CEMENTED BACKFILL MATERIAL CONTAINING VANADIUM-TITANIUM SLAG AND PREPARATION METHOD THEREOF

FIELD OF TECHNOLOGY

[0001] The present invention relates to the technical field of mine backfill materials, and more particularly to a cemented backfill material containing vanadium-titanium slag and preparation method thereof.

BACKGROUND

[0002] Backfill mining technology improves resource utilization and enables green mining by filling underground mined-out areas with solid waste such as waste rock and tailings, representing the development trend in mine exploitation. Currently, traditional cemented backfill mainly uses Portland cement, which accounts for 25%-40% of the total backfill cost, with the binder cost representing approximately 70%-80%. To reduce costs, the key is to seek alternative cementitious materials to replace cement.

[0003] Titanium slag is an industrial solid waste with high TiO2 content and low utilization value, with limited disposal methods, mainly in applications such as cement admixtures and mine backfill cementitious materials; however, these methods are insufficient to address the annual output of more than 2 million tons of vanadium-titanium slag in China. The present invention aims to utilize multiple solid wastes, including vanadium-titanium slag, slag, desulfurized gypsum, and steel slag, to develop a cementitious backfill material suitable for lead-zinc tailings, thereby meeting backfill requirements, reducing costs, and improving applicability.

SUMMARY

[0004] The present invention is directed to the research and development of a novel cementitious backfill material suitable for mine backfill applications with lead-zinc tailings. This material uses vanadium-titanium slag as the main raw material, supplemented by the synergistic utilization of slag, desulfurized gypsum, and steel slag, with the goal of meeting mine backfill performance requirements while optimizing backfill costs and enhancing the material's applicability.

[0005] The cemented backfill material of the present invention comprises two main components: the cementitious material and the aggregate. The mass ratio of cementitious material to aggregate is 1:4, wherein the cementitious material is a specific mixture of vanadium-titanium slag, slag, steel slag, and desulfurized gypsum. The aggregate mainly consists of vanadium-titanium slag and lead-zinc tailings. The preferred composition of vanadium-titanium slag is: CaO 30-40 parts, SiO2 10-30 parts, TiO2 5-20 parts, Al2O3 5-15 parts, MgO 1-10 parts, Fe2O3 1-5 parts, SO3 1-5 parts. Steel slag, slag, and desulfurized gypsum also have corresponding preferred compositional ranges.

[0006] During the preparation process, the raw material ratio of the cementitious material and aggregate is first determined, and then the raw materials are ground to the required specific surface area. Next, the cementitious material raw materials are mixed with water, and the moisture content is adjusted until the slurry concentration reaches 70-80%. Finally, the prepared cementitious material and aggregate are mixed with water, and the moisture content is adjusted until the concentration reaches 70-80%, thus obtaining the cemented backfill material.

[0007] Compared with the prior art, the present invention offers significant advantages. Firstly, vanadium-titanium slag is used in both the cementitious material and the aggregate, greatly increasing its utilization rate and effectively solving the problem of its stockpiling. Secondly, the composition of the cementitious material in the present invention is simpler, requiring no activators or early strength agents, thereby reducing raw material costs.

Additionally, due to the synergistic effect of multiple solid wastes, the material still exhibits excellent cementing and rheological properties, including compressive strength and fluidity. This gives it broad application prospects in the field of mine backfill.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] To more clearly illustrate the technical solutions in the embodiments of the present invention or the prior art, the drawings required in the description of the embodiments or prior art will be briefly introduced below. Obviously, the drawings described below are only embodiments of the present invention; those skilled in the art may obtain other drawings based on the provided drawings without creative effort.

[0009] FIG. 1 is the XRD spectrum of the raw materials for the cemented backfill material containing vanadium-titanium slag provided by the present invention;

[0010] FIG. 2 is the particle size distribution diagram of vanadium-iron slag in the raw materials shown in Figure 1;

[0011] FIG. 3 is a schematic diagram of the morphology of hydration products in the embodiment provided by the present invention.

