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Project Summary

Cost Comparisons of Selected Technologies for the Control of Sulfur Dioxide from Copper Smelters

The U.S. nonferrous metals production industry is a significant contributor of sulfur dioxide, trace metal, and particulate air emissions. Most of the domestic copper smelting capacity is based on obsolescent technology that is both capital- and energy-intensive and hampered by considerable emission control problems. Because systems used to control sulfur dioxide emissions also must remove particulate contaminants, effective control of total particulate and trace element emissions is accomplished as a "byproduct" of sulfur dioxide control. When it can be operated under autothermal conditions, the sulfuric acid plant is recognized as the technology of choice for controlling sulfur dioxide emissions from smelters.

Unfortunately, much of the problem of sulfur dioxide control in the nonferrous industry is associated with the weak sulfur dioxide off-gas streams. Because weak sulfur dioxide streams do not permit autothermal acid plant operation, they cannot be economically controlled by acid plant technology. In copper smelting, the major sources of weak sulfur dioxide off-gases are the reverberatory furnace and multihearth roaster, followed by fugitive emissions that emanate from the converter operation, matte tapping, slag tapping, and ladle transfer. The status of development and use of a number of technologies for wet scrubbing and for process changes based on oxygen smelting technologies were evaluated to determine which could be considered promising for near-term application to sulfur dioxide control at domestic smelters. Cost models were developed for those processes believed to be sufficiently promising for such application.

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

Primary nonferrous smelters accounted for about 6 percent of the total sulfur dioxide emitted in the United States in 1980. These considered of 15 copper smelters (largely in the western section of the country), 5 lead smelters (not including Bunker Hill, which is now closed), and 7 zinc smelters. Several of the copper smelters currently use production curtailment programs to limit their emissions to comply with ambient air sulfur dioxide standards.

The total allowable sulfur input for the 13 western primary copper smelters (based on State Implementation Plans and allowable sulfur dioxide emissions) is 6572 Mg (7244 tons) per day. The sulfur dioxide emissions at this sulfur input would total about 375 Mg (414 tons) per hour, which is equivalent to 87.5 1000-MW power plants emitting at a level of 516 ng/J (1.2 lb of sulfur dioxide per million Btu). These relatively high emission levels may contribute to problems of sulfate-related visibility reduction, high concentrations of sulfur dioxide in the ambient air, and acid rain generation in the West.

A typical conventional reverberatory smelting furnace can vary in size from 30.5 to 40.2 meters long by 7.8 to 12.2 meters wide (approximately 100 to 132 feet by 25.5 to 40 feet). Typical capacity is about 944 Mg (1040 tons) of concentrate per day. The reverberatory furnace can receive its copper ore concentrate either as a "green" or wet feed or as a calcine. The wet-feed process is one of the most endothermic processes for production of copper. The use of calcined feed (as opposed to wet feed) reduces the energy consumption, gas flow, and amount of sulfur dioxide generated in the reverberatory furnace, because the moisture and a portion of the sulfur have been removed in the roasting step.

Currently, continuous controls are not applied to reverberatory furnaces for reduction of sulfur dioxide emissions. All of the sulfur removed from the concentrate in the smelting furnace is discharged to the atmosphere as sulfur dioxide. As much as 38 percent of the sulfur contained in the concentrate may be converted to sulfur dioxide in the conventional green charge reverberatory furnace and emitted in an off-gas stream containing approximately 1 to 1.5 percent sulfur dioxide by volume. Fluid-bed roasting of the concentrate before smelting in the reverberatory smelting furnace can reduce the sulfur emitted to about 10 to 15 percent of the total concentrate sulfur.

The absence of continuous emission control results from a combination of factors, the most important of which are 1) the cost of installing and operating emission control systems for reverberatory furnace sulfur dioxide emissions, 2) the lack of profitable acid byproduct markets, 3) the cyclical nature of copper market prices, and 4) strong international competition.

The contact sulfuric acid process is the most widely used for removing sulfur dioxide from primary copper smelter effluent gases and is considered to be a well-demonstrated technology of reasonable cost for strong sulfur dioxide streams. Currently, 12 of the 15 active domestic primary copper smelters produce sulfuric acid from strong sulfur dioxide off-gases. Acid plants are not considered economic for the control of sulfur dioxide emissions from reverberatory furnaces, however, because of the low (weak) sulfur dioxide content of the off-gas.

Although sulfuric acid plants can be designed to process feed streams that contain a low percentage of sulfur dioxide, economic considerations usually restrict application to gas streams that have a sulfur dioxide content of at least 3.5 percent so that reaction temperatures can be maintained by the heat released in the sulfur dioxide oxidation reaction. Metallurgical single-stage and dual-stage absorption sulfuric acid plants constructed in the past were commonly designed to operate autothermally on feed streams containing 4.0 and 4.5 percent sulfur dioxide, respectively. Nonautothermal operation requires supplemental heating by natural gas and is therefore more costly.

