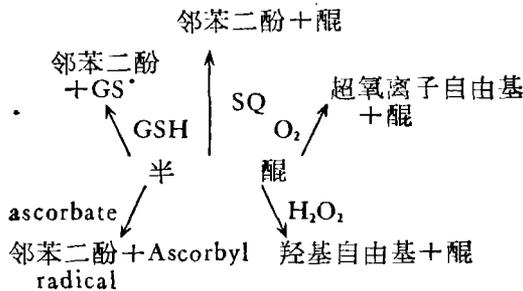


半醌自由基在生物体内产生活性氧的途径<sup>[8]</sup>为



因此富集于骨组织的 FA 大分子因其含有活性基团而对大骨节病具有病理学意义。

腐殖酸在体液 (pH = 7.2—7.4) 内,其

阴离子基团主要是羟基和处于羟基同环的羟基及多羟苯环的羟基,因此有可能与  $\text{Ca}^{2+}$  络合而随之一起在骨组织参与了矿化过程而发生积累。已有文献报道,腐殖酸和  $\text{Ca}^{2+}$  的络合能力与羟基含量成正比<sup>[9]</sup>。可以认为腐殖酸中的羟基、羧基的空间构型对于它与  $\text{Ca}^{2+}$  的络合作用起一定的影响。关于这一积累的机制还有待于进一步研究。

### 参 考 文 献

- [1] 彭安、杨春林等,环境化学,7(5)1(1988).
- [2] Kalyanaraman, B., Felix, C. C. and Sealy R. C., *Environ. Health Perspectives* 64, 185(1985).
- [3] 曾述之等,江西腐殖酸,(4),49(1982).
- [4] 白乃彬,环境化学,(6)5(1987).
- [5] Choudhry, G. G., *Toxicological and Environmental Chemistry* 4: 261—295 (1981)
- [6] Boveris, A., Cadenas, E. and Chance, B. *Fed. Proc.* 40(2), 195 (1981).
- [7] Peng An, Yang Chunlin, xxv International Conference on Coordination Chemistry, pp. 658 Nanjing (1988).
- [8] Curan, S. F. et al., *FEBS Lett.* 176: 155—160 (1984).
- [9] Shirya, R., Kumada, K., *Soil Sci. and Plant Nutr.* 22(3): 345—349 (1976).

(收稿日期: 1989年8月21日)

## 铜矿废石风化及形成酸性废水特征

戴昭华 王志海

(中国科学院生态环境研究中心)

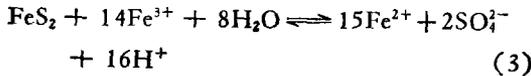
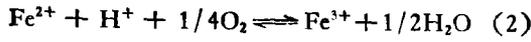
**摘要** 矿山酸性废水中元素的含量与季节和淋洗量有关。元素间相关性和硫与铁的摩尔比表明酸性废水在形成和迁移过程中有次生化合物形成,并对酸水的化学平衡起到一定的控制作用。硫的形态分析结果表明四价硫是可能的中间产物。

废石中硫化物风化产生酸性废水是一个复杂的过程,受到氧,微生物,气象及水文地质条件等多种因素的控制。为了治理酸性矿山废水对矿山周围生态环境所产生的危害,有必要了解硫化物在自然条件下风化产生酸性矿山废水的过程和特征。根据某矿山酸

性废水主要是来源于黄铁矿型废石风化的特点,着重研究了该矿山废石中黄铁矿在自然条件下风化产生的酸性废水特征。

许多学者认为黄铁矿氧化反应如下<sup>[1,2,3]</sup>

$$\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)$$



在这一反应过程中,反应(1)是缓慢的,但反应(3)是很快的,因此反应过程中决定速率的是反应(2).在微生物的作用下,反应(2)可以大大加快,从而使整个反应速度加快<sup>[4,5]</sup>.也有学者对黄铁矿氧化过程提出异议,并提出其氧化过程中可能产生亚硫酸盐或硫代硫酸盐或单质硫类型的中间产物<sup>[6]</sup>,这些产物再进一步氧化成硫酸盐.

根据某矿山酸性废水的分析结果,笔者认为该矿山的酸性废水不仅具有高酸度和某些元素含量高的特点,而且该矿山含黄铁矿废石风化释放元素的量与降雨量之间有关.根据硫的形态分析结果,认为在废石中的黄铁矿风化释放出的硫先被氧化成四价硫,随着酸性废水的迁移以及与大气氧的作用,四价硫被氧化成六价硫.根据酸性废水中元素间的相关性以及硫与铁的摩尔比的变化,认为铁、铝、钙、镁等次生矿物的形成对该矿山酸性废水的化学平衡起着重要的作用.

