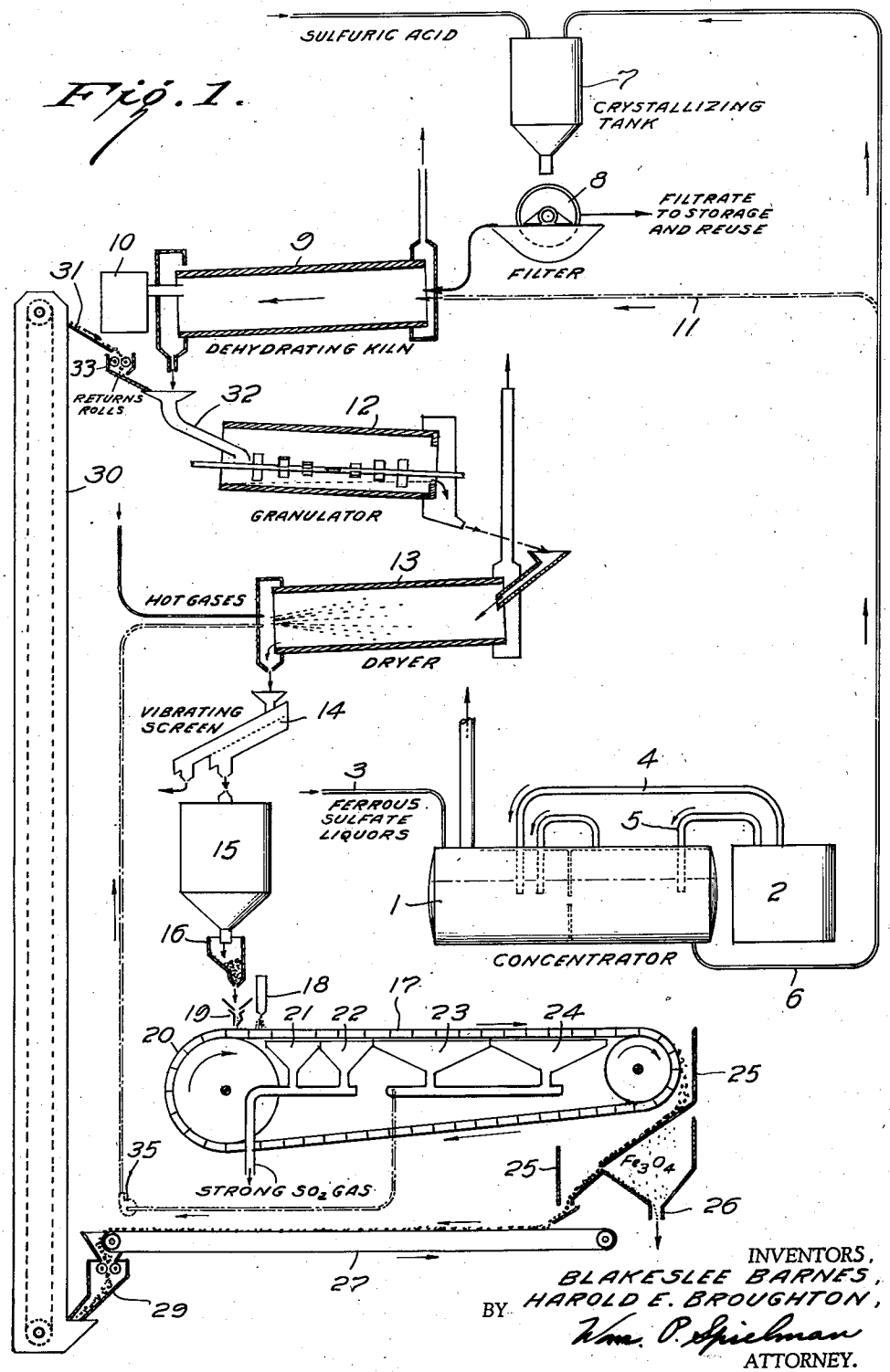
May 28, 1940. B. BARNES ET AL 2,202,414

PRODUCTION OF SULPHUR DIOXIDE FROM METAL SULPHATES

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Fig. 1.



