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(54) Title **COMPOSITION OF A CEMENT ADDITIVE MATERIAL AND APPLICATION THEREOF TO IMPROVE PROPERTIES OF CEMENTITIOUS PRODUCTS**

(57) Abstract

A composition of a cement additive material to improve durability of cementitious structures, is disclosed. The cement additive composition comprises an admixture of one or more of divalent magnesium metal silicates with capacity to act as a latent hydraulic binder in said composition activated by a hydration process under aqueous conditions, and in particular the divalent metal silicate is magnesium-dominated silicate, preferably comprising mineral groups of olivines, orthopyroxenes, amphiboles, talc and serpentines or mixtures thereof. Applications of the compositions are also disclosed, in particular to utilize a property of hydration as a major trigger for the latent hydraulic reaction of magnesium silicates, particularly for said olivines, when exposed to water and brines, in order to obtain a cementitious material becoming self healing.

COMPOSITION OF A CEMENT ADDITIVE MATERIAL AND APPLICATION THEREOF TO IMPROVE PROPERTIES OF CEMENTITIOUS PRODUCTS

The field of the present invention

The present invention concerns a composition of a cement additive material to improve durability of cementitious structures, as defined in the following claim 1.

More specific, the present invention relates to products made from cementitious mineral admixtures. The mixtures will include a cement additive product, a new ingredient, purposed as a latent hydraulic binder for cementitious mineral admixtures, mortars and concrete structures for industrial applications and for construction purposes. The utilized ingredient will increase the durability of the product over its whole lifetime, and when in contact with external humid, wet or submerged aquatic environment.

The invention also relates to several applications of the inventive latent hydraulic binder for cementitious products as appearing in claims 6-14.

Background of the invention

The present invention relates to the field of cementitious materials such as Portland Cement and geopolymers. The purpose of the invention is to apply divalent magnesium-iron solid solution silicates (for example the mineral groups olivine, orthopyroxene, amphibole, talc and serpentine), here called "magnesium silicates", as latent hydraulic binders for cementitious mineral admixtures, thereby increasing the integrity, volume, weathering and/or lifetime of the cementitious mineral admixture structure.

The invention relates the integrity- and/or durability enhancement of cementitious structures over time by including/adding magnesium silicates in cementitious mineral admixtures as a latent hydraulic binder, and to increase its capacity to handle weathering and exposure to flow of water mixtures on and through the cementitious materials.

Metamorphism is the mineralogical and structural adjustment of solid rocks to physical and chemical conditions that have been imposed at depths below the near surface zones of weathering and diagenesis and which differ from conditions under which the rocks in question originated.

Inorganic materials that have pozzolanic or latent hydraulic binding effects are commonly used in cementitious materials. Hydraulicity is defined as “the property of limes and cements to set and harden under water whether derived from a naturally hydraulic lime, cement or a pozzolan”. A latent hydraulic binder reacts in more slowly and due to a trigger in a particular manner in order to change the properties of the cementitious products. It will come to a full strength on its own, while very slowly. These have the purpose of either stretching the need for lime clinker in the cementitious mineral admixture, or improve the properties of the cementitious mineral admixture.

Disclosure of the state of art.

With regard to the state of art, reference is made to the following patent publications: FR-2.939.429, US-2015/18905, WO-2016/094506 and US-2008/196628.

All these documents deal with cement mineral admixtures for producing concrete to defend the cement construction from a reaction with CO_2, named a carbonation process. Carbonation is a well known reaction for all lime-cement mixtures and change its mineral composition from CaO (lime) to $CaCO_3$ (Calcium carbonate) and this happens naturally over time due to weathering. The magnesium silicates will also react with the CO_2 and the minerals formed due to carbonation will expand into gaps and cracks of the cementitious structure in order to keep the structure sealed.

In more detail, the mentioned patent FR-2.939.429 pertains to the carbonation of magnesium silicates. This is particularly relevant in the injection and sealing of reservoirs containing CO_2. FR-2.939.429 discloses the use of magnesium-olivine i cement/concrete mixtures for the sealing of drill wells into geological formation rock for the purpose of storing of CO_2 in geologic formations.

