Ain Shams Univeristy
Faculty of Science
Chemistry Department

Physico-chemical and Mechanical Characteristics of Some Blended Cement Pastes

A Thesis Submitted By

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M.Sc., (Chemistry), (1998)

For The Fulfillment of The Degree of Ph.D.in Chemistry

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بسم الله الرحمن الرحيم

اللَّهُ نُورُ السَّمَاوَاتِ وَالْأَرْضِ

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Dedication

To soul of my parents
To my dear husband
To my lovely son and daughter

To soul of my par
To my dear husband
To my lovely son and daughter

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CHAPTER I

INTRODUCTION AND OBJECT OF INVESTIGATION

IA. Introduction

IA.1. Introductory remarks

Portland cement was developed from natural cements made in Britain in the early part of the nineteenth century, and its name is derived from its similarity to Portland stone, a type of building stone that was quarried on the Island of Portland in Dorset, England **(Jönsson and Tillman, 1999).**

Portland cement (often referred to as OPC, from (Ordinary Portland Cement) is the most common type of cement in general use around the world because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. It usually originates from limestone. It is a fine powder produced by grinding Portland cement clinker (more than 90%), a limited amount of calcium sulfate (which controls the setting time) and up to 5% minor constituents as allowed by various standards such as the European Standard EN197-1.

Portland cement is commercially produced by burning an intimate mixture of calcareous and argillaceous raw materials in rotary kilns to a temperature of approximately 1350 - 1450˚C. Limestone and clay are the most common materials used in the manufacture of Portland cement. The fused product of the kiln is called clinker. The clinker is cooled and ground with a few percent of gypsum to produce what is called Portland cement.

Cement can be defined as material with adhesive and cohesive properties that makes it capable of binding fragments to a compact whole. Such a definition leads to a restriction of the designation of building materials binding with stones, bricks and building blocks in the constructional purposes and engineering works. In its broadest sense, the word cement denotes any kind of binding agent **(Hewlett, 1998).**

Hydraulic cements are the cements of interest in the making of concrete which have the property of setting and hardening under water, due to chemical reactions. Hydraulic cement when mixed with enough water to form a plastic mass (paste), the mixture starts to set, loses its plasticity and becomes hard. The paste continues to harden and develops strength. Most important engineering properties of concrete such as strength, volume stability and permeability to water are mainly determined by the properties of the hardened cement paste. The essential constituents of Portland cement clinker are lime, silica, alumina and iron oxide which are combined to form tricalcium silicate; C_3S (Alite), β-dicalcium silicate; β-C_2S (Belite), tricalcium aluminate; C_3A and a ferrite phase as C_4AF (tetracalcium aluminoferrite).

The properties of Portland cement are mainly controlled by the relative properties of C_3S, β-C_2S, C_3A and C_4AF in the cement clinker. For instance, high early strength is derived from high content of C_3S. Low heat of hydration results from low content of C_3S and C_3A and high resistance to sulfate attack is attributed to low content of C_3A **(Shondeep and Harsh, 1993).**

Several types of Portland cement are manufactured having different characteristics. The classification of the various types of Portland cement is based on the rate of hydration, the rate and extent of heat of hydration as well as the resistance of the hardened cement paste against the attack by aggressive solutions. The characteristics of each type are influenced by the relative properties of the major phases and gypsum content, as well as the fineness of cement.

Manufacturing of Portland cement is a resource exhausting, energy intensive process that releases large amounts of the greenhouse gas CO_2 into the atmosphere. Production of 1 ton of Portland cement requires about 2.8 tons of raw materials, including fuel and other materials. As a result of calcination of limestone, manufacturing of 1 ton of cement generates about 1 ton of greenhouse gas, **Davidovits et al., (1993)** reported that the amount of carbon dioxide released during chemical reactions, the cement CO_2 emission based on the calcination of limestone could reach BaU (Business as Usual) value of 1800-million tons in the year 2000. At present, efforts have been made to promote the use of pozzolans to partially replace Portland cement. Recently, another class of cementitious materials, produced from an alumino-silicate precursor activated in a high alkali solution, has been developed

IA.2. Pozzolana and blended cement

A pozzolana is defined as a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious materials but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties [**(ASTM C618-12a),** and **ASTM C125, (2010)].**

The broad definition of a pozzolana imparts no bearing on the origin of the material, only on its capability of reacting with calcium hydroxide and water. A quantification of this capability is comprised in the term pozzolanic activity **(Snellings et al., 2012).**

Blended cements are made by partial replacement of ordinary Portland cement by siliceous or alumino-silicate materials such as silica fume, blast-furnace slag, metakaolin, fly ash, etc. In addition, natural or artificial pozzolanas are used as active siliceous additives. The use of blended cements to make mortar and concrete was common in practice recently, due to technological, economical, and environmental benefits. Such blending materials modify the strength, pore structure, permeability and durability of hardened cement paste, mortar and concrete.

