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Study on Geochemical Behaviour of Gangue Potential Acidic Release

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Geochemical behaviour of gangue potential acidic release has been investigated through soaking experiments under different conditions of liquid/solid ratio and soaking period. The results show that leachate pH ranges 6.99-7.71 (neutral or weakly alkaline) during immersion test which lasted for 30 days. The closed state where soaking test was performed inhibited the oxidation and dissolution of sulfur minerals containing in coal gangue, thereby affecting acidic release of gangue and making leachate weakly alkaline, resulting in only a small number of heavy metals Co, Cu, Mn and Sr at exchangeable state dissolved by water (dissolution rate $\leq 62.79\%$) with the exception of Cr (completely dissolved) in gangue soaking. Under alkaline conditions, dissolution rates of Co, Cr, Cu, Mn and Sr carbonates, iron and manganese oxide phase, organics matter and residual are extremely low ($\leq 16.67\%$). During soaking test, dissolution release rates of sulfur containing minerals in gangue with acid production (H_2SO_4) capacity of 57.56 Kg/t range merely 2.70-10.34%. Along with the proceeding of soaking, enhancement of dissolution-release rate of sulfur containing minerals will lead to the solubilization-release of harmful trace elements in gangue. Hence, acidic release of gangue has a potentially considerable impact on environment.

Keywords: Gangue, Potential acidic release, Heavy metal, Geochemical behaviour.

INTRODUCTION

Gangue is a byproduct during coal mining and processing, belonging to industrial solid waste. In coal mining of China, every exploited 100 million tons of coal lead to 14 million tons of gangue disposal. There are over 1,600 gangue hills with cumulative accumulation of up to 3 billion tons in China now, occupying land of about 110 million m^2 and the disposal amount of gangue increases year by year with the growth in coal production^{1,2}. A large amount of gangue is piled up in open air for years, subjected to long-term weathering, rain leaching, soaking, erosion and other effects and accompanied by a series of physical and chemical changes, releasing a large amount of harmful substance that penetrates into underground with leaching water or into rivers and reservoirs. As a result, groundwater, surface water and soil are polluted and thus human health and normal growth of flora and fauna will be endangered^{3,4}.

Release of potential acidity of gangue, which exists in certain form is only presented under specific conditions, is one of the main pathways to facilitate the precipitation of hazardous trace elements in gangue⁵. Cumulative weathering destructs the internal structure of gangue and ions in mineral lattice are converted from original compounds into free-state⁶. Sulfide

minerals in gangue such as iron sulfide react with water and air sufficiently, acidifying aqueous solution intensely to facilitate the precipitation and release of toxic heavy metals such as Hg, Pb, Zn and Cu in gangue. Finally, gangue heavy metal sulfates overflow with leaching water in the form of overflowing fountain out of ground surface, so springs of high salinity are formed and then drained either directly into surface water or directly into underground aquifers. Accordingly, environment of surface water and groundwater is severely polluted⁷⁻⁹.

Acidic release is the main route of heavy metal dissolution release of gangue. Sulfur comprising minerals in gangue are oxidized to form acidic mine waste water¹⁰, leading to the gradual concentration of Fe, Mn, Cu, Zn, F^- and SO_4^{2-} in gangue leachate of open systems with prolonged leaching time¹¹. Acidic drainage potential of gangue has been thoroughly investigated through simulation experiments about pyrite oxidation time under water-saturated conditions and that the oxidation time of pyrite in gangue under water-saturated conditions may reach several hundred thousand years has been determined¹². Szczepanska and Twardowska¹³ launched a study on 380 gangue hills in Poland, drawing a conclusion that the pollution caused by gangue stems from salinity, sulfur content and potential acidity and proposed that gangue hill surrounding

mines as long-term contamination source of groundwater can last for decades and enhance with evolution, in which the main pollution indicators are TDS, SO_4^{2-} , Mn, Fe, Zn and high acidity.

Sulfur containing mineral oxidation rate of gangue in open system is evidently higher than that of closed system¹². Oxidation of sulfur containing minerals directly affects the formation of acidic water¹⁴, thereby affecting the dissolution release of heavy metals in gangue. Based on gangue soaking tests in closed system under conditions of varied liquid/solid ratio and different soaking time, dissolution release characteristics of pH, Co, Cr, Cu, Mn, Pb and Sr in leachate have been analyzed and geochemical behaviour of potential acidic release in gangue-water reaction system discussed, providing theoretical foundation for possible environmental risks when gangue is stacked in leaching environment.

