



## 煤矿酸性废水处理技术研究进展

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引用本文:

唐鸿鹄, 张雄星, 董英荻, 曾勇, 刘丙建, 王丽, 韩海生. 煤矿酸性废水处理技术研究进展[J]. 北科大: 工程科学学报, 2025, 47(8): 1763–1776. doi: 10.13374/j.issn2095–9389.2024.10.15.002

TANG Honghu, ZHANG Xiongxing, DONG Yingdi, ZENG Yong, LIU Bingjian, WANG Li, HAN Haisheng. Research progress on the treatment of acid coal mine drainage[J]. *Chinese Journal of Engineering*, 2025, 47(8): 1763–1776. doi: 10.13374/j.issn2095–9389.2024.10.15.002

在线阅读 View online: <https://doi.org/10.13374/j.issn2095–9389.2024.10.15.002>

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# 煤矿酸性废水处理技术研究进展

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**摘 要** 煤矿酸性废水具有产量大、污染范围广、持续时间长、出水水质水量不稳定等特点, 已成为煤炭行业棘手的环境问题之一。本文总结分析了煤矿酸性废水的污染现状、成因和基本特征, 目前井下采空区积水和煤矸石堆积产生的淋滤污染是形成煤矿酸性废水的两大主要来源; 同时, 结合大型煤矿厂和中小型煤矿厂产生酸性废水的方式不同, 从源头控制、路径堵截、末端治理三个方面概括总结了目前已有的煤矿酸性废水处理技术, 并针对当前煤矿废水治理中酸难利用和重金属难回收等困境, 提出“资源综合利用”回收有价、“以废治废”酸碱中和、整体综合治理等思路。

**关键词** 煤矿酸性废水; 基本特性; 处理技术; 有价组分回收; 综合治理

**分类号** X752

## Research progress on the treatment of acid coal mine drainage

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**ABSTRACT** Acid coal mine drainage has emerged as one of the most challenging environmental problems in the coal industry because of its large output, wide pollution range, long duration, and unstable water quality and quantity. This paper summarizes and analyzes the pollution situation, causes, and basic characteristics of acid coal mine drainage. To date, leaching pollution is caused by underground goaf water and coal gangue accumulation, which are the two main sources of acid coal mine drainage. Containing a large amount of soluble iron, manganese ions, and suspended solids, acid coal mine drainage has a low pH, unstable effluent quality and quantity, wide pollution range, and long duration. Acid coal mine drainage production differs between large coal mine factories and small and medium coal mine factories. A large amount of water in underground goaf accumulates after the closure of small and medium coal mine factories, resulting in the oxidation of coal and producing acid coal mine drainage. Large coal mines have not been closed mainly because of the large accumulation of coal gangue, producing leaching pollution and discharging a large amount of acid coal mine drainage. Given the difference in acid coal mine drainage production between the two types of mines, they require different treatment methods. To control acid coal mine drainage pollution, closed coal mines in China mainly apply terminal treatment technologies, such as

收稿日期: 2024–10–15

**基金项目:** 湖南省科技创新计划项目(2023RC3067); 湖南省自然科学基金资助项目(2023JJ20071); 湖南省伴生萤石综合回收利用氟化工工程技术研究中心开放课题(CF-SZX-2023002)

common chemical neutralization, SRB microbial, wetland system construction, and biochar adsorption technologies, which have been developed and utilized in recent years. However, owing to the continuous pollution of water sources, the treatment of acid coal mine drainage pollution in large coal mine plants depends only on terminal treatment, which is time-consuming, costly, and inadequate treatment effect. Hence, increasing source control and path interception technologies is necessary. Source control technologies, such as sterilization, coverage, passivation, and carrier-microencapsulation technologies, have been developed, and path control technologies, such as the roadway closed filling technology, have been used, but they are not yet mature. This paper summarizes existing technologies for acid coal mine drainage treatment from three aspects: source treatment, path blocking, and end treatment. These technologies are based on different processes that produce acid drainage in large coal mines and small and medium coal mines. The path management mode requires the study of the sources, channels, and propagation paths of pollutants, given that this mode mitigates goaf and groundwater pollution by blocking sources and propagation paths, controlling pollution areas, and cutting off the connection between water layers. In view of the challenges in acid utilization and heavy metal recovery in the current acid coal mine drainage treatment, this paper proposes the following concepts: “comprehensive utilization of resources” to recover valuable substances, “treating waste with waste” acid-base neutralization, and overall comprehensive treatment.

**KEY WORDS** acid coal mine drainage; fundamental characteristic; treatment technology; valuable element recovery; comprehensive treatment

随着产业结构调整,全国中小型煤矿陆续整合,并有大量中小型煤矿被关闭,“十一五”期间我国煤矿数量减少九千余座。“十三五”期间我国累计关闭煤矿 7448 处<sup>[1]</sup>.到“十四五”末,预计全国煤矿数量控制在 4000 处以内<sup>[2-4]</sup>.许多煤矿关闭后,由于未能及时采取有效治理措施,导致煤矿酸性废水污染问题严重,对生态环境造成严重危害<sup>[5-9]</sup>.

中小型煤矿厂经产业结构调整,关闭后井下采空区大量积水,导致煤系氧化产生酸性废水.而未关闭的大型煤矿厂在煤矿生产过程中也会大量排放煤矿酸性废水.大型煤矿厂主要由于煤矸石大量堆积,产生淋滤污染排放大量酸性废水.根据两类矿厂产生废水方式不同,治理方式也存在差异.目前国内关闭煤矿主要采用末端治理技术治理废水污染,最常见的为化学中和法<sup>[10]</sup>,以及近年来开发利用的硫酸盐还原菌(SRB)微生物技术<sup>[11]</sup>和人工湿地系统<sup>[12]</sup>等,而大型煤矿厂治理酸性废水污染由于污染水源不绝,仅依靠末端治理不但耗时长、成本大,治理效果也不理想,需增加源头控制和路径堵截技术.国内外学者提出了多种源头控制技术,如杀菌法<sup>[13]</sup>和覆盖法<sup>[14]</sup>.目前路径治理技术发展尚不成熟,如巷道封闭充填技术<sup>[15]</sup>,但采用路径治理模式实现过程减量的目的,进而对煤矿酸性废水后续阶段的治理是非常有益的.为了更有效地实施路径治理模式,要深入研究煤矿酸性废水污染物源头、通道以及传播路径等要素.

因此,若采用单一的末端治理存在成本高、二次污染等问题,亟需探索更为全面的治理手段来清洁高效地解决煤矿酸性废水污染问题.本文总

结并分析了中国国内煤矿酸性废水的基本情况,明晰其形成原因,探讨了煤矿酸性废水污染综合防治的思路,旨在为煤矿酸性废水综合性治理提供新方向.

