



Project Summary

Evaluation of Hazardous Waste Incineration in a Lime Kiln: Rockwell Lime Company

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During a one-week test burn, hazardous waste was used as supplemental fuel and co-fired with petroleum coke in a lime kiln in eastern Wisconsin. Detailed sampling and analysis was conducted on the stack gas for principal organic hazardous constituents (POHCs), particulates, particulate metals, HCl, SO₂, NO_x, CO, and THC and on process streams for metals and chlorine. POHCs were also analyzed in the waste fuel. Sampling was conducted during three baseline and five waste fuel test burn days. Results show average destruction and removal efficiencies (DREs) greater than 99.99% for each POHC and little change in pollutant emissions from baseline to waste fuel test conditions. In addition, material balance results show that 95% of chlorine enters the process from the limestone feed and the chlorine exits the kiln in the baghouse dust and lime product at 61% and 38%, respectively.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Cofiring hazardous wastes in high-temperature industrial processes is an attractive alternative to incineration, because it makes use of the heat content of the waste. Many cofiring devices, which include cement and dolomite kilns, glass furnaces, steel furnaces, and some industrial boilers, provide temperatures and residence times similar to those required for incinerators dedicated to hazardous wastes. In addition to the savings derived from the heat value, using existent equipment saves the capital required to build a separate incinerator and may thus provide an environmentally acceptable alternative to conventional hazardous waste disposal.

Because of their high energy use, lime kilns are an excellent example of this concept. Such kilns typically operate at temperatures over 1093°C (2000°F), have gas residence times exceeding 1.5 seconds, and have a highly turbulent combustion zone. However, the need exists for data that show the effect of cofiring hazardous waste on the emissions from the lime process.

The State of Wisconsin Department of Natural Resources (DNR) and the U.S. Environmental Protection Agency (EPA), Region V, issued a temporary permit to

Rockwell Lime Company to conduct a hazardous waste test burn. This test would allow the burning of hazardous liquid waste as supplemental fuel along with petroleum coke. The waste fuel would replace natural gas as a fuel component.

Through a contract with the Industrial Environmental Research Laboratory, Cincinnati, OH (IERL-Ci), Monsanto Research Corporation (MRC) performed the sampling and analysis of stack gases and process samples during the test burn conducted at the Rockwell Lime Company in Rockwood, Wisconsin.

The primary objectives of the sampling and analysis were to (1) determine the effects of cofiring petroleum coke and hazardous waste on the emissions from the kiln, (2) determine the fate of the principal organic hazardous constituents (POHCs) and determine destruction and removal efficiencies (DREs), (3) determine the fate of chlorine and trace metals in the kiln process, (4) determine the concentration of SO_2 , NO_x , particulates, HCl, metals, total hydrocarbons, and carbon monoxide in the stack gas at baseline and waste fuel test burn conditions, and (5) evaluate kiln operation during hazardous waste fuel burning conditions. This testing provides the Wisconsin DNR and EPA Region V with the data necessary to determine whether a permit can be issued to Rockwell Lime Company to burn hazardous waste. The testing also will provide the EPA-ORD with additional data in their research on the incineration of hazardous waste and the environmental problems associated with incineration.

Facility and Process Description

The Rockwell Lime Company's lime kiln in Rockwood, Wisconsin, approximately 10 miles north of Manitowoc, produces lime at approximately 1.3×10^6 kg (1,430 tons) per week, which varies based upon product demand. The process involves heating limestone to approximately $1,100^\circ\text{C}$ ($2,000^\circ\text{F}$) in a horizontal rotary kiln. Calcining is achieved by interfacing the hot gases with the limestone, which

drives off the CO_2 from the limestone, leaving the lime product (CaO).

