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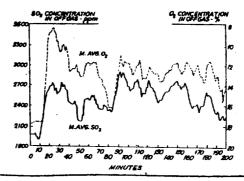
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54) Titre: SULFIDE ROASTING WITH LIME.

(57) Abrégé :

Metalliferous sulfides and arsenides are suspension roasted at a temperature between 600°C and 750°C in a reactor space which has finely divided lime substantially uniformly suspended throughout the reactor space to capture substantially all the oxides of sulfur and arsenic generated by the roasting reactions. Capture of the oxides of sulfur and arsenic is further improved by maintaining a minimum free oxygen content in the offgas.



## SULFIDE ROASTING WITH LIME

## Field of the Invention

The present invention relates to the roasting of metalliferous sulfides and arsenides, and more particularly, to the suspension roasting of metalliferous sulfides while minimizing emission of sulfur and arsenic oxides.

10 Prior Art

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Metalliferous sulfides ores or ore concentrates must frequently be roasted to facilitate subsequent processing for metal recovery. For example, many gold ore deposits exist as oxidized and sulfide fractions. The oxidized portions can be directly processed by known means, e.g. cyanide leaching, but the sulfide portion is often refractory to such processing and must be oxidized by roasting, aqueous oxidation at superatmospheric temperatures and pressures or bacterial oxidation. Aqueous oxidation can be uneconomical depending on the grade of the ore and bacterial oxidation requires long treatment times which increases costs by introduction of

Roasting refractory gold ores is both rapid and cost effective but steps must be taken to minimize sulfur and arsenic oxide emissions. Most roasting facilities, particularly in the U.S., must be equipped with acid plants or scrubbers in order to capture sulfur dioxide before it is released to the atmosphere. Acid plants require large capital expenditures and can present operational inefficiencies if the offgas has low sulfur dioxide concentrations. In addition to capital costs and operational inefficiencies, nearby markets for the generated acid are essential because sulfuric acid markets

large volumes of low grade waste sulfate solutions.

are sensitive to transportation distances. Scrubbing, particularly wet scrubbing, presents problems in disposing of the sludge so generated.

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Metals", M. Jennings, Ed., TMS, 1991 and entitled "Time Roasting of Refractory Precious Metal Ores" discloses a process for batch roasting a mixture of refractory gold ore and lime in a fixed bed over which an oxidizing gas is passed. Taylor et al teach that their process is kinetically sensitive, depending upon the rate of sulfide oxidation and the rate of sulfation of the lime. Although the Taylor et al process works well on a laboratory scale, commercial considerations require a continuous process which can treat large quantities of ore or ore concentrates in short periods while minimizing sulfur dioxide emissions.

### Description of the Invention

Particulate metalliferous sulfides and/or arsenides and lime are introduced into a reactor space. The reactor 20 space is maintained at a temperature between about 500°C and 800°C. The sulfides and/or arsenides and lime are suspended in the reactor space by passing a gas therethrough. A free oxygen-containing gas is supplied to the reactor space to oxidize the sulfides and/or arsenides 25 to metalliferous oxides and oxides of sulfur and arsenic. The lime is added to the reactor space in amounts substantially stoichiometrically sufficient to react with the oxides of sulfur and arsenic and the lime is sufficiently finely divided to be substantially 30 homogeneously suspended throughout the entire reactor space whereby the suspended lime substantially completely reacts with and captures the oxides of sulfur and arsenic.

## Description of the Drawings

Figure 1 is a graph showing the inverse correlation of the concentration of sulfur dioxide in the offgas versus the oxygen content in the offgas. In the graph in Figure 1 the oxygen content of the offgas is inverted to more clearly show the inverse correlation.

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Figures 2 to 4 schematically depict three types of suspension roasters that can be used to roast metalliferous sulfides in accordance with the process of the present invention.

#### Detailed Description of the Invention

The process in accordance with the present invention will be described in conjunction with roasting of refractory gold ores but is not limited thereto as will become apparent to those skilled in the art. Minor modifications may be necessary to roast other metalliferous sulfides but such modifications are clearly within the skills of a practicing artisan. Furthermore, as used herein the term "lime" refers to calcium oxide, limestone or hydrated lime.

