



Project Summary

Destruction and Removal of POHCs in Iron Making Blast Furnaces

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At least one steel company utilizes organic waste liquids as a heat and carbon content source to partially replace the coke that is used to charge the blast furnaces. The waste liquids fed to the blast furnace are likely to contain hazardous constituents. Temperature and residence time in the blast furnace favor total destruction of the principal organic hazardous constituents (POHCs) of the waste fuel, but verification of destruction efficiencies has not been attempted up to now. Also, reduction reactions that occur in a blast furnace may promote the formation of products of incomplete combustion (PICs).

Tests were conducted while feeding waste fuel to a blast furnace located at a major steel mill. The primary objectives of the test program were to determine the fate of the POHCs of the waste fuel; to look for formation of PICs, notably dioxins and dibenzofurans; and to determine relative emissions of volatile organic components of waste oil from the waste fuel storage tank compared with emissions of these components from the combustor.

This Project Summary was developed by EPA's Hazardous Waste Engineering 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

With the passage of the Hazardous and Solid Waste Amendments of 1984, more

liquid hazardous wastes categories will be banned from land disposal facilities. At the same time, energy intensive industries are continuously seeking new sources of less expensive fuel. Because many hazardous waste products can readily be used as fuels, a market based on these wastes has been developing in the United States. Among the high-temperature industrial furnaces and processes that already burn hazardous waste as supplemental fuel are cement kilns, lime and dolomite kilns, clay processing kilns, phosphate rock calciners and dryers, iron ore dryers, brick and tile tunnel kilns, mineral wool furnaces, glass melt furnaces, and steel blast furnaces.

Organic waste liquids can be burned in iron-making blast furnaces to provide a twofold benefit to the user; not only can they replace natural gas as a fuel source, but they can also provide a carbon source, thus partially reducing coke requirements. This practice of burning wastes in the furnace is also attractive from a waste disposal viewpoint since it offers high residence time for destruction of Principal Organic Hazardous Constituents (POHCs) in a high-temperature environment.

Because the disposal of hazardous wastes in industrial furnaces is currently exempt from the Resource Conservation and Recovery Act (RCRA) performance regulations enforced at incineration facilities, little attempt has been made to determine how successful iron-making blast furnaces are in achieving destruction and removal of POHCs. To gain further insight into this, testing was

conducted during the burning of liquid waste fuel in an industry-typical blast furnace located at LTV Steel's Indiana Harbor Works, East Chicago, Indiana.

The primary objectives of this test were as follows:

- Determine the destruction and removal efficiency (DRE) and fate of waste oil POHCs by monitoring blast furnace gas and combustor flue gas for identified POHCs.
- Determine formation of products of incomplete combustion (PICs) and, if detected, their fate.
- Determine relative emissions of volatile organic components of waste oil from the waste fuel storage tank compared with emissions of these components from the combustor.

As a secondary objective, the presence of dioxins and dibenzofurans in the emissions/effluent at levels greater than one part per trillion was also investigated.

Approach

The blast furnace system, depicted in Figure 1, is used to produce molten iron from iron ore and other iron-bearing materials. A moving bed of iron ore, carbon (as coke), and limestone descends through the blast furnace tower. In the combustion zone, located between the descending bed and the hearth of the

furnace, oxygen of the hot blast air and steam react with carbon to produce carbon monoxide and hydrogen. Temperatures in the combustion zone exceed 3000°F. The hot CO and H₂ travel upward through the descending bed. In the lower part of the furnace where the temperature is very high, the iron oxides are reduced to elemental iron by the coke. In the upper part of the furnace tower where the temperature has decreased to 1700°F, the iron oxides are reduced by the carbon monoxide and the hydrogen. The molten iron and slag are collected in discrete layers on the hearth of the furnace and are removed through tap holes at regular intervals.

Unconsumed CO and H₂, which are produced in excess to drive the iron oxide reduction to completion, yield an off-gas with a heating value of 90 BTU/SCF. To recover this heat energy, about a third of the off-gas is burned in stoves that preheat the blast air, while the remaining two-thirds is burned in process boilers. Products of combustion from the stoves are emitted to the atmosphere through a stack.

For the purposes of the test, the set of blast air preheating stoves was considered to be a downstream combustion process and was included in the scope of the test. Sampling was performed upstream and downstream of the stoves while the process boiler streams were not investigated.

Natural gas was originally used as the fuel source for the blast furnace. This has been replaced by a waste oil mixture consisting of waste organic liquids supplied by Cadence Chemical Company and Number 6 fuel oil.

