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Cement Replacement Materials

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Preface

Since its discovery over 150 years ago, portland cement has become
almost a 'wonder' material, and a household name. The raw materials
needed for its manufacture are available in most parts of the world, and
the energy requirements for its production are relatively modest.
Nevertheless many countries have severe shortages of cement, although
their needs are vast. China, for example, has a current annual production
of about 150 million tonnes, yet its estimated needs by the turn of the
century are some 300 million tonnes. The search for alternative binders or
cement replacement materials has thus become a challenge for national
development and forward planning. In many developed countries, on the
other hand, apart from the need to save energy, there is an urgent
requirement to project concrete as a reliable and durable construction
material.

From economic, technological and ecological points of view, cement
replacement materials have an undisputed role to play in the future of the
construction industry. Small amounts of inert fillers have always been
acceptable as cement replacements, but if the fillers have pozzolanic
properties, they impart not only technical advantages to the resulting
concrete but also enable larger quantities of cement replacement to be
achieved. Many of these mineral admixtures are industrial byproducts,
and correctly considered as waste, so that the resulting benefits in terms
of energy savings, economy, environmental protection and conservation of
resources are substantial. The most outstanding technical benefit of
incorporating mineral admixtures in concrete is improved durability of the
concrete to various types of chemical attack, mainly due to its reduced
permeability arising from a pore refining process. But these concretes are
also sensitive to temperature and moisture conditions, and need early and
longer moist curing than that for normal portland cement concrete.

That the entire third volume in the series 'Concrete Technology and
Design' should be devoted to cement replacement materials is thus
appropriate and timely. There are seven chapters, dealing with natural
pozzolanas, calcined clay, shale and other soils, slag cements, condensed
silica fume, rice husk ash and fly ash. Each chapter is written by a
distinguished researcher well known for his/her contribution to our
knowledge and understanding of cement and concrete.

Each chapter is relevant to all countries of the world. Natural pozzolanas have been widely used in the construction of dams, bridges and other large works. In many developing countries, supplementation of cement production with natural pozzolanas is particularly attractive, and there are currently many projects to develop known deposits of such materials. In Italy, for example, pozzolanic cements are in regular production. Fly ash, ground granulated blastfurnace slag and condensed silica fume are all well-known and well-established mineral admixtures. The improvements in the properties of fresh and hardened concrete resulting from the pozzolanic behaviour of these admixtures are well understood by scientists and engineers. But these materials are not available in many countries, and calcined soil pozzolanas may then represent the best economic and technical choice of materials for supplementing cement production.

Rice husk ash has special relevance to many countries. Some 420 million tonnes of rice are produced worldwide annually, from which some 16 million tonnes of pozzolanic ash could be extracted. However, only some 30 000 tonnes of cements based on rice husk ash are currently available. Apart from reducing the demand on portland cement and reducing its cost, incorporation of rice husk ash will provide cement to rural areas which are traditionally deprived of cement Further, the husks have a fuel value of about 14 MJ/kg, which means that one tonne of rice husks is equivalent to about half a tonne of coal or nearly half a tonne of fuel oil. Future development work should concentrate on utilizing this heat value of the husks.

The aim of this volume is to present a critical assessment of the various cement replacement materials currently used in the world. Each chapter provides a continuing story from the chemical and mineralogical composition of the material, and its chemical reactions with portland cement, to the engineering benefits imparted to the concrete in its fresh and hardened states. Special emphasis is given to aspects of durability, specifications and mix design, and to the savings in energy that can be achieved. Equal emphasis is given to the need to have a clear understanding of these materials, and in particular, their sensitivities to bad and inadequate moisture curing.

Some of the mineral admixtures discussed in this volume have the potential of extending the use of concrete as a structural material. Others make concrete available for the building of houses, roads and schools. This book will help to ensure the effective and productive use of cement replacement materials in the concrete industry in all parts of the world

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Abstract

Natural pozzolanas have been in use for many centuries. When mixed with lime, they have provided cement for long lasting and spectacular constructions. However, although their occurrence is quite widespread, there use is somewhat limited. Since the mid-sixties, utilization in the USA and elsewhere has been overshadowed by the increasing popularity of fly ash, mainly due to cost. Many developing countries, however, have turned to pozzolanas, when available, to supplement often insufficient portland cement supplies.