## 1 煤矿酸性废水基本特性

### 1.1 污染现状

中国作为世界煤炭储量第三大国,在煤炭生产和消费方面位居首位<sup>[16]</sup>.在煤炭生产过程中会产生大量煤矿废水.据统计,我国吨煤开采产生的矿井水为  $1.87 \text{ m}^3$ ,每年产生煤矿矿井水约为  $6.88 \times 10^9 \text{ m}^3$ <sup>[17]</sup>.以贵州鱼洞河流域煤矿酸性废水为例<sup>[18]</sup>,24 个矿井每年产生的煤矿酸性废水约为  $5 \times 10^7 \text{ m}^3$ .其排放方式有三种:第一是从煤矿矿井口直接排放,该方式受降雨、季节影响较大;第二是通过暗河和溶洞间接排放,此方式致使桃子冲岩溶泉、鱼洞泉等泉点以  $1500 \sim 2000 \text{ m}^3 \cdot \text{h}^{-1}$  的排放量受到污染;第三是煤矸石淋滤污染,其对地表水的污染较大<sup>[19]</sup>.

### 1.2 形成原因

由于许多矿床(特别是煤系)中含有黄铁矿( $\text{FeS}_2$ )等在还原气氛下发展形成的含硫矿物质,经开采暴露后,由于井下采空区积水或淋滤污染等,且在水、氧气和微生物的协同作用下,产生大量酸性矿井水.其主要反应如下<sup>[20]</sup>:

(1)  $\text{FeS}_2$  在水、氧气和微生物的作用下被氧化;(2) 当 pH 值小于 7.0 时,  $\text{Fe}^{2+}$  进一步氧化为  $\text{Fe}^{3+}$ ;(3) 当 pH 值大于 3.5 时,  $\text{Fe}^{3+}$  以  $\text{Fe}(\text{OH})_3$  形式沉淀;(4)  $\text{Fe}^{3+}$  进一步消耗更多的黄铁矿,不断产生大量的  $\text{H}^+$ ;(5) 其他金属硫化矿物也会受到水、氧气和

微生物的作用而逐渐氧化溶解<sup>[21]</sup>. 其主要反应构成循环, 如图 1 所示.

随着一系列反应, 矿山中的金属离子大量溶入酸性甚至强酸性的矿井水中, 使得废水中金属离子增多, 产生了煤矿酸性矿山废水 (ACMD). 其对地下水系和地表水系造成了严重污染和破坏<sup>[22]</sup>.

煤矿酸性废水的来源有两种, 一种是井下采空区积水, 一种是煤矸石堆积产生的淋滤污染. 井下采空区积水是导致煤系氧化产生酸性废水的主要原因. 大量中小型煤矿关闭后, 遗留许多采空区, 而采空区成为地下水汇聚的空间, 煤层中硫化矿物在上述一系列反应中形成酸性废水 (图 2). 一旦酸性水在采空区下渗或溢出地表后通过河道补给岩溶水, 就会使得岩溶水遭受污染. 这是一种煤矿闭坑后的遗留问题. 随着越来越多的中小型煤矿停采、关闭, 采空区积水水位不断升高, 并在矿区适宜地点溢出, 成为地表水体以及土壤的“长期性污染源”, 对当地居民的生活及生产用水水源构成严重威胁.

此外, 大型煤矿厂会堆积大量煤矸石, 在雨水、空气和微生物作用下, 产生淋滤污染排放大量酸性废水, 淋滤污染导致的酸性废水的形成及影响如图 3 所示.

1.3 主要特征

(1)pH 低且含有大量可溶性铁锰离子及悬浮物.

煤矿酸性废水特征通常为 pH 低、Fe、Mn 和  $\text{SO}_4^{2-}$  浓度高<sup>[23]</sup>, 含有大量悬浮物 (SS) 和多种重金

属离子 ( $\text{Cd}^{2+}$ 、 $\text{Pb}^{2+}$ 、 $\text{Cu}^{2+}$ 、 $\text{Zn}^{2+}$ 、 $\text{As}^{5+}$  等)<sup>[24]</sup>.

由于煤矿酸性废水的产生往往依赖不同场地条件, 如季节、天气、地貌等, 因此, 不同场地的煤矿酸性废水特征差异很大, 如表 1 所示. 例如, 唐艳<sup>[25]</sup>以贵州省花溪麦坪仁和煤矿酸性废水为研究对象, 发现研究区煤矿酸性废水酸性极强 (pH 为 2.76), 且含有大量 Fe (质量浓度为  $102.5 \text{ mg}\cdot\text{L}^{-1}$ )、Mn (质量浓度为  $8.2 \text{ mg}\cdot\text{L}^{-1}$ ), 同时 SS 浓度为  $520 \text{ mg}\cdot\text{L}^{-1}$ ; 周坤强等<sup>[26]</sup>研究发现桑树湾煤矿主井废水的 pH 为 3.59, TFe 浓度为  $398.895 \text{ mg}\cdot\text{L}^{-1}$ , Mn 浓度为  $15.170 \text{ mg}\cdot\text{L}^{-1}$ .

(2)出水水质水量不稳定.

由于煤矿酸性废水产生来源不同, 且在地质气候、季节变化、开采条件等的影响下, 其出水水质、水量以及废水特点也常有变化. 如贵州都匀市菠萝冲煤矿<sup>[31]</sup>枯水期排水量要低于  $1000 \text{ m}^3\cdot\text{d}^{-1}$ , pH 为 3.44, 悬浮物质量浓度为  $450 \text{ mg}\cdot\text{L}^{-1}$ , Fe 质量浓度为  $60 \text{ mg}\cdot\text{L}^{-1}$ , Mn 质量浓度为  $7 \text{ mg}\cdot\text{L}^{-1}$ ; 丰水期排放体积超过  $5000 \text{ m}^3\cdot\text{d}^{-1}$ , pH 低至 2.8, Fe 质量浓度为  $437.8 \sim 860.3 \text{ mg}\cdot\text{L}^{-1}$ , 是枯水期的几倍到十几倍, 硫酸盐质量浓度则为  $3268.1 \sim 5987.4 \text{ mg}\cdot\text{L}^{-1}$ , 属于强酸性矿山废水, 丰水期水质比枯水期差.

(3)污染范围广持续时间长.

