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Effects of Weathering on the Release of Heavy Metals from Coal Gangue

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The effect of weathering on the release of heavy metals from coal gangue was revealed. The XRD, SEM and Tessier five-step extraction method were applied to analyze mineral composition, mineral structure and chemical specification of heavy metals from coal gangue. The results showed that after 7-year weathering, the release rate of heavy metals with high mobility, such as Co, Cu and Pb, was 21.69, 36.49 and 36.73 %, respectively. The release rate of Cr and Zn was only 1.46 and 1.32 %, respectively. Both Mn and Fe were enriched and increased by 42.85 and 15.51 % with an increase of S content. Also, the formation of large amounts of iron colloids due to the weathering could facilitate the adsorption and complexation heavy metals. As a result, residual percentage content of heavy metals Cd, Co, Cu, Ni, Pb and Zn increased by 0.52, 12.85, 0.90, 4.53, 3.47 and 0.01 %, respectively.

Keywords: Weathering, Release of heavy metals, Influence mechanism, Coal gangue.

INTRODUCTION

Coal gangue is the by-product during coal mining and manufacturing processes and represents the major solid waste during the process of coal production. At present, around 4 billion tons of coal gangue is stacked and piled on ground surface in China, which is then affected by long-term weathering, rainwater leaching, soaking, scouring and other processes. Due to the occurrence of a series of physical and chemical changes, large amounts of harmful substances have been released accompanying with leaching, which then seep into the ground, rivers thus cause the pollution of surface water, underground water and soil environment and further endanger the ecological safety of regions around coal gangue piled and stacked sites[1,2].

Weathering process is an important part of the geochemical cycling of coal gangue[3]. When solid and dense coal gangue and associated crystal minerals are in contact with atmosphere, water and some biological substances, the weathering process occurs. With the involvement of water as one important vector, multiple geochemical reactions occur, including hydrolytic reaction, hydration reaction, redox reaction and ion exchange reaction[4]. On one hand, the result of this series of reactions leads to the release of large amounts of harmful substances from dissolved coal gangue. On the other hand, mineral composition, chemical composition and crystal structure of coal gangue is altered and the mineral crystal structure of coal gangue is gradually shattered until the formation of loose deposits. Meanwhile, the activity, bioavailability and danger of heavy metals are mainly determined by the chemical property and specifications of heavy metals. After long-term weathering process, mineral crystals of coal gangue have underwent dissolution, precipitation, complexation, adsorption, oxidation, reduction and other geochemical reactions. Also, the mobility and transformation ability of heavy metals, as well as their imposed pollution hazards, have been significantly altered with the change of corresponding chemical specifications[5-7].

The influence of trace heavy metals from coal gangue on surrounding ecological environments is manifested by the fact that the total amount of trace heavy metals from coal gangue could be used to determine their ecological effects on surrounding environment[5] and that combining the amount of the release of heavy metals with the release rate during the coal gangue-water interaction process further determines the degree of pollution on surrounding environments[8]. With more and more studies available, the conclusion drawn from former method that tests the influence of the amount of trace elements on environment is difficult to be accepted. As to the second method, because of the distinction between samples and experimental method, heavy metals from coal gangue could impose no impact[9] or significant impact[6] on surrounding environment, two totally different conclusions.

In order to clarify the environmental effect of heavy metals derived from coal gangue after chemical weathering process, this paper analyzes chemical components, mineral composition, chemical specifications and variations of heavy metals derived from coal gangue caused by weathering and further provides a mechanistic of the release of heavy metals from coal gangue. Therefore, the results could provide a scientific basis for the selection of coal gangue stacked and piled sites and for the comprehensive utilization of coal gangue landfill sites.

EXPERIMENTAL

Collection and processing of samples: Coal gangue samples used in this study were collected from coal gangue stacked and piled sites in Sangshuping of Hancheng mining zone, Shannxi Province, China, (35° 40'58.8 "N, 110° 33'43 .6 "E) on 27 April, 2011. The collected coal gangue could be divided into two types, the unweathered type (*i.e*., fresh coal gangue) and the weathered type (*i.e*., 7-year coal gangue) as shown in Fig. 1. During the sampling process, the current situation of coal gangue and the growth conditions of plants around the sampling sites were carefully observed. Fresh coal gangue granules were crushed and shattered to form uniform and shiny particles with large pores. Also, no any vegetation was found on the surface of fresh coal gangue particles. By contrast, 7-year weathering coal gangue displayed loose state with small pores in the absence of particle form. Also, vegetation was found distributed on the surface of such coal gangue.

