**RESEARCH**

# Sulfate diffusion in coal pillar: experimental data and prediction model

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## Abstract

The stability of coal pillar dams is crucial for the long-term service of underground reservoirs storing water or heat. Chemical damage of coal dams induced by ions-attacking in coal is one of the main reasons for the premature failure of coal dams. However, the diffusion process of harmful ions in coal is far from clear, limiting the reliability and durability of coal dam designs. This paper investigates sulfate diffusion in coal pillar through experimental and analytical methods. Coal specimens are prepared and exposed to sulfate solutions with different concentrations. The sulfate concentrations at different locations and time are measured. Based on experimental data and Fick's law, the time-dependent surface concentration of sulfate and diffusion coefficient are determined and formulated. Further, an analytical model for predicting sulfate diffusion in coal pillar is developed by considering dual time-dependent characteristics and Laplace transformations. Through comparisons with experimental data, the accuracy of the analytical model for predicting sulfate diffusion is verified. Further, sulfate diffusions in coal dams for different concentrations of sulfate in mine water are investigated. It has been found that the sulfate concentration of exposure surface and diffusion coefficient in coal are both time-dependent and increase with time. Conventional Fick's law is not able to predict the sulfate diffusion in coal pillar due to the dual time-dependent characteristics. The sulfate attacking makes the coal dam a typical heterogeneous gradient structure. For sulfate concentrations 0.01–0.20 mol/L in mine water, it takes almost 1.5 and 4 years for sulfate ions to diffuse 9.46 and 18.92 m, respectively. The experimental data and developed model provide a practical method for predicting sulfate diffusion in coal pillar, which helps the service life design of coal dams.

**Keywords** Sulfate diffusion · Coal dam · Underground reservoirs · Time-dependent · Analytical model · Chemical damage

## 1 Introduction

Coal mining leaves huge underground void spaces that have a great potential for the storage of water (Menéndez et al. 2019; Li 2021; Zhang et al.2021a, b; Ma et al. 2022). In recent 20 years, more than 30 coal mine underground reservoirs with a water storage capacity of about 25 million m[3] have been constructed in western China, which significantly benefits the environment and local community in the water-shortage areas (Gu et al. 2021). In the UK, the approximate mass of water lying in abandoned coal mines was 2.79 billion tonnes which can be used for heat storage (Gluyas et al. 2020). Coal dams or pillars are the main load-bearing structures for underground spaces after mining. Coal pillars are normally considered as short-term structures for conventional mining (Wang et al. 2021a, b). However, the utilization of underground spaces after coal mining for water and heat storage poses a huge challenge for the long-term stability of coal pillars or dams, especially bearing in mind water-coal interaction (Bian et al. 2021; Liu et al.2021; Liu et al. 2022a, b; Liu et al.2022a, b).

Figure 1 illustrates a schematic diagram for underground water reservoir in a coal mine. After coal seam is subtracted, mining goaf is formed. Coal pillars and reinforced concrete

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**Fig. 1** Schematic diagram for underground water reservoir
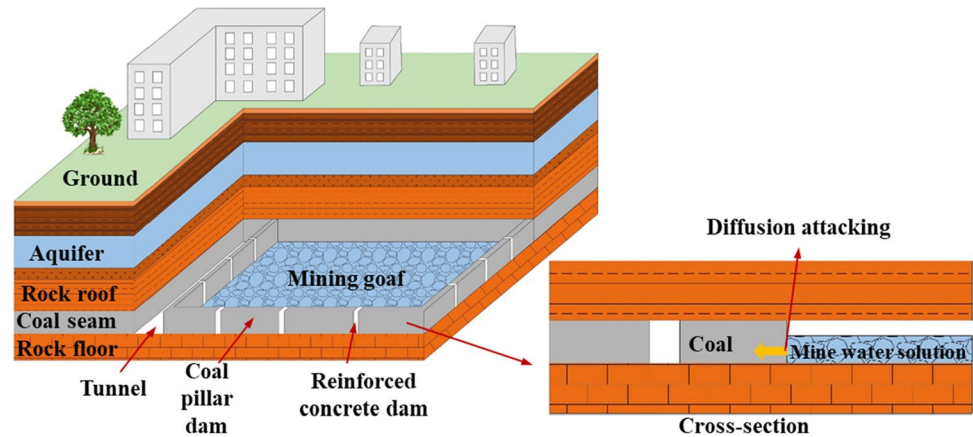


structures are grouped as the dams of water reservoir (Song et al. 2020). Gu (2015) developed a theoretical framework for the design of underground water reservoir and proposed that the elastic zone of coal pillar as a dam must be at least twice the height of the coal pillar. Li et al. (2017) proposed an evaluation method for the suitability of underground water reservoir based on the height of water conduction fracture zone in coal mines. Yao et al. (2019) developed an elastic–plastic model for the design of coal dam width with considerations of upper pressure, water pressure and water content in coal. Liu et al. (2019) assessed the suitability for the construction of underground water reservoir in 14 abandoned mines in Xuzhou city and found that 6 of them were suitable for emergency water supply in urban settings. The theoretical models and frameworks provided key references for the construction of underground water reservoir (Fan and Ma 2018).

With the service time increasing for coal dam in underground water reservoir, the degradation and failure of coal dam have attracted attentions (Wang et al. 2019). Yao et al. (2020) investigated water immersion in coal dam by placing dry coal samples under saturated humidity conditions and found that moisture content in coal was stable at about 22% after 80 h when the shear strength reduced by about 15%. Zhang et al. (2021a, b) analysed the failure mechanisms of coal dam in underground water reservoir and found coal softening induced by water was one of the main reasons for coal dam failure. Ai et al. (2021) tested the pore structure and mechanical properties of coal soaking into water for 3 h to 20 days and found as the water soaking time increased, the average pore sizes expanded and new pores developed. Moreover, the compressive strength and elastic modulus decreased by 20% when the coal was soaked for 100 h. Through considering more factors affecting the stability of coal dam, the underground water reservoir has been more reliable.

Mine water is a complex aqueous solution with chemical ions which unavoidably attack the coal pillar. Balucan et al.