EXPERIMENTAL

Gangue samples in this study were collected on April 27, 2011, in Gangue field of Sangshuping coal mine in Hancheng, Shaanxi Province, China (latitude 35°40'58.8"N and longitude 110°33'43.6"E). Gangue was fresh and unweathered. Four or five samples were collected at each one of three sampling sites in gangue field and then mixed. After impurities were removed and ground, samples were filtered with nylon sieve of 0.5 mm mesh and then stored.

Experimental design and methods

Mineral composition analysis: Gangue samples were characterized by XRD to determine mineral composition.

Gangue digestion: HCl-HNO₃-HF-HClO₄ electric heating plate digestion method was applied to gangue sample digestion.

Elemental determination: Contents of heavy metal Co, Cr, Cu, Mn, Pb and Sr were determined with inductively coupled plasma emission spectrometer (ICP-OES).

Soaking test: The pretreated gangue samples 100, 142.86, 200, 333.33 and 1000 g were placed into 2 L of plastic bottle, respectively. The deionized water 1000 mL with a pH of 6.4 adjusted with nitric acid was added to each bottle and mixtures of liquid-solid mass ratio of 10:1, 7:1, 5:1, 3:1 and 1:1 were prepared, respectively. Intermittently vibrate these bottles and then the pH of supernatant was determined directly after different soaking periods (1, 3, 5, 10, 20 and 30 days). After filtered with 0.45 μm hydrophilic membrane, contents of Co, Cr, Cu, Mn, Pb and Sr were measured. The pH was determined with a PHS-4CT pH meter and concentrations of heavy metals determined with ICP-OES.

Five-step extraction experiment: Chemical speciation of heavy metals in gangue was studied on the basis of five-step sequential extraction method by Tessier *et al.*¹⁵.

Step 1. Exchangeable: Add 8 mL of 1 mol/L MgCl₂ (aq) (adjusted with NaOH until pH = 7) and vibrate it at room temperature for 1 h.

Step 2. Bound to carbonates: Add 8 mL of 1 mol/L aqueous sodium acetate (adjusted with acetic acid until pH = 5) and vibrate it at room temperature for 5 h.

Step 3. Bound to iron and manganese oxides: Add 20 mL of 0.04 mol/L NH₂OH·HCl (aq) prepared with 25 % aqueous sodium acetate and vibrate it at 96 ± 3 °C for 6 h.

Step 4. Bound to organic matter: Add 3 mL of 0.02 mol/L HNO₃ (aq) and 5 mL of 30 % H₂O₂ (aq), then adjust with HNO₃ until pH = 2 and vibrate continuously at 85 ± 2 °C for 2 h. After cooling to room temperature, add 5 mL of 3.2 mol/L CH₃COONH₄ prepared with 20 % HNO₃ (aq), dilute the solution up to 20 mL and vibrate continuously at 25 ± 1 °C for 0.5 h.

Step 5. Residual: Residual was treated through HCl-HNO₃-HF-HClO₄ electric hot plate digestion method.

Quality control: Parallel samples 10 % for experimental analysis were tested in all groups with relative standard deviation (RSD) of 0.3-13.5 %, meeting the demand of test. The accuracy of heavy metal determination was verified with national standard substances and recoveries are 75.2-109.3 %, according with the requirements of quality control. Moreover, all analytical instruments for analysis were within valid period, so the experimental data and results are accurate and reliable.

Statistics: Software Excel2007, SPSS16.0, Origin 8 are used for statistical analysis of experimental data through correlation analysis and comparative analysis *etc.* to investigate heavy metal characteristics of gangue.

RESULTS AND DISCUSSION

The chemical properties of the gangue are shown in Table-1. SiO₂ and Al₂O₃ are major components of gangue and Cr (0.018 %), Cu (0.0028 %), Co (0.0031 %), Pb (0.033 %), Fe (2.40 %), Mn (0.04 %) and Sr (0.036 %) are trace harmful toxic heavy metals that can be dissolved and released from gangue through weathering and leaching into water, thus jeopardizing the ecological environment^{16,17}. Sulfur content is high in gangue (1.89 %), supposing all the sulfur is reductive, according to Sobek acid yield calculation method¹⁸ and then the total potential acidity (H₂SO₄) in gangue is estimated of 57.56 kg t⁻¹ approximately, showing a strong acid producing capacity.