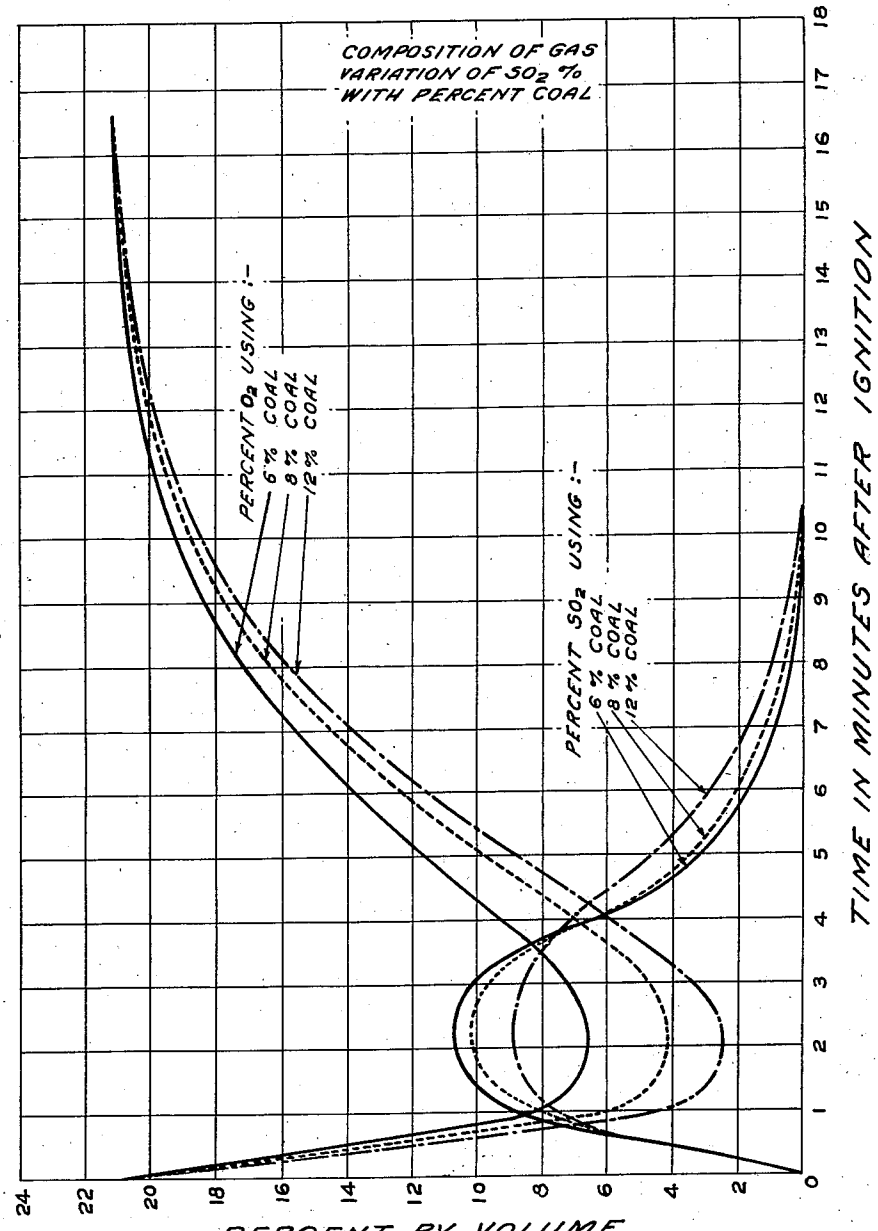
INVENTORS,
BLAKESLEE BARNES,
HAROLD E. BROUGHTON,
BY Wm. P. Spielman
ATTORNEY.

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Fig. 2.



INVENTORS
BLAKESLEE BARNES,
HAROLD E. BROUGHTON,
BY Wm. P. Spielman
ATTORNEY.