Details of a carbonation process.

Magnesium silicates can be carbonised (e.g. altered by CO_2), and therefore will increase the cement-plug lifetime for the cement admixtures in wells when exposed to CO_2, particularly those penetrating carbon-dioxide storage (CCS) reservoirs. (FR-2.939.429). That patent shows features of the reaction of olivine with CO_2 producing magnesium carbonate, creating a self healing cement in actual conditions in the well.

Below is an example of a carbonation process of the magnesium end member olivine reacting with carbon-dioxide.

Carbonation:

Mg_2SiO_4 +	$2CO_2$	→	$2MgCO_3$ +	SiO_2
Forsterite (olivine)	carbon-dioxide		Magnesite	quartz

The carbonation process happens naturally where CO_2 reacts with forsterite.

Details of a hydration process.

An object of the present invention is to improve the properties of a cementitious mineral admixture by adding a pozzolanic or latent hydraulic binder that reacts through hydration i.e. with H_2O and other aqueous solutions. There are a multitude of pozzolans and latent hydraulic binders used in the cementitious mineral admixtures containing lime (CaO), and water. Pozzolans includes a number of natural and manufactured materials, such as ash, slag etc. The pozzolans impart specific properties to cement. Pozzolanic cements may have superior strength at a later age and may be more resistant to weathering.

The present invention.

The present invention pertains to the pozzolanic or latent hydraulic reaction through the hydration, i.e. the reaction with water and/or aqueous solutions like seawater or other brines with magnesium silicates (divalent magnesium-iron solid solution silicates, i.e. the mineral groups olivine, orthopyroxene, amphibole, talc and serpentine). In our invention, the sealing properties and resilience of the resulting product is independent of carbonization.

The composition of a cement additive material to improve durability of cementitious structures according to the invention is characterized by an admixture of one or more of divalent magnesium dominated silicates with capacity to act as a latent hydraulic binder in said composition activated by a hydration process under aqueous conditions.

The preferred features of the composition appear in the following claims 2 - 5. According to a particular preferred embodiment, the composition includes a mixture of Portland cement and water, of an ordinary W/C number, and added olivine in a range of from 5 – 50 % based on weight.

According to an essential aspect of the invention, there is disclosed application of a composition of a cement additive material according to the preceding claims as a latent hydraulic binder for cementitious mineral admixtures, mortars and concrete structures for industrial applications and for construction purposes, as appearing in claim 6.

The further and preferred embodiments appear in claims 7-14.

Further disclosure of the invention, an example:

Olivine group minerals $(Mg,Fe)_2SiO_4$ are silicates with magnesium and iron as major cations, while calcium and minor elements may substitute in the divalent cation sites. While reactions between crystalline minerals and H_2O are generally regarded as slow, the magnesium silicates do react even at room temperatures. Fine powders of olivine, when mixed with water may increase the pH of the water to over 9. This is the origin of the term “ultrabasic rocks” and the end-member of the reactions utilized in our invention.

The hydration reactions described here happen at the very low end of the pressure- and temperature range generally discussed in metamorphic petrology. Diagenesis, weathering and very low grade metamorphism are the main processes. In geochemical reactions, an added forcing on a reaction can be geochemical instabilities, where minerals or solutions not in equilibrium seeks to react towards a steady state. In our invention we are utilising anthropogenically induced geochemical instabilities to induce low, very low grade metamorphism, diagenesis and weathering. Over time, even olivine grains covered in an aqueous solution and left at room temperature will weather to alteration minerals.

Below is shown some of the reactions of end-member olivines (forsterite and fayalite) when hydrated in reaction with H_2O. It may occur according to these but not limited to the following reaction equations:.