TABLE-1
CHEMICAL PROPERTIES OF THE GANGUE

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O
Wt. %	49.90	31.57	2.30	0.31	0.35	1.07	0.14
S	Cr	Cu	Co	Pb	Fe	Mn	Sr
1.89	0.018	0.0028	0.0031	0.033	2.40	0.04	0.036

Gangue minerals: Gangue minerals were determined with X-ray diffraction (Fig. 1) and results are shown in Table-2.

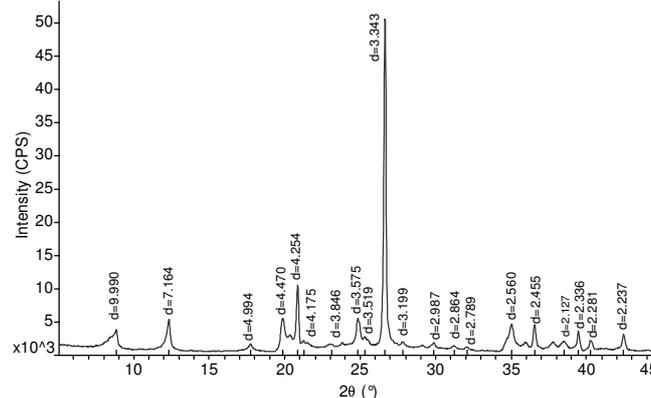


Fig. 1. Minerals compositions of the gangue measured by X-ray

TABLE-2
MINERALS COMPOSITIONS OF THE
GANGUE MEASURED BY X-RAY

Minerals compositions	Quartz	Anatase	Illite	Illite smectite mixed layer	Kaolinite	Pyrite
Content (%)	44	0.8	31.3	22.0	1.9	

The mineralogy in gangue of Sangshuping is relatively simple, consisting of quartz (SiO_2), anatase (TiO_2), illite ($\text{KAl}_2[(\text{Al}, \text{Si})\text{Si}_3\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$), kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and pyrite (FeS_2), with content of 44, 0.8, 31.3, 22 and 1.9 %, respectively.

Chemical speciation of heavy metals: The amount of heavy metals correlates to environmental pollution levels. On the other hand, anthropogenic heavy metal pollution and potential hazard to ecological environment can be objectively and comprehensively assessed from chemical speciation analysis of heavy metals^{19,20}. Relative contents of chemical speciation (exchangeable, carbonates, iron and manganese oxides, organic and residual) of Co, Cr, Cu, Mn, Pb and Sr trace metals in gangue are shown in Fig. 2.

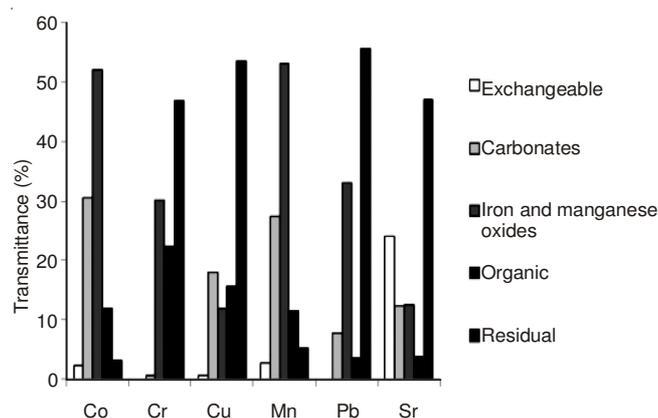


Fig. 2. Chemical speciation of trace metals

It can be judged from chemical speciation of heavy metals in Fig. 2 (greater than 10 % as main speciation) that gangue Co mainly exists in forms of carbonates, iron and manganese oxides and organics, Cr of iron and manganese oxides, organics and residual, Cu of carbonates, iron and manganese oxides, organics and residual, Mn of carbonates, iron and manganese oxides and organics, Pb of iron oxides, manganese oxides and residual and Sr of exchangeable, carbonates, iron and manganese oxides and residual.

