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Review paper

Using Different Methods of Nanofabrication as a New Way to Activate Supplementary Cementitious Materials; a Review

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ABSTRACT: Reducing the consumption of cement with simultaneous utilizing waste materials as cement replacement is preferred for reasons of environmental protection. Blended cements consist of different supplementary cementitious materials (SCMs), such as fly ash, silica fume, Ground Granulated Blast Furnace Slag (GGBFS), natural pozzolans, etc. These materials should be chemically activated to show effective cementitious properties. The present review article reports three different methods of nanofabrication, using ultrasound irradiation, solvothermal/hydrothermal process and microwave irradiation, that were used for activation of two types of SCMs. Based on the obtained results, these methods are suggested as effective methods for nanomodification of supplementary cementing materials.

Keywords: Microwave Irradiation, Nanomodification, Pozzolanic Activity, Supplementary Cementitious Materials, Ultrasound Irradiation.

INTRODUCTION

Environmental Issues of Cement Production

Among most important problems in recent years, climate change and global warming can be mentioned that are resulted by greenhouse gas emission. Carbon dioxide, as a major environmental pollutant leads to greenhouse effects. One of the most important industries and building operations causing carbon dioxide emission is the cement and concrete related industries so that cement production (including direct fuel for mining and transporting raw material) consumes approximately 633 billion Joules per ton, and releases about 1 ton of CO_2. Worldwide, the cement industry alone is estimated to be responsible for about 7% of all generated CO_2 (Pacewskaa and Wilińska, 2013; Najimi et al., 2011). On the other hand, many industrial wastes such as fly ash, silica fume, blast furnace slag and copper slag are pollutive; hence requiring proper collection, disposal and storage. Therefore Basic effort is to find a suitable replacement for economically and ecologically unfavorable cement by another component or components as supplementary cementitious materials (SCMs).

Application of these materials in cement and concrete decreases the depletion of

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natural resources, reduces pollutant emissions and increases the concrete durability, thus is environmentally friendly and economically beneficial (Shi et al., 2008; Targan et al., 2003).

Supplementary Cementitious Materials

Different Supplementary Cementitious Materials (SCMs), such as fly ash, silica fume, Ground Granulated Blast Furnace Slag (GGBFS), natural pozzolans, etc. are used to fabricate blended cements.

A pozzolan is defined as (ASTM C125) ‘‘a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties”. Pozzolans were the first cementitious materials used by early civilizations and some of the most important historical buildings rely on pozzolanic cement systems. The use of pozzolans can improve various physical properties of the resulting concrete. Pozzolans are obtained from various sources and can be naturally occurring minerals or industrial by-products (Lin et al., 2008; Sobolev, 2009).

Ground Granulated blast-furnace slag (GGBFS) or Iron slag is defined as the glassy granular material formed when molten blast-furnace slag is rapidly chilled as by immersion in water (ASTM C125, 1993; Duran Atis and Bilim, 2007). Fast cooling causes weak crystallization and converts the molten slag into fine aggregate sized particles (smaller than 4 mm), composed of predominantly noncrystalline material.

GGBFS shows pozzolanic behavior similar to that of natural pozzolans, fly ash and silica fume, because of its high content of silica and alumina in an amorphous state. Unlike other Pozzolans, it can be hydrated without addition of any cement. The use of GGBFS in concrete increases the workability and reduces bleeding of fresh concrete or mortar. It improves strength, reduces heat of hydration, reduces permeability and porosity and reduces the alkali–silica expansion. Industrial slag is one of the main constituents of SCMs which has been available since the inception of metal extraction from ores through metallurgical processes (Lawrence et al., 2005; Cyr et al., 2006).

Copper slag is the waste material of matte smelting and refining of copper such that each ton of copper generates approximately 2.5 tons of copper slag (Najimi et al., 2011).

It is well known that hydration of Portland cement results in formation of hydrated calcium silicates C-S-H, calcium hydroxide CH, hydrated calcium aluminates and sulfoaluminates (AFm, AFt) as well as similar products with iron ions (some abbreviations used in cement chemistry: C – CaO, S – SiO_2, H – H_2O). In a mixture of portland cement and pozzolan, a pozzolanic reaction occurs between $Ca(OH)_2$ which is the product of cement hydration, and pozzolan. The pozzolanic reaction progresses like an acid-base reaction of lime and alkalies with oxides (SiO_2 + $A1_2O_3$ + Fe_2O_3) of the pozzolan. This secondary pozzolanic reaction yields a denser microstructure because the $Ca(OH)_2$ is consumed and CSH paste is formed. Another benefit of using mineral admixtures, which leads to an increase in strength development, is due to heterogeneous nucleation. This process enhances the chemical activation of the hydration of cement (Wu et al., 2017).

Activation of SCMs

One of the major problems of selecting the appropriate pozzolanic material is its reactivity since the use of high reactive aluminosilicate materials as an addition to lime mortars produce hydraulic, durable mortars with sufficient mechanical strength. Pozzolanic activity can be defined as the reactivity capacity with $Ca(OH)_2$ and hardening capacity in humid medium. Although some other properties have effects on the pozzolanic activity, the references states that the pozzolan's strength is especially affected by the chemical composition, fineness and the amount of its glassy phase (Madani et al., 2016; Pourghahramani and Azami, 2015)

The methods that are known as activating pozzolanic materials, can be divided into three groups: thermal method, mechanical method, and chemical method. Thermal activation methods refer to those processes related to heat treatment, and can be classified into two categories: calcination of pozzolans and elevated temperature curing of pastes containing pozzolans. Mechanical methods have been used to increase the reactivity of siliceous materials such as quartz and basic or devitrified volcanic rocks, which are not regarded as likely sources of active pozzolan, by grounding them into ultrafine powders. This is due to the presence of a disturbed layer of highly reactive material which is formed on the surface of the mineral particles as a result of prolonged grinding. Acid-treatment is a chemical method for increasing the reactivity of an effective pozzolan, particularly at early stages (Souri et al., 2015; Owaid et al., 2014; Jafari Nadoushan and Ramezanianpour, 2016).

Nanotechnology in Concrete

The nanoscience and nano-engineering, sometimes called nanomodification, of concrete describe two main ways of application of nanotechnology in concrete research (Scrivener, 2009; Raki, 2009; Ojo and Mohr, 2009; Ltifi et al., 2011)

Nanoscience deals with the measurement and characterization of the nano and microscale structure of cement-based materials to better understand how this structure affects macroscale properties and performance through the use of advanced characterization techniques and atomistic or molecular level modeling. Nano-engineering encompasses the techniques of manipulation of the structure at the nanometer scale to develop a new generation of tailored, multifunctional, cementitious composites with superior mechanical performance and durability potentially having a range of novel properties such as: low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks. Concrete can be nano-engineered by the incorporation of nanosized building blocks or objects (e.g. nanoparticles and nanotubes) to control material behavior and add novel properties, or by the grafting of molecules onto cement particles, cement phases, aggregates, and additives (including nanosized additives) to provide surface functionality, which can be adjusted to promote specific interfacial interactions (Sanchez and Sobolev, 2010). Nanosized particles have a high surface area to volume ratio, providing the potential for tremendous chemical reactivity and also unique physical properties. Accordingly, fragmentizing of the SCMs particles to nanometer scale leads to increase in their chemical activity. Up to now, various techniques have been developed to fabricate nanomaterials through top- down or bottom- up approaches.

In our previous researches we used three methods of nanofabrication, ultrasound irradiation (Askarinejad et al., 2012), microwave irradiation and solvothermal (Askarinejad et al., 2016), for activating natural pozzolans, GGBFS (Askarinejad et al., 2013) and copper slag.

Ultrasound irradiation is used for fabrication or alteration of different materials in nano scale. Ultrasound induces chemical changes due to cavitation phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm, and a lifetime of a few microseconds. This method has showed significant influence on pozzolanic activity of natural pozzolans (Askarinejad and Morsali, 2008; Askarinejad and Morsali, 2009a,b; Alavi and Morsali, 2010).

Hydrothermal or solvothermal processing where high temperature, high pressure aqueous solutions, vapors and/or liquids react with solid materials, is a well-known process in mineralogy and geology fields for formation, alteration or deposit of minerals, ores or rocks. High temperature, high pressure solutions, vapors and/or liquids can act on materials as: a) transfer medium of pressure, temperature, and mechanical energy; b) adsorbate, which plays a role of catalizer or reaction accelerator; c) solvent which dissolves or precipitates the solid materials; and d) reagent which forms hydroxides, oxides, oxyhydroxides and/or salts. These actions can also be used in processing of inorganic materials: preparation, formation, alteration, sintering, etching, etc. Particularly, the hydrothermal processing is suitable for the preparation of powders; from nano-particles to single crystals (Prabakaran and Rajeswari, 2009; Aslani et al., 2009; Jin et al., 2008; Iwakai et al., 2011; Feng et al., 2011; Askarinejad et al., 2010).

