 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at *Fibers* **2017**, *5*, 47; doi:10.3390/fib5040047

# Enhancement experiment on cementitious activity of copper mine tailings in geopolymer system

Lin Yu[1,2,a], Zhen Zhang[1,a], Xiao Huang[1,a], Binquan Jiao[1,2*], Dongwei Li[1*]

[1]State Key Laboratory for Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China;

[2]City College of Science and Technology, Chongqing University, Chongqing, 400044, China

Corresponding email: *litonwei@cqu.edu.cn (D.W Li) and *j.binquan@cqu.edu.cn (B.Q Jiao)

[a]These authors contributed equally to the work.

**Abstract:** Copper mine tailings are the residual products after the purification of precious copper from copper ores, and their storage can create numerous environmental problems. Many researchers have used copper mine tailings for preparation of geopolymer. This paper studies the enhancement of the cementitious activity of copper mine tailings in geopolymer system. First, copper mine tailings are activated through a mechanical grinding activation. Afterward, the mechanically activated copper mine tailings are further processed through thermal activation and alkaline roasting activating. The cementitious activity index of copper mine tailings is characterized through the degree of concentration of alkali leaching silicon and aluminum. It was observed that the Si and Al alkali leaching concentration of mechanical activated tailings was increased by 26.03% and 93.33%, respectively. The concentration of Si and Al was increased by 54.19% and 119.92%, respectively. For alkaline roasting activating, roasting time, temperature and (C/N ratio) were evaluated through the orthogonal test, and the best condition was activation for 120 min at 600℃ with C/N ratio is 5:1. In this study, the SEM, XRD and IR analysis show that mechanically activation, thermal activation and alkaline roasting activating can improve the cementitious activity index of copper mine tailings.

**Keywords:** copper mine tailings, mechanical activation, thermal activation, alkaline roasting, alkali leaching

## 1. Introduction

Concrete is widely used construction material with annual production of more than 10 billion tons around worldwide [1]. Ordinary Portland cement (OPC) is main constituent of concrete. One ton of cement is produced at cost of 1.5 tons of raw material and 0.7 tons of carbon dioxide emission into the atmosphere [2]. So, cement production not only consumes a large amount of natural resources but also emits carbon dioxide, causing atmospheric pollution. The cement industry is responsible for 7% of the total emissions of carbon dioxide across the world [3-5]. China is the largest cement producer and consumer in the world, and facing air pollution [6]. Therefore it is important to find alternative of cement. Geopolymers are new type of “cementing material” due to cementitious activity. They have more advantages over OPC, because of better performance and cost-effective production [7-8]. Geopolymers are formed through geopolymerization processes; in which (a) solid aluminosilicates are activated by alkali solution to generate aluminate and silicate tetrahedral monomers, (b) the monomers form silica-alumina oligomers, which subsequently form inorganic polymeric material, (c) the inorganic polymeric materials condense and harden into geopolymers [8].

Geopolymers as cement alternatives are used for building materials and solidification of heavy metals. In addition to fly ash and metakaolin, various aluminosilicate minerals, clays, solid wastes, and their mixtures also have been used to synthesize geopolymers [9]. Glukhovsky and Krivenko have used alkali activated metallurgical slag in construction materials in the 1950s [10]. The first concept of geopolymers and geopolymerization time has been proposed by Davidovists in 1972 [11], Davidovits and Orlinski have summarized the progresses on geopolymers throughout the 1980s [12-14]. While, Wastiels et al [15] first time has described alkaline activation of fly ash based geopolymer. In 1990s, Rahier et al [16-20] synthesized aluminosilicate glasses at low temperature and carried out studies on metakaolin based geopolymers. Numbers of silicon and aluminum constituting raw materials have been used for alkali activation, but very few studies conducted on geopolymerization of copper mine tailings [21-24]. Until now, Zhang et al and Ahmari et al [25-26] have checked the effect of different factors i.e. activators (type and concentrations) and curing temperature on alkali-activated binder based on copper mine tailings, and concluded that these can be used as raw materials for preparation of geopolymer. But there are some limitations i.e. use of high curing temperature and concentration of alkali solution. So, some modifications are required to overcome these limitations.

The main objective of this study is to investigate the effects of mechanical grinding, thermal activations and alkaline roasting activating on the improvement of the cementitious activity index of copper mine tailings in geopolymer system. The mechanical grinding per formed by laboratory ball mill. Then the tailings will be activated at five different temperatures (400℃, 500℃, 600℃, 700℃, 800℃) for various durations. Orthogonal tests are designed to analyze the optimal set of the experimental parameters; mass ratio of copper mine tailings to NaOH (C/N ratio)，roasting time and roasting temperature. The cementitious activity index of copper mine tailing are identified by the leaching analysis. Scanning Electron Microscope (SEM), IR and XRD analysis are used to investigate the particle morphology and mineral composition of copper mine tailings.

## 2. Materials and Methods

### 2.1 Materials

The source material used in this experiment was copper mine tailings. The samples were collected from Yangla copper industry in Yunnan, China. The chemical composition of the copper mine tailings listed in Table 1. It can be seen that it mainly consisted of silica and alumina with substantial amount of iron and calcium. The particle size distribution and cumulative distribution were analyzed by LSPSDA (Mastersizer 2000 Malverng England) and shown in Figure 1. It can be seen that the particle sizes of less than 100 μm account for sixty percent of the mine tailings. Morphological characters tested by using the SEM (FEL NOVA400, America) as presented in Figure 2. Results showed that copper mine tailings were unevenly distributed with irregular shapes; large particles having smooth and angular surface, and small particles are adsorbed on the surface

*Preprints* (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at *Fibers* **2017**, *5*, 47; doi:10.3390/fib5040047

of large particle. The XRD analysis was performed with a D/max-RB diffractometer using $CuK_a$ radiation (40 kV and 100 mA), at 4°/min ranging from10° to 70°. The main crystalline materials in the copper mine tailings were: quartz ($SiO_2$), albite ($NaAlSi_3O_8$), Chlorite $(Mg,Al)_6(SiAl)_4O_{10}(OH)_8$ and dolomite ($CaMg(CO_3)_2$) as shown in Figure 3. The Fourier transform infrared spectroscopy analysis was performed by Fourier Transform Infrared spectroscopy (Nicolet5DXC FT-IR) in the range of 400-4000 $cm^{-1}$. The sodium hydroxide solution is made by dissolving sodium hydroxide in de-ionized water.

