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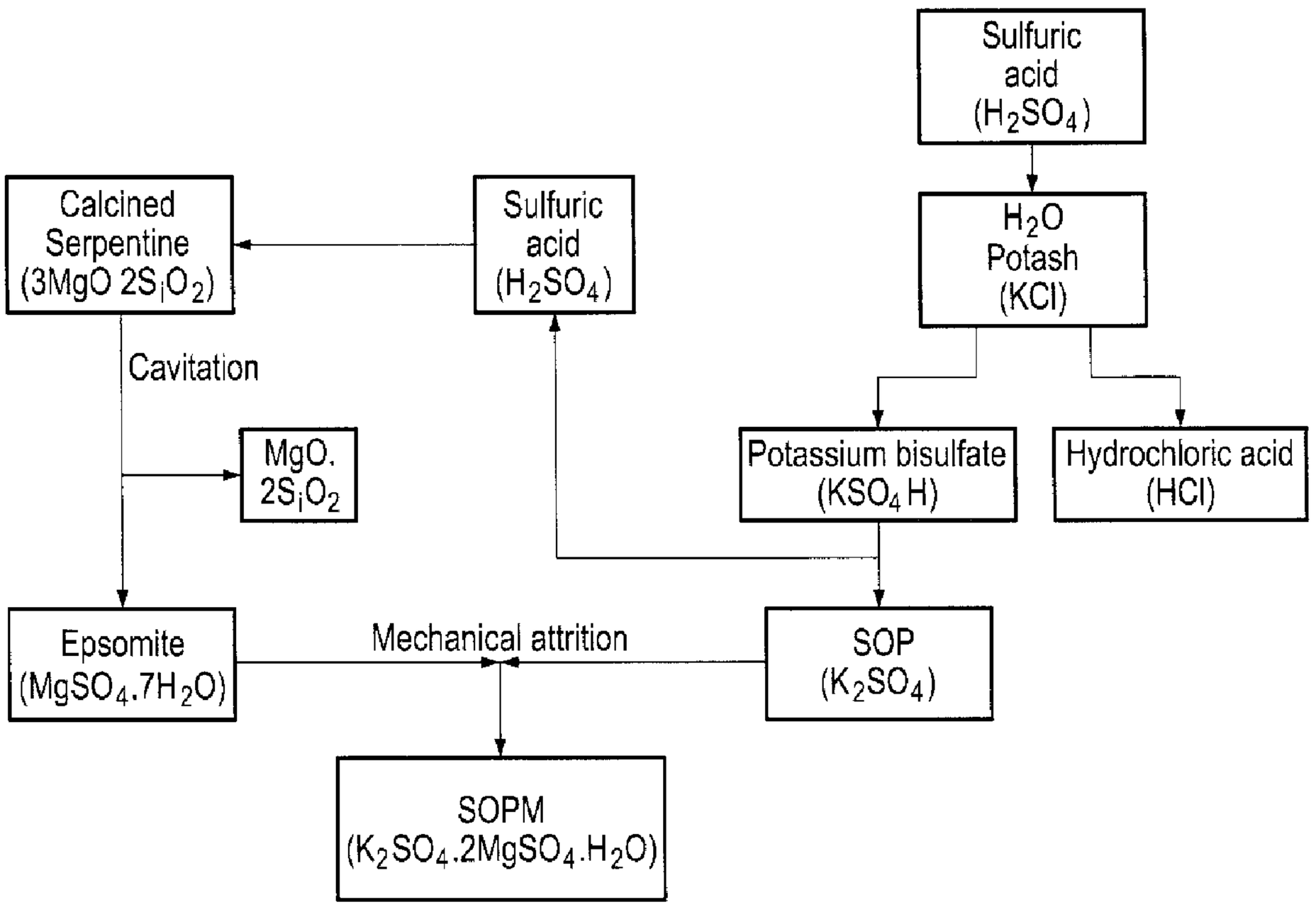
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(54) Titre : FERTILISANT AU POTASSIUM ET MAGNESIUM
(54) Title: POTASSIUM MAGNESIUM FERTILIZER



(57) Abrégé/Abstract:
A method for producing a double sulfate of potassium and magnesium by dry mechanical attrition of potassium sulfate and magnesium sulfate hexahydrate, comprising obtaining potassium sulfate by sulfatation of potash to bisulfate of potassium and disproportionation of the bisulfate of potassium to potassium sulfate in a water-methanol solution, and obtaining magnesium sulfate hexahydrate by sonic-assisted partial sulfatation of calcined serpentinic silicate.

