International Proceedings of Chemical, Biological and Environmental Engineering, V0l. 96 (2016)
DOI: 10.7763/IPCBEE. 2016. V96. 9

Study on the Law of Static Acid Production of Waste Rocks of Different Ages at Dexing Copper Mine

Qiong Wang[1], Yi Liu[2], Yuli Han[3], and Lianbi Zhou[1 +]

[1] Beijing General Research Institute of Mining & Metallurgy, China

[2] China Science and Technology Museum, China

[3] College of forestry, Beijing Forestry University, China

Abstract. Waste rocks and tailings of a mine generate acid wastewater due to oxidization during long-term accumulation, and this may cause serious harm to the environment. 1-year, 5-year and 20-year waste rock of Dexing Copper Mine are taken in the experiments to carry out research on the law of static acid production. The experiment result indicates the sulphur content of waste rock of 4 different ages are all relatively high, much higher than the background value of soil, thus with extremely high risk of acid production, and waste rock, except for 1-year ones, all produce acid. The cause of no acid production of 1-year waste rock possibly lies in the mass existence of internal neutral substances; with the ongoing oxidization, consumption of neutral substances leads to the decrease of total amount and being enveloped by other minerals, and thus reaction is difficult to occur as a result.

Keywords: acid mine drainage, waste rock, static prediction, different ages

1. Introduction

Sulfide minerals (usually FeS_2) generate acid upon oxidation due to corrosion in rainfall or gushing water in pits, and subsequently act with the original compounds in minerals and release the metallic ions therein and finally acid wastewater of mine is formed. As acid wastewater of mine features high acidity, high concentration of heavy metal ions, large volume of generation and long duration, and big fluctuation with seasonal and ore deposit conditions and as well as water yield, it has attracted world-wide concerns. Acid wastewater of mine may corrode pipelines and mining equipment if discharged without treatment, and seriously damage the ecological environment of water bodies if it runs into rivers, and thus affect the normal growth of aquatic organisms; and it may damage the granular structure of soil when it runs into soil, and cause plants unable to normally absorb water and nutrients [1], [2]; and finally affect the health of man directly by metal enrichment [3]. As most metal mines are of primary sulfide deposit in China and a considerable proportion of coal mines are of medium/high-sulfur coal, acid wastewater exists extensively in the mines and during coal mining in China [4].

Dexing Copper Mine is located in Dexing City, Shangrao Region of Jiangxi Province, one of the largest porphyry open-pit copper mine in China. Since the mining commenced in 1958, the generated acid wastewater of mines has caused severe acidification and seriously affected the ecological environment of water bodies [5]. As for acid wastewater of mine, prevention is much more important than treatment. The first step of prevention is to predict the potential of waste rock and tailings so as to better control the generation of acidic wastewater at the source [6]. At present, prediction methods mainly include static prediction and dynamic prediction; therein, static prediction is a rapid and low-cost method to evaluate the acid generation potential of solid wastes of mines, mainly including acid-base account (ABA) and net acid generation (NAG) test. In this

[+] Corresponding author. Tel.: + (86 10) 63299510; fax: +(86 10)68324912.
E-mail address: zhoulianbi@aliyun.com

paper, waste rock of different ages (1-year, 5-year and 20-year) are chosen for chemical component analysis and static evaluation for the purpose of providing a theoretical basis for the prevention and treatment of acid wastewater of mine of mines.

2. Materials and Methods

2.1. Sampling and Processing

Waste rock are taken from Dexing Copper Mine, ground by crusher to a size <5 mm. The samples can be weighed and taken directly for dynamic leaching, but it needs further screening by 200-mesh sieve (<75 μm) for static evaluation. Chemical compositions of waste rock are analyzed before and after test.

2.2. pH1:2 and EC1:2

First, $pH_{1:2}$ and $EC_{1:2}$ of samples are tested, i.e. the electric conductivity of samples of 1:2 solid-to-liquid ratio. Testing method: 25g samples with size <75μm (screened by 200-mesh sieve) are weighed and put into a beaker, 50g distilled water is added and mixed up, and pH and EC are measured after standing for more than 12 hours (overnight).

2.3. ABA Test

Maximum potential acidity (MPA, kg t-1, calculated by H_2SO_4) should be calculated by formula (1), therein, TS indicates the percentage of sulphur content in the samples.

$$MPA=TS\times 30.6 \quad (1)$$

Test of acid neutralizing capacity (ANC, kg t^{-1}, calculated by H_2SO_4) of samples : 1 or 2 drops of 1:3 HCl is added in 0.5 g sample to conduct bubbling level test [7]; 2 g sample is added into a 250 mL conical flask, HCl is taken and transferred according to Table I, 20 mL distilled water is added, the bainmarie is heated (80~90 ℃) until the reaction is finished; while cooled down to room temperature, distilled water is added to 125 mL, pH is measured, NaOH is added until pH becomes 5, 2 drops of 30% H_2O_2 is added and NaOH droplets are added again, and finally ANC is calculated by Formula (2).

$$ANC=(Y\times MHCl/WT)\times 49 \quad (2)$$

In the equation, Y indicates the volume of HCl (mL) actually consumed, MHCl indicates HCl concentration (mol L^{-1}), and WT indicates sample weight (g).

