

TECHNICAL DATA IN SUPPORT OF REGULATIONS
FOR CONTROL OF SULFUR DIOXIDE EMISSIONS AT
ARIZONA COPPER SMELTERS
October 1975

I. Background

On July 27, 1972 EPA disapproved Arizona's control strategy for the attainment of the National Ambient Air Quality Standards (NAAQS) for sulfur oxides and granted an 18 month extension for the promulgation of regulations to include measures that would insure attainment of these standards.

The available ambient air quality data prior to May 1973 measured in the vicinity of the major sources of sulfur oxides within the state, the seven copper smelters, had been challenged in court and in public hearings. EPA therefore established a network of ground level monitoring sites for the collection of sulfur oxides data to be used in evaluating control strategies and determining the amount of control required of each smelter in order to achieve the standards.

The emission limitations in paragraph (e) of the proposed regulations are based on the use of the proportional model that assumes a direct relationship between source emissions and ambient air quality. Source emission data have been supplied by each of the smelters and the ambient air quality data used in the model was obtained from the EPA monitoring sites and from data collected by the smelter's monitoring networks and from data collected by the State of Arizona.

Emission limitations of paragraph (f) are based on an evaluation of the configuration of each smelter and on sulfur balance and operating data obtained directly from the smelter. Appendix A contains the results of an evaluation of the possible control techniques available to each smelter. Section V of Appendix A contains an evaluation of the amount of positive control possible through reasonably available retrofit control technology.

Under the provisions of applicable State regulations, each smelter has embarked on a control program to reduce the effect of their emissions on the ambient levels of sulfur oxides. These control programs include a wide range of permanent control measures and dispersion techniques. The amounts of positive control anticipated through these control programs range from approximately 42% reduction in emissions with production curtailment to well over 90% reduction in emissions with process

changes and sulfuric acid-producing facilities. The control programs are in varying stages of completion. The emission limits established in this document are based on the smelter configuration at the time the State implementation plan was submitted to EPA (January 31, 1972) and are based on the maximum production capacity of the smelter and current sulfur balance information obtained from each smelter.

The regulations contain 3 paragraphs relating specifically to control measures. Paragraph (d) pertains to the control of fugitive emissions.

Paragraph (e) establishes an emission limit that will allow attainment of the NAAQS. EPA has determined that in most cases this emission limit is not achievable through the application of currently reasonably available retrofit control technology but could be achieved through weak gas stream treatment process changes or permanent production curtailment. EPA is not now requiring process changes or permanent production curtailment but anticipates that as retrofit control technology improves this emission limit can be met.

Paragraph (f) provides for interim measures until such time as the emission rate of paragraph (e) can be met. Paragraph (f) establishes an emission limitation that can currently be met with reasonably available retrofit control devices (acid-producing facilities) and allows the use of dispersion techniques and other measures to avoid ground level concentrations in excess of the standards on an interim basis.

The methods used to determine the amount of control required and the emission limitations are included in this document.

II. Air Quality Data

EPA established monitoring stations in the vicinity of each of the copper smelters in Arizona in the late summer or fall of 1973. The purpose of these stations was to collect short term ambient air quality data to be used in the determination of required emission limitations. Both continuous monitoring systems and 24-hour bubbler sampling systems were installed. The location of the stations was selected to either approximate the location of potentially high concentration areas or to supplement the existing smelter and/or State networks. In many instances the availability of power or property access precluded locating in the desired area.

Several of the smelters also operate monitoring networks. Some of the networks have been in operation for several years (Douglas) while others are more recent (Hayden). All of the smelter companies have provided past data from their monitoring sites to EPA and several continue to submit data on a routine basis.

The State of Arizona also operates at least one monitoring site near each smelter.

Data from the EPA network and, where possible, from the smelter networks, has been summarized in Table 1. The highest two 3-hour and highest two 24-hour concentrations are included. The period of record available to EPA of individual smelter network data varied from only 4 months in the Hayden area to 21 months of data from several Phelps-Dodge stations*. The EPA stations were operational in the fall of 1973 and continued through October 1974. The continuous data is available through most of October 1974 and 24-hour bubbler data were obtained through October 1974 and in some cases a few November samples were taken.

III. Emission Reduction Requirements

The amount of control, or reduction in emissions required to meet the ambient air quality standards, is determined using the following relationship between ambient air quality levels and emissions:

$$100 \frac{A-B}{A-C} = \text{percent reduction required}$$

where A is measured air quality level
 B is the ambient air quality standard value
 C is the background level
 (considered to be zero in smelter locales)

and

$$\frac{(\text{current emissions})(100 - \text{percent reduction required})}{100} = \text{maximum allowable emissions}$$

The percent reduction in emissions required to meet all NAAQS is calculated for each smelter area and is also given in Table 1. This method assumes a direct relationship between the total plant emissions and the ambient SO₂ concentrations in the vicinity of the smelter. Such an assumption is not unreasonable where the smelter is the single source of SO₂ in the area. In the case of the Hayden area, where there are two smelters, some additional assumptions are required and are given below. The application of this formula to data from each area is given in subsequent paragraphs.

* Data is continuously supplied by the smelters, including KCC and ASARCO at Hayden, and the listings are available but not summarized or analyzed.

