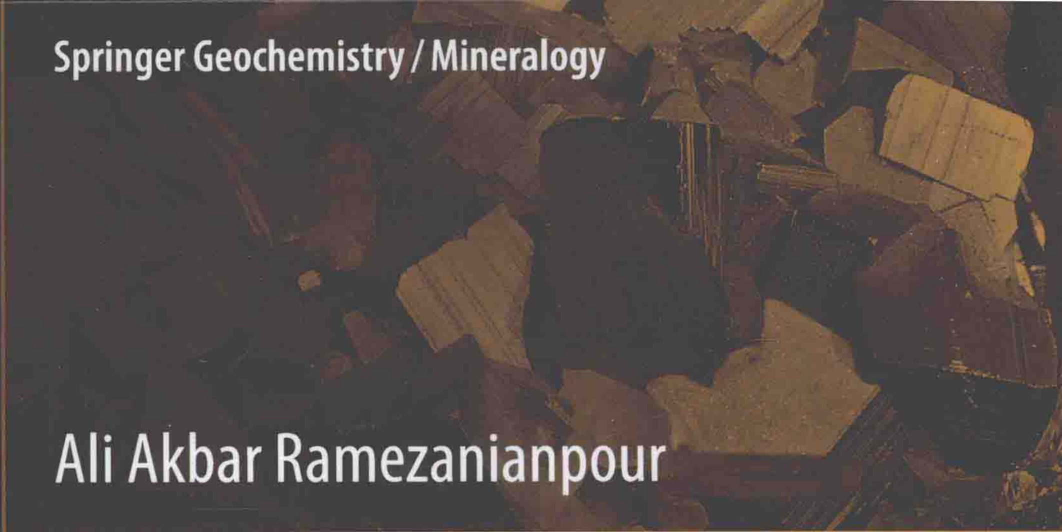

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Ali Akbar Ramezanianpour

# Cement Replacement Materials

## Properties, Durability, Sustainability

Amirkabir University of Technology
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Concrete Technology & Durability Research Center

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# Preface

Sustainability is an important issue all over the world. Carbon dioxide emission has been a serious problem in the world due to the greenhouse effect. Today many countries agreed to reduce the emission of $CO_2$. Many phases of cement and concrete technology can affect sustainability. Cement and concrete industry is responsible for the production of 7 % carbon dioxide of the total world $CO_2$ emission. The use of supplementary cementing materials (SCM), design of concrete mixtures with optimum content of cement, and enhancement of concrete durability are the main issues toward sustainability in concrete industry.

The aim of this book is to present the latest findings in the properties and application of supplementary cementing materials and blended cements currently used in the world in concrete. It consists of eight chapters. The book opens with the Chap. 1 on natural pozzolans, a material which has been used for over 2500 years. This is followed by the Chap. 2 on fly ash, a by-product of the combustion of pulverized coal and the most consumed artificial pozzolans in the cement industry all over the world. The Chap. 3 deals with the granulated ground blast furnace slag, a by-product of the metallurgical industry used as a hydraulic binder in large projects located in severe environments. In Chap. 4, silica fume a by-product in the production of silicon and silicon alloys and a super pozzolan for enhancement of concrete durability is discussed. The Chap. 5 deals with metakaolin (MK), commercially available since the mid-1990s, and one of the recently developed supplementary cementing materials. Metakaolin differs from other supplementary cementitious materials (SCMs), like fly ash, silica fume, and slag, in that it is not a by-product of an industrial process. It is produced by heating kaolin, one of the most abundant natural clay minerals, to temperatures of 650–900 °C. Rice husk ash (RHA), an artificial pozzolan from the combustion of rice husk in a control process and a very reactive material is explained in the Chap. 6. Increasing the rice production and the usage of rice hull in electricity generation and also incorporation of rice husk ash in concretes with enhanced durability, are the main reasons for the better future of rice husk ash. The Chap. 7 deals with the properties of Portland limestone cements. Perhaps the main advantage of producing Portland-limestone cements is that by introducing limestone into cement, the total volume of cement would increase, or in other words, the amount of clinker required to produce a certain amount of cement would decrease. This would result in a substantial amount of energy saving in the production of cement as the consumption of natural raw materials and the fuel needed for production of clinker would be reduced. Finally, the role of supplementary cementing materials on sustainable development is included in the Chap. 8 of this book. Supplementary cementing materials have proven to be economic environmental alternatives to typical concrete mixes. More researches are needed for further applications of supplementary cementing materials to reduce energy consumption for the production of clinker cements and reduction of carbon dioxide emission in the cement and concrete industry.

