Plant for the treatment and the oxidation of antimony minerals, wherein an antimony mineral with any granulometry and humidity, eventually crushed, is carried by a hot gaseous stream, subjected to milling, drying, subsequent separations and then introduced in a rotary kiln in a state of extreme subdivision and oxidized dispersed in a gaseous compressed oxidizing stream.

6 Claims, 3 Drawing Figures
The composition of a hand sorted mineral:

<table>
<thead>
<tr>
<th>Sb</th>
<th>Pb</th>
<th>As</th>
<th>FeO</th>
<th>Gaunue</th>
</tr>
</thead>
<tbody>
<tr>
<td>42-45</td>
<td>27-30</td>
<td>0.1-0.2</td>
<td>0.5-1</td>
<td>1-2</td>
</tr>
</tbody>
</table>

with a humidity of 6 - 7 percent and a granulometry of 5 - 10 cm with 25 percent of fine materials.

The process practiced in the plant covered by the present invention differentiates from the processes used until now for the oxidation of antimony minerals, particularly of those containing sulfur, owing to the fact that the rotary kiln used in the plant is utilized in ways completely different from those traditionally used, a fact which allows to realize an oxidation reaction of the mineral in equicurrent with the oxidizing air and to complete the reaction itself in countercurrent within the same kiln.

Besides, in the system covered by the present invention, the said rotary kiln is coupled with an equipment which allows to introduce the mineral into the kiln in a state of extreme subdivision and dispersed in a gaseous stream constituted by air and/or oxidation oxygen. Such coupling allows to considerably increase the separation yield of the antimony from the gangue, to achieve large economies in the fuel consumption and to attain a high processing capacity.

The plant of the present invention, differentiates from those using turbulent-layer- or fluidized-bed kilns because although it has in common with these latter the thorough mixing between the mineral and oxidizing agent necessary to attain a very high velocity and depth of oxidation and consequently a high processing capacity, it has the advantage, in respect of the said kilns, that the velocity of the gaseous fluids inside the kiln covered by the present invention can be varied within much wider limits, because there is no necessity for maintaining the solid material into fulfidization; this definitively allows, besides a greater flexibility of operation, also a better separation of the gangue from the oxide produced.

The plant covered by the present invention, combines the advantages of the traditional rotary kiln and the fluidized-bed- or the turbulent-layer kilns in a single unit and allows to realize considerable fuel economies and high specific outputs in comparison with the traditional rotary kilns.

The plant covered by the present invention allows, moreover, the use of simpler and less expensive equipment and plants, improving also the kinetics of the heretogeneous reactions occurring therein.

The plant covered by the present invention will be now described on the basis of the attached drawings, wherein: FIG. 1 shows schematically, the part of the plant where the milling and the drying of antimony minerals is achieved. FIG. 2 is the plan view of the part of the plant related to the roasting of antimony minerals. FIG. 3 is the cross-sectional view AA of FIG. 2.

With reference to FIG. 1, the plant related to the present invention comprises the hopper 1 which is loaded with the material to be ground and dried, having a different origine and granulometry such as, for example, those pointed out.
The material undergoes a first dimensional reduction down to 20 – 25 mm passing through a crusher as in the cited example of the handsorted mineral.

In the case where the pre-crushing is not necessary as in the cited example of the flotation concentrate, the crushed 2 will be bypassed by the material without being put in motion.

The material through the chute 3 is admitted to a duct 4, crossed by a hot air stream, which carries it through a ball mill 5, where the material is ground down to the final dimension, all below 20 mesh.

The classifier 6 recycles, through chute 7, the material which did not reach the prescribed dimensions. The mixture air-material is made to go through the cyclone 8 which separates the material carried by the air. The material is collected in a hopper 9, from which, then, it can be taken for the subsequent roasting phase. The air purified in the cyclone 8 almost totally of the mineral powder carried, goes back through the duct 10 and the fan 11 into the duct 4 and pushes more mineral into the mill 5.

The drying of the mineral is insured by heating suitably the carrying air in the cycle, so as to perform the drying at the same time as the grinding.

To this end a hot air source 12 is used, constituted by a furnace where fuel, in particular fuel oil is introduced, so as to add through the valve 13 an amount of hot air sufficient to keep the temperature at the desired levels in the various points of the cycle. The same amount of air is eliminated through the bag filter 14, the regulation valve 15, the auxiliary fan 16, and the stack 17, in order to keep the air volume in the cycle constant.

