**Introduction**

Cement soil is an artificial mixed material formed by stirring natural soft soil and cement slurry (or powder) via mechanical stirring or jet punching processes [1, 2]. It is primarily a mixture of cement and soil [3, 4]. Because of its low price, wide material availability, simple construction process, and excellent performance, cement soil is widely used in foundation treatments and roadbed engineering [5, 6]. In practical engineering, groundwater is often polluted by acidic and alkaline pollutants, the pH of which can have a significant impact on the strength characteristics of cement soil [7, 8]. Additionally, the erosion of cement soil in a sulfate environment is also significant [9, 10]. Bai et al. (2007) compared and analyzed the stress-strain curve of cement soil in clear water and a chemical solution environment using indoor simulation experiments and established the relationship between the compressive strength and erosion time [11]. Dong et al. (2011) tested the strength...
of cement-solidified sodium-sulfate-contaminated soil of different content through laboratory simulation experiments and discovered the relationship between the resistivity and compressive strength of contaminated cement soil [12]. Liu et al. (2014) simulated a seawater erosion environment using different concentrations of sodium chloride, magnesium chloride, and magnesium sulfate solutions and evaluated the effects of the solution concentration on the unconfined compressive strength and microstructure of cement soil [13]. Chen et al. (2016) studied the influence of corrosive medium environment on the mechanical properties of cement soil and found that trace sodium sulfate corrosion solution was conducive to its hydration and compaction [14]. Kampala et al. (2021) analyzed the influence of a sulfate medium on the compaction characteristics and strength development of cement soil and derived a curve for the relationship between the unconfined compressive strength and optimum moisture content [15]. These studies aside, there have been few studies on the compressive strength of cement soils containing additives in corrosive environments.

Metakaolin (MK) is an anhydrous calcium aluminate (Al₂O₃·2SiO₂, AS₂) formed by the calcination and dehydration of kaolin (Al₂O₃·2SiO₂·2H₂O, AS₂H₂) at a certain temperature (500ºC–900ºC) [16, 17]. Coal-bearing metakaolin (CMK) – composed of active silica and alumina – is produced via the calcination of coal kaolin [18, 19]. Recently, MK has been widely used to improve the mechanical properties, impermeability, and durability of cement-based materials [20-23]. Siddique et al. (2009) summarized the research progress on MK in concrete, the results of which showed that MK could improve the corrosion resistance of concrete [24]. Janotka et al. (2010) studied the influence of low-grade MK on the strength of cement mortar and found that it could improve its strength and impermeability [25]. Hassan et al. (2012) evaluated the effect of MK on the rheology of concrete and found that the plastic viscosity and yield strength of concrete were positively correlated with the MK content [26]. Deng et al. (2016) partially replaced cement with MK in cement soil and found that MK greatly enhanced its penetration resistance [27]. Wang et al. (2022) discussed the effects of MK on the permeability characteristics of cemented silty sand and determined the relationship between the permeability coefficient and unconfined compressive strength [28].

Nonetheless, in general, there have been few studies on the impact of CMK incorporation into cement soil, particularly on its durability. In this study, the compressive strength of CMK cement soil was studied using laboratory simulation experiments, along with five CMK samples cured in different concentrations of sodium sulfate (Na₂SO₄) solution. X-ray diffraction (XRD) technology was used to analyze the chemical reactions of Na⁺ and SO₄²⁻ in the CMK cement soil and scanning electron microscopy (SEM) technology was used to determine its microstructure. The average pore size was calculated from the 500× magnification SEM image using Image-ProPlus6.0 analysis software and the mechanism of CMK cement soil curing in a Na₂SO₄ environment was discussed.

**Materials and Methods**

**Experimental Materials**

The soil was collected from a construction site in Taiyuan, Shanxi Province, China. The soil particles were passed through a 2.0 mm sieve. Table 1 lists the particle-size distributions. The coefficients of uniformity (C_u) and curvature (C_c) are 0.76 and 3.65, respectively, which is poorly graded sandy soil according to the Chinese GB50021-2001 standard [29]. The ordinary Portland cement (OPC) was produced in Taiyuan, China. The 28 d compressive strength of the cement is 42.5 MPa, and the particle size distribution range is 5 μm~10 μm. Table 2 lists the chemical composition of the cement. The CMK was obtained from Shanxi Bright

