ijcrr
Vol 04 issue 09
Category: Research
Received on:29/03/12
Revised on:08/04/12
Accepted on:17/04/12

OPTIMIZATION OF ZEOLITE SYNTHESIS USING MICROWAVE ASSISTED ACID DIGESTION METHOD

Chintan Pathak[1], V.K. Srivastava[1], D.N. Singh[2]

[1]Department of Sciences, School of Technology, Pandit Deendayal Petroleum University, Gandhinagar (Gujarat)
[2]Department of Civil Engineering, Geotechnical Engineering Division, Indian Institute of Technology, Powai, Mumbai

E-mail of Corresponding Author: vks1_999@yahoo.co.in

ABSTRACT

Introduction: Application of microwave irradiation is a relatively new development in materials processing. Recent development of microwave digestion for extremely acidic conditions like high temperatures – pressures gives more rapid, efficient and precise digestion. **Methodology:** This study optimizes the temperature and time, for dissolution of silica under acidic condition using microwave irradiation. The etched silica can be utilized for the synthesis of new species of aluminosilicates through various techniques like precipitation/evaporation. **Result and Discussion:** In our study, we have synthesized fly ash zeolite by using the microwave acid digestion method. This calls for utilization of industrial byproduct-fly ash in zeolite synthesis using silica reduction technology.

Keywords: Synthesis, Zeolite, Silica Reduction Technology (SRT), Etching

INTRODUCTION

In the last decade, the use of microwave digestion became increasingly popular. The use of closed vessel microwave assisted digestion system under high temperature and pressure has now become practical. Compared to traditional method[1-3], this procedure promotes the nucleation and crystal growth, allows shorter digestion time, gives homogeneous heating throughout the reaction vessel, activation time needed can be drastically reduced (from 24-48 h to 30 m) and good recoveries[3]. Furthermore, it requires a small amount of acids, reduces risks of external contamination, improved detection limits and improved overall accuracy. Studies have shown that the use of a microwave is easy, rapid, efficient, robust, reliable and cheap method[4-6].

Microwave can transfer energy directly to the reactive species, so-called "molecular heating" and promote transformations that are currently not possible using conventional heat. Energy is applied directly to the reactants; however the bulk heating is reduced by use of simultaneous cooling. This allows for enhanced reactions of larger, more heat sensitive molecules, as the temperatures are low enough to eliminate thermal degradation[7-8]. The key features of this device shall be mainly useful for the synthesis of zeolites: short digestion time, no loss of volatile elements, no acid fumes, no sample contamination, no cross contamination, operation is unattended, minimum quantity of acid (mainly hydrofluoric acid (HF)) is required, complete documentation including reaction kinetics, closed vessel technology[9-11]. This instrument is used to digest small amounts of material for chemical analysis by placing the sample in a Teflon crucible adding acid and microwaving the sample for a certain amount of time.

Microwave digestion inherited some disadvantages[12-14]; most of these problems are associated with the usage of HF. It has been found[15] that for digestion of silica, addition of HF proved to be necessary. In order to insure the maximum digestion of silica from fly ash, it has been opined by the previous researchers[16-20] that the microwave can be employed for complete heating of fly ash samples as compared to the conventional hydrothermal method. Based on this, the main objectives (viz., less activation and digestion time, maximum silica digestion, more nucleation and better crystal growth of zeolites) of the present work have been planned. The aim of this study is to try to understand key parameters – temperature, effect of HF; based on that modify and further improve microwave digestion method for optimum silica reduction[21-24].

1. Experimental

MATERIAL

In the early alkali aluminosilicate synthesis[25-26] of the low silica zeolites, it has been proposed that the hydrated alkali cation 'templates' stabilizes the formation of the zeolite structural sub-units. Alkali hydroxide, reactive forms of alumina and silica, and H_2O are combined to form a gel. Crystallization of the gel to zeolite occurs at a temperature near 100°C. The reactive gel is heated to crystallize the molecular sieve product[27].

Fly ash samples from the Bhusaval Thermal Power Station (BTPS), Bhusaval, Maharashtra, India; were collected for the present study. The ash sampling was done from hoppers and representative samples were prepared for three fields by mixing the collected samples. The hydrofluoric acid was procured from Merck Ltd. and is used for fly ash dissolution and subsequently for synthesis of zeolite.