Co, Cr, Cu, Mn and Pb at exchangeable state are rare in gangue (< 3 %), mainly due to exchangeable state proving to be the most unstable form among the five speciation states of heavy metals. They are susceptible to environmental changes, soluble in water and prone to migration and not easy to accumulate in gangue. When exposed to a solution containing a large number of cations, ion exchange will occur and heavy metals be released²¹⁻²². Among the six heavy metals, Co, Cu and Mn carbonates of the highest relative contents account for 30.43, 18.05 and 27.42 %, respectively and heavy metal carbonates (such as MnCO_3) exist in gangue via precipitation or co-precipitation, wherein pH is the main factor affecting

the stability of carbonates²³. Therefore, heavy metals can be converted from carbonates to exchangeable state and then released with a weak acid stronger than carbonic acid.

Iron and manganese oxides are relatively stable, significantly impacted by redox electric potential²⁰. Under reductive circumstances, Co, Cr, Cu, Mn and Pb in gangue with higher levels of iron and manganese oxides may be released. Co, Cr and Cu in forms of organics are of relatively high contents, accounting for 11.94, 22.44 and 15.75 %, respectively. Cobalt may be present in cobalt pyrite (Fe, Co) S_2 or Co_2CuS_4 , Cr in chromite (Mg, Fe) Cr_2O_4 and Cu in chalcopyrite CuFeS_2 or chalcocite Cu_2S . Co, Cr and Cu are coordinated and adsorbed in organic states and these heavy metals released under oxidation conditions. Residual in crystal lattice is stable but Cr, Cu, Pb and Sr that mainly exist in residual released by strong acid.

Evolution of leachate pH under varied liquid/solid ratios: During the entire soaking test period (0 to 30 days), pH of all leachates with different liquid/solid ratios firstly increased abruptly in the initial 0-5 days, then decreased in day 5 to 10 and finally rose slowly in day 10 to 30 (Fig. 3).

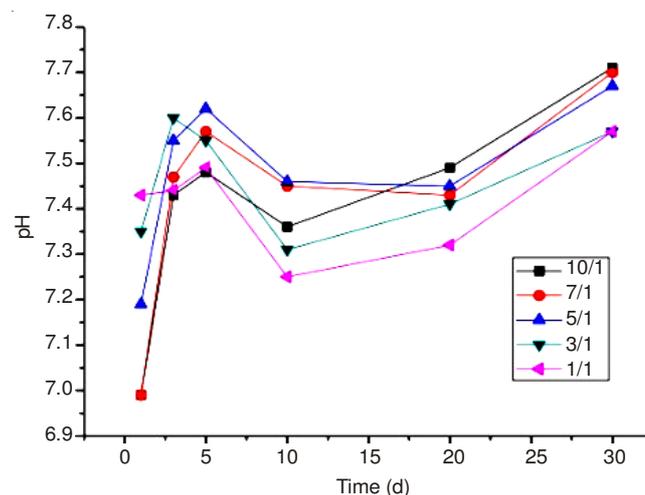


Fig. 3. Change of pH in leachates from gangue in different liquid/solid ratios

Because Hancheng gangue contains aluminum, silicon, sulfur and other minerals, initially, the dissolution of alkaline gangue minerals (such as CuO) soaked in water improved pH. With evolution, pH decreased attributed to acid generated from sulfur containing mineral dissolution or carbonate mineral solubilization buffering effect (pH from 7.4 to 7.8) or solubilization buffering effect (pH from 6.1 to 7.3) of silicate minerals (such as kaolinite and montmorillonite)²⁴. However, after 10 days, dissolution rate of alkaline minerals constantly surpassed sulfur containing mineral dissolution produced acid or solubilization buffering effect of silicates or carbonates, so the pH would increase continuously and slowly.

In Fig. 3, leachate pH under different liquid/solid ratios varied in range of 6.99-7.71, neutral or weakly alkaline. The variance of pH decreased as continuous declination of liquid/solid ratio: pH variance is 6.99-7.71 at liquid/solid ratio of 10/1, while pH variance 7.43-7.57 at 1:1. Liquid-solid ratio vs. pH shows a good linear relationship: liquid/solid ratio =

12.28* pH - 0.376 and $R^2 = 0.897$. This correlation relates to the solubilization effect of alkaline, sulfur containing and silicate minerals in gangue. Smaller liquid/solid ratio causes more significant solubilization effect of alkaline, sulfur containing and silicate minerals and thus slighter pH variance of leachate.

Evolution of heavy metals in leachate under varied liquid/solid ratios: Heavy metal concentrations in gangue leachates of different liquid/solid ratios evolved distinctly, which can be divided into three categories-concentrations of Co, Pb and Mn had been declining; that of Cu declined at the first time then increased afterwards and decreased finally; those of Cr and Sr increased in general (Fig. 4).