The term 'pozzolana' has two distinct meanings. The first one indicates the pyroclastic rocks, essentially glassy and sometimes zeolitised, which occur either in the neighborhood of Pozzuoli (the ancient Puteoli of the Roman times) or around Rome **(Davidovits et al., 1993)** . The second meaning includes all those inorganic materials, either natural or artificial, which harden in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement clinker).

For a long time the use of pozzolanas has been mostly restricted to Italy, where considerable reserves of natural pozzolanas are found and to Greece (Santorin earth). In other countries the interest in these materials is of relatively recent date and has arisen from the need for re-using some waste materials such as fly ashe and silica fume. This historical background can help explain why so many countries have long distrusted pozzolana containing cements, despite the millenary use of lime-pozzolana mortars and the almost 100-year experience in pozzolanic cements. In any case, results of a variety of studies have substantially confirmed that pozzolanic cements can yield concrete showing a high ultimate strength and great resistance to aggressive attack.

The more commonly accepted classification concerns the origin of pozzolanas and therefore a first subdivision is between natural and artificial materials. Natural materials do not require any further treatment apart from grinding; artificial pozzolanas result from chemical and/or structural modifications of materials originally having no or only weak pozzolanic properties. The latter can be residues of certain production methods or products manufactured from selected raw materials.

Donatello et al., (2010) reported a wide range of test methods for assessing pozzolanic activity. These can be categorised as either direct or indirect methods. Direct methods monitor the presence of $Ca(OH)_2$ and its subsequent reduction in abundance with time as the pozzolanic reaction proceeds, using analytical methods such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) or classical chemical titration.

Indirect test methods measure a physical property of a test sample that indicates the extent of pozzolanic activity. This may involve measurement of properties such as compressive strength, electrical conductivity **(Frias et al., 2005 ; McCarter and Tran, 1996** and **Paya et al., 2001).**

Mostafa and Brown, (2005) determined the heat of hydration of high reactive pozzolans in blended cements. Compressive strength test methods have been used to assess the pozzolanic activity of catalytic cracking residues was studied by **Tseng et al., (2005)**, coal bottom ash **Cheriaf et al., (1999)**, glass powders **Shi et al., (2005)**, crushed bricks **Wild et al., (1996)**, silica fume **Mostafa et al., (2001),** and **Agarwal, (2006)** and sewage sludge ash **Monzo et al., (1999)** and **Pan et al., (2003)**.

Tseng et al., (2005) and **Shi et al., (1999)** found results from an indirect pozzolanic activity test are often corroborated using direct tests to confirm that pozzolanic reactions are occurring.

There is a research was to assessed if different test methods for pozzolanic activity correlate with each other was done by **Babak and Mohammad, (2010)**.

IA.3. Kaolinite and metakaolinite (K and MK)

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral **(Deer et al., 1992).**

Metakaolin (MK) is a supplementary cementitious material (SCM) derived from heat treatment of natural deposits of kaolin. Typically, metakaolins show high pozzolanic activity due to their amorphous structure and high surface area **(Ambroise et al., 1985)**.

In Portland cement concrete, MK reacts at normal temperatures with calcium hydroxide in cement paste to form mainly calcium silicate hydrates (C–S–H), C_2ASH_8 (gehlenite hydrate), and C_4AH_{13} (tetracalcium aluminate hydrate) **(Rojas and Cabrera, 2002)**. The formation of secondary C-S-H by this reaction both reduce total porosity and refine the pore structure, improving the strength and impermeability of the cementitious matrix **(Bensted and Barnes, 2002** and **Khatib and Wild, 1996)**.

