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Mineral release processes and mechanisms of raw coal from Feicheng, China

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ABSTRACT

In this study, samples from 3 major mining seams in the mining area of Feicheng in Shandong Province, China, were studied. The release of minerals from raw coal samples with different particle diameters was measured. The characteristics and patterns of the minerals released from residual coal in the groundwater environment after the coalfield was closed are discussed. The following results were obtained. 1) The cumulative amounts of minerals that were leached from the coal samples correlated significantly with the particle diameter. This relationship between the amount of cumulative leaching of the coal sample minerals and the particle diameter was described by the following equation: $y=ax^b$. 2) The different coal compositions resulted in different amounts of mineral release from the samples. 3) The quantities of the minerals released from the coal samples in water were constrained by changes in the residues on the surfaces of the coal samples. These results provide a theoretical basis for determining potential water pollution sources in abandoned coalmines. In addition, these results could be used to restore water circulation systems and to restore the use of groundwater resources. These processes are important for using mine water from abandoned coalmines.

Keywords: North-China-type coal field, mineralisation, leaching, groundwater pollution.

INTRODUCTION

The primary source of mine water is groundwater from the surrounding supply regions. This groundwater is altered by physical, chemical and biochemical reactions between the solid and liquid phases when the groundwater encounters the coal and rock strata [1]. Mine water quality is significantly affected by the duration of contact, geological structures, coal-derived associated mineral compositions and environmental conditions [2]. In addition, the quality of mine water is further complicated by the leaching of stone dust, coal dust and other organic materials into the water. This leaching results from human activities when mine water passes through coal mining faces, tunnels and gob areas [3].

Abandoned coalmines threaten the safety of water environments and pose serious problems worldwide [4]. The groundwater in the Tual region of the former Soviet Union was severely polluted by a large number of abandoned coalmines [5]. In addition, a groundwater catchment in the Appalachian Mountains (US) with an area of 4,000 km^2 was polluted by abandoned coalmines [6]. Recently, a number of coalmines have been closed in China. However, the environmental impacts of mine water can become more serious after mine closure [7-9]. After closure, the mineralisation of the mine water in the Dafeng Mine in the Feicheng mining area of Shandong Province reached 3,996 ml/L. Additionally, the sulphide concentrations reached 2,300 ml/L, and the contamination levels greatly exceeded the standard levels. Groundwater is abundant in the mining area of Feicheng. The groundwater resources and renewable groundwater resource areas that are threatened by pollution due to coalmine closure have reached more than 0.3 billion t/a and 1,000 km^2, respectively. Abandoned coalmine pollution results from the underground structural damage that results from decades of mining and the release of multiple contaminants that pose long-term and continuous threats to groundwater sources in mining areas.

Several types of studies have been conducted to determine the effects of mine water from abandoned coalmines on the surrounding environment. 1) Several studies have analysed and simulated mine water pollution, including the evolution characteristics of groundwater quality, water purification analyses and preliminary investigations of simulation models for water quality. [10-12] 2) Simulation studies have been conducted regarding mine water rebound in abandoned mines. P.L. Younger conducted many of these studies and established three simulation models [13]. In addition, D. Banks [14] created a groundwater recirculation model that was based on the relationships between volume and water levels. This model was established according to different elevations and water storage volumes. 3) Finally, the treatment and comprehensive use techniques of mine water have been evaluated. An abandoned coalmine serves as the catchment area for groundwater where groundwater dissolution takes place. A number of treatment measures and theoretical methods have been proposed for using water resources from abandoned coalmines, including the construction of aquafarms [15] and wetland ecosystems [16, 17]. However, most current studies treat the mine water from an abandoned mine as a pollution source. Thus, current studies have focused on the effects of mine water rebound on external environments (rivers, groundwater and other water systems) after coalmine closure [18]. Here, we consider mine water as a potential resource that has been polluted. Therefore, studies on flooded mine water from abandoned coalmines that restore the original resource value of mine water and increase the usable water source are important for the increasingly severe global crisis of water scarcity [19, 20].

