HYDROTHERMAL REACTIVITY OF SOME SILICEOUS MATERIALS

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بسم الله الرحمن الرحيم

﴿ سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنتَ الْعَلِيمُ الْحَكِيمُ ﴾

صدق الله العظيم

بسم الله الرحمن الرحيم

PHYSICO-CHEMICAL STUDIES OF SOME SILICEOUS MATERIALS

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To My Family.

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NOTE

The candidate has attended courses for one year in Physical and Inorganic chemistry covering the following topics:-

(1) Advanced surface chemistry.

(2) Advanced electro-chemistry.

(3) Statistical thermodynamics

(4) Quantum chemistry

(5) Solvent extraction

(6) Nuclear chemistry.

(7) Inorganic reaction mechanism

(8) Application on group Theory.

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CHAPTER I

INTRODUCTION AND OBJECT OF INVESTIGATION

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IA. INTRODUCTION

Building materials are variable and a large number of these are known to be formed from various starting materials under hydrothermal conditions. Most of these types are made from lime-silica in different forms and different proportions. Lime - clays like quartz and kaolin could be used in making durable and strong bodies by the introduction of the autoclave technique.

The basic chemical aspects and research on hydrated calcium silicates and areas of related tec-hnology have been given in review papers by Talyor[1-4] and Bessey[5]. Crystallographic data for these compounds were also given by Heller and Talyor[6] and in a special report published by U.S. High Way Research Board[7].

Autoclaved sand-lime block normally consists of quartz grains held together in a matrix of crystalline or poorly-crystalline calcium silicate hydrates. The calcium silicate hydrates are not necessarily a single phase with a definite chemical composition, but may represent a number of phases which may occur singly or together in the autoclaved blocks. These hydrates are not usually formed on hydration of Portland cement under hydrothermal conditions as well as in some kinds of autoclaved materials. In another investigation pseudo-crystalline calcium silicate hydrate (I) [CaO/SiO_2 molar ratio =1.3, loss on ignition 14.4%] or crystalline xonollite was mixed with calcium hydroxide or silica and hydrothermally treated in an autoclaved at 130-210^{o}C for one hour. The hydrothermal reaction proceeded only partially under the conditions studied for all the systems except that of calcium silicate hydrate (I), and calcium hydroxide in which 50 % of calcium hydroxide reacted to produce hydrated C_3S. The crystallinity of the starting calcium silicate hydrate was one of the most important factors for the autoclaved hydrothermal reaction(8).

The hardening mechanism of mixtures of calcium hydroxide with clay in the autoclave was studied by Differential Thermal Analysis (DTA) and X-ray analysis(9). In the initial stage of the hydrothermal treatment of lime-clay mixtures, calcium hydroxide reacts with the liberated alumina and silica present in the structure of clay.

Calcium hydroxide is absorbed on the surface of the clay and reacts with the superficial OH-groups, forming hydrated calcium aluminosilicates. As a result of this reaction, the strength of the samples increase because Ca^{+2} ions can bind two neighbouring particles of clay. The last stage of the reaction is the disintegration of clay particles and the formation of hydrated calcium aluminates and silicates. On the other hand, the kinetics of the interaction of lime and silica under hydrothermal treatment was studied by Arestova[10]. The chemical interaction in $CaO-SiO_2-H_2O$ systems during hydrothermal treatment at 150 and 175^oC was studied for CaO/SiO_2 ratios of 0.8:1 and 0.5:1 and solid/liquid ratio of 1:3. The reaction rate increased with increasing calcium oxide content and temperature and was practically constant during 45 minutes treatment in spite of decreasing activation energy from 13.65 to 4.45 and from 10.7 to 1.76 K.Cal./mole for the mixture with CaO/SiO_2 ratio 0.8:1 and 0.5:1, respectively. The reaction rate was controlled by the diffusion of components through layers of colloidal reaction products.

Vinogradov[11] explored the possibilities of autoclaving a mixture of aragonite, calcium hydroxide, gypsum and quartz. Polymorphic transformation of aragonite to calcite was insignificant, amorphous $CaCO_3$ and $CaSiO_3$. $CaCO_3$. $Ca(OH)_2$. $2.87H_2O$ were formed. Vinogradov and Kroichuk[12] also autoclaved a mixture of quartz sand and pure calcium hydroxide (Blaine area = 2500 Cm^2/g). They found that at 250^oC granular CSH (A) (is probably scawtite) was identified. In samples with C/S = 1.0 the sequence + $C_2SH_2 \longrightarrow CSH(I)$ CSH (A) $\longrightarrow$ Xonolite was observed. Palm et.al.[13]

elucidated the role of the ionic composition of the liquid phase of autoclaved concrete on the mechanism and rate of reaction of its components.