METHOD

Microwave digestion: The fly ash with 40 % of HF (AR) is exposed to microwave irradiation for the acid digestion of the fly ash, in closed vessels, maintaining the liquid to solid ratio 10. The activation temperature is maintained from 45 to 110 ^{o}C. The activation time given is 5 m. At the end of these activation periods, the deep brown colored mixture was obtained which was then filtered using watman filter paper no. 41 (5-A) and liquid was collected into propylene bottle. Filter paper was dried in hot air oven at 65 ^{o}C for around 6-8 h. The solid dried residue was scraped and collected in polythene bag. The experimental set up consisting microwave digester is shown in Fig.-1 (a) and 1 (b):

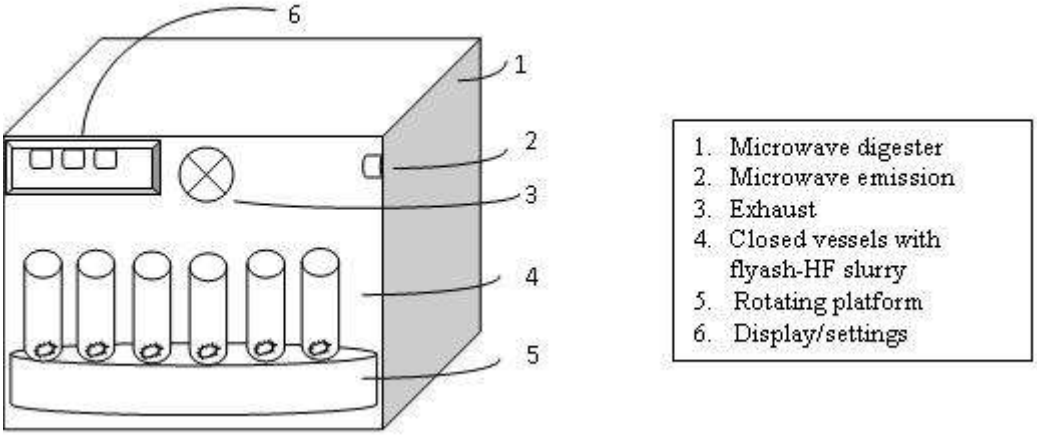


Fig.-1 (a): Schematic of Microwave Digester

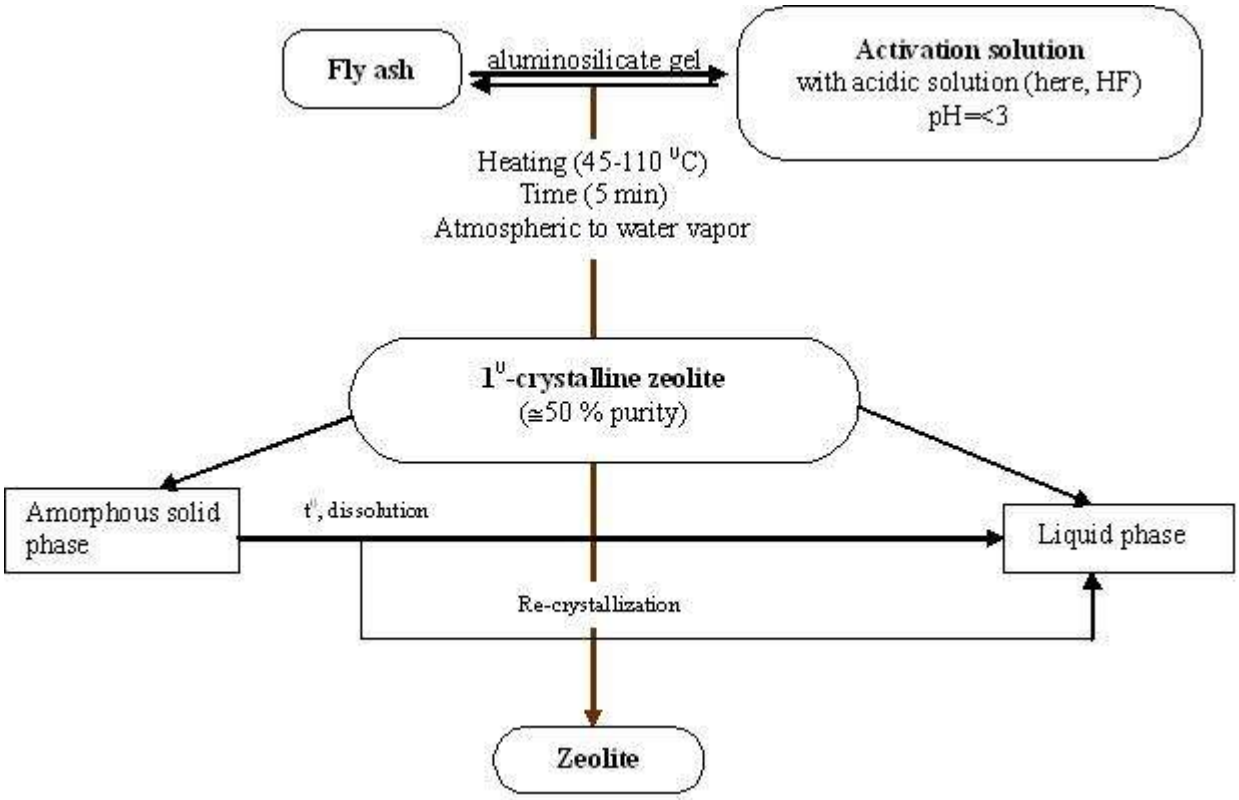


Fig.-1 (b): A Flow chart of the synthesis process for microwave digestion of fly ash