Gold frequently occurs in ores which contain sulfides such as pyrites, pyrrhotite, arsenopyrite or nonferrous sulfides. The gold values may or may not be present as sulfides but are distributed throughout the other sulfide minerals that are present in the ore. The gold values must be liberated from such sulfide minerals before the gold values can be recovered by further processing, such as leaching with cyanide solutions. Carbonaceous materials are also frequently associated with gold ores and interfere with the leaching process by prematurely adsorbing gold values which have already been dissolved. Elimination of such carbonaceous materials by roasting, therefore, further increases the efficiency of subsequently hydrometallurgical processing.

The process in accordance with the present invention relies on suspension roasting to provide a continuous roasting process with high throughput rates. roasting connotes that ore or ore concentrate particles are suspended by flowing gases. Accordingly, the gold ore must be sufficiently comminuted in order to be suspended by flowing gases. Ore concentrates, i.e. sulfide or arsenic minerals which have been concentrated by physical means, such as magnetic separation and/or flotation, are generally sufficiently finely divided so that further. comminution is rarely required. If the ore is to be roasted without prior concentration, the ore should be crushed and ground by conventional methods to provide a particle size distribution of about 100% minus 10 U.S.S. mesh, advantageously about 80% minus 48 U.S.S. mesh. Although very finely divided ore or ore concentrates can be roasted more rapidly, efficient subsequent processing may require that the ore or ore concentrate be somewhat coarse or that very finely divided roasted ore or ore concentrates be agglomerated after roasting.

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Particulate gold ore or ore concentrates and lime are fed into a heated reactor space through which a gas having a sufficient velocity to suspend the particulate feed material and to disperse the lime uniformly throughout the reactor space is passed. A free oxygencontaining gas, i.e. air, oxygen-enriched air or combustion gases containing free oxygen, is introduced to oxidize the mineral sulfides or arsenides to the corresponding metal oxide and oxides of sulfur and arsenic which react with and are captured by the lime. Roasting carried out in accordance with the present invention insures that at least about 90%, and advantageously 95% or more, of the oxides of sulfur and arsenic are captured by the lime.

An important feature of the present invention is that the lime which is introduced into the reactor spaces be added in amounts substantially sufficient to react stoichiometrically with the sulfur dioxide released during roasting and that the lime be sufficiently finely divided 5 so that it can be substantially homogeneously suspended throughout the entire reactor space regardless whether the ore or ore concentrate is present as a dense fluidized bed or as a circulating fluid bed as described hereinafter. If substantially all the oxides of sulfur and arsenic are 10 to be captured before being released to the atmosphere, it is apparent that sufficient amounts of lime must be present to react with and capture the generated oxides of sulfur and arsenic. Beyond the bare stoichiometric minimum required, additional amounts of lime may be 15 required depending upon the particle size distribution of the lime and the condition of roasting both of which can effect the surface area of the lime which is as important as the actual weight of lime added to the reactor. is not obvious is that the lime be sufficiently finely 20 divided so that it can be uniformly distributed throughout the reactor space. When the lime is uniformly distributed throughout the reactor space, a number of factors which influence the reaction between the oxides of sulfur and arsenic and lime are maximized thereby increasing the 25 overall efficiency of the removal of oxides of sulfur and arsenic from the offgas. Suspension of the lime throughout the reactor space insures that a maximum of the lime's surface area will be exposed to the flowing gases thereby significantly increasing the potential for 30 reaction with the oxides of sulfur and arsenic contained in the flowing gases. This is particularly important inasmuch as the sulfur dioxide-lime and arsenic oxide-lime reactions are primarily gas-solid type reactions. dispersion of lime throughout the reactor space maximizes 35

the time the gases containing oxides of sulfur and arsenic are exposed to the lime which insures more complete reaction. If the lime were retained solely within the bed of a dense phase fluid bed reactor or in the bed of a rotating kiln or the like, the time of contact between the lime and the oxides of sulfur and arsenic can be one half or less as compared to that when the lime is suspended throughout the reactor space.