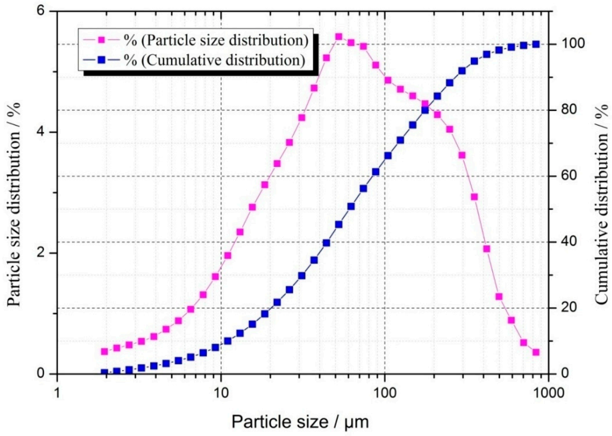
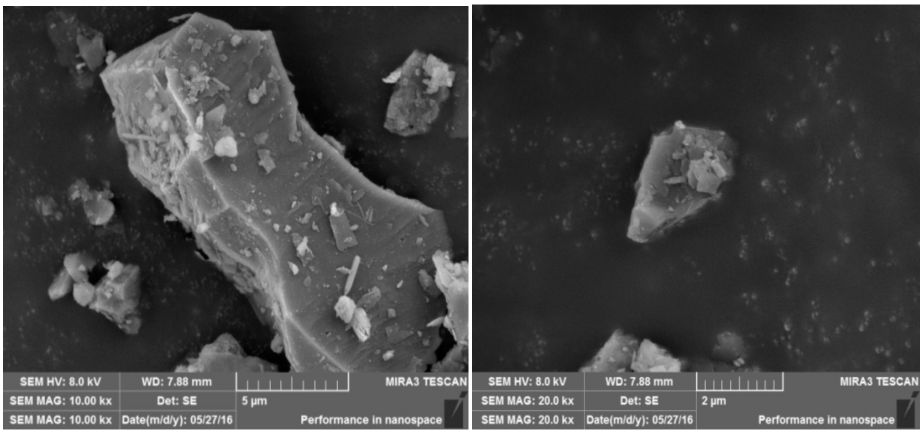



**Figure 1. Particle size and cumulative distribution of mine tailings**



10000x 20000x

**Figure 2 SEM images of raw copper mine tailings powder**

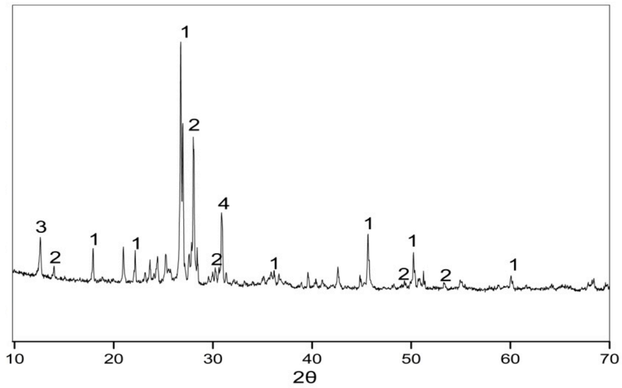



**Figure 3 XRD pattern of mine tailings powder（1 quartz, 2 albite, 3 chlorite, 4 dolomite）**

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

**Table 1 Chemical composition (wt%) of mine tailings**

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $K_2O$ | $Na_2O$ | MgO | $SO_3$ |
|---|---|---|---|---|---|---|---|
| 58.5 | 13.3 | 10.7 | 5.4 | 4.0 | 2.8 | 1.9 | 0.6 |

## 2.2 Methods

### *2.2.1 Mechanical activation of copper mine tailings*

The laboratory ball mill (SN-500, China) was used to improve the activity index of copper mine tailings, and the grinding media was steel balls. 1 kg of copper mine tailings were activated each time. Milling time and the mass ratio of ball are two important factors that influence the mechanical grinding of copper mine tailings. In current study, samples were grounded for different periods (1h 1.5h 2h 2.5h 3h 3.5h 4h 4.5h) at speed of 200 r/min, and the milled samples were denoted by M1, M1.5…M4.5 in the subsequent description (Table 2). Balls and powder used in ratio of 10:1.

**Table 2 The experiment layout of the mechanical grinding of copper mine tailings**

| No. | Milling time(h) |
|---|---|
| M1 | 1.0 |
| M1.5 | 1.5 |
| M2 | 2.0 |
| M2.5 | 2.5 |
| M3 | 3.0 |
| M3.5 | 3.5 |
| M4 | 4.0 |
| M4.5 | 4.5 |

### *2.2.2 Thermal activation of copper mine tailings*

The TG-DSC (Netzsch STA 449C, Germany) was used to examine the melting characteristics of samples. The experiments were carried out at temperature range 10℃ to 1200℃ at air gas atmosphere. One of the best performance mechanical grinding activated copper mine tailings was used in the thermal activation. Activating time is another important factor in the thermal activation. Four times periods (60 min, 90 min, 120 min, 150 min) in each activation temperature were selected to test the effect of temperature and activation time on thermal activation of copper mine tailings. Table 3 summarized the parameters of thermal activation of copper mine tailings and the samples were denoted by TM1, TM2…TM20 in the subsequent description.