The kiln, with refractory linings, is 2.4 m (8 ft) in diameter and 67.1 m (220 ft) long. The kiln rotates at approximately one revolution per minute and has a gentle slope to allow material to pass through by gravity. It also has a counter-current flow pattern, that is, solids travel in one direction and hot gases and dust emissions travel in the opposite direction, as shown in Figure 1. Limestone is fed into the upper end of the kiln at approximately 15,440 kg/hr (34,000 lb/hr). At the opposite end of the kiln, a mixture of coal and natural gas is burned at approximately 1,450 kg/hr (3,200 lb/hr) and 142 m^3/hr (5,000 ft^3/hr) to provide a heat input of approximately 14,700 kw (50 million Btu/hr) or approximately 6.5 million Btu/ton of lime product. As the limestone feed travels down the inclined rotating kiln, it passes through various temperature zones, and the hot gases calcine the limestone into the lime product. The product is produced at approximately 7,720 kg/hr (17,000 lb/hr). After transformation in the kiln, the lime product is air cooled and either directly stored in silos or hydrated prior to storage.

Primary air mixed with the gas, coke, and secondary (heated) air from the lime product cooler is fed to the kiln to provide oxygen for the combustion of the coke and natural gas (or waste fuel). The kiln exhaust gases pass through a series of large radiator coolers that cool the gases before they enter the baghouse; this removes particulates and SO_2 from the gas stream. The gases then pass through the induced draft fans and out the stack at approximately 200°C (392°F) and 5.5 m/s (18 ft/s). The collected dust is stored in a silo and mixed with water to granulate. Some of the dust is sold and the remainder is disposed of in the quarry. No dust is reinjected into the kiln.

During baseline conditions, a blended combination of petroleum coke and natural gas was used to fire the kiln. During the waste fuel runs, a temporary 1-inch diameter stainless steel pipe was placed on the burner pipe with its nozzle pointed into the flame, and the waste fuel

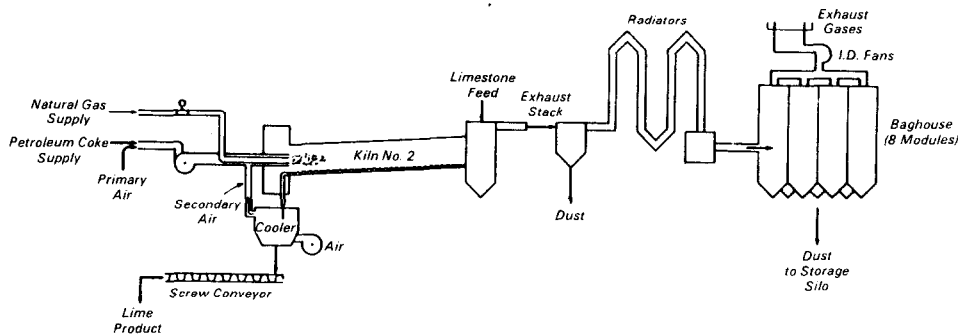


Figure 1. Schematic diagram of lime kiln process.

and petroleum coke were fed unblended to fire the kiln.

The hazardous waste fuel was trucked to the site and stored in a 5,000-gallon tanker between kilns 1 and 2 near the burner end. The diaphragm-type waste fuel pump, located next to the tanker, pumped fuel through the stainless steel pipe to the flame. Air was added to the pipe to supply oxygen for combustion and to cool the pipe.

The waste fuel consisted primarily of lacquer thinner solvents, alcohols, still bottoms, paint wastes, and a small fraction of chlorinated hydrocarbons (0.4%). Tetrachloroethylene and trichloroethylene were spiked to the waste fuel before the test to bring the total chlorine content to approximately 3.0%, which would allow easier evaluation of the destruction of the chlorinated species. During test conditions, the waste fuel ranged from 8% to 36% of the Btu input to the kiln, and petroleum coke ranged from 64% to 90%. Comparatively, under baseline conditions, the petroleum coke averaged 90% and the natural gas averaged 10% of the Btu input to the kiln.

