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Hydraulic activity of water-cooled slag and air-cooled slag at different temperatures

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Abstract

Water-cooled slag (WS) and air-cooled slag (AS) with similar chemical compositions and produced from the same blast furnace were investigated for their hydraulic activities at different temperatures. The kinetics of hydration of WS–lime and AS–lime pastes were investigated at room temperature, 100°C, and 180°C by the determination of unreacted lime and combined water. The hydration products were identified by XRD. The variations in mechanical properties were correlated with the reaction kinetics and the types of the hydration products. The change in the mechanism of slag hydration was also predicted. The AS studied exhibited significant reactivity at room temperature. Increasing the temperature to 100°C has no significant effect on the reactivity of either type of slag except during early hydration. However, the reactivity of AS increased much more than WS with hydrothermal activation at 180°C. Calcium silicate hydrate (CSH) and plazolite formed in AS mixes. CSH, plazolite, and α-C_2SH formed in WS mixes at 180°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Air-cooled slag; Water-cooled slag; Calcium silicate hydrates; Gehlenite; Hydrothermal; Plazolite

1. Introduction

Cement containing water-cooled slag (WS) has long been used in Egypt. Alternatively, there are many other unexploited slag by-products, such as air-cooled blast furnace slag (BFS) and steelmaking slag, available. The feasibility of utilizing these types of slags has been ignored, due to the judgment that air-cooled slags (AS) are hydraulically unreactive. Consequently, little of these materials are used, or their use is limited to low value applications [1–3]. Based on the previous reported results [4–9], we conducted a comparative study [10] of the hydraulic reactivity of AS and WS produced from the same blastfurnace and the same raw materials. Although the reactivity of AS is lower than that of WS at room temperature, it is still can be exploited as a hydraulic material. Even, if these slags still cannot fulfill the requirements of the standard specifications for blended cements [11,12], their hydraulic activities can be exploited in building materials, such as autoclaved building materials or bricks. The latter may be an economical alternative for developing countries, since little technology is required.

Generally, utilization of by-products is not simply controlled only by their reactivities, because many solid waste by-products contain excess reactive silica and alumina. When these materials are blended with cements or used as ingredients in autoclaved building materials, silica and alumina can react and hydrates containing both silica and alumina may form. Among these are hydrogarnets ($C_3AS_XH_{6-2X}$), gehlenite hydrate (C_2ASH_8), and even zeolites [13]. Formation of them can lead to very different properties of the final products.

Studies in the system CaO–Al_2O_3–SiO_2–H_2O at room and higher temperatures contribute to our knowledge of the behaviour of different solid waste by-products and their hydration products. The general complexity and the practical difficulties of exploring reactions over a wide range of temperatures appear to have limited the practical studies

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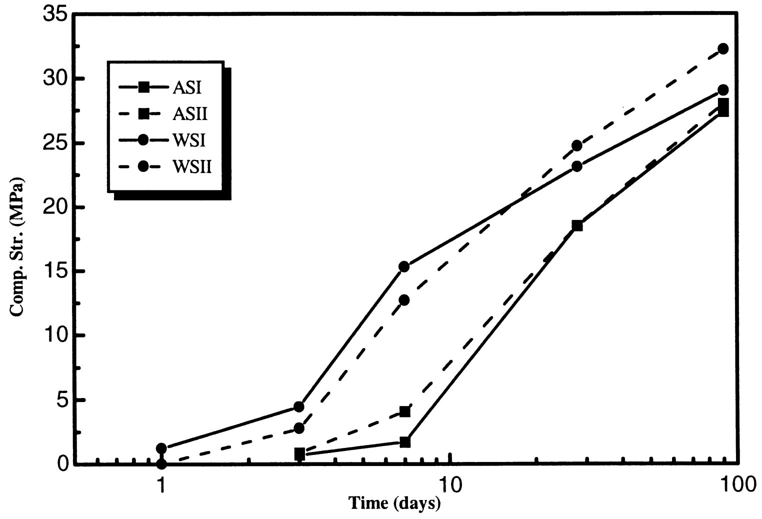

Fig. 1. Compressive strengths of AS–lime and WS–lime mixes cured at room temperature.

in this system [13–15]. In order to define the stability fields of these hydrates relative to those of C_3AH_6 and calcuim silicate hydrate phases (the main binding phases), the $CaO-Al_2O_3-SiO_2-H_2O$ system has been studied by many authors [16,17] using the thermodynamic calculations and solubility product data. Damidot and Glasser [16] defined the stable phases and assemblages of this system. At 25°C there are 37 phases assemblages coexisting with the aqueous phase, 1 invariant point, 18 boundary curves, and 9 hydrates. This study [16] also indicated the phase digram does not change significantly between 25°C and 85°C. The variations of the solubility products with temperature appear only to modify the positions of the crystallization surfaces of the hydrates. Variation in temperature does not induce new phases or destabilise others. However, this digram does not seem to be applicable for temperatures higher than 85°C above which;

- C_2ASH_8 is no longer stable [15].
- Calcium silicate hydrate (CSH) is transformed into crystallized Ca-silicate hydrate.
- Zeolite-type compounds, such as gismondine and phillipsite, may form.

