The hydrogeochemical characteristic of different sulfide-containing gangue during leaching

Y Q Sun 1, 2, 3, L Duan 1, 2, M Yao 1 and W P Li 1

1 School of Environmental Science and Engineering, Chang’an University, Xi’an 710054, China
2 Key Laboratory of Subsurface Hydrology and Ecological Effect in Arid Region of Ministry of Education, Xi’an 710054, China

E-mail: sunyqiao@126.com

Abstract. This investigation examined the hydrogeochemical characteristics of different sulfide-containing gangue samples from the Hancheng mining area in Shaanxi, China. The changes in the hydrogeochemical properties during the leaching experiments on gangue samples containing different levels of sulfur (LSG-Low sulfur gangue, MSG-Moderate sulfur gangue and HSG-High sulfur gangue) were investigated by analyzing the major physical and chemical constituents (pH, EC, TDS, Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻, F⁻, and Fe). The results indicated that the release of SO₄²⁻ and H⁺ from the dissolution of sulfide minerals resulted in low Ca²⁺ and HCO₃⁻ concentrations at pH levels below 4.7 for the HSG leachate. Also for the HSG samples, the molar ratio of SO₄²⁻/Fe exceeded twice that which was expected, meaning the higher SO₄²⁻ concentrations in the HSG samples result from more than just the oxidation of pyrite. Additionally, the leachate of three sulfide-containing gangue samples exhibited changes in the hydrogeochemical facies with the majority of changes occurring in the cation-type and anion-type facies. The HSG samples were of a [Cl-SO₄] type for sulfide dissolution, the unaffected LSG samples were of a [Ca-HCO₃] type, and the MSG samples were of a [Ca-HCO₃-SO₄] type.

1. Introduction

Coal gangue is the solid waste that is generated during coal mining [1-2]. There are approximately 1500 coal gangue dumps in China that together contain a combined weight of four billion tons. This is highly problematic as this waste has the potential to severely impact the surrounding environment as well as human health due to the harmful elements contained within the gangue [3-5]. However, due to the high sulfide content of this gangue, there are limited applications for this waste. The hydrogeochemistry of this sulfide-rich substance plays a key role in its environmental impact [6-8]. More specifically, the aqueous oxidation
processes associated with the sulfide minerals in the gangue produce sulfuric acid, which causes water pollution and soil acidification in addition to harming human health [9-10].

There is a need for investigations to focus on the hydrogeochemical behavior of gangue-water, such as its low pH, resulting drainage with sulfuric acid, and the dissolution of heavy and toxic metals. Sulfur-rich gangue has been classified into the following three types by the National Coal Board (NCB) depending on its sulfur content [11]: low content, with total sulfur <1%; moderate content, with total sulfur between 1-2%; and high content, with total sulfur>2%. In contrast, the Chinese determined the standard sulfur content ranges in coal grade divisions according to its different utilizations. Additionally, not only has sulfur coal gangue been identified in China [12-13], but it has also been identified in several other countries, such as Upper Silesia[14], Northern Iran[15], and India[9]. Furthermore, it is important to continue investigating this area because a large amount of sulfide-containing coal is currently being used as fuel, and consequently, the amount of oxidized sulfur is high [16-18]. Furthermore, sulfur coal gangue is associated with the atmospheric dispersion of fine particles, the spontaneous combustion of gangue dumps, the leaching of elements, and the formation of acid drainage as caused by natural weathering and/or oxidation processes.

The chemistry of gangue leachate depends upon, amongst other factors, the hydrogeological environment, the accompanying gangue material, and the interaction time in gangue-water. Geochemical processes are responsible for releasing sulfur and carbonate buffering into the gangue-water. High sulfide-containing coal gangue may lead to the leaching of harmful elements as well as the release of organic pollutants. Moreover, cations and silica are released for the gangue-water interaction of primary and secondary minerals [19-20]. Contaminants/pollutants from gangue typically flow through the common pathways in gangue dumps during dispersion. Investigations of gangue pollutants are often limited to identifying the release extent of heavy metals as well as their source, cause, and prevention [21-23]. Thus, investigations into the geochemical processes that affect sulfide-containing gangue during gangue-water interactions are often overlooked.