Each chapter begins with a introduction followed by production, physical, chemical, and mineralogical properties, hydration reactions and pozzolanic activity, effects on properties of fresh concretes, effects on the mechanical properties of hardened concretes, effects on durability of concretes and their applications in concrete.

Author has tried to include his 35 years of experience in the field of concrete technology specially the engineering properties and durability of concretes containing cement replacement materials in this book. The author's findings on natural and artificial pozzolans in numerous research projects in Iran and all over the world during these years are discussed in different chapters.

The author wishes to thank Prof. R. D. Hooton, Dr. Amir. M. Ramezanianpour, Mr. M. Mahdikhani, and Mr. H. Bahrami, for their assistances in preparation of some parts of the book. Particular thanks are extended to the Springer Publisher for publishing this book. I would also like to thank Mrs. Hashemi for processing this publication.

May 2013 Ali A. Ramezanianpour

# Contents

# Chapter 1
# Natural Pozzolans

## Introduction

Pozzolan is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Natural pozzolan is a raw or calcined natural material that shows pozzolanic properties. Volcanic ash or pumicite, tuffs, shales and opaline cherts and diatomaceous earths are examples of natural pozzolans.

The oldest example of hydraulic binder was a mixture of lime and a natural pozzolan, a diatomaceous earth from the Persian Gulf at about 5000 B.C. [1]. The next applications of natural pozzolans goes back to about 1600 B.C. in Mediterranian region on the Aegean Island of Thera, now called Santorin, and the other in 79 A.D. on the bay of Naples, Italy. Both pozzolans were volcanic ashes or pumicites with high volcanic glassy form.

The Romans and Greeks used natural pozzolan-lime mixture as binding materials for many structures over 2000 years ago. Such mortars consist of six parts of a natural pozzolan, two parts by volume of lime, and one part by volume of sand. These mortars were used as the first hydraulic cements in aqueducts, bridges, sewers, water tanks and other types of structures. Some of these structures are still exist in countries like Italy, Iran, Greece and Spain. Most recent structures such as the Suez Canal in Egypt built in 1880, the sea walls and marine structures in the islands of the Aegean Sea and the harbors of Alexandria in Egypt are among many structures built with pozzolanic materials. Many monuments from Roman's era are in use today in many parts of the Europe. This is attributed to the high durability of pozzolanic materials in various environmental conditions [2].

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## Natural Pozzolan Classification

There have been several classifications for pozzolans and natural pozzolans. Establishment of a precise classification of natural pozzolans seems very difficult because this common name includes materials which are very different in terms of chemical composition, mineralogical nature and geological origin. Their common property is their reaction with lime and hardening by time. One of the proposed classification for natural pozzolans is shown in Fig. 1.1. This classification is based on the origin of pozzolans [3]. In this classification, Natural pozzolans are those materials which do not require any further treatment apart from grinding to react with lime. In this classification, artificial pozzolans are the materials with low pozzolanic activity and need further treatments to achieve pozzolanic activity.

In another classification, natural pozzolans are classified in four categories based on the principal lime reactive constituent present. They are volcanic tuff, unaltered volcanic glass, calcined clay or shale, and raw or calcined opaline silica [4].

## Production

### *Pyroclastic Rocks*

Explosive volcanic eruptions which project minute particles of melted magma into the atmosphere result in pyroclastic rocks formation. The rapid pressure decrease during eruption causes the gas release from magma. Therefore a microporous structure is usually observed in such rocks. Due to the rapid cooling process, a glassy state is formed. The ground deposit materials are mixed with other materials from the base of the volcano. The pozzolanic activity of the melt magma is low due to the slow rate of cooling and more crystal forming. Figure 1.2 shows the microstructure of Bacoli pozzolan in Italy [5].