Experimental Program

Table 1 summarizes the test program. Measured pollutants in the stack gas include POHCs (tetrachloroethylene (PERC), trichloroethylene (TCE), methylene chloride (MeCl_2), 1,1,1-trichloroethane (CH_3CCl_3), methyl ethyl ketone (MEK), and toluene), particulate matter, particulate trace metals, hydrogen chloride, sulfur

dioxide, nitrogen oxides, carbon monoxide, total hydrocarbons, and oxygen. In addition, the distribution of metals and chlorine was measured in all of the process input and output streams. Waste fuel, coke, baghouse dust, and lime product samples were submitted for sulfur analyses. Coke samples were analyzed for ash and Btu content. Waste fuel samples also were analyzed for POHCs and Btu content.

Sampling was conducted under baseline conditions (i.e., no waste fuel burned) on April 15, 29, and 30. Sampling at waste fuel conditions (i.e., waste fuel burned) was conducted from May 2 to May 6. A Quality Assurance (QA/QC) Project Plan was reviewed and approved prior to the test program. A full description of the QA/QC results involving replicates, blanks, spikes, and standards is provided in the full report.

Results and Discussion

Waste Fuel

A detailed summary of the waste fuel composition for two waste fuel samples collected is shown in Table 2. Tables 3 and 4 show the concentration of each POHC and other properties for the five waste fuel samples (one sample per day, Runs 4-8).

POHC Destruction and Removal Efficiencies

The complex combustion chemistry for organic materials is perplexing when a

Table 1. Summary of Rockwell Lime Kiln Sampling and Analytical Program

Parameter	Sampling method	Analytical method
Stack Gas		
POHCs ^a	Volatile organic sampling train (VOST)	GC/MS, thermal desorption and SIM
Particulate matter	EPA Method 5	EPA Method 5
Metals on particulate	EPA Method 5	ICP
Hydrogen chloride	Impinger absorption in 0.5 M NaOAc (back half of EPA Method 5)	Specific ion electrode
Carbon dioxide and oxygen	EPA Method 3	Fyrite
Nitrogen oxides	Continuous	Chemiluminescence photometric analyzer
Sulfur dioxide	Continuous	Pulsed fluorescence TECO analyzer
Carbon monoxide	Continuous	Infrared-EPA Method 10
Total hydrocarbons	Continuous	Flame ionization detector
Oxygen	Continuous	Teledyne's micro-fuel cell
Waste fuel		
POHCs	Grab - composite	GC/MS
Metals	Grab - composite	ICP
Chlorine, sulfur	Grab - composite	ASTM D240-64
Btu content	Grab - composite	ASTM D482-IP4
Baghouse dust		
Metals	Grab - composite	ICP
Chlorine, sulfur	Grab - composite	XRF
Lime product		
Metals	Grab - composite	ICP
Chlorine, sulfur	Grab - composite	XRF
Dry limestone feed		
Metals	Grab - composite	ICP
Chlorine	Grab - composite	XRF
Primary fuel coke		
Metals	Grab - composite	ICP
Chlorine, sulfur	Grab - composite	XRF
Btu content	Grab - composite	ASTM D240-64

^aTetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, methyl ethyl ketone, and toluene.

broad range of organic compounds in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO₂ in the combustion process, but trace amounts of organic chemicals survive oxidation and are only partially reacted. Accordingly, the test burn investigated the amount of destruction of the organic compounds in the hazardous waste.

The DRE for an incineration/air pollution control system is defined by the following equation:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} (100) \quad (1)$$

where DRE = destruction and removal efficiency, %

W_{in} = mass feed rate of principal organic hazardous constituent(s) (POHCs) fed to the incinerator

W_{out} = mass emission rate of principal organic hazardous constituent(s) (POHCs) to the atmosphere (as measured in stack prior to discharge).