Beaudonin and Feldman[14] investigated mechanical properties of autoclaved cement-fly ash pastes of varying composition. Correlations were obtained between values of intrinsic modulus of elasticity, microhardness, and terms reflecting the chemical composition of fly-ash, when 30-35% silica or 60-70% fly ash was added to the cement, tobermorite was formed, and the product had a high compressive strength and low permeability[15]. Steam curing increased the strength of Portland cement and pozzolanic Portland cement containing clay[16].

Pashchenko and Sai[17] produced high strength cellular products by autoclave treatment of Loess clay and lime mixtures, the products were microporous with a uniform pore distribution. Relation between structure and mechanical properties of autoclaved areated concrete were obtained by Alexanderson[18] where binders consisted mainly of cement and lime. Shrinkage decreased with increasing crystallinity (11.3 Å tobermorite) while compressive strength increased up to an optimum value.

Leont'ev et.al.[19] described the manufacture of autoclaved concrete using a synthesized binder based on quartz ferrous tailings. The high resistance of autoclaved binder to sodium chloride and magnisium sulphate was attributed to the presence of low basic hydrosilicates, tobermorite and hydrogarnet.

Budnikov[20] showed that metakaolin and clay calcined at 800°C react with calcium hydroxide under steam pressure in both their silica and alumina portions. It was found that bentonites and kaolin react slowly while tripoli reacts rapidly. The hydrothermal reaction with calcium hydroxide considerably increases the heats of wetting and the solubility of products in 10 % NaOH solution and greatly increases the refractoriness of the product. Butt et.al.[21] found that by mixing kaolin and bentonite clays, with varying calcium oxide contents up to 10%, moulding in a cylindrical form and treatment in an autoclave up to 8 atmospheres for 4 to 10 hours, calcium hydrosilicates, and several calcium hydroaluminates were formed. It was found that, Loess clay is the best source for the manufacture of building materials in the described method.

Budnikov et al[22] observed that, briquettes containing 8% calcium oxide, varying ratios of kaolinite and sand, were exposed for 24 hours to steam at 8 atmospheres. The tensile strength increased with increasing kaolinite content. When activated kaolinite lime and /or gypsum mixtures exposed to hydro-thermal treatment C_4AH_{13} or $C_3A.\ 3CaSO_4.\ 31\ H_2O$ were formed.

Budnikov [23] indicated that, under hydrothermal conditions, aluminium oxide in clay can interact with calcium hydroxide to form hydrated calcium aluminate while silica forms hydrated calcium silicate, both improving the setting properties of building materials The product has good hydraulic properties and its strength increases with time when the samples are kept under water. A thermal treatment of the solid mixture at 100-1000°C increases its strength. Tripolites and argillaceous clay can be used in the brick manufacture with the products having the same mechanical properties as common brick.

The time needed for the manufacture of the new clay calcium carbonate bricks is only 12-14 hours. Budnikov[24] observed that, the presence of clay in raw materials does not decrease the strength of bricks made from sand and lime by hydrothermal process at 8 atmospheres for 8 hours. During this process the alumina and silica of clay react with calcium hydroxide, forming hydrated calcium aluminate and calcium silicates. Both of these compounds act as binders in the lime-clay building materials. The compressive strength of the bricks made by this process, when stored under water decreased at first and they increased reaching after six months, a value of 236 kg.Cm^{-2} and after one year a value of 265 kg.Cm^{-2}

The production of building bricks from a pressed mixture of clay and quick lime was also reported in the literature[25]; the bricks were exposed to the action of saturated steam of 6 to 8 atmosphere. From analytical determinations, it has been concluded that hydrates of tricalcium aluminate and dicalcium silicate were formed if the lime content is very low; less basic hydrate may have occured. If the clays are precalcined up to 1000^{o}C before they are mixed with lime and steam-treated, generally mechanical strength is reduced. Therefore, in industrial clay-lime bricks manufacturing precalcination is claimed to be unsuitable. Effect of manufacturing conditions on the strength of calcareous marl-sand bricks was alsO investigated[26]. Samples containing 25-35 % calcareous marl calcined at 950^{o}C had the highest compressive strength (600 kg. Cm^{-2}).

Horio et.al.[27] studied the reaction between normal Portland cement and finely powdered quartz in suspension form under hydrothermal conditions (140-250^{o}C) for 0.5-6 hours. The hydration products were