

Leaching characteristics and pollution risk assessment of potentially harmful elements from coal gangue exposed to weathering at different time

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Research Article

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Abstract

This study explored the fresh coal gangue present in the goaf of the Hongqi Coal Mine and the coal gangue present on the surface of the mining area (weathered over a period of one year) to study the migration mechanism of pollutants when different types of coal gangue backfill goaf. Static immersion comparative experiments were conducted to determine the dissolution characteristics of Fe^{3+} , Mn^{2+} , SO_4^{2-} , and other major pollutants present in the two types of coal gangue. The results revealed that under the same soaking conditions, weathered coal gangue released more polluting elements than fresh coal gangue. Moreover, the ion concentration in the soaking solution fluctuated significantly. Meanwhile, the Fe^{3+} concentration presents a “wave-like” trend, and the Mn^{2+} and SO_4^{2-} concentrations fluctuated significantly during the early stages (1–7 d). The trend changed during the middle and late periods (after 7d). The Mn^{2+} content in the soaking solution of the fresh coal gangue decreased slowly, while the Mn^{2+} content in the weathered coal gangue increased steadily. The changes in the pH exhibited a “logarithmic trend”, and the pH of the fresh group was slightly higher than that of the weathered group. Based on the evaluation of the geo-accumulation index, combined with the pollution level evaluation standard, it was found that the levels of heavy metal elements produced by the weathered coal gangue are significantly higher than the levels produced by fresh coal gangue, which are more likely to pollute groundwater and damage the ecological environment.

1 Introduction

China is the largest coal mining country. The annual production of raw coal was 3.90 billion tons in 2020, accounting for nearly 50% of the global coal production. Coal remains an important source of fuel and raw materials (Yang and Xu 2021). Coal gangue is a carbon-containing solid waste produced during the process of coal mining and washing. It accounts for approximately 10–20% of the coal produced. It is kept piled up (4.5 billion tons) and covers an area of approximately 15,000 km^2 (Li et al. 2015; Zhou et al. 2014a). Coal gangue contains a variety of trace elements, heavy metals, organic matter, and other substances. The leaching and weathering effects cause the pollutants in coal gangue to enter the ecosystem. This results in pollution and damage to the surrounding ecological environment (Bian et al. 2008; Sun et al. 2009; Zhou et al. 2014b). Deng Weinan et al. simulated the soaking and leaching experiment to study the release and migration patterns of contaminants (Deng and Wu 2013). They reported that at the beginning of the leaching experiment, the concentrations of the contaminants in the leaching solution were high. With an increase in the volume of leaching water, the concentrations of the pollutants in the leaching liquid gradually decreased. The pollutants were released continuously during the soaking experiments. The accumulation of coal gangue on the surface water and soil environment significantly impacts the environment.

To address the problem of coal gangue pollution, the Jizhong Energy Group has successfully developed two new mining technologies (new domestic mining technology for studying coal gangue backfilling the goaf). One of the methods involves the use of ground gangue to backfill the underground. The other method involves the process where coal gangue is not poured into the well but directly backfilled. The gangue produced by mining is filled into the permanent coal pillar under the building. When the gangue is not raised in the well, it can be used to replace the coal resources that could not be mined following the original method (Xu 2009). The most efficient method of waste management involves the reduction in the production of wastes and the reuse of solid wastes. The commonly used methods include hydraulic filling, wind filling, mechanical filling, and self-slipping filling, among

which the first two methods are more efficient and effective than the others (Bian et al. 2008; Zhang et al. 2013). The technology of using coal gangue as a filling material to backfill goaf not only helps fill the collapsed area but also helps reduce the accumulation of solid wastes. However, there are a large number of pollutants in the gangue. These toxic substances may be transferred to the adjacent environment, causing pollution (see Figure 1). The oxidation of sulfide minerals in gangue results in the production of acidic wastewater containing toxic heavy metals (Novikova and Gas'kova 2013). Due to the weak affinity of Mn with other heavy metal elements, the sulfur in the gangue also affects the content of Mn (Gao et al. 2021), indirectly causing environmental pollution. Tang et al. found that the concentrations of Cu, Pb, and Zn increased in the reclaimed soil in the subsidence area filled with coal gangue in the Huainan mining area (Tang et al. 2018). When a large amount of the pollutants are released, they not only infect the surrounding soil but also infiltrate the groundwater through the surface water. This pollutes the vadose zone and endangers human health through the food chain (Li et al. 2021). Through environmental risk assessment, Hussain R et al. found that coal and coal wastes pose a high risk in their research on coal mining pollution in Hancheng County, Shanxi Province, and food and plants face medium to high risks (Hussain R et al. 2018).

There are many researches on coal gangue, these studies mainly focus on the utilization of coal gangue, and lack of attention to environmental risks (Li and Wang 2019). Fresh and weathered coal gangue were analyzed to compare and study the environmental pollution caused by the two types of coal gangue. The coal gangue obtained from the gangue hill and used for our studies was weathered for 1 year. The fresh coal gangue obtained from the goaf roadway was used as the experimental materials. The static immersion experiment was conducted using deep karst water as the immersion liquid to study the release law of Fe^{3+} , Mn^{2+} , SO_4^{2-} , and other major pollutants present in the two kinds of coal gangue. The change in pH of the soaking solution were also discussed and analyzed. The geo-accumulation index method was used to study the pollution caused by heavy metals. The results can help in the selection of the filling materials required during the production process of coal. Further, this approach seems to be promising in the prevention and control of groundwater pollution in mining areas. It might also help in achieving the effective implementation of water environmental protection strategies in fragile ecological areas.

2 Sample Collection And Experiment

2.1 Overview of the sampling area

The sampling area is located in Jining City and Tai'an City in the southwestern Shandong Province. The three mining areas of Baizhuang, Hongqi, and Zhaizhen (Figure 2), all of which belong to the Luxi Stratigraphic Division of the North China Stratigraphic Region, were chosen. The terrain of this area dips slowly from southwest to northeast, with the vast Yellow River flooding the alluvial plain. It is characterized by a semi-humid climate with hot summers, long frost-free periods, and a high average annual temperature (13–14°C). It is the region with the most abundant heat resources. The average annual rainfall ranges between 600 and 800 mm. The coal-bearing strata in this area are located mainly in the Upper Carboniferous and Lower Permian regions. The Permian coal resources are rich in coal. The coal-bearing strata and coal seam thickness are stable. Gas coal is the main type of coal present, and the base of the coal strata is composed of Ordovician limestone, which is rich in water and has a high groundwater phreatic level. Most of the coal mines in the southwestern Shandong region are of the low-sulfur non-spontaneous combustion type. The gangue is alkaline and is primarily composed of siltstone, mudstone, and carbonaceous mudstone. The gangue lithology is primarily sandstone, mudstone, limestone, and

carbonaceous mudstone, containing pyrite, kaolinite, and coal debris. In addition to SiO_2 , Al_2O_3 , Fe, Mg, Ca, and other constant elements, other heavy metals such as Pb, Ag, Cd, Cr, As, and Mn (toxic heavy metal elements) were also present (Shen 2020).

2.2 Sample collection

The samples used in the experimental study consist of two parts. The first part involves the collection of coal gangue samples from the Hongqi Coal Mine. In the mine outside the gangue pile, 10 sample points were selected from top to bottom using the "snake sampling method". Each sample point contained the same amount of gangue which was put in a clean polypropylene bag for storage to form the weathered coal gangue sample. Following this, 10 samples of equal amounts of coal gangue were collected at equal intervals in the 3112 working face roadway buried 358 meters deep. The samples were immediately put into clean polypropylene bags to form the fresh coal gangue samples. The final samples of coal gangue were collected separately. The pretreatment method was followed by crushing. The quarter method was used to screen out coal gangue samples of particle sizes in the range of 0.45–3.2 mm.

The second part involves the collection of the soaking liquid. The three water samples were taken from the Baizhuang Coal Mine and Zhaizhen Coal Mine. Water sample No.1 is the Ordovician limestone karst water collected from the Bai Zhuang Coal Mine, taken from the 8506 working face, buried at a depth of 250 m. The water pressure was 1.9 MPa. Water samples No.2 and No.3 were taken from the Zhaizhen Coal Mine. Water sample No.2 was taken from the hydrological hole of the 11504 W transport pipeline, from a depth of 549.8 m and water pressure of 2.8 MPa. Water sample No.3 was taken from the trackway of the south wing of the third mining area, from a depth of -395.07 m. The water pressure was 2.05MPa. All water samples were stored in polyethylene bottles.