### 一、样品采集与分析

样品采集:在酸水沟(从废石堆至入河口)上设置了9个采样点(见图1),分别在雨季(9个样点取样)和旱季(5个样点取样)进行酸性废水样品采集.在酸水沟支流上设置了一个样点(11)收集雨季样品(因旱季无水),在流经矿体水流上设置了一个样点(10)

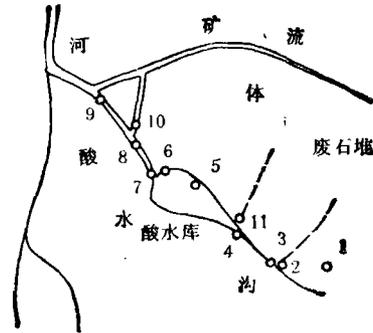


图1 采样位置示意图

进行样品采集,共收集67个酸水样品.用银盐沉淀法在现场收集了14个沉淀样品做硫的形态分析.在废石堆上不同处进行随机取样,获得的废石样品经破碎混匀供分析用.

样品分析:所有水样的pH值均在现场用便携式pH计(±0.01pH单位变化)测定.水样中硫、铁、铝、钙、镁的含量和废石的化学组成用X-射线荧光测定(测定条件见表1).废石中元素含量的分析样品制备是将样品破碎混匀后取出5克样,在玛瑙研磨机上研细至200目,用硼酸衬底,在压力为20吨条件下制成φ30mm的圆片,用标准参考物GSD为标准进行元素分析.水样的分析样品制备是将φ50mm的定量滤纸制成具有30mm直径的蜡圈,将100μl水样滴在滤纸中心,待自然扩散后在50℃下干燥.分析标准以同样的方法制备,并以接近水样酸度且不含被测元素的水溶液制备空白样.用表1中的分析条件进行样品分析.另用一个样品制出

表1 样品分析条件

条件 \ 元素	Fe	Al	Ca	Mg	S	S 形态
分析线	K <sub>α</sub> ±0.5°					
功率	40kV/30mA	40kV/30mA	40kV/30mA	40kV/30mA	40kV/30mA	40kV/30mA
分析晶体	LiF	PE	PE	TAP	Ge	Ge/Ge
计数器	SC	FC	FC	FC	FC	FC
计数时间	10s	20s	20s	20s	20s	扫描步进 0.005°
准直狭缝	细	粗	粗	粗	粗	/

10 个分析样品,用于分析重现性,铁、铝、钙、镁和硫的分析变化率分别为 2.60%, 3.90%, 4.01%, 4.11% 和 3.28%。废石的矿物组成用 X-射线衍射进行半定量分析。硫的形态分析是将沉淀样品经低温干燥,研细压片,以硫酸钾作参考标准,用双晶 X-射线荧光进行谱强度分布扫描,将扫描结果送入 IBM-PC 计算机,用自编的 SULTS 硫形态解析程序进行计算(方法另发表)。

## 二、结果与讨论

废石中若干元素的含量和矿物组成分别列于表 2 和表 3。结果表明该矿山废石中的硫化物主要是黄铁矿,黄铜矿及其它硫化物很少。因此,认为该矿山酸性废水主要是由黄铁矿风化产生的。

酸性废水的分析结果(见表 4)表明该矿山废石风化是十分强烈的,尤其在雨季期间更为明显。还表明酸性废水具有较高的酸度,雨季 pH 值平均为 2.52,旱季 pH 值平均约为 2.73,而且废水中某些元素的含量也很高,在雨季期间酸水沟中铁、钙、铝、镁、硫的平均值分别为 1170.3ppm, 185.7ppm, 600.5 ppm, 494.5ppm 和 3173.1ppm,旱季期间的平均值分别为 840.9ppm, 228.3ppm, 592.0 ppm, 471.8ppm 和 2856.6ppm。由表 4 中的变异系数可以看出,无论在雨季还是旱季,酸水沟中铁的浓度变化较大,其次是硫。图 2 给出酸水沟中硫在旱季、雨季期间连续数日无雨和连续几天降雨时的分布状况,可以

表 2 废石中若干元素的含量

元素	含量(%)	元素	含量(ppm)
Na	0.33	Pb	9.6
Ca	1.18	Zn	74.5
Mg	1.19	Mn	150.0
S	1.50	Cu	169.1
Fe	3.41		
K	3.46		
Al	11.53		