Table I: Bubbling level and acid amount and concentration in ANC test

Reaction intensity	Bubbling level	HCl concentration /(mol L^{-1})	HCl volume/mL	NaOH concentration/(mol L^{-1})
No reaction	0	0.5	4	0.1
Mild	1	0.5	8	0.1
Medium	2	0.5	20	0.5
Strong reaction	3	0.5	40	0.5
Extremely strong reaction	4	1.0	10	0.5
	5*	1.0	60	0.5

Note: * indicates being used in samples (e.g. limestone) with extremely high ANC content (>400 kg t^{-1}, calculated by H_2SO_4).

Net acid generating potential (NAPP, kg t^{-1}, calculated by H_2SO_4) is calculated by Equation (3) [7].

$$NAPP=MPA-ANC \quad (3)$$

2.4. NAG Test

2.5 g sample is put into a 500 mL conical flask, 250 mL 15% H_2O_2 is added, and let stand overnight; heated until bubbling, and distilled water is added to 250 mL after cooling, and the measured pH is NAG_{pH}.

2.5. ABCC Curve

2g sample of waste rock is taken (<75μm) and placed in a 250ml volumetric flask, and 100ml distilled water is added. HCl droplets are added until pH=2.5, therein, droplets of HCl of 0.5mol/l concentration is added for 1-year waste rock, and HCl droplets of 0.1 mol/l concentration is added for waste rock of other ages. 0.1ml HCl droplets are added evenly every time, the pH after each droplet adding is recorded to draw a curve.

3. Results

Results of static acid production of waste rock of different ages at Dexing Copper Mine are shown in Table II.

Table II: Results of static evaluation of waste rock of different ages

Abandoned time	$pH_{1:2}$	$EC_{1:2}$/ ($\mu S\cdot cm^{-1}$)	Total sulfur	MPA/ (kg t^{-1})	ANC (kg t^{-1})	NAPP (kg t^{-1})	NAG_{pH}
1 year	6.85	1262	23.9%	731.34	53.9	677.44	2.54
5 years	2.24	585	8.53%	261.02	9.8	251.22	2.02
10 years	2.3	565	4.76%	145.66	4.9	140.76	3.24
20 years	2.88	232	2.23%	68.24	13.65	54.59	3.76

3.1. Initial pH and EC of Leachate

$pH_{1:2}$ of waste rock of different ages characterize the acidification condition of the waste rock under the current state, 1-year refuse is neutral, indicating it's not oxidized or neutralized due to relatively big ANC though it has been oxidized, the possibility of the latter is higher; however, the 5-year, 10-year and 20-year waste rock show relatively strong acidity, therein, pH of 5-year and 10-year waste rock is the lowest, and pH of 20-year refuse is slightly higher.

$EC_{1:2}$ of waste rock of different ages represent the existing status of soluble ions in waste rock. EC of 1-year refuse is the highest, indicating there are the most soluble ions in it; the ECs of 5-year and 10-year waste rock are close; EC of 20-year refuse is the lowest, possibly due to reduction of internal soluble ions for years of oxidation, leaching and lowering acid generation rate.

3.2. Results of Leachate ABA and NAG Tests and Analysis

The sulphur content in earth crust is 0.06% and it's generally 0.01%～0.50% in soil, the sulphur contents of the waste rock of 4 ages are all relatively high, the sulphur content of 1-year refuse is 100 times higher than that of the background value of soil, thus the risk of acid generation is extremely high.

The static evaluation results indicate that the waste rock of 4 ages comply with NAPP>0，NAG_{pH}<4.5, and thus it can be confirmed that the waste rock of 4 ages have the potential of acid generation.

The quantities of acid generation of ABA test and NAG test are not consistent, the value for NAG is lower than that for NAPP, because the value of NAG test is the quantity of acid generated by direct oxidation of sulphur, however, it's calculated in accordance with total-sulphur content in NAPP test, and thus the capacity of acid generation of waste rock is overestimated.

3.3. Results of ABCC Curve Analysis

The curve of acid neutralization characteristics of waste rock of 4 ages is shown in Fig 1.

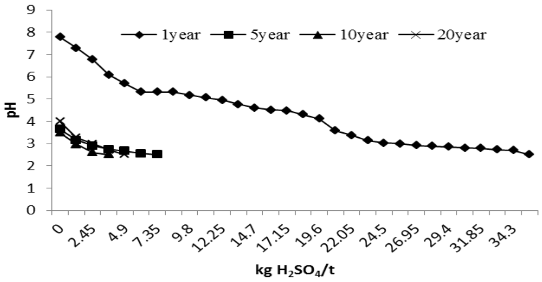

Fig. 1: ABCC curve for waste rock of different ages

ABCC curve reaction reflects the effective acid neutralizing capacity in waste rock within a short time. The mineral components can be confirmed by comparing the ABCC curve for different categories of samples with the ABCC curve for standard minerals. The waste rock of 4 ages are of the same refuse category, thus there isn't any substantial difference in mineral composition. However, with the oxidizing reaction over years, some neutral substance in waste rock may reduce largely or even disappear, and will not appear in waste rock in later years.

