ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

ENERGY-SAVING THROUGH REDUCED FIRING TEMPERATURE USING Li_2O ADDITIVE IN SANITARY-WARE CERAMICS.

Aman Bhardwaj, Lakshya Mathur, SK Saddam Hossain, Prof. Ram Pyare.
Department of Ceramic Engineering, Indian Institute of Technology (BHU), Varanasi, India.

Manuscript Info

Manuscript History:

Received: 14 January 2016
Final Accepted: 29 February 2016
Published Online: March 2016

Key words:
Lithia, Spodumene, Viscous flow Sintering, Firing Temperature, Flux.

Corresponding Author

Aman Bhardwaj.

Abstract

The Fluxing action of Lithia (Li_2O) was investigated by addition of Lithium Carbonate and Spodumene to sanitary ware body. Rectangular specimens were prepared by Slip Casting method prior to firing at 1150°C and 1200°C. The effect of Lithium oxide in sanitary ware body was found to be favorable for reducing maturing temperature up to 50°C. The presence of lithia reacting with other oxides and silicates formed a liquid phase of lower viscosity, which accelerated the densification through viscous flow sintering, without compromising the mechanical strength. Phase development of the fired bodies were also discussed and well correlated with the final properties. Lowering the sintering temperatures leads to reduction in fuel consumption and environment harmful gases.

1. Introduction:-

The energy conservation is an essential step towards overcoming the mounting problems of the worldwide energy crisis and environmental degradation (1). The ceramic industry has high energy demands, also they are recognized for great percentage of the energy cost in the total production cost (2). There are high amount of Green House gases like CO_2 & Poisonous CO, SO_2 etc. evolved, which are harmful to the environment (3).

Traditionally, Feldspar is being used as a flux which introduces alkaline oxides such as Na_2O, K_2O, Li_2O etc. providing a liquid phase at elevated temperatures and thus promoting densification (4-8). Additionally, Quartz also participates in the fusion of feldspar and controls the viscosity of the liquid phase (9).

Lithia is a very effective flux, especially when used in conjunction with potash and soda feldspars. Lithium Carbonate and Spodumene are the two major mineralogical sources of Li_2O. Spodumene is a lithium alumina-silicate with the formula $Li_2O \bullet A1_2O_3 \bullet 4SiO_2$ has a pyroxene structure (10, 11). It has a melting temperature of 1420 °C, density of 3.2 gm/cm^3 and Moh's hardness of 6.5 to 7. Li_2O content varies from 4 to 8% (12-14). Several works have been published showing primary fluxes like soda & potash feldspar incorporated with spodumene and other fluxes like Colemanite or Nepheline synite, has potential to reduce the firing temperature up to 100°C in Porcelain tile composition (15-17).

In the present Investigation, we have studied the effect of incorporating Li_2O with other primary fluxes to achieve better densification even at certain low firing temperatures in sanitary-wares particularly.

2. Material and Methods:-

2.1. Raw Material:-

Preparation of sanitary ware composition was done by using Ball Clay, China Clay, Quartz and Potash feldspar. Priority was given in the use of local available clays. Chemical analysis of the raw materials used is listed in Table (I).

Table (I): Chemical analysis of Raw-materials (in weight %).

Oxides	Clay (K-4)	Clay (555-Grade)	Potash Feldspar ($8\%K_2O$)	Quartz
SiO_2	52.8	66.74	70.6	98.89
Al_2O_3	33.74	21.22	17.3	-
Fe_2O_3	0.41	1.22	0.1	.029
TiO_2	0.06	3.34	-	-
MgO	0.66	0.129	-	0.085
CaO	-	0.232	0.3	0.468
Na_2O	1.28	0.027	3.3	-
K_2O	0.7	0.849	8.1	0.055
L.O.I	9.1	6.238	0.92	0.375

Laboratory grade lithium carbonate with a purity of 99% was used. Spodumene was imported and the chemical composition was determined by using the X-ray fluorescence (XRF) spectrometer according to ASTM C114-00 (18) listed in Table (II).

Table (II): XRF Result of Spodumene

Oxides	Concentration (wt %)
Li_2O	6.80
SiO_2	61.89
Al_2O_3	23
Fe_2O_3	0.08
P_2O_5	0.27
MnO_2	0.04
CaO	0.18
Na_2O	0.45
K_2O	0.40

2.2. Sample Preparation:-

Lithia was introduced by two sources as-

[1] Lithium Carbonate (S-1, S-2 and S-3)

[2] Spodumene (S-4, S-5 and S-6)

Batch S-0 was taken as base composition. Weight percentage composition for different samples is listed in Table (III).