May 28, 1940. B. BARNES ET AL 2,202,414

PRODUCTION OF SULPHUR DIOXIDE FROM METAL SULPHATES

Filed Dec. 3, 1938 3 Sheets-Sheet 3

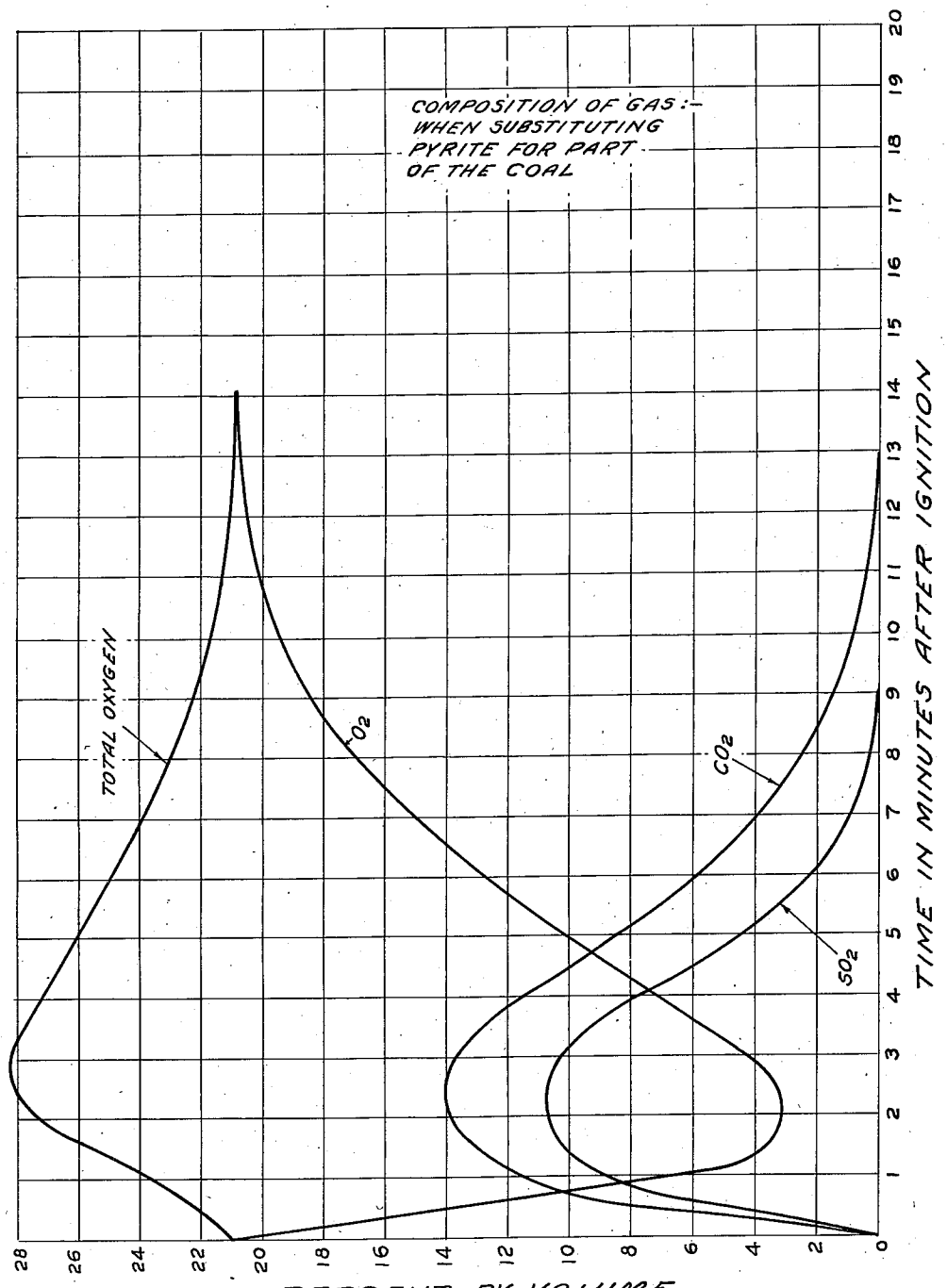


Fig. 3.

INVENTORS
BLAKESLEE BARNES,
BY HAROLD E. BROUGHTON,
Wm. P. Spielman
ATTORNEY.

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UNITED STATES PATENT OFFICE

2,202,414

PRODUCTION OF SULPHUR DIOXIDE FROM METAL SULPHATES

Blakeslee Barnes, New York, N. Y., and Harold E. Broughton, Hackensack, N. J., assignors to Chemical Construction Corporation, New York, N. Y., a corporation of Delaware

Application December 3, 1938, Serial No. 243,706

14 Claims. (Cl. 23—177)

This invention relates to the production of sulphur dioxide gases from heavy metal sulphates such as iron sulphate, copper sulphate, zinc sulphate, and the like. More particularly, the invention relates to a method of obtaining from heavy metal sulphates of this class a sulphur dioxide gas of sufficient strength and free oxygen content for catalytic oxidation by the contact sulphuric acid process.

The roasting of heavy metal sulphates for metallurgical purposes has been practiced for many years, and the sulphur dioxide gases obtained from this source have frequently been converted to sulphuric acid by the chamber process since this process will operate on relatively weak gases. Such ores as iron pyrites, zinc sulphate and the like have also been roasted in Herrshoff furnaces and similar heavy equipment under conditions such that a 6–7% sulphur dioxide gas has been obtained. Heavy metal sulphates of this class have also been mixed with fuel if necessary and sintered on the Dwight-Lloyd sintering machine, but heretofore the sulphur dioxide gases recovered by this process have been too weak for catalytic conversion.