The filter 14 has the function of holding those mineral parts which are not separated by the cyclone because of its yield, lower than 100 percent; the said mineral held by the filter 14 goes back to the hopper 9 through the duct 18.

The said drying system allows to dry the mineral without exceeding the temperature limits at which the oxidation of the mineral could initiate, by conveniently controlling the temperature of the carrying air. For example it is possible to keep the mineral temperature below 190°C.

To this end the drying is performed utilizing as a drying fluid, a mixture of air and of the combustion products of the burner 12 in order to decrease the percentage content of the oxygen of the mixture itself and to rigorously control the operation temperature.

The control of the temperature and of the effectiveness of the drying is performed in the following manner: at the inlet of the ball mill 5, the temperature of the drying air is controlled by the dry bulb thermometer 19, which signals are used to adjust the flow capacity of the fuel of the hot air generator 12 by means of the pneumatic valve 20. The wet bulb thermometer 21 controls the effectiveness of the drying by varying the flow capacity of the drying mixture by means of the valve 13 and it acts in series on the flow meter 22 which controls by means of the valve 15 the amount of air to be expelled from the drying circuit.

The same system of pneumatic haulage which insures a continuous ventilation through the mill guarantees the maintenance of a constant temperature by removing the heat eventually produced by the working process and preventing some portions of the material remaining in the mill from reaching high temperature levels, such as, for example above 190°C.

It is necessary to consider that the air flow through the cycle is obviously limited and that the temperature itself is also limited because of the necessity of avoiding overheating of the material beyond a determined temperature, for example 190°C. These facts condition the amount of humidity which can be possibly removed from the material, but not the type of the mineral to be fed, because the amount of mineral to be put into operation from the hopper 1 in order to obtain a product having the most idoneous humidity level is determined as a function of its initial humidity.

As an applicable example, however not limiting the present invention, the results obtained using the minerals indicated in the hereinabove preceding examples are given below.
3,759,500

percent, to two storage tanks 24. From the said storage tanks which function alternatively so as to insure the necessary elasticity to the plant, the mineral, by means of the continuous extractors 25 is fed into a Redler 26, which conveys it to the dosing scale 27 from which it passes to the continuous feeder 28 and then, by means of the injector-mixer 29 it is introduced into the rotary kiln 30 in a state of dispersion in the air and/or oxygen, which, compressed in the compressor 31, arrives to the said injector-mixer through the duct 32.

The said dispersion of the mineral in the air and/or oxygen is subjected in the first zone of the kiln to a temperature of 1,200° - 1,300 °C, maintained by means of the burner 33 and by the heat of oxidation of the material itself.

The time for the reaction completion is of 3-4 seconds, which corresponds to the time taken by a particle suspended in the gas to go through the reaction zone of the kiln.

The thermo-fluidodynamic conditions realized in the kiln permit to obtain antimony oxide in such a form that as it is gradually formed, it is removed from the grain surface in combustion, by the combustion air and/or oxygen itself, in such a way that the continuously renewed gaseous atmosphere surrounding the mineral grain facilitates the transfer of the oxide vapors and insures the most complete oxidation of the mineral contained therein.

The turbulent oxidation in equipollent is extremely complete and to this one, it must be added the further oxidation sustained by the drosses and the slags in their re-flowing towards the hottest zone of the kiln. This further oxidation occurs in countercurrent and it insures a progressive and more complete elimination of the metal eventually still present, until its almost total elimination is obtained.

In fact the particles which, because of parasitic phenomena, should eventually fall on the walls of the kiln before the end of the trajectory inside the kiln itself, are compelled by the 2-3 percent slanting of the cylindrical chamber of the rotary kiln, to cover again the route in a reverse direction towards the feeding zone; in this way, as it is hereinabove said, the oxidation reactions are continued until the antimony is almost totally eliminated from the starting material.

A portion of the oxide formed inside the kiln, and precisely the Fe₂O₃ and gangue particles have such a granulometric characteristic and specific weight that they do not reach the terminal portion of the kiln itself and fall onto the bottom wall; then they are compelled by the rotation of the kiln and by its slanting to displace themselves slowly towards the feeding zone, from which they are continuously discharged into a water tank 34.

This material which constitutes about 3-4 percent of the feed is characterized by a very low percentage of Sb (around 4-5 percent) and it is eliminated.

