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Project Summary

Assessment of Atmospheric Emissions from Quenching of Blast Furnace Slag with Blast Furnace Blowdown Water

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Use of blast furnace blowdown water to quench hot blast furnace slag is a possible alternative to the treatment and disposal of this wastewater. Because this alternative is not without possible detrimental effects on air quality, however, an environmental assessment program was undertaken to evaluate the air emissions arising from quenching blast furnace slag with blowdown water from a blast furnace scrubber wastewater recirculating system.

Fifteen test runs were conducted at two different slag temperatures, 1100 and 1500°F (593 and 816°C). Results of this laboratory-scale assessment of simulated blast furnace slag quenching with mill service (baseline) water versus blast furnace blowdown water indicated that particulate emissions increase at a more pronounced rate with high slag temperatures when blowdown water is used, presumably because of its higher total dissolved solids content. The quenched slag was not considered hazardous, based on the extractive procedure (EP) toxicity tests. Although minor quantities of organic pollutants evolve during quenching, the data showed no relationship between these pollutants and slag temperatures, slag characteristics, or water quality. Also, no correlation was found between quench water quality or slag temperature and emissions of sulfur dioxide, ammonia, and fluorides.

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

Blast furnace blowdown water can be disposed of in several ways. One option is to use the water for slag quenching. Evaporation of blast furnace blowdown water in slag quenching can eliminate the discharge of this contaminated liquid stream. Effluent limitation guidelines and standards proposed by the U.S. Environmental Protection Agency designate this disposal method as Alternative I of the Best Available Technology for handling blast furnace wastewater. Because this solution is not without possible detrimental effects on air quality, however, several approaches were considered for measuring air emissions from slag quenching during Phase 1. of this two-phase study. The approach finally decided upon (because it did not require the active cooperation and participation of a steel plant) was to use a specially designed container partially filled with blast furnace slag and heated in a custom-designed propane-fired furnace. After the desired bulk slag temperature was achieved, the test water was continuously sprayed onto and evaporated from the slag surface while the slag temperature was maintained by the furnace. Resulting emissions were captured for analysis.

This laboratory method had the advantage of allowing work to be performed under controlled conditions, which permitted accurate measurements to be made of the slag, the water, and the emissions. It also allowed a comparison of results between the use of mill service water and blast furnace blowdown water for quenching. The disadvantages were that it was not possible to collect emissions from the quenching of fresh molten slag, no runoff water could be generated because of the inherent design of this approach, and water evaporated in a semisealed container that probably excluded potential reactions with air.

About 25 lb (11.3 kg) of slag was poured into containers at a blast furnace and transported to the experimental furnace. Blowdown water was obtained from another blast furnace (with a scrubber water system with a high recycle rate) and transported to the laboratory in Teflon-lined drums. Mill service water was used as a baseline for comparison. Fifteen test runs were conducted at two different slag temperatures.

Equipment Design

Figure 1 shows the general arrangement of the experimental setup. The slag pots were designed to withstand the severe thermal stress of being continuously heated for 4 to 6 hours while the slag was simultaneously quenched inside the pot. They also had to withstand the high temperatures of the molten slag.

Test Design

The main objectives of the test were to correlate air emissions and slag characteristics as a function of water quality and slag temperature. For comparison, two types of water were used: (1) typical mill service water used for slag quenching, and 2) blast furnace blowdown water from a treatment system run at a high recycle rate that meets Best Available Technology (BAT) limitations with respect to percentage recycle and blowdown rate per ton of hot metal. The water was analyzed for dissolved solids, priority pollutants, trace metals, and organics.

Air Sampling Approach

The steam and air emissions generated from slag quenching with the two different types of water were sampled and analyzed for various pollutant species. The results of the mill service water tests served as a baseline against which to evaluate emissions from the use of the contaminated blowdown water.

For most of the test runs, 15 liters of quench water was added at a relatively continuous rate throughout the test period.