We have now discovered that heavy metal sulphates, and particularly hydrated ferrous sulphates such as are obtained as by-products from the sulphuric acid leaching of ilmenite in pigment manufacture and from the pickling of iron and steel, can be roasted and/or sintered in admixture with carbonaceous fuel in such a manner that a sulphur dioxide gas suitable for catalytic conversion by the contact sulphuric acid process is obtained. We have found that the production of a gas of sufficient strength and oxygen content from these sources is dependent upon the close control of a number of factors as will subsequently be described.

It is therefore a principal object of the present invention to provide a method of roasting and/or sintering heavy metal sulphates in admixture with carbonaceous fuel in such a manner as to obtain a strong sulphur dioxide gas suitable for catalytic conversion. Another object of the invention is to provide a granulated charge of a mixture of finely divided heavy metal sulphate and carbonaceous fuel which can be ignited and sintered or roasted in a current of air with rapid evolution of a strong sulphur dioxide gas and the production of a hard, dense metal oxide sinter of low sulphur content. Further objects include the control of moisture content, amounts of fuel, size of granulation, and other variables in order to obtain the optimum results. Still further objects will be apparent from the following description, when taken with the drawings attached hereto, and will be pointed out in the appended claims.

While the broader principles of the invention may be applied to any heavy metal sulphate capable of reduction by a carbonaceous fuel, we believe that its most important commercial advantages are obtained in the treatment of ferrous sulphate. Accordingly, the invention will be described in detail with particular reference to ferrous sulphate monohydrate obtained from spent pickle liquors or from the manufacture of titanium pigments, but it should be understood that this description illustrates the broad principles of the invention as well. The invention in its broader aspects is limited only by the scope of the claims annexed hereto.

On the attached drawings, Fig. 1 illustrates diagrammatically a process for the concentration and recovery of hydrated ferrous sulphate from spent pickle liquor or from titanium oxide manufacture and the production of a strong sulphur dioxide gas therefrom. Fig. 2 is a graph showing the compositions of gases obtained when roasting ferrous sulphate from this source. Fig. 3 is a similar graph showing the results obtained when a mixture of carbon and pyrite is used as fuel.

Our invention is based on the discovery that a strong sulphur dioxide gas is obtainable from heavy metal sulphates only when they are burned rapidly. In order to obtain such rapid combustion, we have found that the sulphates must be mixed with carbonaceous fuel and granulated and then burned in a relatively thin, porous layer while passing a strong current of air through them. The complete desulphurization of the material by such an air blast would, of course, give a very dilute gas, but we have found that more than 95% of the sulphur is evolved as sulphur dioxide in the first portions of the products of combustion, so that a strong gas is obtained when these products are separated from the remainder.

The success of this method of operation will depend to a considerable extent upon the granulation of the charge, and this should be closely controlled once the optimum conditions for any given raw material have been established. Thus, for example, we have found that for the roasting of hydrated ferrous sulphate, a granulation of ¼" is to be preferred. Using this particle size, a charge about 6 inches deep and 35 lbs.

per sq. ft. of surface area produces the best results.

The amount of fuel employed also has an important influence on the results obtained. Too much carbonaceous fuel results in too high a combustion temperature, which gives a sinter high in sulphur and a gas having an excess of carbon dioxide and a deficiency of free oxygen, while too little fuel produces a very dilute gas and a sinter of low mechanical strength. An amount of fuel roughly equivalent to 6–12% of coal on a heat evolution basis produces the best results with most heavy metal sulphates, and a part of this fuel charge may be made up of sulphur-containing material such as a free sulphur, pyrite, or other heavy metal sulphides, thereby increasing the strength of the resulting SO_2 gases. However, it is necessary in all cases to have at least 3% of carbon present based on the total weight of the charge, since sulphur alone will not produce a gas free of sulphur trioxide.

The further details of the process as applied to hydrated ferrous sulphate will be discussed in conjunction with the equipment illustrated in Fig. 1. Referring to this figure, a concentrator for waste ferrous sulphate liquors is shown at 1, this concentrator being of the well-known drum type operating with hot products of combustion from an oil burning furnace 2. Waste ferrous sulphate liquors are introduced at 3 and passed in counter-current with hot gases passing through the pipes 4 and 5 and the concentrated liquor leaves through outlet pipe 6. This liquor may be cooled and mixed with strong sulphuric acid in a cooling and crystallizing vessel 7 and crystals of ferrous sulphate heptahydrate removed therefrom in a rotary filter of the Oliver type such as the filter 8, after which the filtrate is preferably returned to the pickling plant for reuse.

