HARDENED SLAG CEMENT PASTES OF LOW POROSITY

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OF LOW POROSITY

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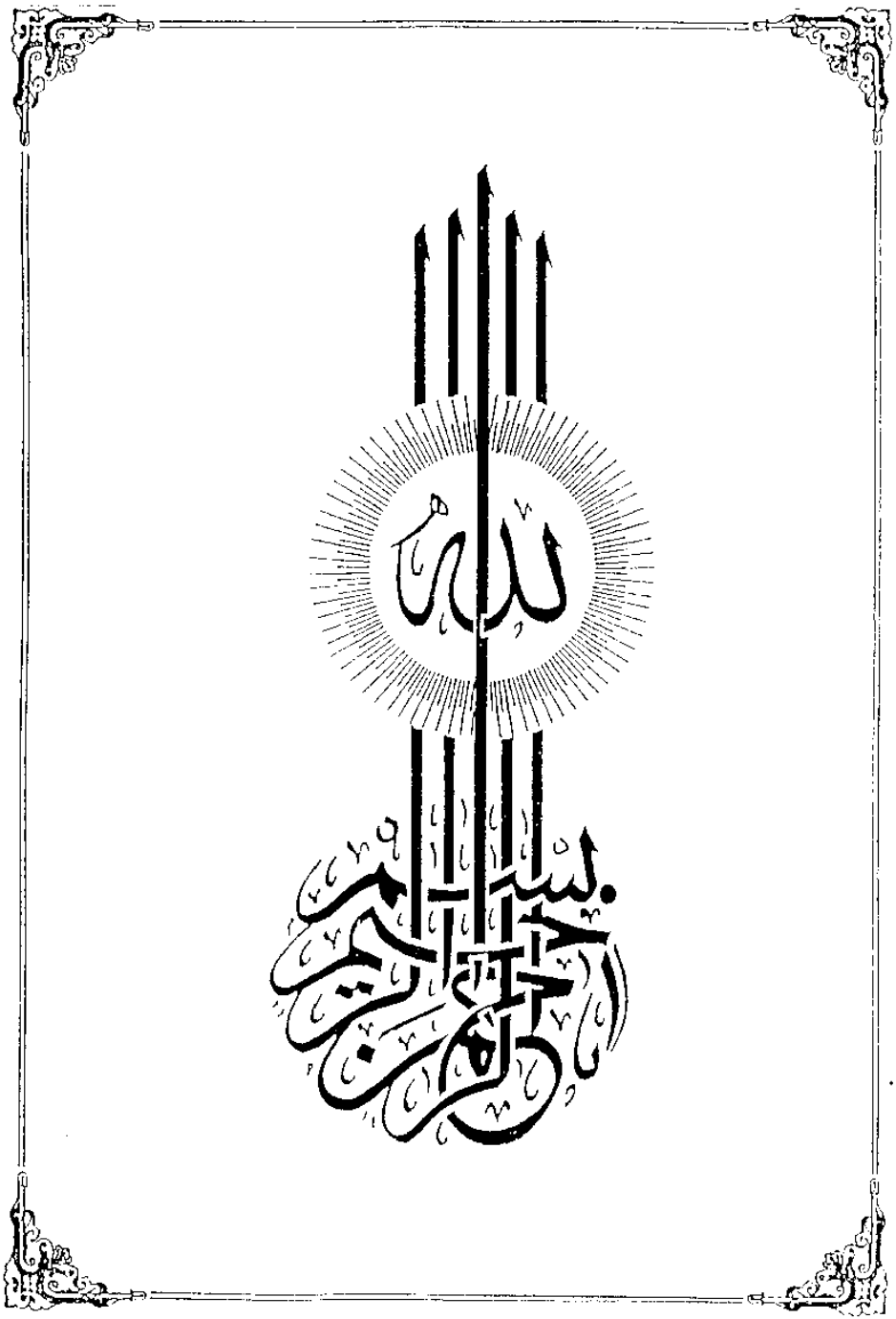

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CHAPTER I

INTRODUCTION AND OBJECT OF INVESTIGATION

The reaction that produces cement hydrates in the dense paste of cement powder with water is of fundamental interest to the building materials industry. The reaction between water and granulated blast-furnace Slag cement has features of interest concerning the variety of applications for this economically valuable type of cement. It also has further interest in connection with the reactivities of solids in general.