Abstract

A method for producing a double sulfate of potassium and magnesium by dry mechanical attrition of potassium sulfate and magnesium sulfate hexahydrate, comprising obtaining potassium sulfate by sulfatation of potash to bisulfate of potassium and disproportionation of the bisulfate of potassium to potassium sulfate in a water-methanol solution, and obtaining magnesium sulfate hexahydrate by sonic-assisted partial sulfatation of calcined serpentinic silicate.

TITLE OF THE INVENTION

Potassium magnesium fertilizer

FIELD OF THE INVENTION

[0001] The present invention relates to fertilizers. More specifically, the present invention is concerned with production of potassium magnesium sulfate.

BACKGROUND OF THE INVENTION

[0002] Potassium is an essential component in fertilizers. In the case of intensive cultures requiring frequent applications of fertilizer, potassium chloride (KCl), also referred to as potash, which is the most abundant source of potassium, is not suitable because chloride can lead to soil sterilization if present in too large amounts. Thus potassium sulfate (K_2SO_4) is preferred to potassium chloride, the sulfate group having a positive agronomic value per se.

[0003] Since magnesium is also an element required by some crops such as tobacco, potatoes or corn for example, it has been found useful to use a naturally occurring double sulfate of potassium and magnesium, such as langbeinite ($K_2SO4 . 2MgSO_4$), known as SOPM.

[0004] To meet an increasing use of SOMP, and in view of the depletion of natural sources thereof, synthetic potassium sulfate is now typically mixed with magnesium sulfate to duplicate naturally occurring SOPM. But mere mixing of the components does not lead to an end product having the required physical properties of the naturally occurring true double salt. When using a solution of the components, leonite rather than langbeinite crystallizes out, with a K/Mg ratio of 2/1 rather than 1/1.

[0005] In view of the relatively high pricing of potassium sulfate and the desired chemical and physical properties of SOPM such as absence of chlorides, hardness and particle size, new methods for obtaining SOPM from much cheaper potash and a low cost source of magnesium

have been developed. A method for the formation of SOPM comprising the reaction of potassium acid sulfate $KHSO_4$ on a source of magnesium ($3MgO.2SiO_2.2H_2O$) has been presented (WO2016/187688A1). Another method to SOPM via magnesium chloride is also known (Canadian patent 2,611,479). However, these methods led to problems with K/Mg ratio control and separation of phases, along with large water handling due in part to the hydrated state of the source of magnesium. Preparation of potassium sulfate from potassium chloride via magnesium sulfate has also been reported (US patent 8,409,542).

[0006] Therefore, there is a need in the art for a method for producing potassium magnesium fertilizer.

SUMMARY OF THE INVENTION

[0007] More specifically, in accordance with the present invention, there is provided a method for producing a double sulfate of potassium and magnesium by dry mechanical attrition of potassium sulfate and magnesium sulfate hexahydrate, comprising obtaining potassium sulfate by sulfatation of potash to bisulfate of potassium and disproportionation of the bisulfate of potassium to potassium sulfate in a water-methanol solution, and obtaining magnesium sulfate hexahydrate by sonic-assisted partial sulfatation of calcined serpentinic silicate.

[0008] There is further provided a method for producing a double sulfate of potassium and magnesium with a molar potassium-magnesium ratio of 1.0 ± 0.05 using potash, calcined serpentinic silicate and sulfuric acid as starting materials, comprising a solid-solid reaction between potassium sulfate and magnesium sulfate hexahydrate, wherein the potassium sulfate is obtained by reacting sulfuric acid with the potash followed by disproportionation of a resulting potassium bisulfate to potassium sulfate and sulfuric acid in a water-methanol mixture; and the magnesium sulfate heptahydrate is obtained by cavitation-assisted sulfatation of the calcined serpentinic silicate.

