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Systematic analysis of natural pozzolans from Greece suitable for repair mortars

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Abstract Natural pozzolans were used as pozzolanic cement in concrete mixtures to increase the long-term strength, the concrete durability, and other material properties of Portland cement many centuries ago. The most common pozzolan is the volcanic ash, a siliceous or aluminosiliceous material, which is highly vitreous, coming from volcanic eruptions. In the Greek territory, 39 reactive volcanoes have been recorded both in insular and in terrestrial areas. The reactivity of pozzolans, in the case of lime-based mortars, is attributed to their content in amorphous silica which reacts with $Ca(OH)_2$ from lime, in environmental conditions, and forms C–S–H compounds responsible for the strength gain. Their use in building materials was diachronic. The significant properties of mortars containing pozzolans derive from the mechanism of its gradual strengthening attributed to the reaction of silicates with lime to form secondary cementitious phases which increase the durability and the dense structure of the mortars. In the present paper, two natural pozzolans from Greece are analyzed in order to record their morphological and analytical microstructure as well as their thermal and physical properties. The results revealed that the pozzolans tested, are materials of high quality and can be used for the production of compatible repair mortars. Also, valuable criteria could be instituted for the selection of reactive pozzolans which could be used for conservation purposes. Among others, crucial parameters for compatibility between old mortars and new ones are the surface features (color, texture, and roughness), the composition (type of binder, granulometry of aggregate), and the pore size distribution.

Keywords Natural pozzolans · TG–DTA · SEM · TEM

Introduction

Pozzolan is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property, but will in a finely divided form—and in the presence of moisture—chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties[1]. They were formed from a combination of minerals, mainly consisting of silica and alumina with smaller and variable quantities of other minerals containing calcium, magnesium, iron, potassium, and sodium. Natural pozzolans has to contain reactive silicates or alumino-silicates which react with calcium hydroxide and alkalis to form compounds possessing cementitious properties. The grains must be fine enough, with size range till 250 μm, in order to provide a sufficient reactive surface area for the solid-state chemical reactions in order to react with the alkalis and calcium hydroxide from the cement to produce cementitious compounds. Their strength mechanism is affected of the chemical composition of the pozzolan as the greater the composition of alumina and silica along with the vitreous phase in the material, the better the pozzolanic reaction and strength display. More than 2,000 years ago, Greeks and Romans built structures that survive today that took advantage of the pozzolan–lime reaction so the use of pozzolanic materials in the construction industry has been a common practice for many years. The materials with the best pozzolanic characteristics have not always been used in a country where there are natural pozzolans of volcanic origin like tuff. The importance of using natural pozzolans in the cement industry requires a complete evaluation of

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their effects on concrete. The use of supplementary materials like natural pozzolans has improved the durability of concrete [2]. Possible technological benefits from the use of natural pozzolans in concrete include enhanced impermeability and chemical durability, improved resistance to thermal cracking, and increase in ultimate strength.

Natural pozzolans are usually deriving from volcanic eruptions. In the Greek territory, 39 reactive volcanoes have been recorded both in insular and in terrestrial areas as the famous center of Thira. The Pozzolanic reaction simply consists of an acid–base reaction between calcium hydroxide ($Ca(OH)_2$), and silicic acid (H_4SiO_4, or $Si(OH)_4$). The reactivity of pozzolans, in the case of lime-based mortars, is attributed to their content in amorphous silica which reacts with $Ca(OH)_2$ from lime[3], in environmental conditions, and forms C–S–H compounds responsible for the strength gain[4]. Pozzolans should contain reactive SiO_2 not less than 25% by weight [5].

Natural pozzolans have been found as binders in combination with lime in mortars in various Greek monuments of different historic periods producing mortars with increase durability and strength [6, 7]. The recourses of pozzolanic materials could be either from well-known centers such as Thira or by the use of available local materials such as clay (possible of lower quality) [8]. Romans were the first that recorded the hydraulic properties of pozzolans and widely used them in construction [9].

The composition of the Byzantine mortars which were mainly based on hydraulic lime or hydrated lime and pozzolanic materials as brick dust and pozzolana were well chosen by the size dimension of the aggregates according to the dimension of the joint, so that in the case of thick joints they can be called rather concrete than mortar [10]. According to the modern theories, thick joints decrease the strength of the masonry, therefore, several hypotheses had been tried to explain the use of thick joints in the ancient times. Nevertheless, wherever these type of joints were used the behavior of the masonry seems to have been good even if large deformations took place in the structural elements. Several cases exist of structural elements like arches and piers which suffered large displacements due to soil and structure settlements without failure or even without important cracks.