据统计, 美国的阿肯色等 11 个州内, 仅由选矿尾矿池和废石堆产生的废水污染, 即可导致 14000 多千米长河流水质急剧下降<sup>[33]</sup>. 据研究, 矿厂产生的酸性废水通常会持续几百年, 个别矿厂

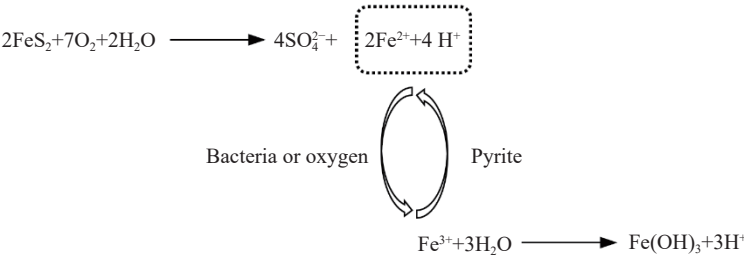


图 1 黄铁矿氧化反应机理

Fig.1 Pyrite oxidation reaction mechanism

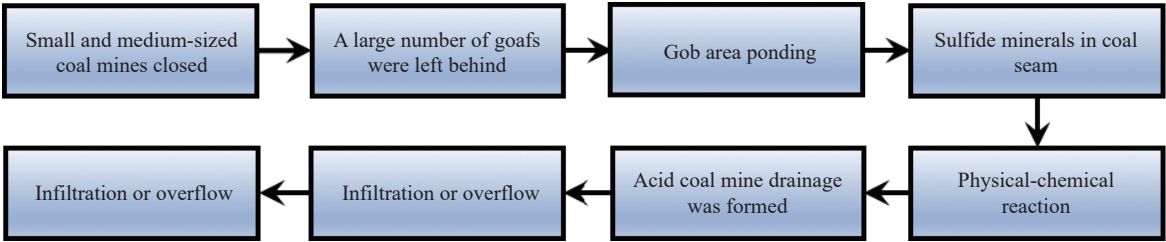


图 2 井下采空区积水导致的煤矿酸性废水的形成过程

Fig.2 Formation process of acid coal mine drainage caused by water accumulation in underground goaf

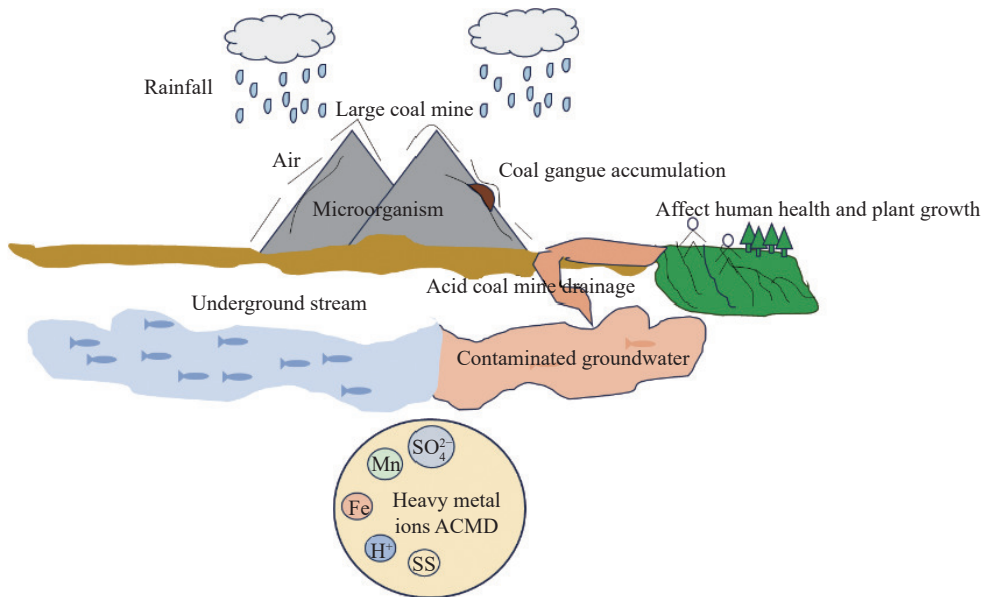


图 3 淋滤污染导致的 ACMD 的形成及影响

Fig.3 Formation and influence of ACMD caused by leaching pollution

表 1 煤矿酸性废水的主要理化性质<sup>[18,25-32]</sup>

Table 1 Main physical and chemical properties of acid coal mine drainage<sup>[18,25-32]</sup>

| Name of coal mine                                                      | pH   | Concentration/(mg·L <sup>-1</sup> ) |         |       |       | Reference |
|------------------------------------------------------------------------|------|-------------------------------------|---------|-------|-------|-----------|
|                                                                        |      | TFe                                 | Mn      | COD   | SS    |           |
| Sunjiashai Jinzhuchong Coal Mine, Guizhou Province                     | 3.5  | 296.4                               | 5.2     |       |       | [18]      |
| Huaxi Maipingrenhe Coal Mine, Guizhou Province                         | 2.76 | 102.5                               | 8.2     | 115   | 520   | [25]      |
| Sangshuwan Coal Mine in Wuma River Basin, Guizhou Province             | 3.59 | 398.90                              | 15.17   | 71.80 | 85.00 | [26]      |
| An abandoned coal mine, Guizhou                                        | 5-6  | 5-55                                | 0.5 ~ 3 | 10    |       | [27]      |
| Xiajiazhuang Coal Mine, Zibo City, Shandong Province                   | 3.5  |                                     |         | 103   | 3     | [28]      |
| Abandoned Maochong Coal Mine in Huaxi District, Guizhou Province       | 2-3  | 200 ~ 400                           | 7-14    |       |       | [29]      |
| Abandoned coal mines in Fenghuangshan area of Zhijin, Guizhou Province | 2-3  | 300                                 | 20      |       | 200   | [29]      |
| Water quality of Shandi River Basin in Yangquan City, Shanxi Province  | 2.5  | 400                                 | 100     |       |       | [30]      |
| Pineapple Chong Coal Mine in Duyun City, Guizhou Province              | 2.8  | 437.8-860.3                         |         |       |       | [31]      |
| Xiaoyi Piandian Coal Mine. Shanxi Province                             | 4-5  | <14                                 | <2.4    |       |       | [32]      |

Note: COD is chemical oxygen demand.

酸性矿山废水甚至会持续上千年之久<sup>[34]</sup>. 同样, 废弃煤矿若未采取治理措施, 也会源源不断向外排放煤矿酸性废水<sup>[35]</sup>.

2 煤矿酸性废水处理技术

目前国内处理煤矿酸性废水普遍采用石灰中和法等传统末端治理技术, 存在易造成二次污染、重金属离子去除不完全、沉淀的重金属难以分离并资源化利用等缺点. 对煤矿酸性废水污染的防治研究应当基于其产生源头、迁移路径、污染物组成等要素, 由单一的末端治理技术转向针对源头、路径、末端等更为全面的治理手段, 这将是清

洁高效地解决煤矿酸性废水污染的根本途径.

2.1 源头控制

源头控制技术从煤矿酸性废水形成的机理及影响因素<sup>[36]</sup>出发, 主要原理为: 使金属硫化矿物与水和空气隔绝或减少其接触、抑制微生物的活性, 从而大幅度降低煤矿酸性废水的产生量<sup>[37-38]</sup>, 实现“不要产生、阻碍产生”. 由于未关闭的大型煤矿厂主要是通过煤矸石堆积产生淋滤污染排放大量酸性废水, 因此适用源头控制技术, 而关闭煤矿由于施工条件限制等导致该技术应用困难. 研究人员探索发现了杀菌法、覆盖法、表面钝化法等源头治理技术如表 2 所示.