(2016) investigated the microstructures of coal treated by acid solution and found the porosity of coal was improved due to the dissolution of kaolinite. Yang et al. (2021) investigated the effect of acetic acid on coal structure and found that acetic acid was sensitive to kaolinite and aromatic hydrocarbons in coal. Xu et al. (2021) investigated the effects of acid and alkali on the erosion effect of coal and found the higher the concentration of the solution, the more pronounced the erosion effect on the coal. Li et al. (2020) discussed the mechanical properties and failure characteristics of coal rock with different combinations of acid solutions and found and hydrofluoric acid can effectively dissolve minerals containing kaolinite and calcite. Wang et al. (2021a, b) carried out experiments on coal deterioration induced by sulfate attacking and found the strength can be reduced by 50% for coal with 0.4% of sulfate ion. Therefore, chemical ions in mine water have significant effects on the microstructures and mechanical properties of coal dam.

Coal mine water is normally rich in sulfate because most coal deposits contain a variety of sulfides (0.5%–3.0%) (Finkelman et al. 2019). Sulfate ions induced coal damage is driven by the sulfate diffusion in coal, which significantly threatens the long-term performance of coal dam. However, the diffusion process of sulfate or other harmful ions in coal has rarely been investigated. Moreover, there is no suitable analytical model for predicting sulfate diffusion in coal dam. This limits durable design and accurate failure prediction of coal dam, obstructing the long-term safe service of underground water reservoirs.

This paper investigates the sulfate diffusion in coal pillar through experiments and analytical methods. Coal samples are prepared and exposed to solutions with different sulfate concentrations. The sulfate ion concentrations at different locations are measured at different exposure time. The concentration of sulfate in the exposure surface of coal and diffusion coefficient of coal are determined

based on Fick's law. Further, empirical models for surface concentration and diffusion coefficient are both formulated as a function of time and external solution concentration. A novel analytical model for describing sulfate diffusion in coal pillar is then developed by Laplace transformation considering the dual time-dependent behaviour of surface concentration and diffusion coefficient. The developed model is verified with experimental data. Finally, the sulfate diffusion process, concentration distribution and service life of a coal dam are predicted.

## 2 Experimental program

Coal samples from Lingxin Coal Mine located in Ningdong mining area where the sulphate content in the mine water solution is high were prepared. The dimensions of the sample were 200 mm in length $\times$ 100 mm in width $\times$ 75 mm in height and the direction of sulfate diffusion was along the length. The sulfate diffusion in coal pillar dam is a typical one-dimensional diffusion process, i.e., from the mine water in mine goaf to the tunnel along the coal dam width direction (Fig. 1). To model the one-dimensional diffusion process, only one surface was set as a diffusion surface while other surfaces were coated with epoxy resin which prevents sulfate diffusion (Fig. 2). The sulfate concentration in mine water is normally varying from geochemistry conditions. To cover a wide range of sulfate concentration and accelerate sulfate diffusion, the sulfate concentrations in water solution were prepared as 0.1 mol/L, 0.5 mol/L and 1 mol/L, respectively. The coal samples were exposed to the prepared sulfate solutions for 30 days. Coring and grinding were carried out along the sample with 2 cm spacing to obtain the coal powder on days 1, 3, 5, 7, 10, 10, 15, 20 and 30, respectively. Figure 2 shows a typical cored sample. The sulfate ion concentration in the coal powder was measured by Dionex ICS-900 Ion Chromatography at the University of Science and Technology Beijing. With the measured concentrations of sulfate ion in coal exposed to different sulfate solutions at different time and locations, the sulfate diffusion process can be analysed.

## 3 Experimental results

### 3.1 Experimental data

The concentration values of sulfate ions in coal exposed to different sulfate solutions are given in Table 1. The concentration was expressed as the mass percentage and 120 concentration values were obtained in total. It can be seen that, the concentration of sulfate ion varied with time, distance and external solution from 0.026% to 0.675%. Figure 3 illustrates the sulfate ion concentration of coal at different locations on day 1. The distance is the diffusion depth or length from the surface of coal specimen. It can be found that, the longer the distance is, the smaller the concentration of sulfate ion is. Moreover, the larger the sulfate concentrate in the external solution is, the larger the concentration in coal is. Figure 4 shows the concentration of sulfate ion in coal as a function of exposure time at the distance of 9 cm. It can be seen that, with the diffusion time increasing, the concentration first increases rapidly then is close to lineally increase. This is because the concentration difference in coal and solution is initially large then gradually decreases. In addition, the larger the solution concentration is, the larger the concentration of sulfate in coal is. Therefore, sulfate diffusion in coal pillar is a typical time-dependent process affected by external solution concentration.

### 3.2 Determination of surface concentration and diffusion coefficient by Fick's law

In 1855, Fick (1855) first derived the now well-known Fick's law for diffusion process (movement of molecules from higher concentration to lower concentration) which can be expressed as follows:

$$J = -D\frac{d\varphi}{dx} \tag{1}$$

where, $J$ is the diffusion flux; $D$ is the diffusion coefficient; $\varphi$ is the concentration; $x$ is the location or position, the dimension of which is diffusion length.

It is clear that, Fick's first law (Eq. (1)) postulates that the diffusion flux goes from areas with high concentration to areas with low concentrations and the magnitude is proportional to



