Cause investigation analysis and experimental argumentation about acidic water in the oil shale open pit of Maoming City

Junguang Zhou¹, Wang Ji², Chang Sha², Chaoyi Pan², Qingwei Guo³, Jingsong Wang⁴*, Sili Cheng⁵*

¹ College of Civil Engineering, University of South China, Hengyang, Hunan, 421001, China;
² South China Institute of Environmental Science, Ministry of Environmental Protection, Guangzhou, Guangdong, 510530, China

* Corresponding author: Jinsong Wang, E-mail: xhwjs@163.com

Abstract: This paper analyzes the sources and causes of the natural history of Maoming city open pit water, combined with the experimental research on the reasons of present continuous mine water acidification, and taking the total mass of H⁺ dissolved in water as an indicator. The results show that the main reason for the continuous acidification of the open pit mine is the accumulation of contaminated soil at random and the leaching of acid from the soil. Acidic substances mainly come from the accumulated waste slag around the pit. In the background of the construction of open-pit mine ecological park, rain, vegetation restoration, river governance slag pollution is the key to acidic mine water.

1. Introduction
The Maoming City Open-pit Mine is located about 3km north of Maoming City. The oil and gas resources of the mining area, especially the oil shale resources, played a huge role in the oil shortage period in the early days of the founding of China. However, environmental pollution and resource depletion caused by extensive and large-scale exploitation of oil shale resources are increasingly hindering the sustainable development of Maoming City. After stop mining oil shale, forming a 5.2km long, wide 1km, an average depth of 20m mining, deep mining goaf maximum 60m [1]. The original mining drainage, wastewater, groundwater and rainwater could not be effectively diverted and treated, and gradually accumulated into a lake with a total water volume of 90 million m³. Monitoring results show that the pH of the water body is stable between 3~4 years. Acidic water washes and erodes the shore, causing geological disasters such as landslides and landslides. The acidified water quality also greatly hinders the natural restoration of the water ecological environment in the pit. At the end of 2015, the open pit mine was handed over to the local government for management. On the basis of restoring the natural ecology, the open pit mine was turned into a domestic first-class open-pit mine park [2], and the management of acid water has become the primary problem.

2. Sampling and monitoring
On February 2017, Maoming City Environmental Monitoring Station deployed 11 groundwater wells in Mutang Village, Yaxiang Village, Poxin Village, Qidong Village and Lishan Village near the open pit. It is found that the groundwater level is much lower than the pit water level, and there may be only a few small springs that may exchange with the pit water, so the groundwater impact can be basically eliminated.
On November 2017 and April 2018, the research team conducted a sub-sampling of the Jianjiang diversion canal, and monitored the water samples in the front, middle and end sections of the canal that was diverted from the Jianjiang water into the open pit, all of which could reach the surface three types water standard.

According to the information provided by Maoming City Environmental Protection Bureau, in 2016, the water supply was 76.36 million m$^3$, and in 2017, the water supply was 5630 m$^3$. The average recharge water body reached 66.33 million m$^3$, accounting for 73.7% of open-pit mine water. However, with reference to the water quality monitoring data of the two-year open pit mine of the Maoming Environmental Protection Bureau$^3$, the pH of the water has not improved significantly. The lowest pH value of 3.03 was observed in March 2017 and July 2017, and the highest pH value of 3.92 was monitored in September 2016. The data were below the minimum surface water limit.

On November 9, 2017, during the raining process, the research team collected surface runoff samples from 11 major catchment points(contains a small amount of sediment) around the pit, at the same time, collect rainwater samples that have not flowed through the surface as a control. When it rained on March 19, 2018, a second batch of water samples was collected at the same point.

The water quality of the open pit mine was continuously monitored in November 2017 and April 2018 in order to compare with the existing pH of the open pit mine. Dividing six water body cross sections and Sampling five meters underwater, simultaneously collecting sediment samples in the left, middle and right cross sections of each water body. The collected mud depth is between 20m and 40m.

The research team collected a total of 64 water samples, collecting 24 soil samples near the rain sampling point. The research team measured the pH of the water sample on site, soil and mud samples were dried after removing grass and stones, soaked according to the ratio of soil to water 1:5, measuring soil leachate with a pH meter$^4$.

3. Results and discussion

Because the soil and accumulated water components in the open-pit mine area are more complicated, the experimental evidence of the acidification of open-pit mineral water in this subject is based on the $H^+$ dissolution amount corresponding to the pH drop value as the calculation basis and reference basis.

Referring to the sampling situation of the site investigation, the main reasons affecting the pH of the pit water may be:

1. After the rainwater flows through the surrounding soil, it turns into acid into the pit and brings in acidic silt;
2. The washed soil is deposited in the pit and continues to dissolve acidic substances;
3. The rock and sediment components at the bottom of the pit are acid-prone and continue to release acidic substances.