[0009] There is further provided a method for producing a double sulfate of potassium and magnesium, comprising submitting potassium sulfate and magnesium sulfate to a solid-solid

reaction.

[0010] Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of specific embodiments thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] In the appended drawings:

[0012] FIG. 1 is a schematic diagram of a method according to an embodiment of an aspect of the present invention.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0013] In a nutshell, there is provided a method for producing a potassium-magnesium fertilizer from potash and serpentinic silicate.

[0014] According to an embodiment of an aspect of the present invention illustrated in the diagram of FIG. 1, the method comprises forming potassium sulfate SOP (K_2SO_4) from potash (KCl), forming magnesium sulfate ($MgSO_4$) from dehydrated magnesium silicate, and combing the two resulting sulfated metals in equimolar proportions to yield SOPM.

[0015] Formation of potassium sulfate SOP (K_2SO_4)

[0016] Sulfuric acid (H_2SO_4) 93%w/w is reacted with potash (KCl) at a temperature in a range between 120 and 140°C, yielding potassium bisulfate (KSO_4H) and hydrochloric acid (HCl) (see US patent 4,588,573A). The evolution of chlorine as hydrochloric acid is essentially complete. The resulting potassium bisulfate (KSO_4H) is dissolved with a minimum amount of water and the

volume of this solution is doubled with methanol (CH_3OH) at a temperature in a range between 25 and 30°C; due to the insolubility of potassium sulfate in the water-methanol mixture, the potassium bisulfate (KSO_4H) disproportionates into potassium sulfate (K_2SO_4), which precipitates, and sulfuric acid (H_2SO_4), which remains in solution in the water-methanol mixture. Solid potassium sulfate (K_2SO_4) is recovered with 99%w/w of the potassium of the starting potash and less than 0.1% w/w of the chloride in the solid phase (precipitate). The methanol (CH_3OH) in the sulfuric acid water-methanol mixture can be recovered by distillation, and sulfuric acid (H_2SO_4), of a concentration of about 20-30% w/w sulfuric acid, can be directed to the formation of magnesium sulfate ($MgSO_4$) as will be described hereinbelow.

[0017] Thus, a potassium sulfate deprived of chloride is obtained from potassium chloride (potash (KCl) with recovery of hydrochloric acid and recycling of sulfuric acid resulting from the disproportionation of bisulfate of potassium, as per relations (1) below :

[0018] (1) Formation of K_2SO_4 from KCl

$$2KCl + 2H_2SO_4 \xrightarrow{130°C} 2KHSO_4 + 2HCl$$

$$2KHSO_4 + H_2O + CH_3OH \xrightarrow{30°C} K_2SO_4 + H_2SO_4 \bullet H_2O \bullet CH_3OH$$

$$H_2SO_4 \bullet H_2O \bullet CH_3OH \xrightarrow{\text{Distillation}} H_2SO_4 \bullet H_2O + CH_3OH$$

[0019] Formation of magnesium sulfate ($MgSO_4$).

[0020] The source of magnesium is serpentinic silicate of general formula 3MgO $2SiO_2$ $2H_2O$ with iron contaminant at the level of 6% along with traces of nickel, chromium, aluminum and manganese. The tailings is first calcined, i.e. submitted to a thermal treatment at about 700°C, to remove the 13% w/w of structural water; this thermal treatment improves greatly the reactivity, oxidize the iron contaminant to ferric state and destroy traces amounts of chrysotile fibers remaining in these tailings of serpentinic silicates as described in the art (CA 2,248,474).

[0021] The iron content of the resulting anhydrous magnesium silicate $3MgO\ 2SiO_2\ 0.1\ Fe_2O_3$ is then reduced to 4% by demagnetisation.