Microwave energy has been extensively used for synthesis and sintering of ceramic materials. The most important reasons of using microwave energy over conventional processing are fast and volumetric heating, high heating rates, limited grain growth and forming more uniform grain sizes throughout the ceramic body.

Microwave-heating is also a rapid and highly effective method having an extensive application in nano material synthesis (Paul and Robeson, 2008).

These methods have been used for synthesizing a wide range of nanomaterials so far.

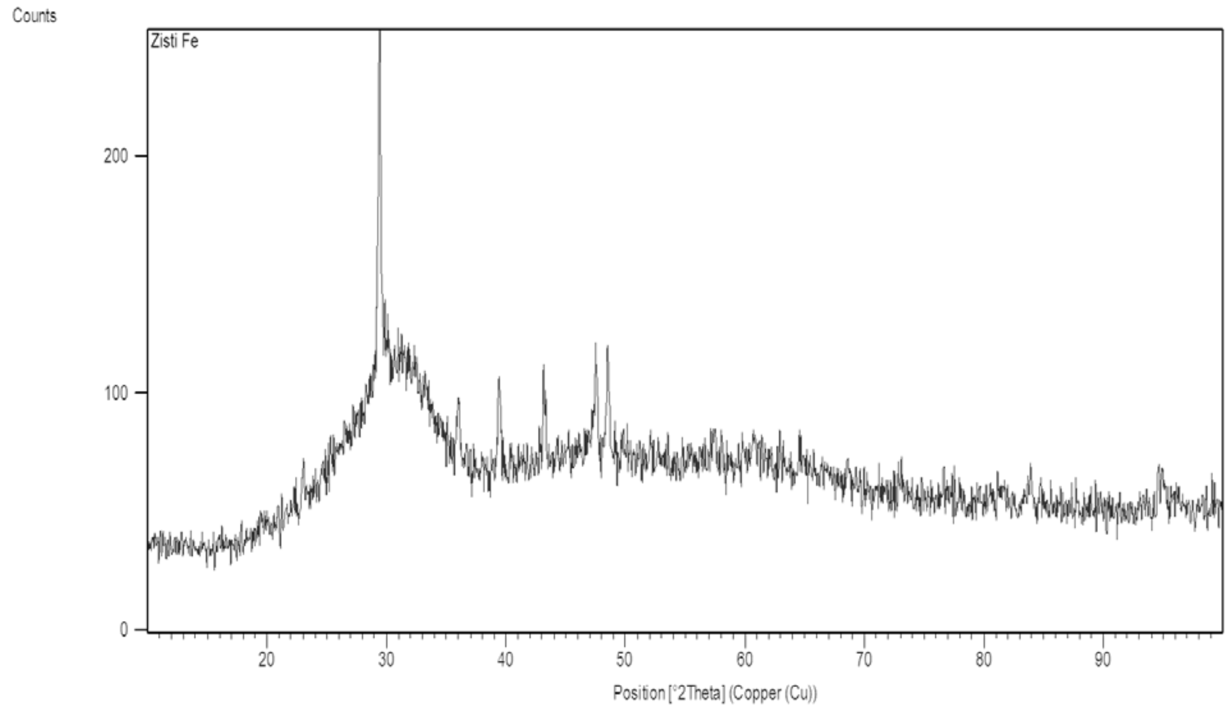
In this paper we review the application of these three methods of nanofabrication for activation of three kinds of pozzolanic materials.

Characterization of Pozzolanic Materials

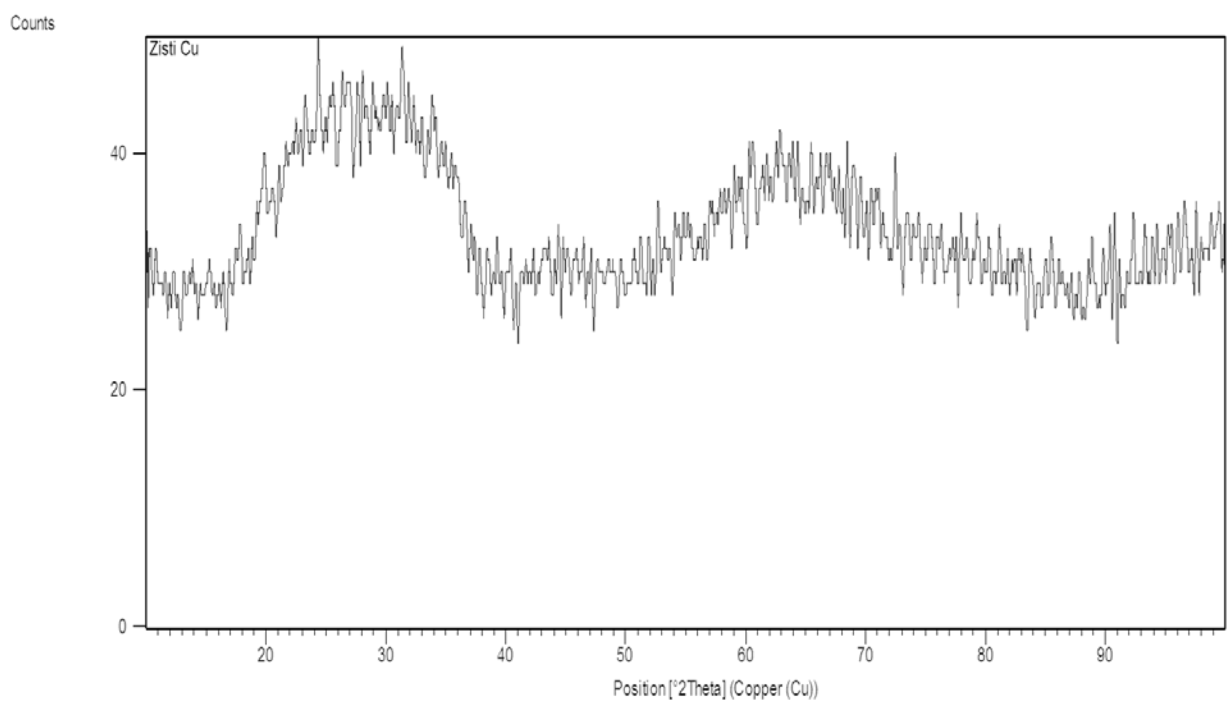
Four different types of natural pozzolans (p1, p2, p3, p4), a sample of GGBFS and a sample of copper slag were investigated in our researches. In order to investigate the chemical composition, particle size, crystal structure and pozzolanic activity of the pozzolanic materials, all the samples were characterized by different methods before being activated by nanomodification.

X-Ray Diffraction (XRD) Analysis

XRD analysis was used to investigate the crystal structure of pozzolanic materials. XRD patterns of GGBFS, copper slag and four natural pozzolan samples (p1, p2, p3, p4) are given in Figure 1 (a, b, c, d, e, f) respectively. According to Figure 1(a), GGBFS has a mostly amorphous structure but the peak related to SiO_2 is given in 30º of 2Ө. Figure 1(b) is corresponding to copper slag sample. As it can be observed, copper slag has amorphous structure. The diffraction peaks shown in Figures 1(c) to 1(f) which are related to natural pozzolan samples, accord with Diopside [$CaMg(SiO_3)_2$], Analcime [$NaAl(SiO_3)_2\ H_2O$], Clinochlore [$(Mg_5Al)(Si, Al)_4\ O_{10}\ (OH)_8$], Quartz ($SiO_2$), Muscovite [$KAl_2Si_3AlO_{10}(OH)_2$], Calcite ($CaCO_3$) and Albite [$Na(Si_3Al)O_8$] phases respectively. All the natural pozzolan samples has high crystallinity. X-ray powder diffraction (XRPD) measurements were performed using a Philips X'Pert X-ray diffractometer with mono chromatised Co-Kα radiation.


