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Mechanical Performances and Microstructures of Cement Containing Copper Tailings†

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The physical and chemical properties of copper tailings have been investigated. The standardized mortars specimen, where cement was replaced by 5, 10, 15, 20, 25, 30 and 35 % of copper tailings were prepared. Its compressive and flexural strengths were tested, the microstructures were examined by scanning electron microscope and pore structures were investigated by mercury intrusion porosimetry. The results show that when copper tailings are less than 15 %, it can increase compressive strength and flexural strength and improve cement performances, while more than 15 % would go against the strength. The best mixing amount of copper tailings is 15 %. Therefore, copper tailings can be used as cement admixture to solve the problem of environmental pollution. It suggested that copper tailings can be recovered and recycled.

Keywords: Copper tailings, Strength, Microstructures, Porosity.

INTRODUCTION

Copper tailings are generated during flotation process from copper industry as a kind of industrial by-product. As a result of current technology and economic level, recovery of copper tailings are relatively difficult, mainly heaped up somewhere, accumulative total accumulation amount of copper tailings in China is quite large nearly more than 2.4 billion tons[1]. The accumulated copper tailings not only occupy a lot of land, but also pollute the environment. Therefore, utilization of copper tailings as cement mixing materials, for one thing can decrease the rate of land using and saving environmental costs. The cement and concrete industry find a new kind of low cost raw materials.

In the past decade, finding out ways to reuse copper tailings or slag, many researchers investigate if it can be widely used as a construction material. Onuaguluchg and Eren[2] studied the impact of copper tailings at 0, 5 and 10 % addition level by mass of cement on the fresh and hardened properties of mortars, the use of pre-wetted tailings blended mortars showed higher strength and abrasion resistance, rate of water absorption, acid and chloride resistance higher than those of the control mixture. The use of pre-wetted tailings at 5 % addition level seems to be the best reuse approach. Moura and Goncalves *et al.*[3] reported the copper slag additions of 20 % (relative to the cement weight) in concrete presented greater mechanical and durability performance, increasing rate compressive strength and splitting tensile strength is, respectively 30.4 and 17.6 %, absorption rate by capillary suction and carbonation depth are lower. Isabel Sánchez de Rojas *et al.*[4] measured the replacement of 30 % cement of copper tailings reduces the flexural and compressive strength in a similar way to fly ash. However, after 28 days, the reduction is less than the percentage of substitution. Al-Jabri *et al.*[5,6] and Wu *et al.*[7] indicated high strength concrete incorporating copper slag as a fine aggregate less than 40 % can achieve high strength and good workability, durability concrete that comparable or better to the control sample. Copper tailings could also be reused for producing autoclaved sand-lime brick[8,9] and autoclaved aerated concrete[10].

This experiment focuses on the feasibility of the copper tailings as an activity mixture, explore its influence on cement strength. The standardized mortars specimen, where cement was replaced by 5, 10, 15, 20, 25, 30 and 35 % of copper tailings were prepared. Its compressive and flexural strengths were tested, pore structures were investigated by mercury intrusion porosimetry (MIP) and the microstructures were examined by scanning electron microscope (SEM).

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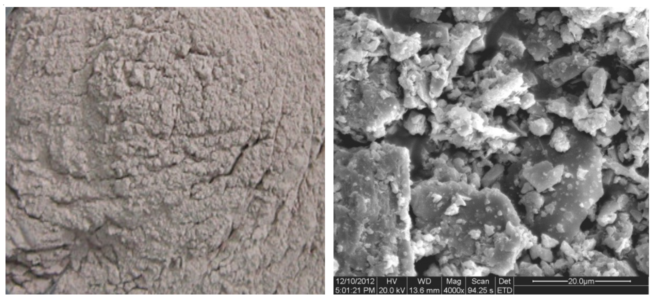
EXPERIMENTAL

Raw materials: The main raw materials are copper tailings and Portland cement from Chu Zhou cement plant (china). Fig. 1(a) is macro appearance and (b) is scanning electron microscopic image. It can be seen that copper tailings are light pink powder. The particle sizes of D10, D50 and D90 are 2.58, 12.12 and 85.10 µm determinated by laser diffract instrument, mainly range from 3-90 µm. So it shows that copper tailings are small and smooth.



