

Influence of Dispersing Agent in Formation of β -Dicalcium Silicate from Rice Husk

Syed Hassan Javed, Mohsin Kazmi, Umair Aslam* and Nadeem Feroze
*Department of Chemical Engineering, University of Engineering and Technology,
Lahore, 54890, Pakistan.
umairaslam@uet.edu.pk**

(Received on 3rd December 2012, accepted in revised form 19th April 2013)

Summary: Present experimental work describes the synthesis of β -dicalcium silicate from rice husk by using dispersing agent during formation of calcium hydro silicate (CSH) gel. The growth of CSH gel retards the impeller mixing phenomenon. This type of problem can be resolved by using dispersing agent. Amorphous silica was obtained from HCl treated rice husk. Calcination temperature of rice husk was maintained at 600 °C for 90 minutes. In the presence of water, amorphous silica was treated with calcium oxide by using 0.2 % dispersing agent to develop CSH gel. The CSH gel was developed in oven for 12 hours at 90 °C followed by drying at 105 °C for 12 hours in an oven. Dried gels were heated up to 900 °C to obtain beta form of dicalcium silicate. The CSH gel and β -dicalcium silicate were examined by XRD, FTIR, SEM and TGA. It was observed that by using pretreated rice husk truly amorphous silica can be obtained. It was also observed that dispersing agent facilitated the formation of CSH gel. Observations further revealed that such amorphous CSH gel started converting into beta form of dicalcium silicate at 600 °C.

Key words: Amorphous silica, Calcium hydro silicate gel, Dicalcium silicate, Dispersing agent, FTIR, SEM, TGA, XRD.

Introduction:

Dicalcium and tricalcium silicates are two major constituent of the Portland cement. Less CO₂ emission and low energy consumption to produce β -dicalcium silicate are main motivations to produce it commercially. Conventionally, Portland cement is produced by solid-state reactions carried out at around 1450 °C. It is a complex material having adhesive properties due to presence of di and tricalcium silicates. Beta form of dicalcium silicate appears at 1300 °C to 1350 °C whereas tricalcium silicate at 1400 °C to 1450 °C, during manufacturing process of Portland cement [1, 2]. Hydrothermal techniques at low pressure or at high pressure consume less energy to produce reactive β -dicalcium silicate [3, 4]. Particularly for hydrothermal techniques, silica should be in amorphous form for CSH gel formation. These gels are the mixtures of various types of CSH gels convertible to β -dicalcium silicate at low temperatures [5]. Among various sources to obtain amorphous silica, the rice husk is more suitable. Approximately 18% rice husk is obtainable from rice paddy. Nearly same percentage of rice husk ash (RHA) can be obtained from rice husk. Therefore, from every metric ton of paddy, ~180 kg of rice husk and ~32.5 kg good quality rice husk ash (RHA) can be obtained for commercial utilizations. Growing interest of utilization of this silica in synthesis of beta form of dicalcium silicate is motivated by economic implications and environmental problems [6, 7]. Because of low

consumption of CaO, low formation temperature and economic utilization of rice husk, dicalcium silicate is getting edge over conventional Portland cement [8].

Many papers [9-11] have addressed the synthesis of reactive β -dicalcium silicate by hydrothermal technique either at high pressure or at low pressure from RHA. Each method has its own advantages, characteristics and applications. Hydration behavior of β -dicalcium silicate obtained by hydrothermal techniques at high pressure is faster than at low pressure [12]. Generally, high pressure range varies from 16 to 20 atm and renders beta dicalcium silicate of large surface area. At normal pressure, β -dicalcium silicate is relatively of low surface area and takes longer hydration period.

Extracting silica in amorphous form from RHA without carbon contents is the basic need to produce CSH gel. Calcinating the rice husk at > 800 °C reduces both carbon contents and amorphous silica and eventually crystal silica dominates which acts as inert during CSH gel growth. On the other hand, calcinating the rice husk at < 600 °C, both carbon and amorphous silica dominate in RHA. The carbon contents and crystal silica both are obstructions in the amorphous CSH gel formation. Amorphous CSH gel is easily convertible into β -dicalcium silicate cement by thermal treatment [13].

*To whom all correspondence should be addressed.

Gel of CSH looks like flocks in morphology and absorbs large quantities of water during formation process. Presence of metallic compounds in rice husk is also responsible for incomplete burning and crystal formation in RHA. Metallic compounds are removable by treating the rice husk with acids of various strengths. Many researchers boiled rice husk with concentrated H_2SO_4 , HCl and HNO_3 and obtained white amorphous silica at 800°C [14, 15]. They reported that using hydrochloric acid, rice husk renders 97.64% amorphous silica. Rice husk boiled in HCl has its own disadvantages such as difficulties in self-burning and formation of complex compounds.

