Title: ALKALI FREE ALUMINATE SULFATE BASED SHOTCRETE ACCELERATOR AS STABLE SUSPENSION OR REDISPERSIBLE SOLID

Abstract: Described is a shotcrete accelerator which is a solid comprising at least one of jarbanite and hydronium alunite or an aqueous suspension or slurry of the solid, and a method of producing the shotcrete accelerator as a solid. The solid shotcrete accelerator is dispersible in water yielding stable aqueous dispersions or slurries. Extended shelf life of the solids and aqueous dispersions and reduced transport costs are the main advantages compared to existing technologies.
ALKALI FREE ALUMINATE SULFATE BASED SHOTCRETE ACCELERATOR AS STABLE SUSPENSION OR REDISPERSIBLE SOLID

Technical field

The invention relates to aluminium sulfate based shotcrete accelerators, in particular alkali-free aluminium sulfate based shotcrete accelerators (AFA).

Background of the invention

Accelerators for accelerating the setting and hardening of compositions comprising hydraulic binders such as concrete, mortar or shotcrete are well known to the skilled person. Conventional accelerators often include alkali metals but these accelerators often are associated with undesired drawbacks. Alkali-free accelerators are a well-known and growing technology for the application of shotcrete. The chemistry of these accelerators is based on aluminium sulfate, in particular on combinations of aluminium salts such as aluminium sulfate, aluminium hydroxide and aluminum hydroxysulfates, which can be used in form of a suspension.

The suspensions based on aluminum sulfate are generally unstable due to non-controlled phase assemblage of aluminium-sulfate phases resulting e.g. in segregation or gel formation. Thus, suspensions based on aluminium sulfate are generally unstable over a period of a few hours to a few months. They may segregate, agglomerate or gel, depending on the production and storage conditions.

Approaches to circumvent this instability include the use of stabilizers or fluidizers which improve the situation in delaying the stability problem over a certain period of time but the inherent instability remains. The current approaches have the further disadvantage that the number of constituents increases by addition of stabilizers, fluidizers, etc. which make the system
more complex and less robust. The object of this prior art approach is to stabilize something which is not stable.

WO 2015/092004 is directed to methods for producing a shotcrete accelerator, wherein one method comprises reacting sulfuric acid and aluminium hydroxide. It is mentioned that aqueous suspensions obtained by the methods may comprise jurbanite.


**Summary of the invention**

The object of the invention was to overcome the problems of the prior art discussed above. Specifically, the object was to provide stable suspensions and slurries and redispersible solids of aluminate sulfate based accelerators, in particular alkali free aluminate sulfate based accelerators, for shotcrete applications. In particular, it should be possible to provide the accelerator in solid form, wherein the solid is easily redispersible in water to obtain stable dispersions or slurries which are the common usage form for accelerators. The use of common stabilizers or fluidizers should not be necessary to achieve redispersibility of the solids and stability of the dispersions.

As mentioned above suspensions based on aluminum sulfate are generally unstable due to non-controlled phase assemblage of aluminium - sulfate phases. The invention concerns a new way of producing the accelerator so as to tailor the phases in equilibrium in the suspension. This was achieved in analyzing which phases are formed in the Al2O3-SO3-H2O system, in studying what their stability domain is and identifying new ways of producing the most interesting ones in a stable form. Thus, the present invention had a complete other approach to tackle the problem of stability of aluminium sulfate based suspensions compared to the prior art approach: instead of stabilizing
suspensions which are unstable, the invention relates to the provision of stable phases.

Accordingly, the present invention relates to a shotcrete accelerator which is a solid comprising at least one jurbanite and hydronium alunite or an aqueous suspension or slurry of the solid.

The present invention also relates to a method for producing the inventive shotcrete accelerator, wherein the method comprises

a) reacting a mixture of a 1) at least one sulfate compound selected from sulfuric acid and aluminium sulfate, a 2) aluminium hydroxide and optionally a 3) water, wherein the molar ratio of Al to SO₄ is in the range of from 2/3 to 3/2, at a temperature in a range of 40°C to 140°C,

b) cooling down the reaction mixture to obtain a solid, and optionally
c) dispersing the solid obtained in water to obtain a suspension or slurry, wherein the water content in the mixture is set to a water content A so that the molar ratio of H₂O to Al is in a range of from 5.5 to 6.7, or wherein the water content in the mixture is set to a water content B which is greater than water content A and the water content is reduced to the water content A in the course of reacting step a) by temporarily allowing partial removal of water from the mixture through evaporation.