TABLE 1

Date	Concentration (ppm 3-hour average) ($\mu\text{m}/\text{m}^3$ 24-hour average)	averaging time (hours)	Reduction required to* meet standards (percent)
<u>Phelps Dodge/Ajo</u>			
11 Nov 1973	1.65	3	69.7
2 Nov 1973	1.35	3	63
1 Nov 1973	784	24	53.4
8 Jan 1974	662	24	44.9
<u>Phelps Dodge/Douglas</u>			
17 Jan 1974	3.81	3	86.9
8 Dec 1973	3.37	3	85.2
20 May 1974	1395	24	73.8
8 Dec 1973	1031	24	64.6
<u>Phelps Dodge/Morenci</u>			
10 Nov 1973	4.10	3	87.8
11 Feb 1974	3.51	3	85.8
21 Dec 1973	2335	24	84.4
14 Jan 1974	1502	24	75.7
<u>Kennecott and ASARCO/Hayden</u>			
20 Oct 1973	3.17	3	84
13 Oct 1973	2.67	3	82
4 Jun 1974	2.33	3	79
8 Nov 1973	2319	24	84
<u>Magma/San Manuel</u>			
12 Oct 1973	2.32	3	78.4
20 Oct 1974	1.98	3	74.9
14 Nov 1974	.39	24	64.1
12 Oct 1973	.36	24	61.1
<u>Inspiration</u>			
10 Sep 1974	4.43	3	88.7
12 Mar 1974	3.67	3	86.4
5 Nov 1974	2193	24	83.4
2 Nov 1974	1617	24	77.4

* Calculated from proportional rollback

The rollback or proportional model is not adequate for the purpose of determining the effect of certain dispersion techniques such as taller stacks or intermittent controls. It cannot take into account the fact that emissions may come from different heights and locations within the smelter, thus it cannot be used, for example, to evaluate the effect of changing the emission points of fugitive emissions from building emissions to venting them through a stack. Use of a diffusion model would be preferable to use of the rollback model in relating emissions to air quality, however most of the smelters are located in areas with elevated terrain features and current diffusion models do not, with precision, handle the effects of various topographic elements. Also meteorological variables in areas of rough terrain are not easily quantified. The meteorological input data for diffusion modeling must be extrapolated from existing National Weather Service stations located at considerable distances from the smelters, since complete data are not available locally. For these reasons it is not surprising that modeling results vary considerably with different modeling techniques and do not generally compare favorably with actual measured short term data. The rollback model was therefore accepted as containing fewer assumptions and as providing reasonable results for total source control.

Operating data were supplied to EPA by each smelter. These data contained average production figures and sulfur balance data as well as specifics for particular days of interest. In some cases actual emission data were supplied by the smelter, while in other cases emissions were calculated from the sulfur balance figures supplied.

In the subsequent paragraphs the calculations of the emissions that will achieve the NAAQS are discussed. All calculations are in terms of tons of sulfur and have been calculated for an averaging time of one day. The regulations refer to emissions in terms of pounds per hour averaged over a six hour period. This is required for this compliance testing program where 24-hour tests are impractical. Had hourly operating or emission data been available from the smelters, the calculations would have been based on the shorter averaging period. The variable nature of the smelting process is recognized and hourly data would have been preferable. However, use of the emission data for the same day as the air quality data provides as accurate a relationship as is available from past records.

A. Hayden, Arizona

There are two smelters in relatively close proximity at Hayden, Arizona, one operated by ASARCO, Incorporated and the other by the Kennecott Copper Corporation. In this discussion the first will be identified as ASARCO, the second as KCC.

EPA operated two continuous and four 24-hour bubbler SO₂ monitoring sites in the vicinity of the two smelters from mid-1973 until October 1974 when the bubbler sites were discontinued and the continuous monitors turned over to the State of Arizona.

The two smelters operate a Joint Control Center for meteorological and SO₂ monitoring and maintain 7 sampling sites in the Hayden vicinity.

High SO₂ concentrations have been recorded at all sites on occasion but the two sites where high concentrations most frequently occur are the Globe Highway Joint Control site and the monitoring site at Reese-Montgomery Ranch to the WNW of the smelter complex. The highest concentrations on record in the EPA office have occurred at the Reese-Montgomery Ranch site.

The highest 24-hour average concentration occurred on November 8, 1973 when the 24-hour bubbler sampler indicated a concentration of 2319 ug/m³. Based on the proportional rollback formula, this concentration, when compared to the primary NAAQS for SO₂, indicates a reduction of 84.3% is required in SO₂ emissions in order for the standard to be met in the Hayden area. On the 8th of November 1973 the emissions from the two smelters were as follows:

KCC	32.85 T/D sulfur
ASARCO	461 T/D sulfur

These numbers are based on actual daily estimates of emissions in the case of ASARCO and on average November sulfur balance data and actual daily production rates for KCC. They represent the best available information. Applying the 84.3% reduction requirement to the total emissions for that day yields a value of 77.8 T/D allowable sulfur emissions $((1 - .843)494 = 77.8 \text{ T/D S})$.

Each smelter has a different production capacity, has different SO₂ control systems, emits different quantities of SO₂ and is obviously located differently with respect to the sampling site. Also emissions come from different locations within the smelter complex and from different heights. These facts tend to make the use of the rollback formula and the assumption of a direct proportionality of emissions to ambient concentrations somewhat doubtful. Several attempts were made to find a suitable diffusion model for use in this situation where both the configuration of the smelters and their emissions and the meteorology