**Table 3 Copper mine tailings thermal activation parameters**

| Sample name of MT | Calcination temperature/℃ | Calcination time/min |
|---|---|---|
| TM1 | 400 | 60 |
| TM 2 | 400 | 90 |
| TM 3 | 400 | 120 |

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

| | | |
|---|---|---|
| TM 4 | 400 | 150 |
| TM 5 | 500 | 60 |
| TM 6 | 500 | 90 |
| TM 7 | 500 | 120 |
| TM 8 | 500 | 150 |
| TM 9 | 600 | 60 |
| TM 10 | 600 | 90 |
| TM 11 | 600 | 120 |
| TM 12 | 600 | 150 |
| TM 13 | 700 | 60 |
| TM 14 | 700 | 90 |
| TM 15 | 700 | 120 |
| TM 16 | 700 | 150 |
| TM 17 | 800 | 60 |
| TM 18 | 800 | 90 |
| TM 19 | 800 | 120 |
| TM 20 | 800 | 150 |

### *2.2.3 Alkaline roasting activating of copper mine tailings (ARMT)*

Three fundamental technological factors affecting the cementitious activity index of the copper mine tailings, such as roasting time, temperature and (C/N ratio) were evaluated through the orthogonal test. First, the copper mine tailings were mixed with NaOH solution, the solution was prepared by adding sodium hydroxide flakes to de-ionized water. Then put the mixture in oven for drying to a particular time. The copper mine tailings and NaOH mixtures were roast in muffle furnace at a certain temperature for different time (Table 4). These tailings were activated by alkaline roasting are named as ARMT in subsequent description. The parameters with their respective levels and orthogonal experiment layout presented in table 4 and 5, respectively.

**Table 4 Levels of factors**

| Levels | factors | | |
|---|---|---|---|
| | A<br>roasting time（min） | B<br>roasting temperature (℃) | C<br>C/N ratio |
| 1 | 60 | 550 | 5:1 |
| 2 | 90 | 600 | 7.5:1 |
| 3 | 120 | 650 | 10:1 |

**Table 5 Orthogonal experiment layout**

| No. | A | B | C | result |
|---|---|---|---|---|
| ARMT1 | 1(60 mim ) | 1(550℃) | 1 (5:1) | $y_1$ |
| ARMT2 | 1 | 2(600℃) | 2(7.5:1) | $y_2$ |
| ARMT3 | 1 | 3(650℃) | 3(10:1) | $y_3$ |
| ARMT4 | 2(90 min) | 1 | 2 | $y_4$ |

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

| | | | | |
|---|---|---|---|---|
| ARMT5 | 2 | 2 | 3 | $y_5$ |
| ARMT6 | 2 | 3 | 1 | $y_6$ |
| ARMT7 | 3(120 min) | 1 | 3 | $y_7$ |
| ARMT8 | 3 | 2 | 1 | $y_8$ |
| ARMT9 | 3 | 3 | 2 | $y_9$ |

#### *2.2.4 Leaching test*

The leaching analysis was performed to study the effects of different activation methods on dissolution of silica and alumina species from copper mine tailings. Due to the reason that first step of geopolymerization processes is to dissolve solid aluminosilicate materials in alkaline solution to generate aluminates and silicate tetrahedral monomers, the leaching test can be used to measure the cementitious activity of copper tailings. A sample of 1 g copper mine tailings was immersed in 100 ml NaOH solution (1 M) in a polyethylene beaker stirred evenly, and sealed. After curing (7 days) in a standard curing box at 20±1℃, the solution was filtrated and diluted 100 times. Concentration of Al and Si in the solution was analyzed by using inductively coupled plasma optical emission spectrometer (ICP-OES), made by Thermo Electron Corporation in the USA (Model ICAP 6300). During ARMT alkaline leaching experiment, in order to ensure the concentration of sodium hydroxide solution is 1M, it is necessary to adjust sample (tail mining contains NaOH) and NaOH concentration in solution. Table 6 shows the mixture ratios for ARMT in alkaline leaching experiments.

**Table 6 Mixture ratios for ARMT in alkaline leaching experiments**

| sample | The sample quantity(g) | The quantity of NaOH in the solution (g) |
|---|---|---|
| ARMT1、ARMT6、ARMT8 | 1.200 | 3.800 |
| ARMT2 、ARMT4 、ARMT9 | 1.133 | 3.867 |
| ARMT3、ARMT5、ARMT7 | 1.100 | 3.900 |

## 3 Results and discussions

### 3.1 Mechanical activation of copper mine tailings

#### *3.1.1 Leaching test*

Silicon and aluminum concentrations from leaching experiment are given in Table 7 and illustrated in Figure 4. It can be seen from results that maximum leaching concentrations of activated silica is 47.02 µg/ml (M3) and alumina is 18.98µg/ml (M4.5) after mechanical grinding. The percent increase in leaching concentration is 26.03% (Si) and 93.33% (Al) after activation as compared to raw mine tailings, which are significantly higher than those in the copper mine tailings before the activation.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

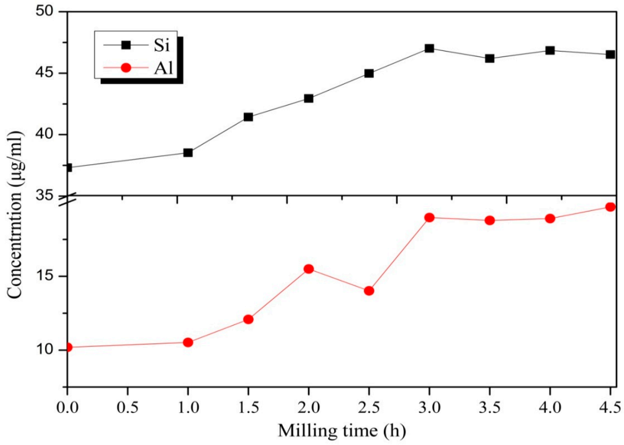



**Figure 4 Silicon and aluminum concentration in mechanical activation of copper tailings alkali leaching**

**Table7 Silicon and aluminum concentration in mechanical activation of copper tailings alkali leaching**

| Sample | Si (μg/ml) | Al (μg/ml) |
|---|---|---|
| Raw | 37.31 | 10.19 |
| M1 | 38.53 | 10.52 |
| M1.5 | 41.43 | 12.08 |
| M2 | 42.94 | 15.50 |
| M2.5 | 44.98 | 14.02 |
| M3 | 47.02 | 18.98 |
| M3.5 | 46.19 | 18.79 |
| M4 | 46.85 | 18.91 |
| M4.5 | 46.52 | 19.70 |