The use of mine water is important for addressing the shortage of water resources in mining areas. Among the 13 planned large-scale coal areas in China (with the exception of the Yunan-Guizhou area), the Huainan and Huaibei area and the eastern Inner Mongolia (Northeast) area have relatively abundant water resources. In contrast, the other 10 areas have water scarcity issues [21]. Thus, it is important to use mine water to alleviate inadequate water supply problems in mining areas and to satisfy production demands for domestic water. Water quality data from 154 coalmines in China indicated that the pH of mine water ranged from 3.42 to 8.94, with a mean value of 7.67. In addition, the mine water in most coalmines is neutral or weakly alkaline. Furthermore, mineralisation ranges from 356.00 to 7,399.29 mg/L, with a mean value of 1,650.15 mg/L. Thus, mine water is commonly highly mineralised.
Several studies have shown that mine water quality can improve with time, which has been verified in many countries (including China, the US and the UK) [22, 23]. However, due to the uncertainty of pollution sources, unknown pollution mechanisms, unclear treatment prospects and the early stage of water use from closed coalmines, the treatment of pollution in mine waters requires further research. Many researchers have studied the use of mine water and abandoned coalmines [24, 25]. However, few researchers have studied the characteristics and patterns of mineral release in abandoned coalmines. The release of related ions from abandoned coal in abandoned coalmines determines the investments and profits of mine water treatment.

Thus, this process is considered by many decision-makers. Therefore, the characteristics and patterns of mineral release from residual coal in underground spaces and groundwater environments after coalmine closure were discussed in this study. Specifically, indoor leaching experiments were conducted with the coal samples. Our results provide a theoretical basis for the use of mine water resources from closed coalmines.

EXPERIMENTAL SECTION

Sampling

Coal samples collected from 3 major mining seams at the Caozhuang Coalmine of the Feicheng Mining Bureau were used as the experimental samples in the present study. The coal samples come from the 3rd seam (Sample 1), 8th seam (Sample 2) and 9th seam (Sample 3). Table 1 lists the major compositions of the coal samples from the different seams (data provided by the China Geological Environmental Monitoring Institute).

There are 10 mining seams in the mining area of Feicheng. The 3rd coal seam is in the Permian Shanxi formation and occurs at a depth of 190m. The 8th and 9th coal seams belong to the Carboniferous Taiyuan group and occur at depths of 309 and 319m, respectively. These 3 seams represent the major coal mining seams in Feicheng and are the main mining seams in the coalfields typical of North China. Raw coal was selected from this mine as the experimental samples. In addition, this research provides important references for similar areas.

Table 1 Major composition of the samples

Seam	Water	Ash	Volatile	Total sulphur	Phosphorous	Chemical composition of ash (%)		
						SO_3	CaO	MgO
Sample 1	1.4	22	39	0.6	0.0188	2.26	5.13	0.67
Sample 2	1.4	28	42	2.9	0.0055	7.5	9.73	1.19
Sample 3	1.3	26	42	2.2	0.0288	3.78	4.56	0.69

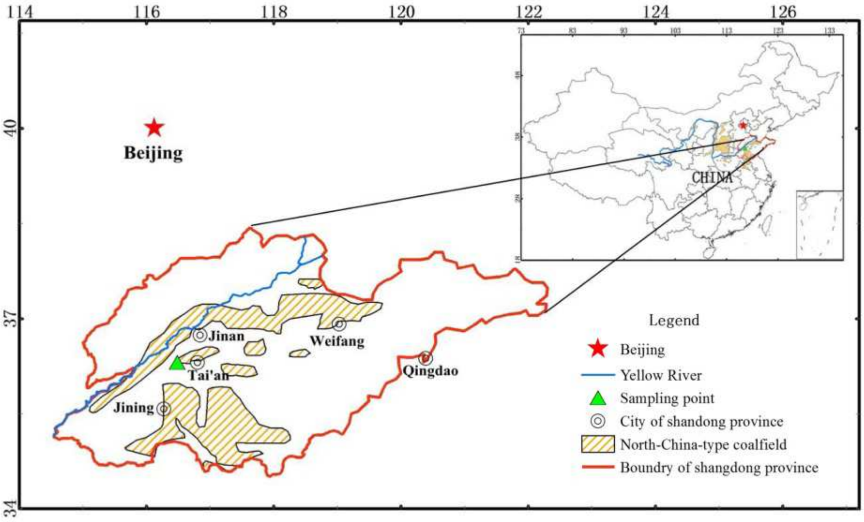

Fig. 1 Location map of the sampling point

Methods

The still water leaching method was used here to investigate the characteristics and patterns of mineral release to water from coal samples with different particle diameters. The release process was also studied. The degree of mineralisation was used as an index for quantifying mineral release. The experimental steps are listed below.