could be used to more accurately predict the ambient concentrations and the effect of various changes. In addition, a five day intensive field investigation was conducted in April 1975 to attempt to describe the input parameters to the model. The results of these efforts indicate that the currently available diffusion models do not accurately describe the behavior of the emissions from the two smelters in Hayden. The field investigation led to the conclusion however that the Globe Highway station is occasionally subject to high concentrations due in large part to fugitive or low level emissions and that while there may be fugitive emissions traveling as far as the Reese-Montgomery Ranch site, the concentrations there are probably primarily due to emissions from the stacks. Diffusion modeling produced concentrations that were not realistic based on actual measured data from the available sites. In general the modeling results were much lower than actual measurements unless adjustments were made for topography and with those adjustments, the results appeared to be unrealistically high. As a result, the proportional model or direct relationship of emissions and ambient concentrations appears to be the most reasonable representation. The rollback model required some adjustment to address the contribution from each smelter. This was done by apportioning the reduction requirements according to the maximum production capacity of each smelter. The amount of input sulfur at maximum concentrate feed rate for Kennecott is 1500 T/D at 30% S equals 450 T/D input S. For ASARCO the maximum concentrate feed rate is 2000 T/D at 29.4% S equals 588 T/D input S. Thus KCC would contribute about 43% of the uncontrolled sulfur emissions and ASARCO 57%. These same figures applied to the allowable emissions results in an emission rate of 34 T/D S limit applied to KCC and 44 T/D S limit for ASARCO in order to meet the primary standard.

Annual averages determined from the four bubbler sites indicate that less control is required to meet the annual average NAAQS than the 24-hour standard.

The short term 3-hour standard is 0.50 ppm or 1300 ug/m³. Data from Reese-Montgomery Ranch site supplied the highest 3-hour averages. A concentration of 3.17 ppm was recorded on October 20, 1973. Using the rollback formula a reduction of 84.2% is required to meet the 3-hour standard. KCC emissions on that day were estimated from average October sulfur balance data for KCC and the production rate on that day to be 97.6 T/D S. ASARCO emissions were supplied by the smelter and were 223 T/D S. Without controls the emissions would have been 307 T/D S from KCC and 321 T/D S from ASARCO. Applying the 84.2 % reduction requirement to the actual emissions results in an emission rate of 50.6 T/D S needed to meet the secondary standard. These emissions were again apportioned on the basis of the relative smelter capacity resulting in an allowable emission rate of 22 T/D S applied to KCC and a rate of 29 T/D S applied to ASARCO.

B. San Manuel, Arizona

The Magma Copper Company operates a smelter at San Manuel. They also operate an extensive monitoring network in the vicinity with locations as far away as Oracle and Reddington. Ambient air quality data were made available to EPA by the Magma Copper Company. Data were collected at monitoring sites in the vicinity of the smelter and the period of record used in this analysis was generally from February 1973 through November 1974. Additional data are available but have not been analyzed.

EPA collected data at four monitoring sites in the vicinity of this smelter from September 1973 until October 1974. Those data have been used in conjunction with the smelter's data to determine the SO₂ concentration distribution.

The emission limitation established to meet both the primary and secondary standards was determined using only measured SO₂ data and applying the rollback formula to determine the emission reduction requirements. Diffusion modeling results prepared by EPA, and also a modeling study completed for Magma Copper Company by Stanford Research Institute, were reviewed and an attempt was made to reconcile the modeling results with the measured data. Model predictions were quite good for 24 hour and longer averaging periods but did not compare well with short term concentrations.

High concentrations have been recorded at all stations within five miles of the smelter. The highest values were reported at the smelter's Townsite and Golf Course locations and the EPA Slag Pile site. On the 14th of November 1974 a concentration of 0.39 ppm 24-hour average was reported at the smelter's Golf Course station. This is the highest 24-hour average for the period of EPA's record.

Information was supplied by the Magma Copper Company for the actual production and emission rates on specific dates. These data were used to determine the emissions that could be allowed and still meet the NAAQS. On the 14th of November 1974 the total sulfur emitted to the atmosphere was 394 tons. Applying the rollback formula to the 24-hour measure concentration on that day results in a required of reduction of 64.1%. Reducing the emission rate on that day by 64.1% results in an emission rate of 141 T/D required to meet the primary standard.

The highest measured 3-hour concentration was 2.32 ppm measured at the Townsite location on October 12, 1973 and the next highest 1.98 ppm occurred at the EPA North Slag site on October 20, 1974. Calculations using rollback and applied to actual emissions on those days resulted in

the use of the October North Slag data to specify the allowable emission rate. On October 20th the total sulfur emitted was 306 tons. The proportional reduction requirement determined by comparing the 1.98 ppm to the .5 ppm standard is 74.7%. Reducing the 306 tons of emissions by 74.7% results in an allowable emission rate of 77.3 T/D ($306(1 - 0.747) = 77.3$). Thus, the 77.3 T/D emission rate is the one that must be met to achieve all NAAQS.

C. Douglas

The Phelps Dodge Corporation operates a smelter at Douglas, Arizona. They also operate an extensive monitoring network in the vicinity and have provided EPA all of the data from their network. EPA operated 3 stations in the vicinity from fall 1973 until October 1974. Data from both networks have been reviewed and form the basis for the emission calculations.

The smelter at Douglas is located in open relatively flat terrain. A number of modeling studies have been done for the Douglas area. Contrary to modeling studies for other smelters located in areas with elevated topographic features, modeling results here tend to underestimate the actual measured concentrations indicating that the model does not adequately account for the specific meteorological conditions that produce high ground level concentrations of SO_2 . It is also quite possible that short term emission data are not sufficiently accurate to allow realistic short term model predictions.

The highest reported short term concentrations in the Douglas area have been measured at the smelter's Pirtleville site. The maximum 3-hour concentration was 3.81 ppm measured on January 17, 1974. Using the rollback formula a reduction of 86.9% is required when this concentration is compared to the 3-hour NAAQS. Phelps Dodge Corporation supplied to EPA data concerning production and emission rates on specific dates. On January 17, 1974 the total sulfur emissions were listed as 597 tons. Applying the reduction requirement of 86.9% to this 597 T of S results in an allowable emission rate of 78.2 T/D of S to achieve the secondary NAAQS for SO_2 ($597(1 - .869) = 78.2$).

