Research on Application Technology of Molybdenum Tailings Sand Concrete

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Abstract. Molybdenum tailings sand is used as a fine aggregate to replace part of the construction sand, which can effectively solve the environmental pollution problems caused by the molybdenum tailings pond and has high utilization value. After testing the physical properties, chemical analysis, radioactivity and other indicators of molybdenum tailings sand, the results show that the molybdenum tailings sand basically meets the conditions of construction sand. By increasing the proportion of molybdenum tailings in concrete, the concrete performance will decrease in viscosity, slump loss and strength with the increase of the blending ratio. Therefore, the ratio of molybdenum tailings to substitute fine aggregate is between 40%-50%, should not exceed 60%. The problems of viscosity and strength of molybdenum tailings sand concrete still need to be solved through adjusting the concrete mix proportion or optimizing the admixture formula.

1. Introduction
Molybdenum is one of the important metal elements. Its alloys are widely used in important fields such as metallurgy, electrical, chemical, and aerospace. China’s proven molybdenum metal reserves are 1.7 million tons, ranking second in the world only after the United States. The waste slag discharged by the molybdenum ore after beneficiation is currently discharged in the form of mud, which forms a molybdenum tailings reservoir over time. The piled molybdenum tailings occupy a large amount of land, and waste land resources, and cause pollution to the natural ecological environment. Besides, the tailings reservoir has a high dam body, which has great safety hazards. Many experts and scholars agree that how to effectively develop and utilize a large amount of long-term shelving molybdenum tailings is the primary task of developing a circular economy of molybdenum mining. The best treatment method for molybdenum tailings is to make sand from molybdenum tailings sand, which is used as a fine aggregate to replace part of the construction sand. Especially in nowadays the sandstone resources are very scarce and the sandstone materials are in short supply, the economy benefits of molybdenum tailings sand are more prominent. For example, the current price of molybdenum tailings sand in Shaanxi Province is nearly 70 yuan/ton cheaper than the mechanism sand, and the current inventory of molybdenum tailings sand in Shaanxi Province is nearly 60 million tons. Study on application technology of molybdenum tailings sand concrete has significant economic and social benefits.

The molybdenum tailings sand mentioned in this paper refer to the waste particles with a particle size less than 4.75 mm. About whether molybdenum tailings sand can be used as a building material for industrial application, and what is its specific properties and possible hazards to concrete, there is no specific knowledge or understanding. Scientific and systematic experimental research must be carried out. First, molybdenum tailings sand used as a fine aggregate in the construction industry
should comply with the relevant requirements of the current national standard "Sand for Construction" GB/T14684. Secondly, the properties, mechanical properties and durability of the mixture of molybdenum tailings sand concrete should be in line with the relevant provisions of the current national standards. Finally, the radioactivity of molybdenum tailings sand concrete should comply with the relevant provisions of the current national standard "Limits of Radionuclides in Building Materials" GB 6566.

2. Experimental

2.1. Performance tests of Molybdenum tailings sand

This are performance tests of molybdenum tailings sand produced by a large molybdenum mine in Shan’xi Province. Based on relevant standards, specifications and test procedures, the tests mainly include the particle gradation, fineness modulus, stone powder content, physical index, radioactivity, stability, micromorphology and X-ray diffraction etc.

2.1.1. Particle grading and fineness modulus

After testing, the fineness modulus of molybdenum tailings sand is 0.9. According to JGJ52-2006 standard, it is classified as superfine sand. The test results are shown in Table 1.

| Project                          | Nominal diameter of square hole sieve/mm | Fineness modulus (μf) |
|----------------------------------|----------------------------------------|-----------------------|
| Cumulative screening /%          | 0                                      | 4.75                  |
|                                  | 0                                      | 2.36                  |
|                                  | 1                                      | 1.18                  |
|                                  | 4                                      | 0.600                 |
|                                  | 25                                     | 0.300                 |
|                                  | 57                                     | 0.150                 |
|                                  | 77                                     | 0.075                 |
|                                  | 0.9                                    |                       |

2.1.2. Physical index

The physical indexes of molybdenum tailings sand are tested according to the national standard "Sand for Construction" GB/T 14684. The results are shown in Table 2.