The aim of this research is to evaluate the methods by which each type of slag can be employed in building materials by normal or higher temperature curing. In the present study, the kinetics of hydration and hydration products of slag–lime reactions were investigated in pastes at room temperature, 100°C, and 180°C. This

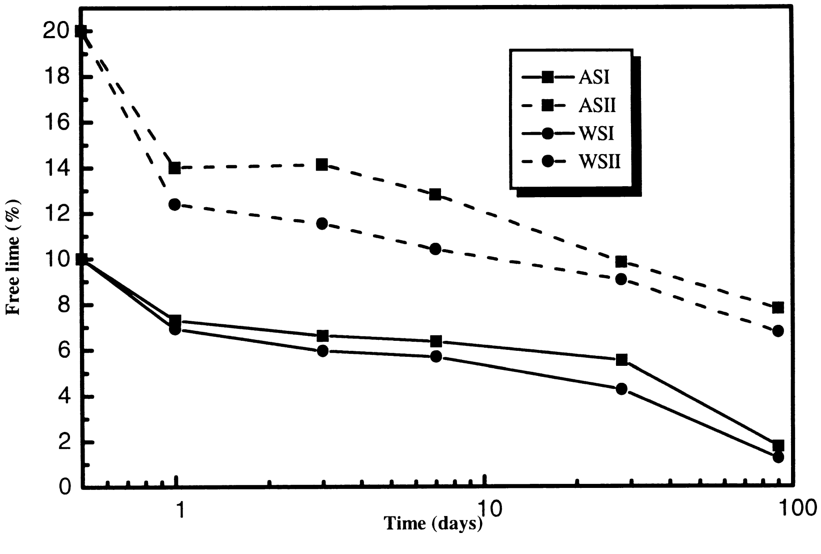

Fig. 2. Free lime contents of AS–lime and WS–lime mixes cured at room temperature.

Table 1
Combined water contents of AS and WS mixes cured at room temperature

	Combined water (%)				
Mix	1 day	3 days	7 days	28 days	90 days
WSI	1.36	1.81	2.16	4.83	5.34
WSII	2.39	2.65	3.31	5.38	5.46
ASI	1.06	1.70	2.20	3.99	3.77
ASII	2.10	2.32	2.69	4.74	3.73

investigation was carried out using pastes to correlate the physico-mechanical properties of the samples with the degree of hydration and with the hydration products that formed.

2. Materials and methods

The AS and the WS used throughout this investigation were obtained from Halwan Steel in Egypt. These slags were also obtained from the same blastfurnace. WS is produced by rapid cooling (quenching in water) to be used in the production of blended cement. AS is constrained to be produced by slow cooling in air due to inadequate granulation facilities. Slags were ground in a ball mill to attain a Blaine surface area of 300 m^2/kg. The WS and AS have nearly the same chemical composition. The X-ray diffractograms of WS show it to be completely vitreous. AS is composed of gehlenite ($Ca_2Al_2SiO_7$) although a glassy phase is also present. The details of the characterization of WA and AS are given in another paper [10].

Hydration kinetics of AS–lime and WS–lime reactions were followed using two mixes of each. Low-lime mixes (ASI) and (WSI) for AS and WS, respectively, contained 10% of $Ca(OH)_2$ and high-lime mixes (ASII) and (WSII) for AS and WS, respectively, contained 20% of $Ca(OH)_2$. The slag and hydrated lime mixes were prepared by mixing appropriate proportions of the starting materials in a ball mill for 1 h. All samples were prepared using a water/solid ratio of 0.22. Cylindrical specimens were moulded by hand in stainless steel moulds having a diameter of 2 cm and a height of 2 cm. They were cured at 100% relative humidity for 12 h to attain initial setting. The specimens were then cured as follows: at room temperature, in water, for 1, 3, 7, 28, and 90 days; at 100°C for 0.5, 1, 3, 7, and 14 days; and at 180°C for 0.5, 2, 6, 12, and 24 h.