DESCRIPTION OF THE EMBODIMENTS

[0012] The present invention relates to a cemented backfill material containing vanadium-titanium slag and its preparation method, which is particularly suitable for mine backfill with lead-zinc tailings. The backfill material mainly comprises a cementitious material and aggregate, with a mass ratio of cementitious material to aggregate of 1:4. The cementitious material is a mixture of vanadium-titanium slag, slag, steel slag, and desulfurized gypsum in specific proportions, while the aggregate is mainly composed of vanadium-titanium slag and lead-zinc tailings.

[0013] In the cementitious material, the weight proportion of vanadium-titanium slag is 0-30 parts, slag is 30-60 parts, steel slag is 30-42 parts, and desulfurized gypsum is 10-16 parts. In addition, the chemical compositions of vanadium-titanium slag, slag, steel slag, and desulfurized gypsum also have corresponding preferred ranges.

For example, the preferred composition of vanadium-titanium slag is: CaO 30-40 parts, SiO2 10-30 parts, TiO2 5-20 parts, Al2O3 5-15 parts, MgO 1-10 parts, Fe2O3 1-5 parts, SO3 1-5 parts.

[0014] Regarding the preparation method, the raw material ratio of the cementitious material and aggregate is first determined, and then the raw materials are ground to the required specific surface area. Next, the cementitious material raw materials are mixed with water, and the moisture content is adjusted until the slurry concentration reaches 70-80%. Finally, the prepared cementitious material and aggregate are mixed with water, and the moisture content is adjusted until the concentration reaches 70-80%, thus obtaining the cemented backfill material.

[0015] A series of tests were conducted to verify the effectiveness of the present invention. First, compressive strength tests were performed on the backfill material specimens. The test results showed that the compressive strength of the backfill material gradually increased with the extension of curing age. Second, compressive strength tests were conducted on neat paste block specimens, and the results showed that the neat paste blocks of the present invention exhibited good compressive strength. Additionally, heavy metal ion leaching concentration tests were performed, and the results showed that the leaching concentration of heavy metal ions in the neat paste specimens of the present invention was much lower than the limit value of Class III underground water quality standards, indicating that the heavy metal components were effectively solidified.

[0016] In summary, the cemented backfill material containing vanadium-titanium slag and its preparation method provided by the present invention meet the performance requirements for mine backfill, achieve cost optimization, enhance applicability, and possess excellent environmental protection characteristics.

[0017] The following comparative experiments illustrate the advantages of the present invention:

[0018] **Example 1-1**

[0019] In this example, a preparation method for backfill material using vanadium-titanium slag–steel slag–slag–desulfurized gypsum-based cementitious material, with lead-zinc tailings and vanadium-titanium slag as aggregate, is provided.

The cementitious material mainly consists of the following components by mass percentage: vanadium-titanium slag 10.5%, slag 31.5%, steel slag 42%, desulfurized gypsum 16%. Binder-to-aggregate ratio is 1:4 (vanadium-titanium slag: lead-zinc tailings = 1:2), and slurry concentration is 70%.

[0020] The chemical compositions of vanadium-titanium slag, slag, desulfurized gypsum, steel slag, and lead-zinc tailings are shown in Table 1.

[0021] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg. Backfill material specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 70.7 mm × 70.7 mm × 70.7 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0022] After casting and forming, the specimens are cured to different ages for compressive strength testing.

[0023] **Example 1-2**

[0024] This example provides a method for preparing neat paste blocks using vanadium-titanium slag–steel slag–slag–desulfurized gypsum-based cementitious material. The cementitious material mainly consists of the following components by mass percentage: vanadium-titanium slag 10.5%, slag 31.5%, steel slag 42%, desulfurized gypsum 16%. Water-to-binder ratio is 0.32.