In sol-gel technique, formation of CSH gel takes place by using stoichiometric ratios of amorphous silica and calcium oxide in the presence of large quantities of water [16, 17]. Proper mixing improves the quality of the gel. By using impellers for mixing, the flocks of CSH gel grow as mixing proceeds. Such flocks become six to eight times larger by taking up the water and eventually terminate the mechanical mixing phenomenon. Properly formed CSH gel is usually amorphous in nature and convertible to reactive beta dicalcium silicate cement at relatively low temperatures. Practically by impeller mixing the formation of amorphous CSH gels is difficult to grow. This kind of problem can be resolved by using the dispersing agents.

In the present work above mentioned problems have been addressed by treating rice husk with dilute HCl and by using superplasticiser of carboxylic ether based with brand name Gelenium-51 (Degussa) as dispersing agent in CSH mixtures. The objective of the work was to obtain commercially viable reactive β -dicalcium silicate at low temperatures.

Results and Discussion

The XRD patterns generated for R1 and R2 by XRD machine are shown in Fig. 1. Both patterns have broad peaks diffused at 22.2° which is a characteristic of amorphous silica [18]. Pattern of R2 is not truly amorphous due to short peak at 26° indicating presence of crystal silica whereas R1 is truly amorphous silica. It is evident from these patterns that HCl treated rice husk (R1) generates truly amorphous silica by removing metallic compounds from rice husk. By appearance, R2 was black and R1 was white in color.

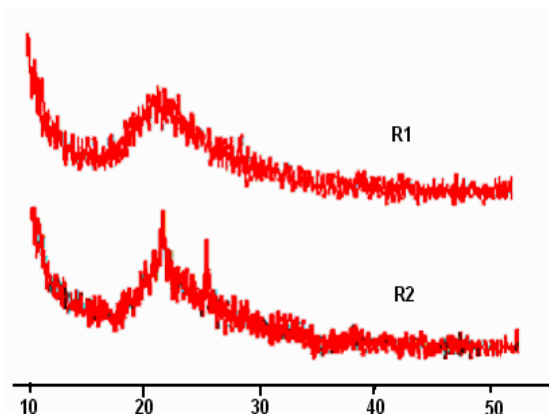


Fig. 1: XRD patterns of RHA. R1 from treated and R2 from untreated RH.

The quality of CSH gel is directly related to the quality of β -dicalcium silicate. The CSH gels were also analyzed by XRD machine to find out its amorphous nature. The XRD patterns of the CSH gels prepared from R1 and R2 are shown in Fig. 2. Gel obtained by using R1 is truly amorphous in nature (upper pattern) whereas lower pattern was obtained by using R2 which is not amorphous. Reaction between RHA and calcium hydroxide determines the pozzolanic property of amorphous silica. Many authors [19- 21] determined pozzolanic properties of silica by using this type of reaction and claimed that RHA is a better pozzolanic material. Particle size, burning conditions of RH, reaction temperature, pressure and time of reaction are the major precursors of CSH gels formation by sol-gel technique.

It was reported that at $<40^\circ\text{C}$, the mixture is combination of various CSH gels and become unconvertible to β -dicalcium silicate [22]. During synthesis of CSH gels the reaction temperature for mixtures in each case was maintained at 85°C to 90°C to eliminate negative thermal effects. In Fig. 2 the reaction conditions for both CSH gels were same. The upper XRD pattern is a product of complete reaction of CSH gel, however, lower XRD pattern represents the incomplete reaction, presence of crystals of R2 and calcium hydroxide. Therefore, product obtained from R1 is of our interest. It was also observed that product obtained without dispersing agent showed XRD pattern similar to lower pattern of Fig. 2. Comparing XRD patterns it is evident that role of dispersing agent was positive in formation of amorphous CSH gel within 12 hours. In fact dispersing agent provides the space for reacting particles.

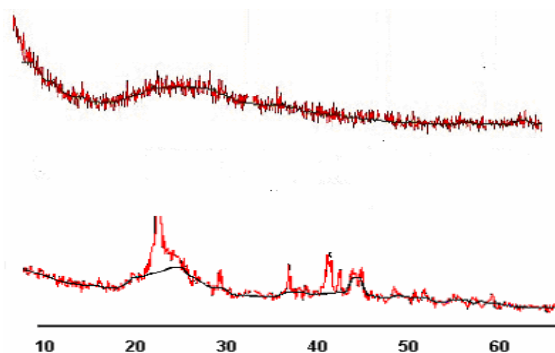


Fig. 2: XRD of Gels prepared from R1 (upper) and R2 (lower).

