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Project Summary

Hot Metal Desulfurization, BOF Charging, and Oxygen Blowing: Level 1 Environmental Assessment

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An EPA/IERL-RTP Level 1 environmental assessment of fumes generated at one plant during external hot metal desulfurizaton (HMDS), hot metal charging to the basic oxygen furnace (BOF), and during oxygen blowing of the BOF was performed. The purpose of the work was to develop preliminary information on the organic and inorganic matter generated in these processes.

Fumes generated (before emission control) during HMDS contain about 0.64 kg of particulate and 1 x 10⁻³ kg of organic/Mg of metal desulfurized (1.27 and 2 x 10⁻³ lb/ton, respectively). Although a small amount of possibly carcinogenic polynuclear aromatic hydrocarbons (PNA) were detected, none of the organic categories was found in sufficiently high concentration to be of environmental concern. Sufficiently high concentrations of some metals (e.g., lead, mercury, antimony, and arsenic) were found to require highly efficient dust capture and environmentally sound disposal.

Fumes generated (before control) during BOF hot metal charging contain about 5.3×10^{-2} kg of particulate and 5.8×10^{-4} kg of organic/Mg (of hot metal charged (10.6 $\times 10^{-2}$ and 11.6 $\times 10^{-4}$ lb/ton, respectively). No PNA was detected and none of the organic category concentrations is high enough for environmental con-

cern. Sufficiently high concentrations of some metals (e.g., arsenic, lead, mercury, and cadmium) were found to require good dust capture and disposal. Dust from the BOF baghouse, which collects fumes from hot metal transfer and charging, scrap charging, tapping, and slagging, also contained about 100 mg PNA/kg (0.2 lb/ton) of dust. The source of the PNA was not determined.

About 11 kg of particulate and 0.004 kg of organic/Mg of steel (22 and 0.008 lb/ton, respectively) processed in the BOF is captured by the primary emissions control scrubber during the oxygen blow period. Although no PNA was found in the scrubber water, a small amount (<1 mg/kg solids) was found in the solids removed from the primary clarifier. None of the organic concentrations is high enough for environmental concern. The concentrations of lead, selenium, manganese, copper, and zinc in the clarified recycle water would be of concern if discharged to surface waters.

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

This report describes the results of an EPA/IERL-RTP Level 1¹ assessment of fumes generated at one plant (Kaiser Steel Company, Fontana, CA) in three phases of the manufacture of steel. The Level 1 approach, which measures particulates, inorganics, and organics, is a unified approach designed to indicate whether or not significant amounts of hazardous materials may be generated, and possibly emitted, by a process. The data obtained are useful in assessing potential environmental problems and allow priorities for future research efforts to be established.

The purpose of this study is to determine if the processes involved, rather than the plant as a whole, are potential generators of hazardous materials. Therefore, this work concentrates primarily on characterization of the fumes generated by the processes rather than on measuring discharges to the environment As such, the results can be extrapolated, with appropriate caution, to similar processes at other plants.

The processes included in this study are external desulfurization of molten metal produced by the blast furnace, charging of hot metal into the basic oxygen furnace (BOF), and oxygen blowing of the BOF.

Summary

Sampling and analysis of fumes generated during external desulfurization of blast-furnace-produced hot metal, during hot metal addition to the basic oxygen furnace (BOF), and during oxygen blowing of the BOF at the plant were conducted. EPA/ IERL-RTP Level 1 protocols¹ were used. Statements regarding the degree of environmental concern are based on comparison of the data obtained with published MEGs data.²

Hot Metal Desulfurization

Molten metal produced by the blast furnace is cast into torpedo rail-cars. If the metal sulfur content exceeds desirable levels for specific further processing, the sulfur is removed from the metal, while still in the torpedo car, at the hot metal desulfurization station (HMDS). To accomplish this, appropriate amounts of calcium carbide (CaC₂) and calcium carbonate (CaCO₃) are blown into the metal (with nitrogen gas) through a lance submerged in the metal. Furnes generated in the process are collected by side-draft hoods and collected in a baghouse. One to three cars can be

desulfurized simultaneously. All sidedraft hoods operate during desulfurization regardless of the number of cars being processed.