Fig.1 Fresh coal gangue and 7-years weathering coal gangue

During sample collection process, three sampling sites were established for each type of coal gangue (fresh *versus* weathered coal gangue), with four or five samples collected from each sampling site. Collected samples were mixed well with impurities removed, shattered and then filtered through 0.5 cm nylon sieve and all processed samples were saved for further analysis.

Mineral analysis: Mineral composition analysis: coal gangue samples were analyzed by using XRD (D/MAX2500X-ray diffraction) to determine mineral composition.

Mineral structure analysis: coal gangue samples were analyzed by using SEM (JSM-6700F cold field emission scanning electron microscope) to determine mineral structure.

Analysis of the content of heavy metals: Coal gangue digestion: HCl-HNO_3-HF-$HClO_4$ electric heating plate digestion method was used for the digestion of coal gangue samples.

Element measurement: Inductively coupled plasma emission spectrometer (ICP-OES) was used to determine the content of heavy metals, such as Co, Cr, Cu, Mn, Pb and Sr.

Specification analysis of heavy metals: In this study, Tessier *et al*.[10] five-step sequential extraction method was used to study the chemical specifications of heavy metals derived from coal gangue.

Step 1. Exchangeable phase: Add 8 mL 1 mol/L $MgCl_2$ solution, which is adjusted with NaOH until pH value reaches 7. The solution is then shaken under room temperature for 1 h.

Step 2. Carbonate phase: Add 8 mL 1 mol/L CH_3COONa solution, which is adjusted with CH_3COOH until pH value reaches 5. The solution is then shaken under room temperature for 5 h.

Step 3. Fe-Mn oxides bound phase: Add 20 mL 0.04 mol/L $NH_2OH{\cdot}HCl$ configured with 25 % CH_3COOH solution, which is then continuously shaken for 6 h under 96 ± 3 °C conditions.

Step 4. Organic matter bound phase: Add 3 mL 0.02 mol/L HNO_3 solution and 5 mL 30 % of H_2O_2 solution, which is then adjusted with HNO_3 until pH value reaches 2. The solution is then continuously shaken for 2 h under 85 ± 2 °C conditions; after the solution is cooled to room temperature, 5 mL 3.2 mol/L CH_3COONH_4 configured with 20 % HNO_3 solution is added until the final volume is 20 mL. The solution is then continuously shaken for 0.5 h under 25 ± 1 °C conditions.

Step 5. Residual phase: HCl-HNO_3-HF-$HClO_4$ electric heating plate digestion method is applied for digestion purpose.

For each step, the extract first goes through 0.45 µm sieve and inductively coupled plasma emission spectrometer (ICP-OES) is used to determine the chemical specifications and content of heavy metals, such as Co, Cr, Cu, Mn, Pb and Sr.

Quality control: All samples used for experimental analysis underwent 10 % parallel sample test, with relative standard deviation (RSD) within the range of 0.3 and 13.5 %. Therefore, our samples met all test requirements. Also, the measurement accuracy of all heavy metals passed the requirement of national standard verification procedures, with the recovery rate within the range of 75.2 and 109.3 %, which also met the quality control requirement. In addition, all used analytical instruments were within the qualification period. Therefore, our experimental results were both accurate and reliable.

Data and statistics: Experimental data were statistically analyzed by using Excel 2007, SPSS16 and Origin8 software. Also, correlation analysis, comparative analysis and other methods were used to study the mechanism of the release of heavy metals from coal gangue.

RESULTS AND DISCUSSION

Mineral composition and structure: The mineral composition of coal gangue was determined by using X-diffraction method, with the results shown in Table-1 and Fig. 2. Also, the mineral structure determined by using SEM scanning method was shown in Fig. 3.