To investigate the effect of dispersing agent on surface morphology of CSH gels the SEM analyses was performed. In Fig. 3 the continuous phase of amorphous gel is visible. Amorphous gels usually are combinations of various calcium silicate phases. Such phases cannot be identified in present SEM. In Fig. 4 the phase is discontinuous and un-reacted particles either of calcium hydroxide or of un-reacted silica are visible.



Fig. 3: SEM of CSH gel prepared using pretreated rice husk.

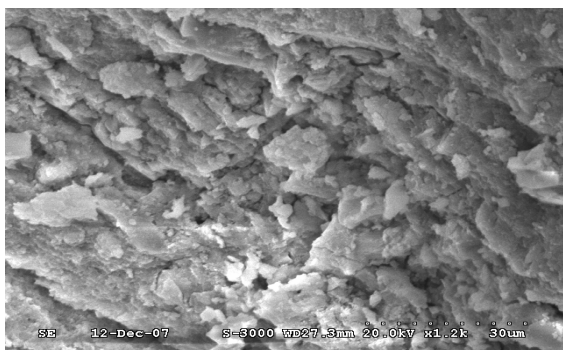


Fig. 4: SEM of CSH gel prepared using untreated rice husk.

The Chemical composition of CSH gels are strongly affected by Ca/Si ratio. For example, the Ca/Si = 2 renders beta form of dicalcium silicate whereas Ca/Si = 1 may form wollastonite. Mechanical strengths of such gels are not comparable to ordinary Portland cement. The dried gels are brittle, having weak strengths and may take long time to become stable by absorbing CO₂ from environment.

The CSH gels may acquire reasonable strengths if compressed to high pressure. The dried amorphous CSH gel is shown in Fig. 5.



Fig. 5: Dried white gel prepared from CaO and amorphous silica (Ca/Si=2).

The thermal degradation behavior of CSH gels was studied by thermal analyzer under nitrogen environment. To this end, the rise in temperature was adjusted to 10°C/min up to 1000°C. The thermal degradation behavior and the weight loss are shown in Fig. 6.

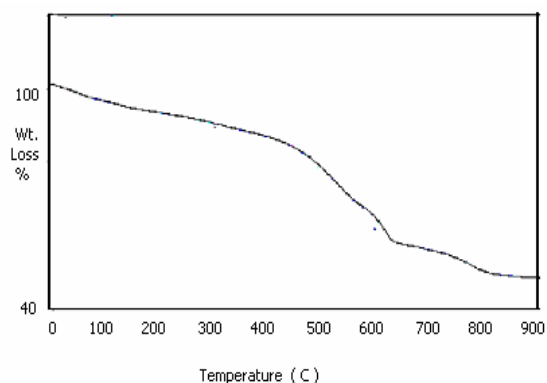


Fig. 6: Thermogravimetric curve of CSH gel.

Approximately, 55% weight loss was observed up to 900 °C. Major weight loss was observed from 450 °C to 650 °C. The stability in sudden weight loss was observed from 800 °C to 900 °C. Major weight loss is due to the decomposition of various phases of different compositions each having its own decomposition temperature where as stability in weight loss is due to formation of β -dicalcium silicate.

Using the data from thermogravimetric analyses the dried CSH gels were heated gradually from 500 °C to 900 °C without using any stabilizing agents. Rapid cooling technique was employed to cool down the heated samples as a requirement of obtaining the β -dicalcium beta silicate. The samples were ground to 200 mesh and analyzed by XRD machine within 3 hours of its formation and are shown in Fig. 7. No formation of β -dicalcium silicate can be seen up to 600 °C. At 700 °C, XRD pattern is close to the pattern of β -dicalcium silicate which is further improved at 800 °C. At 900 °C, no phase other than β -dicalcium silicate was observed. The calcination time for each sample was kept constant for 30 minutes. Calcination time plays an important role in formation process. It was observed that by maintaining the temperature for four hours at 800 °C, XRD pattern was very similar to XRD pattern obtained at 900 °C for 30 minutes. By using hydrothermal technique at high pressure, CSH gel usually is hillebrandite which decomposes into β -dicalcium silicate at 700 °C where as by using normal pressure hydrothermal technique (sol-gel) the CSH gel is a complex compound of CSH gels which decomposes at higher temperatures.

