STUDY ON THE CORROSION RESISTANCE OF EARLY-STRENGTH COAL GANGUE-BASED SPRAYED COMPOSITE MATERIALS

by

Xiao-Xi BI[a,b], Jun-Wu XIA[a], Pei-Tao QIU[b*], Zhi-Jun ZHANG[b], and Yan-Mei MA[a]

[a] China University of Mining and Technology, Xuzhou, Jiangsu, China
[b] School of Civil Engineering, Xuzhou University of Technology, Xuzhou, China

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On the basis of the basic performance research of gangue aggregate, the early strength sprayed composite material was prepared by using gangue to completely replace the aggregate and sulphoaluminate cement as the cementitious material, and its corrosion resistance was studied. The research results show that the early strength gangue-based sprayed composite material (RSCG) has good working performance. With the increase of corrosion time, the strength of RSCG gradually decreases. The main corrosion components are gypsum ($CaSO_4{\cdot}2H_2O$) and calcium sulfonate. The expansion products are generated and expanded in smaller capillaries, which is the main reason for the generation and expansion of cracks. Based on the experimental research, the equation of the corrosion reaction of gangue-based sprayed composite material and the surface sulfate ion concentration equation are given.

Key words: *early strength, coal gangue, injection, corrosion*

Introduction

Coal gangue coexists with coal-bearing strata and is a sedimentary rock system dominated by gray, gray-black and gray-green colors [1]. It mainly includes sandstone gangue, calcareous rock gangue and aluminous rock gangue. Since the chemical composition of coal gangue is rich in SiO_2 and Al_2O_3, it is similar to the sand and stone aggregates commonly used in concrete, so it can be used as coarse and fine aggregates in concrete [2, 3]. This cannot only reduce the secondary environmental problems caused by the accumulation of coal gangue, but also realize the resource recycling of coal gangue. In underground space engineering, the most commonly used is spray composite material. As a special composite material, it is a composite material formed by sending a concrete mixture of cementitious materials, aggregates*, etc.* mixed in a certain proportion into the spraying equipment, and then spraying it at high speed with the help of compressed air or other power transmission [4, 5]. Compared with traditional poured concrete, sprayed composite materials have the characteristics of faster construction speed, more flexible structure, and stronger adaptability. It is especially suitable for construction on various complex-shaped curved surfaces and harsh construction environments. Shotcrete has significant support functions in the field of underground space. It is mainly used in underground tunnel support, rock mass reinforcement, shaft lining and many other scenarios, providing an indispensable guarantee for the safe and stable

* Corresponding author, e-mail: qpt198959@163.com

operation of underground space projects [6, 7]. This paper will use coal gangue to replace the coarse and fine aggregates of shotcrete to prepare an early strength coal gangue-based high performance shotcrete composite material, and study its basic mechanical properties and corrosion properties to explore the possibility of its efficient use in underground space, aiming to provide more ideas for future research by experts and scholars.

Trial plan

The cement used is the sulphoaluminate cement produced in Changzhi, Shanxi Province. Its chemical compositions are showed in tab. 1.

Table 1. Chemical composition of sulphoaluminate cement [%]

Composition	CaO	Al_2O_3	SiO_2	Na_2O	SO_3	TiO_2	Fe_2O_3	MgO	K_2O	P_2O_3	Others
Content	40.76	33.66	7.41	0.16	9.00	1.26	2.43	0.92	0.29	0.29	0.19

Table 2. Aggregate crushing value determination value

Aggregate type	Group 1 [%]	Group 2 [%]	Group 3 [%]	Average [%]
Aggregates	11.67	11.38	11.58	11.54
Coal Gangue	23.26	24.46	23.81	23.84

The aggregate used in this experiment is a recycled aggregate, which is coal gangue sand made from coal gangue discarded in mining projects after crushing and screening, tab. 2. The ordinary sand is considered as the natural aggregate. The particle size distribution of the fine aggregate is given in tab. 3.

Table 3. Particle size of fine aggregate

Sieve size [mm]	0.16	0.315	0.63	1.25	2.5	5.0	10.0
Aggregate particle size	2-10	8-20	20-35	35-55	50-70	70-85	90-100

The test uses secondary fly ash, and the main performance indicators are shown in tab. 4.