**Fig. 2** Coal sample preparation and coring

**Table 1** Concentration of sulfate ions in coal exposed to sulfate solution

| Time (d) | Distance (cm) | Concentration (%) for solution 0.1 mol/L | Concentration (%) for solution 0.5 mol//L | Concentration (%) for solution 1 mol/L |
|---|---|---|---|---|
| 1 | 1 | 0.198 | 0.211 | 0.255 |
| | 3 | 0.114 | 0.146 | 0.204 |
| | 5 | 0.057 | 0.083 | 0.145 |
| | 7 | 0.035 | 0.059 | 0.095 |
| | 9 | 0.026 | 0.029 | 0.068 |
| 3 | 1 | 0.224 | 0.246 | 0.270 |
| | 3 | 0.196 | 0.219 | 0.248 |
| | 5 | 0.155 | 0.183 | 0.210 |
| | 7 | 0.121 | 0.153 | 0.180 |
| | 9 | 0.093 | 0.125 | 0.160 |
| 5 | 1 | 0.286 | 0.316 | 0.347 |
| | 3 | 0.256 | 0.284 | 0.320 |
| | 5 | 0.221 | 0.268 | 0.299 |
| | 7 | 0.204 | 0.238 | 0.273 |
| | 9 | 0.172 | 0.201 | 0.243 |
| 7 | 1 | 0.330 | 0.332 | 0.376 |
| | 3 | 0.300 | 0.319 | 0.359 |
| | 5 | 0.273 | 0.294 | 0.333 |
| | 7 | 0.256 | 0.263 | 0.306 |
| | 9 | 0.221 | 0.231 | 0.289 |
| 10 | 1 | 0.357 | 0.378 | 0.401 |
| | 3 | 0.324 | 0.356 | 0.388 |
| | 5 | 0.308 | 0.343 | 0.368 |
| | 7 | 0.288 | 0.320 | 0.342 |
| | 9 | 0.279 | 0.292 | 0.329 |
| 15 | 1 | 0.369 | 0.396 | 0.437 |
| | 3 | 0.351 | 0.385 | 0.422 |
| | 5 | 0.342 | 0.352 | 0.406 |
| | 7 | 0.318 | 0.343 | 0.385 |
| | 9 | 0.303 | 0.333 | 0.376 |
| 20 | 1 | 0.403 | 0.448 | 0.519 |
| | 3 | 0.385 | 0.433 | 0.506 |
| | 5 | 0.373 | 0.417 | 0.487 |
| | 7 | 0.360 | 0.396 | 0.469 |
| | 9 | 0.343 | 0.387 | 0.454 |
| 30 | 1 | 0.465 | 0.517 | 0.675 |
| | 3 | 0.455 | 0.496 | 0.657 |
| | 5 | 0.446 | 0.489 | 0.643 |
| | 7 | 0.422 | 0.470 | 0.624 |
| | 9 | 0.407 | 0.466 | 0.611 |

the concentration gradient. Further, Fick's second law can be derived from Fick's first law for describing the concentration change with respect to time and location, which can be expressed by a partial differential equation as follows (Tang and Gulikers 2007):

$$\frac{\partial \varphi(x,t)}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} \tag{2}$$

where $\varphi(x, t)$ is the concentration at location $x$ and time $t$.

The boundary condition and initial value of the diffusion problem in the coal sample exposed to sulfate solution can be described as follows, respectively:
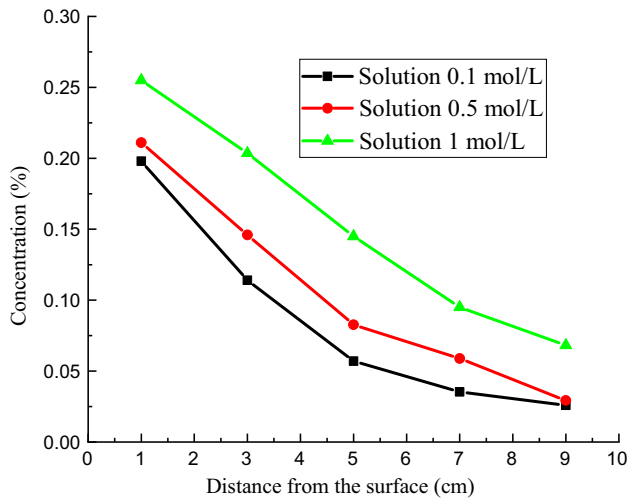
$$\varphi(0, t) = \varphi_s \tag{3}$$

**Fig. 3** Concentration of sulfate ion in the coal specimen being exposed 1 day
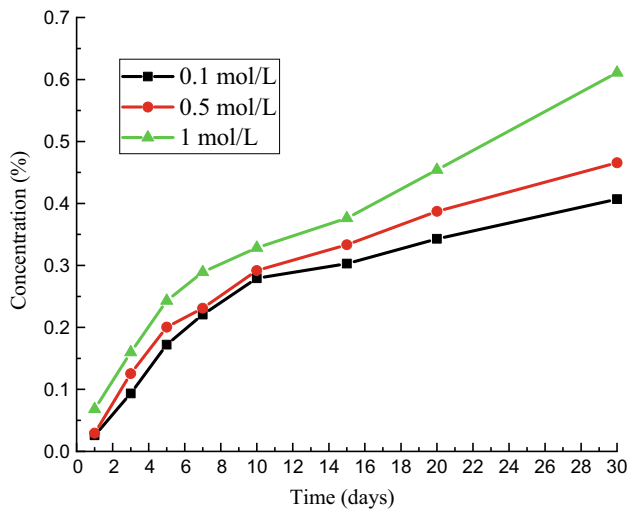


**Fig. 4** Concentration development as a function of time at the distance of 9 cm

$$\varphi(x, 0) = 0 \tag{4}$$

where $\varphi_s$ is the surface concentration that is the concentration at the surface of the coal pillar or dam exposed to the solution. It should be mentioned that, the surface concentration would be varying with exposure time. The initial concentration of sulfate ion in the coal, i.e., $\varphi(x, 0)$, is zero.

By combining Eqs. (2)-(4), the solution of Fick's second law can be derived as follows:

$$\varphi(x, t) = \varphi_s erfc\left(\frac{x}{2\sqrt{Dt}}\right) \tag{5}$$

where *erfc* is the complementary error function that can be calculated as follows:

$$erfc(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt \tag{6}$$

According to the experimental data in Table 1, the surface concentration of coal sample and diffusion coefficient can be obtained by non-linear fitting of Eq. (5). Figure 5 illustrates a typical fitting curve for coal exposed to 0.1 mol/L solution in the first 24 h. It can be seen that, the experimental data can be well described by Fick's second law. The coefficient of determination $R^2$ is 0.983. The determined surface concentration and diffusion coefficient of coal for external solution 0.1 mol/L on day 1 are 0.23% and $1.29 \times 10^{-8}$ m$^2$/s, respectively. It should be noted that, the determined diffusion coefficient by the fitting of Fick's law is an apparent diffusion coefficient representing the average diffusion during the fitted period (ASTM 2016). Table 2 shows all the determined surfaced concentration and diffusion coefficient of coal exposed different solutions for different time. It can be seen that, the surface concentration varies from 0.230% to 0.682% and the diffusion coefficient varies from $1.29 \times 10^{-8}$ to $8.19 \times 10^{-8}$ m$^2$/s.