Surprisingly, the shotcrete accelerator of the invention can be provided as a redispersible solid. The solid can be dispersed in water easily to produce stable dispersions or slurries, which solid content can be varied to a large extent. The addition of common stabilizers or fluidizers is not necessary. Extended shelf life of the solids or the aqueous dispersions/slurries and reduced transport costs are the main advantages compared to existing technologies. The reduced transport costs are due to possibility of transporting the accelerator as a solid and produce the dispersion or slurry on site of usage, whereas conventional accelerators must be transported as a dispersion/slurry.
Thus, the invention allows producing either redispersible solid, e.g. in form of blocks (bulky pieces), flakes or powder, or stable suspensions (no agglomeration and no gelling) at various solid contents with long shelf life. The solid can be stored as solid or redispersed in water at any time, e.g. immediately after the synthesis to months later.

The invention also relates to the use of the inventive shotcrete accelerators. Preferred embodiments are given in the dependent claims.

**Brief description of the figures**

- Fig. 1: XRD spectrum of synthesized pure phase of jurbanite
- Fig. 2: XRD spectrum of synthesized pure phase of alunogen
- Fig. 3: XRD spectrum of mixture of synthesized phases of jurbanite and alunogen prepared according to example 1
- Fig. 4: XRD spectrum of mixture of synthesized phases of hydronium alunite and alunogen prepared according to example 2
- Fig. 5: Photograph of solid product obtained in example 1
- Fig. 6-10: Diagrams of performance tests related to strength development of samples.

**Detailed description of the invention**

Accelerators for compositions or construction materials, respectively, comprising a hydraulic binder such as shotcrete are known to the skilled person, and are substances or admixtures, which accelerate the setting and/or hardening of compositions comprising a hydraulic binder such as shotcrete. Accelerators can be used in powder or liquid form. Typical examples of hydraulic binders are cement, lime and slaked lime, where cement is preferred. Typical examples for compositions or construction materials comprising a hydraulic binder, e.g. cement, are shotcrete, cement suspensions, e.g. for injections, mortar and concrete.
Accelerators suitable for shotcrete are designated shotcrete accelerators. Shotcrete includes sprayed concrete and sprayed mortar. Shotcrete usually comprises cement as the hydraulic binder. There exist wet and dry spray methods for applying shotcrete.

Wet sprayed concrete or mortar means delivery of a ready-mixed concrete or mortar comprising e.g. aggregate, cement, water and sprayed concrete admixtures to the nozzle in a workable mix. For spraying, the wet concrete or mortar is mixed at the nozzle with air and shotcrete accelerators and then applied. Dry sprayed concrete or mortar means delivery of a ready-mixed concrete or mortar comprising e.g. aggregate, cement and sprayed concrete admixtures but without mixing water. This ready-mixed formulation is either completely dry (dust dry) or is dampened by the inherent moisture in the aggregate. For the spraying operation, the dry concrete is mixed at the nozzle with water and shotcrete accelerators and then applied.

Shotcrete methods are used for instance when formwork is not possible or for the fabrication of linings or reinforcing layers in underground constructions, mining or hollow spaces, e.g. in tunnels, galleries or ducts. Shotcrete methods are also suitable for stabilization or compaction of natural formations, such as rocks, declivities, excavations and building grounds.

The shotcrete accelerator of the invention is a solid comprising jurbanite and/or hydronium alunite or an aqueous suspension or slurry of the solid, wherein the solid preferably comprises jurbanite or jurbanite and hydronium alunite. In a preferred embodiment the solid further comprises $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$.

