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CA 2779152 C 2017/10/10

(11)(21) **2 779 152**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2010/10/28
(87) Date publication PCT/PCT Publication Date: 2011/05/05
(45) Date de délivrance/Issue Date: 2017/10/10
(85) Entrée phase nationale/National Entry: 2012/04/27
(86) N° demande PCT/PCT Application No.: BR 2010/000355
(87) N° publication PCT/PCT Publication No.: 2011/050434
(30) Priorité/Priority: 2009/10/30 (US61/256,621)

(51) Cl.Int./Int.Cl. *C05D 1/04* (2006.01), *C05B 13/00* (2006.01)

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(54) Titre : PROCEDE AMELIORE POUR PRODUIRE UN THERMOFERTILISANT A PARTIR DE MINERAUX PORTEURS DE POTASSIUM

(54) Title: ENHANCED PROCESS TO PRODUCE A THERMOFERTILISER FROM POTASSIUM-BEARING MINERALS

(57) Abrégé/Abstract:
The present invention proposes a simplified and enhanced process route to produce thermofertiliser obtained from potassium and phosphorous-bearing minerals where these elements can be or not in the citric acid or water insoluble forms. The process described also comprises the use of specific additives, at the beginning of the process or immediately before the beginning of the thermal treatment step, in order to increase the potassium and phosphorous contents in the product and the overall efficiency of the process and also to promote the production of a high quality thermofertiliser.

ABSTRACT

The present invention proposes a simplified and enhanced process route to produce thermofertiliser obtained from potassium and phosphorous-bearing minerals where these elements can be or not in the citric acid or water insoluble forms. The process described also comprises the use of specific additives, at the beginning of the process or immediately before the beginning of the thermal treatment step, in order to increase the potassium and phosphorous contents in the product and the overall efficiency of the process and also to promote the production of a high quality thermofertiliser.

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ENHANCED PROCESS TO PRODUCE A THERMOFERTILISER FROM POTASSIUM-BEARING MINERALS

Field of the invention

The present invention refers to an enhanced process to produce a thermofertiliser from potassium-bearing minerals, more specifically silicate minerals and phosphate rock using a thermal treatment process route.

Background of the invention

It is common knowledge that potassium can be extracted from potassium-bearing minerals, like slate ores, using either thermal or hydrometallurgical methods or combinations of both. There are studies about the dissolution of potassium from potassium minerals (feldspar, mica) and from glauconite in inorganic acids. Fogler and Lung (1975), among other researches, shows a study about the dissolution of potassium feldspar in HF and HCl acid mixtures.

Preliminary studies conducted by Eichler (1983), from Universidade Federal de Lavras, in Minas Gerais state, Brazil, were assayed mixtures with 50% (p/p) of potash-bearing ore and 50% (p/p) limestone. The researchers concluded that for the use as a potash source, the mineral have to be calcinated jointly with a source of limestone. Because of this, these mixtures were calcined at 1,100°C during lab tests, and assayed agronomic. The results conducted in maiz culture, shown that the efficiency of potassium absorption was equivalent when compared with traditional potash fertilizer (KCl). The main focus of the mentioned study is to test the feasibility of the use of a specific silicate mineral, called Verdete, as a potash source for the production of fertilizers, which was confirmed.

These results, from Eichler (1983), related to the agronomic assay indicate that, even being the final product a compound that has low solubility in water and a quite high solubility in citric acid, the agronomic efficiency is satisfactory, mainly when comparisons are made between these product and the one obtained from a traditional potash source, as KCl, which is completely soluble in water.

The route studied by Eichler (1983) comprehends only the calcination step. The proposed process in the present invention describes a thermal treatment route that comprehends more than a calcination treatment; it goes further, through a sintering step that promotes and applies specific conditions for the generations of micro fusion in the particles of the mixtures, which is one of the main characteristics of the route proposed in the describe invention.

