International Journal of Coal Science & Technology (2022) 9:56
https://doi.org/10.1007/s40789-022-00520-1

RESEARCH

Environmental risk assessment of industrial byproduct gypsum utilized for filling abandoned mines

XueHong Du[1] · Xiangdong Li[1] · Qiyan Feng[1] · Lei Meng[2,3] · Yue Sun[4]

Received: 3 June 2021 / Accepted: 16 June 2022

Abstract
In response to the basic policy of green and low-carbon circular development to solve resource, environmental and ecological problems, gypsum is considered to be a filling material for mine backfilling. To explore the potential risks of gypsum to the groundwater environment due to the backfilling of abandoned mines, a sequential batch leaching experiment was carried out in this paper, which used three types of industrial waste gypsum, namely, phosphorus gypsum (PG), titanium gypsum (TG) and flue gas desulfurization gypsum (FGDG). COMSOL Multiphysics 5.4 software was used to simulate and solve the migration process of the leached metal elements in the mine floor when these three gypsum types were used as filling materials to observe the concentration distributions and diffusion distances of the metal elements from these three gypsum types in the mine floor. The results show that (1) during repeated contact of the three types of industrial waste gypsum with the leaching medium, the pH levels changed, and the changes in pH affected the leaching patterns for the heavy metal elements in the gypsum. (2) Based on the concentrations of the metal elements that were leached from the three types of gypsum, it can be determined that these three types of gypsum are not classified as hazardous solid wastes, but they cannot be ruled out with regard to their risk to the groundwater environment when they are used as mine filling materials. (3) When the three types of gypsum are used as filling materials, the concentration distributions of the metal elements and their migration distances all exhibit significant changes over time. The concentration distributions, diffusion rates and migration distances of the metal elements from the different gypsum types are affected by their initial concentrations in the leachate. The maximum migration distances of Zn in the floor from the PG, FGDG and TG are 8.2, 8.1 and 7.5 m, respectively.

Keywords Industrial solid waste gypsum · Coal mine back-filling · Leaching of metal elements · Patterns of migration

1 Introduction

In China, metal or nonmetal mineral assets have a large outputs and reserves, which are an important pillar of national economic and social development. Reasonable filling and governance of the mined-out areas in mines have become a prerequisite for the green mining of mineral resources. Filling mines has become a focus of the government's attention to the control object. Due to the large amounts of accumulated water that are stored in the mine pits, the accumulated water dissolves any harmful substances in the pits and then flows out through slope cracks or leftover abandoned roadways, which poses a very great threat to the underground and surface waters, as shown in Fig. 1. With the increasing promotion of coal mine filling and mining technology, the demand for solid waste for use in mine backfilling has also increased greatly. For example, coal gangue and fly ash are often used in mine backfilling, but the annual gangue

✉ Xiangdong Li
xdli123@126.com

[1] School of Environment Science and Spatial Informatics, China University of Mining and Technology, Xuzhou 221116, China

[2] The National and Local Joint Engineering Laboratory of Internet Application Technology On Mine, China University of Mining and Technology, Xuzhou 221008, Jiangsu Province, China

[3] IoT Perception Mine Research Center, China University of Mining and Technology, Xuzhou 221008, Jiangsu Province, China

[4] Jiangsu Vocational Institute of Architectural Technology, No. 26 Xueyuan Road, Xuzhou 221433, China

Published online: 08 August 2022

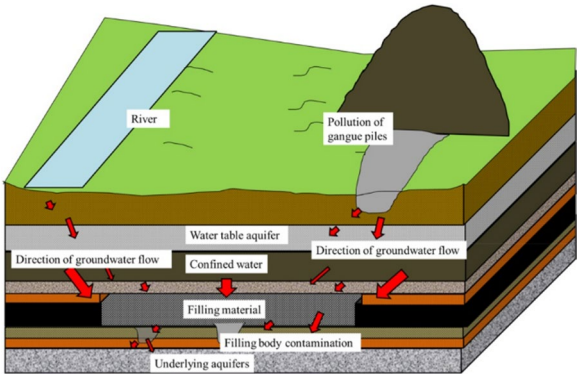

Fig. 1 Diagram of groundwater pollution in a mining area

discharges only account for 10%–20% of coal production, and an insufficient supply of filling materials that is caused by long-term filling has inevitably become a problem (Wang et al. 2019a; b; Fallgren et al. 2021).

China produces very large amounts of industrial byproduct gypsum each year. There are three main types of byproduct gypsum that are produced by industrial activities: titanium gypsum (TG), which is produced by neutralizing acidic liquid wastes with lime or calcium carbide slag during the production of sulfuric acid titanium dioxide; phosphorus gypsum (PG), which is produced by phosphorite that is eroded by sulfuric acid during the production of phosphoric acid; and flue gas desulfurization gypsum (FGDG), which is produced by removing the sulfur oxides in flue gas in most power plants in China by using the limestone gypsum method. In 2020, the total PG production was 74 Mt, which represented a yearly decrease of 1.3%, and the utilization rate was approximately 44%. The FGDG emissions from thermal power plants totaled approximately 73 Mt, which represented an increase of approximately 1%. TG emissions rank third, with an output of approximately 30 Mt, but their utilization rates were very low at approximately 8% (Yang 2021). In response to the basic policy of green and low-carbon recycling development to solve resource, environmental and ecological problems, gypsum is considered to be a filling material for mine backfilling (Al Heib et al. 2010; Li et al. 2020, 2021; Zhang et al. 2017, 2021), which not only provides an economic, safe and relatively environmentally friendly method for the large-scale disposal of solid waste but also promotes the waste-free and harmless green mining of mines. However, although the main component of the three types of gypsum is $CaSO_4 \cdot 2H_2O$, they still contain impurities. When gypsum is used to fill the goaf of a coal mine and this occurs in an acidic or alkaline mine water environment for a long period, this increases the leaching of metal elements that are contained in the gypsum and will cause a risk of migration to the mine floor and could affect the groundwater.