The Source Assessment Sampling System (SASS) was used to collect samples during four periods of desulfurization. The sample was taken in the duct before the fume entered the baghouse and, thus, represents the amount of fumes generated by the process and not the amount emitted to the environment. A sample of the dust collected by the baghouse was also obtained and analyzed.

Table 1 is a summary of the particulate and total organic matter results.

BOF Hot Metal Charging

After scrap metal is charged into the BOF vessel, molten iron is added. The fumes generated during this addition are collected by two side-draft hoods and captured in a baghouse. The baghouse also captures fumes generated

during hot metal transfer, reladling, scrap charging, tapping, and slagging.

Samples were taken from one of the charging fume control dusts with the SASS train. Twenty-four periods of hot metal charging were sampled to obtain a reasonable amount of sample. Since the SASS train was not "cleaned up" (samples recovered) between runs, data for individual charges were not obtained. Also obtained and analyzed was a sample of the dust collected by the baghouse. Results from this sample cannot be compared to the SASS train samples since fumes from other sources enter the baghouse.

Given in Table 2 are the results obtained for particulates and total organics.

BOF Oxygen Blowing

After hot metal is charged, oxygen is blown into the vessel (fluxes are also added) to reduce the carbon content and produce steel. At Kaiser, a suppressed combustion system is used and results

Table 1. HMDS Total Particulate and Organic Matter Summary

Sample Type	Concentration in Gas mg/Nm³	Generated, kg/Mg Steel Desulfurized	
A. Particulate			
Probe, cyclone washes	1 <i>75</i>	0.018	
>10 μ cyclone dust	3123	0.318	
>3 μ cyclone dust	1 <i>754</i>	0.179	
>1 μ cyclone dust	900	0.092	
<1 μ dust (filter)	298	0.030	
TOTAL:	6250	0.637	
B. Organic	·····		
All particulates	<i>3.8</i>	3.87 x 10 ^{−4}	
Organic module	<i>6.1</i>	6.21 x 10 ⁻⁴	
TOTAL:	6.1 9.9	1.01 x 10 ⁻³	

Table 2. BOF Hot Metal Charging Particulate and Organic Summary

Sample Type		mg/Nm ³	kg/Mg Hot Metal Added	
A. F	Particulate			
F	Probe, cyclone washes	98.6	6.65 x 10 ⁻³	
>	>10 μ cyclone dust	274.0	1.85 x 10 ^{−2}	
>	>3 μ cyclone dust	<i>205.8</i>	1.40×10^{-2}	
	>1 μ cyclone dust	<i>123.9</i>	8.42×10^{-3}	
<	<1 μ dust (filter)	85 .1	5.77 x 10 ⁻³	
	TOTAL:	787.4	5.33 x 10 ⁻²	
В. С	Drganic	•••••••••••••••••••••••••••••••••••••••		
1	\// particulates	0.7	4.7 x 10 ^{−5}	
C	Organic module	_7.9_	5.4 x 10 ⁻⁴	
	TOTAL:	8.6	5.8 x 10 ⁻⁴	

Componentian in Con-

in gas produced during oxygen blowing with a high (>20 percent) carbon monoxide content. Direct sampling of the gas was not done. The gas produced is cleaned in a scrubber. Samples of the water going to and coming from the scrubber and solids removed from the water treatment clarifiers were obtained and analyzed. The results are given in Table 3.

Conclusions

- Fumes generated (before emission control) during external hot metal desulfurization (HMDS) contain about 0.64 kg of particulate and 1 x 10⁻³ kg of organic/Mg (1.27 and 2 x 10⁻³ lb/ton, respectively) of metal desulfurized.
- Organics in the HMDS fumes are predominately aliphatic hydrocarbons, ethers, ketones, and esters. A small amount of polynuclear aromatic hydrocarbons (possibly including some carcinogens) was detected. None of the organic category concentrations are high enough to be of environmental concern.
- Significantly high concentrations of lead, mercury, barium, antimony, strontium, arsenic, copper, manganese, and chromium were found in the HMDS fumes. It is important that fume collection and baghouse dust collection efficiency be high.
- Dust captured by the HMDS baghouse is sufficiently high in content of strontium, chromium, and arsenic to be of concern for landfill disposal. (The dust is recycled at the plant tested.)
- Only about 10 percent of the organic matter generated by HMDS is capture by the baghouse.
- Fumes generated (before emission control) during hot metal charging to the basic oxygen furnace (BOF) vessel contain about 5.3 x 10⁻² kg of particulate and 5.8 x 10⁻⁴ kg of organic/Mg (10.6 x 10⁻² and 11.6 x 10⁻⁴ lb/ton, respecively) of hot metal charged.