DRE calculations are based on combined efficiencies of the destruction of the POHC in the incinerator or the lime kiln and the removal of the POHC from the gas stream in the air pollution control system. The presence of POHCs in solid discharges from the air pollution control devices is not accounted for in the DRE calculation as currently defined by EPA. RCRA, Part 264, Subpart O regulations for hazardous

Table 2. Results of Capillary GC/MS Analysis of Major Components of Waste Fuels

Waste fuel component	Concentration, wt %	
	Number 4 ^a	Number 7 ^a
Acetone	0.23	0.22
Methyl ethyl ketone (MEK) (POHC)	2.48	3.17
1,1,1-Trichloroethane $CH_3 CCl_3$ (POHC)	0.24	0.22
1-Butanol	0.32	0.37
Trichloroethylene TCE (POHC)	1.73	2.16
2-Ethoxyethanol	0.85	0.92
Methyl isobutyl ketone	1.06	1.16
Toluene (POHC)	11.0	12.5
Tetrachloroethylene (Perc) (POHC)	2.17	2.49
Butyl acetone	0.27	0.32
Ethylbenzene	1.42	1.58
Xylene (isomer No. 1)	4.92	5.58
Xylene (isomer No. 2)	1.43	1.60
2-Butoxyethanol	1.99	2.07
2-Ethoxyethyl acetate	5.91	6.37
C_3 -Benzene (isomer No. 1)	0.28	0.32
C_3 -Benzene (isomer No. 2)	0.46	0.57
C_{10} -Alkane	0.80	0.94
Alkane $>C_8$	0.24	0.28
Alkane	0.14	0.18
C_{11} -Alkane	1.26	1.48
2-Cyclohexen-1-one or 3,5,5-Trimethyl (isomer)	0.15	0.18
Alkane $>C_6$	0.27	0.24

^aAverage of split sample.

Table 3. Concentration of POHCs

Run No.	POHCs concentration, wt % ^a					
	MeCl ₂	MEK	$CH_3 CCl_3$	TCE	Perc	Toluene
4	0.101	2.48	0.238	1.73	2.17	10.97
5	0.097	2.75	0.239	1.64	2.02	10.55
6	0.106	2.48	0.228	1.78	2.05	10.95
7 ^b	0.120	3.17	0.216	2.16	2.49	12.50
7 ^c	0.120	3.17	0.216	2.16	2.49	12.50
8	0.116	2.59	0.282	1.89	2.56	12.90

^aNo waste fuel burned on baseline runs 1-3.

^bRuns 7A-7C.

^cRuns 7D-7F.

waste incinerators require a DRE of 99.99% for all principal organic hazardous constituents of a waste during trial burns unless it can be demonstrated that a higher or lower DRE is more appropriate based on human health criteria. Specification of the POHCs in a waste is subject to best engineering judgment, considering

the toxicity, thermal stability, and quantity of each organic waste constituent. DRE requirements in the Subpart O regulations do not apply to metals or other noncombustible materials.

Toluene, MEK, Perc, and TCE were present in high concentration for organic compounds (see Table 2). Spikes of Perc