(a) (b)

Fig. 1. Particle image of copper tailings

The mineral composition mainly depends on the chemical composition, so mineral composition of copper tailings is complex, there is a marked regional difference. The most mineral composition of copper tailings is gangue mineral, other are rock, sulfide minerals, *etc*. X-ray diffraction of copper tailings is shown in Fig. 2, it can be seen that the main mineral composition are A quartz, B calcite, C dolomite and a little amount of D magnetite, E muscovite and F clinochlore. Above all, copper tailings are complex mixtures.

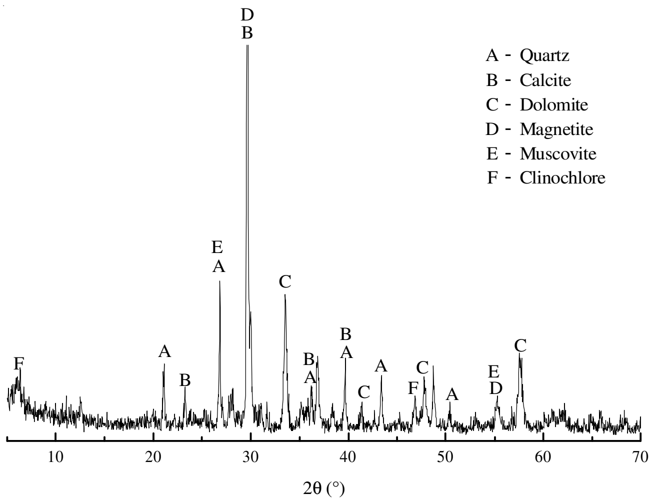


Fig. 2. XRD pattern of copper tailings

The percentages of copper tailings added in cement are as follows: 0 % (for the control mix), 5, 10, 15, 20, 25, 30 and 35 %. The water requirement of normal consistency and setting time of each experimental group were tested according to China standard GB/T1346-2001. The determination of flexural and compressive strengths of the 4 cm × 4 cm × 16 cm specimens are realized in mortars with sand/cement in a proportion of 3/1 and a W/C ratio of 0.5 prepared following the method established in the China standard GB/T17671-2005. The results are obtained at 3, 28 and 90 days. The pore structures of specimens was determined by mercury intrusion porosimetry.

The copper tailings and Portland cement in desired proportion were mixed by hand. The mixtures were with w/c = 0.5. The pastes were transferred to little bottles and sealed for curing. At each testing age, samples were taken out. The surface was discarded and the paste was ground with absolute alcohol to check hydration. After filtration the ground samples were moved to the drying oven at 50-60 ºC to dry for 24 h. Finally, samples were cooled at room temperature for hydration products test. Hydration products were identified by differential thermal analysis (DTA) and by SEM.

RESULTS AND DISCUSSION

Normal consistency: The results given in Fig. 3 show that the standard consistency gradually increases with the increase content of copper tailings. However, when the dosage of copper tailings is 0-10 %, the standard consistency changes are not obvious, but the changes gradually increase significantly more than 10 %. Copper tailings have small particle size, large specific surface area, large contact area between particles, the same quality of the copper tailings need water is more than the cement, therefore, it demand much more water to achieve the standard consistency. When the small dosage of copper tailings (0-10 %), grain fineness variation is not obvious, standard consistency is small. When copper tailings content more than 10 %, relatively large amounts of water, normal consistency are gradually increasing and changes are higher.

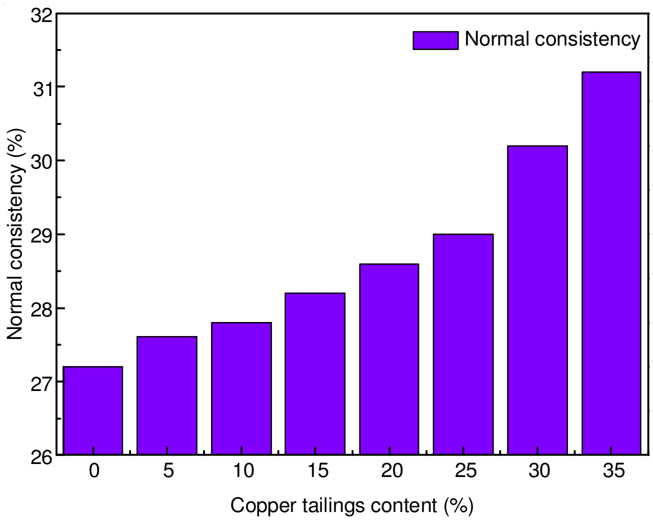


Fig. 3. Normal consistency of cement with different proportions of copper tailings

