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# 煤矸石生态修复利用及其重金属污染防控 研究进展

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**摘要:** 煤矸石是我国大宗固废之一,其堆存占用了大量土地资源,同时长期堆存可产生地质灾害、环境污染等一系列生态环境问题,严重制约了煤炭行业的可持续发展。煤矸石大规模消纳迫在眉睫,而煤矸石生态修复利用是实现煤矸石大规模消纳的有效途径。本文综述了国内外煤矸石中的元素和矿物组分、煤矸石生态修复利用技术、煤矸石生态修复利用中重金属释放风险及其污染防控措施,并提出了煤矸石生态修复安全利用建议。煤矸石中富含氮、磷、钾和有机质等营养元素和物质,且矿物以石英和黏土矿物为主,可为煤矸石生态修复利用提供必要的物质基础。煤矸石可通过填沟造地和制备植生基质实现煤矸石生态修复利用。但部分煤矸石中重金属和硫含量高,存在产酸和重金属释放风险,使大规模生态修复利用受到了一定的制约。微生物技术、氧化菌抑制技术及重金属钝化技术等技术手段可有效控制煤矸石中重金属释放。针对重金属和硫含量高的煤矸石,需加强对煤矸石生态修复利用过程中重金属的环境行为研究,同时研发物理、化学和微生物多途径联用技术,抑制产酸和重金属释放,实现煤矸石生态修复安全利用。同时加强监测煤矸石生态修复过程中重金属的潜在生态环境风险,实现煤矸石生态修复安全利用。

**关键词:** 煤矸石; 生态修复; 重金属; 污染防控; 植生基质

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## A critical review on the ecological restoration utilization and prevention and control of heavy metal pollution of coal gangue

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**Abstract:** Coal gangue is a major industrial solid waste in China, which occupies a large amount of land and causes a serious ecological issues, such as geological disaster and environmental pollution. The extensive accumulation of coal gangue poses a significant constraint on the sustainable development of the coal industry. Therefore, it is urgent to find large-scale disposal methods for coal gangue. The ecological restoration utilization of coal gangue is an effective way to achieve large-scale disposal. The paper presents a comprehensive overview of the constituents and minerals in coal gangue, as well as the ecological restoration utilization technologies employed for the material. The release risk of heavy metals during the ecological restoration utilization processes, and prevention and control of heavy metal pollution are also discussed. Furthermore, some valuable recommendations for ensuring the safe utilization of coal gangue in ecological restoration are proposed. Coal gangue is comprised of sand and clay minerals, containing abundant N, P, K, organic matter, and other nutrients that serve as essential material foundation for ecological restoration utilization of coal gangue. Coal gangue can be utilized for ecological restoration utilization through backfill ditches and create land while also serving as a soil-functional planting substrate. However, the presence of high levels of heavy metals and sulfur in certain coal gangue samples presents a potential environmental risk associated with the release of heavy metals, thereby impeding the ecological restoration utilization of coal gangue. The use of techniques such as microbial technology, oxidation inhibition technology, and immobilization technology of heavy metals can effectively control the release of heavy metals in coal gangue. The environmental behavior of heavy metals during the process of ecological restoration utilization of coal gangue, which contains high levels of heavy metals and sulfur, should be further investigated to ensure its ecological restoration utilization. Integrated technologies encompassing physical, chemical, and microbial approaches need to be employed, inhibiting acid production and the release of heavy metals to achieve ecological restoration safe utilization of coal gangue. In addition, the monitoring of potential ecological and environmental risks of heavy metals in the ecological restoration process of coal gangue should be strengthened, ultimately achieving ecological restoration safe utilization of coal gangue.

**Keywords:** coal gangue; ecological restoration; heavy metal; prevention and control of pollution; plant substrate

## 0 引言

煤矸石属于矿山大宗固体废弃物,在煤炭开采与洗选过程中产生,占原煤产量的 10%~30%<sup>[1]</sup>。我国是煤炭生产大国,煤矸石是我国大宗工业固废之一,煤矸石排放量占我国工业固废年排放量的 25%<sup>[2]</sup>。我国由煤矸石堆存形成的规模较大的煤矸石山达 2 600 多座<sup>[3]</sup>,全国一百多个地市堆存煤矸石,赤峰、大同、淮南等地市堆存量超过 1 000 万 t<sup>[4]</sup>。2021 年我国煤矸石产生量达到 7.43 亿 t,预测 2025 年我国煤矸石产生量将达到 8.00 亿 t<sup>[5]</sup>。