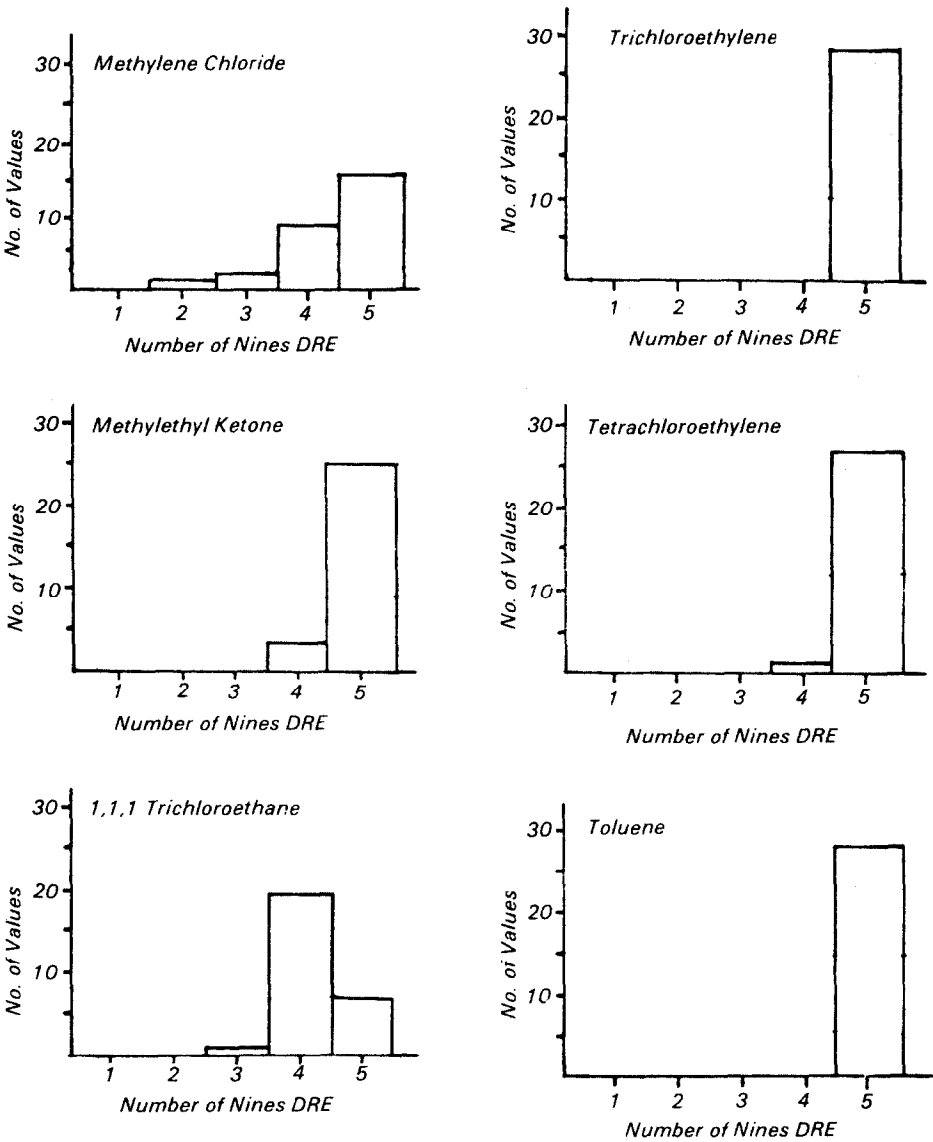


Figure 2. Destruction and removal efficiencies.

and TCE were added to the waste fuel prior to the test burn to obtain the higher concentrations. Perc, TCE, methylene chloride, and 1,1,1-trichloroethane were selected because the chlorinated hydrocarbons are, in general, difficult to destroy thermally. All six of the compounds except methylene chloride were found in the top twenty constituents of the waste fuel. All six compounds are listed as hazardous in RCRA Part 261, Appendix VIII.

Approximately six VOST sampling runs were made each day (Runs 1-8). Destruction and removal efficiencies, calculated for waste fuel runs 4-8, are summarized in Figure 2.

In general, DREs ranged from 99.60% to >99.999% for all compounds and averaged 99.9989%. Only four runs had DREs less than 99.99%; three of these were for methylene chloride, the fourth for 1,1,1-trichloroethane.

DREs for methylene chloride (MeCl₂) ranged from 99.60% to <99.999% and averaged 99.983% ± 0.15% (95% confidence limits).

Methyl ethyl ketone (MEK) had an average DRE of 99.999% ± 0.0002% (95% confidence limit) and ranged from 99.998% to greater than 99.999%. These high destruction efficiencies were consistent throughout the test runs.

DREs for 1,1,1-trichloroethane (CH₃CCl₃) ranged from 99.989% to 99.999% and averaged 99.997% ± 0.004% (95% confidence limits). Only Run No. 4E had a DRE less than 99.99%.

DREs for trichloroethylene (TCE) were greater than 99.999% for all runs. TCE was spiked to the waste fuel prior to testing to increase its concentration and

allow easier detection of TCE in the stack gas. Spiking of TCE to concentrations greater than approximately 1.3% by volume was not possible due to permit requirements which specified a maximum of 3.0% by volume for chlorine.

DREs for tetrachloroethylene (Perc) also were greater than 99.99% for all runs. Like TCE, Perc was spiked to the waste fuel to the maximum allowable concentration described in the test burn permit prior to the test.