Counts
Zisti Fe
200
100
0
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))

(a)


Counts
Zisti Cu
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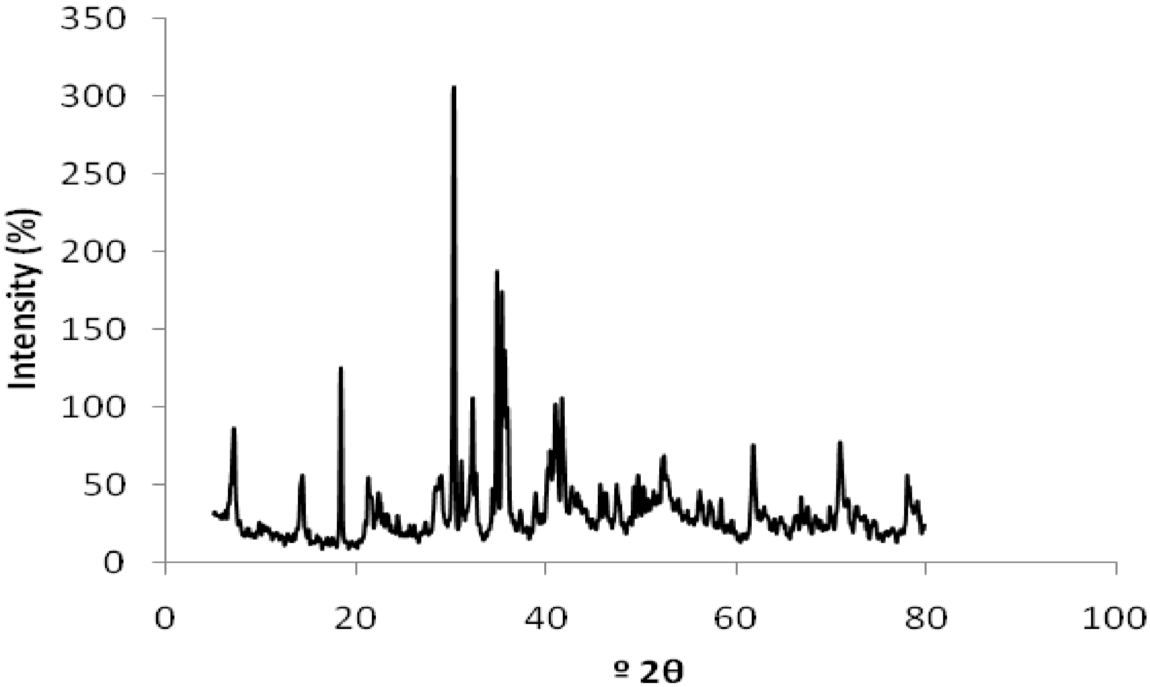
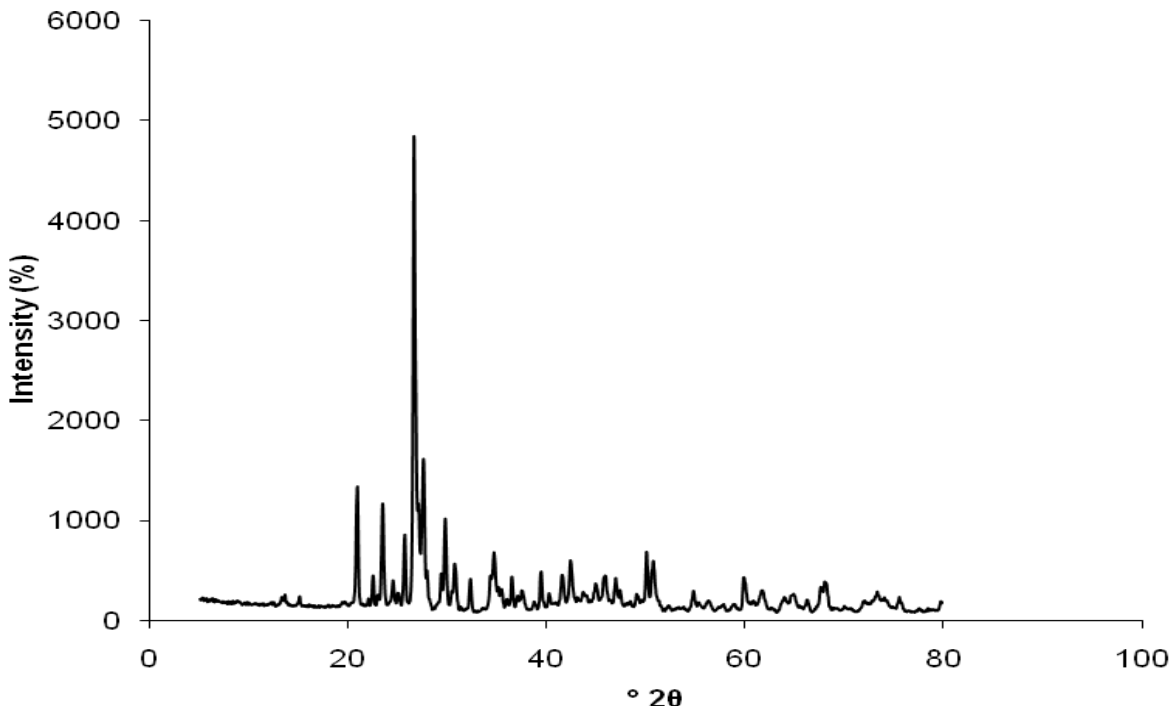
20
0
20
30
40
50
60
70
80
90
Position [°2Theta] (Copper (Cu))

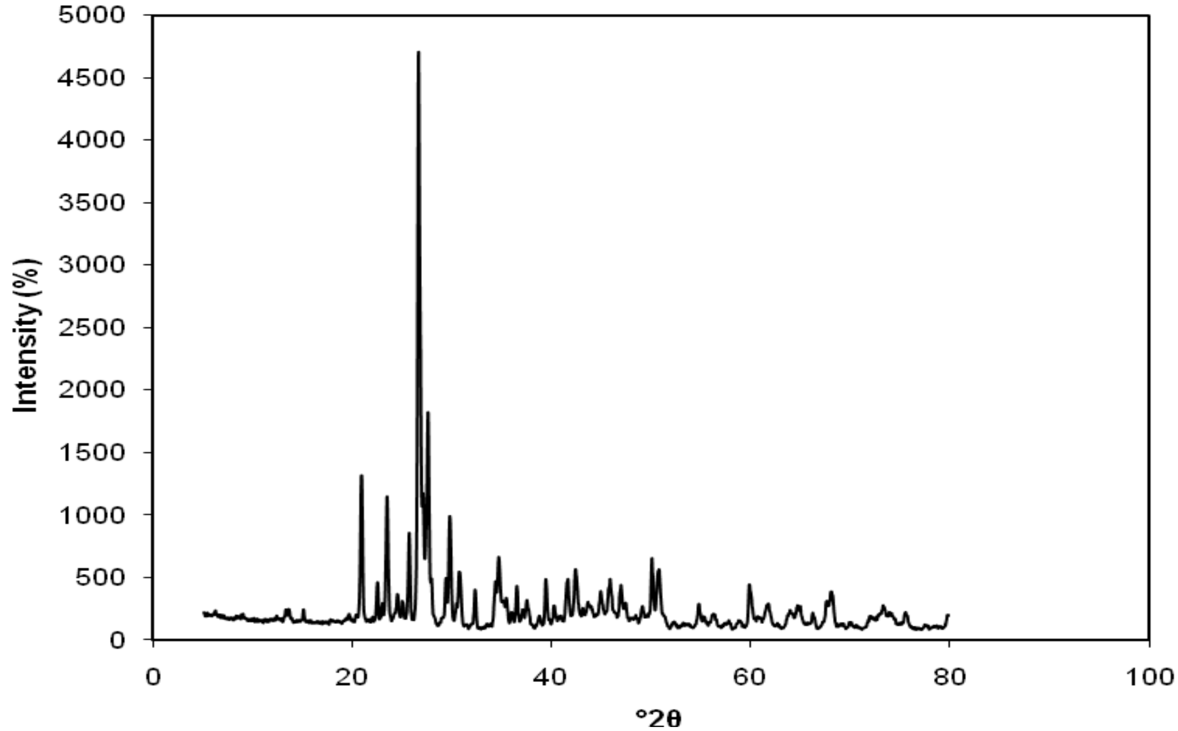
(b)


350
300
250
200
150
100
50
0
0
20
40
60
80
100
Intensity (%)
º 2θ

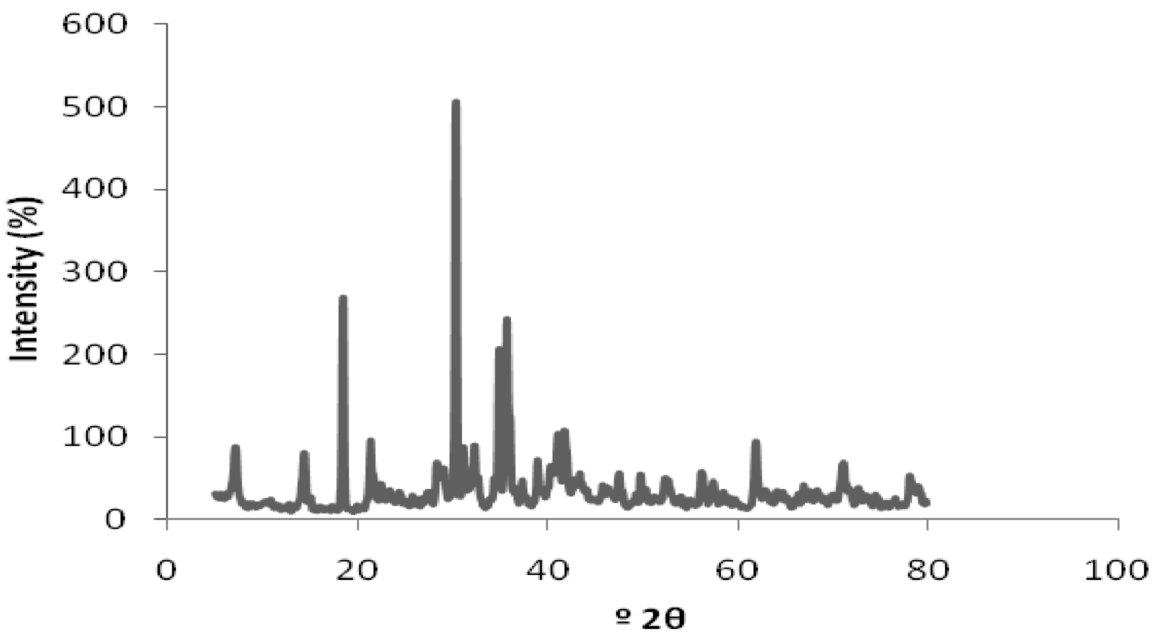
(c)