Jurbanite has the chemical formula $\text{Al}(\text{SO}_4)\text{OH} \cdot 5\text{H}_2\text{O}$. Hydronium alunite has the chemical formula $(\text{H}_3\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$. 
\[ \text{Al}_2(\text{SO}_4)_{3-x}\text{H}_2\text{O}, \text{ wherein } 14 < x < 20, \text{ is in particular alunogen. Alunogen has a variable water content, the most common and most stable are } \text{Al}_2(\text{SO}_4)_{3-1.7}\text{H}_2\text{O} \text{ and } \text{Al}_2(\text{SO}_4)_{3-1.8}\text{H}_2\text{O}. \]

Preferred embodiments of the shotcrete accelerator are the following solids or an aqueous suspension or slurry thereof:

a) a solid comprising pure jurbanite or jurbanite mixed with another solid,

b) a solid comprising jurbanite and \( \text{Al}_2(\text{SO}_4)_{3-x}\text{H}_2\text{O}, \text{ wherein } 14 < x < 20, \) or

c) a solid comprising jurbanite, hydronium alunite and \( \text{Al}_2(\text{SO}_4)_{3-x}\text{H}_2\text{O}, \text{ wherein } 14 < x < 20. \)

The following indications of weight proportions are based on the dry weight of the shotcrete accelerator. The same weight proportions equally apply when based on the solid.

It is preferred that the shotcrete accelerator comprises a total amount of jurbanite and/or hydronium alunite and optionally \( \text{Al}_2(\text{SO}_4)_{3-x}\text{H}_2\text{O}, \text{ wherein } 14 < x < 20, \) in the range of from 80 to 100% by weight, more preferably from 95 to 100% by weight, based on the dry weight of the shotcrete accelerator.

It is preferred that the shotcrete accelerator comprises a total amount of jurbanite and/or hydronium alunite in the range of from 30 to 100% by weight, more preferably from 50 to 100% by weight, based on the dry weight of the shotcrete accelerator. The shotcrete accelerator may, for instance, comprise a total amount of jurbanite and/or hydronium alunite in the range of from 30 to 99% by weight, more preferably from 50 to 97% by weight, based on the dry weight of the shotcrete accelerator.

Depending on the alternative synthesis routes discussed below, the main phase is either jurbanite or hydronium alunite. Hence, in the route where hydronium alunite is the main phase, the amount of jurbanite is usually low or even absent and vice versa. Accordingly, in one embodiment, the shotcrete accelerator
preferably comprises from 50 to 100% by weight, more preferably from 80 to 100% by weight, of jurbanite, based on the dry weight of the shotcrete accelerator, or, in another embodiment, the shotcrete accelerator preferably comprises from 30 to 100% by weight, more preferably from 50 to 100% by weight, of hydronium alunite, based on the dry weight of the shotcrete accelerator.

In one embodiment, the shotcrete accelerator may, for instance, comprise from 50 to 99% by weight, more preferably from 80 to 97% by weight, of jurbanite, based on the dry weight of the shotcrete accelerator, or in another embodiment, the shotcrete accelerator may, for instance, comprise from 30 to 99% by weight, more preferably from 50 to 97% by weight, of hydronium alunite, based on the dry weight of the shotcrete accelerator.

The shotcrete accelerator preferably comprises from 0 to 50% by weight, more preferably from 0 to 20% by weight, of \( \text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O} \), wherein \( 14 < x < 20 \), based on the dry weight of the shotcrete accelerator. In one embodiment, the shotcrete accelerator preferably comprises from 1 to 50% by weight, more preferably from 3 to 20% by weight, of \( \text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O} \), wherein \( 14 < x < 20 \), based on the dry weight of the shotcrete accelerator.

In a preferred embodiment the shotcrete accelerator comprises, based on the dry weight of the shotcrete accelerator, from 50 to 100% by weight, more preferably from 80 to 100% by weight, e.g. 50 to 99% by weight or 80 to 97% by weight, of jurbanite and from 0 to 50% by weight, more preferably from 0 to 20% by weight, e.g. 1 to 50% by weight or 3 to 20% by weight, of \( \text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O} \), wherein \( 14 < x < 20 \).

The shotcrete accelerator can be a solid or an aqueous suspension or slurry of the solid. As explained below the shotcrete accelerator is preferably produced in solid form.
The solid shotcrete accelerator can be e.g. in form of a powder, flakes or blocks. The solid is in particular a dispersible or redispersible solid, i.e. it can be dispersed in water resulting in an aqueous dispersion or slurry.

