Available online at www.sciencedirect.com
SciVerse ScienceDirect
Procedia Engineering 21 (2011) 1124 – 1131
Procedia Engineering
www.elsevier.com/locate/procedia

2011 International Conference on Green Buildings and Sustainable Cities

Novel fiber-reinforced composite materials based on sustainable geopolymer matrix

A. Natali [a*], S. Manzi[a], M. C. Bignozzi[a]

[a]Dipartimento di Ingegneria Civile, Ambientale e dei Materiali,
Facoltà di Ingegneria - Università di Bologna, Via Terracini 28, 40131 Bologna, Italy

Abstract

Geopolymers are representing the most promising green and eco-friendly alternative to ordinary Portland cement and cementitious materials, thanks to their proven durability, mechanical and thermal properties. However, despite these features, the poor tensile and bending strengths usually exhibited by geopolymers due to their brittle and ceramic-like nature, can easily lead to catastrophic failure and represent the main drawback limiting the use of those materials in several applications. Fiber reinforced geopolymer composites may be considered a solution to improve flexural strength and fracture toughness. Different types of dispersed short fibers are here investigated as a reinforcing fraction for a geopolymer matrix based on an alkali-activated ladle-slag. It has been demonstrated that both organic and inorganic fibers can lead to a significant flexural strength enhancement. Moreover, the investigated geopolymers exhibit an increase in toughness, thus determining a switch from a brittle failure mode to a more ductile one.

Selection and/or peer-review under responsibility of APAAS

Keywords: geopolymer; composite; ladle-slag; waste management

1. Introduction

In the last 20 years, the increased need to design and formulate green materials significantly contributed to develop innovative researches on environmentally friendly substitutes for Portland cement, along with ways of reusing industrial waste and by-products.

* Corresponding author. Tel.: +39-051-2090363.
E-mail address: annalisa.natali2@unibo.it.

doi:10.1016/j.proeng.2011.11.2120

To this end, geopolymer materials have attracted a great attention and are still increasing their popularity in construction industry and building engineering because of their capability to restrain CO_2 emissions, together with their rapid strength development, low shrinkage and excellent corrosion and fire resistance. Producing geopolymer binders would not be so detrimental to environment as producing ordinary Portland cement (OPC), thanks to the lower process-temperature characterizing geopolymers production technology [1-3].

Geopolymers have been recently regarded as promising substitutes for OPC in different applications fields, including that of engineered fiber reinforced composite materials based on cementitious or inorganic matrices [4-8]. In the past years, in facts, fiber reinforced composite materials have been playing an important role in rehabilitation and repair of damaged masonry and concrete structures, thanks to their performing properties such high strength to weight ratio, corrosion resistance and ease of application.

Woven fabrics, mats or unidirectional fibers, such as carbon, E-glass, Kevlar or basalt fibers have been so far the most widely used to cast continuous fiber-reinforced composites in civil engineering applications. More recently, structural composite materials obtained from inorganic matrix have been designed to deal with the major drawbacks deriving from the use of organic polymer resins. As a matter of fact, a significantly low resistance to UV radiation and high-temperatures is largely limiting organic matrix use in a wide field of applications [6].

With the aim to go on with the research on inorganic matrices, fiber reinforced composite materials based on geopolymers are currently being investigated. Different types of fiber reinforcements have already been employed in various geopolymer systems to improve their flexural strength, impact behaviour and failure mode [4, 8]. It has been reported that adding reinforcing fibers to a brittle matrix helps to control micro and macro-cracks diffusion through the material by generating a bridging effect [4, 8-13], as well as to change the post-cracking behavior of the material from a brittle fracture mode to a ductile one, thanks to its enhanced strain energy dissipation ability [9, 11, 14-16].

This study investigates the effect of different fibers on a geopolymer matrix based on recycled waste. Ladle slag, a by-product coming from steel production process, has been used as novel raw material to synthesize sustainable geopolymer matrix [17]. Different types of short fibers were embedded in the novel matrix. High Tenacity (HT) carbon, E-glass, polyvinyl alcohol (PVA) and polyvinyl chloride (PVC) fibers were chosen and several tests have been carried out in order to determine the adhesion of each type of fiber to the matrix and their ability to improve the geopolymer's flexural strength and toughness. Results from mechanical and microstructure characterization of all obtained geopolymer composites are here reported and discussed.