Toluene was the POHC of highest concentration in the waste fuel (average 11.6% by weight). DREs for toluene were above 99.999% for all runs. Data for toluene was very consistent during all waste fuel test runs.

Stack Samples

Results for stack conditions and particulate, hydrogen chloride, sulfur dioxide, nitrogen oxides, carbon monoxide, and total hydrocarbon emissions for baseline and waste fuel runs are summarized in Table 5. The overall stack rate averaged 917 m³/min (32,420 ft³/min) and the dry stack rate averaged 487 dscm/min (17,210 dscf/min). As evidenced by the high standard deviations the CO and, to a lesser degree, the SO₂ fluctuated. Minor kiln upsets (i.e., coke feed chute cleaning, clumps of coke falling to kiln, change in process conditions) created high CO excursions. An increase in SO₂ by ~200 ppm, followed by a reduction in NO_x by ~50 ppm and a subsequent increase in CO by ~500 ppm occurred quite often over a 15 minute period. These trends are expected when a lower intensity flame occurs (or kiln upset). However, as revealed by Figure 2, the kiln upsets had little or no effect on the DRE results.

Table 4. Waste Fuel Conditions

Run number ^a	Chlorine content, % (vol.)	Sulfur content, %	PCB concentration, ppm	Heat value, Btu/lb	Specific gravity, g/cc	Feed rate, gal/min	Mass rate, g/min
4	3.14	0.10	1.0	12,301	1.031	0.76	2,990
5	2.66	0.08	1.0	12,084	1.042	1.21	4,770
6	3.04	0.065	1.0	12,267	1.035	2.05	8,020
7	3.05	0.06	1.0	13,612	0.986	0.78 ^b	2,910
						2.90 ^c	10,820
8	3.51	0.11	1.0	14,064	0.971	2.88	10,590

^aNo waste fuel burned during Run Nos. 1, 2, and 3.

^bRuns 7A-7C.

^cRuns 7D-7F.

Table 5. Average Stack Emissions

Parameter and unit	Baseline			Waste fuel		
	Range	Average	Standard deviation	Range	Average	Standard deviation
Stack rate, m ³ /min	805 - 975	917	76	791 - 938	847	52
Stack velocity, m/sec	5.0 - 6.0	5.7	0.4	4.9 - 5.8	5.2	0.3
Particulates						
mg/dscm	24.0 - 35.0	28.7	4.7	24.9 - 48.7	35.3	8.0
kg/hr	0.66 - 1.1	0.9	0.2	0.68 - 1.4	1.0	0.3
HCl, ppm	0.74 - 3.9	2.0	1.4	2.5 - 6.0	4.4	1.2
SO ₂ , ppm	123 - 730	553	110	183 - 1,924	596	240
NO _x , ppm	306 - 460	386	49	288 - 552	446	64
CO, ppm	10 - 4,900	477	966	10 - 4,540	599	1,409
THC, ppm	6.7 - 12.7	8.2	1.9	1.5 - 10.0	3.5	1.1

Chlorine, Sulfur and Metals Balance

Chlorine and sulfur material balances are summarized for baseline and waste fuel conditions in Table 6. The majority of chlorine (for either baseline or waste fuel conditions) enters the kiln in the limestone feed and exits the kiln in the lime product and baghouse dust. Sulfur (for either baseline or waste fuel conditions) enters the kiln in the petroleum coke and exits the kiln distributed in the lime product (~9%), baghouse dust (~27%), and stack gas (~64%).

Typical metals material balance is shown in Table 7. There was no difference for baseline and waste fuel conditions for distribution of metals in the kiln process. As shown in Table 7, the majority of mass entering the kiln is contributed by the limestone feed, except for zinc. The mass exiting the kiln is distributed between the lime product and baghouse dust.

