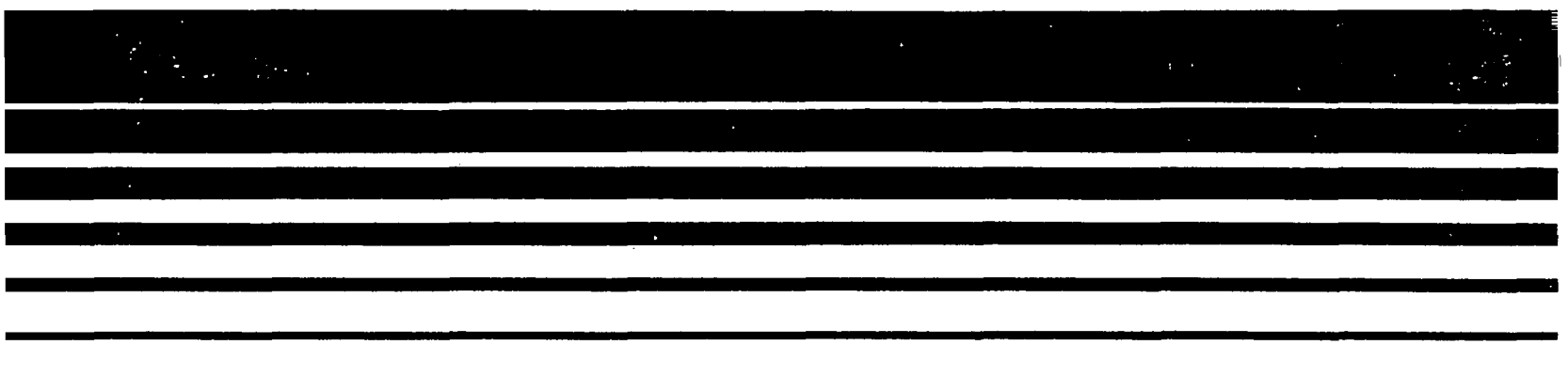


Air



NSPS Revision Nonferrous Smelter Reverberatory Furnace

**Emission
Test Report
Phelps Dodge
Morenci, Arizona**





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FINAL REPORT
PRIMARY COPPER SMELTER
NSPS REVISION
EMISSIONS TESTING AT
THE PHELPS DODGE SMELTER
MORENCI, ARIZONA

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1.0 INTRODUCTION

This report presents the results of a field testing effort conducted at the Phelps Dodge smelter at Morenci, Arizona. This effort, conducted under U. S. EPA Contract 68-02-3542 Work Assignment No. 6, was part of a series of efforts designed to provide background data for a portion of the revision of the New Source Performance Standards for the primary copper industry. During the study, the emissions from the fugitive gas collection hooding serving the reverberatory furnace matte tapping and slag skimming operations were measured.

The particulate and sulfur dioxide emission rates were determined using the combined EPA Reference Methods 5 and 6. Visible emissions (used as a surrogate for particulate and sulfur dioxide) were monitored using the techniques of EPA Reference Methods 9 and 22 (proposed) to determine the capture efficiency of the fugitive gas collection systems.

The emission rates from these tests are used in conjunction with observations of matte and slag production to calculate emission factors for the mass of particulate and sulfur dioxide emitted per mass of matte or slag produced.

Radian personnel performed all particulate, sulfur dioxide, and visible emissions testing. Research Triangle Institute (RTI) personnel made process observations during testing.

The remaining sections of this report present a summary of the results, a process description, sampling and analytical methodologies, quality assurance documentation, and results.

2.0 SUMMARY OF RESULTS

The particulate and sulfur dioxide testing performed at the Phelps Dodge Morenci smelter yielded average results of 17 pounds of particulate and 300 pounds of sulfur dioxide per hour of matte tapping and 1.9 pounds of particulate and 17 pounds of sulfur dioxide per hour of slag skimming.

These tests were performed intermittently due to the nature of the two processes evaluated. Only reverbratory fugitive emissions were measured. Fugitive emissions from matte tapping were obtained at the No. 5 furnace and fugitive emissions from slag skimming were taken at the No. 3 furnace. Thus, the results are more meaningful if expressed in terms of mass of pollutant per unit of production.

The average pounds per hour pollutant emission rates were converted to the following average pound per unit of production emission factors: 0.076 pounds of particulate and 1.3 pounds of sulfur dioxide per ton of matte production and 0.024 pounds of particulate and 0.21 pounds of sulfur dioxide per ton of slag production. These emission rates and factors are presented in Table 2-1. The matte and slag production rates used for these emission factors are estimated from observation of the matte tapping and slag skimming operation made by RTI during the emissions testing. This information "Primary Copper Smelter NSPS Revision Emission Testing, Process Observations, December 17, 1981" prepared by RTI is included as Appendix A. Additional information, including copies of the operator logs, have been requested from Phelps Dodge by RTI. Therefore, it should be realized that the process observations, in particular the production rates, may be subject to small changes; emission factors in this report are based upon the data given in Table 2-1.

TABLE 2-1. SUMMARY OF EMISSION RATES CALCULATED FROM PARTICULATE TESTING AT MORENCI

	<u>Estimated Production</u>		<u>Particulate</u>		<u>Sulfur Dioxide</u>			
Test	Tons	Taps	Lb/Hr*	Lb/Ton**	Lb/Hr*	Lb/Ton**	ppm	DSCFM
<u>Matte Tapping</u> (Reverb No. 5)								
EMB-004 MMT	185	8	19	0.1	290	1.6	683	42600
EMB-006 MMT	250	10	18	0.072	290	1.2	491	59200
EMB-008 MMT	275	11	15	0.054	310	1.1	516	60200
Average			17	0.076	300	1.3	557	54000
<u>Slag Skimming</u>								
EMB-003 MSS	80	2	2.0	0.025	15	0.19	188	8000
EMB-005 MSS	90	3	2.5	0.028	30	0.33	367	8200
EMB-007 MSS	60	2	1.2	0.020	7.6	0.13	100	7600
Average			1.9	0.024	17	0.21	215	7933

*Lb. of pollutant/hr. of sampling.

**Lb. of pollutant/ton of matte or slag produced during sampling.

3.0 PLANT DESCRIPTION

3.1 Process Description

A block flow diagram of a typical primary copper smelter is shown in Figure 3-1. The Phelps-Dodge smelter at Morenci has two reverberatory furnaces in operation, No. 3 and No. 5. Both furnaces are charged with copper ore concentrate and are fired with natural gas and/or fuel oil. Fluxing agents are also added to the furnace with the concentrate. In the furnaces, the levels of sulfur and iron in the concentrate are reduced to the point where iron sulfide (FeS) and copper sulfide (Cu_2S) are present in approximately equal amounts. This mixture is called matte. Excess FeS is converted via an exothermic reaction to iron oxide (FeO) and sulfur dioxide (SO_2). The FeO then combines with the silica-based fluxing agents and forms slag. This slag floats on top of the matte which facilitates their separation. The discharges from the furnace are the furnace off gases, the slag, and the matte.

The off gases containing SO_2 , particulate, metal fumes, and combustion products leave the furnace and enter waste heat boilers and then a dust collection system. The recovered dust is combined with the reverberatory furnace feed and recycled to the furnace.

Removal of the slag layer from the furnace for disposal at a slag dump is by a process referred to as "slag skimming". Molten slag exits the furnace through a skimming port and is conveyed to a ladle by way of a trough or "slag launder". The port, slag launder, and transfer point from the slag launder to the ladle are all hooded. These hoods are designed to collect fugitive gases from the slag skimming operation and convey them through a duct to a blower and then to a discharge stack.