表 2 源头治理技术及其机理和优缺点分析<sup>[13, 37, 39-50]</sup>

Table 2 Source treatment technology and its mechanism and advantages and disadvantages<sup>[13, 37, 39-50]</sup>

| Treatment technique        | Action mechanism                                                                                                                        |                                                                                                                                                                                                                                                                                  | Advantages                                                                                                                                                                                                                                                                                   | Defects                                                                                                                                                        | Reference |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Sterilization method       | The sterilization method can inhibit or even kill microorganisms, thereby inhibiting the production of acid wastewater from coal mines. |                                                                                                                                                                                                                                                                                  | Sodium dodecyl sulfate, sodium alkyl sulfonate, and sorbic acid                                                                                                                                                                                                                              | It is greatly affected by environment, climate, and other conditions and may kill beneficial bacteria and produce drug-resistant bacteria.                     | [13, 37]  |
| Coverage method            | Inorganic material coverage                                                                                                             | An inorganic material is applied on the surface of waste rock or tailings, acting as a low-permeability impermeable layer that reduces the contact of water and oxygen with sulfide minerals.                                                                                    | The strong redox sensitive organic compounds are used to coordinate with insoluble ions and form soluble complexes. The insoluble ions are separated and released through an electrochemical reaction and precipitate on the surfaces of sulfide minerals, forming a dense protective layer. | It is easily affected by rain and snow and has little inhibitory effect on the acid production in bottom tailings or waste rock.                               | [39]      |
|                            | Organic material coverage                                                                                                               | Organic mineral materials are used as the covering layer.                                                                                                                                                                                                                        | Similar to the coverage of electrodeless materials, it has a long-term inhibitory effect on the oxidation of sulfide minerals.                                                                                                                                                               | Greatly affected by the weather and material drying                                                                                                            | [40–41]   |
| Surface passivation method | Inorganic material passivation                                                                                                          | A dense inert protective film is formed on the surfaces of sulfide minerals after the addition of a passivator.                                                                                                                                                                  | Mainly phosphate and silicate                                                                                                                                                                                                                                                                | Excessive phosphate causes the eutrophication of the surrounding water body. This technology has high requirements when used in an acid–base environment.      | [42]      |
|                            | Organic material passivation                                                                                                            | Similar to inorganic materials                                                                                                                                                                                                                                                   | Mainly diethylenetriamine (DETA), triethylenetetramine (TETA), and humic acid                                                                                                                                                                                                                | It is mainly used in laboratory research, but its long-term stability in the field cannot be confirmed. It has some shortcomings, such as biological toxicity. | [43–46]   |
|                            | Carrier-microencapsulation                                                                                                              | The strong redox sensitive organic compounds are used to coordinate with insoluble ions to form soluble complexes. Insoluble ions are separated and released through an electrochemical reaction and precipitate on sulfide minerals’ surfaces to form a dense protective layer. | It can specifically identify the sulfide minerals in tailings, improve the utilization rate of passivation agent and reduce the waste of resources.                                                                                                                                          | Long-term monitoring is required when using this technology to prevent the passivation layer from being destroyed in an acidic environment.                    | [47–50]   |

2.1.1 杀菌法

微生物能够加快黄铁矿的氧化, 而杀菌法<sup>[37]</sup>能够抑制甚至杀灭微生物, 从而抑制煤矿酸性废水的产生. 已有研究采用十二烷基硫酸钠、烷基磺酸钠和山梨酸等作为杀菌剂来抑制黄铁矿氧化. 如 Zhang 和 Wang<sup>[13]</sup> 采用杀菌剂十二烷基硫酸钠来抑制 FeS<sub>2</sub> 氧化, 使得亚铁离子质量浓度从最初的 8.9 g·L<sup>-1</sup> 下降到 6.8 g·L<sup>-1</sup>, 在一定程度上抑制了酸性矿山废水的形成. 但杀菌法受环境、气候等条件的影响较大, 且可能杀死有益菌群, 产生抗药性细菌.

2.1.2 覆盖法

覆盖法主要是用无机材料或者有机材料作为低渗透性防渗层铺设在废石或尾矿表层, 以减少水和氧气与硫化矿物的接触.

(1)无机材料覆盖技术.

无机材料覆盖技术使用无机矿物材料铺在尾矿表面, 使得硫化矿物与 H<sub>2</sub>O 和 O<sub>2</sub> 的接触变少. Wang 等<sup>[39]</sup> 发现 Atikokan 发电站的粉煤灰作为无机材料覆盖层抑制尾矿氧化的效果很好, 对于 pH 低至 3.8 的尾矿渗滤液, 采用粉煤灰覆盖后, 其出水呈碱性, 重金属含量也逐渐下降. 无机材料覆盖技术<sup>[37]</sup> 优点很多, 如来源广泛、易施工、防水隔氧性能好等, 但存在易受雨雪影响、对底部尾矿或废石的产酸过程抑制作用不大等缺点.

(2)有机材料覆盖技术.

有机材料覆盖技术即使用有机矿物材料作为覆盖层. 如 Lu 等<sup>[40]</sup> 探索了污泥和污泥粉煤灰对尾矿氧化的抑制作用, 合理调配的污泥粉煤灰混用

相比于单独使用污泥对尾矿氧化的抑制效果更好; Demers 等<sup>[41]</sup>进行了实验室试验和野外试验, 表明土壤污泥混合物对硫化矿物氧化具有长期性的抑制效果. 有机材料覆盖技术的优点与无机材料相似, 但其存在受天气影响较大、材料干化等缺点.

2.1.3 表面钝化法

表面钝化法通过加入钝化剂, 在硫化矿物表面生成一层致密的惰性保护膜, 阻碍氧气、水、微生物与硫化矿物之间的反应, 从而减少煤矿酸性废水的产生. 表面钝化法包括无机材料钝化、有机材料钝化和载体-微胶囊化技术等.

(1)无机材料钝化技术.

无机钝化剂主要有磷酸盐、硅酸盐等. Kang 等<sup>[42]</sup>研究了硅酸钠、硅酸钙和  $\text{KH}_2\text{PO}_4$  钝化剂对硫化矿物氧化的抑制效果,  $\text{KH}_2\text{PO}_4$  在用量为 0.05、0.1 和  $0.3 \text{ mol}\cdot\text{L}^{-1}$  时, 氧化抑制效率(以  $\text{Fe}^{2+}$  的释放量计)分别为 67%、94% 和 96%. 而采用  $\text{Na}_2\text{SiO}_3$  和  $\text{CaSiO}_3$  涂层, 其铁氧化量分别减少 94% 和 84%. 无机材料钝化技术也存在一些缺点, 如采用过量的磷酸盐会使周围水体富营养化, 同时此技术对酸碱环境要求较高, Al、Fe 等形成的氢氧化物保护层在中性条件下才能发挥效果.

(2)有机材料钝化技术.

