



## Leaching Properties of Fly Ash in Strong Alkaline Solution

C. CHEN<sup>1</sup>, W.L. GONG<sup>2</sup>, Q. LI<sup>1</sup>, L.F. SHEN<sup>1</sup> and J.P. ZHAI<sup>1\*</sup>

<sup>1</sup>State Key Laboratory of Pollution Control and Resource Reuse and School of the Environment, Nanjing University, Nanjing 210093, P.R. China

<sup>2</sup>Vitreous State Laboratory, The Catholic University of America, Washington D.C., USA

\*Corresponding author: Tel/Fax: +86 25 83592903; E-mail: jpzhai@nju.edu.cn

(Received: 11 October 2010;

Accepted: 25 April 2011)

AJC-9841

Dissolution properties of fly ash in strong alkaline solution have been studied by leaching in 7.5 M potassium hydroxide solution at room temperature. The solid to liquid ratio is 40 and the leaching time is from 6 to 168 h. Results show that the mass of silica and aluminum leached out increase with time but the rate decrease. Silica and aluminum tend to leach out to alkaline solution in the same rate at the beginning and then the rate of silica change to a little higher and the silica and aluminum tend to precipitate to amorphous "gel" phase. The leaching rate of metal ions are in the order of barium > calcium > magnesium > titanium > iron. Almost all the metal ions tend to precipitate to "gel" phase at beginning of leaching which make the "gel" phase rich in iron and calcium.

**Key Words:** Leaching, Fly ash, Alkaline solution.

### INTRODUCTION

Fly ash is a solid waste coming from power plants. In 2009, ca. 37.5 million tons of fly ash was produced by US coal-fired power plants and only 35 % has been reused in various applications<sup>1</sup>. Most of the others were disposed of in landfills which occupy much cultivated field and give lots of pollution to the air and groundwater around the landfill area. In this decade, fly ash has been applied to many fields. For examples, Magudeswaran *et al.*<sup>2</sup> studied the activated fly ash blended cement. Deshmukh *et al.*<sup>3</sup> analyzed the fly ash for agricultural use. Dakshene and Jain<sup>4</sup> advised that the alkali activated fly ash could be used for the adsorptive removal of tartrazin (E 102). Besides these, fly ash also has been used as a major component for geopolymer materials which is an inorganic silica-aluminum material. Davidovits<sup>5</sup> suggested that geopolymer material has similar properties as classic portland-cement but dramatically reduced CO<sub>2</sub> emissions.

Until now, the theory suggested by Xu and van Deventer<sup>6</sup> has been widely accepted to explain the reaction process of the geopolymerization. The theory is as follow: firstly, the silica-aluminum resources dissolve to free Si and Al species in the strongly alkaline solution and then the free Si and Al species reorganized to gel binders leading to the setting of the materials. So, the dissolving of the resources materials should be very important for the geopolymerization. Unfortunately, the papers about the leaching properties of fly ash in strong alkaline solution are very few. Mikuni *et al.*<sup>7</sup> studied how the

alkaline concentration and temperature affect the dissolution properties of fly ash in alkaline solution. Panagiotopoulou *et al.*<sup>8</sup> compared the dissolution properties of many aluminosilicate minerals. Lee and van Deventer<sup>9</sup> investigated the structural reorganization of fly ash in alkaline silicate solutions. However, all of the papers above only focused on the dissolution behaviour of silica, aluminum and calcium in leaching alkaline solutions. The results do not show the properties of other elements like iron, magnesium, titanium and the distribution of the elements in the alkaline solution and the solid reaction products. In this paper, the above issues are investigated.

### EXPERIMENTAL

The fly ash used in this paper was received from a power plant on Orlando, Florida. Table-1 shows chemical composition of the fly ash. As it shows, the main composition of the fly ash is the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> > 70 %) which implies the potential used as raw materials for geopolymer. After quantity-XRD process calculation, the fly ash contained 77 wt % glass particles, 13.4 wt % mullite and quartz and 9.6 wt % unburned carbon (Table-2 and Fig. 1). About 80 % of the fly ash particles were between 10 m and 100 μm.