The particular fluid dynamic regime realized in the kiln, allows to limit the draggings with the double advantage of having a purer oxidized material and a very high yield, because the gangue re-flowing into the kiln continues its oxidative process.

The oxide produced inside the kiln, proceeding with the gaseous stream inside the kiln itself, meets such a regime of temperature so as to prevent subsequent chemical transformations and reactions, avoiding in this way the harmful incrustations of oxysulfides, otherwise unavoidable and frequently occurring in other processes.

At the kiln outlet the gas containing the Sb oxide fumes, which in going through the chamber 35 lets to decent eventual dragged heavy parts, is subjected to a sudden cooling by means of an introduction of cold air through the outlet 36; the said cold air, decreases the gas temperature to a value lower than 400°C.

This cooling has beneficial effects on the quality and on the granulometry of the oxide which in this way acquires such characteristics so as to make it marketable. To that it must be added, moreover, that the operations downstream the kiln are helped, since the further processings are facilitated and the equipment is thermically stressed to a lesser degree.

The oxides which are dragged by the gas downstream the kiln and which have lost the greater part of the iron and of the gangue present in the feed, are first sent to a hot cyclone (not shown in the drawings), where the fallout of a portion of the solid material contained in the gas takes place and subsequently in a dry filtration system (not shown in the drawings) comprising a set of filtering sleeves where the residual portion of the solid is recovered.

In this way it is possible to obtain the separation of the oxide into two distinct fractions, the first of which, dropped into the site of the cyclone shows more current chemical characteristics and a coarser granulometry, as compared to the fraction recovered on the filters, which having a content of Sb oscillating around 75-80 percent and a granulometry which is 90 percent below 400 mesh, displays adequate marketable characteristics.

The oxide obtained in the cyclone has still sufficient purity to make it directly reducible to metal.

The plant covered by the present invention allows a complete oxidation of the mineral and a high processing capacity, since it presents both the advantages of the operating speed proper to fluid-bed- or turbulent-layer kilns, thus affording a high processing capacity, and the advantages of rotary kilns, insuring the absolute completeness of the operation.

The advantages and the characteristics of the present invention will be furtherly illustrated by the following example, related to a way of performing, chosen as a demonstration and not as a limitation of the invention itself.

Example 7

The example refers to the production of antimony oxide starting from a flotation concentrate with the following characteristics:

<table>
<thead>
<tr>
<th>CHEMICAL ANALYSIS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>54 %</td>
</tr>
<tr>
<td>Fe</td>
<td>7 %</td>
</tr>
<tr>
<td>S</td>
<td>32 %</td>
</tr>
<tr>
<td>As</td>
<td>1.5 %</td>
</tr>
<tr>
<td>humidity: 6.65%</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GRANULOMETRIC ANALYSIS</th>
<th>% partial</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 + 0.8</td>
<td>0.10</td>
</tr>
<tr>
<td>0.3 + 0.6</td>
<td>0.10</td>
</tr>
<tr>
<td>0.1 + 0.3</td>
<td>4.10</td>
</tr>
<tr>
<td>0.07 + 0.1</td>
<td>5.40</td>
</tr>
<tr>
<td>0.06 + 0.07</td>
<td>6.30</td>
</tr>
<tr>
<td>0.05 + 0.06</td>
<td>12.50</td>
</tr>
<tr>
<td>0.04 + 0.05</td>
<td>15.30</td>
</tr>
<tr>
<td>0.038 + 0.04</td>
<td>18.40</td>
</tr>
<tr>
<td>&lt;0.038</td>
<td>37.90</td>
</tr>
</tbody>
</table>
The rotary kiln has the following characteristics:

- Length: 20m
- Diameter: 1.2m
- Slanting: 2%

The operation initiates by setting the kiln at a proper regime by means of a naphta burner until the optimal distribution curve of temperatures throughout the kiln is reached. Once this condition has been reached the feeding of the mineral is initiated.

The kiln as well the throwing device affords a considerable flexibility of processing, so that the kiln can be operated in a continuous way with feedings which can be varied from 500 to 1,000 Kg/h, providing that the mixing air capacity is varied accordingly, in such a way as to have always a ratio equal to 2–3 cu.m of air per kg of the material fed.

The fuel consumption is reduced to a very considerable extent since, owing to the exothermic character of all the reactions taking place, the process is almost an autogeneous one.