The digestion was performed in closed vessels (volume 100 ml). Reaction parameters are temperature, reaction time (5 m) and sample to reagent ratio (L/S = 10) kept constant (shown in Table-1 and 2). The heating cycle was based on the power settings from 400, 800 and 1600 Watt. Digestion pressure is atmospheric pressure. 1 g of fly ash was taken into the digestion vessels with 10 ml of HF. No stirring was provided. It is then allowed for around 15 m of natural digestion with HF. The initial temperature of digester was maintained at 37 ^{o}C. After the final temperature is achieved, microwave digester was kept at that temperature as per the set program and heating duration of 5 m. Finally, after the completion of microwave process, the digesting vessels were allowed to cool within the digester only. All the vessels were taken out of the digester. Safety precautions should be taken while opening the vessels. A relaxation time of 5-10 minutes was allowed for the mixture. The mixture was later transferred to a filtration unit for the separation of solid residue and the liquid supernatant. The resultant liquid was collected into the propylene bottles and kept for further analysis. In order to separate out the solid residue from the filter paper, the filter paper was kept in the hot air oven at around 65 ^{o}C for about 12 h for complete drying. All the solid particles left over on the surface of the filter paper, were scraped and stored in polythene bags for further analysis.

Table-1: Symbols and Parameters which are considered for the study

Symbols	
Ws	Wt. of solids
W1	Initial weight of filter paper
W2	Weight of filter paper after drying (filter paper + undigested silica)
W3	Weight of undigested silica (W2-W1)
W4	Weight of digested silica (Ws-W3)

L/S	**Temp.** (°C)	**Time** (min)
10	45 – 200	5
		10
		15

Table-2: Sample dissolution for different temperature, time and source of fly ash

Time (min)	**Sample designations for different temperature, time and source of fly ash**																	
	Temperatures (^{o}C)																	
	45	**50**	**55**	**60**	**70**	**80**	**90**	**100**	**110**	**120**	**130**	**140**	**150**	**160**	**170**	**180**	**190**	**200**
A	F1-A-45	F1-A-50	F1-A-55	F1-A-60	F1-A-70	F1-A-80	F1-A-90	F1-A-100	F1-A-110	F1-A-120	F1-A-130	F1-A-140	F1-A-150	F1-A-160	F1-A-170	F1-A-180	F1-A-190	F1-A-200
	F2-A-45	F2-A-50	F2-A-55	F2-A-60	F2-A-70	F2-A-80	F2-A-90	F2-A-100	F2-A-110	F2-A-120	F2-A-130	F2-A-140	F2-A-150	F2-A-160	F2-A-170	F2-A-180	F2-A-190	F2-A-200
	F3-A-45	F3-A-50	F3-A-55	F3-A-60	F3-A-70	F3-A-80	F3-A-90	F3-A-100	F3-A-110	F3-A-120	F3-A-130	F3-A-140	F3-A-150	F3-A-160	F3-A-170	F3-A-180	F3-A-190	F3-A-200
B	F1-B-45	F1-B-50	F1-B-55	F1-B-60	F1-B-70	F1-B-80	F1-B-90	F1-B-100	F1-B-110	F1-B-120	F1-B-130	F1-B-140	F1-B-150	F1-B-160	F1-B-170	F1-B-180	F1-B-190	F1-B-200
	F2-B-45	F2-B-50	F2-B-55	F2-B-60	F2-B-70	F2-B-80	F2-B-90	F2-B-100	F2-B-110	F2-B-120	F2-B-130	F2-B-140	F2-B-150	F2-B-160	F2-B-170	F2-B-180	F2-B-190	F2-B-200
	F3-B-45	F3-B-50	F3-B-55	F3-B-60	F3-B-70	F3-B-80	F3-B-90	F3-B-100	F3-B-110	F3-B-120	F3-B-130	F3-B-140	F3-B-150	F3-B-160	F3-B-170	F3-B-180	F3-B-190	F3-B-200

C	F1-C-45	F1-C-50	F1-C-55	F1-C-60	F1-C-70	F1-C-80	F1-C-90	F1-C-100	F1-C-110	F1-C-120	F1-C-130	F1-C-140	F1-C-150	F1-C-160	F1-C-170	F1-C-180	F1-C-190	F1-C-200
	F2-C-45	F2-C-50	F2-C-55	F2-C-60	F2-C-70	F2-C-80	F2-C-90	F2-C-100	F2-C-110	F2-C-120	F2-C-130	F2-C-140	F2-C-150	F2-C-160	F2-C-170	F2-C-180	F2-C-190	F2-C-200
	F3-C-45	F3-C-50	F3-C-55	F3-C-60	F3-C-70	F3-C-80	F3-C-90	F3-C-100	F3-C-110	F3-C-120	F3-C-130	F3-C-140	F3-C-150	F3-C-160	F3-C-170	F3-C-180	F3-C-190	F3-C-200

Characterization

Determination of dissolved silica

The solution obtained after separation of activated fly ash residue, was subjected to elemental analysis for the determination of silica content[28]. The results obtained are presented in Table-4 and 5.