A number of laboratory investigations of gypsum leaching have been reported in recent decades and have provided quantitative estimates of the amounts of toxic elements released. Wei et al. (2015) used a H_2SO_4/HNO_3 mixture, deionized water and seawater for leaching treatments. When seawater was used as the leaching medium, the heavy metal concentrations that were released from titanium gypsum were the largest, especially the Mn and Hg concentrations, which were 5.0 and 34.2 times those of deionized water, respectively. In addition, the leaching concentration of an H_2SO_4/HNO_3 mixture as the leaching medium is also greater than that of deionized water, which indicates that TG has a strong ability to release heavy metals in solid–liquid leaching systems. When studying and analyzing the drainages, erosion gully waters and depression waters of a PG storage field in the karst mountainous area of Guizhou, Wang et al. (2019a, b) found that the concentrations of heavy metals such as Pb, Cd, Cr, As, and Hg exceeded Class III of the China Surface Water Environmental Standard (GB3838-2002). Water standards, erosion and PG leaching that are caused by natural rainfall are the main reasons for heavy metal migration. Zhong et al. (2018) investigated the paddy soil within 50–200 m of a PG storage yard and found that the cadmium contents in the soil reached 1.14–2.86 mg/kg, and the soil samples exceeded the soil environmental quality standard (GB15618–1995). Compared with TG and PG, the utilization rate of FGDG in China is the highest at approximately 80%. Although studies have shown that desulfurized gypsum can be used for mine backfilling, the leakage risk of pollutant elements that affects the safety of the groundwater environment cannot be ignored, especially when the desulfurized gypsum is located in a water environment. Hao et al. (2017) indicated that 25% of total Pb, 77.4% of Mn, and 51.8% of Zn occurred as easily soluble forms in the FGD gypsum from Shanxi Province. Wang et al. (2017a, b) used the column leaching mode to conduct acid leaching experiments on two samples of FGDG from power plants in Wuhan and Zhejiang. The outputs exceeded the standard limit of Class V water quality in the Groundwater Quality Standard Water (GB/T 14848–93). The highest leaching amounts of Pb, As, Cr and Ni in the sample reached 3.92, 0.11, 0.2 and 0.47 mg/L, respectively, in the leaching medium with pH = 4.0, which exceeded the maximum allowable concentrations (e.g., 0.1 mg/L). Wang et al. (2018) pointed out that the current consumption of FGDG in China is usually relatively high at approximately 20–60 t/hm^2, which may lead to excessive accumulation of contaminated elements in soil within a few years if it is used in large quantities every year.

Yang et al. (2007) considered that the contaminated elements in the fill material could penetrate into the aquifer through the mine floor rock layer via water seepage and diffusion, which would cause permanent damage to the

groundwater environment. In their research on the migration of heavy metals, scholars have paid more attention to how heavy metal elements migrate in the soil and how they accumulate in rivers and other sediments. Tabelin et al. (2019) used a coal mine as the research object and analyzed the whole process of heavy metal elements from their release to entering the soil and finally leaching into the groundwater and also established a heavy metal migration model. Jiang and Liang (2007) studied the heavy metal migration model in the saturated–unsaturated state and simulated the process of groundwater pollution of coal gangue leachates by using numerical calculations and laid a foundation for the study of pollutant migration patterns. Sui et al. (2013) studied the dispersibility and seepage characteristics of the unsaturated soil of a slag field and simulated the migration of pollutants in the slag field in unsaturated rock and a soil medium by using COMSOL Multiphysics software. This work indicates that COMSOL Multiphysics software can be used for pollutant migration simulation.

Based on the previous research foundation, the author found that (1) the types of gypsum in the industrial byproduct gypsum leaching experiment and the research conditions were relatively simple. (2) There are many studies on the use of industrial solid waste gypsum for mine backfilling, but few studies have discussed the migration process during backfilling of the metal elements contained in gypsum. Therefore, this study selects TG, PG, and FGDG as the research objects. In addition, the samples were placed in acidic, alkaline and deionized waters to analyze the leaching characteristics of the metal elements. At the same time, the coupling numerical simulation method of the seepage field and concentration field was established to explore the diffusion characteristics and migration patterns of heavy metal elements when different types of gypsum were used as filling materials. This paper will further improve the theoretical system for recycling solid waste resources in mine filling work and has a certain degree of reference significance for protecting the groundwater environment.

2 Methods

2.1 Gypsum samples

The phosphorus gypsum, titanium gypsum and FGD gypsum used in the experiment were collected from a phosphate fertilizer plant, titanium powder plant and thermal power plant, respectively. All samples were dried in a 328 K oven for 19 h before the experiment and were then screened with a 200 mesh for subsequent use. The main chemical components of the industrial waste gypsum are given in Table 1.

Table 1 Main chemical components of industrial waste gypsum

Chemical composition	Mass fraction (wt%)		
	FGDG	TG	PG
MgO	0.3	0.155	0.055
Al_2O_3	1.42	3.324	0.66
SiO_2	3.12	2.716	5.93
SO_3	44.62	40.27	53.7
CaO	31.45	40.82	36.5
Fe_2O_3	0.34	6.45	0.575
K_2O	≤ 0.4	≤ 0.1	≤ 0.4
ZrO_2	≤ 0.10	≤ 0.1	≤ 0.10
pH	8.9	8.3	5.0

2.2 Sequential batch extraction leaching

The sequential batch extraction process is performed by regularly adding fresh leaching medium in the process of the leaching experiment to simulate the leaching conditions where the disposed gypsum experiences repetitive percolation of rainwater and/or acid mine drainage (AMD) solutions with low pH and the leachate coexists with the gypsum for a considerable period of time. The repetitive extractions help us to determine the highest concentrations of each constituent that are likely to leach out into natural environments (Dutta et al. 2009).

In a typical run, 40 g of each of three gypsum samples were extracted with 200 mL of diluted H_2SO_4 (pH = 1.8 and 3.1) for one week. The gypsum was separated from the extracting medium, and fresh diluted sulfuric acid was then added and the run continued for another week. The same procedure was repeated for four cycles. The leachate from each cycle was collected, the pH of the leachate was noted, and the trace elements in the leachate were analyzed. A series of experiments was performed by using the above procedure with NaOH solutions (pH = 10.4 and 11.7).

The elemental concentrations (except As and Hg) in the leachates were determined by inductively coupled plasma emission spectrometry (ICP). The As and Hg concentrations in the leachates were estimated by using atomic fluorescence analysis (AFS).

2.3 Numerical simulation of heavy metal element migration

Taking the working face of a mining area as the research background, the length of the working face is 120 m and is nearly horizontal, and the filling goaf and the coal seam floor constitute a system of upper and lower media. The

mine floor consists of limestone with a thickness of 20 m, and the thickness of the filling area is 5 m. The model is divided into a free triangle mesh, and the mesh of the filling area is added to ensure the reliability of the results. The entire mesh consists of 2525 domain units and 265 side units. To better observe the migration of metal elements in the filling process, an observation point was defined at the middle line of the working face and at the center of the bottom of the filling area, with coordinates (60, − 6). The boundary labels of the model and the location of the observation point are shown in Fig. 2.

The subsurface flow module in the COMSOL Multiphysics software contains the most commonly used basic differential equations and boundary conditions used in calculations of seepage flow. The Darcy equation model is a general seepage equation based on Darcy's law and the continuity equation of water flow. The expression is (Whitaker 1986):

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot \rho\left[-\frac{k}{\mu}(\nabla p + \rho g \cdot \nabla D)\right] = Q_{\mathrm{m}} \tag{1}$$

where ε is the porosity, ρ is fluid density (kg/m^3), k is the permeability,μ is the fluid viscosity (Pa s), p is the pressure (Pa), D is the direction that represents vertical elevation (m), and Q_{m} is the source item.