煤矸石堆存不仅占用了大量的土地资源,其无序堆放还可能导致矸石堆自燃、滑坡等生态环境风险。同时,煤矸石因富含硫和重金属等污染物,会释放有害气体和重金属,从而导致环境污染<sup>[6-7]</sup>。在“双碳”背景下,如何开展煤矸石的资源化利用,实现煤矸石的“减量化、资源化、无害化”成为了重要的课题<sup>[8-9]</sup>。尽管煤矸石常通过矸石发电、井下填充、有价金属回收、建筑材料利用和农业生产等途径进行综合利用,但是因其用量有限或相关产品/技术受成本

和市场制约,难以开展煤矸石的大规模利用<sup>[10]</sup>。煤矸石大量堆存依旧是践行“绿水青山就是金山银山”的“绊脚石”。

2014 年,国家发展和改革委员会等十部委联合发布的《煤矸石综合利用管理办法(2014 年修订版)》指出:“新建(改扩建)煤矿及选煤厂应节约土地、防止环境污染,禁止建设永久性煤矸石堆放场(库)”,煤矸石用地愈发紧张。煤矸石规模化生态利用,可腾退压占土地,成为了煤矸石处理处置的新方向<sup>[11]</sup>。煤矸石中富含有机质、氮、磷、钾等植物生长的必要元素,为煤矸石生态修复利用提供了物质条件<sup>[12]</sup>。但是煤矸石会因其产酸使本身富集的重金属释放,造成水土污染<sup>[13]</sup>。因此,如何实现煤矸石生态修复利用,同时控制其产酸和重金属释放,对煤矸石规模化生态利用具有重要意义。本文在总结煤矸石中的矿物和元素组成特征的基础上,分析煤矸石在生态修复中的应用、煤矸石中重金属释放风险、煤矸石生态修复中的重金属污染防控技术,以期降低煤矸石在生态修复过程中环境风险,为煤矸石大规模生态修

复利用提供借鉴。

## 1 煤矸石中的元素和矿物特征

### 1.1 煤矸石中的元素

#### 1.1.1 主量元素

煤矸石往往含有  $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{CaO}$ 、 $\text{MgO}$ 、 $\text{K}_2\text{O}$  等无机物, Ti、Co 等微量稀有金属元素, 碳、氢、氧、氮、硫和有机质<sup>[4]</sup>, 其中,  $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$ 、 $\text{MgO}$ 、 $\text{Fe}_2\text{O}_3$ 、 $\text{CaO}$  是主要成分, 可占到煤矸石主要化学成分的 80% 以上。根据  $\text{SiO}_2$ 、 $\text{Al}_2\text{O}_3$  和  $\text{CaO}$  的比例关系可以把煤矸石分为黏土岩质煤矸石、砂岩质煤矸石、铝质煤矸石和钙质煤矸石(表 1)<sup>[15-16]</sup>, 不同类型煤矸石

矿物组分不同。《煤矸石分类》(GB/T 29162—2012) 中还根据煤矸石中钙镁含量将其划分为钙镁型煤矸石( $w_{\text{CaO}+\text{MgO}} > 10\%$ )和铝硅型煤矸石( $w_{\text{CaO}+\text{MgO}} \leq 10\%$ ); 其中, 硅铝型煤矸石按铝硅比划分为低级铝硅比煤矸石( $m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2) \leq 0.3$ )、中级铝硅比煤矸石( $0.3 < m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2) \leq 0.5$ )和高级铝硅比煤矸石( $0.5 < m(\text{Al}_2\text{O}_3)/m(\text{SiO}_2)$ )。如安徽省淮河能源矿区煤矸石中  $\text{SiO}_2$  和  $\text{Al}_2\text{O}_3$  成分占比范围分别为 59.57%~77.76% 和 13.49%~26.43%, 属于硅铝型煤矸石<sup>[7]</sup>。不同类型煤矸石的化学成分(质量分数)见表 1。

表 1 不同类型煤矸石的化学成分(质量分数)

