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(54) **Title**: CATALYST COMPOSITION, METHOD OF PRODUCING THE SAME AND THE USE OF THE SAME

(57) **Abstract**: The present invention relates to a catalyst composition consisting of ammonium chloride, aluminum chloride, and magnesium oxide and uses thereof. Moreover, the invention relates to a method for obtaining a catalyst composition for reinforcing cement, comprising a combination of a) ammonium chloride and optionally one or more additional chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, and barium chloride; b) aluminum chloride, and c) magnesium oxide and optionallyone or more other metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably calciumoxide; by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition and thenadding the remaining additives.

Title: Catalyst composition, method of producing the same and the use of the same

Background

The present invention relates to a catalyst composition, a method of producing the same and uses of the same.

Patent EP 1 349 819 (corresponding to US 7,316,744) of the present inventor discloses a composition for reinforcing cement, which contains: a) sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride and/or ammonium chloride; b) aluminum chloride; and c) silica and/or zeolite and/or apatite. EP 1 349 819 is incorporated by reference in its entirety.

This composition for reinforcing cement according to EP 1 349 819 is commercially available from PowerCem Technologies B.V. under the registered trade names of PowerCem and RoadCem.

In a preferred embodiment of the composition of EP 1 349 819, this composition comprises a combination of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement.

The composition for reinforcing cement according to EP 1 349 819 shows excellent performances in the field. For example, in road construction or soil consolidation.

However, the present inventor has recently discovered that for certain applications it is desirable to provide a catalyst composition having an increased reactivity.

It is an aim of the present invention to provide a catalytic composition for reinforcing cement having a higher reactivity. Another aim of the invention is provide novel uses for this catalytic composition. In addition novel methods for producing the additive composition for reinforcing cement according to EP 1 349 819 are desired.

Summary of the invention

This aim is obtained by the following four aspects of the present invention.

In a first aspect, the present invention is related a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide.

The total quantity of I) may be 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; based on the total weight of I) + II) + III).

The total quantity of II) may be 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, based on the total weight of I) + II) + III).

The total quantity of III) may be 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, based on the total weight of I) + II) + III).

The second aspect of the present invention relates to a method for obtaining a additive composition for reinforcing cement, comprising a combination of :

a) ammonium chloride and optionally one or more additional chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, and barium chloride;

b) aluminum chloride,

c) silica and/or zeolite and/or apatite; and

magnesium oxide and optionally one or more other metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably calcium oxide; and

by firstly combining I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide to form the catalytic composition and

by then adding optionally one or more additional chlorides of group a), and optionally one or more other metal oxides and silica and/or zeolite and/or apatite of group c).

It should be noted that the ammonium chloride I) of the present catalyst composition is the same as the ammonium chloride added in group a) of the additive composition. However, it should be noted that additional ammonium chloride may be added.

It should be noted that the aluminum chloride II) of the present catalyst composition is the same as the aluminum chloride added in group b) of the additive composition. However, it should be noted that additional aluminum chloride may be added.

In other words, the present invention relates to a novel method for obtaining a additive composition for reinforcing cement, comprising a combination of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition.

In a third aspect the present invention is related to the use of a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide for lowering the pH of cement.

In other words, the third aspect of the present invention is related to a method for lowering the pH of cement by the addition of a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide, preferably in an amount of between 1 and 15 weight percent based on the weight of the cement.

In a fourth aspect, the present invention relates to use of a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide for addition to cement for oil well cementing.

In other words, this fourth aspect of the present invention relates to a method of cementing a wellbore, comprising the steps of: i) drilling a wellbore; ii) introducing a casing string into the wellbore; iii) preparing a cement slurry based on a combination of cement and a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide; iv) pumping said cement slurry into the wellbore; and v) allowing said cement slurry to set.

Moreover, the invention relates to a cement slurry for cementing a wellbore, comprising i) cement, ii) water; and iii) a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide.

In an embodiment, said cement slurry comprises between 50 and 85 wt%, preferably between 65 and 75 wt% of I) cement, and between 20 and 40 wt%, preferably between 25 and 30 wt% of II) water, and between 0.1 and 10 wt%, preferably between 1 and 3 wt%, more preferably between 1.5 and 2.5 wt% of catalyst composition III).

In an embodiment, the total quantity of components from group I) may be 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; most preferably 10 wt.% based on the total weight of I) +II) + III).

In an embodiment, the total quantity of components from group II) may be 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, most preferably 30 wt.% based on the total weight of I) +II) + III).

In an embodiment, the total quantity of components from group III) may be 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, most preferably 20 wt.% based on the total weight of I) +II) + III).

<u>Detailed description of the invention</u>

Extensive studies by the present inventor have revealed that with the use of the composition of EP 1 349 819 (viz. comprising sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement) a certain combination of specific components are responsible for the activation of the remaining components. The present catalytic composition comprises these specific components and imposes reactivity on the other components to a full oxidation reaction when water is added to the dry mixture.

Based on this remarkable and surprising finding, the inventor has arrived at the present invention.

Without wishing to be bound by a theory, the following is observed. Several of the components of the RoadCem or PowerCem product of EP 1 349 819 comprise water of crystallization in their crystal structures. This water of crystallization reacts with some of the reactive components, such as aluminum chloride. This crystal water is e.g. believed to deactivate aluminum chloride in a preliminary oxidation reaction. The release of this water of crystallization is increased during the process of mixing the components together in which mixing process optionally crushers are used which generate heat.