### 3.3 Time-dependent surface concentration and diffusion coefficient

Since the surface concentration and diffusion coefficient of coal are dependent on time and solution concentration, it is necessary to establish an empirical model based on the experimental data for predicting sulfate diffusion in coal pillar. The empirical model for surface concentration is
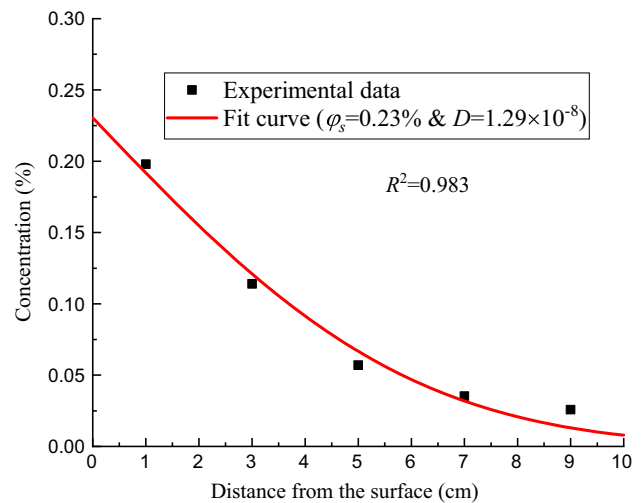


**Fig. 5** Determination of surface concentration and diffusion coefficient according to Fick's law

**Table 2** Surface sulfate concentration and diffusion coefficient for different exposure time

| Time (d) | Soultion 0.1 mol/L | | Soultion 0.5 mol/L | | Soultion 1 mol/L | |
|---|---|---|---|---|---|---|
| | Surface concentration (%) | Diffusion coefficient ($\times 10^{-8}$) | Surface concentration (%) | Diffusion coefficient ($\times 10^{-8}$) | Surface concentration (%) | Diffusion coefficient ($\times 10^{-8}$) |
| 1 | 0.230 | 1.29 | 0.342 | 1.85 | 0.289 | 3.21 |
| 3 | 0.247 | 2.03 | 0.265 | 3.05 | 0.288 | 4.27 |
| 5 | 0.300 | 3.03 | 0.332 | 3.92 | 0.361 | 5.57 |
| 7 | 0.343 | 3.33 | 0.353 | 3.73 | 0.390 | 5.95 |
| 10 | 0.359 | 5.08 | 0.390 | 4.91 | 0.414 | 6.71 |
| 15 | 0.378 | 5.04 | 0.435 | 5.67 | 0.445 | 7.63 |
| 20 | 0.409 | 5.76 | 0.456 | 5.95 | 0.529 | 7.38 |
| 30 | 0.476 | 4.97 | 0.520 | 8.04 | 0.682 | 8.19 |

consisted of a power function which can be expressed as follows:

$$\varphi_s = s_1(\varphi_{ex})^{s_2} t^{\partial} \tag{7}$$

where, $\varphi_{ex}$ is the magnitude of sulfate concentration of external solution; $t$ is the exposure time; $s_1$, $s_2$, and $\partial$ are the fitting parameters. $s_1(\varphi_{ex})^{s_2}$ can be regarded as a term of external environmental coefficient for surface concentration, which is constant for a given sulfate solution. $t$ is the magnitude of time in day. For simplification, $s_1(\varphi_{ex})^{s_2}$ can be defined as $\varphi_{s0}$.

The empirical model for diffusion coefficient is also proposed as a power function as follows:

$$D = d_1(\varphi_{ex})^{d_2} t^{\beta} \tag{8}$$

$d_1$, $d_2$, and $\beta$ are the fitting parameters. $d_1(\varphi_{ex})^{d_2}$ can be regarded as a term of external environmental coefficient for diffusion coefficient, which is also constant for a given sulfate solution. $t$ is the magnitude of time in day. For simplification, $d_1(\varphi_{ex})^{d_2}$ can be defined as $D_0$.

Figure 6 illustrates the fitted results for the surface concentration of coal by Eq. (7). $s_1$, $s_2$ and $\partial$ are 0.238, 0.098 and 0.262, respectively. The coefficient of determination $R^2$ is 0.910. Figure 7 illustrates the fitted results of the diffusion coefficient of coal by Eq. (8). $d_1$, $d_2$ and $\beta$ are $2.731 \times 10^{-8}$, 0.173 and 0.343, respectively. The coefficient of determination $R^2$ is 0.909. It can be seen that, the surface concentration and diffusion coefficient of sulfate increase with time and external solution concentration. The empirical models have good agreements with experimental data. The surface concentration and diffusion coefficient are both time-dependent and affected by the external solution concentration. The time-dependent behaviour indicates that the diffusion process of sulfate is affected by coal damage, i.e., with the chemical damage of coal accumulating, the surface concentration of coal is increased and the diffusion coefficient is improved. Therefore, the
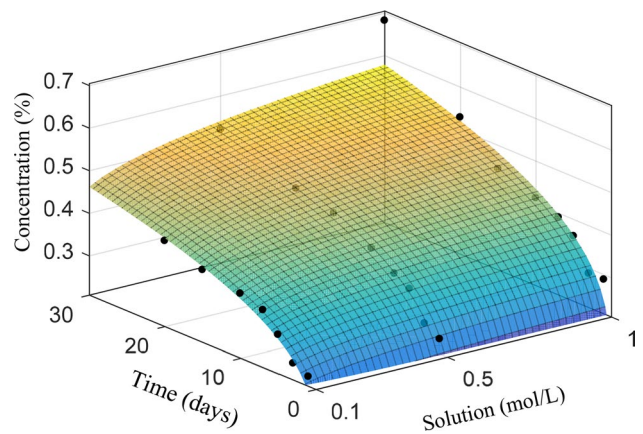