Table 1 Chemical composition(mass fraction)of different types of coal gangue

类型	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	单位: %
									资料来源
黏土岩质煤矸石	59.44	23.43	32.98	2.52	1.06	—	3.47	1.34	[18]
砂岩质煤矸石	64.79	18.00	3.82	1.42	4.18	1.62	4.55	—	[19]
铝质煤矸石	42.17	48.41	0.07	0.94	3.77	—	—	1.35	[20]
钙质煤矸石	21.71	4.82	4.43	1.61	64.17	0.64	—	0.36	[21]

#### 1.1.2 营养元素

煤矸石中往往含丰富的 N、P、K 等营养元素, 同时还含有大量的有机质。煤矸石中 N 含量一般在 0.19%~0.87% 之间,  $\text{P}_2\text{O}_5$  占比一般在 0.25%~0.50% 之间,  $\text{K}_2\text{O}$  占比一般在 0.11%~5.00% 之间, 有机质占比一般在 5%~25% 之间<sup>[10,22-23]</sup>。与全国第二次土壤普查养分等级划分标准相较, 煤矸石中 N 和 P 含量较高, 为较丰富~丰富等级和丰富等级; K 含量变化较大, 部分煤矸石 K 达到了丰富等级, 部分 K 含量较为缺乏; 煤矸石有机质含量高, 为丰富等级(>4%)。煤矸石中不同营养元素生物可利用性有一定差异。以淮河能源矿区煤矸石为例, 其水解性氮含量较低, 有效磷含量极低, 不易被植物吸收利用, 但煤矸石中速效钾含量较高, 最高达 552 mg/kg, 处于二级及以上标准, 可作钾肥<sup>[7]</sup>。除此之外, 煤矸石中 Si 含量较高, 也常用作硅肥的原料<sup>[24]</sup>。煤矸石中营养元素丰富, 可为煤矸石制肥和生态修复提供物质基础。

#### 1.1.3 重金属元素

煤矸石中往往含有一定含量的重金属元素, 这些重金属元素往往以独立的硫化物矿物或类质同相的形式赋存于煤矸石中<sup>[25]</sup>。随着含重金属的硫化物矿物的分解, 煤矸石中重金属也随之释放。国内外煤矸石样品中部分煤矸石重金属含量超过了农用地

土壤污染风险筛选值<sup>①</sup>, 存在重金属释放风险(表 2)。中国不同矿区煤矸石中重金属超过土壤风险筛选值<sup>①</sup>的比例不高, 但部分煤矸石中 Cu 和 Cr 含量可分别达到 368.79 mg/kg 和 337.25 mg/kg<sup>[26]</sup>。赞比亚煤矸石中 Cd 含量在 0.97~1.17 mg/kg 之间, 英国威尔士煤矸石中 Zn 和 Cu 含量也较高, 均有一定的环境风险<sup>[27]</sup>。不同成矿年代煤矸石重金属含量不同。对中国煤矸石样品分析发现, 晚石炭纪和早二叠纪煤矸石中 Pb、Se 和 As 含量最高, 二叠纪煤矸石中 Cr、Cd、Be、Cu 和 Zn 含量最高, 且煤矸石形成年代越晚, 重金属富集程度越低<sup>[21]</sup>。尽管部分煤矸石中重金属含量未超过风险筛选值, 但重金属元素可通过淋溶作用随酸性淋溶液进入土壤, 并在土壤中富集, 依然存在一定的生态环境风险<sup>[2]</sup>。

## 1.2 煤矸石中的矿物

石英与高岭石和伊利石等黏土矿物是煤矸石中的主要矿物, 一般占比较高。不同矿物赋存比例与煤矸石类型相关。如砂岩类煤矸石中石英含量较高, 黏土岩类煤矸石则含有相当高比例的高岭石、伊利石等黏土矿物<sup>[23]</sup>。除此之外, 煤矸石中还常含有黄铁矿等矿物, 其是煤矸石产酸的主要原因。郭彦霞等<sup>[23]</sup>总结了各国煤矸石中矿物赋存情况(表 3), 表明我国煤矸石中高岭石含量较丰富, 为煤矸石资源化利用