The matte is removed from the furnace by a process called "matte tapping". The molten matte exits the furnace through a tapping port and

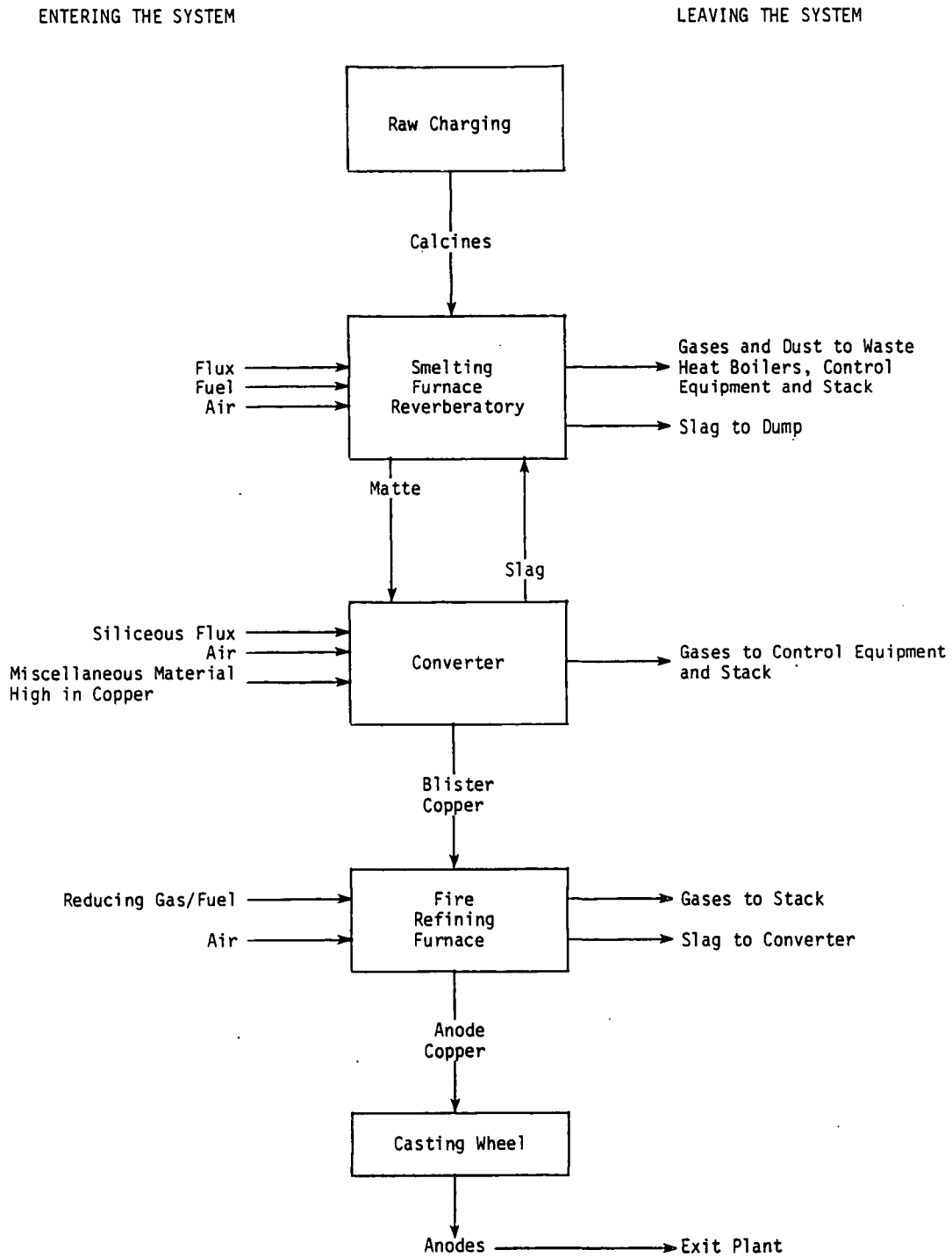


Figure 3-1. Typical Primary Copper Smelter Flowsheet

conveyed to a ladle by way of a trough or "matte launder". The port, matte launder and point of transfer from the launder to the ladle are all hooded. As in the slag skimming process, these hoods are designed to collect fugitive gases from the matte tapping operation and convey them through a duct to a blower and then to a discharge stack. The ladle of molten matte is transferred by way of overhead cranes to converters for further refining.

In the converters, FeS is oxidized to FeO and SO_2 . Quartz is added to the converters and binds the FeO to form a slag containing approximately four percent copper. This slag is periodically recycled to the reverberatory furnace via ladles and an overhead crane. "White metal" consisting of Cu_2S remains after the removal of the iron. At this stage, the converter blowing cycle starts. The Cu_2S is converted to a 98 percent pure copper called "blister copper." Cold copper scrap is periodically added during the blowing step to absorb the heat produced by the exothermic reaction.

The blister copper is transferred to an anode furnace in batches, again by ladles and cranes. Air blowing into the anode furnace removes the remaining sulfide and results in copper containing Cu_2O as an impurity. The Cu_2O is then reduced with reformed natural gas and produces a 99+ percent pure copper which is ready for the anode pouring step and casting. Casting 99+ percent pure copper into the anodes is the final production operation that takes place at most smelters. The copper anodes, which weight about 750 lbs each, are then shipped by rail car to another facility where they are refined one last time by means of electrolysis. This step removes trace amounts of noble and precious metals, leaving pure copper as the final product.

3.2 Sampling Port Description

Emission rates for particulate and sulfur dioxide from the fugitive gas collection hooding for matte tapping and slag skimming operations were determined during this effort. During the pretest site survey for the Phelps Dodge smelter at Morenci, and as a result of subsequent discussions with EPA/EMB and RTI, two sampling locations were selected. One was for the emissions from the slag skimming operations, while the other was for the emissions from the matte tapping operations.

The first location is in a duct which carries emissions captured by hooding at two of the three slag skimming locations on the No. 3 reverberatory furnace. The second location is in the duct which carries emissions from all tapping and skimming locations on the No. 5 reverberatory furnace. Only emissions from the matte tapping operations at the No. 5 reverberatory were sampled, thus requiring coordination to assure sampling was performed when matte tapping only was in progress. The configuration of the duct work and these ports are further described in Section 4.0.

4.0 SAMPLING METHODOLOGY

The emission rates for particulate and sulfur dioxide from the fugitive gas collection hooding serving the matte tapping operations for the No. 5 reverberatory and the slag skimming operations for the No. 3 reverb were determined during this effort. In addition, the visible emissions escaping these hooding systems were monitored. This section describes the sampling locations and the methodologies utilized to collect these samples and data.

4.1 Sampling Locations

4.1.1 Matte Tapping Emissions

The No. 5 reverberatory has eight tap bays and two skim bays. The gases from these bays were conveyed to one common duct, through two fans in series, and on to the main converter stack. The sampling ports were downstream of the fan and upstream of the junction with the other gases which are also conveyed to the main duct. The ports were located in a long horizontal run of the main fugitive gas duct as it crossed the top of the reverberatory/converter building. These ports were two duct diameters upstream of the 90° elbow, which turns the duct down the side of the building. The duct diameter at the ports was 53".

The ports were installed specifically for these tests and were accessible from an existing catwalk. The catwalk was enlarged for these tests. One port axis was horizontal and the other was vertical. An "A" frame was also constructed above the duct to support the sampling train. The ports were 3" pipe nipples approximately 6" in length. Electrical power was available at the sampling ports. Figure 4-1 is a sketch showing the matte tapping emission sampling port locations. This test plane meets the eight and two diameter criteria as described in EPA Method 1.