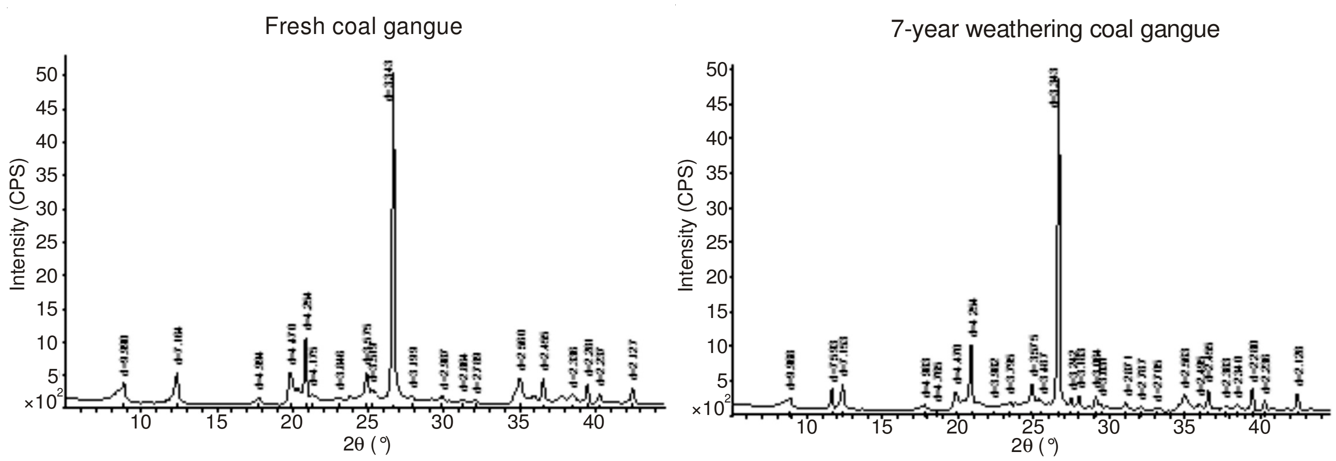

Fig. 2. X-diffraction of coal gangue

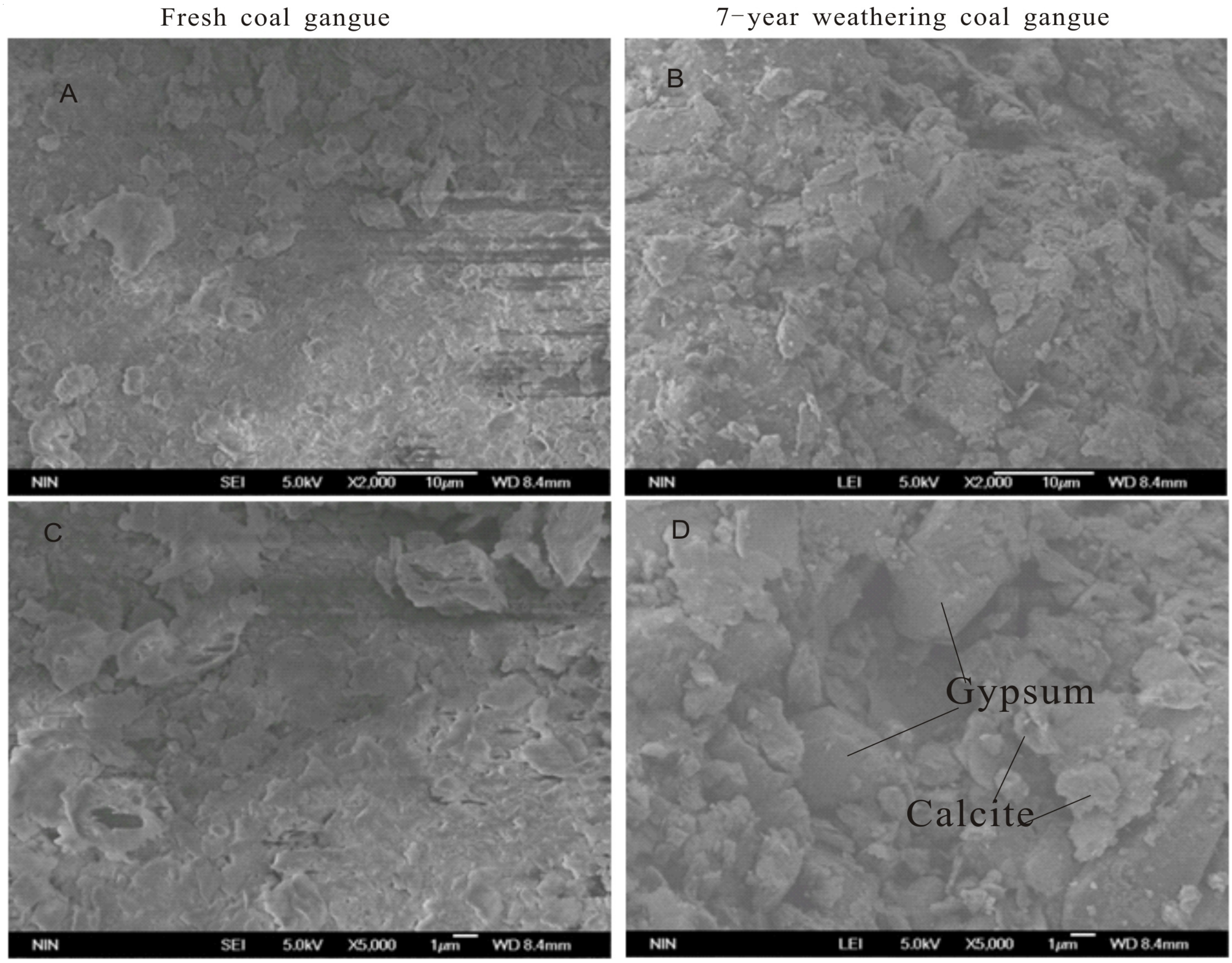

Fig. 3. SEM of coal gangue: (A) magnification 2000x from fresh coal gangue; (B) magnification 2000x from 7-year weathering coal gangue; (C) magnification 5000x from fresh coal gangue; (D) magnification 5000x from 7-year weathering coal gangue

TABLE-1
MINERAL COMPONENTS CONTENT OF COAL GANGUE (%)

Composition	Fresh	7-year weathering	Difference
Quartz	44.0	57.4	13.4
Plagioclase		2.6	2.6
K-feldspar		1.9	1.9
Calcite		1.2	1.2
Pyrite	1.9	0.9	-1.0
Anatase	0.8		-0.8
Gypsum		5.0	5.0
Illite Mixed-layer illite and smectite	31.3	16.0	-15.3
Chlorite		2.0	2.0
Kaolinite	22.0	13.0	-9.0

It can be seen from both Table-1 and Fig. 2 that after 7-year weathering process, due to the damage and breakage of clay mineral crystal lattice, the content of quartz in weathered coal gangue increased by 13.4 %, whereas the content of pyrite, mixed-layer illite/smectite and kaolinite decreased by 1, 15.3 and 9 %, respectively. Also, compared with fresh coal gangue, the content of anatase in weathered coal gangue was reduced from 0.8 to 0 %. After 7-year weathering process, five new minerals are formed, including plagioclase feldspar, K-feldspar, calcite, gypsum and chlorite, with corresponding content as 2.6, 1.9, 1.2, 5 and 2 %, respectively.

Under the influence of weathering and leaching processes, mineral crystal lattice of illite, mixed-layer illite/smectite and kaolinite was shattered and damaged to form weathering minerals, such as plagioclase feldspar, potash feldspar and chlorite.

Since pyrite represents the major sulfur-bearing mineral of coal gangue, the oxidation of pyrite could significantly lower down the content of pyrite in coal gangue, which is an important factor that leads to the discharge of acidic wastewater and contributes to the release of harmful trace heavy metals derived from coal gangue[11,12].

The formation of secondary minerals, such as calcite and gypsum, is probably due to the hydrated combination of Ca^{2+} from calcium-bearing minerals of coal gangue, HCO_3^- and CO_3^{2-} from the dissolution of CO_2 in surrounding environment and SO_4^{2-} and Ca^{2+} from the dissolution release of sulfur-bearing minerals. As a result, minerals of $CaCO_3$, $CaSO_4$ and $CaSO_4·2H_2O$ are formed, which then precipitate and are adsorbed on the surface of weathered coal gangue. Under the influence of water leaching process, these minerals will continue to dissolve and disperse to surrounding environments.