有机钝化剂主要有二乙烯三胺(DETA)<sup>[43]</sup>、三乙烯四胺(TETA)<sup>[44]</sup>、腐殖酸<sup>[45]</sup>等. 如 Reyes-Bozo 等<sup>[46]</sup>发现腐殖酸和生物固体对硫化矿物表面改性的

能力, 薄膜浮选试验<sup>[46, 51]</sup>结果表明腐殖酸和生物固体吸附在黄铁矿表面, 腐殖酸质量分数为 1.5% 时浮上来的黄铁矿占黄铁矿总质量的 17%, 10%(质量分数)的生物固体用量可使黄铁矿回收率达到 40%, 黄铁矿表面疏水性增强, 这有利于阻碍黄铁矿与水的接触, 进而减少酸性废水的产生量. 然而, 有机材料钝化技术目前主要应用于实验室研究, 其野外长期稳定性还无法证实, 且存在有一定生物毒性的缺点.

(3)载体-微胶囊化技术.

载体微胶囊化技术对尾矿中硫化矿物的识别具有特异性, 其主要机理<sup>[47]</sup>是: 使用强氧化还原敏感性的有机物(如邻苯二酚等)作为钝化剂(PA), 与本不可溶的离子  $\text{M}^{3+}$ (如  $\text{Al}^{3+}$ 、 $\text{Fe}^{3+}$ 、 $\text{Ti}^{4+}$ 、 $\text{Si}^{4+}$ 等)配合形成可溶性配合物, 其稳定存在于溶液中, 随着电化学反应不可溶的离子又分离释放出来, 并沉淀在硫化矿物表面生成致密的保护层, 机理图如图 4 所示. 日本北海道大学学者们探索了 Ti-邻苯二酚(cat)<sup>[48]</sup>、Al-cat<sup>[49]</sup>及 Fe-cat<sup>[50]</sup>作为黄铁矿的钝化材料, 发现了金属离子从释放到生成氢氧化物保护层的过程及其机理. 由于此技术可以特异性识别尾矿中的硫化矿物, 因此其具有很好的应用前景. 但在使用该技术时需要进行长期监测, 防止钝化层在酸性环境下被破坏而失效.

2.2 路径堵截

针对煤矿酸性废水污染, 采用路径治理的模式(图 5)应当遵循“一矿一策”的原则, 需要研究

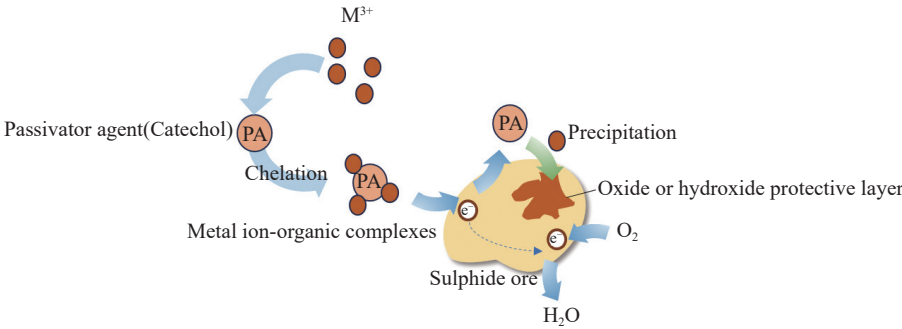


图 4 载体-微胶囊化技术钝化原理图

Fig.4 Passivation principle diagram of carrier-microencapsulation technology

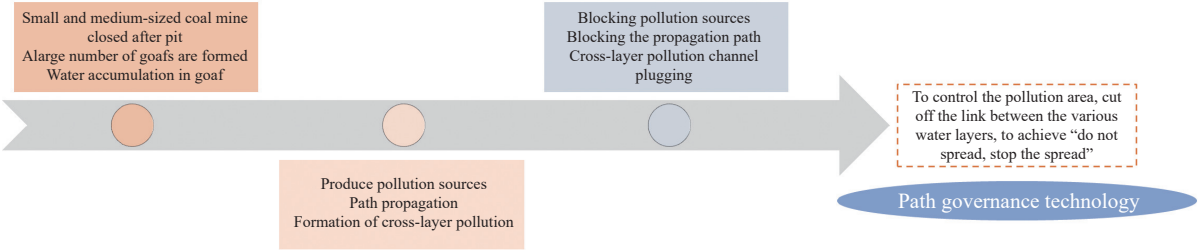


图 5 路径治理模式内容及目的

Fig.5 Content and purpose of the path treatment model

污染物源头、通道和传播路径等要素,并通过对源头进行阻断和对传播路径封堵等方式,以处理采空区及地下水的污染,控制污染区域,切断各个土层之间的联系,达到“不要传播、阻止扩散”的目的,实现排放过程减量。由于其主要针对采空区积水产生的煤矿酸性废水污染,因此适用于关闭中小型煤矿废水治理。

### 2.2.1 源头阻断

煤矿酸性废水污染治理除了闭坑后的集中再处理,一些研究也开始围绕前期的源头封堵开展,提前采取措施降低酸性废水污染的矿井水对周边的影响。李曦滨<sup>[19]</sup>研究了源头封堵技术对鱼洞河流域酸性废水的治理,通过多分支水平定向钻探技术以及地面高压注浆控制技术,对所探测的导水通道和裂隙进行注浆改造,实现对顶板含水层与采空区之间水力联系的阻断。

### 2.2.2 采空区污染物控制及传播路径封堵

为对废弃采空区进行有效控制,使用注浆的方式向采空区及其上覆岩体裂隙注入大量填充物,可以避免大量废弃矿井水的产生。注入顶板岩石破碎充填物,可对多种污染物协同控制,首先吸附过滤矿井水中的悬浮物,同时充填的顶板砂岩可以接触去除 Fe,并可消耗井下生产过程中混入矿井水中的大部分有机质(石油类污染物)。杨建<sup>[52]</sup>对井下采空区污染物的去除进行了深入研究,通过注入顶板岩石破碎充填物,吸附过滤矿井水中悬浮物,铁离子的去除率达到 20%,TOC(总有机碳)和 UV<sub>254</sub>(表示腐殖质类大分子有机物以及含 C=C 双键和 C=O 双键的芳香族化合物)的平均去除率分别为 67.45% 和 65.40%。

对采空区治理也可构筑挡水墙,隔断不同含水层之间的水力联系,实现对采空区积水的封闭隔离,减少废弃矿井水的传播。冀红娟和贾立庆<sup>[53]</sup>对矿井老空水治理进行研究,该工程通过井下密闭加固以及帷幕注浆的方式,封堵了老窑区和老巷道等通道,在进入矿井前截断老窑水及巷道水,以实现“堵水截流”,截断了头屯河与北东老空水的水力联系通道,减少了矿井污水的传播。吕华等<sup>[54]</sup>对淄博市洪山、寨里煤矿的串层污染防治采取路径封堵的方式,通过切断污染途径、干预地下流场、预控制等技术手段减少矿区污染,改善研究区水质。