In addition, the equation that is used in this software to describe fluid flow in saturated unsaturated porous media is the Richards equation (Bear 2012):

$$\rho\left(\frac{C_{\mathrm{w}}}{\rho g} + S_{\mathrm{c}}S\right)\frac{\partial p}{\partial t} + \nabla \cdot \rho\left[-\frac{K_s}{\mu}K_r(\nabla p + \rho g \cdot \nabla D)\right] = Q_{\mathrm{m}} \tag{2}$$

where, C_{w} is water capacity;S_{c} is effective saturation (dimensionless);$S_{\mathrm{c}} = \left(\theta_{\mathrm{s}} - \theta_{\mathrm{r}}\right)/(1\,m \cdot \rho g)$, where θ_{s} and θ_{r} denote the volume fractions of the fluid at saturation and after drainage, respectively; S is a storage coefficient (1/m); K_{s} is saturated permeability; and K_{r} is relative permeability.

Assuming that the fluid experiences seepage motion only under the action of gravity, it conforms to Darcy's law of motion (Huang et al. 2014):

$$u = -\frac{k}{\mu}\nabla p \tag{3}$$

where u is the fluid seepage velocity vector (m/s).

During the process of pollutant migration, both molecular diffusion and mechanical dispersion follow Fick's first law, and these two effects occur at the same time. Because dispersion and diffusion are difficult to distinguish, the two are generally referred to as the hydrodynamic dispersion coefficient, and the hydrodynamic dispersion equation is written as follows (Bachmat and Bear 1964):

$$\frac{\partial}{\partial x}\left(D_{\mathrm{h}}\frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x}(uC) = \frac{\partial C}{\partial t} \tag{4}$$

where D_{h} is the hydrodynamic dispersion coefficient.

2.4 Initial values and boundary conditions

Assuming that the goaf is full of water, the gravitational potential energy of the mine water produces a pressure head on the floor. Combined with the experimental results of the metal element release patterns in gypsum, Zn is taken as an example for the numerical simulation. The initial value of the inflow concentration is the final leaching concentration of Zn when deionized water is used as the leaching medium. The boundary conditions and governing equations are shown in Tables 2 and 3, respectively.

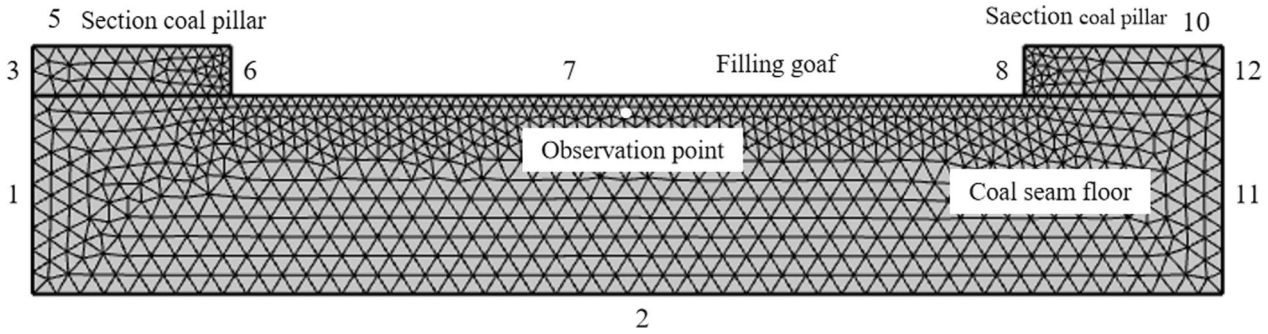

Fig. 2 Mine filling numerical subdivision model

Table 2 Setting of boundary conditions

Component	Boundary condition	Equation	Boundary label
Richards' equation (dl)	Pressure head	$H_p = \frac{p}{\rho g}$	6,8
	No flow	$-n \cdot \rho u = 0$	1,2,3,5,10,11,12
Transport of diluted species in porous media (tds)	No flux	$-n \cdot J_j = 0$	1,3,5,10,11,12
	Inflow	$c_j = c_{0,j}$	6,7,8
	Outflow	$n \cdot D_j \nabla c_j = 0$	2

Table 3 Parameters of floor in the model

Variable	Unit	Description	Value
K_s	m/d	Saturated hydraulic conductivity	1.2×10^{-7}
θ_s		Porosity/void fraction	0.25
θ_r		Residual saturation	0.01
ρ	kg/m^3	Fluid density	1×10^3
D_m	m^2/d	Coefficient of molecular diffusion	1×10^{-9}
H_p	m	Pressure head	5
μ	Pa s	Fluid viscosity	0.89×10^{-3}

3 Results

3.1 Sequential batch extraction

3.1.1 Changes in pH of the leachate

The time evolution of the leachate pH values for different leaching media (e.g., diluted H_2SO_4 pH = 1.8 and 3.1; deionized water; diluted NaOH pH = 10.3 and 11.7) at solid–liquid ratios of 1:5 is shown in Fig. 3. Leaching was conducted