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In order to insure that the lime be substantially uniformly or homogeneously distributed throughout the reactor space, the lime should have a particle size distribution of about 100% minus 325 U.S.S. mesh and advantageously about 80% minus 400 U.S.S. mesh. In most instances, the average particle size of the lime will be significantly less than the average particle size of the metalliferous sulfides. It has been found that hydrated lime because of its hydrated water content and its inherently small particle size (i.e. at least about 75% minus 200 USS mesh), and hence large surface area, provides the best overall results. In addition to its fine particle size and enormous surface area, the fresh surfaces produced by dehydration of the hydrated lime during roasting also increase its reactivity. calcined calcium carbonate can also be used but must be comminuted to provide the particle size distribution described hereinbefore. When using calcined lime better results are obtained if lime has been calcined at lower temperatures because lime calcined at higher temperatures is significantly less reactive than lime calcined at lower temperatures.

Particulate sulfides and finely divided lime are introduced, either as a mixture or separately, into a reactor space heated to a temperature between about 500°C and 800°C, advantageously between about 600°C and 750°C. Lower or higher roasting temperatures can be employed but

lower temperatures provide slower roasting reactions and lower throughput rates while higher temperatures can cause mechanical problems, such as sticking, and can be less energy efficient. Depending upon the sulfur content and the organic carbon content of the feed material, roasting may be autogenous or require exogenous heat. If exogenous heat is required such heat can be supplied by heating the suspending gas, either indirectly or more efficiently directly by combusting a fuel with the suspending gas. Thermal efficiency is improved by recovering heat from the offgas whether direct or indirect heating is employed.

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A free oxygen-containing gas must be supplied to the reactor space to oxidize the particulate sulfide minerals. Air, oxygen-enriched air or combustion gases containing free oxygen can be employed. Whatever the source of the free oxygen-containing gas, sufficient oxygen must be present to react stoichiometrically with the sulfides and arsenides to form the corresponding metal, sulfur and arsenic oxides. However, it has been found that large excesses of free oxygen in the offgas are highly desirable in insuring substantially complete capture of the generated sulfur dioxide. The amount of sulfur dioxide in the offgas is inversely correlated with the oxygen content in the offgas as shown in Figure 1. A certain amount of excess oxygen is needed to promote the conversion of SO2 to SO3. The free oxygen also reacts and eliminates most, if not all, of any carbonaceous material associated with the ore or ore concentrates. Roasting can also oxidize and volatilize any arsenic associated with the ore and the volatilized arsenic oxide is also captured by the lime.

In Figure 1 the volumetric concentration of free oxygen is inversely plotted as a moving average against time as a dotted line which the volumetric concentration of sulfur dioxide is directly plotted as a moving average against time as a solid line. Reference to Figure 1

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clearly demonstrates a high inverse correlation between the free oxygen content and the sulfur dioxide content in the offgas. In view of the relationship shown in Figure 1, it is advantageous to maintain the free oxygen content of the offgas at a minimum of at least about 3%, by volume, and more advantageously at least about 8%, by The formation of calcium sulfate from calcium volume. oxide, sulfur dioxide and oxygen at the roasting temperatures is quite energetic -- a Gibbs energy of formation of about -55 Kcal/per gram mole. This reaction is sufficiently energetic as to cause localized fusion of the calcium sulfate which can produce adverse effects such as reduction of surface area by the fusion itself and/or by agglomeration of the lime particles, both of which processes diminish the activity of the lime. during test runs agglomerated nodules of crystalline calcium sulfate (CaSO4, or anhydrite) were observed. believed, although the invention is not limited thereto, that by having a high free oxygen content in the offgas sufficient oxygen is provided for the oxidation of sulfur dioxide and the greater amounts of free oxygen insure that the sulfur dioxide concentration is sufficiently low to minimize any problems associated with localized fusion of calcium sulfate.

High throughput rates and completeness of roasting are best realized by using a suspension type reactor which may be one of the types shown in Figures 2 to 4. Other types of reactors, such as rotary kiln, can be employed if provisions are made for insuring that the lime is suspended throughout the reactor space. A rotary kiln equipped with flights for lifting the finely divided lime to near the top of the kiln where upon being released it falls through the reactor space can be employed but is not nearly as efficient the suspension type reactors shown in Figures 2 to 4.

