Research progress of key technologies for preparing concrete admixtures by multiple activation of iron-containing tailings

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Abstract: Iron tailings are an excellent secondary resource. Reasonable use, it can not only alleviate the problem of resource shortage, but also solve some environmental pollution problems. Therefore, it has a good development prospect. The resource utilization of iron tailings has always been a hot spot of social concern. The article reviews the results achieved by the predecessors. In addition, outlines the method of activation of iron tailings and the influence of its strength and durability as a concrete composite admixture. At last, the prospects of the research on the utilization of iron tailings are put forward.

1 Introduction

Iron tailings are industrial solid wastes produced after iron ore is processed, refined and sorted. At present, most iron ore companies choose to stack a larger part of the tailings for backfilling treatment, and only a small part is used. According to statistics, iron tailings in my country the comprehensive utilization rate is only 11.27% [1]. Not only occupy space and waste land resources, but also cause environmental pollution. China has rich iron ore resources. As of the end of 2011[2], 4,011 iron ore mines have been identified nationwide, with reserves of 5.667 billion tons, and basic reserves of 19.276 billion tons. Stone resource reserves are 74.39 billion tons. By 2011, china has 4203 mines, the amount of rough iron ore mined reached 1.327 billion tons. It is conceivable that the iron tailings produced are even more astronomical. At the same time, the Chinese economy is booming, industrialization and urbanization continue to advance, the demand for steel continues to increase. It is foreseeable that a large amount of iron tailings will be produced in the future.

After entering the 21st century, the effective utilization of resources appears to be particularly important, the secondary utilization of iron tailings is even more important. In order to solve the above problems, the comprehensive utilization of iron tailings[3] and increasing its utilization rate have become a research hotspot in recent years. The multiple activation of iron-containing tailings as admixtures to prepare concrete is one of the effective ways of resource utilization of iron tailings. In recent years, domestic and foreign scholars have conducted continuous research on this and have achieved certain results. The article summarizes and looks forward to the method of activation of iron tailings and its influence on the strength and durability of concrete as a composite admixture.

2 Iron tailings activation method

Iron tailings are divided into monometallic iron tailings and polymetallic iron tailings, whether they are Anshan high-silicon type iron tailings or Maanshan Iron and Steel high-alumina type iron tailings. These tailings are inherently inert and must be modified to stimulate their activity if they want to be used. At present, there are various activation methods, which can be activated by mechanical force, chemical activation, thermal activation[4], etc.

2.1 Mechanical activation of iron tailings

In 2002, Shujun Gao[5] et al. selected three iron tailings in Nanjing, Maanshan and Meishan. ND2 type planetary ball mill is used for grinding, the particles are squeezed each other through mechanical force, shear force and grinding action. Furthermore, the inside of the tailings particles is depolymerized, cracks are formed on the surface and inside of the particles, the material composition is gradually uniform, so that some polar molecules or ions that can decompose the slag enter the inside, improve the activity of the tailings. The strength of concrete made with different grinding time and different age of mineral particles. The results show that the best grinding for 2-4 hours can increase the compressive strength by 1.5 to 7 times. At the same time, it was discovered during the grinding process that there is a limit to the fineness of the particle, otherwise agglomeration will occur[6] and the specific surface area will decrease instead.

In 2013, Mengyi Chen[7] et al. selected some iron ore tailings in Hubei. Using a 5kg small ball mill, mechanical

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force is used to distort the crystal lattice of the iron tailing crystals, reduce the degree of crystallinity, change its microstructure, increase the activity of the iron tailings. The mortar strength test was carried out on the iron tailings powder. The compressive strength of tailings powder with different fineness, different blending amount and different curing conditions was measured. The results show that the sand activity index is 69% when the specific surface area is 751m^2/kg. The strength contributions of tailings powder blended with 20% of this fineness under autoclave curing for 3, 28, and 56 days are 14.02, 20.08, and 22.86 MPa, respectively.