1) Standard experimental samples with particle diameters of 5, 2, 0.6, 0.25 and ≤0.05cm (pulverised coal with the smallest particle diameter) were prepared from coal samples 1, 2 and 3. The samples with a particle diameter of 0.25 cm weighed 800 g and the other samples weighed 400 g.

2) Still water leaching experiment. Distilled water was added to the samples with different particle diameters (400g of each sample) based on a coal: water ratio of 1:5. The coal samples were immersed in distilled water for 24h. Then, the distilled water was replaced with clean distilled water, and the coal samples were immersed for an additional 24h. The distilled water was replaced 5 times. After each immersion, the leachate was added to a flask before chemically analysing the leachate.

3) Still water leaching extension experiment. Distilled water was added to samples with a particle diameter of 0.25 cm at a coal: water ratio of 1:5. The coal samples were immersed in distilled water for 72 h before the distilled water was replaced by clean distilled water, and the coal samples were immersed for an additional 72 h. The distilled water was replaced 8 times. After each immersion, the leachate was added to a flask before leachate analysis.

The experiments were conducted exclusively at the Shandong Geological Environmental Monitoring Station and were performed according to their requirements. The leachates were analysed at the Shandong Geological Environmental Monitoring Station laboratory. The following gravimetric method was used to determine the degree of mineralisation:

$$C=\frac{W\text{-}W_0}{V}*10^6+\frac{1}{2}C_1 ,$$

Where：

C – mineralisation degree of the water sample, mg/L;
W – total mass of the evaporation pan and residue, g;
V – volume of the water sample, mg;
W_0 – mass of the evaporation pan, g; and
C_1 – bicarbonate content in the water sample, mg/L.

RESULTS AND DISCUSSION

Relationships between the amounts of leaching and particle diameter

We obtained the cumulative amounts of leached minerals from the coal samples with different particle diameters by chemically analysing the coal leachates (Table 2). Large differences occurred between samples with the same mass with regard to the amounts of leaching that resulted from the different particle diameters. Table 2 shows that the cumulative amounts of the leached minerals gradually increased with decreasing particle diameter. This trend was basically observed in all 3 coal samples. Due to the relatively small amount of minerals leached from sample 3, the cumulative leaching was slightly less for the particle size 0.25 cm than for 0.6 cm. Overall, the cumulative amount of leaching generally increased with decreasing particle diameter.

Table 2 Cumulative amounts of mineral leaching

Particle diameter (cm)	Cumulative amounts of mineral leaching (mg)		
	sample1	sample2	sample3
5	483.94	207.34	283.88
2	579.56	618.12	316.44
0.6	1081.04	2363.24	486.28
0.25	1863.38	2776.08	440.58
0.025*	3312.98	4263.08	608.93

* *These data were calculated based on the mean values.*

Based on the cumulative amounts of minerals leached from the 3 coal samples with different particle diameters, the data from the leaching experiments of the 3 coal samples were fitted with different curves. As a direct test method, there are 3 major forms of relationships obtained from the coal sample leaching experiment:

Logarithm form $y=a\ln x+b$

Exponentiation form $y=ax^b$

Index form $y=ae^{bx}$,

Where *y* is the cumulative leaching amount, *x* is the particle diameter and a and b are the regression coefficients. The coefficient of determination (R^2) was obtained from a regression analysis of the y and x variables and was used to evaluate the goodness of fit. The F-test was used to test the significance of the regression equation at a significance level of 0.05.

The 3 fitting relationships shown above were used to fit the experimental leaching data. A comparison of the fitting results indicated that the exponential fit was the best relationship with regard to precision, followed by the logarithmic and index relationships. Therefore, we used the exponential relationship to fit the cumulative amounts of minerals leached from the 3 coal samples with the particle diameters. These results are listed in Table 3.

Table 3 Exponential fitting results of the cumulative amounts of mineral leaching and the particle diameters

Sample	Coefficient a	Index b	Coefficient of determination (R^2)	Significance test of the regression equation	
				F	Sig
sample1	117.2848	-0.33844	0.9637	161.596	0.00105
sample2	1469.26	-0.30272	0.80854	28.8703	0.01262
sample3	380.4642	-0.13233	0.84338	178.938	0.0009

The coefficient of determination of the fitting results for coal sample 1 reached 0.96, which indicates that the goodness of fit was excellent. The coefficients of determination for coal samples 2 and 3 were also greater than 0.8 and passed the significance test ($p<0.05$). These results indicate that the cumulative amount of mineral leaching was correlated with the particle diameter. In addition, the establishment of regression equations was meaningful. Therefore, the particle diameter (using $y=ax^b$) was suitable for describing the correlations between the cumulative amounts of mineral leaching and the particle diameters.