Complete elemental analysis of fly ash was carried out using inductively coupled plasma - atomic emission spectrometer (ICP-AES). Model: ARCOS from M/s. Spectro, Germany. The excited electrons emit energy at a given wavelength as they return to ground state after excitation by high temperature argon plasma[29-30]. The fundamental characteristic of this process[31] is that each element emits energy at specific wavelengths peculiar to its atomic character. The energy transfer of electrons when they fall back to ground state is unique to each element as it depends upon the electronic configuration of the orbital. The energy transfer is inversely proportional to the wavelength of electromagnetic radiation, $E = hc/\lambda$ ... (Where h is Planck's constant, c the velocity of light and λ is wavelength), and hence the wavelength of light emitted is also unique. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the sample being analyzed[32]. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can qualitatively and quantitatively find the elements from the given sample relative to a reference standard[28].

RESULTS AND DISCUSSION

Results of various tests conducted on the samples are being presented here. The results indicate that the temperature above 200 ^{o}C, does not have much effect on the silica dissolution. At lower temperature only, it can be possible to achieve the required amount of digestion of silica (shown in Table-3, Fig.-2). The effects of digestion with temperature change on samples are illustrated in Fig.-3 and Table-4. For most of the elements, observed temperature suggested by the original methods[33-35], (60-65 ^{o}C) was found to be optimal. The recoveries for Si, Al, Fe and other trace elements were best when the sample was irradiated at 60-65 ^{o}C. Fig.-4 and -5 and Table-5 shows the effect of digestion with respect to time change on elemental recovery. Recovery of the elements remained unaffected in most of the cases; which in this case, too, seem to be optimized by the digestion time. Compared to the conventional digestion methods, microwave method consumes less time and increases efficiency in fly ash sample digestion. The expenses and costs need to be explored for pilot plant

experimentation, with the available technology. It can be concluded that the establishment of an efficient, cost effective, fast route (from hours to minutes) and environment friendly way of the synthesis of fly ash zeolite gives good recoveries using fluoride-containing medium with microwave irradiation.

Table-3: Bulk Solid Dissolution (% by Wt.) (time=5 min)

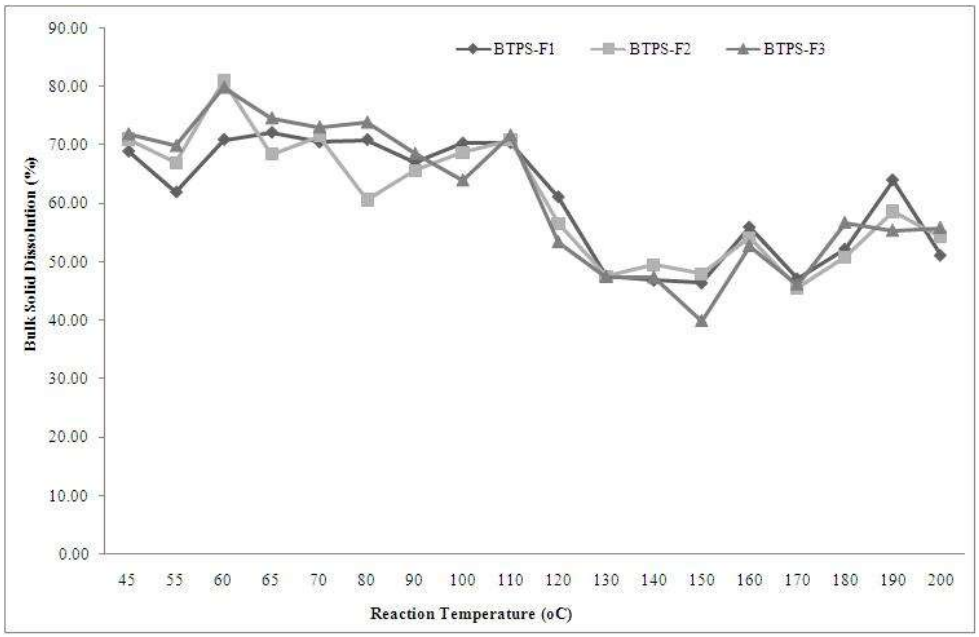
Solid Samples	Temperature (^oC)																	
	45	55	60	65	70	80	90	100	110	120	130	140	150	160	170	180	190	200
BTPS-F1	69.00	62.00	71.00	72.23	70.56	70.99	67.20	70.39	70.46	61.17	47.57	46.84	46.39	56.00	47.13	52.22	64.10	51.13
BTPS-F2	71.00	67.00	81.00	68.46	71.55	60.67	65.64	68.74	70.93	56.61	47.55	49.50	47.94	54.19	45.60	50.86	58.67	54.32
BTPS-F3	72.00	70.00	80.00	74.74	73.15	74.00	68.62	64.08	71.77	53.49	47.52	47.40	39.93	52.82	46.23	56.78	55.43	55.90