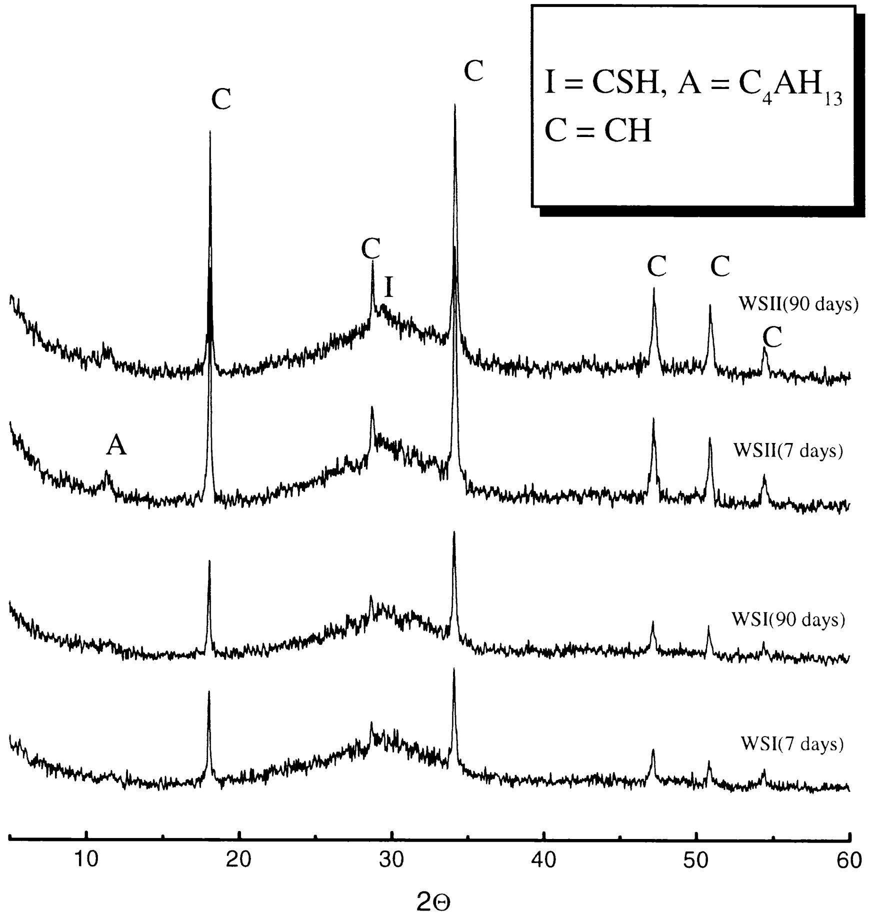

Fig. 3. XRD of WS–lime mixes cured at room temperature.

Samples cured at room temperature and 100°C were tested wet for their compressive strengths at each age. Samples cured at 180°C were tested for compressive strength after drying at 105°C for 24 h. A specimen from the core was then taken to complete the investigation. For phase analysis, hydration reaction were stopped by immersion of approximately 10 g of each ground specimen in about 100 ml of a (1:1) methanol/acetone mixture and stirred magnetically for 30 min. The solid sample was filtered off, washed with methanol, then dried at 105°C for 24 h. Free lime was determined using the modified Franke method [18]. The dried samples were also tested for combined water and examined by XRD. A Scintag/VAX 3100 XRD system with $CuK_{\alpha}1$ radiation was used. The combined water contents were calculated from the loss on ignition at 900°C after correction for the loss in weight due to free lime and the gain in weight due to the oxidation of ferrous iron and sulfides.

3. Reactivity at room temperature

The variations in the compressive strengths of the AS–lime and WS–lime mixes cured at room temperature with hydration age are shown in Fig. 1. The AS mixes show nearly no gain in strength in the first 3 days. However, the compressive strengths show marked increases at longer times. Mix ASII shows only slightly higher compressive strengths than mix ASI. These data reveal the low reactivity of AS at early ages (1–7 days) and higher reactivity at later ages of hydration (7–90 days) and the strength gain to be independent of the amount of CH present.

The WS–lime mixes generally show higher compressive strengths than the AS–lime mixes at all ages of hydration. This reflects the higher relative activity of WS with respect to AS, especially at early ages. Mix WSI shows slightly higher compressive strengths than mix WSII at early ages of hydration, but at later ages (28–90 days), the reverse occurs.