When a high grade aluminum chloride is used in the preparation of the RoadCem or Powercem products, this grade is lowered upon storage. Higher grade aluminum chloride is more expensive than lower grade aluminum chloride and when the higher quality does not provide an additional reactivity since it has deactivated, it is not of any commercial use to start with a high grade aluminum chloride. With the catalyst and method of preparation of the additive of the present invention, this deactivation does not occur since the catalyst composition in only mixed with the remaining (water of crystallization containing) components shortly before it is used. In that case, there is not sufficient time for the deactivation to occur and the higher reactivity of aluminum chloride is maintained. The technical effect, is to supply a highly reactive catalyst composition.

In this case the catalyst composition is prepared and stored separately from the remaining components. Shortly before using RoadCem or PowerCem product of EP 1 349 819 the catalyst composition is mixed with the remaining components.

An additional advantage of the present catalytic composition as revealed by research carried out by the present inventors is that it is possible to use a better grade (higher purity) aluminum chloride, such as 99% (2N), 99.9 % (3N), 99.99 % (4N) or even 99.999 % (5N) Aluminum chloride, in the preparation of e.g. the RoadCem or PowerCem product of EP 1 349 81.

In a first aspect, the present invention thus relates to the catalytic composition as such.

In a second aspect, the present invention relates to the method of manufacturing a composition for reinforcing cement using the present catalyst composition as pre-mix.

In third and fourth aspects, the present invention relates to specific uses of said catalytic composition.

The catalyst composition can be added to cement to increase the reactivity of cement and provide a high energetic value of the cement. Thus the present invention relates to the use of the catalyst composition to reinforce cement for high-demanding applications, for example cementing of wellbores (fourth aspect of the present invention).

The catalyst composition of the present invention, viz. the catalyst will in the future probably be marketed by PowerCem Technologies B.V. under the trademark of RC-C (RoadCem-catalyst).

Definitions as used in the present description

The following definitions are used in the present description and claims to define the stated subject matter. Other terms not cited below are meant to have the generally accepted meaning in the field.

“Cement” as used in the present description means: a salt hydrate consisting of a fine-ground material which, after mixing with water, forms a more or less plastic mass.

“Pozzolan” as used in the present description means: a material which, when combined with calcium hydroxide, exhibits cementitious properties.

“E-fly ash” as used in the present description means: pulverised coal fly ash. E-fly ash is a fine powder which consists mainly of spherical glassy particles having pozzolane properties.

“E-bottom ash” as used in the present description means: a burned, dehydrated clay which is coloured brown-black.

"boiler sand" as used in the present description means: certified E-bottom ash.
“WI fly ash” as used in the present description means: a fine dustlike/powdery material that is formed as a residual product in the incineration of domestic waste and comparable industrial waste.

“WI bottom ash” or "slag" as used in the present description means: a material consisting for 50% of an amorphous mass and for the rest of other materials, such as glass, rubble/ceramics, slag-like material and small amounts of iron and non-combusted organic material.

Cement is a salt hydrate consisting of a fine-ground material which, after mixing with water, forms a more or less plastic mass. Cement hardens both under water and in the outside air and which is capable of bonding materials suitable for that purpose to form a mass that is stable also in water. The cement standards according to European standard NEN-EN-197-1 are as follows: CEM I is Portland cement; CEM II is composite Portland cement; CEM III is blast furnace slag cement; CEM IV is pozzolan cement and CEM V is composite cement.

The catalyst composition can be added to pozzolan materials. The effect of the catalyst composition is that it activates the pozzolan characteristics of e.g. fly ash or bottom as (preferably E-fly ash or E-bottom ash) to hydrolyze these ashes.

A pozzolan is a material which, when combined with calcium hydroxide, exhibits cementitious properties. Pozzolans are a siliceous or aluminosiliceous material, which is highly vitreous. Pozzolans are commonly used as an addition or “supplementary cementitious material" or SCM to Portland cement concrete mixtures to increase the long-term strength and other material properties of Portland cement concrete, and in some cases reduce the material cost of concrete. Pozzolans are primarily vitreous siliceous materials which react with calcium hydroxide to form calcium silicates; other cementitious materials may also be formed depending on the constituents of the pozzolan. The most commonly used pozzolan today is fly ash, though silica fume, high-reactivity metakaolin, ground granulated blast furnace slag, fly ash and other materials are also used as pozzolans. Many pozzolans available for use in construction today were previously seen as waste products, often ending up in landfills. Use of pozzolans can permit a decrease in the use of Portland cement when producing concrete; this is more environmentally friendly than limiting cementitious materials to Portland cement.

E-fly ash (pulverised coal fly ash) is a fine powder which consists mainly of spherical glassy particles having pozzolane properties (i.e. the particles cement with lime and water into stable compounds that do not dissolve in water). E-fly ash is released in pulverised coal-fired power plants, where the fly ash is separated from the flue glass flow by means of electrostatic filters. The properties of E-fly ash are influenced by the origin of the coal, the process conditions in the power plant and the manner of transportation of the ash. E-fly ash may cause environmental problems when released into the atmosphere.

E-bottom ash is released in pulverised coal-fired power plants. E-bottom ash is released as "heavy" ash particles during the combustion process. The material is a burned, dehydrated clay which is coloured brown-black. A distinction may be made into porous (sintered) and dense (molten) E-bottom ash granules. If the E-bottom ash is certified, it is also referred to as "boiler sand".

Bag house dust is a material that has physical properties that are comparable to E-fly ash.