**Fig. 6** Time-dependent surface concentration and fitting results ($R^2 = 0.910$)
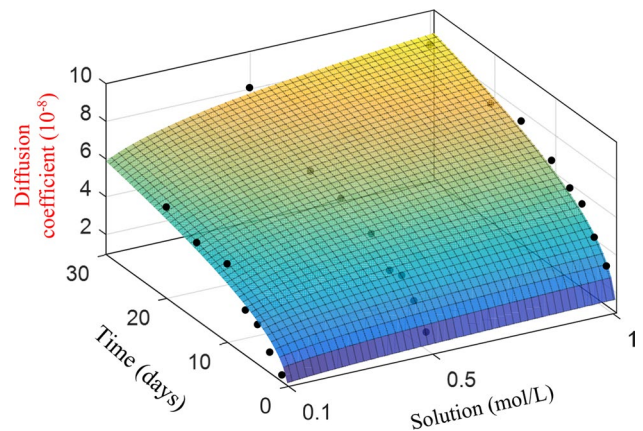


**Fig. 7** Time-dependent diffusion coefficient and fitting results ($R^2 = 0.909$)

conventional solution of Fick's second law is not able to predict the sulfate diffusion in coal pillar due to the time-dependent surface concentration and diffusion coefficient.

There is a well-justified need to develop a predict model for dual time-dependent diffusion of sulfate in coal.

## 4 Prediction model and verification

### 4.1 Dual time-dependent analytical model

According to Fick's second law and the empirical models for surface concentration and diffusion coefficient, the following equations can be obtained for describing sulfate diffusion in coal pillar as follows (Tang and Gulikers 2007):

$$\begin{cases} \frac{\partial \varphi(x,t)}{\partial t} = D(t)\frac{\partial^2 \varphi(x,t)}{\partial x^2} \\ \varphi(0,t) = \varphi_s(t) \\ \varphi(x,0) = 0 \end{cases} \tag{9}$$

where $D(t)$ and $\varphi_s(t)$ are given in Eqs. (8) and (7), respectively.

To solve the above partial differential equation, Laplace transformation method is employed (Doetsch 2012). Assume the following equation:

$$T(t) = \int_0^t t^\beta dt = \frac{t^{\beta+1}}{\beta+1} \tag{10}$$

Thus, Eq. (9) can be transformed into:

$$\begin{cases} \frac{\partial \varphi(x,T)}{\partial T} = D_0\frac{\partial^2 \varphi(x,T)}{\partial x^2} \\ \varphi(0,T) = \varphi_s(T) \\ \varphi(x,0) = 0 \end{cases} \tag{11}$$

where $\varphi_s(T)$ can be expressed as follows:

$$\varphi_s(T) = \varphi_s[(\beta+1)T]^{\frac{\alpha}{\beta+1}} \tag{12}$$

Perform Laplace transform on $T$ in $\varphi(x,T)$, it can be obtained that:

$$\overline{\varphi}(x,p) = L[\varphi(x,T)] = \int_0^\infty \varphi(x,T)e^{-pT}dT \tag{13}$$

where $p$ is a complex variable in Laplace transform

Thus, Eq. (11) can be transformed into:

$$\begin{cases} p\overline{\varphi}(x,p) = D_0\frac{d^2\overline{\varphi}(x,p)}{dx^2} \\ \overline{\varphi}(0,p) = \overline{\varphi}_s(p) \\ \varphi(x,0) = 0 \end{cases} \tag{14}$$

where $\overline{\varphi}_s(p)$ can be expressed as follows:

$$\overline{\varphi}_s(p) = L[\varphi_s(T)] = \varphi_s(\beta+1)^{\frac{\alpha}{\beta+1}}L\left[T^{\frac{\alpha}{\beta+1}}\right] \tag{15}$$

According to the table of Laplace Transforms, $L\left[T^{\frac{\alpha}{\beta+1}}\right]$ can be expressed as a gamma function as follows:

$$L\left[T^{\frac{\alpha}{\beta+1}}\right] = \frac{\Gamma\left(\frac{\alpha}{\beta+1}+1\right)}{p^{\frac{\alpha}{\beta+1}+1}} = \frac{\frac{\alpha}{\beta+1}\Gamma\left(\frac{\alpha}{\beta+1}\right)}{p^{\frac{\alpha}{\beta+1}+1}}, \frac{\alpha}{\beta+1} > -1 \tag{16}$$

Substituting Eq. (16) into Eq. (15), $\overline{\varphi}_s(p)$ can be expressed as follows:

$$\overline{\varphi}_s(p) = \varphi_s(\beta+1)^{\frac{\alpha}{\beta+1}}\frac{\frac{\alpha}{\beta+1}\Gamma\left(\frac{\alpha}{\beta+1}\right)}{p^{\frac{\alpha}{\beta+1}+1}} \tag{17}$$

The general solution of Eq. (14) can be obtained as follows:

$$\overline{\varphi}(x,p) = Ae^{-x\sqrt{\frac{p}{D_0}}} + Be^{x\sqrt{\frac{p}{D_0}}} \tag{18}$$

If the location of coal is far from the exposure surface, i.e., $x \to \infty$, the sulfate concentration is zero. Therefore, $\overline{\varphi}(x,p)$ can be derived as follows:

$$\overline{\varphi}(x,p) = \overline{\varphi}_s(p)e^{-x\sqrt{\frac{p}{D_0}}} \tag{19}$$

The inverse Laplace transform of $\overline{\varphi}(x,p)$ can be obtained as follows:

$$\varphi(x,p) = L^{-1}\left[\overline{\varphi}(x,p)\right] = L^{-1}\left[\overline{\varphi}_s(p)e^{-x\sqrt{\frac{p}{D_0}}}\right] \tag{20}$$

Substituting Eq. (17) into Eq. (20), the sulfate distribution $\varphi(x,p)$ can be expressed as follows:

$$\varphi(x,p) = L^{-1}\left[\varphi_s(\beta+1)^{\frac{\alpha}{\beta+1}}\frac{\frac{\alpha}{\beta+1}\Gamma\left(\frac{\alpha}{\beta+1}\right)}{p^{\frac{\alpha}{\beta+1}+1}}e^{-x\sqrt{\frac{p}{D_0}}}\right] \tag{21}$$

