THESIS

ON

SURFACE STRUCTURES OF CALCIUM SILICATE PASTES

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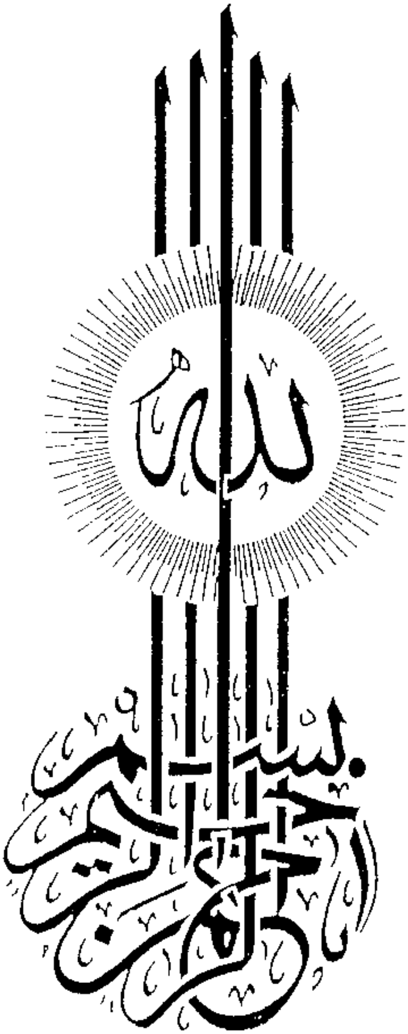

بسم الله الرحمن الرحيم

SURFACE STRUCTURES OF CALCIUM SILICATE PASTES

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Part of this Thesis has been accepted for publication in the "Proceedings of the Tenth Conference on the Silicate Industry", to be published by the "Scientific Society of the Silicate Industry" - Budapest - Hungry.

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NOTE

The candidate has attended postgraduate courses for two years in Physical and Inorganic Chemistry covering the following topics:-

1) Advanced surface chemistry.
2) Chemistry of the solid state.
3) Techniques of Inorganic Chemistry.
4) Structural Inorganic Chemistry.
5) Electrochemistry.
6) Polarography

He has successfully passed a written examination in these courses.

Prof. F. G. Baddar
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CONTENTS

Page.

CHAPTER I : Introduction and Object of Investigation....

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CHAPTER I

1.1 INTRODUCTION .

The chemical composition and physical state of the compounds produced in the hydration of Portland Cement have been an 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 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 cement hydration and of the physico-chemical conditions under which they are produced and formed having a particular structure. Earlier work in the lime-silica-water system, especially at ordinary temperatures[1], has shown that it is extremely difficult to assign a simple chemical formula to any phase, and in some cases wide differences of composition occur within the phase, in water content and in $CaO : SiO_2$ ratio. On the other hand, products with the same composition are often represented by several phases. Consequently chemical analysis alone cannot hope to unravel the system. Further, the products of hydration occur in very fine crystalline state, often called gels.

Consequently microscopic and petrographic methods, so useful in other fields of cement chemistry, have yielded indefinite and controversial character.

The most obvious method to overcome these difficulties was believed at one time to be through the use of X-ray methods;[2] but here again the results have been rather meagre, partly because of the fine-grained character of the material but mainly because most of the compounds have large unit cells of low symmetry, so that the X-ray powder patterns overlap and defied analysis. Moreover, owing to the difficulty of avoiding the presence of more than one phase there has been considerable divergence in the description of the patterns obtained.

Possibly of considerable importance, however, is the fact that, by reason of the colloidal states of the solid phases, complete thermodynamic equilibrium was actually not attained in any case. The solids may have remained significantly different in colloidal particle size in different investigations and even in different experiments within a single investigation. The resultant differences in adsorptive capacity may have contributed materially to the differencies in results obtained. Differences in adsorptive capacity are directly related to differences in surface areas of the colloidal solids, produced in the hydration reactions as well as in their pore structure.