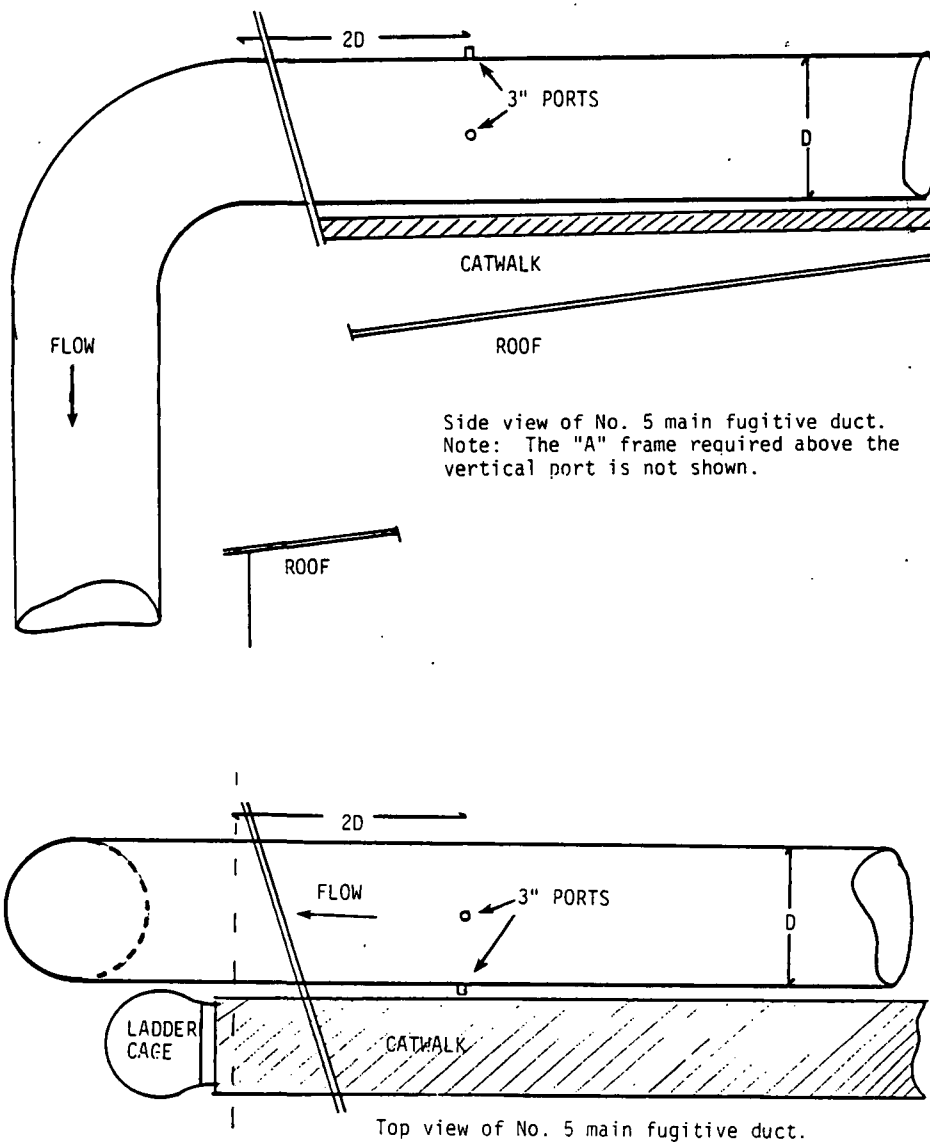


Figure 4-1. Sketches Showing the Locations of the Matte Tapping Emission Sampling Ports at the Phelps Dodge Morenci Site

Due to the availability of a more favorable site, approximately 225 feet downstream of the first, matte tapping emission sampling operations were moved to the second site after the first run.

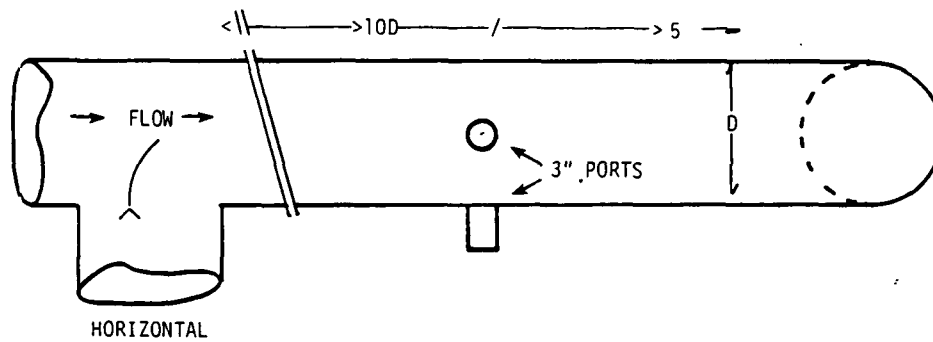
These ports had been installed after the pretest site survey by Phelps Dodge for their own use. The duct diameter and conditions were the same for both locations. However, the gas velocity measured at the second site was greater than for the first site. Adjustments to some of the hood dampers overnight could account for this increased gas flowrate.

4.1.2 Slag Skimming Emissions

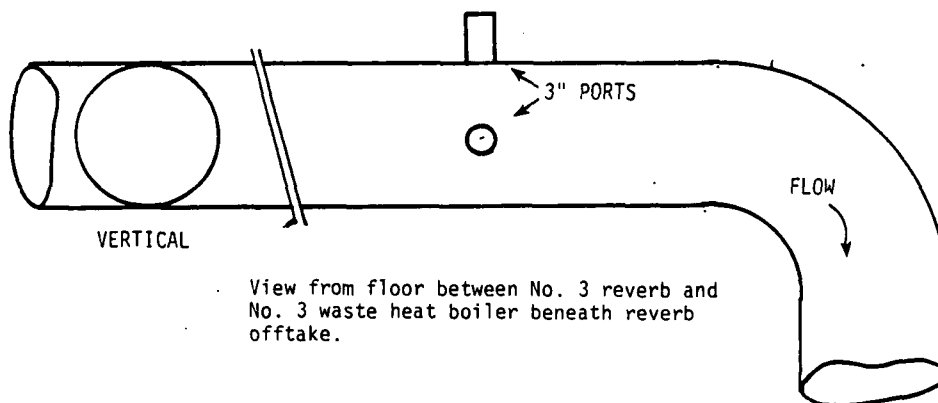
Unlike the No. 5 reverb, the slag skimming bay ventilation system was isolated sufficiently to permit sampling without interference from simultaneous matte tapping. The two 3" sampling ports were in an 18" diameter duct which served two of the three skim bays for the No. 3 reverb. This test plane met the eight and two diameter criteria with more than ten duct diameters downstream from any disturbance, and approximately five diameters upstream of any disturbance. The duct was horizontal and just below the reverberatory gas offtake. Figure 4-2 is a sketch showing the slag skimming emissions sampling port locations.

4.2 Sampling

Radian determined the emission rates by EPA Reference Methods 1, 2, 3, 5, and 6 (Code of Federal Regulations, 40, Protection of the Environment, Parts 53 to 80, Revised as of July 1, 1980). Radian performed EPA Reference Methods 1 and 2 the first day at the plant at both sampling sites. When the decision was made to move the matte tap testing to a more accessible sampling location, Methods 1 and 2 were again performed at that site.



View toward No. 3 reverb from between No. 3 reverb and No. 3 waste heat boiler beneath reverb offtake.



View from floor between No. 3 reverb and No. 3 waste heat boiler beneath reverb offtake.

Figure 4-2. Sketches Showing the Locations of the Slag Skimming Emission Sampling Port at the Phelps Dodge Morenci Site

During each test, Radian also performed EPA Reference Method 3 using a calibrated Fyrite®.