2.3 Immersion experiments

The pre-processed and crushed gangue samples were divided into two parts: one was analyzed using the X-ray diffraction (XRD) technique to determine the mineral composition. The other part of the sample was used for static immersion experiments. First, equal amounts of fresh gangue samples and weathered gangue samples were weighed (10 g). The karst water samples of No.1, No.2, and No.3 were put into polyethylene bottles (solid-liquid ratio: 1:10 (g/mL)). The samples were labeled as FS1, FS2, FS3, WS1, WS2, and WS3. These were then put into a constant temperature incubator. The samples were subjected to intermittent agitation. The samples were collected at intervals of 1, 2, 4, 7, 15, 25, and 35 d. The supernatant was drawn, filtered, and collected to obtain 20 mL of the soaked water samples. The concentrations of the contaminants in the solution were determined using the inductively coupled plasma mass spectrometry (ICP-MS) technique. The pH, Oxidation-reduction potential (ORP), Electrical conductivity (EC), Total dissolved solids (TDS), and Dissolved oxygen (DO) values for the immersion solution were determined using a Hach Hydrolab multiparameter water quality analyzer. The experimental process followed is shown in Figure 3.

3 Results And Discussion

3.1 Dissolution of the main pollutants in coal gangue

The X-ray fluorescence spectrometry was used to determine the chemical composition of fresh gangue and weathered gangue collected from the Hongqi Coal Mine. The ICP-MS technique and the ion chromatograph ICS-

600 were used to analyze the three types of karst water collected to determine the various parameters (Table 1 and Table 2). The main components of fresh gangue samples are SiO_2 , Al_2O_3 , CaO , MgO , and Fe_2O_3 , and the main components of weathered coal gangue samples are SiO_2 , Al_2O_3 , MgO , and Fe_2O_3 . The results reveal that the amount of calcium and magnesium ions in fresh coal gangue is higher than the amounts present in weathered coal gangue. The pH values of the three karst water samples were 7.64, 7.69, and 9.54 for the neutral water, neutral water, and weakly alkaline water, respectively. The TDS contents were 480.3, 1251.7, and 543.7 mg/L, respectively, which indicated that the salinity of water samples No.1 and No.3 was low (freshwater). Water sample No.2 belonged to the medium salinity group (brackish water). The major cations in water sample No.1 were $\text{Ca}^{2+}+\text{Mg}^{2+}$, and the ions present in samples No.2 and No.3 were predominantly Na^+ . The dominant anion in the three water samples was SO_4^{2-} .

Table 1
Analysis of the chemical composition of the coal gangue samples (%)

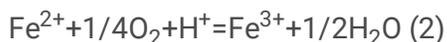
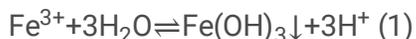
Chemical composition	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	MnO
Fresh coal gangue	33.359	22.872	22.557	12.189	5.632	0.655	0.084
Weathered coal gangue	49.765	36.382	0.971	3.034	2.738	0.722	0.018

Table 2
Chemical composition of karst water (mg/L)

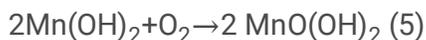
Water samples	Cation		Anion				pH	TDS
	$\text{Ca}^{2+}+\text{Mg}^{2+}$	Na^+	Fe^{3+}	Cl^-	SO_4^{2-}	HCO_3^-		
1	190.14	50.8	0.32	68.33	114.39	83	7.64	480.3
2	286.57	1000	0.71	82.63	1224.58	99	7.69	1251.7
3	56.87	1000	0.09	6.92	368.97	78	9.54	543.7

The concentrations of the polluting elements in the leachate change with an increase in time, and the analysis of the graph drawn from the experimental data shows that the dissolved concentration of Fe^{3+} changes significantly with an increase in the soaking time (Fig. 4). In each group, the trend in the changes in the Fe^{3+} ions is roughly similar, and the solubility decreases significantly. The solubility rises again after two peak dissolution values. The leaching solution of both groups reached the first peak dissolution value on day 1. Following this, the extent of dissolution gradually decreased. A low peak of dissolution was observed on day 4, and a new peak appeared on day 7. This can be attributed to the static immersion method. During the initial process of the experiment, the water-gangue action can only activate and cause the rapid release of the metal on the surface. The concentration gradually decreases in the subsequent sampling solution (Cao et al. 2010). Following sufficient contact by stirring, Fe^{3+} dissolves again at a faster rate. The solubility drops sharply after day 7 and then rises sharply until day 35. This is because Fe^{3+} is formed during the process of hydrolysis. The formation of $\text{Fe}(\text{OH})_3$ precipitated in the gangue soaking solution is also observed. The adsorption of inorganic particles (Zhao et al. 2019) is observed, shifting the balance to the right, as shown in formula (1). Thus, the concentration of Fe^{3+} decreases. The gangue in the pyrite was exposed to oxygen and water. Under these conditions, oxidation occurs to produce acid and ferrous sulfate (Burt and Caruccio 1986). Fe^{2+} is unstable in solution and undergoes oxidation to form Fe^{3+} (Equation 2) causing the Fe^{3+} concentration to rise.

During the experimental period, the two types of gangue Fe^{3+} presented “wave-like” behavior. The total solubility of the weathered gangue in the leaching solution is higher than that of the fresh gangue. This is because the oxidation product of pyrite in weathered gangue (Fe^{3+}) is mainly precipitated on the surface in the form of amorphous hydrated oxides. This accelerates the rate of release of Fe^{3+} during the soaking process (Wu et al. 2014).



Coal gangue contains a large number of harmful trace elements such as Mn^{2+} , which causes serious environmental pollution (Cai et al. 2008). The trend in the solubility of Mn^{2+} contained in coal gangue is presented in Figure 5. The fresh coal gangue reached the peak solubility value on the 4th day. The solubility continued to decline in the time period of 4–25 d. Following this, the concentration increased in the range of 25–35 d. The concentration of the weathered coal gangue increased and then decreased in the range of 0–2 d and 2–4 d, respectively. After 4 days, the manganese content in WS2 and WS3 (except WS1) and the dissolution value increased till the end of the experiment. The overall change in the trend of fresh and weathered groups represents a downward curve and an upward curve. As can be seen from Table 1, the content of manganese was not high. In comparison, the content of fresh gangue was 8 times higher than that of weathered gangue. Fresh gangue also contained more Ca^{2+} and Mg^{2+} (mainly derived from calcite and calcium feldspar). The dissolution of calcite in gangue results in the consumption of a part of H^+ (formula 3) and an increase in the OH^- concentration in the solution during soaking. The soluble manganese salt undergoes a precipitation reaction with OH^- in the alkaline environment (formula 4). The generated $\text{Mn}(\text{OH})_2$ is quickly oxidized into hydrated manganese dioxide (formula 5). Under these conditions, the Mn^{2+} content in the fresh gangue soaking solution decreases continuously. The sulfide precipitated following the weathering of coal gangue results in the formation of a reducing environment in the soaking liquid. This enhances the activity of Mn^{2+} and results in the continuous dissolution of the unit into the soaking liquid. In addition, Mn^{2+} is characterized by a variety of valences, among which the tetravalent manganese salt is unstable and can be easily reduced to Mn^{2+} in the acidic medium. This increases the Mn^{2+} content in the soaking solution.

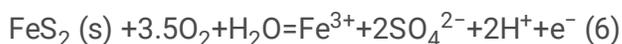


During the experimental period, the solubility of the sulfate ions changed (Fig. 6). In karst water No.1, the concentration of SO_4^{2-} decreased till day 6 days, but the overall trend appeared upward. After day 6, three phases of opposite dissolution trends were observed. Little floating was observed under these conditions. The overall solubility of SO_4^{2-} in the weathered gangue was approximately twice that observed in the fresh group. The changes in the karst water of No.3 were similar to the changes in No.1. The concentration of SO_4^{2-} in FS3 rapidly declined during 0–1 d (Fig. 6c). The dissolution trend observed after 4 d was almost the same as the trend observed with weathered gangue. The solubility of the weathered group was higher than that of the fresh group.

The two groups of change images were similar to “radical sign”, roughly for the first rise. Following this, equilibrium is achieved as the soaking solution contains more dissolved oxygen at the beginning of the experiment. Pyrite was oxidized in the short term and accelerated the dissolution of SO_4^{2-} . As the experimental time was increased, the extent of dissolution of dissolved oxygen in the soaking solution increased. The rate of mineral decomposition decreased. The concentration of dissolved SO_4^{2-} did not fluctuate much in the middle and late stages. The concentration of SO_4^{2-} in FS3 dropped rapidly and then increased suddenly, giving rise to a “V”-shaped fluctuation after 1 day. This can be related to the presence of carbon-containing organic matter in fresh coal gangue (Fan and Lu 1999). During soaking, it adsorbs the sulfide minerals in the coal gangue to reduce solubility. A new dissolved state is reached following stirring.

In karst water No.2, the changes in the SO_4^{2-} concentration in both groups followed the rising-declining-rising-declining cycle. The image of ion concentration in this group presents two “high points” and three “low points”, and the overall change resembles the “M” shape (Fig. 6b). The oxidation mechanism (Pandey et al. 2007) revealed that Fe^{3+} (an additional oxidant) exerts an oxidizing effect on sulfides. This prompted the release of SO_4^{2-} in the gangue. Fe^{3+} could be easily hydrolyzed. It was precipitated as iron hydroxide. Its redox potential and oxidizing capacity were reduced. The solubilities of the sulfides decreased in the absence of Fe^{3+} .