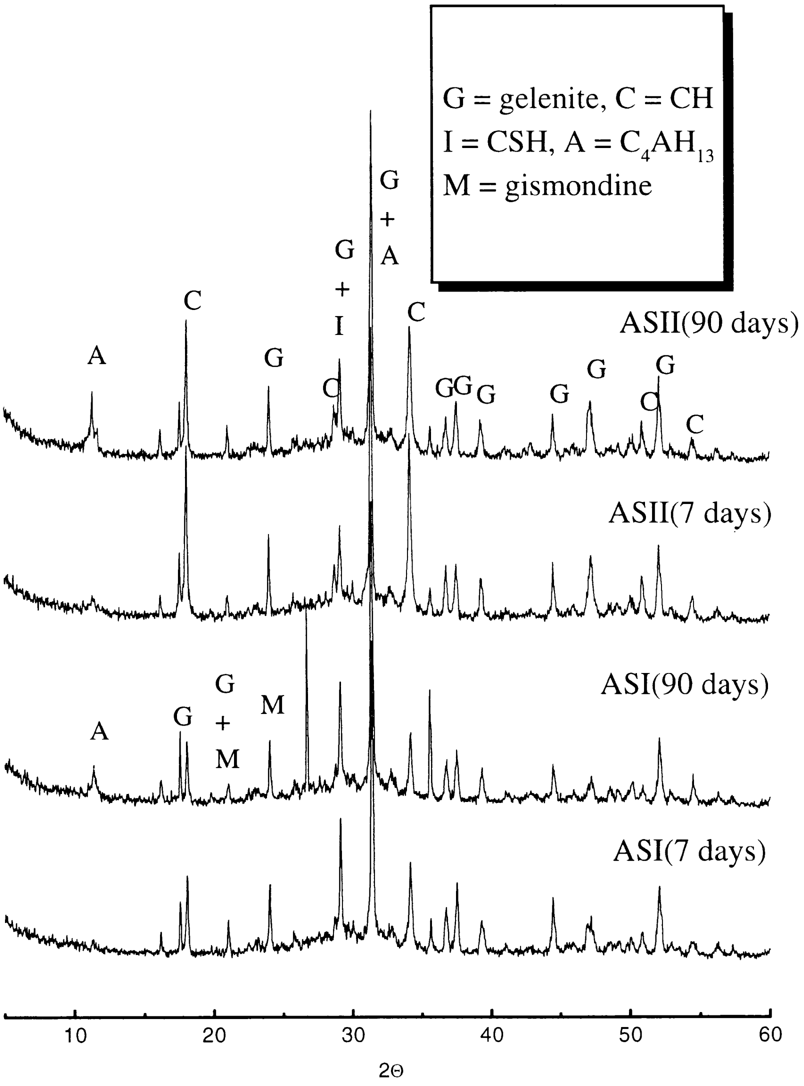

Fig. 4. XRD of AS–lime mixes cured at room temperature.

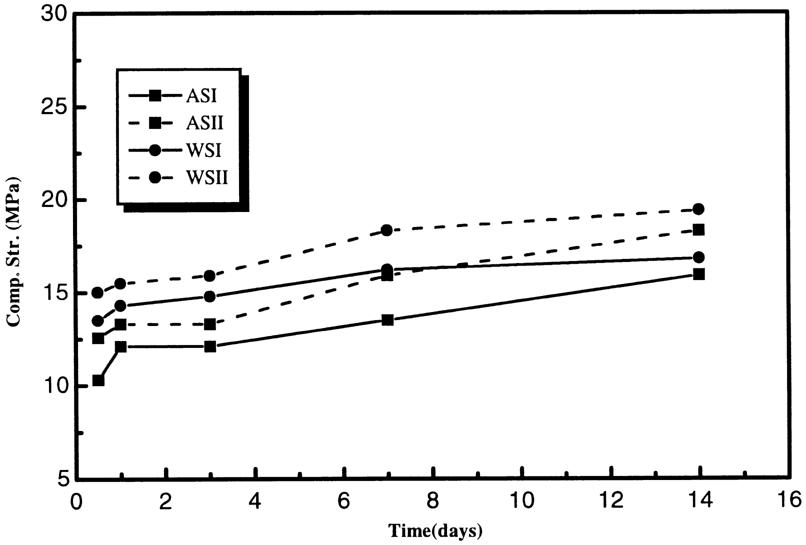

Fig. 5. Compressive strengths of AS–lime and WS–lime mixes cured at 100°C.

As with AS mixes, a strong dependence of the strength gain on CH content is not observed.

The kinetics of hydration of each mix were studied by determining the free lime contents and the chemically combined water contents (Wn) with hydration time. The results of the free lime determinations are shown in Fig. 2. The free lime contents decrease sharply during the first day in all mixes. This decrease is greater in high-lime mixes than in low-lime mixes. This indicates the initial rate of hydration depends on the initial lime content. It is well established that the rate of reaction during the initial period of hydration is governed by two processes: (a) nucleation and growth of the hydration phases, and (b) phase boundary interactions [19–21]. During this acceleratory period, the rate increases due to rapid surface hydration of AS and WS forming a coating of hydration products, which slow the subsequent reaction and eventually cause it to become diffusionally controlled. With additional hydration time, there are further slight continuous decreases in free lime at decreasing rates, up to 90 days. As expected, mixes ASII and WSII show higher free lime contents at all ages of hydration due to the higher the original lime content (20%). The differences between AS and WS reactivity at room temperature is confirmed by the lower free lime contents in the WS mixes.

Combined water contents (Wn) show a continuous increase with increasing hydration time up to 28 days for all mixes (Table 1). Mixes with higher initial lime contents (ASII and WSII) generally show the higher combined water contents up to 28 days. This confirms the increasing extents of hydration of both types of slags with increasing the initial mixing lime contents. After 28 days, the combined water increases marginally for WS mixes but declines for AS mixes. The results of combined water

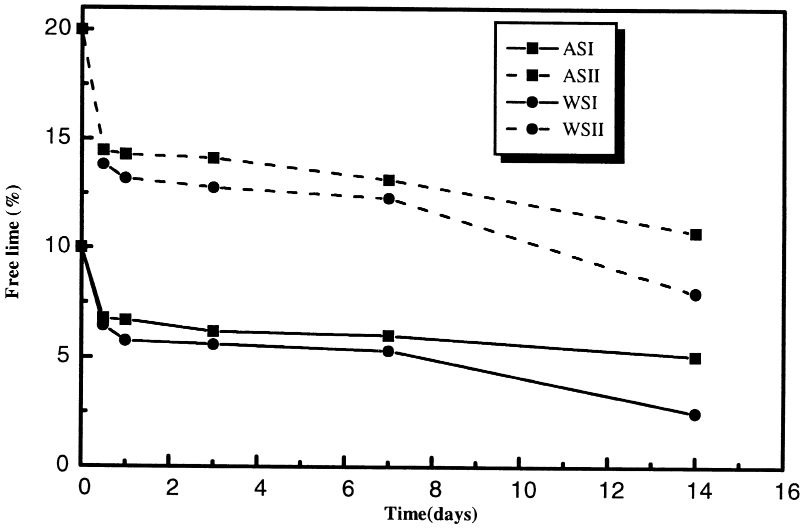

Fig. 6. Free lime contents of AS–lime and WS–lime mixes cured at 100°C.