Similar calculations were made to determine the requirements needed to meet the primary standards. The highest 24-hour average concentration was also measured at the smelter's Pirtleville station on December 9, 1973. This concentration was 2437 ug/m^3 . Rollback indicates an 85% reduction requirement. Applied to the emission rate of 669 tons of sulfur on that day, the allowable emission rate is 100 T/D of sulfur.

Less reduction is required to meet the annual standard.

D. Morenci

The Phelps Dodge Corporation operates a smelter at Morenci. Ambient monitoring data are available from nine smelter monitoring sites and for a one year period from EPA monitoring sites. These data were used to develop the emission limitations.

This smelter is located in an extremely rugged terrain area. Monitors that are located less than two miles from the smelter may differ in elevation by nearly 1500 feet. The rugged terrain features and the possible effects of mountains and valleys on the meteorological model inputs resulted in a decision to use actual measured data.

The highest measured concentrations occurred at the smelter's monitoring location called Cadillac Point, and the highest reported 3-hour average of 4.10 ppm was measured on November 10, 1973. Comparing this concentration to the 3-hour secondary standard using the rollback formula results in a required emission reduction of 87.8%. Phelps Dodge Corporation supplied operating data for the smelter on specific dates from these data it was determined that the emission rate on November 10th was 725 tons of sulfur. Reducing this emission rate by the required 87.8% results in an allowable emission rate of 88.45 T/D of sulfur to meet the secondary NAAQS ($725(1 - .878) = 88.45$).

The highest 24-hour average concentration also occurred at Cadillac Point. The concentration was 1.29 ppm and was recorded December 22, 1973. Comparing this value with the primary standard yields a reduction requirement of 90.7%. An emission rate of 996 tons of sulfur was calculated from data supplied by the smelter for this data. A 90.7% reduction in emissions leaves an allowable of emission rate of 92.6 tons of sulfur to meet primary standard.

Less reduction is required in order that the annual standard be attained.

E. Ajo

The Phelps Dodge Corporation operates a smelter in Ajo. EPA established a monitoring network in 1973 composed of four 24-hour bubbler sites and two continuous SO₂ monitors. These sites were discontinued or turned over to the State in October 1974. The smelter has operated 4 stations with continuous monitors since mid-summer 1973. Data from all sites have been made available to EPA. These data were used to determine the allowable emission rates.

Diffusion modeling was attempted to provide a more accurate representation of the relationship between air quality levels and emissions than can be obtained through the use of the proportional or rollback model. Results were compared with actual measured data. Model predictions were generally lower than measured data except where topographic considerations were entered in the model calculations and those results appeared to be higher than might be anticipated. There did not appear to be a simple calibration or adjustment technique to apply to the model to compensate for the difference. For that reason, actual measured data was used.

The highest measured 3-hour concentration of 1.65 ppm was reported on November 11, 1973 at the South Tailings Pond Phelps Dodge monitoring site. The second highest concentration of 1.35 ppm was measured at the EPA Oxidation Pond site on the 2nd of November 1973.

Operating data for the smelter on specific dates was supplied by the Phelps Dodge Corporation and this data indicated emissions to the atmosphere of 132.3 tons of sulfur on the 11th of November and 49.2 tons of sulfur on the 2nd.

Using the rollback model a reduction in emissions of 69.7% would be required to meet the secondary standard on the 11th and 63% reduction required for the 2nd. Applying these values to the actual emission rates on those days resulted in allowable emission rates as follows:

$$11 \text{ Nov } 73: (1 - .697)132.3 = 40.1 \text{ T/D S}$$

$$2 \text{ Nov } 73: (1 - .63)49.2 = 18.2 \text{ T/D S}$$

The lower emission rate would of course apply and becomes the maximum emission rate allowable.

Reduction requirements to meet the 24-hour standard are based on the concentration of 784 ug/m^3 measured on the 1st of November 1973 at the EPA Oxidation Pond station. Using the rollback formula a reduction of 53.4% is required. Emissions on that day were calculated from the actual concentrate feed processed and average sulfur balance data, and totalled 65.96 tons of sulfur emitted to the atmosphere. The allowable emissions to meet the primary standard are then equal to 30.7 T/D sulfur $((1 - 0.534)65.96 = 30.7)$.

Annual average concentrations resulted in lower emission reduction calculations.

F. Miami

The Inspiration Copper Company operates a smelter at Miami. Air quality data in the area are limited to the data from the EPA smelter monitoring sites and from the State monitoring sites. Only the EPA monitoring data were used in this analysis. EPA operated one continuous monitor and 3 bubbler samplers in the vicinity of Miami from approximately October 1973 through October 1974. The sampling site at Jones Ranch was considered to be in an area where stack emissions would result in maximum concentrations and the measured data from that site are used to establish emission limits.

This smelter is located in an area of extremely complex topography. Diffusion modeling results did not compare favorably with actual measured data due in part to the lack of appropriate emission and meteorological input data.

The highest measured 3-hour concentration was reported on September 10, 1974. This was 4.43 ppm. The second highest value, 3.67 ppm, occurred on March 12, 1974.

Production data were made available by the smelter for specific dates and average monthly input sulfur data were used to calculate emission requirements.

Based on the high 3-hour average concentration measured September 10, 1974, the rollback determined reduction required is 88.7%.