The concentration of SO_4^{2-} in the three groups of karst water was always higher in the weathered group than the concentration observed in the fresh group. This can be attributed to the loose structure of the weathered gangue. Under the effect of long-term weathering, the internal structure of the gangue was destroyed. The ions in the mineral lattice were decomposed and freed. From the original chemical state to the free state, the solubility of pollutants also increased (Xiao et al. 2006). According to the data, the weathered gangue contains a large number of sulfides floating on the gangue surface. This can be attributed to the role of atmospheric rainfall and surface water immersion. The pyrite contained in the open-air coal gangue is formed following the weathering Hydrolysis reaction as follows:



Therefore, the concentration of the dissolved SO_4^{2-} in weathered coal gangue is higher than that in fresh coal gangue. A comparison of the graph of No.1, 2, and 3 soaking liquids reveals that the SO_4^{2-} detection value for the weathering group is greater than that of fresh coal gangue at each stage of the experiment.

It can be concluded that the concentrations of dissolved Fe^{3+} , Mn^{2+} , and SO_4^{2-} were higher in the weathered gangue.

Table 3
Comparison of the changes in ion concentration at different weathering levels (mg/L)

	FS1	WS1	FS2	WS2	FS3	WS3
Fe ³⁺	1.02	1.12	2.71	2.81	0.422	0.696
Mn ²⁺	0.016	0.018	0.066	0.098	0.023	0.153
SO ₄ ²⁻	146.10	188.74	1375.16	1442.96	447.06	507.45

The data in the table presents the maximum leaching amount of pollutant ions in the soaking solution of each group. The concentration of Fe³⁺, Mn²⁺, and SO₄²⁻ in the soaking solution of the weathering group is higher than the concentration of each ion in the fresh group. The results revealed that the amount of pollutants in the weathered coal gangue is significantly higher than that in the unweathered gangue.

A part of the sample was in an anoxic state during the experiment. Following the process of intermittent stirring, the gangue samples came in full contact with the immersion solution. Intermittent stirring increased the movement of the molecules in the solution to a certain extent. This also hindered the process of adsorption and the process of forming colloids (He et al. 2014). Both influence the rate of dissolution of each ion.

3.2 Changes in the pH of the soaking solution under the influence of different types of coal gangue

The pH of the soaking solution of the three groups was weakly alkaline during the whole experiment (Fig. 7). The detected values were not much different. With an increase in the soaking time, the final pH of the fresh group increased and became higher than that of the weathered group. The trend of pH change in the fresh group and the weathering group was similar, and the overall image was similar to the "logarithmic curve". The graph recorded for the change in the pH of solution No.3 presents a decreasing tendency, which is opposite to the trend presented by the graph recorded for the change in pH of solutions No.1 and 2. The pH value of the soaking solution in the three groups increased and decreased significantly before and after 6 days. Following this, the change occurred within a small range (8.0–8.5) till the end of the experiment. Alkaline pH is reached due to the presence of a large amount of SiO₂ and Al₂O₃ in the gangue and the presence of a large amount of calcium, magnesium, and aluminum ions and salts in the karst water samples (Table 1 and 2). The fluctuations in the pH of the soaking solution decrease as the solution balances with the single, multiple weak acids and weak alkalis. Under the action of oxygen, moisture, and microorganisms in the air, the reducing sulfide minerals on the surface of the coal gangue are first oxidized. Following this, a certain oxide layer is formed on the surface of the coal gangue. The oxide layer contains reducing sulfur oxidation products that can significantly reduce the pH of the soaking liquid (Srace et al., 2004). Under these conditions, the pH of the weathering group is lower than that of the fresh group.

The overall pH was weakly alkaline, and the oxidation and dissolution of sulfide minerals contained in the gangue were inhibited under the closed state. This affected the acidic release of the gangue. With the passage of time, the pH value of the fresh gangue and weathered gangue soaking solution was finally stabilized between 8.0–8.5. This was in line with the surface water environmental quality standard. The maximum concentration of each of the dissolved elements is listed in the following table with reference to the water quality standard (Class III; Environmental Quality Standard for Surface Water (GB3838-2002)):

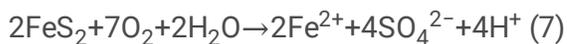
Table 4
Evaluation indicators of environmental effects for pollutants in immersion solutions

Element Name	Maximum concentration in the immersion solution (mg/L)	Class III water quality standard
	Fresh	Weathered
SO ₄ ²⁻	1375.16	1442.96
Fe ³⁺	2.71	2.81
Mn ²⁺	0.06	0.15

As can be seen from Table 1, the maximum concentration of SO₄²⁻ in the soaking solution of the two groups exceeds the value presented in the water quality standard of type III. The concentration of Fe³⁺ is close to that presented in the water quality standard. The concentration of Mn²⁺ in the soaking solution of the weathering group exceeds that presented in the water quality standard (2) in the soaking solution of the weathered gangue. The solubility of each substance is higher than that in the fresh gangue group. In general, the environment is affected, and in comparison, the harm caused by the weathered gangue to the environment is greater than the harm caused by fresh gangue.

Correlation analysis can measure the closeness of the correlation between the two variable factors. Pearson's correlation coefficients for each ion in the leachate and soaking solution were calculated separately for the fresh and weathered groups using SPSS Statistics 26 software. The correlation heat range was further plotted using Origin 2021, as shown in Figure 8.

It can be seen from Figure 8 that the pH of the soaking solution of each group has a significant correlation with SO₄²⁻, indicating that SO₄²⁻, as the main pollutants present predominantly and has a certain influence on the fluctuation of pH. The oxidation of pyrite in coal gangue produces acid, and the corresponding chemical reaction is presented as follows:



When the H⁺ concentration increases, the pH of the soaking solution decreases. The SO₄²⁻ p-value in Figure 8 shows that the content in the weathering group is higher than the content in the fresh group, indicating that the more the content of SO₄²⁻ in the gangue, the lower the pH of the soaking solution. This is in line with the analysis results presented in Figure 7. The pH of the weathering gangue soaking solution is slightly lower than the pH of the fresh gangue soaking solution.

It was found that the pH of soaking solution No.1 and No.2 positively correlated with the sulfate ions, and the sulfate ions of soaking solution No.3 were negatively correlated (Figure 8). This indicated that the trend of pH change in the first two groups of the soaking solution increased with the ion concentration, while the trend of pH change in soaking solution No.3 decreased with an increase in the ion concentration, making the graph of pH change in soaking solution No.3 opposite to the graph of pH change in soaking solution No.1 and No.2. This is consistent with Figure 7.

4 Evaluation On Water Pollution And Geo-accumulation Index Of Soaking Liquid

To further explore the influence of the pollution causing ability of the dissolved ions in the leaching solution, the geo-accumulative index method was used to evaluate and analyze the samples taking into account not only the environmental geochemical background values but also the influence of the anthropogenic factors and natural diagenesis to determine the degree of contamination caused by certain heavy metals at the sampling site. The following equation was used:

$$I_{geo} = \log_2(C_n/kB_n)$$

8,

where I_{geo} is the cumulative pollution index of heavy metals, C_n is the measured concentration of pollutants, B_n is the geochemical environmental background value of the pollutants, and K is the correction coefficient ($K=1.5$). According to the standard of the cumulative index, the pollution degree is classified as shown in Table 5.

Table 5
Pollution level of the cumulative index

I_{geo}	≤ 0	0~1	1~2	2~3	3~4	4~5	>5
Pollution level	1	2	3	4	5	6	7
Pollution degree	None	Light	Medium	Moderate	Heavy	Severe	Extremely

With reference to the background values of soil elements in China released by the Chinese General Environmental Monitoring Station and the experimentally measured data has been presented in a columnar comparison chart (Figure 9). The contamination index of the element Fe in the soaking solution was higher than that of manganese, while the contamination levels of element Mn in FS1, FS2, FS3, and WS1, WS2, and WS3 solutions were moderate, heavy, moderate, and moderate, severe, and heavy respectively. In addition, it is obvious that the ground cumulative pollution index of the unweathered gangue soaking solution was less than that of the weathered gangue group, namely $WS1 > FS1$, $WS2 > FS2$, $WS3 > FS3$. Under natural denudation conditions, rainfall leaching and surrounding fluid soaking, the degree of weathering has a significant impact on the content of heavy metals, causing a large amount of pollutant elements to be released into the environment (Hua et al. 2018), thereby affecting the surrounding water environment.

