Pergamon

Cement and Concrete Research, Vol. 25, No. 2, pp. 332-338, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00018-6

ACTIVATION OF GYPSUM ANHYDRITE -SLAG MIXTURES

Manjit Singh and Mridul Garg
Scientists
Central Building Research Insitute, Roorkee (India)

(Refereed)
(Received June 17, 1993; in final form October 27, 1994)

ABSTRACT

Gypsum anhydrite-slag mixtures were produced by blending anhydrite with granulated blast furnace slag, $Ca(OH)_2$ and small amounts of $Na_2SO_4.10H_2O$ and $FeSO_4.7H_2O$ as activators. A mechanism of conversion of anhydrite into gypsum through transient double salts in presence of activators is suggested. Activation of granulated slag with the gypsum anhydrite and $Ca(OH)_2$ to form ettringite and tobermorite has been discussed. The correlation between gain in strength and hydration products is reported.

Introduction

Over 4 million tonnes of phosphogypsum and 10 million tonnes of slag are produced annually from phosphoric acid fertilizer and steel plants in India. Phosphogypsum has limited scope of utilization as building material due to presence of P_2O_5, F, organic matter, alkalies in it as impurities. Impairment of strength and workability by these impurities has been reported earlier (1,2). Several processing techniques and uses of phosphogypsum have been suggested by various workers (3,5). Unlike phosphogypsum, the slag has also been used to small extent mainly in the production of blended cements.

To invigorate the increased application of phosphogypsum and blast furnace granulated slag together, investigations were carried out to inactivate the impurities of P_2O_5 and F in the phosphogypsum at elevated temperature so that it can be easily blended with the slag. Phosphogypsum was calcined at 700-800°C to make β-anhydrite. It is well known that gypsum anhydrite reacts with water very slowly and therefore, it has to be activated by the activators particularly alkali/alkaline sulphates, carbonates or combination of small quantities of portland cement, $Ca(OH)_2$ and alkali sulphate (6).

The present paper brings out the mechanism of strength development in the gypsum anhydrite - slag mixtures. The role of activators in transferring the gypsum anhydrite to gypsum and combination with granulated slag to form basic cementitious materials is reported.

Experimental

Materials

Phosphogypsum anhydrite (produced by calcination at 750°C for 4 hours) and granulated blast furnace slag of chemical composition (Table 1) were used for the preparation of gypsum anhydrite-slag mixtures.

Activators

Analytical grade $Ca(OH)_2$,Na_2SO_4. $10H_2O$ and $FeSO_4$. $7H_2O$

TABLE - 1

Chemical Composition of Phosphogypsum Anhydrite and Slag (wt.%)

Constituents	Phosphogypsum Anhydrite	Slag
P_2O_5	00.69	-
F	00.97	-
Organic matter	-	-
SiO_2 + insoluble in HCI	01.26	33.83
R_2O_3 (Al_2O_3 + Fe_2O_3)	00.50	22.93
CaO	38.60	34.93
MgO	00.06	07.46
SO_3	54.20	-
Mn_2O_3	-	00.099
S	-	00.84
Loss on Ignition	00.32	00.00

Preparation and Evaluation of Gypsum Anhydrite-slag Mixtures

Gypsum anhydrite (Fineness, 3500 cm^2/g) was blended with the ground granulated slag (Fineness, 4200 cm^2/g) in the proportions; 70:24, 65:30, 60:35 and 50:50 parts by weight containing $Ca(OH)_2$ (2-3%), Na_2SO_4. $10H_2O$(1.5-2%) and $FeSO_4$. $7H_2O$ (1.0-1.5%) by the weight of gypsum anhydrite-slag mixtures respectively. These proportions were designated as L,R, Q and N. The selection of Na_2SO_4. $10H_2O$ and $FeSO_4$. $7H_2O$ activators is mainly based on the work reported earlier (7).

The gypsum anhydrite-slag mixtures were tested for physical properties such as consistency, setting time, compressive strength, water absorption, chemically combined water and soundness as per IS:4031-1968, Specification for methods of physical testing for hydraulic cements, IS:2542 (part 1)-1978, Specification for methods of test for gypsum plaster, concrete and products and IS:6909-1973, Specification for supersulphated cement.

The 5 cm. cubes of gypsum anhydrite-slag mixtures were cured at 27°C over 90% RH for a period of 1 day to 28 days.

The formation of hydraulic products during progressive hydration of gypsum anhydrite-slag mixtures were monitored by differential thermal analysis (DTA) (Stanton Red Croft Simultaneous thermal analyser 1200 UK) at rate 10° using α-Al_2O_3 as control material and infra red spectroscopy (IR) (IR Model 833, Perkin Elmer U.K.).

