REACTIVITY AND CEMENTITIOUS PROPERTIES OF MICROWAVE-IRRADIATED COPPER TAILINGS

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This research investigates the reactivity and cementitious properties of copper tailings irradiated with microwave at different power. The dissolution quantities of Si^{4+}, Al^{3+} species of the microwave-irradiated copper tailings were tested by inductively coupled plasma optical emission spectrometer (ICP-OES). The microwave irradiated copper tailings and the microstructure of the copper tailings-based cement were examined by X-ray diffraction (XRD), differential thermal analysis (TG-DTA) and scanning electron microscope (SEM). The results show that the free water and constitutional water of copper tailings can be taken away and the firm bonds of Si-O and Al-O are damaged by microwave irradiation. The solubility of SiO_2 and Al_2O_3 is improved, resulting in the improvement on the reactivity and cementitious property of copper tailings. The copper tailings irradiated at 800 W have the best cementitious properties. The dissolution quantities of Si^{4+} and Al^{3+} species are 37.3 $mg{\cdot}g^{-1}$ and 34.7 $mg{\cdot}g^{-1}$ respectively, which are increased by 56.7% and 31.4% when compared with the original copper tailings. When 30% copper tailings is incorporated in the cement paste, the 28-d compressive strength is 69.6 MPa, which is higher than the 17.5 MPa obtained from the cement paste with unirradiated copper tailings. Irradiated copper tailings promote the hydration of cement paste, improve the crystallization degree of hydration products and compact the pore structure. In addition, the heavy metals elements in the copper tailings could be effective immobilized in the cement pastes.

Keywords: copper tailings; reactivity; microwave irradiation; cementitious properties

1. Introduction

Copper tailings as a kind of industrial by-product are produced during the flotation process from copper industry. According to the relevant statistics, the tailings become abundant year after year, and the total output of copper tailings is more than 2.4 billion tons in China [1]. Large amounts of piled copper tailings occupy valuable land, so it becomes a serious problem for saving the farm land resources. Copper tailings are easy to cause air pollution or get into the rivers and lakes after washing out by the acid rain [2]. Copper tailings may also contain the

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flotation agent produced from the flotation process. The leaching of harmful substances to pollute water or soil will affect agriculture and fishing production seriously [3, 4]. In recent decades, most of copper tailings are abandoned as a waste, or simply used for backfilling or road construction. Therefore, seeking for efficient technologies to profitably use this industrial waste becomes an urgent work for industry.

A large number of industrial wastes, such as fly ash [5], slag [6], and coal bottom ash [7], can be widely used with the Portland cement production, which provides a guidance for the use of copper tailings. It is an effective way of solving the problem of copper tailings accumulation, and its pozzolanic activity is the basis to judge whether it can be used as the cementitious supplementary material. In order to achieve the effective utilization of copper tailings resources, it needs to enhance the reactivity. At present, most studies are focused on the direct use of copper tailings in cement or concrete, while there is few research focused on activating copper tailings [8-10]. Microwave activation has the advantages of short processing time and high efficiency. Material could be internally heated by microwave radiation. The microwave effect is different from the conventional heating method. The high heating rate could be obtained by changing the microwave power source, where the maximum value of temperature is reflected inside the material rather than the surface[11].To establish the method of preparing the highly reactive copper tailings, the microwave irradiation could be used. To lay the foundation of the large and effective use of copper tailings, investigating the activity of copper tailings and improving their cementitious properties will improve the overall performance of cement and cement-based materials, and increases the utilization amounts of the copper tailings in cement products [12-14].

This paper explores the reactivity of copper tailings by microwave irradiation in the cement products. A detailed analysis of the microstructure of the copper tailings-based cement is performed by SEM microscopy, X-ray diffraction and TG-DTA. In addition, mechanical, thermal as well as some functional properties of the copper tailings-based cement are also investigated [15].

2. Experimental

Raw materials. The copper tailings are obtained from Langya mountain mining industry company (China). The cement clinker and desulfurization gypsum are provided by China United Cement Chuzhou Co, Ltd. The chemical compositions of raw materials are shown in Table 1. The main components in copper tailings include CaO, SiO_2, Fe_2O_3, Al_2O_3 and MgO, and traces of Mn, Zn, Cu, Ti elements. The XRD pattern of copper tailings is shown in Fig.1. The main crystalline phases are quartz, calcite, dolomite, muscovite and clinochlore.