## 2.3 末端治理

末端治理即在煤矿酸性废水排出后,对污水进行收集处理,通过物理、化学、生物等方法来对

煤矿酸性废水进行处置。末端治理是目前国内治理煤矿废水采用最多的一种模式,发展已较为全面,其中常见的技术方法包括化学中和法、可渗透反应墙(PRB)处理技术、吸附法、膜分离法、微生物法和人工湿地法等,末端治理技术及其机理和优缺点分析如表 3 所示。

### 2.3.1 化学中和法

化学中和法是目前处理煤矿酸性废水最常用的一种方法,目前煤矿酸性矿山废水治理系统<sup>[55]</sup>通常是采用氢氧化钠、碳酸钠、碳酸氢钠、石灰石等来中和酸性废水。

织金县凤凰山地区废弃煤矿废水处理工程<sup>[10]</sup>中,选用石灰作为中和和沉淀剂。调试及试运行期间效果较好,出水中 TFe、TMn 质量浓度平均值低于 1.0 mg·L<sup>-1</sup>,Fe 和 Mn 的平均去除率分别为 99.76% 和 91.07%,该工程每吨废水的处理运行成本仅为 1.06 元,对煤矿酸性废水处理具有较好的参考价值。

化学中和法虽然应用最为广泛,但生成的 CaSO<sub>4</sub> 较多,易造成二次污染。废水中的部分重金属如氢氧化亚铁等由于溶度积较大,利用中和法并不能完全去除,且沉淀的重金属部分会与石膏混合,难以分离并资源化利用。

### 2.3.2 吸附法

吸附法主要是利用其固体表面对水中的离子或分子物质的吸附作用来达到去除污染物的目的。唐艳<sup>[25]</sup>对贵州煤矿酸性废水的处理研究中,当使用活性炭时,对固体悬浮物(SS)的最大去除率约为 85%、对 SO<sub>4</sub><sup>2-</sup>的最大去除率约为 92%、对 Fe<sup>2+</sup>和 Mn<sup>2+</sup>的最大去除率约为 90%。

同时,生物炭吸附技术也是一种潜在的吸附技术<sup>[56]</sup>。生物炭是指通过热解生物质原料制得的含碳芳香化固体物质<sup>[60]</sup>,具有来源广、孔隙发达的特点,其对酸性废水中重金属离子的吸附机理如图 6 所示。生物炭技术具有成本较低、制备简便,并可有效吸附煤矿酸性废水中金属离子的优点,可能是未来煤矿酸性废水治理领域极具发展潜力的处理技术。

### 2.3.3 PRB 井下原位处理技术

PRB 技术原位处理煤矿酸性废水存在处理能力强、可操作性、作用时间长以及经济效益性强等优势。PRB 反应介质包括零价铁、碳酸盐、活性炭、离子交换树脂、螯合剂和微生物等<sup>[62]</sup>。可渗透反应墙技术示意图如图 7 所示。

对采空区进行 PRB 原位处理不仅可以克服传统处理技术高成本、易产生二次污染的缺点<sup>[61]</sup>,并

表 3 末端治理技术及其机理和优缺点分析<sup>[10-12,23,25,27,55-67]</sup>

Table 3 End treatment technology and its mechanism and advantages and disadvantages<sup>[10-12,23,25,27,55-67]</sup>

| Treatment technique            | Action mechanism                                                                                                                                                                                                                                     | Advantages                                                                                                                                                                                  | Defects                                                                                                                                                                                                                                                                        | Reference    |
|--------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| Chemical neutralization method | Removal of heavy metal ions in wastewater through a chemical neutralization reaction                                                                                                                                                                 | Sodium hydroxide, sodium carbonate, sodium bicarbonate, limestone, etc., raw materials are easily available and widely used.                                                                | It easily causes secondary pollution. Some heavy metals, such as ferrous hydroxide, in the wastewater cannot be completely removed because of the large solubility product. The precipitated heavy metal part mixes with gypsum and is thus difficult to separate and recycle. | [10,55]      |
| Adsorption method              | Pollutants are removed through the adsorption of ions or molecular substances in water on a solid surface.                                                                                                                                           | Activated carbon, biochar adsorption technology, etc., low cost, simple preparation                                                                                                         | Small application scale                                                                                                                                                                                                                                                        | [25, 56-60]  |
| PRB treatment technology       | The basic principle is to set up a highly permeable reaction barrier underground. Barrier construction usually uses specific reaction media, such as zero-valent iron or activated carbon, to promote the decomposition or adsorption of pollutants. | It has the advantages of strong processing capacity, operability, long action time and strong economic benefits and can also promote the natural balance of groundwater in the mining area. | Long processing time, limited by geological conditions, may cause soil pollution                                                                                                                                                                                               | [61-63]      |
| Membrane separation method     | The selective separation of heavy metal ions is driven by the pressure difference and potential difference between the reverse-osmosis and electrodialysis membranes.                                                                                | The ion removal rate is high, and the process is easy to operate and control. Temperature control is flexible.                                                                              | The membrane cost and operation cost are high, so it is not suitable for treating large amounts of wastewater.                                                                                                                                                                 | [64-65]      |
| Microbiological method         | Microorganisms are added to the acid wastewater of the coal mine for oxidation treatment.                                                                                                                                                            | Low cost, high metal ion removal rate, no secondary pollution                                                                                                                               | The requirements for temperature and pH are high.                                                                                                                                                                                                                              | [11,23, 66]  |
| Artificial wetland method      | A constructed wetland is an ecosystem composed of substrates, plants, and microorganisms. Heavy metals in wastewater are removed from water through physical, chemical, and biological effects.                                                      | Adsorption matrix improvement, functional microbial enhancement and dominant plant enrichment, low operating cost, strong buffering performance                                             | The area is large, the effluent's pH barely meets the standard, the method is unsuitable for high-concentration and low-pH wastewater, and the removal effect of $\text{SO}_4^{2-}$ is not good.                                                                               | [12, 27, 67] |