2. Experimental

2.1. Materials

The geopolymer matrix was prepared with metakaolin (MK), obtained by calcination of a commercial kaolin with Si:Al ratio of 1.44 (Argirec B24, AGS Mineraux, Clerac, France) at 700°C for 5h, and ladle slag (LS), supplied by Acciaieria di Rubiera SpA, Casalgrande, RE, Italy. LS was previously sieved to obtain a grain size distribution ≤ 0.063 mm. Grain size distribution curves of LS and MK, determined by a laser particle-size analyzer (Master Sizer 2000, Malvern Instruments), are reported in Fig. 1; main oxides composition for kaolin and ladle slag are listed in Table 1.

Sodium silicate solution, with a SiO2:Na2O ratio of 1.99 (kindly supplied by Ingessil, Montorio, VR, Italy) and 8M NaOH solution were used as alkaline activators.

HT-carbon fibers (average fiber diameter: 10 µm, tensile strength: 5490 MPa) were supplied by Torayca-Toray Industries, Tokyo, Japan; commercial E-Glass fibers (average fiber diameter: 10 µm, tensile strength: 2500 MPa) were supplied by Betontex, Casalecchio di Reno, BO, Italy; PVA fibers (average fiber diameter: 18 µm, tensile strength: 1800 MPa) were supplied by Thermofibers S.r.l, Lanzo, TO, Italy and PVC fibers (average fiber diameter: 400 µm, tensile strength: 215 MPa) were supplied by Fili&Forme, S. Cesario sul Panaro, MO, Italy.

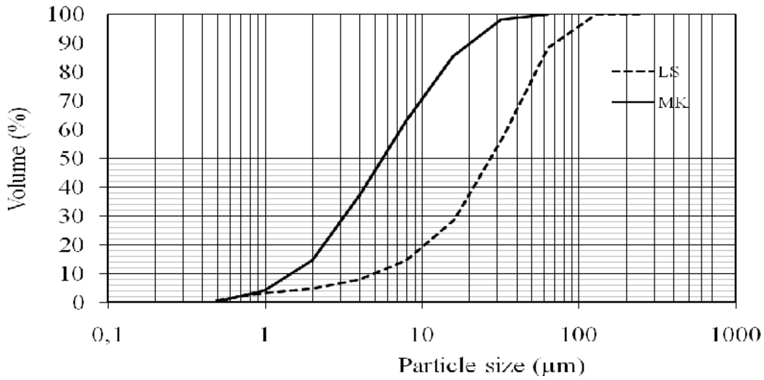

Fig. 1. Grain size distribution for metakaolin and ladle slag

Table 1. Chemical oxide composition of metakaolin and ladle slag (wt.%)

	CaO [%]	SiO_2 [%]	Al_2O_3 [%]	Fe_2O_3 [%]	TiO_2 [%]	MgO [%]
MK	0.08	47.6	37.7	1.6	1.7	-
LS	54.5	16.4	11.1	8.7	0.3	4.0

2.2. Samples preparation

The mix design for all the geopolymer samples is reported in Table 2. A reference sample (GS) was firstly prepared by combining in a planetary mixer both LS and MK, in a ratio of 3:2 respectively [17] and mixing for 5 min. The alkaline solutions were blended together and then added to the previously mixed solid fraction, up to obtain homogeneous and workable slurry. No further water additions, that would have been detrimental to mechanical properties [17], were necessary to achieve the adequate workability (Tab. 2).

The four different fibers, appositely selected, were cut to obtain a 7±1 mm length and used to prepare fiber-reinforced geopolymers, named as follows FtypeGS (e.g. FpvcGS means geopolymer matrix reinforced by PVC fibers). Regardless the fiber type, the same amount of fiber (1% wt. fraction on the total mixture) was added to MK and LS in the above reported ratio, then the slurry was mixed for 5 min. Specimens were cast in prismatic moulds of 2x2x12 cm and cured in a humid atmosphere (RH > 90%) at room temperature for 7 days.

2.3. Samples characterization

Pore size distribution measurements were carried out on all specimens by a mercury intrusion porosimeter (MIP, Carlo Erba 2000) equipped with a macropore unit (Model 120, Fison Instruments).