表 3 废石中主要矿物组成

矿物名称	含量(%)
石英	50
云母类	42
长石	4.5
黄铁矿	3.5

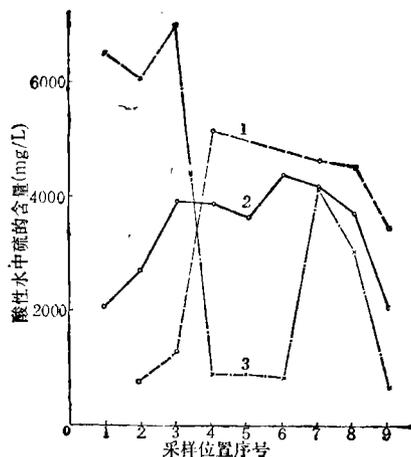


图 2 不同采样时间酸水沟中硫的分布状况  
1.旱季分布曲线; 2.雨季无雨时分布曲线; 3.雨季下雨期间分布曲线

表 4 不同季节酸性废水元素含量 (ppm)

元素		pH	Fe	Ca	Al	S	Mg
雨 季	含量范围	2.22—2.86	56.6—3623.6	50.9—421.5	125.8—1174.7	502.6—7536.4	92.3—1118.3
	平均值	2.52	1170.3	185.7	600.5	3173.1	494.5
	变异系数(%)	7.13	81.59	44.03	52.52	59.01	55.23
旱 季	含量范围	2.33—3.33	13.8—1897.9	133.7—285.6	139.0—1013.0	806.0—5206.0	221.2—784.0
	平均值	2.73	840.9	228.3	592.0	2856.6	471.8
	变异系数(%)	12.50	94.74	22.32	60.20	62.79	49.07

看出,在旱季和雨季无雨期间酸水沟源头的水中硫的含量较低,而降雨期间硫的浓度很高,说明在雨季降雨期间废石中硫化物风化释放元素的速率增加。在降雨期间这种元素释放速率增加的现象主要是由于降雨时大气氧被雨水带入废石堆内,在强烈的微生物作用下,黄铁矿的氧化速率增加;其次是因在无雨和少雨时硫化物风化产物在堆内形成次生矿物,在降雨时又被溶解和冲刷从堆内排出。由图 2 还可以看出,酸水库排水(样点 7)中硫的含量随季节变化较小,即使在连续降雨期间,酸水库的水位不断上升,但排出水中硫的含量仍没有明显差异,表明该酸水库对控制和调节酸性排水的水质起着重要作用。

根据一元回归计算方法求出酸性废水中元素含量之间及 pH 值与元素含量的对数值之间的相关关系,结果表明酸性废水的酸度与铁、铝、硫、镁的含量之间呈显著性相关(相

关系数列于表 5),其关系式为:

$$C_i = \exp(A_i + B_i \text{pH}) \quad (4)$$

式中  $c_i$  为元素  $i$  (铁、铝、硫、镁)的浓度,  $A_i$  和  $B_i$  为回归系数。从表 5 中的相关系数可以看出,酸性废水的 pH 与铁、铝、硫、镁、钙均有较好的相关性,即置信系数均有  $P < 0.001$ 。证明该矿山酸性废水的酸度不仅受到硫氧化成酸的影响,还受到铁、铝、镁、钙的影响。这些元素对酸性废水的酸度的影响主要是通过形成次生矿物对酸性废水的化学平衡起控制作用而引起的<sup>[7]</sup>。

酸性废水中的硫与铁的摩尔比列于表 6。结果表明不同点位所采集的样品中的 S/Fe 比有显著性差异,相同点位不同时间采集的样品同样差异很大,且所有比值均大于 3。而无论是黄铁矿( $\text{FeS}_2$ )还是黄铜矿( $\text{CuFeS}_2$ )风化,其风化产物的硫与铁之比都应为 2 左右。即使不考虑其它铁化合物的风化,其结

表 5 酸性废水中元素与 pH 之间及元素间的相关系数\*

相关系数 元素	元素					
	pH	Fe	Ca	Al	S	Mg
pH		-0.957	-0.650	-0.925	-0.946	-0.926
Fe	+++		0.270	0.919	0.966	0.903
Ca	++	+		0.618	0.626	0.639
Al	+++	+++	++		0.986	0.983
S	+++	+++	++	+++		0.978
Mg	+++	+++	++	+++	---	

\* 相关系数临界值( $R_{\text{临}}$ ): $\alpha = 0.05$  时,  $R_{\text{临}} = 0.27$ ;  $\alpha = 0.001$  时,  $R_{\text{临}} = 0.44$ 。+表示有相关性,++表示相关性较好,+++表示相关性显著。