The solid is stable since solid phases are included. The solid, preferably in form of powder or flakes, can be stored as solid for months and redispersed in water just before use on site of application.

The solid of the shotcrete accelerator or the dispersion or slurry thereof essentially includes only pure active substances. Neither fluidizers nor stabilizers are required.

Apart from the components mentioned above, the solid and the aqueous dispersion or slurry may optionally include other components. In the following other components refer to components which are different from jurbanite, hydronium alunite, $\text{Al}_2(\text{SO}_4)_3 \times \text{H}_2\text{O}$, wherein $14 < x < 20$, and water.

The solid and the aqueous dispersion or slurry may optionally comprise one or more other components such as other aluminium compounds and/or common additives for improving certain properties. Other aluminium compounds refer to other reaction products obtained from the raw materials used, such as e.g. $\text{Al}_{16}(\text{SO}_4)_6(\text{OH})_{18} \cdot 37\text{H}_2\text{O}$.

Examples for suitable additives are $\text{Mg(OH)}_2$ or $\text{Ca(OH)}_2$ or reaction products thereof, amines like DEA (diethanolamine) or TEA (triethanolamine); thixotropic agents, e.g. sepiolite, formiates; and fluorides. The additives can optionally be added to the solid or to the aqueous dispersion or slurry.

In principle, the solid or the aqueous dispersion or slurry thereof may optionally comprise fluidizers and/or stabilizers as additives. However, it is preferred that the solid or the aqueous dispersion or slurry thereof do not contain any fluidizer or stabilizer. Examples of stabilizers and fluidizers are polycarboxylates, hydroxycarboxylic acids, phosphoric acids, salts of phosphoric acids or
hydroxycarboxylic acids, sepiolite or bentonite. Phosphoric acids are e.g.
orthophosphoric acid, metaphosphoric acid and pyrophosphoric acid.

The content of additives in the shotcrete accelerator is preferably less than 15%
by weight, more preferably less than 10% by weight, based on the dry
weight of the shotcrete accelerator.

In particular, it is preferred that the shotcrete accelerator is an alkali-free
accelerator. Moreover, it is preferred that the shotcrete accelerator is free of
fluidizer and stabilizer. Alkali-free means that the alkali content, calculated as
Na₂O equivalent, is less than 1% by weight, preferably less than 0.5% by
weight, based on the dry weight of the shotcrete accelerator. As known in the
field of cement applications, Na₂O equivalent refers to Na₂O + 0.658 K₂O. Free
of fluidizer and stabilizer means that the total amount of fluidizer and stabilizer
is less than 0.1% by weight, preferably less than 0.01% by weight, based on
the dry weight of the shotcrete accelerator. It is generally preferred that the
shotcrete accelerator does not contain any fluidizer or stabilizer. Typically, the
chloride content should be < 0.1% with respect to corrosion.

In particular, the aqueous dispersion or slurry of the solid is obtained by mixing
the solid with water. Additives may be added separately or together with the
water. The solid content of the aqueous dispersion or slurry may be adjusted in
broad ranges. The solid content of the aqueous dispersion or slurry is e.g. in
the range of 35 to 90% by weight, preferably 40 to 75% by weight, more
preferably 40 to 60% by weight. The dispersion of the solid in water may
cause partial dissolution and other reactions of the solid with the water.

The invention also relates to a method for producing the shotcrete accelerator
according to the invention. The method comprises in step a) reacting a mixture
of a) at least one sulfate compound selected from sulfuric acid and aluminium
sulfate, a2) aluminium hydroxide and optionally a3) water, wherein the molar
ratio of Al to SO₄ is in the range of from 2/3 to 3/2, at a temperature in a range
of 40°C to 140°C, preferably 50 to 130°C, more preferably 60°C to 120°C.
The mixture comprises and preferably essentially consists of 1) at least one sulfate compound selected from sulfuric acid, and aluminium sulfate, a2) aluminium hydroxide and optionally a3) water, wherein the addition of water is usually preferred. The sulfate compound is sulfuric acid and/or aluminium sulfate, wherein aluminium sulfate is preferred. In a preferred embodiment the mixture comprises and preferably essentially consists of aluminium sulfate, aluminium hydroxide and water.