Central Board of Irrigation, (1971) reported that the clay minerals gain a distinct pozzolanic activity when burned at temperatures between 600 and 900°C. The use of burned clays for the preparation of hydraulic mortars dates back to ancient times and is particularly widespread in India . **Mielenz et al., (1950)** and **Ambroise et al., (1992)** studied the effect of calcination on natural pozzolanas and Pozzolanic behavior of thermally activated kaolin. Owing to the chemical composition of clay and related materials, these artificial pozzolanas are mostly composed of silica and alumina. The loss of combined water due to the thermal treatment causes the crystalline network of the clay minerals to be destroyed, while silica and alumina remain in a messy, unstable, amorphous state. Heating does not affect anhydrous minerals such as quartz or plagioclase, so that pozzolanic activity depends only on the clay mineral content as well as on the thermal treatment conditions. The burning or retorting of certain oil shales produce ashes which harden when mixed with water **(Ambroise et al., 1985)**. Their chemical composition varies largely according to their origin. The silica content can vary between 22%, **(Ambroise et al., 1994),** 42%, **(Laubenheimer, 1968),** and conversely lime can vary between 55%. **(Ish-Shalom et al., 1990),** and 22%, **(Laubenheimer, 1968)**. Hardening results from the presence of cementitious compounds such as C_2S, CA and C. **Khedaywi et al., (1990)** concluded that the burned shales have a more complicated mineralogical composition than burned clays depending on their composition, temperature and duration of burning. Shale burned at temperatures ranging between 750 and 840˚C contains β-quartz, β-cristobalite, calcite, α-F_2O_3 and muscovite, which are already present in shale, and gehlenite, anorthite, wollastonite, orthoclase, anhydrite, β-C_2S, CA and CaO formed during the burning process. In any case, oil shale ashes should possess pozzolanic properties as they consume lime when they are mixed with water and hydrated lime or Portland cement.

Bich et al., (2009) studied the effect of heating temperature on kaolin. Kaolin samples were heated between 500 and 850 °C. X-ray diffraction (XRD), differential thermal analysis (DTA), and Infra-Red (IR) spectroscopy were used to determine their mineralogical composition and degrees of crystallinity and dehydroxylation. The reactivity of the heated samples was evaluated by the determination of the residual quantity of $Ca(OH)_2$ by differential thermal analysis (DTA) performed on hydrated mixtures of 50% metakaolin and 50% $Ca(OH)_2$. There was no direct relationship between the pozzolanic activity of metakaolin and the degree of dehydroxylation. Highest activity was obtained when the degree of dehydroxylation was 95%.

Konan et al., (2009) compared the surface properties between kaolin and metakaolin in concentrated lime solutions. Kaolinite and metakaolinite are clay minerals with different structural properties. In the case of kaolinite, the octahedral layers, centered on aluminum cation, have hydroxyl groups on their external surfaces that probably do not interact strongly with the hydroxyl ions in solution. Interactions between kaolinite and alkaline solutions, rather than just considering proton exchanges at the clay mineral surfaces, are explained by an adsorption of calcium and hydroxyl ions not only at the edges of the clay particles but also onto the faces. Metakaolinite obtained after a thermal treatment at 700˚C for 5h of kaolinite was fully dehydroxylated. The complete dehydroxylation and disintegration of the original kaolinite structure means the formation of an unstable metakaolinite form and the change of the Al atom coordination number from 6 to 4, or to 5. Both forms with the coordination numbers 5 and 4 are reactive, which means ready for hydration. The dehydroxylation is accompanied by the formation of amorphous metakaolinite, which is favorable to a surface dissolution of clay particles in a calcium hydroxide solution. Metakaolin adsorbs larger quantities of calcium hydroxide than kaolin. When metakaolin reacts with calcium hydroxide, C-S-H gel and gehlenite like hydrate (C_2ASH_8) are the most important hydrated phases which form on the surfaces of solid.

Serry et al., (1987) and **Mejia et al., (2008)** investigated the influence of the calcination temperature of kaolin on the mechanical properties of mortars and concretes containing metakaolin. They found that the thermal transformation of kaolin showed that the temperature and time of thermal treatment have a significant importance on the properties of concretes containing metakaolin as an addition. **Ambroise et al., (1992)** showed that the metakaolin (MK) is a reactive aluminosilicate which is formed by the dehydroxylation of kaolin precursor upon heating in the ~700-800°C temperature range.

Aluminium (Al) ions substitute for silicon (Si) ions to a maximum A1/Al+Si ratio of 0.14, **Mitsuda et al., (1992)**, higher A1 concentrations in