

DESCRIPTION

MARINE ENGINEERING ADMIXTURE

BACKGROUND OF THE INVENTION

[0001] 1. Technical Field

[0002] The invention relates to the technical field of marine engineering materials, in particular to a marine engineering admixture.

[0003] 2. Description of Related Art

[0004] The seawater environment has a huge impact on the corrosion resistance and durability of marine engineering facilities. The development of land reclamation and infrastructure construction in coastal areas is faced with harsh climate environments such as high temperature, high humidity, high salt spray, deep water and large waves, which puts forward very high requirements for the performance of marine building materials. However, ordinary Portland cement (OPC) has poor corrosion resistance and high heat of hydration, and because the concrete has very low early tensile strength and small elastic modulus, which can easily lead to serious temperature cracks in concrete, especially large-volume concrete, thus seriously affecting the strength and durability of marine the structures.

[0005] The coupling effect of multiple factors such as temperature field, humidity field, harmful ion erosion, super typhoon, etc. in the marine environment has caused serious damage to the safe service and durability of concrete structures, resulting in the service life of the concrete building being much lower than the expected value of the code design. The most serious and common durability problems faced by marine engineering cement concrete at home and abroad are dissolution, corrosion and chlorine-induced steel corrosion of cement-based material. The instability of hydration products in seawater is a problem in the research and application of OPC for marine engineering structures.

[0006] Calcium hydroxide (CH) (the Portland cement hydration product) and hydrated

calcium silicate (CSH) gel are both easily dissolved or corroded in seawater media. Adjusting the clinker composition and introducing a large amount of auxiliary cementing materials are important ways to reduce the heat of hydration, improve the corrosion resistance and block Cl⁻, but it still cannot overcome the stability problem of the products. Early research by the University of California, Berkeley shows that reducing the proportion of CH in cement products and introducing aluminum components into the CSH gel to form a calcium aluminum silicate (CASH) gel can significantly improve its resistance to seawater corrosion. European studies on ancient Roman marine structures with a history of thousands of years show that the formation of stable zeolite products in seawater in the cement is an important reason for its long-term corrosion resistance. These studies suggest that the design and introduction of products that are stable in seawater media is an important way to develop high corrosion-resistant cementing materials. At present, Norway, the United States, Lafarge, and China have established marine engineering cement standards, and produced and applied the marine engineering cement standards in engineering. The harsh marine construction environment and lack of special cement admixtures lead to poor construction quality. The lack of Cl⁻ rapid online detection technology in service leads to poor durability of marine engineering. Therefore, the development of special admixtures, on-site non-destructive Cl⁻ measurement, early diagnosis technology for steel corrosion and long-term service performance testing is the main trend in this field.

BRIEF SUMMARY OF THE INVENTION

[0007] Based on the existing research and development experience and enlightenment of cement-based marine engineering materials at home and abroad, with the focus of increasing the stable products and composite chlorine resistance in seawater media, high-corrosion, high-strength, long-term stable marine Portland cement is developed to meet the requirements of marine engineering durability. The invention is to provide a marine engineering admixture that is compounded from a large amount of metallurgical industrial waste, such as superfine slag

powder, coal ash, and desulfurized gypsum by adding a suitable amount of actuator in a certain proportion, which can effectively reduce the heat of hydration of concrete and improve the durability of marine engineering concrete.

[0008] The above objective of the invention is reached through the following technical solutions:

[0009] According to the first aspect, the marine engineering admixture of the invention comprises the following raw materials in parts by weight: 50-90 parts of superfine slag powder and 10-50 parts of coal ash, or further comprises 1-10 parts of an actuator, and the above raw materials are compounded in proportion and then stirred well, thus obtaining the marine engineering admixture.

[0010] In some embodiments, the marine engineering admixture comprises the following raw materials in parts by weight: 55-80 parts of superfine slag powder and 15-40 parts of coal ash, and 1-8 parts of an actuator. The reasonable ratio of the superfine slag powder and the coal ash used in marine engineering concrete can effectively reduce the heat of hydration of concrete, reduce temperature cracks in concrete, and improve the durability of concrete. The addition of the actuator can excite activity and improve early strength.

[0011] The superfine slag powder of the invention is superfine slag powder S95 with a specific surface area of 400-450 m²/kg, preferably 420 m²/kg.

[0012] The coal ash of the invention meets the relevant technical indicators of GB/T1596-2017 "Coal Ash Used in Cement and Concrete" and has a water content of $\leq 1.0\%$ and a SO₃ content of $\leq 3.0\%$.