Applying this figure to the September 10 concentrate change rate of 546.5 tons and the average September sulfur content of the concentrate (21.82%) results in an allowable emission rate of 13.5 T/D S ($119(1 - .887) = 13.5$) required to meet the secondary standard.

The highest 24-hour average of 2193 ug/m³ occurred on November 5, 1974. A rollback reduction requirement of 83.4% is indicated from this value. Emissions on this date were determined from the concentrate processed, average November sulfur content of the concentrate and an estimate of the amount of sulfur removed through limited operation of the new acid plant. Based on information supplied by the smelter, approximately 57% of the furnace and converter off-gases were processed

through the acid plant. An efficiency of 99.5% was assumed for the acid plant. Process losses were estimated at 7% of the input sulfur (5% in slag and 2% in acid sludge). Total emissions were calculated from total input sulfur:

$$\begin{array}{rcl}
 436.9 \times 24.45\% & = & 106.82 \\
 \text{process loss} & - & \underline{7.48} \\
 & & 99.34 \\
 \\
 \text{processed in acid plant} & \times & \underline{.57} \\
 & & 56.62 \\
 \\
 \text{converted to acid} & & 56.34 \\
 \\
 \text{emitted to atmosphere} & 99.3 - 56.34 = & 42.96
 \end{array}$$

The reduction required to meet the primary standard is 83.4%, thus:

$$\begin{array}{rcl}
 42.96 & \text{emissions November 5} & \\
 - \underline{35.83} & \text{reduction required} & \\
 7.13 & \text{T/D emissions allowable} &
 \end{array}$$

The estimated annual average concentration of sulfur oxides indicates that less control is required to meet the annual average NAAQS.

IV. Emissions allowable through use of RACT

The following paragraphs contain the determination of the amount of emissions that can be controlled through the installation of a sulfuric acid producing facility designed to process all gaseous emissions from the converters in each smelter. The calculations are based on the processes used and the stacks in existence on January 31, 1972 and the latest information on production rates and sulfur balance as provided by the individual smelter.

All calculations are based on the maximum operating capacity of the smelter in terms of daily concentrate feed rate. The acid plant size required to process all converter emissions at the maximum production rate is determined and used as a basis for calculating the allowable emissions with this control system. Where an acid plant is used for the treatment of other than converter emissions it is assumed that this will continue in operation and will operate at the same efficiencies as prescribed for converter off-gases.

The emission rates determined in the subsequent paragraphs are based on the utilization of a double absorption acid plant where no acid plant is currently installed or where such an acid plant exists. The assumed conversion efficiency for such a plant is 99.5%. Where a smelter has installed a single absorption acid plant this plant has an assumed conversion efficiency of 97%. Emission rates from these plants have been set at 650 ppm for the double absorption plant and 2600 ppm for the single absorption plants.

Studies of existing operational sulfuric acid plants indicate that the efficiency of conversion of SO_2 to SO_3 decreases due to catalyst deterioration between screenings. EPA tests conducted on two single absorption acid plants indicate that with a twelve-month catalyst cleaning cycle the difference in emissions due to deterioration appears to be of the order of magnitude of 30 percent.¹ The value of 30 percent was calculated as the difference between the performance of two plants--one at each end of the catalyst cycle. This difference in emissions reflects not only catalyst deterioration but other factors as well, such as a difference in emissions due to design or construction variations between the two acid plant vendors. More recent results of tests on a double absorption acid plant indicate no deterioration.² However, discussions with an acid plant designer indicated that up to a 10 percent increase in emissions was expected before renewal of the catalyst.³ Catalyst deterioration, therefore, has to be taken into account when predicting the expected emissions concentration from an acid plant.

¹Background Information for New Source Performance Standards; Primary Copper, Zinc and Lead Smelters, Vol 1: Proposed Standards, EPA, OAQPS, RTP NC, October 1974, p. III-3.

²Ibid, p. VI-19.

³Ibid, p. VI-20.

The typical conversion efficiency for a single absorption acid plant at the beginning of the catalyst cleaning cycle is 97 percent. Although, as noted above, the conversion efficiency can deteriorate between catalyst cleanings, it is reasonable to expect no more than a 10 percent change.

The overall acid plant efficiency also varies with the volumetric flow rate and the sulfur dioxide concentration of the gas stream to the acid plant. EPA tests indicate instantaneous sulfur dioxide emission concentrations may vary from 1,000 ppm to 7,000 ppm during normal operating conditions due to these flow rate and gas stream concentration variations. These tests indicated that, by providing an allowance of 10-20% over the vendor's guaranteed emission concentration, and averaging the concentrations over a 6-hour period, the average emission concentration will be within specified limits.⁴

Increasing the averaging time beyond six hours does not significantly affect the average emission concentration. A 10% allowance for catalyst deterioration and a 20% allowance for variations in input SO₂ concentrations and volumetric flow rates increases the allowable emission concentration from the acid plant from the vendor guarantee of 2000 ppm to 2600 ppm. This allowance is reflected in the emission rates established in paragraph (f) of the regulations. Similarly the allowable emissions for a double absorption acid plant are increased from 500 to 650 and the corresponding efficiency is assumed to be 99.5%

The allowable emissions after the installation of an acid producing facility of sufficient capacity to process all converter emissions were calculated according to the following general formulae:

- a. Calculation of total input sulfur that can be processed through acid plant operating at maximum capacity:

$$\text{acid plant capacity} \div (98/64) = \text{daily tonnage SO}_2 \text{ converted to H}_2\text{SO}_4$$

$$\frac{\text{SO}_2 \text{ converted to H}_2\text{SO}_4}{\text{acid plant efficiency}} = \text{tons SO}_2 \text{ daily to acid plant}$$

$$\frac{(\text{ratio S to SO}_2)(\text{tons SO}_2 \text{ to acid plant})}{(\text{percent of SO}_2 \text{ into smelter emitted by converters})} = \text{total sulfur input to smelter that can be processed at maximum capacity of acid plant}$$