① 《土壤环境质量 农用地土壤污染风险管控标准(试行)》(GB 15618—2018)。

表 2 各地区煤矸石中重金属含量

Table 2 Content of heavy metals in coal gangue from various regions

地区	单位: mg/kg								
	Zn	Cu	Cd	Pb	Cr	Hg	As	Mn	资料来源
中国不同地区	1.96~204.99	3.63~368.79	0~0.71	0.85~62.22	3.20~337.25	0.02~0.20	0~14.26	17.61~3 662.34	[26]
中国陕西省	—	35.25~55.50	—	418.50~664.50	341.75~359.50	—	—	—	[28]
中国山东省	3.20~57.53	22.00~47.30	0~2.50	33.30~75.30	48.93~115.62	1.15~1.78	2.92~3.49	—	[29]
赞比亚	36.62~63.56	1.51~44.28	0.97~1.17	58.67~70.18	—	—	—	—	[27]
英国威尔士	38.86~485.00	17.03~675.00	0.34~0.52	10.42~153.11	—	—	—	—	[25,30]

提供了有力条件。DUAN 等<sup>[31]</sup>对山西、河北、重庆、新疆四个具有代表性的地区的煤矸石中矿物组分进行了研究,表明方石英、高岭石和黄铁矿是其主要矿物。煤矸石中主要矿物与土壤中相似<sup>[32]</sup>,具有制备植生基质的潜力。但是煤矸石中还常含黄铁矿,在氧气、水和微生物共同作用下可产生硫酸,不利于其生态修复规模化利用。

表 3 不同国家煤矸石矿物组分

Table 3 Mineral compositions of coal gangues in various countries

矿物	单位: %					
	中国	捷克斯洛伐克	德国	西班牙	英国	苏联
伊利石	10~30	10~45	41~66	20~60	10~31	5~30
高岭石	10~67	20~45	4~25	3~30	10~40	1~60
绿泥石	2~11	0~15	1~3	0~7	2~7	—
石英	15~35	10~50	13~27	5~57	15~25	—
铁矿石	2~10	0~25	0.5~5	—	2~10	0.2~8

资料来源:文献[23]。

## 2 煤矸石生态修复利用

### 2.1 煤矸石用于填沟造地

填沟造地等是煤矸石大规模生态修复利用途径之一。《土地复垦质量控制标准》(TD/T 1036—2013)对土地复垦定义为“对生产建设活动和自然灾害损毁的土地,采取整治措施,使其达到可用的状态。矸石山可根据当地自然环境,可复垦为耕地、林地和草地”。煤矸石填沟造地一般要求隔层填埋,覆土阻燃,并且要考虑煤矸石产酸和重金属释放等生态环境风险。《固体废物处理处置工程技术导则》(HJ 2035—2013)要求在处置过程中,对于含硫量大于 1.5% 的煤矸石,应采取措施防止自燃。部分省区针对填沟造地建立了一些地方标准。山西省出台的《煤矸石填埋造田技术规程》(DB14/T 1114—2015)规定,煤矸石填埋造田需采取隔层填埋,当煤矸石填埋厚度达到 5 m 时,必须上覆压实土层,厚度为 0.3~0.5 m,形成覆土阻燃系统;最终封场覆土要求总厚度达到 0.8~1.0 m。因煤矸石中本身含有硫和重金属等有害物质,

贵州省正在立项的地方标准《煤矸石填沟造地技术规程(试行)》要求填沟造地的煤矸石固定碳含量应≤15%,全硫含量<3.0%、且含量为 1.5%~3.0% 的煤矸石要采取相关阻隔措施;煤矸石中重金属浸出要低于《污水综合排放标准》(GB 8978—1996)中第一类污染物最高允许排放浓度和第二类污染物一级标准限值要求。

煤矸石填沟造地复垦的场地在符合相关标准并具备农作物种植条件的情况下可作为农用地。煤矸石填沟造地复垦耕地伴随着复垦时间的持续,土壤有机碳含量和微生物丰度往往有不同程度的积累和恢复,且复垦后合理的农业耕作活动更有助于土壤质量的持续改善<sup>[33]</sup>。靳东升等<sup>[34]</sup>在煤矸石填埋场复垦土壤种植玉米、大豆、苜蓿和紫云英,发现种植植物可以提高复垦土壤的养分含量,增加复垦土壤中真菌的多样性。BAI 等<sup>[35]</sup>也发现植物修复增强了煤矸石修复区土壤磷的生物转化,降低了土壤中几种有害金属元素的含量,显著改变了微生物群落的结构和功能,改善了整体土壤生态环境。HU 等<sup>[36]</sup>将煤矸石作为填充基质的复垦土地种植玉米,发现填充前控制煤矸石的 pH 值,且覆盖较厚的土壤,可以显著提高土壤质量和促进玉米生长。