Let $m = \varphi_s(\beta+1)^{\frac{\alpha}{\beta+1}}$ and $n = \frac{\alpha}{\beta+1}$, Eq. (21) can be changed as follows:

$$\varphi(x,p) = L^{-1}\left[m\frac{n\Gamma(n)}{p^{n+1}}e^{-x\sqrt{\frac{p}{D_0}}}\right] \tag{22}$$

Further, the above equation can be transformed into:

$$\varphi(x,p) = mnL^{-1}\left[\frac{\Gamma(n)}{p^n}\frac{1}{p}e^{-x\sqrt{\frac{p}{D_0}}}\right] \tag{23}$$

According to the table of Laplace transform, it can be obtained that:

$$L^{-1}\left[\frac{\Gamma(n)}{p^B}\right] = T^{n-1} \tag{24}$$

$$L^{-1}\left[\frac{1}{p}e^{-x\sqrt{\frac{p}{D_0}}}\right] = erfc\left(\frac{x}{2\sqrt{D_0T}}\right) \tag{25}$$

Therefore, according to the convolution theorem of Laplace transform (Doetsch 2012), $\varphi(x, T)$ can be expressed as follows:

$$\varphi(x, T) = mn \int_0^T \tau^{n-1} erfc\left(\frac{x}{2\sqrt{D_0(T-\tau)}}\right) d\tau \tag{26}$$

Equation (26) is just the analytical model for predicting dual time-dependent diffusion of sulfate in coal. Next, the model would be verified with experimental data and used to predict sulfate diffusion in underground coal dam.

## 4.2 Verification with experimental data

With the parameters $m$, $n$ calculated from experimental results, the dual time-dependent model was used to predict the sulfate concentration in coal sample. The calculated results were compared with experimental data. Figure 8 illustrates a typical example from the model and experiments for external solution 0.5 mol/L and location 5 cm. It can be seen that, with time increasing, the sulfate concentration gradually increased. The predicted concentration from the analytical model has a good agreement with experimental data. Further, all the predicted data and its error with experimental results are given in Table 3. It can be found that, the average error for solution 0.1 mol/L, 0.5 mol/L and 1.0 mol/L are 16.25%, 9.45% and 15.37%, respectively. Moreover, the errors for 80% of data points are smaller than 20%. The relative large errors occur for data on day 1 because the concentrations are very small. Therefore, the developed model can well predict sulfate diffusion in coal pillar considering both time-dependent diffusion coefficient and surface concentration. It should be mentioned that, the
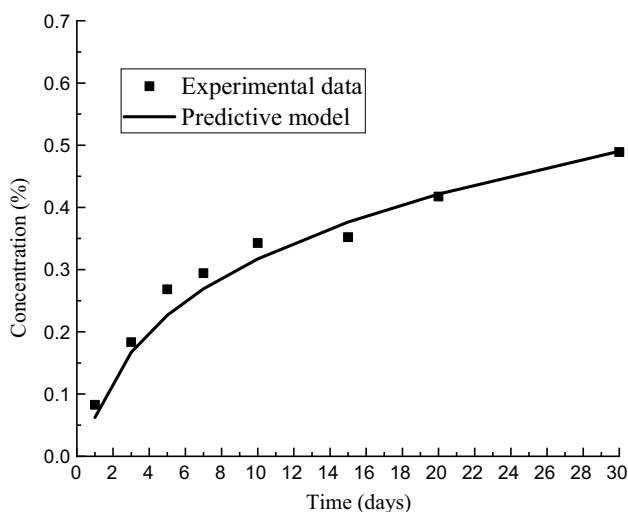
developed model can also be used to predict other ions diffusion in coal.

## 5 Predicting sulfate diffusion in coal pillar dam

The sulfate concentration in mine water varies from mining regions, mines and working faces, e.g., 0.05–0.18 mol/L in Shendong mining region (Zhou and Wang 2017), 0.12 mol/L in Lingxin coal mine (Wang et al. 2021a, b) and 0.17 mol/L in Ningdong mining region (Jiang et al. 2020). Thus, the sulfate concentrations in mine water are set as 0.01, 0.05, 0.10 and 0.20 mol/L for discussions. The coal dam width $W$ is considered as 18.92 m with reference to (Yao et al. 2019). Figure 9 illustrates the sulfate concentration development as a function of time at the middle of the coal dam ($x = 0.5W$). It can be seen that, with the service time of coal dam increasing, the sulfate gradually diffuses into the coal dam and the concentrations at the middle of the coal dam are almost zero before 1.5 years then are close to linearly increase. The larger the mine water concentration of sulfate is, the larger the sulfate concentration in coal is. For the mine water with sulfate concentrations 0.01 mol/L, 0.05 mol/L, 0.1 mol/L and 0.2 mol/L, the sulfate concentrations at the middle of coal dam serviced 10 years are 0.36%, 0.52%, 0.60% and 0.69%, respectively. Figure 10 shows the sulfate concentration at the end surface of coal dam ($x = W$). It can be found that, the concentrations at the end surface of coal dam are almost zero before 4 years then non-linearly increase. From 0 to 10 years, the concentration increasing rates first are zero then increase but finally are almost constant. For the mine water with sulfate concentrations 0.01, 0.05, 0.10 and 0.20 mol/L, the sulfate concentrations at the end surface of coal dam serviced 10 years are 0.05%, 0.11%, 0.14% and 0.19%, respectively. In general, it takes almost 1.5 and 4 years for sulfate ions reaching the middle and end of coal dam, respectively.

The sulfate concentration distribution in the dam significantly affects the deterioration and structural bearing capacity of coal dam. Figure 11 illustrates the distribution of sulfate concentration in the coal dam in the 5th year. It can be seen that, the further the coal from the exposure surface, the sulfate concentration is smaller. From the end surface to the exposure surface, the concentration gradients gradually increase. For the mine water with sulfate concentrations 0.01 to 0.20 mol/L, the concentrations in coal dam from the exposure surface 12.00 m to 18.92 m are similar in the 5th year. Therefore, the coal dam attacked by sulfate is a typical heterogeneous gradient structure. With the service time increasing, the closer the coal is to the mine water with rich sulfate ions, the deterioration of coal is more significant.