In addition to E-fly ash and E-bottom ash, there is also the so-called WI fly ash and WI bottom ash (WI = Waste Incineration), which both have properties that are completely different from the properties of E-fly ash and E-bottom ash.

WI fly ash consists of a fine dustlike/powdery material that is formed as a residual product in the incineration of domestic waste and comparable industrial waste. The incineration takes place in waste incineration plants and concerns the ash that can be separated from the crude flue gases from such a plant by means of electrostatic filters.

WI bottom ash (previously called "slag") consists for 50% of an amorphous mass and for the rest of other materials, such as glass, rubble/ceramics, slag-like material and small amounts of iron and non-combusted organic material. WI bottom ash is formed during the combustion of domestic waste and comparable industrial waste.

Preferred embodiments of all aspects of the present invention

The present invention is preferably a mixture of noble metals (e.g. aluminum) and non-noble metals (e.g. magnesium) which combined give a synergistic reaction to the formation of stable crystalline structures.

For an optimum composition of the catalyst, the total quantity of components from group I) may be 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; most preferably 10 wt.% based on the total weight of I) +II) + III).

For an optimum composition of the catalyst, the total quantity of components from group II) may be 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, most preferably 30 wt.% based on the total weight of I) +II) + III).

For an optimum composition of the catalyst, the total quantity of components from group III) may be 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, most preferably 20 wt.% based on the total weight of I) +II) + III).

The present catalyst is preferably used in an amount of 0.1 to 15 wt.% based on the amount of pozzolan materials, preferably in an amount of 0.5 to 10 wt.%, more preferably in an amount of between 1 and 5 wt.%, such as for example 2 wt.%, 3 wt.%, or 4 wt.%.

Preferred pozzolan materials for use in the present invention are ashes as disclosed above for the binder composition and the construction composition.

Without wishing to be bound to any specific theory, experimental results indicate that the components which are present in the catalyst form crystalline structures when added to cement material which are well bonded together and are homogeneously distributed, in between the cement particles, and thereby bind the cement particles. Hardened cement which is prepared without this binder or with known binders has a relatively open structure when viewed on a microscopic scale, with crystalline agglomerations which are not homogeneously distributed. Consequently, the interaction between the crystalline agglomerations and also between the cement particles and the crystalline agglomerations is poor.

The crystalline compounds which are formed by this additive are surprisingly homogeneously distributed and may be in the form of acicular (viz. needle-like) structures. The homogeneous distribution results in an optimum strength and stability. The water in the cement is bound in and to the crystalline structures. Consequently, there are no local concentrations of water, and therefore the formation of potential weak spots is avoided.

The present catalyst composition has been found be induce the forming of nanoscale crystalline compounds. Hence, the function of the catalyst of the present invention is the formation of durable crystal structures.

The catalyst composition according to the present invention can be prepared by combining the required components and dry-mixing them. The catalyst composition according to the invention is preferably assembled from the abovementioned components in pure form (> 97%, or even >98 %, or even > 99 %).

First aspect of the present invention

In a first aspect, the present invention thus relates to the catalytic composition as such and the use thereof.

The sole components of the catalyst composition are ammonium chloride, aluminum chloride, and magnesium oxide. Thus the catalyst composition is constituted by these three components. No other components are present.

The present catalyst composition can for example be considered as a pre-mix having enhanced activity for an additive composition (e.g. a composition for reinforcing cement).

Said composition for reinforcing cement – which is prepared using the present catalyst composition as pre-mix - contains: a) sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride and/or ammonium chloride; b) aluminium chloride; and c) silica and/or zeolite and/or apatite. Group a) of said composition for reinforcing cement – which is prepared using the present catalyst composition as pre-mix - may contains at least sodium chloride and calcium chloride.

Group c) of said composition for reinforcing cement – which is prepared using the present catalyst composition as pre-mix - may contain silica and/or zeolite. Optionally only silica is present in group c). However, at least some of the silica and/or zeolite may be replaced by cement, preferably Portland cement.

Said composition for reinforcing cement – which is prepared using the present catalyst composition as pre-mix - may also contains magnesium oxide and/or calcium oxide. The additive composition comprising at least ammonium chloride in group a) and at least additional magnesium oxide can be prepared using the catalyst composition of the present invention as a premix.

The composition for reinforcing cement – which is prepared using the present catalyst composition as pre-mix - may contain sodium chloride, potassium chloride, magnesium chloride, calcium chloride, ammonium chloride, aluminium chloride, magnesium oxide, silica and/or zeolite.

Additional components for the additive composition that can be prepared using the present catalyst composition are: magnesium hydrogen phosphate, magnesium sulfate and/or sodium carbonate.

One embodiment of the additive composition is:

10 to 55% by weight of sodium chloride

5 to 40% by weight of potassium chloride

0.5 to 5% by weight of ammonium chloride (* part of the catalyst composition)

5 to 40% by weight of magnesium chloride

5 to 45% by weight of calcium chloride

1 to 15% by weight of aluminium chloride (* part of the catalyst composition)

0.5 to 10% by weight of silica

0.2 to 8% by weight of magnesium oxide (* part of the catalyst composition)

1.5 to 10% by weight of magnesium hydrogen phosphate

1.5 to 8% by weight of magnesium sulfate

1 to 10% by weight of sodium carbonate

0 to 20% by weight of cement based on the total weight of these components.