Testing for particulate, sulfur dioxide, metals, and organics was conducted with

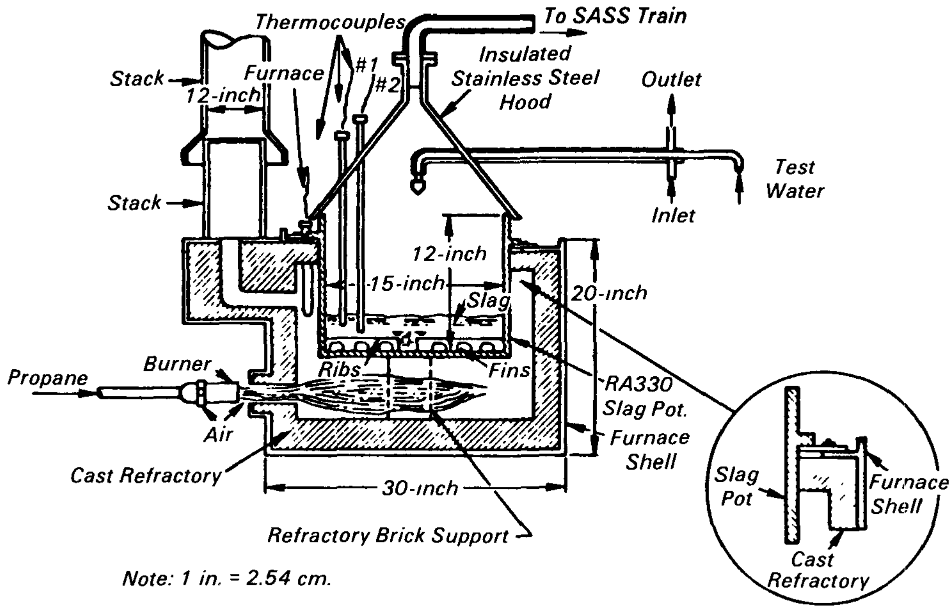

Figure 1. *General arrangement of the experimental setup (not to scale).*

a Source Assessment Sampling System (SASS) Train. Testing for hydrogen sulfide, ammonia, fluoride, and cyanide during a slag heat was conducted with separate trains.

Test Results

The evaluation of the test data in terms of water quality, slag temperature during quenching, and slag characteristics is presented under the following subcategories: particulate emissions, hydrogen sulfide, sulfur dioxide, hydrogen cyanide, hydrocarbons C_1 to C_7 and C_7 to C_{16}, organic emissions, metals, and toxicity of the quenched slag. All emissions except permanent gases are expressed in terms of milligrams or micrograms per liter of water evaporated on the slag surface during quenching. In all cases, the water evaporated is the same as the water applied.

Particulate Emissions

The level of particulate emissions was related to two conditions: the total dissolved solids (TDS) content of the quench water (450 mg/liter for the mill service water versus 2491 mg/liter for the blast furnace blowdown water) and the temperature of the slag. Emissions were:

Type of water	TDS content, mg/liter	Avg. slag temp., °F(°C)	Particulates, mg/liter of H_2O evap.
Mill service	450	1125 (607)	34.7
Mill service	450	1523 (828)	51.5
Blast furnace blowdown	2491	1116 (602)	156.8
Blast furnace blowdown	2491	1633 (889)	395.2

Considerably less particulate emissions were generated during blast furnace slag quenching with blast furnace blowdown water than were generated during coke quenching with semidirty water. No firm conclusions can be drawn, however, until data on slag quenching emissions from actual production facilities are available.

Hydrogen Sulfide, Sulfur Dioxide, Hydrogen Cyanide, Ammonia, and Fluorides

Results of the samples collected are:

Hydrogen Sulfide (H_2S)

Type of water	Slag temperature, °F (°C)	Slag sulfur content, %	Slag basicity	H_2S, mg/liter
Mill service	1142 (617)	1.29	1.130	23.2
Mill service	1428 (776)	1.01	0.880	Not detected
BF blowdown	1117 (603)	1.20	1.102	5.9
BF blowdown	1411 (766)	1.21	1.078	0.1

Several studies have been conducted of H_2S emissions during BF slag quenching. The exact mechanism of H_2S emissions is not well understood, and no specific attempt is made here to project the H_2S data generated during these tests.

Sulfur Dioxide (SO_2)

Type of water	Slag temperature, °F (°C)	Slag sulfur content, %	SO_2 mg/liter
Mill service	1120 (604)	1.30	165
Mill service	1523 (828)	1.01	360
BF blowdown	1116 (602)	1.25	350
BF blowdown	1633 (889)	1.22	164

The SO_2 content does not show any relationship to water quality, slag sulfur content, or quench temperature.

Hydrogen Cyanide (HCN)

Type of water	Slag temperature, °F (°C)	Total cyanides in water mg/liter	HCN, mg/liter
Mill service	816 (436)	0.03	<0.0057
Mill service	1443 (784)	0.03	<0.012
BF blowdown	1059 (571)	0.12	0.0027
BF blowdown	1476 (802)	0.12	0.0008

The HCN data show a possible breakdown of cyanide both at low- and high-temperature slag quench.

Ammonia

Type of water	Slag temperature, °F (°C)	Ammonia (N) in water, mg/liter	Ammonia, mg/liter
Mill service	1040 (560)	<0.2	1.4
Mill service	1443 (784)	<0.2	3.5
BF blowdown	1099 (593)	33.3	33.6
BF blowdown	1472 (800)	33.3	10.1

When blast furnace blowdown water is used, the ammonia appears to break down at higher quench temperatures. Also, the ammonia emissions are higher if the quench water contains higher ammonia concentration.