The sulfuric acid is generally a concentrated sulfuric acid. Sulfuric acids include water and are defined by their content of H₂SO₄. A suitable sulfuric acid has e.g. a content of H₂SO₄ of at least 50 % by weight. Sulfuric acids having a content of H₂SO₄ in the range of 60 to 90 % by weight are particularly preferred.

The sulfate compound used is preferably aluminium sulfate. All common commercial products of aluminium sulfate can be used, including technical grade aluminium sulfates. Aluminium sulfate includes anhydrous aluminium sulfate, hydrates of aluminium sulfate and mixtures thereof, wherein hydrates of aluminium sulfate are generally preferred. Aluminium sulfate forms a number of different hydrates, e.g. the hexadecahydrate and the octadecahydrate.

All commercial products can be used as aluminium hydroxide. The aluminium hydroxide may be amorphous aluminium hydroxide or crystalline aluminium hydroxide or mixtures thereof. All crystal modifications of aluminium hydroxide are suitable, e.g. γ-Al(OH)₃, designated as gibbsite, β-ΑιΟ(ΟΗ)₃, designated as bayerite, triclinic Al(OH)₃, designated as nordstrandite. Apart from Al(OH)₃ also water-poor aluminium hydroxides AlO(OH) such as a-AlO(OH) (diaspore) Oder γ-AlO(OH) (boehmite) are suitable. Bauxite can also be used as aluminium hydroxide.

Optionally water may be added to the mixture. With respect to the water content of the mixture, water introduced e.g. by sulfuric acid or hydrate water is
to be considered so that the mixture may achieve the desired water content by such starting materials. However, generally the addition of water to the mixture is preferred or necessary.

The molar ratio of Al to SO$_4$ in the mixture is in the range of from 2/3 to 3/2, preferably from 0.9 to 1.1.

The reaction of the mixture is usually carried out in a closed system. A closed system means that educts and products, in particular water, can not escape from the system. The reaction can be carried out e.g. under reflux or in a closed reactor. For a reaction under reflux conventional reflux means such as a reflux condenser may be used.

The reaction of the mixture can be carried out by two alternative routes, namely by a stoichiometric route where the desired water content is adjusted initially in the mixture or by a concentration route where water is initially added in excess to the mixture with respect to the desired water content but in the course of the reaction excessive water is removed by evaporation.

According to the first embodiment according to the stoichiometric route, the water content in the mixture is set to a water content A so that the molar ratio of H$_2$O to Al is in a range of from 5.5 to 6.7, preferably from 5.5 to 6.0. As indicated above, water introduced e.g. by sulfuric acid or hydrate water is to be considered for the water content of the mixture.

If the method is carried out according to the first embodiment, the mixture is preferably reacted at a temperature in a range of 90°C to 140°C, preferably from 110°C to 130°C.

In the method according to the first embodiment the mixture melts at the beginning of the reaction. When the melt thickens the reaction is completed and the mixture can be cooled down, e.g. by allowing the mixture to flow out of the reactor. Within minutes it becomes a solid.
Advantages of the first embodiment are that the method is easy, fast and reproducible. Higher temperatures than current production methods are necessary.

According to the second embodiment according to the concentration route, the water content in the mixture is set to a water content B which is greater than water content A mentioned above for the first embodiment and the water content is reduced to the water content A in the course of reacting step a) by temporarily allowing partial removal of water from the mixture through evaporation. The partial removal of water can be effected e.g. by opening the closed system, e.g. by temporarily interrupting reflux or temporarily opening the closed reactor.

The water content B is generally greater than a molar ratio of H₂O to Al of 6.7 and preferably in the range of from more than 6.7 to 24, more preferably in the range of from 9.5 to 13.7.

If the method is carried out according to the second embodiment, the mixture is preferably reacted at a temperature in a range of 50°C to 100°C, preferably from 70°C to 90°C. After the partial removal of water by evaporation, the temperature may be decreased to some extent with respect to the initial temperature, e.g. the temperature may be decreased by 10 to 30°C with respect to the initial temperature.