Over the last forty years, due to an increase in coal mining, there has been a significant increase in the volume of gangue extracted from the Hancheng coal mine and stored on-site. The lack of stringent environmental protection measures, coupled with increased stacking, has resulted in adverse environmental impacts on the ground water and soil in the study area. This study aims to investigate the hydrogeochemical characteristics controlling the leaching of harmful substances from the gangue and to evaluate the evolution of sulfur oxidation in gangue-water. To undertake this research, the leaching of quality parameters were investigated, including parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), total alkalinity, and total hardness (TH). Various cations/anions (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, F$^-$, and Fe) were determined. A hydrogeochemical facies evaluation was also undertaken by plotting a Piper diagram in order to understand the gangue-water geochemistry in the leaching experiment. Overall, a systematic effort was made to investigate the hydrogeochemical characteristics of sulfur and the other chemical elements released into gangue-water.
2. Materials and Methods

2.1. Sample Collection
Coal gangue was collected from three sites in the Hancheng coal mining area, Shaanxi province, China (figure 1) in May 2014. The sample locations were chosen to provide gangue that contained low, moderate, and high sulfur contents. The low sulfur gangue (LSG, 0.04% sulfur content) was collected from the Permian Shanxi formation #3 coal bed; the moderate sulfur gangue (MSG, 1.29% sulfur content) was collected from the Permian Shanxi formation #2 and #3 coal beds; and the high sulfur gangue (HSG, 3.40% sulfur content) was collected from the Carboniferous System Taiyuan formation #11 coal bed. The gangue samples were air-dried in the laboratory and sieved through 0.147 mm nylon sieve meshes.

![Figure 1. Sampling site locations within the Hancheng, Shaanxi province.](image)

2.2. Leaching tests
To investigate the effect of sulfide on the hydrogeochemical processes in gangue, leaching experiments using deionized water were conducted at liquid-solid ratios (L:S) of 10:1, 8:1, 6:1, 4:1, and 2:1. The samples were rotated in a tumbler at 40 rpm for 48 h before being filtered for chemical composition analysis. Leached samples for cation determination were filtered through a 0.45 um Millipore nitrocellulose filter. Then, 10mL of the filtered sample was acidified with ultrapure HNO\(_3\) (10%) until pH<2 was attained. All samples were stored at 4°C in HDPE bottles prior to analysis.

2.3. Analytical Methods
The samples prepared using the leaching method were analyzed for pH, EC, TH, and cations/anions (including Ca\(^{2+}\), Mg\(^{2+}\), Na\(^+\), K\(^+\), Cl\(^-\), SO\(_4^{2-}\), Cl\(^-\), HCO\(_3^-\), F\(^-\) and Fe). Major cations (K, Na, Ca, and Mg) and other trace elements were determined using inductively coupled plasma atomic emission spectrometry (ICP-OES) (American thermoelectric icap6300). The pH was measured using METTLER TOLEDO SG2-ELK, and the EC was measured using METTLER TOLEDO FG3. The total S was determined using an infrared carbon sulfur analyzer (CS-8800), and the mineral composition of the gangue was analyzed by XRD (D/max-2500).

The analytical precision for the cations and anions, as indicated by the ionic balance error, was calculated to be within a ±5% limit for all of the samples. The quality of the analysis was ensured by standardization using blank, spike, and duplicate samples.
3. Results and Discussion

3.1. Chemical characteristics

The mean pH values in the samples were 9.18, 7.46, and 2.96 for LSG, MSG, and HSG, respectively (Table 1). The recorded pH of the LSG and MSG samples were alkaline. The LSG samples had a pH ranging from 8.88 to 9.40, and the MSG samples ranged from 7.37 to 7.58. In contrast, the pH results of the HSG samples were very acidic, ranging from 2.38 to 3.62 (Table 2). The HSG leachates had the highest average EC values (3976.00us/cm), thereby indicating that the acidic condition of the samples resulted in high concentrations of dissolved material during the leaching process. The leachates from the LSG and MSG samples had EC ranges of 172.20-435.00us/cm and 1371.00-2420.00us/cm, respectively. This indicated that in alkaline conditions, the leachate had lower solute concentrations as compared with the leaching process [8, 24]. The average hardness values were 10.75, 23.97, and 8.21mg/L for LSG, MSG, and HSG, respectively.

