SYNTHESIS OF WOLLASTONITE FROM AGRO-WASTE

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ABSTRACT

A study was conducted in the Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan during the year 2008. In this study an attempt was made to produce wollastonite from rice husk by extracting amorphous silica present in hydrated form. The rice husk, an agro-waste material was treated with potassium permanganate and then incinerated in tube furnace at 600ºC for 10 minutes to produce amorphous silica. The amorphous silica was then treated with calcium oxide in presence of water to form calcium hydro silicate (CSH) gel. CSH gels were dried in oven and heated at 800ºC in muffle furnace for 60 minutes. The incinerated samples were ground and passed through 100, 200 and 300 mesh sieves and then analyzed by X-Ray Diffraction (XRD). XRD patterns confirmed the formation of wollastonite.

KEYWORDS: Rice husk; potassium permanganate; wollastonite; Pakistan.

INTRODUCTION

Rice husk an agro-waste material is abundantly available in rice producing areas and is a source of many useful products. Wollastonite, calcium metasilicate ($CaSiO_3$) is a mineral that exists in two forms i.e. β-wollastonite with a fusion point < 1160ºC and α-wollastonite with a fusion point > 1160 ºC (1). Use of natural wollastonite in ceramic composite provides a favourable mineral formation which reduces the porosity and increases the stability to temperature changes. It also improves the dielectric properties thermal expansion coefficient (safety of micro flaw of glazing) and decreases shrinkage during drying and lowers finishing temperature range. Besides it favourably influences the expansion due to moisture. In compounding the glazes, buble formation due to carbon dioxide is avoided by using the wollastonite. In view of its utilities, it is widely used in electric insulators, high strength mortars in opaque glasses as fluxes welding electrodes, refractory moulds and binders fire proofing composites as filler and light weight non-

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flammable products. The use of wollastonite has also been reported in floor tiles, cement boards, sound insulators, paper fillers and steel industry.

Wollastonite has received much attention during last decade and number of researchers attempted to produce it synthetically (2). In nature, wollastonite is formed under high temperature and pressure. Quartz and calcite comes in contract in the presence of high pressure and temperature and forms wollastonite. It has been reported that rocks with calcite and quartz under 2000 bars and at around 800ºC form wollastonite (5). It has also been observed that CaO present as mineralizer in raw batches for producing silica refractories reacts with SiO_2 ad forms wollastonite. Kartal and Akpinar (8) produced wolllastonite from silica fumes, diatomite, waste of marbles, calcite and sodium feldspar in varying ratios and calcined at 1100ºC.

Wollastonite was produced by Kotsis *et al.* (9) at solid state by using limestone and micro SiO_2 and it was observed that formation of β-wollastonite took place without formation of intermediate products. Yun *et al.* (14) produced β-wollastonite from waste glasses and waste shells. Automobile waste glasses and waste shells were mechanically ground in a disk type ball mill for four hours. After milling the mixtures were pressed into disk of 10 mm diameter, without using binder and then heated to 850ºC, 950ºC and 1050ºC for one hour to produce wollastonite. A hydrothermally $CaO-SiO_2-H_2O$ was investigated by Grigoryan *et al.* (6) at 150-200ºC ($CaO:SiO_2$ = 0.95) using modifications of SiO_2 in the presence of mineralizer. It has been reported that tridymite is the most reactive form among all SiO_2 types.

Zao (15) first prepared CSH gel from calcium oxide and silica. The product was then heated to 1200ºC to obtain wollastonite.

Parkison (11) synthesized wollastonite from 47 percent quick lime and 57 percent quartz sand at 1500ºC. Wollastonite produced with this composition contains 4.5 percent free silica.

Ibanez (7) prepared β-wollastonite by solid state reaction using Spanish diatomites plus chalk having SiO_2:CaO molar ratio of 1:1. Demidenko and Podzorova (1) produced β-wollastonite from natural siliceous limestone by calcining at 1100ºC. Fumuja (4) utilized SiO_2 from waste gases of electric furnace and treated with $Ca(OH)_2$ in 1:1 ratio in autoclave. The pressure was maintained at 7-10 atm and temperature 170ºC - 190ºC for 24 hours. The resulting material was fine wollastonite.