Fig. 3 shows different magnification SEM features of coal gangue after 7-year weathering and leaching process. It can be seen that the crystal lattice of coal gangue is damaged. Consequently, the dense and smooth mineral crystals of coal gangue are smashed (magnification 2000 x), the surface of coal gangue becomes rugged, loose and fragile (magnification 5000 x), large coal gangue granules are shattered into small pieces and the crystal structure of gypsum and calcite after weathering process is visible. The damage of mineral crystal lattice is easy to make ions within crystal lattice to convert from original compounds to the free state and thus enhances the mobility of heavy metals.

Element content: According to the detected chemical composition of coal gangue samples (Table-2), it can be seen that during the entire period up to 7 years from coal gangue exploitation and stacking process to weathering process, small amounts of chemical components Al and K were released, with the release rate as 7.45 and 2.66 %, respectively. By contrast, the content of B and Mg increased slightly by 6.54 and 4.89 %, respectively. In addition, the content of Ca and S almost increased doubled by 94.62 and 101.59 %, respectively, indicating the occurrence of significant enrichment.

The dissolution of pyrite (the content of FeS_2 decreased by 1 % consequently) and the formation of acidic water led to the dissolution and release of heavy metals from coal gangue, resulting in the change of the content of heavy metals in coal gangue. However, due to the influence of geochemical reactions within coal gangue-water system (including oxidation, dissolution, precipitation, adsorption, complexation and other reactions), the content of heavy metals in coal gangue, such as Co, Cr, Cu, Pb and Zn, decreased by 21.69, 1.46, 36.49, 36.73 and 1.32 %, respectively. Also, a small portion of heavy metals was dissolved and then released into the environment, whereas the majority of them remained in the coal gangue. However,, the content of heavy metals, such as Mn and Ni, increased by 42.85 and 0.50 %, respectively, indicating the occurrence of enrichment in coal gangue.

Under the influence of weathering, the release rate of heavy metals Co, Cu and Pb from coal gangue was 21.69, 36.49 and 36.73 %, respectively, not less than 20 %, indicating that these three heavy metals were of high mobility during the weathering and leaching process. As a result, these three heavy metals could easily disperse to surrounding environment and they represent heavy metals that could impose a great impact on the environment once they are dissolved and released from coal gangue. By contrast, the release rate of heavy metals Cr and Zn was only 1.46 and 1.32 %, respectively, whereas the content of Mn and Fe increased with an increase of S content in coal gangue. After 7-year weathering process, the content of Mn and Fe increased by 42.85 and15.51 %, respectively.

It can be seen from Table-2 that the influence of natural weathering on Cd, Cr, Ni and Zn in coal gangue was relatively small, whereas the influence of natural weathering on Pb, Mn, Cu, Co, S and Ca was much more significant. For coal gangue before or after weathering process, the content of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn was higher than corresponding Chinese soil environmental background value except Cu from fresh coal gangue and Mn from seven-year weathered coal gangue[13]. Actually, the content of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in coal gangue before or after weathering process was 1.34-806.07 times of environmental background value found in Chinese soils and the content of Zn in coal gangue before or after weathering process was hundreds of times of environmental background value found in Chinese soils, which thus imposed serious environmental problems.

The content of sulfur from 7-year weathered coal gangue was 2.02 times of that from fresh coal gangue. Similarly, the content of iron from weathered coal gangue was 1.16 times of that from fresh coal gangue. In addition, S/Fe molar ratio in weathered coal gangue was 2.4, which was greater than 1.37, the S/Fe molar ratio found in fresh coal gangue, indicating

TABLE-2
CHEMICAL COMPOSITION OF COAL GANGUE (g/kg)

	7-year weathering	Fresh	Release rate (%)	Background value*
Al	287.25	310.38	7.45	
B	12.47	11.71	-6.54	0.04
Ca	53.76	27.63	-94.62	
Mg	5.49	5.24	-4.89	
K	120.79	124.09	2.66	
Fe	27.74	24.01	-15.51	
S	38.15	18.93	-101.59	
Cd	0.0065	0.0065	0.00	0.0008
Co	0.0244	0.0311	21.69	0.0116
Cr	0.1771	0.1798	1.46	0.0573
Cu	0.0176	0.0278	36.49	0.0207
Mn	0.5659	0.3961	-42.85	0.5430
Ni	0.0501	0.0499	-0.50	0.0249
Pb	0.2093	0.3308	36.73	0.0235
Zn	54.0875	54.8125	1.32	0.0680

*Chinese soil environmental background value[13]

that the increase of sulfur content in weathered coal gangue was closely related to the deposition of sulfur-bearing atmosphere (SO_2, SO_3, S) around sites where coal gangue was stacked and piled. Therefore, in such stacking area of coal mine and coal gangue, air pollution represents a serious environmental pollution problem[14]. Especially under dry and windy weather conditions, the influence of coal dust subsidence from coal gangue (especially coal dust from weathered coal gangue) on the surrounding environment where coal gangue was stacked and piled deserved more and more attention.