Baseline vs. Waste Fuel and Kiln Operation

Emissions were evaluated under baseline and waste fuel conditions. For the pollutants listed in Table 5, HCl, NO_x,

Table 6. Chlorine and Sulfur Material Balance

Run number	Percent to kiln		Limestone feed	Total mass in, kg/hr	Lime product	Percent from kiln		Stack gas	Total mass out, kg/hr	Material balance closure, %
	Coke	Waste fuel				Baghouse dust	Percent from kiln			
Chlorine ^a										
Baseline ^a	4	0	96	23	47	52	1	13	55	
Waste fuel ^b	5	2	93	21	34	65	1	20	105	
Sulfur										
Baseline ^a	100	0	NA	59	8	29	63	91	73	
Waste fuel ^b	99	1	NA	54	10	25	65	70	77	

^aAverage values of baseline Runs 1-3

^bAverage values of waste fuel Runs 4-8

Table 7. Typical Rockwell Lime Metals Material Balance^a

Metal	Percent to kiln (by wt)			Total mass in, g/hr	Lime product	Percent from kiln (by wt)		Total mass out, g/hr	Percent closure
	Coke	Waste fuel	Limestone feed			Baghouse dust	Stack gas		
Be	10	0	90	25	75	25	0	16	64
Ca	1	<1	99	3 x 10 ⁶	93	7	<1	3 x 10 ⁶	100
Cr	1	<1	98	811	75	25	<1	700	86
Fe	1	<1	99	13,160	83	17	<1	13,300	101
Mg	<1	0	99	2 x 10 ⁶	90	10	<1	2 x 10 ⁶	100
Ni	20	<1	80	660	74	26	<1	460	70
Pb	14	6	80	<500	55	45	<1	<450	90
Zn	5	53	42	170	41	58	1	100	58

^aAverage values for Runs 1-8.

and THC showed a significant difference in stack emissions under baseline and waste fuel conditions. For the POHCs, only methylene chloride and toluene showed an increase from baseline to waste fuel conditions. All remaining POHCs showed no significant difference in baseline vs. waste fuel emissions.

As described previously, the kiln operation fluctuated as indicated by CO and SO₂ emission variations during waste fuel burning. Kiln fluctuations were caused by several factors, including non-constant fuel rates, product rushes, clumps of coke fed to kiln accidentally, and operator inexperience with burning waste fuel. The fluctuation resulted in occasional kiln O₂ increases and stack gas SO₂ decreases that caused a poorer quality lime product most likely due to excess sulfur. The following items were identified as ways to improve kiln operation under waste fuel conditions:

- Change waste fuel burner configuration such that at low waste fuel rates the waste fuel is mixed with the coke to maintain a flame.
- Decrease the fan speed (i.e., reduce the draft) to lower the O₂ in the kiln, thus lowering the sulfur in the product and increasing the sulfur in the stack.

Conclusions

Constant achievement of at least 99.99% DRE was demonstrated for each POHC (MeCl₂, MEK, CH₃ CCl₃, TCE, Perc, and toluene) in the lime kiln process.

Emissions of pollutants were determined and ranged as follows: particulates 0.7-1.4 kg/hr; HCl 0.04-0.26 kg/hr; SO₂ 123-2,100 ppm; NO_x 280-550 ppm; THC 1.5-10 ppm; and CO 10-5,000 ppm.

Except for HCl, NO_x, THC, MeCl₂, and toluene, emissions for pollutants were statistically not different for baseline and waste fuel conditions.

Typically, sulfur enters the kiln in the petroleum coke and exits the kiln distributed in the lime product, baghouse dust, and stack gas.

Typically, a metal enters the kiln in the limestone feed and exits the kiln in the lime product and baghouse dust.

The kiln operation fluctuated resulting in an occasionally lower-quality lime product. Improving the burner system, reducing draft (and % O₂), and allowing operators sufficient time to run the system may minimize fluctuations and improve product quality.

D. R. Day and L. A. Cox are with Monsanto Research Corporation, Dayton, OH 45407; R. E. Mournighan (also the EPA Project Officer, see below) is with the Industrial Environmental Research Laboratory, Cincinnati, OH 45268. The complete report, entitled "Evaluation of Hazardous Waste Incineration in a Lime Kiln: Rockwell Lime Company," (Order No. PB 84-230 044; Cost: \$16.00, subject to change) will be available only from:

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