Setting time: Fig. 4 shows that the setting time can satisfy the requirements of national standard. The initial setting and final setting time will change with the content of the copper tailings. The dosage of water consumption will increase when copper tailings increase, the time of cement paste lose plasticity become long, initial setting show a trend of gradual increase. Copper tailings are beneficial to accelerate the hydration process of cement, so it can short the time that cement paste

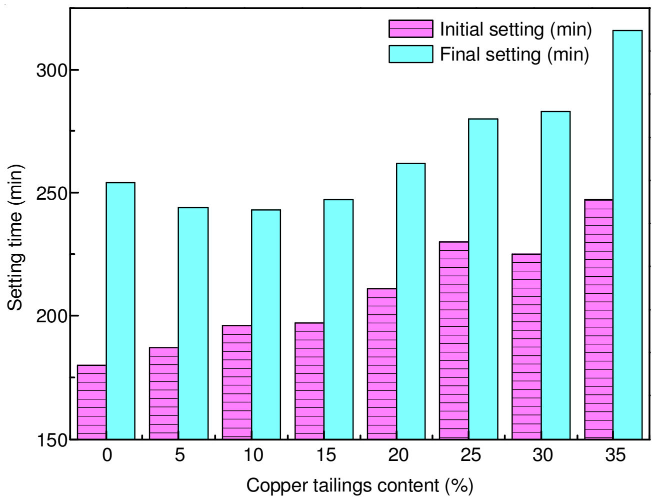


Fig. 4. Setting time of cement with different proportions of copper tailings

cement paste completely lose plasticity when the content of copper tailings is less than 15 %. When the content is more than 15 %, the effect on the cement hydration is less even become blocks, final setting time is longer along with the increase in content. Thus the final setting change is irregular, increase after the decrease.

Mechanical strengths: Table-1 indicates that the changes of the compressive strength are different for 3, 28, 90 days. The compressive strength of 3 and 90 days first enhance gradually but become decrease after reaching a maximum (15 %) with the increase in dosage of copper tailings; the strength value is the highest when copper tailings are 15 %. But at 28 days appear a linear downward trend along with the increase in dosage of copper tailings. At 3, 28 and 90 days's, the flexural strength trend are similar to each other, with the increasing of copper tailings, strength will increase gradually, then decrease when reaching to a maximum (15 %) (Table-1).

Pore structure: The pore structure of prepare samples (A0, A3 and A6) for 3, 28 and 90 days was tested by mercury intrusion porosimetry after weighing quality and calculating volume and density. The results are shown in Table-2. Taking a holistic approach to the Table-2, capillary pores become small from 3 days to 90 days, because cement hydration products are filled in the pores lead to big pores change into small gel pores. With the hydration degree carrying out, much more hydration products mixed with each other to occupy more pore space, gel pores also become smaller and smaller. It's known that at 3, 28 and 90 days, the intraparticle porosity gradually increase from A0, A3 to A6, the intraparticle porosity gradually increase from A0, A3 to A6, while the interparticle porosity gradually decrease from A0, A6 to A3. As a result, the total porosity from high to low in order as A6, A0 and A3. When cement mixed with 15 percentages of copper tailings, activated SiO_2 in copper tailings can neutralize $Ca(OH)_2$ produced by hydration of cement clinker and promote the cement hydration. Besides, small copper tailings play a role in filling the large pore space between cement particles and the close packing effect can reduce porosity and average pore size. When copper tailings are added to Portland cement in proportion of 30%, the content of the clinker mineral in cement is reduced significantly to lead to reducing of $Ca(OH)_2$ formed during clinker hydration and the secondary hydration products. Thus the interparticle and total porosity increases.

Fig. 5 shows the differential distribution curves of porosity (A0, A3 and A6) at 3, 28 and 90 days. The diameter size corresponds to the highest peaks of curve in the graph is critical aperture. The area under the curve and X axis formed is the total porosity. The small critical aperture and area illustrate that the porosity is low and the structure is dense. At 3 days, the critical aperture of A3 and A6 are smaller than A0, A3 has more small pores and fewer large pores than A0, so in order of small the area are, A0 and A6. It suggested that the pore sizes of A0, A3 and A6 become small because the main peaks were moved in the direction of the small pores on the left after 28 and 90 days. The values of critical aperture are similar at 28 days, but the area of A0 is the smallest, then next are A3 and A6. At 90 days, it's obvious that the area of A3 is smaller than A0 and A6. The results are in line with the Table-2 as well as the compressive strength and flexural strength in Table-1.

