

Speciation of Cr in waste rocks of Xinqiao pyrite mine in Tongling, China

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Abstract. Based on the investigation of the characteristics of the waste rocks of Xinqiao pyrite mine in Tongling, the possibility of AMD was discussed, and the speciation of Cr in the waste rocks was studied by the improved five steps sequential extraction method. The results reveal that the NP is less than the AP, the waste rocks have a high acid potential and produce AMD. The speciation of Cr in the waste rocks exist mainly in the silicate, secondly in deoxidize and oxidizable mode. But the Cr contents in the deoxidize mode are correlative to the total contents in waste rocks, if the waste rocks react with the AMD, the Cr in the deoxidize and oxidizable modes may easily release from the waste rocks. So the Cr has high environmental risk.

Introduction

Waste rocks are the non-economic material removed from a mine to access the ore body. Under the earth surface conditions, the hazard of waste rocks is controlled by the speciation of the heavy metal elements other than the total content of the heavy metal [1]. Most of the studies deal with the contamination of waste rocks by heavy metals using only the generation of AMD and the total metal content as a criterion to assess its potential effect as contaminant [2,3,4,5]. And many scholars have done a lot of researches on the modes of occurrence, distribution characters of heavy metals around mine tailing reservoirs [6,7,8,9]. But there are few studies on the speciation heavy metals in waste rocks. The speciation is a good indicator and has been used to assess metal mobility, availability and toxicity.

Cr is a sort of heavy metal in white or cyan. The abundance of lead elements in lithosphere is 13.16 mg/kg. The background value in world soil is 35 mg/kg, 26 mg/kg in China soil and 26.4 mg/kg in Anhui soil [10,11]. The lead is not the necessary element of creature but the accumulative contamination. The lead in soil can get in the human body by eating, breath and skin absorption and harm the health.

The objective of this study is to identify and quantify the speciation in which Cr is present in Xinqiao pyrite mine to gain a more precise understanding of the potential and actual impacts of elevated level of the metal, and to evaluate processes of Cr release under changing environmental conditions and how much contamination release into the environment.

Site description

Tongling city of Anhui province is one of the important mineralization areas in China, lies in the middle of the iron-copper-gold polymetallic metallogenic belt of the Middle and Lower Reaches of Yangtze River. The eastern suburb of Tongling city is an important mining area for nonferrous metals. The Xinqiao pyrite mine is in the center of the suburbs. The north of the city distributes farmland and water network which connects to the Yangtze River. The Xinqiao pyrite deposit is a large copper-bearing

pyrite mineral deposit. The waste rocks stripped by surface mining are piled up on the hillside near the mine. Parts of the waste rocks are used to back-fill the mining tunnel. The sulfur-concentrates from which Cu, Au and Ag have been separated are transported to other places to produce vitriol, so no tailings are produced.

Mining activities in Tongling city has been booming for very long time. The exploitation of mineral resources brings huge economic benefits to the development of the society, but it leads to a series of environmental contamination problems at the same time. One of the universal problems of mining activities is the pollution of heavy metal elements.

The main metal minerals in the crude mine ores are shown in table 1. It shows that the content of S is much higher than CaO. In other words, the content of S might be higher than CaO in the waste rocks, and it might be AMD generation.

Table 1 Analytical results of the chemical components of the crude ores in Xinqiao pyrite mine[12]

Mine	Au	Ag	Cu	S	Fe	Cr	Zn	As	CaO	MgO	Al ₂ O ₃	SiO ₂
content	0.82	14.00	0.40	36.27	33.73	0.067	0.21	0.054	3.06	1.44	2.85	14.12

Note: The unit of Au and Ag is 10^{-6} , and the unit of others is 10^{-2} .

Materials and methods

The 7 waste rocks samples were taken from the waste heap of Xinqiao pyrite mine by color at random. Heavy metal concentrations of samples were measured in the central geological laboratory of Anhui province. The waste rocks were then broken up by hammer, and also ground to 200 micron with a carnelian mortar. The resulting powder samples were kept in polyethylene plastic bags. The concentrations of heavy metals elements were measured by AFS (230E), AAS(ZEEEnit60) and ICP-OES (Iris advantage). The S element was tested by the non-aqueous titration combustion method, the acid potential values gained by the counting method[10]are maximal, and were counted in the light of the S element content. The neutralization potential was tested by the improved neutralization potential acid-alkali counting method [13].

The speciation of Cr(exchangeable, carbonate, deoxidize, oxidizable and slag) was obtained by the improved five steps sequential extraction method of Förlsner [14], then added 1-2 drops of dense nitric acid to the solution. The acidized solution was tested with ICP-AES (Iris advantage). The content of the slag mode is gained by the total content of the elements less the content of the elements of each of the other speciation.

Results and discussion

Neutralization potential and possibility of producing AMD of the waste rocks

AMD is water with $\text{pH} < 5$, originating from mine tailing ponds, waste rock piles and oxidation of sulphide ores. AMD is not the most serious contamination, but the deliquescent components might possibly result in harmful influence.