The test plan consisted of three sampling runs conducted on successive days (8/15/84-8/17/84). Selected blast furnace and stove set operating data for each of the three runs are summarized in Tables 1 and 2, respectively.

Liquid waste feed characterization may be found in Table 3. Eleven detected compounds were selected as POHCs for the test. This selection was based upon concentration, toxicity, and degree of chlorination of the compounds. Those POHCs with feed concentrations below 1000 ppm may yield suspect results for DRE because it is likely that emission rates for compounds with such low feed concentrations will be below the detection limits. This inhibits verification of DRE, which is determined as shown in Figure 2.

The target for acceptable DRE performance was chosen to be 99.99%, which is also the RCRA standard for incineration of non-PCB wastes. DREs were determined across the blast furnace itself and across the total system (blast furnace + stove set).

A summary of the process stream sampled and the analyses performed may be found in Table 4.

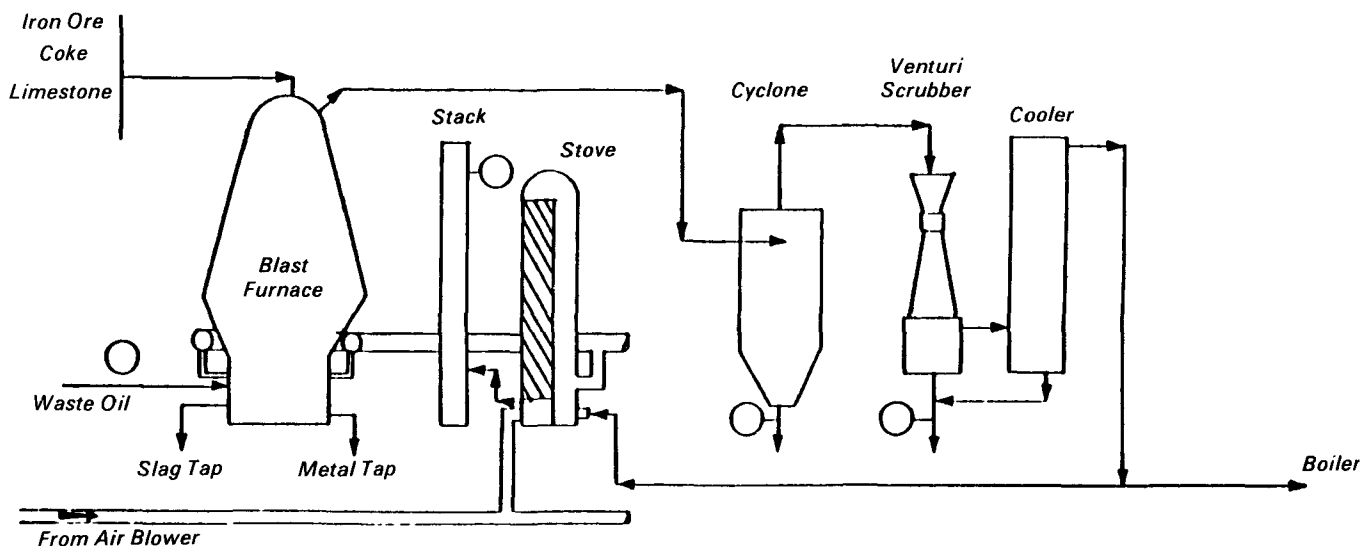


Figure 1. Blast furnace process flow.

Table 1. Summary of Blast Furnace Operating Data

Parameter	Run 01	Average Value Run 02	Run 03
Blast Air Temperature, °F	1,743	1,770	1,756
Blast Air Flowrate, dsc fm x 10 ³	116.5	116.6	116.2
Blast Air Pressure, psig	31.5	30.4	30.2
Total Oxygen in Blast, %	23.4	23.4	23.4
Flame Temperature °F (calculated)	3,389	3,487	3,402
Furnace Top Temperature °F	337	379	325
Top Gas Heating Value, Btu/scf (calculated)	90.7	89.3	91.5
Total Blast Gas Volume, scfm x 10 ³	128.3	127.1	127.9
Waste Oil Injection, gpm	60.6	59.5	60.4
Waste Oil Heating Value, Btu/lb	14,776	14,708	14,851

Table 2. Summary of Stove Operation Data for Periods of Blast Furnace Gas Combustion

