



Project Summary

Organic Emissions from Iron Ore Sintering Plants: Determination of Causes and Methods of Abatement

Robert A. Stoehr

This report summarizes a laboratory project to develop basic information on the emission of organics from iron ore sinter beds. Samples of sinter mix and sinter mix components (including several types of iron ore fines, blast furnace flue dust, rolling mill scale, anthracite coal, and limestone) were obtained from three sinter producers.

Small samples were heated in a tube furnace under a 100 ml/min flow of N₂ or air. A combination of total organic analysis and full chromatographic analysis was used to determine the rate of organic emissions as a function of temperature and to characterize the nature of the emissions. Maximum emissions were observed between 300° and 500°C. Substantial emissions occurred as low as 100° and as high as 800°C. They were less in air than in N₂, indicating that combustion occurred even at comparatively low temperatures where the fixed carbon does not burn. Mill scale and blast furnace flue dust were shown to be the major sources of the organic emissions.

These results suggest procedures for recycling the hydrocarbon bearing gases through the hot sinter bed to produce complete combustion and for thermally pretreating the offending components.

This Project Summary was developed by EPA's Industrial Environmental

Research Laboratory, Research Triangle Park, NC, 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

The goal of this project was to develop basic information on the conditions under which organics are emitted from iron ore sinter beds and to investigate techniques for their elimination at the source.

Iron ore sintering is one of the principal methods for agglomerating iron ore fines into a feed material suitable for the blast furnace. Furthermore, it is a unique agglomerating method in that it permits the recycling of certain waste materials which are high in iron value and fuel value, including rolling mill scale and blast furnace flue dust and filter cake. Iron ore fines, iron ore concentrates, coke, coke breeze, anthracite coal, and limestone are used in various proportions to complete the mix.

The materials are blended, mixed with a controlled amount of moisture, agglomerated on a balling drum or disc, then fed onto the travelling grate of a downdraft sintering machine. The material is ignited from the top. Suction in the windboxes pulls air down through the bed. The ignited layer, or "flame front," moves down through the bed as

the bed moves along the machine on the travelling grate. The flame front reaches the bottom of the bed just before the bed reaches the discharge end of the line.

Hydrocarbons enter the sinter mix with a number of components; principally with blast furnace flue dust and filter cake, and oil-coated mill scale. They are volatilized in the preheating zone below the flame front; since the conditions are reducing, they either do not burn or burn incompletely. Temperatures are not high enough in the windboxes to ensure burning of the hydrocarbons after they leave the bed. The organics emitted from the bed may be subsequently condensed or allowed to escape into the atmosphere.

The experiments of this project were designed to obtain basic information on the conditions under which organics are emitted from sinter bed materials to aid in the control of the process and the design of systems for improved pretreatment of components and recycling of the off-gas.

Experimental Procedures

Sinter mix samples were obtained from three major producers of iron ore sinter: Bethlehem Steel, Jones and Laughlin Steel, and United States Steel. Samples were shipped in sealed cans. In addition to samples of the complete mix, samples of the sinter mix components were supplied by the producers. These components included rolling mill scale, blast furnace flue dust, Quebec ore concentrate, Mesabi ore fines, Venezuela fines, calcine, black sand, and anthracite coal.

The general experimental procedure was to place the specimen on a porous support in a vertical combustion tube, heat it at a prescribed rate while passing a controlled atmosphere through it, and analyze the effluent gases for organics using a gas chromatograph (GC) with a flame ionization detector.

From the beginning, it was realized that the emissions should be analyzed continuously so that the total quantity of organics emitted could be determined. This proved to be impossible when the GC was used in a conventional manner, because a long time (nearly 1 hr) was needed to provide good separation between the organics from C₁ to C₂₄.

Several unsuccessful techniques were used in efforts to overcome this problem before a truly effective procedure was developed. The unsuccessful techniques included

capturing the off-gas in gas sampling bottles which were stored until they could be analyzed, absorbing the organics in hexane or benzene for later analysis, capturing the organics by condensation at liquid nitrogen temperatures, and measuring emissions by measuring weight loss as the specimen is heated.

A successful technique involved a combination of total organic analysis, which could be performed on a nearly continuous basis, and full chromatographic analysis, which could be performed at selected temperatures.

The eventual apparatus for testing sinter mix components is shown in Figure 1. A 3.0-g sample was placed on a vertical 13-mm diameter silica glass tube (C). A fritted silica disc supported the sample. The tube was heated in a resistance-wound tube furnace (B). A thermocouple directly in the sample measured the sample temperature independently of the furnace temperature.