This chapter reviews the types and behaviour of natural pozzolanas. As with many aspects of the behaviour of hydrated cement, the portland cement–pozzolana–water reaction is not well characterized. In addition, the relationship between the lime–pozzolana reaction and the mechanical properties of the cement have not been defined other than in qualitative terms. Nevertheless it is recognized that the reaction is influenced by the chemical and mineralogical composition of both the pozzolana and the cement, their relative finenesses, conditions of ambience, curing time and the effect of admixtures. The literature, much of which has come from Italy, Germany and the USA, indicates that most elements of modern concrete technology, and in particular, the use of chemical admixtures and polymer impregnation, have included portland–pozzolana cements in their scope. Apart from reducing cost, compared to plain portland cement concrete, the benefits of portland–pozzolana blends are essentially associated with improvements in durability, and in particular, resistance to sulphate attack and a reduction in the effects of the alkali–aggregate reaction. This chapter concludes by indicating some of the factors involved in developing natural pozzolana deposits.

1.1 Introduction

The Romans were fortunate builders in that certain volcanic soils in Italy were found to be suitable for producing a hydraulic mortar. One such soil was found near the town of Pozzuoli, near Naples, and although the Romans called the material 'pulvis puteolanus', it subsequently became known as a pozzolana. The Romans used lime–pozzolana mortars extensively in building and in the colonization and settlement of their empire; evidence has been found of the use of mortars containing trass in old Roman buildings along the Rhine.

Since pozzolanas are of volcanic origin they are found in regions where geologically recent volcanic activity has occurred. Sersale[1] has pointed out, however, that pozzolanas are only formed when volcanic activity has produced an explosive type of eruption. The violent projection of melted magma into the atmosphere results in the formation of glassy material; less violent eruptions produce volcanic ash which is much less reactive with lime even though it may have a similar chemical composition. According to Sersale, Vesuvius has only produced pozzolanas once and this was during the famous eruption which destroyed Pompeii and Herculanum in 79 AD.

The natural pozzolana deposits in Italy which occur near Vesuvius, around Pozzuoli, Naples and Rome, have been in use for many centuries, originally in lime mortars and then in portland cement concrete. Sersale[1] states that in 1977, 15 million tonnes of pozzolanic cement were produced in Italy and while a range of pozzolanic materials were probably used, the contribution of natural pozzolanas is no doubt significant.

Natural pozzolanas have been used in Greece[2], Germany[3] and in the Canary Islands[4]. Lea[2] indicates that trass deposits have also been worked in Romania and the USSR. In the United States, the first large use of pozzolanas was in the costruction of the Los Angeles aqueduct from 1910 to 1912 where more than 100000 tonnes was used[5]. Since then, natural pozzolanas have been used in the construction of a number of dams, bridges and other large works, but mainly in the western United States where pozzolanas are found. They have been used for many decades in Japan for concrete structures in marine environments and viable deposits have been located in Canada, New Zealand and in a number of other countries.

Supplementation of cement production with natural pozzolanas has proved particularly attractive in developing countries and in recent years there have been projects to develop known deposits in Indonesia[6], Tanzania[7], Trinidad[8], Dominica[9] and other countries.

1.2 Classification

The name pozzolana was originally reserved for vitreous pyroclastic material produced by violent eruptive volcanic action. It is now used as a generic term to describe all materials which exhibit reactivity with lime and which set, harden and develop strength in the presence of water. The range of pozzolanic materials continues to increase, but their origin, structure, and chemical and mineralogical composition vary widely. Sersale[1] and Massazza[10] have expressed reservations in the use of the word 'pozzolana' to cover the whole range of these materials and it is probably more correct to refer to them as mineral additives. Accordingly, classes of mineral additives would include natural pozzolanas, calcined clay and shales, fly ash, silica fume and ash from agricultural residues. However, since conventional use of the generic term pozzolana still prevails, it is used in this context in this book.

Table 1.1 Classification of natural pozzolanas

Activity type	Essential active constituent
1	Volcanic glass
2	Opal
3a	Kaolinite-type clay
3b	Montmorillonite-type clay
3c	Illite-type clay
3d	Mixed clay with vermiculite
4	Zeolites
5	Hydrated oxides of aluminium
6	Non-pozzolanas

Mielenz et al.[11] proposed one of the first classifications of natural pozzolanas, which is given in Table 1.1.

In a later paper, Mielenz et al.[12] added activity type 3e in which attapulgite-type clay was the active constituent. In this classification system, only activity types 1, 2 and 4 are natural pozzolanas. Types 3 and 5 react with lime, but are only considered pozzolanic after they have been calcined.