***3.1.2 Effect of Mechanical activation on the particle size distribution***

Figure 5 shows the cumulative particle size distribution of copper mine tailings milled for different time. The curves shift slowly to the left side with increase of milling time; While, after 3 hours, the curves begin to shift to the right side. It illustrates that the particle size of copper mine tailings is gradually decreased with increase in milling time up to 3hours and then increased. Moreover, the particles having size <10 μm of M3 is increased by 20% than the original sample (reach to 31.45%). While, particles having grades/size<44.00μm reach to 89.63%. Average particle sizes D50 and D90 at different grinding time for copper mine tailings are presented in Table 8 and illustrated Figure 6. It can be seen from that the average particle sizes D50 and D90 are rapidly decreased with increase in grinding time, ad after three hours of grinding, the average particle sizes D50 and D90 reach to their minimum sizes 16.98 μm and 44.53 μm, respectively. After 3 hours, continuous grinding resulted in gradual increase of particles size, which suggests that the previously broken small copper tailings particles start to bond together. Therefore, three hours is the optimal mechanical grinding time under this condition.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

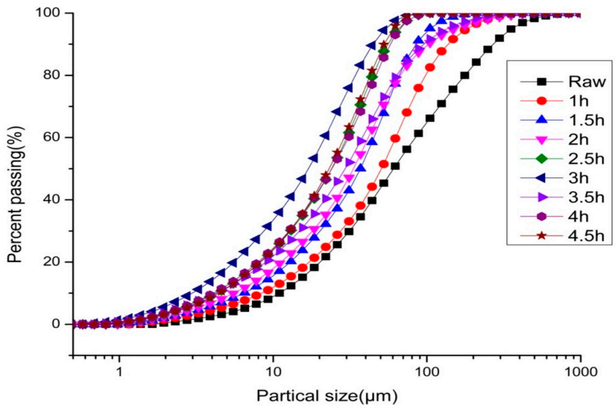



**Figure 5** The particle size of mine tailings milling for different time

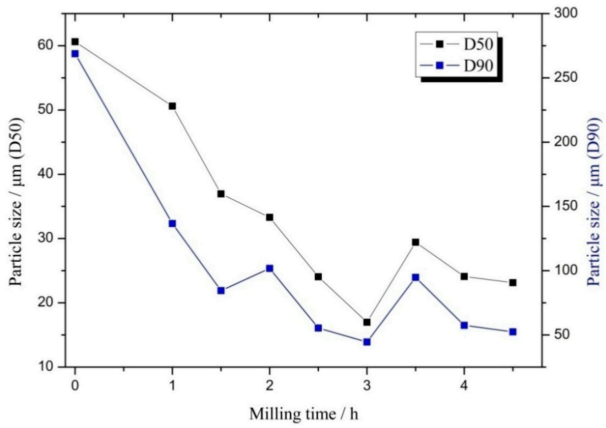



**Figure 6** The particle size variation of D50 and D90 withmilling time

**Table8 Characteristic particle diameters of copper mine tailings milled for different time**

| Milling time | 0 | 1h | 1.5h | 2h | 2.5h | 3h | 3.5h | 4h | 4.5h |
|---|---|---|---|---|---|---|---|---|---|
| D50 | 60.63 | 50.60 | 36.96 | 33.30 | 24.05 | 16.98 | 29.43 | 24.11 | 23.14 |
| D90 | 268.8 | 136.7 | 84.52 | 101.8 | 55.40 | 44.53 | 94.79 | 57.49 | 52.43 |

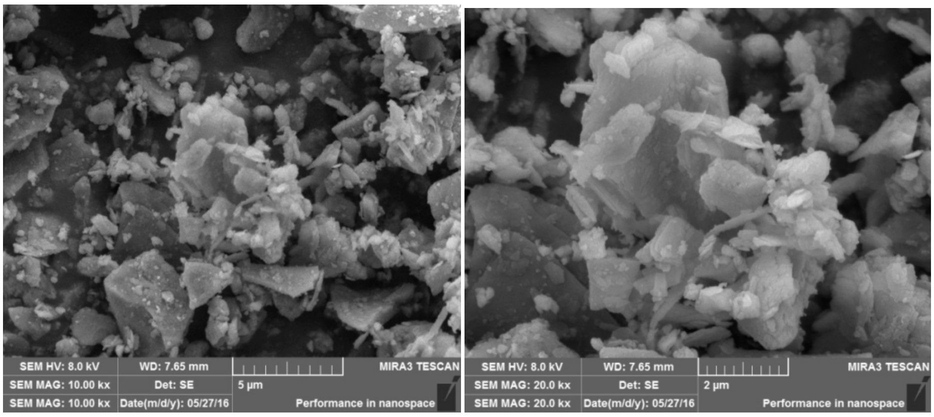
### *3.1.3 Particle morphology and mineral composition*

Figure 7 shows the SEM images of M3 copper mine tailings. It can be seen that copper mine tailings have particles of different sizes. Smaller sized particles are attached to the surface of larger particles. Silicon and aluminum ions are easily leached down due to presence of smaller sized particles (as a result of mechanical grinding).

Figure 8 shows the XRD patterns of raw and M3 copper mine tailings. It can be analyzed that no significant difference among diffraction peaks are observed, which indicates that no new phase generated. The crystalline silica exhibits less intense peaks after the activation, which indicates that some of the crystalline silica has been broken, and the intensity of albite diffraction peak is increased, that is mostly because the larger particles copper mine tailings containing albite and mechanical grinding make the particle breakage. Grain refinement makes silicon aluminum leaching more easily. It can be seen from Figure 9, Si（$Al^{IV}$）-O-Si asymmetric stretching band is

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1
Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

reduced from 1005.41 $cm^{-1}$ to 1004.99 $cm^{-1}$and Si-O bend vibration (533.30 $cm^{-1}$ and 462.43 $cm^{-1}$) are reduced to 530.84 $cm^{-1}$ and 461.52 $cm^{-1}$, respectively. It indicates that the polymerization degree of [$SiO_4$] and [$AlO_6$] of copper mine tailings are reduced. That is because Si-O and Si($Al^{IV}$)-O-Si bound of copper mine tailings are gradually broken in the mechanical activation. Which result in the cementitious activity index of copper mine tailings is improved.