Table 1. Chemical data of leaching samples.

| Sulfur content | Low (0.04%) | Middle (1.29%) | High (3.40%) |
|----------------|-------------|----------------|--------------|
|                | mean | max | min | mean | max | min | mean | max | min |
| PH             | 9.18 | 9.40 | 8.88 | 7.46 | 7.58 | 7.37 | 2.96 | 3.62 | 2.38 |
| EC (μs/cm)     | 274.84 | 435.00 | 172.20 | 1,831.40 | 2,420.00 | 1,371.00 | 3,976.00 | 7,330.00 | 1,830.00 |
| TH (mg/L)      | 10.95 | 16.15 | 5.44 | 23.97 | 32.01 | 6.01 | 8.21 | 14.21 | 4.23 |
| K+ (mg/L)      | 2.332 | 2.916 | 1.720 | 2.416 | 3.916 | 1.900 | 1.781 | 2.365 | 1.466 |
| Na+ (mg/L)     | 4.788 | 11.630 | 1.365 | 1.992 | 3.441 | 0.413 | 0.614 | 1.077 | 0.241 |
| Ca2+ (mg/L)    | 8.978 | 13.220 | 4.666 | 20.949 | 27.110 | 2.795 | 6.675 | 12.460 | 2.758 |
| Mg2+ (mg/L)    | 1.977 | 3.146 | 0.770 | 3.023 | 4.896 | 1.187 | 1.537 | 1.745 | 1.449 |
| HCO3- (mg/L)   | 105.287 | 157.713 | 55.465 | 67.812 | 89.949 | 49.677 | 0.000 | 0.000 | 0.000 |
| Cl- (mg/L)     | 3.412 | 4.555 | 1.914 | 16.491 | 29.000 | 9.233 | 212.466 | 398.500 | 115.230 |
| SO42- (mg/L)   | 5.126 | 5.871 | 4.107 | 36.021 | 59.550 | 24.141 | 100.236 | 127.770 | 85.980 |
| F (mg/L)       | 2.182 | 3.963 | 1.190 | 1.503 | 1.584 | 1.446 | 0.008 | 0.010 | 0.006 |
| Fe (mg/L)      | 9.533 | 11.290 | 7.851 | 36.028 | 46.700 | 17.190 | 24.890 | 27.390 | 23.400 |

The results from the cation analysis indicated that Ca2+ and Mg2+ were the dominant elements; together they averaged 61%, 84%, and 77% of the total cations in the LSG, MSG, and HSG samples, respectively (Figure 2). Ca2+ was the major constituent with average concentrations of 8.978, 20.949, and 6.675mg/L, respectively (table 1). For comparison, the dominance of Ca2+ in the samples followed the following sequence: MSG (74%) > HSG (63%) > LSG (50%). Together, K+ and Na+ averaged 39%, 15%, and 23% of the total cations in the LSG, MSG, and HSG samples, respectively (figure 2).