[0022] The sulfatation of this magnesium silicate then uses sulfuric acid (H_2SO_4), of a concentration of about 20-30% w/w sulfuric acid, recycled from the formation of potassium sulfate described hereinabove, as per relation 2 below, yielding a slurry of 30% solid in an acid 20-30% w/w of sulfuric acid. With such a weak acid the reaction is expected to be slow and incomplete, even at high temperature. Surprisingly, it was found that cavitation near ambient temperature, i.e. at a temperature in a range between 30 and 50°C and under a pressure of 20-25 psi, allowed the reaction to proceed efficiently and rapidly. The ratio of acid/calcined serpentine is adjusted to extract two of the three atoms of magnesium in the magnesium silicate $3MgO\ 2SiO_2$. After a 30 min contact time, more than 95% of the initial sulfuric acid is reacted. pH adjustment using MgO and filtration yields a neutral and clean solution of magnesium sulfate at pH 6. The residual $MgO\ 2SiO_2$ along with precipitated iron hydroxide is then easily filtered with no difficulties was met with silica filtration when magnesium is completely dissolved.

[0023] The solution of magnesium sulfate is then evaporated by distillation to crystallize out magnesium sulfate as an heptahydrate, i.e. Epson salt: $MgSO_4.7H_2O$. The residual solid is discarded as an insoluble and inert material.

[0024] (2) Formation of $MgSO_4.7H_2O$ from calcined serpentine

$3MgO\bullet 2SiO_2\bullet 2H_2O\bullet 0.1\ FeO/Fe_2O_3 \xrightarrow{700°C} 3MgO\bullet 2SiO_2\bullet O.1\ Fe_2O_3+2H_2O$

$3MgO\bullet 2SiO_2\bullet 0.1Fe_2O_3 + 2H_2SO_4 + 5H_2O \xrightarrow[2.\ MgO]{1.Cavitation} 2MgSO_4\bullet 7H_2O + MgO\bullet 2SiO_2+0.1Fe_2O_3$

$2MgSO_4\bullet 7H_2O\bullet xH_2O \xrightarrow{distillation} 2MgSO_4\bullet 7H_2O + x\ H_2O$

[0025] Thus magnesium sulfate ($MgSO_4$) is obtained from dehydrated magnesium silicate.

[0026] Production of sulfate of potassium and magnesium (SOPM)

[0027] It was found that mechanical attrition of the two solid components, i.e. one mole of potassium sulfate with two moles of hydrated magnesium sulfate, was very efficient. It was discovered that such a dry mechanical treatment, such as ball milling for example, facilitates greatly the formation of the double salt, and that the resulting double salt is much less hydrophilic than the starting magnesium sulfate as the water liberated from the Epsom salt transforms the solid mixture into a slurry. This slurry may then be partly dried at 150°C to the consistency of a thick paste and then pelletized with a standard rotation pelletizer into particulates approximately spherical and having a desired diameter, for example in a range between about 5 and about 7 mm. The pellets can then be then dried at 200°C to yield SOPM with a formulation corresponding to $K_2SO_4.2MgSO_4.1H_2O$. Relation 3 below describes the formation of SOPM from K_2SO_4 and $MgSO_4.7H_2O$.

[0028] (3) Formation of SOPM

$K_2SO_4 + 2MgSO_4 \bullet 7H_2O$ —Ball Milling 30°C→ $K_2SO_4 \bullet 2MgSO_4 \bullet 4H_2O \bullet 10H_2O$

$K_2SO_4 \bullet 2MgSO_4 \bullet 4H_2O \bullet 10H_2O$ —1. 150°, 2. Pelletizing→ $K_2SO_4 \bullet 2MgSO_4 \bullet 4H_2O + 10H_2O$

$K_2SO_4 \bullet 2MgSO_4 \bullet 4H_2O$ —200°C→ $K_2SO_4 \bullet 2MgSO_4 \bullet 1H_2O + 3H_2O$

[0029] A chloride-free double sulfate of potassium and magnesium of the langbeinite structure was thus obtained starting from potash and serpentinic silicate. Moreover, the obtained material is shaped at a dimension ensuring it does not break at a free fall of 3 meters and is not dusty, allowing easy blending and field applications. If heating is conducted at 250°, the anhydrous double sulfate is obtained.

[0030] The following non limitative examples describe implementations of the method.