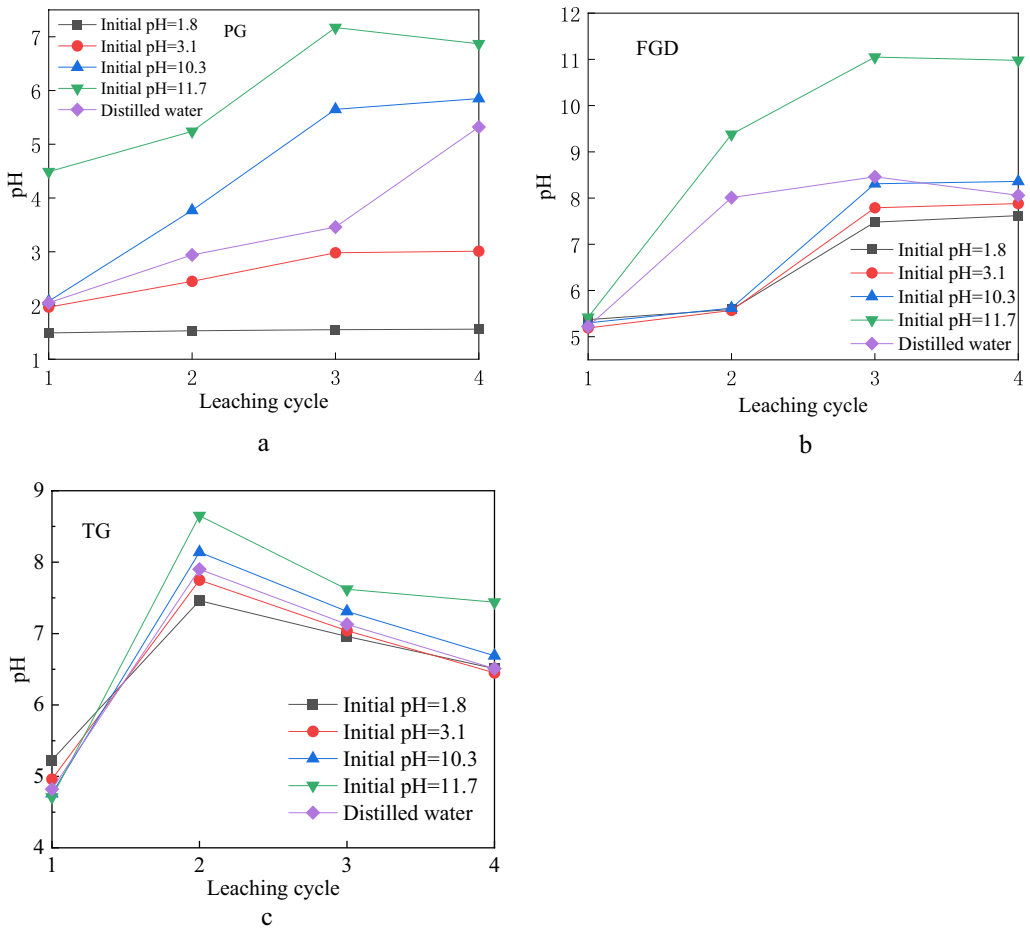

Fig. 3 Time evolution of the leachate pH during sequential batch extraction

in 4 cycles spanning a seven-day period. During the repeated contact of gypsum with the leaching medium, the leachate pH values change accordingly.

Most of the PG leachate is strongly acidic, especially the PG leachate in the first cycle, which is most acidic, with a pH range of 1.49–4.49, which indicates strong acidity, probably because both alkaline and acidic leaching media can effectively leach out the residual acidic substances in phosphorus gypsum (Chen and Mao 2007). As the time and pH of the leaching medium increase, the pH values of the leachate increased accordingly, especially under deionized water and NaOH, and the pH of the fourth cycle leachate reached a range of 5.32–6.87. However, the pH change of the leachate was not obvious when it was leached under H_2SO_4 (pH = 1.8 and 3.1), and the values at the end of the experiment were 1.56 and 3.01, respectively, and when compared with the initial pH values, only increased by 0.7 and 1.04, respectively, which indicate that the leachate pH under strong acidic conditions did not change over time (Fig. 3a). The pH changes of the FGD and titanium gypsum leachates exhibited obvious effects over time. Figure 3b shows that the pH range of the FGDG leachate in the H_2SO_4 leaching medium is 5.19–7.18, which neutralizes the acidity of H_2SO_4 and may be due to the alkalinity of FGD itself. When NaOH is used as the leaching medium, the pH values of the leachate are lower than the initial pH of the leaching medium even under alkaline conditions, which may be due to the Ca^{2+} ions that are released by FGDG that replace the Na^+ ions in NaOH, which thus decreases the pH (Wang et al. 2017a, b). The pH values of the leachates obtained from TG in acidic or alkaline leaching media over time are similar to those of the deionized water leachate. In the first period, the pH values were in the range of 4.71–5.23, and the pH values of the second cycle reached 7.48–11.05, which were the peak values among the four cycles; then, the pH exhibited a small decrease. This is because TG has a good buffer effect and can maintain pH stability. Therefore, even under the different leaching media conditions, the pH levels of the leachate did not show large differences.

3.1.2 Leaching of metal elements

Figure 4a, d show that the leaching characteristics of Zn and Mn in PG were relatively similar. The leaching concentrations of the metal elements decreased with increasing pH (except for deionized water). At pH = 11.7, the released metal element concentrations were the smallest, which shows that alkaline conditions are not conducive to the leaching of metal elements in phosphorus gypsum, which may be caused by the formation of phosphate precipitates of the metal elements under alkaline conditions (Brückner et al. 2020). During the release process of Mn, the concentration that was released in the leaching medium with an initial pH of 1.8 was the largest, which reached 0.073 and 3.3 mg/L, which was followed by deionized water, and the concentrations in both of these media were very similar. During the Zn release process, the concentration at pH = 1.8 was the largest only in the first cycle. From the second cycle to fourth cycle, the released concentrations were the largest when deionized water was used as the leaching medium. Furthermore, the concentrations of the leached metal elements gradually decreased under all conditions, and the concentration was close to 0 in the fourth period. This indicates that when PG is exposed to acidic solvents (such as acid rain or acidic mine water) or nonacid precipitation, this will promote the release of the metal elements in phosphorus gypsum and the released metal element concentrations gradually decrease during repeated contact.

The Zn concentrations released by TG in NaOH (pH = 10.3 and 11.7) were greater than those in H_2SO_4 (pH = 1.8 and 3.1), and the leachate was in a weakly alkaline state from the second cycle onward (Figs. 3, 4b). Although the acidic leaching medium can consume the alkalinity of TG itself, the pH decreases slowly, and the release of metal elements under low pH conditions is less obvious. This phenomenon can be explained as the result of the buffering effect of titanium gypsum on the acidity, which is similar to the conclusion obtained by Wei et al. (2015). Figure 4e shows the pattern of change for the Mn leaching concentrations in TG. Except for the leaching medium with an initial pH of 1.8, the leaching concentrations of Mn under other conditions were quite low and were even below the detection limit. This may be because the leachate pH in the first cycle was in the range of 4.71–5.23, which represents weakly acidic conditions. Thus, the acidic conditions had certain effects on the release of the metal elements in TG. Then, with increasing pH, the Mn concentrations significantly decreased. When extracting Mn from gypsum with a leaching medium of pH = 11.7, only very small amounts of Mn were released in the first cycle, and the concentrations in later cycles were below the detection limit. This result may be because Mn is in a weakly alkaline condition in the form of oxyhydroxide, or hydroxide precipitates, or is adsorbed in the solid phase (Neculita and Rosa 2019), which results in extremely small amounts present in the leachate that can even be lower than the detection limit.