Today, natural pozzolans are used as binder for the production of repair mortars in order to produce repair materials compatible to old authentic mortars [11, 12] and also in cement industry. The importance of adding pozzolan in concrete was mainly the increased durability, sulfate resistance, and cost reduction [2, 13]. The addition of natural pozzolan for the production of repair mortars for the conservation of historic masonry is due to the need of producing materials compatible to old mortars.

For the production of repair mortars, the required specific materials are not often available at the market. The materials for conservation undergo detailed tests regarding their quality and compatibility with the initial materials used. Some of the criteria for compatibility of the repair mortars with the old mortars are the surface features (color, texture, and roughness), the composition (type of binder and granulometry of aggregate) the physical properties the thermal characteristics and the pore size distribution [14].

Materials and Methods

Two natural pozzolans available at the Greek market named A and B from insular origin of the area of Cyclades (different places), were tested morphological, analytical physical and thermal in order to record their properties.

The morphological and analytical characterization was performed by scanning and transmission electron microscopy. Scanning electron microscopy was performed with a 20 kV JEOL 840A SEM and an OXFORD INCA EDS analyzer. Structural characterization was performed with a transmission electron microscope 100 kV JEOL100CX TEM.

The thermal stability of the pozzolans was estimated by means of a Setaram TG-DTA SETSYS 16/18.

The pore size distribution of the pozzolans were determined by particle size analysis (Malvern Mastersizer Scirocco 2000), the specific gravity was measured with LeChatellier method.

Results

According to SEM analysis, the morphology of grains for the two samples show angular, quite rough texture, from rounded to elongated particles (Figs. 1, 2). In addition, the qualitative and the quantitative elemental microanalysis of the samples allowed the determination of the elements.

The morphology of the grains from sample A is angular, crystalline with two main categories of size distribution as is shown in Fig. 1. Some of them seem to have a layer or platy texture.

As can be seen, the morphology of pozzolan B is different than the previous sample as is shown in Fig. 2 where no special texture, rather an amorphous and finer one is apparent. The fineness is an important parameter as it is known that the finer materials are usually more reactive [15].

In each sample, almost 30 points were analyzed by EDS and the average is indicated in Table 1. The same elements were detected in the two samples with small fluctuation.

Table 1 shows indicatively the average stoichiometry of 60 microanalysis from the studied samples. Pozzolan from sample B contain a greater percentage of Si and Al than this of sample A. Silicon is present in different forms in the

Fig. 1 SEM micrographs of sample A grains

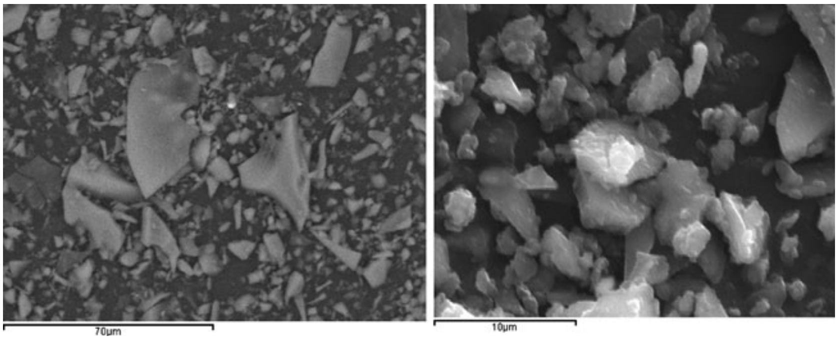

Fig. 2 SEM micrographs of sample B grains

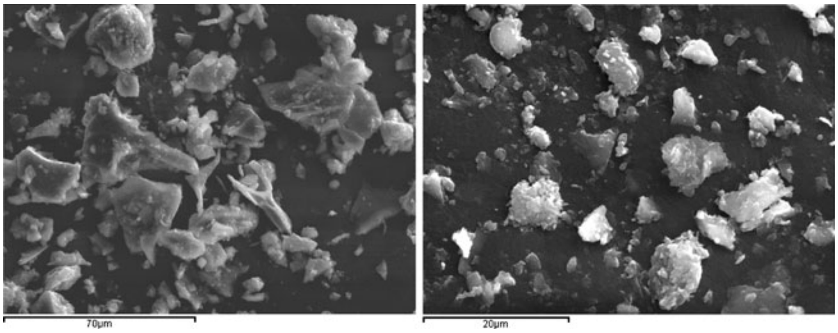

Table 1 Average energy dispersive spectroscopy microanalysis of 60 grains from samples A and B