Table 1

Chemical compositions of raw materials (*wt* %)

materials	copper tailings	cement clinker	desulfurization gypsum
SiO_2	37.02	21.79	2.32
Al_2O_3	7.34	5.32	1.22
Fe_2O_3	11.64	3.31	0.49
CaO	26	64.8	31.43
MgO	3.34	2.17	1.53
SO_3	-	-	33.56
Loss	11.61	0.6	22.49
Total	96.95	97.99	93.04
K_2O	0.42	-	-
Na_2O	2.25	-	-
Mn	0.18	-	-
Zn	0.11	-	-
Cu	0.68	-	-
Ti	0.19	-	-
B	0.025	-	-
Ba	0.052	-	-
Cr	0.02	-	-
As	0.0042	-	-
Pb	0.006	-	-

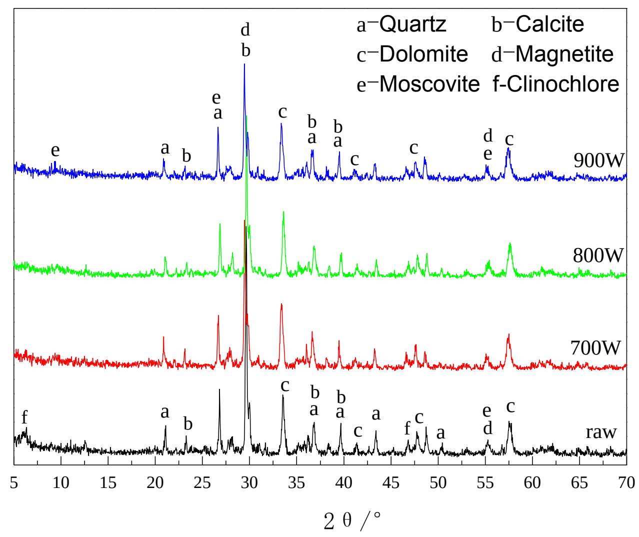


Fig.1 XRD pattern of copper tailings
Quartz, PDF No. 47-1301, Calcite, PDF No. 43-0697, Dolomite, PDF No. 36-0426, Magnetite, PDF No. 19-0629, Moscovite, PDF No. 52-1380, Clinochlore, PDF No. 09-0472

Experimental methods. The copper tailings were heated by microwave irradiation. When the temperature was below 400 ℃, the reactivity of copper tailings is low. When the temperature reached 500 ℃, the copper tailings particles were sintered. So the heating temperature was chosen as 400 ℃.

Copper tailings are irradiated for at 400 ℃ 10 minutes in the high temperature microwave muffle furnace. The powers are 500 W, 600 W, 700 W, 800 W, 900 W, 1000 W and 1100 W. After the irradiation process, the tailings were took out, grinded, and then sealed for storing.

The original copper tailings or irradiated copper tailings were soaked in 1 mol/L NaOH solution for 14 days at 20 ℃, and then processed in the water-bathing vibrator oscillate for 8 hours. After the filtration, the Optima-4300 DV type inductively coupled plasma emission spectrometer was used to test Si^{4+}, Al^{3+} dissolution and analysis the pozzolanic activity of the copper tailings.

The mix proportions of copper tailings-cement pastes are given in Table 2. The 0.08 mm square hole sieve residue of the samples were less than 2%. The cement pastes with water/solids ratio of 0.4 were cast into 2×2×2 cm cubes and vibrated 60 seconds on the table vibrator. The pastes were cured in a moist curing room at 20±3 ℃. The specimens were demoulded after 24 h and left in the moist curing room until the 3 and 28 days compressive strength measurement. After compressive strength test, the samples were grounded with absolute alcohol to stop hydration. After filtration, the ground samples were dried in the drying oven with 50～60 ℃ for 4～5 hours.

Using DX-2700 type X-ray diffraction to analyze the mineralogical compositions. The work conditions include the Cu Kα line, the 30 mA tube current, and 40KV tube voltage. The American QUANTA200 scanning electron microscopy was used to analyze microstructure. The accelerating voltage is 20KV. The Germany STA 449C type synchronous was used to conduct the thermograms analyze with the temperature rate of 10 ℃/min.