Surface area determination of colloidal solids using low-temperature nitrogen adsorption has become a common procedure since the development of the Brunauer-Emmett-Teller theory[3] Surface area measurements make it possible to demonstrate the presence of colloidal structure, to detect changes in this structure, and under some circumstances to estimate the dimensions of the submicroscopic structural units which comprise the solid. The surface area of hydrated cement is essentially the surface area of the colloidal hydration protucts since the surface of the original cement is comparatively small. Although surface areas by nitrogen adsorption have been reported for hardened cement pastes[4,5] and hydrated calcium silicates[6] water vapour has been used more oftem than nitrogen as the adsorbate in surface area measurements of these materials. Some of the reasons for this practice have been summerized by Powers.[7]

Powers and Brownyard[8] were the first to measure the Specific areas of hardened Portland Cement pastes using the BET method with water vapour as the adsorbate. Practically all investigators who published specific area values in the field of cement chemistry used the BET method. Greenberg[9], used nitrogen adsorption, but nitrogen surface values for tobermorites, the main hydration products in cement pastes, are unreliable. Nitrogen adsorption, in almost every instance, leads to a smaller specific surface area than water vapour adsorption. Kalousek[10] believed that nitrogen measured only the external surfaces. He attributed the difference between the two to the layer structure of tobermorite gel, and to the ability of water and the inability of nitrogen to penetrate between the layers of the gel. However, later work has shown that water cannot penetrate between the layers of strongly dried tobermorite gel, even when the gel is soaked in water.[11] Thus, the difference between water and nitrogen adsorption may be a, consequence of the pore structure of the gel. Water, because of its smaller size and strong dipole character, may be able to measure the specific surface area and pore volume of spaces which are inaccessible to nitrogen. There is evidence that water measures the total surface area and pore volume of the gel.[12]

Mikhail, Copeland and Brunauer[13] in their study of the pore structure and surface area of hardened cement pastes, concluded that nitrogen can be excluded from the pores in hardened cement pastes by two mechanisms. Either the pores can be too narrow to admit the nitrogen molecules or the pore entrances can be too narrow. This latter mechanism may be one of the reasons why surface areas by nitrogen adsorption undergo large decreases when partially dried pastes are stored in a closed system[14]. Surface areas available to nitrogen are not only lower than those available to water but are sometimes more responsive to the environmental history of the specimen after hydration has stopped.

The above results show that cement pastes, like other high area solids, exhibits dependence of the area measured by gas adsorption techniques on the gas used in the determination. Investigations of hardened pastes of portland cement were performed similar to the investigations of the pore structures and surface areas by nitrogen adsorption.[13]

Adsorption-desorption isotherms were determined using Organic[15] vapours of different molecular areas and polarities: the vapours used were cyclohexane, isopropanol and methanol. The surface areas and pore volumes accessible to each were obtained and compared to those obtained with nitrogen and water vapour.

Mikhail and Selim[15] explared the relative importance of the effects of size and polarity of the adsorbate molecules on the pore structures of cement pastes by considering the adsorption of molecules of different sizes and polar natures. Their results were explained by visualizing the microstructure of the paste as consisting of aggregated masses of the basic structural units, mainly tobermorite gel sheets, with the masses separated by pores of an average size larger than the average size of pores within the aggregated masses. The pore system within these masses is designated the internal pore system, and between the masses the external pore system. The main conclusions were as follows:

1. Cyclohexane and isopropanol measure only the external pore system. Whereas methanol and nitrogen can partly be admitted to the internal pore system. Water seems to measure the entire pore structure of the paste.

2. The external pore system contains both S(small) and L (large) pores. There is evidence that the internal pore system also contains both S and L pores. Cyclohexane and isopropanol are excluded from the internal pore system because the aggregated masses have narrow entry ways to the internal pore system.

3. Study of the hydraulic radii shows that the entry ways to the pores have a size distribution.