The study also confirms the potential of the use of a thermofertiliser obtained by the process described by the proposed invention, which proposes the use of the silicate minerals, such as Verdete, as one of the potash sources, associated with phosphate rock and other additives, aiming to increase the grade of nutrients potash and phosphorous and also to allow the solubilization of them in citric acid.

Patent US 4,334,908 describes the production of a vitreous fertilizer that was obtained from raw material with high water solubility ($NH_4H_2PO_4$, KH_2PO_4 and $CaHPO_4$), these materials were mixed with feldspar or granite where the feldspar and granite was introduced aiming become the P and K, present in the raw materials, insoluble in water. This invention uses raw materials with high cost that were processed to decrease the water solubility. This patent has an objective to reduce the water solubility of products obtained whose raw materials have originally had high water solubility, and therefore spent cost not necessary. The process described in this document starts with the use of pure raw materials that already have high solubility in water. This process also aims to make these materials insoluble in water and to promote a slow release of its nutrients from the fertilizer produced. The process described in the present invention propose a different product and goes in the inverse way, it comes from materials insoluble in water to become then soluble in citric acid, to avoid nutrient loses in the final thermofertiliser produced.

Patent US 4,313,753 describes a process where a mixture of a potassium source, such as caustic potash or potassium carbonate, and a silicon source, as fly ash, is dried and calcined at the temperature of 600°C to 1,000°C. According to this process the silicon content in the fly ash reacts with the potassium resulting in a potassic product having high solubility in citric acid. As the previous patent document, this one has the objective to reduce the water solubility of raw materials, which has originally high water solubility. The complexity of equipment and process can be result in a high costly project.

The main differences between the two processes described and the one disclosed in the present invention is the use in the proposed process of raw materials that already have the potash in a water soluble form that is transformed to a citric acid soluble form and also the thermal treatment stage that promotes calcination and sintering stages in a joint operation, in one embodiment. The use of this raw material associated with the proposed flow sheet facilitates the overall chemical process applied and promotes the use of ores that already have the potash with the water-insoluble characteristic that is required by the final product obtained. Due to this characteristic these raw materials do not need to be processed in order to change its characteristics of solubility in water.

The roast-leach method for extraction of potassium is also extensively studied over the years. Mazumber, Sharma and Rao (1993) disclosed a route for extraction of potassium from glauconite sandstone. They described the roast kinetics with calcium chloride and after the roasting potassium is recovered from potassium chloride through leaching using distilled water. Further developments in such route were made but for industrial use the route concept has been considered of high cost and low efficiency nowadays. Direct acid leaching is also known as an alternative route of the roast and leaching treatment for obtaining products containing high grade of the element of interest, as the potash.

It is also known that the use of sintering process route for iron ore and also a mixture of phosphate concentrate and slag, being the latter one to produce a phosphate fertilizer. Such arrangement is describe in the patent document BRPI 9501458-6, filed by Usiminas in the Brazilian Patent and Trademark Office. This application uses aciaria LD clinker (slag) in sintering processes for production of agricultural thermo-phosphate fertilizers comprising mixing the slag with phosphates, lime and/or dolomite, sodium salts, solid carbonaceous fuel, water and recovered fines in a mixer. The focus of this process is to overcome the economic and environmental problems of storage of slag. Besides the differences between the overall process of this document and the invention proposed, the source of Ca and silica in the document is the slag used as the focus of the invention, which also may contain other elements not related to the characteristic of the final product. In the proposed invention the first step involves the use a silicate mineral, as the Verdete ore, which also supplies potash to the final product, as the main source of silica. These differences promote a final product with the desirable solubility in citric acid. What also contributes for these results is the thermal treatment process proposed that also promotes the calcination in a way to make the potash of the raw materials easily available.