<table>
<thead>
<tr>
<th>Particle size /mm</th>
<th>2.00~0.50</th>
<th>0.50~0.25</th>
<th>0.25~0.075</th>
<th>0.075~0.005</th>
<th>&lt;0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content /wt.%</td>
<td>18.0</td>
<td>25.0</td>
<td>21.0</td>
<td>24.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>Other</th>
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</thead>
<tbody>
<tr>
<td>Content /%</td>
<td>18.81</td>
<td>5.86</td>
<td>3.34</td>
<td>66.35</td>
<td>1.04</td>
<td>0.41</td>
<td>0.31</td>
<td>2.53</td>
<td>1.35</td>
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</table>

<table>
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<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
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</thead>
<tbody>
<tr>
<td>Content /%</td>
<td>52.62</td>
<td>45.42</td>
<td>0.45</td>
<td>0.85</td>
<td>0.17</td>
<td>0.11</td>
<td>0.13</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Kaolin Technology Co., Ltd., China. Particles smaller than 2 μm account for more than 90% of the total mass. Table 3 lists the chemical composition of the CMK. The sodium sulfate reagent was analytically pure anhydrous Na$_2$SO$_4$ with a purity of more than 99%, produced by the Tianjin Reagent Factory Co., Ltd., China. The pH of the Na$_2$SO$_4$ reagent was maintained between 5 and 8 at room temperature.

### Sample Preparations

Prior to sample preparation, sandy soil was dried in an oven at 105ºC for 24 h. Table 4 lists the mix proportions for the preparation of the CMK cement soil. During the sample preparation, the sandy soil, CMK, cement, and distilled water were weighed, as listed in Table 4. All mixtures were poured into a mixer for two min to ensure uniform stirring of the slurry. The slurry was then added in two steps to a 70.7 mm × 70.7 mm × 70.7 mm steel mold. After adding one-third of the slurry, the steel mold was vibrated on a vibration table for one min to ensure that all air was exhausted. The sample surface was scraped flat using a scraper, and the steel mold was wrapped in plastic. After 24 h, the mold was removed. The samples were cured in a constant-temperature water tank for 7 d. Finally, all the CMK cement-soil samples were removed and placed in solutions of different Na$_2$SO$_4$ concentrations to continue curing for 28 d. The concentrations of the Na$_2$SO$_4$ solutions were 0, 4.5 g/L, 9 g/L, 18 g/L and 36 g/L, respectively, according to the Chinese GB50021-2001 standard [29]. The samples in the five different environments were denoted as NS0, NS1, NS2, NS3, and NS4.

### Testing Methods

The compressive strengths of the CMK cement-soil samples at 28 d were tested using a WDW-100 electronic universal testing machine at a loading rate of 0.3 kN/s. Phase composition tests of the CMK cement-soil samples were performed at 28 d using a Shimadzu Suzhou XRD-6000 X-ray diffractometer, the scanning angle ranging from 2°~60° and the speed being 6°/min. Microscopic images of the CMK cement-soil samples at 28 d were captured using a Hitachi TM-3000 scanning electron microscope, at magnifications of 500× and 5000×.

After the test, the XRD peaks were analyzed using MDI Jade 6.0 software, to determine the phase composition of the CMK cement soil. Additionally, Image-ProPlus6.0 analysis software was used to process and analyze the SEM images at 500× magnification to obtain the pore distribution of the CMK cement soil.

### Results and Discussion

#### Compressive Strength

Fig. 1 shows the compressive strength of the CMK cement soil cured in different Na$_2$SO$_4$ solution concentrations at 28 d. In general, compared with the CMK cement soil cured in clear water (Na$_2$SO$_4$ concentration of 0), the compressive strength of the CMK cement soil increases to differing degrees with increasing Na$_2$SO$_4$ solution concentration. When the Na$_2$SO$_4$ solution concentration is less than 18 g/L, the compressive strength of the CMK cement soil increases with increasing Na$_2$SO$_4$ solution concentration. When the Na$_2$SO$_4$ concentration is greater than 18 g/L, the compressive strength of the CMK cement soil decreases with increasing Na$_2$SO$_4$ solution concentration. Within the scope of the experiment designed in this study, when the Na$_2$SO$_4$ solution concentration is 18 g/L, the strength of the CMK cement soil reaches its maximum value, indicating that a moderate Na$_2$SO$_4$ solution concentration has a crucial enhancing effect on the CMK cement soil strength. It should be noted that the relationship between the compressive strength of the CMK cement soil and the CMK content has been previously reported [30, 31]. When the CMK content is 3%, the strength of the CMK cement soil reaches its maximum value. Consequently, the CMK cement soil with 3% CMK content cured in different concentrations of Na$_2$SO$_4$ solution was selected for microscopic analysis.