Bicarbonate (HCO3-) is the dominant anion in the LSG and MSG samples with average values of 105.287mg/L (ranging from 55.465-157.713mg/L) and 67.812mg/L (ranging from 49.677-89.949mg/L), respectively. For the dissolution of pyrite during the HSG leaching process, the pH value is lower than 4.7 (ranging from 2.38-3.62 mg/L; mean of 2.96 mg/L) (table 1). The contribution of HCO3- is 0% (figure 2). The dissolution of gypsum and pyrite minerals (Table 4) in the samples contributes to the SO42- concentration; thus, the SO42- results increased to 4.107-5.871mg/L (mean of 5.126mg/L), 24.141-59.550mg/L (mean of
36.021 mg/L), and 85.980-127.770 mg/L (mean of 100.236 mg/L) in the LSG, MSG, and HSG samples, respectively. Therefore, the SO\textsubscript{4}\textsuperscript{2-} percentage in the samples followed the following sequence: HSG (32%) > MSG (30%) > LSG (4%) (figure 2). Additionally, the Cl\textsuperscript{-} concentration in the samples followed the following sequence: HSG (68%) > MSG (13%) > LSG (3%). In contrast, the low F\textsuperscript{-} contribution was the following: LSG (2%) > MSG (1%) > HSG (0%).

### Table 2. Mineral composition of the gangue used in the leaching experiments.

| Mineral phase          | LSG (wt%) | MSG (wt%) | HSG (wt%) |
|------------------------|-----------|-----------|-----------|
| Quartz                 | 40        | 35        | 16        |
| Plagioclase            | 2         | 1         | 2         |
| Potassium feldspar     | 1         | /         | 1         |
| Calcite                | 4         | /         | /         |
| Chlorite               | /         | /         | 7         |
| Montmorillonite        | /         | 1         | 2         |
| Illite                 | 11        | 12        | 13        |
| Ammonium Illite        | /         | /         | /         |
| Kaolinite              | 26        | 34        | 32        |
| Dolomite               | 1         | /         | /         |
| Gypsum                 | /         | 8         | 8         |
| Pyrite                 | /         | /         | 8         |
| Anatase                | /         | /         | 1         |
| Jarosite               | /         | 4         | 5         |
| The amorphous phase    | 15        | 5         | 5         |

**Figure 2.** Average percent contribution of individual ions.
3.2. Hydrochemical facies of leaching

The Piper diagram (figure 3) reveals the similarities and differences in the sample compositions from the three gangue sites. The results are consistent with the other results in this study, and they confirm the hydrochemistry characteristics from the different sulfur-containing gangue samples in the experiment. As indicated in the left ternary diagram of Figure 3, the LSG and MSG samples were [Ca] type. The right ternary diagram indicates that the [HCO$_3$], [HCO$_3$-SO$_4$], and [Cl-SO$_4$] types are present in the LSG, MSG and HSG samples, respectively. Therefore, the LSG and MSG samples are predominantly [Ca-HCO$_3$] and [Ca-HCO$_3$-SO$_4$] types, respectively. The HSG samples are dominated by the sulfur mineral dissolution (pyrite, gypsum, and jarosite; table 2), which, as noted previously, results in these samples having lower pH values and a lack of carbonate formation. The chemical type of the HSG samples is chloride-sulfate water. Furthermore, it should be noted that the differences in the hydrogeochemical facies in the LSG, MSG, and HSG samples of [Ca-HCO$_3$], [Ca-HCO$_3$-SO$_4$], and [Cl-SO$_4$], respectively, are observed in the ternary diagram (Figure 3). The differences are possibly influenced by the mineral composition and the sulfur contained in the gangue as well as by the interaction with water during the leaching process. This will affect the chemical characteristics and the water-gangue interactions.

![Figure 3. The Piper Diagram for gangue leaching samples.](image)

3.3. pH changes with pyrite oxidation

During the leaching experiments, pyrite was identified as one of the main sulfide minerals in the HSG samples (table 2). Pyrite oxidation releases free H$^+$ into the solution, which results in low pH values and a high SO$_4^{2-}$ concentration leached from the gangue. The chemical reaction to produce sulfuric acid in the solution is:

$$\text{FeS}_2(s) + 7/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)$$

$$3\text{FeS}_2(s) + 11.25\text{O}_2 + 10.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) \downarrow + 6\text{H}_2\text{SO}_4 \quad (2)$$

The gangue leaching increased the sulfate content and lowered the pH in the leachate as well as elevated the iron and SO$_4^{2-}$ concentrations (Chemical quation.1).