In 2014, Chaomei Meng[8] et al. selected a high silicon iron tailings in Liaoning Province. Using the SYM-cement ball mill, through different grinding time, it is found that the grinding process can be roughly divided into three stages: first the tailings particles are broken and the specific surface area of the material increases; then aggregation occurs and the free energy decreases; finally the tailings particles agglomerate Phenomenon; the final result shows that the tailings particles have the best activity after 3.5 hours of grinding, the 30% of the tailings powder is added to the cement mortar test. The 28d compressive strength is greatly improved, can be used as a concrete cementing material to prepare concrete.

In 2016, Chunai Piao[9] et al. selected an iron tailings in Qian'an, Hebei. Using a 5kg laboratory ball mill, the effects of different grinding times on the specific surface area, density, particle size and microstructure of iron tailings particles were studied. Through orthogonal solidification, the results show that as the grinding time of iron tailings increases, the particle density first decreases and then increases, the specific surface area first increases and then decreases, the grinding time is 2 hours, the density is the smallest, which is 2.75g /m^3, the specific surface area is 770m^2/kg. According to the activity study and IR analysis, the compressive strength and activity index of the tailings particles at different ages are all maximum.

In 2017, Fahai Zhang[10] et al. selected a certain subway tailings. Use a 0.08mm square hole sieve for sieving, then use a laboratory ball mill to grind, control different grinding times, orthogonally compare the results, and perform electron microscope analysis, X-ray diffraction analysis, infrared spectrum and intensity analysis at the same time. The results show that with the lengthening of the grinding time, the absorption capacity of the English band of the tailings is strengthened and the degree of activation is deepened; under different grinding times, the silicon-oxidation bond in the tailings will be broken and reorganized, which improves its activity.

In 2020, Xiaowei Cui[11,12] and others selected skarn iron tailings in Shangluo City, Shaanxi Province. Use DHG-9075A electric heating blast drying oven to control the water content within 1%, use a laboratory grinder to grind for 60min, 80min, 100min, 120min. The specific surface area tester, X-ray diffractometer, American Fourier infrared spectrometer, thermal analyzer were used to analyze the influence of grinding time on tailings particles. The results show that mechanical force can destroy the internal structure of iron tailings, break chemical bonds, increase defects, improve activity. However, the agglomeration phenomenon still needs attention, the grinding time is controlled at 100min, which is more suitable for higher activity index.

Recent years, the research on the activation of iron tailings by mechanical force has been continuously deepened, and the mechanism of mechanical force activation has gradually become clear. As a result, relatively suitable grinding fineness, specific surface area, and grinding time have been obtained. However, further research is needed to utilize iron tailings in the project.

Table 1 Summary of existing research on mechanical activation of iron tailings

years	scholar	Tailings Origin	Test equipment	Results
2002	Shujun Gao[5]	Nanjing etc.	ND2 ball mill	The best activity in 2~4h, the compressive strength increased by 1.5~7 times
2013	Mengyi Chen[7]	Hubei	5kg small ball mill	When the specific surface area is 751m^2/kg, the activity index is 69%
2014	Chaomei Meng[8]	Liaoning	SYM-Cement Ball Mill	3.5h best activity
2016	Chunai Piao[9]	Qian'an, Hebei	5kg laboratory ball mill	2h best activity
2017	Fahai Zhang[10]		5kg laboratory ball mill	Increased activity
2020	Xiaowei Cui[11,12]	Shaanxi	5kg laboratory ball mill	High activity index in 100min

2.2 Chemically activated iron tailings

In 2008, Yongchao Zheng[13] and others selected Beijing Miyun iron tailings, cement clinker, slag, desulfurization gypsum, diagenetic agents. The iron tailings are classified and screened to obtain particles with a particle size of less than 50μm, mixed with cement clinker and desulfurized gypsum to an average particle size of 5μm. The coarse aggregate with a particle size greater than 50 μm is mixed with a diagenetic agent, cured for 1 day at room temperature and relative humidity at 90%, then the mold is removed, and then cured by steam. The results show that the activity of tailings is improved through chemical activation. The composition of raw materials, the amount of diagenetic agent and curing conditions will affect the performance of the material. At last, a high-strength material with a strength greater than 100MPa was successfully prepared. The mixing amount of tailings reaches 70%, the total solid waste usage reaches 87%.