For these reasons, primary copper smelters using reverberatory furnaces have not attained the emission limitations specified by the State Implementation Plans as required by the Clean Air Act of 1967. Recognizing the difficulties of the smelting industry, Congress included a provision in the Clean Air Act Amendments of 1977 for the issuance of a "primary nonferrous smelter order" (N.S.O.) to any existing smelter applying and qualifying for such an order. The N.S.O., which constitutes a delayed compliance order, is unique to primary nonferrous smelters and is provided "in recognition of the economic circumstances of the industry." The law permits any smelter that operates processes from which sulfur dioxide emissions cannot be controlled to meet the applicable State Implementation Plan requirements by the application of a continuous emission control technology to apply for and operate under the N.S.O. until such technology is "adequately demonstrated to be reasonably available (as determined by the Administrator, taking into account the cost of compliance, nonair quality health and environmental impact, and energy consideration)." This program places the responsibility for developing the necessary technology upon the smelting industry and requires compliance by January 1988.

Control Approaches Studied

This study was undertaken to develop the tools needed by the U.S. Environmental Protection Agency to conduct an independent evaluation of the "reasonable availability" of technologies considered to have reached, or to be approaching, an "adequately demonstrated" status. The two primary approaches available to smelters for the control of sulfur dioxide emissions are 1) process modifications that produce a strong higher-concentration sulfur dioxide off-gas that can be controlled by conventional acid plant technology, or 2) removal of the sulfur dioxide from weak off-gas by wet scrubbing.

The INCO flash furnace represents a process replacement of the reverberatory furnace with an alternative smelting technology that produces a strong off-gas. The oxygen-fuel and oxygen-sprinkle processes represent modifications to reverberatory furnaces that use oxygen enhancement to produce a stronger off-gas.

Scrubbing processes include the lime/limestone process, which is a nonregenerative flue gas scrubbing system that disposes of the sulfur fixed in an absorbent, and the magnesium oxide and citrate processes, which involve regenerative flue gas scrubbing that converts the sulfur dioxide to a strong stream in the regeneration process for subsequent recovery.

Several other processes, such as the Noranda, Mitusbishi, and Outokumpu Oy processes, also warrant consideration as possible ways of achieving reduced sulfur dioxide emissions and profitable, energy-efficient operation.

Process Modifications

Modifying existing furnace operations to increase the sulfur dioxide content of the off-gas can be an effective approach to emission control when coupled with sulfur dioxide recovery or a gas scrubbing system (e.g., when there is no market for acid, scrubbing equipment costs would be less because of the lower-volume gas stream). Alternative pyrometallurgical processes are of interest for the following reasons: they produce a strong sulfur dioxide gas stream that can be sent to a sulfuric acid plant, they reduce energy consumption, they decrease gas-stream volumes, and they subsequently reduce operating costs.

The full report presents descriptions and costs of process modifications that would enable existing copper smelters to increase sulfur dioxide concentration and make recovery more practicable.

Process modification principally entails the introduction of oxygen into the furnace so that oxygen-enriched air or pure oxygen is used in the smelting process. Descriptions of the process modifications and the estimated capital and annual operating costs for installation and operation are presented for plant models based on the INCO oxygen flash furnace smelting process, the oxygen-sprinkle process, and the oxygen-fuel smelting process. The Outokumpu Oy, Noranda, and Mitsubishi continuous processes are also described, but in less detail. Whenever possible, existing equipment was assumed to be modified to minimize costs; however, because the modifications are affected by plant-specific considerations such as equipment arrangement and layout, costs could vary widely. In each case, the acid or oxygen plants were assumed to be new units. Existing converters were utilized, and as the copper percentage of the matte increased, a reduction in blowing costs and labor was assumed. A "greenfield" installation would be more costly than a retrofitted installation, as it would entail additional costs for ore handling, blending, and preparation facilities, as well as converters, buildings, utilities, rail facilities, working capital, and other items. A computer-aided cost estimation model for process modifications developed for this project is described.

Intrinsic benefits of this modification vary with the extent of the replacement of air with oxygen. The use of oxygen can significantly reduce the energy required to produce blister copper. For example, a smelter based on the INCO flash furance, which utilizes pure oxygen, requires only about 70 percent of the energy input of a conventional green charge reverberatory smelter. The use of oxygen in smelting also reduces and/or replaces the fossil-fuel requirements. This, in turn, increases the sulfur dioxide concentration in the off-gas and effects a corresponding decrease in off-gas flow, which reduces the energy and equipment size required to handle this gas. A 30-fold reduction in gas cleaning equipment size (volumetric flow rate) can be realized with pure oxygen smelting; thus, the increased sulfur dioxide concentration lowers the capital cost of control equipment and power requirements of sulfur recovery. For example, a sulfuric acid plant that uses a 4 percent sulfur dioxide stream costs about 1.8 times as much as one handling a 12 percent stream for the same daily acid production. Power required per ton of sulfuric acid by a plant (either single- or double-contact) using the 4 percent stream would be 91.7 percent greater than that required by a plant using 12 percent stream.