表 6 酸性废水中硫与铁的摩尔比

样点号	S/Fe 摩 尔 比						
1	9.436	8.193	7.319	3.703	3.155	3.731	/
2	6.851	6.508	7.079	4.325	4.852	5.724	101.48
3	5.145	4.325	5.705	3.526	3.515	3.600	11.394
4	4.008	3.578	6.083	10.509	/	/	4.766
5	4.812	5.018	10.676	7.276	8.500	6.471	/
6	6.300	5.969	7.129	29.569	12.029	10.632	9.957
7	4.739	4.850	4.643	5.127	4.213	4.730	4.834
8	4.452	4.901	5.033	4.496	4.683	4.594	/
9	5.415	6.642	12.718	10.105	7.551	6.994	/

果也表明铁的风化产物因形成次生化合物而使 S/Fe 比增加。

大多数学者认为黄铁矿氧化直接生成硫酸盐,但也有人推测黄铁矿在氧化过程中可能形成亚硫酸盐或硫代硫酸盐或单质硫的中间产物<sup>[6]</sup>。笔者用银盐沉淀法取样,用双晶 X-射线荧光扫描得到硫的谱强度分布,用 SULTS 程序解析,结果表明该矿山酸性废水中有大量的四价硫存在(见表 7)。虽然因取样方法的局限性,未能证明黄铁矿风化过程中是否有单质硫为中间产物,但本方法却有力地证明了黄铁矿风化过程中释放出的硫在氧化形成酸过程中,四价硫可能是重要的中间产物。由表 7 的结果还可看出,随着采样点远离废石堆,四价硫的比例迅速下降,表明酸性废水在离开废石堆出露地表之后,酸性水与大气氧接触,四价硫很快被氧化成六价硫。样点 9 的四价硫比例上升是因大量流经矿体的酸性水进入酸水沟所引起的,同时也证明矿体表面风化在微生物作用弱的情况下同样有四价硫中间产物存在。

表 7 酸性废水中硫的形态分析计算结果(%)\*

形态 \ 点位	1	3	5	7	9
四价硫	72	70	29	28	63
六价硫	28	30	71	72	37

\* 相对于硫总量的百分数。

### 三、结 束 语

1. 该矿山废石风化产生的酸性废水具有高酸度及某些元素含量高的特点,且废水酸度及元素含量随季节和降雨量而变化。降雨量越大,由废石风化释放出元素的量越大,

这种现象可能是由于降雨时,随雨水带入围内的大气氧在微生物作用下使黄铁矿风化速度加快,以及降雨量大时将无雨和少雨时黄铁矿风化产物形成的次生矿物溶解洗出所引起。

2. 根据酸性废水的 pH 与元素含量的对数值之间的相关性及 S/Fe 摩尔比,认为不仅废石风化释放的硫被氧化成酸对酸水的酸度起到关键作用,而且铁、铝等元素的次生矿物的形成对该废水的酸度也有一定影响。

3. 根据该酸性废水中硫的形态分析计算结果,认为该矿山废石中黄铁矿风化释放出的硫在氧化形成酸过程中,四价硫可能是重要的中间产物,并在迁移过程中被氧化成六价硫。

总之该矿山废石在自然条件下风化是十分强烈的,产生某些大量金属元素和硫含量高的高酸度废水。因此,研究该矿山酸性废水的形成及其特征,对回收自然资源及消除该矿山地区及废石堆下游河道的水体酸化给生态环境带来的影响有重要价值。

### 参 考 文 献

- [1] Stumm, W. and Morgan, J. J., *Aquatic Chemistry*, pp 383 Wiley-interscience, New York, 1981.
- [2] McKibben, M. A. and Barnes, H. L., *Geochim. Cosmochim. Acta*, 50, 1509(1986).
- [3] Sullivan, P. J. et al., *Environ. Geol. Water Sci.*, 11, 289 (1988).
- [4] Taylor, B. E. et al., *Nature*, 308, 538 (1984).
- [5] 钟慧芳等, *微生物学报*, 27(3), 264(1987).
- [6] Lowson, R. T., *Chem. Rev.* 82, 461 (1982).
- [7] Sullivan, P. J. et al., *Environ. Geol. Water Sci.*, 11, 283(1988).
- [8] Nordstrom, D. K. et al., *Chemical Modelling in Aqueous System*, pp. 51, Ed. by E. A. Jenne, Am. Chem. Soc., Washington, 1978.