Flexural strength of geopolymer samples was determined by an Amsler Wolpert testing machine (100 kN) with three point bending geometry after 7 curing days; load-deflection curves were also recorded for fiber reinforced and unreinforced specimens, in order to determine their energy absorption capability by defining flexural toughness indices and residual strength factors, according to ASTM C1018-97.

The amount of energy absorbed during fracture and ductility of reinforced specimens were also determined by Charpy impact strength tests on 2x2x4 cm samples. A Zwick Charpy pendulum, equipped with a 15 J hammer, was used. All mechanical tests were conducted on batches of at least 3 samples and reported results are an average value of 3 tests.

Microstructure observations were performed on fracture surfaces by a Philips XL20 scanning electron microscope (SEM) and phase recognition of the investigated geopolymer matrix samples was acquired by energy dispersive X-ray (EDX 9800 microanalysis).

Table 2. Reference and fiber-reinforced geopolymer samples mix design

Samples	MK [g]	LS [g]	NaOH [g]	Na_2SiO_3 [g]	Fiber type	Fiber amount (wt. %)
GS	140	210	105	105	-	0
FcGS	140	210	105	105	Carbon HT	1
FgGS	140	210	105	105	E-Glass	1
FpvaGS	140	210	105	105	PVA	1
FpvcGS	140	210	105	105	PVC	1

3. Results and discussion

Pore size distributions for fiber-reinforced and unreinforced (dashed line) geopolymer samples are reported in Fig. 2. Reported data (Tab. 3) show clearly that the addition of reinforcing fibers generally resulted in a reduction of the intruded volume, except from FpvaGS: specific intruded volume for the investigated samples lies in the range of 52.5-129.1 mm3/g, where the highest values were recorded for the reference sample (GS) and PVA reinforced sample (FpvaGS). A remarkable difference in the pore network distribution between carbon, glass and PVC reinforced samples and the reference one can be pointed out, the latter showing a more homogeneous and uniform distribution. The pores structure for the unreinforced sample, in fact, comprises a system of mesopores from 20 to 200 nm that was not observed in the fiber-reinforced specimens, whose pores distribution is mainly defined by smaller pores (4-20 nm) (Fig. 2). Nevertheless, despite the reduction of the intruded volume found in most reinforced samples, their average pore radius (Rav) was found to be slightly higher after the addition of fibers (Tab. 3), especially for glass and PVA reinforced samples.

Besides increasing average pore radius, fiber addition has a direct effect on mechanical properties. Flexural strength (Rf) is indeed strongly increased for all fiber-reinforced samples, whose strength increments (Δ Rf) range between 30-70% if compared to unreinforced geopolymer. Maximum values were found for carbon fiber reinforced sample (FcGS) (Tab. 3). Increased mechanical strength for fiber-reinforced samples resulted in accordance with the lower total porosity values and the bridging effect adduced by the dispersed fibers. Even FpvaGS, whose total porosity was found higher than the reference sample's one, exhibited a clear flexural strength gain.

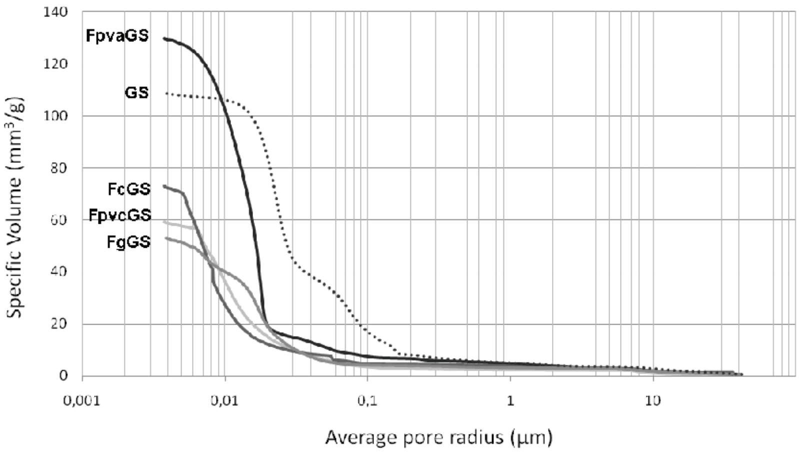

Fig. 2. Pore size distribution for geopolymer samples

Table 3. Physical and mechanical properties of geopolymer samples

Samples	Specific intruded volume [mm^3/g]	R_{av} [μm]	R_f [MPa]	Δ R_f [%]
GS	108.3	0.006	6.9	-
FcGS	72.2	0.009	11.7	+ 70
FgGS	52.5	0.016	9.0	+ 30
FpvaGS	129.1	0.016	11.2	+ 62
FpvcGS	58.5	0.009	10.0	+ 45

This is likely to be due to the stronger crack-bridging behavior of PVA fibers due to a high-grade adhesion to the geopolymer matrix and, thus to a more efficient load transfer mechanism.