Table (III): Sample Composition (in weight %)

Raw-Materials	S-0	S-1	S-2	S-3	S-4	S-5	S-6
Clay (K-4)	37	37	37	37	37	37	37
Clay (555-Grade)	23	23	23	23	23	23	23
Potash Feldspar	25	24	23	22	23	21	19
Quartz	15	15	15	15	15	15	15
Lithium Carbonate	0	1	2	3	0	0	0
Spodumene	0	0	0	0	2	4	6

For the preparation of slip, all the raw materials were crushed and sieved. Sieves with different mesh sizes were used to obtain a particle size distribution. Around 30-35% of water was added. For better dispersion, de-flocculants like sodium silicate (0.5%) was added to the slurry prior to mixing. The prepared slip was kept on agitation for 24 hours to obtain better homogeneity and develop plasticity. Then it was casted into rectangular samples using Plaster of Paris moulds and left for 12 hours.

2.3. Drying & Firing:-

The test specimens were removed from the mould and allowed to dry in the open atmosphere for 24 hours. Then the bodies were dried for 6 hours at 110°C in an electric air oven. Sintering was done at 1150°C and 1200°C in a muffle furnace with a soaking time of 2 hours with an average heating and cooling rate of 4°C/min & 2.5°C/min respectively.

3. Results and Discussion:-

It was found that replacing Potash feldspar by Lithium carbonate and Spodumene didn't affect the behaviour of the composition in the pre-firing stages as green strength and workability found same as of base composition. Several Physical and Mechanical properties of the fired product was determined as given below-

3.1. Apparent Porosity & Bulk Density:-

The boiling water method according to ASTM C20 (19) was used to determine the apparent porosity (A.P.) and the bulk density (B.D.) and the results are plotted in Fig (I) to Fig (IV) Respectively.

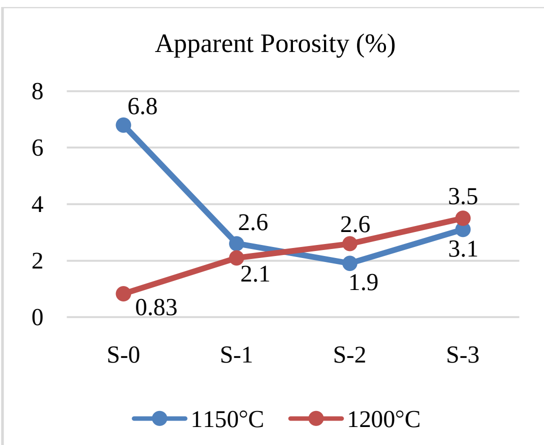

Fig (I): Effect of addition of Li_2CO_3 on A.P.

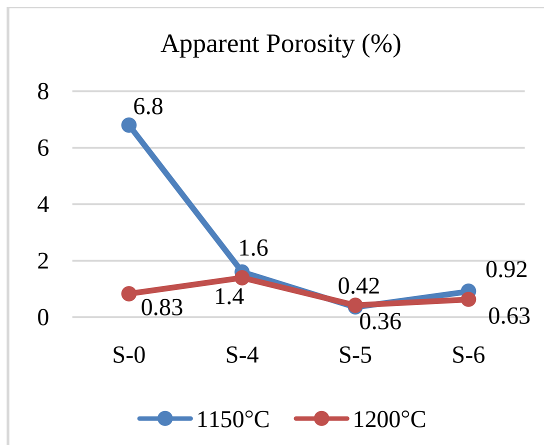

Fig (II): Effect of addition of spodumene on A.P.

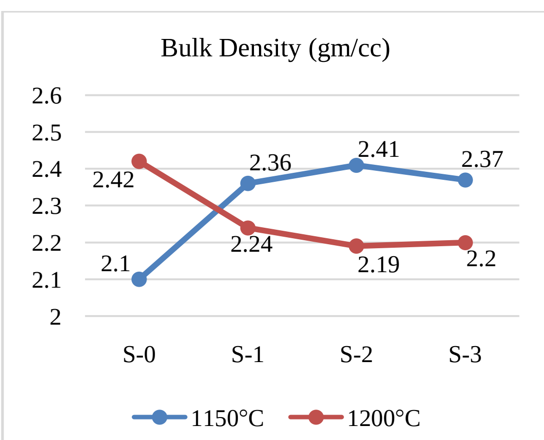

Fig (III): Effect of addition of Li_2CO_3 on B.D.