$3Mg_2SiO_4$ +	SiO_2 +	H_2O	→	$2Mg_3Si_2O_5(OH)_4$
Forsterite	Quartz	water		Serpentine

and

$2\ Mg_2SiO_4$ +	$3H_2O$	→	$Mg_3Si_2O_5(OH)$ +	$Mg(OH)_2$
Forsterite olivine	water		Serpentine	Brucite

and

$3Fe_2SiO_4$+	$2H_2O$	→	$2Fe_3O_4$	$3SiO_2$	+	$2H_2$
Fayalite	water		Magnetite	aqueous silica		hydrogen

The purpose of the present invention is to utilize a similar reaction pattern of magnesium silicates in hydration reactions (with water (H_2O) and associated aqueous solutions (e.g. brines)), in that the composition is used as enhancers in cementitious mineral admixture materials, as a pozzolan, a latent hydraulic binder, as a filler, for the use of producing amorphous silica in the latent reaction, and to provide a natural anti-fouling agent in cementitious concrete and/or mortar structures in general.

As disclosed above the present invention is a cement additive material that is a pozzolanic or latent hydraulic binder of made from magnesium silicates that improve the properties of a cementitious mineral admixture and the outcome of the products made from the admixture. Our product is a cement additive material that is a latent hydraulic binder that is activated through hydration, and is intended for cementitious mineral admixtures for the purpose of increasing the integrity of the created structures produced over time. The product may also be used for its faster, pozzolanic effects.

While a function of product that is a cement additive is that the magnesium silicate material is as a filler in the cementitious mineral admixture material, the latent hydraulic binder reaction by the magnesium silicates will at low-, very low metamorphosis, diagenesis and weathering reactions of the magnesium silicate with water form reactive products such as magnesium silicate hydrates, amorphous silica and hydrogen. These reactions and alterations the original minerals causes the reactive products to expand into gaps, pores and other pressure shadows in the cementitious structure with amorphous and crystalline alteration materials.

The minor elements of naturally occurring magnesium silicates and traces from accessory minerals, containing elements like Nickel, Zinc and Chromium may in addition improve the interactions with steel, notoriously corroded in contact with corrosive water and brines. Magnesium silicate outcrops frequently are vegetation free, and we are suggesting this is grounds to utilise magnesium silicates due to the content of minor amounts of anti-biofouling agents.

It is known that the most used experimental olivine (San Carlos olivine) with water will metamorphose to talc (Mg_3,$(Si_4O_{10})(OH)_2$), and quartz minerals below 70ºC and to serpentine minerals (for example Mg_6,$(Si_4O_{10})(OH)_8$) above 70ºC while giving the water a higher pH due to the H_2 produced in the reaction and dissolved into water. The higher pH water is naturally and by less oxidizing to iron and steel and reduce the weathering and weakening of cement and associated structures inside and outside to the cementitious mineral admixture. Mixing materials lowers the Gibbs free energy compared to the pure end-members. The initiation of reactions will happen at lower temperatures for magnesium silicates in cementitious mineral admixtures, than for the pure end-members alone. The ΔT above initiation of reactions will influence the rate of reaction, as the rate be dependent on the temperature as described by the Arrhenius' equation. Therefore, the processes in the mixtures will speed up and/or occur at even lower temperatures than model mineral end-members. At diagenetic and very low grade metamorphism pressures and temperatures, the magnesium silicates will reduce and/or replace the need for quartz additives that prevent the growth of unwanted minerals (e.g. promoting Tobermorite in lieu of the high Ca/Si ratio phases).

Structures like road constructions or buildings for homes and offices will decay over time due to weathering and other external factors like climate, as well as due to internal structural decay. Adding magnesium silicates as a cement additive product working as a latent hydraulic binder will reduce weathering by low temperature metamorphism involving hydrous alteration of the magnesium silicates over time.

Our product will have the same outcome as crystalline quartz flour for compressive strength and permeability at higher pressures and temperatures. Alternatively it may work like slag, which is also a latent hydraulic binder for cementitious mineral admixtures.