Mineral release pattern

The still water leaching extension experiment results indicated that the cumulative amounts of leaching were different between the coal samples with the same particle diameters due to the differences in coal quality. According to Table 1, coal sample 2 contained high SO_3, CaO and MgO contents. The release of these compounds resulted in an increase in the degree of mineralisation in the leachates. Figure 3 shows that the cumulative amount of minerals leached from coal sample 2 was significantly higher than those from the other two coal samples. After 8 cycles of leaching, the accumulated mineral release from coal sample 1 was 1,788.4mg, the cumulative amount of minerals released from coal sample 3 was 1,165.6mg， and the cumulative amount of minerals released from coal sample 2 was 7,569mg, which was 4 times that from coal sample 1 and more than 7 times that from coal sample 3. The trend lines of the cumulative amounts of minerals released from coal samples 1 and 3 are relatively consistent with one another and basically parallel one another. In sharp contrast, the trend line of the cumulative amount of minerals leached from coal sample 2 rises sharply before gradually stabilising.

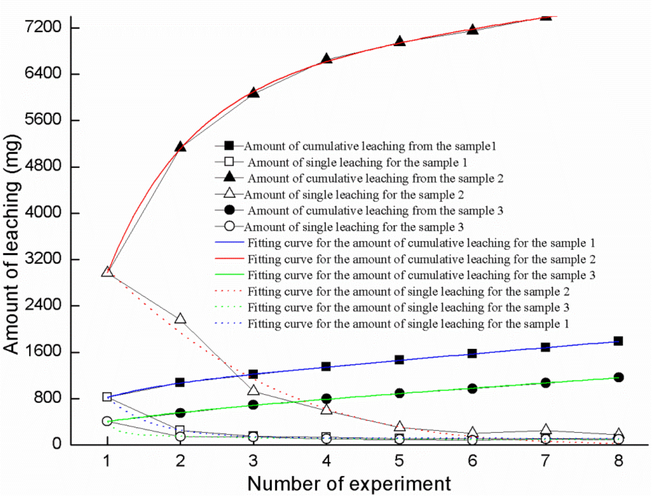

Fig. 2 Amounts of minerals leached from the coal samples and the fitting curves

The release patterns of minerals from the 3 coal samples show that the amounts of minerals released from the coal samples in water were the largest in the first leaching experiment. Subsequently, the amounts of minerals released from the coal samples decreased rapidly. This change was particularly significant in coal samples 1 and 3. The amounts of minerals released from the coal samples gradually stabilised in the subsequent leaching experiments. The amount of minerals released from coal sample 1 in the first leaching experiment was 820 mg, whereas the amount of minerals released from coal sample 1 in the second leaching experiment was 250 mg, which was 3 times less than that in the first leaching experiment. A similar release pattern was also observed in the leaching experiments of coal sample 3. Due to the relatively high S, Ca and Mg contents, the single release curves of coal sample 2 decrease slowly; however, the single amounts of minerals released from coal sample 2 were relatively large. For instance, the amounts of minerals released from coal sample 2 in the first and second leaching experiments were 1,485.8 mg and 1,080.6 mg, respectively. Table 4 lists the fitting equations for the amounts of minerals released from the coal samples.

Table 4 Fitting equations for the amounts of minerals released

Type	Sample	Fitting equation	Coefficient of determination
Single release	Coal sample1	y=1772.74exp(-x/0.62)+1772.74exp(-x/0.62)+113.15	R^2=0.998
	Coal sample2	$y=\exp(8.384-0.3261x-0.0404x^2)$	R^2=0.971
	Coal sample3	y=1.03E7exp(-x/0.09+180.2756exp(-x/1.87)+87.59	R^2=0.983
Cumul-ative release	Coal sample1	y=-395.911+906.96ln(x+2.887)	R^2=0.996
	Coal sample2	y=-5704.6exp(-x/23.6)-7973.58exp(-x/1.09)+11638.4	R^2=0.994
	Coal sample3	y=-1874.08+1130.8ln(x+6.547)	R^2=0.998

