



Project Summary

Control of Air Pollution Emissions from Molybdenum Roasting

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Molybdenum, a relatively rare element, occurs principally as molybdenite (MoS_2) and wulfenite (PbMoO_4). Molybdenite is the commercial source of molybdenum. In 1979, three primary molybdenum mines accounted for about 68% of the domestic production with the balance obtained as a principal byproduct chiefly from 16 porphyry copper mines. This latter form is presently our sole source of rhenium, which is recovered in the processing of molybdenite.

While a minor metal in terms of commercial volume, molybdenum is widely used in the form of molybdenum oxide as an alloying agent in ferrous metals, its principal application, and is essential for tool steels. Molybdenum compounds are also used in chemicals, catalysts, pigments, lubricants, and electronics. In 1979, the value of U.S. exports of molybdenum ore, concentrates, and products was about three quarter billion dollars.

Molybdenum oxide is derived from a concentrate of molybdenite via a thermal process known as roasting. In practice, the concentrate is processed in a vertical multiple hearth type furnace to produce the oxide. The roasting results in the generation of particulate and weak sulfur dioxide emissions. This program was undertaken to: (1) determine the capabilities of a unique fabric filtration system using Teflon®* coated bags in a hot, corrosive atmosphere for particulate and trace element control and (2) explore and evaluate the

feasibility of a variety of weak SO_2 control systems for application to the molybdenum roaster and potentially to other smelter weak SO_2 off-gases.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in three separate reports (see Project Report ordering information at back.

Introduction

This project was undertaken jointly by Molycorp and the IERL-Ci because of mutual interest in addressing the problems of weak SO_2 stream control. At the time the tests were conducted, Molycorp was concerned with the problem of controlling sulfur dioxide emissions and eliminating a visible plume in order to meet state requirements. The IERL objectives were similar. The first task was to characterize the pollution control capabilities of the Teflon® coated fabric filter for removal of particulate and trace metals in the flue gas prior to atmospheric discharge or treatment in a sulfur dioxide control system. The second task was to determine the technical feasibility of applying a flue gas wet scrubbing system for weak stream (about 1%) sulfur dioxide control. The joint study was subdivided into three tasks: (1) characterization of emissions and particulate control, (2) a study of alternatives for control of weak sulfur dioxide emissions, and (3) a pilot-plant scale test study of one of the approaches identified in the second task. The magnesium oxide system was selected for this study. The results of these tasks achieved our objectives and aided Moly-

*Mention of tradenames or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

corp in developing a plan to modernize their smelter.

At the time these tests were conducted, Molycorp, Inc. operated two multi-level hearth roasters at its facility in Washington, Pennsylvania. The plant processed 10 million pounds of molybdenum per year. In the roasting process, molybdenum disulfide concentrate was oxidized by air to molybdenum trioxide and sulfur dioxide. Particulate control was achieved by a baghouse, followed by a spray cooler and a packed bed scrubber. The scrubber water was recirculated with blow-down. A diagram showing the process flow, flue gas handling and baghouse is given in Figure 1. The baghouse employs Teflon® coated fabric filter bags, a unique application in the nonferrous industry.

Emissions Characterization and Particulate Control

The sampling and analysis effort described in this report was conducted to characterize the particulate emissions from the molybdenum roaster performance of the associated particulate control devices consisting of a high-temperature baghouse and a spray scrubber-packed bed clean-up facility. The characterization was accomplished by chemical analyses of all streams, flow-rate measurements, grain-loading determinations, and particle-size distribution measurements under different operating conditions. Spark Source Mass Spectrometry (SSMS) was used to semiquantitatively analyze the samples. From these results, 15 elements were selected for quantitative determination. The selection was based on concentration level, volatility, and toxicity. The elements investigated more fully were:

Arsenic	Bismuth	Nickel
Lead	Antimony	Copper
Molybdenum	Cadmium	Manganese
Mercury	Silver	Iron
Selenium	Zinc	Rhenium

The quantitative analytical results were combined with the total mass flow in each individual stream to derive an elemental flow rate. These data were used to establish material balances around the roaster and the baghouse.