6000
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
Intensity (%)
° 2θ

(d)



(e)



(f)

Fig. 1. X- ray powder diffraction pattern of: a) GGBFS; b) copper slag; c,d,e,f) natural pozzolans before being activated

X-Ray Fluorescence (XRF) Analysis

XRF was used for determination of chemical composition of Fe and Cu slag samples. Table 1 shows the results of XRF analysis of GGBFS and copper slag. As it can be observed the amount of SiO_2, which is one of the reactants of pozzolanic reaction, in both slag samples is considerable. The significant difference between copper slag and Fe slag is that Fe slag has considerable amount of CaO. As CaO is one of the reactants of secondary hydration (pozzolanic) reaction, Fe slag can have cementitious properties itself and can drive the pozzolanic reaction without the need of residual $Ca(OH)_2$ of cement hydration. As natural pozzolan samples had crystal structure, determination of their chemical composition was possible by XRD analysis.

Table 1. XRF analysis results of GGBFS and copper slag

Compound	In Iron Slag (%)	In Copper Slag (%)
Na_2O	0.814	0.768
MgO	5.992	0.996
Al_2O_3	9.053	7.052
SiO_2	32.594	28.945
SO_3	2.339	1.904
K_2O	1.053	2.212
CaO	42.327	1.173
TiO_2	3.325	0.711
MnO	1.578	-
Fe_2O_3	0.819	54.534
P_2O_5	-	0.097
Sr	0.07	-
Y	0.011	-
Zr	0.027	-
Cu	-	0.585
Zn	-	0.824
Mo	-	0.199

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is one of the most common methods of observing nanostructures. SEM was used in order to observe the morphology and estimate the particle size distribution of pozzolanic material samples. SEM images of GGBFS, copper slag and four natural pozzolan samples (p1, p2, p3, p4) are given in Figure 2 (a, b, c, d, e, f) respectively. All the images show agglomerated particles in micrometer scale without regular distribution. The samples were characterized with a SEM (Philips XL 30) with gold coating.

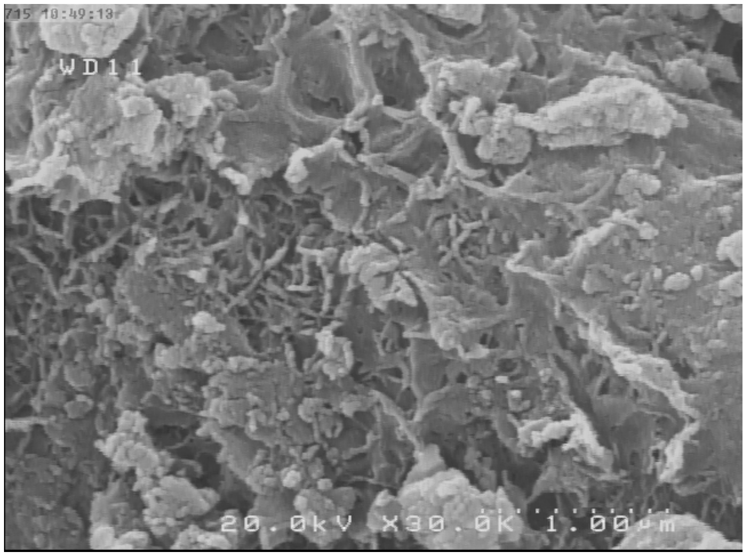
Thermal Gravimetry/Differential Thermal Analysis (TG/DTA)

In the thermogravimetric analysis, the calcium hydroxide content is determined based on the weight loss between 400-500 °C. $Ca(OH)_2$ consumption was calculated in time using thermal gravimetry studies for all the samples. By mixing 50% natural pozzolan, copper slag or GGBFS and 50% $Ca(OH)_2$ powder in presence of enough water for 9 days, pozzolanic reaction was performed. Pozzolanic reaction (Velosa and Cachim, 2009) (reaction 1) is defined as the reaction of silica, alumina and iron oxide of pozzolan with calcium hydroxide of cement hydration and alkalies that results the compounds such as CSH (Calcium Silicate Hydrate) and CAH (Calcium Aluminate Hydrate) gels. Thus, the percentage of reacted $Ca(OH)_2$ versus time determine the amount of pozzolanic reactivity.

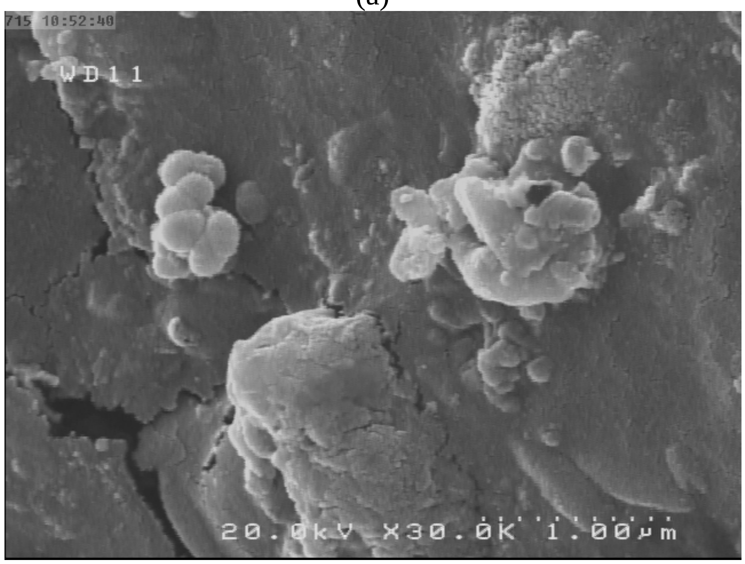
$$\text{pozzolan} + Ca(OH)_2 \rightarrow \text{C-S-H} + \text{C-A-H} + \ldots \quad (1)$$

All samples were analyzed by TG/DTA method by using a STA-449 C device (Jupiter model) of Netzsch Company in a static air atmosphere with heating rate of 10 °C/min from 25 to 600 °C.

Figures 3(a, b, c, d, e, f) show DTG curves of lime-pozzolan mixtures related to GGBFS, copper slag and four natural pozzolan samples (p1, p2, p3, p4), respectively.


715 10:49:13
WD11
20.0kV X30.0K 1.00μm

(a)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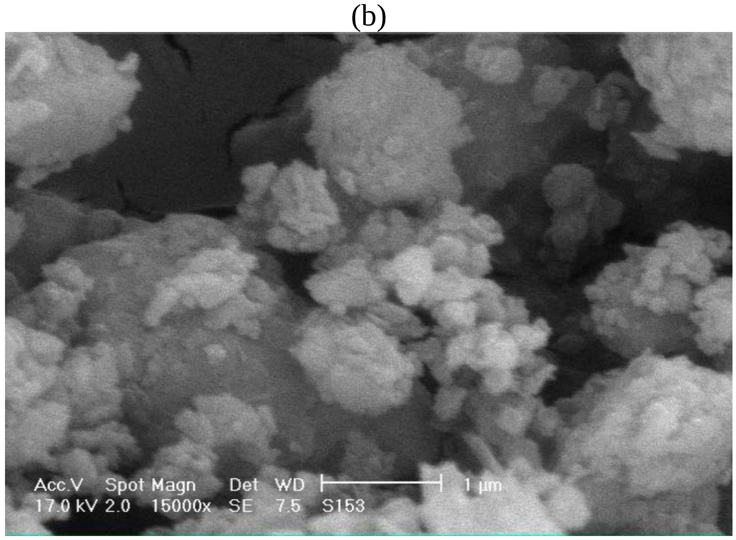
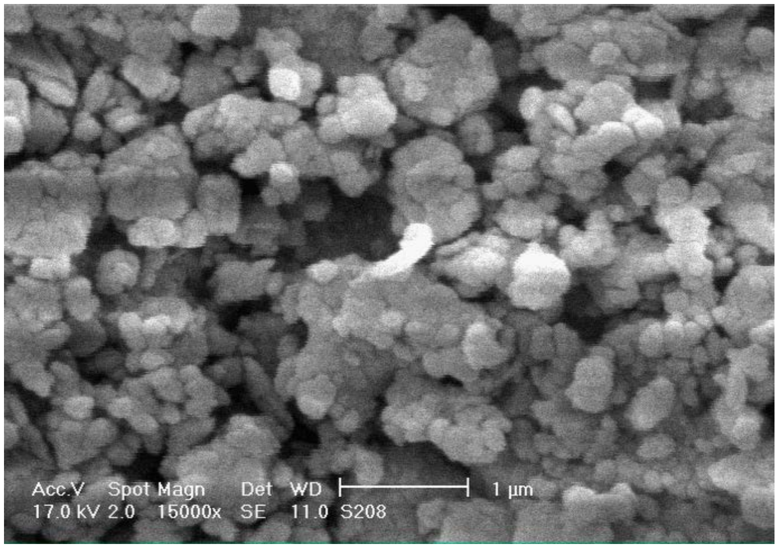
WD11
20.0kV X30.0K 1.00μm

