Effects Of Deep Karst Water On The Release Of Potentially Toxic Metal Ions From Coal Gangue In Abandoned Coal Mine Region

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Abstract

A great amount of coal gangue was left out in mine goaf after the mines closed or abandoned, and they underwent the soaking of the groundwater from the underlying aquifers with the release of potentially toxic metals. A series of large-capacity immersion test was conducted to study the metal Mn and its leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels. We obtained the results including XRF, pH, ORP, EC, and the concentration of Mn, which showed a big difference between site karst water and lab solutions with different pH levels. All results may provide reference for security theory and contamination control technology of deep karst water in abandoned coal mines.

Keywords: immersion test, XRF, site karst water

Introduction

Potentially toxic metal ions from coal gangue in abandoned coal mines substantially affect the quality and uses of water supplies in mining area all over the world [Iii CAC 2008; Azam S and Li Q, 2010]. The mining activity of coal mines in Shandong province of China has experienced aross the whole century. With the closure and integration of numerous coal mines, safety and environmental issues induced by closed mines have become increasingly prominent, including surface subsidence or landslides, unstable foundations of high buildings or buildings rupture, poor-quality mine water, and surface water or ground water contamination, etc [Hasheela I et al., 2014; Wang LG et al., 2008]. The effect of closed mines on the surrounding environment involves so many aspects, but relatively speaking, groundwater pollution pose more serious threats to human survival [Atanacković et al., 2016; Xia Z et al., 2007]. After the closure of coal mines, a large amount of solid waste such as the abandoned coal, coal gangue and waste structures are left in the goaf [Zhou HY 2012; Peng B et al., 2018]. When ground water rebound, toxic potentially toxic metals contained in solid waste, such as chromium (Cr), cadmium (Cd), copper (Cu), manganese (Mn), lead (Pb), zinc (Zn) and arsenic (As) are continuously released into the water and cause water pollution [Zheng L et al., 2016; Tang Q et al., 2018]. In recent years, many researches related to potentially toxic metals release or migration focus on the effects of pH levels of leaching solutions, grain sizes of different solid waste, mineral structure, chemical compositions, solid–liquid ratios, temperatures, etc on solid waste during the process of static and dynamic leaching tests [Lin H et al., 2017; Roessler JG et al., 2015; Othmani MA et al., 2013]. In China, especially in North China, a great majority of coal-bearing strata overlay the Ordovician limestone karstic aquifers, which are deeply buried.These coal mines almost have special karst groundwater and large mining depth, whose greater liquidity and hydrochemistry environment sensibility further aggravated the crisis of site karst water contamination in abandoned coal mines. However, very detailed studies of site karst water on the release of potentially toxic metal ions from coal gangue under this special conditions have been reported.

The main objective of this research was to investigate the effect of site karst water using coal gangue as experimental material with regard to potentially toxic metals, and compare its difference from other pH levels of leaching solutions. A series of large-capacity immersion test was performed to study the potentially toxic metals and leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels. The release mechanism of potentially toxic metal Mn was investigated, and the relevant influencing factors were analysed and discussed during the leaching process, covering liquid-solid ratio, contact time and temperature, pH changes, oxidation reduction potential (ORP), electrical conductivity (EC), etc. The results are supposed to serve as a reference for the evaluation of potentially toxic metals pollution of Ordovician limestone water occurring in abandoned or closed coal mines and the forecast of the ecological risks induced by coal gangue, and examine the safety for applying coal gangue to the goaf.

Methods

In this paper the study area is Baizhuang coal mine, which is located in the west wing of Taishan Mountain and at the southern foot of famous Taoshan Mountain (seen in Fig 1). It lies in Midwest of Feicheng coal field, located in Feicheng, Shandong Province, east of China. The range of coal mine is west to fault F_7 and adjacent to Chazhunag coal mine and Guozhuang coal mine, north to fault F_{1-1} and fault F_{1-2}, east to fault F_{21} and adjacent to Taoyang coal mine, south to fault F_{3-1} and adjacent to fault BF_5 along with Xinglong coal mine. Baizhuang coal mine has its strike of about 4 km long, inclination of about 3.9 km wide, and area of 15.6708 km^2. The regional stratigraphic classification of Baizhuang coal mine belongs to stratigraphic subregion of western Shandong in North China, and the whole area has steady deposition. Its strata thickness, lithology, and stratigraphic contacts are essentially the same as for stratigraphic subregion of western Shandong. And its strata correspond to Quaternary, Permian, Carboniferous, Ordovician and Cambrian from above to below respectively. Baizhuang coal mine is surrounded by faults, and its northern part is influenced by the traction of boundary F_1 fault to form an accompanying asymmetric syncline along the F_1 fault group. In this area there has quite a few aquifers such as Quaternary sandstone aquifer, first, second and fourth limestone aquifers of Taiyuan Formation, fifth and sixth limestone aquifers of Benxi Formation and Ordovician limestone aquifer. Moreover, Ordovician limestone aquifer has strong water yield property, adequate recharge water and close hydraulic relationship with the fifth limestone aquifer. For karst coal mines in North China, the strong Ordovician limestone aquifer often poses a huge threat to coal seam floor, especially for the closed or abandoned mines, Ordovician water always flow into the goaf and react with the leftover coal gangue.