In the determination of particulate and sulfur dioxide rates, EPA Reference Methods 5 and 6 were combined within a single sampling test. A very prominent portion of this testing was the sequencing and communication involved to coordinate the sampling with the plant operations. Walkie talkies, provided by the U.S. EPA, were the main source of communication. RTI officials observed when the slag was being skimmed and the matte being tapped. This information was relayed to the sampling team and the sampling commenced. If the plant operations ceased, then word was sent to terminate the sampling. This aspect of the testing went smoothly. The U.S. EPA requested that Radian sample each traverse for 2 1/2 minutes per point and sample each of the six points twice. The reasoning was that since each tap had a duration of only a few minutes, the sampling would be biased if only one point was sampled per tap (5-minute sampling point). With 2 1/2 minute sampling points, at least two points across the duct would be sampled per tap.

A schematic drawing of the sampling train and related equipment is shown in Figure 4-3. Gas volume was measured with a dry gas meter calibrated against a standard dry gas meter. Stack temperature was measured by Type K, chrome-alumel, thermocouple calibrated against a mercury thermometer. Velocity pressure and pressure drop across the orifice were measured using Magnehelic® gauges having ranges from 0-1 and 0-3 inches H₂O, respectively.

A leak check of the entire train was conducted before and after each run and the leak rate noted. The leak check was performed at either 15" Hg vacuum or the highest vacuum obtained during the run. Pitot lines were leak checked at 3" H₂O before and after each run to insure proper velocity pressure measurements. The barometric pressure was read daily from an aneroid barometer. The measured static pressure of the stack gas was added to this atmospheric pressure to obtain the actual stack pressure.

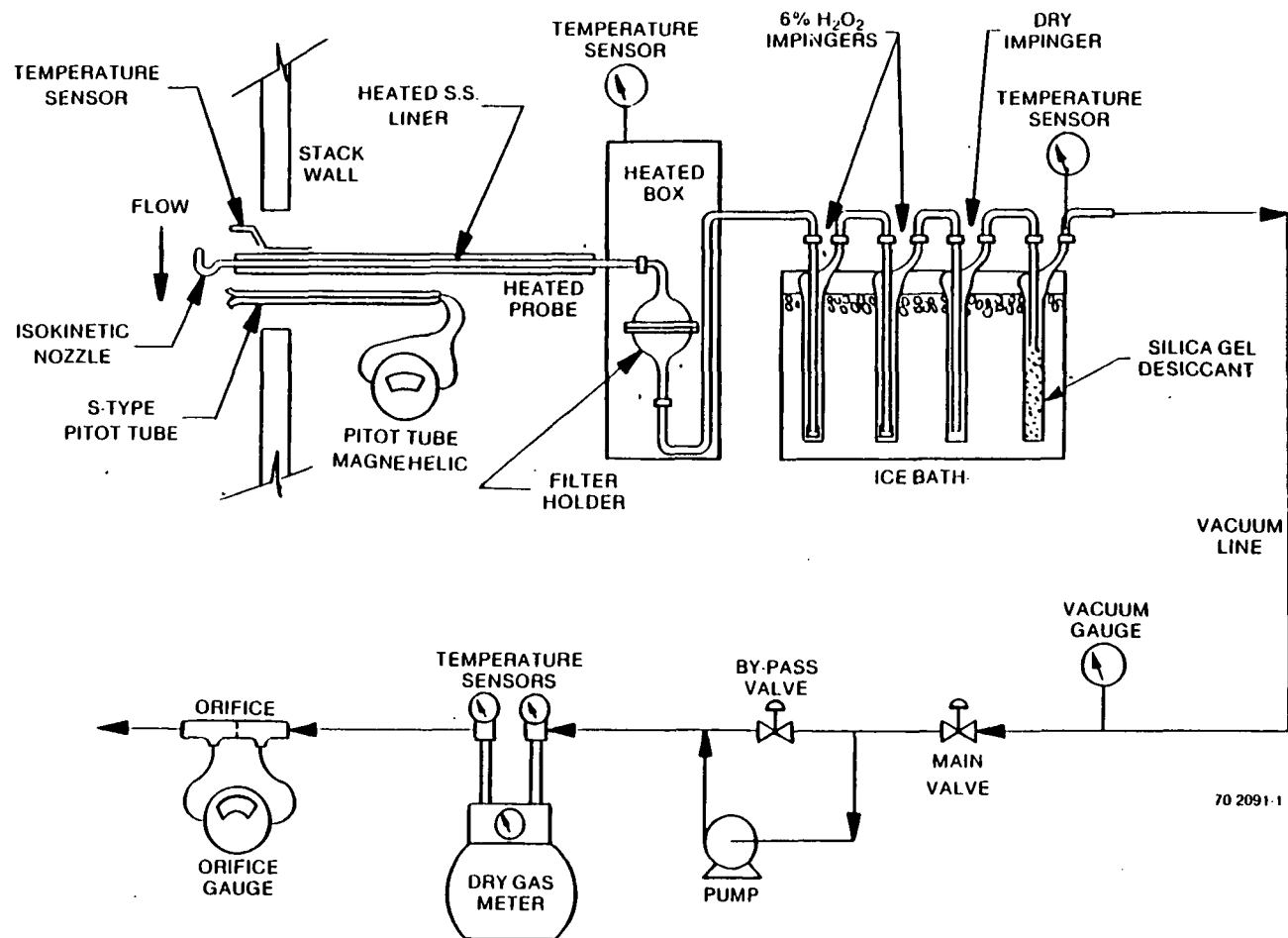


Figure 4-3. A Schematic of the Combined EPA Method 5 and 6 Sampling Apparatus

Dry gas meter volume was noted at the beginning of sampling for each point. The velocity pressure (ΔP) was read and the sampling rate (ΔH) adjusted by a predetermined factor to obtain an isokinetic sample. Stack temperature, hot box temperature, gas temperature at the exit of the final impinger, dry gas meter inlet and outlet temperature, and vacuum on the train were all recorded at each sample point. Data forms containing the above information for each run are included in Appendix C.

Both the probe liner and nozzle were brushed and rinsed with acetone to collect particulate while at the sampling location. The hot box/cold box assembly was taken to the mobile lab for the remaining portion of the sample recovery. All glassware upstream of the filter and the front half of the glass filter holder were rinsed with acetone into the probe wash sample container. The filter was removed and placed in its original petri dish. Care was taken to recover all fragments of the filter. Impingers were weighed to obtain final weights to allow calculation of the moisture fraction, and the H_2O_2 impingers were quantitatively transferred to polyethylene containers, marked, and sealed for shipment.

4.3 Visual Emissions Observations

Visual emission observations were made to visibly evaluate various hood capture systems and pollution control equipment at the Phelps Dodge Company copper smelting facilities in Morenci, Arizona.

All visible testing was performed by certified observer Mr. Craig Beskid, Engineer, of Radian Corporation (Texas Air Control Board certification date 9-24-81). The testing was performed using visible emissions observations of particulate matter escaping capture of the hooding system or pollution control equipment as a surrogate for sulfur dioxide (SO_2) emissions that were not captured. Results from this visible emissions testing, along with simultaneous SO_2 and particulate measurements, will provide input for revision of the New Source Performance Standards (NSPS) for the primary copper industry.

4.3.1 Observation Sites - Morenci Smelter

Two streams from the Morenci smelter were visually evaluated:

- The No. 3 reverberatory furnace slag skimming fugitive emissions escaping capture by the hooding system, and
- The No. 5 reverberatory furnace matte tapping fugitive emissions escaping capture by the hooding system.

Figures 4-4 and 4-5 show the position of the observer for each launder and reverberatory furnaces No. 3 and No. 5, respectively.