| Serial number | Test items       | Unit   | Test value |
|---------------|------------------|--------|------------|
| 1             | Bulk density     | kg/m³  | 1390       |
| 2             | Compact density  | kg/m³  | 1620       |
| 3             | Apparent density | kg/m³  | 2720       |
| 4             | Voids            | %      | 49         |
| 5             | Moisture content | %      | 6.4        |
| 6             | Stone powder content | %  | 24.6    |
| 7             | MB value         |        | 2.0        |
| 8             | Mica content     | %      | 0.0        |
| 9             | Water absorption rate | % | 1.0       |
| 10            | Rugged           | %      | 4          |
| 11            | Light matter content | % | 0.0     |
| 12            | Organic content  | / qualified |   |
| 13            | Sulfide and sulfate content | %  | 0.34    |

Through the analysis of the test results of the above indicators, we can know that most of the performance indexes of molybdenum tailings sand meet the requirements of relevant standards and specifications. But their performance characteristics are also remarkable. Such as, the content of stone powder is reaching up to 24.6%. If applied in concrete, the molybdenum tailings sand will result in
higher water demand, higher concrete viscosity and more cracking problems. The large void ratio will certainly affect the compactness and the strength of the concrete. But when used in combination with machine-made sand, its void ratio can reach 42% which is in line with the standard requirements. The detection of harmful substances is qualified, and it will have no impact on durability. In this test, since the fineness of the molybdenum tailings sand was too fine, the alkali activity measurement experiment could not be performed temporarily.

2.1.3. Radioactivity
The test is according to the current national standard “Limited Radionuclides for Building Materials” GB 6566. And the test results are shown in Table 3.

| Test items | Indicator requirements | Test results |
|------------|------------------------|--------------|
| radioactivity | Internal illumination line index ≤1.0 | 0.1 |
| | External illumination line index ≤1.0 | 0.4 |

The test results show that the radioactivity of molybdenum tailings sand meets the requirements of relevant national standards.

2.1.4. Chemical composition
The chemical composition test of molybdenum tailings sand, see Table 4.

| Test items | Indicator requirements | Test results |
|------------|------------------------|--------------|
| Fe₂O₃ | 3.56 |
| Al₂O₃ | 4.40 |
| SiO₂ | 67.18 |
| CaO | 7.72 |
| MgO | 1.92 |
| f-CaO | 0.06 |
| f-MgO | 0.00 |
| Cl⁻ | 0.00 |
| SO₃ | 0.34 |

The chloride ion content is basically zero, and it will not cause corrosion to the steel bars. The content of SO₃ is in the normal range.

2.1.5. Chemical composition
The crystal phase and crystal form of molybdenum tailings sand were analyzed by XRD. The results are shown in Figure 1.

As shown in Figure 1, the molybdenum tailings sand mainly contains crystalline silica, a small amount of mica and molybdenum ore.
2.2. Concrete performance test of molybdenum tailings sand

2.2.1. Experimental raw materials for main performance testing
Cement(C P.O 42.5 Cement), Sand(S1, Machine sand Mx=3.0), Sand(S2, Molybdenum tailings sand Mx=0.9)Gravel(G, grain size of 5-31.5mm), Fly ash(F, Level II), Mineral powder(GGBS,S95 level) Polycarboxylate superplasticizer(Point-400S polycarboxylate superplasticizer).

2.2.2. Concrete performance measurement
This test selects the C30 concrete mix ratio which has the largest concrete demand. The concrete test was carried out according to the Standard Test Method for Performance of Ordinary Concrete Mixture GB/T50080-2016. The test items include the initial slump, expansion, bulk density and 1h slump loss, inverted slump cylinder emptying time, 7d compressive strength, 28d compressive strength and other indicators.

| Substitution ratio of molybdenum tailings sand | W (kg/m³) | C (kg/m³) | S1 (kg/m³) | S2 (kg/m³) | G (kg/m³) | F (kg/m³) | GGBS (kg/m³) |
|------------------------------------------------|--------|---------|---------|---------|--------|-------|-------------|
| 0                                              | 170    | 270    | 800    | 0       | 1050   | 50    | 50          |
| 20%                                            | 170    | 270    | 640    | 160     | 1050   | 50    | 50          |
| 40%                                            | 170    | 270    | 480    | 320     | 1050   | 50    | 50          |
| 60%                                            | 170    | 270    | 320    | 480     | 1050   | 50    | 50          |
| 80%                                            | 170    | 270    | 160    | 640     | 1050   | 50    | 50          |