The geo accumulation was evaluated. It was observed that the contamination degree in fresh gangue in the study area was lower than that in the weathered gangue, where the contamination level of Fe^{3+} was much higher than that of Mn^{2+} . This can be attributed to the fact that FeS_2 in gangue is oxidized to produce Fe^{2+} . Following this, it is oxidized to Fe^{3+} to increase the concentration of iron ions. The calcium salts in the soaking solution have an inhibitory effect on the release of Mn^{2+} (Wang et al. 2017), while Fe^{2+} ions are oxidized to Fe^{3+} . Fe^{3+} can react with $FeS_2(s)$ to form Fe^{2+} and SO_4^{2-} . Thus, the concentration of iron ions in the soaking solution remains relatively high. The mechanism of oxidation of pyrite is shown in Figure 10. During the process of coal gangue backfilling the goaf, attention should be paid to groundwater pollution caused by weathered coal gangue and Fe^{3+} . As the degree of weathering of coal gangue increases, the pollution index of Fe^{3+} and Mn^{2+} increases, causing water pollution.

The toxicity caused by heavy metals is related to the total content and the form of existence. Different forms of existence have different environmental effects, which directly affect the toxicity, migration, and circulation of pollutants in nature. This paper studies the release of two types of pollutants from fresh and weathered coal

gangues. Karst water also contains a certain amount of mineral ions. There is still a lack of detailed research on the specific quantitative analysis of mineral dissolution in gangue and ions in an aqueous solution. Therefore, the potential pollution risks caused during the backfilling of goafs by coal gangue under different weathering degrees need to be further explored. This study can provide a certain reference value for groundwater protection in mining areas.

5 Conclusion

The release of major pollutants from fresh and weathered gangue in the Hongqi Coal Mine was studied. The amount of pollutants released by weathered gangue in the soaking solution was higher than that by fresh gangue. The contrast difference was maximum for Mn^{2+} (~ 7 times). The amount of SO_4^{2-} dissolved in the three main pollutants was the maximum (as high as 1442.96 mg/L). Throughout the experiment, the solubility of the contaminants varied inconsistently. The solubility of Fe^{3+} showed a “wave-like” change, and that of Mn^{2+} was curved up (weathering group) and down (fresh group). The graph representing the solubility of SO_4^{2-} was similar to the “radical sign”.

The pH of the two types of coal gangue soaking solution was slightly alkaline (8.0–8.5) and the pH of the weathered gangue soaking solution was lower than that of the fresh group. This could be attributed to the presence of SO_4^{2-} . The results of geo-accumulative risk assessment show that weathered gangue causes more pollution than fresh gangue. Both Fe^{3+} and Mn^{2+} in the two types of coal gangue cause pollution. Among them, the pollution level of Fe was significantly higher than that of Mn^{2+} . The level increased with the weathering years. It may have a certain degree of impact on the groundwater environment. There is a lack of research on the correlation between the elements and the occurrence of the elements. The effect of the minerals present in karst water on the release of coal gangue pollutants should also be studied.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

All authors contributed to the study conception and design. Jin-feng Peng was the main author of the manuscript and has made major contributions to the operation throughout the experiment, including data collection, data analysis and article conception. Long-qing Shi has contributed to the operation in experiment guidance, especially the guidance of the geological work and the data analysis. Dong-jing Xu was responsible for leading the planning, execution, and the review of the research activities. He was also the main funder of the study. Jin-jin Tian is mainly responsible for studying literature collection, analyzing the experiment data. Tian-hao Liu is mainly responsible for drawing guidance and chart correction. Bin-bin Jiang. helped refine these ideas, performed additional analysis and revised this article. Fa-cai Zhang was mainly responsible for article revision and data verification. The first draft of the manuscript was written by Jin-feng Peng and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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References

1. Bian Z, Dong J, Lei S, Leng H, Mu S, Wang H (2008) The impact of disposal and treatment of coal mining wastes on environment and farmland. *Environmental geology* 58(3):625-634
2. Burt RA, Caruccio FT (1986) The effect of limestone treatments on the rate of acid generation from pyritic mine gangue. *Environmental geochemistry and health* 8(3):71-78
3. Cai F, Liu Z, Lin B, Li W, Lu Z (2008) Study on trace elements in gangue in Huainan mining area. *Journal of Coal* (08):892-897
4. Cao Y, Zhang S, Liu H (2010) Study on the characteristics of dynamic leaching and static leaching dissolution of heavy metals in coal gangue. *Journal of Hebei Engineering University (Natural Science Edition)* 27:76-80
5. Deng W, Wu C (2013) Study on the characteristics of pollutant release from coal gangue simulated soaking and leaching experiments. *Coal Technology* 32(05):142-144
6. Fan W, Lu Z (1999) Development of Jinguang wall and floor tiles using coal gangue. *Journal of Jiaozuo Engineering College* (01):45-50
7. Gao H, Huang Y, Li W, Li J, Ouyang S, Song T, Lv F, Zhai W, Ma K (2021) Explanation of heavy metal pollution in coal mines of china from the perspective of coal gangue geochemical characteristics. *Environmental Science and Pollution Research* 1-11
8. He B, Zhang Y, Li X (2014) Experimental study on the dissolution of the main pollution components of coal gangue. *Silicate Bulletin* 33(09):2217-2222

9. Hua C, Zhou G, Yin X, Wang C, Chi B, Cao Y, Wang Y, Zheng Y, Cheng Z, Li R (2018) Assessment of heavy metal in coal gangue: distribution, leaching characteristic and potential ecological risk. *Environmental Science and Pollution Research* 25(32):32321-32331
10. Hussain R, Luo K, Chao Z, Xiaofeng Z (2018) Trace elements concentration and distributions in coal and coal mining wastes and their environmental and health impacts in Shaanxi, China. *Environmental Science and Pollution Research* 25:19566-19584
11. Li C, Zhao L, Ren Q (2015) Analysis of the current situation and prospect of comprehensive utilization of coal gangue. *Environment and Development* 27(03):72-74
12. Li C, Zheng L, Jiang C, Chen X, Ding S (2021) Characteristics of leaching of heavy metals from low-sulfur coal gangue under different conditions. *International Journal of Coal Science & Technology*
13. Li J, Wang J (2019) Comprehensive utilization and environmental risks of coal gangue: A review. *Journal of Cleaner Production* 239:117946
14. Novikova S, Gas'kova O (2013) Influence of natural fulvic acids on the solubility of sulfide ores (experimental study). *Russian Geology and Geophysics* 54(5):509-517
15. Pandey PK, Sharma R, Roy M, Pandey M (2007) Toxic mine drainage from Asia's biggest copper mine at Malanjkhand, India. *Environmental geochemistry and health* 29(3):237-248
16. Shen L (2020) Research on coal gangue composition and its reuse technology. *Energy and Energy Conservation* (05):62-63
17. Sracek O, Choquette M, Gélinas P, Lefebvre R, Nicholson RV (2004) Geochemical characterization of acid mine drainage from a waste rock pile, Mine Doyon, Quebec, Canada. *Journal of contaminant hydrology* 69(1):45-71
18. Sun R, Liu G, Zheng L, Chou CL (2009) Characteristics of coal quality and their relationship with coal-forming environment: a case study from the Zhuji exploration area, Huainan coalfield, Anhui, China. *Energy* 35(1):423-435
19. Tang Q, Li L, Zhang S, Zheng L, Miao C (2018) Characterization of heavy metals in coal gangue-reclaimed soils from a coal mining area. *Journal of Geochemical Exploration* 186:1-11
20. Wang H, Wu Y, Fu T (2017) Effects of different types of accompanying anionic calcium salts on the release of pollutants from weathered coal gangue. *Journal of Environmental Engineering* 11(05):3043-3050
21. Wu H, Li X, Li J (2014) Acid production and pollutant release behavior of sulfur iron ore tailings during simulated weathering. *Environmental Chemistry* 33(03):447-451
22. Xiao L, Liang B, Lu h (2006) Experimental analysis of leaching release characteristics of some substances in coal gangue. *Journal of Safety and Environment* (02):19-22
23. Xu G (2009) Hebei Promotes Filling Technology in Empty Mining Areas. *China Land and Resources News* (002)
24. Yang F, Xu H (2021) Analysis of the development path of ecological environmental protection and comprehensive utilization of resources in the coal industry in the 14th Five-Year Plan. *China Coal* 47(05):73-82
25. Zhang M, Gao S, Liu W (2013) Prospects for filling solid waste mining areas. *Science and Technology Innovation and Application* (21):122-123

26. Zhao L, Sun Y, Luo S (2019) A comparative study on the dissolution characteristics of inorganic nitrogen and heavy metals in gangue of coal mines in Mianlianta and Baode. *Arid Zone Resources and Environment* 33(10):172-177
27. Zhou C, Liu G, Fang T, Sun R, Wu D (2014a) Leaching characteristic and environmental implication of rejection rocks from Huainan Coalfield, Anhui Province, China. *Chemosphere* 143:54-61
28. Zhou C, Liu G, Wu D, Fang T, Wang R, Fan X (2014b) Mobility behavior and environmental implications of trace elements associated with coal gangue: a case study at the Huainan Coalfield in China. *Chemosphere* 95:193-199