In the method according to the second embodiment the mixture dissolves at beginning and the solution turns into yellowish. This indicates complete solution and start of the reaction. The partial removal of water by evaporation is preferably started when complete solution of the starting material occurs. When the water removal has reached the desired level so that the water content is reduced to the water content A, the system is again closed in order to avoid further evaporation. When the mixture starts to thicken due to growth of crystals, the reaction is complete and the reaction mixture can be cooled down,
e.g. by allowing the mixture to flow out of the reactor. For instance, within 5 to 10 minutes the mixture becomes a solid.

Advantages of the second embodiment are that the method is easy, fast and reproducible. Evaporation of water is necessary.

The reaction time within the reactor until starting cooling down may be e.g. in the range of about 30 min to 4 h. In the first embodiment (stoichiometric route) the reaction time may be e.g. in the range of 30 min to 2 h. In the second embodiment (concentration route) the reaction time may be e.g. in the range of 1 to 4 h.

The reaction may optionally be carried out as a hydrothermal synthesis. The reaction can be carried out e.g. at atmospheric pressure or overpressure, e.g. at a pressure of at least 2 bar, e.g. in a range of 3 to 15 bar.

When the reaction is completed the reaction mixture is cooled down. Usually the reaction mixture is cooled to room temperature, e.g. to about 15 to 25°C, but cooling down to lower temperatures than room temperature is also possible. It is preferred to cool down the reaction mixture quickly, e.g. by removing the reaction mixture from the reactor. Cooling down can alternatively be effected by spraying.

When the reaction mixture is cooled down it becomes a solid, usually within a few minutes. The solid obtained may be dried and/or comminuted, if necessary. The solid obtained may be used as such or stored. Optionally, the solid may be dispersed in water to obtain the aqueous suspension or slurry. Thus, the shotcrete accelerator in form of the solid or the aqueous suspension or slurry is obtainable by the method of the invention.

The solidification of the reaction mixture upon cooling down is a particular feature of the inventive method. Since the shotcrete accelerator is produced as a solid the method is a direct solid synthesis. The solid obtained by the method
is dispersible in water. While the shotcrete accelerator is directly produced as a solid by the inventive method, conventional commercial methods generally produce a shotcrete accelerator in form of a suspension or solution.

The invention also relates to the use of the shotcrete accelerator of the invention as an accelerator for a construction material comprising a hydraulic binder and in particular for shotcrete. The shotcrete accelerator may be added to the shotcrete or the construction material e.g. in an amount of 0.1 to 15 % by weight, preferably 5 to 10 % by weight, more preferably 5 to 8 % by weight, based on the amount of hydraulic binder contained in the shotcrete or construction material, respectively, wherein the shotcrete accelerator is preferably a dispersion having a solid content in the range of 40 to 60% by weight. In other words, the amount of the shotcrete accelerator, preferably in form of a dispersion, added to the shotcrete or construction material, respectively, is e.g. such that the solid content of the shotcrete accelerator added is 0.04 to 9 % by weight, preferably 2 to 6 % by weight, based on the amount of hydraulic binder contained in the shotcrete or construction material, respectively. As mentioned above, typical examples for construction materials comprising a hydraulic binder, e.g. cement, other than shotcrete are cement suspensions, e.g. for injections, mortar and concrete.

Examples

Example 1 (Precipitation by concentration)

Aluminium sulfate hydrate \((\text{Al}_2(\text{SO}_4)_{13}\cdot14\text{H}_2\text{O})\) and aluminium hydroxide powders were mixed in a weight ratio of 8:1 with 4 weight parts of water at 80°C in a closed reactor. After a few minutes the solution turns yellowish showing that all starting materials were dissolved and the reaction had started. The reactor was then opened to allow evaporation of water. When 3 to 3.5 weight parts of the water were evaporated, the reactor was closed and temperature was set to 60°C. After some time (about 1 to 3 hours), the mix thickens due to growth of the crystals in the solution. The mixture was then
rapidly cooled down to room temperature and became a solid within five to ten minutes. Fig. 5 is a photograph of the solid obtained which is broken down to blocks and eventually ground to a powder, respectively.

