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FLUIDISATION AND ITS APPLICATION TO THE ROASTING OF SULPHUR-BEARING MINERALS.

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Fluidisation is a recent technical achievement which, however, the writer thinks, will not be entirely new to members. This matter has been the subject of numerous publications, especially in English. But the literature on the subject becomes more extensive every day, and recently a French study appeared (1). The writer apologises for repeating what is probably known to many members.

Fluidisation - in the absence of a better expression - may be defined as a technical process consisting of the creation of a dense mass of finely divided solids maintained in suspension by a current of ascending gas. Such a mass of solids constitutes what is called a "bed". These fluidised beds possess peculiar physical properties.

For a long time past suspensions in gas of relatively small quantities of solids have been used for technical purposes. For example, for purely physical purposes, the separation and classification of ground products, and for chemical purposes, the combustion of pulverised coal and flash-roasting. These solid-gas mixtures retain, however, properties which make them very much akin to gases and, especially, the weight of solids in suspension is of the order of a fraction of kg per cubic metre. On the contrary, in the fluidised masses, the density of the mixture is much higher and can exceed a ton per cubic metre. The difference is obvious.

A fluidised mass acquires properties which to a certain degree are analogous to a liquid. Its appearance resembles on the whole a boiling liquid which bubbles owing to the steam engendered. Such a mass possesses a separation surface at a definite level which, although irregular, forms nevertheless a fairly clearly defined demarcation with the gaseous phase above. The fluidised beds obey hydrostatic laws, and their overflow can therefore be controlled, provided an appropriate technique is applied. Among other things it is possible to apply to these masses the notion of pressure and specific heat. From the purely scientific point of view, the properties and dynamics of fluidised beds are the subjects of numerous theoretical studies in the last few years, mainly in the United States. A Congress of the American Chemical Society was entirely devoted to this question (2).

(1) Une technique nouvelle: LA FLUIDISATION - Historique, Théorie et Applications - par G.GENIN - L'INDUSTRIE CHIMIQUE et le PHOSPHATE REUNIS - 38ème année - Nos 407 et 408 Juin et Juillet 1951.
(2) INDUSTRIAL & ENGINEERING CHEMISTRY - Volume 41 - June 1949, Pages 1098 and following.

What is the origin of this new technique ? It evolved during the last world war in the oil industry as a consequence of the applications of fluid catalysis. Certain reactions among gases, as is well known, are made possible or greatly accelerated by the use of solid catalysers. Instead of allowing the catalytic masses to rest on the shelves the idea was conceived to utilise finely divided catalysers in order to increase very considerably their specific surface. Thus in 1940 the first basic patents were taken out by the STANDARD OIL DEVELOPMENT COMPANY. The considerable resources at the disposal of the oil industry quickly permitted a rapid expansion of the application of fluid catalysis.

Fluidisation appears therefore to be a means considerably to increase the contact between gases and solids. Applied to the catalytic process, fluidisation does not allow the solid to intervene directly in the reaction, and one of its advantages is to allow a continuous flow of the catalyser towards a separate apparatus for its regeneration, which is often necessary in reactions between hydrocarbons when undesirable sediments modify the acting surface.

Quite naturally, the idea which followed was to apply the technique developed in connection with catalytic operations to reactions as between gases and solids where the latter play the role of reagents. Thus a wide field was opened up in regard to fluidisation which entered into the field of inorganic chemistry. The well-known American DORR COMPANY made a contract with the STANDARD OIL DEVELOPMENT COMPANY which allowed them to apply the technique developed by the former in fresh fields. Through their own research work, the Dorr Company rapidly developed such techniques and finally were able to apply them industrially.

After this short outline, considerations of a more practical nature should be discussed. How is a fluidised bed to be realised ? In principle, in the most simple manner: all that is needed is a receptacle, the bottom of which is perforated by numerous holes to admit the gas, which for roasting is air, above which a certain thickness of a sufficiently divided solid matter is introduced. Under the impact of the flow of the ascending gas the mass is fluidised, and becomes absolutely homogenous as far as composition and temperature is concerned; it acquires properties which are almost those of a liquid, as mentioned above. One can assume that each solid particle is coated by a gaseous film which is constantly renewed.

This explanation is admittedly somewhat simple, and it is quite an art to construct a perforated bottom which allows the solid matter to be supported before the gas is blown through to allow fluidisation to take place.

The fluidised masses may be the object of heat exchanges of a varying nature. The exchanges can be carried out within the masses by using hot gases for the supply of heat or by allowing them by an inverse process to introduce into the gases passing through the mass calories which are retained in a sensitive or latent form, e.g. as a result of combustion. On the other hand, it is possible for example to allow the fluidised masses to flow into exchanger tubes, in order to transmit or to receive heat through the walls of the latter.