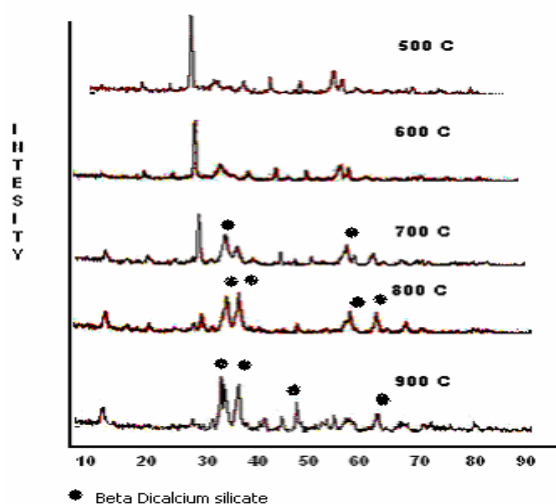


Fig. 7: XRD patterns of heated CSH gels.

The FTIR spectra obtained at 900°C is shown in Fig. 8. The FTIR spectra were obtained within two hours of calcinations.

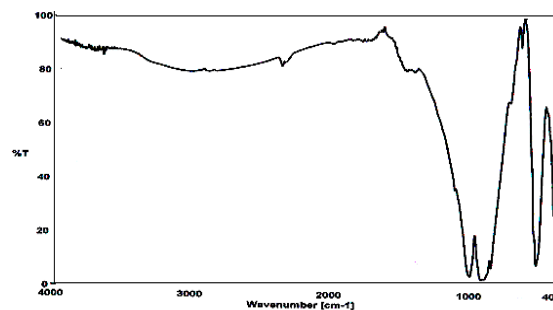


Fig. 8: FTIR spectra of β -dicalcium silicate (900°C).

The broad peak at 3400 cm^{-1} is usually due to the water absorbed at the surface of the product. In Fig. 8, peak at 3400 cm^{-1} is due to the absence of water. Bands at 800 – 1000 cm^{-1} is a characteristic of stretching vibration whereas at 400 – 600 cm^{-1} is characteristic of bending vibrations of Si-O bonds in SiO_4 tetrahedra. The main peaks attributed to β -dicalcium silicate are the stretching modes of Si-O located at 900 and 1000 cm^{-1} .

The SEM of β -dicalcium taken at 700 °C and 900 °C are shown in Fig. 9 and 10 respectively. Discontinuous phase with unreacted particles are visible in SEM image in Fig. 9. In Fig. 10, spherical shaped particles of β -dicalcium are visible. The small size spherical shaped particles of β -dicalcium are responsible of stabilization at room temperature.

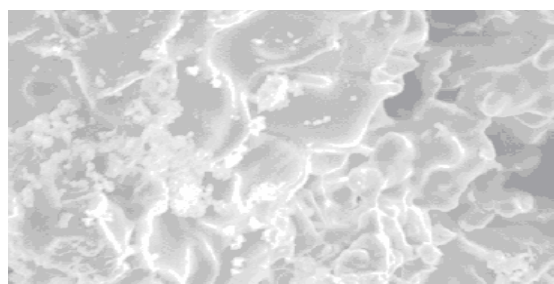


Fig. 9: SEM of β -dicalcium (700°C).

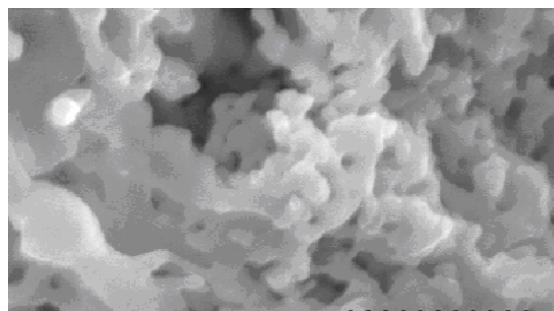


Fig. 10: SEM of β -dicalcium silicate (900°C).

Experimental

Sample Preparation

Rice husk samples were prepared by washing and drying in oven for 24 hours at 105°C. Samples were treated with 4% HCl for 24 hours at room temperature followed by washing and drying in oven for 24 hours. Such samples were designated as R1. As a reference, another rice husk sample was prepared without acid treatment and designated as R2. Dried samples were heated gradually in tube furnace (Carbolite) up to 600 °C for 90 minutes and cooled at room temperature. Samples were ground to fine powder with a maximum particle size of 200 mesh.