Table 2
Combined water contents of AS and WS mixes cured at 100°C

	Combined water (%)				
Mix	0.5 days	1 day	3 days	7 days	14 days
WSI	2.03	2.65	2.51	2.38	3.31
WSII	3.14	3.59	3.60	3.61	4.12
ASI	2.27	3.21	3.30	3.32	3.78
ASII	2.92	3.35	3.41	3.34	3.89

contents support the conclusion that the reactivity of WS is higher. Thus, the compressive strengths, free lime values, and Wn values are consistent.

The variations in the XRD patterns of the WS–lime mixes and AS–lime mixes cured at room temperature for 7 and 90 days are shown in Figs. 3 and 4, respectively. The main phase detected is CSH. Calcium aluminum oxide hydroxide hydrate (C_4AH_{13}) [JCPDS# 33-0255] appears in both AS mixes but only in the high-lime WS mix (WSII). The zeolite gismondine ($CaAl_2Si_2O_8.4H_2O$) [JCPDS# 20-0452] forms in the low-lime mix (ASI) by 90 days.

4. Reactivity at 100°C

The compressive strengths of slag mixes hydrated at 100°C for 0.5, 1, 3, 7, and 14 days are shown in Fig. 5. At this temperature, the compressive strengths of high-lime mixes (ASII and WSII) are higher than that of low-lime mixes (ASI and WSI) at all ages. WS–lime mixes continue to produce higher compressive strengths than the corresponding AS–lime mixes. This indicates the reactivity of WS is still higher than that of AS. The mixes show the most rapid increases in strength during the first 3 days of hydration. After that a slow continuous increase in strength with time is observed. These results illustrate the effect of increasing the temperature from room temperature to 100°C tends to primarily enhance early reactivity.

The results of the free lime determinations are shown in Fig. 6. The free lime contents show sharp decreases during the first 12 h of hydration, followed by slower continuous decreases. The changes in combined water contents are also prominent during early hydration (Table 2).

XRD patterns of WS–lime mixes and AS–lime mixes cured for 14 days at 100°C are shown in Fig. 7. Calcium

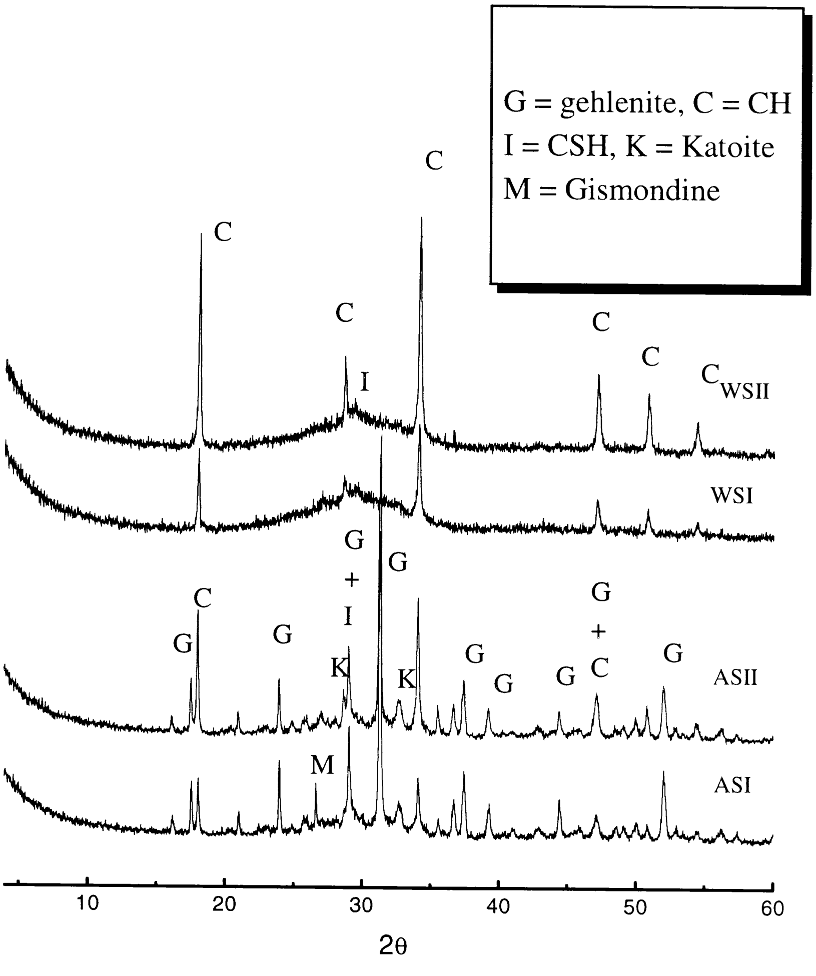

Fig. 7. XRD of WS–CH and AS–CH pastes cured at 100°C for 14 days.