⁴Ibid, p. 4-7.

b. Method of calculating total plant emission limitation

$$\text{Emission limit} = 2(I \times (R+F)) + A$$

where I = total sulfur input into plant at maximum design capacity of acid plant

R = fraction of total sulfur emitted from reverberatory furnaces

F = fraction of total sulfur emitted as "ground smoke" or fugitive emission

A = allowable SO₂ emissions from acid plant and is determined by subtracting the SO₂ in H₂SO₄ produced from the total SO₂ input

The emissions calculated in this fashion allow for all reverberatory and fugitive emissions to be released through a stack serving the facility. The requirements of paragraph (d) are presumed to have been met in this calculation and the assumption here is that all fugitive emissions will be vented to a stack. In reality it is doubtful that all fugitive emissions can be so vented and the emission limit thus calculated is therefore higher than what will in fact be emitted from the stacks. The amount of this difference varies with the percentage of total input sulfur emitted as fugitive and the amount that will be controlled or vented to a stack in accordance with paragraph (d) of the regulation. An allowance of 5% of the input sulfur is made in the subsequent calculations for the fugitive emissions vented to a stack. Estimates of losses from buildings are not included.

The percentage of total sulfur emitted from the converters and reverberatory furnaces, the percentage emitted as fugitive and the amount of sulfur lost in the process such as in slag, blister copper or scrubber sludge were all based on information provided by each smelter or by the smelter owner. It is recognized that these are estimates and may vary from day to day, and certainly may vary from hour to hour. This makes it difficult to relate these estimates to the hourly average emission limitation established in paragraphs (e) and (f) unless assumptions are made that the sampling time for compliance testing and the allowances that have been made by including fugitive emissions, by use of a conversion efficiency in the acid plant less than what a vendor would normally guarantee, all provide an increase in the emission limit that mask nearly all the large fluctuations that might be expected over the short time periods.

The subsequent paragraphs discuss the calculations and emission rates determined for each smelter where the current operating procedures and installed control equipment are not sufficient when operating at design specifications to meet the emission limitations required to achieve the NAAQS.

The Inspiration Copper Company smelter at Miami has been completely redesigned and treatment of all electric furnace and converter off-gases should provide sufficient control to enable them to meet the specified emission limit.

The Kennecott smelter at Hayden operates a double absorption acid plant to process converter and roasting off-gases and currently available emission data indicate they can operate well within the specified emission limitation.

The Phelps Dodge smelter at Ajo operates an absorption system for weak gas streams and with this system the emissions will be within specified limits.

The remainder of the smelters will need some control in addition to the installation of an acid plant to process converter off-gases. For these smelters the regulations provide an alternative to meeting the emission limits by a specified time. This alternative allows the smelter to make application for use of such supplementary control systems as may be required to meet the NAAQS until such time as the control of weak gas streams becomes reasonably available. A condition for the approval of such supplementary systems is the installation and operation of an acid producing facility designed to process all converter off-gases. The following paragraphs specify the emission limits from such facilities. Where a smelter has additional acid producing facilities to accommodate other than converter off-gases, it is required that these remain in operation, and the emission limits include the current reduction from such facilities.

The data supplied by each smelter included maximum tons per day of concentrate processed, average sulfur content of the concentrate and estimated average sulfur balance data including the percentages of sulfur emitted from the converters, roasters and reverberatory furnaces as well as process losses and the amount of sulfuric acid produced. The estimated amount of fugitive emissions varied greatly from smelter to smelter and most smelters indicated the figures were only gross approximations. For the purposes of the calculations of emissions allowable after installation of an acid producing facility and assuming most fugitive emissions are vented to a stack, a figure of 5% of the input sulfur was selected as being representative of the vented fugitive emissions. The emissions from the converters, roasters and reverberatory furnaces were then adjusted to account for this 5% fugitive emission. The adjustment was proportioned to each source according the percentage of the total emissions contributed from each source.

A. ASARCO/Hayden

1. Operational data from ASARCO/Hayden smelter

maximum production rate	
(concentrate feed rate)	2000 T/day
percent sulfur concentrate (average)	29.4%
input sulfur at maximum production rate	588 T/day

2. 1973 Average sulfur balance data

<u>Emissions</u>	<u>% input sulfur</u>	<u>tons/day at max. production</u>
converter	28.2	165.7
reverbertory furnaces	16.2	95.0
roasters	23.3	136.9
fugitive	5.0	29.4
Process Losses		
slag, dust, blister	3	18
Converted to acid	24.4	143
TOTAL	100.1	588

3. Acid plant capacity required to process all converter off-gases:

Total converter off-gas = percent of input converted to H_2SO_4 plus percent converter emissions (24.4 + 28.2)

Total sulfur available from converter off-gases = 52.6% (588 T/day S) = 309.3 T/D S

Assume all S emitted as $\text{SO}_2 = 618.6 \text{ T/D } \text{SO}_2$

Acid plant capacity required to process all converter off-gases with an acid plant conversion efficiency of 96.1%:

$$618.6 \times .961 \times \frac{98}{64} = 910.3 \text{ T/D H}_2\text{SO}_4$$

A 910.3 T/D acid plant will convert 297.2 T/D S to H_2SO_4

4. Allowable emissions from acid plant:

$$\begin{aligned} A_E &= \text{amount of input sulfur not converted to acid} \\ &= 309.3 - 297.2 \\ &= 12.1 \text{ T/D S} = 24.2 \text{ T/D SO}_2 \end{aligned}$$