10000x 20000x

**Figure 7 SEM images of M3**

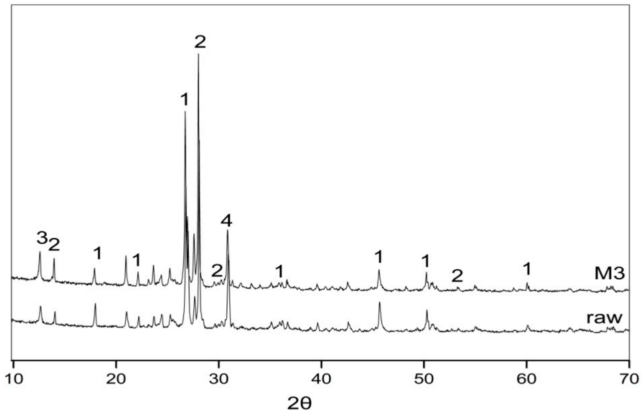



**Figure 8 XRD result of raw and M3**

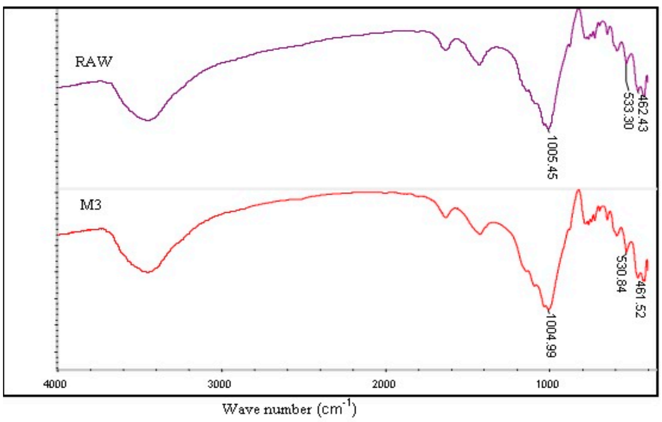



**Figure 9 FTIR spectra of raw and M3**

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

### 3.2 Thermal activation of copper mine tailings

#### *3.2.1 TG-DSC*

The TG-DSC curves of the copper mine tailings (at the temperature range between 10℃ and 1200℃ under air gas atmosphere) are shown in Figure 10. Based on the results, the first phase of slight decrease in weight of mine tailings is observed at temperature range of 10℃-400℃, which is due to removal of adsorbed water from mine tailing. While, the significant decrease in weight is observed at temperature range of 400℃-800℃. In this temperature range, the weight is reduced by about 5% and there is an obvious exothermic peak at the same time. While, at temperature range between 800℃ and 1200℃, there is no significant exothermic or endothermic reaction and samples weight also don not have significant change. Hence, the Thermal activation temperature was set in the range of 400℃ to 800℃.

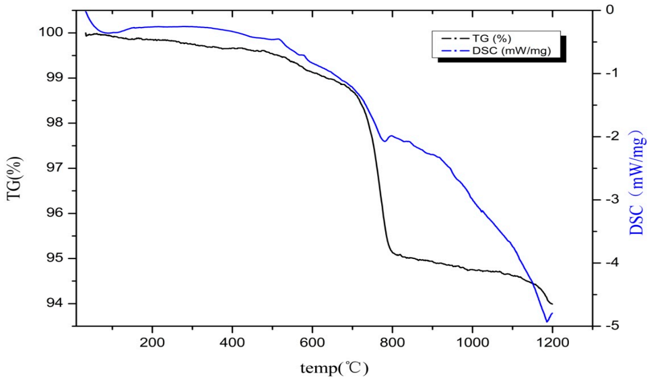



**Figure 10 TG-DSC curve (10℃~1200℃; Gas atmosphere: air)**

#### *3.2.2 Leaching test*

The experimental results from the thermal activation of copper tailings at different temperatures and different durations are shown in Table 9 and Figure 11. Highest leaching concentrations of silicon (57.53 μg/ml) and aluminum (22.41 μg/ml) are observed at activation temperature of 600℃ for 120 min. The amount of the concentration increase from the raw copper mine tailings is 20.22 μg/ml for silicon and 12.22 μg/ml for aluminum ; the percent increase in leaching concentration is 54.19% (Si) and 119.92% (Al) after activation as compared to raw mine tailings. During thermal activation process, water present in copper tailings is removed and crystal structure is destroyed and then restructured, which increase the cementitious activity of silica and alumina and ultimately improve the activity index of copper mine tailings.

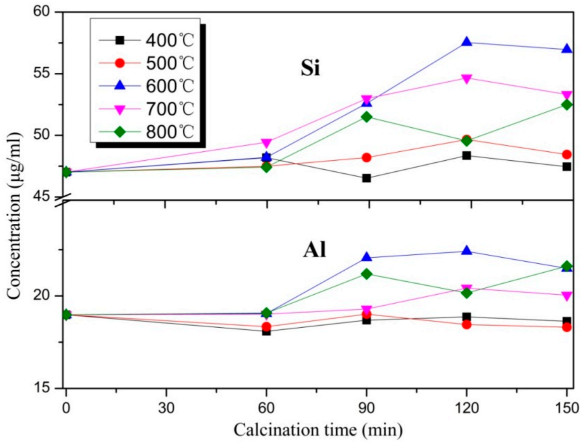



**Figure 11** Silicon and aluminum concentrationsin the thermal activation of copper tailings alkali leaching

**Table 9 Silicon and aluminum concentrations in thermal activation of copper tailings alkali leaching**

| NO. | Calcination temperature(℃) | Calcination time(min) | Si(μg/ml)) | Al(μg/ml)) |
|---|---|---|---|---|
| TM 1 | 400 | 60 | 48.19 | 18.09 |
| TM 2 | 400 | 90 | 46.53 | 18.68 |
| TM 3 | 400 | 120 | 48.36 | 18.87 |
| TM 4 | 400 | 150 | 47.46 | 18.63 |
| TM 5 | 500 | 60 | 47.49 | 18.34 |
| TM 6 | 500 | 90 | 48.20 | 19.02 |
| TM 7 | 500 | 120 | 49.66 | 18.45 |
| TM 8 | 500 | 150 | 48.45 | 18.31 |
| TM 9 | 600 | 60 | 48.22 | 19.02 |
| TM 10 | 600 | 90 | 52.59 | 22.06 |
| TM 11 | 600 | 120 | 57.53 | 22.41 |
| TM 12 | 600 | 150 | 56.96 | 21.49 |
| TM 13 | 700 | 60 | 49.44 | 19.02 |
| TM 14 | 700 | 90 | 52.98 | 19.29 |
| TM 15 | 700 | 120 | 54.66 | 20.42 |
| TM 16 | 700 | 150 | 53.32 | 20.04 |
| TM 17 | 800 | 60 | 47.42 | 19.08 |
| TM 18 | 800 | 90 | 51.50 | 21.19 |
| TM 19 | 800 | 120 | 49.56 | 20.16 |
| TM 20 | 800 | 150 | 52.50 | 22.61 |