**Fig. 8** Comparisons of the data from experiments and analytical model for solution 0.5 mol/L and location 5 cm

**Table 3** Concentration of sulfate ions from the analytical model and errors

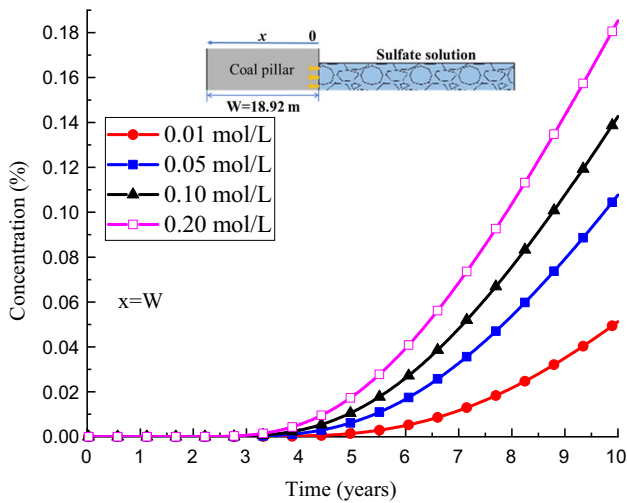| Time (d) | Distance (cm) | Solution 0.1 mol/L | | Solution 0.5 mol//L | | Solution 1 mol/L | |
|---|---|---|---|---|---|---|---|
| | | Model | Error (%) | Model | Error (%) | Model | Error (%) |
| 1 | 1 | 0.135 | 31.86 | 0.163 | 22.74 | 0.177 | 30.76 |
| | 3 | 0.079 | 30.28 | 0.105 | 28.05 | 0.118 | 42.23 |
| | 5 | 0.042 | 27.12 | 0.062 | 24.88 | 0.073 | 49.86 |
| | 7 | 0.019 | 45.95 | 0.033 | 43.16 | 0.041 | 56.34 |
| | 9 | 0.008 | 70.37 | 0.016 | 44.19 | 0.022 | 68.13 |
| 3 | 1 | 0.210 | 6.06 | 0.250 | 1.49 | 0.269 | 0.47 |
| | 3 | 0.168 | 14.42 | 0.206 | 5.84 | 0.225 | 9.47 |
| | 5 | 0.130 | 15.98 | 0.167 | 8.80 | 0.185 | 11.67 |
| | 7 | 0.099 | 18.21 | 0.133 | 12.85 | 0.150 | 16.58 |
| | 9 | 0.072 | 22.42 | 0.104 | 17.39 | 0.119 | 25.36 |
| 5 | 1 | 0.252 | 11.68 | 0.298 | 5.66 | 0.320 | 7.75 |
| | 3 | 0.216 | 15.76 | 0.261 | 7.94 | 0.283 | 11.52 |
| | 5 | 0.182 | 17.38 | 0.227 | 15.49 | 0.248 | 16.99 |
| | 7 | 0.152 | 25.54 | 0.195 | 18.23 | 0.216 | 21.02 |
| | 9 | 0.125 | 27.40 | 0.166 | 17.28 | 0.186 | 23.43 |
| 7 | 1 | 0.283 | 14.30 | 0.334 | 0.48 | 0.358 | 4.87 |
| | 3 | 0.250 | 16.41 | 0.301 | 5.79 | 0.325 | 9.58 |
| | 5 | 0.220 | 19.58 | 0.269 | 8.47 | 0.293 | 12.08 |
| | 7 | 0.191 | 25.27 | 0.240 | 9.02 | 0.263 | 13.90 |
| | 9 | 0.165 | 25.27 | 0.212 | 8.21 | 0.235 | 18.72 |
| 10 | 1 | 0.319 | 10.63 | 0.375 | 0.86 | 0.402 | 0.12 |
| | 3 | 0.290 | 10.52 | 0.345 | 2.96 | 0.372 | 4.04 |
| | 5 | 0.262 | 15.01 | 0.317 | 7.37 | 0.344 | 6.44 |
| | 7 | 0.236 | 18.30 | 0.290 | 9.15 | 0.317 | 7.36 |
| | 9 | 0.211 | 24.49 | 0.265 | 9.22 | 0.291 | 11.43 |
| 15 | 1 | 0.363 | 1.57 | 0.427 | 7.80 | 0.457 | 4.56 |
| | 3 | 0.338 | 3.64 | 0.401 | 4.33 | 0.432 | 2.37 |
| | 5 | 0.314 | 8.19 | 0.376 | 6.86 | 0.407 | 0.26 |
| | 7 | 0.290 | 8.83 | 0.353 | 2.69 | 0.383 | 0.66 |
| | 9 | 0.268 | 11.68 | 0.329 | 1.18 | 0.359 | 4.47 |
| 20 | 1 | 0.398 | 1.18 | 0.467 | 4.23 | 0.500 | 3.64 |
| | 3 | 0.375 | 2.57 | 0.444 | 2.44 | 0.477 | 5.65 |
| | 5 | 0.353 | 5.29 | 0.422 | 1.02 | 0.455 | 6.73 |
| | 7 | 0.331 | 7.88 | 0.400 | 1.05 | 0.433 | 7.82 |
| | 9 | 0.310 | 9.44 | 0.378 | 2.30 | 0.411 | 9.46 |
| 30 | 1 | 0.452 | 2.79 | 0.530 | 2.44 | 0.567 | 15.99 |
| | 3 | 0.432 | 5.01 | 0.510 | 2.77 | 0.547 | 16.72 |
| | 5 | 0.413 | 7.41 | 0.490 | 0.25 | 0.528 | 17.90 |
| | 7 | 0.394 | 6.62 | 0.471 | 0.13 | 0.508 | 18.55 |
| | 9 | 0.375 | 7.80 | 0.452 | 2.87 | 0.489 | 19.91 |
| Total average error | | | 16.25 | | 9.45 | | 15.37 |

For the design and stability analysis of coal dam, the gradient mechanical performance should be considered.