Results and Discussion

Evaluation of Gypsum anhydrite-slag mixtures

The physical properties of gypsum anhydrite-slag mixtures are depicted in Table - 2. It can be seen that mix composition N has comparatively lower values of consistency, setting time, water absorption, soundness (expressed as cold expansion) and higher values of chemically combined water than the mix compositions L, R and Q. However, the chemically combined water was found to increase with the progress of hydration from 1 day to 28 days in all the compositions. The enhancement in the chemically combined water with increase in the curing period may be ascribed to the increased formation of dihydrate gypsum from the anhydrite. The effect of curing period on the strength development of gypsum anhydrite-slag mixtures is shown in Fig. 1. Data show increase in the strength with the inrease in curing period. Maximum compressive strength was obtained for the mix composition N.

Hydration of Gypsum Anhydrite-Slag Mixtures

Anhydrite possesses close packing of Ca^{2+} and SO^{2-}_4 ions and therefore it either does not combine or reacts very slowly with water. It is, therefore, important to activate the

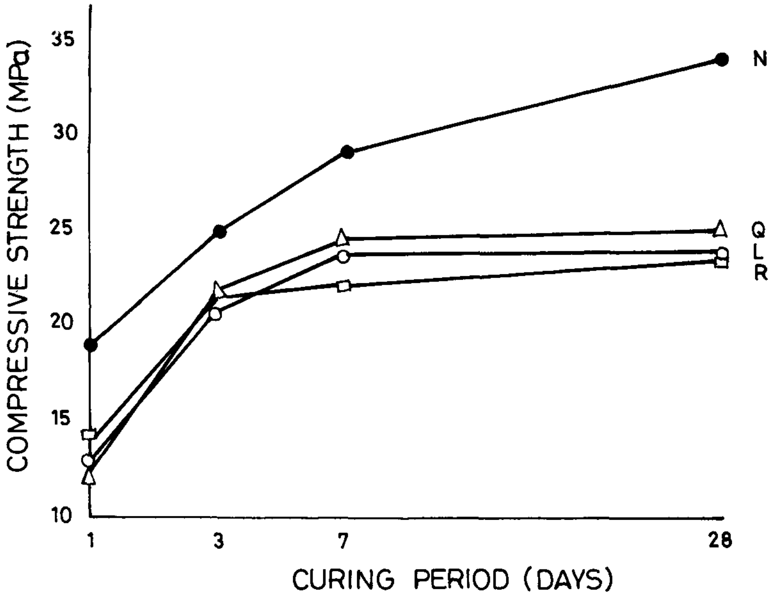

FIG.1

Effect of curing period on compressive strength of gypsum anhydrite-slag mixtures

TABLE - 2

Physical Properties of Gypsum Anhydrite-Slag Mixtures

Mixes Gypsum anhyd-rite-slag	Consis-tency (%)	Setting time (Minutes) Initial	Final	Water Absorp-tion (%)24h	Sound-ness Expn. (mm)	Chemically combined water (%) 1d	3d	7d	28d
70 24 (L)	28.42	90	300	10.84	0.81	3.8	5.1	5.1	5.36
65 30 (R)	28.50	75	240	10.50	0.80	3.8	5.2	5.41	5.60
60 35 (Q)	27.80	65	210	10.01	0.76	3.91	5.4	5.60	5.66
50 50 (N)	27.42	54	186	09.55	0.70	4.0	5.4	5.68	5.84

setting and hardening of gypsum anhydrite-slag mixtures. In order to find out the effect of different activators on the strength development of anhydrite-slag mixtures, the DTA and IR of hydrated product of mix composition N was chosen obviously on the basis of attaining maximum strength. The results are reported below:

DTA

Fig. 2 clearly manifests formation of two endotherms at 145-150°C and 200-220°C due to presence of ettringite ($C_3A.\ 3CaSO_4.\ 32H_2O$) and gypsum. Endotherms at 145-150°C are predominent and reduced with the increase in the curing period from 1 to 28 days. However, the endotherms at 200-220°C are increased with the progress in curing on account of enhanced inversion of anhydrite into gypsum. The exotherms at 372-413°C and 880-890°C may be attributed to the inversion of $CaSO_4$ (III)→$CaSO_4$ (II) and devitrification of slag respectively. No endotherm was observed for tobermorite (CSH) at lower temperatures (120-140°C), probably overlapping with the ettringite could have been occurred.