The sample heating tube was connected to the GC through a 3.17-mm (0.125-in.) diameter heated stainless steel line (D). A heated glass fiber filter (E) in the line removed particulates. The eight-port gas sampling valve (F) was in a heated compartment on top of the GC. Each time the sample valve was

actuated, a 1-ml gas sample was injected into the GC. This sample valve resulted in much less variability than the hypodermic syringes used previously.

A 3.0-g sinter mix sample size was chosen because it allowed all of the off-gas to go through the sample line and valve without overloading the flame ionization detector in the GC. The gas flow rate was standardized at 100 ml/min.

To perform total organic analysis, a short (25.4 cm or 10 in. long) column of SP 2100 on 80/100 Supelcoport was used at a constant oven temperature of 250°C. This caused all of the organics to be eluted to the flame ionization detector (FID) in a single peak. The FID responded specifically to organic carbon. Tests have verified that other carbon (such as CO₂) does not interfere. Because only one peak needs to be observed, sample repetition time could be as short as 15 sec.

For full chromatographic separation of the organics, a 1.83 m (6 ft) long column of SP 2100 on 80/100 Supelcoport was used. The column oven temperature was programmed, starting at 50°C and heating at 10°C per minute to a final temperature of 250°C. This produced a separation of the or-

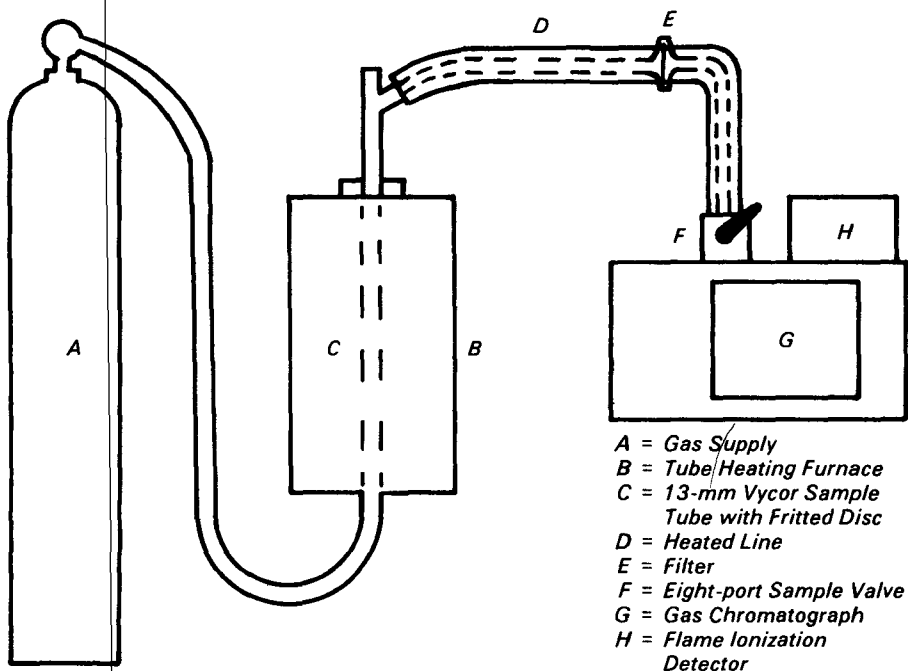


Figure 1. Sinter mix component apparatus.

ganics from C₁ to C₂₄, but it took more than 1 hour from sample to sample, including the oven cooling time.

Results and Conclusions

Major conclusions from these experiments include:

1. Mill scale and blast furnace flue dust are the major sources of organic emissions from sinter beds.
2. The range of temperatures over which substantial emissions occur varies with the producer and the components used in the mix. It may extend from 100° to nearly 800°C.
3. Higher oxygen potentials result in lower organic emission rates. Combustion of some of the hydrocarbons occurs, even though the temperatures are too low for ignition of the fixed carbon.
4. The full chromatographic analyses reveal that the emissions are predominantly of low molecular weight, indicating that thermal decomposition is occurring. This effect becomes more pronounced at higher temperatures. The percentage reduction of emissions in air is much greater in the complete sinter mix than in the individual components. The greater reductions achieved on the complete mix probably indicate that the oxidation of organics at these temperatures requires a surface, and that the iron oxides and other materials, which are more prevalent in the complete mix, provide such a surface.
5. Thermal pretreatment of the offending components could effectively remove the hydrocarbons while leaving the fixed carbon.
6. The analytical procedures developed for this project could be applied to monitoring organic emissions on industrial sinter lines.

*Robert A. Stoehr is with the University of Pittsburgh, Pittsburgh, PA 15261.
Robert C. McCrillis is the EPA Project Officer (see below).*

The complete report, entitled "Organic Emissions from Iron Ore Sintering Plants: Determination of Causes and Methods of Abatement," (Order No. PB 83-116 897; Cost: \$8.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
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81

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