One embodiment of the additive composition is:

15 to 45% by weight of sodium chloride

8 to 32% by weight of potassium chloride

0.5 to 2% by weight of ammonium chloride (* part of the catalyst composition)

8 to 32% by weight of magnesium chloride

7.5 to 30% by weight of calcium chloride

1.5 to 6% by weight of aluminium chloride (* part of the catalyst composition)

0.5 to 2% by weight of silica

0.2 to 4% by weight of magnesium oxide (* part of the catalyst composition)

1.5 to 6% by weight of magnesium hydrogen phosphate

1.5 to 5% by weight of magnesium sulfate

1 to 6% by weight of sodium carbonate

3 to 10% by weight of cement based on the total weight of these components.

In an Example of EP 1 349 819 (See Table 1) the following composition is given for the additive composition: (% by weight of total composition). NaCl: 30; NH_4Cl: 1; $AlCl_3.6H_20$: 3; KCl: 16; $CaCl_2$. $2H_2O$: 15; $MgCl_2.6H_2O$: 16; MgO: 2; $MgHP0_4.3H_2O$: 3; $MgSO_4.7H_2O$: 2.5; Na_2CO_3: 3; Amorphous SiO_2: 1; Portland cement 52.5 R (Blain 530m2/kg).: 7.5

This composition has a pH of approx. 9-9.5 (1 part additive and 20 parts water,T = 16.8 C) and a conductivity of 53.1 mS (T = 16.8 C)

Group a) of the additive composition of EP 1 349 819 are alkali metal and alkaline earth metal chlorides. Ammonium chloride is always present as it is present in the catalyst composition. It is preferred since it provides the highest reactivity in combination with aluminum chloride and the metal oxides.

Group b) of the additive composition of EP 1 349 819 is composed of aluminum chloride and is important for the formation of crystalline compounds. Aluminum chloride is always present and preferred, but may also be partially replaced by other chlorides of trivalent metals, such as iron (III) chloride.
Moreover, one or more metal oxides are present. Magnesium oxide is always present as part of the catalytic composition. The effect of these metal oxides is that they take part in the chain reaction that lead to a crystalline matrix. The metal oxides form clusters with other ions that are formed into oxides.

In European patent application EP 1 829 840 of the present inventor a binder composition is disclosed comprising an ash, an additive composition and a cement.

The binder composition of EP 1 829 840 comprising:

a) an ash in an amount of 30.0 - 70.0 wt.%, based on the total weight of the binder composition;

b) an additive composition in an amount of 0.1 - 5.0 wt.%, based on the total weight of the binder composition, wherein the additive composition comprises one or more components from group (b1) and one or more components from group (b2), wherein group (b1) consists of metal chlorides and wherein group (b2) consists of silica, zeolite and apatite, and wherein the one or more components from group (b1) make up 70.0 99.0 wt.% of the total weight of the components (b1) and (b2) and wherein the one or more components from group (b2) make up 1.0 30.0 wt.% of the total weight of the components (b1) and (b2);

c) a cement in an amount of 25.0 - 69.9 wt.%, based on the total weight of the binder composition.

The present catalytic composition can also be used in this binder composition instead of the additive composition of group b). Thus the present invention also relates to a binder composition comprising: i) an ash in an amount of 30.0 - 70.0 wt.%, based on the total weight of the binder composition; ii) a catalyst composition, consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide; iii) a cement in an amount of 25.0 - 69.9 wt.%, based on the total weight of the binder composition.

In addition to that the present application relates to a composition for construction comprising a basic component and the present binder composition, and also to a method for obtaining the same and uses thereof. EP 1 829 840 is incorporated by reference herein in its entirety.

An advantage of such a binder composition is that the binder composition, when used in a composition for construction, converts hexavalent chromium that is present in the composition into trivalent chromium, and that said chromium compounds, as well as any harmful radon that may be present in the composition, will not find their way into the environment. Such an advantage is achieved to a lesser extent, or even not at all, with a binder composition that comprises amounts of ash, additive composition and cement that do no fall within the scope of present invention.

The amount of component a) in the binder composition may be 40-65 wt.%, in particular 50-60 wt.%, since this will provide optimum results if the binder is used in a construction composition. Preferably, the ash of component a) is selected from E-fly ash, E-bottom ash, bag house dust and a combination thereof. The amount of component b) in the binder composition may be 0.1-2.0 wt.%, preferably 0.5 to 1 wt.% of the total binder composition, as it has been found that good binding properties are obtained in particular in this range, whilst the composition is cost-effective.

In European patent application EP 1 829 840 (incorporated by reference herein in its entirety) of the present inventor a construction composition and a method for making a construction product is disclosed, comprising:

an ash in an amount of 90.0-99.9 wt.%, based on the total weight of the construction composition, wherein the ash is fly ash or bottom ash;

an additive composition in an amount of 0.1-10.0 wt.%, based on the total weight of the construction composition, wherein the additive composition comprises a component from group (2a) and a component from group (2b), wherein group (2a) consists of metal chlorides and wherein group (2b) consists of silica, zeolite and apatite, and wherein group (2a) comprises 70.0-99.0 wt.% of the total additive composition and group (2b) comprises 1.0-30.0 wt.% of the total additive composition, wherein group (2a) comprises at least one component from group (2a1) and a component from group (2a2), wherein group (2a1) consists of sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride, and ammonium chloride, and wherein the group (2a2) consists of aluminum chloride; and

cement, in an amount of 0.0-5.0 wt.%, based on the total weight of the construction composition.