Based on the single release curves of the 3 coal samples, after coal samples 1 and 3 were leached 3 times and coal sample 2 was leached 4 times, the release amounts of the coal samples levelled off. During the mineral release process, we discovered a layer of soft residues on the surfaces of the coal particles that became thicker with leaching time. This layer of surface residue on the coal particles acted as a “protective membrane” and prevented the release of minerals. In addition, the thickness of this “protective membrane” continued to increase and became more effective at preventing the release of minerals, resulting in stable, low amounts of released minerals from the coal samples. As shown in Fig. 3, almost no protective membrane occurred on the particle surfaces in section a (i.e., the first 3 leaching experiments), and the minerals were released rapidly and in large amounts. The protective membrane gradually formed in section b (during the 4th and 5th leaching experiments); the mineral release rate decreased, and the amounts released during single events gradually decreased. In section c, the protective membrane was relatively thick, and the release amount tended to be stable and low.

According to Fig. 3, the total amount of minerals released from coal sample 1 was 1,788.4 mg, and the total amounts of minerals released from coal samples 2 and 3 were 7,869 mg and 1,165.6 mg, respectively. When only the masses of SO_4^{2-}, Mg^{2+} and Ca^{2+} were considered, according to Table 1, the amounts of minerals that could be released from coal samples 1, 2 and 3 were 6,962.96, 15,303.6 and 5,168.2 mg, respectively. The percentages of the total mineral release to the potentially releasable minerals were 25.68%, 51.4% and 22.6%, respectively. These percentages would be lower if other ions were considered. This phenomenon indicated that the release of minerals from abandoned coal (a pollution source in the groundwater) is constrained due to the protective membrane. In this case, the single releases decrease rapidly, which results in reduced effects on the groundwater quality.

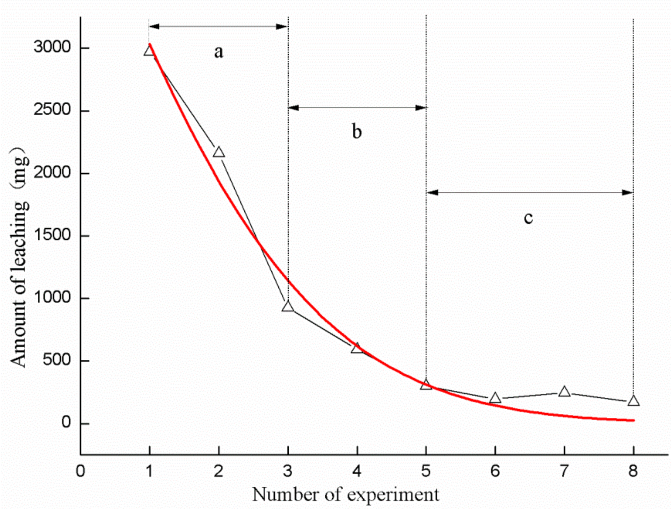

Fig. 3 Mineral release pattern of Sample 2

CONCLUSION

In this study, the characteristics and patterns of mineral releases from coal samples in a aqueous environment were investigated through still water leaching experiments. The experimental results showed that the compositions of the coal samples differed between the different seams. In addition, a large difference occurred among the coal samples with regard to the amounts of minerals released into the water. Furthermore, the effects of the coal samples on the groundwater were different. Therefore, when calculating the amounts of minerals released from abandoned coal, the coal should be comprehensively analysed. A significant correlation occurred between the amount of minerals leached from the coal sample and the particle diameter. The correlation between the amount of cumulative minerals leached from the coal samples (which were collected from the abandoned coalmine in the Feicheng mining area) and the particle diameter was described by the following equation: $y=ax^b$. When the coal samples released minerals to the water, a layer of the residues on the coal surface gradually increased. This residue layer acted as a “protective membrane” on the surfaces of the coal particles, preventing additional mineral release and decreasing the mineral release rate. Eventually, the amounts of minerals released gradually stabilised [26].

When treating an abandoned coalmine, the mean particle diameter and volume of the abandoned coal should be measured according to the fitting equations of the amount of leaching versus particle diameter. Next, we can predict the approximate cumulative amount of leaching based on the regression equations of the cumulative amounts of mineral leaching and the particle diameter to treat the mine water of an abandoned coalmine. Decision-makers can estimate their investments and profits from treating the mine water. Therefore, the present study provides a theoretical basis for comprehensively treating and utilising mine water in abandoned coalmines and is promising for turning abandoned coalmines into “underground water reservoirs”. In addition, this study is important for addressing water scarcity issues that are becoming more severe.

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