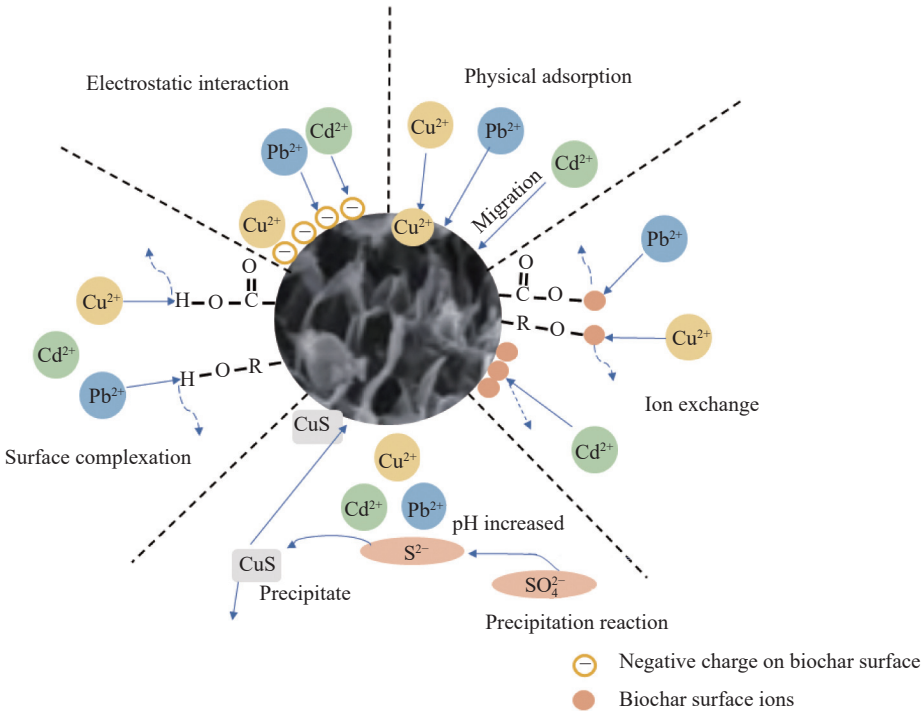


图 6 生物炭对煤矿酸性废水中不同重金属离子的吸附机理

Fig.6 Adsorption mechanism of biochar for different heavy metal ions in ACMD

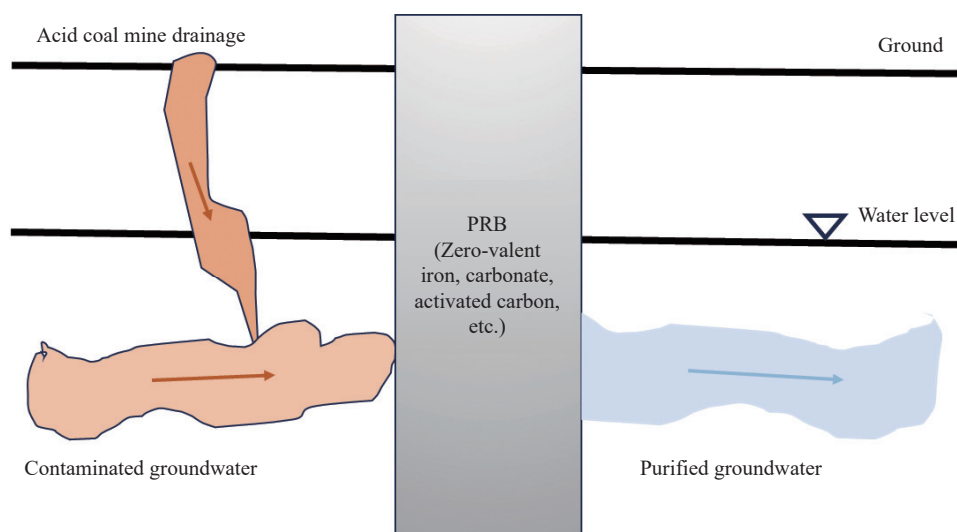


图7 可渗透反应墙技术示意图

Fig.7 Schematic of PRB technologies

且还可以促进矿区地下水的自然平衡。熊玲等<sup>[63]</sup>采用碳酸盐岩作为 PRB 反应介质来处理煤矿酸性废水, 结果 pH 由进水的 2.5 上升到出水的 7.0 左右,  $\text{Fe}^{3+}$  的去除率超过 99.5%, 出水中铁质量浓度低于  $0.5 \text{ mg} \cdot \text{L}^{-1}$ 。

#### 2.3.4 膜分离法

膜分离法则是通过反渗透膜和电渗析等技术利用膜两侧产生的压力差及电位差为推动力, 选择性地分离重金属离子, 主要包括微滤、超滤、纳滤、反渗透和电渗析等技术<sup>[64-65]</sup>(表 4)。陈明等<sup>[66]</sup>通过电渗析来处理含铜酸性废水, 经电渗析处理后不仅可以使淡化室废水中脱铜率和脱氢率达到 97.08% 和 99.20%, 淡化液达到污水综合排放标准, 还可以有效富集废水中的铜、铁、氢离子。膜分离法的离子去除率高, 容易操作和控制, 温度控制灵活, 但膜成本和运行费用较高, 不适合处理量大的废水。

#### 2.3.5 微生物法

微生物法是一种常见的酸性矿山废水处理技术<sup>[11]</sup>, 即向煤矿酸性废水添加一定量的微生物, 对其进行氧化处理<sup>[23]</sup>, 其具有成本低、金属离子去除率高和无二次污染等优点, 其缺点是对温度和 pH 的要求较高。Sahinkaya 等<sup>[67]</sup>研究了 SRB 处理技术, 其应用于酸性矿山废水时可溶性金属离子的去除率最低达到 82%, 最高达到 99.9%, 总金属去除率则在 80% ~ 99.9% 的范围内。

#### 2.3.6 人工湿地法

人工湿地是由基质、植物、微生物三者共同组成的一个生态系统, 通过物理、化学和生物作用将

废水中的重金属从水体去除。吸附基质改良、功能微生物强化及优势植物富集是改善人工湿地系统、提高对煤矿酸性废水处理效率的主要手段。

##### (1) 吸附基质改良。

土壤基质是人工湿地系统中最重要的一部分, 既是微生物的载体, 支撑着植物的生长, 也在煤矿废水悬浮物、重金属的去除中起着关键作用。最初采用纯土壤(如黄土、赤泥)作为人工湿地法中的基质来治理煤矿酸性废水, 但其所取得的效果并不理想, 且有容易堵塞的缺点。因此基质改良是提高人工湿地法处理效率的关键所在。通过添加其他辅料(如煤渣、沸石、活性污泥等)改善土壤内部环境, 使混合的土壤基质具有发达的土粒结构、大吸附量和高渗透率等特点, 从而提高人工湿地系统对污染物的去除效率。程丽芬等<sup>[12]</sup>研究了不同基质的湿地系统对山西高家窑煤矿废水的处理效果, 结果发现对全磷、全氮、汞去除效果最好的是河沙和湿地土壤的混合基质, 对硫化物去除率最高的为湿地土壤, 其次是两者混合基质。这说明单一基质吸附性能较差, 虽然湿地土壤中含有较多的微生物和有机物, 但空气状况较差, 向湿地土壤中添加河沙可以改善其透气性, 从而提高对废水中污染物的去除效率。

##### (2) 功能微生物强化。

除了吸附基质改良, 还可通过微生物强化处理技术来提高人工湿地对酸性废水的处理效率。矿山水环境中存在变形菌门、绿弯菌门、拟杆菌门、放线菌门、硝化螺旋菌门和蓝细菌门等细菌群落, 其中变形菌门为 AMD 中的丰富物种, 绿湾