[0013] The actuator of the invention is one or a mixture of two or more of triisopropanolamine, triethanolamine, ethylene glycol, desulfurized gypsum, calcium oxide, and sodium sulfate.

[0014] Further, the desulfurized gypsum is power plant desulfurized gypsum or sintered desulfurized gypsum.

[0015] In a certain embodiment, the marine engineering admixture is composed of, by weight, 60 parts of superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 35 parts of coal ash and 5 parts of desulfurized gypsum.

[0016] In a certain embodiment, the marine engineering admixture is composed of, by weight, 65 parts of superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 32 parts of coal ash and 3 parts of sodium sulfate.

[0017] In a certain embodiment, the marine engineering admixture is composed of, by weight, 70 parts of superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 22 parts of coal ash, 5 parts of desulfurized gypsum, and 3 parts of sodium sulfate.

[0018] According to the second aspect, the marine engineering concrete of the invention is concrete C30, comprises any of the above-mentioned marine engineering admixtures in a dosage which is 30% to 35% of the total weight of the concrete, and further comprises cement, medium sand, gravel, additives and water.

[0019] In a certain embodiment, the dosage of the marine engineering admixture is 33% of the total weight of the concrete.

[0020] Compared with the prior art, the invention has the following beneficial effects:

[0021] 1. The marine engineering admixture of the invention is compounded from metallurgical solid waste such as superfine slag powder and coal ash, as the main raw materials according to a certain proportion by adding an appropriate amount of activator materials. On one hand, it reduces the use of cement and effectively reduces the heat of hydration of concrete; moreover, it is also beneficial to reducing the temperature cracks in concrete and improving the durability of marine engineering concrete such as resistance to sulfuric acid and chloride ion.

[0022] 2. The marine engineering admixture of the invention can increase the density of concrete materials, form a low-permeability, high-density, low-defect concrete structure, fundamentally improve the corrosion resistance of the concrete structure in the ocean, and improve the carbonization resistance, impermeability and freezing resistance of concrete.

[0023] 3. The invention can increase the early strength and improve the working performance of concrete by adding an activator.

[0024] 4. The marine engineering admixture of the invention uses solid waste as the main raw material, which has positive significance for resource regeneration and environmental protection, and the product processing technology is controllable and easy to implement.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The invention will be further detailed below with reference to examples.

[0026] The marine engineering admixture prepared in the following examples comprises the following raw materials in parts by weight: 50-90 parts of superfine slag powder and 10-50 parts of coal ash, or further comprises 1-10 parts of an actuator, and the above raw materials are compounded in proportion and then stirred well, thus obtaining the marine engineering admixture.

[0027] The superfine slag powder is superfine slag powder S95 with a specific surface area of 400-450 m²/kg.

[0028] The coal ash meets the relevant technical indicators of GB/T1596-2017 "Coal Ash Used in Cement and Concrete", its water content is $\leq 1.0\%$, and the SO₃ content is $\leq 3.0\%$.

[0029] The actuator is one or a mixture of two or more of triisopropanolamine, triethanolamine, ethylene glycol, desulfurized gypsum, calcium oxide, and sodium sulfate.

[0030] Desulfurized gypsum is power plant desulfurized gypsum or sintered desulfurized gypsum.

[0031] Further description is carried out through Examples 1 to 3. The raw materials are put into a mixer according to the following ratio, stirred for 4 minutes, and mixed well to obtain the marine engineering admixture. The difference is as follows.

[0032] Example 1

[0033] The marine engineering admixture is composed of, by weight, 60 parts of

superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 35 parts of coal ash, and 5 parts of desulfurized gypsum.

[0034] Example 2

[0035] The marine engineering admixture is composed of, by weight, 65 parts of superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 32 parts of coal ash, and 3 parts of sodium sulfate.

[0036] Example 3

[0037] The marine engineering admixture is composed of, by weight, 70 parts of superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$, 22 parts of coal ash, 5 parts of desulfurized gypsum, and 3 parts of sodium sulfate.

[0038] Test data

[0039] The concrete test was carried out with the configured marine engineering admixture. The concrete C30 was designed. The mix ratio was the mix ratio of the commonly used pumped concrete. The water consumption was basically unchanged. The concrete slump was controlled to $180 \pm 30 \text{ mm}$ by adjusting the dosage of the additive. The mix ratio of the concrete C30 is shown in Table 1, where:

[0040] Comparative Example 1 adopts the reference concrete.