In 2010, Dezhong Li[14] et al. selected Beijing Miyunshou iron and steel tailings, cement clinker, blast furnace slag, desulfurization gypsum, and water reducer. Use WL-1 ball mill to feed 5kg each time for classifying grinding. The tailings are ground in the first stage, blast furnace slag is added in the second stage, water reducing agent and gypsum are added in the third stage to obtain a mixture. Orthogonal experiment discusses the mild influence factors of the mixture specimen. The results show that the mixing time of 60min, the water reducing agent content of 1%, the tailing particle size of 0.16~2.5mm are reasonable. The 28d compressive strength of the obtained concrete is 97.63MPa.

In 2013, Anling Wang[15] et al. iron tailings in Qian'an, Hebei. Use a ball mill to grind to a fineness of 430kg/m^2±20kg/m^2, mix with slag powder in different proportions. Orthogonal experiment analysis results explore the effect of fineness on activity. The results showed that the activity of the mixture was improved, the activity increased by about 15% to 35% in 28 days. It proves that the composite effect of iron tailings powder and slag powder is good, the research on preparing concrete can be carried out.

In 2015, Beixing Li[16] et al. selected Beijing Miyun iron tailings, Huaxin Cement, Guizhou Hongfu phosphorous slag, limestone, dihydrate gypsum, and triethanolamine as a grinding aid. Use a 5kg laboratory ball mill for step grinding. The specific steps are shown in Figure 1. The results show that the iron tailings-phosphorus slag-based composite admixture (TPCMA) improves the volatilization activity of the mixture during the hydration process through the refinement of the phosphorus slag. When the effective mixing time Q=42.5min, the overall uniformity of TPCMA is better, at the same time the activity index can reach 82%. At the same time, the mixture can produce a large amount of calcium silicate hydrate (CSH) and ettringite under the action of calcium hydroxide and gypsum, showing a certain strength.

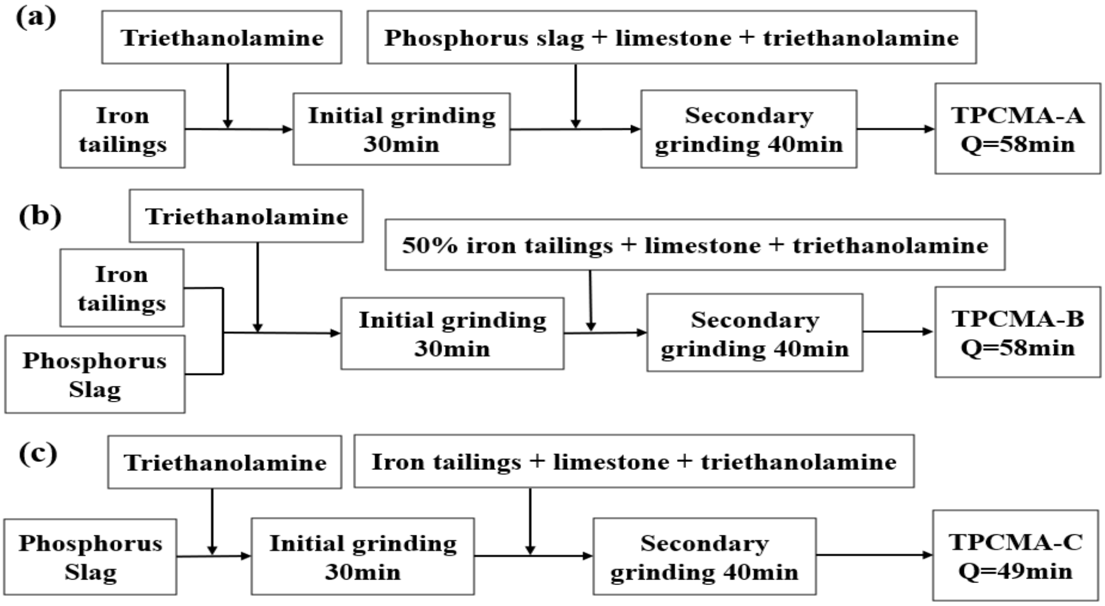

Figure 1 Flow chart of different cascade grinding sequence[16]