The alkaline solutions used for the experiment were 7.5M potassium hydroxide solution which prepared by the chemically pure agents and deionized water. The HCl solution (HCl/H<sub>2</sub>O = 1:20) were prepared by the saturated HCl solution (37.5 %) and deionized water. All of the solutions were stored at least 24 h before use.

TABLE-1  
CHEMICAL COMPOSITION OF THE FLY ASH (%)

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI <sup>a</sup>
Fly ash	46.7	24.1	1.36	7.74	0.39	0.87	2.53	1.40	0.47	9.56

<sup>a</sup>LOI = Loss on ignition at 960 °C

TABLE-2  
MINERAL COMPOSITION OF THE FLY ASH (%)

Oxides	Quartz	Mullite	Fe <sub>2</sub> O <sub>3</sub>	Glass	LOI	Total
Fly ash	2.45	7.3	3.78	76.93	9.56	100

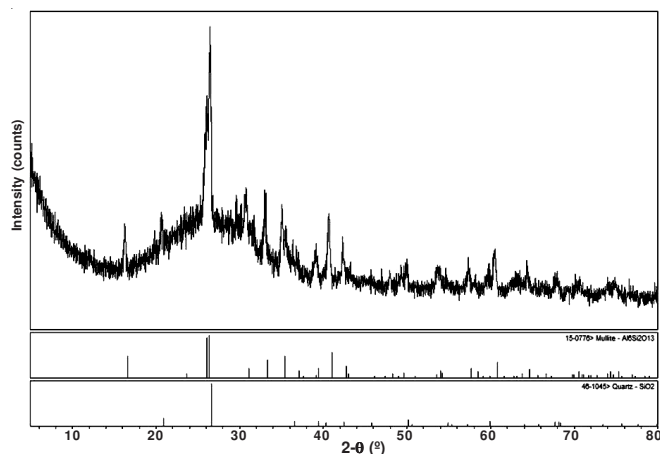


Fig 1. XRD pattern of original fly ash

Leaching experiments were conducted with 2.5 g ( $m_0$ ) fly ash with 100 g alkaline solution. The solution-to-fly ash ratio (W/S = 40) was used in all leaching experiments. The fly ash and the alkaline solutions were mixed in a 250 mL Teflon bottles. Then the bottles were fixed in a water-base which had a shaking instrument to keep the fly ash particles suspend in the alkaline solution. The reaction time was from 1 to 336 h and the temperature was room temperature. After leaching, the mixture solutions were filtered with 0.6  $\mu$ m filter membrane with a vacuum pump. The filter residue were washed and put in 100 % absolute ethanol to stop further hydration, then dried at 105 °C, weighted ( $m_1$ ) and stored in a dry box. The compositions of filter solutions were detected by DCP.

The mass and composition of solid reaction products was gained from dissolving it with HCl solution (1:20). 0.5 g ( $m_2$ ) solid reaction products were mixed with 150 mL HCl solution in a 250 mL Teflon bottles and fixed in the same equipments for leaching experiment. The temperature was maintained at

room temperature. The reaction time was 3 h. After it, the mixture solutions were also filtered with 0.6  $\mu$ m filter membrane with a vacuum pump and then the filter residue were washed, dried at 105 °C and weighed ( $m_3$ ). The filter solutions were also detected by DCP.