The main phases of the solid formed were
1. \( \text{Al(SO}_4\text{)OH-5H}_2\text{O} \) (jurbanite)
2. \( \text{Al}_2(\text{SO}_4)_3\times\text{H}_2\text{O} \), wherein \( 14 < x < 20 \) (alunogen, most probably \( x = 17-18 \))

Traces of \( \text{Al}_{10}(\text{SO}_4)_6(\text{OH})_8-37\text{H}_2\text{O} \) can be observed.

The solid can be either kept as solid or redispersed as a suspension in water.

**Example 2** (direct precipitation from stoichiometry)

Aluminum sulfate hydrate \( (\text{Al}_2(\text{SO}_4)_3-14\text{H}_2\text{O}) \) and aluminium hydroxide were mixed with water (weight ratios 8:1:0.8) at 120°C. After some minutes the solids were molten. The mix was kept at 120°C while mixing for about 1 hour. Upon starting to thicken, the mix was then flowed out from the reactor and cooled down to room temperature. Within minutes it became a solid.

The main phases of the solid formed were
1. \( (\text{H}_3\text{O})\text{Al}_2(\text{SO}_4)_2(\text{OH})_6 \) (hydronium alunite), more than 50%
2. \( \text{Al}_2(\text{SO}_4)_3-x\text{H}_2\text{O} \), wherein \( 14 < x < 20 \) (alunogen, most probably \( x = 17-18 \))
3. \( \text{Al(SO}_4\text{)OH-5H}_2\text{O} \) (jurbanite), only traces

The solid can be either kept as solid or redispersed as a suspension in water.

**Analysis by x-ray diffraction (XRD)**

The solids prepared in the examples were analysed by XRD from which the above mentioned main phases were determined.

Fig. 3 is a XRD spectrum of the solid prepared according to example 1 showing a mixture of phases jurbanite and alunogen. All peaks marked with black circle
are jurbanite, all other peaks belong to alunogen. Fig. 4 is a XRD spectrum of the solid prepared according to example 2 showing a mixture of phases hydronium alunite and alunogen. All peaks marked with black circle (-) are hydronium alunite, all other peaks belong to alunogen.

The solid prepared according to example 1 was subjected to a refinement process. Fig. 1 is a XRD spectrum of the refined solid showing pure phase of jurbanite. Fig. 2 is a XRD spectrum of alunogen showing pure phase of alunogen as a reference.

Performance tests

The solids prepared in the examples were tested as shotcrete accelerators added to cementitious compositions to prepare minishots and compared with commercial shotcrete accelerators. The performance was tested by determining the strength development of the cementitious compositions to which the shotcrete accelerator has been added. The strength development was evaluated continuously by ultrasound wave velocity measurement of the modulus of the cement paste.

Acc2 is an aqueous dispersion of the solid obtained in Example 1. Acc1 and Acc3 are aqueous dispersions of solids obtained by the synthesis route of precipitation by concentration similar to the process of Example 1. Acc4 is an aqueous dispersion of the solid obtained in Example 2.

The commercial shotcrete accelerators used are all Sigunit® products of Sika Schweiz AG which are aqueous alkali-free Al based accelerators.

In the following tables the compositions of the minishots based on cement pastes prepared are given. The amount of the accelerators is given in % based on the weight of the binder. Those dosages correspond to dispersions. In all instances the solid content of the accelerator in the dispersion is around 50%. The strength development of minishots MS1 to MS22 are shown in Fig. 6 (MS1
to MS4), Fig. 7 (MS5 to MS8), Fig. 8 (MS9 to MS12), Fig. 9 (MS13 to MS16),
and Fig. 6 (MS17 to MS22), respectively.

Table 1

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* cement grade
** type of Sigunit® accelerator

Table 2

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* cement grade
** type of Sigunit® accelerator
*** GGBS = Ground granulated blastfurnace slag; SF = slag superfine
## Table 3

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* cement of Holcim, Suisse  
** type of Sigunit® accelerator
Claims

1. A shotcrete accelerator which is a solid comprising at least one of jurbanite and hydronium alunite or an aqueous suspension or slurry of the solid.

