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REDUCTION OF SULPHATE MINERALS AND BRIQUETTES THEREFOR.

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This invention relates to the production of alkali-metal, and alkaline earth metal, sulphides by the reduction of the corresponding sulphates, and while it applies particularly to the production of barium sulphide, it is also applicable to other sulphides such as those of calcium, strontium, and sodium. It has for its object an improvement in the method of carrying out this process for producing such sulphides.

According to the customary practice for the production of barium sulphide, which is typical of the other alkaline earth sulphides, the finely ground barytes (barium sulphate mineral) is mixed with more or less finely ground reducing material, such as coal or other carbonaceous material. The proportion of coal to mineral is generally 1 to 4, which is in excess of that theoretically required by the reaction. The average fineness of the mineral is generally 50 to 100 mesh. The charge in this form is fed into a suitable furnace, the operation being of the batch type, where it is heated to a red heat or higher, which effects the reduction of the barium sulphate to barium sulphide. The resulting product known as "black ash" contains barium in the forms of the sulphide, of the unconverted barium sulphate, and of barium rendered unavailable due to the deleterious reactions also occurring in the furnacing operation.

The furnace usually employed is of the rotating reverberatory type, from 9–20 feet in length, and 6–10 feet in diameter, directly heated by a coal grate, oil or gas burner at one end; but other types of furnaces are occasionally used, heated either by direct contact with combustion products or by heat transfer through an intervening wall.

Our invention is especially advantageous where the furnacing operation is continuous and involves direct contact of hot products of combustion with the barytes to be reduced, as is the case in the customary method above described.

It has long been recognized that silica, which is universally present in barytes ores, is an objectionable constituent, so that, in the mining of the barytes, as much silica is removed as is practicable without too great an increase in the cost of the mining and refining of the mineral. For the production of sulphides it has heretofore been considered necessary to use a high grade barytes ore, that is, one having less than 4% of silica. A high grade barytes mineral may also be defined as a mineral containing 94% or more of barium sulphate, about half the impurities consisting of silica. The low grade mineral run down to well under 90% of barium sulphate and contain more than 4% of silica. The reason for this demand for a mineral contaning more than 94% barium sulphate, is the poor yield, running in some cases less than 60%, which is obtained with mineral containing substantially more than 4% silica. As a result, the comparatively large deposits of low grade mineral have heretofore been practically unavailable as a source of supply for the production of barium sulphide—a compound which is used in enormous quantities in the production of the white pigment, lithopone.

Our invention is based to a great extent upon the discovery that where the sulphate mineral is heated by direct contact with hot products of combustion, these hot products have a deleterious action on the furnace charge; this deleterious action seems to be due, at least in part, to an acceleration of the chemical reaction between the barium and the silica, and is accentuated when the degree of subdivision of the charge is increased—probably because of the greater surface which is thereby exposed to the hot gases.

Our invention consists in preventing these hot products of combustion from contacting with a great proportion of the furnace charge in so far as is compatible with the efficient handling and heating of such charge. This we do by first molding or pressing the furnace charge into the form of small dense masses, tablets or briquettes which are relatively impervious to the hot combustion gases, and which have sufficient coherence to retain their shape throughout the furnacing operation. For proper handling these masses should be less than four inches in diameter or length, and are preferably of from one-half to two inches in diameter and/or length. Small masses or tablets substantially less than one-half inch in diameter expose more surface to the chemical action of the hot gases than is desirable. Briquettes having one or more dimensions in excess of four inches may of course be used, and come within the scope of our invention, but no special advantage is gained by this increase in size.

By subjecting the furnace charge in this form to hot combustion products, the tablets or briquettes are easily brought to the temperature required for the reduction of the sulphate by the powdered coal in admixture therewith, while at the same time the proportion of mineral which is subjected to the chemical action of these combustion gases is confined approximately to the surface layers of said tablets or briquettes.

Although the increase in the yield of sulphide when using a high grade mineral is sufficient to justify the use of our process with such mineral, the outstanding importance of this new process is most clearly demonstrated by the remarkable increase in yield which is obtained when it is used with a low grade mineral containing, say, from 80 to 90% of barium sulphate and 8% or more of silica. A typical illustration of this increased yield is given in the following table:

Type of charge.	Yield with— Poor mineral A. ($BaSO_4$: 89%. SiO_2: 10%.) Per cent.	Good mineral B. ($BaSO_4$: 94%. SiO_2: 3%.) Per cent.
Usual operation	60.3	81.5
Briquettes (¾" dia.)	91.4	94.1

The furnacing conditions for our process are those ordinarily used in the prior art, namely, a three-hour reduction period with the charge temperature of from 950 to 1150° C.

The tablets or briquettes mentioned above may be prepared in various ways, but we prefer the following procedure: One part of coal and about four parts of barytes mineral, each preferably ground or pulverized to a fineness of 100 mesh, are thoroughly mixed together, and with the resulting mixture there is incorporated a suitable binding material such as crude petroleum, sulphite process waste liquor, starch, molasses or other similar material. The resulting mass is then pressed in a suitable mold, preferably at a high pressure, into tablets or briquettes; these may have practically any form, although we prefer the pillow shape.

In addition to the prevention of direct contact of the combustion products with a large proportion of the furnace charge at very high temperatures, an advantage of considerable importance in introducing the furnace charge in the form of dense, compact masses results from the fact that the mineral and coal are tightly packed together, and remain in intimate contact throughout the furnacing operation, thus facilitating the reaction between the solid phases carbon and barium sulphate in the mineral; and also from the fact that since contact with hot combustion products is confined to the surfaces of the tablets, the degree of subdivision of the mineral and coal before being mixed and molded may be greatly increased, thereby still further increasing the degree of intimate contact of the mineral and coal while they are being subjected to the high temperature required for reduction of sulphate to sulphide.

Although throughout the above specification and following claims, we describe the furnace charge and the tablets or briquettes as consisting essentially of ore and coal, it will be understood that by the word coal we mean to include any carbonaceous material which will function like coal in effecting reduction of the sulphate to sulphide.

We claim:

1. The process of treating a low grade barytes ore containing more than 4% of silica to reduce the sulphate therein to sulphide, which comprises mixing from four to six parts of finely powdered ore with about one part of finely powdered coal and with a binder, pressing the resulting mixture into tablets or briquettes, and bringing said tablets or briquettes into contact with hot products of combustion until the reduction of the sulphate to sulphide is practically complete.

2. A process as set forth in claim 1 in which the smallest dimension of the tablets or briquettes is in excess of half an inch, and the temperature to which they are heated is from about 950 to 1150 ° C.

3. As a new article, powdered sulphate ore containing more than 4% of silica and held together in the form of substantially non-porous tablets or briquettes by a suitable binder, which depends upon its coking properties for its binding action.

4. As a new article, barytes containing more than 4% of silica mixed with powdered coal in the proportion of four to six parts of finely powdered ore to one part of coal, and held together in the form of substantially non-porous tablets or briquettes by a suitable binder, which depends upon its coking properties for its binding action.

5. As a new article, barytes containing less than 90% of barium sulphate and more than 4% of silica mixed with powdered coal in the proportion of four to six parts of finely powdered ore to one part of coal, and held together in the form of substantially non-porous tablets or briquettes by a suitable binder, which depends upon its coking properties for its binding action.

In testimony whereof we affix our signatures.

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