**Data calculation:** Typically, the data gained from the chemistry experiment and DCP-AES were calculated as follows:

(1) The unit mass of element (i) in leaching solution was given by:

$$M_i = \frac{C_i \cdot V_{al}}{m_0} \quad (1)$$

(2) The unit mass of element (i) in reaction product was given by:

$$M_i' = \frac{C_i' \cdot V_{hc} \cdot m_1}{m_0 \cdot m_2} \quad (2)$$

(3) The partition coefficient of element (i) was given by:

$$P_i = \frac{M_i}{M_i'} \quad (3)$$

(4). The rate of the element (i) leaching out was given by:

$$R_i = \frac{M_i + M_i'}{C_{0-i}} \quad (4)$$

here,  $C_i$  is the concentration of element (i) in the leaching solution gained by DCP.  $C_i'$  is the concentration of element (i) in the HCl solution gained by DCP.  $C_{0-i}$  is the composition of element (i) in the raw fly ash gained by XRF.  $V_{al}$  is the volume of the alkaline leaching solution.  $V_{hc}$  is the volume of the HCl solution.

## RESULTS AND DISCUSSION

The original data gained from DCP were presented in Table-3. All the data in the Table-3 have been calculated by the eqn. 1 to 4 and the results were showed from Figs. 2-6.

**Dissolution of silica and aluminum:** Results of the dissolution of silica and aluminum are summarized in Figs. 2 and 3 as a function of leaching time. As the Fig. 2, the mass of

TABLE-3  
ORIGINAL LEACHING RESULTS GAINED FROM DCP (ppm)

Sample ID	Al	Si	Fe	Ca	Mg	Ba	Ti
FA-L6 h-solution	25.52	18.74	9.74	34.89	7.95	0.15	2.85
FA-L24 h-solution	415.72	682.35	0.38	0.12	0.05	0.14	0
FA- L72 h-solution	703.38	1245.50	1.23	0.10	0.07	0.13	0
FA- L120 h-solution	902.33	1660.00	1.15	0.08	0.07	0.10	0
FA- L168 h-solution	1028.50	1985.90	1.20	0.09	0.05	0.05	0
FA- L6 h-products	34.79	30.73	36.61	65.67	9.91	4.16	6.35
FA-L24 h-products	26.90	32.00	99.43	102.07	26.39	9.12	20.03
FA- L72 h-products	35.40	53.46	202.95	133.62	47.72	14.30	41.43
FA- L120 h-products	36.29	77.17	308.18	162.15	64.48	18.66	58.82
FA- L168 h-products	65.34	128.08	370.49	172.52	75.98	20.62	80.92