Table 4. Main technical indicators of secondary fly ash

Fineness 0.045 mm [%]	Water demand ratio [%]	Loss on ignition [%]	Density [gcm^{-3}]	Water content [%]	Intensity activity index [%]
6.0	89	3.43	2.20	0.1	81.6

The fiber used in this experiment is polyvinyl alcohol fiber. The main performance indicators are in tab. 5.

Table 5. Main performance indicators of polyvinyl alcohol fiber

Length [mm]	Diameter [mm]	Tensile strength [MPa]	Elongation [%]	Elastic modulus [GPa]	Density [gcm^{-3}]
6	0.02	1550	6.5	42	1.4

We use the polycarboxylic acid high performance water reducing agent. Test mix ratio is seen in tab. 6.

Table 6. Test mix ratio

Group	P·O [g]	R·S·A [g]	Water [ml]	Natural sand [g]	Coal gangue sand [g]	Water reducing agent [g]
P·O + S (POS)	450	0	225	1350	0	4.5
P·O + CGS (POCG)	450	0	225	0	1350	4.5
R·S·A + S (RSS)	0	450	225	1350	0	4.5
R·S·A + CGS (RSCG)	0	450	225	0	1350	4.5

Note: P·O – Ordinary Portland cement; R·S·A – Sulphoaluminate c ment; S – Natural sand; CGS – Coal gangue sand.

Theoretical derivation

The corrosion of gangue-based spray composites can be regarded as a 1-D corrosion problem. According to the diffusion-reaction equation of chromium sulfate ions, its transport equation can be expressed [8]:

$$\frac{\partial U_{so_4^{2-}}}{\partial t} = \frac{\partial}{\partial x}\left[D(x,t)\frac{\partial U_{so_4^{2-}}}{\partial x}\right] - \frac{\partial U_c}{\partial t}$$
$$U_{so_4^{2-}}(x,0) = U_0,\ U_{so_4^{2-}}(0,t) = U_s(t),\ \ x \in (0,l) \tag{1}$$

where $U_{SO_4^{2-}}$ is the free sulfate ion concentration, U_c – the sulfate ions consumed in the reaction, $D(x, t)$ – the diffusion coefficient, which is the initial concentration of the sulfate ions, l – the overall height of the section, x – the section location, t – the corrosion time, and $U_s(t)$ – the sulfate ion concentration on the concrete surface.

As a function $U_s(t)$ with the corrosion time as the independent variable, it characterizes the change of sulfate ion concentration on the concrete surface with time. The function $U_s(t)$ is defined:

$$U_s(t) = U_0 + U_a(1 - \mathrm{e}^{-gt}) \tag{2}$$

where U_0 is the initial concentration of the sulfate ions in the concrete, U_a – the increase in the ion concentration after stabilization, and g – the dimensionless fitting parameters.

According to previous research results, the linear relationship between and water-cement ratio is approximately a linear function, namely:

$$U_a = b_1\left(\frac{w}{c}\right) + b_2 \tag{3}$$

where b_1 and b_2 are the fitting parameters, and w/c – the water-cement ratio. By eqs. (2) and (3), we may get:

$$U_s(t) = U_0 + \left[b_1\left(\frac{w}{c}\right) + b_2\right](1 - \mathrm{e}^{-gt}) \tag{4}$$

Here, eq. (4) can characterize the sulfate ion concentration on the surface of the gangue-based spray composites.

Test process

This paper uses slump and expansion as evaluation indicators of composite material fluidity, and the test method refers to the specification GB/T 50080-2016. The test block is subjected to corrosion test under dry-wet cycle. After reaching the specified number of dry-wet cycles, the strength test is carried out. At the same time, the damage of the concrete surface after dry-wet cycles should be observed and the appearance should be described. When the compressive strength test is carried out on the test pieces subjected to dry-wet cycles, a group of comparison test pieces with standard curing should be taken for compressive strength test at the same time. The appearance morphology and element distribution of the corroded material were analyzed using a scanning electron microscope combined with an X-ray spectrometer. We prepare the test block according to the GB50056-2015.

Results and discussion

Based on the study of mechanical properties, the hydration reaction of RSCG was deeply analyzed.

It was found that the hydration mechanism of RSCG has certain particularities due to the secondary hydration reaction, fig. 1.