Hydration products and microstructures: The hydration samples (copper tailings/cement (CT/C) = 0/100, 15/85 and

TABLE-1
CEMENT MORTAR MECHANICAL STRENGTHS

Sample	Portland cement (W %)	Copper tailings (W %)	Compressive strength (MPa)			Flexural strength (MPa)		
			3d	28d	90d	3d	28d	90d
A0	100	0	26.5	55.7	57.4	5.3	8.0	9.0
A1	95	5	27.4	54.0	56.3	5.9	8.2	8.4
A2	90	10	28.9	52.6	56.4	5.9	8.3	8.6
A3	85	15	29.4	50.3	57.8	6.0	8.5	9.3
A4	80	20	28.6	47.8	54.8	5.8	7.5	8.6
A5	75	25	25.7	45.8	49.8	5.5	7.3	8.0
A6	70	30	24.0	42.5	47.7	5.2	7.0	7.6
A7	65	35	22.9	39.6	45.9	4.8	6.6	7.4

TABLE-2
POROSITY OF CEMENT

Sample	Interparticle porosity (%)			Intraparticle porosity (%)			Total porosity (%)		
	3d	28d	90 d	3d	28d	90 d	3d	28d	90 d
A0	2.65	1.97	1.56	9.48	6.60	5.82	12.13	8.57	7.38
A3	0.07	1.25	0.92	10.96	7.78	6.24	11.02	9.03	7.16
A6	1.64	1.61	1.01	11.94	10.20	9.24	13.58	11.81	10.25

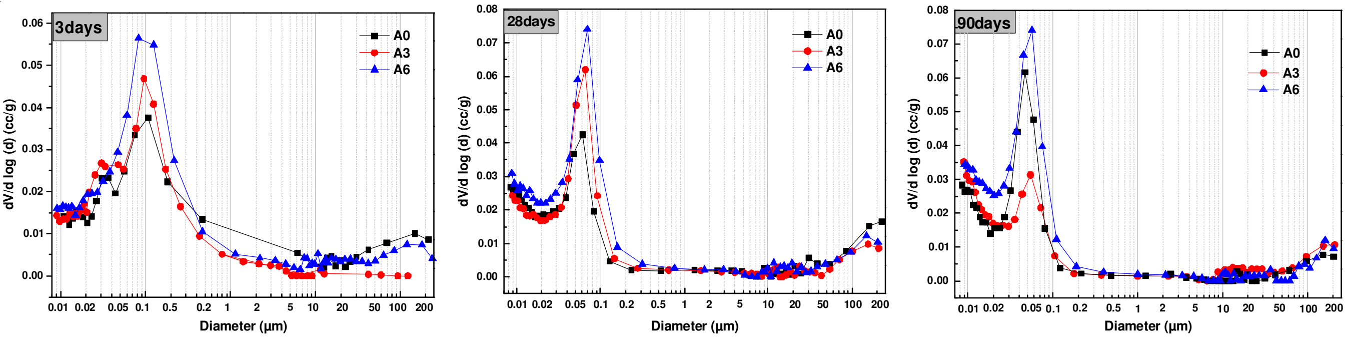


Fig. 5. Porosity of A0, A3, A6 at 3, 28 and 90 days

30/70, cure time is at 3d and 28d) are tested by DTA (Fig. 6). In Fig. 6, there are three endothermic peaks at the DTA. The first is formed from hydrated calcium silicate (main is CSH) at 90 ºC; the second calcium hydroxide (CH) at 440 ºC. The third calcium carbonate ($CaCO_3$), which result from the reaction between $Ca(OH)_2$ in the past with CO_2 in air during curing process of the samples, of non-crystallization and crystallization at 700 ºC. It can be seen that CSH peak and CH peak are feebler with the increase of adding copper tailings at 3d and 28d. However, CH peak that copper tailings/cement ratio is 15/85 is obvious feebler at 28d than at 3d. It means that there is more hydrated calcium silicate added copper tailings, it is because activated SiO_2 from copper tailings lead to accelerate of hydration rate.

