



Recipe development of low-cost wollastonite-based phosphate cements

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HIGHLIGHTS

- Cements with adapted properties can be produced from natural wollastonite.
- Initial materials and processing conditions affect the cement's properties.
- Highly pure wollastonite is not mandatory for structural applications.
- Temperature controlled curing process replaces use of retarders.

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ABSTRACT

Compositions of low-cost wollastonite-based phosphate cements (Wo-PC) were developed as materials, which are suitable for a continuous manufacturing process of structural or functional elements. The composition influences the curing temperature and time, the porosity as well as the microstructure and the mechanical properties. The initial substances were adapted in order to minimize the material costs on the one hand and to maximise the cement's hardness within the test series on the other hand. Scanning electron microscopy (SEM) and energy disperse spectroscopy (EDX) showed the material's structure and distribution of additives depending on their concentration. Additionally, evidenced macroporosity, mesoporosity and microporosity reveal the potential of Wo-PC as functional and structural materials for loadbearing elements. Compositions with a suitability for various applications, such as foams or bulk materials for structural applications, were established and a base for a tailored processing of Wo-PC was built.

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1. Introduction

Fibre or textile reinforced mineral composites demand matrix materials with aligned properties [1–3]. In recent years, international research activities were intensified in order to substitute the energy-intensive ordinary Portland cement, e.g. [4–6]. One possible alternative to Portland cement are chemically bonded phosphate cements. They are used in shielding systems, nuclear waste stabilisation as well as high temperature structural and biomedical applications [7]. They can also be used as an inorganic resin for textile reinforced composites with improved properties for indoor and outdoor applications [8]. However, the cost factor of the material limits the actual quantity of realised objects. In current literature and references therein, a lot of information about magnesium phosphate cements can be found, see e.g. [9–14]. However, the initial materials for magnesium-based cements are more expensive

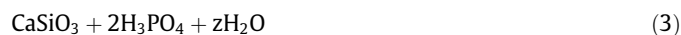
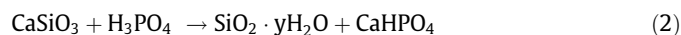
than those for calcium-based cements. Research on calcium phosphate cements for structural applications is done only by a small group of scientists and some aspects on the processing properties of these materials are still unknown or a well-kept secret [15–20]. In general, phosphate cements can be generated by the reaction of metal cations with phosphate anions in an aqueous solution [21]. The phosphate ions can be provided either by phosphate salts or by phosphoric acid. One suitable source for the metal cations is the silicate mineral wollastonite with its chemical composition $\text{Ca}_3[\text{Si}_3\text{O}_9]$. If phosphoric acid is used as a phosphate ion source, the Wo-PC is formed within an acid-base reaction via the following steps:

1. Gradual dissolution of the sparsely soluble wollastonite in the low pH solution associated with the release of cations.
2. Reaction of the phosphate anions with the released cations from wollastonite and arrangement of a coordinated network by gelation and salt formation resulting in the consolidation to a solid material [7,21].

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The first step is an endothermic process, whereas the second one is exothermic. Thus, the structure of this cement consists of silica, sometimes quartz and some remaining wollastonite powder embedded in a matrix of calcium phosphates, i.e. brushite (Eq. (1)), monetite (Eq. (2)) and calcium dihydrogen phosphate monohydrate (Eq. (3)).