A more recent system of classification has been proposed by Massazza[13] and this is shown in slightly amended form in Figure 1.1. It can be seen that the natural pozzolanas can be divided into three groups. Pyroclastic rocks, materials of volcanic origin, can be subdivided into the true pozzolanas, unaltered incoherent materials and pyroclastic rocks which have been diagenetically altered after deposition. It should be noted that diagenetic processes are distinct from metamorphism and cause more superficial alteration such as densification, cementation, and in some instances, recrystallization. The true pozzolanas consist predominantly of silica with alumina and ferric oxide being the next major constituents. Typical chemical compositions for these materials are shown in Table 1.2. As mentioned, true pozzolanas are formed by violent ejection of the molten magma when the subsequent rapid quenching produces a glassy material containing entrapped gas bubbles. The reactivity of the pozzoland with lime is increased as the vitreous compound increases. Sersale[14] points out that reactivity is also related to the specific surface area of the pozzoland, a property related to the vesicular nature of pyroclastic materials.

The chemical composition of the true pozzolanas is dependent on the composition of the ejected magma. For the two true pozzolanas found in Italy, the material found near Naples and Pozzuoli (sometimes referred to as Phlegraean) consists mainly of a pumiceous glass containing sanidine (a high-temperature form of the potassium feldspars) though plagioclase and pyroxene inclusions are sometimes found. The Phlegraean pozzolanas have been classified as alkali-trachytic from a mineralogical point of view. On the other hand, the material found near Rome (sometimes referred to as Latian pozzolana) contains leucite in crystalline and altered forms, as well as augite
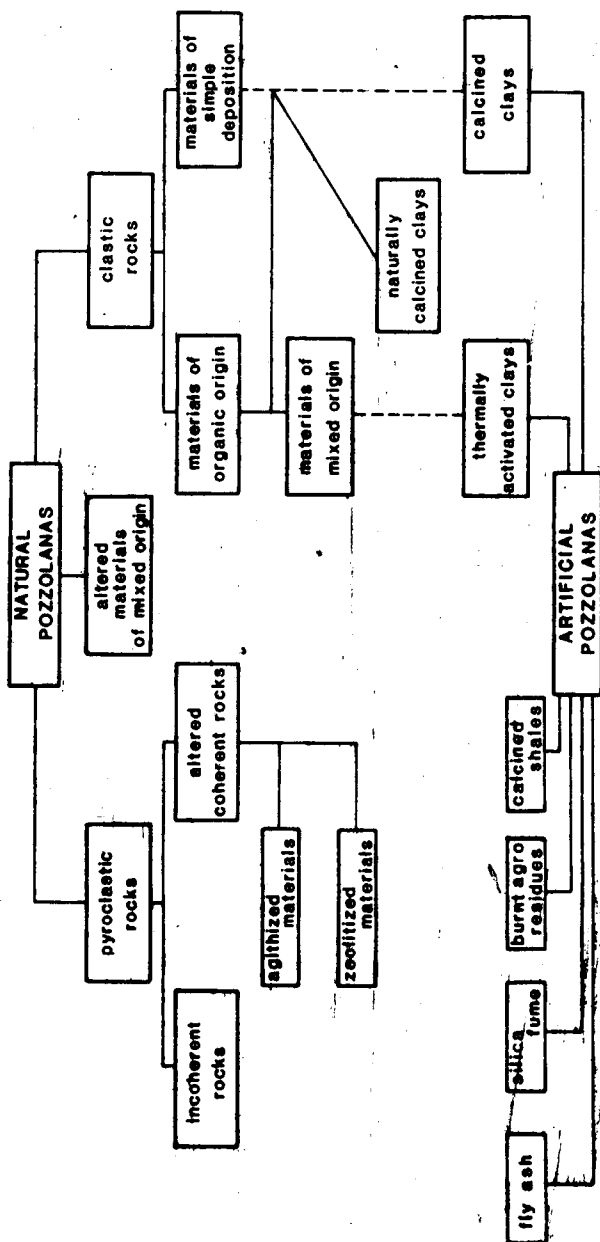
Figure 1.1 Classification of pozzolanic materials. Adapted from Massazza[13]