[0041] Comparative Example 2 is to add Superfine slag powder S95 with a specific surface area of $420 \text{ m}^2/\text{kg}$ to the raw material composition of the reference concrete, while correspondingly reducing the amount of cement used.

[0042] Effect examples 1 to 3 refer to the addition of the marine engineering admixture obtained in examples 1 to 3 to the raw material composition of the reference concrete, and the addition amount is 33% of the cementing material, while correspondingly reducing the amount of cement used.

[0043] The mechanical properties of concrete are shown in Table 2. The durability of concrete is measured in accordance with GB/T 50082-2009 Standard for Test Methods of

Long-term Performance and Durability of Ordinary Concrete, and the results are shown in Tables 3-6.

[0044] Table 1: Mix ratio of concrete C30 (/kg)

No.	Cement	Coal ash	Superfine slag powder	Marine engineering admixture	Medium sand	Gravel	Additive	Water
Comparative Example 1	324	54	0	0	790	1007	5.67	192
Comparative Example 2	252	54	72	0	788	1004	5.67	192
Effect Example 1	252	0	0	126	788	1004	5.67	192
Effect Example 2	252	0	0	126	788	1004	5.67	192
Effect Example 3	252	0	0	126	788	1004	5.67	192

[0045] Table 2: Mechanical properties of concrete

No.	Compressive strength/Mpa			Breaking strength/Mpa		
	3d	7d	28d	28d	60d	90d
Comparative Example 1	13.6	24.2	33.0	5.5	6.3	6.5
Comparative Example 2	12.3	20.4	37.6	5.6	6.5	6.7
Effect Example 1	11.1	20.0	33.5	5.9	6.2	6.6

Effect Example 2	12.2	20.3	33.1	6.2	6.8	7.0
Effect Example 3	11.7	19.9	33.7	5.7	6.5	6.8

[0046] It can be seen from Table 2 that the compressive strength of concrete mixed with the marine engineering admixtures (Effect Examples 1 to 3) is basically slightly lower than that of the reference concrete (Comparative Example 1) in the early stage, and gradually exceeds that of the reference concrete in the later period. The flexural strength of the concrete is close to that of the reference concrete.

[0047] According to GB/T50082-2009, the dry shrinkage resistance of concrete was tested, and the dry shrinkage values of different ages were tested. The results are shown in Table 3.

[0048] Table 3: Dry shrinkage resistance of concrete

Dry shrinkage rate/ $\times 10^{-6}$	Comparative Example 1	Comparative Example 2	Effect Example 1	Effect Example 2	Effect Example 3
1d	65.23	53.26	34.93	34.85	35.65
3d	126.12	112.70	91.55	88.04	82.15
7d	174.95	164.94	122.04	130.82	135.69
14d	216.28	194.77	173.75	172.10	173.66
28d	246.73	214.82	203.08	204.75	211.04
45d	263.48	226.56	208.66	208.87	221.95
60d	276.67	238.14	215.68	214.01	225.96

[0049] It can be seen from Table 3 that the dry shrinkage rate of the concrete mixed with the marine engineering admixtures (Effect Examples 1 to 3) is significantly lower than that of the reference concrete (Comparative Example 1), and slightly better than the concrete with the same content of superfine slag powder (Comparative Example 2). It shows that the marine engineering

admixture is beneficial to reducing the early shrinkage of concrete.

[0050] According to GB/T50082-2009, carbonization test was carried out on test specimens cured standardly for 28d. In a carbonization box, the CO₂ concentration was 20%, the temperature was 20°C±3°C, and the relative humidity was 70%±5%. The test results are shown in Table 4.

[0051] Table 4: Carbonization resistance test results of concrete C30

Test item	Comparative Example 1	Comparative Example 2	Effect Example 1	Effect Example 2	Effect Example 3
14d carbonization depth (mm)	3.2	2.9	3.0	2.7	2.7
28d carbonization depth (mm)	5.7	5.1	5.2	4.2	4.9
60d carbonization depth (mm)	8.2	7.0	5.9	5.4	6.0

[0052] It can be seen from Table 4 that compared with the reference concrete (Comparative Example 1), the carbonization depth of the concrete mixed with marine engineering admixtures (Effect Examples 1 to 3) has different degrees of reduction, and with the continuation of the carbonization time, this reducing trend becomes more and more obvious, indicating that mixing with marine engineering admixtures can improve the carbonization resistance of concrete to a certain extent.