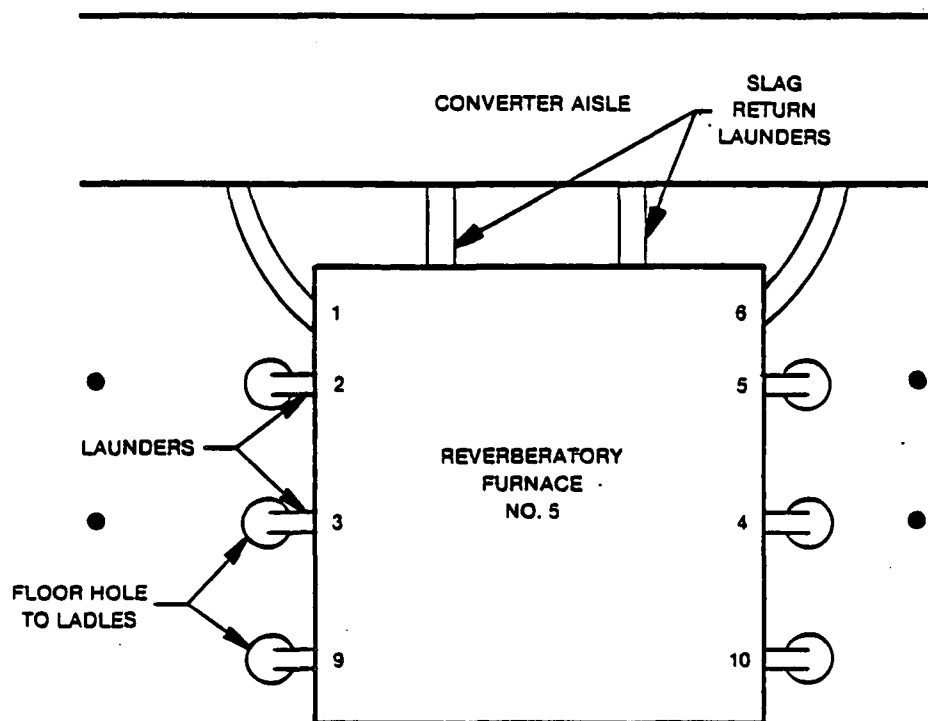
4.3.2 Methodology

Two visible emissions methods were employed in the testing. The technique of EPA Method 9, "Visual Determination of the Opacity of Emissions From Stationary Sources" was used to determine the opacity of fugitive hood emissions and scrubber stack emissions. The technique of proposed EPA Method 22, "Visual Determination of Fugitive Emissions from Material Processing Sources" was used to determine the accumulated time that fugitive emissions were observed escaping each hooding system evaluated.

All in-plant observations were made from a position approximately 15 feet directly in front of each launder.

4.3.3 Method 9

A certified observer is generally used by control agencies to evaluate the opacity of an emission source. The observers are instructed at opacity training schools. In order to become certified, observers must evaluate plume opacity with ± 7.5 percent accuracies relative to transmission measurement of plume opacity. Upon passing the course, they are certified by the school for six months as capable of evaluating plume opacity by visual inspection.



- Identifies observer location points

Figure 4-4. Visible Emissions Observer Locations for the No. 5 Reverberatory Furnace at Morenci Matte Tapping Operations.

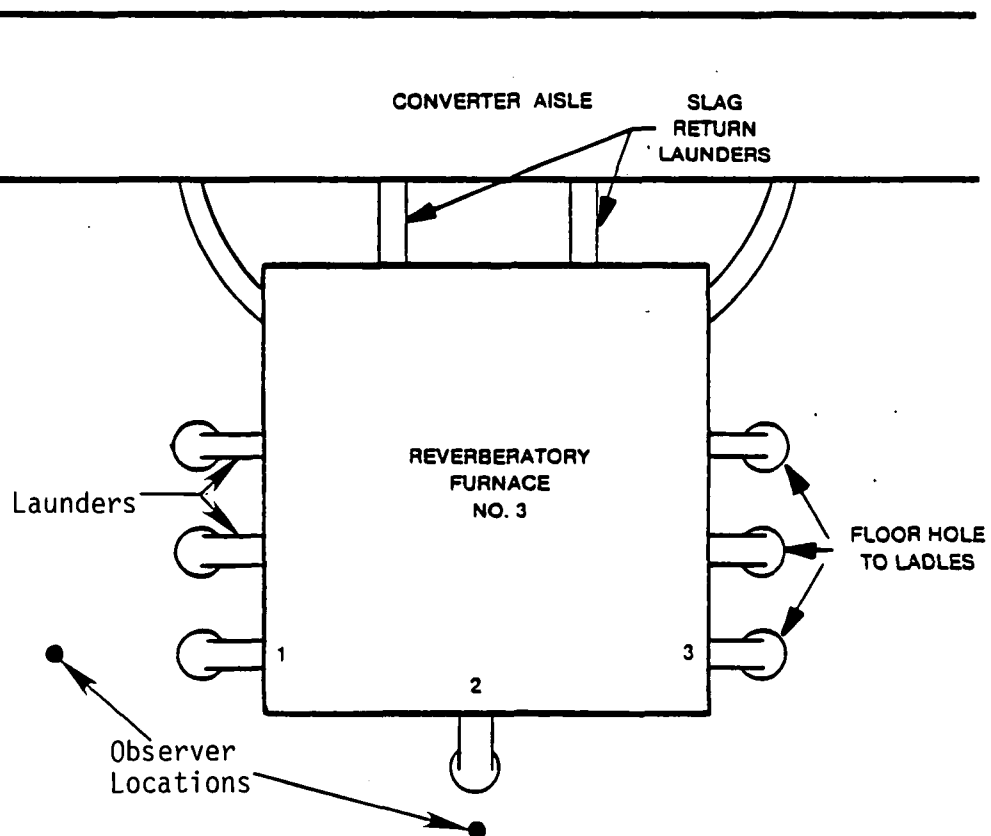


Figure 4-5. Visible Emissions Observer Locations for the No. 3 Reverberatory Furnace at Morenci for Slag Skimming at Taps 1, 2, and 3.

When observing a plume, Method 9 requires that the observer stand:

- at a distance from the plume sufficient to provide a clear view of the emissions,
- with his line of vision approximately perpendicular to the plume direction, and
- with the sun oriented in the quadrant to his back.

The method also requires that readings be made at 15-second intervals over a minimum six-minute period at the point of greatest opacity in the plume. The average of these minimum 24 readings is reported as the average visual opacity. Data forms with these recorded readings are contained in Appendix D.

For the purpose of this study, modifications to Method 9 were necessary. First, Method 9 was performed indoors at the Morenci smelter reverberatory furnaces. This was an improper position relative to the emissions, the light source, and the background. The emissions were read most often with light from above the emissions as the emissions escaped the hooding system. All opacity observations were made consistently using the furnace facing approximately two feet above the launders as background. Most observations were performed during a simultaneous stack test. Also, all observations were halted during excessive visual interferences caused by fugitives from other sources or moving equipment and personnel.

4.3.4 Method 22

This method is used to determine the amount of time that any fugitive visible emissions occur during the observation period. Fugitive emissions include emissions that:

- escape capture by process equipment exhaust hoods,
- are emitted during material transfer, building housing material processing or handling equipment, and
- are emitted directly from the process equipment.

Since this procedure does not require certification according to Method 9, a trained opacity observer is not required. However, it is necessary that the observer be educated in the general procedures for determining the opacity of emissions. Mr. Craig Beskid of Radian Corporation performed all the Method 22 testing. The modifications to Method 22 are identical to the modifications previously listed for the Method 9 observations.

4.3.5 Limitations of the Methods

Both Methods 9 and 22 were modified for conditions at the observation sites. The modifications to each method were made to minimize method limitations and to include process dependent effects on emissions, light deficiencies, and observer positions. The extent of these modifications were determined during the observations at each smelter process point. The modifications and limitations of the methods, including their effect on the observations, are discussed below.