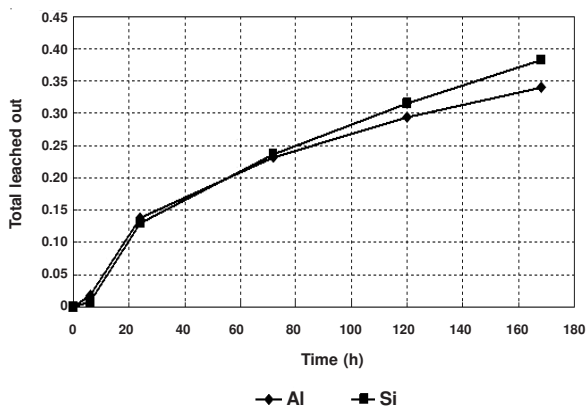


Fig. 2. Total Al and Si leached out

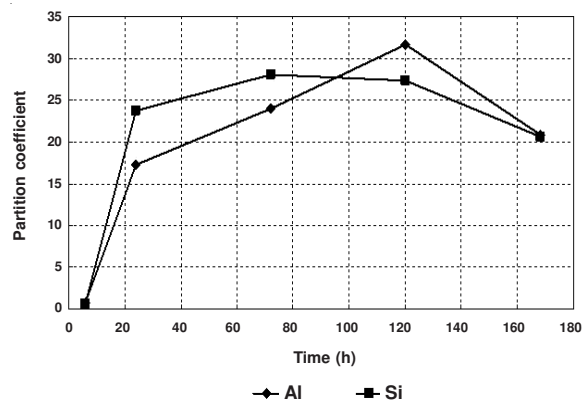


Fig. 3. Partition coefficient of Al and Si

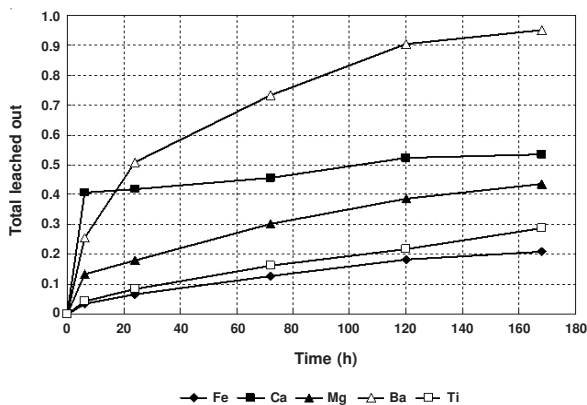


Fig. 4. Total Fe, Ca, Mg, Ba and Ti leached out

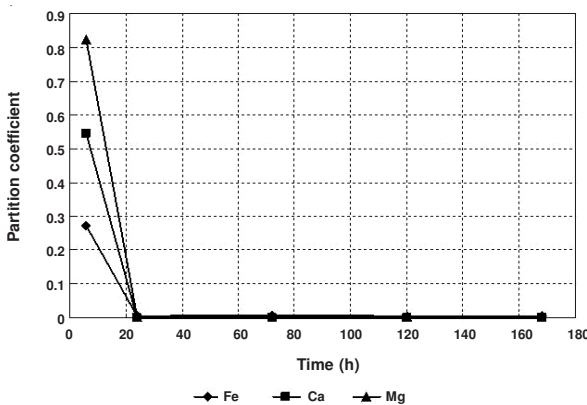


Fig. 5. Partition coefficient of Fe, Ca and Mg

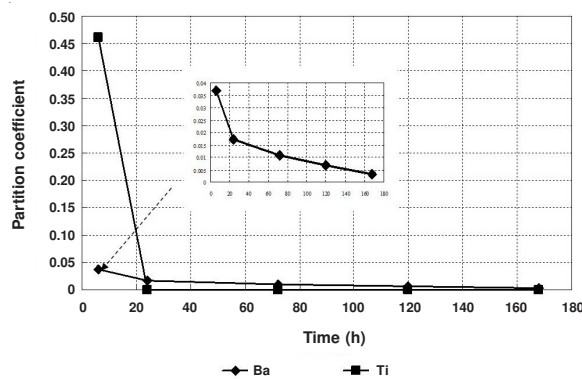


Fig. 6. Partition coefficient of Ba, Ti and Sr

silica and aluminum leached out grow with the time and reach 38.2 and 33.9 % after 168 h, respectively. However, during the whole leaching process, the rate of leaching is decreasing gradually. Take the silica for example, *ca.* 13.2 % silica is leached out in the first 24 h (average 0.55 %/h) while the result only increases to 38.2 % in the next 144 h (average 0.17 %/h). At the early stage of the leaching, there are no apparent difference between the leaching rates of silica and aluminum while it is clear that the leaching rate of silica observed a little higher than aluminum after 72 h. Fig. 3 shows the change of partition coefficients of silica and aluminum as a function of time. It could be seen that both the curves of silica and aluminum experience a growth at the beginning and then flow down. The results could be explained that when the concentrations of solution are low, the silica and aluminum tend to leach out to the alkaline solution. However, after the concentrations of solution reach a "saturate" point, the silica and aluminum change tending to precipitate to solid products. The results are consistent with the hypothesis of the formation of geopolymerization suggested by Xu and van Deventer<sup>10</sup>. As the hypothesis, there are three stages of the geopolymerization *viz.*, the dissolution of solid reactants, transferring of the dissolved species from the solid surface into a gel phase, nucleation and condensation of the gel phase. It is presumed that the present phenomena should belong to the stage 1 and 2. With the help of the XRD, we know that only the quartz and mullite which origin from the raw fly ash could be detected in the XRD patterns of reaction products (Figs. 1 and 7) and no new crystalline minerals are found during the leaching process. The results