Chemical specifications of heavy metals: Changes of chemical specifications of trace heavy metals in coal gangue could directly reveal the changing characteristics of heavy metal toxicity and environmental behavior and through analysis of changes of chemical specifications of heavy metals, it is possible to carry out objective and comprehensive assessment of the extent of heavy metal pollution caused by anthropogenic activities and of the potential hazards imposed by heavy metals on ecological environments[15,16].

A comparison between fresh coal gangue and 7-year weathered coal gangue regarding chemical specifications of heavy metals in different percentages was shown in Fig. 4. It could be seen that before or after weathering process, chemical specifications of heavy metals in percentages, such as Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, all varied through time.

Although weathering and leaching process caused a decrease of exchangeable percentages of heavy metals, such as Cd, Co, Mn and Ni, in coal gangue, with corresponding value decreased by 0.07, 1.40, 1.10 and 0.33 %, respectively,

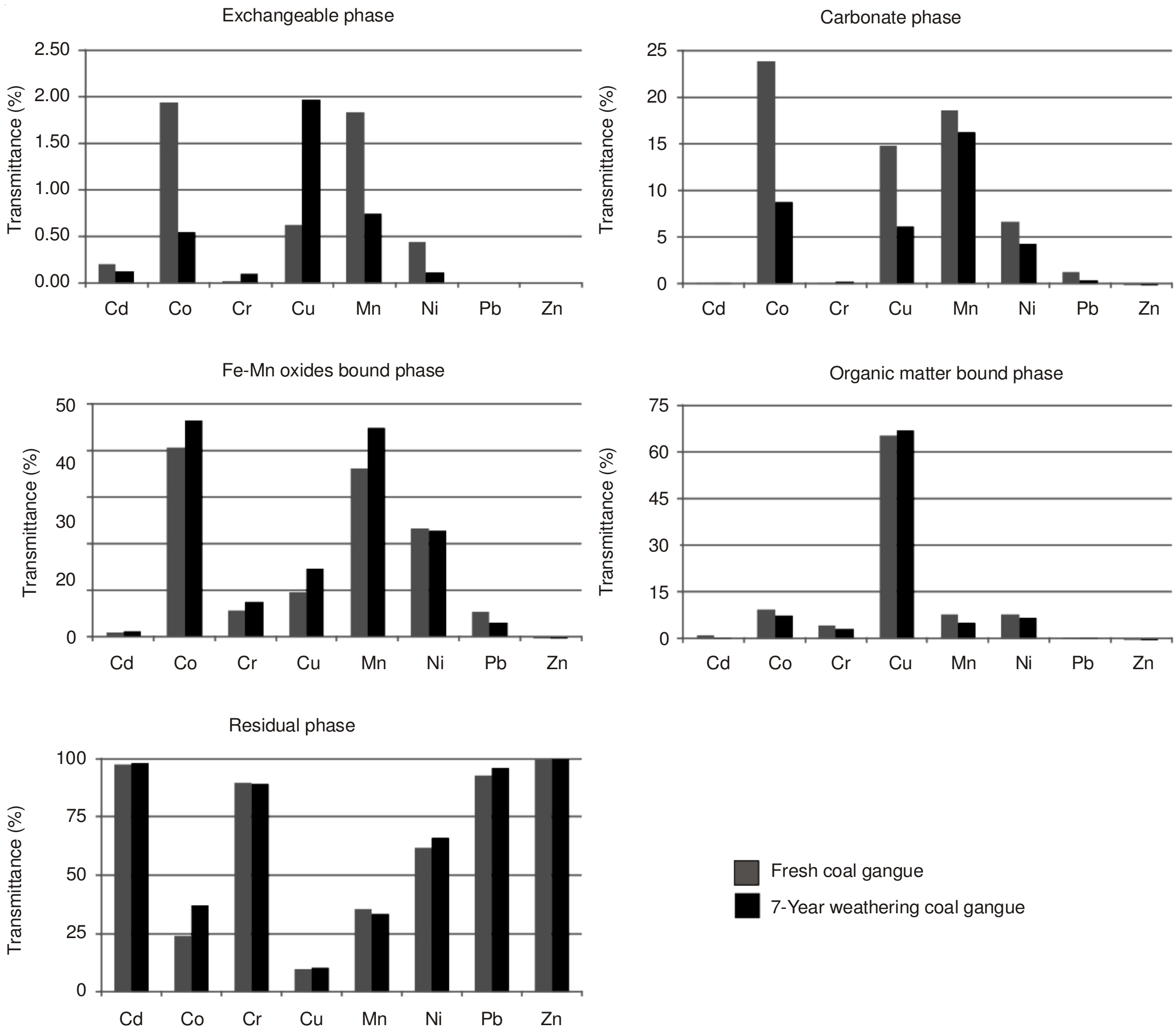

Fig. 4. Chemical specifications percentage of heavy metals

but due to the fact that Cr-bearing organic matter bound state and Fe-Mn oxidation bound state could undergo exchangeable transformations under the influence of weathering process, the percentage content of Cr and Cu in weathered coal gangue increased by 0.09 and 1.34 %, respectively.

During the oxidation and dissolution process of pyrite, a large amount of H^+ was released. As a result, the carbonate state of heavy metals in coal gangue was dissolved and released, with the percentage content of Co, Cu, Mn, Ni, Pb and Zn decreased by 15.07, 8.70, 2.36, 2.35, 0.89 and 0.01 %, respectively.

Due to the influence of weathering process, the Fe-Mn oxidation bound phase percentage content of Cd, Co, Cr and Cu increased by 0.16, 5.61, 1.82, 4.94 and 8.68 %, respectively. By contrast, the percentage content of organic matter and sulphide of heavy metals decreased, with the order from the highest to the lowest as Mn > Co > Cr > Ni > Cd > Pb > Zn.