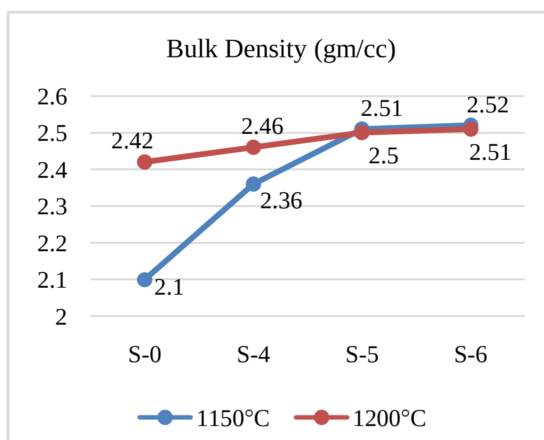

Fig (IV): Effect of addition of spodumene on B.D.

It has been observed that sample S-0 has highest and S-5 has the lowest porosity amongst samples fired at lower temperature (1150°C). Maximum bulk density was also found for sample S-5.

3.2. Water Absorption (W.A.):-

Water absorption is an important property to be measured for sanitary ware especially and was determined according to ASTM C20 (19). It was found that sample S-5 has negligible water absorption even in unglazed condition as shown in Fig (V) & (VI).

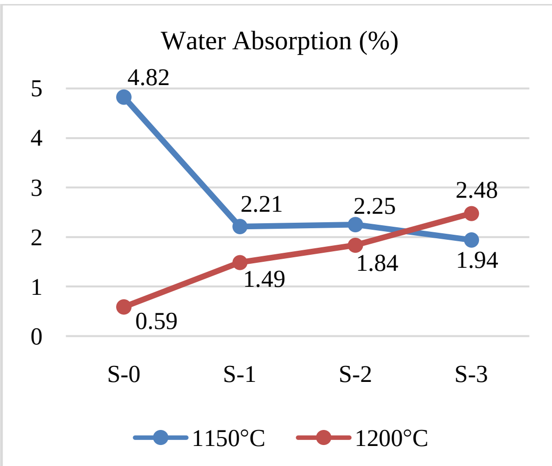

Fig (V): Effect of addition of Li_2CO_3 on W.A.

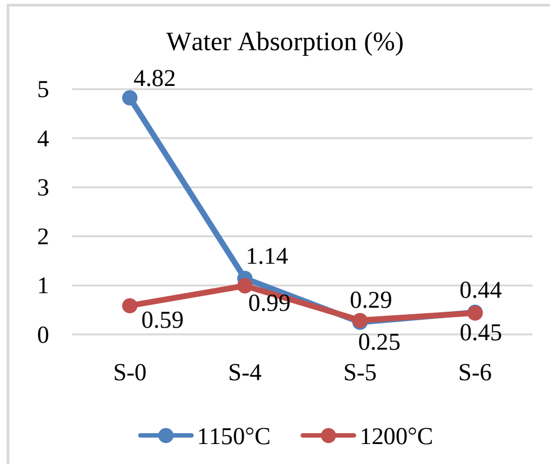

Fig (VI): Effect of addition of spodumene on W.A.

3.3. Modulus of Rupture (M.O.R.):-

The M.O.R. was determined according to ASTM C-133/97 (20) and shown in Fig (VII) & Fig (VIII). It was observed that samples S-0 to S-4 doesn't have good flexural strength when fired at 1150°C whereas S-5 was found positive. These results show a possibility of Bloating in sample S-1 to S-3 due to the de-composition of Lithium carbonate at elevated temperature evolving carbon dioxide.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2 \text{ (g)}$$