The latent hydraulic binder reaction by hydration without calcium in solution in this invention works by altering the minerals to secondary minerals with a lower density and therefore also a higher volume. Due to pressure-gradients on micro scales, the secondary minerals produced will seek to form in voids, pores, cavities and cracks, thereby sealing the cementitious product when it is exposed to aqueous solutions externally and internally. These are particularly important where weaknesses in the cementitious product occurred during the emplacement of the mixtures. Even during curing of the cement mineral admixture containing our cement additive material, the volume of the cementitious mineral admixture increases, compared to ordinary cementitious mineral admixtures that shrink during curing. Hydration is a major trigger for the latent hydraulic reaction of magnesium silicates, particularly for olivines. By adding magnesium silicates, the cementitious materials become self healing when exposed to water and brines.

Used in oil and gas wells, it improves the exposure resilience to fluids that are penetrating the structure made up by the cementitious mineral admixture, while potentially creating natural reactive bonding with the side rock and buffering the corrosion of steel in the well. Already established methods used in well maintenance and the plugging and abandonment (P&A) process today can still be enabled by use of this new latent hydraulic binder for cementitious mineral admixtures. This make it easier for the industry to take the new cementitious into use.

The olivines have a particular wetting angle being much smaller than most other solids to water, and the use of this magnesium silicate will change the adhesion of olivine-containing cementitious mineral admixtures to steel and other iron products.

Our tests show that cementitious materials that have been produced with pores and fractures are filled by low temperature metamorphic minerals when the materials are exposed to water and brines.

Thus there is provided a cement capable of binding suitable aggregate into a concrete that can set and harden underwater.

Examples of use:

The chemical properties of magnesium silicates make the mineral suitable for improvement of the outcome of cementing and plugging of wells that are drills that are trying to reach reservoirs. The minor elements of magnesium silicates and the commonly accessory minerals will improve the interactions with steel. This invention can be used for the management of wells, including, but not limited to open petroleum reservoirs, inside casing/liner/tubing/conductor, between casing/liner/tubing/conductor and geological formation, in open hole as kick-off plug for drilling/kicking off for new wellpath, as barrier as part of plug and abandonment, as well as permanent plug and abandonment, both conventional and by use of perf and wash technology. Invention can be used in oil producers, new and old, gas producers, new and old, water producers, new and old, injection wells, new and old, Geothermic wells, new and old, water wells, new and old or any combinations of these. Exploration well, appraisal wells, development wells will also be areas of use for invention. Well integrity problems due to degraded cement sheaths are a known cause of leaks through active and abandoned wells. Development of an improved well plugging material that hinders leakage through well plugs is likely to have major positive environmental impact, as it improves long-term well integrity and reduces leakages to the environment. Our invention, as a cement additive material added to cementitious mineral admixture materials, magnesium silicates will increase the cement-plug lifetime for the drilling, abandonment of oil and gas wells in general, but also those penetrating present or future carbon-dioxide storage reservoirs. Current practices on P&A involves massive retrieval (“pulling”) of steel tubulars. This is an environmental work hazard due to the application of rotating methods (cutting/milling) that can threaten workers, all the while very costly in rig time. The reduction of steel corrosion from our product will possibly reduce the amount of steel pulling needed and enable piercing practices currently underway (so called perforate-wash-cement). Likewise, the acoustic properties of olivine are significantly different from both the surrounding rocks, steel and mud, making logging easier if applied as an annular sealant material. The addition of the cement additive product will make ordinary wells described above safer for the future by using this invention in the cementitious material also in areas that may become CCS reservoirs, as shown by FR-2.939.429.

This invention is suitable to be used in cement, mortar and/or concrete products to reduce biofouling and corrosion of steel and iron, weathering and carbonation of the cement material (also as a part of concrete).

The corrosion of constructions were concrete containing e.g. Portland cement is widely known and is more prone to this in environment with rough weather and were exposed to CO_2 and salt conditions. This intervention will better resist these conditions and hence increase the lifetime of concrete constructions in general.

An Experiment.

