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PREFERENTIAL SULPHATIZATION OF COMPLEX ORES

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This invention relates to the preferential or selective sulphatization of mixed metallic oxides and silicates. More specifically the invention relates to the treatment of complex ores, which because of their earthy character and the intimate association of their mineral constituents, are not amenable to known methods of ore dressing and separation. It is particularly directed to the hydrated type of ore, consisting of a complex aggregate of minerals, including metallic oxides and hydro-silicates, in the smelting of which it is impossible to avoid reduction of the minor metallic components, the latter therefore appearing in the product as alloying impurities.

As an example of the type of ore to which the invention is particularly directed, may be cited the nickel chromiferous iron ores of Cuba, Greece and Borneo. These ores range in analysis, on dry basis; iron 46 to 52, chromium 2 to 3, nickel and cobalt up to 1.2%. These deposits represent large tonnages of comparatively high grade iron ore, which it has hitherto been found impossible to utilize to any substantial degree in the manufacture of commercial steel products, such use having been limited to special products in which the content of nickel and chromium could be effectively utilized.

A purpose of the invention is therefore to remove the nickel, which because of its chemical stability, is not susceptible to removal in the course of steel-making operations.

Certain ores of this character, tend to run higher in alumina, than is desirable for normal smelting practice; a further purpose of this invention is therefore to effect some decrease in the alumina.

The process also admits of chromium removal, but to a degree commensurate with a loss in iron. As it is a specific purpose of the invention to maintain as nearly as possible the original iron content of the ore, the process contemplates only an incidental removal of chromium, which element may, however, be removed to an effective degree in subsequent process steps, well known in the metallurgical art.

A known method of treating metallic oxides and silicates, so as to facilitate their removal, is to convert them to soluble sulphates by roasting them at suitable temperatures in the presence of a sulphatizing agent. In the case of complex iron ores, such as those above referred to, the purpose of sulphatization is to effect a preferential conversion of certain undesired components to soluble sulphates, removable by leaching, without incurring serious losses of soluble iron in the leach solution.

Previous investigators, having in view a selective sulphatization of non-ferrous oxides and silicates, associated with iron oxides, have used as indirect sulphatizing agents, metallic sulphides and sulphates, alkaline metal sulphates, or their chemical equivalents; as more direct sulphatizers, they have used mixtures of sulphur dioxide and air. All of these have been utilized under various conditions within limits of temperature, time and concentration. However, the fact that the partial pressure of sulphur trioxide (which is the effective reagent from whatever source derived) is an important factor in any system of selective sulphatization and that it must be effectively controlled, seems to have been entirely ignored. This fact has now been fully demonstrated in the course of experiments in the sulphatizing of ores, and the knowledge thereby gained has been usefully applied to an adequate solution of the problem. In the case of the Cuban ores, for example, it has been shown that nickel and alumina may be removed and the ore beneficiated to a degree adequate for normal steel making operations, by exercising the proper control of partial pressure and temperature during the sulphatizing reactions.

The presence in an ore of several sulphatizable components, which it is desired to sulphatize in a preferential or selective manner, complicates the problem of controlling the degree of conversion of the respective components to their soluble sulphates; particularly is this so in the case of the readily sulphatizable iron, which is present in predominant proportions. The difficulty of control can be appreciated, if due consideration be given to the fact, that conversion to sulphate is reversible within certain ranges of temperature, to the extent that the sulphate formed, tends to dissociate. Such dissociation, depending on the particular element from which the sulphate is derived, may take the form of a direct reversion to the original oxide or, in certain cases, to the reduced metal; or, again, it may pass through an intermediate stage as basic sulphate, before reverting to the oxide. Whatever be the mechanism of dissociation, it is necessarily accompanied by a secondary dissociation of the SO_3 radicle set free by the reversion of the sulphate, so that sulphur dioxide and oxygen are produced.