Table 1.2 Chemical composition of some natural pozzolanas

Pozzolana type	Location	Chemical composition (%)								
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	L.o.I
Incoherent pyroclastic	Bacoli (Naples, Italy)	53.8	18.20	4.29	9.05	1.23	3.08	7.61	0.65	3.05
	Segni (Roman)	45.47	19.59	9.91	9.27	4.52	0.85	6.35	0.16	4.03
	Salone (Roman)	43.26	15.98	9.40	7.92	3.98	0.77	5.96	0.10	9.77
	Casteggio (Italy)	45.83	8.95	3.61	14.85	3.08	0.51	1.82	1.40	19.14*
	Vizzini (Italy)	49.01	16.28	11.25	4.72	5.09	0.84	0.17	0.15	12.30
	Santorin (Greece)	63.80	13.00	5.70	4.00	2.00	3.80	2.50	—	4.8
	Auvergne (France)	46.60	17.60	11.80	9.84	5.58	3.14	1.76	0.02	0.24
	California (USA)	70.76	12.85	1.38	1.08	0.43	—	—	—	n/s
Coherent pyroclastics	Yellow tuff (Italy)	54.68	17.70	3.82	3.66	0.95	3.43	6.38	—	9.11
	Rhenish trass (Germany)	52.12	18.29	5.81	4.94	1.20	1.48	5.06	—	11.10
	Trass (Indonesia)	60.02	17.76	6.80	4.49	0.96	3.88	2.62	—	2.62
Materials of mixed origin	Sacrofano (Italy)	89.22	3.05	0.77	2.28	—	—	—	—	4.67
Materials of organic origin	Washington State (USA)	85.97	2.30	1.84	—	0.61	0.21	0.21	—	ns
Naturally burned clays	Porcellanite (Trinidad)	56.79	25.79	7.61	0.06	0.28	0.10	0.42	0.57	7.60

*of which CO_2 = 11.5%

n/s: not stated

and traces of mica, olivine, zeolitic and clay minerals, and fluorite; the different crystals are cemented in an altered glassy phase. The Latian pozzolanas belong to the leucitic (alkaline basaltic) group with respect to mineralogical composition. With respect to mineralogy, Sersale[14] notes that the quality of a pozzolana seems to be associated with a composition containing alkaline feldspars in preference to anorthite since the glassy phase decreases with an increase in the amount of anorthite.

Apart from the Italian pozzolanas, materials which can be classified as incoherent pyroclastics have been identified on the Greek island of Santorin (known as Santorin earth), in Japan 'Shirasu' found in the southern part of Kyushu[15], on the west coast of the United States (vitreous rhyolites) and in the Bombay area in India (also vitreous rhyolite). While it is most likely that other deposits exist, their mineralogical description and indeed exploitation has to date been limited.

Coherent pyroclastic pozzolanas are volcanic deposits which have undergone diagenesis. Sersale[16] has shown that the most significant feature of diagenesis for pozzolanic reactivity is zeolitization, though other cementing reactions occur in the transformation from a true pozzolana. Sersale has classified these materials as lithic tuffs, the actions of diagenesis leading to the process of lithification. The German trasses are classified as tuffs and as would be expected they are also found in Italy. Sersale[16] has examined the mineralogical nature of tuffs from Italy, West Germany and from Tenerife in the Canary Islands. He found that the matrix which cemented the rock fragments together consisted of the zeolite minerals, herschellite, analcime, phillipsite and chabazite. The mineralogical character of the rock fragments reflected the nature of the incoherent material. Hence the Latian tuff was leucitic while the Neopolitan yellow tuff was alkali-trachytic.

Pozzolanic tuffs and trass are found in many countries and as such are probably the most widely available natural pozzolanas. Sersale[17] notes, however, that where true pozzolanas are available they are preferred because the presence of rock fragments in the lithic material increases the grinding time. Lithification provides many tuffs and trasses with inherent compressive strength, as high as 30 MPa[1], and as a consequence they have been quarried as building stone.

The second group of natural pozzolanas in Massazza's classification comprises altered materials with a high silica content. These pozzolanas have been formed by a process which includes the deposition of materials of different origins in stagnant water, leaching of the soluble oxides and chemical conversion to produce a generally light or white-coloured porous and light rock. The chemical composition of such a material, known as Sacrofano earth, is shown in Table 1.2. These materials are frequently interbedded or mixed with clay which reduced their pozzolanicity.

The third group of material pozzolanas includes materials of clastic and

pelitic origin. The materials in this group include the clays and diatomaceous earths. It is well known that lime will react with clay to impart strength and stability, but strength development is sufficiently small to preclude their use as a portland cement replacement. However, as discussed in Chapter 2, calcination at appropriate temperature conditions can significantly promote the pozzolanicity of clays. (Clays fix lime but have no pozzolanic activity: in fact clay minerals are not destroyed but are transformed by lime.) Diatoms are siliceous organic residues and in some soils can lead to silica contents as high as 94%. More frequently, the diatoms are mixed with clay and other sediments. Diatomaceous soils can exhibit pozzolanicity either before or after grinding. In some instances due to the presence of clay, the soil needs to be calcined to exhibit adequate pozzolanic characteristics, as is done for the Danish material known as moler. Calcined diatomaceous clays were used by the Bureau of Reclamation in the United States in the construction of the Monticello dam completed in 1957 and the Twitchell dam completed in 1958[18], Massazza notes that other deposits have been located in Canada, Algeria, Germany and the USSR, but their exploitation for cement replacement is not thought to be extensive. Lea has suggested that because of the skeletal nature of the diatoms, the water demand of mixes with them will increase significantly. As a consequence, the strength of the mix will decrease disproportionately due to the increase in the water–cement ratio.