Although being largely known, fusion route or independent potassium extraction techniques such as calcination followed by leaching can be considered of high cost and ineffective in many cases. The route proposed is adequate for the use of silicate minerals similar to the Verdete ore, which is a potash source not widely used in the industry for producing thermofertilisers. This type of ore brings benefits to the overall process and to the final product, as less energetic costs in the comminution step, a low relation between the amount of gangue and minerals (less than 1) and also a high potash content (about 10% K_2O), what implies in the reduction of use of noble raw materials, as KCl, which is more expensive.

Verdete ore, a kind of slate that occurs in Cedro de Abaeté, Minas Gerais State in Brazil is a source of potassium, which contains in its structure the minerals biotite, muscovite and feldspars, as the potassium sources, according shown in the Table 1. The K_2O content in the Verdete ore is about 10%, generally in the range of 9-12%. The Verdete ore can be one of the silicate minerals used as raw material in the process described by the present invention.

Table 1 – Mineralogical distribution in each fraction

	Size distribution (μm)					
Mineral	**-500/+300**	**-300/+212**	**-212/+150**	**-150/+106**	**-106/+74**	**-74/+38**
Biotite	5.89	5.80	5.51	5.66	5.73	5.64
Muscovite	75.13	73.51	75.64	74.23	70.30	64.63
Feldspars	18.98	20.69	18.85	20.11	23.97	29.73
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Brief description of the invention

This invention aims to overcome the technical and economical scenarios showed by others technologies and processes routes by proposing a simplified thermal treatment process route to obtain the thermofertiliser.

In this way the present process route comprises the use of additives at the beginning of the process or, alternatively, immediately before the thermal treatment step depending upon the size distribution of the additive. Further, a variety of resources of raw materials can be used in order to increase the potassium and phosphorous contents in the product and the overall efficiency of the process and also the quality of the thermofertiliser produced.

Brief description of the drawings

Figure 1 is a flowchart of the process provided by the present invention.

Description of preferred embodiments

A thermal treatment process is described as a method to produce a thermofertiliser based on sintering of mixtures containing phosphate rock, potassium-bearing minerals, preferred Verdete ore, limestone and other potassium sources water soluble, as sylvinite and muriate of potash (Potassium Chloride) aiming to increase the potassium content in the thermofertiliser. The described method increases overall nutrients extraction and improves process cost effectiveness.

The main novelty of the thermal treatment route proposed is the micro fusions on the surface of particles created by the sintering occurred during the thermal treatment, where the chemical reactions take place. Sodium carbonate, calcium-sodium borate, magnesium chloride or sulphate salts (as calcium and magnesium sulphates) can also be used to increase the potassium and phosphorous extraction from the ores and to reduce the temperature in the thermal treatment step.

Due to this characteristic, the process does not comprise a fusion reaction, what represents an advantage compared with the fusion process and other traditional routes in terms of energy consumption, achieving about 40% of saving. Also, the fusion process route can generate by-products (slags), what the proposed process avoids. The mass recovery of the proposed process is higher than the other routes and does not generate solid residue.

The process begins with a comminution step. After grinding between 2mm and 0.037mm, the raw materials are mixed and are optionally subjected to an agglomeration process, depending of the choice of the equipment that will be used to sinter these materials in the next step of the process. The thermal treatment occurs preferably in rotary kilns, that avoids the necessity of the agglomeration step. On the other hand, as an alternative the process can use a sintering roaster that will bring the necessity of a previous agglomeration stage for the raw materials.

In the thermal treatment step the temperature is between 300°C and 1,600°C, preferably between 850°C and 1,300°C and the residence time needs to be in the range of 1 and 10 hours, preferably between 1 and 4.5 hours.

Coal, oil, gas, biomass or any other energy source can be used to provide energy to the process. After thermal treatment the material must be cooled down up to the room temperature using air, water or any other cooling operation known. If necessary, after cooling, the material is grinded to adjust the particle size to achieve commercial product specifications. Besides, and optionally, micronutrients can be added to the final product, depending upon the marketing necessities, as boron, manganese, copper, cobalt and molybdenum.