Figures

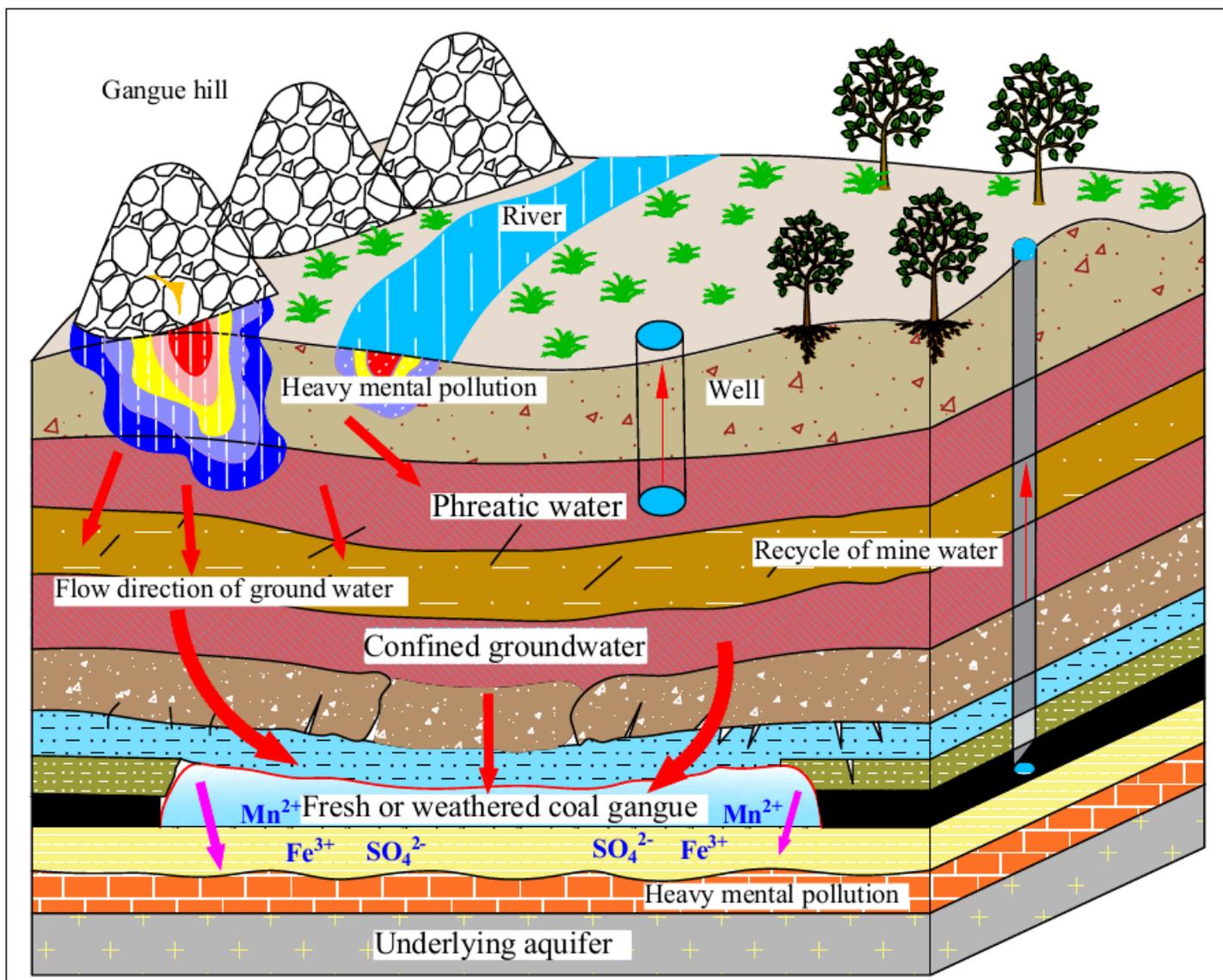


Figure 1

Schematic diagram of groundwater pollution caused by backfilling of coal gangue in goaf

