HYDRAULIC REACTIVITY OF SOME ARTIFICIAL POZZOLANIC MATERIALS

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قالوا

سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا
إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ

صدق الله العظيم

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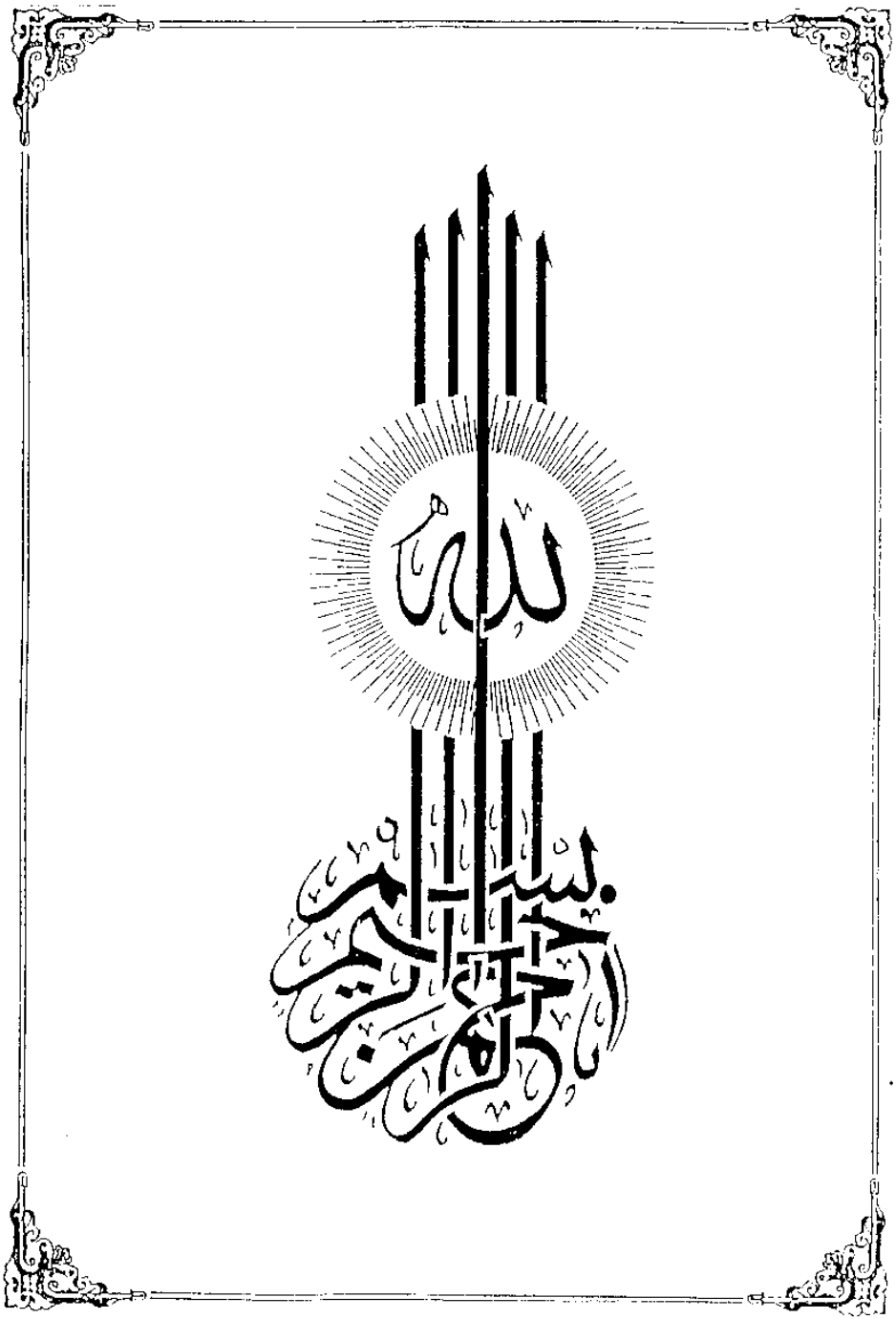

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CONTENTS

Page

CHAPTER I:

Introduction and Object of Investigation.

I.A. Introduction 1

I.B. Object of investigation 59

CHAPTER II:

Materials and Experimental Techniques

II.A. Materials and preparation of the cement pastes 60

A.1. Starting materials 60

A.2. Preparation and burning of clays 65

A.3. Preparation of the various pozzolanic cement mixtures 65

(1) Mixing with $Ca(OH)_2$ 65

(2) Mixing with Portland cement 66

II.B. Methods of physicochemical measurements 67

B.1. Compressive strength 67

B.2. Hydration kinetics 67

B.2.1. Chemically-combined water 68

B.2.2. Free lime determination 68

B.3. Identification of phases produced upon hydration . . . 69

B.3.1. X-ray analysis 69

B.3.2. Scanning electron microscopy (SEM) 69

CHAPTER III:

Results and Discussion

III.A. Physico-chemical properties of the hard lime-burnt clay pastes 70

III.A.1. Hydraulic reactivity of artificial pozzolanas made from burnt mixed clay using lime as an activator 70

A.1.a. Compressive strength 70

A.1.b. Hydration kinetics 76

A.1.b.(i) Combined water contents 76

A.1.b. (ii) Free lime contents 79

A.1.c. Phase composition of the formed hydrates . . . 81

A.1.d. Morphology and microstructure 82

III.A.2. Hydraulic reactivity of artificial pozzolanas made from burnt kaolinite clay using lime as an activator 83

A.2.a. Compressive strength 83

A.2.b. Hydration kinetics 83

A.2.b. (i) Combined water contents 83

A.2.b. (ii) Free lime contents 87

III.A.3. Hydraulic reactivity of artificial pozzolanas made from burnt montmorillonite clay using lime as an activator 89

A.3.a. Compressive strength 89

A.3.b. Hydration kinetics 91

A.3.b. (i) Combined water contents 91

A.3.b. (ii) Free lime contents 93

A.3.c. Phase composition of the formed hydrates . . . 95

A.3.d. Morphology and microstructure 95

III.B. Physico-chemical properties of the hardened Portland cement-burnt clay pastes 97

III.B.1. Hydraulic reactivity of artificial pozzolanas made from burnt mixed clay using Portland cement as an activator 97

B.1.a. Compressive strength 97

B.1.b. Hydration kinetics 102

B.1.b. (i) Combined water contents 102

B.1.b. (ii) Free lime contents 107

B.1.c. Phase composition of the formed hydrates . . 107

B.1.d. Morphology and microstructure 109

III.B.2. Hydraulic activity of arificial pozzolanas made burnt kaolinite clay using Portland cement as an activator 111

B.2.a. Compressive strength 111

B.2.b. Hydration kinetics 116

B.2.c. Phase composition of the formed hydration products 120

III.B.3. Hydraulic activity of artificial pozzolanas made from burnt montmorillonite clay using Portland cement as an activator

B.3.a. Compressive strength 122

B.3.b. Hydration kinetics 127

B.3.b (i) Chemically-combined water contents 127

B.3.b. (ii) Free lime contents 131

B.3.c. Phase composition of the formed hydrates . . 131

B.3.d. Morphology and microstructure 132

CHAPTER IV:

Summary and Conclusions 134

References 138

Arabic Summary

CHAPTER I

INTRODUCTION
AND
OBJECT OF INVESTIGATION

I- INTRODUCTION AND OBJECT OF INVESTIGATION

I.A- Introduction

"Pozzolana" is defined as natural or artificial solids involving constituents which react with Ca^{2+} or $Ca(OH)_2$ and form new binding compounds under the presence of water. "Constituents", we say, means minerals, crystals, noncrystalline materials, glasses and "artificial" means chemical or physical treatment for natural materials. Fly ash is one of possolanas in this meaning.

"Pozzolanic reactivity" is defined as index of reaction degree at ordinary temperature between pozzolanas and Ca^{2+} or $Ca(OH)_2$ with water or between pozzolanas, water and material which produces $Ca(OH)_2$ under the presence of water.

As the definition of "pozzolana" says, the mere physical absorption is excluded from pozzolanic reaction because this term means the formation of binding compounds by the reaction. In general the chemical reaction has absorption process as one of reaction processes and after that process forms new compounds, but we interpretate here such a physical absorption process as so-called induction period and evaluate the degree of pozzolanic reaction of this period as zero.

In the definition of "pozzolanic reactivity", properties of reaction products or aggregate system which involves raw materials and reaction products are not mentioned. The reason is that the

properties of paste which involves reaction products are substantially independent from pozzolanic reactivity. For example, strength, which is one of the representative properties of paste, is strongly influenced by the kinds, shapes, sizes and distribution of hydration products and pores, has not so good correlation with the degree of reaction.

The base of pozzolanic reactivity can be defined so that the difference of free energy between source system and products system or magnitude of activation energy from source system to products system, in the reaction system of pozzolanas, Ca^{2} [or $Ca(OH)_2$] and water, or pozzolanas, water and materials which form $Ca(OH)_2$ under the presence of water. The nature of pozzolanic reactivity is determined by the character of pozzolanas, that is, the composition and structure of pozzolanas.

In the many papers, the term of "pozzolanic activity" or "pozzolanicity" other than reactivity has been used. Some of them[1,2] used the pozzolanic activity for the test results of strength of pozzolanic cements. ISO[3] uses the "pozzolanicity" for the test results of $Ca(OH)_2$ concentration in the liquid of cement suspension. The concept of these terms is not always authorized or standardized and gives us unnecessary confusion. In this paper, the authors uses only the term of "pozzolanic reactivity", as defined at the first.