In the HSG leaching samples, a high sulfide-containing mineral concentration (table 2) and a low pH indicated that leaching of these samples was affected by acid mine drainage and the
pyrite oxidation. The maximum acidification produced by the complete oxidation of the sulfur minerals in the gangue leaching was investigated. In all of the HSG samples, the pH of the samples ranged between 2.38 and 3.62 for about 8% pyrite oxidation and dissolution. In these samples, a lower concentration of dissolved total Fe was detected (table 1); this being an indication of the rapid precipitation of the mineral phases of Fe (Chemical quation.2) for the FeS₂ oxidation [22].

High Fe and SO₄²⁻ concentrations (figure 2) in the HSG samples may be due to the oxidation of pyrite, the dissolution of iron-bearing minerals and gypsum, and the subsequent transformation of oxidation products under acidic conditions. The SO₄²⁻/Fe molar ratio recorded in these samples was more than twice the expected levels from pyrite dissolution alone, which is a result that suggests the occurrence of the dissolution of gypsum and jarosite (Table 2). The saturation indices of gypsum were less than zero, thus indicating that gypsum was unsaturated in the HSG samples. As the HSG samples were strongly corrosive to sulfur-containing minerals during leaching, minerals, such as gypsum and pyrite, dissolved during leaching further reduce the pH of the solution. During the HSG samples leaching, the neutralization process resulting from carbonate mineral dissolution was much less than that resulting from the pyrite dissolution. Therefore, the pH values of the HSG samples were lower, even though more silicate minerals were available for dissolution buffering during leaching.

4. Conclusions
The hydrogeochemistry characteristics of the LSG, MSG, and HSG leached samples were investigated in order to analyze the reaction between sulfur-containing minerals in the gangue and water. Ca²⁺ was found to be the major ion released from the gangue during the experiments. Furthermore, it was found that the pH values of the HSG samples were very acidic (2.38-3.62) due to the dissolution of pyrite. Additionally, the molar ratio of SO₄²⁻/Fe in the HSG samples was more than twice that which was expected, which suggested that the higher SO₄²⁻ concentrations in the HSG samples affected the oxidation of pyrite as well as the dissolution of other sulfur minerals in the gangue. Furthermore, the [Ca-HCO₃⁻], [Ca-HCO₃⁻·SO₄], and [Cl-SO₄] facies were the main hydrogeochemical facies in the LSG, MSG, and HSG samples, respectively. Sulfur mineral dissolution and lower pH levels were responsible for a lack of carbonate formation and chloride-sulfate type water formation in the HSG samples. The present results have the potential to aid in providing a scientific basis during coal gangue landfill treatments and comprehensive applications.

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References
[1] Shealy M and Dorian J P 2010 Growing Chinese coal use: Dramatic resource and
environmental implications Energy Policy 38(5): 2116–22

[2] Shujie Y 2005 Some Aspects of the Coal Industry Sustainable Development in China In ESobczyk & J KickiEds, International mining forum 2005 new technologies in underground mining, safety and sustainable development Proceedings of the Sixth International Mining Forum 2005 CRC Press Cracow-Szczyrk-Wieliczka Poland: 5–12

[3] Fan J S, Sun Y Z, Li X Y, Zhao C L, Tian D X, Shao L Y and Wang J X 2013 Pollution of organic compounds and heavy metals in a coal gangue dump of the Gequan Coal Mine China Chinese Journal of Geochemistry 32: 241–47

[4] Meng L, Feng Q, Zhou L, Ping L and Meng Q 2009 Environmental cumulative effects of coal underground mining Procedia Earth and Planetary Science 11: 1280–84

[5] Boularbah A, Schwartz C, Bitton G and Morel J L 2006 Heavy metal contamination from mining sites in South Morocco: 1 Use of a biotest to assess metal toxicity of tailings and soils; 2 Assessment of metal accumulation and toxicity in plants Chemosphere 63: 802–17