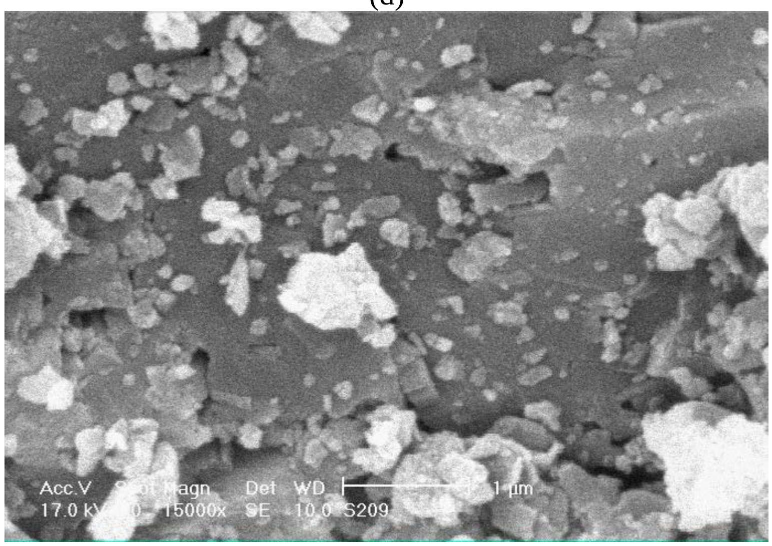
(b)


Acc.V Spot Magn Det WD 1 μm
17.0 kV 2.0 15000x SE 7.5 S153

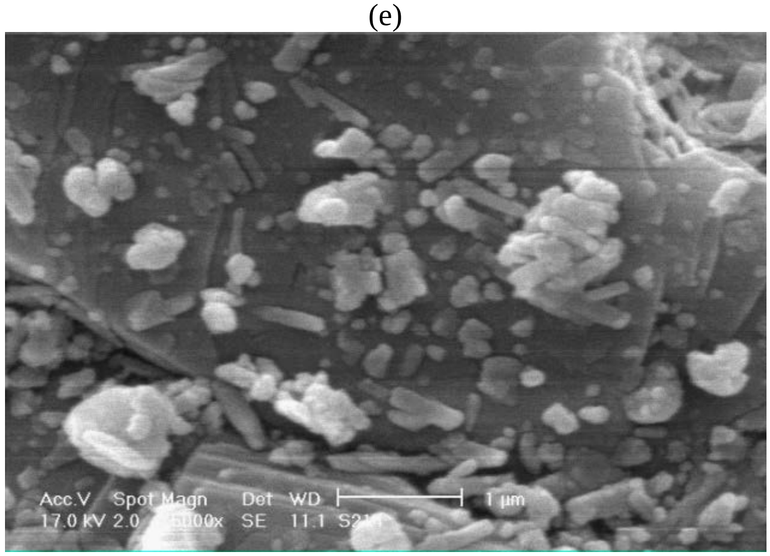
(c)



(d)



(e)



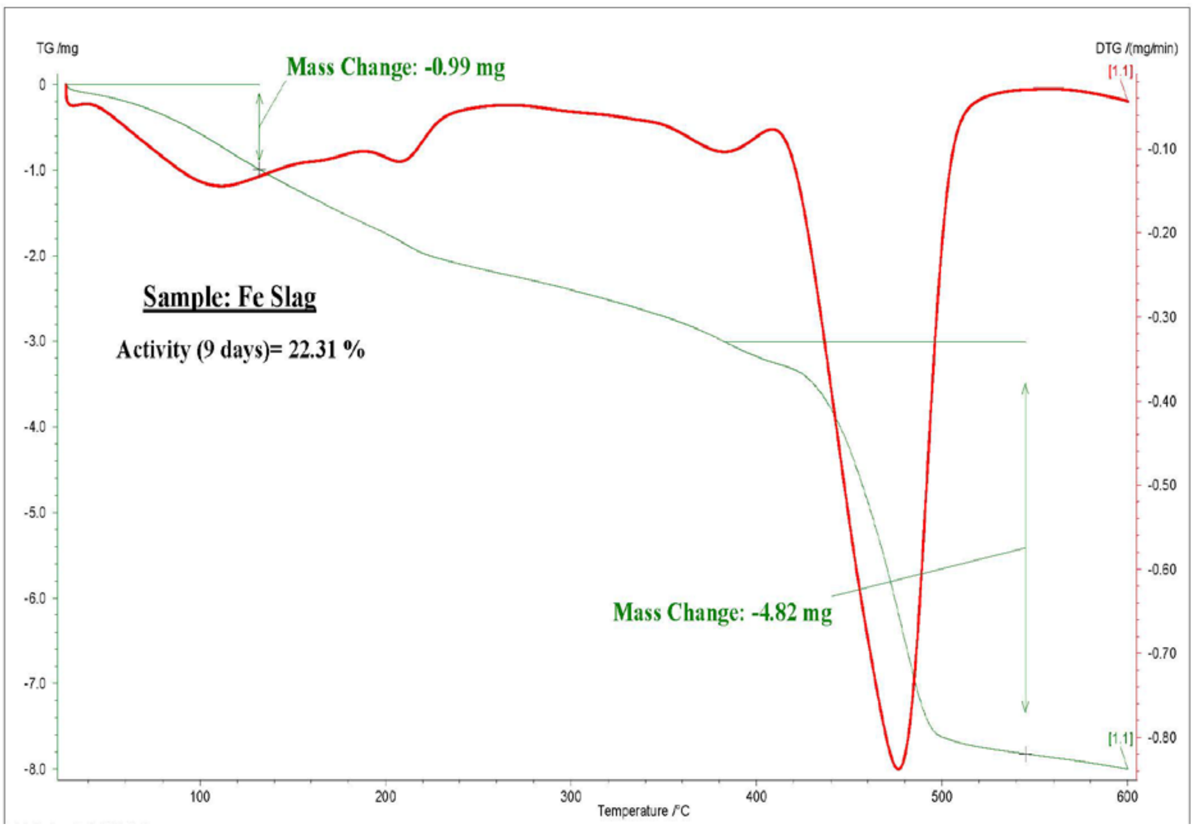
(f)

Fig. 2. SEM images of: a) GGBFS; b) copper slag; c,d,e,f) natural pozzolans before being activated