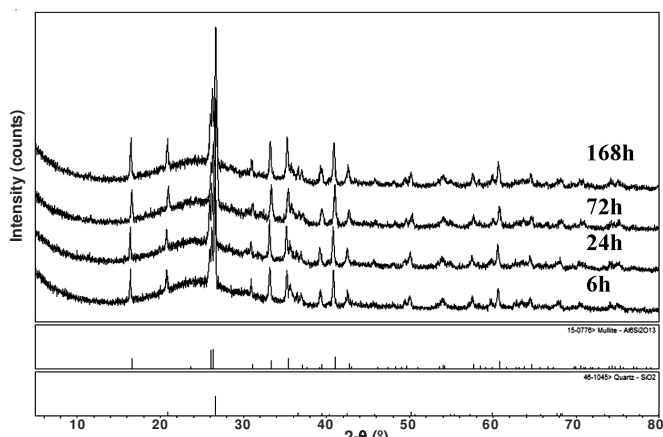


Fig. 7. XRD patterns of leaching products

make sure that the solid products forming during the leaching must be an amorphous "gel" phase which can not be detected by XRD. Fig. 8 shows the backscattering electron images of the polished reaction products after 3d. As the images, there is an apparent "gel" phase (white area A) coating on the surface of the un-reacted particles (black area B) which is consistent with the XRD and the hypothesis for geopolymerization. According to the leaching theory, the "gel" phase should be a "block" for the OH<sup>-</sup> diffuses to the reaction surface which leads to the decrease of the leaching rate.

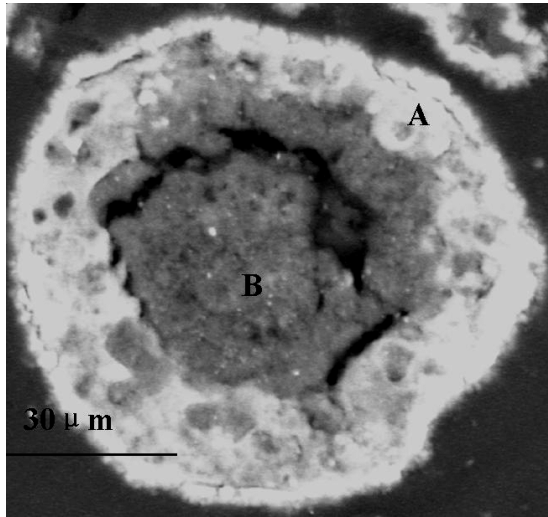


Fig. 8. Backscattering electron images of leaching products after 72 h

**Dissolution of metal ions:** Results of the dissolution of metal ions are summarized in Figs. 4-6 as a function of leaching time. As the Fig. 4, the metal ions show apparent different leaching rates. The rates are in the order of: barium > calcium > magnesium > titanium > iron. After 168 h, ca. 95 % of barium in the original fly ash has been leached out. At the same time, the Mg, Ti and Fe only reach 43, 28 and 20 %, respectively. The leaching rates of barium, magnesium, titanium and iron gradually decrease during the leaching process as the silica and aluminum while it is very strange that the calcium show high dissolution at the beginning of the leaching (0 to 40 % before 6 h) and then followed by slow increasing (40 to 53 % from 6 to 168 h). Fig. 5 shows the change of partition coefficients of metal ions as a function of time. As the Fig. 5, it could be seen that the partition coefficients almost drop down to zero at the early leaching process. The results reveal that almost all the metal ions tend to precipitate to solid products at the early period of the leaching. Mikuni *et al.*<sup>7</sup> suggested that the calcium dissolved relatively large amount in genuine water and no marked dissolution was detected with increasing concentrations of the alkaline leaching solution and presumed that it may be due to the formation of C-S-H gel. Based on the EDS results (Figs. 9 and 10), both the main compositions of the two areas are silica and aluminum. However, they show much difference in the iron and calcium. The peak of iron and calcium are much higher in the "gel" phase than the un-reacted particles (the other metal ions can not be detected because of the low content). It suggests that the iron and calcium enriches to the "gel" phase through the leaching process.