The heptahydrate crystals are introduced into a rotary dehydrating kiln 9 where the greater part of their water of crystallization is removed by counter-current contact with hot gases from an oil or gas fired furnace 10. Instead of introducing heptahydrate crystals into this dehydrator, the concentrated liquor from the concentrator 1 may be dehydrated directly, as indicated by the dotted flow line 11.

It should be understood that the invention in its broader aspects is not limited to the above method for obtaining hydrated ferrous sulphate and similar heavy metal sulphate crystals. On the contrary, there are a number of other methods available for accomplishing this purpose; for example, waste ferrous sulphate liquors may be mixed with strong sulphuric acid, concentrated and filtered at temperatures above 65° C. whereby ferrous sulphate monohydrate is obtained, as described in the Smith and Belding Patent No. 2,185,095 dated December 26, 1939. Alternatively, instead of concentrating the waste liquors, they may be subjected to artificial refrigeration with or without the preliminary addition of sulphuric acid, whereby crystals of ferrous sulphate heptahydrate are obtained. The broad principles of the invention are directed to the production of a strong sulphur dioxide gas from solid heavy metal sulphate crystals, and these crystals may be obtained from any source and by any suitable method.

The ferrous sulphate leaving the dehydrator 9 may have a water content of about 14–20% and is preferably in the form of ferrous sulphate monohydrate containing about 16% of water. These crystals are finely divided, and are preferably of a size sufficiently small to pass through a standard 6 mesh sieve. The finely divided particles are fed to a rotary granulator or pelleting mill 12, which is preferably of the type known as a pug mill and consists of a rotary shell equipped with internal paddles moving in a direction opposite to its direction of rotation. This mill is charged with the hydrated ferrous sulphate described above together with a metal oxide such as iron oxide, an amount of carbonaceous fuel sufficient to produce a gas of optimum strength for the subsequent roasting operation, and a binder such as waste sulphite liquor, crude molasses residues, or water.

Pellets or granules of very uniform size are obtained from the pug mill granulator and these are introduced into a drier 13 for suitable reduction in their moisture content. This drier is preferably of the rotary type in which the granules pass downwardly in counter-current contact with drying gases of relatively high temperature. Waste gases of low sulphur dioxide content from the subsequent sintering step are well suited for use as the heating and drying medium as they are available at temperatures of 700–800° F., or hot gases from other sources may be used. For best results, the pellets or granules should preferably be dried to a final temperature of 170–180° F. and a total moisture content of not more than 12%.

The dried and hardened pellets are then classified on a vibrating screen of ¼" mesh size, the oversize material being crushed and returned to the granulator for reworking. When proper working conditions are maintained in the granulator and drier it will be found that not more than 10–15% of oversize material is obtained and care should be taken that not more than 10% of fines are mixed with the pellets passing through the screen.

The dried and sized pellets are retained in a storage hopper 15 and are supplied as needed to the feeding device 16 of a roasting and/or sintering machine of the moving grate type, such as a Dwight-Lloyd machine, a Greenwalt machine, or the like. A machine of the Dwight-Lloyd type is illustrated at 17 and operates as follows:

The machine is essentially a steel framework supporting a closed track around which travel a series of movable grates or pallets 20 for carrying the charge, together with a driving mechanism, an igniter 18, a feed hopper 19 and a plurality of suction or wind boxes 21, 22, 23, and 24 directly beneath the upper pallet track section. Exhaust fans are connected with these wind boxes for drawing air through the charge on the pallets 20 and for carrying away the products of combustion.

The operation of the machine is continuous. As each pallet passes under the feed hopper it receives a charge of combustible material and carries it under the igniter 18 where a flame is directed upon the top surface to start the charge burning. The pallet then passes over the first wind boxes, 21, 22 which draw a blast of air through the charge and receive the first portions of the resulting products of combustion. Continuing its travel it then passes over the remaining boxes 23 and 24 which draw further amounts of air through the charge and carry off the remaining products of combustion, and its speed of travel is so adjusted that the pallet leaves the last suction box zone at the moment

when the charge has been completely sintered. The pallet then passes around the curved track section and discharges the sinter cake into a trough 25, from which a portion of it is withdrawn for sale as at 26. The remainder falls upon a conveyor 27 which carries it to the hopper 29 of an elevator 30, the outlet 31 of which is adjacent the return rolls 33 which discharge into the feed inlet 32 of the granulator 12. Here the sinter cake is crushed to 6 mesh size and mixed with ferrous sulphate, carbonaceous fuel and a binder to form a new charge for granulation.