表 4 膜分离技术分类及原理、特点<sup>[64-65]</sup>

Table 4 Classification, principle, and characteristics of membrane separation technology<sup>[64-65]</sup>

| Membrane separation technique | Principle                                                                                                                                                                                                 | Feature                                                                                                                                                                                          |
|-------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Microfiltration               | Microfiltration membrane is used to screen liquid substances, which penetrate particles or molecules smaller than membrane pores under pressure, separating different particles or molecules.             | It is often used in wastewater treatment in the petroleum industry. Compared with the traditional filtration method, it is more moderate and can reduce energy consumption.                      |
| Ultrafiltration               | It is mainly used to intercept some macromolecular substances in a solution, separating macromolecular substances and small molecular substances.                                                         | Ultrafiltration membrane can be used to separate macromolecular organic matter from wastewater and then discharge wastewater, and the separated wastewater often has low organic matter content. |
| Nanofiltration                | A membrane separation process driven by the pressure difference between ultrafiltration and reverse osmosis.                                                                                              | The pore size of the membrane is in a range of several nanometers and can separate organic matter with low and high molecular weight and can separate salt compounds in water.                   |
| Reverse osmosis               | The separation of liquid and mixture is realized by using pressure to intercept small molecular substances with a reverse-osmosis membrane.                                                               | It can effectively separate salts, bacteria, and other substances dissolved in water, which can be used for wastewater recovery.                                                                 |
| Electrodialysis               | Under the action of a DC electric field, charged particles are driven by potential difference, and the electrolyte in a solution is separated by the selective permeability of the ion exchange membrane. | After using this technology for solution separation, it can better desalinate or purify the solution. It is simple and efficient and has been widely used in wastewater treatment.               |

菌门在沉积物和湿地土壤中的丰富程度较高, 蓝细菌细胞外会生成多糖等能吸附金属离子的物质. 王能等<sup>[27]</sup> 分析了贵州某废弃煤矿酸性废水处理系统中的细菌群落结构, 结果表明湿地系统沉积物和植物根际土壤中土微菌属 (*Pedomicrobium*) 和硝化螺旋菌属 (*Nitrospira*) 的丰富度指数 (Chao 指数和 ACE 指数)<sup>[27]</sup> 较高, 分别为  $8.38\% \pm 1.51\%$  和  $14.75\% \pm 0.46\%$ , 湿地中此类微生物可强化对 Fe、Mn 的去除.

(3) 植物富集.

此外, 植物富集也是人工湿地法的一大优势. 人工湿地中植物可通过吸收和吸附等作用去除废水中的金属离子, 常见的此类植物有水葱、水麦冬、香蒲、芦苇、石菖蒲、梭鱼草和金丝草等, 如菖蒲对废水中 Mn 具有很好的生物富集能力<sup>[27]</sup>. 程丽芬和张欣<sup>[68]</sup> 研究了 5 种水生植物对煤矿废水的适应性和净化效果, 5 种植物中对煤矿酸性废水适应性最好的是水麦冬和三棱水葱, 对煤矿废水中总氮的去除效果从高到低依次为芦苇、香蒲、三棱水葱、水麦冬、石菖蒲, 综合适应性和去除效果, 香蒲和三棱水葱更适合用于人工湿地法的植物富集.

湿地法的运行成本低, 缓冲性能强, 但占地面积较大, 出水 pH 值较难达标. 该方法对低浓度废水有明显的去除效果, 但不能处理高浓度低 pH 废水, 且对  $\text{SO}_4^{2-}$  去除效果不佳.

3 展望

为了更好地解决我国煤矿酸性废水污染问

题, 对中小型关闭煤矿主要采用末端治理技术 (如中和法、微生物法、人工湿地法等); 对于大型煤矿采用末端治理技术的同时, 还需针对不同煤矿采用有效的源头及路径治理技术, 三者结合达到“去除有害、回收有价”的目的. 同时, 针对当前煤矿废水治理中酸难利用和重金属难回收的困境, 提出“资源综合利用”回收有价、“以废治废”酸碱中和、整体综合治理等思路.

(1) “资源综合利用”回收有价.

煤矿酸性废水中往往含有铁、锰、锌、铜等有价金属元素, 部分甚至含有稀土、锂等稀散、稀贵金属, 单纯回收其中某种金属元素不具有现实意义, 需要探索有价金属综合回收工艺, 并探讨其经济性, 达到“回收有价”的目的. 同时, 针对废水中的酸也可再利用处理. 如可尝试将矿山酸性废水作为矿浆 pH 调整剂用于选矿生产, 既可以节省药剂用量, 又能够保证浮选效果, 同时酸性废水也得到较妥善的处置.

(2) “以废治废”酸碱中和.

针对煤矿酸性废水末端治理中最常用的化学中和法, 其关键之一是对经济、高效中和剂的选取. 煤矿酸性废水呈酸性甚至强酸性, 且往往产生量较大, 若能从废水产地周边企业、工厂获取廉价的废碱液、废碱渣等作为中和剂, 有望达到“以废治废”的效果, 既能够使煤矿酸性废水的治理排放达标, 又能节约成本, 实现其经济性.

(3) 整体综合治理方案.

目前国内针对煤矿酸性废水的综合治理技术

还不够成熟, 源头、路径和末端治理相结合的整体综合治理方案有望成为未来研究的热点. 首先, 针对大型煤矿产生的酸性废水, 需要将煤矿废水污染防治提前纳入考虑, 做好矿山尤其井下工程历史数据、图纸资料收集, 以便实施源头控制和路径堵截等方案; 其次, 对于关闭的中小型煤矿, 除主要运用末端治理技术外, 对采空区的积水也要实施疏放和切断补给水路径等方案.

## 4 结论

煤矿酸性废水具有 pH 值低, 总铁、总锰、 $\text{SO}_4^{2-}$  含量高, 且有污染范围广、持续时间长、出水水质水量不稳定等特点. 本文基于已有研究归纳总结了煤矿酸性废水的成因和主要特征, 并从源头治理、路径堵截、末端治理三个方面概括分析了已有煤矿酸性废水的处理技术.

(1) 末端治理技术适用于大部分煤矿, 但存在二次污染、成本高的问题, 如中和法中生成的  $\text{CaSO}_4$  较多.

(2) 关闭的中小型煤矿排放的煤矿酸性废水主要来源于井下采空区积水导致的煤系氧化, 除采用末端治理技术外, 还应增加巷道封闭充填、帷幕注浆、建立堵水墙等路径封堵技术, 针对采空区封堵污染源, 减少污水扩散.

(3) 大型煤矿产生的煤矿酸性废水主要来源于煤矸石堆积产生的淋滤污染, 适用源头控制技术, 源头控制和路径封堵技术相比于末端治理更加高效清洁, 在出水前便采取相应措施, 可解决传统末端治理成本高、二次污染的问题. 但源头控制如杀菌法、覆盖法均受环境、气候的影响较大, 路径治理则须遵循“一矿一策”的原则, 操作较困难.

(4) 针对当前煤矿废水治理中酸难利用和重金属难回收的困境, 提出“资源综合利用”回收有价、“以废治废”酸碱中和、整体综合治理等思路, 有望为后续煤矿酸性废水处理提供新思路.

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