[0053] After curing the concrete for 28d, the test results of the water resistance depth and the chloride ion electric flux of the specimens are shown in Table 5.

[0054] Table 5: Results of water impermeability test and chloride ion impermeability

Test item	Comparative	Comparative	Effect	Effect	Effect
-----------	-------------	-------------	--------	--------	--------

	Example 1	Example 2	Example 1	Example 2	Example 3
Water permeation height(mm)	7.2	6.9	5.6	5.2	6.4
Electric flux(C)	2244	2062	1550	1201	1892

[0055] It can be seen from Table 5 that the impermeability of concrete has been significantly improved after mixing with the marine engineering admixtures. After mortar test blocks were immersed in a 10% sulfate solution for the corresponding age, the compressive and breaking strength ratios of the specimens are shown in Table 6.

[0056] Table 6: Compressive strength ratio and breaking strength ratio of mortar specimens after immersion in sulfate solution

Test item	Comparative Example 1	Comparative Example 2	Effect Example 1	Effect Example 2	Effect Example 3
3d Compressive strength ratio%	104	105	102	109	107
3d breaking strength ratio%	104	105	116	120	114
7d Compressive strength ratio%	109	113	108	122	118
7d breaking strength ratio%	109	115	120	120	128
28d Compressive strength ratio%	102	102	106	101	103
28d breaking strength ratio%	113	110	124	116	119
60d Compressive strength ratio%	103	101	107	102	105

60d breaking strength ratio%	100	103	109	108	102
------------------------------	-----	-----	-----	-----	-----

[0057] It can be seen from Table 6 that the compressive strength and breaking strength of the mortar specimens immersed in the sulfate solution are higher than those of the specimens cured in tap water with the same ratio.

[0058] The above are the preferred embodiments of the invention, but the invention should not be limited to the content disclosed in these embodiments. Therefore, all equivalents or modifications made without departing from the spirit disclosed in the invention fall within the protective scope of the invention.

CLAIMS

What is claimed is:

1. A marine engineering admixture, comprising the following raw materials in parts by weight: 50-90 parts of superfine slag powder and 10-50 parts of coal ash, or further comprising 1-10 parts of an actuator, wherein the above raw materials are compounded in proportion and then stirred well, thus obtaining the marine engineering admixture, wherein the superfine slag powder is superfine slag powder S95 with a specific surface area of 400-450 m²/kg.
2. The marine engineering admixture according to Claim 1, comprising the following raw materials in parts by weight: 55-80 parts of superfine slag powder and 15-40 parts of coal ash, and 1-8 parts of an actuator.
3. The marine engineering admixture according to Claim 1 or 2, wherein the superfine slag powder is superfine slag powder S95 with a specific surface area of 420m²/kg.
4. The marine engineering admixture according to Claim 1 or 2, wherein the coal ash meets the relevant technical indicators of GB/T1596-2017 “Coal Ash Used in Cement and Concrete” and has a water content of $\leq 1.0\%$ and a SO₃ content of $\leq 3.0\%$.
5. The marine engineering admixture according to Claim 1 or 2, wherein the actuator is one or a mixture of two or more of triisopropanolamine, triethanolamine, ethylene glycol, desulfurized gypsum, calcium oxide, and sodium sulfate, wherein the desulfurized gypsum is power plant desulfurized gypsum or sintered desulfurized gypsum.
6. The marine engineering admixture according to any of Claims 1-5, composed of, by weight, 60 parts of superfine slag powder S95 with a specific surface area of 420 m²/kg, 35 parts of coal ash, and 5 parts of desulfurized gypsum.
7. The marine engineering admixture according to Claims 1-5, composed of, by weight, 65 parts of superfine slag powder S95 with a specific surface area of 420 m²/kg, 32 parts of coal ash, and 3 parts of sodium sulfate.
8. The marine engineering admixture according to any of Claims 1-5, composed of, by weight,

70 parts of superfine slag powder S95 with a specific surface area of 420 m²/kg, 22 parts of coal ash, 5 parts of desulfurized gypsum, and 3 parts of sodium sulfate.

9. A concrete for marine engineering, wherein the concrete is concrete C30 and comprises the marine engineering admixture according to any of Claims 1-8 in a dosage which is 30% to 35% of the total weight of the concrete, and wherein the concrete further comprises cement, medium sand, gravel, additives and water.

10. The concrete for marine engineering according to Claim 9, wherein the dosage of the marine engineering admixture according to any of Claims 1-8 is 33% of the total weight of the concrete.