Synthesizing wollastonite from calcium oxide and rice husk has been tried in this study. Treatment of rice husk with acids has also been exercised in the past to remove impurities present in rice husk. Boiling rice husk with mineral acids for many hours just to remove the minor impurities is not cost effective for commercial productions. In many commercial operations sufficient oxygen is more important than removal of impurities from the surface of rice husk.

Postassium permanganate as an oxidizing agent is being used in pharmaceutical industry to oxidize functional groups such as aromatic side chain to carboxylic acids and organic sulfones. Potassium permanganate upon heating decomposes and liberates oxygen which can help in combustion of rice husk. Keeping in view this characteristic, it was planned to treat rice husk with various strengths of potassium permanganate to produce wollastonite.

MATERIALS AND METHODS

This study was conducted in the Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan during the year 2008. Rice husk was collected from local rice mill during milling season. The rice husk was first washed with deionized water for five minutes followed by drying in oven at 105ºC for 24 hours. Washed and dried rice husk was treated with 0.05N solution of potassium permanganate for 30 minutes followed by drying in an oven at 105ºC for 24 hours and designated as K1.

The sample K1 was then placed in porcelain crucible and calcined in electric tube furnace. The tube furnace was programmed @ 10ºC per minute upto 600ºC. The furnace allowed to remain at 600ºC for 90 minutes and then allowed to cool down at room temperature.

K1 sample was removed from tube furnace and then ground, passed through 200 mesh sieve for XRD analyses.

X-Ray diffraction analysis

X-Ray diffraction (XRD) method is a powerful technique to identify materials. Sample K1 calcined at 600ºC in tube furnace was analyzed by XRD method. Sample was dried in oven at 105ºC for three hours before carrying out XRD analysis. For XRD analysis, Philips Model PANalytical x-pert pro machine was used under following set conditions for each sample:

Scanning range	=	5-7 degree
Scanning time	=	420 seconds

Voltage	=	35 KV
Intensity	=	35 mA
Step size	=	0.050

Preparation of calcium hydro silicate (CSH)

Amorphous silica present in rice husk ash usually reacts with calcium oxide in presence of water and forms calcium hydro silicate gel (CSH gel). The reaction between amorphous silica and calcium hydroxide is even faster in presence of warm water. This gel looks like flocks in morphology, with a porous structure and large specific surface area. When product is heated, it gradually loses water and forms calcium silicate.

The rice husk ash and calcium oxide (Merk) were taken with equal molar ratio (C/S=1). Following ingredients were taken and mixed with the help of magnetic stirrer at 50ºC.

CaO (Merk)	=	56 g
Rice husk ash	=	66 g
Distilled water	=	500 g

The amorphous silica obtained from rice husk was used to synthesize calcium hydro silicate gels. The calcium hydro silicate gels were prepared by changing reaction temperature of mixture (Table 1).

Table 1. Effect of temperature on gels and wollastonite formation.

Water bath temperature (ºC)	Gel weight after 24 hrs mixing (g)	Excess water found in CSH gel after 24 hours	Furnace heating 800ºC for one hour
50	320	Yes	Partial wollastonite
60	430	Yes	Partial wollastonite
70	560	Yes	Partial wollastonite
80	622	No (Full gel)	Partial wollastonite
90	622	No (Full gel)	Full wollastonite

Formation of calcium hydro silicate gels took place at all temperatures (Table 1). The full gel formation indicated to complete reaction. Full CSH gel was formed at 80C and 90ºC. CSH gels obtained at 50ºC, 60ºC, 70ºC and 90ºC were dried in oven at 105ºC each for 24 hours and subsequently heated in muffle furnace at 800ºC each for one hour. The gels heated in furnace were cooled, ground and passed through 100 mesh sieve for XRD analysis.

RESULTS AND DISCUSSION

XRD analysis of sample K1 was performed in its powdered form. XRD pattern of powdered sample is shown in Fig. 1. It has been reported that diffused peak at 0 = 22ºC is a characteristic of amorphous silica (3). Formation of crystal silica during burning of rice husk depends upon temperature and duration of burning. It has been reported that retrieving silica from rice husk for industrial use is possible by controlling the burning temperature below 700ºC. it has also been suggested that essentially amorphous silica can be produced by maintaining the combustion temperature below 500ºC under oxidizing condition for prolonged periods. Alternatively it can be produced below 680ºC with holding time less than one minute (10).