The present catalytic composition can also be used in this construction composition instead of the additive composition of group b). Thus the present invention also relates to a construction composition comprising: i) an ash in an amount of 90.0-99.9 wt.%, based on the total weight of the construction composition, wherein the ash is fly ash or bottom ash; ii) a catalyst composition, consisting of I) ammonium chloride, II) aluminum chloride, III) magnesium oxide; iii) cement, in an amount of 0.0-5.0 wt.%, based on the total weight of the construction composition.

The ash of this construction composition can be the same as the ash described above for the binding composition. The construction composition may be added in the method for making a construction product, such that the weight of the construction composition comprises 10-90 wt% (wet weight) of the bottom material, e. g. 10-80 wt.%.

In various sectors, cement is used as a binder. Possible applications of cement include the stabilization of soil, when building bored wells, houses, roads and tunnels, the immobilization of pollutants or sludge, the production of concrete, etc. In these applications, additives which increase the binding force of cement are generally added to the cement.

In addition to the uses above, the catalyst composition according to the invention can be used for: i. stabilizing/modifying cement and consolidating sand, sludge and/or soil, such as for the construction and laying of bored wells, roads, dykes, tunnels, foundations and the like; ii. immobilizing pollutants, such as heavy metals, but also fly ash; iii. when injecting cement compositions, such as grouting; When grouting, a mixture or suspension of composition, cement and/or sand in combination with water is injected. 50-100 g of cement and approx. 2 g of composition are added per 100 g of water. In this case, a drum or mixing silo is filled with water, composition according to the invention and cement, and then the metered quantity is injected. The pressure is 10 to 400 bar. iv. the production of concrete.

Second aspect of the present invention

In a second aspect, the present invention relates to the method of manufacturing a composition for reinforcing cement using the present catalytic composition.

All aspects discussed above for the first aspect are also applicable to this aspect of the present invention.

Prior to the use as a composition for reinforcing cement, one or more additional components such as for example one or more zeolites and/or one ore more sulfates (e.g. magnesium sulfate) and/or additional chlorides and/or one or more carbonates (e.g. sodium carbonate) and/or one ore more cements may be added to the catalytic composition according to the present invention.

Thus the present invention relates to a method for obtaining a additive composition for reinforcing cement, comprising a combination of :

a) ammonium chloride and optionally one or more additional chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, and barium chloride;

b) aluminum chloride, and

c) silica and/or zeolite and/or apatite;

magnesium oxide and optionally one or more other metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g.

iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably calcium oxide; and

by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition and

by then adding the optionally one or more additional chlorides of group a), and optionally one or more other metal oxides and silica and/or zeolite and/or apatite of group c).

In other words, the present invention relates to a method for obtaining a additive composition for reinforcing cement, comprising a combination of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition.

<u>Third aspect of the present invention</u>

In a third aspect, the present invention relates to use of said catalytic composition for lowering the pH of cement.

Suspensions based on the catalyst composition described above have a pH of between approx. 9 and 9.6 (1 part composition and 20 parts water, T = 16.8 °C).

When cement is formed, the pH is highly basic having a pH of between 12 and 13. This is caused by the high concentrations of calcium oxide which forms calcium hydroxide when exposed to water. This is not only detrimental to people working with cement since cement can cause chemical burns; but the presence of hexavalent chromium can cause ulcers.

It has surprisingly been found by the present inventor that the catalyst composition according to the present invention regulates the pH balance of cement by lowering the pH of cement in time, possible to a neutral pH. Moreover, the crystalline structure that is formed as cited above is capable of enclosing or entrapping hexavalent chromium thereby rendering it harmless since it cannot leak from the cement.

Tests were conducted by the present inventor.

In Comparative Test 1 a suspension of 50 grams of the catalyst composition according to the present invention constituted of ammonium chloride (1 part), aluminum chloride (3 parts), magnesium oxide (2 parts), in 500 grams of demineralized water. After one hour the pH was 7.86.

In Comparative Test 2 a suspension of 500 grams of cement (CEM I 42,5 N) was mixed with 500 grams of demineralized water. After one hour the pH was 12.50.

In a Test according to the present invention in a fist step a 50 grams of the catalyst composition according to the present invention constituted of ammonium chloride (1 part), aluminum chloride (3 parts), magnesium oxide (2 parts), in 500 grams of demineralized water was prepared. Half of this suspension was added to 500 grams of cement (CEM I 42,5 N). After ten minutes the second half of the suspension was added. After one hour from the addition of the first half of the suspension the pH was 11.72. Indicating that a decrease of the pH by almost 1 pH point was obtained by the addition of the present catalyst. After 48 hours the pH and after 96 hours the pH is still 11.72. This is explained as follows. It is noticed that primary etringites are formed at a pH of approx. 11. After a chemical equilibrium is formed, the pH decreases to values below 11. After a period of several days or weeks, the pH decreases further to values as discussed below.

Thus the present catalytic composition is useful for the lowering the pH of cement. Preferably, the lowering will take place to such an extent that a pH of below 11, preferably below 10, more preferably below 9, even below 8 or a neutral pH between 6.5 and 7.5 is obtained. The person skilled in the art is able to determine the amount of catalyst required by a series of simple test using a standard pH metering device and different amount of catalyst with respect to cement. The amount needed is dependent on the type of cement used.

In an embodiment the amount of catalyst needed is between 1 and 15 wt.% based on the weight of the cement, preferably between 7 and 12 wt.%

Without wishing to be bound to a theory, the following is observed. When water is added to cement, each of the compounds undergoes hydration and contributes to the final product. Only the calcium silicates contribute to strength. Tricalcium silicate is responsible for most of the early strength during first 7 days. Dicalcium silicate, which reacts more slowly, contributes only to the strength at later times. Upon the addition of water, tricalcium silicate rapidly reacts to release calcium ions, hydroxide ions, and a large amount of heat. The pH quickly rises over 12 because of the release of alkaline hydroxide (OH-) ions. This initial hydrolysis slows down quickly with a corresponding decrease in heat.