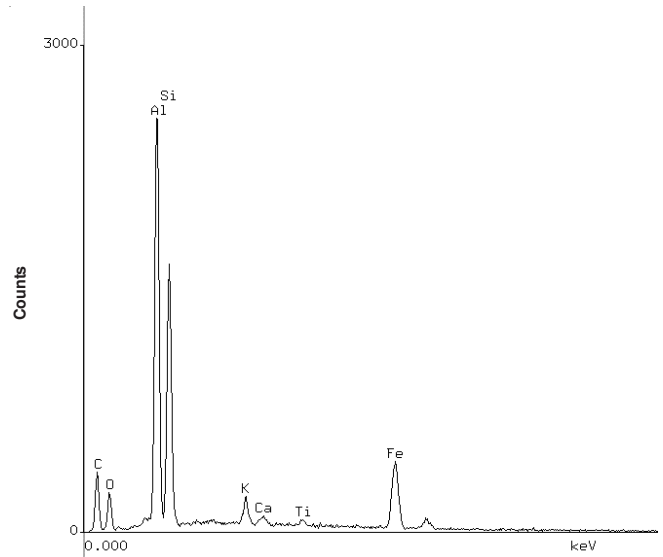


Fig. 9. EDS results of area B of Fig. 9

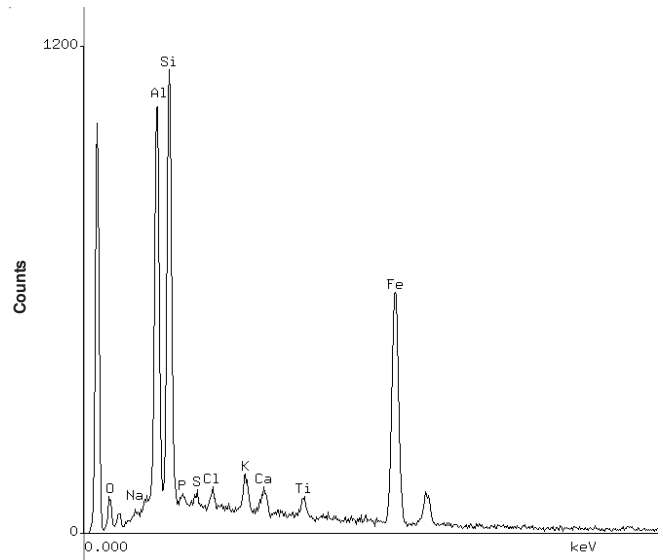


Fig. 10. EDS results of area A of Fig. 9

So the leaching process of fly ash particles in the strong alkaline solution is summarized as Fig. 11:

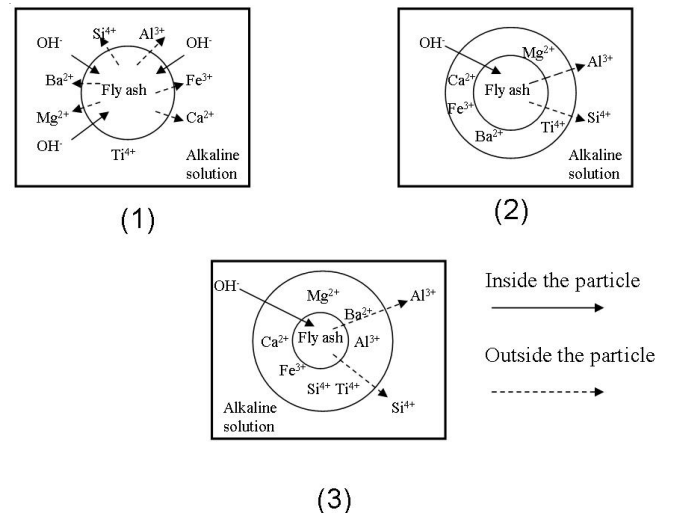


Fig. 11. Mechanism of leaching process

(1) OH<sup>-</sup> in the strong alkaline solution reacts with the fly ash particles and the elements including silica, aluminum, barium, calcium, magnesium, titanium and iron leached out to the solution.