Figure 4c, f show that the metal elements in FGDG were more easily released in the low pH leaching medium. The leaching concentration changes for Zn and Mn were similar; both were liable to be leached under acidic conditions, and the concentrations under each condition gradually decreased and became stable with the extension of time. The release concentrations of Zn and Mn were the largest in H_2SO_4 (pH = 1.8) because FGDG has more impurities and its structure is relatively loose (Lei et al. 2017). For initial pH values of 1.8 and 3.1, higher concentrations of H^+ will destroy the

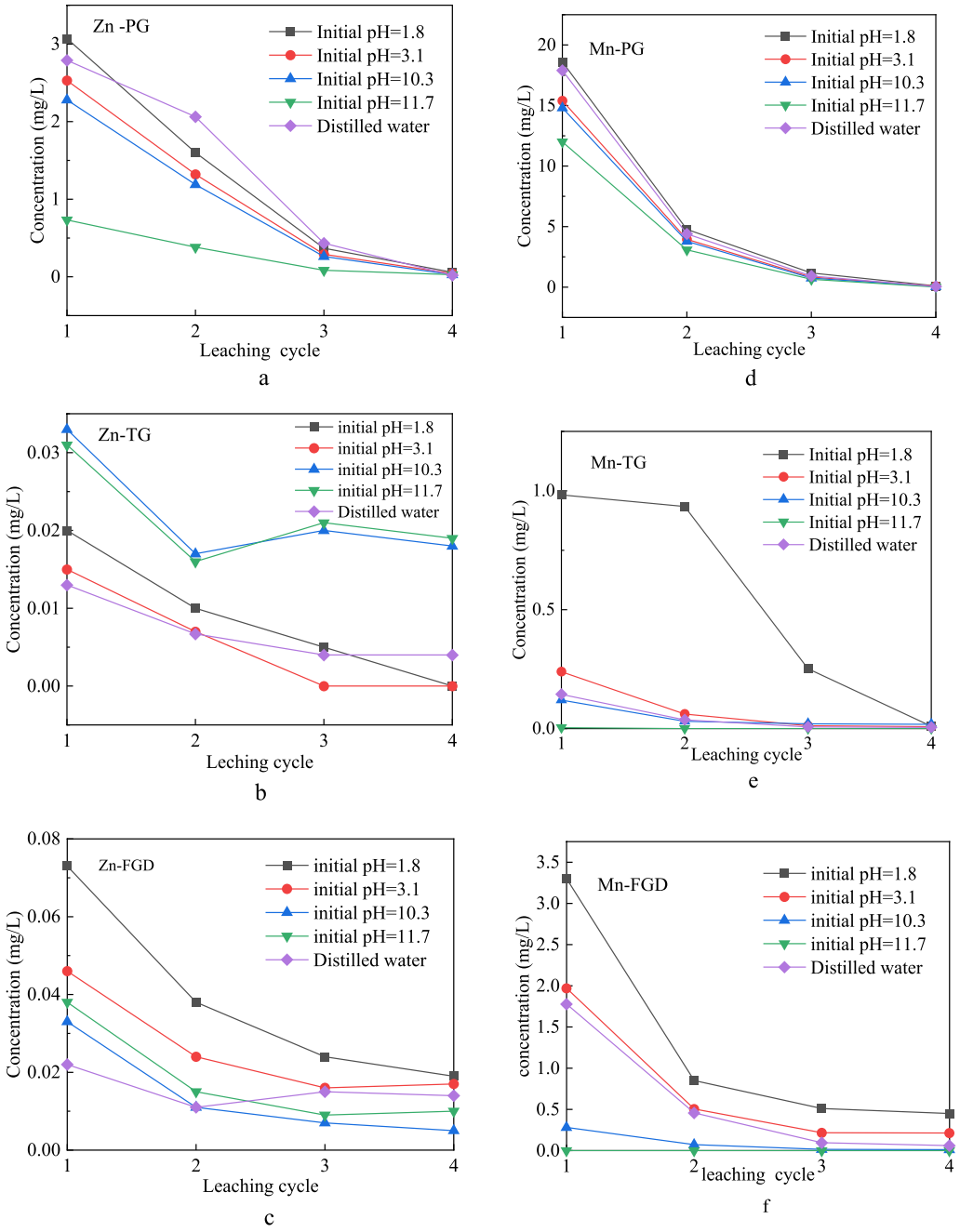

Fig. 4 Leaching concentrations of Zn in PG (**a**), TG (**b**) and FGDG (**c**); leaching concentrations of Mn in PG (**d**), TG (**e**) and FGDG (**f**)

structure of FGDG so that the metal elements are replaced by the H^+ ions in the gypsum particles and dissolve into a water phase. Under initial pH conditions of 10.3 and 11.7, the leaching amounts of Mn in FGDG were extremely low. The Mn concentrations were all lower than the detection limit during the entire leaching process at NaOH (pH = 11.7), which may be due to the presence of Mn in the form of precipitates under strong alkaline conditions. However, Zn is still released under strong alkaline conditions, probably because Zn combines with hydroxyl groups to form soluble substances, which will be leached in strong alkaline leaching media (Kim and Hyun 2015).

According to the leaching tests of the three gypsum types under different leaching media conditions, the maximum leaching amounts of their pollutant elements were compared with the national environmental quality standards, with the details shown in Tables 4, 5 and 6. Although the leaching contents of the heavy metal elements in the three gypsum types are all lower than those specified in the Identification Standards for Hazardous Wastes Identification for Extraction

Table 4 Comparison between the leachable contents of the elements in PG gypsum and the national environmental quality standard limits for hazardous pollutants

Elements	Leachable contents of PG (mg/L)					GB5085.3–2007 limited value (mg/L)	GB8978–1996 limited value (mg/L)	GB/T1484–93 limited value (mg/L)		
	Deionized water	pH = 1.8	pH = 3.1	pH = 10.3	pH = 11.7			III	IV	V
As	0.378	0.399	0.36	0.354	0.347	5	0.5	≤ 0.05	≤ 0.05	> 0.05
Hg	0.0117	0.00547	0.0101	0.00956	0.00365	0.1	0.05	≤ 0.001	≤ 0.001	> 0.001
Cd	0.074	0.082	0.067	0.06	0.035	1	0.1	≤ 0.01	≤ 0.01	> 0.01
Cr	0.16	0.25	0.15	0.11	ND	15	1.5	≤ 0.05	≤ 0.1	> 0.1
Pb	0.31	0.36	0.26	0.21	ND	5	1	≤ 0.05	≤ 0.1	> 0.1
Zn	2.79	3.07	2.53	2.28	0.733	100	2.0–5.0	≤ 1.0	≤ 5.0	> 5.0
Mn	17.9	18.6	15.4	14.8	12	NG	2.0–5.0	≤ 0.1	≤ 1.0	> 0.1
pH	2.05	1.49	1.97	2.08	4.49	NG	6–9	6.5–8.5	5.5–6.5 8.5–9	< 5.5 > 9.0

"ND" represents "not detected"; "NG" represents "not given"

Table 5 Comparison between leachable contents of the elements in TG gypsum and national environmental quality standard limits for hazardous pollutants