Fourth aspect of the present invention

In a fourth aspect, the present invention relates to the use of said catalytic composition for cementing well bores. Moreover, the inventions is related to a cement slurry comprising the catalytic composition of the present invention.

One of the uses of the catalyst composition of the present invention is as an (nano-engineered) additive for oil well cementing. The present catalyst composition improves flexibility and increases compressive strength.

One important use of concrete or cement in the oil and gas field is as so-called “well cementing” or the cementing of the drilling or oil well. For this use deep bores are drilled into the ground or soil. The inside of these bores are covered by a metallic layer or pipe that is used to guide the oil from the oil field up to the surface (= casing string). These metallic layers should adhere to surrounding environment (i.e. soil or rock). In order to obtain this adhesion between the metallic layer (casing or casing string) and the surroundings cement is often used.

Wellbores are protected and sealed by cementing, i.e. for shutting off water penetration into the well, to seal the annulus after a casing string (viz. a long section of connected oilfield pipe) has been introduced down the wellbore, or to plug a wellbore to abandon it.

Cementing is carried out using a cement slurry that is pumped into the well. In this method, usually the drilling fluids that are present inside the will are replaced by cement. The cement slurry fills the space between the casing and the actual wellbore, and hardens to create a seal. This presents external materials entering the well flow and positioning the casing string into place permanently.

A cement slurry is wet cement obtained by mixing dry cement and water and optionally one or more additives.

The cement slurry for cementing a wellbore according to this fourth aspect of the present invention, comprises i) cement, ii) water; and iii) a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide.

In an embodiment of the cement slurry, said slurry comprises between 50 and 85 wt%, preferably between 65 and 75 wt% of: I) cement, and between 20 and 40 wt%, preferably between 25 and 30 wt% of; II) water, and between 0.1 and 10 wt%, preferably between 1 and 3 wt%, more preferably between 1.5 and 2.5 wt% of composition III).

The wet cement (viz. cement slurry) is obtained by the use of mixers (e.g. hydraulic jet mixers, re-circulating mixers or batch mixers) from water and dry cement and one or more additives.

For wellbore cementing Portland cement is most frequently used (calibrated with additives to 8 different API classes). Examples of additives are accelerators, which shorten the setting time required for the cement, as well as retarders, which do the opposite and make the cement setting time longer. In order to decrease or increase the density of the cement, lightweight and heavyweight additives are added. Additives can be added to transform the compressive strength of the cement, as well as flow properties and dehydration rates. Extenders can be used to expand the cement in an effort to reduce the cost of cementing, and antifoam additives can be added to prevent foaming within the well. In order to plug lost circulation zones, bridging materials are added, as well.

The present invention provides catalytic composition to be used as an additive for cement to be used for wellbores.

A method for well cementing is known in the art. After casing string has been run into the bored well, an cementing head is attached to the top of the wellhead to receive the slurry from the pumps. A so-called bottom plug and top plug are present inside the casing and prevent mixing of the drilling fluids from the cement slurry. First, the bottom plug is introduced into the well, and cement slurry is pumped into the well behind it, viz. within the casing and not yet between the casing and its surroundings. Then the pressure on the cement being pumped into the well is increased until a diaphragm is broken within the bottom plug, permitting the cement slurry to flow through it and up the outside of the casing string, viz. outside of the casing and hence between the casing and its surroundings. After the proper volume of cement is pumped into the well, a top plug is pumped into the casing pushing the remaining slurry through the bottom plug. Once the top plug reaches the bottom plug, the pumps are turned off, and the cement is allowed to set.

Since wellbores are very deep, setting or hardening at deep depths and under conditions of high temperature and/or high pressure, and optionally corrosive environments, there are stringent requirements for the cement.

A few of the challenges today with respect to well cementing are discussed below.

Despite recent technological advances with elastomers, polymers, fibres and reactive components that self-heal micro fissures, the cement sheath between the casing string and the surrounding rock/soil is not always able to deliver an acceptable long-term solution for today’s demanding drilling environment. Changes in down hole conditions with pressure and temperature fluctuations impose stresses on the cement sheath. Consequently, shrinking and de-bonding of the cement sheath creates very small micro cracks allowing fluid migration. Besides these external forces that cause cement sheath damage an evaluation of conventional oil well cement sheath on the nanoscopic scale from 1 – 100 nm reveals that the chemical bond between components within the cement itself is relatively brittle.

Examples of the challenges are: i) micro cracks occurring because of fluctuations in pressure and/or temperature inside the well; ii) undesired gas migration due to shrinkage or expansion of the cement; iii) corrosion of the protective casing, which costs hundreds of millions and which reduces longevity.

There are several demands required in the field of well cementing, viz. with respect to density, permeability, shrinkage, bonding, chemical resistance, setting time, viscosity, flexibility, and durability. Moreover, downhole temperature can exceed 200 °C.