[0025] The chemical compositions of vanadium-titanium slag, slag, desulfurized gypsum, steel slag, and lead-zinc tailings are shown in Table 1.

[0026] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg. Neat paste block specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 30 mm × 30 mm × 50 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0027] After casting and forming, the specimens are cured to different ages for compressive strength testing.

[0028] **Example 2-1**

[0029] In this example, a preparation method for backfill material using vanadium-titanium slag–steel slag–slag–desulfurized gypsum-based cementitious material, with lead-zinc tailings as aggregate, is provided. The cementitious material mainly consists of the following components by mass percentage: vanadium-titanium slag 10.5%, slag 31.5%, steel slag 42%, desulfurized gypsum 16%. Binder-to-aggregate ratio is 1:4 (all lead-zinc tailings as aggregate), and slurry concentration is 75%.

[0030] The chemical compositions of vanadium-titanium slag, slag, desulfurized gypsum, steel slag, and lead-zinc tailings are shown in Table 1.

[0031] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg. Backfill material specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 70.7 mm × 70.7 mm × 70.7 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0032] After casting and forming, the specimens are cured to different ages for compressive strength testing.

[0033] **Example 3-1**

[0034] An example of a preparation method for backfill material using vanadium-titanium slag–steel slag–slag–desulfurized gypsum-based cementitious material, with lead-zinc tailings and vanadium-titanium slag as aggregate, is provided. The cementitious material mainly consists of the following components by mass percentage: vanadium-titanium slag 30%, slag 30%, steel slag 30%, desulfurized gypsum 10%. Binder-to-aggregate ratio is 1:4 (vanadium-titanium slag: lead-zinc tailings = 1:2), and slurry concentration is 75%.

[0035] The chemical compositions of vanadium-titanium slag, slag, desulfurized gypsum, steel slag, and lead-zinc tailings are shown in Table 1.

[0036] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg. Backfill material specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 70.7 mm × 70.7 mm × 70.7 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0037] After casting and forming, the specimens are cured to different ages for compressive strength testing.

[0038] **Example 3-2**

[0039] This example provides a method for preparing neat paste blocks using vanadium-titanium slag–steel slag–slag–desulfurized gypsum-based cementitious material. The cementitious material mainly consists of the following components by mass percentage: vanadium-titanium slag 30%, slag 30%, steel slag 30%, desulfurized gypsum 10%. Water-to-binder ratio is 0.32.

[0040] The chemical compositions of vanadium-titanium slag, slag, desulfurized gypsum, steel slag, and lead-zinc tailings are shown in Table 1.

[0041] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg. Neat paste block specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 30 mm × 30 mm × 50 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0042] After casting and forming, the specimens are cured to different ages for compressive strength testing.

[0043] The raw materials are weighed according to the above proportions: vanadium-titanium slag is ground to a specific surface area of 450 m2/kg (particle size distribution as shown in Figure 2), slag to 550 m2/kg, steel slag to 500 m2/kg, and desulfurized gypsum to 450 m2/kg.

Backfill material specimens are prepared according to GB17671-1999 "Test Method for Strength of Cement Mortar," with specimen dimensions of 70.7 mm × 70.7 mm × 70.7 mm, cured at a temperature of 20°C and humidity above 99.5%.

[0044] After casting and molding, curing is performed to different ages for compressive strength testing.

[0045] After casting and molding, curing is performed to different ages for compressive strength testing.

[0046] The fluidity of the filling slurry in Examples 1-1, 2-1, 3-1, and Comparative Example 1-3 was measured according to GB/T 2419-2005 Method for Determination of Fluidity of Cement Mortar.

[0047] The results are shown in Table 2.

[0048] Table 2 Summary of Filling Slurry Fluidity

Example	Initial Fluidity
Example 1-1	≥200
Example 2-1	≥180
Example 3-1	≥180
Comparative Example 1	≥200
Comparative Example 2	≥200
Comparative Example 3	≥100

[0049] It can be seen that the cemented backfill material provided by the present invention exhibits good fluidity, which is sufficient to meet the requirements for mine backfilling.