In an experiment, solid cementitious mineral admixture products were fabricated based on a mixture of Portland cement and water having an ordinary W/C number (W/C = water to cement ratio). To this mixture an olivine, which is a divalent magnesium-iron solid solution silicate, was added in a range of 5-50 % based on weight. A solid cementitious mineral admixture product was prepared and possible changes of their porosity and permeability were measured compared with a standard cementitious mineral admixture product following their exposal towards different brines for a period of about one week.

The measurements showed that porosity of the product, when applying the inventive cementitious mineral admixture, was reduced by as much as 90%, and permeability went down by 70% after said just one week exposed to brines. The experiments show that a more dense and water resistance concrete material is achieved by the present invention.

PATENTKRAV

1. Composition of a cement additive material to improve durability of cementitious structures, characterized in that the composition comprises an admixture of one or more of divalent magnesium-dominated silicates with capacity to act as a latent hydraulic binder in said composition activated by a hydration process under aqueous conditions.

2. Composition according to claims 1, characterized in that the magnesium silicate comprises mineral groups of olivines, orthopyroxenes, amphiboles, talc and serpentines or mixtures thereof.

3. Composition according to claims 1-2, characterized in that the composition comprises traces from accessory minerals containing elements like Nickel, Zinc and Chromium,

4. Composition according to any of claims 1-3, characterized in that it includes a mixture of Portland cement and water, of an ordinary W/C number, and added olivine in a range of from 5 – 50 % based on weight.

5. Application of a composition of a cement additive material according to the preceding claims as a latent hydraulic binder for cementitious mineral admixtures, mortars and concrete structures for industrial applications and for construction purposes.

6. Application of a composition of a cement additive according to claim 5, as a pozzolan, a latent hydraulic binder, as a filler for producing amorphous silica in a latent reaction, as a natural anti-fouling agent in cementitious concrete and/or mortar structures.

7. Application of a composition of a cement additive according to any of claims 4 - 6, as a cementitious mineral admixture material, wherein latent hydraulic binder

reaction by the magnesium silicates at low-, very low metamorphosis, diagenesis and weathering reactions of the magnesium silicate with water, to achieve reactive secondary products such as magnesium silicate hydrates, amorphous silica and hydrogen causing reactions and alterations of the original minerals to produce reactive products to expand into gaps, pores and other pressure shadows of the cementitious structure with amorphous and crystalline alteration materials.

8. Application of a composition of a cement additive according to claim 7, to utilize a property that during curing of the cement mineral admixture containing the abovementioned cement additive material, in that the volume of the cementitious mineral admixture increases, compared to ordinary cementitious mineral admixtures that shrink during curing.

9. Application of a composition of a cement additive according to any of claim 5-8, in utilizing a property of hydration as a major trigger for the latent hydraulic reaction of magnesium silicates, particularly for olivines, when exposed to water and brines, in order to obtain a cementitious material becoming self healing.

10. Application of a composition of a cement additive according to any of claims 5-9, in that said composition including traces from accessory minerals, and elements of Nickel, Zinc and Chromium, utilizes a property to improve interaction with steel, notoriously corroded in contact with corrosive water and brines.

11. Application of a composition of a cement additive according to claims 5-10, of magnesium silicates as a cement additive product working as a latent hydraulic binder to reduce weathering by low temperature metamorphism involving hydrous alteration of the magnesium silicates over time.

12. Application of a cementitious mineral admixture according to the previous claims 1 - 4,

-to increase the cement-plug lifetime for the drilling, abandonment of oil and gas wells, for example those operating penetrating present or future carbon-dioxide storage reservoirs,

- for cementing oil and gas wells.

- to be used in cement, mortar and/or concrete to reduce biofouling and corrosion of steel and iron, weathering and carbonation of the cement material (also as a part of concrete), and

-for concrete elements in building and industrial plants.

13. Application of a cementitious mineral admixture material in according to claim 12, to obtain a reaction pattern where the concrete building element is exposed to aqueous environment, creating hydration processes wherein water reacts with magnesium silicates content of cement compositions.