5. Total allowable emissions

$$\begin{aligned} E_{\text{ASARCO}} &= 2(\text{total emission from reverberatory furnace} + \text{emissions} \\ &\quad \text{from roasters} + \text{fugitive emissions} + \text{acid plant} \\ &\quad \text{emissions}) \\ &= 2(95.0 + 136.9 + 29.4 + 12.1) \\ &= 2(273.4) = 546.8 \text{ T/D SO}_2 \end{aligned}$$

$$546.8 \times \frac{2000 \text{ lbs}}{24 \text{ hrs}} = 45,567 \text{ lbs/hr}$$

B. Magma Copper Co., San Manuel

1. Operational data

Estimated maximum concentrate feed rate	3150 T/D
Average sulfur content of concentrate	32%
Input sulfur at maximum feed rate	1008 T/D

2. 1973-74 Sulfur Balance

<u>Emissions</u>	<u>% of input sulfur</u>	<u>tons/day at max. prod. rate</u>
converters	61.8	623.4
reverberatory furnaces	29.4	295.9
fugitive emissions	5.0	50.4
Process Losses		
slag & blister	3.8	38.2

3. Acid plant capacity required to process all converter off-gases with acid plant conversion efficiency of 96.1%.

SO_2 converted to acid = acid plant efficiency x (tons of SO_2 from converters - sulfur removal in scrubber)

4 tons/day of sulfur is removed in scrubbing process.

SO_2 converted to acid = $.961 \times 2(623.4 - 4)$
= $.961 \times 2(619.7)$
= 1190.5 tons/day

Acid plant capacity = Tons SO_2 converted x ratio of H_2SO_4 to SO_2
= $\frac{98}{64} \times 1190.5$
= 1823 Tons per day acid plant capacity

4. Allowable emissions from acid plant (A_E)

A_E = amount of input SO_2 not converted to acid
= input from converter - amount converted and removed
= $1246.8 - (8 + 1190.5)$
= 48 Tons/day SO_2 allowable emissions from acid plant.

5. Total allowable emissions:

$$\begin{aligned} E_{\text{MAGMA}} &= 2(\text{total sulfur emitted from reverberatory furnaces} + \\ &\quad \text{fugitive emissions} + \text{acid plant emissions}) \\ &= 2(295.9 + 50.4) + 48.3 \\ &= 2(346.3) + 48.3 \\ &= 741 \text{ T/D SO}_2 \end{aligned}$$

$$741 \times \frac{2000 \text{ lbs}}{24 \text{ hrs}} = 61,750 \text{ lbs/hr}$$

C. Phelps-Dodge/Morenci

1. Operational data

maximum production rate (concentrate feed)	2778 T/day
percent sulfur in concentrate	38.46%
input sulfur from concentrate	1,068.4

2. Sulfur balance data (as of 1974)

<u>Emissions</u>	<u>% of input sulfur</u>	<u>tons/day at max. prod. rate</u>
converters	47.9	511.7
reverberatory furnaces	26.9	287.4
fugitive	5.0	53.4
roaster acid plant	0.8	8.5
Process Losses		
slag & blister	2.35	25.1
roaster acid sludge	0.42	4.5
Sulfur converted to H ₂ SO ₄	16.62	177.6

An additional 20 Tons/day of sulfur is input directly to the converters in scrap increasing the total emissions from the converters to 531.7 T/day.

3. Acid plant capacity required to process all converter off-gases.

efficiency of a single absorption acid plant = 96.1%

SO₂ converted to acid = acid plant efficiency x tons of SO₂ available

SO₂ converted to acid = .961 x 2(531.7 - 8.5 T/day to sludge)

SO₂ converted to acid = .961 x 2(523.2)
= 1005.6

Acid plant capacity = $\frac{98}{64} \times 1005.6 = 1539.8 \text{ T/D}$

4. Allowable emissions from acid plant (A_E)

A_E = amount of input SO₂ not converted to acid
= 1068.4 - 1005.6
= 62.8 T/D SO₂

5. Total allowable emissions

E_{MORENCI} = 2(total sulfur emitted from reverberatory furnaces
and as fugitive + roaster acid plant emissions)
+ allowable emissions from converter acid plant (A_E)

= 2(287.4 + 53.4 + 8.5) + 62.8
= 761.4 T/D SO₂

$761.4 \times \frac{2000 \text{ lbs}}{24 \text{ hrs}} = 63,450 \text{ lbs/hr}$

D. Phelps-Dodge/Douglas

1. Operating data

maximum production rate (concentrate feed)	2368 T/day
average sulfur content of concentrate	37.93%
input sulfur at max. prod. rate	898.2 T/day

2. Sulfur balance estimates

<u>Emissions</u>	<u>% of input sulfur</u>	<u>tons/day at max. prod. rate</u>
converters	38.72%	347.8
reverberatory furnaces	8.34	74.9
roasters	45.58	409.4
fugitive	5.0	44.9
Process Losses (slag, blister, etc.)	2.36	21.2

3. Double contact acid plant required to process sulfur emitted from converters.

Estimated efficiency of double contact acid plant = 99.5%
 SO_2 converted to acid = acid plant efficiency x tons
 SO_2/D from converters
= $.995 \times 2(347.8)$
= 692.1 T/Day

Acid plant capacity = tons SO_2 converted x ratio H_2SO_4 to SO_2
= $692.1 \times \frac{98}{64}$
= 1059.8