An explicit phase analysis of the stoichiometry depending reactions can be found in [22], where thermal hardening and structure of Wo-PC were studied for an acid concentration of 13 mol% and varying molar ratios $r = \text{P}/\text{Ca}$ in the mixture. These investigations showed a sudden increase of the storage modulus at 33% of the total heat conversation by temperature modulated differential scanning calorimetry and dynamic mechanical analysis. Temperatures of more than 60 °C lead to the formation of monetite instead of the brushite phase, which results in worse mechanical properties of the cured material [17,23]. Wo-PC recipes with good mechanical properties and acid contents of 50% phosphoric acid and more are known from the literature [8,24,25]. In recent applications, borax is frequently used as a retarder, whereas its toxicity is a clear disadvantage, especially for large production charges. It is known, that metal ions can retard the setting process and reduce the setting temperature. Especially Al, Zn and Mg ions are contemplated as possible candidates. These metallic ions are participating in the binding phase as amorphous calcium-metal phosphates [25]. The degree of the retarding effect essentially depends on the particular chemical and the physical properties of the dry wollastonite, such as phase composition, particle size, aspect ratio, absorbency, surface area and roughness, which influence the water demand of the chemical reaction, which in turn influences the dissolution characteristics of the mixture. Moreover, the mineral composition of wollastonite powder changes as time goes by because it is strongly hygroscopic. Ca^{2+} ions on the powder surface can be easily replaced by 2H^+ ions. Oxygen and carbon dioxide from the air lead to the formation of more stable compounds such as SiO_2 and CaCO_3 in the powder [8,22,26]. CaCO_3 causes porosity as carbon dioxide is formed during the setting of Wo-PC. Therefore, it is undesirable in most application scenarios and the powder has to be stored under dry conditions in order to limit the amount of CaCO_3 . Consequently, blend-by-blend analyses are necessary for different practical applications with different initial powders when the process window, relating to curing temperature and pot life, has to be determined [8].

The investigations in this study were carried out in order to develop a nontoxic low-cost material, which has acceptable properties for mechanical applications on the one hand and which is easy to handle in a continuous working process on the other hand.

The costs should be low compared to Wo-PC mixtures available on the market, which amount to more than 5 €/kg. Density and basic stability are the most important material properties for mechanical applications. For this purpose, different acid formulations were systematically evaluated, various initial powders were characterised and combined with an optimised acid formulation for a constant acid to powder mass ratio a/p. The resulting Wo-PC were fundamentally characterised to estimate their structure and mechanical properties in order to assess their application potential. The research demonstrates the ability of mixing Wo-PC with adapted properties from low-cost natural wollastonite powders and acid formulations.

2. Materials and methods

2.1. Materials

The used raw materials including their suppliers and oxide compositions are shown in Table 1. Median values of the particle size d_{50} vary from 18 µm to 35 µm and are discussed in detail in Section 3.1. The mineral composition of the powders is commonly not specified. Generally, the clear wollastonite contents of these natural powders range between 80% and 95%. For instance, the CWZ 200 typically consists of 84% wollastonite, 8% calcite, 7% quartz and 2% other minerals according to guiding values of the manufacturer. The costs of wollastonite powders vary from about 0.7 to about 10 €/kg, related to a purchase quantity of 100 kg, whereby the price increases with increasing purity and a higher grinding degree. In addition to the wollastonite powders, different phosphoric acid formulations were used as liquid components. Therefore, chemical grade 85% phosphoric acid was mixed with varying contents of deionized water and additives, which include zinc oxide [27], aluminium hydroxide [28] and magnesium oxide [29].

2.2. Methods

2.2.1. Mix design

The mixing of the acid formulations was realised with the help of a magnetic stirrer and a laboratory shaker. For cement manufacturing, the mixing was performed either manually or by an electrically driven propeller. In the first instance, preliminary tests with varying chronological sequences of mixture and acid concentrations were done. Based on the achieved results, a material development was implemented with the following solution approaches:

- Development of a suitable acid formulation – test series “WCC”.
- Investigation of raw powders and effect of temperatures – test series “WP”.

Within the scope of these test series, the parameter finding for adequate material compositions was performed according to the

Table 1
Chemical composition of the wollastonite powders according to manufacturer's data [30–33].

Contents in %	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	MgO	TiO ₂	K ₂ O	Na ₂ O	S	P
Casiflux A38 (Keramik-Kraft e. K.)	45	50	0.5	0.5	n. s.	0.4	n. s.	n. s.	n. s.	n. s.	n. s.
NYAD M200 (NYCO Minerals)	44.94	52.94	0.28	0.30	0.04	0.75	0.05	0.23	n. s.	n. s.	n. s.
Woll. F (Mineralmühle Leun, Rau GmbH & Co. KG)	45	50	0.3	0.4	n. s.	1.1	n. s.	0.1	0.2	0.02	0.05
WZ 90 (Franz Mandt GmbH & Co. KG)	49	44	0.3	n. s.	n. s.	n. s.	n. s.	n. s.	n. s.	n. s.	n. s.
CWZ 200 (Franz Mandt GmbH & Co. KG)	44.7	50.1	0.13	0.23	n. s.	1.02	n. s.	n. s.	n. s.	n. s.	n. s.

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