Stove Number	Test Run	Mean Blast Gas Flow (scfm)	Air/Fuel Ratio (scf/scf)	Mean Stove Temperatures		
				Wall (°F)	Dome (°F)	Stack (°F)
31	01	25,050	0.75	1,746	2,283	444
	02	25,050	0.73	1,694	2,246	399
	03	25,950	0.74	1,684	2,200	426
32	01	26,050	0.81	1,626	2,271	443
	02	25,730	0.80	1,638	2,246	429
	03	26,580	0.81	1,650	2,247	413
33	01	25,370	0.83	1,681	2,279	448
	02	25,220	0.83	1,636	2,246	431
	03	26,360	0.87	1,656	2,252	432

Table 3. Summary of Liquid Feed Data

	Run 01	Run 02	Run 03
Waste Liquid/Fuel Oil Ratio	.8	.6	.6
Heating value, Btu/lb	14,776	14,708	14,851
Carbon, wt %	67.57	68.27	70.06
Hydrogen, wt %	9.58	9.20	9.28
Nitrogen, wt %	0.26	0.31	0.39
Chlorine, wt %	0.09	0.08	0.08
Sulfur, wt %	0.73	0.30	0.59
Ash, wt %	0.99	0.98	0.77
Oxygen, wt %, by difference	17.88	17.93	17.58
Water, wt %	2.90	2.93	1.25
	100.00	100.00	100.00

	Compound Concentration (ppm by Weight)				Average Mass to Blast Furnace ^a (Kg/hr)
	Run 01	Run 02	Run 03	Average	
Methylene chloride	688	1,023	535	750	9.7
1,1-dichloroethene	1,071	1,880	690	1,213	15.7
Chloroform	33	469	259	254	3.3
1,1,1-trichloroethane	817	965	1,215	999	13.0
Trichloroethene	1,511	719	1,326	1,185	15.4
Benzene	569	547	543	553	7.2
Tetrachloroethene	2,230	3,372	2,787	2,796	36.3
Toluene	65,417	53,342	49,901	56,220	731
m/p-Xylene	2,600	1,500	10,600	9,400	122
o-Xylene	9,500	3,300	3,050	5,280	68.8
Napthalene	810	1,100	730	880	11.4
Volumetric rate, gpm	60.6	59.9	60.4	60.2	--
Mass rate, kg/h	13,067	12,830	13,024	12,974	--

^aMass rate based on average waste/oil feed rate of 60.2 gpm and specific gravity of 0.95. Feed rates for individual test runs ranged from 59.5 to 60.6 gpm.

Results

DREs and Fate of Waste Oil POHCs

A summary of the DREs may be found in Table 5. The results have been segregated into three groups: DREs for POHCs having feed concentrations greater than 1000 ppm; DREs for POHCs having feed concentrations less than 1000 ppm; and DREs for benzene and methylene chloride. Benzene is looked at separately because it is often found in combustion emissions when not detected in the scrubber feed; explanations for this include benzene as an artifact of one of the sorbents, and benzene as a PIC. Methylene chloride is singled out because of its high background concentration typically found in hazardous waste destruction tests; it is commonly used as a solvent during sample train cleanup and analysis.

Across the blast furnace, the target DRE of 99.99% was reached for 8 of the 18 1000+ ppm measurements. For the cases in which feed concentrations were less than 1000 ppm, three of nine DRE measurements were greater than 99.99%. None of the six DRE measurements across the furnace for benzene and methylene chloride met the target.

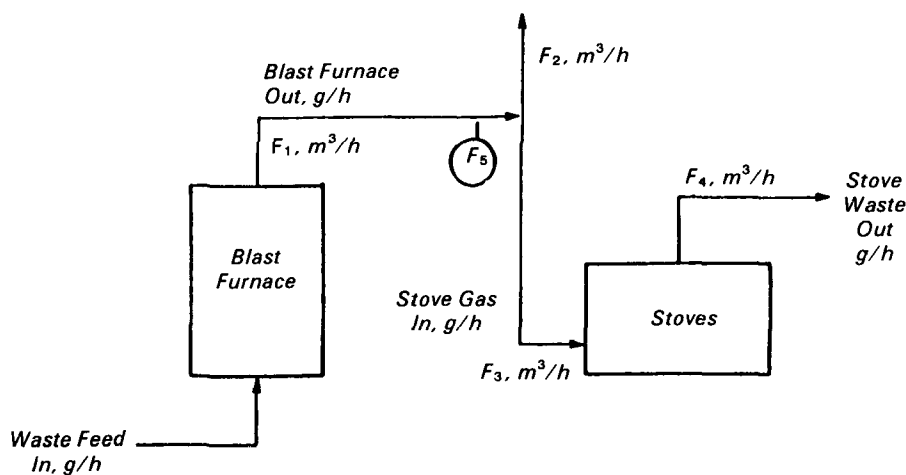
Across the total system, DREs were somewhat higher. The criterion was met in 14 of the 18 1000+ ppm measurements. For feed concentrations below 1000 ppm, three of nine DRE measurements were greater than 99.99%. As was the case with the blast furnace, none of the DREs for benzene and methylene chloride reached 99.99% across the total system.