The major findings were:

- Semiquantitative survey analyses by SSMS for 73 elements indicate that Twin Buttes and Questa concentrates contain low concentrations (ppm range) of most metals. Exceptions are: copper, lead, zinc, iron, and manganese. The Twin Buttes concentrate is high in copper concentrate (24,000 ppm versus 1000 ppm in Questa). The Questa concen-

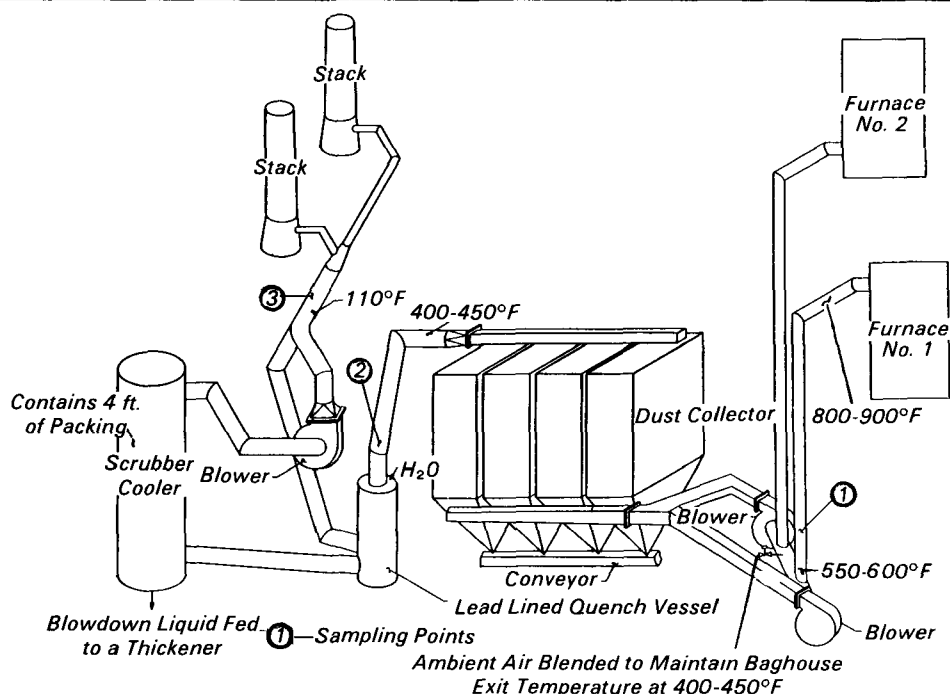


Figure 1. Dust collection system at Molycorp.

- trate shows a high lead concentration (4300 ppm versus 930 ppm in Twin Buttes concentrate).
- Mercury and selenium are volatilized in the roasting process, pass through the baghouse essentially uncontrolled, and are partially removed in the quench scrubber. For mercury, a feed rate of 0.104 gm/hr (2.3×10^{-4} lb/hr) was measured with 0.0014 gm/hr (0.3×10^{-4} lb/hr) reporting to the product; therefore 0.1026 gm/hr was volatilized in the roaster of which 90% was removed in the quench scrubber. For selenium, a feed rate of 68.1 gm/hr (0.15 lb/hr) was measured, with 1.4 gm/hr (0.003 lb/hr) reporting to the product; therefore 66.7 gm/hr was volatilized in the roaster of which 50% was removed in the quench scrubber.
- Pollutant content of the stack gas was, in gm/hr (in lb/hr): molybdenum — 4.5 (0.01), selenium — 3.6 (0.008); lead — 6.8 (0.015); iron — 3.2 (0.007); organics — 6.8 (0.015).
- The baghouse was effective for particulate control. The average inlet loading was 10.3 gm/Nm³ (4.51 grains/DSCF) and 0.1 Mg/hr (223 lbs/hr); the average outlet loading was 0.091 gm/Nm³ (0.040 grains/DSCF) and 1.8 kg/hr (4.04 lbs/hr). This indicates a control efficiency of 99.1% on a concentration basis and

98.2% on a mass basis. One would expect an efficiency of 99% or better for an installation of this type. For zero air leakage (i.e., dilution) the concentration efficiency should equal the mass efficiency. It is not clear if the difference here is real or whether the lower mass efficiency value is attributable to: (1) flow measurement error as the location of the measurement points was less than ideal owing to the limitations imposed by the equipment configuration or (2) interference by acid mist formed by condensation at the outlet test point.

- The source of the plume had been a controversial point. Some observers held that it was caused by the presence of organic material introduced by flotation agents while others felt that the cause was sulfuric acid mist formed in the interaction of the roaster gas with the quench scrubber. It was found that sulfate particles and sulfuric acid mist, not organics, were principally responsible for the visible plume problem. The high oxygen, high SO₂ concentration of the roaster off-gases favors the formation of SO₃ as the flue gas cools. The SO₃ reacts with solids to form sulfates and with water vapor to form sulfuric acid mist. This increases the particulate loading as the gas tem-

perature decreases. Acid dew points were 309°F at the roaster outlet, and 269°F at the baghouse outlet.