It is well known that the dissociation pressures of various sulphates differ according to the metal

from which they are derived. From previous investigations of paired sulphates, heated to various temperatures, it is known that there are also variations in the pressures set up by different types of mixed sulphates. With certain exceptions, the dissociation pressure is generally that due to the less stable member of the pair. On the other hand pairs of certain isomorphous sulphates exhibit the characteristics of a single phase, having a well defined dissociation pressure, intermediate in range between that of the individual members. From this it becomes evident, that, in the case of mixed non-isomorphous sulphates, the member having the highest dissociation pressure, that is to say, the least stable at the selected temperature, is the more readily decomposed to its insoluble form; the other sulphate therefore remaining substantially unaffected.

To better understand the distinctive features of the process herein disclosed, let it be assumed that the ore exists in a simplified form and that its important components, iron oxide, alumina, chromic oxide and nickel oxide are present as pure oxides. By selecting the proper temperature and partial SO_3 pressure, it should be possible to sulphatize one or more of the components in a preferential manner. For example, at a temperature of 700° C. and SO_3 partial pressure of 120 m/m, only the oxides of nickel and aluminum should be sulphatizable. Conversely, the reaction being reversible, it can be shown that under conditions of complete sulphatization of the mixture, the comparative stabilities against reversion, of the sulphates so formed, would run in the order: chromium, iron (ferric), aluminum and nickel, with nickel sulphate as the most stable.

In actual fact however, a complex ore contains other components, silica for example, which intervene and change the characteristic dissociation pressures of the metallic sulphates above referred to. Also the reactivity to sulphatization of each component is appreciably affected by the particular mineralogical form in which it exists in the ore. Nevertheless the general indications above cited hold true, as to the feasibility of selective suphatization and a controlled reversion of the sulphates formed, so long as the components to be separated do not have the character of solid solutions. While the investigations of single and mixed sulphates, above referred to, relate to the total dissociation pressures set up, it is evident that for the purpose in view, viz. a control of the formation of sulphates and their maintenance in a stable form, it is the partial pressure of sulphur trioxide that is the more readily controlled factor.

As a result, a preferred process has now been worked out for the treatment of Cuban ores, such as those of the Mayari and Moa Bay districts; the features of which are as follows.

As is well known, sulphur trioxide is produced by the combination of sulphur dioxide and the oxygen of the air, in the presence of a suitable catalyst, such as platinum or an oxide of vanadium, at a temperature of about 450° C., the purpose being to attain a high degree of conversion of sulphur dioxide and the concentration of trioxide being dependent on the ratio of air and dioxide used in the process. For the purpose of this invention, it has been found that in order to secure the desired results, the generation of the sulphur trioxide, to be used for sulphatizing the ore, should be effected at a point in the system, entirely separate from the zone of sulphatization. The gas, so produced, is then brought into intimate contact with the ore to be sulphatized, said ore being heated to a predetermined range of temperature in a furnace of suitable type. A concentration of 25–30% SO_3, arising from a 2:1 ratio of air and sulphur dioxide and a 90% conversion of SO_2, has given particularly effective results in sulphatization; lower concentrations may be satisfactorily used, but the time factor in sulphatization is correspondingly increased; for this reason it is preferred not to lower the concentration below 15%.

An important feature of the present process is the somewhat higher range of sulphatizing temperatures, 650° C. to 760° C., than that used heretofore. If reference be had to known methods of sulphatizing, by effecting the conversion of sulphur dioxide in contact with the ore to be sulphatized, or by mixing pyrite or similar sulphur bearing material therewith, it will be seen that the required degree of SO_2 conversion cannot be met. For example, in the case of burned pyrite, the percentage conversion of SO_2 to SO_3 at 450° C. is less than 20%; at 500–600° C. with the same rate of flow, the conversion is still less than 50%; and at 700–750° C. it drops to less than 20%. Whether pyrite be roasted with the ore to be sulphatized, or whether a mixture of sulphur dioxide and air be passed over the ore at 400–500° C., it is evident that the reaction rate is too slow for the purpose sought. Any extension of the treatment period, to offset the low reaction rate tends to a corresponding increase in the amount of iron sulphatized.