With respect to the first category, variation of Co and Mn is basically consistent. The concentrations decline slightly, at liquid/solid ratio of 1:1, in the first 3 days and increases slowly from day 3 to 30. However, in the range of 10:1 to 3:1, concentrations decline sharply in the first 5 days and decline slowly from day 5 to 30. Thus, dissolution rate of Co and Mn containing minerals is greater than sedimentation rate at liquid-solid ratio of 1:1, resulting in gradual increase of Co and Mn concentrations in leachate along with soaking time. On contrary, in the range of 10:1 to 3:1, owing to continuous solubilization of gangue alkaline and acidic components, a system in equilibrium would be formed gradually based on slow dissolution of Co and Mn. Concentration variation of Co and Mn affected by liquid/solid ratio is: 1:1 > 3:1 > 5:1 > 7:1 > 10:1. At 1:1, Co and Mn concentration ranges from 0.019 to 0.028 and 0.074-1.75 mg/L, respectively, much higher than other liquid/solid ratios. Thus, the impact of liquid-solid ratio on gangue Co and Mn releasing is significant that smaller liquid/solid ratio lead to higher concentrations of Co and Mn pollutants in leachate and greater liquid/solid ratio will lead to lower concentrations. Under these liquid/solid ratios, Pb content in leachate decreases gradually. Because Pb in exchangeable state is rare (Fig. 2), the neutral or weakly alkaline leachate dissolved

Pb carbonates in gangue, but $Pb(OH)_2$ precipitation was then formed, resulting in that the concentration of Pb in leachate is far below that of Co and Mn.

Concentrations of Cr and Sr in gangue leachate shows an upward trend, overall, influenced by increasing leachate pH (from neutral to weakly alkaline gradually). Because hexavalent or trivalent chromium oxides or hydroxides are insoluble in the initial neutral aqueous solution, Cr concentration of leachate would be reduced. Alkaline leachate with gradually increasing pH is prone to dissociate Cr compounds, so Cr concentration increased gradually. In weakly alkaline leachate, chromium mainly exists in form of hexavalent chromium compound (CrO_4^{2-}) with strong migration capacity and therefore the elution of Cr increases²⁵. It can be seen from Fig. 4 that along with evolution, Sr concentration in leachate increased steadily and gradually in the first 5 days. From day 5 to 30, Sr dissolution and release were maintained in equilibrium, so the Sr concentration of leachate tended to be consistent. Liquid-solid ratio has a significant impact on the solubilization release of Sr in gangue. Sr concentration in leachate gradually increased with the gradual reduction of liquid/solid ratio. Conversely, a greater ratio of liquid/solid would lower the concentration of Sr. Therefore, liquid/solid ratio is the major influential factor of Sr release in gangue.

Copper concentration in leachate decreased initially, then increased and finally decreased slowly. By comparing leachate pH vs. time and Cu concentration vs. time under different liquid/solid ratios, pH and Cu concentration evolved in completely opposite directions-increasing (decreasing) pH accompanied by decreasing (increasing) Cu concentration. This is mainly attributed to gangue Cu in forms of Cu_2O , CuO and Cu_2S etc., which belong to alkaline substances and slightly alkaline leachate after an interval of soaking would hinder the solubilization release of copper, resulting in the decreasing Cu concentration in leachate²⁶.