Particulate loading determinations showed a concentration at the roaster exit of 10.3 gm/Nm³ (4.51 grains/scf). Analysis of the filter for sulfate indicated a sulfate contribution of 0.4%. An average particulate loading of 0.091 gm/Nm³ (0.040 grains/scf) was measured at the baghouse exit. Sulfate contribution accounted for 17% of the particulate matter. Water droplets and acid mist were present in the quench-scrubber exit gases. Water had to be evaporated in order to determine a particulate loading. The EPA method 5 was used. Contributions of sulfuric acid mist accounted for 35%, 50%, 74% and 91% at sampling temperatures of 380°F, 365°F, 300°F and 250°F, respectively. These results point to sulfuric acid mist as the cause of the plume formation. This mist was completely removed in a bench-scale wet electrostatic precipitator.

Alternatives for Control of Weak Sulfur Dioxide Emissions

Processes in the primary nonferrous metals industry produce off-gases containing significant quantities of SO₂. Typically, these streams are classified as "strong" or "weak" depending on their SO₂ concentration. Strong gas streams have SO₂ concentrations greater than 3.5 to 4.0 volume percent while weak gas streams contain between 0.5 and 3.5 volume percent SO₂.

The technology for sulfur dioxide control in emissions from smelters containing weak concentrations, i.e., from about 0.5 to 3.0 percent SO₂, is a slowly developing area. This survey of alternative control technologies was undertaken to provide information to aid in selection of system for pilot-scale testing. The technical feasibility for a number of scrubbing systems has been established through application and full-scale operation at certain smelters. It should be noted that, with the exception of cold sea water absorption, each full-scale scrubber system is unique in the sense that it has been applied at only one smelter site. Some twelve systems were examined for suitability for application to nonferrous smelters and molybdenum roasting in particular.

- CIBA-GEIGY nitrosyl-sulfuric acid process
- CIBA-GEIGY SO₂ sorption-stream stripping process
- Limestone FGD
- Dual Alkali
- Magnesium Oxide

- Wellman-Lord
- Sulf-X
- Endako
- Chiyoda Thoroughbred (2)
- U.S. Bureau of Mines Citrate
- Sodium Carbonate Throwaway
- Dow Basic aluminum sulfate

The magnesium oxide system was selected for pilot-scale testing because of the state-of-development, available information for test design purposes, compatibility with existing pilot plant equipment, and the need to develop applicability data to support analysis of economic feasibility of this system.

Pilot-Scale Test Results for Magnesium Oxide Scrubbing

The magnesium oxide (MgO) system was selected for pilot-scale testing to generate engineering design data for an MgO system which, in turn, could be used as a basis for exploring economic feasibility. Specifically, the tests were designed to quantify the SO₂ removal which could be attained by the MgO system, and to develop data on the MgO system which could be used to design an absorber for treating similar gas streams in other smelter applications.

A schematic of the pilot unit is shown in Figure 2. As shown, the pilot unit consisted of an absorber, reaction tank, and solids separator. For the purpose of these brief tests, the solids produced were disposed of by ponding rather than being dried and regenerated.

The absorber was a 76 cm (30 inch) diameter tower containing two beds of 2.5 cm (1 inch) Tellerette® packing. The upper bed depth was 76 cm (30 inches) and the lower bed was 51 cm (20 inches) deep. The piping and valve arrangement was designed to distribute slurry through both beds or the lower bed only. This permitted scrubbing tests at packing depths of 51 cm (20 inches) and 127 cm (50 inches). Full cone spray nozzles were used for liquid distribution and were arranged so that the edge of the spray contacted the tower wall at the level of the packing.

Gas flow rates through the absorber ranged from 2800 to 4000 Nm³/hr (1700 to 2600 scfm) while slurry flow rates ranged from 0.4 to 2.4 l/sec (6 to 38 gpm). The SO₂ concentration of the gas was controlled by a damper arrangement on the inlet gas stream so that inlet gas strength and flow rate could be maintained at a constant value through dilution without interfering with plant operations. During most tests, the pH of the absorber feed was maintained between 7.5 and 8.0. Slurry exiting the absorber was gravity fed to a 5680 (1500 gallon) reaction tank. The pH of the slurry leaving the absorber ranged from 4.5 to 6.5, and Mg(OH)₂ was added to the reaction tank to raise the pH back to 7.5-8.0.