Flexural toughness and post-cracking ductility of fiber-reinforced samples were also investigated. Load-deflection curves for geopolymer composites, along with unreinforced control samples (GS) were determined (Fig. 3). As shown in Fig. 3, post-cracking behavior is significantly improved by fiber addition. Reinforcing fibers are clearly contributing to extend the area under the non-linear portion of the load-deflection curve and, thus, to enhance the energy absorbed by the material during fracture. All added fibers are able to determine for the reinforced geopolymers a change from a plain linear behavior (GS), where the energy absorption capacity just concerns the simultaneous onset of fracture and initiation of cracking, to a typical ductile behavior, where the energy absorption is mainly determined by micro-cracks growth and propagation and progressive fiber debonding up to failure [15].

Moreover, the energy absorption capacity is significantly influenced by the type of reinforcing fibers used in the mixtures: carbon and PVC fibers show higher fracture toughness and ductility, as it can be seen from the wider curve branch that describe the composites' behavior after reaching the first-crack load. These fibers were demonstrated to have a better bridging behavior within the cracked matrix as they were able to induce a favorable pull-out mechanism that occurred when fracture arose.

To quantify the fracture energy content of the fiber-reinforced geopolymers, toughness indices and residual strength factors have been determined according to ASTM C1018-97 (Tab. 4) [16].
The closer I_5, I_{10} and I_{20} are to values of 5, 10 and 20 respectively, the more the material's behavior can be approximated to perfectly plastic after first crack. Carbon fiber-reinforced sample FcGS shows the best

response after first crack load, providing the higher values for all toughness indices and residual strength factor $R_{5,10}$. The latter represents the average level of strength retained after first crack as a percentage of the first-crack strength.

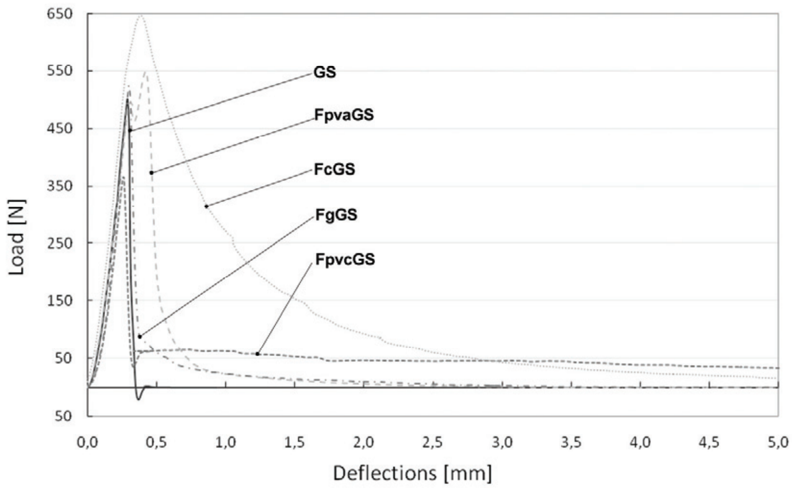

Fig. 3. Load-deflection curves for all geopolymer samples

Table 4. Toughness and residual strength of geopolymer samples

Samples	Resilience* [J/cm²]	Toughness Indices			Residual Strength Factor	
		I_5	I_{10}	I_{20}	$R_{5,10}$	$R_{10,20}$
GS	2.2	1.0	1.0	0	0	0
FcGS	3.1	4.6	6.5	8	38.62	14.41
FgGS	2.2	1.7	1.9	2.0	4.51	1.55
FpvaGS	2.6	3.1	3.4	3.5	4.67	0.86
FpvcGS	2.4	2.0	3.2	4.9	22.47	17.3

* Determined by impact test (Charpy Pendulum)

Microstructure investigations have been performed on cured samples by SEM-EDS to point out gels structure and composition (Fig. 4), as well as fiber-matrix interface (Fig. 5). It can be noticed that the geopolymerization process has successfully occurred and all investigated samples exhibited a mainly amorphous structure (Fig. 4,5). EDX investigations evidence the formation of C-A-S-H gels generated by geo-synthesis for all the samples, although in each sample differences in microstructure were observed. A more homogeneous and close-grained structure was found to be related to higher values of Si:Al ratios in the geopolymer matrix (detected Si:Al values ranged from 1.1 to 3.7).