Furthermore the sulphatizing temperature is necessarily limited to that at which the combination of SO_2 and O can best be effected, say 400° C. to 500° C. Moreover the conflict between the formation of sulphur trioxide in contact wth the ore, the latter acting to some degree catalytically, and the sulphatization of the ore by the gas so formed, makes it impossible to attain the desired control of SO_3 partial pressure. In other words, these known methods do not provide the best conditions, neither in respect to SO_3 concentration, nor in respect to temperature, for effecting a selective conversion of nickel and other minor components of the ore to a form suitable for their removal.

The sulphur trioxide gas is passed into a suitable roasting furnace, so devised as to provide a maximum degree of contact between the ore mixture and the sulphatizing gas. The ore, or advantageously a mixture of ore of 5 to 15% of sodium chloride, should previously be brought to the desired roasting temperature, 650–700° C. In heating the ore, moisture and water of hydration are driven off, their removal being facilitated by passing air over the mixture, during the early stages of the heating period.

The most effective rate of flow for the sulphatizing gas should be determined experimentally. In the initial stages of sulphatization SO_3 is rapidly absorbed by the ore, but as sulphatization proceeds the rate of absorption slows down appreciably; hence the rate of gas-flow into the furnace should be cut down accordingly. By observing the gas leaving the furnace for indications of unconsumed SO_3, and by sampling the ore at different stages of the roast, these conditions may be adequately controlled.

If sulphatization at 650–700° C. be prolonged until 90% or more of the nickel has been sulphatized, it will be found that a substantial propor-

tion of the iron, varying from 20 to 50%, has also been converted to soluble sulphate. To avoid high iron losses in the subsequent leaching of the roasted product, it is essential to cause the reversion of the ferric sulphate to an insoluble form of iron. This may be effected by increasing the temperature during the later stages of roasting to a degree sufficient to decompose, or dissociate, the ferric sulphate. Within certain limits of temperature, say up to 750° C., and provided roasting at this higher temperature be not protracted for too long a period, the greater part of the sulphatized iron may be caused to revert with but slight loss of sulphatized nickel.

A more precise and controllable method of preventing the decomposition of the nickel sulphate, one which is an important feature of this invention, consists in maintaining on the roasted product during the decomposition period, a degree of gas pressure in excess of the dissociation pressure of nickel sulphate at that temperature, but less than the dissociation pressure of ferric sulphate.

In the case of Cuban ore, the roasting temperature in the final period may advantageously be increased about 50° C., say to a temperature of 700–760° C., while maintaining a slow flow of SO_3 gas over the sulphatized ore, so as to impose thereon a total gas pressure, high enough to inhibit reversion of nickel sulphate. This imposed pressure, which may be controlled to the desired value by a valved outlet from the furnace, is due to the combined partial pressures of SO_3 and of its own decomposition products SO_2 and O at that temperature, and also of the inert gas which accompanies the SO_3. It is known that the dissociation pressure of nickel sulphate at 750° C. is only about 38 m/m, which value is the sum of partial pressures of SO_3, SO_2 and O. On the other hand ferric sulphate has a dissociation pressure greatly exceeding the value for nickel sulphate even at substantially lower temperatures, which value increases rapidly as it approaches 700° C., when it attains approximately 560 m/m. Chromium sulphate likewise has high dissociation pressures, whereas the individual pressures of the sulphates of cobalt, manganese and magnesium (which may also be present as oxides or silicates in ores of this type) are still lower than nickel sulphate, within a temperature range of 700–760° C. Aluminum sulphate has a pressure higher than nickel sulphate but substantially lower than the sulphates of iron and chromium.

From this it becomes evident that, the substantial difference between the low dissociation pressures of nickel sulphate (also of cobalt, manganese and magnesium, when these are present in sulphatized form) and the comparatively high pressures of iron and chromium sulphates, renders possible the selective reversion of the latter group to their insoluble form, without greatly affecting the solubility of the nickel and other soluble metallic salts of low dissociation pressure, by maintaining over the mixture a total pressure intermediate between the extreme values aforesaid. In so far as soluble aluminum is concerned, the imposed pressure selected should have a value also higher than that, which would correspond to the dissociation of aluminum sulphate.