The scrubbing slurry contained 4 to 8 weight percent Mg SO₃ · 6H₂O solids. A bleed stream of slurry was removed from the reaction tank and concentrated to approximately 35 weight percent solids in

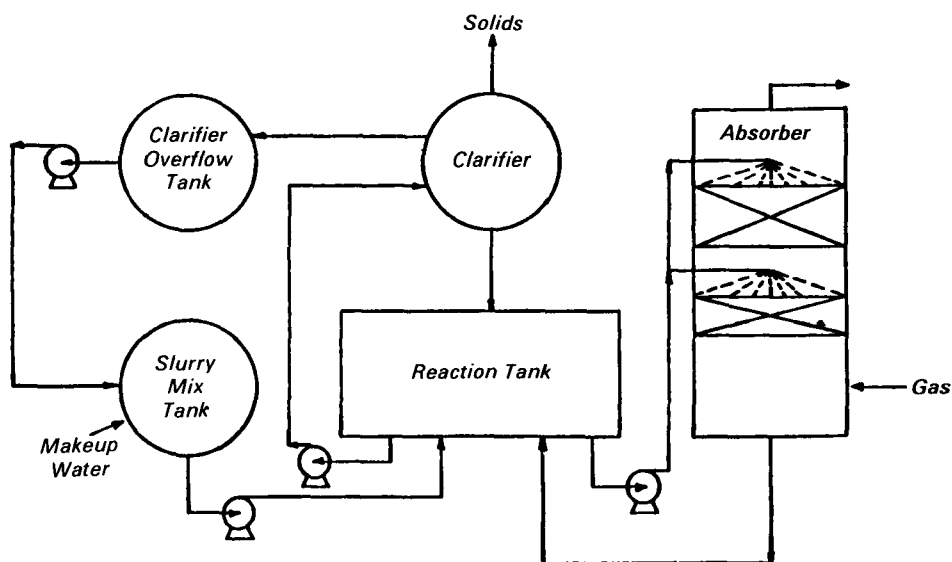


Figure 2. Schematic of the magnesium oxide scrubber.

a clarifier. Overflow from the clarifier was either returned to the reaction tank or used to prepare fresh $Mg(OH)_2$ in the slurry tank.

A well-defined test program was conducted in which the process parameters of interest were varied to observe their effect on SO_2 removal. The data collected during these tests were then correlated in the form of a design equation. As this program was considered preliminary effort, long-term testing to demonstrate reliability and to acquire operability data was considered beyond the scope of this effort and was not attempted.

The statistically designed test plan consisted of a matrix of short-term tests which included all possible combinations of three liquid-to-gas ratios, three gas flow rates, and two packing depths (18 tests). These tests were supplemented with a limited number of tests in which the pH of the scrubbing slurry and the SO_2 concentration of the off-gas were varied. In addition, a longer-term, or steady-state test was scheduled. This test was included to provide data which would be used to complete material balance calculations for the system.

The test results indicate that the MgO scrubbing system is applicable for treating gas streams containing up to about one percent SO_2 . Removal efficiencies of over 90 percent of SO_2 were possible at gas velocities and absorber pressure drops similar to those used in design of utility MgO FGD systems. In the evaluation of the results of the tests conducted at MolyCorp, a correlation was developed which can be used to predict SO_2 removal in the pilot plant for a given set of absorber operating parameters. This correlation was developed based on absorption theory, using the two-film mass transfer model. Regression analysis was used to develop an empirical value for K_gA , resulting in the design equation:

$$R = 1 - \exp[(4.36 \times 10^{-3}) (L/A_c)^{0.899} (pH)^{2.86} (W)^{0.284} (SO_2)^{-0.621} (P) (D)]$$

where

R = fractional efficiency of SO_2 removal

L = absorbent flow rate, liters per second

SO_2 = SO_2 concentration of inlet gas, ppm

W = $MgSO_3$ solids in the absorber feed, % by weight

A_c = absorber cross sectional area, square meters

D = packing depth, centimeters

P = operating pressure, atmospheres

pH = pH of the absorber feed slurry

It is interesting to note that the flue gas flow rate does not appear. This is due to an offsetting effect associated with a

change in gas flow rate into the absorber. By increasing gas rate, more SO_2 enters the absorber and thus tends to lower removal. However, increasing the gas flow rate increases the value of K_gA and thus offsets the effect of additional SO_2 entering the absorber. The reader is cautioned that this is only true because the exponent of (G/A_c) is 1.0 for this test program, and should be re-established for other tests conditions.