To predict the service life of coal dam induced by sulfate attacking, a preliminary method is proposed. The basic assumptions are given as follows: (1) With reference to previous mechanical tests on coal soaking in sulfate solution (Wang et al. 2021a, b), the critical sulfate concentration in coal is assumed as 0.4% with which the strength of coal can be reduced by 50%. (2) For simplification, the coal dam will be out of service if half of the dam loses its
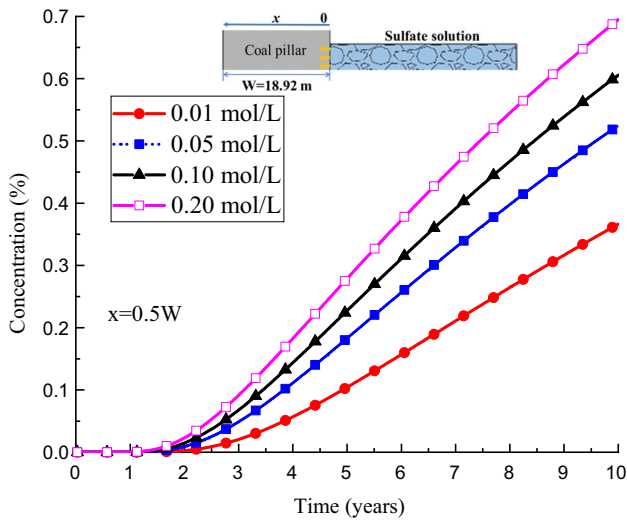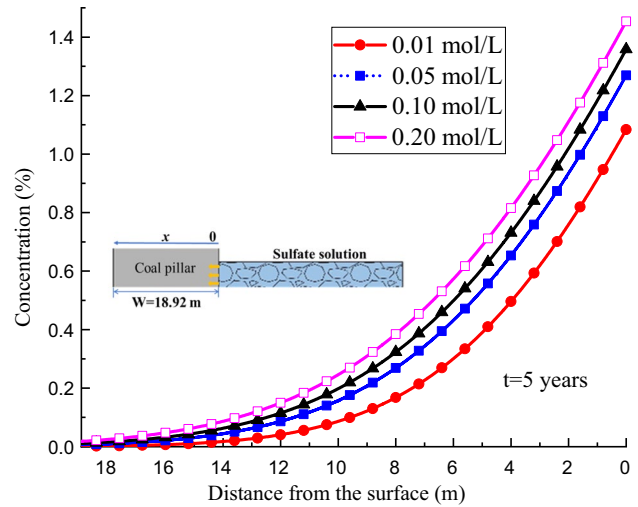
**Fig. 9** Concentration development as a function of time at the distance of half width of the coal dam
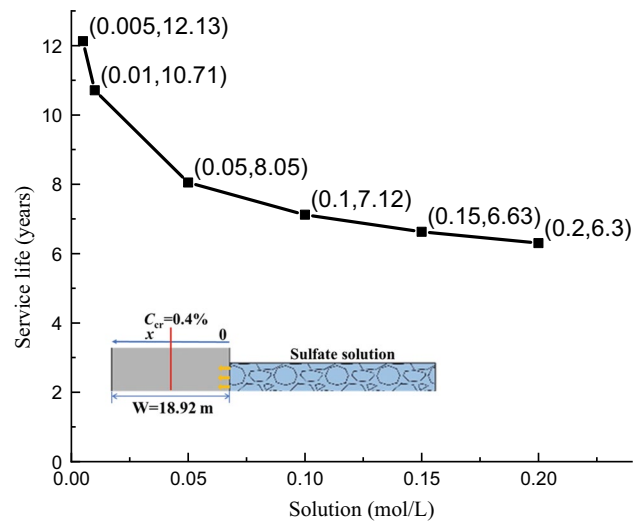


**Fig. 11** Concentration distribution in the coal dam in the 5th year



**Fig. 10** Concentration development as a function of time at the distance of coal dam width



**Fig. 12** Service life for coal dam affected by the sulfate in mine water

50% strength. Based on the above assumptions, the critical failure time of coal dam can be predicted. Figure 12 shows the critical failure time for different concentrations of sulfate in mine water. It can be seen that, the larger the sulfate concentration in mine water is, the earlier the coal dam failure occurs. When the sulfate concentration in mine water is increased from 0.005 to 0.200 mol/L, the service life of coal dam decreases by about 50% from 12.13 to 6.30 years. Moreover, the change of service life is more sensitive for relatively smaller concentration in mine water, i.e., the change rate for mine water with 0.005 to 0.05 mol/L sulfate is larger. Therefore, for coal dam in mines with sulfate mine water, the long-term performance

and service life are significantly affected by the diffusion and attacking of sulfate. It should be mentioned that, the service criterion of coal dam in the above discussion is simplified but the employed method can be a reference for long-term service prediction of underground water reservoir considering the ions-attacking coal dam.

## 6 Conclusions

This paper investigated sulfate diffusion in coal pillar through experiments that obtained the sulfate concentrations at different locations and time. The time-dependent surface concentration of sulfate and diffusion coefficient were determined and formulated. Further, an analytical

model for predicting sulfate diffusion in coal pillar was developed by considering dual time-dependent characteristics and Laplace transformations. The analytical model was then verified with experimental data. Further, sulfate diffusions in coal dam for different concentrations of sulfate in mine water were investigated. Finally, the service life of coal dam was preliminarily discussed. Conclusions are drawn as follows:

(1) The concentrations of sulfate in coal exposed to sulfate solution increase with time. The closer the location to the exposure surface, the concentration is larger. The larger the concentration in external solution, the larger the concentration in coal is.

(2) The sulfate concentration of exposure surface and diffusion coefficient in coal are both time-dependent and increasing with time. Empirical models for the time-dependent surface concentration and diffusion coefficient are obtained as power functions in which parameters are determined by non-linear fitting of Fick's law.

(3) Conventional Fick's law is not able to predict the sulfate diffusion in coal pillar due to the dual time-dependent characteristics. A novel analytical model is developed by Laplace transforms and Fick's law. The model can well predict sulfate diffusion in coal pillar and be used for coal dam design and long-term performance prediction.

(4) The sulfate attacking makes coal dam be a typical heterogeneous gradient structure. For sulfate concentration 0.01–0.20 mol/L in mine water and coal dam width 18.92 m, it takes almost 1.5 and 4 years for sulfate ions reaching the middle and end of coal dam, respectively. If the sulfate concentration in mine water is increased from 0.005 to 0.200 mol/L, the service life of the coal dam decreases by about 50% from 12.13 to 6.30 years.

## Declarations

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