Sample	O	Na	Mg	Al	Si	K	Ca	Fe	Total
A	40.35	2.16	0.90	7.53	39.88	5.65	0.41	3.12	100.00
B	36.24	1.58	0.15	8.49	45.88	5.12	0.92	1.62	100.00

Fig. 3 TEM images of sample A grain of the mica group of sheet silicate minerals (**a**) and sample B grain of amorphous Silicon (**b**)

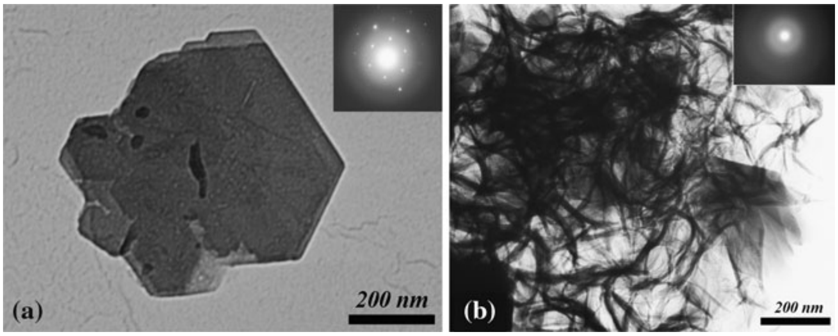

Fig. 4 Particle size distribution of sample A

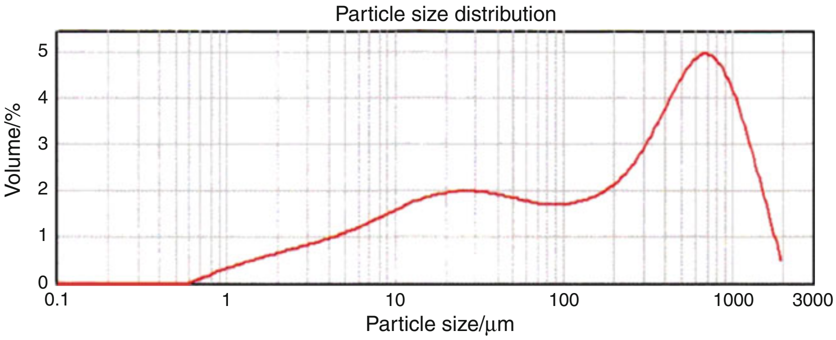

Fig. 5 Particle size distribution of sample B

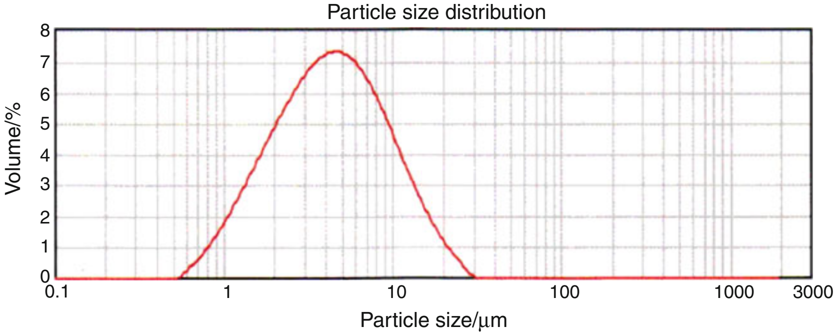

Table 2 Physical characteristics of the pozzolans

Samples	$D(0.9)$/µm	$D(0.5)$/µm	$D(0.1)$/µm	Spec. surface area/m^2/g	Spec. gravity (Le Chatelier)
A	818	138	5.98	0.34285	2.170
B	18.73	4.967	1.542	1.74138	2.403