(收稿日期: 1989 年 8 月 17 日)

**Reclamation Treatment of the Scraps of Chrome Leather — Animal Test of the Feed Protein Powder.** Jiang Tingda, Zhang Chunping (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11(3)**, 1990, pp.2—6

The proteins extracted from scraps of chrome leather were mixed with bran and used as feed protein powder. The feeding test for mice showed that the animals grew faster by using the feed additive protein powder, compared with fishpowder after six weeks. No abnormal variations were observed in organs of the mice. The feeding test with the feed additive protein powder for chickens and middling hens showed that growth of the animals was accelerated in comparison with the group fed with fishpowder after 27 and 17 days respectively. The rate of layeggs in the initial stage was 40% higher than that of feeding fishpowder group. No abnormal variations were observed in organs, and chrome had not been detected out in muscle, liver and egg at ppm level.

**Study on Copper Pollution from Fertilizing the Soil with Sludge.** Wang Hongkang, Yan Shoucang (Beijing Agricultural University): *Chin. J. Environ. Sci.*, **11(3)**, 1990, pp.6—11

The pot and plot experiments have been conducted for studying the effect of copper pollution on wheat and rice in calcareous soil fertilized with sludge containing copper. The results demonstrated that high concentrations of copper in soil affected on the growth of the crops and their yields. Rice was more susceptible to it than wheat, and reduced the yield about 10% when the soil had been treated with copper by 100 ppm. The order of absorption and accumulation of copper within the organs was as follows: root >> stem > leaf > grain. The copper content in grains of wheat and rice both were not higher than 20 ppm. In the soil fertilized with the sludge, the variation of available copper, its cation speciation and soil capacity were also studied in the paper. It is suggested that 130 ppm of copper as a critical value, and 800 ppm as a maximum permissible limit in sludge as it is fertilized to calcareous soil.

**Structural Influence of Fulvic Acid in Rat Bone Formation.** Yang Chunlin et al. (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11(3)**, 1990, pp.11—15

The influence of fulvic acid from Beijing weathered coal on the structure of rat bone has been studied. Emphasis was put on the fluorescent spectrum, ultra-violet spectrum and gel chromatographic properties of water extract of the rat bone injected with fulvic acid. The results showed that the evidence incorporating of fulvic

acid into rat bone and the pathogenic significance of this incorporation in causing Chinese Kaschin-beck disease was evaluated.

**Weathering of Copper Mine Waste Rock and Characteristics of Acid Wastewater.** Dai Zhaohua, Wang Zhihai (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing): *Chin. J. Environ. Sci.*, **11(3)**, 1990, pp.15—19

In this paper the characteristics of acid mine water generated from weathering of copper mine waste rock have been described according to the survey in situ. The acidity and concentration of some elements in the acid water were higher. Except that the content of some elements released from the rock weathering affected by seasons, it was affected by rainfall, even if in a season. According to the relationship between elements and the molar ratio between sulfur and iron in the acid water, it was considered that some secondary minerals were formed during generation and transportation of the acid water and controlled the chemical equilibria and acidity of the acid water. Tetravalent sulfur might be an important intermediate product during the process of acid generation from pyrite weathering on the basis of sulfur speciation analysed, and it was rapidly oxidized to hexavalent sulfur during transportation of acid water.

**Tolerance and Purification Capacity of Some Species of Trees against Sulfur Dioxide** Li Yichuan, Liu Houtian (Chinese Research Academy of Environmental Sciences, Beijing); Ma Liangqing, Du Shicai (Chongqing Bureau of Forestry, Sichuan Province): *Chin. J. Environ. Sci.*, **11(3)**, 1990, pp.20—23

In order to determine the threshold doses of acute and chronic injury by SO<sub>2</sub>, the saplings fumigated with SO<sub>2</sub> in the open top chamber were conducted. According to the principle that purification capacity of SO<sub>2</sub> by trees is in a function of sulfur intensity accumulated in leaves and its transfer rate out of leaves, the purification capacity of a tree can be estimated in varied sulfur contents in the leaves before and after fumigation. The experimental results show that the trees *Cunninghamia lanceolata*, *Camptotheca acuminata*, *Cinnamomum pilyphyllum* possess strong tolerance and higher purification capacity against SO<sub>2</sub>, but the capacity of *Robinia pseudacacia* etc are lower. Chongqing is a city with heavier SO<sub>2</sub> pollution, so the said trees can be selected for greening around the urban districts.

**The Function of the Root Microecosystem in the Process of Dyeing Wastewater Treatment by the Hyacinth.** Sun Tianhua, Liu Zhenghong, Lin Shaoning (China Textile University