An example of preferred product criteria for cement for wells are the following:

- Density: value < 1300 kg/m^3
- Permeability: material has to be impermeable
- Shrinkage: material may not shrink, expansion is preferred
- Bonding: good bond required with steel
- Chemical resistance: high chemical resistance required
- Thickening time: materials needs to be workable up to 6 hours
- Viscosity: preferably 300 CP
- Flexibility: stretch of 2% without fracturing

Known Portland cement consists of five major compounds and a few minor compounds. The composition of a typical Portland cement is as follows: 50 wt.% of tricalcium silicate (Ca_3SiO_5 or $3CaO.SiO_2$); 25 wt.% of dicalcium silicate (Ca_2SiO_4 or $2CaO.SiO_2$); 10 wt.% of tricalcium aluminate ($Ca_3Al_4O_6$ or $3CaO.Al_2O_3$); 10 wt.% of tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$ or $4CaO.Al_2O_3.Fe_2O_3$); 5 wt.% of gypsum ($CaSO_4.2H_2O$)

Without wishing to be bound to any specific theory, experimental results discussed in prior patent applications of the present inventor US 13/654,920 and US 13/540,181 (both incorporated by reference in its entirety) indicate that the components which are present in the composition for reinforcing cement used in the present application form crystalline structures when added to cement material which crystalline structures are well bonded together and are homogeneously distributed, in between the cement particles, and thereby bind the cement particles.

Without wishing to be bound to a theory, the following is observed. When water is added to cement, each of the compounds undergoes hydration and contributes to the final product. Only the calcium silicates contribute to strength. Tricalcium silicate is responsible for most of the early strength during first 7 days. Dicalcium silicate, which reacts more slowly, contributes only to the strength at later times. Upon the addition of water, tricalcium silicate rapidly reacts to release calcium ions, hydroxide ions, and a large amount of heat. The pH quickly rises over 12 because of the release of alkaline hydroxide (OH-) ions. This initial hydrolysis slows down quickly with a corresponding decrease in heat.

The reaction slowly continues producing calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Ions precipitate out of solution accelerating the reaction of tricalcium silicate to calcium and hydroxide ions, also called Le Chatelier's principle. The evolution of heat is then dramatically increased again.

The formation of the calcium hydroxide and calcium silicate hydrate crystals provide "seeds" upon which more calcium silicate hydrate can form. The calcium silicate hydrate crystals grow thicker which makes it more difficult for water molecules to reach the anhydrate tricalcium silicate. The speed of the reaction is controlled by the rate at which water molecules diffuse through the calcium silicate hydrate coating. This coating thickens over time causing the production of calcium silicate hydrate to become slower and slower. The majority of space is filled with calcium silicate hydrate, what is not filled with the hardened hydrate is primarily calcium hydroxide solution. The hydration will continue as long as water is present and there are still anhydrate compounds in the cement paste.

Dicalcium silicate also affects the strength of concrete through its hydration. Dicalcium silicate reacts with water in a similar manner as tricalcium silicate, but much more slowly. The heat released is less than that by the hydration of tricalcium silicate because the dicalcium silicate is much less reactive. The other major components of Portland cement, tricalcium aluminate and tetracalcium aluminoferrite also react with water. Heat is evolved with cement hydration. This is due to the breaking and making of chemical bonds during hydration.

The strength of cement bound products is very much dependent upon the hydration reaction just discussed. Water plays a critical role, particularly the amount used. The strength of the product increases, when a lower amount of water is used. The hydration reaction itself consumes a specific amount of water. The empty space (porosity) is determined by the water to cement ratio. The water to cement ratio is also called the water to cement factor (abbreviated by wcf) which is the ratio of the weight of water to the weight of cement used in the slurry. The wcf has an important influence on the quality of the cement produced.

Low water to cement ratio leads to high strength but low workability. High water to cement ratio leads to low strength, but good workability. A person skilled in the art of cement is able to determine the optimum water cement factor based on the component used in the slurry and the purpose of the cement slurry.

Time is also an important factor in determining product strength. The product hardens as time passes. The hydration reactions get slower and slower as the tricalcium silicate hydrate forms. It takes a great deal of time up to several years for all of the bonds to form, which eventually determines the product's strength for the life of the well.

When the catalytic composition according to the present invention is used as additive, moisture remains necessary for hydration and hardening. The five major compounds of the hydration process of cement still remain the most important hydration products but the minor products of hydration probably change. Furthermore, the rate at which important hydration reactions occur and the relative distribution of hydration products changes as a result of the addition of the present inventive composition. In addition, the crystallization of calcium hydroxide accordingly occurs at different rates and the reduction of heat generation from the hydration reactions occurs. There are more crystals formed during the reactions and the relevant crystalline matrix is much more extensive.

When adding the present composition, the water changes chemically in sphere, electrical load, surface tension and reaches a chemical/physical equilibrium in the matrix. This complex process depends of the type and mass of materials involved in the cement slurry. Similar to the chemical processes physical aspects are part of the equilibrium process in the matrix when the amount of water, trapped as free water is reduced and the crystals grow into the empty void space. This makes the product less permeable to water and more resistant to all types of attack that are either water dependant or water influenced. A bigger fraction of the water is converted to crystalline water than is the case with the reactions in the absence of the present inventive composition. The reduced porosity and increased crystalline structural matrix increases compressive, flexural and breaking strength of the product and change the relative ratio between these strengths.

As before the strength of the product increases when less water is used to make a product. The hydration reaction itself now tends to consume a different amount of water. When the present inventive composition is mixed with oil well cement it is also possible to use salt water and achieve a good end result.

In other words, the present invention relates to a catalyst composition for pozzolan compositions, comprising: a) one or more chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride and /or ammonium chloride, preferably ammonium chloride; and b) aluminum chloride, and c) one or more metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably magnesium oxide or calcium oxide, most preferably magnesium oxide.