Table-4: Optimization of Silica Reduction Potential with respect to Temperature (at time = 5 min)

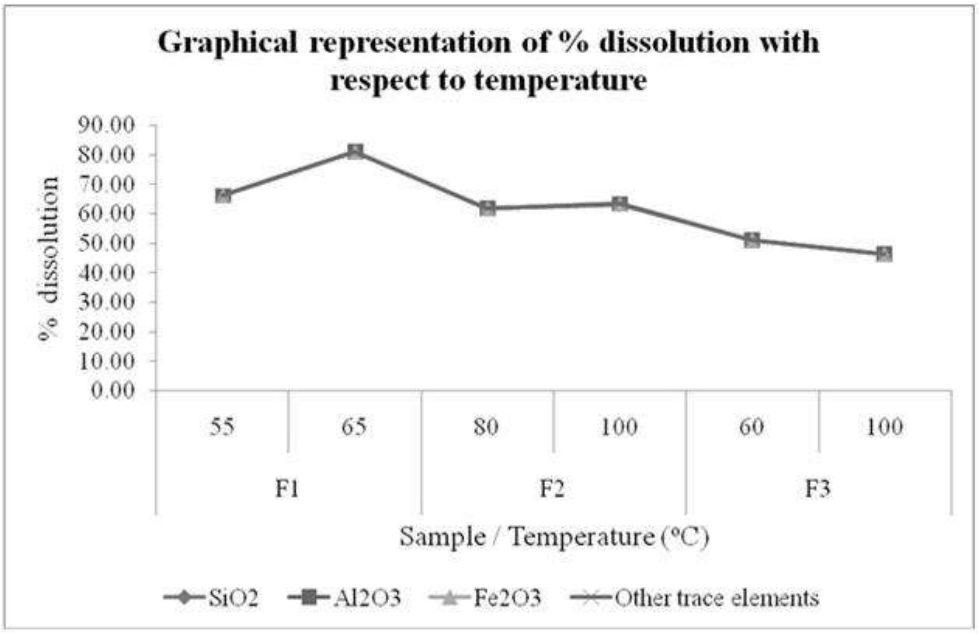
Sample	Temperature (^oC)	Initial conc. (%)				Loss of bulk solid (%)	ICP result (%)				Silica reduction (%)			
		SiO_2	Al_2O_3	Fe_2O_3	Other trace elements		Si	Al	Fe	Other trace elements	SiO_2	Al_2O_3	Fe_2O_3	Other trace elements
F1	55	63.85	26.05	5.14	4.96	62.00	1.26	0.0001	0.0002	60.74	65.99	0.0109	0.1363	33.86
	65	63.85	26.05	5.14	4.96	72.23	1.55	0.0000	0.0000	70.68	81.01	0.0029	0.0208	18.97
F2	80	63.28	27.06	4.63	5.03	60.67	1.17	0.0000	0.0001	59.50	61.69	0.0027	0.0801	38.23
	100	63.28	27.06	4.63	5.03	68.74	1.20	0.0001	0.0001	67.54	63.21	0.0070	0.0763	36.71
F3	60	61.99	29.29	3.76	4.96	80.00	0.95	0.0000	0.0001	79.05	51.03	0.0024	0.0489	48.92
	100	61.99	29.29	3.76	4.96	64.08	0.86	0.0000	0.0000	63.22	46.17	0.0032	0.0108	53.82

Time	Sample	Temperature (^oC)	Initial conc. (%)				Loss of bulk solid (%)	ICP result (%)				Silica reduction (%)			
			SiO_2	Al_2O_3	Fe_2O_3	Other trace elements		Si	Al	Fe	Other trace	SiO_2	Al_2O_3	Fe_2O_3	Other trace elements
5	F1	55	63.85	26.05	5.14	4.96	62.00	1.26	0.03	0.02	60.69	65.99	3.64	13.63	16.74
		65	63.85	26.05	5.14	4.96	72.23	1.55	0.01	0.00	70.67	81.01	0.98	2.08	15.93
	F2	80	63.28	27.06	4.63	5.03	60.67	1.17	0.01	0.01	59.48	61.69	0.91	8.01	29.39
		100	63.28	27.06	4.63	5.03	68.74	1.20	0.02	0.01	67.51	63.21	2.35	7.63	26.81
	F3	60	61.99	29.29	3.76	4.96	80.00	0.95	0.01	0.01	79.04	51.03	0.79	4.89	43.29
		100	61.99	29.29	3.76	4.96	64.08	0.86	0.01	0.00	63.21	46.17	1.08	1.08	51.67
10	F1	55	63.85	26.05	5.14	4.96	74.00	0.54	0.01	ND	73.45	28.03	1.61	ND	ND
		65	63.85	26.05	5.14	4.96	74.00	0.59	0.02	ND	73.39	30.78	2.59	ND	ND
	F2	80	63.28	27.06	4.63	5.03	77.00	0.60	0.01	ND	76.39	31.80	1.32	ND	ND
		100	63.28	27.06	4.63	5.03	75.00	0.76	0.01	ND	74.23	39.91	1.78	ND	ND
	F3	60	61.99	29.29	3.76	4.96	72.00	2.03	0.03	0.06	69.89	109.16	3.21	49.04	61.41
		100	61.99	29.29	3.76	4.96	72.00	1.84	0.01	0.03	70.12	98.89	0.89	30.45	30.24