Using 99.99% as the criterion, successful DRE was consistently achieved for the following POHCs: trichloroethene (across blast furnace and total system), tetrachloroethene (blast furnace and total system), toluene (total system only), and o-xylene (total system only).

Analysis of the scrubber water for semi-volatile POHCs found that, with one exception, POHC concentrations were either below the detection limit or did not exceed concentrations in makeup water. For Run 3, the mass rate of toluene in the blowdown, corrected for concentrations in the makeup, was 7800 g/hr or about 1 percent of the toluene in the feed.

PIC Formation and Fate

Scrubber makeup water, scrubber discharge water, and blast furnace and stove off-gas were sampled for volatile



$$\text{System DRE}_i = \frac{(\text{Waste Feed In, g/h})_i (F_3/F_1)_i - (\text{Stove Waste Out, g/h})_i}{(\text{Waste Feed In, g/h})_i (F_3/F_1)_i}$$

$$\text{Blast Furnace DRE}_i = \frac{(\text{Waste Feed In, g/h})_i - (\text{Blast Furnace Out, g/h})_i}{(\text{Waste Feed In, g/h})_i}$$

Subscript *i* is for each component

Figure 2. Diagram for definition of blast furnace DRE and system DRE.

Table 4. Analytical Methods

Sample/Component	Analytical Method
Waste Oil	
—POHCs	Extraction, followed by GC/MS
—Ultimate composition (C, H, S, O, N, Cl)	ASTM
heating value and H ₂ O	
Blast Furnace and Combustion Process Emissions	
—POHCs and PICs by VOST	Purge and trap, followed by GC/MS
—POHCs and PICs by MM5	Extraction, followed by GC/MS
—Chlorides	Ion chromatography
—Dioxins/dibenzofurans	High resolution GC/MS
—Particulate matter	EPA Method 5
—Method 3 fixed gases (O ₂ , CO ₂ , CO, H)	GC/TC
Scrubber Water	
—POHCs and PICs	GC/MS
—Dioxins/dibenzofurans	High resolution GC/MS
Waste Oil Feed Tank Vent Gas	
—POHCs	VOST sampling and analysis for identification. GC/FID for concentration

Carbon disulfide was found in significant concentration in the blast furnace and stove off-gases and is typical of incomplete combustion from operation at reducing conditions. Concentrations were not quantitated due to the water solubility of the carbon disulfide that limited sample recovery during the purge trap and analytical method. Chloromethane was also found in the gaseous emissions but not detected in the waste oil feed. No "nonfeed" compounds were detected in the scrubber waters. Several such compounds were found in the off-gases during Run 2 (Table 6).

Storage Tank Vapor Phase

Integrated bag samples of vapors exiting the waste feed storage tank during truck off-loading were analyzed on-site using GC/FID. Samples of the vapors for GC/MS analysis were also collected directly from the bag using a VOST train.

An important factor limiting the amount of information and the quality of data that could be obtained from the vent gas sampling effort was the high concentration of hydrocarbons in the vent gas. The data gathered indicate that total hydrocarbon (THC) concentration as benzene ranged from 1 to 6 percent by volume. This high THC concentration resulted in condensation of organic constituents on the interior of the Tedlar bags before VOST sampling and the GC/FID analysis.

No quantitative data could be obtained from the GC/MS analysis because the Tenax tubes were saturated with hydrocarbons after sampling less than 0.1 scf of vent gas. Organic compounds identified in the vent gas by GC/MS are listed below:

Methylene chloride
1,1-Dichloroethene
Chloroform
1,1,2-Trichloro-1,2,2-Trifluoroethane
2-Butanone
1,1,1-Trichloroethane
Trichloroethene
Benzene
5-methyl-1 hexanol
Tetrachloroethene
Toluene
Xylenes

and semi-volatile compounds not found in the waste fuel. Classification of these compounds as PICs is avoided because they may have originated in the blast air or the iron ore/coke mixture, neither of

which was analyzed. Baseline emission testing (no waste liquid feed) could not be conducted without upsetting the carbon and heat balances of the blast furnace.

