STEAM-CURING OF BLASTFURNACE SLAG-ALITE PASTES

Presented to

Faculty of Science

Ain Shams University

Cairo

By

MAHMOUD AHMED TAHER

B. Sc.

Submitted in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

(Physical Chemistry)

1987

بسم الله الرحمن الرحيم

سبحانك لا علم لنا إلا ما علمتنا

إنك أنت العليم الحكيم

صدق الله العظيم

بسم الله الرحمن الرحيم

STEAM - CURING OF
BLASTFURNACE SLAG-- ALITE PASTES

Thesis Advisors

Approved

Prof. Dr. S.A. Abo-El-Enein — S. A. Abo-El-Enein

Prof. Dr. H. El-Diadamony Ahmed — H. El-Diadamony

Prof. Dr. M.A. Shater

Head of Chemistry Department

Nabil M. Guirguis

ACKNOWLEDGEMENTS

The present research work has been carried out under the supervision of :-

- **Dr. Salah A. Abo-El-Enein,** Professor of Physical Chemistry, Dept. of Chemistry, Faculty of Science, Ain Shams University, Cairo.
- **Dr. Hamdi El-Didamony,** Professor of Inorganic Chemistry, Dept. of Chemistry, Faculty of Science, Zagazig University, Zagazig.
- **Dr. Magda A. Shater,** Research Professor of Chemistry G.O.H.B.P.R., Dokki, Cairo.

To whom the author is deeply indebted for their unlimited assistances, critical reading of the entire manuscripts and for their general advices in the preparation of the dissertation.

The author wishes to express his great indebtedness to Dr. Adel M. Amin, Researcher of Chemistry, G.O.H.B.P.R., Dokki, Cairo.

Finally, particular gratidue is expressed to my father, mother and wife for their assistance and continuous encouragement during all phases of the preparation of the thesis.

CONTENTS

CHAPTER (I)

I. INTRODUCTION AND OBJECT OF INVESTIGATION

CHAPTER (I)

I. INTRODUCTION AND OBJECT OF INVESTIGATION

I. INTRODUCTION:

I.1. Introducing Remarks:

In the operation of blastfurnace , the iron oxides ore is reduced by means of cock to metallic iron, while the silica and alumina constituents combine with the lime and magnesia to form a molten slag which collects on the top of the molten iron at the bottom of the furnace. Blastfurnace slag issues from the blastfurnace as a molten steam at a temperature of 1400-1500°C. Its conversion into products suitable for various usage depends on the subsequent processing; widely different products are obtained according to the kind of process used in cooling the molten slag.

When the slag is allowed to cool slowly, it solidifies into a grey, crystalline, stony material, known as air-cooled, lumps or dense slag. This forms the material used in a road-stone and as a concrete aggregate. More rapid chilling with a limited amount of water, applied in such a way as to trap stream in the mass, produces a porous, boneycombed material which resembles pumice. This light-weight material is called foamed slag and after crushing and grinding is used as a light-weight aggregate.

Slag woll is normally made by reheating cold slag from a slag bank sometimes with added siliceous or other materials. The process is carried out in cupola from which the remelted slag is tapped in thin stream. As it issues from the tap hole it is chilled quickly by means of a jet of air; or air and steam, crushing the slag to form vitreous threads which felt together into a light-weight mass. The product is an excellent thermal insulator.

Slag which is to be used in the manufacture of the various slag cements is chilled very rapidly either by pouring into a large excess of water or by subjecting the slag steam to jets of water, or of air and water. The process is to cool the slag so quickly that crystallization is prevented and it solidifies as a glass. At the same time the quenching breaks up the material into small particles varying from glassy beads to light-weight mass. The product is called granulated slag and is principally used as cement of one type or another. Minor quantities are sold for glass-making, as a branive, or as a sand for concrete.

The chemical composition of slag can vary over a wide range depending on the nature of the ore, the composition of the limestone flux, the cock consumption, and the kind of iron being made. It can also change over the years with alterations in the sources and kinds of ore being melted. These variation, affect the relative contents of the four major constituents, lime, silica, alumina, and magnesia, and also the amounts of the minor components, sulphur in form sulphide, and ferrous and manganese oxides. In general the lime content may range from 30 to 50 %, silica 28 to 38 %, alumina 8 to 24 %, magnesia 1 to 18 %, sulphur 1 to 2.50 % and ferrous and manganese oxide 1 to 3 %, except in the special case of ferro-manganese production when the manganese oxide content of slag may be considerably higher[1].

Alite is the principal cementing constituent in Portland cement. Very detailed X-ray work [2] showed that the phase formed in Portland cement contains MgO and Al_2O_3 and differs slightly from pure C_3S (called alite).

The alite in Portland cement is not pure C_3S but contains various other oxides in solid solution[3] and these have some influence on its strength. The more significant of these are MgO, Al_2O_3 and Fe_2O_3. The Mg^{2+} ion substitute, directly for Ca^{2+} with a limit of about 2 % MgO weight replacement at 1500°C. The limit of solubility of Al_2O_3 is about 0.9 % weight, 3 Al^{3+} ions replacing 3 Si^{4-} ions, the balance of charge being maintained by the introduction of Al^{3+} in interstitial positions. When MgO and Al_2O_3 are taken into solid solution only 1 % MgO is required to stabilize the monoclinic form of C_3S to room temperature, but when the content of each is below about three-quarters of their individual saturation values the triclinic form is found. Fe_2O_3 dissolves in C_3S to the extent of 1 % Fe_2O_3 by weight at 1400-1500°C as a solid solution of hypothetical C_3Fe in C_3S. The limit of solubility is unaffected by the simultaneous presence of Al and Mg ions.