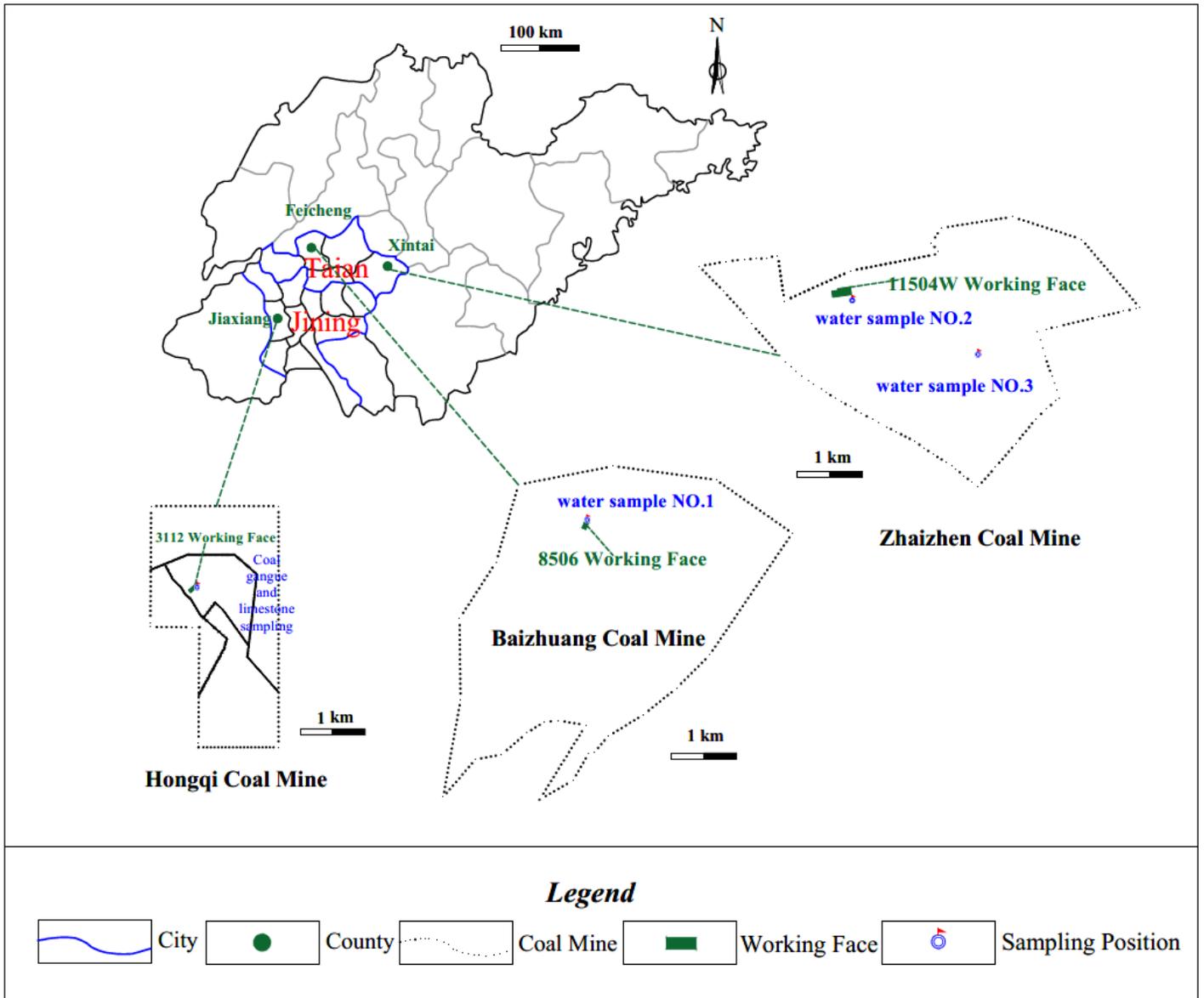


Figure 2

Location map of the sampling area

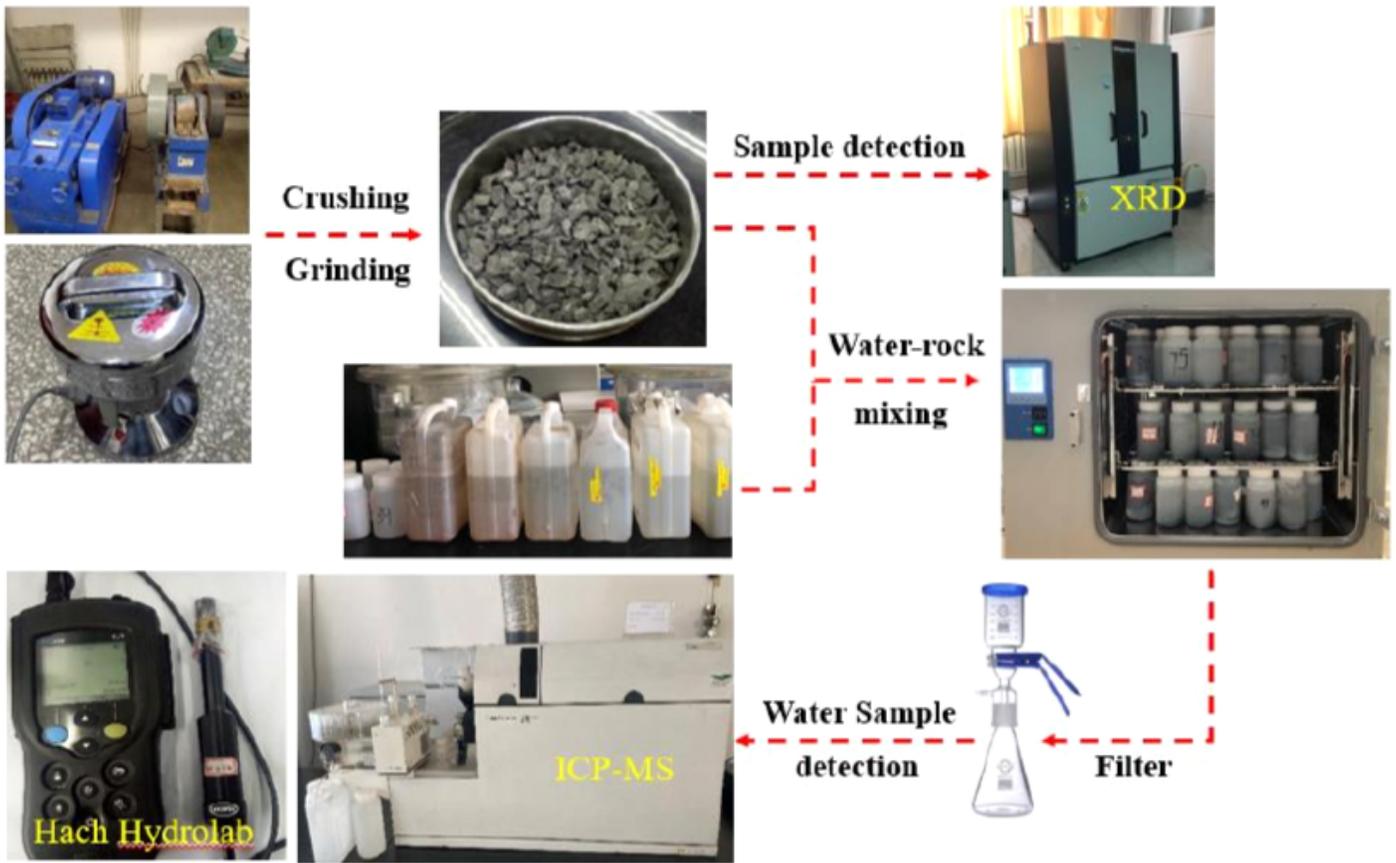


Figure 3

Gangue soaking experiment

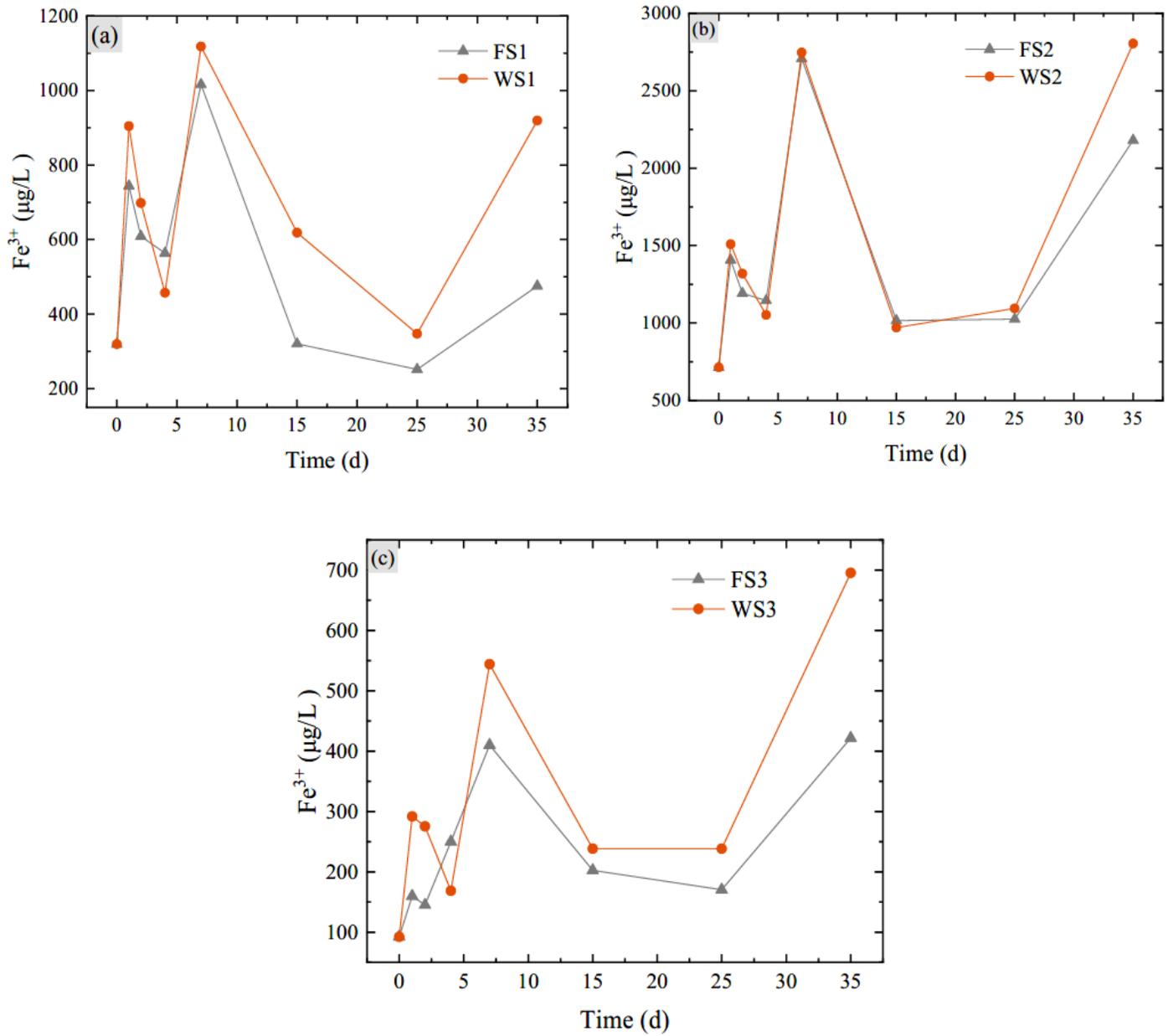


Figure 4

Trend of change in the Fe^{3+} concentration in the leachate of the two kinds of coal gangue