3. Results and discussion

Cementitious properties of copper tailings. The microwave irradiated copper tailings enhance the reactivity. The microwave irradiated copper tailings, Portland cement clinker and desulfurization gypsum are mixed to prepare the cement paste specimens according to the proportions of 30%:66%:4%. The 3-day and 28-day compressive strengths are shown in Table 2. The compressive strength of the sample with irradiated copper tailings is higher than that of the specimen with original copper tailings. The compressive strength is the highest when the power is 800W. The 3-day and 28-day compressive strengths gradually increase as the powder increases from 500 W to 800 W and reduces with higher powder. The compressive strength has a relationship with the reactivity of copper tailings. It means that the reactivity of 500 W to 800 W copper tailings are greater than the original copper tailings, while the activity starts to decrease after 900 W. The microwave irradiation is an effective way in enhancing the reactivity of the copper tailings.

Table 2

Compressive strengths of the cement pastes with irradiated copper tailing addition

Sample	microwave irradiation power of irradiated copper tailings (W)	Portland cement clinker (%)	copper tailings (%)	Desulfurization gypsum (%)	compressive strength(MPa)	
					3 d	28 d
A_0	-	66	30	4	31.3	52.1
A_1	500	66	30	4	30.9	57.4
A_2	600	66	30	4	33.8	61.1
A_3	700	66	30	4	39.5	64.2
A_4	800	66	30	4	46.6	69.6
A_5	900	66	30	4	42.8	62.1
A_6	100 0	66	30	4	43.4	55.9
A_7	110 0	66	30	4	37.0	48.5

Composition and microstructure of irradiated copper tailings. Fig. 1 shows the XRD patterns of samples of original copper tailings and copper tailings irradiated by 700 W,800 W and 900 W. Compared with the original copper tailings, the intensities of diffraction peaks of the quartz in irradiated copper tailings are reduced. The microwave radiation seems to reduce the crystallinity of the quartz. The diffraction peaks of clinochlore are apparent in the original copper tailings, but the diffraction peaks disappear after irradiation. It shows that the clinochlore decomposes and the crystallization water in the clinochlore minerals is moved out.The clinochlore lattice was broken to generate the SiO_2 and Al_2O_3. The diffraction peaks of dolomite and magnetite are not changed significantly. Thus, the microwave irradiation mainly contributes to the transition of clinochlore and quartz from crystalline to amorphous transition, and the reactivity of copper tailings is improved.

Si^{4+}, Al^{3+} contents of irradiated copper tailings. Table 3 shows the dissolution results of the irradiated copper tailings. The dissolved Si^{4+} and Al^{3+} ions have significant relationship with the pozzolanic activity. The dissolved quantities of Si^{4+} and Al^{3+} of 700 W and 800 W irradiated copper tailings are higher than those of the original copper tailings. In the 800 W-irradiated copper tailings, the dissolution quantities of Si^{4+} and Al^{3+} are the highest. Compared with original copper tailings, the amounts of Si^{4+} and Al^{3+} ions are improved by 56.7% and 31.4%, respectively. However, the amounts of dissolved Si^{4+} and Al^{3+} ions decrease when the power is 900 W but are still higher than that of the original copper tailings.

Fig. 1 shows that the intensity of quartz is reduced after microwave irradiation, which enhances the Si^{4+} dissolution. In addition, the clinochlore crystal is changed into amorphous state due to microwave irradiation, resulting in the formation of SiO_2 and Al_2O_3 species. When the copper tailings are irradiated under 800W, the Si^{4+} and Al^{3+} dissolution quantities increase, but decrease as the power increase to 900 W. The sharp reduction is due to the recrystallization of copper tailings. Therefore, the reactivity will decrease when the power is too high. The reactivity improvement is the best when the irradiation power is 800W. This is consistent with the compressive strength results.

Table 3

Si^{4+} and Al^{3+} dissolution quantities

microwave Power (W)	Si^{4+} dissolution quantity ($mg \cdot g^{-1}$)	Increase percentage (%)	Al^{3+} dissolution quantity ($mg \cdot g^{-1}$)	Increase percentage (%)
0	23.8	0	26.4	0
700	36.5	53.4	33.7	27.7
800	37.3	56.7	34.7	31.4
900	31.8	33.6	31	17.4

TG-DTA and XRD analysis of copper tailings-cement paste. The cement pastes of A_0 and A_4 are tested by differential thermal analysis, and the results are shown in Fig. 2.