The total quantity of components from group a. may be 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; based on the total weight a. + b. + c. The total quantity of components from group b. may be 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, based on the total weight a. + b. + c. The total quantity of components from group c. may be 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, based on the total weight a. + b. + c.

The composition disclosed above may be used for addition to cement for oil well cementing. The composition disclosed above may be used for lowering the pH of cement.

The present invention also relates to a method for obtaining a composition for reinforcing cement, comprising a combination of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition and then adding the remaining additives.

The present invention also relates to a binder composition comprising: i) an ash in an amount of 30.0 - 70.0 wt.%, based on the total weight of the binder composition; ii) a catalyst composition, comprising: a) one or more chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride and /or ammonium chloride, preferably ammonium chloride; and b) aluminum chloride, and c) one or more metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably magnesium oxide or calcium oxide, most preferably magnesium oxide; iii) a cement in an amount of 25.0 - 69.9 wt.%, based on the total weight of the binder composition.

The present invention moreover relates to a construction composition comprising: i) an ash in an amount of 90.0-99.9 wt.%, based on the total weight of the construction composition, wherein the ash is fly ash or bottom ash; ii) a catalyst composition, comprising: a) one or more chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride and /or ammonium chloride, preferably ammonium chloride; and b) aluminum chloride, and c) one or more metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably magnesium oxide or calcium oxide, most preferably magnesium oxide; and iii) cement, in an amount of 0.0-5.0 wt.%, based on the total weight of the construction composition.

According to the best mode of the invention, 12.5 kilogram of Dyckerhoff cement API Class G is mixed with 4.75 kilogram water and 375 of the catalyst composition, comprising one part ammonium chloride to two parts magnesium oxide to three parts aluminum chloride.

Embodiments disclosed in the present invention for one aspect of the invention are, were applicable, also intended to be used for other aspects of the inventions, and vice versa.

The present invention is further explained in the appended claims.

CLAIMS

1. Catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide.

2. Composition according to Claim 1, wherein the total quantity of I) is 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; based on the total weight of I) + II) + III).

3. Composition according to one of the preceding claims, wherein the total quantity of II) is 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, based on the total weight of I) + II) + III).

4. Composition according to one of the preceding claims, wherein the total quantity of I) is 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, based on the total weight of I) + II) + III).

5. Method for obtaining a additive composition for reinforcing cement, comprising a combination of :

a) ammonium chloride and optionally one or more additional chlorides, selected from the group consisting of: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, strontium chloride, and barium chloride;

b) aluminum chloride,

c) silica and/or zeolite and/or apatite; and

magnesium oxide and optionally one or more other metal oxides, preferably selected from the group consisting of: oxides from metals from Group II of the Periodic Table, oxides from metals from Group VIII B of the Periodic Table (e.g. iron oxide), more preferably oxides from metals from Group II of the Periodic Table, even more preferably calcium oxide; and

by firstly combining I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide to form the catalytic composition and

by then adding the optionally one or more additional chlorides of group a), and optionally one or more other metal oxides and silica and/or zeolite and/or apatite of group c).

6. Method for obtaining a additive composition for reinforcing cement, comprising a combination of sodium chloride, potassium chloride, ammonium chloride, magnesium chloride, calcium chloride, aluminum chloride, silica, magnesium oxide, magnesium hydrogen phosphate, magnesium sulfate, sodium carbonate, and cement by firstly combining ammonium chloride, aluminum chloride, and magnesium oxide to form the catalytic composition.

7. Method according to any one of claims 5-6, wherein I) is added to a total quantity of I) of 1 to 25 % by weight, preferably 5 to 15 % by weight, more preferably 8 to 13 % by weight; based on the total weight of I) + II) + III).

8. Method according to any one of claims 5-7, wherein II) is added to a total quantity of I) of 10 to 50 % by weight, preferably 20 to 40 % by weight, more preferably 25 to 35 % by weight, based on the total weight of I) + II) + III).

9. Method according to any one of claims 5-8, wherein III) is added to a total quantity of III) of 5 to 40 % by weight, preferably 10 to 30 % by weight, more preferably 15 to 25 % by weight, based on the total weight of I) + II) + III).

10. Use of a catalyst composition consisting of I) ammonium chloride, II aluminum chloride, and III) magnesium oxide for lowering the pH of cement.

11. Method for lowering the pH of cement by the addition of a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide, preferably in an amount of between 1 and 15 weight percent based on the weight of the cement.

12. Use of a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide for addition to cement for oil well cementing.

13. Method of cementing a wellbore, comprising the steps of: i) drilling a wellbore; ii) introducing a casing string into the wellbore; iii) preparing a cement slurry based on a combination of cement and a catalyst composition consisting of I)

ammonium chloride, II) aluminum chloride, and III) magnesium oxide; iv) pumping said cement slurry into the wellbore; and v) allowing said cement slurry to set.

14. Cement slurry for cementing a wellbore, comprising i) cement, ii) water; and iii) a catalyst composition consisting of I) ammonium chloride, II) aluminum chloride, and III) magnesium oxide.

15. Cement slurry according to claim 14, comprising between 50 and 85 wt%, preferably between 65 and 75 wt% of I) cement, and between 20 and 40 wt%, preferably between 25 and 30 wt% of II) water, and between 0.1 and 10 wt%, preferably between 1 and 3 wt%, more preferably between 1.5 and 2.5 wt% of catalyst composition III).