The concrete performance test was carried out by adjusting the admixture dosage to make the initial expansion of the concrete within the range of 600±20 mm. The concrete test results are shown in Table 6:

| Substitution ratio of molybdenum tailings | Admixture dosage (%) | T₀ (mm) | T₁h (mm) | Bulk weight (kg/m³) | Initial inverted slump bucket emptying time (S) | Initial 1h inverted slump bucket emptying time (S) |
|------------------------------------------|----------------------|--------|---------|--------------------|-----------------------------------------------|-----------------------------------------------|
| 0                                        | 2.3                  | 600    | 585     | 2402               | 7.2                                           | 13.8                                          |
| 20%                                      | 2.6                  | 600    | 560     | 2400               | 12.4                                          | 13.8                                          |
| 40%                                      | 2.9                  | 585    | 460     | 2388               | 17.6                                          | 20.4                                          |
| 60%                                      | 3.4                  | 600    | 500     | 2374               | 23.2                                          | 34.5                                          |
| 80%                                      | 4.1                  | 610    | 550     | 2365               | 34.7                                          | 44.6                                          |

Through the concrete mixture performance test results, the following conclusions can be drawn:
(1) With the increase of the amount of molybdenum tailings sand, the adsorption of additives becomes more and more obvious, and the dosage of additives needs to be increased continuously.
(2) With the increase of the amount of molybdenum tailings sand, the slump loss of concrete shows an inverted U-shaped trend. The initial fluidity loss becomes larger and larger, and after reaching 40%, the trend becomes smaller. The analytical reason is that when the amount of molybdenum tailings sand
increases, the concrete gets more sticky. So the dispersing effect of the admixture is poor, and the reaction rate is slow, and some admixtures have a post-lag reaction.

(3) When the amount of molybdenum tailings sand increases continually, the viscosity of the concrete becomes significantly large, the flow rate becomes very slow, and the emptying time of the inverted slump barrel after the initial loss is longer and longer. When the dosage reaches 80%, the concrete is very sticky which is unfavorable to concrete construction.

(4) With the increase of the amount of molybdenum tailings sand, the bulk density of concrete shows a downward trend.

(5) When molybdenum tailings sand replace 40% of manufactured sand, concrete work-ability is improved, and the bleeding problems of concrete can be effectively solved.

Compressive strength tests were carried out for 7d and 28d. The strength data are shown in Figure 2:

![Figure 2. C30 concrete compressive strength](image)

As shown in Figure 2, the concrete compressive strength at 7 days and 28 days decrease with the increase of the proportion of molybdenum tailings sand, and the strength decreases distinctly when the substitution ratio reaches 60% or more. Therefore, it is recommended that the proportion of molybdenum tailings should not exceed 60%.

3. Conclusions

(1) After analyzing the existing test data of molybdenum tailings sand, the test performance indexes of physical properties, chemical analysis and radioactivity of molybdenum tailings meet the requirements of relevant standard specifications.

(2) For the application technology of molybdenum tailings sand concrete, refer to the current national standard “Technical Regulations for Iron Tailings Sand Concrete Application” GB 51032, which is used to guide the use of molybdenum tailings sand.

(3) When replacing some river sand with molybdenum tailings sand, the concrete will become sticky and the fluidity will get slow as the substitution ratio increases, which is not conducive to construction and will decrease the strength. Therefore, the ratio of molybdenum tailings sand to replaces river sand and machine sand is preferably between 40% and 50%, and is recommended not to exceed 60%.

(4) The molybdenum tailings sand concrete will have obvious viscosity problems, and it needs to be further solved in the actual application process. The mixing ratio can be improved by keeping the water-to-binder ratio constant, increasing the water consumption and cement dosage, and at the same time, the admixture can be selected. The reduced mother liquor is compounded with a viscosity reducing agent to further optimize the performance of the admixture.
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