Figure 2 depicts a stationary or dense fluid bed reactor 10 equipped with cyclone dust collector 12. Solids, i.e. particulate sulfides and lime are fed to reactor 10 at solids inlet 14 which solids are retained above plenum chamber 16 by constriction plate 18, and roasted sulfides are removed from reactor 10 via solids port 20. Suspending or fluidizing gas is introduced into plenum chamber 18 via gas inlet 22. Fluidizing gas introduced into reactor 10 via gas inlet 22 and constriction plate 18 fluidizes the solid sulfides as bed 24 while suspending the more finely divided lime throughout the reactor space shown in less dense spots at The fluidizing gas containing free oxygen flows from reactor 10 to cyclone 12 via conduit 28. Effluent gas from cyclone 12 can be vented to the atmosphere or sent to heat recovery, via outlet 30. Disengaged solids, i.e. lime, sulfides and oxidized sulfides, are returned to reactor 10 via conduit 32 or are recovered or bled from the system via outlet 34.

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20 Figure 3 depicts a circulating fluid bed reactor 50 equipped with cyclone solids collector 52. Solids, i.e. particulate sulfides and lime are fed to reactor 50 at solids inlet 54 which solids are retained above plenum chamber 56 by constriction plate 58. Suspending or 25 fluidizing gas is introduced into plenum chamber 58 via gas inlet 62. Fluidizing gas introduced into reactor 50 via gas inlet 62 and constriction plate 58 fluidizes the solid sulfides as bed 64 while suspending particulate sulfides and finely divided lime throughout the reactor space shown in less dense spots at 66. 30 The fluidizing gas containing free oxygen flows from reactor 50 to cyclone 52 Effluent gas from cyclone 52 can be via conduit 68. vented to the atmosphere or sent to heat recovery, via Disengaged solids, i.e. lime, sulfides and outlet 70. oxidized sulfides, are returned to reactor 50 via conduit 35

72 or are recovered or bled from the system via outlet 74. In continuous operations between about 10% and 90%, advantageously between about 20% and 80%, of the disengaged solids are recovered as product. The amount of disengaged solids recovered as product is dependent upon the roasting conditions and the amount of sulfur that can be tolerated in the roasted product.

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Figure 4 depicts a transport reactor 100 equipped with cyclone solids collector 102. Solids, i.e. particulate sulfides and lime are fed to reactor 100 at solids inlet 104. Suspending gas is introduced into reactor 100 via gas inlet 112. Suspending gas introduced into reactor 50 via gas inlet 112 suspends and transports the solid sulfides and finely divided lime throughout the reactor space shown in less dense spots at 116. suspending gas containing free oxygen flows from reactor 100 to cyclone 102 via conduit 118. Effluent gas from cyclone 102 can be vented to the atmosphere or sent to heat recovery, via outlet 120. Disengaged solids, i.e. lime, sulfides and oxidized sulfides, are returned to reactor 100 via conduit 122 or are recovered or bled from the system via outlet 124. In continuous operations between about 10% and 90%, advantageously between about 20% and 80%, of the disengaged solids are recovered as product. The amount of disengaged solids recovered as product is dependent upon the roasting conditions and the amount of sulfur that can be tolerated in the roasted product.

The circulating fluid bed depicted in Figure 3 is particularly useful in the practice of the process in accordance with the present invention. Because a portion of the fluidized bed is intentionally transported from the reactor, the velocities of the suspending gas and free oxygen-containing do not have to be as carefully controlled so that an extra degree of freedom is gained.

For example, as noted hereinbefore the capture of sulfur dioxide is inversely correlated with the amount of free oxygen in the offgas and the extra degree of freedom afforded by the circulating fluid bed reactor permits the independent introduction of a free oxygen-containing gas to the reactor without concern as to whether or not the stability of the fluidized bed would be perturbed. Another example of the desirability of the circulating fluid bed is the greater freedom for the rate at which solids are fed to the reactor thereby offering greater content of the potential for agglomeration. hereinbefore, even in a transport type reactor some of the formed calcium sulfate agglomerates. Such agglomeration of feed material or products in fluidized or other moving beds is a well known source of operating difficulties.