The product obtained have two main nutrients, phosphorus and potassium, also having a better efficiency when used in acid soils because the high calcium and magnesium oxides (basic products) contents can correct the soil acidity, therefore reducing the use of neutralizing agents. It also contains silicon, calcium and magnesium as important nutrients for crops.

In order to evaluate the final product quality, the potassium and phosphorous contents in the thermofertiliser can be extracted using a citric acid solution, achieving up to 85-95% extraction. This result shows that the nutrients K and P are in a low water solubility form, what is one of the main benefits of the proposed process for the product. This characteristic promotes less loses by natural leaching in the ground during the final use of the product as a fertilizer.

During the overall process, the main transformation promoted by the present invention involves about 60 to 90% of the insoluble material that comes from the raw materials (insoluble in both water and citric acid). The mentioned material comprehends the K insoluble (K_2O) – that is in the composition, for example, of the Verdete ore – or the

P insoluble (P_2O_5) from the phosphate rock. All these raw materials are transformed into a soluble only in citric acid form. Besides, the raw materials that are already soluble in water have its solubility in citric acid increased and its solubility in water decreased in about 15 to 50%. This characteristic of the process promotes a generation of a final product as described, having a low solubility in water and a high solubility in citric acid, qualities desired by the composition of the thermofertiliser, that avoids the mentioned loses of nutrients in its agronomic use.

Initial laboratory tests indicated that a composition comprehending raw materials and additives for starting the process that can improve the solubilization of potassium is: 15 to 48 % of Verdete ore (or another source, being potassium-bearing minerals), 25 to 46% phosphate rock, 4 to 12% of potassium chloride, 10 to 22% of dolomite and 4 to 15% of sodium carbonate.

Unique features and advantages:

- Increased extraction of value nutrients, such as potassium and phosphorous from potassium-bearing minerals, as the Verdete ore and phosphates rocks;
- Better deposit exploitation in the case of Verdete ores deposits;
- Product with high agronomy efficiency due to the low solubility in water and high solubility in citric acid;
- Reduced energy consumption;
- Two or more nutrients provided by the same product;
- High mass recovery without generation of solid residues;
- Nutrients with low water solubility but soluble in citric acid solution with high availability to crops.

<u>Example 1:</u>

A mixture containing 30.3% of Verdete ore (12.5% K_2O), 37.9% of phosphate rock (30.0% total P_2O_5 and 9.0% P_2O_5 soluble in 2% w/w citric acid solution), 7.6% of muriate of potash (KCl - 60.0% K_2O), 15.1% of dolomite and 9.1% of soda ash (Na_2CO_3) was heated in an oven for 1 (one) hour in a constant temperature of 1,100°C. The size distribution of all raw materials used to prepare the mixture were 90% minus 44 μm (0.044 mm). After the heating process, the mixture was cooled, weighed and analyzed the contents potassium and phosphorous soluble in 2% w/w citric acid solution. The mass loss was of 17.7%, K_2O and P_2O_5 soluble in 2% w/w citric acid solution were 8.4% and 0.0% respectively. Excluding the K_2O and P_2O_5 soluble in 2% w/w citric acid solution in the raw materials, muriate of potash and phosphate rock, the potassium and phosphorous extraction yields were 59% and 0% respectively, and K_2O, soluble in water, that comes from the muriate of potash has its solubility in water reduced in 36%, became soluble only in citric acid. The phosphorous and potassium contents soluble in 2% w/w citric acid solution in the thermofertiliser were 4% and 8% respectively, or 00-04-08 (N, P_2O_5 and K_2O contents).