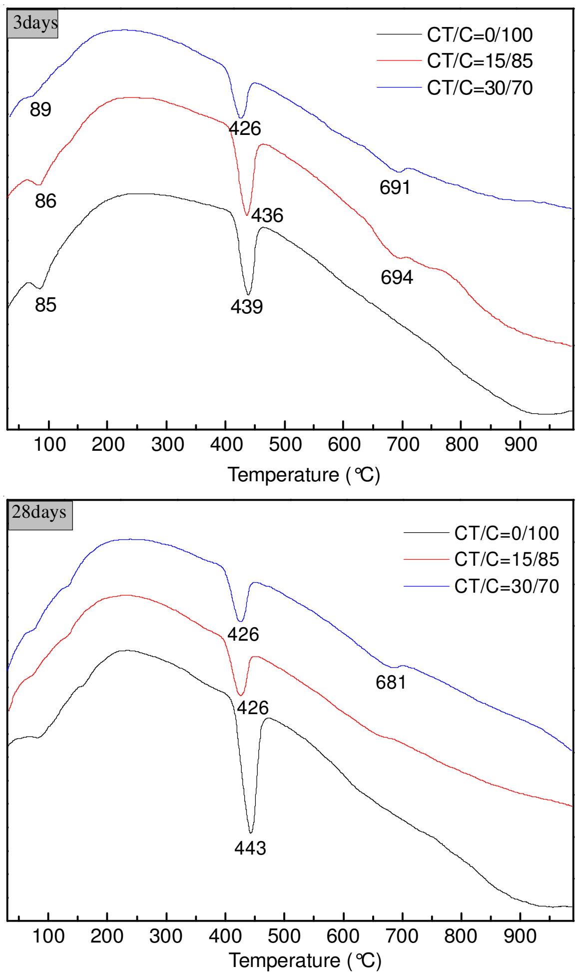


Fig. 6. DTA curves of 3 days and 28 days hydration products

The hydration samples (CT/C=0/100, 15/85 and 30/70, cure time is at 1, 3, 28 and 90 days) are analyzed by SEM (Figs. 7-9). Compared with 1 day and 3 days, the fastest speed of hydration is C_3A, followed by C_4AF, C_3S and C_2S are slow, but it can be observed that hydration products like the fibroid C-S-H gel, hexagonal flake $Ca(OH)_2$ and rods AFt were generated. The C-S-H gel radiant grow outward from the surface of cement particles. The $Ca(OH)_2$ grow up apparently from 1 day to 3 days. There are much more structure of C-S-H gel, $Ca(OH)_2$ at 3d compared with 1d, crystals also grow up and microstructure began to be dense. Among A0, A3, A6, the hydration products crystal of A3 are better than the A0 and A6 crystal are minimal.

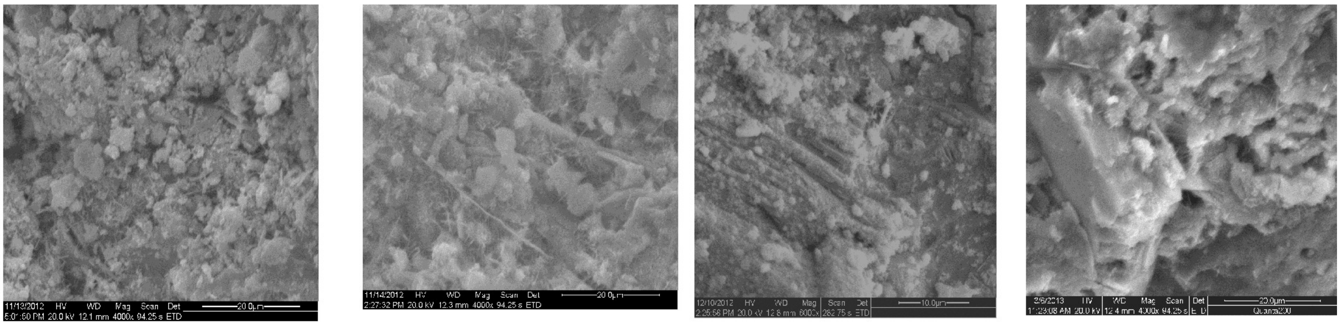
At 28 days, C_3A and C_4AF hydration degree are about 65-80 %, many AFt begin to transform into AFm, AFm and $Ca(OH)_2$ grow up and become lamellar crystal. The number of C-S-H gel increase significantly, interweave and overlap with $Ca(OH)_2$ and AFm forming a relatively complete network structure to fill the pore structure. Compared with A0 and A3, A6 has a negative effect on strength because of more pore and loose structure.