Calcium oxide (Merck Germany) was heated to 1000 °C for one hour followed by cooling at room temperature to assure the formation of calcium oxide. Calcium oxide and RHA samples were mixed together with Ca/Si ratio of 2.0 in ten times water by weight of solids. Superplasticiser 0.2% of solids was incorporated to form suspension. The mixtures were boiled for one hour and then placed in an oven for 12 hours at 90 °C for gel formation. The gels were further dried in oven at 105°C for 24 hrs after removing excess water by ordinary filter paper. The gels were ground to fine powder and tested by XRD machine (Philips Model Panalytical X-pert pro). Samples were also analyzed by thermogravimetric analyzer (TA instruments model Q600). The muffle furnace was programmed with 10°C/min rise in temperature from room temperature to 900 °C to calcine the dried samples. The heated gels were drawn from 500 °C to 900 °C from muffle furnace after every 100 °C rise in temperature. Each sample was cooled rapidly at room temperature, ground to fine powder and tested by XRD, FTIR and by SEM machines.

Conclusions

Results have shown that white amorphous silica as a starting material is helpful in formation of amorphous CSH gel by hydrothermal technique at normal pressure. Treating rice husk with dilute HCl renders white amorphous silica by calcinating at 600 °C. Superplasticisers as dispersing agent are helpful in formation of CSH gel and are the better replacement of impeller mixing. Amorphous CSH gels found to be convertible into reactive β -dicalcium silicate in the range of 700 °C to 900 °C. Continuous phase of CSH gel was observed by SEM results. Nano size particles in SEM confirmed the formation of β -dicalcium silicate at 900 °C.

Acknowledgement

The funding and support provided by University of Engineering and Technology Lahore Pakistan, is acknowledged.

References

1. F. Lin and C. Meyer, *Cement and Concrete Research*, **39**, 255 (2009).
2. S. Tsivilis, E. Chaniotakis, G. Kakali and G. Batis, *Cement and Concrete Composites*, **24**, 371 (2002).
3. K. Yanagisawa, X. Hu, A. Onda and K. Kajiyoshi, *Cement and Concrete Research*, **36**, 810 (2006).
4. N. S. Gajbhiye and N. B. Singh, *Material Research Bulletin*, **45**, 933 (2010).
5. F. A. Rodrigues, *Cement and Concrete Research*, **33**, 823 (2003).
6. M. Wang, C. G. Lee and C. K. Ryu, *International Journal of Hydrogen Energy*, **33**, 6368 (2008).
7. W. Zhao and J. Chang, *Materials Letters*, **58**, 2350 (2004).
8. N. B. Singh, *Progress in Crystal Growth and Characterization of Materials*, **52**, 77 (2006).
9. M. Georgescu, J. Tipan, A. Badanoiu, D. Crisan and L. Dragan, *Cement and Concrete Composites*, **22**, 315 (2000).
10. I. G. Richardson, *Cement and Concrete Research*, **38**, 137 (2008).
11. M. Nehdi, J. Duquette and A. El Damatty, *Cement and Concrete Research*, **33**, 1203 (2003).
12. H. Ishida, K. Sasaki and T. Mitsuda, *Journal of American Ceramic Society*, **75**, 353 (1992).
13. H. Ishida, K. Mabuchi, K. Sasaki and T. Mitsuda, *Journal of American Ceramic Society*, **75**, 2427 (1992).
14. Q. Feng, H. Yamamichi, M. Shoya and S. Sugita, *Cement and Concrete Research*, **34**, 521 (2004).
15. S. Chandrasekhar, P. N. Pramada and L. Praveen, *Journal of Materials Science*, **40**, 6535 (2005).
16. K. E. Kurtis and F. A. Rodrigues, *Cement and Concrete Research*, **33**, 509 (2003).
17. F. A. Rodrigues, *Cement and Concrete Research*, **33**, 1525 (2003).
18. A. Proctor, *Journal of American Oil Chemists Society*, **67**, 576 (1990).
19. D. G. Nair, A. Fraaij, A. A. K. Klaassen and A. P. M. Kentgens, *Cement and Concrete Research*, **38**, 861 (2008).
20. S. K. Agarwal, *Cement and Concrete Research*, **36**, 1735 (2006).
21. J. Payá, J. Monzó, M. V. Borrachero, E. Peris-Mora and L. M. Ordóñez, *Waste Management Series*, **1**, 493 (2000).
22. K. Luke, *Cement and Concrete Research*, **34**, 1725 (2004).