It can be seen from Figure 1.1 that Massazza has included Gaize and Gliezh in the third classification of pozzolanas. Gliezh is a shale found in Central Asia which is calcined by subsurface coal fires and is thus rendered pozzolanic. Porcellanite, found in Trinidad[8] is a similar material and is thought to have been formed by sintering of bituminous or lignitic clays and silts through spontaneous combustion caused by the breakdown of pyrites. Gaize is a soft highly siliceous material found in France. It has a high proportion of siliceous organic material and quartz, and the matrix consists of opal mixed with clay and, in some cases, chalcedony. It is generally calcined before use as a pozzolana.

1.3 Pozzolanic activity

It is interesting to note that Lea[19] at the 1938 Conference on the Chemistry of Cement indicated that 'the source of the pozzolanic properties of trass, the Italian pozzolanas and other similar materials has been the subject of considerable controversy'. Lea repeated this sentence word for word in the last edition of his book[2] published in 1970. At the 1980 Conference on the Chemistry of Cement, papers by Sersale[1] and Takemoto and Uchikawa[15] proposed mechanisms for pozzolanic activity which indicated that the lime–pozzolana reaction is still by no means well understood.

One proposal suggested that the lime–pozzolana reaction was due to the

presence of zeolites in the pozzolanas. It was considered that the zeolites absorbed lime through a base exchange mechanism. Sestini and Santarelli[20] have shown that the exchange activity of the pozzolanas they examined was very low and the explanation could not be used to explain the considerable amounts of lime combined in their experiments. Others have shown that zeolites do not occur in many pozzolanas[21] and that the lime–pozzolana reaction produces new compounds which could not be explained by the base exchange mechanism.

Sersale[1] has quoted R. Dron's view that the pozzolanic reaction can be interpreted by considering the solubility of feldspars-like structures in a lime solution. He considers that the tetrahedral silica units are held in position in the interior of the material by oxide ions at the apexes of the tetrahedron. At the surface, however, the oxide ion is converted to a hydroxyl group, that is

$$O^{2-} + H_2O \rightarrow 2(OH)^-$$
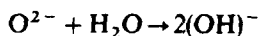
This destroys the spatial equilibrium of the unit within the material and allows it to pass into the lime solution where it reacts with the calcium ions to form insoluble calcium silicate hydrates. The removal of one silica unit permits another to be at the interface between the material and the solution and hence the mechanism can continue. Sersale considers that this mechanism can occur more easily in pyroclastic pozzolanas because the bonds between the silica tetrahedra are weaker. For zeolitic pozzolanas, the reaction would accelerate when the solution penetrated into the 'open' structure. Finally, the mechanism would explain the faster rate of reaction for finely divided and porous pozzolanas.

Takemoto and Uchikawa[15] consider that the pozzolanic particles are protonically attacked by water in the highly alkaline lime solution, dissociating the Si OH group on the surface of the particle to SiO_4^{4-} and H^{2+}. As a result the particle surface is negatively charged and absorbs Ca^{2+} which causes alkalis in the pozzolana to dissolve into the liquid phase. The Ca^{2+} at the particle surface reacts with silica and alumina to form a film or layer which thickens with time. Osmotic pressure resulting from the difference of concentration between the inside and the outside of the layer causes it to rupture. As a result of differences in the diffusion characteristics of the calcium aluminate and calcium silicate hydrates, the calcium aluminate hydrates precipitate away from the pozzolana while the calcium silicate hydrates are found at the surface of the pozzolana. Takemoto and Uchikawa refer to the mechanism as diffusion-controlled dissolution.

Drazaj et al.[22] have investigated the kinetics and mechanism of the reaction in the zeolitic tuff–CaO–H_2O system and their findings support the mechanism proposed by Takemoto and Uchikawa. They found that the reaction consisted of the diffusive dissolution of the zeolite mineral and lime and that the reaction was limited by the diffusion of calcium and hydroxyl ions through the C–S–H and the interface layer of the zeolite. They observed that the