Investigated samples showed that both organic (Fig. 5a) and inorganic (Fig. 5b) fibers are able to sufficiently adhere to the geopolymer matrix. However, polymer fibers seem more efficient in controlling and preventing the micro-cracks propagation (Fig. 5). In particular, PVC fibers were observed to have the best adhesion properties, probably due to their sensibly higher diameter. The strong bond between these fibers and the matrix, however, did not make the pull-out more difficult and, thus, did not affect the toughness of the material significantly.

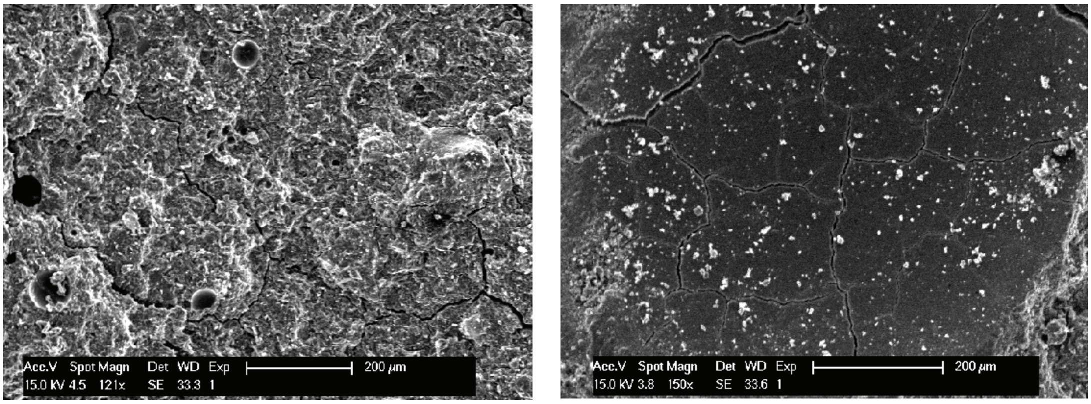

Fig. 4. (a) SEM observation for GS sample, 120 X; (b) SEM observation for GS sample, 150 X

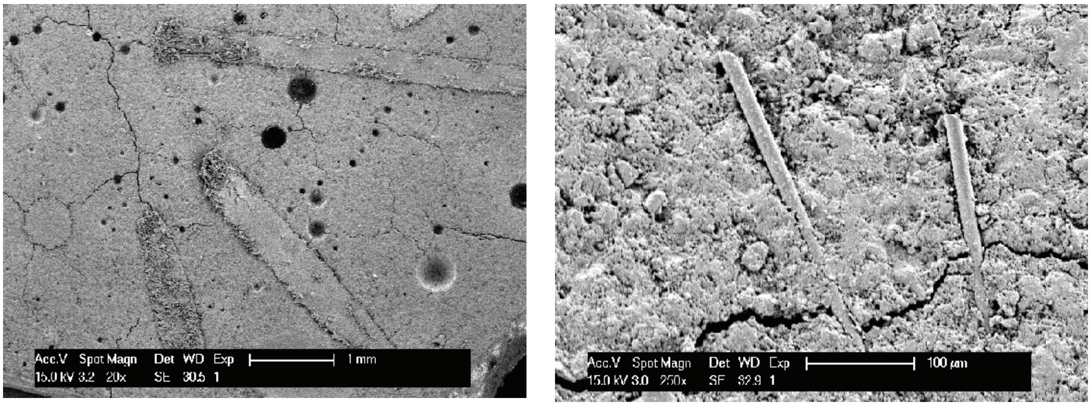

Fig.5. (a) SEM observation for FpvcGS sample, 20 X; (b) SEM observation for FgGS sample, 250 X