#### XRD Analysis

Fig. 2 shows the XRD patterns of the CMK cement soil with 3% CMK content cured in different
concentrations of Na$_2$SO$_4$ solution at 28 d. The main phases of the CMK cement soil are quartz, ettringite, calcium aluminate hydrate, calcium hydroxide, calcium aluminate silicate hydrate, albite, calcium silicate hydrate, calcite, and gypsum. The CMK cement soil is reinforced mainly through the hydrolysis and hydration of MK and cement, the interaction between the soil particles and hydration products, and carbonation [32]. Moreover, the interaction between the soil particles and hydration products manifests as an ion-exchange agglomeration reaction and a pozzolanic reaction. Additionally, Na$^+$ and SO$_4^{2-}$ participate in chemical reactions in the CMK cement soil. The chemical reactions between Na$^+$ and the CMK cement soil can be expressed as follows [33]:

$$\text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} + 8\text{H}_2\text{O}$$

$$3\text{Ca}_3\text{O}_2\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O} + 4\text{NaOH} = 3\text{Ca(OH)}_2 + 2\text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O}$$

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 2\text{NaOH} = 3\text{Ca(OH)}_2 + \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 4\text{H}_2\text{O}$$

$$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 6\text{SiO}_2 = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$$

The reaction equation shows that calcium hydroxide (Ca(OH)$_2$) is the product of the Na$^+$ reaction. As shown in Fig. 2, the peak value of calcium hydroxide increases as the reaction progresses – that is, as the Na$_2$SO$_4$ solution
concentration increases, more calcium hydroxide is produced. Moreover, the hydration reactions of cement produce large quantities of calcium hydroxide [34].

As shown in Fig. 1, when the Na$_2$SO$_4$ solution concentration is less than 18 g/L, the compressive strength of the CMK cement soil increases with increasing Na$_2$SO$_4$ solution concentration. This is because the production of calcium hydroxide continues to improve the overall CMK cement-soil strength in three ways: First, Na$_2$O$_3$ in the sandy soil and CMK to produce calcium silicate hydrate (3CaO∙Al$_2$O$_3$∙6SiO$_2$) owing to the presence of Na$^+$. Moreover, Na$^+$ has a larger ionic radius in albite, which can cause an ion exchange with Ca$^{2+}$ in the calcium hydroxide [35]. All calcium hydroxides are produced by the hydration of cement and CMK, as well as by the reaction between Na$^+$ and the cement soil. After ion exchange, the diffusion layer of the electric double layer in the cement-soil system weakens. Consequently, the volume of bound water is reduced, thereby increasing the direct cohesion of soil particles and improving the strength of the soil [36]. Additionally, the generated Ca$^{2+}$ chemically reacts with active SiO$_2$ and Al$_2$O$_3$ in the sandy soil and CMK to produce calcium silicate hydrate (3CaO$\cdot$2SiO$_2$$\cdot$3H$_2$O) and other products in alkaline environments [37]. These hydration products bond with the soil particles to form a cemented network structure, which continues to increase the strength of the cement soil. Finally, part of the free calcium hydroxide is carbonized with carbon dioxide in air and water to produce calcite (CaCO$_3$), which also enhances the strength of the cement soil [38].

The chemical reactions between SO$_4^{2-}$ and CMK cement soil can be expressed as follows [39]:

$$CaSO_4 + 2H_2O = CaSO_4\cdot2H_2O$$

$$3CaSO_4 + 4CaO\cdotAl_2O_3\cdot19H_2O + 14H_2O = 3CaO\cdotAl_2O_3\cdot3CaSO_4\cdot32H_2O + Ca(OH)_2$$

$$3CaSO_4\cdot3CaO\cdotAl_2O_3\cdotCaSO_4\cdot18H_2O + 14H_2O = 3CaO\cdotAl_2O_3\cdot3CaSO_4\cdot32H_2O$$

