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Magnesium fertilizer from serpentinite

Serpentinites are minerals whose basic ingredients are the products of serpentinization of magnesium olivines, that is magnesium silicates in the form of olivine, serpentine, talcum and some quantities of magnesium carbonate.

Serpentinites occur in the form of vast deposits not deep under the soil surface. They are easily accessible and are usually excavated by the strip mining method. Poland has big deposits of serpentinites in the Walbrzych voivodship.

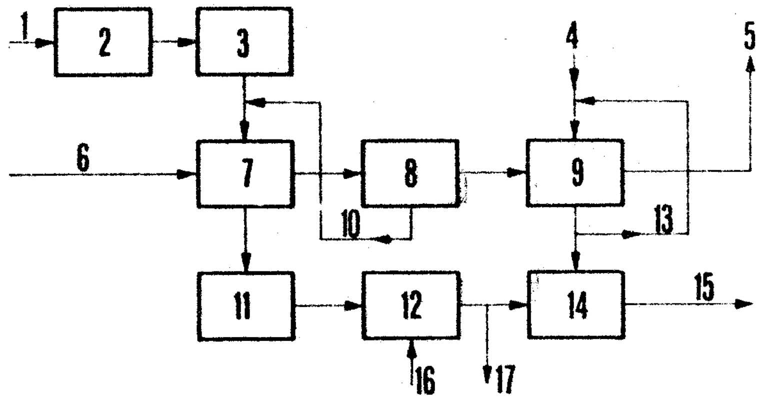
Serpentinites from strip mines are very seldom subjected to chemical processing aimed at recovering magnesium compounds and other elements such as nickel, chromium and iron contained in serpentinites in an amount of less than one to more than ten percent by weight.

The Chemical Engineering Institute of Warsaw Technical University has developed a method of producing phosphate fertilizer by exposing phosphorites to the action of gaseous SO_3*. Then, by analogy to this method tested on an industrial scale, a process of serpentinite decomposition by the dry method, also using gaseous SO_3 was developed. The purpose of the study was to produce a magnesium fertilizer with magnesium sulphate as its main component, since this compound is the best source of fertilizer magnesium. The magnesium fertilizer production process was an intermediate stage in investigations aimed at obtaining pure magnesium sulphate and magnesium oxide from serpentinite. The dry method of producing magnesium fertilizer from raw materials containing serpentinites depends on the action of gaseous sulphur trioxide on the comminuted raw material. MgO reaction in the magnesium raw material varies from 65 to 85%.

Strip-mined serpentinites of any content of MgO constitute the raw material in the dry-method production of magnesium fertilizers. Before reaction the raw material is comminuted and ground. After grinding the raw material does not need to be dried.

Gases containing SO_3 mixed with inert gases (oxygen, nitrogen, etc.) or 100% pure SO_3 e.g. desorbed from oleum can be used for the production of magnesium fertilizers. SO_3 concentration in the gas has no effect on the quality of the final product. Also the presence of water vapour in the gas (as a result of which some part of SO_3 is bound in the form of sulphuric acid vapours) has no influence on the implementation of the process by the dry method. Gases containing SO_3 to be used for the dry production of magnesium fertilizers can, therefore, come from any installation producing sulphuric acid by the contact method, or from the so-called wet catalysis process.

The product obtained from the process is magnesium fertilizer plus post-reaction gases. Water contained in the SO_3 carrying gas and in the magnesium raw material is bound by magnesium sulphate. Consequently, the product is a mixture composed of anhydrous and monohydrate magnesium sulphate. Since soluble MgO concentration in the product should be as high as possible,



Flow-sheet for the production of magnesium fertilizer from serpentinite: 1 – Serpentinite from the mine, 2 – Comminution of serpentinite, 3 – Batch feeding of serpentinite, 4 – Water, 5 – Waste gases, 6 – Gases containing SO_3, 7 – Proportioning of serpentinite with gaseous SO_3, 8 – Dry dedusting of gases, 9 – Wet scrubbing of gases, 10 – Dust, 11 – Cooling of product, 12 – Saturation with steam, 13 – Serpentinite + $MgSO_4$ aq suspension, 14 – Granulation, 15 – Granulated magnesium fertilizer, 16 – Water vapour, 17 – Powdered magnesium fertilizer

* See PTR No. 12/79

the average $MgSO_4$ hydration degree should not exceed a unit.