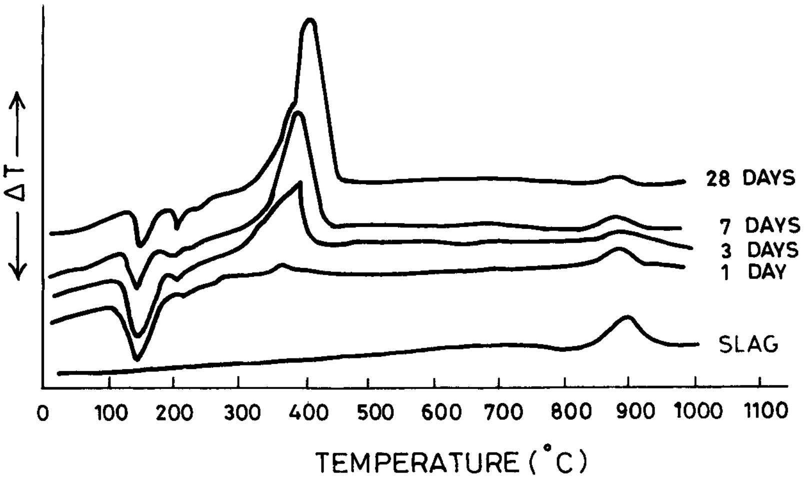

FIG. 2
DTA of gypsum anhydrite-slag mixture N hydrated for different curing period

IR

IR of anhydrite-slag mixtures hydrated for different periods is shown in Fig. 3. The absorption bands of gypsum (602,616,1145,1624,3410 cm^{-1}) ettringite (1116, 1130, 2244,2432 cm^{-1}) unreacted anhydrite (598, 674 cm^{-1}) and slag (242,254,264, 270, 468, 1358, 1486, 2344, 2932 and 2432 cm^{-1}) can be identified in anhydrite-slag mixtures, hydrated from 1 to 28 days. No absorption band for tobermorite was found in the 1 dav cured samples. Tobermorite (920,1000,1040 cm^{-1}) bands can be noticed in 3, 7 and 28 days cured samples. No absorption bands however, were detected for the complex such as $Na_2SO_4Fe_2(SO_4)_3$, Na_3FeSO_4. $3H_2O$ and Na_2SO_4. $CaSO_4$.

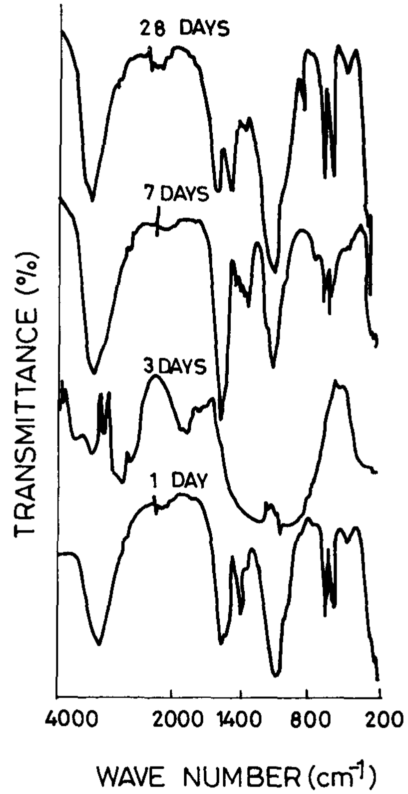

FIG. 3.

IR Spectra of gypsum anhydrite - slag mixture N hydrated for different curing periods

On the basis of the results obtained form DTA, and IR, the strength development in the anhydrite-slag mixtures (Fig 1) can be correlated with the hydration of gypsum anhydrite and slag duly activated by chemical activators. The plausible mechanism for the attainment of strength in the gypsum anhydrite seems to take place by the production of dihydrate gypsum ($CaSO_4$. $2H_2O$) through the formation of transient unstable salts (Na_2SO_4. $Fe_2(SO_4)_3$.Na_3FeSO_4.$3H_2O$ and $Na_2SO_4CaSO_4$) during hydration. These salts are formed by the concentration of colloidal particles of activators on the molecules of anhydrite ($CaSO_4$) upon their surface in the unsaturated solution. As a result, potential nucleating centres are established by the concentration of colloidal particles of activators on the molecules of anhydrite ($CaSO_4$) upon their surface in the unsaturated solution. As a result, potential nucleating centres are established around which crystallization starts in when solution turns supersaturated. The unstable salts are decomposed to various ions (Ca^{2+} ions, activator cations, SO_4^{2-} ions) binding water to anhydrite to form interlocking needles interspersed with prismatic and tabular shaped crystals. Hence the role of activators may be contemplated to increase the rate of dissolution of anhydrite.

$$\underset{\text{Anhydrite}}{CaSO_4} \xrightarrow[Na_2SO_4.10H_2O]{H_2O} Ca^{2+}+SO^{2-}_4 + Na^+ \xrightarrow{H_2O} \underset{\text{gypsum}}{CaSO_4.2H_2O} \quad \ldots\ldots\text{ (1)}$$

$$CaSO_4 \xrightarrow[FeSO_4.7H_2O]{H_2O} Ca^{2+}+So_4^{2-} + Fe^{3+} \xrightarrow{H_2O} CaSO_4.2H_2O \quad \ldots\ldots\text{ (2)}$$