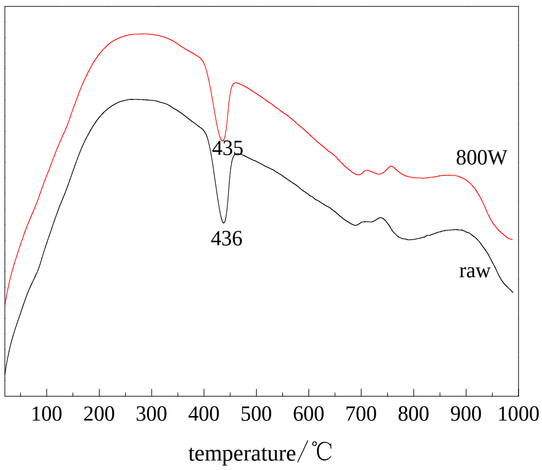


Fig.2 DTA curves of 28d hydration samples

The $Ca(OH)_2$ endothermic peaks in the range of 435 ~ 436 ℃ are present in the DTA curves, and the mass losses corresponding to original copper tailings and 800 W irradiated copper tailings are 3.05% and 2.92% respectively (Fig. 3). The XRD patterns of 28-d cured samples of A_0 and A_4 are showed in Fig. 4.

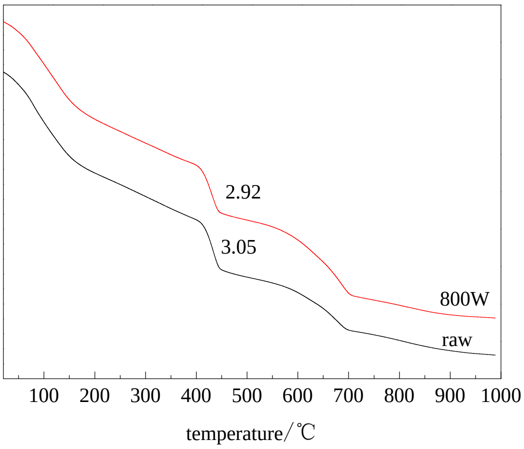


Fig.3 TG curves of 28d hydration samples

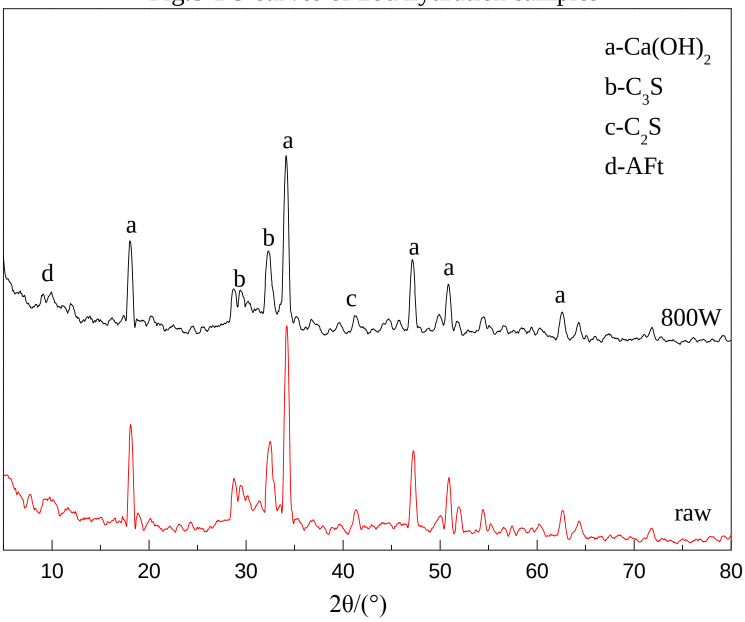
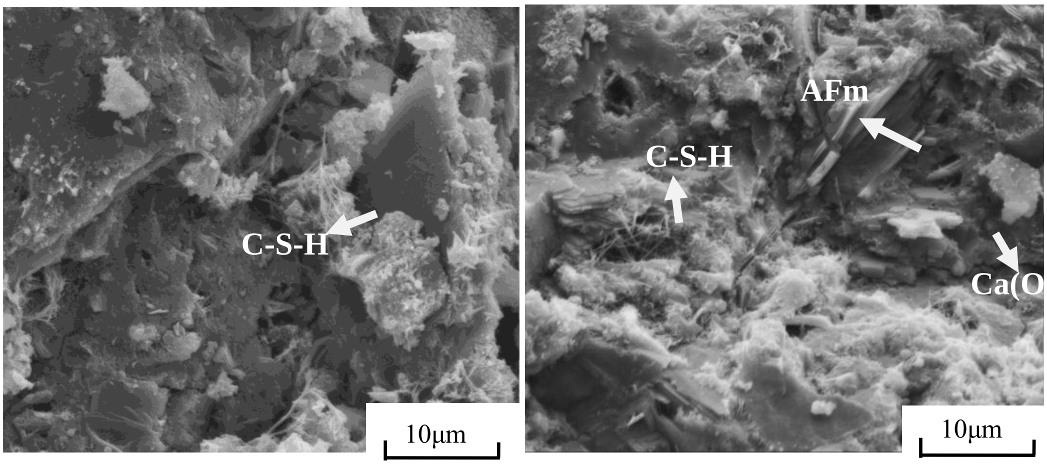