<u>Example 2:</u>

A mixture containing 48.0% of Verdete ore (12.5% K_2O), 40.0% of phosphate rock (30.0% total P_2O_5 and 9.0% P_2O_5 soluble in 2% w/w citric acid solution) and 12.0% of muriate of potash (KCl with 60.0% K_2O) was heated in an oven for 1 (one) hour in a constant temperature of 1,200°C. The size distribution of all raw materials used to prepare the mixture were 90% minus 44 µm (0.044 mm). After the heating process, the mixture was cooled, weighed and analyzed the contents potassium and phosphorous soluble in 2% w/w citric acid solution. The mass loss was of 13.4%, K_2O and P_2O_5 soluble in 2% w/w citric acid solution were 8.3% and 10.8% respectively. Excluding K_2O and P_2O_5 soluble in 2% w/w citric acid solution in the raw materials, muriate of potash and phosphate rock, the potassium and phosphorous extraction yields were 0% and 68% respectively; e K_2O, soluble in water, that comes from the muriate of potash has its solubility in water reduced in 43%, became soluble only in citric acid. The phosphorous and potassium contents soluble in 2% w/w citric acid solution in the thermofertiliser were 11% and 8% respectively, or 00-11-08 (N, P_2O_5 and K_2O contents).

<u>Example 3:</u>

A mixture containing 32.1% of Verdete ore (12.5% K_2O), 40.1% of phosphate rock (30.0% total P_2O_5 and 9.0% P_2O_5 soluble in 2% w/w citric acid solution), 8.0% of muriate of potash (KCl with 60.0% K_2O), 16.0% of dolomite and 3.8% of ulexite was heated in an oven for 1 (one) hour in a constant temperature of 900°C. The size distribution of all raw materials used to prepare the mixture were 90% minus 44 µm (0.044 mm). After the heating process, the mixture was cooled, weighed and analyzed the contents potassium and phosphorous soluble in 2% w/w citric acid solution. The mass loss was of 14.5%, K_2O and

P_2O_5 soluble in 2% w/w citric acid solution were 6.1% and 4.2% respectively. Excluding K_2O and P_2O_5 soluble in 2% w/w citric acid solution in the raw materials, muriate of potash and phosphate rock, the potassium and phosphorous extraction yields were 9% and 0% respectively, e K_2O, soluble in water, that comes from the muriate of potash has its solubility in water reduced in 13%, became soluble only in citric acid. The phosphorous and potassium contents soluble in 2% w/w citric acid solution in the thermofertiliser were 4% and 6% respectively, or 00-04-06 (N, P_2O_5 and K_2O contents).

CLAIMS

1. Process to produce thermos fertilizer from a potassium-bearing mineral, comprising the steps of:

(i) grinding the raw potassium-bearing material;
(ii) screening the grinded raw material;
(iii) mixing the screened raw material with additives,
(iv) thermal treating the mixture in a temperature between 300 and 1,600°C, so that calcination and sintering occurs jointly and micro fusions are formed in the material;
(v) cooling the material,
(vi) secondary grinding the cooled material,
(vii) final screening the grinded material; and
(viii) final mixing the grinded material with nutrients.

2. Process, according to claim 1 wherein the raw material is grinded between 2 and 0.037 mm in the first grinding step (i).

3. Process, according to claim 1 wherein the grinding step (i) is followed by an agglomeration step.

4. Process, according to claim 1, wherein the thermal treatment occurs in a temperature between 850 and 1,300°C.

5. Process, according to claim 1, wherein the residence time in the thermal treatment is between 1 and 10 hours.

6. Process, according to claim 1, wherein the energy source for the thermal treatment is selected from a group consisting of coal, biomass, oil and gas.

7. Process, according to claim 1 wherein the cooling step uses air or water.

8. Process, according to claim 1 wherein the additives are selected from a group comprising limestone, sylvinite and muriate of potash.

9. Process, according to claim 1 wherein the micronutrients are selected from a group comprising boron, manganese, copper, cobalt and molybdenum.

10. Process, according to claim 1 wherein the raw material source contains citric acid and water insoluble forms of potassium and phosphorous.

Drawings

FIGURE 1