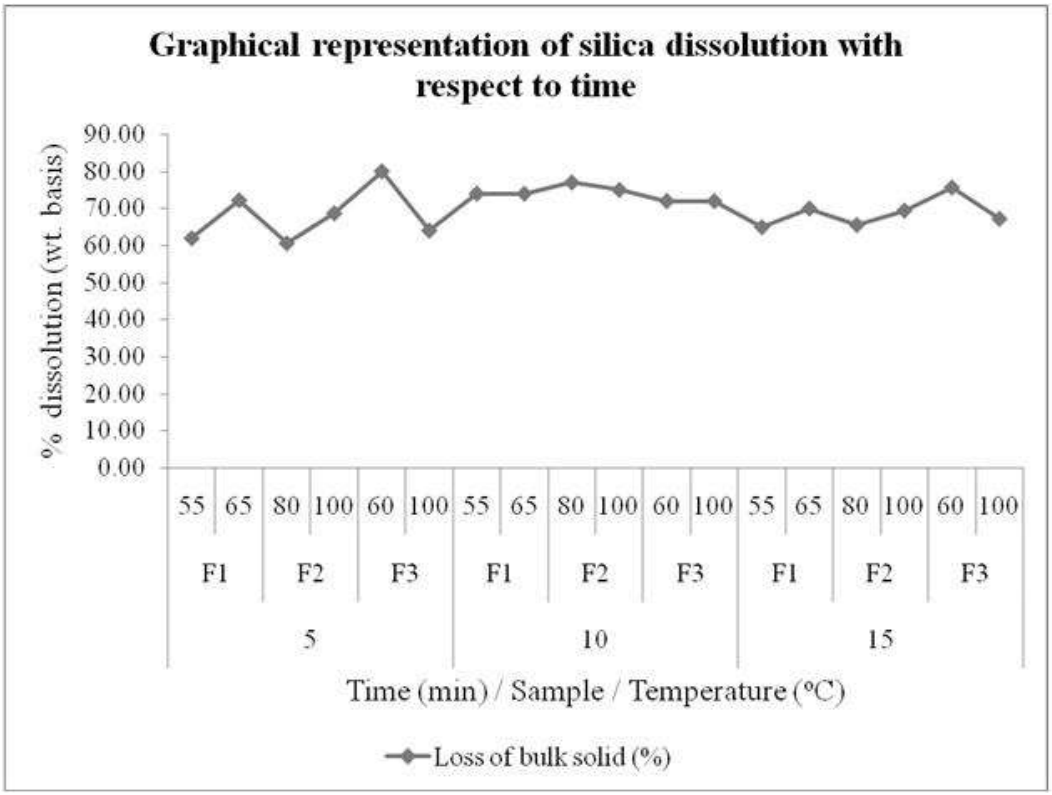
Table-5: Optimization of Silica Reduction Potential with respect to Time



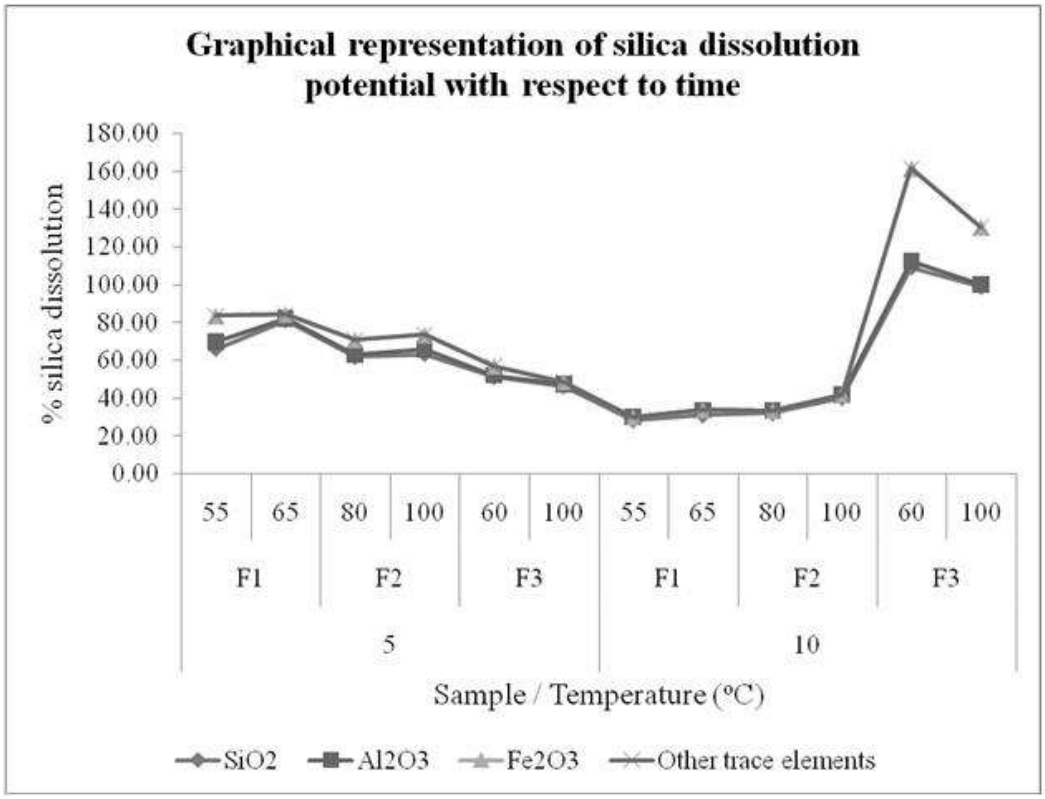
Graph.-2: Graphical representation of bulk solid dissolution and optimization of temperature