The correlation between actual and predicted SO_2 removal efficiency is quite good with a correlation coefficient of 0.98. The absorber design equation can be used to predict the performance of a particular absorber design configuration. However, this equation has been proved valid only for specific conditions and ranges of absorber operating parameters explored in this program. In using the equation, the most obvious restriction is that it is only applicable for use with an MgO scrubbing system processing gas in an absorber packed with 2.5 cm (1 inch) Tellerette® packing. This design equation is not applicable to other absorber configurations (e.g., a spray tower) or other types or sizes of packing material. The other principal restriction is that the scrubber operating parameters selected for an absorber design must be within the range in which the parameters were tested during the program. Specific ranges for these parameters are presented in Table 1. The applicable range for each parameter represents the range over which the parameters were varied during the test program.

Another significant result of the test program was determination of the absorber pressure drop as a function of various absorber operating parameters. Of the parameters which were examined during the test program, only packing depth and gas velocity were found to have a significant impact on the pressure drop in the absorber (Figure 3). Based on theoretical considerations and on measurements made on the pilot absorber, pressure drop was found to be a linear function of packing depth. That is, a doubling in the packing depth results in a doubling of the pressure drop in the absorber.

The relationship between gas velocities and pressure drop is somewhat more

complex. Pressure drop appears to increase exponentially with increasing gas velocity. This is an important consideration in designing an absorber since the gas velocity would be selected based on a trade-off between absorber cross section and pressure drop. Relatively low gas velocities result in a larger absorber with a lower pressure drop. The trade-off which must be evaluated is an economic one; the capital costs for a larger absorber versus the operating costs of overcoming a high pressure drop.

The major conclusions of the pilot-scale tests are:

- 1) The MgO scrubbing system which was tested at MolyCorp's Washington, Pennsylvania plant was capable of removing over 90 percent of the SO_2 from an off-gas stream containing up to 9000 ppm SO_2 . The use of a packed absorber in conjunction with the MgO sorbent was the major factor which contributed to the good system performance. This is due to the high (relative to a spray tower) liquid residence time and overall area for mass transfer which exist in a packed absorber. The relatively long liquid residence time in the absorber helped promote dissolution of $MgSO_3$ solids in the absorber which effectively increased the liquid phase alkalinity of the scrubbing slurry.
- 2) An equation was developed to correlate the results of the pilot-scale tests. The correlation of experimental data was excellent and the equation can be used to design an MgO absorber using identical packing material treating a gas stream which is similar in composition to the one at MolyCorp. In using the design equation, the level of absorber operating parameters should be in the range of parameters examined during the pilot-scale tests.
- 3) For most operating conditions, plugging of the absorber bed was not a problem. However, at very high SO_2 removal efficiencies (95 percent) $MgSO_3$ solids did begin to accumulate in the absorber. In order to prevent such accumulation, the SO_2 concentration at the outlet of the packed bed should be maintained above 500 ppm. If additional SO_2 removal is required, a clear

Table 1. Range of Absorber Operating Parameters Applicable to Design Equation

Operating parameter	Applicable range
Gas Velocity (m/sec)	1.8 to 2.6
pH	6.0 to 8.0
Liquid Velocity (l/sec·m ²)	1.0 to 5.4
Weight Percent Solids	4 to 10
SO_2 Concentration (ppm)	2000 to 9000