[0031] For the formation of potassium sulfate, in a one liter three necks flash, 29,82 g (0.4 mole) of KCl were treated with 42.6g (0.4 mole at 92%w/w) of sulfuric acid by slow addition over 30 minutes. The evolution of HCl was brisk and directed via a condenser to a collecting flash kept at 0°C with an ice/salt bath. After addition of the sulfuric acid, the reacting mixture, under mechanical stirring, was treated with water addition, 25 ml over a period of 45 minutes at 130°C. By titration, the total evolution of HCl was then 14.3g close to the theoretical amount of 14.58g.

[0032] The solid in the reaction flask was cooled to 30°C and dissolved in 100 ml of water. To this stirred solution, 100 ml of methanol at 30°C was added slowly, over five minutes. The precipitated potassium sulfate was filtrated and rinsed with methanol (2 displacements).

[0033] The yield of the reaction was 98.1% w/w of the expected K_2SO_4 , with only 0.003%w/w of chlorides. After recovery of methanol from the filtrate by distillation, the water-sulfuric acid solution contained 96% w/w of the expected acid.

[0034] For the formation of magnesium sulfate, the serpentinic silicate used as a source of magnesium ($3MgO.2SiO_2.2H_2O.0.1\ FeO/Fe_2O_3$) was calcined at 700°C, reduced in size to 80% minus 100 mesh and demagnetized (1,100 Gauss). This anhydrous magnesium silicate (284.3g) was reacted with 196.1g of sulfuric acid (30% w/w H_2SO_4) giving a slurry of 30% w/w solid. The reaction was achieved by circulating this slurry through a cavitation tube (20 psi, 5 gal/min) at 30°C for ten minutes. The filtration of the reaction after neutralization with 13g of MgO mixture yield 170g of unreacted solid. The soluble fraction, after evaporation at 50°C under vacuum yield 496g of a white solid, $MgSO_4.7H_2O_3$ corresponding to the extraction of two of the three magnesium atoms of the starting magnesium silicate.

[0035] For the formation of double sulfate of potassium and magnesium, a dry mixture of 174.27g of K_2SO_4 and 492g of $MgSO_4.7H_2O$ was placed in a 5 liter ball mill with 0.5 liter of cylindrical ball 1 cm in diameter by 1 cm. The milling was done for 30 minutes at 25°C. During this treatment, the initial dry mixture turned wet by the release of water from the highly hydrated magnesium sulfate. The reaction mixture was decanted over a screen to separate the cylindrical

balls with a minimum rinsing and the resulting slurry was evaporated to a paste texture, at 150°c amendable to pelletizing. The paste was then pelletized in a rotary pelletizer (Zhengzhou Weslite Machinery Equipment Co) to produce green pellets, which were further dried at 200°C for hardening. These pellets 5 to 6 mm in diameter could withstand a 3 meter fall on a hard surface without breaking and had a composition corresponding to $K_2SO_4.2MgSO_4.1H_2O$. A further heating at 250° yield the anhydrous double sulfate.

[0036] There is thus provided a method for producing a double sulfate of potassium and magnesium with a molar potassium-magnesium ratio of 1.0 ± 0.05 using potash, calcined serpentinic silicate and sulfuric acid as starting materials and forming the desired double sulfate by a solid-solid reaction between potassium sulfate and magnesium sulfate hexahydrate.

[0037] The method comprises obtaining the potassium by the action of sulfuric acid on potash followed by the disproportionation of the potassium bisulfate to potassium sulfate and sulfuric acid in a water-methanol milieu.

[0038] The method comprises the preparation of magnesium sulfate heptahydrate by the cavitation assisted sulfatation of calcined serpentinic silicate.

[0039] The method comprises the formation of a double sulfate of potassium and magnesium of the langbeinite type by mechanical attrition of a dry mixture of potassium sulfate and magnesium sulfate hexahydrate followed by partial dehydration, pelletizing and drying at 200°C.

[0040] There is provided a method for producing a double sulfate of potassium and magnesium by dry mechanical attrition of K_2SO_4 and $2MgSO_4.7H_2O$ followed by pelletization, the K_2SO_4 being obtained by sulfatation of KCl to bisulfate of potassium that disproportionates to K_2SO_4 in water-methanol milieu and the $MgSO_4.7H_20$ being obtained by sonic assisted partial sulfatation of calcined serpentinic silicate.