Magnesium fertilizer obtained as a result of gaseous SO_3 reaction on the magnesium raw material is a powder of a granulometric composition close to that of the magnesium raw material used. The product of the reaction contains free SO_3 both absorbed and weak-bound, in the form of appropriate pyrosulphates. In this connection it requires treatment with gases containing water vapour (saturation with superheated steam, seasoning in atmospheric air) or adding not more than 8% by weight of water, which is connected with granulation of the raw dusty product. After saturating with superheated steam, or after granulation, the final product in the form of magnesium fertilizer is obtained. This fertilizer is dry, does not get lumped and has the form of a non hygroscopic white powder containing more than 50% of parts which are soluble in water.

The powdered magnesium fertilizer can be easily granulated. In the course of granulation the water gets bound to form magnesium sulphate hydrates. This process is accompanied by the emission of a small amount of heat. Thus, the fertilizer granules are hard; they do not stick to one another and require no drying.

Magnesium fertilizer contains magnesium sulphate of various degrees of hydration. The fertilizer in its powdered form contains a mixture of anhydrous and monohydrate $MgSO_4$. The granulate hydration degree varies from 1 to 6.5 depending on the way the granulation process was effected and on the amount of water supplied.

Magnesium fertilizer produced by the dry method from a raw material containing 30% MgO (which is the average MgO content in serpentinites and in mixtures of serpentinites and magnesites) contains about 16% MgO in the form of magnesium sulphate.

Field tests of magnesium fertilizers produced by the dry method were started in 1978 at the Agricultural Academy in Warsaw (in pots and in experimental plots). In 1980 pot tests of the product were also carried out by the Cultivation, Fertilizing and Soil Science Institute at Pulawy. The results of these agricultural tests have shown that magnesium sulphate contained in the fertilizer produced by the dry method is equally efficient as the analytically pure compound and much better than raw serpentinite. The waste gases from the reactor contain inert components of the gas used for the reaction, carbon dioxide produced as a result of SO_3 reaction with carbonates and dust which in some part is the reacted magnesium raw material.

Thanks to the high speed of gaseous SO_3 reaction with the non-reacted magnesium raw material and using a reagent stream countercurrent, SO_3 can be removed completely from the gas inflowing to the reactor.

The process as described here is cheap and requires no special equipment or expensive corrosion-resistant constructional material and therefore it can successfully compete with the wet processes and the recovery of magnesium from sea water.

The process includes the preparation of serpentinite (storage, comminution, grinding), batch feeding of the ground serpentinite and of the gas containing sulphur trioxide, reaction in the gas – solid body system, scrubbing of waste gases and final treatment of the product of gaseous SO_3 reaction with the magnesium raw material.

To attain the preset degree of MgO reaction to $MgSO_4$ it suffices to grind the serpentinite to a grain size 10% bigger than 0.15 mm.

In the system of automated control of the ratio of streams containing the raw materials (which has been developed), an amount of SO_3 equal to the required amount of serpentinite is fed to the reactor. The system is sensitive neither to the rapid changes in the composition and quantity of serpentinite nor to the concentration of SO_3 in gases taken from the installation for the production of sulphuric acid.

The solid product of reaction is first saturated with superheated water steam, then cooled. The result is powdered magnesium fertilizer. Water or dust suspension obtained in the process of wet dust removal from post-reaction gases, is used for the granulation of the product of reaction of gaseous SO_3 with serpentinite (saturation being avoided).

Since SO_3 is not present in waste gases, they can be dry-dedusted, and the dust goes back to the process. Then the gases are scrubbed with the use of water, and the slurry from the scrubber circuit is used for granulation of the magnesium fertilizer.