Incoherent natural pozzolans have been formed in Italy since 1500 B.C. after a tremendous explosive volcanic eruption. It has been widely used as Santorin earth since ancient times. The incoherent glassy rhyolites have been found in the United States [6], Indi [7] and Turkey [8]. Rhenish trass which is a natural pozzolan of volcanic origin is included among the tuffs or compact and coherent materials, but incoherent layers of glass have been found in its deposits. It has been found in the Valley of the Rhine River in Germany and has been used for many years [9, 10].

Volcanic pozzolans are usually deposited in compact layers known as tuffs which originate from weathering and cementation of loose particles by diagenetic or other natural processes. Weathering can cause zeolitisation or orgillation. It means that it can transform the glass of the pozzolans into zeolitic minerals or clay minerals. The degree of transformation reached by the original deposit depends on the intensity of the diagenetic actions as well as on their duration. Zeolitisation improve the properties of pozzolans whereas argillation usually reduces the pozzolanic properties [11].

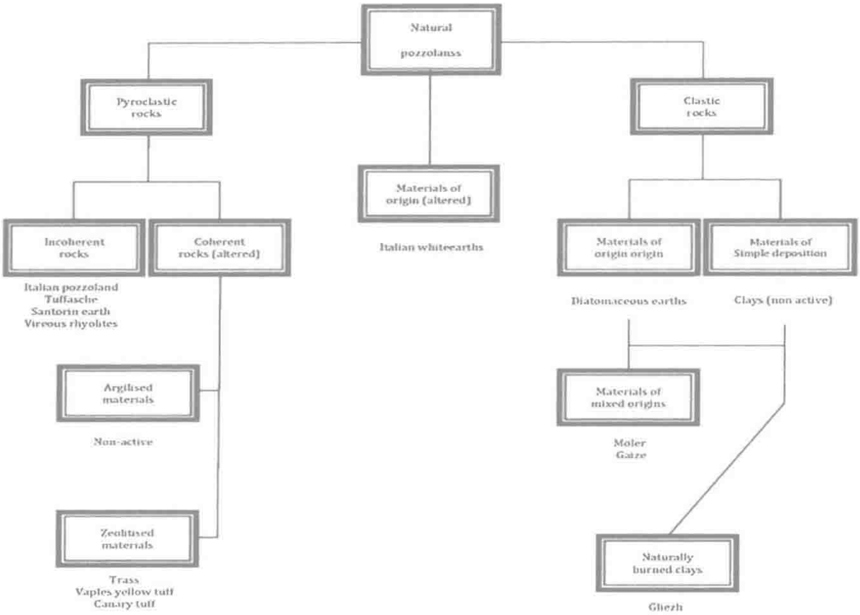
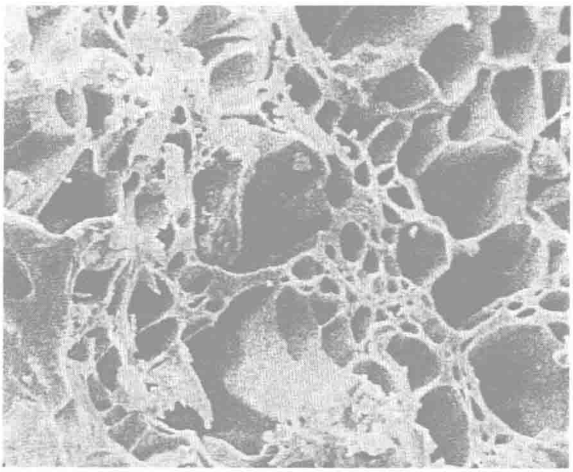



**Fig. 1.1** Classification of pozzolans

**Fig. 1.2** SEM image of Bacoli pozzolan [5]



The transformation of volcanic pozzolan, incoherent and mostly glassy, into compact and zeolitised tuffs is found in some deposits. An example is the Naples natural pozzolan. Deposits of volcanic tuffs have been discovered in Italy, Greece, United States, Spain and Iran. Figure 1.3 shows the deposit of volcanic tuffs known as trass in the Albors Mountain, north of Iran.