Table 2 shows that the difference in the contents of S element in 7 samples is large, from 0.04% to 3.44%, so that AP counted from the S content is also very different. What's more, the difference in NP of the samples is also very large because their mineral components are different. As a single sample is concerned, if $\text{NP} > \text{AP}$, the waste rock don't produce AMD. There are two samples with the NP almost equivalent to the AP; in the others, the NP is less than the AP. In other words, the waste rocks generally produce AMD. If the waste rocks are handled unreasonably, they will pollute groundwater and result in deterioration of the soil and water eco-environment.

Table 2 Test results of the waste rocks and the the possibility of producing AMD

Sample No.	S%	AP	HCl (ml)	NaOH (ml)	NP	Possibility of producing AMD
R1	0.42	13.12	2.40	23.00	2.50	Yes
R2	0.04	1.20	2.40	23.70	0.75	Uncertainty
R3	0.05	1.56	2.40	23.20	2.00	Uncertainty
R4	1.42	44.37	2.00	11.90	20.25	Yes
R5	0.62	19.37	4.20	0.60	103.50	No
R6	0.33	10.31	2.10	20.40	1.50	Yes
R7	3.44	107.5	2.50	23.60	3.50	Yes

Table 3 Sequential extraction experimental results of Cr in the waste rocks [mg/kg]

Speciation	R1	R2	R3	R4	R5	R6	R7
Exchangeable	0	0	0	0	0	0	0
Carbonate	0.3	0	0.7	2.2	5.7	0.2	0.9
Deoxidize	12.9	48.4	13.9	47.9	50.8	6.5	73.6
Oxidizable	1.6	9.6	0.4	2.3	1.9	0.8	4.0
Silicate	42.0	74.6	68.9	76.7	33.6	36.7	57.2
Total content	56.9	132.8	83.9	129.0	92.0	44.2	135.8

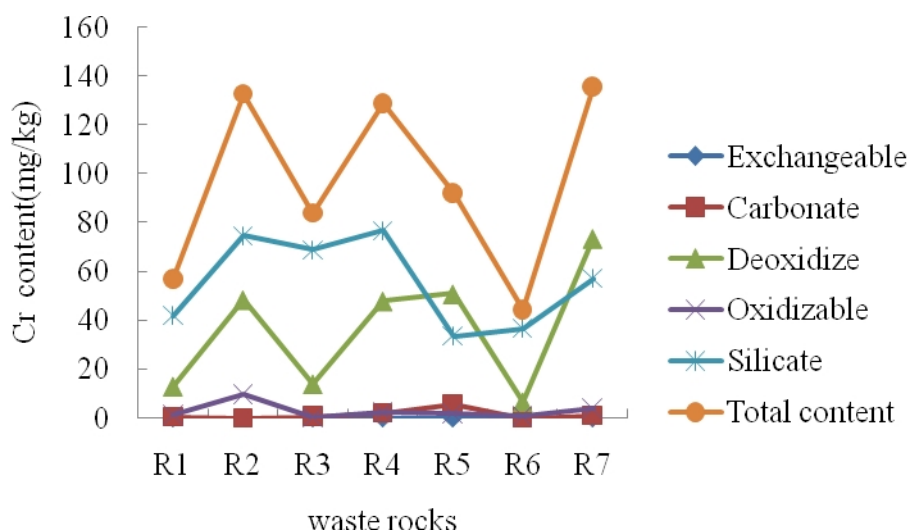


Fig. 1 Speciation of Cr in the waste rocks

The speciation of Cr in the waste rocks

The speciation of Cr in the extracting solutions of the waste rocks is listed in Table 3. Fig 1 shows the corresponding data of Table 3. It can be seen that the exchangeable mode of all samples are not detected. The contents of carbonate, exchangeable and oxidizable modes are low. Cr distributes mainly in the silicate(except sample R5 and R7). And most of Cr is in the stable state. The Cr contents in the deoxidize are higher, especially in sample7, reaching 73.6mg/kg. Its percentage of all Cr content amounts to 54.16%. In all samples, the percentage of Cr content in the deoxidize mode is largest in sample R5, reaching 55.16% of the total Cr content.

From Fig. 1 we can know that the Cr contents in the deoxidize mode are correlative to the total contents in waste rocks. The Cr in the deoxidize modes in waste rocks can transform to the exchangeable mode, so that the Cr element can release and migrate from the waste rocks into the water and soil. Especially, when the waste rocks react with the AMD, the heavy metals will leach from the waste rocks, transfer to the solution, migrate to the surroundings, and pollute and exacerbate the environment.

Conclusions

Generally speaking, the NP is less than the AP of the waste rocks in Xinqiao pyrite mine, so the waste rocks have a high acid potential and produce AMD.

The Cr in the waste rocks mainly exists in the silicate, secondly in deoxidize, oxidizable mode, carbonate mode, and exchangeable is hardly detected. The Cr contents in the deoxidize mode are correlative to the total contents in waste rocks. In other words, the higher the contents of the Cr in waste rocks, the higher those in the deoxidize modes. Under the oxidation condition, especially when the waste rocks react with the AMD, the heavy metals in the deoxidize and oxidizable modes may easily release from the waste rocks, transfer to other modes, and eventually pollute the environment.

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