1.2. The Hydrothermal Treatment of Blastfurance Slag:

Granulated blastfurnace slag, because of its low water requirements, low heat of hydration, low volume change and high corrosion resistance, is now widely used in cements as well as in autoclaved building materials.

This main advantages favour the use of slags in autoclaved materials; these are: (i) omission of the process of combining lime, and (ii) economization of lime stone and fuel.

In most of the hydrothermal reaction involving blastfurnace slag, lime (or hydrated lime) or Portland cement clinker were always used as activators for slag hydration[4-10].

Papuashvili and others[11], studied the autoclave hardening of slag binder and showed that in highly reactive mixtures the unreacted $Ca(OH)_2$ was high at low autoclaving pressures and decreased as the autoclaving pressure was raised. In comparison with spong alite-lime mixtures, the slag - CaO mixtures were less cementatious and exhibited lower compressive strength. The results also showed that autoclaving pressures of about 2 atm. yielded highest compressive strength for variously reactive specimens.

In 1972, Fender[12] studied the effect of steam curing on the hardening of slag Portland cement, made by mixing granulated blastfurnace slag and Portland cement clinker and the resulting mixture was ground with gypsum to attain a mixture with a specific surface area of 3500-4000 cm^2/g. The slag-Portland cement was steam cured for 3 + 6 + 4 hours at 95°C. The compressive strength of samples cured under normal conditions and of steam - cured samples (183, 284 kg/cm^2) were determined after 7 days with a water/cement ratio of 0.40.

In 1972, a method was developed(13) to determine the optimum amount of the individual components of autoclaved binders required to provide a maximum strength of the products. In order to arrive at the composition of the cement, the maximum amount of CaO has to be determined bound to a slag on steam curing. In this case the ratio of $CaO:SiO_2$ was assumed to be 2.00. The amount of ground sand or lime has then to be calculated providing a $CaO:SiO_2$ ratio of 0.9 - 1.2. Formula was given in order to calculate the amount of lime, sand and free CaO.

Kamel(14), established the optimum autoclaving conditions for a Portland blastfurnace slag cement. Autoclaving for longer time or at higher pressure gave lower strength due to metastable phase formation. It was found that the presence of fine sand does not cause any difference in optimum autoclaving conditions.

Other investigators (15), showed that granulated blastfurnace slags from Egyptian metallurgical plants consisted of β-C_2S, gehlenite, $CaCO_3$ and glassy slag when ground with cement clinker in a ball mill, gypsum was added to control the setting time. Steam cured specimens give a higher compressive strength than those cured near normal conditions.

In 1977, Japanese Scientists(16) made a light-weight building material with a good fire-resistance by mixing blastfurnace slag with lime, gypsum and amosite. The mixture was stirred at 70°C for 6 hours, cooled, moulded, pressed, kept at room temperature for 24 hours, steam cured at 80°C for 3 hours and dried at 100°C, the moulded product had a compressive strength of 21 kg/cm^2.

Karl et al[17] mixed lime with slag 7.95 : 92.05 % or lime, cement and slag 4.5 : 4.5 : 91 % with required water amounts. The strengths were 165-180 and 240-245 kg/cm^2, respectively, while a control with pulverized slag had strength of $\leqslant$ 150 kg/cm^2.

Kamel and Shater[18], studied the suitability of granulated blastfurance slag and lime as a binder for autoclaved calcium silicate bonded building materials. They found that the strength developed by autoclaving slag-lime binders was close to that obtained with Portland cement. The autoclaved pastes contained tobermorite as the predominant phase and some xonolite and hillebrandite. Hardening of quartz sand, blastfurnace slag, β-C_2S containing slurry, water and lime mixtures was also studied under hydrothermal treatment in relation to the use of mixtures of deep wells giving good mechanical strength[19].

In a process of the manufacture of steam-hardened shaped articles of cement[20], water and slag as addition agents were used. The mixture was compressed and shaped in a mould then exposed to steam pressures of 7 - 15 atm. for 7 - 12 hours for producing particles having compressive strength of 1300-1700 kg/cm^2.

From the investigation of physico-chemical properties of blast-furnace slag[21], it was found that the granulated slag is a suitable siliceous raw material for the autoclave production of porous concrete, especially in combination with silica sand with the addition of lime as a binder.

Mironov et al [22], studied the effect of acidic and basic blast-furnace slag, on the properties of slag Portland cement, by determining the optimum amount of slag required which depends on the hardening condition, quality of the initial clinker and slag. The addition of large amounts $\leqslant$ 80 % of basic slag, decreases the cement strength. On the other hand, the addition of $\leqslant$40 % slag has no marked effect on cement hardening and strength. But hydrothermal treatment decreases the difference between the strength of cement containing 40 and 80 % of slag.

I.3. Alite Under Hydrothermal Conditions:

Alite is tricalcium silicate aluminate or tricalcium silicate (C_3S), also it has the name Monoclinic• alite[23] which stabilized with Al_2O_3, Fe_2O_3 and/or MgO.

The hydrothermal hardening of alite results in a liberation of a larger amount of free $Ca(OH)_2$; therefore, it can be utilized as an important substance for the manufacture of autoclaved products envolving granulated blastfurnace slag. The calcium hydroxide liberated, as a result of the hydrosthermal curing of alite, activates the hydration