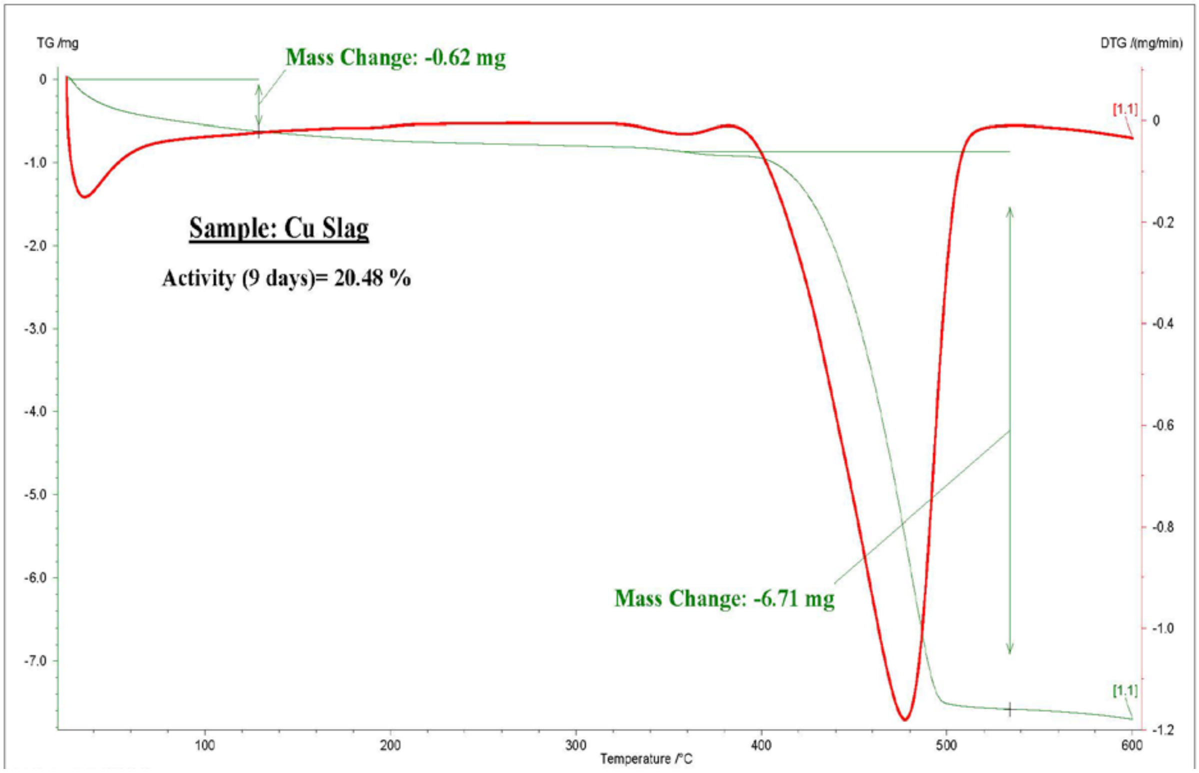
The thermograms show thermal decomposition of $Ca(OH)_2$ that has not contributed in the pozzolanic reaction. Endothermic peaks in DTA curves at about 450 ºC are attributed to the decomposition of $Ca(OH)_2$. The weight loss of $Ca(OH)_2$ is shown on the TGA curves for all the samples. The mass of $Ca(OH)_2$ that is converted to H_2O can be calculated from TGA curves. By subtracting this amount from the initial amount of $Ca(OH)_2$ that was added to the pozzolan sample, the amount of $Ca(OH)_2$ that is consumed in the pozzolanic reaction will be calculated. Thus, Pozzolanic reactivity amount can be estimated. Table 2 shows the initial pozzolanic reactivity percent of all samples.

Table 2. Initial pozzolanic activity of pozzolanic materials

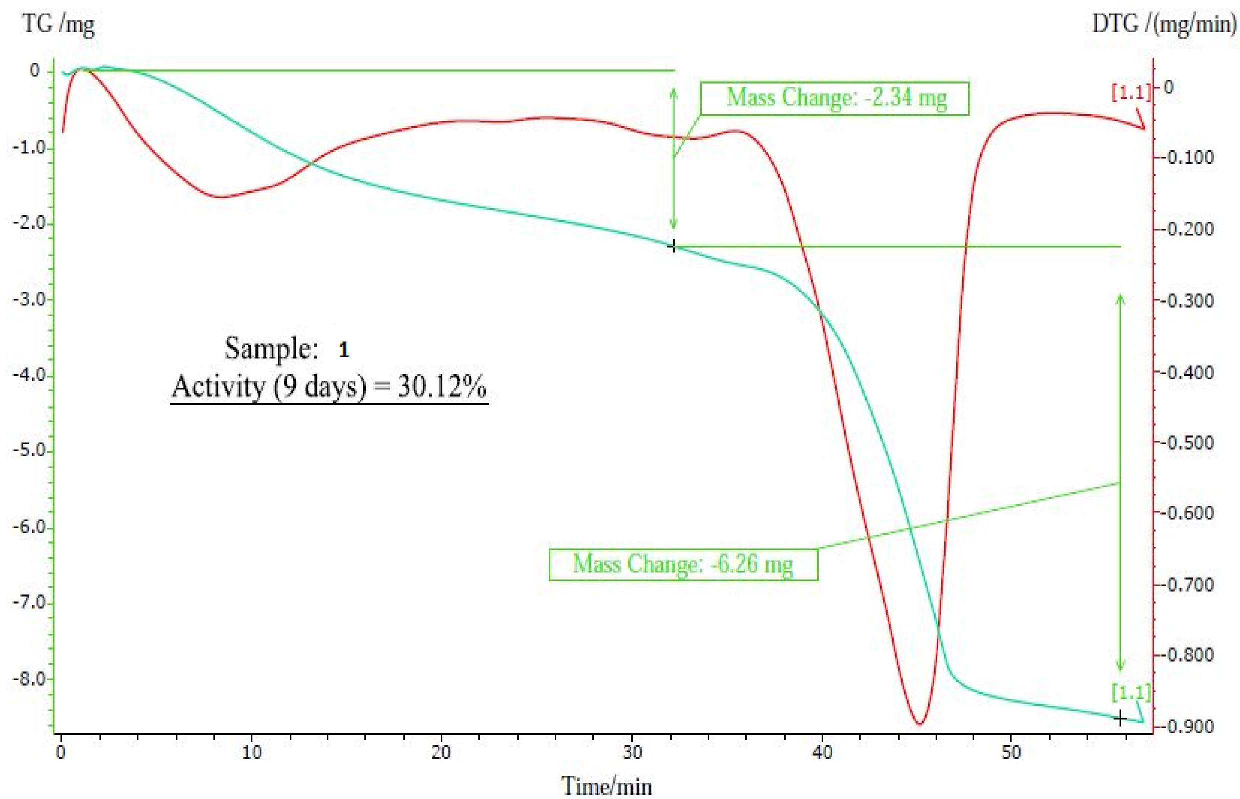
Sample	Pozzolanic Activity (%)
Fe slag	22.31
Cu slag	20.48
P1	30.12
P2	21.09
P3	17.87
P4	13.97



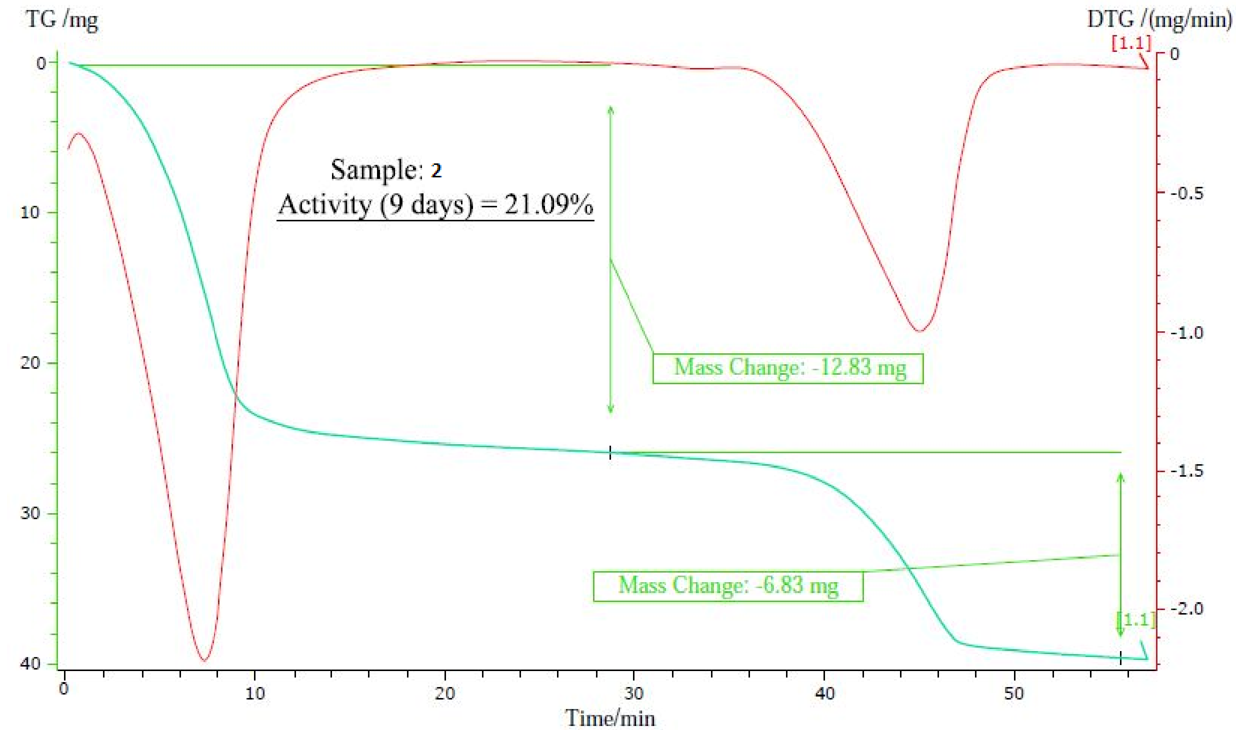
(a)


TG /mg
DTG /(mg/min)
Mass Change: -0.62 mg
Sample: Cu Slag
Activity (9 days)= 20.48 %
Mass Change: -6.71 mg
Temperature /°C