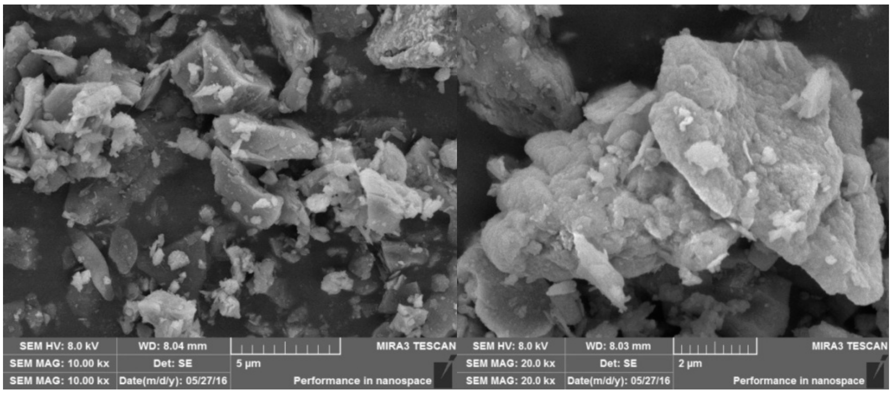
### *3.2.3 Mineral composition and particle morphology*

The SEM images of the copper mine tailings activated at 600℃ for 120 min are shown in Figure 12. It is observed that copper mine tailings particles are irregular in shape and most of particles show a relatively loose and porous surface structure. The thermal activation results in

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

change of mine tailings' structures, which can be observed by their fuzzy appearance of edges and corner. This is because of activation temperature (600℃), which results in soften of most minerals. It indicates that the microstructures of activated copper mine tailings are also changed, which causes the easier leaching of silica and alumina from copper mine tailings.




**c : 10000x** **d : 20000x**

**Figure 12 The SEM images of TM11**

Figure 13 shows the XRD patterns of copper mine tailings activated for 120 min at various temperatures. It can be seen that the crystalline chlorite dissolved at 600℃. This is most likely due to fact that the chlorite crystals are breakdown as the activity temperatures of copper tailings increases. It can be seen from Figure 14 that the Si（$Al^{IV}$）-O-Si asymmetric stretching band of 1004.99 $cm^{-1}$ is disappeared. The Si-O bend vibrationis reduced from 530.84 $cm^{-1}$ and 461.52 $cm^{-1}$ to 529.37 $cm^{-1}$ and 460.96 $cm^{-1}$, respectively. It indicates that extent of polymerization of [$SiO_4$] and [$AlO_6$] are reduced by mechanical milling. That is because Si-O and Si（$Al^{IV}$）-O-Si bound of copper mine tailings are broken during thermal activation, which results to enhance the cementitious activity index of copper mine tailings.

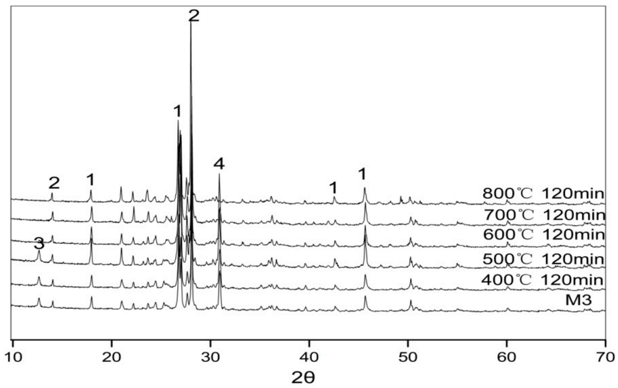



**Figure 13 XRD from various thermal activation conditions of copper tailings (1 quartz, 2 albite, 3 chlorite 4 dolomite)**

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

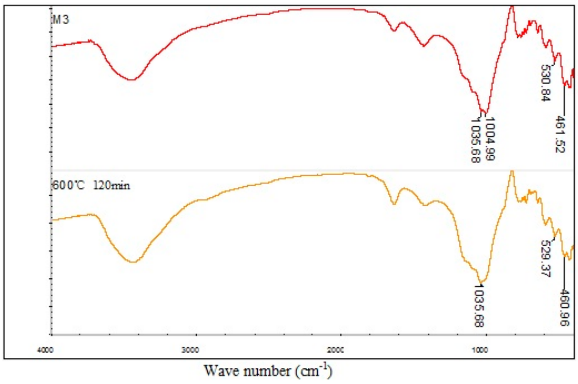



Figure 14 FTIR spectra of M3 and TM11

### 3.3 Alkaline roasting activation of copper mine tailings

#### 3.3.1 *Optimization analysis*

Table 10 shows the orthogonal experimental results and range analysis of Si and Al leaching concentration. For Si leaching concentration, it is shown from range analysis that C/N mass ratio is the most important factor, following by roasting temperature and roasting time, C>B>A. The optimal level of silicon is at $A_3B_2C_1$. It also can be seen that silicon leaching concentration increased with the increment of roasting time and roasting temperature and its concentration is decreased as C/N ratio decreases. For Al leaching concentration, it is effected by different factors in following order: roasting temperature (B)> roasting time (A) > C/N ratio(C). $A_3B_2C_1$ is the optimal level, at which maximum leaching of Al is noted. We can see that Al leaching concentration increased as roasting time increases, moreover, with increase in roasting temperature; first its concentration increased then decreased, and when C/N mass ratio decreased, the silicon leaching concentration decreased. The results indicate that the alkaline roasting activation can largely improve the activity index of copper mine tailings. Overall consideration, we chose condition $A_3B_2C_1$ for the best way to activate copper mine tailings.