The production of low-porosity, high hydraulically reactive and strength bearing material from this kind of cement is one of the most, if not the most important aim which has attracted the attention of numerous investigators in the field. A historical review might help in giving a short account of the work done on this substance with a particular emphasis on its microporosity. This review is not meant to give a full account of all work done in the field but will furnish few examples of the various angles attacked by the various investigators.

I.A. Introduction:

The chemical composition and physical state of the compounds produced in the hydration of granulated blastfurnace Slag cement have been the object of study for many decades. Nevertheless, despite the numerous and careful researches devoted to it, the complexities of the system prevented decisive conclusions, and still very little is known

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regarding the essential structural and physico-chemical reactions that determine the basic events in the hydration of cement.

The basic knowledge required is one which will provide a complete description of the distinct phases produced in Slag cement hydration and of the physico-chemical conditions under which they are produced and formed having a particular structure.

The most important constituent of concrete and mortar made with Slag cement is the hydration products; and the most important product obtained in the hydration of cements, is the calcium silicate hydrates, which consist of a range of phases which vary widely in both composition and of crystallinity. As a group, these are characterised by a common structural resemblance to tobermorite itself, a compound of approximate composition $C_5S_6H_6$ and which was originally discovered in Scotland as a natural mineral[1]. The compounds or phases in the group as a whole are described as tobermorite - like hydrates or tobermorites in general. Tobermorites constitute about 80% of the total hydration products of different cements. Tobermorites are colloids with a very large specific surface area (about 250 m^2/g). The surface is hydrophilic, the ions in the surface readily adsorb water. Tobermorites are formed as an immediate product in almost all reactions in which calcium ion and silicate ions are brought together in the presence of water.

It is not the intention to present a full scale discussion of the tobermorite - like hydrates. However, a discussion of certain aspects of the system seems desirable in order to show the complexity of the syste

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$CaO - SiO_2 - H_2O$, which is the main constituent of Slag cement studied in the present investigation.

Taylor[2], in 1950, called the hydrate, ranging in $CaO : SiO_2$ ratio up to 1.5, calcium silicate hydrate (I) or C-S-H (I). The $CaO : SiO_2$ ratio in the hydrate rises sharply at lime saturation. Taylor called this high-lime hydrate, calcium silicate hydrate (II) or C-S-H (II).

The hydraulic reactivity of Slag depends on the presence of alkaline activators. The only crystalline component of blastfurnace Slag possessing cementitious properties at normal temperature and pressures of water vapour is β-C_2S. From this similarity in setting characteristics of C_2S and of granulated blastfurnace Slag in the presence of lime, it was concluded that, the fundamental constituents in the Slag giving rise to hydraulic reactivity, were C_2S and C_2AS.

Feret[3], also concluded that the hardening agent was C_2S but the hydraulic quality depends on Al_2O_3 as well as CaO. A defficiency of one could be componsated by a larger amount of the other up to a limiting point where increasing CaO content make granulation to a glass difficult.

The hydration of Portland cement - granulated Slag mixtures is more complex than that of Portland cement, since both constituents react with water. We have here, therefore, to consider the hydration of the Slag as influenced by the calcium hydroxide liberated from the Portland cement. No hydration products can be observed when ground granulated Slag is placed in water. This is ascribed to the formation of acidic surface films as a small amount of Ca^{++} ions is released into solution.

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In a calcium hydroxide solution, reaction occurs, removing this film and hydration continues as the lime breaks into the silica frame work of the Slag. Provided a continuous supply of lime is available, the Slag can combine with up to about a tenth of its weight of CaO in three months.[4] Granulated Slag contains some calcium sulphide[5] which reacts with water to give $Ca(OH)_2$ and $Ca(SH)_2$, but the amount of lime so produced from the sulphide on the surface of the Slag particles can only provide a very minor amount of lime to the solution.

The hydration products clearly identified,[6] in set of blast-furnace Slag cements are:

(1) A tobermorite - like calcium silicate hydrate phase which probably contains alumina in solid solution, for not all the alumina can be accounted for in the other hydration products. This phase may also contain magnesia in solid solution because free $Mg(OH)_2$ can not be detected in the set cement.[7]

(2) Hexagonal tetra calcium aluminate hydrate or its solid solutions, or intergrowth with 3 CaO (Al_2O_3, Fe_2O_3) Ca SO_4. 12 H_2O.