[6] Chandra A P and Gerson A R 2011 Redox potential Eh and anion effects of pyrite FeS2 leaching at pH1 Geochimica et Cosmochimica Acta 75: 6893-911

[7] Romero A, Gonzalez I and Galan E 2011 Stream water geochemistry from mine wastes in Pena de Hierro, Ritinto area, SW Spain: a case of extreme acid mine drainage Environmental Earth Sciences 62: 645-56

[8] Tao X Z, Wu P, Tang C Y, Liu H and Sun J 2012 Effect of acid mine drainage on a karst basin: a case study on the high-As coal mining area in Guizhou province, China Environmental Earth Sciences 65: 631-38

[9] Murkute Y A 2014 Hydrogeochemical characterization and quality assessment of groundwater around Umrer coal mine area Nagpur District, Maharashtra, India Environmental Earth Sciences 72: 4059-73

[10] Kuenzer C, Zhang J, Tetzlaff A, Van Dijk P, Voigt, S and Mehl H 2007 Uncontrolled coal fires and their environmental impacts: Investigating two arid mining regions in north-central China Applied Geography 271: 42–62

[11] Spears D A, Rippon J H and Cavender P F 1999 Geological controls on the sulphur distribution in British Carboniferous coals: a review and reappraisal International Journal of Coal Geology 401: 59-81

[12] Wen X Q, Zeng F G and Zhang H 2013 Geochemical characteristics of the coal gangues from the Du’erping coal mine, Xishan coalfield, North China Chinese Journal of Geochemistry 32: 227-34

[13] Xue Q, Lu H J, Zhao Y and Liu L 2014 The metal ions release and microstructure of coal gangue corroded by acid-based chemical solution Environmental Earth Sciences 71: 3235-44

[14] Szczepanska J and Twardowska I 1999 Distribution and environmental impact of coal-mining wastes in Upper Silesia, Poland Environmental Geology 383: 249-58

[15] Shahhоеiny M, DoulatiArdejani F, Shafaei S Z, Noaparast M and Hamidi D 2013 Geochemical and mineralogical characterization of a pyritic waste pile at the AnjirTangen Coal Washing Plant, Zirab, Northern Iran Mine Water and the Environment 32: 84-96
[16] Tang Z and Yang W 2000 Efficient and environment friendly use of coal Fuel processing Technology 62: 137-41

[17] Zhang J, Han C and Xu Y Q 2003 The release of the hazardous elements from coal in the initial stage of combustion process Fuel processing Technology 84: 121-33

[18] Su S, Li B, Cui S and Tao S 2011 Sulfur Dioxide emissions from combustion in china: From 1990 to 2007 Environmental Science and Technology American Chemical Society Publications Beijing Peking University: 1–8

[19] Medina A, Gamero P, Querol X, Moreno N, Leon B D, Almanza M and Vargas G, Izquierdo M and Font O 2010 Fly ash from a Mexican mineral coal I : mineralogical and chemical characterization Journal of Hazardous Material 181: 82-90

[20] Sun W, Wu Q, Dong D and Jiao J 2012 Avoiding coal–water conflicts during the development of China's large coal-producing regions Mine Water and the Environment 311: 74–78

[21] Ribeiro J, Silva E F D, Jesus A P D and Flores D 2011 Petrographic and geochemical characterization of coal waste piles from Douro coalfield International Journal of Coal Geology 87: 226-36

[22] Silva L F O, Querol X, Boit K M, Vallejuelo F O and Madariaga J M 2011 Brazilian coal mining residues and sulphide oxidation by Fenton’s reaction: an accelerated weathering procedure to evaluate possible environmental impact Journal of Hazardous Materials 186: 516-25

[23] Zhang Y, Feng Q Y, Meng Q J, Lu P and Meng L 2012 Distribution and Bioavailability of metals in subsidence land in a coal mine China Bulletin of Environmental Contamination Toxicology 89: 1225-30

[24] Lee J E and Kim Y 2008 A quantitative estimation of the factors affecting pH changes using simple geochemical data from acid mine drainage Environmental Geology 55: 65-75