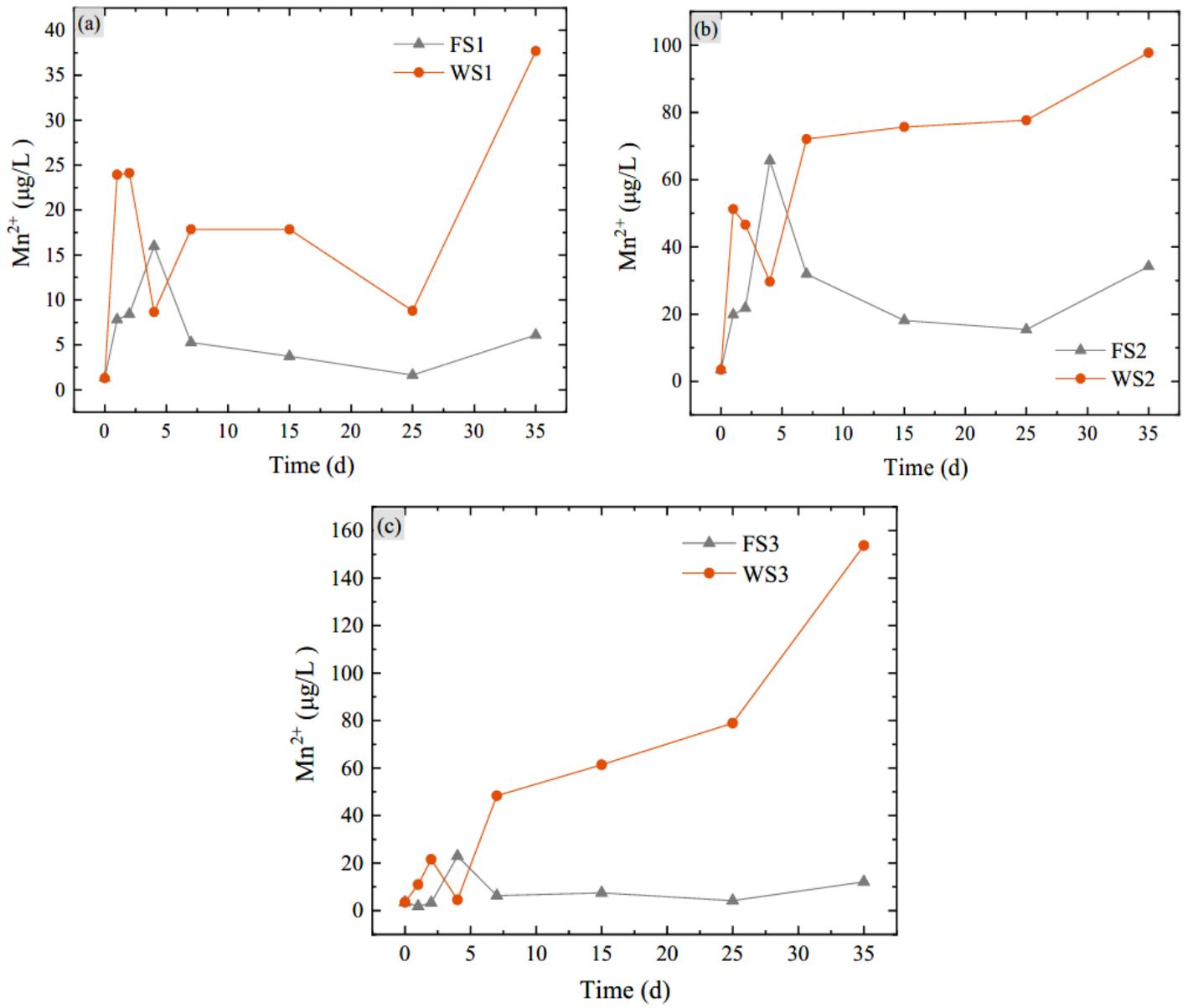


Figure 5

Trend in the change of Mn^{2+} concentration in the leachate of two kinds of coal gangue

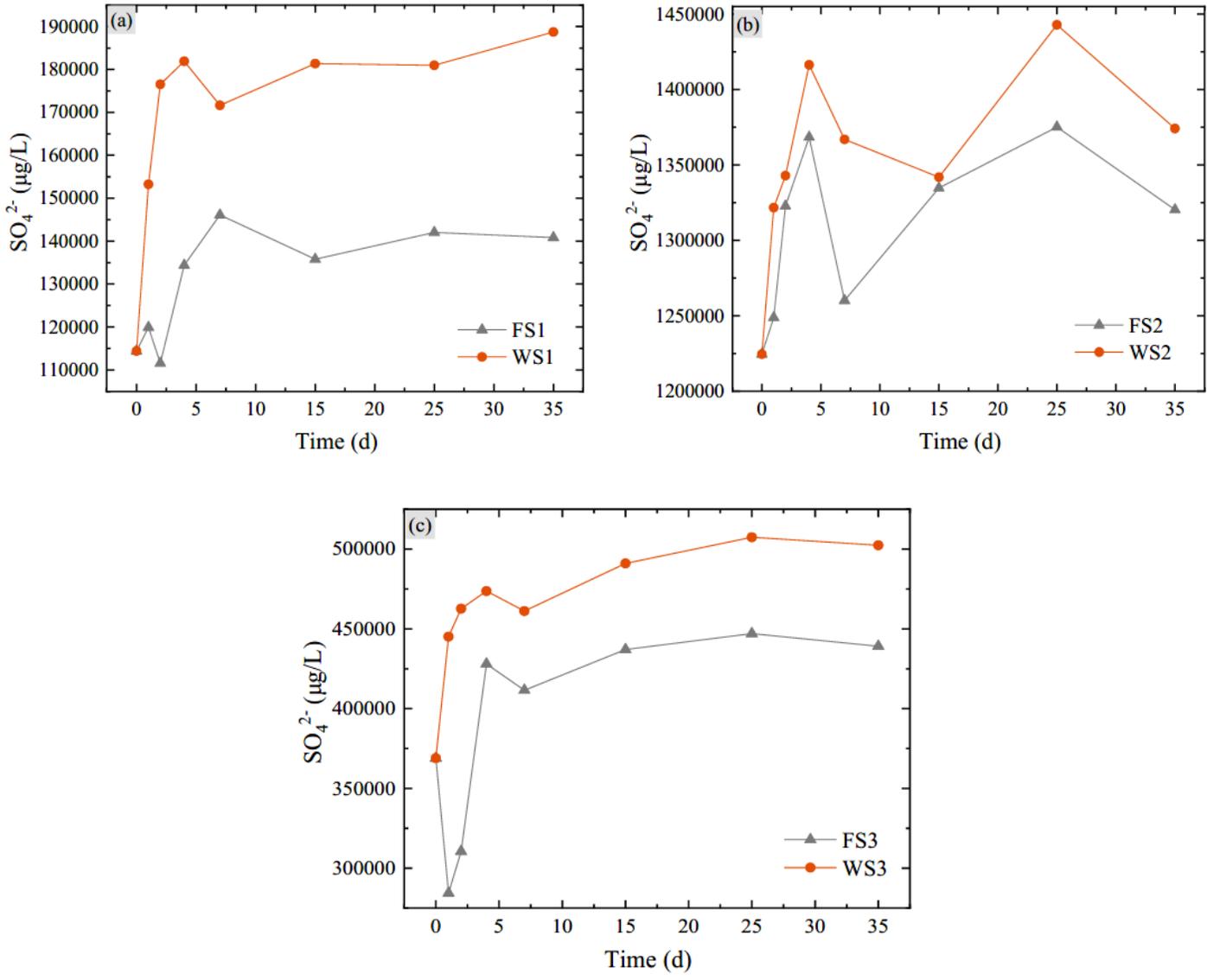


Figure 6

Trend in the changes of SO_4^{2-} concentration in the leachate of the two kinds of coal gangue