(3) An ettringite type phase 3 CaO (Al_2O_3, Fe_2O_3) 3 Ca SO_4. 31 H_2O.

(4) Calcium hydroxide.

Investigations, for a long time, debated the question whether the lime in excess of CaO : SiO_2 ratio of 0.8 should be regarded as adsorbed or whether it is in solid solution. Brunauer, Copeland and Bragg[8] advanced arguments in favour of the viewpoint that the extra lime is not adsorbed physically. On the other hand Taylor and Hawison[9] advanced

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arguments for the extra lime being part of the crystal structure. It seems probable that the extra lime is a rather special type of solid solution. However, it is most unlikely to provide the whole explanation, because the C-spacing normally decreasing with rise in the Ca : Si ratio.

The $CaO : SiO_2$ ratio is not the only variable in the system. The $H_2O : SiO_2$ ratio also varies in wide ranges. The water content of the calcium silicate hydrate depends on the drying conditions employed.[10]

Such variations in the lime - silica ratios and in the water - silica ratios are due to several factors. One of these factors, is the difference in the structure, the degree of crystallinity and morphology of the tobermorite obtained in the reaction. For a given $CaO : SiO_2$ ratio, every recent investigator reports a somewhat different x-ray diffraction patterns; and even the same investigator reports somewhat different patterns for different methods of preparation. Variations in the crystal structure and morphology of a tobermorite of a given $CaO : SiO_2$ ratio may cause variations in the free energy content and in solubility. Thus, it may happen, that tobermorite, with a ratio 1:1 is in equilibrium with a calcium ion concentration of 3 millimoles per litre[11] whereas, in other cases, it is in equilibrium with a concentration of about 6 millimoles per litre.[12]

Modification of the course of hydration of the cement pastes can lead to physical as well as physico-chemical changes, and these are reflected as changes in the rates of hydration, engineering properties and microstructure of the formed hydrates, as well as changes in the compressive strength of the hardened cement pastes.

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Modification of the course of hydration have attracted the attention of several investigators in the field. The ultimate aim of such studies is to be able to control the microstructure of the hardened pastes so that specified properties could be tailord for specified applications.

Brunauer and Co-workers,[13] in a series of 6 papers, reviewed the effect of changing water to cement ratio. Decreasing water to cement ratio was found to produce better, high-strength cement pastes. Reducing water/cement ratio, hinder the workability and moulding of the cement pastes; and to counteract such a difficulty several additives have been used, some of them act as accelerators and others act as retarders for the process of hardening. The effect of each group of additives on the hardening of cement pastes have been met with several investigations.

The original work of Werner and Giertz - Hedstrom[14] could indicate that the strength of hardened cement pastes and concrete should be a function of the concentration of the hydrated cement. Giertz - Hedstrom,[15] 1938, reviewed all related investigations that support the dependence of strength on concentration of hydrates. In 1947 Shinohara[16] and Powers and Brownyards[17] independently published work based on a similar basis. Powers and Brownyard adopted the term Gel-space ratio analogous in concept to Feret cement-space ratio. The same concepts, later, used by Taplin,[18] in 1959. In a dissertation published in 1953, Dzulynsky[19] published a study of strength in relation to cement hydration in which ideas similar to those reviewed above were developed.

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By determining the compressive strength of different type I cements, it was noticed[19] that cement gels low in C_3A are stronger than those high in C_3A. Although there is such evidence that the strength of cement gel is a function of its chemical composition, there is no evidence that some of the chemical species present do not contribute to strength. By means of simple demonstration, Gzernin[20] made it clear that the physical state of the solid material may be responsible for strength. Such strength is presumably due to the proximity of surfaces and van der Waal's forces. Since all the major components of hydrated cement are found in substances having high specific surface areas, all contribute to at least the van der Waal's source of strength. On the other hand, it seems unlikely that the strength of cement gel is due, exclusively, to physical forces. It seems probable that there are many points of chemical binding between the particles. Whether or not all chemical species contribute to this source of strength cannot be said. As to the relative importance of the two sources of strength, one can only speculate. When specimen of cement paste is dried in such a way as to avoid excessive stresses during drying, the specimen becomes stronger as its evaporable water is lost: in fact, if some of the chemically combined water is removed, there is gain in strength. In terms of van der Waal's forces, this gain of strength could be accounted for in terms of the reduction in average distance between surfaces in the cement gel.

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