2. The shotcrete accelerator according to claim 1, wherein the solid further comprises $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$.

3. The shotcrete accelerator according to claim 1 or claim 2, wherein the solid comprises jurbanite and $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$, or wherein the solid comprises jurbanite, hydronium alunite and $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$.

4. The shotcrete accelerator according to any one of claims 1 to 3, wherein the total amount of jurbanite and/or hydronium alunite and optionally $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$, is in the range of from 80 to 100% by weight, preferably from 95 to 100% by weight, based on the dry weight of the shotcrete accelerator.

5. The shotcrete accelerator according to any one of claims 1 to 4, wherein the total amount of jurbanite and/or hydronium alunite is in the range of from 30 to 100% by weight, preferably from 50 to 100% by weight, and/or the total amount of $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$, is in the range of from 0 to 50% by weight, preferably from 0 to 20% by weight, each based on the dry weight of the shotcrete accelerator.

6. The shotcrete accelerator according to any one of claims 1 to 5, wherein the total amount of jurbanite and/or hydronium alunite is in the range of from 30 to 99% by weight, preferably from 50 to 97% by weight, and/or the total amount of $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, wherein $14 < x < 20$, is in the range
of from 1 to 50% by weight, preferably from 3 to 20% by weight, each based on the dry weight of the shotcrete accelerator.

7. The shotcrete accelerator according any one of claims 1 to 6, wherein the solid is in form of powder, flakes or blocks.

8. The shotcrete accelerator according any one of claims 1 to 7, wherein the shotcrete accelerator is an alkali-free accelerator and/or wherein the shotcrete accelerator is free of fluidizer and stabilizer.

9. A method for producing a shotcrete accelerator according to any one of claims 1 to 8, comprising
   a) reacting a mixture of a1) at least one sulfate compound selected from sulfuric acid and aluminium sulfate, a2) aluminium hydroxide and optionally a3) water, wherein the molar ratio of Al to SO₄ is in the range of from 2/3 to 3/2, at a temperature in a range of 40°C to 140°C,
   b) cooling down the reaction mixture to obtain a solid, and optionally
   c) dispersing the solid obtained in water to obtain a suspension or slurry,
   wherein the water content in the mixture is set to a water content A so that the molar ratio of H₂O to Al is in a range of from 5.5 to 6.7, or wherein the water content in the mixture is set to a water content B which is greater than water content A and the water content is reduced to the water content A in the course of reacting step a) by temporarily allowing partial removal of water from the mixture through evaporation.

10. The process according to claim 9, wherein aluminium sulfate, aluminium hydroxide and water are mixed in step a).

11. The process according to claim 9 or claim 10, wherein the water content B is so that the molar ratio of H₂O to Al is in the range of from more than 6.7 to 24.
12. The process according to any one of claims 9 to 11, wherein the mixture is reacted at a temperature in a range of 90°C to 140°C, if the water content is set to the water content A, or wherein the mixture is reacted at a temperature in a range of 40°C to 100°C, if the water content is set to the water content B.

13. The process according to any one of claims 9 to 12, wherein reacting the mixture is carried out under reflux or in a closed reactor, wherein in the case of setting the water content to the water content B, the partial removal of water is carried out by temporarily interrupting reflux or temporarily opening the closed reactor.

14. The shotcrete accelerator according any one of claims 1 to 8, obtainable according to a method according to any one of claims 9 to 13.

15. The shotcrete accelerator according to claim 14, which is a solid and wherein the solid further comprises Al₂(SO₄)₃·xH₂O, wherein 14 < x < 20.

16. Use of a shotcrete accelerator according any one of claims 1 to 8, 14 and 15 as an accelerator for shotcrete or for a construction material comprising a hydraulic binder.
**INTERNATIONAL SEARCH REPORT**

**INTERNATIONAL APPLICATION No**

PCT/EP2016/065028

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**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C04B22/14 C04B40/00 C01F7/74

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**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C04B COIF

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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* Further documents are listed in the continuation of Box C.

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**Date of the actual completion of the international search**

1 September 2016

**Date of mailing of the international search report**

12/09/2016

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**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

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**Authorized officer**

Gatterer, Irene
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