The reactions taking place in the beds are either endothermic or exothermic. In the first case, the reactors, this is the usual name for the receptacles or furnaces in which the reactions take place consist of several beds situated at different levels. The solids of the upper bed overflow by gravity to the lower beds and meet a counter-current of hot gases, thereby obtaining a rational transfer of heat. A lower compartment can be used with advantage to re-heat the combustion air, and for cooling the calcined material.

Those modi operandi are only mentioned in passing, as the roasting of sulphur-bearing minerals which interest this meeting is an essentially exothermic operation. Generally speaking, it requires only a very simple reactor with a single bed.

Thus the principle of the FLUO-SOLID apparatus - trade mark of the DORR COMPANY for its process - can be traced, a principle which is of special interest to the Superphosphate industry:

- The furnace, or reactor, consists simply of a chamber in sheet-iron lined ~~on the inside~~ with refractory material and equipped with a special perforated bottom destined to carry the bed. Below the bottom is a box receiving the air delivered by a compressor. Above the perforated bottom is the fluidised bed, the height of which remains constant; a feeding system brings the mineral, pyrites for example, to the furnace where it falls into the bed, and the roasted material is evacuated like a liquid by an overflow situated at a given height above the bottom. The free space above the bed allows of a certain amount of decantation of the finest portion of the mineral which is carried away. The compressor has blown air through the bottom and through the bed and the gases which escape and which contain SO2 leave near the top of the chamber. The gases deposit the greatest portion of their dust in one or several hot cyclones and finally pass through a waste boiler before entering the electro-static precipitator or the washing tower which normally forms part of a sulphuric acid plant.

The operation of the furnace is therefore completely continuous: the pyrites introduced penetrate into the fluidised bed and are immediately roasted. Exchanges are vigorous, and the reaction takes place almost instantaneously. The homogeneity of the masses is such that no segregation is observed and that the matter leaving the over-flow is perfectly roasted.

What are the advantages of the FLUO-SOLIDS process ? What are its limitations ? What are its drawbacks ? How does this process fare as compared with the other known methods of roasting in mech-anical furnaces or flash-roasting ? These are a number of questions which will be answered briefly.

The primary advantage is certainly the simplicity of the process and of the apparatus. The latter is completely static and has no moving part, with the exception of the exterior apparatus such as the air compressor and the feeding mechanism, the construction of which does not present any problem. For this reason, the construct-ion of the reaction chamber and its immediate accessories can be made entirely from refractory material. Experience has shown that the lining is subject to negligible wear and tear, and that its life is exceptionally long.

The absence of moving parts permits of a construction which is 100% air-tight, and the sulphurous gasses are practically not in direct contact with the metal parts. The air-tightness allows of a rigid control of the composition of the roasting gases. There is no other air for roasting than that which is blown in and its delivery is completely controlled. Consequently it is possible to obtain a gas with 14 or 15% SO_2, if desired, with a very low O_2 and SO_3 content which considerably reduces corrosion. As the purifying apparatus forms part of the sulphuric acid plant and is of dimensions proportionate to the volume of the traversing gases, it is possible to use smaller and less costly purifiers. The air necessary for the oxidation of SO_2 can be introduced into the circuit after purification and ahead of the chambers or the catalyser, as the case may be.

The possibility of rigidly controlling the mineral supply and the volume of air blown in, as well as the constancy of the temperature in the fluidised mass are factors which render the use of a FLUO-SOLIDS reactor very easy, and allows making the installation automatic with the aid of adequate measuring apparatus equipped with suitable controls.

A desired or accidental interruption has no disadvatageous consequences. The quantity of hot material in the furnace is sufficiently large to allow an immediate restart when air is admitted again. Some industrial installations abroad used for the roasting of auriferous pyrites are regularly stopped every week-end and started up again on Monday without difficulty.

The mineral supply can be assured with various methods of introducing the mineral into the furnace by a screw feeder, by blowing in with the aid of compressed air, by a vibrating hopper etc. In some instances the thermic balance is sufficiently favourable to allow the pumping of mineral sludge into the reaction chamber which is an advantage in certain cases, for example, where the mineral is concentrated near the roasting installation.

The FLUO-SOLIDS process requires certain conditions in regard to the physical and chemical composition of the mineral. In the case of pyrites normally the granules should be less than 3 mm. although in certain special cases this process can be successfully applied to minerals passing through a 10 mm. screen. It goes without saying that flotation concentrates are suitable for roasting by fluidisation. But as it will be seen, rock-like minerals need only a relatively slight grinding.

As mentioned above, humidity, especially in the case of pyrites with a 45% S content, is in no way an obstacle to roasting. But this question may cause an incidence in the operations of acid manufacture which follow.