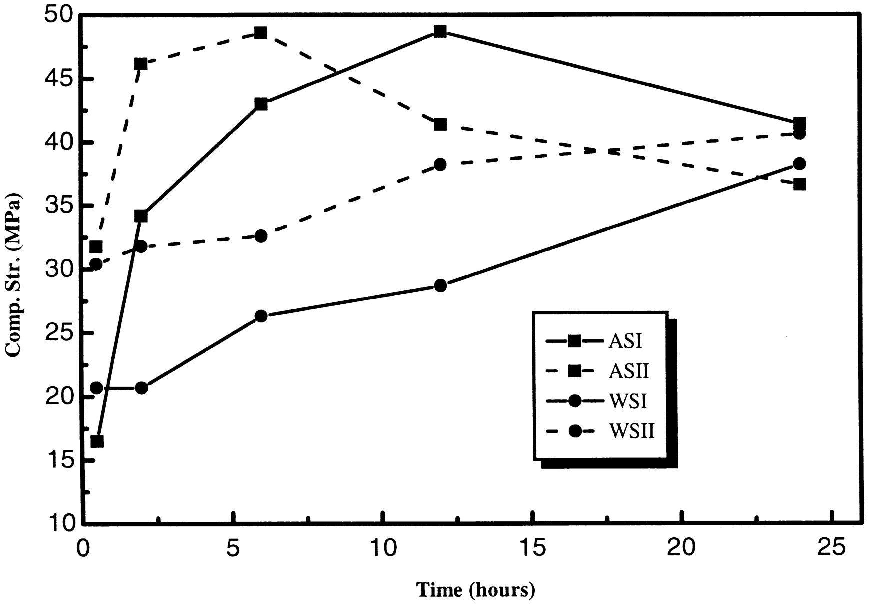

Fig. 8. Compressive strengths of AS–lime and WS–lime mixes cured at 180°C.

aluminum oxide hydroxide hydrate (C_4AH_{13}) [JCPDS# 33-0255] is unstable at 100°C, and its peaks are absent from all mixes. Rather, AS mixes produce katoite [JCPDS# 77-1713] (with the approximate composition $Ca_3Al_2(SiO_4)_{0.64}(OH)_9$). Katoite is a member of the hydrogarnet series. Gismondine ($CaAl_2Si_2O_8.4H_2O$) is still observed in mix ASI.

These results reveal that increasing the temperature to 100°C enhances both reactivity and strength gain during early hydration. However, hydration at 100°C has little effect on the diffusionally controlled later hydration.

5. Reactivity at 180°C

The changes in the compressive strengths of the slag–lime mixes with autoclave curing for 0.5, 2, 6, 12, and 24 h at 180°C are shown in Fig. 8. The compressive strengths of both AS mixes increase dramatically during the first 2 h. Further, slow strength gains occur and strength maxima appear to be attained. Mix ASII attains a strength maximum at 6 h whereas mix ASI reaches its maximum strength at 12 h. In contrast to curing at room temperature and 100°C, the compressive strengths of AS mixes exceed those of the WS

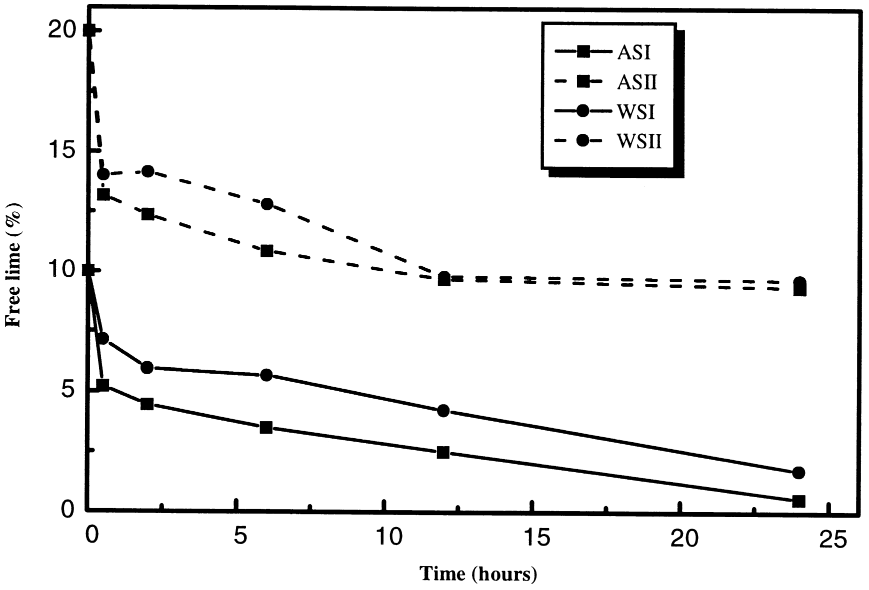

Fig. 9. Free lime contents of AS–lime and WS–lime mixes cured at 180°C.

Table 3
Combined water contents of AS and WS mixes cured at 180°C

	Combined water (%)				
Mix	0.5 h	2 h	6 h	12 h	12 h
WSI	1.06	2.10	3.12	3.99	3.77
WSII	2.10	2.32	3.41	4.74	3.73
ASI	2.76	3.55	4.98	6.80	6.90
ASII	2.60	3.33	4.48	5.23	5.47

mixes in the interval from 2 to 12 h. Mix WSII has a higher compressive strength than mix WSI at all autoclaving times but the difference between them narrows with increasing autoclaving time.