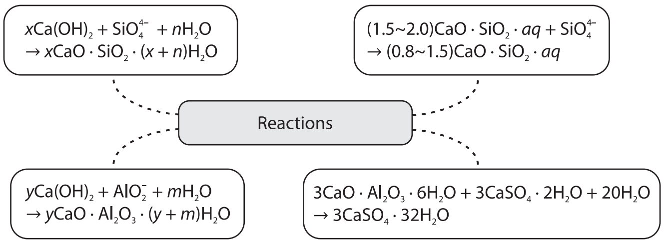

Figure 1. Hydration reaction of RSCG

As the corrosion time increases, the compressive strength of both RSCG and RSS materials shows a downward trend, and the decline rate is significant, see figs. 2 and 3. This indicates that corrosion has a greater impact on the strength of both materials. As the corrosion time increases, although the compressive strength of RSS has always been higher than that of RSCG, the decrease rate of the two is similar. Especially when the corrosion time reaches 45 days, the compressive strength of the two is not much different (RSS is slightly higher). By 90 days, the compressive strengths of the two tend to be the same, about 30 MPa.

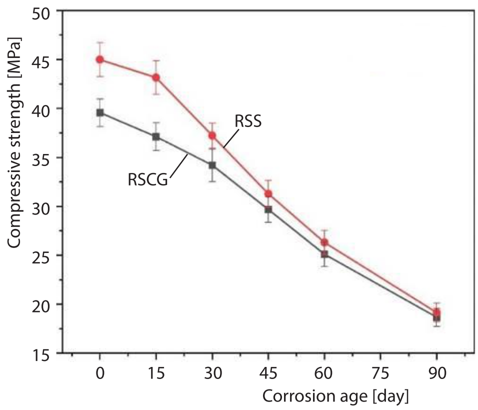

Figure 2. Compressive strength of materials after different corrosion times

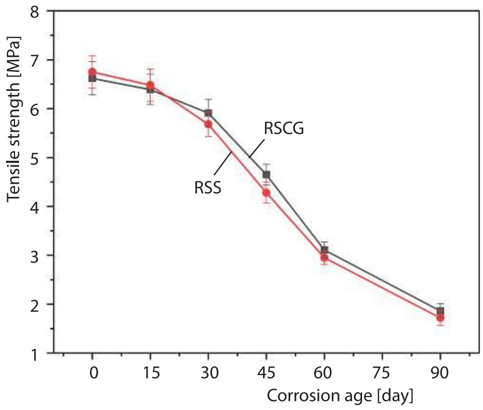

Figure 3. Splitting tensile strength of materials after different corrosion times

As corrosion progresses, the rough particles and cracks generated on the surface gradually increase, making the surface of the material more rough and uneven. Observation under an electron microscope found that the originally dense and flat surface will turn into a rough surface full of cracks and holes, fig. 4. The main reason is that sodium sulfate accumulates on the surface of shotcrete, and the uncorroded sulfur and sodium elements increase significantly compared to those after 45 days of corrosion, as shown in figs. 5 and 6. It reacts with calcium hydroxide, $Ca(OH)_2$, and other hydration products (such as ettringite) in concrete to generate secondary products with volume expansion characteristics. The main components are gypsum, $CaSO_4 \cdot 2H_2O$, and ettringite. The expansion products (gypsum and ettringite) are generated and expanded in smaller capillaries, causing local stress concentration, leading to the generation and expansion of cracks. Obvious pits and holes appeared on the surface.