Before or after weathering process, except Co, Cu and Mn with residual percentage content less than 50 %, the rest of heavy metals, such as Cd, Cr, Ni, Pb and Zn, had their residual percentage greater than 60 %. In particular, residual percentage content of Cd, Pb and Zn was up to 90 %. Weathering process damaged the crystal structure of coal gangue to make it crush, but residual percentage content of heavy metals in coal gangue was unchanged as mineral structure was damaged except corresponding residual percentage content of Cr and Mn decreased by 0.75 and 2.54 %, respectively. Due to the dissolution of iron-bearing minerals and the existence of organic matters, iron colloids were formed, which then had complex adsorption or complexation reactions with the release of heavy metals due to the influence of weathering and leaching events, causing different degree of increase of residual percentage content of heavy metals such as Cd, Co, Cu, Ni, Pb and Zn.

The effect of weathering on the total amount of heavy metals in coal gangue, such as Cd, Cr, Ni and Zn, was relatively small, but its effect on their chemical specifications was significant.

The dissolution and release of exchangeable and carbonate-bound heavy metals would directly affect the surrounding ecological environment. With an extension of weathering time and weathering extent, piled and stacked coal gangue would become a long-term source for the release of harmful elements. As the life cycle of coal gangue (weathering early stage → weathering middle stage → weathered late stage) enters the late stage (completely decomposed)[17], the mobility and transformation of the bioavailability (exchangeable phase + carbonate phase + Fe-Mn oxides bound phase + organics/ sulfide bound phase) of heavy metals within coal gangue[18] could impose negative impacts on surrounding ecological environments.

This is especially true for the scenario when the content of heavy metals in coal gangue is higher than Chinese soil environmental background value. For example, the dissolution, release and mobility of heavy metals with corresponding bioavailability content more than 60 %, such as Co, Cu and Mn and one particular heavy mental with bioavailability content of Ni as 33.71 %, could all impose potential harmful effects on the surrounding ecological environment and the potential harmful effects could increase gradually with an increase of weathering time.