In view of the above-mentioned causes, the research team conducted actual measurement and laboratory research, and finally measured the main reason for the acidification of the pits.

3.1 Rainwater and surface runoff

On November 9, 2017, Maoming City moderate rain. The research team collected surface runoff samples from 11 major catchment points(contains a small amount of sediment) around the pit, at the same time, collect rainwater samples that have not flowed through the surface as a control. The measured pH values in Table 2.1—1

| pH at different points | A0 | A1 | A2 | A3 | A4 | A5 | A6 | B7 | B8 | B9 | B10 | B11 |
|-----------------------|----|----|----|----|----|----|----|----|----|----|------|-----|
|                       | 6.64 | 4.29 | 3.61 | 3.68 | 3.31 | 3.68 | 3.85 | 3.14 | 4.38 | 2.91 | 3.22 | 4.97 |

It can be seen that the pH of A0 rainwater was 6.7, and the remaining sampling points A1, A2, A3, A4, A5, A6, B7, B8, B9, B10, and B11 were all acidic. It shows that rainwater flows through the soil around the mining area, which will dissolve acidic substances, causing the rainwater pH to decrease. At different sampling points, the corresponding pH values also differ.
The second collection of rain measured results

On March 19, 2018, Maoming City was a shower at 9 am with a rainfall of about 20 mm. The research team collects surface runoff at the same point in open pit mine. The measured surface rainwater pH dropped rapidly from 6.7 to about 3.8-4. The same result as the first collection of rainwater.

3.2 Calculation of $H^+$ leaching caused by rainfall

According to the information provided by the Maoming Environmental Protection Bureau, the open-pit mine pits have a total rainfall area of 7.6 km$^2$. The average annual rainfall of open pits is 8.954 million m$^3$ per year. In October 2017, the open surface water surface area was 4.5 km$^2$, accounting for 58.52%. Hydrological monitoring shows that about 5.24 million m$^3$ of rainfall in the rain-collecting area does not flow directly into the pit through the surrounding soil. And another part of about 3.714 million m$^3$ of rainwater flows through the surrounding soil and enters the pit. This part of the rainwater is acidified by the soil to carry $H^+$. So based on the total amount of rain flowing through the soil, in this paper, according to the data in Table 2.1, from the $H^+$ leaching amount of the lowest pH value of the water sample and the $H^+$ leaching amount of the average pH value of the water sample, the amount of $H^+$ brought into the open-pit mine water in one year is calculated.

1. Maximum $H^+$ leaching amount: $10^{-2.9} \text{mol/L} \times 1 \text{g/mol} \times 3.714 \times 10^6 \text{m}^3 = 4.569 \text{t/a}$
2. The average $H^+$ Leaching amount: $10^{-3.74} \text{mol/L} \times 1 \text{g/mol} \times 3.714 \times 10^6 \text{m}^3 = 0.676 \text{t/a}$

3.3 Simulated flushing soil $H^+$ leaching

In November 2017, 24 soil samples were collected at the catchment point. The average sediment concentration of surface runoff measured by the laboratory is 5.235kg/m$^3$. Weigh 5.2g of soil sample in equal proportions, and add 1.0L of pure water with a pH of 7.0 to soak the sample. After three days of leaching, the pH of the leachate was basically stable, and the lowest pH was found to be 5.25. This pH was used as the maximum dissolved amount of soil $H^+$. The measured open-pit mine has 3.714 million m$^3$ of rainwater inflow every year. Therefore, the maximum sand mass brought into the open pit every year is about 19442.8t/a. Therefore, it is possible to calculate the maximum amount of $H^+$ dissolved after the soil enters the pit due to rain erosion:

$$ \frac{(19442.8 \text{t/a})}{5.2g} \times 10^{-5.25} \text{mol/L} \times 1.0L \times 1 \text{g/mol} = 21.01 \text{kg/a}$$

3.4 Open pit mine wall and pit bottom sludge leaching experiment

The research team divides the pits into six cross sections from west to east (W1, W2, W3, W4, W5, W6). Mud samples of different cross sections are dried, take 200g of dried sample and add 1.0L of pure water with a pH of 7.0 to soak the sample. When soaked to the second day, the pH value stabilized and the pH of all sample leaching solutions was greater than 6. There was no significant change in continuous monitoring for 10 days. Therefore, it can be judged that at current stage the soil at the pit wall and the bottom of the pit is not the main cause of acidification in the open pit.