4. Allowable emissions from acid plant

A_E = amount of SO_2 not converted to H_2SO_4
= $695.6 - 692.1$
= 3.5 T/D

5. Total allowable emission rate

$$E_{\text{DOUG}} = 2(\text{total sulfur emitted from roasters, reverberatory furnaces and as fugitive}) + \text{allowable acid plant emissions } A_E$$

$$= 2(409.4 + 74.9 + 44.9) + 3.5$$

$$= 2(529.2) + 3.5$$

$$= 1061.9 \text{ T/Day SO}_2$$

$$1061.9 \times \frac{2000}{24} = 88,490 \text{ lbs/hr}$$

V. Designated Liability Area

A designated liability area is defined as the geographic area within which emissions from a source may significantly affect ambient air quality. A simplified modeling approach was used to determine the extent of the area surrounding each smelter where violations of the standards could conceivably occur. No attempt was made to incorporate terrain effects. From this model Figure 1 was developed which relates the emission rate of the source to the radius of the area within which exceedances of the standard can be expected. The radius defines the designated liability area as distance from the stack (or stacks) serving the facility. Based on Figure 1, the radius of the designated liability areas for each source is as follows:

	<u>Emission Rate</u>	<u>Radius</u>
ASARCO/Hayden	23 T/hr	10 miles
MAGMA/San Manuel	31	15 miles
PD/Morenci	32	15 miles
PD/Douglas	44	22 miles

For the purposes of application to use supplementary control systems an "isolated source" is defined as a source that can and will assume legal responsibility for all violations of the applicable national standards in the designated liability area.

These designations should apply as long as the existing SO₂ sources in each area remain the only SO₂ sources. Should new sources locate in these areas, the designated liability area will be subject to re-evaluation.

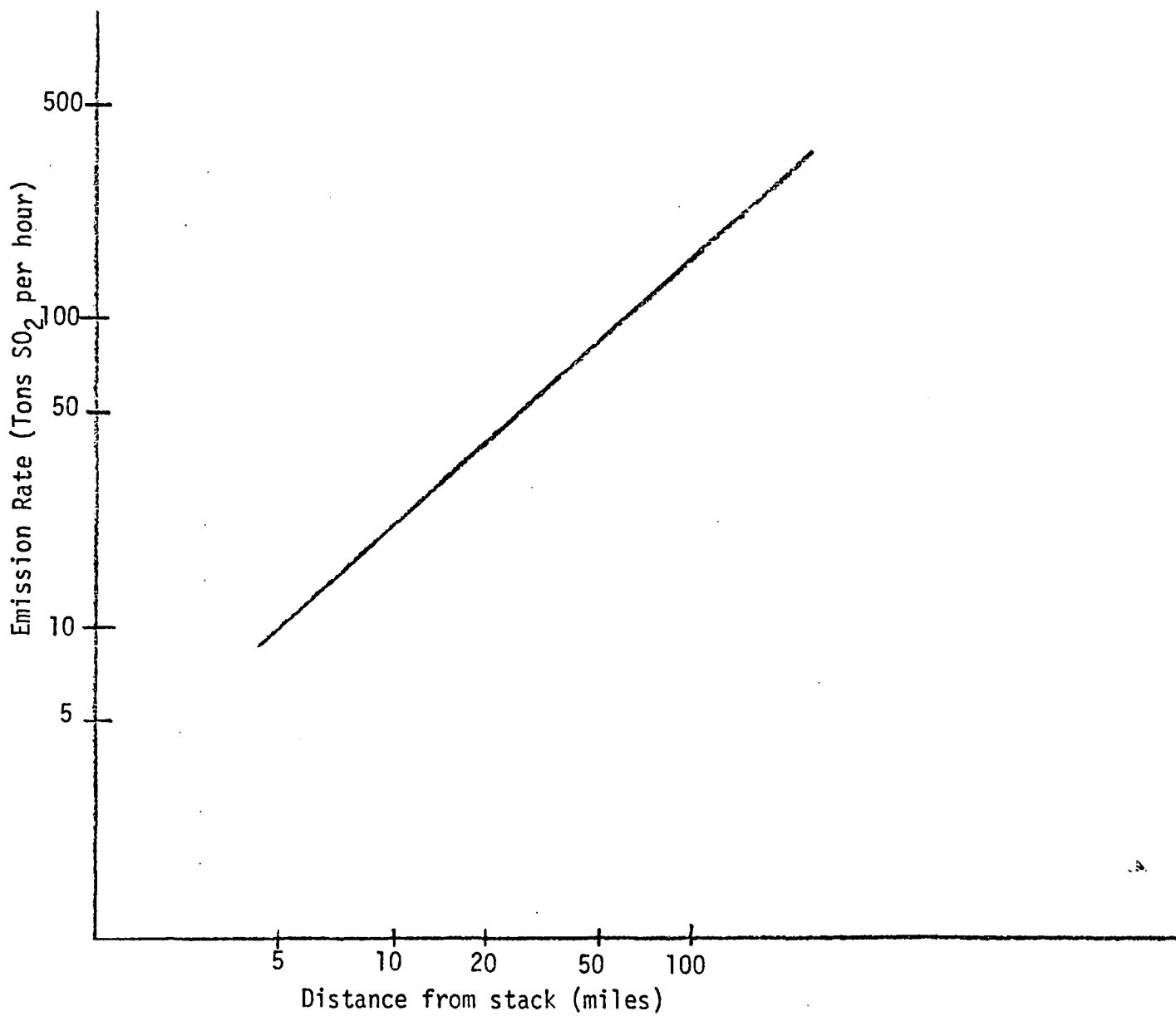


FIGURE 1. Radius of Designated Liability Area