The crystalline hydrates formed in the reaction between lime

and pozzolana in the presence of water were summarized by Massazza[4] as hexagonal calcium aluminate hydrate (C_4AH_x), calcium carbo-aluminate hydrate ($C_3A.CaCO_3.H_{12}$), calcium aluminate monosulfate hydrate ($C_3A.CaSO_4.H_{12}$), calcium silicoaluminate hydrate which were identified by means of DTA, powder X-ray diffraction and electron diffraction analysis.

The kinds and compositions of produced hydrates are generally related to the character, that is, chemical composition, crystal structure of constituents of pozzolana, and the conditions of hydration. However, there are no remarkable difference between hydrates formed in paste and those of suspension hydration at later age.

Ludwig and Schwiete[5] studied the hydration in the system $Ca(OH)_2$ and two kinds of trasses containing 50-70 % of glass phase, feldspar, quartz analcite etc. in suspension and paste. They confirmed the formation of C_4AH_{13} and C_3S_2 hydrate in the case without gypsum, and ettringite and monosulfate hydrate with gypsum.

Amicarelli, Sersale and Sabatelli[6] studied the suspension hydration of argillified pyroclasts in lime saturated solution. They found C_2ASH_8, C_4AH_{13} and tobermorite-like calcium silicate hydrate in clayish pozzolana containing large amount of halloysite, C_2ASH_8 and tobermorite in zeolitic pozzolana containing chabazite and $C_3A.CaCO_3.H_{12}$ and tobermorite in tuff containing leucite and halloysite at the age of 20 days. The amount of combined lime was 17 % by weight of added lime. Hydrogarnet, or C_2ASH_8 and

hydrogarnet, were formed at the later stage of 70 - 150 days, when the combined lime was from 46 to 60 %.

In the five years old paste intially containing 40 % of lime and 60 % of calcined pozzolana, Sabatelli, Sersale and Americarelli[7] observed two typical different cases consisting of C-S-H (I) and C_2ASH_8, and C-S-H (I), C_2ASH_8, C_4AH_{13} and $C_3A.CaCO_3.H_{12}$.

In the authors' study, the hydrates produced in the paste hydration of pozzolana-$Ca(OH)_2$ in W/S = 0.56 - 0.46 at 20°, 40° and 60°C using five kinds of Japanese natural pozzolanas and one kind of fly ash were classified into three cases according to pozzolanas, that is, (1) C-S-H only, (2) C-S-H, $(C_3A\ CaCO_3\ H_{12}C_4AH_{13})$ss and hydrogarnet in later age, (3) C_2ASH_8, hydrogarnet, and a little amount of C-S-H. The first case was Beppu white clay consisting of opal. The second case was tuff containing volcanic glass and shirasu containing volcanic glass and plagioclase. The third case was Kanto loam containing much allophane. The formation of hydrogarnet in allophane rich pozzolana was accelerated in the increased amount of $Ca(OH)_2$ and in the rise of temperature.

Regourd, Hornain and Mortureux[8] recognized silicoaluminates of $C_3A.CS.H_{12}$ and $C_3A.3CS.H_{31}$ near C_3A grains in the hydrated paste of C_3S-C_3A and C_3S-C_3A-$CaSO_4.2H_2O$ at 28 days by SEM with energy dispersive X-ray analysis (EDX). These hydrates might be produced in the pozzolana system.

The concentration of Ca^{2+} in the liquid of the system pozzolana-

$Ca(OH)_2$ is kept between 2 m mole/l and 9 m mole/l[9]. The former corresponds to the value equilibrating to C-S-H and the latter corresponds to the value in the liquid equilibrating to $Ca(OH)_2$ coexisting with alkalies. The molar CaO/SiO_2 ratio is closely related to the concentration of Ca^{2+} in the liquid.

Drzaj, Hocevar, Slokan and Zajc[10] studied kinetics and mechanism of reaction in the system zeolitic tuff-CaO-H_2O at 65°C using the 1:1 mixture of CaO and three kinds of tuffs and one kind of heulandite hydrate in W/S = 50/6 at 65°C. They determined the relative decrease of the minerals in reactants and the relative increase of the amounts of CSH (I), tobermorite, tetracalcium aluminate hydrate, nekoite, osumilite in products by powder X-ray diffraction referring the SEM observation. They described that the initial reaction was the diffusive dissolution of zeolite and $Ca(OH)_2$ as it agreed with Fick's first low, and that the reaction was diffusion-controlled topochemical reaction limited by the diffusion of Ca^{2+} and OH^- through the membrane of CSH (I) gel, which formed on the surface of zeolite grain in the processes of zeolite + $Ca(OH)_2$ + CSH (I) + tobermorite, and the interface layer between zeolite and CSH (I) gel membrane. They also pointed out that CSH (I) formed in the early stage of reaction and that tobermorite formed as final product through heterogeneous nucleation on the solid [CSH (I)] -liquid (solution) interface.

The mechanism of the hydration in the system pozzolana-