Here, SO$_4^{2-}$ reacts with the cement soil to form gypsum (CaSO$_4$$\cdot$2H$_2$O), which has an expansion effect on the cement soil [40]. Additionally, gypsum reacts with calcium aluminate hydrate (4CaO$\cdot$Al$_2$O$_3$$\cdot$19H$_2$O) and monosulfur calcium aluminate hydrate (3CaO$\cdot$Al$_2$O$_3$$\cdot$CaSO$_4$$\cdot$18H$_2$O) to form ettringite (3CaO$\cdot$Al$_2$O$_3$$\cdot$3CaSO$_4$$\cdot$32H$_2$O). Ettringite is characterized primarily by its filling and expansion effects [41]. When the generation of ettringite is low during the early stages, the space network structure formed by the intersecting ettringite crystals and calcium silicate hydrate fills the gaps in the cement-soil particles. This reduces the porosity and increases the strength. However, during the later stages, with an increase in the number of ettringites, the expansion effect is not conducive to cementation between the soil particles, contributing to a decrease in the cement-soil strength.

As shown in Fig. 1, when the Na$_2$SO$_4$ solution concentration is greater than 18 g/L, the compressive strength of the CMK cement soil decreases with increasing Na$_2$SO$_4$ solution concentration. This is because large quantities of Na$^+$ and SO$_4^{2-}$ participate in the reaction. Sodium hydroxide (NaOH) undergoes a chemical reaction with the calcium silicate hydrate produced by the hydration of cement and CMK, leading to poor cementation between the soil particles. This is reflected in the reduction in the cement-soil strength. Furthermore, the gypsum and ettringite generated by excessive SO$_4^{2-}$ exhibit expansion effects, generating a large swelling force. This increases the volume of the soil particles and damages its internal structure, causing a reduction in the cement-soil strength.

**SEM Analysis**

Fig. 3 shows SEM images of the CMK cement soil with 3% CMK content cured in different concentrations of Na$_2$SO$_4$ solution at 28 d. As shown in Fig. 3a), the soil particles of the CMK cement samples cured in clean water are bonded through flocculent cementitious products. However, some pores remain between soil particles. The strength of the flocculent cementitious products is low, and they are relatively loosely arranged. Once the soil particles are disturbed by external forces, their internal microstructures can be easily destroyed.

Fig. 3(b-d) shows SEM images of the CMK cement-soil samples cured in different concentrations of Na$_2$SO$_4$ solutions. When the Na$_2$SO$_4$ solution concentration is less than 18 g/L, more and more flocculent cementitious products are generated from the hydration reaction of the CMK cement soil with increasing Na$_2$SO$_4$ solution concentration. This flocculent cementitious product wraps the soil particles from all sides, promoting firmer soil particles. With increasing Na$_2$SO$_4$ solution concentration, an increasing number of needle-shaped and rod-shaped ettringites are generated by the hydration reaction of the cement soil. The pores between the soil particles are effectively filled with ettringite, thereby reducing the number of pores. The structural units of the soil particles are granulated to ensure that the soil structure is stable.

As shown in Fig. 3e), when the Na$_2$SO$_4$ solution concentration exceeds 18 g/L and reaches 36 g/L, a large quantity of ettringite crystals are generated during the hydration reaction of the CMK cement soil. In addition to filling the pores between the soil particles, these ettringite crystals are attached to the surface of the soil particles, forming a part of the acicular soil particle structure. Because of the expansion effect produced by ettringite crystals, the volume of the CMK cement soil expands rapidly, and the pores become larger. When the expansion effect produced by ettringite is greater than the cementation effect between the soil particles, the soil is damaged, leading to a decrease in the cement-soil strength [42].
To obtain the pore distribution of CMK cement soil cured in different concentrations of Na\textsubscript{2}SO\textsubscript{4} solution, SEM images of the CMK cement soil at 500× magnification were processed using Image-ProPlus 6.0 analysis software. Fig. 5 shows the original SEM images and binary images of the CMK cement soil with 3% CMK content cured in different concentrations of Na\textsubscript{2}SO\textsubscript{4} solution at 28 d. The size of the pores was calculated using the black and white binarized images, the classification and statistical parameters of which are listed in Table 5.