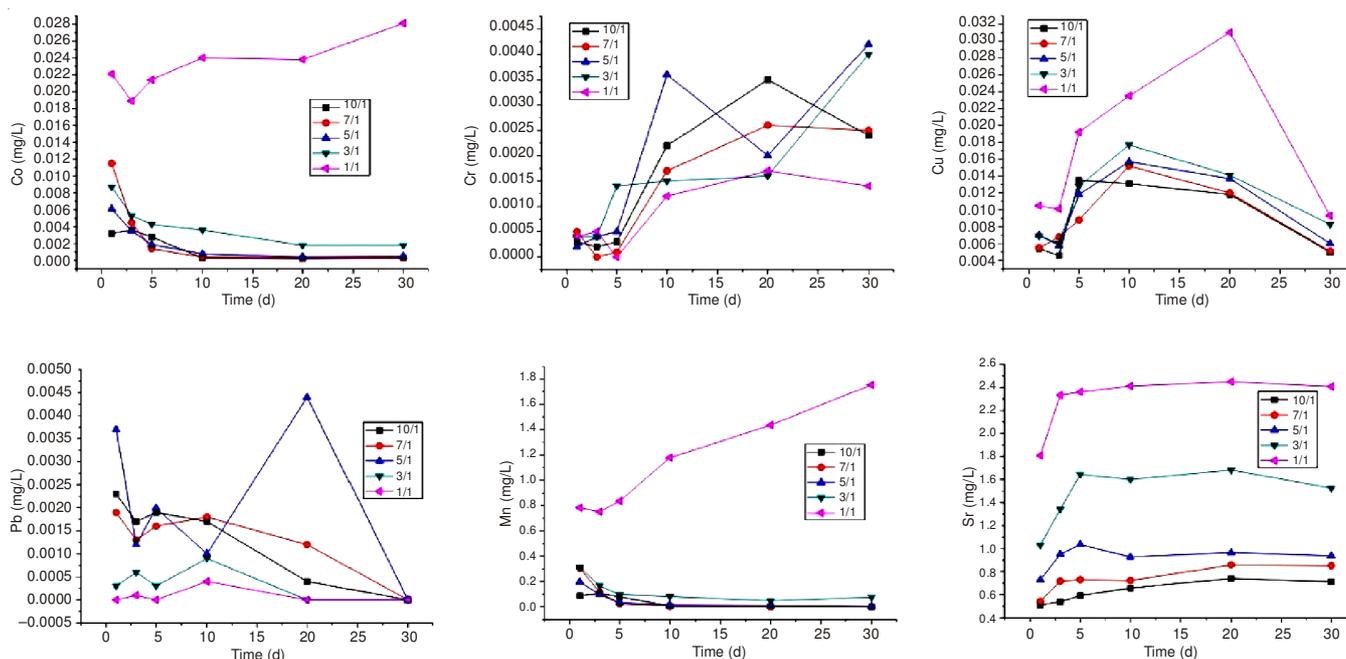


Fig. 4. Heavy metal concentrations in gangue leachates of different liquid/solid ratios evolved with time

Correlation analysis of leachate pH and heavy metals:

Correlation analysis results of gangue leachate pH and the 6 heavy metals of Co, Cr, Cu, Pb, Mn and Sr are exhibited in Table-3.

TABLE-3
CORRELATION ANALYSIS OF LEACHATE
pH vs. HEAVY METALS (n = 30)

	pH	Co	Cr	Cu	Mn	Pb	Sr
pH	1						
Co	-0.228	1					
Cr	0.338	-0.345	1				
Cu	-0.167	0.422*	0.1	1			
Mn	-0.151	0.963**	-0.217	0.476**	1		
Pb	-0.395*	-0.369*	-0.275	-0.14	-0.373*	1	
Sr	0.059	0.810**	-0.057	0.593**	0.810**	-0.555**	1

*Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level

It can be seen from Table-3 that the pH of neutral and weakly alkaline (pH 6.99-7.71) leachate correlates rarely to a variety of heavy metals, merely negatively to Pb at level of 0.05. This may be ascribed to that although activated lead minerals constantly dissolved during soaking, the dissolved trace heavy metal Pb was converted into hydroxide precipitate²⁷ in neutral or weakly alkaline solution, or adsorbed by colloidal iron and organics in residual skeleton, or forming secondary minerals of trace heavy metals, resulting in decreasing Pb concentration in leachate as leachate tended to be slightly alkaline. Leachate pH is positively correlated to Cr, indicating that as the pH increases, migration capacity of Cr-containing compounds in leachate increases, facilitating the solubilization release of Cr-containing minerals.

Positive and negative correlations between heavy metals in leachate co-exist, demonstrating that evident synergy and antagonism occur between heavy metals in gangue during leaching process. Heavy metals Co, Mn and Sr in leachate shows highly significant positive correlation ($P \leq 0.01$), implying that they are chemically similar with co-solubilization characteristics in gangue. Affected by other factors, heavy metals Cu, Mn and Sr in leachate exhibit a significant positive correlation ($P \leq 0.01$).