In order to provide the skilled artisan with a better appreciation of the process in accordance with the present invention the following illustrative examples are given:

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#### Example I

An auriferous sulfide ore containing 4.2 ppm Au and 7% sulfur was ground to 100% passing 200 mesh. It was roasted in a circulating fluid bed furnace at the rate of 20 kg/hour in three different campaigns. Except for Campaign II-d, when the temperature was controlled at 780°C, the roasting was carried out at a temperature of 700°C. The calcine was analyzed for sulfur content and the sulfur capture was calculated. The results of the three campaigns are presented in the following table.

5	Campaign Number	Roaster Operating Conditions	Sulfur Capture - %
	I-a	No Additive, 3% O <sub>2</sub> in offgas, Temp. 700°C	11
	I-b	No Additive, 6.5%1 O <sub>2</sub> in offgas, Temp. 700°C	N/A
10	I-c	No Additive, 18% O <sub>2</sub> in offgas, Temp. 700°C	23
	II-a	Lime Stone added at 2 kg/hr, Temp. 700°C	13
15	II-b	Lime Stone added at 4 kg/hr, Temp. 700°C	15
	II-c	Lime Stone added at 8 kg/hr, Temp. 700°C	19
20	II-d	Lime Stone added at 4 kg/hr, Temp. 780°C	21
	III-a	Lime added at 1.5 kg/hr, (42% of stoichio- metric), Temp. 700°C	21
25	III-b	Lime added at 3.0 kg/hr, (84% of stoichio- metric), Temp. 700°C	68
30	III c-i	Lime added at 4.5 kg/hr, (126% of stoichiometric), Temp. 700°C, O <sub>2</sub> in offgas less than 8%	94
	III c-ii	Lime added at 4.5 kg/hr, (126% of stoichiometric), Temp. 700°C, $O_2$ in offgas less than 14%	96
35	III c-iii	Lime added at 4.5 kg/hr, (126% of stoichiometric), Temp. 700°C, O <sub>2</sub> in offgas less than 18%	98

It should be noted that III-c was not really divide into sub-campaigns. The sulfur capture data merely represents the calculated capture during times of high, medium and low oxygen contents. The data do of course show our point that excellent sulfur capture is possible. It should be noted that hydrated lime was used during campaign III.

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## EXAMPLE II

An auriferous ore containing 5.7 ppm Au and 3.7% S was roasted at the rate of 20 kg/hr in a circulating fluid

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bed under a constant temperature of 700°C. Besides silicates, the ore also contained dolomite, a calcium magnesium carbonate. The calcium assay of the ore was 5.0%. Ore of two different particle sizes was tested in the two separate campaigns. The sulfur capture results, calculated on the basis of calcine sulfur analyses were as follows:

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10	Campaign	Campaign		Sulfur Capture - %		
		Particle Size	Oxygen	in offg	as - %	
	Number	0100	3	6	19	
15	IA	100% passing 20 mesh	62	N/A	76	
	V	100% passing 65 mesh	82	84	93	

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EXAMPLE III

The ore form Example II was subjected to flotation to produce a sulfide concentrate containing 36 ppm Au and 23% sulfur. The concentrate was roasted in a circulating fluid bed at the rate of 12 kg/hr maintaining a temperature of 675°C in two different campaigns, with and without the addition of lime to capture sulfur. flotation concentrate particle size was about 80 passing 325 mesh. The concentrate still contained some residual dolomite. The sulfur capture results are presented in the following table.