For purposes of the present invention, the construction of the above described sintering machine is modified by providing a means for collecting as a separate fraction the products of combustion evolved near the feed end of the moving grates by the first wind boxes 21 and 22. As is shown in Fig. 2, the combustion or sintering of a highly porous mass of granulated or pelletized ferrous sulphate will produce during the first few minutes a strong sulphur dioxide gas containing the major part of the sulphur, after which the sulphur dioxide content of the gas soon falls to zero. By providing a separate gas take-off and suction fan for the first two wind boxes 21 and 22 a gas of satisfactory characteristics for the contact sulphuric acid process is obtained, while the remaining products of combustion are collected separately in the boxes 23 and 24 and discharged by the blower 35 into the drying kiln 13, or into the dehydrating kiln 9, or into the concentrator 1 as desired.

The principles of the invention will be illustrated in greater detail in conjunction with the following specific examples to which, however, it is not limited.

Example 1

50–60 parts of crystalline ferrous sulphate obtained as a by-product from the treatment of ilmenite or other iron-titanium ores and having a total water content of 14–20% are ground if necessary to 6 mesh size and mixed with 25–40 parts of iron oxide, which may be partly in the form of fine flue dust and partly sintered Fe_3O_4 crushed to 6 mesh particle size. From 6 to 12 parts of finely divided carbon are added, depending on the water content of the ferrous sulphate crystals, the larger amounts being used when more water is present. The mixture is thoroughly blended and granulated in the pug mill granulator 12 with the addition of about 8 parts of water or waste sulphite liquor as a binder. The pellets or granules are then introduced into the rotary drying kiln 13 where they pass in countercurrent contact with hot products of combustion having a temperature of 600–800° F., preferably those obtained from the last wind boxes of the sintering machine 17. The size, inclination and speed of rotation of the kiln 13 are such that the pellets leave the kiln with a temperature of 170–180° F. and a total water content of not over 12%, and preferably about 8–10%. The pellets are then passed over a double vibrating screen, having upper openings of ¼ inch in size and lower openings of about 10 per inch. The material remaining on the upper screen and that passing through the lower screen is preferably passed through crushing rolls and then returned to the granulator 12.

The pellets remaining on the lower screen are fed onto the moving grate of the sintering machine 17 in a relatively thin, porous layer about 6 to 7 inches deep. They are then ignited by the pilot flame 8 which is sufficiently intense to light off the charge in about one-half minute. A suction of 4 to 7 inches of water is maintained on the wind boxes by the exhaust fans, and the current or blast of air so produced is sufficient to burn out more than 99% of the sulphur in the first eight to nine minutes of combustion. Complete desulphurization and sintering are obtained in about 15–20 minutes, depending on the amount of water in the charge and the amount of fuel used, and a sintered magnetite (Fe_3O_4) suitable for blast furnace reduction is produced.

The composition of the gases issuing from the wind boxes 21 and 22, and representing the first portions of the products of combustion is illustrated on Fig. 2 of the drawings. These gases will average about 7% SO_2 by volume with a sulphur recovery of 94–95% and an oxygen content of about 10% by volume. Their temperature is about 780–800° F., and they are therefore well suited for direct introduction into a contact sulphuric acid plant provided with a vanadium catalyst.

Example 2

Iron sulphate obtained by the concentration and dehydration of waste ferrous sulphate liquors from titanium pigment manufacture has about the following composition:

	Per cent
$FeSO_4$	40.0
$Fe_2(SO_4)_3$	31.9
Free H_2SO_4	5.7
Total water	16.3
Balance (probably Fe_2O_3)	6.1

A charge was prepared containing 55% of this material, 29.5% of sintered magnetite in the form of crushed returns from the sintering machine, 7.5% of coal and 7.5% of pyrite, all of a particle size small enough to pass through a 6 mesh sieve. 0.5% of water was added and the mixture was granulated, dried and hardened, screened and fed to the sintering machine 17, as described in Example 1. The sulphur dioxide content of the gases evolved from this mixture is shown on Fig. 3 of the drawings, from which it is apparent that a strong gas suitable for catalytic oxidation by the contact sulphuric acid process is obtained by collecting as a separate fraction the gases evolved during the first 5–6 minutes of combustion. After about 18 minutes total combustion time at gas temperatures of 830–840° F., a good hard and dense sinter was obtained having a sulphur content of 0.17.% Part of this sinter was returned for the preparation of another batch; the remainder was available for use as a blast furnace charge.