Fresh coal gangue exactly mined out from Baizhuang coal mine were collected as the main experimental samples. After five samples (roughly 1 kg each one) gathered in the tunnel of the buried depth of 430 m and stored in clean polypropylene bags, a process of sample pooling and crushing was conducted, and then the coal gangue with 3–8 mm in diameter was sieved to homogenize for subsequent analysis by use of classifying (seen in Fig.2). After that these coal gangue

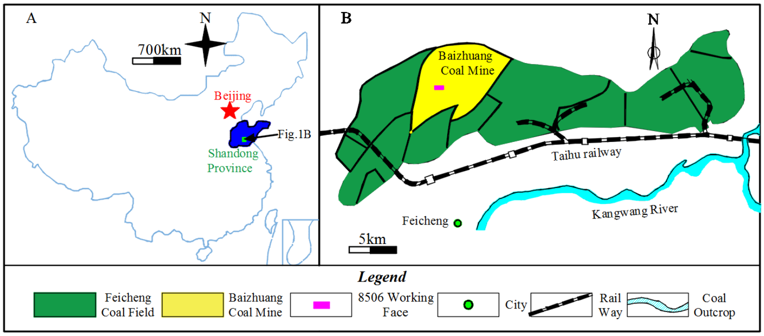

Figure 1 Geographic location of Baizhuang coal mine in China.

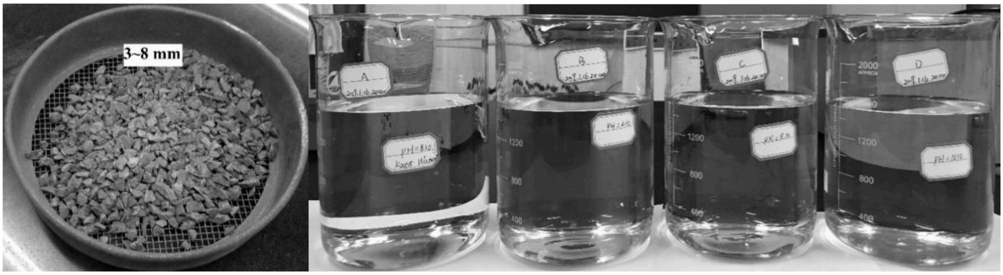

Figure 2 Coal gangue of particle sizes 3–8 mm (left) and the leaching solutions (right).

Table 2 The major elements content and potentially toxic metal elements content in the original coal gangue sample.

Elements Unit	Si g/kg	Al g/kg	Fe g/kg	K g/kg	Mg g/kg	Na g/kg	Ca g/kg	Mn g/kg
Coal gangue	305.7	120.9	33.0	26.9	10.1	2.68	2.18	0.217

samples were dried for 24 h at 105°C, which were finally placed in an airtight container as the samples of immersion test. Whereas Ordovician limestone water samples were collected from full hole of east wing belts I located in the drilling O_{38} of 8506 working face in this coal mine, and then they were stored in polyethylene bottles and brought into the lab.

According to the experience of immersion research, this test was conducted to study the release of potentially toxic metals at the solid: liquid ratio 1:10 (g/mL). An equivalent amount of coal gangue samples was weighed and put into large beakers with the leaching solutions including site karst water, pH= 5.3, 7.3, and 9.3 (marked respectively A, B, C, and D, seen in Fig. 2). The initial pH value of three leaching solutions was selected in view of pH level of site karst water (pH=7.3), which was adjusted with diluted H_2SO_4 or NaOH. One hundred and sixty gram of gangue sample was mixed with 1600 ml leaching solutions in large-capacity beakers, which were shook in stable temperature Horizontal shaking bath with oscillation frequency of 80 r/min and amplitude of 20 mm at 25°C. After a certain shaking time (12 h, 24 h, 36 h, 48 h, 72 h, 96 h, 144 h, and 216 h), 10 mL leaching solution was taken out from the beakers and then was kept under seal and labelled as testing solutions. Notably, the leaching solutions need to be stirred for one hour before sampling, and after that a supernatant liquid resting for half an hour was extracted and finally filtered into polyethylene bottles using a 0.45 μm aperture microporous membrane and stored at 4 °C until experimental analysis. After four testing solutions were collected, the content of potentially toxic metal Mn was determined by ICP atomic emission spectrometer (ICP-AES). The value of pH, ORP and EC was determined by Hach Hydrolab Multi-Parameter Water Quality Analyzer. 36 testing solutions were obtained for this experiment.