3.5 Estimation of the total amount of $H^+$ carried by rainwater

When rainwater flows through the soil, it dissolves out $H^+$, it causes the pH of the rain to become sour. At the same time, rainwater flows into the open pit mine, bringing a lot of soil. The soil is soaked in the pit and also produces a small amount of $H^+$. Therefore, the total amount of $H^+$ brought in by the rain should be the sum of the above two $H^+$:

The maximum amount of $H^+$ contributed by rainwater and soil:

$$ 4.569 \text{t/a} + 21.01 \text{kg/a} = 4.569 \text{t/a} $$

Average $H^+$ amount contributed by rainwater and soil:

$$ 0.676 \text{t/a} + 21.01 \text{kg/a} = 0.676 \text{t/a} $$

3.6 summary

Based on field research and experimental results, at present, the most important reason for the acidity
of open pit mines is the impact of rainfall. Surface rainwater flows through the soil around the pit, and the acid released from the soil causes the water in the pit to continue to become sour.

4. Analysis of sources of soil acid

Based on the monitoring data and on-site investigation and analysis of open pits, the main reasons for the acidity of the soil around the open pit mine in Maoming City are as follows.

4.1. Oil shale waste slag weathering

The Maoming open-pit mine began mining oil shale in 1955 and ceased production in 1995, the total amount of soil discharged reached 181.57 million m$^3$. The slag treatment method produced at that time was: One layer of soil then a layer of oil shale slag, both of hey are all piled up in two open areas in the north and south. After years of weathering, these refinery slags have been combined with the soil. Su Dagen and Yang Dongsheng$^{[5]}$ has component analysis of Maoming dry distillation oil shale slag. The results showed that the slag contains about 0.11% sulfur. These sulfides are oxidized in the soil and air. Then with the rainwater flows into the pit to make the water body sour.

4.2. Ore sulfide is oxidized

The total area of the open-pit oil shale deposit in Maoming City is 193.43 km$^2$. The maximum cumulative thickness of oil shale is 46.33m, the average oil content of oil shale is 6.03%, and the highest is 13.66%$^{[6]}$. Huge oil shale reserves, including raw quartz, kaolin, clay, mica, carbonate and pyrite. Mining caused a large amount of exposed rock layers, the sulfide in the rock layer is exposed to the air for a long time and is gradually oxidized. Then it is washed into the water body due to rain:

$$2S^{2-} + 7O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+$$

5. Conclusions and recommendations

Although 2016-2017 upstream Jianjiang contributed a total of 120 million m$^3$ of fresh water. However, acidic substances in the soil are also continuously leached by surface runoff in open pit mines. Therefore, how to effectively solve the impact of rainfall surface runoff is the key to solving the problem of continuous acidification of open-pit mine water.

1) The surface vegetation around the open pit is sparse, and the coverage is less than 30%. The water storage capacity is extremely weak and the surface runoff coefficient is high. Reduce the exposed surface area of open pit mines, carry out vegetation restoration and prevent soil erosion, minimize surface runoff. Appropriately reduce the slope of the ground in the tailings slag accumulation area to avoid forming a large depth of flushing grooves.

2) In the area around the pit, building flood intercepting ditch is provided to divert the rainwater to block the rainwater from entering the pit. At the same time, the most important things are to dredge the waste intercepting ditch and drainage ditch, improve the corresponding drainage facilities to quickly drain the rainwater. The water supply and drainage system should be improved first when carrying out the corresponding infrastructure construction of open pit mines. Collect rainwater from different areas and then discharge them centrally.

3) Improving the soil base layer and reducing the impact of acidified soil on vegetation. The soil can be improved by appropriately transferring the soil or applying calcium carbonate in the areas where the soil has been severely acidified. In some areas where soil conditions are poor and vegetation is not suitable for survival but artificial buildings or man-made landscapes can be constructed as appropriate to enrich the ecological environment around the open pit mine.

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Reference

[1] Tu Ningyu, Liu Yang, Jin Renhe. Study on Main Ecological and Environmental Problems Caused by Mining of Oil Shale Open-pit Mine in Maoming City [J]. Guangdong Chemical Industry, 2011, 38(07): 86-87.

[2] Maoming City Planning and Design Institute. 《Maoming Open-pit Mine Ecological Restoration Protection Area Master Plan（2016-2030）》 Report 3. 2016. 1.

[3] 《Open pit mine sampling monitoring results》. Maoming City Environmental Monitoring Station.

[4] Chen Xiao, Kang Ronghua, Luo Yao, Ma Xiaoxiao, Ye Zhixiang, Duan Lei. Present Situation and Trend of Surface Water Acidification in Sichuan Basin [J]. Chinese Science Bulletin, 2012, 57(25): 2419-2424.

[5] Su Dagen, Yang Dongsheng. Study on application of rare earth oil shale slag in cement industry [J]. Journal of South China University of Technology (Natural Science Edition), 1995(02): 139-145.

[6] Xi Huifeng, Mu Jianchun, Wang Zhigang, Wu Yonghe, Li Shengqiang, Yu Chenglong. Discussion on the Present Situation and Application of Maoming Oil Shale Waste Slag [J]. New building materials, 2012, 39(04): 58-60.