[0050] The setting time of the filling slurry in Examples 1-1, 2-1, 3-1, and Comparative Examples 1-3 was measured in accordance with *GB/T 1346-2011 Test Methods for Water Requirement of Standard Consistency, Setting Time, and Stability of Cement*.

[0051] The test results are shown in Table 3.

[0052] Table 3 Summary of Setting Time of Filling Slurry (h)

Example	Initial Setting Time	Final Setting Time
Example 1-1	18	26
Example 2-1	15	23
Example 3-1	17	26
Comparative Example 1	17	25
Comparative Example 2	20	30
Comparative Example 3	15	24

[0053] By comparing Comparative Example 1, it can be concluded that when the raw materials are 60% slag, 30% steel slag, and 10% desulfurized gypsum, the lower the proportion of vanadium-titanium slag, the shorter the final setting time.

[0054] By comparing Comparative Example 2 and Example 3-1, it can be concluded that when the raw materials are 30% vanadium-titanium slag, 30% slag, 30% steel slag, and 10% desulfurized gypsum, the lower the proportion of vanadium-titanium slag, the shorter the final setting time.

[0055] By comparing Comparative Example 3, Example 1-1, and Example 2-1, it can be concluded that when the raw materials are 10.5% vanadium-titanium slag, 31.5% slag, 42% steel slag, and 16% desulfurized gypsum, the lower the proportion of vanadium-titanium slag, the shorter the final setting time.

[0056] By comparing Comparative Example 1, it can be seen that appropriate addition of vanadium-titanium slag can reduce the final setting time.

[0057] In summary, in the aggregate used for preparing the filling material in the present invention, the lower the proportion of vanadium-titanium slag, the shorter the final setting time. Moreover, appropriate addition of vanadium-titanium slag can reduce the final setting time.

[0058] According to GB17671-1999 Method for Determination of Strength of Cement Mortar, filling material specimens were prepared with dimensions of 70.7mm × 70.7mm × 70.7mm, and cured under standard conditions at 20°C and humidity above 99.5%, with the curing atmosphere similar to that of the mined-out area underground. The compressive strength at different ages was tested.

[0059] The test results are shown in Table 4:

[0060] Table 4 Summary of Compressive Strength of Filling Specimens (MPa)

Example	3d	7d	28d
Example 1 - 1	0.53±0.03	1.54±0.08	3.00±0.15
Example 2 - 1	1.04±0.05	2.56±0.13	3.95±0.20
Example 3 - 1	0.69±0.03	2.23±0.11	3.26±0.16
Comparative Example 1	1.76±0.09	2.03±0.10	5.11±0.26
Comparative Example 2	1.04±0.05	1.72±0.09	2.61±0.13
Comparative Example 3	2.63±0.13	6.33±0.32	7.32±0.37

[0061] It can be seen that while the composition is simplified, the synergistic effect of multiple solid wastes still enables good cementing performance.

[0062] Below, Examples 1-2 and 3-2 are compared to demonstrate that the neat paste blocks prepared by the present invention possess good compressive strength. According to GB17671-1999 Method for Determination of Strength of Cement Mortar, neat paste block specimens were prepared with dimensions of 30mm × 30mm × 50mm, and cured under standard conditions at 20°C and humidity above 99.5%, with the curing atmosphere similar to that of the mined-out area underground. The compressive strength at different ages was tested.

[0063] Please refer to Table 5, which is the summary table of compressive strength for Examples 1-2 and 3-2 of the present invention;

[0064] Table 5 Summary of Compressive Strength of Neat Paste Specimens (MPa)

Example	3d	7d	28d	90d
Example 1 - 2	3.27±0.16	23.92±1.20	33.50±1.68	36.62±1.83
Example 3 - 2	14.02±0.70	16.20±0.81	31.33±1.57	34.53±1.73

[0065] It can be seen that while the composition is simplified, the synergistic effect of multiple solid wastes still enables good cementing performance.