Elements	Leachable contents of TG (mg/L)					GB5085.3–2007 limited value (mg/L)	GB8978–1996 limited value (mg/L)	GB/T14848–93 limited value (mg/L)		
	Deionized water	pH = 1.8	pH = 3.1	pH = 10.3	pH = 11.7			III	IV	V
As	0.0014	0.0007	0.001	0.0016	0.0129	5	0.5	≤ 0.05	≤ 0.05	> 0.05
Hg	4E−5	ND	ND	ND	ND	0.1	0.05	≤ 0.001	≤ 0.001	> 0.001
Cd	ND	0.008	0.005	ND	ND	1	0.1	≤ 0.01	≤ 0.01	> 0.01
Cr	ND	0.05	0.03	ND	ND	15	1.5	≤ 0.05	≤ 0.1	> 0.1
Pb	ND	ND	ND	ND	ND	5	1	≤ 0.05	≤ 0.1	> 0.1
Zn	0.013	0.02	0.015	0.033	0.031	100	2.0–5.0	≤ 1.0	≤ 5.0	> 5.0
Mn	0.144	0.983	0.239	0.12	0.004	NG	2.0–5.0	≤ 0.1	≤ 1.0	> 0.1
pH	4.82	5.23	4.96	4.76	4.71	NG	6–9	6.5–8.5	5.5–6.5 8.5–9	< 5.5 > 9.0

"ND" represents "not detected"; "NG" represents "not given"

Table 6 Comparison between leachable contents of the elements in FGD gypsum and national environmental quality standard limits for hazardous pollutants

Elements	Leachable contents of FGD (mg/L)					GB5085.3–2007 limited value (mg/L)	GB8978–1996 limited value (mg/L)	GB/T14848–93 limited value (mg/L)		
	Deionized water	pH = 1.8	pH = 3.1	pH = 10.3	pH = 11.7			III	IV	V
As	ND	0.0005	0.0003	ND	ND	5	0.5	≤ 0.05	≤ 0.05	> 0.05
Hg	ND	ND	ND	ND	ND	0.1	0.05	≤ 0.001	≤ 0.001	> 0.001
Cd	ND	0.006	ND	ND	ND	1	0.1	≤ 0.01	≤ 0.01	> 0.01
Cr	0.03	0.08	0.05	ND	ND	15	1.5	≤ 0.05	≤ 0.1	> 0.1
Pb	ND	0.07	ND	ND	ND	5	1	≤ 0.05	≤ 0.1	> 0.1
Zn	0.022	0.073	0.046	0.033	0.038	100	2.0–5.0	≤ 1.0	≤ 5.0	> 5.0
Mn	1.78	3.3	1.97	0.281	ND	NG	2.0–5.0	≤ 0.1	≤ 1.0	> 0.1
pH	5.22	5.37	5.19	5.3	5.42	NG	6–9	6.5–8.5	5.5–6.5 8.5–9	< 5.5 > 9.0

"ND" represents "not detected"; "NG" represents "not given"

Toxicity (GB 5085.3–2007), gypsum is not classified as hazardous solid waste, but the influence of leached heavy metal elements on groundwater quality cannot be ignored. The maximum leaching amounts of the pollutant elements in PG exceed the limit defined in the Quality Standards for Ground Water (GB/T 1484–93) Class III water quality standard. The maximum leaching concentrations of Hg, Cd, Cr, Pb, and Mn reached 0.0117, 0.082, 0.25, 0.36, and 18.6 mg/L, respectively, which all exceeded the limits of the Class V water quality standards. The maximum Mn concentration from TG exceeded the limit defined in the groundwater quality standard V class water quality standard. When the leaching media consisted of deionized water, H_2SO_4 (pH = 1.8, pH = 3.1) and NaOH (pH = 10.3), the Mn concentrations were 0.144, 0.983, 0.239, and 0.12 mg/L, respectively. The leaching results for FGDG are similar to those of TG. When the leaching media consisted of deionized water, H_2SO_4 (pH = 1.8, pH = 3.1) and NaOH (pH = 10.3), the Mn concentrations exceeded the groundwater quality standard V water limit and were 1.79, 3.3, 1.97, and 0.281 mg/L, respectively. It is worth noting that the limit defined in the Class III water quality standard is based on the human health benchmark value, and water is not suitable for drinking if it exceeds the limits of Class IV and V water quality standards.

3.2 Numerical simulation result analysis

COMSOL Multiphysics software was used to simulate the migration and diffusion of the leached metal elements in the mine floor when PG, FGDG and TG were used as the filling materials, and the concentration distributions of Zn from the different gypsum samples at 10a, 100a and 200a were obtained, as shown in Fig. 5. At the same time, to facilitate the analysis of the metal element concentration distributions and migration and diffusion changes, curves of the concentration distributions of Zn at the observation point with the passage of time and the increase in distance along the mine floor direction were drawn, as shown in Figs. 6 and 7.

According to Fig. 5, for the different gypsum types, the concentration distributions of the metal elements and the migration distances exhibited significant changes over time. According to the cloud charts, the migration distances for PG, FGDG and TG at 10a were 1.8, 1.6 and 1.2 m, respectively. Figure 7 shows that the Zn migration distances at 200a were analyzed in detail, and the migration distances for PG, FGDG and TG reached 8.2, 8.1 and 7.5 m, respectively. When filling with different gypsum contents, the Zn concentration distributions were significantly different, which were caused by the different initial concentrations. When the filling body of the goaf consisted of PG, the initial concentration of the leached metal elements was greater than those of the other two gypsum types, which thus affected the concentration distribution range of the metal

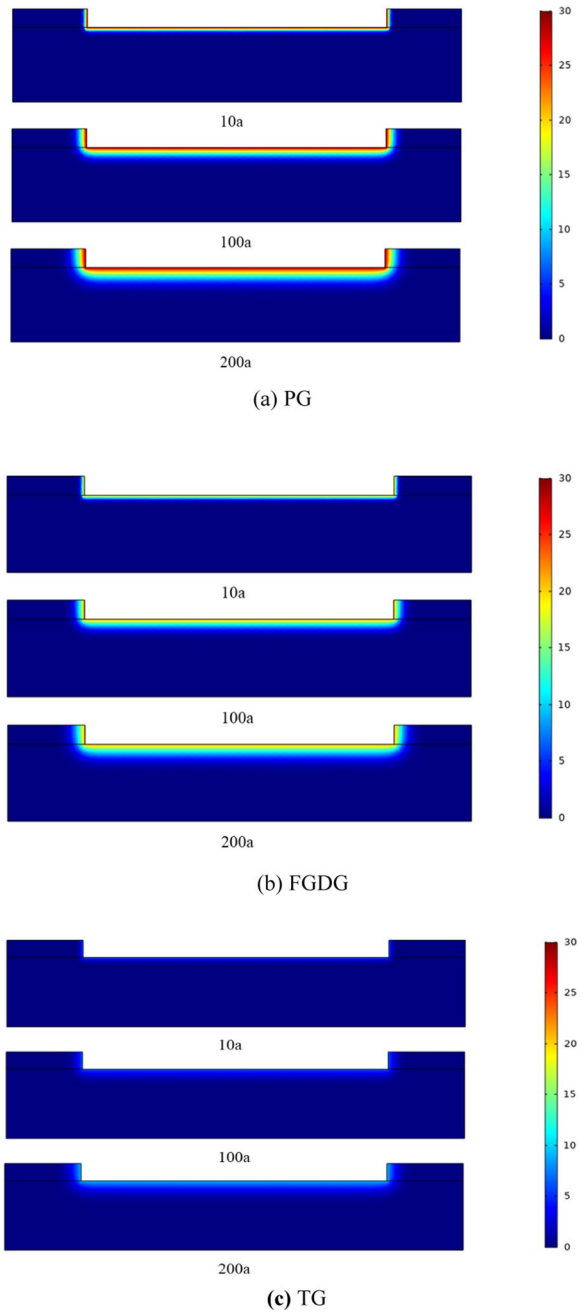

Fig. 5 Cloud maps of the Zn concentration distributions at 10a, 100a and 200a (10^{-5} mol/L)

elements. In addition, it can also be found that in all cases, the metal element concentrations near the filling area were the greatest, and the diffusion ability of the metal elements decreased with increasing depth, which are similar to the results obtained by Song et al. (2018).