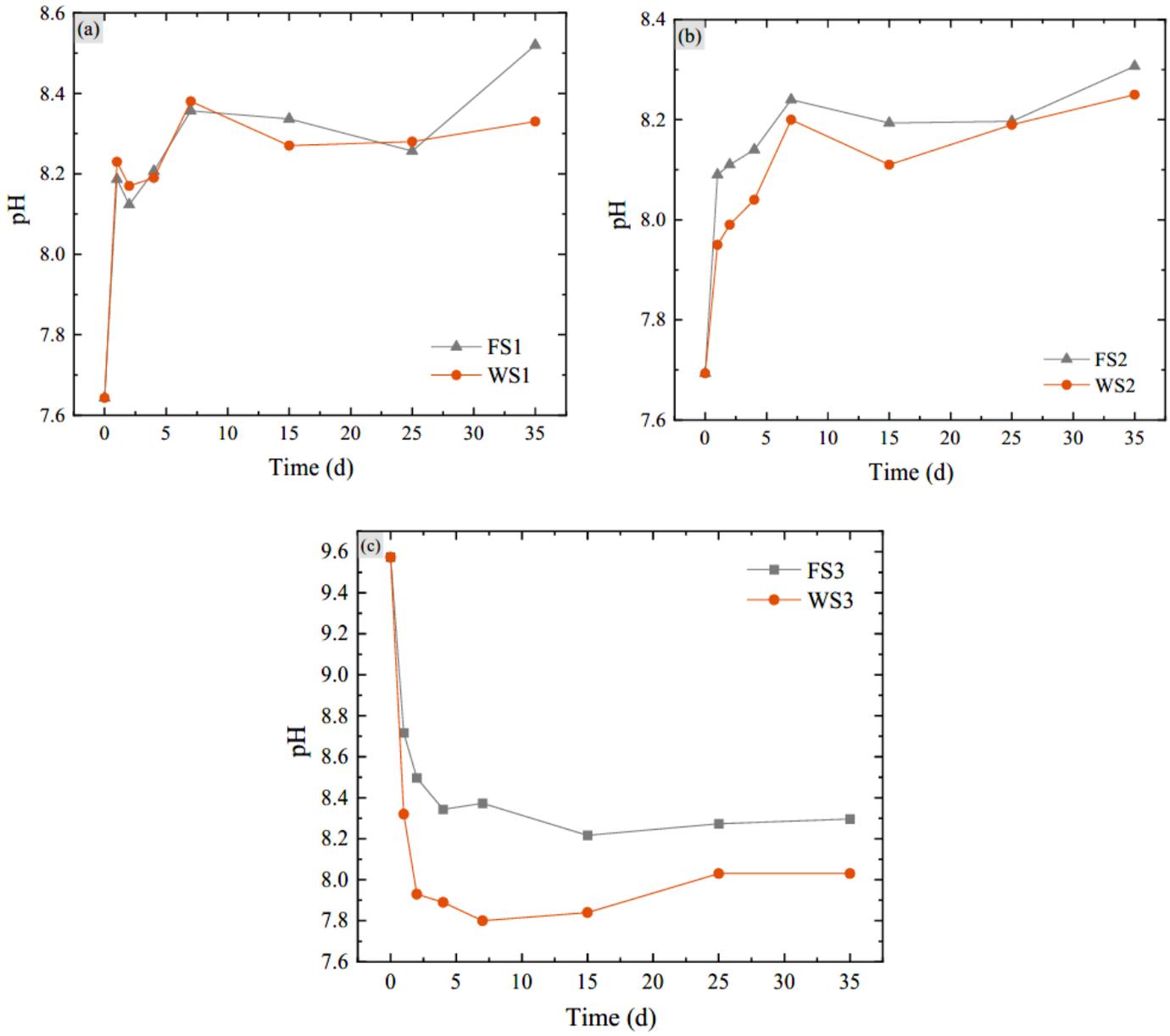


Figure 7

Trends in the change of pH of different leaching solutions

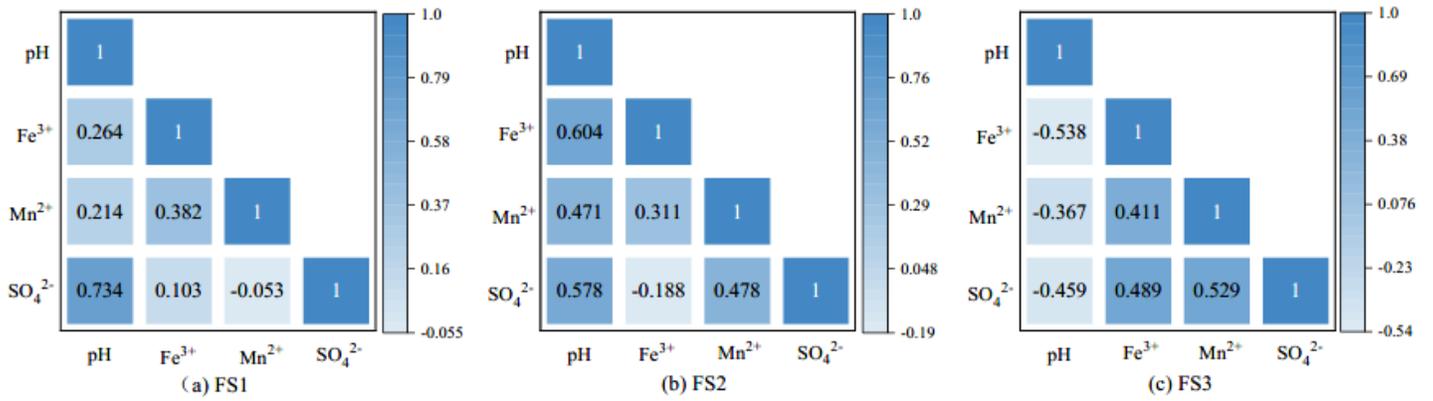


Figure 8

Heat range diagram for correlation between the pH of the immersion solution and each ion

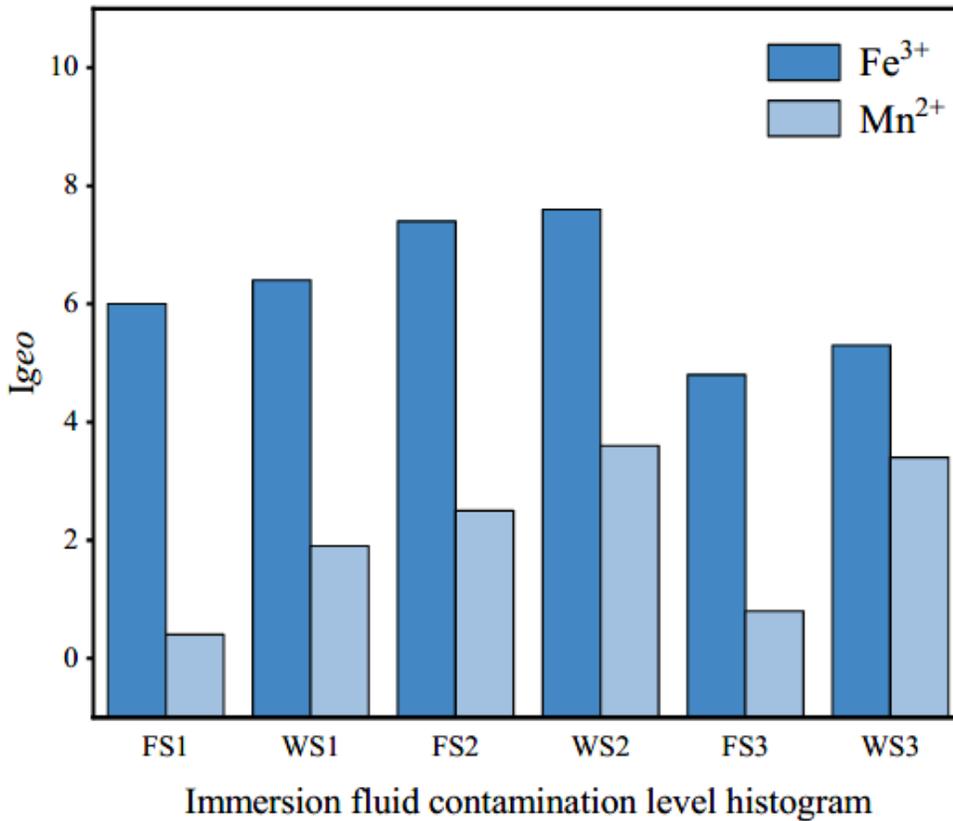


Figure 9

Histogram of the immersion fluid contamination level

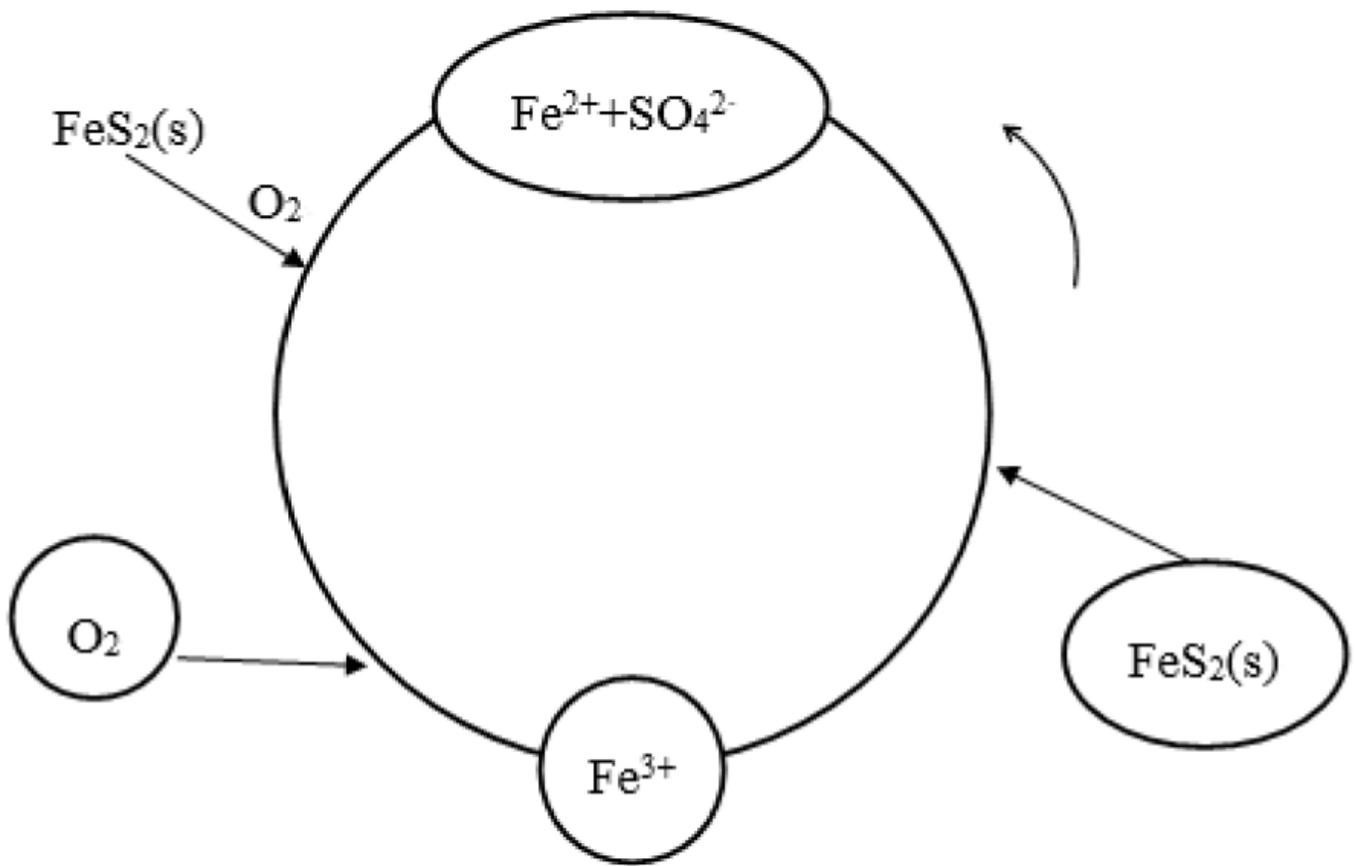


Figure 10

Schematic diagram of the pyrite oxidation cycle