Graph-3: Graphical representation of % dissolution with respect to temperature (ICP results)



Graph-4: Graphical representation of bulk solid reduction with respect to time (% Wt. basis)



Graph-5: Graphical representation of % dissolution with respect to time (ICP results)

CONCLUSION

It is necessary to study the desired properties of synthesized zeolite. Different synthesis methods should be used or the zeolite must be modified, to meet the specifications. Zeolite synthesis, -modification, -characterization and -application thus are strongly related. A simplified description of the structure types, interrelationship between structural subunits, the effect of several parameters on the synthesis of fly ash zeolite through microwave digestion process; needs to be investigated further. The increasing requirements for the environmental protection have resulted in the search for more effective, inexpensive and ecologically safe solutions and zeolites are one of the alternatives, which due to their peculiar structure are widely used for various environmental processes[33-35]. The demand for an easily accessible and inexpensive source of zeolites has raised interest in synthesis of these minerals. The extraction of natural zeolites[13] from the deposits has certain disadvantages, like comparatively more expensive, causes degradation of the environment despite their better efficiencies. On the other hand the disposal and storage of fly ash as waste from the Thermal Power Plant's is a large problem in the power generation industries. The dumped fly ash may be a significant resource for the production of the zeolite. Such secondary optimization of wastes supports activities aiming at lithosphere protection and is consistent with the guidelines for sustainable development. The non-biodegradability of these materials is a major disadvantage since landfill disposal is environmentally undesirable and incineration is very expensive[14]. It is suggested that the use of zeolite may prove very economical, technically feasible and environmentally acceptable technology, particularly those prepared cheaply from fly ash, aluminum refining wastes and other solid waste materials containing silica and alumina may find application in many fields while simultaneously providing a solution to various environmental problems. The synthesizing capability of microwave from fly ash to zeolite has positive impacts on utilization of wastes coming from solid fuel combustion by converting the fly ash into valuable raw material and simultaneously accomplishing the lithosphere protection effect.

ACKNOWLEDGEMENT

The authors acknowledge the immense help received from the scholars whose articles are cited and included in references of this manuscript. The authors are also grateful to authors / editors / publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed.

REFERENCES

1. ASTM C 618 94. (1994). Specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in portland cement concrete. Annial Book of ASTM standards, 04.02. 296-8.
2. Walker, A.H., Michel, J., Benggio, B., Mcketrick, B., Scholz, D., Boyd, J. and Walker, W. (2003). Selection guide for oil spill applied technologies: volume 1 - decision making. Scientific and environmental associates, Inc.
3. Auerbach, S.M., Carrado, K.A. and Dutta, P.K. (2003) Handbook of zeolite science and technology. Marcel Dekker, Inc., New York.
4. Barnes, I. (2001). Speciality and novel uses of fly ash and fly ash components. Proceedings of the International Workshop on Novel Products from Combustion Residues: Opportunities and Limitations, Morella, Spain. 23-33.
5. Barrer, R.M. (1984). Synthesis of zeolites. In: Drzaj B, Hocevar S, Pejovnik S, editors.