4. Conclusions

New fiber-reinforced composite materials based on sustainable geopolymer matrix have been investigated. All the selected fibers were found to have good adhesion properties, being able to control micro-cracks propagation along the matrix and creating a favorable bridging effect. A better behaviour of polymer fibers has been observed compared to that one showed by glass fibers. Moreover, obtained results showed that a fraction equal to 1% wt. of reinforcing fibers embedded in the geopolymer matrix is able to determine a flexural strength increment, ranging from 30% up to 70% depending on the fiber type, compared to the unreinforced material. Geopolymers added with PVC and carbon fibers exhibited the best energy absorption capacity: for those types of fibers the post-crack behavior is significantly improved, resulting in an enhanced ductility of the material after reaching the first crack load.

References

[1] Davidovits J. *Geopolymer Chemistry and Applications*. Saint-Quentin: Institut Géopolymère; 2008, p. 3-18.

[2] Pachego-Torgal F, Castro-Gomes J, Jalali S. Alkali-activated binders: A rewiew, Part 1. *Construction and Building Materials* 2008; **22**:1305-1314.

[3] Xu H, Van Deventer JSJ. The geopolymerisation of alumino-silicate minerals. *International Journal of Mineral Processing* 2000; **59**:247-266.

[4] Zhao Q, Nair B, Rahimian T, Balaguru P. Novel geopolymer based composites with enhanced ductility. *Journal of Materials Science* 2007;**42**:3131-3137.

[5] Giancaspro JW, Papakonstantinou CG, Balaguru PN. Flexural Response of Inorganic Hybrid Composites With E-Glass and Carbon Fibers. *Journal of Engineering Materials and Technology* 2010;**132**:1-8.

[6] Giancaspro JW, Papakonstantinou CG, Balaguru PN. Mechanical behavior of fire-resistant biocomposite. *Composites Part B : Engineering* 2009;**40**:206-211.

[7] Hammell J, Balaguru P, Lyon R. Influence of reinforcement types on the flexural properties of geopolymer composites. In: *Materials and process affordability - Keys to the future; Proc. 43rd International SAMPE Symposium, May 31st – June 4th*, Anaheim, CA ; 1998, p. 1600-1608.

[8] Silva FJ, Thaumaturgo C. Fibre reinforcement and fracture response in geopolymeric mortars. *Fatigue & Fracture of Engineering Materials & Structures* 2006;**26**:167-172.

[9] Dias DP, Thaumaturgo C. Fracture toughness of geopolymeric concretes reinforced with basalt fibers. *Cement and Concrete Composites* 2005;**27**:49−54.

[10] Toutanji H, Xu B, Gilbert J, Lavin T. Properties of poly(vinyl alcohol) fiber reinforced high-performance organic aggregate cementitious material: Converting brittle to plastic. *Construction and Building Materials* 2010;**24**:1-10.

[11] Li W, Xu J. Mechanical properties of basalt fiber reinforced geopolymeric concrete under impact loading. *Materials Science and Engineering* 2009;**505**:178-186.

[12] Lin T, Jia D, He P, Wang M. In situ crack growt.h observation and fracture behavior of short carbon fiber reinforced geopolymer matrix composites. *Materials Science and Engineering A* 2010;**527**:2404–2407.

[13] Zhang Z, Yao X, Zhu H, Hua S, Chen Y. Preparation and mechanical properties of polypropylene fiber reinforced calcined kaolin-fly ash based geopolymer. *Journal of Central South University of Technology* 2009 ;**16**:49- 52.

[14] Yunsheng Z, Wei S, Zongjin L, Xiangming Z, Chungkong C. Impact properties of geopolymer based extrudates incorporated with fly ash and PVA short fiber. *Construction and Building Materials* 2008;**22**:370-383.

[15] Toutanji H, Xu B, Gilbert J, Lavin T. Properties of poly(vinyl alcohol) fiber reinforced high-performance organic aggregate cementitious material: Converting brittle to plastic. *Construction and Building Materials* 2010;**24**:1-10.

[16] Barr BIG, Liu K, Dowers RC. A toughness index to measure the energy absorption of fibre reinforced concrete. *International Journal of Cement Composites and Lightweight Concrete* 1982;**4**:221-227.

[17] Bignozzi MC, Barbieri L, Lancellotti I. New Geopolymers based on Electric Arc Furnace Slag. *Advances in Science and Technology* 2010;**69**:117-122.