- Organics in the BOF hot metal charging fumes are predominately esters, ketones, and ethers. The concentrations found at this plant are not high enough for environmental concern.
- Significantly high concentrations of strontium, selenium, arsenic, copper, chromium, lead, mercury, barium, antimony, and cadmium were found in the BOF hot metal charging fumes. It is important that fume collection and capture efficiency be high.
- Dust captured by the BOF secondary emissions control baghouse is sufficiently high in content of the metals cited in 8 above to be of concern for landfill disposal. (The dust is recycled at the plant tested.)
- 10. The organic content of the BOF baghouse dust was about 540 mg/kg (1.1 lb/ton) of dust. As much as 20 percent of the organic could be polynuclear aromatic hydrocarbons, and could include some known carcinogens. This suggests possible environmental problems with the disposal of the dust and indicates that the baghouse outlet should be tested to determine PNA emissions.
- About 11 kg of particulate and 0.004 kg of organic/Mg (22 and 0.008 lb/ton, respectively) of steel processed in the BOF is captured by the primary emissions control scrubber during the oxygen blowing period.
- 12. Organics in the BOF scrubber water were mostly silicones, ethers, alcohols, ketones, and similar compounds. No PNA was found in the scrubber water; however, a small amount (<1 mg/kg solids) of PNA was found in solids removed from the primary clarifier. None of the organic categories, in either the clarified recycle water or scrubber discharge water, was in sufficient concentration to be of environmental concern.</p>

Table 3. BOF Oxygen Blowing Water Treatment Samples

Sample Type	In Sample, kg/min		kg/Mg Steel Processed	
	Solids	Organic	Solids	Organic
Scrubber discharge water	137	0.36		
Recycle water	1.5	0. 32		
Net Captured			11	0.004
Primary clarifier solids = Abou Secondary clarifier solids = Al				

13 The concentrations of lead, selenium, manganese, copper, and zinc in the clarified water would be of concern if discharged to surface waters. (This water is totally recycled at the plant tested.)

Recommendations

Although organic matter is generated during hot metal desulfurization and the data indicate a substantial fraction (possibly >90 percent) of the organic is not captured by the baghouse, the low concentrations found indicate that no additional work in this area is needed. Significantly high concentrations of some metals (including lead, mercury, antimony, and arsenic) were found in the fumes generated and dust captured. Additional testing (e.g., leaching) may be needed to assess the degree of hazard if the dust is landfilled, rather than recycled as for the plant tested.

The data suggest that additional work may be needed to assess BOF secondary fume generating processes (hot metal transfer, scrap charge, tapping, etc.) and possibly emissions from this source. About 100 mg PNA/kg secondary emission control baghouse dust was found. but PNAs were not detected in fumes from hot metal charging. Testing should include further analysis of the dust to determine if it constitutes a hazardous waste, testing of each process step to determine which is generating the PNA. and testing of the baghouse outlet to determine if unacceptable amounts of PNA are being released to the environment. Significant amounts of some metals (e.g., arsenic, chromium, lead, antimony, and cadmium) were found in both the hot metal charging fumes and in the secondary emissions control baghouse dust.

The data suggest that little organic matter is generated during BOF oxygen blowing. No additional testing in this area is recommended. The clarified scrubber water (recycled at the plant tested) contains sufficiently high concentrations of lead, selenium, manganese, copper, and zinc to present problems if discharged to surface waters. More accurate quantitation of the concentrations and masses generated may be needed for plants where the water is discharged rather than recycled.

References

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R. C. McCrillis is the EPA Project Officer (see below).

The complete report, entitled "Hot Metal Desulfurization, BOF Charging, and Oxygen Blowing. Level | Environmental Assessment," (Order No. PB 81-179 251; Cost: \$12 50, subject to change) will be available only from:

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