The results of free lime determination are shown in Fig. 9. The free lime contents of all mixes show sharp decreases during the first 0.5 h of hydration. After this, the free lime contents decrease at slow rates. The free lime contents of AS mixes are lower than those of the corresponding WS mixes at all curing times. This indicates the reactivity of AS to be higher than that of WS under these hydrothermal conditions.

Combined water contents (Wn), as shown in Table 3, increase with increasing curing time reaching nearly constant values at 12 h. The higher Wn values for AS mixes again illustrates the enhancement of AS reactivity associated with hydrothermal treatment. Generally, the combined water contents of mix ASI were higher than those of mix ASII.

XRD analyses confirmed the enhanced reactivities of both slags due to hydrothermal treatment. Fig. 10 shows a strong reduction in the hump characteristic of vitreous slag with increased autoclaving time and intensification of peaks characteristic of CSH. Calcium aluminum silicate hydrate (plazolite; $Ca_3Al_2(SiO_4)_{1.53}(OH)_{5.88}$), [JCPDS# 75-1690] is formed in both slag mixes. α-C_2SH [JCPDS# 81-1987] is present also in the high-lime mix (WSII) after 24 h of curing. Peaks characteristic of CSH and plazolite developed in the AS mixes (Fig. 11).

The relative increase in the compressive strengths of AS mixes compared to the WS mixes may be due to the formation of crystalline plazolite, which was previously reported to increase the strengths of compacts of BFS activated by cement and gypsum [22]. It seems the forma-

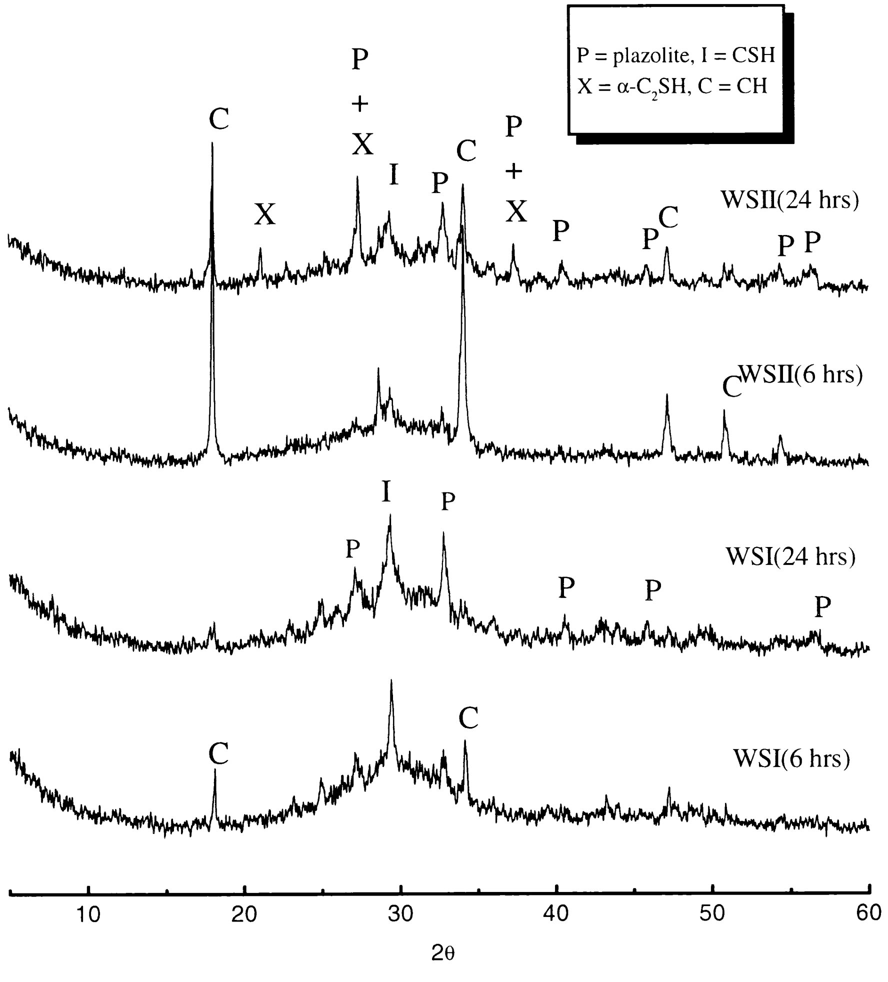

Fig. 10. XRD of WS–lime mixes cured at 180°C at different times.