The formation of gypsum, thus involves a dissolution-nucleation growth process. The above mechanism can be linked with the findings of Hajjouji and Murat (8) who have established that the nucleation rate is very specific to the nature of the metallic cation employed as "Chemical activator" to accelerate the setting and hardening of the gypsum anhydrite. According to them, the formation of gypsum crystal size does not depend on the growth rate but actually on the nucleation rate. With the increase in the nuleation rate, gypsum crystal and porosity are reduced and consequently the nigh strength of the hardened anhydrite is attained. The increased transformation of gypsum from anhydrite with the increase in the curing period can be correlated with the increase in the intensity of gypsum endotherms (Fig. 2.).

Besides conversion of anhydrite into gypsum, the activation of granulated slag takes place when anhydrite combines with Al_2O_3 contributed by the slag in presence of $Ca(OH)_2$ to form ettringite ($C_3A.\ 3CaSO_4.32H_2O$). $Ca(OH)_2$ interacts with SiO_2 content of slag to form tobermorite compounds. $Na_2SO_4.10H_2O$ can also effect the enhancement of early strength of slag. The mechanism of the reaction is yet to be established. However, Yuan and Xin (9) have shown that a synthetic $C_3A\bar{S}_3H_{32}$ is formed if the $CaSO_4/Al_2O_3>3$ in the raw materials. If the ratio is between 1-3,the hydration products may contain the ettringite in two types: high and low sulphur or solid solution of low sulphur type of ettringite and $C_4AH_{13,}$ if $CaSO_4/Al_2O_3<3$, the solid solution of metastable product and C_4AH_{13} may be formed. In the alkali slag system, SO^{2-}_4 ions penetrate into the vitreous phase of slag disturb the stati electric balance of the system, cause the rupturing of slag, thereby improving the reactivity of slag. At the same time the presence of SO^{2-}_4 effects the CaO/SiO_2 and H_2O/SiO_2 parameters of CSH phase. It penetrates the CSH and changes the composition and structure of CSH.

Conclusions

1. The gypsum anhydrite-slag mixtures of low water absorption, high strength and high stability can be produced by blending in equal proportions, duly accelerated by small

quantities of $Ca(OH)_2$ and chemical activtors ($Na_2SO_4.10H_2O$ + $FeSO_4.\ 7H_2O$).

2. The attainment of high strength in the anhydrite - slag mixture is due to rapid conversion of anhydrite into gypsum, through formation of double salts with the activators and due to formation of ettringite and tobermorite compounds.
3. The development of high strength and stability of anhydrite - slag mixtures may be utillized in making prefabricated building materials such as boards, tiles, artificial marble, masonry etc.

Acknowledgement

The work reported in this paper forms a part of normal research programme at the Central Building Research Institute, Roorkee (India), and is published by permission of the Director. Thanks are due to Shri R.S. Srivastava, and Shri S.K. Malhotra, Scientists for carrying out IR and DTA of the samples respectively.

References

1. Manjit Singh, Effect of Phosphogypsum impurities on the morphology and physical characteristics of set plaster, 9th CIB Congress, Stockholm, Sweden, Vol. 4, pp. 239-250, (1983).
2. A.A. Tabikh and F.M.Miller, Cement and Concrete Research, Vol. 1, pp. 663-678. (1971).
3. Manjit Singh, Utilisation of by-product phosphosgypsum for building materials, Building Research Note No. 9, CBRI Publication, Roorkee, India, (1988).
4. Lee Koo Jong, Lee Kyong Won, Cho Duk Ho, Studies on utillization of by-product gypsum, Chem. Abstr. Vol. 115, 14219h, (1991).
5. H.Olmez and E. Erden, The effects of phosphogypsum on the setting and mechanical properties of portland cement and trass cement, Cement and Concrete Research, 19(3), pp. 377-384, (1989).
6. Manjit Singh, Mridul Garg and S.S. Rehsi, Durability of phosphogypsum based water-resistant anhydrite binder, Cement and Concrete Research, Vol. 20, No. 2, pp. 271-276, (1990).
7. Manjit Singh, Correlation between microstructure and mechanial properties of anhydrite cement, 14th Conference on Sillcate Industry and Silicate Science, Budapest, Hungary, May 6-10, pp. 172-178, (1985).
8. A. El Hajjouji and M. Murat, Strength development and hydrate formation rate. Investigation on anhydrite binders. Cement and Concrete Research Vol. 17.pp.814-822, (1987).
9. Chen Zhi Yuan and Liao Xin, the selection of simulation agents for alkali-slag cement, 9th Intl. Cong. on the Chemistry of Cement, New Delhi, India, Vol. III, Theme II, pp. 305-311, (1992).