Results and discussion

XRF analysis of coal gangue

The major elements content and potentially toxic metal elements content in the original coal gangue sample are determined using X-ray Fluorescence Spectrometry (XRF) at Shandong University of Science and Technology, which are shown in Table 2. The XRF results revealed that SiO_2 was major constituent. From this table, we can see that the main potentially toxic metal was Mn (0.217 g/kg).

Results of immersion test

Through Hach Hydrolab Multi-Parameter Water Quality Analyzer, we can acquire the pH, ORP and EC of coal gangue at different solutions over time displayed in Fig. 3.

As we all know, pH is one of the important parameters to measure the extent to environmental degradation. From Fig.6 we can know that the changing trend of all pH curves is consistent on the whole. After 36 h the pH changing curves of C and D samples remained stable, but that of A and B samples have a big drop down to 8.28 after 72 h and to 8.26 after 216 h respectively. Although initial pH values vary, the variation range of all pH values at four kinds of solutions has been primarily centered on pH of 8-8.7 throughout time, which maintain the weakly alkaline. It also showed the acid buffering capacity of coal gangue. Due to this capacity the pH values of four solutions including site karst water could keep constant for a long time [Lin H et al., 2017]. Moreover, every testing pH value of sample at a solution of site karst water after 24 h (A) was almost higher than that of three other immerse solutions (B, C and D), the pH values of all solutions were successively observed, A>B>D>C, which indicate the effect of site karst water on coal gangue differs considerably from lab configuration cases in terms of solution pH. Additionally, there is a substantial difference of pH variation over time at A and C samples with the same pH of 7.3.The pH at A sample over time fluctuated larger than that at C sample, the former varies from 7.3 to 8.7, mostly at pH of 8.5 above, yet the later with almost no change, mostly at pH of 8.0. Again, it confirmed that the different effect mechanism of site karst water.

It is well known that electrical conductivity (EC) reflects the activity of the electrolyte in solutions (that is, ion concentration), which can also show the interactive intensity between solid phase and liquid phase. The EC values of all solutions were observed in the following order, C>A>D>B. It can been seen from Fig.6 that the conductivity at a solution of site karst water (A) first increased up to 733 µS/cm slightly after 36 h and then fluctuated up or down from 661 µS/cm to 764 µS/cm, and finally decreased all the way up to 636.3 µS/cm after 216 h, with the EC values ranging from 1098 µS/cm to 1291 µS/cm. Compared with A, the conductivity at a solution pH of 7.3 (C) has a similar changing trend, and it fluctuated first from 1098 µS/cm to 1291 µS/cm, and then decreased to 1146 µS/cm from 96 h to 216 h, with the EC values ranging from 636.3 µS/cm to 764 µS/cm. Whereas the conductivity at a solution pH of 5.3 and 9.3 (B and D) over time had nonlinear growth, changing from 1.2 µS/cm to 76.3 µS/cm (B), from 25.4 µS/cm to 92.6 µS/cm (D), respectively. The two samples increased faster in early stage before 96 h than that in later stage. Meanwhile, there is almost a difference of 15 µS/cm between the two solutions, and the conductivity variation of the two solutions over time can be calculated by solving the fitting formula, namely, $EC=-0.0016T2+0.6536T+6.7655$ and $EC=-0.0013T2+0.5829T+25.178$, where EC is the conductivity value, and T is the immerse time. And the correlation coefficient is 0.983 and 0.993, respectively. From the above results, we can also know site karst water (A) has a relatively higher ion concentration except C.