[0066] Fresh paste from neat paste blocks prepared in Examples 1-2 and 3-2 was taken, and neat paste specimens were prepared according to GB17671-1999 Method for Determination of Strength of Cement Mortar, with dimensions of 30mm × 30mm × 50mm, cured under standard conditions at 20°C and humidity above 99.5%, with the curing atmosphere similar to that of the mined-out area underground. The leaching concentrations of heavy metal ions at different ages were tested. The leaching concentration of heavy metal ions from lead-zinc tailings was measured at the State Key Laboratory of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The instrument model used was SHIMADZU 2030 inductively coupled plasma mass spectrometer, with a detectable range of 5~260 amu, a detection limit below 0.1 ppt, a detector counting range of 1~109, and a resolution below 1 amu, suitable for trace element determination. The results are shown in Table 6:

[0067] Table 6 Heavy Metal Pollution Characteristics of Neat Paste Specimens (ug/L)

Element **Sample Name**	Cd	Cr	Cu	Sb	As	Pb	Zn
Vanadium-titanium slag	0.004	1.734	0.139	1.159	2.521	0.005	0.002
Example 1 - 2 (3d)	0.007	30.252	0.126	0.951	1.208	0.010	0.007
Example 1 - 2 (7d)	0.004	22.475	0.098	0.566	1.043	0.006	0.005
Example 1 - 2 (28d)	0.001	17.813	0.043	0.292	0.740	0.003	0.004
Example 3 - 2 (3d)	0.007	18.521	0.135	0.914	1.191	0.189	0.005
Example 3 - 2 (7d)	0.005	13.617	0.078	0.561	1.119	0.117	0.003
Example 3 - 2 (28d)	0.002	12.869	0.057	0.286	0.956	0.094	0.002
Class III groundwater standard (ug/L) ≤	5	50	1000	5	10	10	1000

[0068] The present invention provides a cemented backfill material containing vanadium-titanium slag and its preparation method, wherein the filling material comprises a cementitious material and aggregate at a mass ratio of 1:4. The cementitious material mainly includes vanadium-titanium slag, slag, steel slag, and desulfurized gypsum, while the aggregate mainly consists of vanadium-titanium slag and lead-zinc tailings.

The chemical compositions of vanadium-titanium slag, slag, steel slag, and desulfurized gypsum have corresponding preferred ranges, for example, the preferred composition of vanadium-titanium slag is: CaO 30-40 parts, SiO2 10-30 parts, TiO2 5-20 parts, etc.

[0069] In terms of preparation method, the raw material ratios of the cementitious material and aggregate are first determined, and then the raw materials are ground to the required specific surface area. Next, the raw materials of the cementitious material are mixed with water, and the moisture is adjusted until the slurry concentration reaches 70-80%. Finally, the prepared cementitious material and aggregate are mixed with water, and the moisture is adjusted until the concentration reaches 70-80%, thereby obtaining the cemented backfill material.

[0070] Test results show that the filling material of the present invention exhibits good fluidity, setting time, and compressive strength. In particular, heavy metal ion leaching concentration tests indicate that the leaching concentration of heavy metal ions in the neat paste specimens of the present invention is far below the limit value of the Class III groundwater quality standard, demonstrating effective solidification of heavy metal components. Furthermore, the hydration reaction process of the filling material was further verified by observing the morphology of the hydration products using scanning electron microscopy (SEM).

[0071] Overall, the cemented backfill material containing vanadium-titanium slag and its preparation method provided by the present invention not only meet the performance requirements for mine backfilling, but also offer advantages such as cost optimization and environmental protection. Meanwhile, this method does not require the addition of activators, early strength agents, or other admixtures, reducing raw material costs, and the slurry concentration is low, making it economical, practical, and conducive to emission reduction.