All of the above compounds were also found in varying quantities in the waste oil feed samples. Naphthalene was the only waste oil feed POHC not detected in the storage tank vapor.

Table 5. DRE Results in Percent

	Blast Furnace							
	Run 01	Run 02	Run 03	Mean	Run 01	Run 02	Run 03	Mean
For feed concentration ≥ 1000 ppm:								
1,1-dichloroethene ^a	99.968	>99.995	--	>99.972	99.994	>99.998	--	>99.991
1,1,1-trichloroethane ^a	--	--	99.964	--	--	--	>99.935	--
Trichloroethene ^a	99.998	--	99.996	>99.998	99.997	--	99.997	99.997
Tetrachloroethene ^a	99.997	99.999	99.999	99.999	99.999	99.998	99.999	99.999
Toluene	99.987	99.991	99.981	99.986	99.998	99.999	>99.999	99.999
m/p-Xylene ^b	99.940	99.988	99.977	99.968	99.981	99.999	99.960	99.980
o-Xylene ^b	99.993	99.979	99.973	99.982	99.998	99.996	99.993	99.996
Naphthalene ^b	--	99.790	--	--	--	99.977	--	--
For feed concentration < 1000 ppm								
1,1-dichloroethene ^a	--	--	>99.954	--	--	--	>99.982	--
Chloroform ^a	>99.700	>99.998	99.973	>99.890	99.876	99.995	99.972	99.948
1,1,1-trichloroethane ^a	>99.955	>99.997	--	>99.972	99.944	99.967	--	99.949
Trichloroethene ^a	--	>99.990	--	--	--	99.998	--	--
Naphthalene ³	99.860	--	99.640	99.763	99.993	--	99.962	99.977
Methylene chloride ^a	>99.897	>99.968	>99.847	>99.904	99.823	99.941	99.841	99.868
Benzene ^a	98.886	99.143	98.539	98.856	99.954	99.853	98.833	99.547

^aBy VOST analysis.^bBy MM5 analysis.**Table 6. Non-Feed Compounds Detected at Outlet of Stoves—Run 02**

	Concentration g/Sample (Total)	ID Confidence Level ^a
Unknown ^b	180	1
5-Methyl-2-furancarboxaldehyde	200	2
1,1-Dimethoxyheptane	230	2
Benzoic acid + 1,1-Di-methoxyoctane ^c	250	2
Methyl hexadecanoate	1,970	2
Methyloctadecanoate	2,060	2

^aID Confidence Levels. (1) tentative, (2) confident, and (3) confirmed^bApparent molecular weight is 142, probable empirical formula is C₈H₁₄O₂^cConcentration reported represents total of two co-eluting compounds

Dioxins/Dibenzofurans

All scrubber water, blast furnace off-gas, and stove off-gas samples were screened for dioxins and dibenzofurans with high resolution GC/MS. Neither class of compounds was detected at the 1-ppb detection limit for the aqueous samples or 1 ppt detection limit for the gas samples.

Conclusions

For reasons mentioned previously, the DRE results for feed concentrations below 1000 ppm as well as the results for benzene and methylene chloride are not reliable enough to draw conclusions

from them. Therefore, attention should be focused on those POHCs having feed concentrations greater than 1000 ppm. Taking this into consideration, the LTV Steel Blast Furnace shows considerable potential as a hazardous waste incinerator.

In looking at the blast furnace alone, 99.99% DRE was only consistently attained in the cases of trichloroethene and tetrachloroethene. But following downstream combustion in the stove set, DREs of 99.99% were consistently measured for 1,1-dichloroethene, toluene, and o-xylene in addition to the trichloroethene and tetrachloroethene.

The analysis for PICs is of limited value since there was no baseline emission testing and neither the blast air nor the iron ore/coke mixture was analyzed. Based upon the analyses undertaken, it would appear that carbon disulfide and chloromethane are likely PICs.

A comparison of the volatile organic emissions from the waste fuel storage tank relative to the emissions of these components from the combustor could not be made since quantitation of tank vapor emissions was not possible. However, with the exception of naphthalene, all of the waste feed POHCs were detected in the tank vapor phase.

Dioxins and dibenzofurans were not present at detectable levels in the effluent and emission streams.

Recommendations

In future tests, analysis of blast air and the iron ore/coke mixture should be undertaken to allow for more accurate determination of PICs and DREs. Additionally, a test program is recommended to determine venting rates of the individual components of the tank vapor phase in order to compare these rates with those from the blast furnace emissions.