Figure 6 shows that during the filling processes of the three gypsum materials, the Zn concentrations gradually increased with time. When titanium gypsum was used as the filling material, the Zn concentrations changed most

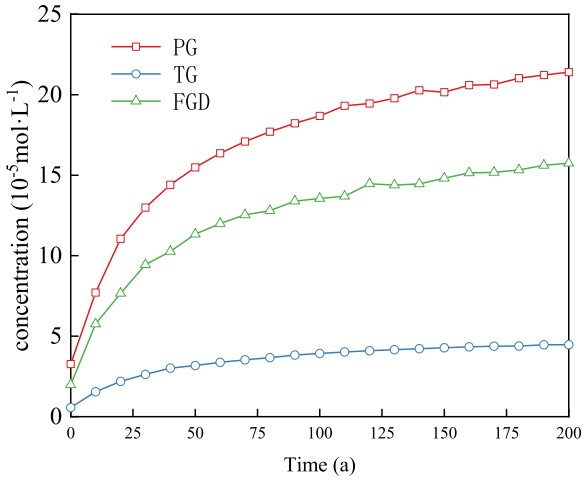

Fig. 6 Zn concentration distribution curves at the observation point over time (10^{-5} mol/L)

slowly, while when phosphorus gypsum and FGD gypsum were used as the filling materials, the changes in Zn concentrations were relatively obvious. The PG and FGDG concentrations increased the fastest during the initial period of 0–25a, which indicated that the metal elements in the PG and FGDG diffused most rapidly in the mine floor at the early stage and then gradually stabilized. The order of the concentration change rates is PG > FGDG > TG, and the Zn concentrations in the three materials at the end of the simulation are 2.14×10^{-4}, 1.57×10^{-4} and 4.46×10^{-5} mol/L. These results show that the diffusion rates and concentration distribution changes of the elements are affected by their initial concentrations.

Figure 7 shows that during the gypsum filling process, the metal element concentrations all exhibited downward trends, especially for the cases of phosphorus gypsum and FGD gypsum. The Zn concentration distributions from the different gypsum samples exhibited significant differences along the depth direction of the mine floor from 0 to 6 m and at approximately 6 m and deeper, the differences in the Zn concentration distributions began to decrease. As shown on the right part of Fig. 7, the concentration distribution at 4–10 m is enlarged, and it can be observed that there are generally no differences in the migration distances of the metal elements for the three gypsum types after 8.2 m. Therefore, due to the differences in the initial metal element concentrations, the concentration distributions and migration distances of the elements in the migration and diffusion processes of the bottom plate are different, among which the changes in concentration distributions and element diffusion rates were the largest in the initial stage, and the differences among the different gypsum types gradually decreased in the later stage. The maximum Zn migration distances from PG, FGDG and TG in the mine floor reached 8.2, 8.1 and 7.5 m, respectively.

4 Conclusions

(1) During the process of repeated contact of the three types of industrial waste gypsum with the leaching medium, the pH changes accordingly, and the pH changes will affect the leaching patterns of the heavy metal elements in gypsum. The pH levels of the PG leachate are low in both alkaline and acidic environments, which range from 1.49 to 4.49. In the H_2SO_4 (pH = 1.8) leaching medium, the Zn and Mn release concentrations were the highest, which were 3.07 and 18.6 mg/L, respectively, while in NaOH (pH = 11.7), the Zn and Mn release concentrations were the lowest. The leaching medium of NaOH (pH = 10.3 and 11.7) was not conducive to the release of harmful elements from PG. FGDG can effectively neutralize the acidity and alkalinity of the leaching medium. Moreover,

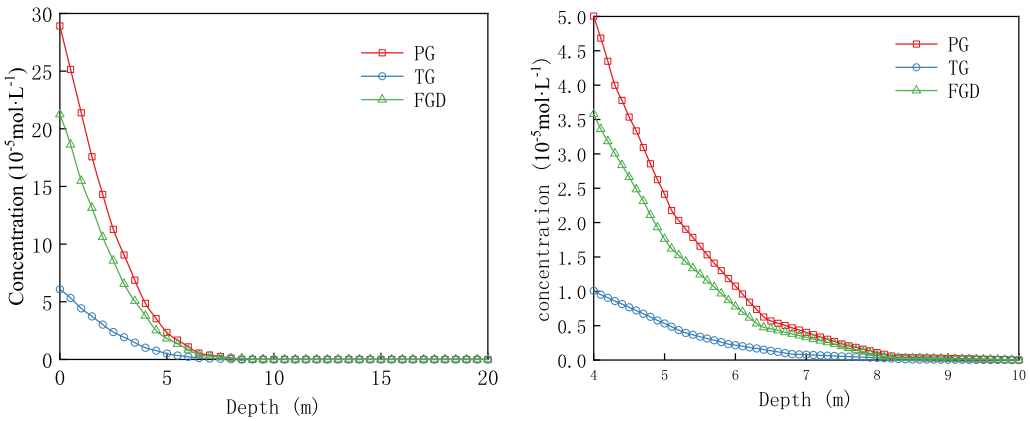

Fig. 7 Zn concentration distributions at different depths along the mine floor direction at 200a (10^{-5} mol/L)

the metal elements in FGDG were easier to leach. In H_2SO_4 (pH = 1.8), the Zn and Mn release concentrations were 0.073 and 3.3 mg/L, respectively. With increasing leaching times, the metal element concentrations for each condition gradually decrease and then tend to become stable. There were no significant differences in the pH values of the TG leachate under the different conditions. Because TG has a buffering effect on the acidity, the metal element releases are not obvious when the leaching medium is H_2SO_4 (pH = 1.8 and 3.1).