Gangue-water interaction: During stacking process, gangue reacts with air and oxygen in ambience, moisture and microorganisms to oxidize sulfur containing minerals on the surface of gangue and oxide layer is formed superficially. Gangue was sealed in soaking experiments of different conditions of liquid/solid ratio and soaking time. It was observed that, in the initial soaking & extraction (0-1 day), oxides on gangue surface were dissolved to produce various contaminants rapidly with the aid of water and oxides of reductive sulfur significantly decreased the pH of leachate. Simultaneously, Co, Cr, Cu, Pb, Mn and Sr in oxides were dissolved to certain extents, corresponding to results performed by Sracek *et al.*²⁸. Along with the proceeding of gangue-water interaction, oxidation-dissolution rate of sulfur containing minerals in the absence of oxygen decreased, leachate being weakly alkaline and except that the concentration of Cr

increased with prolonged leaching time, concentrations of heavy metals Co, Mn and Sr became consistent gradually, while Cu and Pb concentrations tended to decrease.

Along with evolution, Co, Mn and Sr concentrations impacted by gangue-water interaction reached dissolution-precipitation equilibrium rapidly after 5 days. Additionally, leachate after gangue soaking is neutral or weakly alkaline, not conducive to precipitation of certain trace elements but to the dissolution of ionic Cr in alkaline solution wherein chemical state changes, so that Cr concentration gradually increased with soaking time.

Combined with the present speciation of trace elements in gangue for analysis, water soluble/exchangeable ratio is tabulated in Table-4. Due to the effect of leachate pH, the soaking test only partially dissolved exchangeable heavy metals Co, Cu, Mn and Sr in water (minimum dissolution rate of 0 % and a maximum of 62.79 %) except that exchangeable Cr was completely dissolved when immersed. Under alkaline soaking conditions, carbonates, iron and manganese oxides, organics and residual did not precipitate at all.

TABLE-4
DISSOLUTION RATE OF EXCHANGEABLE HEAVY METALS

Water soluble/exchangeable	Co	Cr	Cu	Mn	Sr
Minimum	0.45	0	4.32	0.049	10.38
Maximum	18.30	116.67	62.79	34.98	42.53

Chemical behaviour during gangue acidic release:

During gangue-water interaction process, dissolution reactions of sulfur containing and alkaline minerals and dissolution of carbonates and aluminosilicates *etc.* destroy internal structure of gangue, facilitating the decomposition and dissociation of ions in mineral lattice and enabling the ions to present at free state in leachate. The acidity of leachate directly affects concentrations of heavy metals in leachate, not only the solubility of sulfides but also the formation of secondary precipitation of heavy metals in solution⁵, but the impact of leachate acidity on the release pathway of heavy metals in gangue is not evident. Heavy metals will precipitate in form of hydroxide in neutral or weakly alkaline (pH 6.99-7.71) leachate. In this gangue-water reaction system, formulae of mineral dissolution and precipitation are presented as follows:

Pyrite dissolution reaction: $\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$

Carbonate dissolution reaction: $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
 $\text{CaMg}(\text{CO}_3)_2 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$

Aluminosilicate dissolution reaction: Me-Al-silicate + $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{nHCO}_3^- + \text{H}_4\text{SiO}_4 + \text{Me}^{\text{n}+} + \text{Al-silicate}$ (Me: Na^+ , K^+ , Ca^{2+} , Mg^{2+} and other cations). Alkaline oxide hydrolysis: $\text{MnO} + \text{H}_2\text{O} \rightarrow \text{nM}^{\text{n}+} + 2\text{OH}^-$

Heavy metal precipitation reaction: $\text{M}^{2+} + 2\text{OH}^- \rightarrow \text{M}(\text{OH})_2$ (M as heavy metals) from the above reactions, it can be seen that the dissolution of pyrite can further promote dissolution reactions of carbonates and aluminosilicate minerals that buffer the increase of H^+ concentration and formation of OH^- in leachate, which lead to pH increase of leachate, precipitating Pb^{2+} as $\text{Pb}(\text{OH})_2$ and reducing the concentration of Pb in leachate. With the proceeding of

reaction, aqueous dissolved oxygen was continuously consumed and oxidation rate of sulfur containing minerals decreased. Concentrations of heavy metals in leachate tend to be consistent or decrease except chromium. Because soaking test was conducted in sealed system, where the oxidation reaction could not be completely preceded, the sulfur containing minerals could not be completely oxidized and dissolved, thereby inhibiting the gangue mineral structure decomposition and release of trace heavy metals. On the other hand, organic matter and iron-manganese colloids contained in gangue would adsorb heavy metals released during soaking, resulting in elevated heavy metal concentrations in Fe-Mn phase and organic phase.