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Campaign Number	Lime Addition	Sulfur Capture - %	
VI	No	20	
VII	Yes, 65% of stoichio- metric requirement	75	

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Although the present invention has been described in conjunction with preferred embodiments, it is to be

understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

#### WHAT IS CLAIMED IS:

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- A process for roasting particulate metalliferous minerals of at least one member selected from the group consisting of sulfides or arsenides which comprises introducing the minerals and lime into a reactor space, maintaining the reactor space at a temperature between about 500°C and 800°C, suspending the minerals and lime by passing a gas through the reactor space and supplying a free oxygen-containing gas to the reactor space to oxidize the minerals to metalliferous oxides and oxides of sulfur and arsenic, the lime being added to the reactor space in amounts substantially stoichiometrically sufficient to react with the oxides of sulfur and arsenic and the lime being sufficiently finely divided to be substantially homogeneously suspended throughout the entire reactor space whereby the suspended lime substantially completely reacts with and captures the oxides of sulfur and arsenic.
- 2. The process described in claim 1 wherein the reactor space is maintained at a temperature between about 600°C and 750°C.
- 3. The process described in claim 1 wherein the lime is added to the reactor space as hydrated lime.
  - 4. The process as described in claim 1 wherein sufficient free oxygen-containing gas is supplied to the reactor to provide offgas having a free oxygen content greater than about 3%, by volume.
  - 5. The process as described in claim 1 wherein sufficient free oxygen-containing gas is supplied to the reactor to provide offgas having a free oxygen content greater than about 8%, by volume.

- 6. The process as described in claim 1 wherein suspended solids are conveyed to means for disengaging the suspended solids from the suspending gas and a first portion of the disengaged solid is recovered as product and a second portion is recycled to the reactor space.
- 7. The process described in claim 6 wherein the portion recovered as product amounts to between about 20% and 80% of the disengaged solids.

- 8. The process as described in claim 6 wherein a circulating fluidized bed is established within the reactor space.
- 9. The process as described in claim 1 wherein at least about 90% of the oxides of sulfur are captured by the lime.
- A process for roasting particulate 20 metalliferous minerals of at least one member selected from the group consisting of sulfides or arsenides which comprises establishing a circulating fluidized bed within a reactor space, introducing the minerals and hydrated lime into the fluidized bed, maintaining reactor space at a temperature between about 500°C and 800°C, suspending 25 and circulating the minerals and hydrated lime by passing gas through the reactor space, supplying a free oxygen containing gas to the reactor space to oxidize the minerals to metalliferous oxides and oxides of sulfur and arsenic, and to provide an offgas containing at least 30 about 3% free oxygen and suspended solids, passing the offgas to means for disengaging the suspended solids and recirculating a portion of the disengaged solids to reactor space, the hydrated lime being added to the fluidized bed in amounts at least substantially 35

stoichiometrically sufficient to react with the oxides of sulfur and arsenic and the hydrated lime being substantially homogeneously suspended throughout the entire reactor space whereby the suspended hydrated lime substantially completely reacts with and captures the oxides of sulfur and arsenic.

11. The process as described in claim 1 wherein the reactor space is maintained at a temperature between about 600°C and 750°C.

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12. The process as described in claim 10 wherein the metalliferous minerals contain auriferous minerals.

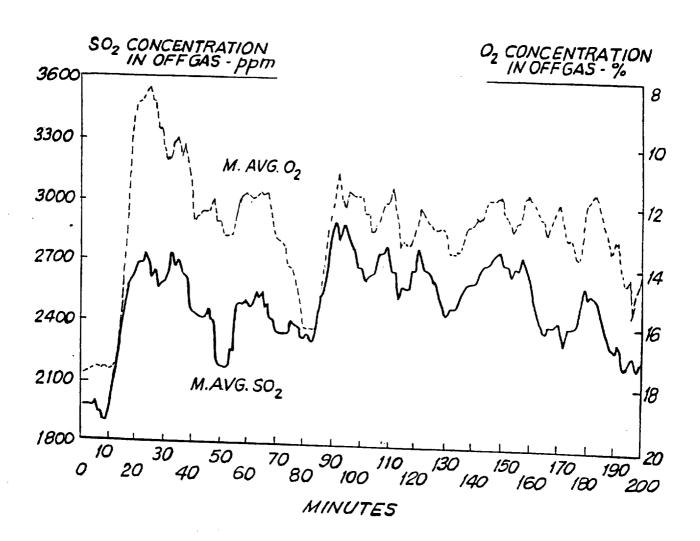


FIG. 1