4.3.5.1 Method 9 Limitations

Visible emissions best evaluated by this method are from stack plumes, while observations at the Morenci smelter were performed on fugitive emissions. The procedures for Method 9 specify outdoor observations. The majority of observations at the Phelps Dodge smelter were performed indoors. Indoor observations decrease observed opacities due to a decrease in the amount of light and background contrast.

Method 9 procedures implicitly include provisions for a cyclic process such as a varying process load. However, characterization of fugitive emission opacity for an intermittent process such as slag skimming or matte tapping is not addressed.

Other limitations to obtaining an accurate opacity assessment of the fugitive emissions is listed below.

- Inability to obtain proper observer position relative to the light source.
- Inconsistent amount of light.
- Visible emissions interferences due to hood leaks and nearby processes (increases observed opacity).

4.3.5.2 Method 22 Limitations

The most significant modifications and limitations to the Method 22 observations are listed below.

- Visible emissions interference due to hood leaks and nearby processes (increased recorded emission time).
- Less than adequate amount of light (<100 lux, decreases visibility of emissions).
- Inability to attain proper observer position relative to light source (may increase or decrease visibility of emissions, highly dependent on position of light source).

4.4 Process Observations

The matte tapping from the No. 5 reverberatory and slag skimming from the No. 3 reverberatory were observed from the furnace floor during sampling. The observers also coordinated the sampling and communicated with the two-way radio.

At Morenci, the No. 5 reverberatory tap and skim bays were served by a single hooding system. Samples were collected from a location common to other types of bays. Thus, it was necessary to sample only during the tapping operation and stop sampling if a skim or lancing in preparation of a skim began. The observer noted the times for the start of any lancing operations, the initiation of metal flow (at which time sampling could begin), and the completion of the top or the start of lancing for another tap or skim (at which time sampling was stopped). The observer also noted the extent that each ladle was filled and any other information which was thought to be pertinent. Simultaneous taps occurred several times during the sampling. For these, sampling was stopped only during lancing, but was resumed as soon as metal flow at the second bay began. Sampling continued if just one of the taps were completed.

The observer's task at the No. 3 reverberatory skim bay was essentially the same as above. However, the duct work in which the sampling ports were installed served only two of the three skim bays for the furnace and none of the tap bays. The observer, as for the No. 5 reverberatory, recorded the times of lancing and metal flow and skim completion, as well as the time of any interfering operations. The observer also noted the extent to which each ladle was filled and any other information thought to be pertinent.

The process observation for Morenci was performed primarily by RTI with support from Radian. Coordination of the sampling activities was performed by Radian. The process observations document provided by RTI is Appendix A in this report. Operating logs from the Morenci have been requested. This information will be used to corroborate the data used, and, where possible, confirm some assumptions which were made for matte and slag production notes and schedules.

5.0 ANALYTICAL METHODOLOGY

This section deals with the handling, preparation and analysis of all the recovered samples. EPA Reference Methods 3, 5, and 6 were performed using the same reference stated in Section 4.2.

In determining the dry molecular weight of the flue gas, the EPA's Reference Method 3 was used. Radian used a Fyrite during each test. During mid-run, the flue gas was hand pumped through a pitot line into a sealed container holding either CO₂ or O₂ absorbing solution. The gas was thoroughly mixed with the solution and the CO₂ or O₂ percentile was read off the scale on the container. This procedure was done at least twice. Once both CO₂ and O₂ percentages were established, the remainder of the gas was assumed to be composed of nitrogen.

Upon return to Radian's Austin laboratories, final weights were obtained for all filters and the acetone/deionized water wash residues in compliance with EPA Reference Method 5. Filters were desiccated for 24 hours and weighed to a constant weight. Initial and final weighing was performed on a Mettler semi-micro balance. The acetone/deionized water wash was quantitatively transferred to equilibrated tared glass beakers and taken to dryness. These samples were then desiccated 24 hours and weighed to a constant weight. Acetone and deionized water blanks, 100 mL, were treated in this same manner, and the samples corrected for these blanks.

Using EPA Reference Method 6, the H₂O₂ samples containing the SO₂ were diluted up to 500, 1000, or 2000 mL in volumetric flasks depending on the SO₂ concentration. A 5 mL aliquot was pipetted into a 250 mL Erlenmeyer flask and 20 mL of 100% isopropanol added. Two to four drops of thorin indicator were added and the sample titrated to a pinkish-orange endpoint with .01 N Ba(ClO₄)₂. The equation in Method 6 for calculation of SO₂ concentration was followed. The Ba(ClO₄)₂ was standardized daily

against 0.01 N H_2SO_4 prepared from a purchased analytical concentrate.
Blanks and QA audit samples were titrated as was a duplicate of every tenth sample.

6.0 QUALITY ASSURANCE

The work performed at the Phelps Dodge Morenci smelter incorporated a comprehensive quality assurance/quality control (QA/QC) program as an integral part of the overall sampling and analytical effort. The major objective of the QA/QC program was to provide data of known quality with respect to:

- completeness,
- accuracy,
- precision,
- representativeness, and
- comparability.

The quality assurance function was organized to provide independent review and assessment of project activities and their ability to achieve the stated data quality objectives. The QA coordinator for the project had the responsibility of evaluating the adequacy and effectiveness of the QC system and providing assurance that it was, in fact, responsive to the specific needs of the program.

While the system of QA activities was necessarily independent of the technical effort per se, the QC system was an integral part of the daily technical effort. It was designed to provide an overall system for generating data of a specified quality. This section provides an assessment of the QC program and a summary of resulting data quality as determined by the QA audit.

6.1 Source Sampling Audit Results

As part of the quality assurance program for this project a performance and systems audit was performed during the period 13 November to 14 November 1981. Audit activities, results and conclusions are presented below.

6.1.1 Systems Audit

A systems audit is an on-site qualitative review of various aspects of a total sampling and/or analytical system to assess its overall effectiveness. The systems audit results represent a subjective evaluation of a set of interactive systems with respect to strengths, weaknesses and potential problem areas. The audit was designed to evaluate the following:

- Adherence to accepted procedures in performing reference method source sampling,
- Adequacy of internal quality control procedures
- Equipment and facilities,
- Qualification and training of personnel,
- Calibration procedures and documentation,
- Sample handling, custody and storage, and
- Data recording, review and handling.

The systems audit checklists, which are presented in Appendix B, delineate the specific aspects of the sampling/analytical system which are deemed to be especially important in obtaining quality data. The activities which were observed during the audit included determinations of:

- Velocity and volumetric gas flowrate (EPA Method 2)
- Gas phase molecular weight (EPA Method 3),
- Gas phase moisture (EPA Method 4),
- Particulate concentration (EPA Method 5),
- Gas phase (SO₂) concentration (EPA Method 6), and
- Visible fugitive emissions (EPA Method 9 and proposed Method 22).

As indicated on the audit checklists, careful compliance with accepted sampling procedures was observed for all sampling activities. The sampling crew exhibited an obvious familiarity with the equipment and methods used. Internal QC checks such as pre- and post-test leak checks of sampling train, intermediate calculation of isokinetics, replicate Fyrite analyses, etc., were carefully followed. The facilities and procedures used in sample handling and storage were judged to be quite adequate. All data records were well organized and utilized preformatted data sheets in most instances. All equipment calibration data was complete and similarly well organized. Overall, the systems audit indicated an efficient, well orchestrated sampling effort which was judged to be adequate for achieving the data quality for each of the EPA Methods as shown in Table 6-1.

6.1.2 Performance Audit

A performance audit is a quantitative assessment of the data quality of a sampling and/or analytical system. Both field and laboratory (analytical) operations were addressed in the performance audit for this program. Audit activities included:

- field checks of dry gas meter/control console calibration,
- field check of the laboratory balance (Mettler PC4400),
- field checks of the Fyrite analyses,
- checks of field calculations,
- check of the data reduction program used for the sampling data reduction, and
- analysis of SO₂ audit samples.