Zeolites: synthesis, structures, technology and applications.1-26.
6. Breck, D.W. (1974). Zeolite molecular sieves. NY, USA: Wiley.
7. Ch Baerlocher, Ch., Meier, W.M. and Holson, D. (2001) Atlas of zeolite framework types. Amsterdam: elsevier.
8. Cundy, C.S. and Cox, P.A. (2003). The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. Chem. Rev 103, 663−701.
9. Das, A.K., Chakraborty, R. and et al (2001). ICP-MS multielement determination in fly ash after microwave-assisted digestion of samples. Talanta, Elsevier. 54, 975–981.
10. Flanigen, E. M. (1980). Pure appl chem. 52: 2191-2211.
11. Fukui, K. et al. (2009). Utilization of NaCl for phillipsite synthesis from fly ash by hydrothermal treatment with microwave heating. Advanced Powder Technology. 20, 35–40.
12. Galarneau, A., Renzo, F.D., Fajula, F., Vedrine, J., eds. (2001). Zeolites and mesoporous materials at the dawn of the 21st centuary. Stud surf sci catal. 135.
13. Gottardi, G. and Galli, E. (1985) Natural zeolites. Berlin: Springer.
14. Guthrie, G.D. (1997). Environ health persp. 105:1003-1011.
15. Hayes, B.L. (2002). Microwave Synthesis – chemistry at the speed of light. CEM publication. 1: 11-20.
16. Kim, D.S., Chang, J.S. and et al (2004). Synthesis of zeolite beta in fluoride media under microwave irradiation. Microporous and Mesoporous Materials, Elsevier. 68, 77–82.
17. Kokatailo, G.T., Fyfe, C.A., Feng, Y., Grondey, H., Gies, H. and Marler, B. (1995). Stud surf sci catal. 94:78-100.
18. Lister, R.A. and Peterson, T.J. (1996) Recent developments in dry ash handling. In: Raju VS, Datta M, Seshadri V, Agarwal VK, Kumar V, editors. Ash ponds and ash disposal systems. New Delhi: Narosa Publishing House. 86-96.
19. Mumpton, F.A. (1978). In: Sand LB, Mumpton FA, editors. Natural zeolites, occurrence, properties and use. London: Pergamon.
20. Murty, AVSR. (1996) Fly ash in construction of road and embankment. In: Raju VS, Datta M, Seshadri V, Agarwal VK, Kumar V, editors. Ash ponds and ash disposal systems. New Delhi: Narosa Publishing House. 222-37.
21. Newsam, J.M. (1992). Solid state chemistry: compounds. New York: oxford university press, 234-280.
22. Ojha, K. et al. (2004). Zeolite from fly ash: synthesis and characterization. Bull. Mater. Sci., Indian Academy of Sciences. 27(6), 555–564.
23. Querol X., Moreno N., Uman J.C., Alastuey A., Herna´ndez E., Lo´pez-Soler A., Plana F., (2002) Synthesis of Zeolites from coal fly ash: an overview. International Journal of Coal Geology, 50, 413– 423.
24. Querol, X., Uman J.C., Plana, F., Alastuey, A., Soler, A.L., Medinaceli, A., Valero, A., Domingo M.J., Rojo, E.G. (1999) Synthesis of Zeolites from Fly Ash in a pilot Plant Scale. Examples of Potential Environmental Applications. International Ash Utilization Symposium, Center for Applied Energy Research.
25. Querol,X., Alastuey, A. Ä S. and et al (1997). A Fast Method for Recycling Fly Ash: Microwave-Assisted Zeolite Synthesis. Environ. Sci. Technol. 31, 2527-2533.

26. Rayalu, S. et al. (2000). Highly crystalline faujasitic zeolites from flyash. Journal of Hazardous Materials. B77, 123–131.
27. Sherwood, P.T. and Ryley, M.D. (1996) The use of stabilized pulverized fuel ash in road construction. Road Res Lab, Ministry of Transport. 49:1-44.
28. Singh, D.N. and Kolay, P.K. (2002). Simulation of ash – water interaction and its influence on ash characteristics. Progress in Energy and Combustion science. 28: 269.
29. Source: Liebau, F., Gies, H., Gunawardne, R.P. and Marles, B. (1986). Zeolites. 6:373-377.
30. Thomas, J.M., Terasake, O., Gai, T.L., Zhou, W. and Gonzales-calbet, J. (2001). Acc chem res. 34:583-594.
31. Thostenson, E. and Chou, T.-W. (1999). Microwave processing: fundamentals and applications. Composites: Part A. 30, 1055–1071.
32. Treacy, M.M., Higgins, J.B. and Ballmoos, R.V. (1996). Zeolites. 16:327-802.
33. Tschernich, R.W. (1992). Zeolites of the world. Phoenix: Geoscience press.
34. Usmen, M.A., Baradan, B. and Yazici, S. Geotechnical and geo-environmental properties of stabilized lignite fly ash. Environmental Geotechnology edited by Usmen MA and Acor YB. 419-427, Rotterdam, Brockfield: AA Baikema.
35. Xavier, Q., Juan, C.U., Flicia, P., Andres, A., Angel, L., Alejandro, M., Antonio, V., Manel, J.D. and Ezequil, G.R. (1999) Synthesis of zeolites from fly ash in a pilot plant scale: examples of potential environmental application. Proceedings of the 1999 International Ash Utilization Symposium, October 18-20, Lexington, Kentucky, USA.