The release mechanism of heavy metals from weathered coal gangue: Within coal gangue, Cu, Pb, Zn and other elements often appear as sulfur-bearing minerals such as galena, sphalerite, chalcopyrite and azurite. Due to the influence of weathering process, these sulfur-bearing minerals would undergo chemical reactions, resulting in the formation of a large amount of H^+, which would then facilitate the dissolution and release of carbonate heavy metals from coal gangue. As heavy metals are transformed from organic matter phase and sulfide bound phase to exchangeable phase and then released into the environment, are transferred to form iron-manganese oxide phase, or are adsorbed on residual phase, the content of Fe-Mn oxides and residual heavy metals would increase and the adsorption and enrichment of heavy metals would slow down the release rate of heavy metals to some level, but the total amount of heavy metals released would not reduce as weathering effect is enhanced through time.

After coal gangue had been explored and piled, it was stacked and placed in environment different from underground environment, coal gangue would be affected by multiple factors such as water, air and anthropogenic activities. As a result, its composition and morphology would change. Due to the influence of weathering and leaching events, pyrite, the major sulfur-bearing mineral of coal gangue, would have oxidation and hydrolysis reactions with both water and oxygen, with the product Fe^{2+}, Fe^{3+}, SO_4^{2-} and H^+. The dissolution reaction of pyrite is shown as following[11]:

Oxidation of pyrite: $$FeS_2 + 7/2O_2(aq) + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

Iron oxidation: $$Fe^{2+} + 1/4\ O_2(aq) + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \quad (2)$$

Iron reduction: $$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

After pyrite is oxidized and dissolved, acidic water is formed and released, which would then facilitate the dissolution and release of trace heavy metals from coal gangue. Also, the input of H^+ would promote the desorption of exchangeable heavy metals that are adsorbed on the surface of coal gangue. Meanwhile, under the influence of acidic water, heavy metals with carbonate phase, organic phase, or sulfide phase would be slowly released from coal gangue.

The content of organic matters increased from 59.18 % in fresh coal gangue to 71.89 % in weathered coal gangue. Also, large amounts of organic matters and iron colloids caused by pyrite reaction exist in coal gangue. These colloids could interact with many heavy metals *via* adsorption or complexation. Therefore, under the influence of above mentioned desorption, dissolution, adsorption and complexation process, Mn and Ni element would gradually get enriched in weathered coal gangue. In particular, the content of Mn in 7-year weathered gangue could be increased by 42.85 %. By contrast, a few heavy metals, such as Co, Cr, Cu, Pb and Zn, could undergo rainwater leaching process. Ultimately, they could get dissolved in the water body and then released to the environment.

Conclusions

• Under the influence of weathering process, the hard and dense coal gangue would be crushed and shattered to loose structure. Consequently, mineral composition of coal gangue would be altered. After 7-year weathering process in the mining zone of Hancheng, the content of quartz in coal gangue increased by 13.4 %, whereas the content of pyrite, mixed-layer illite/smectite and kaolinite decreased by 1, 15.3 and 9.0 %, respectively. Five new minerals were formed after weathering process, including plagioclase feldspar, potash feldspar, calcite, gypsum and chlorite, with corresponding contents as 2.6, 1.9, 1.2, 5 and 2 %, respectively.

• Under the influence of weathering process, only portions of heavy metals have been dissolved and released. For heavy metals with high mobility, such as Co, Cu and Pb, corresponding release rate was 21.69, 36.49 and 36.73 %, respectively. By contrast, the release rate of heavy metals Cr and Zn was only 1.46 and 1.32 %, respectively. Also, the content of Mn and Fe was enriched with an increase of S content in coal gangue. For 7-year weathered coal gangue, the content of Mn and Ni increased by 42.85 and 15.51 %, respectively.

• After 7-year weathering process, the bioavailability percentage of heavy metals, such as Cd, Co, Cu, Ni, Pb and Zn, decreased by 0.52, 12.85, 0.90, 4.53, 3.47 and 0.01 %, respectively, whereas for heavy metals Cr and Mn, corresponding bioavailability increased by 0.75 and 2.54 %, respectively. Except Co, Cu and Mn, the majority of heavy metals before or after weathering events, such as Cd, Cr, Ni, Pb and Zn (61.76-99.94 %), was adsorbed to the crystal structure of residuals. Due to the adsorption and complexation effect of iron colloids and organic matters after weathering process, the residual content of most heavy metals was enhanced except Cr and Mn.

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