[0041] It can be appreciated that a more direct approach to potassium sulfate and to SOPM is desirable to circumvent the limitations of mere mixing of species, sulfating with bisulfate or preparing K_2SO_4 via $MgSO_4$ or $MgCl_2$.

[0042] The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

Claims

1. A method for producing a double sulfate of potassium and magnesium by dry mechanical attrition of potassium sulfate and magnesium sulfate hexahydrate, comprising obtaining potassium sulfate by sulfatation of potash to bisulfate of potassium and disproportionation of the bisulfate of potassium to potassium sulfate in a water-methanol solution, and obtaining magnesium sulfate hexahydrate by sonic-assisted partial sulfatation of calcined serpentinic silicate.

2. A method for producing a double sulfate of potassium and magnesium with a molar potassium-magnesium ratio of 1.0 ± 0.05 using potash, calcined serpentinic silicate and sulfuric acid as starting materials, comprising a solid-solid reaction between potassium sulfate and magnesium sulfate hexahydrate, wherein the potassium sulfate is obtained by reacting sulfuric acid with the potash followed by disproportionation of a resulting potassium bisulfate to potassium sulfate and sulfuric acid in a water-methanol mixture; and the magnesium sulfate heptahydrate is obtained by cavitation-assisted sulfatation of the calcined serpentinic silicate.

3. A method for producing a double sulfate of potassium and magnesium, comprising submitting potassium sulfate and magnesium sulfate to a solid-solid reaction.

4. The method of claim 3, comprising forming the potassium sulfate by reacting sulfuric acid with potassium chloride.

5. The method of claim 3, comprising forming the potassium sulfate by reacting sulfuric acid with potassium chloride and disproportionating a resulting potassium bisulfate to potassium sulfate and sulfuric acid.

6. The method of claim 3, comprising forming the potassium sulfate by reacting sulfuric acid with potassium chloride and disproportionating a resulting potassium bisulfate to potassium sulfate and sulfuric acid in a water-methanol solution.

7. The method of claim 6, further comprising recovering methanol by distillation and recycling sulfuric acid.

8. The method of any one of claims 4 to 7, wherein the potassium chloride is in the form of potash.

9. The method of any one of claims 3 to 8, comprising forming the magnesium sulfate by sulfatation of magnesium silicate.

10. The method of any one of claims 3 to 8, comprising forming magnesium sulfate by cavitation-assisted sulfatation of magnesium silicate.

11. The method of claim 10, wherein the magnesium silicate is in the form of dehydrated magnesium silicate.

12. The method of any one of claims 10 and 11, wherein the magnesium silicate in the form of calcined serpentinic silicate.

13. The method of any one of claims 3 to 12, comprising forming the magnesium sulfate by calcining serpentinic silicate and reacting a resulting anhydrous magnesium silicate with sulfuric acid of a concentration of about 20-25% w/w acid under cavitation.

14. The method of any one of claims 3 to 12, comprising forming the magnesium sulfate by calcining serpentinic silicate and reacting a resulting anhydrous magnesium silicate with sulfuric acid of a concentration of about 20-30% w/w acid under cavitation at a temperature in a range between 30 and 50°C.

15. The method of claim 14, further comprising neutralizing, filtration and distillation.

16. The method of any one of claims 3 to 15, wherein said solid-solid reaction comprises mechanical attrition of a dry mixture of the potassium sulfate and magnesium sulfate hexahydrate.

17. The method of claim 16, further comprising partial dehydration, pelletizing and drying.

18. The method of any one of claims 3 to 17, wherein the potassium magnesium sulfate has a molar potassium-magnesium ratio of 1.0 ± 0.05.