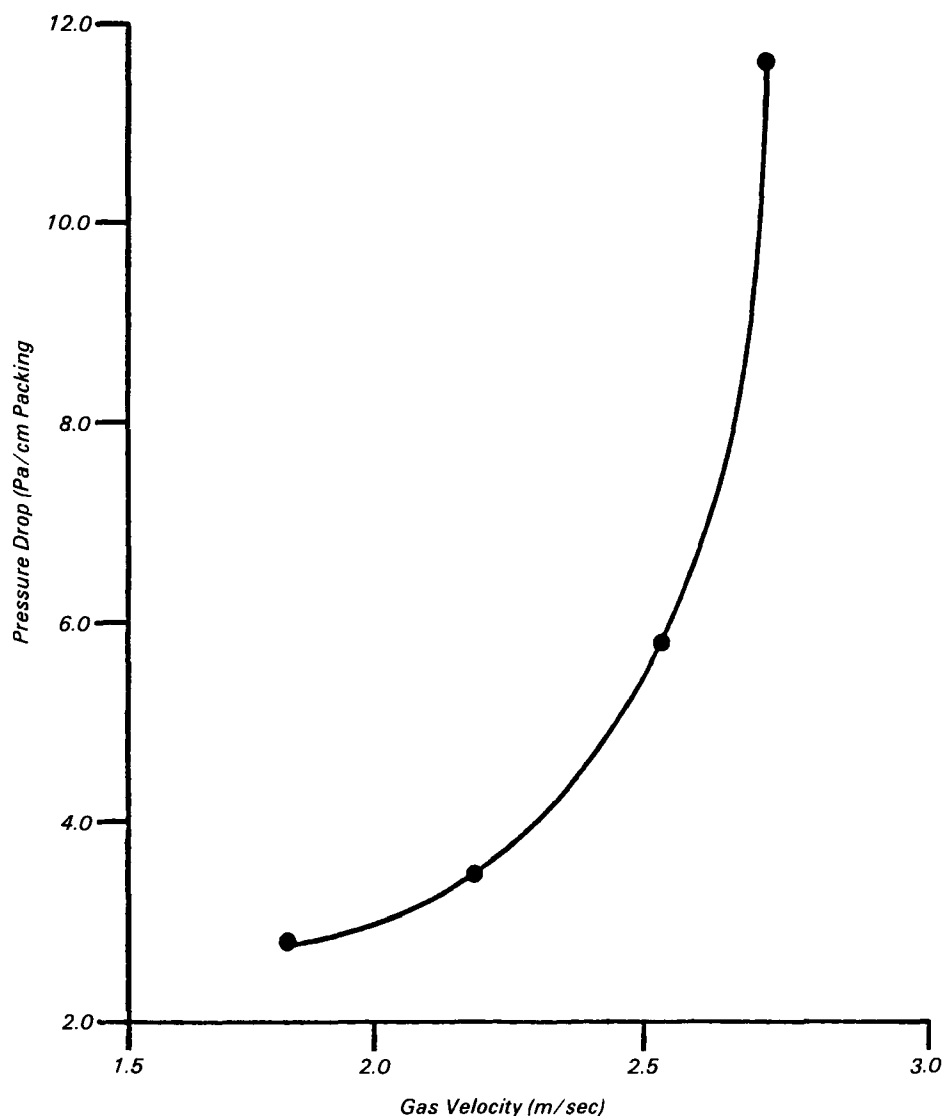


Figure 3. Absorber pressure drop as a function of gas velocity

SO₂ removal efficiencies and lower absorber pressure drops than those reported by utility applications. The principal reason for the superior performance is the absorber design used, a packed absorber in the pilot tests versus a venturi type absorber in the utility systems. In general, the packed absorber appears well suited to treating off-gas streams which contain high concentrations of SO₂ (up to 9000 ppm).

liquor spray installed above the packing should permit absorber operation without plugging.

- 4) Process control of the pilot-scale MgO system was not difficult. Measurement of reaction tank pH provided an indicator which could be used to accurately control the Mg(OH)₂ feed rate to the system. Also, changes in gas flow rate (over the range tested) did not require any corresponding changes in other absorber operating parameters to maintain a constant SO₂ removal efficiency.
- 5) Because the pilot unit was not operated as a closed-loop system, there were certain issues which were not addressed during the test program. Of these, it appears that buildup of

MgSO₄ (aq) will have the largest impact on test results. This is due to the fact that as MgSO₄ (aq) concentration builds up, MgSO₄ (aq) solubility decreases, thus decreasing available liquid phase alkalinity in the scrubbing slurry and possibly decreasing the SO₂ removal efficiency. Theoretically, a decrease in alkalinity can be offset by a corresponding increase in liquid flow rate to the absorber, but tests should be conducted to confirm this fact prior to using the design equation.

- 6) A comparison of the pilot plant test results to those reported for utility applications of the MgO system indicates that the system tested at Molycorp was generally superior. The Molycorp pilot tests resulted in higher

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The complete report consists of three volumes, entitled "Control of Air Pollution Emissions from Molybdenum Roasting," (Set Order No. PB 83-264 184; Cost: \$33.00, subject to change)

"Volume I. Emissions Characterization and Particulate Control," (Order No. PB 83-264 192; Cost: \$11.50, subject to change)

"Volume II. Alternatives for Control of Weak Sulfur Dioxide Emissions," (Order No. PB 83-264 200; Cost: \$13.00, subject to change)

"Volume III. Pilot Scale Test Results for Magnesium Oxide Scrubbing," (Order No. PB 83-264 218; Cost: \$14.50, subject to change)

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