In table II, the effective neutralization capacity is remarkably smaller than the measured ANC value; there shows an obvious descending process in the ABCC curve for 1-year waste rock, indicating the neutralization capacity is released gradually in this area, it's a feature of calcite ($CaCO_3$) neutralization, and there isn't such area in the ABCC curve of waste rock of other ages.

4. Conclusions

Interpretation on pH and EC: Acid is generated in 5 years, 10 years and 20 years, the initial pH values are 6.85, 2.24, 2.3 and 2.68 respectively, and the EC values are $1262\mu S\cdot cm^{-1}$, $585\mu S\cdot cm^{-1}$, $565\mu S\cdot cm^{-1}$ and $232\mu S\cdot cm^{-1}$ respectively, and all show acidic property except for 1-year waste rock.

The sulphur contents of the 4 ages are all very high, much higher than that of the background value of soil, therefore, there is extremely high risk of acid generation. The results of ABA and NAG tests proved this point. The results of the both tests indicate the waste rock of 4 ages all have the potential of acid generation. 1-year waste rock don't generate acid probably because they contain massive neutral substances; with the oxidation, consumption of neutral substances leads to reduction of total quantity and they could be possibly enveloped in other minerals, and thus reaction can hardly occur, and thus pH of 5-year and 10-year waste rock turns acidic; pH of 20-year waste rock grows higher slightly, possible because of the fact that the reduction of metal sulfides leads to slow acid production rate.

Acid generating quantities of waste rock of different ages of NAG test is smaller than the results of ABA test, probably because the maximum acid generating quantity is calculated by total sulphur content, and this might overestimate the risk of acid generation of waste rock.

ABCC curve indicates that the effective neutralization capacity is lower than ANC value, and the neutral substances of 1-year waste rock and waste rock of other ages may be different.

During mine refuse stacking, it's advised to place fresh waste rock on the top layer to effectively reduce generation of acid wastewater [8]; if dry covering method is adopted to prevent acid wastewater, it's advised to add some waste rock of younger age and not generating acid in a certain period of time in a single layer or multiple layers if cheap covering materials are available; during refuse yard reconstruction, the acid wastewater generating intensity of waste rock should be taken into consideration; and a long-term acid generating model can be further established for waste rock to provide a basis for numerical simulation during the work of acid wastewater prevention. It's predictable that acid generation must last a very long period of time, but its environmental impact cannot be overlooked though the acid generating rate is slowing down, because the quantity of refuse is huge.

5. Acknowledgements

The project was financially supported by the International Technology Cooperation Special Project (2012DFA90500): Research on Key Technology Cooperation for Comprehensive Improvement to Acidic Pollution in Metallic Mine Dump.

6. References

[1] Qun Yang, Ping Ning, Fangyuan Chen, et al. Status Quo and Prospect of the Treatment Technology for Acid Mine Drainage, Metal mine. 1 (2009) 131-134. (In Chinese)

[2] Yuanhong Luo, Liangqi Lei, Yaohui Chang. Discussion on Acidic Mining Drainage Production and Prevention in Carbonate Rock Area, Environmental Science and Management. 7(2011)81-83. (In Chinese)

[3] Lei Wang, Zeqin Li, Lei Jiang. Acidic Mine Waste Water Hazards and Countermeasures Research, Environmental Science and Management. 10(2009)82-84. (In Chinese)

[4] Runcai Bai, Bin Li, Sanchuan Li, et al. Development and Status of the Treatment Technology for Acid Mine Drainage, Journal of Yangtze River Scientific Research Institute. 2(2015) 14-19. (In Chinese)

[5] Yuhu Chang, Yuanyi Zhao, Chong Cao, et al. Characteristics of Heavy Metals Content and Assessment of Health Risk in Different Environment Media in the Dexing Copper Mining Area, Acta Geologica Sinica. 5(2015)889-908. (In Chinese)

[6] Weijun Qiu. Prevention and control of acid wastewater produced in metallic mines, Gold. 3(2014)73-76. (In Chinese)

[7] Zengpin Ning, Tangfu Xiao, LianBi Zhou, et al. Prediction of Acid Rock Drainage (ARD) Generation Potential in an Antimony Mining Area, Earth and Environment. 3(2009) 249-253. (In Chinese)

[8] Yunzhang Rao, Shuitai Xu, Jianping Pan, et al. Study on Distribution Rules of Acid Mine Drainage and Heavy Metal Pollution of Sulphide Mineral in the Waste Rock Site, Journal Os Southern Institute of Metallurgy. 5(2003): 90-94. (In Chinese)