It will of course be understood that the values given above refer to the individual dissociation pressures of the various sulphatized components. Because of their influence on each other and depending on their respective proportions, the dominant dissociation pressure of any one group of mixed sulphates will vary from the values indicated. In the same way, the presence of intervening components of the ore, silica for example, will influence the values. However, the wide disparity between the two groups, namely nickel, cobalt, manganese and magnesium on the one hand, and iron and chromium on the other, allows sufficient latitude in which to select the gas pressure to be imposed. Such selection, in view of the complex factors involved, is best determined experimentally and for practical purposes may be expressed as the total pressure, corresponding to a specific SO_3 partial pressure.

By way of illustration it may be stated that when the decomposition of nickel and iron sulphates was carried out at 750° C. the total pressure was 737 m/m, corresponding to an SO_3 partial pressure of 237 m/m. The partial pressure of nickel sulphate at this temperature is but 4 m/m, that of ferric sulphate exceeds the total pressure figure of 737 m/m. Consequently the decomposition of ferric sulphate can continue unopposed, the nickel sulphate remaining practically unaffected. By actual analyses prior to, and subsequent to decomposition, it has been shown that by maintaining the conditions above specified the incidental reversion of nickel sulphate may be limited to 2.5% whereas the iron sulphate may be decomposed to the extent of 97–98%.

It is further to be observed that the above SO_3 partial pressure of 237 m/m is close to, but slightly less than, that due to the decomposition of aluminum sulphate. From this, it is evident that decomposition of any aluminum sulphate present would not be avoided, under the conditions specified. To maintain both nickel and aluminum in soluble condition as sulphates, but revert substantially all the iron, it would be necessary to maintain an SO_3 partial pressure in excess of that due to the decomposition of aluminum sulphate at the decomposition temperature selected. This can be effected by lowering the temperature of decomposition, say to 720° C., at which temperature the SO_3 partial pressure of aluminum sulphate would decrease to about 100 m/m; in consequence any total pressure corresponding to an SO_3 partial pressure in excess of this figure, but lower than that due to the decomposition of ferric sulphate, would be suitable for inhibiting the decomposition of aluminum and nickel sulphates.

With the temperature range and degree of gas pressure established, the third controllable factor, that of time, remains to be considered and particularly in respect to the comparative durations of the two roasting periods, the functions of which are broadly that of sulphatization and restrained or selective decomposition. In the first period at the lower temperature 650–700° C., the initial stages of nickel sulphatization proceed rapidly but the reaction slows down as the absorption of SO_3 becomes less. On the other hand prolongation of the time of sulphatization beyond a certain time promotes a rapid increase in the amount of iron that may be sulphatized at that temperature. At the higher temperature of 700–760° C. the sulphatization of nickel tends to accelerate and at the same time reversion of sulphatized iron is promoted. The most effective combination of the two roasting periods is such that, the first period results in oversulphatization of the ore to the extent that sulphatization of the iron is permitted to proceed to a substantial degree, before changing to the higher temperature.

There is probably some additional sulphatization of nickel at the higher temperature which serves to insure a higher recovery of nickel in a soluble form, but the main purpose of the second period is to decompose iron sulphate without a concomitant decomposition of nickel sulphate. With the Cuban ore referred to, the best results have been obtained by roasting at the higher temperature with a slow and controlled flow of SO_3 for a period representing from 40 to 50% of the total time of roasting. In this manner over 90% of the nickel has been obtained in a soluble form, while the solubility of the iron has been limited to 8% or less. Aluminum to the extent of about 50% has also been rendered soluble.