**Fig. 1.3** Deposit of volcanic tuffs known as trass in the Albors Mountain, north of Iran

Another type of an incoherent natural pozzolan is pumicite. It is a finely divided volcanic ash composed of angular and porous particles of siliceous glass and varying proportions of crystal fragments differing from pumice only in grain size. They occur as stratified or massive deposits, usually as lake beds. Pumicite was also discovered in USA, Iran, and Canada.

Diatomaceous earths and some clays are sedimentary rocks which show pozzolanic properties by reacting with lime. Clays originate from the alteration of igneous rocks. Diatomaceous earth usually forms from the siliceous skeletons of microorganisms known as diatom deposited in fresh or under sea waters. Diatoms and clay minerals are sometimes deposited together under water. Some types of clays such as montmorillonite group can react with lime to produce calcium silicate and calcium aluminate hydrates. They are not usually used as pozzolan for replacement with cement due to their higher water demand in concrete mixtures resulting in low strengths.

Deposits of diatomaceous earths can be found in Canada, United States, Germany, Algeria, Iran, Russia and Denmark [12]. A diatomaceous earth consisting of amorphous opal and montmorillonite has been found in Europe which can react with lime before and after calcination to present pozzolanic activity [13].

## Physical, Chemical, and Mineralogical Properties

### *Physical Properties*

Physical properties of natural pozzolans vary widely. The fineness, specific surface area, the shape of particles, and density of natural pozzolans influence the properties of fresh concrete and the strength development of hardened concrete.

Fineness of natural pozzolans is usually measured by wet sieving method. The amount of the sample retained when wet sieved on a 45 μ sieve is determined in accordance of ASTM Method C430. Several standards specify the maximum residue in percentage retained on a 45 μ sieve. Depending on the grinding system and grinding time, natural pozzolans are produced from a few microns up to 200 μ. Particle size distribution of natural pozzolans can be measured by laser particle size analyzer, X-ray sedigraph, and coulter counter. In some cases the agglomeration of a number of small particles may form a large particle. In most natural pozzolans productions, they contained particles greater than 1 μ.

The specific surface area of natural pozzolans, which is the area of a unit mass, is measurable by different techniques. The most common is the Blaine specific surface area technique, which measures the resistance of compacted particles to an air flow.

A laser particle size analyzer can also be used for determination of the specific surface area of natural pozzolans. The Brunauer-Emmett-Teller (BET) nitrogen adsorption technique has also been used for determining the specific surface of the particles, but the results obtained by this method are usually higher than the results obtained by the Blaine specific surface area technique or particle size analyzer.

The specific surface area of blended natural pozzolans is usually similar to that for the normal Portland cement at about 300–400 $kg/m^2$. Larger surface area with smaller particles of natural pozzolans can be produced by separate grinding. Higher surface area of about 500 $kg/m^2$ has increased the pozzolanic activity of most natural pozzolans.

The shape of particles of natural pozzolans is usually angular or irregular. Some of them have micro porous character and increase the water demand for constant consistency in concrete mixtures. Figure 1.4 shows the Scanning Electron Micrograph of the Jadjroud Trass as an example of the shape of natural pozzolans.

The specific gravity of natural pozzolans is determined according to ASTM C188 test method similar to Hydraulic cements. If natural pozzolan contains water soluble compounds, the use of a non-aqueous solvent, instead of water is recommended. The specific gravity of different natural pozzolans varies over a wide range, like the other physical properties. The specific gravity of volcanic ashes varies between 1.8 and 2.4 and reaches to 2.9 for the high density compacted tuffs.

## *Chemical and Mineralogical Properties*

The chemical composition of natural pozzolans varies within wide ranges and depends on their sources. Silica and alumina are usually high in incoherent volcanic pozzolans. The next oxide elements are iron, calcium and magnesium oxides. The alkali content is not high but may vary between 3 and 10 %. Loss on ignition is generally low but may reach to 9 % in some pozzolans. The chemical analysis of some incoherent volcanic pozzolans is shown in Table 1.1 [14, 15].