In 2016, Chunai Piao[17] et al. selected iron tailings in Qian'an, Hebei. Use P·I 42.5 cement and some water reducing agents including Na_2SiO_3, NaOH, Na_2SO_4, $CaSO_4{\cdot}2H_2O$, the purity of which is greater than or equal to 96%. Use a 5kg ball mill to grind the mixture into different finenesses. Carry out electron microscope analysis, infrared spectroscopy analysis, and test the heat of hydration. The results are measured through orthogonal experiments. The results show that: when the ball mill is pulverized for 2 hours and the $CaSO_4{\cdot}2H_2O$ content is 0.5%, the internal disordered matter increases, at the same time the iron tailings have better activity. The flexural strength and activation index are the maximum at the age of 7, 28 days.

Table 2 Summary of existing research on chemically activated iron tailings

years	scholar	Tailings Origin	Supplementary materials	Results
2008	Yongchao Zheng[13]	Miyun, Beijing	Cement clinker, slag, desulfurization gypsum, diagenetic agent	Material strength is greater than 100MPa
2010	Dezhong Li[14]	Miyun, Beijing	Cement clinker, blast furnace slag, desulfurization gypsum, water reducing agent	28d compressive strength is 97.63MPa
2013	Anling Wang[15]	Qian'an, Hebei	Slag powder	Increase activity by about 15%~35%
2015	Beixing Li[16]	Miyun, Beijing	Cement, phosphorous slag, limestone, dihydrate gypsum, triethanolamine	Activity index reaches 82%
2016	Chunai Piao[17]	Qian'an, Hebei	P·I 42.5 cement and some water reducers include Na_2SiO_3, NaOH, Na_2SO_4, $CaSO_4{\cdot}2H_2O$	Increased iron tailing activity

2.3 Thermally activated iron tailings

In 2007, Xiangpeng Feng[18] et al. selected an iron tailing in Tonghua, Jilin. The Suzhou pure kaolin and tailings were mixed and wet milled at a ratio of 1:1 for 0.5 hours, then dried, and then calcined at a high temperature of 600°C for 2 hours. The mixed materials with different dosages were subjected to the mortar strength experiment, the 28d strength was measured. The results are shown in Table 1. The results show that through wet grinding and mixing and calcination, the tailings react during the heating and dehydration process, the structure is distorted, the activity and the reaction performance are improved. When the mixture content is 50%, the strength of 28d mortar can reach 29.4MPa .

Table 3 Strength test results of wet grinding kaolin-iron tailing mixture mortar[18]

Numbering	Wet grinding tailings mixture (%)	Flexural strength/MPa		Compressive strength/MPa	
		3d	28d	3d	28d
E1	40	3.9	7.8	10.3	33.6
E2	50	3.3	7.3	9.2	29.4
E3	55	2.6	5.9	7.8	24.8
E4	60	2.1	5.7	7.4	19.3

In 2009, Zhonglai Yi[19]et al. selected Gushan iron tailings in Maanshan, Anhui. The tailings are dried at 100°C, and then thermally activated at different temperatures, at last the activated tailings are ground to a specific surface area of 400m^2/kg. The phase change was analyzed by differential thermal analysis (DTA) and thermogravimetry (TG), the strength was tested by the mortar strength test. The results show that the kaolinite in the tailings decomposes during the thermal activation process. After complete decomposition, the activity index reaches the highest. After heating continues, the CaO produced by the decomposition of calcite will react with the SiO_2 and Al_2O_3 produced by the decomposition of kaolin, and the activity will decrease. Therefore, 700°C thermal activation is the best value. At this time, when the tailings content is 30%, the strength of 28d mortar can reach 40.3MPa.