The principles of the process as outlined above, may be applied in an alternative and equally effective manner, by utilizing the ferric sulphate formed in the first roasting period at 650–700° C., as the reagent in the second roasting period at 700–760° C. This can be accomplished by making an addition of raw ore to the product of the first period in amount, such that the nickel and aluminum in the added ore may be sulphated by the subsequent dissociation of the ferric sulphate, available in the initially oversulphated ore. The furnace is then closed and heated to approximately 750° C. and a total gas pressure maintained therein, which corresponds to the selected SO_3 partial pressure; gas in excess of this pressure being allowed to escape from the furnace through a suitable valved connection and recovered for further use on a subsequent batch of ore.

After sulphatization has been completed the treated mass is quickly cooled by quenching in water. This is necessary, because if the mass be permitted to cool in the presence of SO_3 it may, in passing through the temperature range at which iron sulphatizes readily, acquire ferric sulphate, a result it is particularly desired to avoid. On the other hand if residual SO_3 be swept out by a current of air, there is danger of decomposing some of the soluble nickel sulphate and a consequently less efficient removal of nickel from the ore. The cooled mass is submitted to a suitable water leaching for the removal of the soluble sulphates of nickel and aluminum. Recovery of these soluble salts may be effected by any methods known in the art, by precipitation for example, but such methods are outside the scope of the invention, the main purpose of which is to maintain sulphatization under proper control. Obviously the cooling and leaching may be combined as one step. The leached residue may be dried and agglomerated by nodulizing or sintering and is then in suitable condition for smelting in a blast furnace.

In certain cases analysis of the leach solution has indicated that an appreciable amount of chromium sulphate may be brought into solution. However this necessarily involves some additional loss in iron, because of the known inactivity of chromic oxide, causing it to sulphatize at a comparatively slow rate, and also because the same measures that may be taken to inhibit sulphatization of iron or to promote its decomposition if sulphatized, will be similarly effective in respect to the chromium. Therefore, while admitting the feasibility for certain purposes, of removing chromium with some increase in soluble iron, by this process, the preferred practice of the invention is not directed to chromium removal in any substantial degree, said removal may be adequately effected by known metallurgical processes.

It will be obvious to those skilled in the art that the process steps, herein described and the methods devised for controlling partial pressures in the reactions of sulphatization, are applicable to a comparatively wide range of metallic oxides and silicates specifically and to mixtures of sulphatizable inorganic salts in general, selective treatment of which is based, in part on a selective sulphatization to soluble form, in part on a selective reversion therefrom to an insoluble condition.

The specific features of the invention are set forth in the following claims.

We claim:

1. A process for the selective sulphatization of metallic oxides and silicates in iron ores containing them, which consists in, treating the ore with sulphur trioxide gas at a temperature favoring the formation of soluble metal sulphates having comparatively low dissociation pressures, raising the temperature after a predetermined period, so as to dissociate any incidental metal sulphates of high dissociation pressure formed at lower temperature, while maintaining thereon a predetermined degree of reaction gas pressure to inhibit dissociation of those soluble sulphates having low dissociation pressures, cooling the mass and removing the undissociated soluble sulphates by leaching.

2. A process for the selective sulphatization of nickel oxides in iron ores containing them, which consists in, treating the ore with sulphur trioxide gas at a temperature favoring the formation of soluble nickel sulphate, raising the temperature after a predetermined period, so as to dissociate any incidental iron sulphate formed at lower temperature, while maintaining thereon a predetermined degree of reaction gas pressure to inhibit dissociation of soluble nickel sulphate, cooling the mass and removing the undissociated nickel sulphate by leaching.

3. A process for the selective sulphatization of nickel and aluminum oxides in chromiferous iron ores containing them, which consists in, treating the ore with sulphur trioxide gas at a temperature favoring the formation of soluble nickel and aluminum sulphates, raising the temperature after a predetermined period, so as to dissociate any incidental iron and chromium sulphates formed at lower temperatures, while maintaining thereon a predetermined degree of reaction gas pressure to inhibit dissociation of soluble nickel and aluminum sulphates, cooling the mass and removing the undissociated nickel and aluminum sulphates by leaching.