Sulfur/iron molar ratio of 1.33 in gangue indicates that there are other sulfur-containing minerals (such as cobalt pyrite or chalcocite) in addition to pyrite. Fe^{3+} released from gangue pyrite oxidation-dissolution in leachate of $\text{pH} > 3$ was precipitated in form of $\text{Fe}(\text{OH})_3$, but pH has no impact on formation of SO_4^{2-} . Consequently, sulfur/iron molar ratio in leachate is significantly high. The SO_4^{2-} is mainly produced from sulfur containing mineral dissolution and dissolution-release rate of sulfur containing minerals in 30 experimental days ranges from 2.70 to 10.34 % (Fig. 5). Oxidation-dissolution-release rate of sulfur containing minerals with different liquid/solid ratios was increased with prolonged leaching time: 1:1 < 3:1 < 5:1 < 7:1 < 10:1. As liquid/solid ratio increases, sulfur dissolution-release rate becomes higher.

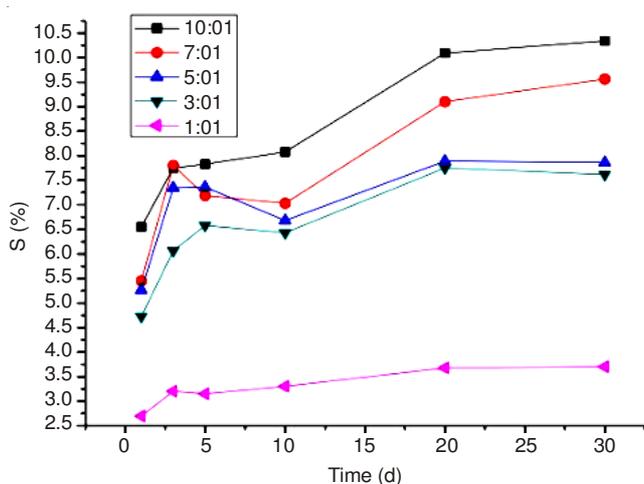


Fig. 5. Dissolution-release rate of sulfur containing minerals within gangue

Dissolution-release rates of Co, Cr, Cu, Mn, Pb and Sr were 0.008-0.260, 0.0003-0.0194, 0.03-0.48, 0.0008-0.53, 0-0.007 and 0.50-2.06 %, respectively, which means that only partial sulfur containing minerals were oxidized and then dissolved affected by the limited oxygen in sealed soaking system, resulting in lower dissolution-release rates of trace heavy metals. The complete dissolution of sulfur containing gangue minerals with great dissolution potential facilitate the dissolution-release of more heavy metals from gangue, so gangue acidic release has a potentially significant impact on environment.

Conclusions

- During the entire soaking period, pH of leachate with

varied liquid/solid ratios is in the overall range of 6.99-7.71, neutral or slightly alkaline, attributed to acid generated from sulfur containing mineral dissolution, hydrolysis of alkaline minerals, carbonate and silicate mineral solubilization buffering effect. The pH firstly increased abruptly, then decreased and finally increased slowly during soaking test lasting for 30 days.

- Heavy metals in gangue leachate vary distinctly under different liquid/solid ratios and different soaking time. Concentrations of Co, Cu, Mn and Sr decrease as liquid/solid ratio increases. Concentrations of Cr and Pb increase overall with liquid/solid ratio. Co, Mn and Pb concentrations decrease with soaking time except when liquid-solid ratio is 1:1. With soaking evolution, Cu concentration initially decreased, then increased and finally decreased slowly. Under different liquid/solid ratios, Cr increased slowly with the extension of leaching time. Strontium concentration increased initially and then tended to be in equilibrium after 5 days.

- Affected by leachate pH, the sealed soaking test could only partially dissolve exchangeable heavy metals Co, Cu, Mn and Sr in water (minimum dissolution rate of 0 % and a maximum of 62.79 %) except that exchangeable Cr was entirely dissolved when immersed. Carbonates, iron and manganese oxides, organics and residual did not precipitate at all under alkaline soaking conditions.

- In the long-term sealed gangue-water soaking system, dissolution-release rate of sulfur containing minerals of high acid producing capacity ranges from 2.70 to 10.34 %. Oxidation-dissolution-release rate of sulfur containing minerals with varied liquid/solid ratios increases with prolonged leaching time. Complete dissolution of sulfur containing minerals with significant potential of solubilization will facilitate the dissolution-release of gangue heavy metals, so gangue acidic release has an underlying significant impact on environment.

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