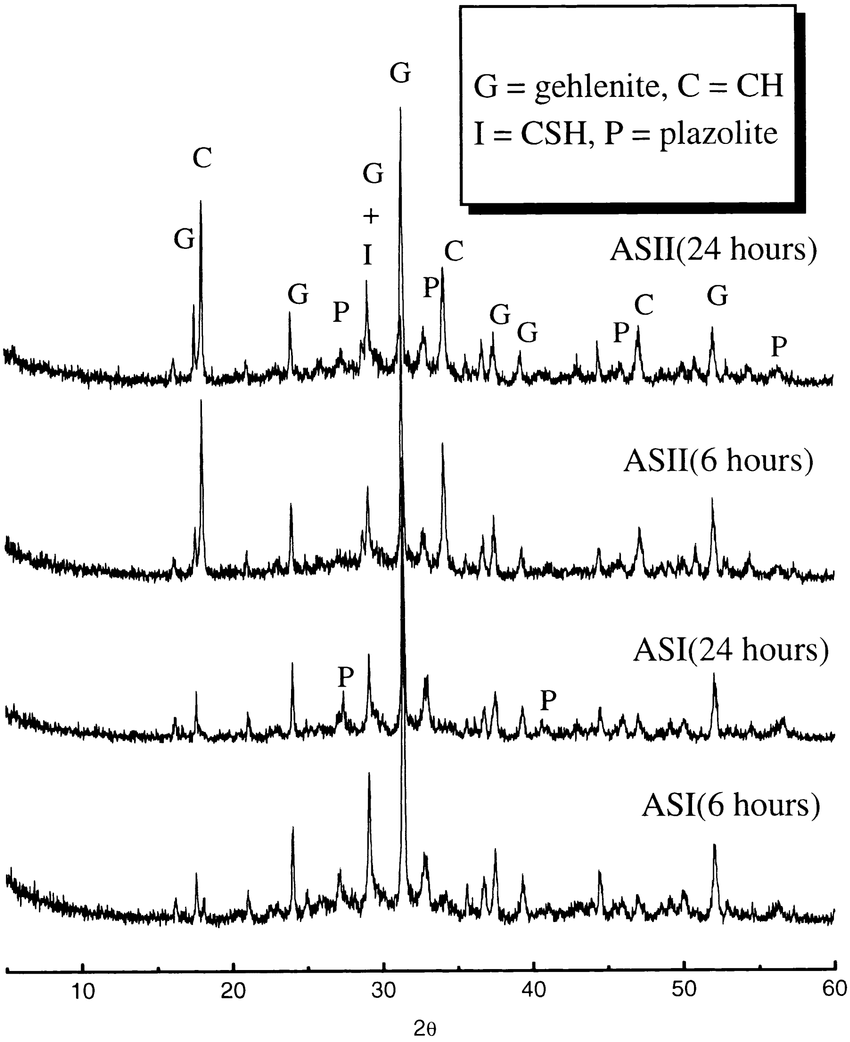

Fig. 11. XRD of AS–lime mixes autoclaved at 180°C at different times.

tion of hydrogarnets (plazolite) and α-C_2SH in WS mixes causes an enhancement of the strength. Alternatively, it well known that the formation of these compounds is associated with low strength [23]. In the present system, the water/solid ratio is very low (0.22), thus strength may be significantly enhanced by an increase in the amounts of crystalline materials. It is also well known that the strengths of cement pastes [24] and similar materials [25] depend on various factors including the porosity in particular and the relative proportions of dense crystalline materials and less dense, poorly crystalline materials.

6. Conclusions

Both AS and WS underwent hydration at room temperature. The hydraulic activity of AS is lower than that of WS, especially at an early age of hydration. Regardless, considerable strengths were attained at room temperature. Thus, AS of suitable compositions still can be exploited as hydraulic materials. Due to the lower ability of AS to fix lime, sufficient CH is present in both low- and high-lime AS mixes to form C_4AH_{13} in addition to CSH. Gismondine was also detected in the low-lime AS mix at 90 days of hydration. C_4AH_{13} formed only in the high-lime WS mix. deSilva and Glasser [13] studied phase equilibria in metakaolin–lime mixes and concluded C_4AH_{13} to be a metastable product which formed during the initial stages of hydration due to the initially high calcium and hydroxide concentration [26,27]. In the present study, C_4AH_{13} proved to be stable provided sufficient calcium and hydroxide remain in the pore solution.

Increasing the hydration temperature to 100°C increases only the early age lime–slag reaction and compressive strengths (up to 1 day). However, reaction at 100°C has little effect on the long-term hydration reaction rates of slags. Thus, the reaction rate appears to be governed by diffusional processes. Calcium aluminum oxide hydroxide hydrate (C_4AH_{13}) was not observed at 100°C. Rather, AS mixes produce hydrogarnet; katoite, and gismondine ($CaAl_2$-

$Si_2O_8{\cdot}4H_2O$) were still observed in mix ASI. Roughly comparing the final compressive strengths at room temperature and 100°C, the compressive strengths of mixes cured at room temperature for 28 and 90 days were much higher.

Hydrothermal treatments enhance the reactivities and the compressive strengths of both types of slag. The hydrothermal reactivity of AS is much higher than that of WS as indicated by the compressive strength, free lime contents, and combined water contents. Hydrothermal treatments intensify the formation of calcium hydrosilicate as well as the hydroganets (plazolite; $Ca_3Al_2(SiO_4)_{1.53}(OH)_{5.88}$) in both slag mixes. α-C_2SH is formed in the high-lime mix (WSII) after 24 h of curing. The formation of plazolite is associated with the development of high compressive strength, especially in AS mixes.

Acknowledgments

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