Fluorides

Type of water	Slag temperature, °F (°C)	Fluorides in water, mg/liter	Fluorides, mg/liter
Mill service	816 (436)	1.84	35.3
Mill service	1443 (784)	1.84	238
BF blowdown	1059 (571)	15.1	32.4
BF blowdown	1476 (802)	15.1	157

The generation of fluorides is not dependent on the concentration in the quench water or the quench temperature.

Hydrocarbons: C_1 to C_7 and C_7 to C_{16}

Grab samples were taken from each test run and analyzed for hydrocarbons C_1 through C_7. In a few cases, methane was detected in the range of 1.2 to 23.7 ppm; in the rest, it was below the detection limit of 1 ppm. The presence of C_2 through C_7 was generally undetectable or at very minor levels.

Organics (C_7 through C_{16}) per liter of water applied did not show any relationship to either quench water type or slag temperature.

Metals

The data for 40 elements were analyzed by Inductively Coupled Argon Plasma (ICAP) Optical Emission Spectrometry for different test conditions. The highest emission rates were found for aluminum, calcium, potassium, sodium, silicon, magnesium, uranium, and boron. In general, the tendency was toward higher emissions with higher slag temperatures, which is in line with particulate emissions. Metals such as arsenic, selenium, and mercury (also determined separately) did not show any relationship to slag temperature or water type used during quenching.

Organics

Only one priority pollutant (3.2 mg/liter of phenol in the blast furnace blowdown water) was detected in the quench water samples. Selected runs, however, showed the presence of the following in the air emissions:

2-Chlorophenol	4 out of 5 samples
2,4-Dimethylphenol	2 out of 5 samples
Phenol	5 out of 5 samples
Fluoranthene	3 out of 5 samples
Naphthalene	4 out of 5 samples
Bis(2-ethylhexyl) phthalate	5 out of 5 samples
Butybenzyl phthalate	5 out of 5 samples
Di-n-butylphthalate	5 out of 5 samples
Diethyl phthalate	3 out of 5 samples
Acenaphthylene	3 out of 5 samples
Anthracene and/or phenanthrene	4 out of 5 samples
Fluorene	3 out of 5 samples
Pyrene	4 out of 5 samples

The levels for phenol, 2-chlorophenol, 2,4-dimethylphenol, and phthalates were relatively high compared with other organic substances, and they bore no relationship to quench water quality or slag temperature. The following are some of the possible explanations for the presence of organics in the air samples. The formation of organics may result from slag/water reactions at high temperature in an oxygen-deficient atmosphere. It is not uncommon for some unburnt coke to be present in slag, which might contribute the required carbon. Also, minute quantities of organics in the quench water below detection limits might have shown up in the air samples. The presence of phthalates is presumably due to binders in the sampling train filter.

Slag Toxicity Data

Eight metals tested for EP toxicity under each quenching condition were well below allowable concentrations. The reactivity tests for cyanide showed negative results; however, three of the four sulfide reactivity tests showed positive results.

Conclusions

The laboratory-scale assessment of simulated blast furnace slag quenching (using mill service water versus blast furnace blowdown water) produced the following major findings and conclusions:

1) The level of particulate emissions is higher when the blowdown water (with a high total dissolved solids content) is used for quenching, and the level of these emissions increases greatly when the temperature of the slag quenched is high. The proportional increase at high temperatures is not nearly as great when mill service water is used.
2) Particulate emissions from slag quenching with blast furnace blowdown water are much lower than those produced by coke quenching with semidirty water with a similar total dissolved solids content.
3) Based on this laboratory-scale evaluation, the particulate emissions generated by high-temperature slag quenching with blast furnace blowdown water are significantly lower than uncontrolled blast furnace cast house emissions.
4) Emissions of metals increase with high-temperature slag quenching.
5) There is no EP toxicity connected with slag quenching, with either clean or blast furnace blowdown water.
6) No specific relationship was found between organic pollutants and the use of blowdown water or slag temperature during quenching.
7) No correlation was found between quench water quality or slag temperature and emissions of SO_2, ammonia, and fluoride. Cyanides appeared to break down at both low- and high-temperature slag quench.

Recommendations

1. Similar tests, carried out with spiked quench water samples, would help to better understand the behavior of toxic organic pollutants during quenching.
2. Laboratory scale tests, similar to those conducted during this project, would help determine the feasibility of using coke plant wastewater as a quenching medium for BF slag quenching.
3. Tests conducted at a plant site that practices hard slag quenching with mill water, blast furnace blowdown water, and (if possible) coke plant wastewater would help verify the test data and findings of this project.

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The complete report, entitled "Assessment of Atmospheric Emissions from Quenching of Blast Furnace Slag with Blast Furnace Blowdown Water," (Order No. PB 84-172 493; Cost: $11.50, subject to change) will be available only from:
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