**Table 10 The orthogonal experimental results and range analysis of Si and Al leaching concentration**

| No | A(time) | B(temp) | C | Si(μg/ml) | Al(μg/ml) | |
|---|---|---|---|---|---|---|
| ARMT1 | 1 | 1 | 1 | 183.25 | 62.91 | |
| ARMT2 | 1 | 2 | 2 | 147.83 | 48.46 | |
| ARMT3 | 1 | 3 | 3 | 159.45 | 49.55 | |
| ARMT4 | 2 | 1 | 2 | 149.23 | 49.13 | |
| ARMT5 | 2 | 2 | 3 | 150.09 | 68.19 | |
| ARMT6 | 2 | 3 | 1 | 198.10 | 79.53 | |
| ARMT7 | 3 | 1 | 3 | 151.95 | 66.35 | |
| ARMT8 | 3 | 2 | 1 | 192.35 | 88.83 | |
| ARMT9 | 3 | 3 | 2 | 175.92 | 57.35 | |
| | Si | | | Al | | |
| | A | B | C | A | B | C |
| kj1 | 163.51 | 161.48 | 191.23 | 53.64 | 59.46 | 70.84 |

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 25 September 2017 doi:10.20944/preprints201709.0118.v1

Peer-reviewed version available at Fibers 2017, 5, 47; doi:10.3390/fib5040047

| | | | | | | |
|---|---|---|---|---|---|---|
| kj2 | 165.81 | 163.12 | 157.66 | 65.62 | 68.49 | 62.14 |
| kj3 | 173.40 | 177.82 | 153.83 | 70.84 | 51.65 | 61.36 |
| R | 9.89 | 16.34 | 37.40 | 17.2 | 16.84 | 9.48 |
| Order | | C>B>A | | | B>A>C | |
| Optimal level | | $A_3$、$B_3$、$C_1$ | | | $A_3$、$B_2$、$C_1$ | |

XRD patterns of alkaline roasting activated copper mine tailings are shown in Figure 15. The crystalline silica and albite exhibit less intensive peaks after the activation, which indicates that some of the crystalline silica and albite has been disintegrated. We can also observe that biotite has generated. It can be seen from Figure 16, the Si（$Al^{IV}$）-O-Si asymmetric stretching band 1033.65 $cm^{-1}$ is disappeared, and 1004.99 $cm^{-1}$ is reduced to 996.51 $cm^{-1}$. The Si-O bend vibration is reduced from 530.84 $cm^{-1}$ to 529.37 $cm^{-1}$and 461.52 $cm^{-1}$ to 458.57 $cm^{-1}$. Wave number 786.93 $cm^{-1}$ represents the [$AlO_4$] bend vibration and its intensity decreased in alkaline roasting activating. The O-C-O asymmetric stretching band is observed at1436.74 $cm^{-1}$, this may be due to intensive reaction of NaOH with $CO_2$ in the presence of air during roasting activation.

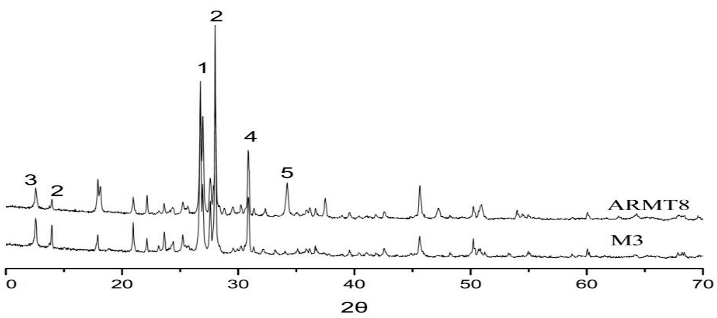



**Figure 15 XRD result of M3 and ARMT8 (1 quartz, 2 albite, 3 chlorite 4 dolomite5biotite)**

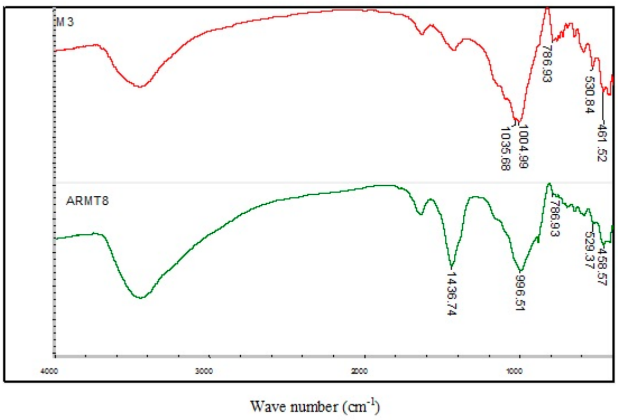



**Figure 16 FTIR spectra of M3 and ARMT8**

## 4 Conclusions

Based on the above study on the combined approach using the mechanical grinding and thermal activation of the copper mine tailings, the following conclusions can be made:

(1) In the mechanical grinding, activation time is one of the main factors that significantly affect the cementitious activity of copper mine tailings. Three hours is the optimal activation time for the copper mine tailings. The percent increase in leaching concentration is 26.03% (Si)

Peer-reviewed version available at *Fibers* **2017**, *5*, 47; doi:10.3390/fib5040047

and 93.33% (Al) after activation as compared to raw mine tailings. When the copper mine tailings are activated for three hours, the average particles of D50 and D90 reaches their minimum sizes and alkali leaching silicon and aluminum concentrations reach their maximum level.

(2) In the thermal activation, activation time and temperature are two most important factors affecting the thermal activation of the copper mine tailings. Optimal thermal activation conditions achieved at 600℃ for 120 min, in which the percent increase in leaching concentration is 54.19% (Si) and 119.92% (Al) after activation as compared to raw mine tailings.

(3) The alkaline roasting activation can largely improve the cementitious activity index of copper mine tailings, and the best condition was activation for 120 min at 600℃with C/N ratio is 5:1.

(4) It is confirmed from SEM images that mechanical grinding activation broke the particles into smaller pieces, and thermal activation caused surface microstructure changes into smaller particles and thus increased the corresponding activation activity of the particles.

(5) Some of the crystalline silica was broken in the mechanical grinding activation, evidenced by less intensive peaks in the crystalline silica from the XRD patterns. Si-O and Si($Al^{IV}$)-O-Si bound of copper mine tailings are broken during activation.

## Author contributions

Lin Yu wrote the main manuscript text. Lin Yu, Zhen Zhang and Xiao Huang participated in the experiments. Binquan Jiao and Dongwei Li supervised the project.