(2) According to the concentrations of metal elements that were leached from the three gypsum types, it can be judged that they are not classified as hazardous solid wastes, but whether they pose a risk to the groundwater environment when they are used as mine filling materials cannot be ruled out. The maximum concentrations of the heavy metals elements leached from PG exceed the limits of the Class III water quality standards for ground water. Among them, the maximum leaching concentrations for Hg, Cd, Cr, Pb, and Mn reached 0.0117, 0.082, 0.25, 0.36, and 18.6 mg/L, respectively, which exceeded the limits defined in the Class V water quality standard. The maximum leaching amounts of Mn from TG and FGDG also exceeded the limits defined in the Class V water quality standard.

(3) When the three types of gypsum were used as filling materials, the concentration distributions and migration distances of the metal elements exhibited significant changes over time. However, the concentration distributions, diffusion rates and migration distances in the mine floor of the metal elements from different gypsum types are affected by the initial concentrations. The concentration distribution changes and element diffusion rates were largest in the early stage, and the differences among the different gypsum types gradually decreased in the later stage. These were ranked as PG > FGDG > TG. Furthermore, the final Zn concentrations that were leached from PG, FGDG and TG were 2.14×10^{-4}, 1.57×10^{-4} and 4.46×10^{-5} mol/L, respectively. The maximum Zn migration distances from PG, FGDG and TG in the mine floor were 8.2, 8.1 and 7.5 m, respectively.

Acknowledgements The authors are grateful to the Xuzhou Key Social Research and Development Program (KC18134) for providing financial support for this study.

Author contributions All authors read and approved the final manuscript.

References

Al Heib MM, Didier C, Masrouri F (2010) Improving short-and long-term stability of underground gypsum mine using partial and total backfill. Rock Mech Rock Eng 43(4):447–461

Bachmat Y, Bear J (1964) The general equations of hydrodynamic dispersion in homogeneous, isotropie, porous mediums. J Geophys Res 69(12):2561–2567

Bear J (2012) Hydraulics of groundwater. Courier Corporation, Chelmsford

Brückner L, Elwert T, Schirmer T (2020) Extraction of rare earth elements from phospho-gypsum: concentrate digestion, leaching, and purification. Metals 10(1):131

Chen YS, Mao JQ (2007) Study on the leaching properties of soluble phosphorus in phosphogypsum. J Guizhou Univ Technol (nat Sci Ed) 01:99–102

Dutta BK, Khanra S, Mallick D (2009) Leaching of elements from coal fly ash: assessment of its potential for use in filling abandoned coal mines. Fuel 88(7):1314–1323. https://doi.org/10.1016/j.fuel.2009.01.005

Fallgren PH, Liang C, Min P, Urynowicz MA, Song J (2021) Facultative-anaerobic microbial digestion of coal preparation waste and use of effluent solids to enhance plant growth in a sandy soil. Int J Coal Sci Technol 8(4):767–779

Hao Y, Li Q, Pan Y et al (2017) Heavy metals distribution characteristics of FGD gypsum samples from Shanxi province 12 coal-fired power plants and its potential environmental impacts. Fuel 209:238–245

Huang G, Cai SJ, Yan ZX et al (2014) One-dimensional seepage laws of backfill-rock in heterogeneous area in under- ground mines. J Univ Sci Technol Beijing 36(01):8–13

Jiang LG, Liang B (2007) Numerical analog simulation of heavy metal pollution transport in variably saturated flow. J Liaoning Tech Univ S2:74–76

Kim J, Hyun S (2015) Nonequilibrium leaching behavior of metallic elements (Cu, Zn, As, Cd, and Pb) from soils collected from long-term abandoned mine sites. Chemosphere 134:150–158

Lei DY, Guo LP, Sun W et al (2017) Study on properties of untreated FGD gypsum-based high-strength building materials. Constr Build Mater 153:765–773

Li L, Gao Q, Xiao B et al (2020) Review and application prospevt of filling cementitious material developed by industrial solid waste. Mine R&d 40(2):19–25

Li J, Yilmaz E, Cao S (2021) Influence of industrial solid waste as filling material on mechanical and microstructural characteristics of cementitious backfills. Constr Build Mater 299:124288

Neculita CM, Rosa E (2019) A review of the implications and challenges of manganese removal from mine drainage. Chemosphere 214:491–510

Song T, Huang Y, Zhang J, Li J (2018) Numerical simulation on migration effects of heavy metal elements in coal gangue backfilling body caused by the lithology of coal seam floor. J China Coal Soc 43(7):1983–1989

Sui SG, Xu SG, Liu WL (2013) Simulation study on pollutant migration of a slag yard for unsaturated geotechnical materials. J Cent South Univ (sci Technol) 44(05):2173–2180

Tabelin C, Sasaki A, Igarashi T, et al (2019) Prediction of acid mine drainage formation and zinc migration in the tailings dam of a closed mine, and possible countermeasures. In: MATEC web of conferences EDP sciences, 2019, vol 268, p 06003

Wang SJ, Chen Q, Li Y et al (2017a) Research on saline-alkali soil amelioration with FGD gypsum. Resour Conserv Recycl 121:82–92

Wang SJ, Wu XQ, Liu C et al (2017b) Research into mobility of heavy metals components in FGD gypsum on the basis of column leaching model. Chin J Environ Eng 11(4):2512–2521

Wang XB, Yan X, Li XY (2018) Environment risk for application of flue gas desulfurization gypsum in soils in China. Sci Agric Sin 51(05):926–939

Wang G, Xu Y, Ren H (2019a) Intelligent and ecological coal mining as well as clean utilization technology in China: review and prospects. Int J Min Sci Technol 29(2):161–169

Wang P, Liu J, Zhu J et al (2019b) Impacts of heavy metal migration onquality of cultivated land and control of pollution risk in phosphogypsum yard in karst mountain area. Bull Soil Water Conserv 39(04):294–299

Wei C, Sun Y, Gao X et al (2015) Study on leaching characteristics of heavy metals in titanium gypsum. Environ Eng 5:131–135

Whitaker S (1986) Flow in porous media I: a theoretical derivation of Darcy's law. Transp Porous Media 1(1):3–25

Yang ZY (2021) Utilization status of industrial by-product gypsum in China and its prospect in the 14th Five-Year Plan. Sulphuric Acid Ind 7:1–4+23.

Yang Q, Li JX, Ding WC (2007) Primary analysis of main approaches, harm and preventions of groundwater pollution. Ground Water 3:72–75+125.

Zhang J, Liu F, Jiang J et al (2017) Experimental study on the mechanical property of composite backfills with phosphorus gypsum. Metal Mine 1:47–50

Zhang K, Li H, Han J, Jiang B, Gao J (2021) Understanding of mineral change mechanisms in coal mine groundwater reservoir and their influences on effluent water quality: a experimental study. Int J Coal Sci Technol 8(1):154–167

Zhong GJ, Xu HZ, Yang G (2018) Analysis of Cd forms and release potential of cultivated soil around phosphogypsum yard. Low Carbon World 7:1–2