From the statistical results of the sample porosity in Table 5, the porosity of the CMK cement soil in Na\textsubscript{2}SO\textsubscript{4} solution is considerably lower than that in clean water. Moreover, with an increase in the Na\textsubscript{2}SO\textsubscript{4} solution concentration, the porosity first decreases before increasing. When the concentration of the Na\textsubscript{2}SO\textsubscript{4} solution is 18 g/L, the porosity reaches its minimum value of 26.52%. This is because the hydration products generated by the reaction between the CMK cement soil and Na\textsubscript{2}SO\textsubscript{4} solution play a far greater role in filling than the hydration products generated by the CMK cement soil. Consequently, the CMK cement-soil porosity decreases, and the CMK cement-soil strength increases in the Na\textsubscript{2}SO\textsubscript{4} solution. When the Na\textsubscript{2}SO\textsubscript{4} solution concentration is too high, the gypsum and ettringite generated by the CMK cement soil and Na\textsubscript{2}SO\textsubscript{4} solution contributes to the expansion. Consequently, the porosity of the CMK cement soil increases and the CMK cement-soil strength decreases in the Na\textsubscript{2}SO\textsubscript{4} solution [43].

Based on the size of the average pore diameter, the microscopic pores of the sample can be divided into the following five categories – that is, micro pores (<2 μm), small pores (2 μm–5 μm), medium pores (5 μm–20 μm), macro pores (20 μm–50 μm), and holes (>50 μm) [44, 45]. From the statistical analysis of the pore distribution shown in Table 5, it is evident that the pore distribution of the CMK cement soil changes owing to the influence of the Na\textsubscript{2}SO\textsubscript{4} solution. The distribution proportions of micro pores, small pores, and medium pores all initially increase before decreasing with increasing Na\textsubscript{2}SO\textsubscript{4} solution concentration – that is, the proportion of all the pores in sample NS3 reaches its maximum. By contrast, the distribution proportion of macro pores first decreases before increasing with increasing Na\textsubscript{2}SO\textsubscript{4} solution concentration – that is, the proportion of NS3 reaches its minimum value. Moreover,
Fig. 4. Original SEM images and binarized images at 500× magnification processed by Image-ProPlus6.0 analysis software of CMK cement soil at 28d.
the proportion of holes decreases with increasing Na$_2$SO$_4$ solution concentration, reaching a minimum in sample NS4. This indicates that the Na$_2$SO$_4$ solution environment changes the pore distribution of the CMK cement soil, accounting for the change in porosity, and ultimately leading to a difference in strength.

Table 5. Mix proportions for the preparation of CMK cement soil samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of various pore areas in the total pore area /%</th>
<th>Porosity /%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;2 μm</td>
<td>2 μm~5 μm</td>
</tr>
<tr>
<td>NS0</td>
<td>3.32</td>
<td>29.96</td>
</tr>
<tr>
<td>NS1</td>
<td>3.55</td>
<td>28.73</td>
</tr>
<tr>
<td>NS2</td>
<td>4.31</td>
<td>27.94</td>
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<tr>
<td>NS3</td>
<td>4.53</td>
<td>26.52</td>
</tr>
<tr>
<td>NS4</td>
<td>4.24</td>
<td>28.28</td>
</tr>
</tbody>
</table>

Conclusions

In this study, CMK was used as a cement-soil additive, and its strength characteristics in an Na$_2$SO$_4$ solution environment were determined. The Na$_2$SO$_4$ solution concentration was varied to determine the influence of the Na$_2$SO$_4$ solution concentration on the compressive strength of CMK cement soil. Based on the laboratory results, the following conclusions could be drawn:

1. The compressive strength of the CMK cement soil cured in different concentrations of Na$_2$SO$_4$ solution differed. When the Na$_2$SO$_4$ solution concentration was 18 g/L, the compressive strength of the CMK cement soil reached its maximum value.
2. In the Na$_2$SO$_4$ solution environment, the albite generated by the reaction contributed to the ion-exchange reaction owing to the presence of Na$^+$, making the soil particle structure unit of the CMK cement soil more compact and increasing its strength.
3. In the Na$_2$SO$_4$ solution environment, ettringite generated by the reaction had a dual effect. When the Na$_2$SO$_4$ solution concentration was appropriate, the ettringite had certain filling and expansion effects on the CMK cement soil due to the presence of SO$_4^{2-}$.
4. The Na$_2$SO$_4$ solution changed the pore distribution in the CMK cement soil, leading to a change in its porosity, causing a change in its strength.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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