At 90 days, C_3A, C_4AF, C_3S hydration degree around 90 % and C_2S the slowest in hydration is 30 %, cement paste gradually hydrate and hardening. The cement hydration degree is high, a lot of gel material cemented together and filled in the space original occupied by the water and wrapped up the $Ca(OH)_2$, greatly increased the density. The dense structure of A3 compared with A0 had good contribution to high compressive strength. The pore sizes of A6 are big, A6 has a negative effect on strength because of more pore and loose structure compared with A0 and A3.

Conclusion

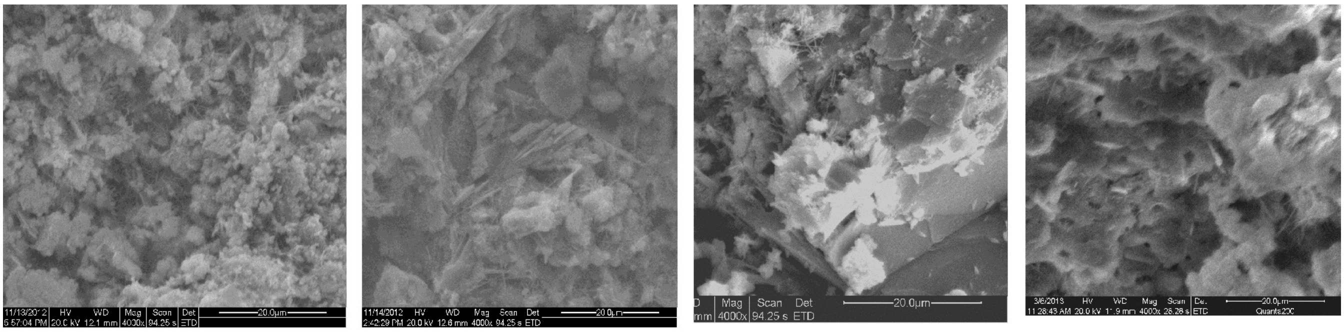
The following conclusions may be drawn through the above analyses. When different contents of copper tailings as mixing materials joined in cement, normal consistency and setting time of different ages can meet the national standard requirements.

When the dosage of copper tailings is 15 %, a large number of hydration products such as C-S-H gel, Ca $(OH)_2$ and AFm are generated and cemented together to fill up the pore space, the cement paste greatly increase the density. The interparticle porosity and total porosity are small compared with control cement as well as the critical aperture. The results show that the compressive strength and flexural strength are good in the end. But 30 % of copper tailings mixed with cement, the pheno-



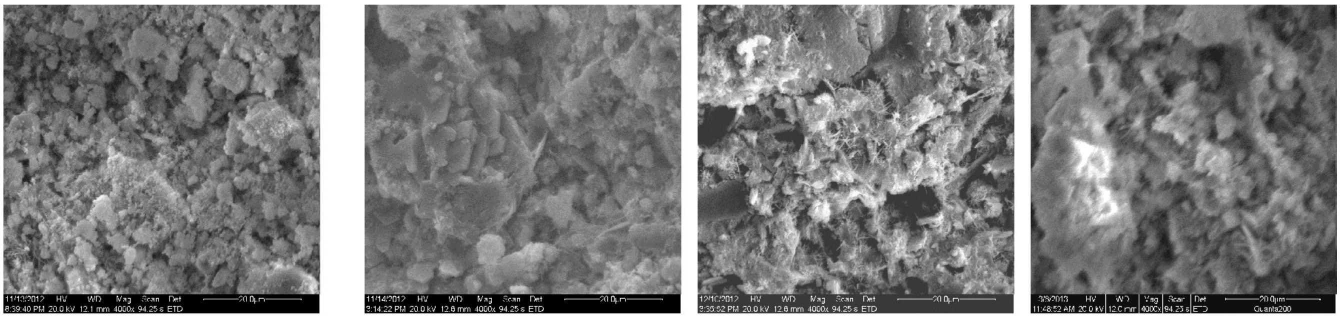
(a) 1d (b) 3d (c) 28d (d) 90d

Fig. 7. SEM images of hydration products (CT/C = 0/100)



(a) 1d (b) 3d (c) 28d (d) 90d

Fig. 8. SEM images of hydration products (CT/C = 15/85)



(a) 1d (b) 3d (c) 28d (d) 90d

Fig. 9. SEM images of hydration products (CT/C = 30/70)

menon which strength and performances degradation occurs. Thus, copper tailings can used as a cement admixture and the best amount is 15 % by weight.

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