## Conflicts of interest

There are no conflicts of interest to declare.

## Reference

1. Mahasenan, N.; Smith, S.; Humphreys, K. The cement industry and global climate change: Current and potential future cement industry co2 emissions. *Greenhouse Gas Control Technologies, Vols I And Ii, Proceedings* **2003**, 995-1000.
2. Gines, O.; Chimenos, J.M.; Vizcarro, A.; Formosa, J.; Rosell, J.R. Combined use of mswi bottom ash and fly ash as aggregate in concrete formulation: Environmental and mechanical considerations. *J Hazard Mater* **2009**, *169*, 643-650.
3. Mechtcherine, V. Strain-hardening cement-based composites material design, properties and applications in construction. *Beton- Stahlbetonbau* **2015**, *110*, 50-58.
4. Mohammadinia, A.; Arulrajah, A.; Sanjayan, J.; Disfani, M.M.; Bo, M.W.; Darmawan, S. Laboratory evaluation of the use of cement-treated construction and demolition materials in pavement base and subbase applications. *J Mater Civil Eng* **2015**, *27*.
5. Wang, A.G.; Deng, M.; Sun, D.S.; Li, B.; Tang, M.S. Effect of crushed air-cooled blast furnace slag on mechanical properties of concrete. *J Wuhan Univ Technol* **2012**, *27*, 758-762.

Peer-reviewed version available at *Fibers* **2017**, *5*, 47; doi:10.3390/fib5040047


6. Qin, W.Z. What role could concrete technology play for sustainability in china? *Proceedings Of the International Workshop on Sustainable Development And Concrete Technology* **2004**, 35-43.
7. Pavlik, Z.; Keppert, M.; Pavlikova, M.; Zumar, J.; Fort, J.; Cerny, R. Mechanical, hygric, and durability properties of cement mortar with mswi bottom ash as partial silica sand replacement. *Cem Wapno Beton* **2014**, *19*, 67-+.
8. Puertas, F.; Santos, R.; Alonso, M.M.; Del Rio, M. Alkali-activated cement mortars containing recycled clay-based construction and demolition waste. *Ceram-Silikaty* **2015**, *59*, 202-210.
9. Polozhyi, K.; Reiterman, P.; Keppert, M. Mswi bottom ash as an aggregate for a lightweight concrete. *Special Concrete And Composites 2014* **2014**, *1054*, 254-+.
10. Sadi, M.A.K.; Abdullah, A.; Sajoudi, M.N.; Kamal, M.F.B.; Torshizi, F.; Taherkhani, R. Reduce, reuse, recycle and recovery in sustainable construction waste management. *Trends In Civil Engineering, Pts 1-4* **2012**, *446-449*, 937-+.
11. Duxson, P.; Provis, J.L.; Lukey, G.C.; Van Deventer, J.S.J. The role of inorganic polymer technology in the development of 'green concrete'. *Cement Concrete Res* **2007**, *37*, 1590-1597.
12. Davidovits, J. Pyramid man-made stone, myth or facts .3. Cracking the code of the hieroglyphic names of chemicals and minerals involved in the construction. *Abstr Pap Am Chem S* **1987**, *193*, 37-Hist.
13. Davidovits, J. Geopolymers and geopolymeric materials. *J Therm Anal* **1989**, *35*, 429-441.
14. Davidovits, J. Geopolymers - inorganic polymeric new materials. *J Therm Anal* **1991**, *37*, 1633-1656.
15. Wastiels, J. Sandwich panels in construction with hpfrcc-faces: New possibilities and adequate modelling. *High Performance Fiber Reinforced Cement Composites (Hpfrcc3)* **1999**, *6*, 143-151.
16. Lofthouse, H. An international journal devoted to innovation and developments in mineral processing and extractive metallurgy. *Miner Eng* **1999**, *12*, 581-581.
17. Rahier, H.; Wullaert, B.; Van Mele, B. Influence of the degree of dehydroxylation of kaolinite on the properties of aluminosilicate glasses. *J Therm Anal Calorim* **2000**, *62*, 417-427.
18. Rahier, H.; VanMele, B.; Wastiels, J. Low-temperature synthesized aluminosilicate glasses .2. Rheological transformations during low-temperature cure and high-temperature properties of a model compound. *J Mater Sci* **1996**, *31*, 80-85.
19. Rahier, H.; VanMele, B.; Biesemans, M.; Wastiels, J.; Wu, X. Low-temperature synthesized aluminosilicate glasses .1. Low-temperature reaction stoichiometry and structure of a model compound. *J Mater Sci* **1996**, *31*, 71-79.
20. Rahier, H.; Simons, W.; VanMele, B.; Biesemans, M. Low-temperature synthesized aluminosilicate glasses .3. Influence of the composition of the silicate solution on production, structure and properties. *J Mater Sci* **1997**, *32*, 2237-2247.
21. Allahverdi, A.; Skvara, F. Sulfuric acid attack on hardened paste of geopolymer cements - part 2. Corrosion mechanism at mild and relatively low concentrations. *Ceram-Silikaty* **2006**, *50*, 1-4.

22. Badanoiu, A.; Voicu, G. Influence of raw materials characteristics and processing parameters on the strength of geopolymer cements based on fly ash. *Environ Eng Manag J* **2011**, *10*, 673-681.
23. Duxson, P.; Provis, J.L. Designing precursors for geopolymer cements. *J Am Ceram Soc* **2008**, *91*, 3864-3869.
24. Marin-Lopez, C.; Araiza, J.L.R.; Manzano-Ramirez, A.; Avalos, J.C.R.; Perez-Bueno, J.J.; Muniz-Villareal, M.S.; Ventura-Ramos, E.; Vorobiev, Y. Synthesis and characterization of a concrete based on metakaolin geopolymer. *Inorg Mater+* **2009**, *45*, 1429-1432.
25. Zhang, L.Y.; Ahmari, S.; Zhang, J.H. Synthesis and characterization of fly ash modified mine tailings-based geopolymers. *Constr Build Mater* **2011**, *25*, 3773-3781.
26. Ahmari, S.; Zhang, L.Y.; Zhang, J.H. Effects of activator type/concentration and curing temperature on alkali-activated binder based on copper mine tailings. *J Mater Sci* **2012**, *47*, 5933-5945.