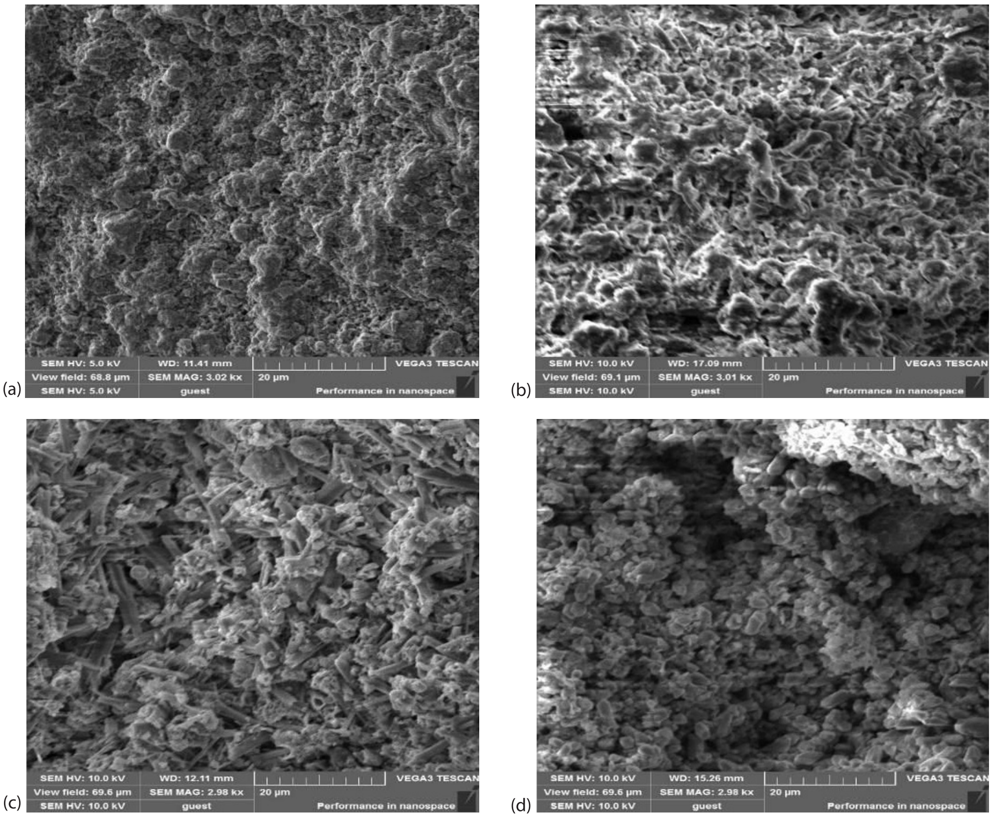

Figure 4. Surface morphology of test blocks after different corrosion times; (a) no corrosion, (b) after 30 days of corrosion, (c) after 45 days of corrosion, and (d) after 90 days of corrosion

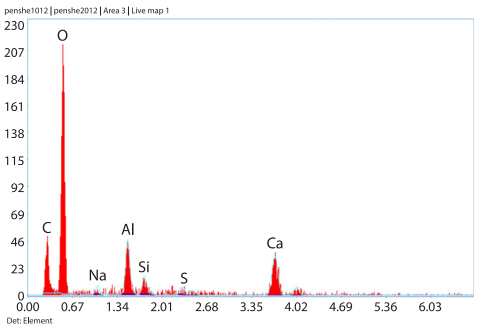

Figure 5. Element distribution on the surface of uncorroded test block

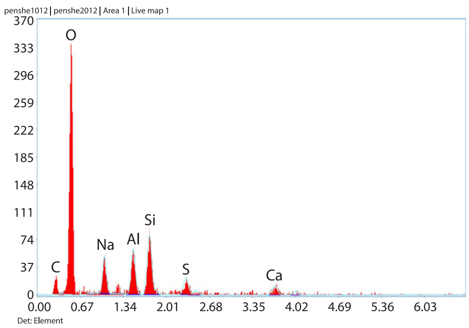

Figure 6. Surface element distribution of the test block after 45 days of corrosion

Conclusions

Compared with ordinary spray composite materials, RSCG can meet the use requirements of various working conditions in underground space. In terms of compressive strength, the peak strength of early-strength coal gangue-based spray composite materials is the highest among the four materials, and the peak strength can be reached in seven days. In terms of flexural strength, compared with the generally low early flexural strength of the other three materials, the flexural strength of RSCG materials from 1-28 days is basically at a higher level. This shows that its basic mechanical properties are more outstanding than the other three spray composite materials, and it is very feasible to use local materials in underground space environments.

From the analysis of the hydration reaction, the coal gangue as aggregate affects cement hydration through two mechanisms. High water absorption accelerates the hydration rate. The activation in the secondary cement hydration reaction consumes CH crystals to form C-S-H gel and AFt crystals, thereby reducing the content of CH crystals and improving the micro-structure and mechanical properties of the concrete. In terms of the corrosion performance, with the increase of corrosion time, the strength of the early-strength coal gangue-based sprayed composite material gradually decreases. The main corrosion components are gypsu, $CaSO_4 \cdot 2H_2O$, and calcium aluminates. The expansion products are generated and expanded in smaller capillaries, which is the main reason for the generation and expansion of cracks.

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Nomenclature

l – overall height of section, [m]
t – corrosion time, [day]
U_a – increase in the ion concentration, [molm^{-3}]
U_0 – initial concentration, [molm^{-3}]
$U_s(t)$ – sulfate ion concentration, [molm^{-3}]
x – section location, [m]

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