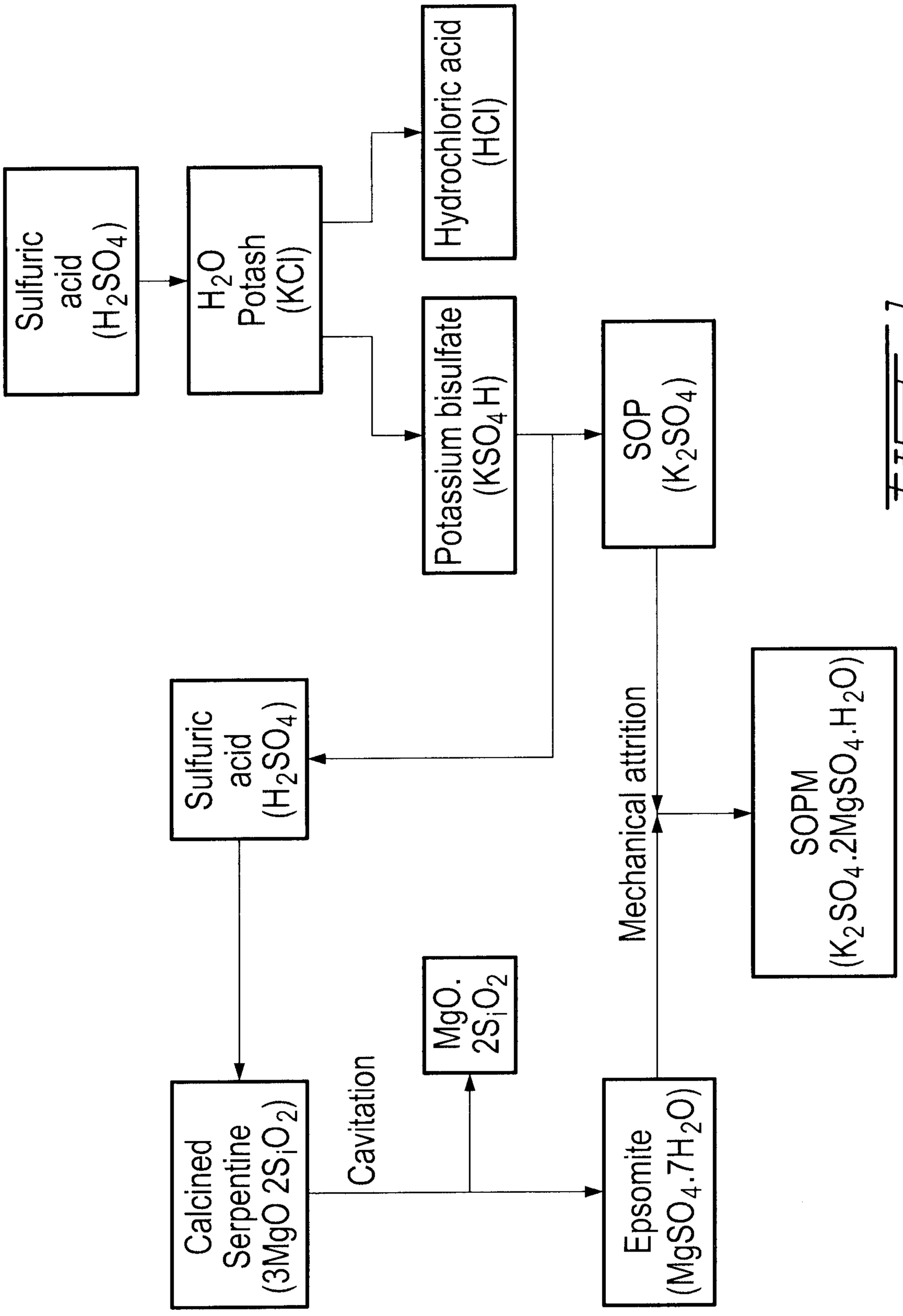
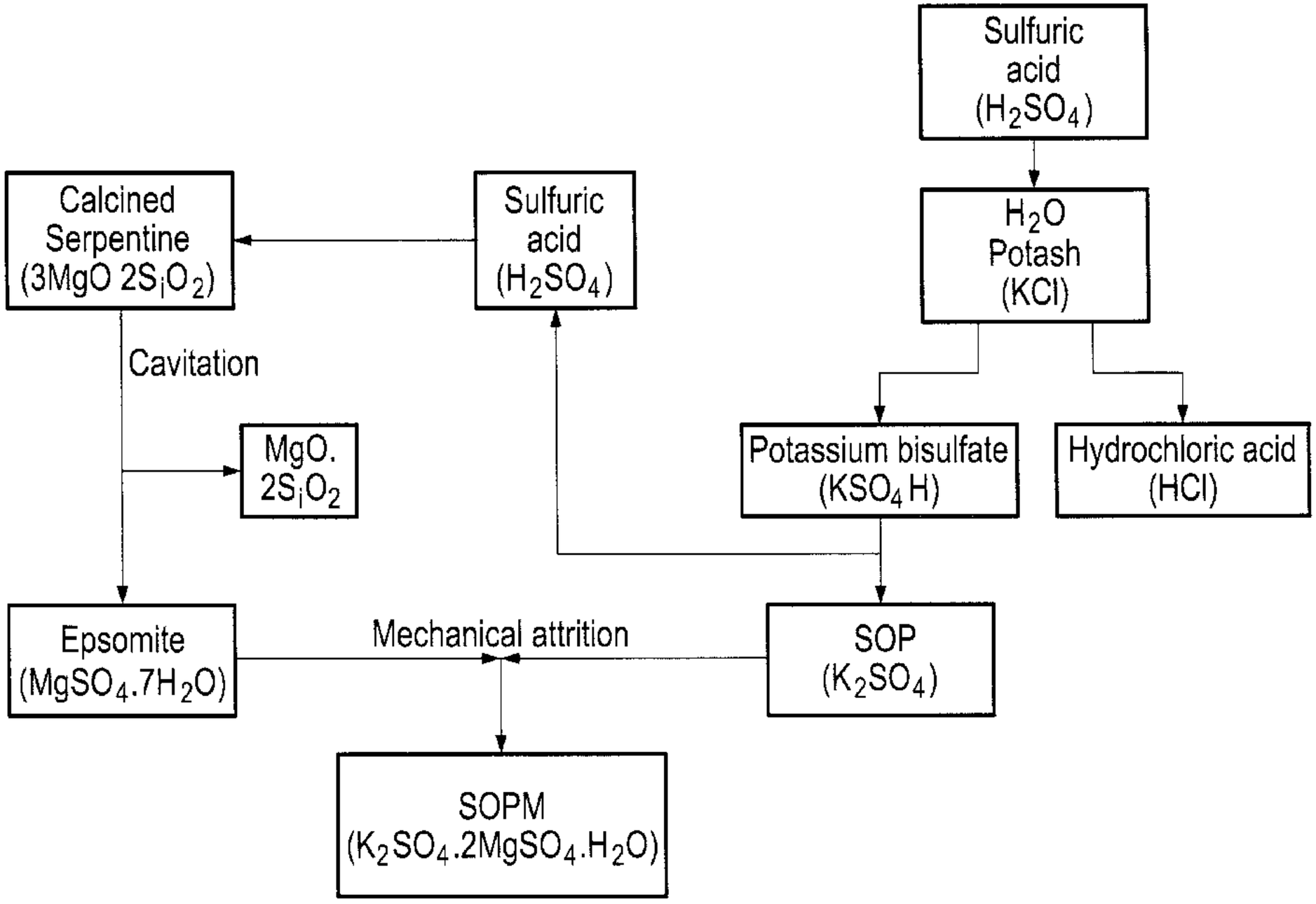

Sulfuric acid (H_2SO_4)
H_2O Potash (KCl)
Hydrochloric acid (HCl)
Potassium bisulfate (KSO_4H)
SOP (K_2SO_4)
Sulfuric acid (H_2SO_4)
Mechanical attrition
SOPM ($K_2SO_4.2MgSO_4.H_2O$)
Calcined Serpentine ($3MgO\ 2S_iO_2$)
Cavitation
MgO. $2S_iO_2$
Epsomite ($MgSO_4.7H_2O$)

Fig-1


Sulfuric acid (H_2SO_4)
H_2O Potash (KCl)
Calcined Serpentine ($3MgO\ 2S_iO_2$)
Sulfuric acid (H_2SO_4)
Cavitation
$MgO.\ 2S_iO_2$
Potassium bisulfate (KSO_4H)
Hydrochloric acid (HCl)
Epsomite ($MgSO_4.7H_2O$)
Mechanical attrition
SOP (K_2SO_4)
SOPM ($K_2SO_4.2MgSO_4.H_2O$)