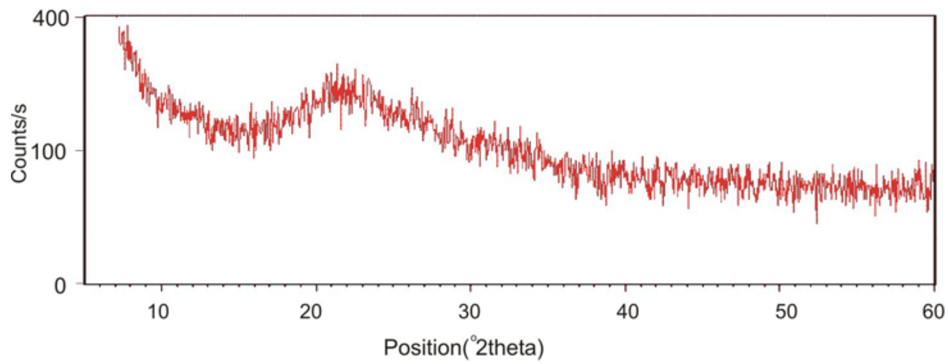

Fig. 1: XRD of sample K1 indicating amorphous silica.

Paya *et al.* (12) reported that $Ba(OH)_2$ solution reacts with amorphous silica and forms barium hydro silicate paste. Like $Ba(OH)_2$ solution, $CA(OH)_2$ solution also reacts with amorphous silica and forms calcium hydro silicate gel. Therefore, formation mechanism of CSH gel may be described as under.

The amorphous silica is stimulated by $Ca(OH)_2$ solution by forming SiO_4 ions. SiO_4 ion reacts with Ca and OH ions in solution phase and forms CSH gel. In other words, CSH gel is formed by dissolution - precipitation process.

Like specific pattern of amorphous silica, XRD of wollastonite also has specific pattern enabling to identify the product formation. One sharp peak of highest intensity at 29 to 30 degrees confirms the formation of wollastonite.

Gels prepared at different temperatures for 24 hours in conical flask with magnetic stirrer were dried in oven for 24 hours and then heated to 800ºC for one hour in electric muffle furnace. The heated products were cooled, ground and passed through 100 mesh sieve. The sieved powders were then put into XRD machine for material identification and patterns obtained are shown in Fig 2 to 6.

In Fig. 2, pattern has one sharp peak at 29.37 degrees confirming the presence of wollastonite, whereas all other peaks belongs to calcite. The presence of calcite is an indication of incomplete reaction between calcium hydroxide and amorphous silica.

In Fig. 3, one peak at 29.3 degrees belongs to wollastonite whereas all other peaks are of calcite. XRD pattern is almost similar to XRD pattern shown in Fig. 2.

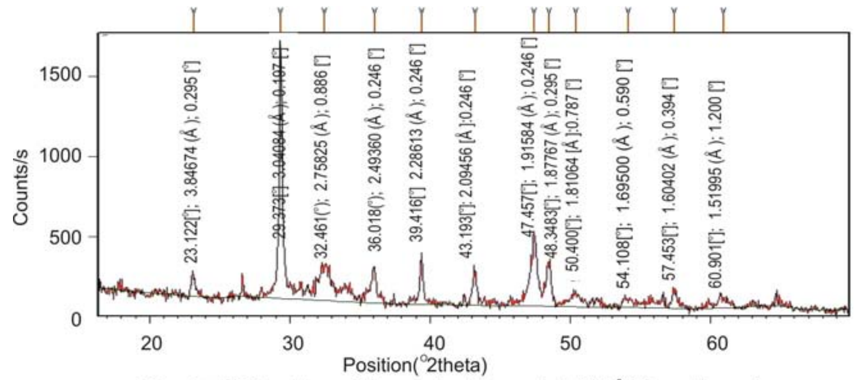

Fig. 2: XRD pattern of the product formed at 800 °C from the gel prepared at 60 °C.