Fig.4 XRD patterns of 28d hydration samples of copper tailings

Compared with the original copper tailings, the intensity of the diffraction peaks of $Ca(OH)_2$ in irradiated copper tailings is reduced. According to the TG-DTA and XRD results, it can be concluded that the portlandite is formed by cement hydration and is consumed due to the pozzolanic reaction of 800 W irradiated copper tailings. It shows that reactive SiO_2 and Al_2O_3 species in the irradiated copper tailings react with $Ca(OH)_2$, so the content of $Ca(OH)_2$ is decreased in the hardened paste. The hydration products improve the compactness of the structure. Therefore, the compressive strengths are increased. This is due to that the free water and constitutional water in the copper tailings is taken off and the firm bond structure of Si-O and Al-O is damaged by microwave irradiation to improve the solubility of SiO_2 and Al_2O_3. This results in the improvement in the reactivity and cementitious property of copper tailings.

SEM analysis of copper tailings cement paste. SEM images of 28-d cured samples of A_0 and A_4 are showed in Fig. 5.



(a) A_0 (b) A_4

Fig.5 SEM images of 28d hydration samples

The microstructures of A_4 are compact and there is a few large pores. The hydration products are more crystallized than those in the A_0 sample. Fibrous C-S-H gel, platy $Ca(OH)_2$ and the layered structure of AFm can be observed in the SEM images of the cement sample incorporated with the copper tailings irradiated at 800 W. The irradiated copper tailings have more reactive SiO_2 and Al_2O_3 species to consume the $Ca(OH)_2$ produced during the hydration of cement clinker, and then the $Ca(OH)_2$ cannot reach saturated and crystallization. This increases the degree of hydration and accelerates the formation of hydration products. It indicates that the higher activity of copper tailings leads to a higher extent of hydration.

Heavy metal dissolution of copper tailings-cement paste. The heavy metals dissolved form the cement mortars were tested by ICP-OES method according to GB5085.3-2007 [16]. The results are shown in Table 4. It indicates that the heavy metals dissolved from the copper tailings-cement pastes are much lower than the standard requirements of for hazardous waste extraction toxicity. It can draw a conclusion that the copper tailings-cement pastes can be used to meet the requirements of GB5085.3-2007.

Table 4

Heavy metal dissolution of copper tailings-cement pastes (mg·L^{-1})

Sample	A_0	A_3	A_4	A_5	GB508 5.3-20 07
Cr	<0.007 1	<0.007 1	<0.007 1	<0.007 1	≤5
Ni	0.018	0.016	0.013	0.014	≤5
Cu	<0.005 4	<0.005 4	<0.005 4	<0.005 4	≤100
Cd	<0.002 5	<0.002 5	<0.002 5	<0.002 5	≤1
Pb	<0.009	<0.009	<0.009	<0.009	≤5
Zn	0.022	<0.001 8	<0.001 8	<0.001 8	≤100
As	<0.083	<0.083	<0.083	<0.083	≤5
Ba	0.63	0.78	0.75	0.71	≤100

4. Conclusions

Reaction reactivity and cementitious properties of copper tailings are improved by microwave irradiation. Irradiated copper tailings are incorporated into the Portland cement. The compressive strengths are increased when the content of copper tailings is 30%. The improvement effect is obvious when the microwave irradiation power is increased from 700 W to 900 W. In addition, strength values are the highest at 800 W. Irradiated copper tailings promotes the cement hydration. The crystallization degree of hydration products is improved to compact the pore structure.

The dissolved amounts of Si^{4+} and Al^{3+} ions from the copper tailings are enhanced due to the irradiation. The dissolved amounts of Si^{4+} and Al^{3+} ions are the highest when the power is 800 W, which are increased by 56.7% and 31.4% when compared with the original copper tailings. The heavy metals elements in the copper tailings are effective immobilized in cement pastes to the pollution when the cement pastes are used.

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