The chemical composition of the minerals to be roasted is often important, since certain elements may lead to the formation of fluxed compounds which may entail the agglomeration and defluidisation of the roasting bed, which is of course a serious matter, which however is less to be feared with the pyrites known to us than with blonde or with chalcopyrites or other copper pyrites. Roasting is usually more delicate when the calcined material forms the basic material of a subsequent metallurgical treatment which may impose additional requirements. But hundreds of the most complex minerals have been treated by fluidisation and in each case it has been possible to conduct the roasting in such a manner as to give entire satisfaction from this point of view.

When roasting pyrites in our industry, generally speaking, the composition of the cinders matters less and the efforts are concentrated on desulphuration. The latter is excellent, and a total residual sulphur content of less than 0.5% is easily obtained. As already mentioned, the roasting of sulphur-bearing minerals is an exothermic operation, which with certain minerals which are rich in sulphur constitutes a disadvantage. As a matter of fact, there is an upper limit of temperature which can be attained in the fluidised bed, and this limit ranges between 800 and 900°C, according to the composition of the mineral. In exceeding this temperature limit, agglomerating fluxes are produced which destroy fluidisation. If the thermic balance is excessive, taking into account the considerable heat carried away by the gases and the loss by radiation, convexion etc., cooling by an appropriate means must be resorted to. The most simple means giving excellent results consists quite simply of injecting water into the reaction chamber. This water is vaporised and maintains the desired temperature. It is quite simple to render this arrangement automatic by controlling the flow of water with the aid of a pyrometer equipped with suitable switches. The presence of water in the roasting gas is not a disadvantage if the acid is produced by the contact process. As a matter of fact, the water thus introduced recondenses in the washing-tower. On the other hand, if the chamber system is employed, other measures of cooling will have to be adopted. But it should be mentioned here that the ease with which the fluidised materials are manipulated allows of using appropriate heat exchangers, the hot water from which may serve to supply a waste-heat boiler similar to that used with the flash-roasting process.

The problems of burning sulphur contained in sulphur-bearing materials, with a sulphur content ranging between 12% and 50% have been definitely solved.

The principal drawback, and actually the only one, of the FLUO-SOLIDS process is the necessity of consuming energy for the blowing of the air through the bottom of the apparatus and the bed, the hydrostatic pressure of which must be overcome. According to the methods of application, the height of the bed regulated by the position of the over-flow, varies between 300 and 1500 mm., and it is advisable to have at one's disposal a compressor, the manometric pressure of which can attain 2 metres of water. The total expenses for energy of this process, calculated for the reaction chamber and its accessories, is 15 to 20 KWH per ton of pyrites. But as in the case of flash-roasting, the high temperature of the gases (about 900°C) permit of an interesting and considerable heat recovery, and a steam production of 700 kgs to 1000 kgs per ton of pyrites which must be put on the credit side of the balance sheet of power consumption.

A minor drawback, of variable importance according to the aim envisaged, is the carrying away of the fine dust by the ascending gas current, and the necessity to make arrangements for its collection. However very often this dust is completely roasted and can be considered a satisfactory product. This is certainly the case when roasting the usual iron pyrites.

To sum up:

Advantages:

- Simplicty of construction;
- Ease of control;
- Absolute control of roasting;
- Possibility of rendering operations automatic;
- Increased desulphurisation;
- Possibility of treating wet minerals or even sludges, except with the lead chamber process.

Drawbacks.

- Power consumption, but possibility of heat recuperation;
- Problem sometimes set by the carrying away of dust;
- Necessity of a slight grinding, in the case of coarse minerals.

Fluidisation is very favourable as compared with the usual roasting processes, owing to its simplicity. It is characterised by low initial costs, by reduced working costs and negligible maintenance costs. As compared with roasting in suspension, it allows of the construction of very large units - a Canadian installation will produce 150 tons of monohydrate acid with a single reaction chamber without necessitating the fine grinding and careful drying which would otherwise be necessary.

The FLUO-SOLIDS process is at the beginning of its industrial development. Applied to the roasting of metallic sulphides, it has already had considerable success in special metallurgical lines, and above all in the very delicate roasting of auriferous pyrites with a view to rendering them suitable for cyanuration. It is being introduced into the zinc and copper industry.

The present lack of sulphur has rendered it necessary to have recourse to all possible sources of sulphur. Many users are taking to roasting pyrites, and for this reason are studying and installing the FLUO-SOLIDS process in the United States, Canada, Gt.Britain and South Africa.

In Belgium the process has awakened interest and an installation studied jointly by the Société Belge DORR-OLIVER and the SOCIETE GENERALE DES MINERAIS is in course of construction in a Superphosphate works. It is to be hoped that it will fulfil expectations.

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