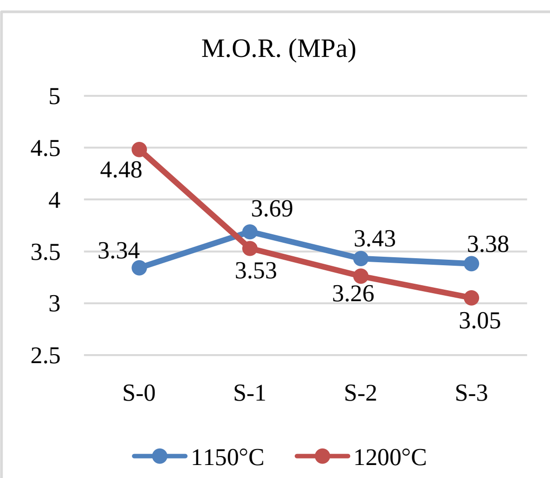

Fig (VII): Effect of addition of Li_2CO_3 on MOR

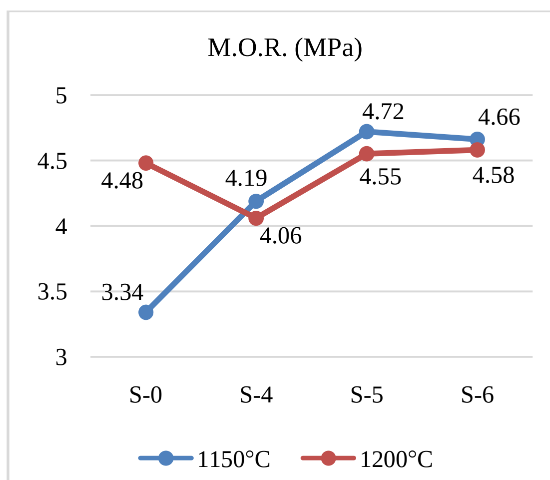

Fig (VIII): Effect of addition of spodumene on MOR

3.4. X-Ray Diffraction (XRD) Analysis:-

XRD was carried out for optimized sample (S-5) and results were recorded in 10° to 50° range of 2ϴ in a "Rigaku Mini Flex-II Desktop X-ray Diffractometer". The XRD pattern of sample S-5 has shown in Fig (IX). Results were studied using JCPDS file to identify the phases developed after sintering. The major phase identified as Quartz and some small peaks corresponding to Mullite were also identified which supported the good mechanical properties shown by the sample.

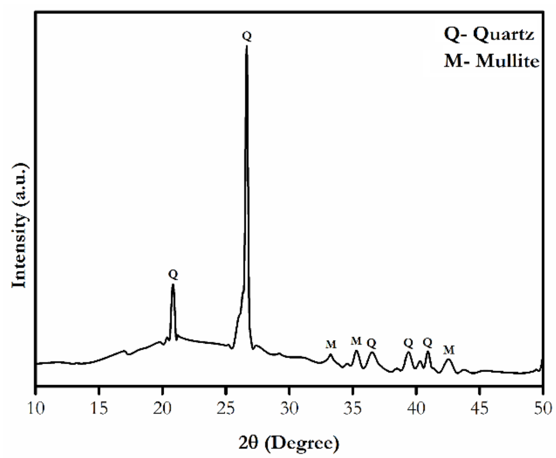

Fig (IX): X-Ray Diffraction for Sample S-5

In summarizing these results, it is observed that Spodumene has contributed to the formation of liquid phase before reacting with the other ingredients of the mixture and the densification of the body was advanced by the presence of this liquid phase by viscous flow. This Sintering action can be explained by the eutectic found at 975°-1000°C, in the Ternary Phase diagram for $Li_2O{\cdot}SiO_2 - SiO_2 - Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, given in Fig (X).

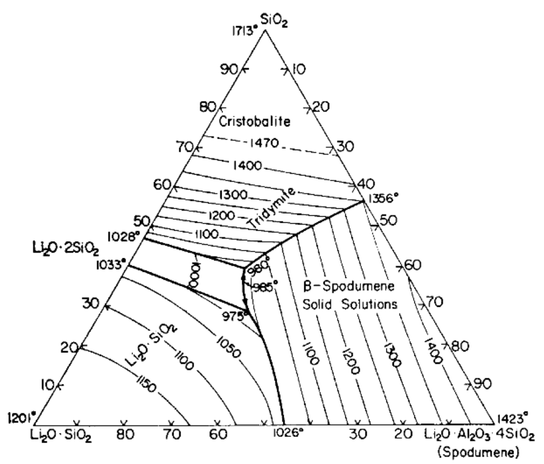

Fig (X): Ternary phase diagram for Spodumene

4. Conclusion:-

After analyzing the results, the outcome of the experiment can be summarized as-

1. Lithia has a very significant fluxing effect in sintering of ceramics. However, Lithium carbonate has a limitation due to bloating, which constraints its uses up to 2% only.
2. Spodumene incorporated with other fluxes in sanitary ware compositions has lowered the firing temperature but didn't narrow the firing range, which represents a technical advantage compared to other

vigorous fluxes. It reveals the possibility of reducing the energy consumption during firing by decreasing maturing temperature by 50˚C.