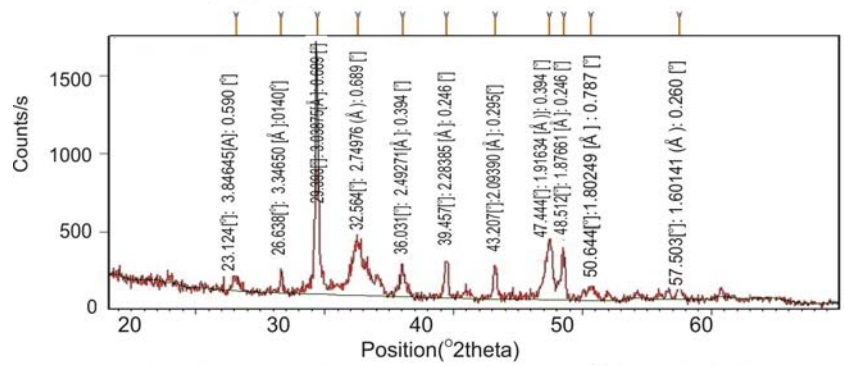

Fig. 3: XRD pattern of the product formed at 800 °C from the CSH gel prepared at 70 °C (100 mesh).

General XRD patterns given in Fig. 4-6 are almost similar. In Fig. 4 sharp peaks are 9 whereas in Fig. 5 and Fig. 6, sharp peaks are 14. The difference

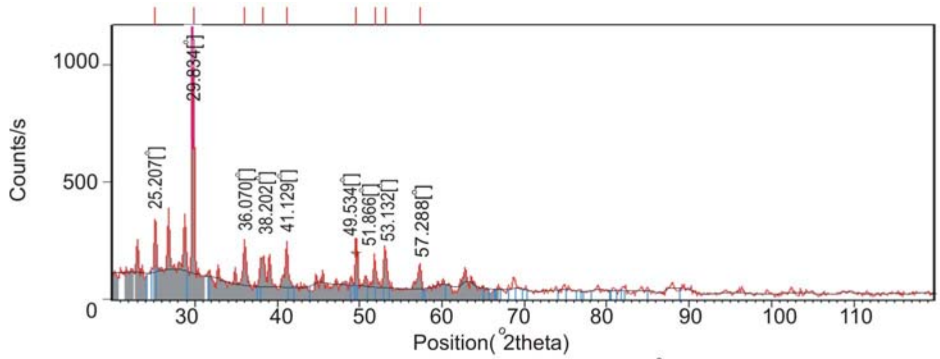

Fig 4 : XRD pattern of the product formed at 800 °C from the gel prepared at 90 °C(100 mesh).

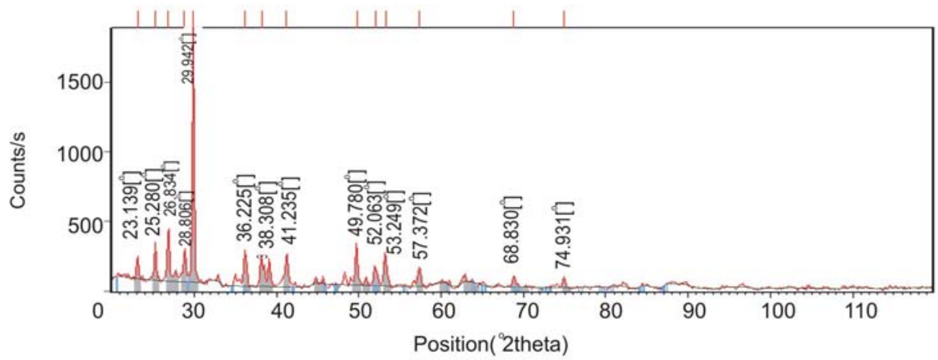

Fig 5 : XRD pattern of product formed at 800 °C from the gel prepared at 90 °C (200 mesh).