(2) Barium, calcium, magnesium, titanium and iron react with the OH<sup>-</sup> in the solution and a thin "gel" phase forms coating on the surface of the fly ash particles. OH<sup>-</sup> must diffuse through the "gel" phase to the un-react fly ash particles and the silica and aluminum must also diffuse through the "gel" phase to the alkaline solution. The rate of leaching decrease.

(3) The silica and aluminum concentrations in the solution reach a "stature" point. The silica and aluminum start precipitating into the "gel" phase which make the "gel" phase thicker and the rate of leaching continue decreasing.

### Conclusion

Measurements of dissolution of fly ash which is an important material for geopolymer manufacturing have been conducted in 7.5M KOH solution at room temperature and the solid to liquid ratio is 40 all the time. The leaching time is from 6 to 168 h. The obtained dissolution properties could be summarized as follows: Extending the leaching time could make more silica and aluminum leached out but the leaching rate decrease. At the early stage of the leaching, silica and aluminum tend to leach out to alkaline solution at the same rate. Then the rate of silica change to a little higher and the

silica and aluminum tend to precipitate to amorphous "gel" phase. The leaching rate of metal ions are in the order of barium > calcium > magnesium > titanium > iron. Almost all the metal ions tend to precipitate to "gel" phase at very beginning of leaching which make the "gel" phase rich in the iron and calcium.

### ACKNOWLEDGEMENTS

The authors are grateful for financial support of this project from the Vitreous State Laboratory (VSL) of The Catholic University of America (CUA). One of the authors, Chen Chen thanks the Chinese Overseas Fellowship Commission for financial support of his visit to VSL/CUA.

### REFERENCES

1. [http://en.wikipedia.org/wiki/Fly\\_ash](http://en.wikipedia.org/wiki/Fly_ash)
2. P.N. Magudeswaran, M. Malathi and S. George, *Asian J. Chem.*, **20**, 21 (2008).
3. N.C. Deshmukh, P.K. Sarway, N.P. Tyagi, A. Bawaria and S. Shrivastava, *Asian J. Chem.*, **17**, 1371 (2005).
4. M. Dakshene and R. Jain, *Asian J. Chem.*, **22**, 7733 (2010).
5. J. Davidovits, *J. Thermal Anal.*, **37**, 1633 (1991).
6. H. Xu and J.S.J. van Deventer, *Int. J. Miner. Process.*, **59**, 247 (2000).
7. A. Mikuni, R. Komatsu and K. Ikeda, *J. Mater. Sci.*, **42**, 2953 (2007).
8. Ch. Panagiotopoulou, E. Kontori, T. Perraki and G. Kakali, *J. Mater. Sci.*, **42**, 2967 (2007).
9. W.K.W. Lee and J.S.J. van Deventer, *Colloids Surf. A*, **211**, 49 (2002).
10. H. Xu and J.S.J. van Deventer, *Colloids Surf. A*, **216**, 27 (2003).

## NEW ZEALAND INSTITUTE OF CHEMISTRY CONFERENCE

27 NOVEMBER — 1 DECEMBER, 2011

THE UNIVERSITY OF WAIKATO, HAMILTON, NEW ZEALAND

#### Contact:

ForumPoint2/Six Hats Conference Management

Postal Address: PO Box 1008, WMC, Hamilton 3240

Location: Level 1, 1088 Victoria Street, Hamilton

Phone: +64 7 981 5860; Facsimile: +64 7 838 1097; Email: [kylie@fp2.co.nz](mailto:kylie@fp2.co.nz)