In 2013, Beixing Li[20] et al. selected a certain silicon-rich iron tailings. Use a laboratory standard ball mill to grind to obtain iron tailings powder with different finenesses, compare the activity index and cement mortar strength under different curing conditions through orthogonal experiments. The results show that the tailings activity is not high under standard curing, 90°C hot water curing, and 200°C high temperature dry heat curing. Under autoclave curing, the activity is higher, with 504m^2/kg, 751m^2/kg, 1120m^2/kg. The specific results of different specific surface areas of are shown in Figure 2. At the same time, SiO_2 reacts with $Ca(OH)_2$ to produce gelling substances, which further improves the strength.

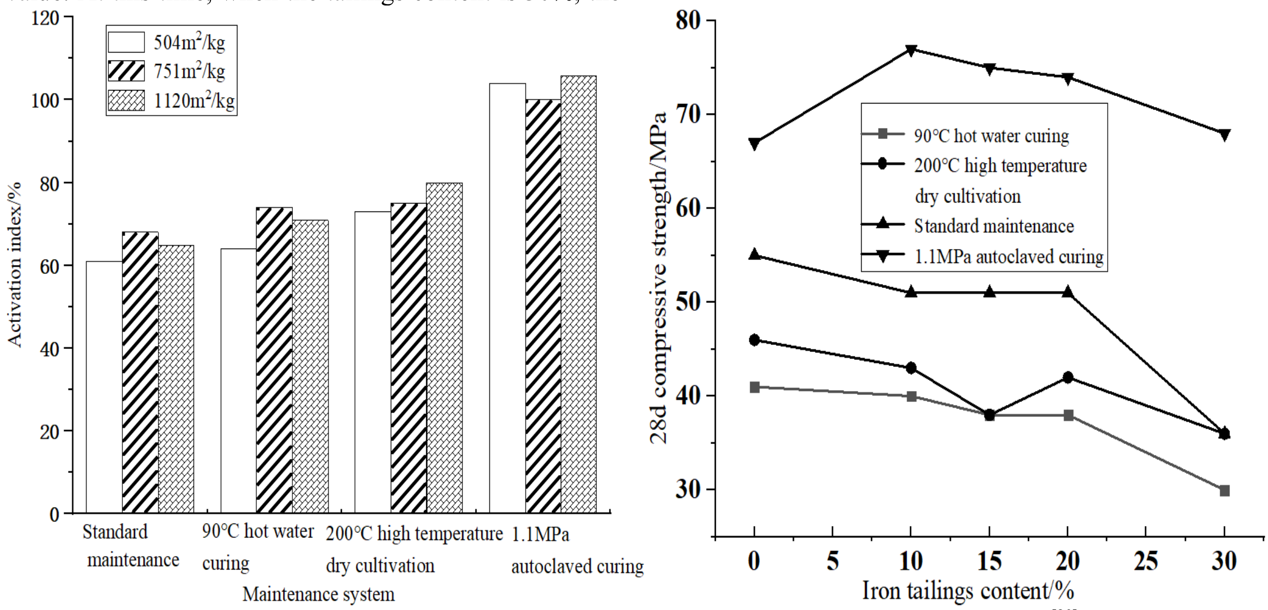

Figure 2 The effect of maintenance system on activity index and compressive strength[20]

In 2015, Ankang Song[21] et al.selected an iron tailing with kaolinite as the main component. The iron tailings are made into strips with a diameter of 5mm, dried at 105°C, calcined in a muffle furnace at a certain temperature. After holding for a certain period of time, they are removed and ground to test the activity index. The comparison results of orthogonal experiments show that the tailings activity is higher when calcined at 700 °C for 1 h and 800 °C for 0.5 h, the activity index is 122%. It is more suitable that the particle size is less than 12μm. It shows that the tailings can produce pozzolanic activity when calcined, and it is a good admixture for preparing concrete.