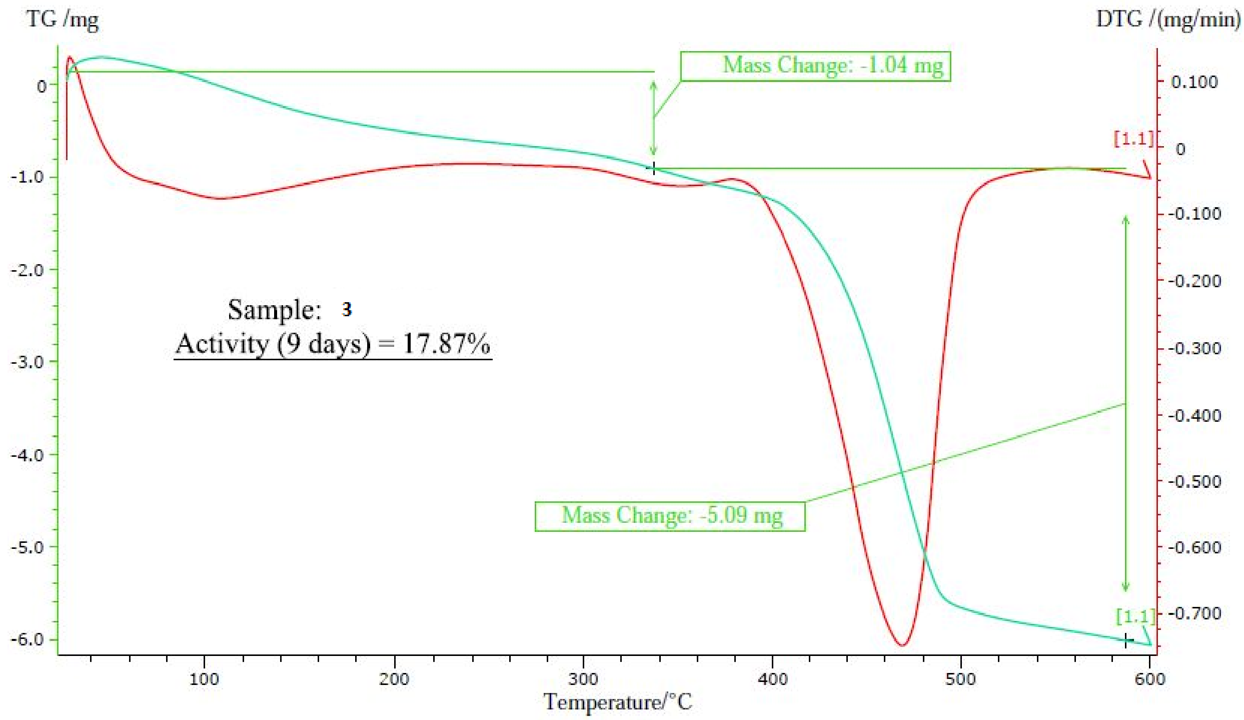
(b)


TG /mg
DTG /(mg/min)
Mass Change: -2.34 mg
Sample: 1
Activity (9 days) = 30.12%
Mass Change: -6.26 mg
Time/min

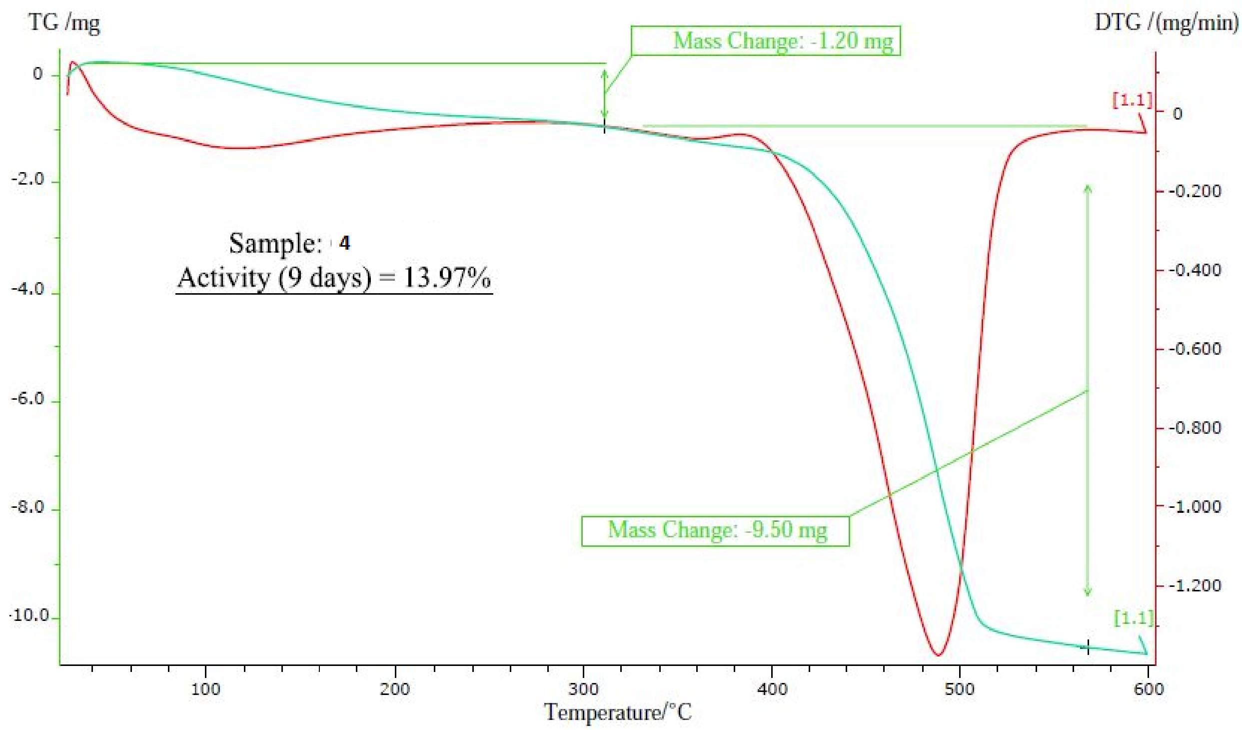
(c)


TG /mg
DTG /(mg/min)
Sample: 2
Activity (9 days) = 21.09%
Mass Change: -12.83 mg
Mass Change: -6.83 mg
[1.1]
[1.1]
0
10
20
30
40
0
-0.5
-1.0
-1.5
-2.0
0
10
20
30
40
50
Time/min

(d)


TG /mg
DTG /(mg/min)
Mass Change: -1.04 mg
Sample: 3
Activity (9 days) = 17.87%
Mass Change: -5.09 mg
[1.1]
[1.1]
0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
0.100
0
-0.100
-0.200
-0.300
-0.400
-0.500
-0.600
-0.700
100
200
300
400
500
600
Temperature/°C

(e)



(f)

Fig. 3. TG/DTA diagrams of: a) GGBFS; b) copper slag; c,d,e,f) natural pozzolans before being activated

Nanomodification of Pozzolanic Materials

Using Ultrasound Irradiation for Activation of Pozzolanic Materials

In order to obtain pozzolanic material nanostructures, 10 g of bulk samples were dispersed in 400 ml water or ethanol in an appropriate vessel and were posited under ultrasound irradiation for 1, 2 or 6 hr with an UP200S ultrasonic processor equipped with a converter/transducer and titanium oscillator (horn) sonicator with frequency of 24 kHz and output power of about 200 W.

The precipitates obtained from sonicating were isolated by vacuum filtration, dried and analyzed by means of XRD and SEM.

The pozzolanic activity (lime binding capacity) of pozzolans and slags was investigated by thermal gravimetry analysis. Table 3 shows the percent of increase in pozzolanic activity as the result of using ultrasound irradiation. The role of solvent and time of sonication on the size and morphology of products were investigated by using different solvents and changing the reaction times. The results given in Table 3 are related to the optimized condition.

Figure 4 shows the SEM image of copper slag nanoparticles obtained by using ultrasound irradiation. As it can be observed Better particle separation and distribution and lower particle size has obtained as the result of ultrasound irradiation. Therefore the increase of 180% in chemical activity of copper slag is corresponded to this particle size reduction.