TABLE 6-1. ATTAINABLE ACCURACY AND PRECISION OF TEST RESULTS
BASED ON THE EPA COLLABORATIVE TESTS OF STATIONARY
SOURCE METHODS**

Parameter	Method	Accuracy (%)	Precision (Standard Deviation) (%)
Volumetric Gas Flow Rate	2	<u>+11</u>	20
Molecular Weight	3	<u>+25</u>	10
Moisture	4	<u>+10</u>	11
Particulate Mass	5	<u>+20</u>	10
SO ₂	6	<u>+20</u>	10
Emissions Opacity	9	<u>+7.5</u>	5
Emissions Visibility*	22	<u>+10</u>	10

*Radian estimate.

**Midgett, M. Rodney, Environmental Science and Technology,
11, No. 7, pp. 655-659.

Results of the performance audit supported the results of the systems audit, indicating that the test data quality should be as shown in Table 6-1.

Performance audit results presented below are expressed in terms of relative accuracy. The relative accuracy for each parameter is calculated as:

$$\% A = \frac{(M-T)}{T} \times 100$$

where,

% A = relative accuracy, percent

M = measured value

T = true value of reference standard

100 = factor for conversion to percentage basis

Dry Gas Meter/Control Console

Field checks of the dry gas meters/control consoles were performed using a Kurz Model 543 flow calibrator (Serial No. 769). The Kurz instrument had recently been calibrated by the manufacturer using an NBS traceable mass flow meter (NBS test numbers 213-21/190522). The calibration factor, Y_i , was determined by averaging triplicate measurements at each of three meter rates (nominally 0.25, 0.50 and 0.75 ACFM).

A second calibration indicated that the dry gas meter correction factors (Y_i) had changed by less than five percent of their original calibration value. Thus, the use of the original calibration factor was appropriate for further data reduction.

Laboratory Balance

The accuracy of the laboratory balance (Mettler PC4400) was checked using a set of NBS traceable Class S weights. Replicate weighings were made on weights ranging from 0.01 g to 100 g. The greatest difference between balance reading and actual weight was observed with the 0.5 g weight. This difference was 0.01 g or 2.0 percent.

Fyrite® Analyses

Ambient air was analyzed during the performance audit using the Fyrite gas analyzer for carbon dioxide and oxygen. The precision and accuracy for these determinations were within the readability of the analyzers (± 0.5 percent). Based on this data and the systems audit results the gas composition determinations should be within the precision and accuracy ranges estimated for this method (Table 6-1).

Field Calculations and Computerized Data Reduction

A check of field measurements and calculations used for determining the location of sampling traverse points (EPA Method 1) indicated that the points were correctly located. Radian's computerized Source Sampling Data Reduction Program was used to reduce all velocity, flowrate, molecular weight, particulate mass and SO₂ data. Example data sets for Methods 2, 3, 4, 5 and 6 were submitted for reduction using this program and the results compared to those obtained by hand calculation using the equations and procedure specified in the Reference Methods. The comparison of results indicated excellent agreement between the two procedures with the magnitude of the difference attributable to rounding differences. The results of this comparison are summarized in Table 6-2.

TABLE 6-2. SUMMARY OF DATA REDUCTION CHECK

Parameter	Data Reduction Program Results	Hand Calculated Results	Accuracy (%)
Velocity (ft/sec)	15.3505	15.3657	-0.04
Volumetric Flow Rate (dscf/min)	24184	24203	-0.08
Molecular Weight (lbs/lb-mole)	28.85	28.85	0.0
Particulate Concentration (gr/dscf)	0.637	0.639	-0.3

Sulfur Dioxide Determinations

The sulfate content of the impinger solutions resulting from the absorption of sulfur dioxide were analyzed per EPA Reference Method 6 using the barium perchlorate-thorin titration method. The data quality for these determinations were assessed by submitting blind EPA Stationary Source Quality Assurance SO₂ Reference Standards. These audit standards were analyzed with the impinger samples. The results for these determinations are summarized in Table 6-3. The percent accuracy for these analyses is within the ± 7.0 percent control limit.

Two of the six Method 5 and 6 tests incorporated a third hydrogen peroxide impinger to document the SO₂ collection efficiency of the impinger train. As shown in Table 6-4, the results from the analyses of these additional impinger solutions indicate the collection efficiency using two impingers was greater than 98 percent.

TABLE 6-3. SUMMARY OF EPA AUDIT SAMPLE ANALYSES

Sample Number	Measured ng SO ₂ /dscf	Actual ng SO ₂ /dscf	Accuracy (%)	Control Limit
8136	805	762.6	+5.6	<u>+7.0</u>
6065	1317	1334.6	-1.3	<u>+7.0</u>

TABLE 6-4. SUMMARY OF EPA METHOD 5/6 IMPINGER COLLECTION EFFICIENCY RESULTS

Sample Number	mM SO ₂ in Impingers 1 and 2	mM SO ₂ in Impinger 3	Collection Efficiency (%)
EMB 007 MSS	98.1	1.9	>98
EMB 008 MMT	99.3	0.7	>99

7.0 CHAIN-OF-CUSTODY

While in the field, all samples were under the care of Michael J. Krall during the period of November 12 through November 24. Throughout this period, all samples were processed for transport back to Radian's Austin laboratories within 24 hours after collection. This involved placing filters in petri dishes and sealing them with tape. Probe washes and SO₂ samples were kept in polyethylene bottles, their lids taped shut, and initial volume noted. All samples were stored in the Radian Mobile Lab on site.

On November 24, the samples were transported by automobile from Deming, New Mexico, to El Paso, Texas. The samples were placed in the custody of Continental Airlines aboard Flight No. 75. Upon arrival to San Antonio, Michael J. Krall transported the samples by automobile to Radian's Austin laboratories where they remained overnight. Final processing of the samples was completed on December 7, and the samples were placed in storage. At no time during the process of collection, storage on site, transport, or final analysis was there any evidence that these samples were tampered with.

8.0 RESULTS

A summary of particulate and sulfur dioxide sampling results of the matte tapping and slag skimming are presented in Tables 8-1 and 8-2. The sampling time for each run was 60 minutes while the total elapsed time from beginning to end was much longer - exceeding 24 hours in some instances.

The particulate and sulfur dioxide results from the computerized data reduction are in units of mass of pollutants per hour (of sampling). These results were converted to mass of pollutants per ton of matte or slag produced (during sampling) using the following expression:

$$\frac{\text{Mass of Pollutant}}{\text{Ton of Production}} = \frac{\text{PMR } \Theta}{(60 \text{ min/hr}) \sum_{i=1}^n M_i T_i L}$$

where: PMR, in pounds per hour, is the pollutant mass rate of particulate or sulfur dioxide as calculated through the computerized data reduction.

Θ , in minutes, is the sampling time.

n is the number of trapping or skimming operations which were sampled. (Note: more than one operation may be in progress during sampling.)

T_i is the fraction of the total duration of the i^{th} tap or skim which was sampled.

M_i is the fraction of the normal ladle which was removed from the furnace during the observed i^{th} tap or skim.

L, in tons, is the weight of a normal ladle of matte or slag as specified by the plant personnel.