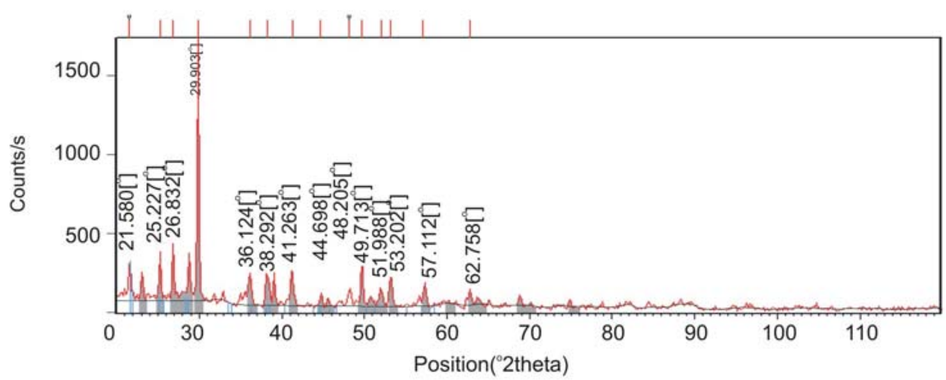

Fig. 6 : XRD pattern of the product formed at 800 °C from the gel prepared at 90 °C (300 mesh).

of peaks is due to reduced mesh size. All peaks in these patterns belong to wollastonite. Comparing all five XRD patterns of wollastonite it can be deduced that good quality wollastonite can be obtained from those gels prepared at 90ºC for 24 hours with equal molar ratios and heated at 800ºC for one hour.

CONCLUSION

Rice husk an agro-waste material can be used to produce wollastonite, which is an important mineral in ceramic industry. The pretreated rice husk with potassium permanganate obtained amorphous silica. The amorphous silica was allowed to react with calcium oxide at 90ºC in presence of sufficient water for 24 hours to form CSH gel. The CSH gel appeared to be flocks in morphology with a porous structure and large specific surface area. When this porous dried gel was heated to 800ºC it gradually lost water and transformed into crystalline wollastonite ($CaSiO_3$). The XRD analysis confirmed the complete conversion of CSH gel into crystalline wollastonite.

ACKNOWLEDGEMENT

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REFERENCES

1. Demidenko, N. I. and L. I. Podzorova. 2005. Wollastonite a Substitute of Asbestos. J. Konstruktsii iz Kompozitsionnykh Materia, n1, pp. 37-39.
2. Encinas, M. 2008. Synthesis and characterization of hydroxyapatite - Wollastonite composite powders by sol-gel processing. Int. J. Applied Ceramic Technology. 5(4): 401-411.
3. Flavio, A. R. 2003. Dicalcium silicate from rice husk, J. Cement and Concrete Res. Vol. 33:1525-1529.
4. Fumuja, J. T. 2004. Wollastonite from hydrothermally Synthesized Calcium hydrometasilicate. J. Amer. Ceramic Society. 88(2):345-349.
5. Greish, Y. E. and P. W. Rown. 2001. Characterization of wollastonite-reinforced hap - Ca Polycarboxylate composites. J. Biomedical Materials Res. 55(4):618-628.
6. Grigoryan, K., G., Harutyunyan and G., Grigoryan. 2006. Wollastonite from hydrothermally synthesized calcium hydrometasilicate obtained from various modifications of silica. J. Amer. Ceramic Soc. 89(1):374-376.
7. Ibanez, A. 1990. "Solid state reaction for producing β-wollastonite" J. Amer. Ceramic Soc. 69(3):374-376.
8. Kartal, A., and Akpinar S. 2004. "Synthesis of wollastonite by using various raw materials. J. Key Eng. Materials, 264(3):2469-2472.

9. Kotsis, LIdiko and Balogh. 1989. Synthesis of wollastonite, J. Ceramic Inte. 15(2):79-85.
10. Mehta, P. 1977. Properties of blended cements made from rice husk ash. J. Amer. Concrete. 74(9):440-442.
11. Parkison, G. 1990. Wollastonite. J. Surface Mining. 16(2). 266-267.
12. Paya, J., J. Monzo and M. V. Borrachero. 2001. Determiantion of amorphous silica in rice husk ash by rapid analytical method, J. Cement and Concrete Res. Vol. 31, p 227-231.
13. Virtal R. L. 2006. Wollastonite. J. Mining Engg. 58(6). 61-62.
14. Yun, S. D., H. R. Park and Y. N. Yound. 2002. Preparation of β-wollastonite glass ceramics. J. Materials Synthesis and Processing. 1(4):205-209.
15. Zao, W. 2006. FTIR spectra for molecular structure of wollastonite. J. Chinese Ceramic Soc. 34(9):1137-1139.