Example 3

Spent pickle liquor from the pickling of sheet metal and containing approximately 8% sulphuric acid and 20% $FeSO_4$ is heated in the concentrator 1 with hot gases, which may be the products of combustion from the furnace 2 or may be the hot gases from the last wind boxes 23 and 24 of the sintering machine, or both. 41% of the water content of the liquor is evaporated after which the remainder is mixed with about 13% of its weight of concentrated sulphuric acid, cooled, and the resulting wet crystals of hydrated ferrous sulphate are filtered off by the filter 8. These crystals are further dehydrated to a total water content of about 16% in

the dehydrating kiln 9, whereupon a material of the following composition is obtained.

	Percent
$FeSO_4$	58.8
$Fe_2(SO_4)_3$	25.0
Water	16.2

A mixture of 30 parts of this material, which corresponds to a ferrous sulphate monohydrate containing some ferric sulphate, together with 20.2 parts of iron oxide returns from the sintering machine and 3.3 parts of coal, all in finely divided condition, were granulated in the granulator 12 with the addition of 2.8 parts of water. The granules were dried and hardened by heating in a current of hot gases to a final temperature of 170–180° F. and a water content of 11%, after which they were fed to the grate of a sintering machine, ignited and burned. Samples collected from the products of combustion gave the following results:

	Percent SO_2 in gas	Percent sulphur recovery
Collecting all gas for first 9 min.	4.6	100
Collecting all gas for first 8 min.	5.2	99+
Collecting all gas for first 7 min.	5.8	98
Collecting all gas for first 6 min.	6.7	96.5
Collecting all gas for first 5½ min.	7.1	93.8

Upon completion of the combustion, 28 parts of a good, hard iron oxide sinter were obtained which contained less than 0.1% of sulphur and were therefore well suited for use in the manufacture of iron and steel.

What we claim is:

1. A method of obtaining from heavy metal sulphates a sulphur dioxide gas of sufficient strength and free oxygen content for catalytic oxidation by the contact sulphuric acid process which comprises mixing said sulphates in the form of finely divided solids with heavy metal oxides and finely divided carbonaceous fuel in the presence of a binder, granulating and sizing the mixture to a fairly uniform size, drying and hardening the granules, igniting and burning the dried granules in a relatively thin, porous layer in about 20 minutes or less while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

2. A method of obtaining from heavy metal sulphates containing water of crystallization a sulphur dioxide gas of sufficient strength and free oxygen content for catalytic oxidation by the contact sulphuric acid process which comprises mixing said sulphates in the form of finely divided solids with an oxide of the corresponding metal and finely divided carbonaceous fuel in the presence of sufficient free water to act as a binder, granulating the mixture, drying the granules to a water content of not more than 12%, sizing the granules to a fairly uniform size, igniting and burning the dried granules in about 20 minutes or less in a relatively thin, porous layer while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

3. A method of producing a sulphur dioxide gas suitable for catalytic oxidation by the contact sulphuric acid process which comprises mixing together a finely divided heavy metal sulphate, a finely divided mixture of carbon and a combustible heavy metal sulphide and a heavy metal oxide in the presence of a binder, granulating and sizing the mixture to a fairly uniform size, drying and hardening the granules, igniting and burning the granules in about 20 minutes or less in a relatively thin, porous layer while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

4. A method of obtaining from hydrated ferrous sulphate a sulphur dioxide gas of sufficient strength and oxygen content for catalytic oxidation by the contact sulphuric acid process which comprises mixing it in the form of a finely divided solid material with iron oxide and with finely divided carbonaceous fuel in the presence of a binder, granulating and sizing the mixture to a fairly uniform size, drying and hardening the granules and igniting and burning them in about 20 minutes or less in a relatively thin, porous layer while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

5. A method of obtaining from hydrated ferrous sulphate a sulphur dioxide gas of sufficient strength and oxygen content for catalytic conversion by the contact sulphuric acid process which comprises mixing it in the form of a finely divided solid material with iron oxide and with finely divided carbonaceous fuel in the presence of a binder, granulating and sizing the mixture to a fairly uniform size, drying and hardening the granules, feeding the granules onto a moving grate in a relatively thin, porous layer and burning them in about 20 minutes or less while passing a current of air therethrough, and collecting as a separate fraction the products of combustion evolved near the feed end of said grate.