As we can see from the above, the pH and EC of all solutions nearly reach unchanged after 96 h, thus reflecting that the dissolution and precipitation of minerals in coal gangue maintaining a dynamic balance. Additionally, the pH changing curve of A sample has a drop after 72 h, and yet with a growth in its EC value at the same time, indicating the minerals in coal gangue dissolved in growth and thus hydrogen ions in growth. Though the ORP values of all solutions in a relatively low level, presenting a weaker redox environment [Lin H et al., 2017], the ORP value of A sample remarkably increased to that close to

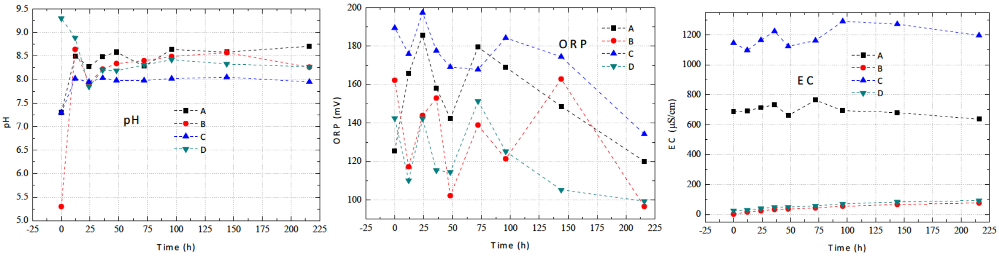

Figure 3 pH, ORP, EC, TDS and DO of coal gangue at different solutions over time.

the maximum after 72 h with highest level in ORP values of four solutions, which showed a relatively higher degree of redox reaction and consisted with the former analysis. All ORP curves fluctuated greatly and decreased overally with a similar variation tendency, and the ORP values of all solutions were observed in the following order, C>A>B>D. There is a higher redox environment after 24 h and 72 h among the four solutions. Moreover, A and C samples curves developed more alike except initial ORP value and that after 72 h, accounting for similar redox environment.

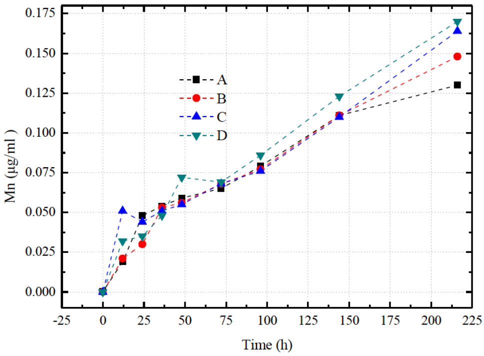

Figure 4 Dissolved quantities of Mn from coal gangue at different solutions over time.

Through ICP atomic emission spectrometer (ICP-AES), we can obtain the concentrations of Mn of coal gangue at different solutions over time depicted in Fig.4. From Fig. 4 we can know that the dissolved quantities of potentially toxic metal elements in coal gangue at different solutions present a approximately similar trends. The dissolved process can be divided into three phases: earlier phase (0-24 h), medium phase (24-144 h) and later phase(after 144 h). The release rate of Mn in earlier immerse phase was very fast and fluctuated greatly, mainly due to the sufficient contact between immerse solutions and the particles of coal gangue with an instable process, causing the quick and instable dissolving of the potentially toxic metals in samples. Then the release rate of Mn in medium phase got relatively slow, mainly because of the blocking of contact channel between immerse solutions and the particles of coal gangue induced by the dissolution of minerals. After that the release rate of Mn in the later phase got more slow and more dispersed than that in medium phase, and later immerse. In addition, compared with the other three samples (B, C and D), the release rate of Mn in sample A was the lowest, but the highest after 24-36 h, and then decreased to a minimum towards the end of immersion, resulting in lower release rate of Mn at the solution of site karst water than that at different pH solution in the lab, perhaps due to more superior self purification capacity, except transient peak in medium phase. However, the curve in sample D (pH=9.3) maintained the highest point during the medium and later phases, indicating the more easily released ability of Mn in slightly alkaline condition than other three conditions.

Conclusions

A series of large-capacity immersion test was conducted to study the Mn and its leaching behaviour of coal gangue under different leaching solutions including site Ordovician limestone karst as opposed to three solution pH levels, the results of XRF, pH, ORP, EC and concentrations of Mn was obtained and analysed.It can be founded that (1) SiO_2 was major constituent and Mn was almost the highest content of potentially toxic metal from coal gangue. (2) although initial pH values vary, the effect of site karst water on coal gangue differs considerably from lab configuration cases in terms of solution pH. From EC values, site karst water (A) has a relatively higher ion concentration except C. From ORP values, A and C samples curves developed more alike except initial ORP value and that after 72 h, accounting for similar redox environment. (3) there was a lower release rate of Mn at the solution of site karst water than that at different pH solution in the lab, perhaps due to more superior self purification capacity. All results may provide reference for security theory and contamination control technology of deep karst water in abandoned coal mines.

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