Table 4 Summary of existing research on thermally activated iron tailings

years	scholar	Tailings Origin	experiment procedure	Results
2007	Xiangpeng Feng[18]	Jilin Tonghua	Mixed and wet milled for 0.5 hours, dried, then calcined at a high temperature of 600°C, kept for 2 hours	Strength up to 29.4MPa
2009	Zhonglai Yi[19]	Maanshan, Anhui	Drying at 100°C, heat activation treatment at different temperatures	700°C heat activation strength can reach 40.3MPa
2013	Beixing Li[20]	A silicon-rich iron tailings	Under different curing conditions	Under autoclave curing, higher activity
2015	Ankang Song[21]	Kaolinite is the main tailings	Drying at 105°C, calcining in a muffle furnace at a certain temperature	Activity index can reach 122%

3 Research on the performance of iron tailings on concrete prepared as admixtures

In 2010, Yunhong Cheng[22,23] et al. selected an iron tailing in Liaoning Province. The iron tailing is activated by mechanochemical means, make cementitious materials instead of cements of different specific gravities, as a blending amount to prepare concrete. Carry out concrete carbonization performance test and concrete sulfate corrosion resistance test on the prepared concrete. The results show that the amount of cement replaced by activated tailings is in the range of 10%-40%. With the increase of the amount, the carbonization resistance and sulfate corrosion resistance increase. When the replacement cement content is 20%, 30% and 40%, the sulfate corrosion resistance of concrete is higher than the standard. Therefor, from these two levels, it is feasible to use tailings as an auxiliary cementing material to prepare concrete.

In 2015, Wei Zeng[24] et al. used iron tailings as basic materials, composite phosphorous slag and limestone as admixtures for concrete. The prepared C20~C55 concrete was compared with the concrete prepared by mixing II grade fly ash and S95 grade slag powder. The results show that the strength of concrete made with iron tailings is not much different from that with grade II fly ash, which is lower than that with grade S95 slag powder. However, the durability of carbonization resistance, chloride ion penetration resistance and frost resistance are slightly lower than the two.

In 2016, Chunai Piao[25] et al. selected iron tailings in Qian'an, Hebei, used mechanochemical coupling to activate the tailings. Cementitious material containing iron tailings powder is prepared, and then used as admixture to prepare concrete. aiming at affecting the durability and resistance of concrete to chloride ions. The permeability, carbonization resistance, freeze-thaw resistance were studied. The results show that the chemical-mechanical activation of iron tailings has a significant ability to reduce the total porosity and pore connectivity of the hardened mixture, its impermeability is improved compared with blank cement and fly ash. At the same time, the frost resistance of concrete is also good. Its resistance to carbonization is lacking, but the impact is not significant.

Table 5 Summary of existing research on the related properties of concrete prepared from iron tailings

years	scholar	Tailings Origin	experiment	Results
2010	Yunhong cheng [22,23]	Liaoning	Carbonization test, sulfate corrosion resistance test	It is feasible to use tailings as an auxiliary cementitious material to prepare concrete
2015	Wei Zeng[24]		Orthogonal contrast	Not much difference in intensity
2016	Chunai Piao[25]	Qian'an, Hebei	Durability, resistance to chloride ion permeability, resistance to carbonization, and freeze-thaw resistance tests	Except for the lack of carbonization resistance, other performances are good

4 Summary and Outlook

Although iron tailings are inherently inert, they can be excited by appropriate methods, such as mechanical activation, chemical activation, and thermal activation, to homogenize the internal results of the tailings, and cause distortions in the internal lattice and occurrence of internal particles. Depolymerization, turning it into an active material similar to natural pozzolanic material. Using iron tailings as an admixture to prepare concrete and even ultra-high performance concrete[26] is one of the reasonable methods for comprehensive utilization of tailings, and it is also an effective way to solve the problem of insufficient resources, which is in line with the development of the society in the new era view.

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