6. A method according to claim 5 in which the granules contain an amount of fuel equivalent, on a heat evolution basis, to 6–12% of coal, and in which at least 3% is carbon.

7. A method of obtaining from hydrated ferrous sulphate a sulphur dioxide gas of sufficient strength and oxygen content for catalytic conversion by the contact sulphuric acid process which comprises mixing it in the form of solid particles of 6 mesh or less in size with carbonaceous fuel of about the same particle size and with iron oxide in the presence of sufficient free water to act as a binder, granulating the mixture to a ¼" particle size, drying and hardening the granules, screening and returning the oversize material for grinding and regranulation, feeding the sized granules onto a moving grate in a relatively thin, porous layer and burning them in about 20 minutes or less while passing a current of air therethrough, and collecting as a separate fraction the products of combustion evolved near the feed end of said grate.

8. A method of producing a sulphur dioxide gas suitable for catalytic oxidation by the contact sulphuric acid process which comprises mixing hydrated ferrous sulphate crystals with iron oxide, pyrite and carbon, all of less than 6 mesh in particle size, granulating and sizing the mixture to a fairly uniform size in the presence of a binder, drying and hardening the granules, feeding the granules onto a moving grate in a relatively thin, porous layer and burning them in about 20 minutes or less while passing a current of air therethrough, and collecting as a separate fraction the products of combustion evolved near the feed end of said grate.

9. A method according to claim 8 in which the granules are dried to a total water content of not over 12%.

10. A method of producing a sulphur dioxide gas suitable for catalytic oxidation by the contact sulphuric acid process which comprises mixing finely divided ferrous sulphate monohydrate with finely divided carbonaceous fuel and iron oxide, granulating the mixture in the presence of a binder, drying and hardening the granules, sizing the granules to a fairly uniform size, igniting and burning the dried granules in about 20 minutes or less in a relatively thin, porous layer while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

11. A method according to claim 10 in which the granules are dried to a final temperature of 170–180° F. and a total moisture content of not more than 12%.

12. A method of producing a sulphur dioxide gas suitable for catalytic oxidation by the contact sulphuric acid process which comprises preparing a charge containing about 50–60 parts of finely divided ferrous sulphate monohydrate, about 25–40 parts of finely divided iron oxide, about 6–12 parts of finely divided carbon and about 8 parts of water, granulating and sizing the charge, drying and hardening the granules to a fairly uniform size, igniting and burning the granules in about 20 minutes or less in a relatively thin, porous layer while passing a current of air through them, and collecting as a separate fraction the first portions of the resulting products of combustion.

13. A method of recovering from waste ferrous sulphate liquors a sintered iron oxide and a sulphur dioxide gas of sufficient strength and free oxygen content for catalytic oxidation by the contact sulphuric acid process which comprises concentrating said liquors and recovering the ferrous sulphate therefrom in the form of finely divided monohydrate, mixing iron oxide, finely divided carbonaceous fuel and water with said ferrous sulphate monohydrate, granulating and sizing the mixture to a fairly uniform size, drying the granules to a total moisture content of not more than 12%, feeding the dried granules onto the moving grate of a sintering machine in a relatively thin, porous layer, igniting and burning the granules to a sintered mass substantially free from sulphur in about 20 minutes or less while passing a current of air therethrough, and collecting as a separate fraction the products of combustion evolved near the feed end of said grate.

14. A method of recovering from waste ferrous sulphate liquors a sintered iron oxide and a sulphur dioxide gas of sufficient strength and free oxygen content for catalytic oxidation by the contact sulphuric acid process which comprises concentrating said liquors and recovering the ferrous sulphate therefrom in the form of finely divided monohydrate, mixing iron oxide, finely divided carbonaceous fuel and water with said ferrous sulphate monohydrate, granulating the mixture to pellets of about ¼" size, drying said pellets by counter-current contact with hot gases to a total moisture content of not more than 12%, feeding the dried granules onto the moving grate of a sintering machine in a relatively thin, porous layer, igniting and burning the granules to a sintered mass substantially free from sulphur while passing a current of air therethrough, collecting as a strong sulphur dioxide gas the products of combustion evolved near the feed end of said grate, and returning the remaining products of combustion to the drying step.

BLAKESLEE BARNES.
HAROLD E. BROUGHTON.