Oxygen smelting also increases matte grade, and higher matte grade requires less time for conversion to blister copper. For example, if the time for converting matte to blister copper is "t" for a 35 percent copper matte, the time required for a 42 percent copper matte becomes 0.8t and that for a 50 percent copper matte becomes 0.65t. Obviously, fewer converters are thus required to produce the same tonnage. In addition, a savings would be realized in blowing time and labor, and the smelter capacity would be increased by such a modification.

Flue Gas Scrubbing

For weak gas streams (i.e., those containing less than about 3.5 percent sulfur dioxide), flue gas scrubbing is required to control sulfur dioxide emissions. In such processes, the smelting furnace off-gases, after particulate removal and temperature conditioning, are contacted with an absorbent medium in an absorber tower or a scrubber.

The gas scrubbing processes are categorized as regenerable or nonregenerable. In the regenerable process, the absorbent is regenerated for reuse by stripping (separating) the sulfur dioxide. The absorbent is then recycled to the absorbing stage. Sulfur dioxide, stripped from the liquid, is recovered by further processing to liquid sulfur dioxide or sulfuric acid. In the nonregenerable process, the spent absorbent is converted to a gypsum byproduct or discarded as waste.

Four gas scrubbing systems were evaluated in this study. The lime/limestone (nonregenerable) and the magnesium oxide (regenerable) scrubbing systems have been used on full-scale smelters in Japan. Pilot plants of the citrate process (a regenerable system) have been operated on smelters in Sweden (by Flakt at Boliden) and in the United States (by the Bureau of Mines).

The study evaluation of scrubbing systems is based on a gas stream that has passed through a waste-heat boiler and an electrostatic precipitator for particulate removal. Most smelters include both of these operations. A generalized scrubber system flow diagram shows the gas pretreatment options and the gas/liquid system. If the temperature of the gas stream is below 205°C (400°F), the stream can go directly to the absorber. If further particulate removal is required, the stream can be "treated" in a venturi scrubber, after which the cooled gas goes to the absorber.

The estimated capital and annual operating costs for each scrubbing system addressed in this study were prepared by utilizing a standardized format.[1] The costs reflect a "study estimate" with a reliability of about ±30 percent. A computer-aided cost-estimating technique used to generate these costs is also described.

[1]Uhl, V. W., A Standard Procedure for Cost Analysis of Pollution Control Operations. U.S. Environmental Protection Agency. EPA-600/8-79-018a. June 1979.

Costs for gas scrubbing systems vary widely depending on the gas pretreatment required and the sludge treatment and disposal alternatives selected. Ancillary items such as bypass ducting, a new stack, sludge pond, etc., will also affect the capital cost. The computer-aided cost-estimating system allows the user to select input parameters for a specific case.

Conclusions

A comparison of the incremental costs for control of sulfur dioxide emissions by process change with those for the addition of flue gas scrubbing shows the kind of decisions the industry faces. For a plant producing 90,720 Mg of copper per year, the approaches based on process change (ranging from $67 to 87 million) and regenerable flue gas scrubbing (at about $70 million) are the most capital-intensive, whereas the approaches based on lime or limestone scrubbing ($36 to 52 million) are much less capital-intensive. The capital costs presented for regenerable flue gas scrubbing are based on the citrate system. Although the sulfur dioxide absorption and stripping components of this sytem have been well demonstrated at pilot scale on smelter off-gas, the developer has not yet demonstrated that a full-scale citrate system can be operated economically. Also, the case presented for citrate scrubbing with the stripped sulfur dioxide fixed as liquid sulfur dioxide, which offers very attractive capital and annualized costs, is based on the marketability of the liquid sulfur dioxide produced. Such a market is unlikely for smelters located in the southwestern United States. On the other hand, a greenfield smelter located near a paper producing area probably could tap a sulfur dioxide market of sufficient size.

In contrast, the estimated annualized costs for process change (which range from 28 to 36 cents per kilogram of copper) appear to make this approach more attractive than these approaches based on add-on flue gas scrubbing (which entail costs of 22 to 29 cents for the lime or limestone processes, and 14 to 17 cents for the citrate process). The advantage of the former is that the annual operating costs for a process change include the costs of operating the smelting furnace and production improvements, whereas those for an add-on flue gas scrubbing system represent an incremental cost in addition to those for operating the smelting furnace.

The decision then becomes one of trading off capital costs for operating costs. The trade-off analysis is difficult because of the variable price of copper, the marketability and price of the sulfur byproduct, the life of the smelter, and the cost of capital. It would be more economical to use a throwaway flue gas scrubbing system in cases where the cost of capital was high and the life of the smelter was limited by its present condition, market viability, or the security of the concentrate supply. Where the life of the smelter is judged to be longer, continuous control of sulfur dioxide would be achieved most economically through process change.

The Project Report was authored by personnel of PEI Associates, Inc., Cincinnati, OH 45246; the author of this Project Summary ***John O. Burckle*** *(also the EPA Project Officer, see below) is with the Water Engineering Research Laboratory, Cincinnati, OH 45268.*

The complete report, entitled "Cost Comparisons of Selected Technologies for the Control of Sulfur Dioxide from Copper Smelters," (Order No. PB 85-215 705/AS; Cost: $23.50, subject to change) will be available only from:
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