4. A process for the selective sulphatization of nickel and aluminum oxides in chromiferous iron ores containing them, which consists in, adding a small amount of an alkaline metal chloride to the ore, heating the mixture to a temperature of 650° C. to 700° C., passing thereover sulphur trioxide gas which has been formed prior to its contact with the mixture, continuing said flow of gas and maintaining said temperature until substantially all the nickel, a large proportion of the aluminum and minor proportions of the iron and the chromium have become sulphatized to soluble metal salts, raising the temperature to from 700° C. to 750° C. and continuing the flow of sulphur trioxide gas until the soluble iron and chromium of earlier sulphatization have been decomposed to insoluble forms, rapidly cooling the mixture and leaching the soluble nickel and aluminum salts from the insoluble residue.

5. A process for the selective sulphatization of nickel and aluminum oxides in chromiferous iron

ores containing them, which consists in treating the ore with sulphur trioxide gas at a temperature of 650° C. to 700° C. for a predetermined period, until substantially all the nickel, a large proportion of the aluminum, and minor proportions of the iron and chromium have been sulphatized, raising the temperature for a further period to a point not exceeding 760° C. to decompose iron and chromium sulphates, while maintaining thereon a total gas pressure which corresponds to an SO_3 partial pressure greater than that of nickel and aluminum sulphates but less than that of iron and chromium sulphates, quenching the mass and removing the nickel and aluminum sulphates by leaching.

6. A process for the selective sulphatization of nickel and aluminum oxides in chromiferous iron ores containing them, which consists in, adding 5% to 15% of an alkaline metal chloride to the ore, treating the mixture with sulphur trioxide gas at a temperature of 650° C. to 700° C. for a predetermined period, raising the temperature for a further period to a point not exceeding 760° C. while maintaining thereon a total gas pressure which corresponds to an SO_3 partial pressure exceeding that of nickel and aluminum sulphates but less than that of iron and chromium sulphates, quenching the mass and removing the nickel and aluminum sulphates by leaching.

7. A process for the selective treatment of iron ores containing oxides and silicates of nickel, whereby the nickel constituents may be rendered soluble preferentially to iron, which consists in, treating the ore with a sulphatizing gas at a temperature to effect the sulphatization of substantially all the nickel and from 20% to 50% of the iron, then raising the temperature to decompose the sulphatized iron, while imposing on the mass a total gas pressure exceeding that derivable from the decomposition of sulphatized nickel at that temperature, controlling said total pressure by maintaining a flow of sulphatizing gas, the partial pressure of which is that corresponding to the total pressure desired.

8. A process for the selective sulphatization of nickel oxides and silicates in iron ores containing them, which consists in, adding to the ore a small amount of an alkaline metal chloride, heating the mixture to a temperature of 650° to 700° C., passing thereover a stream of sulphur trioxide gas until substantially all the nickel and a minor proportion of the iron have been sulphatized, adding thereto fresh ore in amount, such that the sulphatizable components of the latter, when heated to suitable temperature, may react with the gaseous decomposition products of the sulphatized iron derived from the original ore, effecting said decomposition by increasing the temperature to a degree not exceeding 760° C., while maintaining thereon such a degree of total pressure as to correspond to a sulphur trioxide partial pressure intermediate between those of nickel sulphate and iron sulphate, and removing the undecomposed products of sulphatization by leaching.

9. In a sulphatizing roast for complex ores under conditions effecting a substantial sulphatization of several components of the ore, the method of selectively controlling the dissociation of the sulphatized components by maintaining thereon a degree of reaction gas pressure, greater than the dissociation pressures determined for such of the sulphatized components as it is desired to inhibit from dissociation, but inferior to the dissociation pressures of the sulphatized components to be dissociated.

10. A process for controlling the decomposition of mixed sulphates which consists in, heating the sulphates in an atmosphere of sulphur trioxide to a temperature in excess of their appropriate temperature of sulphatization, inhibiting the decomposition of sulphates having lower dissociation pressure by maintaining thereon a degree of gas pressure in excess of said dissociation pressure but inferior to the higher dissociation pressure of those sulphates decomposition of which is desired.

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