Table 3. Pozzolanic activity increase of pozzolan and slag samples after activation by ultrasound irradiation

Sample	Pozzolanic Activity Increase (%)
Fe slag	38
Cu slag	180
P1	32
P2	72.7
P3	78
P4	148.6

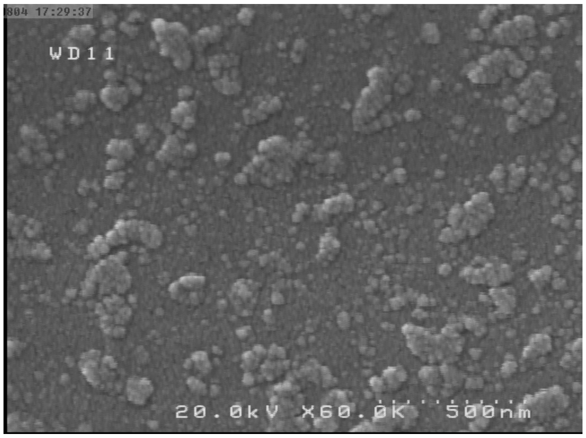


Fig. 4. SEM image of copper slag after being activated by using ultrasound irradiation

Using Solvothermal/Hydrothermal Method for Activation of Pozzolanic Materials

In this method 2 g pozzolanic material and 20 ml distilled water were mixed and charged into a Teflon-lined stainless steel autoclave and heated at 120°C for 10 hr. The product was filtered and dried after the autoclave was cooled to room temperature, and analyzed by means of XRD and SEM. Thermal gravimetry analysis was also used to calculate the pozzolanic activity (lime binding capacity) of pozzolans. The role of solvent and time of the heating on the size and morphology of products were investigated by using different solvents and changing the solvothermal process times.

Table 4 shows the percent of increase in pozzolanic activity as the result of using solvothermal method in optimized condition.

Table 4. Pozzolanic activity increase of pozzolan and slag samples after activation by solvothermal method

Sample	Pozzolanic Activity Increase (%)
Fe slag	36
Cu slag	227
P1	29
P2	83
P3	49
P4	140

Figure 5 shows the SEM image of iron slag nanoparticles obtained by using solvothermal method. Ordered orientation of the particles and the formation of one-dimensional nanostructures as the result of solvothermal method can be observed. As the XRD patterns of products are the same as initial samples, there is not any change in crystallinity of pozzolanic materials after being activated; therefore the increase in pozzolanic activity is as the result of decrease in particle size.

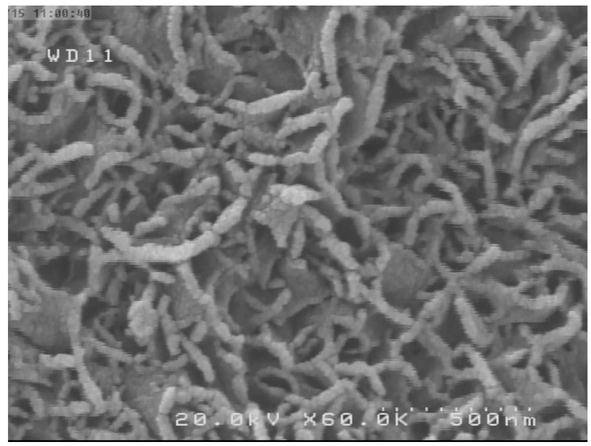


Fig. 5. SEM image of iron slag after being activated by using solvothermal method

Using Microwave Irradiation for Activation of Pozzolanic Materials

In this method 4 g pozzolanic material and 100 ml distilled water were mixed and put in a microwave oven (500 W) at continuous heating for 2 min. The resulting precipitate was separated by centrifuging, dried at 80 °C and analyzed by means of XRD and SEM. The pozzolanic activity (lime binding capacity) of products was investigated by thermal gravimetry analysis.

Figure 6 shows the SEM image of pozzolan nanoparticles obtained by using microwave assisted method. Ordered Orientation of the particles and optimum particle size distribution as the result of microwave irradiation can be observed. As the XRD patterns of products are the same as initial samples, there is not any change in crystallinity of pozzolanic materials after being activated; therefore the increase in pozzolanic activity is as the result of decrease in particle size.

Table 5 shows the percent of increase in pozzolanic activity as the result of using microwave assisted method in optimized condition.

Table 5. Pozzolanic activity increase of pozzolan and slag samples after activation by microwave assisted method

Sample	Pozzolanic Activity Increase (%)
Fe slag	35
Cu slag	99
P1	18
P2	63
P3	44
P4	115

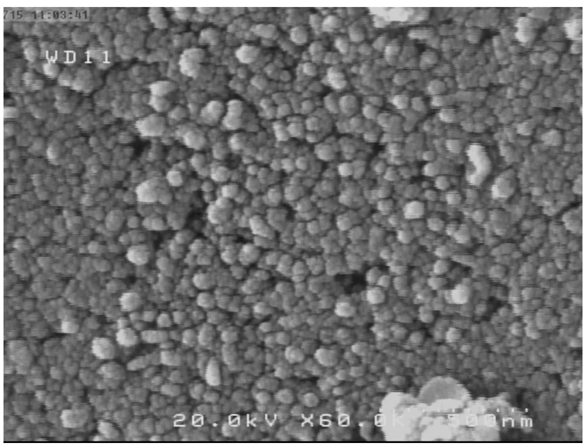


Fig. 6. SEM image of natural pozzolan (P4) after being activated by using microwave assisted method

CONCLUSIONS

Based on the results of applying the ultrasound assisted, solvothermal and microwave assisted processes to increase chemical activity of natural pozzolan, iron and copper slag samples, increasing the time of sonication, heating and microwave irradiation leads to increase in pozzolanic activity of all pozzolanic materials.

Based on the SEM images of pozzolanic material samples before and after activation by all three methods, reducing the size of the particles and as the result increasing the reactive sites of pozzolans and slag samples has considerable direct influence on the rate of the reaction of pozzolanic materials with lime.

The percent of pozzolanic activity increases in all activation processes has higher values for the samples with lower initial activities.

As the XRD patterns of natural pozzolan, copper slag and iron slag samples before and after all processes are identical, no change in the chemical composition and Crystal phase of pozzolanic materials can be observed, thus increase the activity of pozzolanic materials cannot be attributed to increase in amorphous phase of their structure and changes in particle size and morphology of pozzolanic materials is responsible for this reactivity increase.

The results of applying the three methods at optimum conditions for activation of slag and pozzolan samples is presented in Table 6. Also, Figure 7 shows the amount of activity increase of slag and pozzolan samples as the result of applying the three methods with optimal conditions.

The above results prove that using the methods of nano fabrication is a useful and effective route for increasing the chemical activity of SCMs.

Comparing with other methods which are reported for activation of pozzolanic materials (Demirboğa et al., 2004), these methods are simple and rapid, they do not need high temperatures, acids or other chemical compounds and they can be performed in industrial scale.

Therefore using ultrasound irradiation, solvothermal/hydrothermal process and microwave irradiation can be suggested as effective methods for nanomodification of supplementary cementing materials in order to develop more ecofriendly concrete.

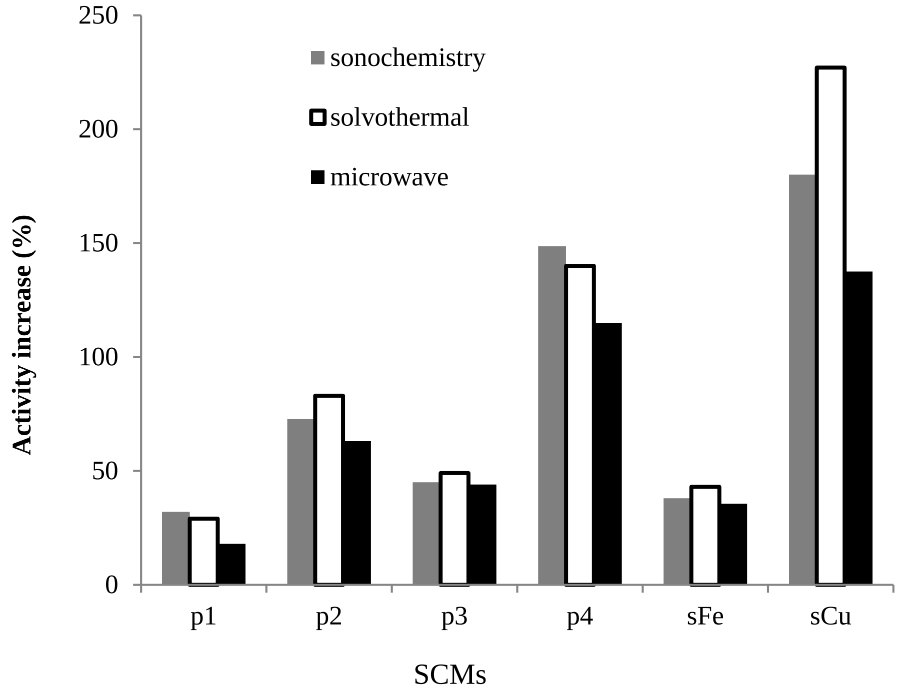


Fig. 7. Diagram of activity increase of slag and pozzolan samples as the result of applying the three methods

Table 6. Pozzolanic activity increase of pozzolan and slag samples after activation by three methods

Sample	Chemical Activity Increase as the Result of Sonication (%)	Chemical Activity Increase as the Result of Solvothermal Treatment (%)	Chemical Activity Increase as the Result of Microwave Irradiation (%)
P1	32	29	18
P2	72.7	83	63
P3	78	49	44
P4	148.6	140	115
Fe slag	30.89	43	35.57
Cu slag	180	227	187

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