TABLE 8-1. MATTE TAPPING DATA SUMMARY

Run	EMB 004 MMT	EMB 006 MMT	EMB 008 MMT	Average
Date	11/12-13/81	11/13-14/81	11/14-15/81	-
Time	1247-0844	1413-1248	1328-1145	-
Lbs Particulate/Hr	19	18	1.9	17
Lbs Particulate/Ton	0.10	0.072	0.054	0.076
Lbs SO ₂ /Hr	290	290	310	300
Lbs SO ₂ /Ton	1.6	1.2	1.1	1.3
Matte Production, Tons	185	250	275	237
Episodes	8	8	11	-
Gas Flow, DSCFM	42,600	59,200	60,200	-

TABLE 8-2. SLAG SKIMMING DATA SUMMARY MORENCI NO. 3 REVERB FURNACE

Run	EMB 003 MSS	EMB 005 MSS	EMB 007 MSS	Average
Date	11/12/81	11/13/81	11/14/81	-
Time	1556-1747	1532-1733	0854-1057	-
Lbs Particulate/Hr	2.0	2.5	1.2	1.9
Lbs Particulate/Ton	0.025	0.028	0.020	0.024
Lbs SO ₂ /Hr	15	30	7.6	17
Lbs SO ₂ /Ton	0.19	0.33	0.13	0.21
Slag Production, Tons	80	90	60	77
Episodes	2	3	2	-
Gas Flow, DSCFM	8,000	8,200	7,600	-

The T_i , M_i , and L terms are presented in Tables 8-3 and 8-4. These were derived from correlating the start and stop times on the data sheets with the process observations. The test results are expressed in units of mass of pollutant per unit sampling time (not clock time). Also, the mass of matte and slag production on those which occurred during sampling not that which occurred during the elapsed time of the test.

Visible Emissions

Two types of visible emission testing were performed: Method 9 which yields results that are a time weighted opacity and Method 22 which indicates the fraction of time visible emissions were present. Neither method produces data on the percent of fugitive emissions captured, but lower opacity reported for Method 9 generally indicates a greater capture efficiency for the hooding system evaluated if all other factors are constant.

Method 9 is generally used for sources where natural lighting conditions are present. The use of Method 9 in indoor locations, where lighting conditions may not be optimal and where observer locations may or may not be a problem, will not produce data as reliable as data gathered under the conditions for which the method was intended.

Reverberatory Furnace No. 5 Matte Tapping (Lancing Emissions Not Included)

Method 9

Matte tapping launder No. 3 hood system was observed most frequently. Based on approximately one hour of observations, the average opacity was 15 percent. Launder Nos. 2 and 4 had average opacities of 10 percent. Based on 14 minutes of observations the launder No. 5 hood system had an average opacity of 35 percent. Table 8-5 presents these results.

TABLE 8-3. SAMPLING SEQUENCING PHELPS-DODGE MORENCI, ARIZONA
 COPPER SMELTER MATTE TAPPING - NO. 5 REVERB

Date	Episode	EMB-004MMT			EMB-006MMT			EMB-008MMT		
		Ti	Mi	L	Ti	Mi	L	Ti	Mi	L
11/12/81	1257-1304	0.8	1	25						
	1334-							1	1	25
	1445-1453	1	1	25						
	1656-1703	1	1	25						
	1705-1709	1	1	25						
	1733-1740	1	1	25						
	1745-1752	1	1	25						
11/13/81	0829-0835	1	1	25						
	0836-0844	1	1	25						
	1213-1223				1	1	25			
	1502-1509				1	1	25			
11/14/81	0756-0806				1	1	25			
	0944-0950				1	1	25			
					1	1	25			
	1058-1106				1	1	25			
	1120-1127				1	1	25			
	1131-1135				1	1	25			
	1244-1248				1	1	25			
	1328-1337							1	1	25
	1402-1409							1	1	25
	1434-1441							1	1	25
	1449-1454							1	1	25
	1509-1513							1	1	25
	1602-1606							6	1	25
	1635-1639							1	1	25
11/15/81	0929-0935							1	1	25
	0945-0951							1	1	25
	1118-1123							1	1	25
	1140-1145							1	1	25

T_i is the fraction of the total duration of the i th tap or skim which was sampled.

M_i is the fraction of the normal ladle which was removed from the furnace during the observed i th tap or skim.

L , in tons, is the weight of a normal ladle of matte or slag as specified by the plant personnel.

TABLE 8-4. SAMPLING SEQUENCING
 PHELPS-DODGE MORENCI, ARIZONA COPPER SMELTER
 SLAG SKIMMING - NO. 3 REVERB

Date	Episode	EMB-003MSS			EMB-005MSS			EMB-007MSS		
		Ti	Mi	L	Ti	Mi	L	Ti	Mi	L
11/12/81	1556-1626	1	1	40						
	1717-1747	1	1	40						
11/13/81	1532-1602				1	1	40			
	1659-1706				1	0.3	40			
	1711-1733				1	1	40			
11/14/81	0854-0924							1	1	40
	1025-1057							1	0.5	40

TABLE 8-5. REVERBERATORY FURNACE NO. 5 - METHOD 9 OBSERVATIONS

Process Observed	Launder Number	Number of Events Observed	Average Opacity	Total Observation Time (Min/Sec)
Matte Tapping	2	7	10	55:00
Matte Tapping	3	7	15	66:00
Matte Tapping	4	7	10	42:00
Matte Tapping	5	2	35	14:00

TABLE 8-6. REVERBERATORY FURNACE NO. 5 - METHOD 22 OBSERVATIONS

Process Observed	Launder Number	Number of Events Observed	Time Emissions Observed (%)	Total Observation Time (Min/Sec)
Matte Tapping	3	1	100	6:38
Matte Tapping	4	1	82	5:00
Matte Tapping	5	1	100	5:33

Method 22

Fugitive emissions were observed escaping capture by launders No. 3 and No. 5 hood systems continuously. The hood system for launder No. 4 was observed for approximately five minutes. Emissions escaped capture 82 percent of the time. Table 8-6 presents these results.

Reverberatory Furnace No. 3 Slag Skimming (Lancing Emissions Not Included)Method 9

Based on over two hours of observations, the average opacity of emissions escaping capture by the launder No. 1 hood system was less than five percent. The average opacity of the emissions from launder No. 2 was also less than five percent. Table 8-7 presents these results.

TABLE 8-7. REVERBERATORY FURNACE NO. 3 - METHOD 9 OBSERVATIONS

Process Observed	Launder Number	Number of Events Observed	Average Opacity (%)	Total Observation Time (min/sec)
Slag skim	1	4	<5	122:00
Slag skim	2	2	<5	33:00

Method 22

Launder No. 2 was evaluated using Method 22 for approximately 30 minutes. Fugitive emissions were observed escaping capture by the hood system three percent of the time.

The visual emissions testing indicate each of the hoods for the matte handling systems on the No. 5 reverb perform equally as well. The system for tap bay No. 5 may be an exception to this with an opacity approximately three times greater than the others. Each of the three tests incorporated approximately equal fractions of the No. 5 bay and the reduced collection efficiency of this hood cannot be verified.

The performance of the skim bay hooding was much better than that of the tap bays as determined from both the visible and sampling data.

Examination of the data presented in Tables 8-1 and 8-2 does not show a strong dependence of the emission rate, mass of pollutant emitted per unit time, on production rate. Thus, the emission factors, mass of pollutant emitted per unit of production, are not constant and in some cases actually decrease with increasing production. A possible explanation for this situation is the strong dependence of the emission rate on the exposed surface area of the molten material and the time it is exposed. This type of dependence would result in reduced emission factors with increased flowrates of molten material. With this approach the exposed surface of molten material in the ladles would be a significant contributor with its contribution being inversely proportional to the matte or slag flowrate in the launder. Sampling was terminated when the flow of molten material stopped, thus emissions from a ladle of material waiting for transfer, were not addressed by this testing protocol.

APPENDICES

At the request of the Project Officer, a number of copies were published without the appendices which consisted of original field data sheets and raw, reduced data. This is one of those copies. Please contact the Project Officer if details of those data are required.