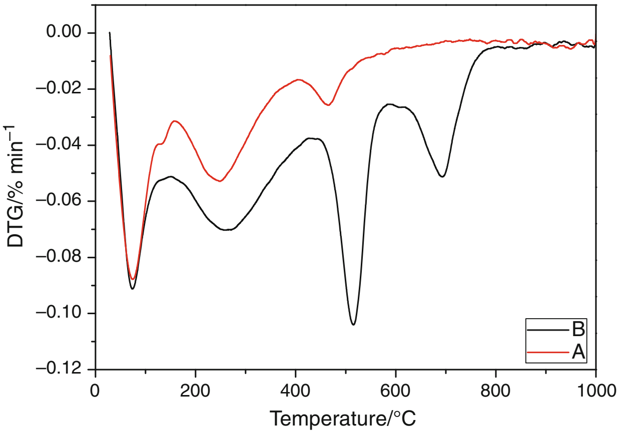

Fig. 7 DTG curves of natural pozzolan sample A and B

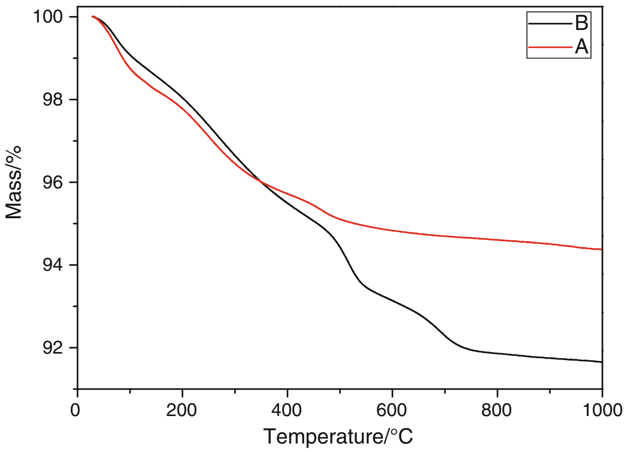

Fig. 6 TG curves of natural pozzolan sample A and B

studied samples. It can be bound as an oxide in minerals and it can also be found in amorphous state.

The morphology of sample A is angular, crystalline of the mica group of sheet silicate minerals as a TEM study has shown in Fig. 3a. The leading use of dry-ground mica was in joint compound for filling and finishing seams and blemishes in gypsum wallboard. The mica acts as a filler and extender, provides a smooth consistency, improves the workability of the compound, and provides resistance to cracking. Sample B contains an amount of amorphous silicon as is shown in Fig. 3b. Figures 4 and 5 show the distribution of the particles measured by Mastersizer Scirocco 2000, given in volume. Sample A is the coarser one while B is the finer. These data are accumulated in Table 2.

The effects of particle size on reactivity of pozzolanic has been demonstrated, where increased fineness led to an increase in early age compressive strength, even in the absence of activators. Particle size is also influential in controlling the mechanism between alkali–silica and pozzolanic reactions. The pozzolanic and alkali–silica reactions follow similar mechanisms. Specifically, both require the dissolution of amorphous silica in an alkaline solution followed by the formation of a product bearing calcium, silica and alkali ions. The main difference between the two reactions is the properties of the resulting products, which can be loosely related to their chemical composition, namely the ratio of alkali to calcium and calcium to silica.

Pozzolan grains from sample A are of two main group sizes, 12 and 82 µm.

Pozzolan grains of sample B have a mean size grain distribution of 8 µm.

Table 2 shows the physical properties of the samples studied.

The mass curves are presented in Fig. 6 and show a greater four step mass loss for sample B pozzolan with a mass loss of 8.5% than the lower 3 step decomposition of sample A with only 4.6% mass loss. Approximately, up to 350 °C the two samples behave similarly. The recorded mass loss along with the DTG peaks (Fig. 7) of the first two steps are almost the same. Above 350 °C, the different thermal behaviors of the two samples can be seen. The third mass loss step for sample A was recorded at slightly lower temperatures than in sample B and corresponds to a smaller mass loss, whereas in sample B, a larger amount of mass is lost in a more rapid step. The major difference between the two studied samples can be seen at temperatures above 500 °C where sample A remains almost stable while sample B continuous to lose mass and a fourth DTG peak appears at 700 °C.

Conclusions

In the studied pozzolans, the morphology of the grains from sample A is angular, crystalline and larger than sample's B. Pozzolan from sample B contain a greater percentage of Si and Al than this of sample A. The amorphous material recorded by TEM from the sample B is amorphous Si. This last parameter in relation to the material's fineness, seem to contribute to the effectiveness of the pozzolans. The heat flow of the DSC curve shows a greater four step endothermic transformation for sample B pozzolan with a mass loss 8.5% than the lower 3 step transformation of sample A with only 4.6% of mass loss.The estimation of chemical, mineralogical and physical properties of natural pozzolans have been proved valuable for the evaluation of pozzolans as proper binders in order to use them for the production of compatible repair mortars used for conservation purposes.

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