In fact the oxidation reaction of antimony sulfide and other chemical compounds contained in the mineral is characterized by an exothermicity equal to about 1,000–1,300kcal/kg of oxidized material; this amount of heat, in particular realizations, can be completely exploited to raise the temperature of the reaction zone.

If, on the contrary, the heat insulation characteristics are such that a portion of the heat of reaction is yielded to the external environment, or in any way they are such that in the reaction zone a temperature equal to 1,100–1,200°C cannot be reached, then the necessary amount of heat is supplied by a solid, liquid or gaseous fuel, the combustion products of which can be mixed with the oxidation products.

The temperature of 1,100–1,200°C is necessary since besides the fundamental reactions:

\[
2\text{Sb}_2\text{S}_3 + 9 \text{O}_2 \rightarrow 2\text{Sb}_2\text{O}_3 + 6 \text{SO}_3
\]

\[
2\text{FeS} + 1/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2
\]

\[
\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2
\]

local phenomena may occur, leading to the formation of higher Sb oxides which, specifically, at these temperatures dissociate to yield Sb_2O_3.

Other characteristics data of the process practiced in the plant are the following: ones which are referred to an optimal feeding equivalent to 600 kg/h of the hereinabove indicated concentrate:

- Air flow capacity: 1200 cu.m/h
- Naphta flow capacity: 30 kg/h
- Vapor velocity: 2 m/sec

The reactions taking place are the classic ones of roasting; the advantage of the herein described process lies on the fact that the said roasting is uniformly distributed and takes place in an almost instantaneous manner in the whole reacting mass.

The amount of volatile products in the fumes outgoing from the kiln is the following:

\[
\begin{align*}
\text{Sb}_2\text{O}_3 & : 100–110 \text{ g/Nm}^3 \\
\text{SO}_3 & : 100–105 \text{ g/Nm}^3 \\
\text{As}_2\text{O}_3 & : 0.5–1 \text{ g/Nm}^3 \\
\text{Hg} & : 0.5–0.7 \text{ g/Nm}^3
\end{align*}
\]

The operation yield attains values which, on the average, oscillate around 98 percent, with loss percentages of Sb in the slags equal to about 1 percent.

The characteristics of the oxide produced at the cyclone, always as an example may vary within the hereinbelow reported limits:

The present invention has been described and illustrated with reference to its preferred realization, but it is intended that variations or modifications may be introduced without the protection limits of the present industrial patent.

What is claimed is:

1. Plant for the treatment and the oxidation of antimony minerals achieving the milling, the drying and the oxidation of the said mineral, wherein it comprises means for the automatic control of the flowing capacity, temperature and humidity, of the hot gaseous stream carrying the said mineral, means for the milling and the drying of the said mineral and means for the feeding and the oxidation of the said mineral in the state of extreme subdivision and dispersed in a compressed oxidizing gaseous stream.

2. Plant for the treatment and the oxidation of antimony minerals according to claim 1, wherein said control means are a regulation valve for the flow capacity of the hot gaseous steam generator, a regulation valve for the flow capacity of the hot gaseous steam carrying the mineral and a regulation valve for the flow capacity of the outgoing hot gaseous stream.

3. Plant for the treatment and the oxidation of antimony minerals, according to claim 1, wherein the said control means are a meter for the flow capacity, in register with the regulation valve of the flow capacity of the hot gaseous stream carrying the said mineral, with the regulation valve of the flow capacity of the hot gaseous outgoing stream and with a wet bulb thermometer, a dry bulb thermometer in register with the regulation valve of the flow capacity of the fuel generator of the said hot gaseous stream.

4. Plant for the treatment and the oxidation of antimony minerals according to claim 1, wherein the said milling and drying means are a ball mill and a hot gaseous stream.

5. Plant for the treatment and the oxidation of antimony minerals according to claim 1, wherein the said feeding and oxidation means are a compressor, an injector-mixer, a burner and a slanted rotary kiln.

6. Plant for the treatment and the oxidation of antimony minerals, according to claim 1, wherein it comprises a charging hopper, a crusher, a classifier, a cyclone, a collecting hopper, a bag filter, a duct for the pneumatic haulage of the mineral, two storage tanks supplied with continuous extractors, a feeding Redler, a dosing scale, a continuous feeder, a rotary kiln, a collecting tank, a decantation chamber, a cyclone and a battery of dry filters.