3. The Lithium ion having extensively small size (90pm), provided by both Lithium carbonate & Spodumene, has the potential to reduce the maturing temperature without decreasing the surface tension. This explains the large range for firing.
4. Reduction in maximum temperature of the kiln leads to reduction in environmental pollution and extending refractory and furnace life cycle.

Acknowledgement:-

We are grateful to the Faculty and Staff of Department of Ceramic Engineering and The Honorable Director, IIT (BHU), Varanasi for providing the proper facilities to accomplish this work.

References:-

1. **Energy Conservation in Ceramic Industry (1994).** the Energy Conservation Centre (ECC), Japan https://www.unido.org/fileadmin/import/userfiles/puffk/ceramic.pdf
2. **BAT (Best Available Techniques) Reference Document (BREF)** entitled "Ceramic Manufacturing (CER)" - The European IPPC Bureau.
https://www.eippcb.jrc.ec.europa.eu/reference/BREF/cer_bref_0807.pdf
3. **Michael Bozsin (1966).** "Air Pollution Abatement in the Ceramic Industry", Journal of the Air Pollution Control Association, 16:6, 332-333, DOI: 10.1080/00022470.1966.10468484
4. **Worral W. E. (1982).** "Ceramic Raw Materials", 2nd edition. Ed. Pergamon Press, Oxford, England, UK
5. **Carty W. M., U. Senapati (1998).** "Porcelain-Raw Materials, Processing, Phase Evolution and Mechanical Behavior", Journal of American Ceramic Society 81 [1] 3-20
6. **Harvey, C.C. and H.H. Murray (1997).** "Industrial clays in the 21st century: A perspective of exploration, technology and utilization", Applied Clay Science, 11(5-6): p. 285-310
7. **Iqbal, Y. and W.E. Lee (1999).** "Fired porcelain microstructures revisited", Journal of the American Ceramic Society. 82(12): p. 3584-3590
8. **Zanelli C., Raimondo M., Guarini G., Dondi M. (2011).** "The vitreous phase of porcelain stoneware: Composition", evolution during sintering and physical properties. Journal of Non-Crystalline Solids. 357(16-17): p. 3251-3260
9. **Drozda F. O. (2003).** "Optimization of closed porosity of pieces of porcelain stoneware" Master's thesis, State University of Ponta Grossa, Ponta Grossa
10. **Dana E.S. (1892).** Dana's system of mineralogy, (6th edition), p. 366-369
11. **Deer W.A., R.A. Howie, and J. Zussman (1978).** "Rock-forming minerals (2nd edition)", v. 2A, single-chain silicates, 527-544
12. **Arlt T. and Angel R. (2000).** "Displacive phase transitions in C-centered clinopyroxenes: spodumene-LiScSi2O6, and ZnSiO3", Physics and Chemistry of Minerals: 27: 719-731
13. **Cameron, M., S. Shigeho, C.T. Prewitt & J.J. Papike (1973).** "High temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene and ureyite", American Mineralogist: 58: p. 594-618
14. **Jolyon Ralph and Ida Chau**, Copyright © 1993-2014, "Spodumene" at Mindat.org
http://www.mindat.org/min-3733.html
15. **Tulyaganov DU, Agathopoulos S, Fernandes H.R. and Ferreira JMF. (2006).** "Influence of lithium oxide as auxiliary flux on the properties of triaxial porcelain bodies", Journal of the European Ceramic Society, 26:1131-1139 http://dx.doi.org/10.1016/j.jeurceramsoc.2005.01.036
16. **Oberzan M, Holc J, Buhb M, Kuscer D, Lavrac I and Kosec M. (2009).** "High-alumina porcelain with the addition of a Li2O bearing fluxing agent", Journal of the European Ceramic Society, 29:2143-2152 http://dx.doi.org/10.1016/j.jeurceramsoc.2009.01.029
17. **J. Llop, M. D. Notari, E. Barrachina, I. Nuñez, I. Nebot-Díaz, J. B. Carda (2010).** "Vitrification studies on Porcelain tile compositions with Spanish raw materials and New Fluxes", QUALIcer'10, Castellón, Spain
18. **ASTM C114-00 (2009).** Standard test methods for Chemical Analysis of Materials, ASTM International
19. **ASTM C20 (2010).** Standard test methods for apparent porosity, water absorption, apparent specific gravity and bulk modulus of burned refractory brick and shapes by boiling water, ASTM International
20. **ASTM C133/99 (2008).** Standard test methods for cold crushing strength and modulus of rupture of refractories, ASTM International