### 2.2 煤矸石用于植生基质制备

因煤矸石富含营养元素和有机质,且其矿物组分与土壤相似,因此,煤矸石具有制备植生基质的物质基础。将煤矸石制备成具有土壤功能的植生基质,实现煤矸石生态修复利用逐渐成了近些年关注的焦点<sup>[37]</sup>。但是煤矸石基质本身物理结构不良,保水保肥等物理性质较差,难以直接作为植生基质使用;且煤矸石中往往含有重金属和硫,制约了煤矸石植生基质的利用(图 1)。

肥料、生物炭、保水剂、粉煤灰等一些材料的添加可以显著改善煤矸石基质理化性质,实现煤矸石植生基质的可持续生态利用。研究表明,在煤矸石种植区施肥,可以快速且有效地提高有机质、全氮、硝态氮、速效磷,以及速效钾等土壤养分含量,促进

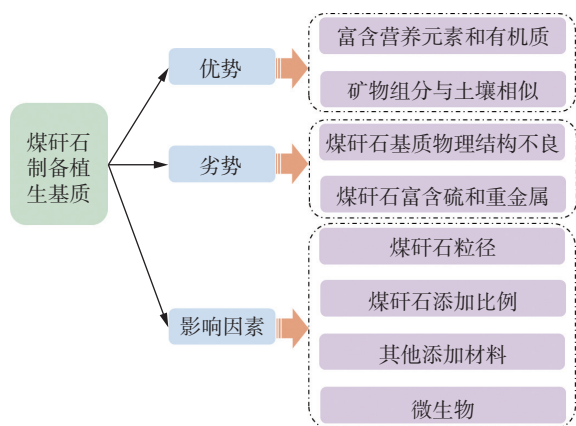


图 1 煤矸石制备植生基质的可行性及影响因素

Fig. 1 Feasibility and influencing factors of preparing plant substrate by using coal gangue

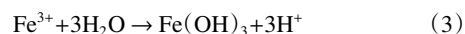
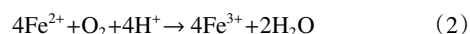
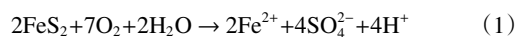
植物生长<sup>[38-41]</sup>。生物炭和保水剂可以增加煤矸石基质土壤疏松度、土壤有机含量和含水量,同时可以提高土壤酶活性<sup>[42-43]</sup>。玉米秸秆和粉煤灰作为主要添加剂可显著改善煤矸石基质理化性质和养分,达到促进植物生长的目的<sup>[44-45]</sup>。菌渣、磷石膏、酒厂污泥等其他固体废弃物也可改善煤矸石基质性质,促进植被的发芽和生长<sup>[46]</sup>。除添加材料外,煤矸石粒径、煤矸石添加比例、微生物群落等会通过影响煤矸石基质的最大持水量、孔隙率、有机质、营养元素等理化性质,进而影响其生态修复效果<sup>[47-49]</sup>。煤矸石粒径可改变基质的孔隙度和持水能力,影响土壤团聚体结构稳定性和土壤养分含量<sup>[50]</sup>。HAN 等<sup>[51]</sup>研究发现厚度为 8~16 cm、粒径范围为 0.5~2.0 cm 的煤矸石覆盖可以最大程度地提高矿区土壤的持水能力。煤矸石添加比例也可显著影响土壤持水和保肥能力等理化性质,进而影响植物生长<sup>[52-54]</sup>。向煤矸石中接种微生物可用于调节煤矸石植生基质中微生物群落结构,缩短生态恢复期<sup>[55]</sup>。YU 等<sup>[56]</sup>对煤矸石基质接种铜绿假单胞菌(LB5Z)发现其可促进植物生长和提高植物对重金属耐受性。有研究发现,膨润土窄食单胞菌 BII-R7 与煤矸石结合可以提高苜蓿种子发芽率,促进苜蓿生长<sup>[57]</sup>。丛枝菌根真菌(AMF)可提高煤矸石基质土壤团聚体稳定性、酶活性、有机质、碳固存能力和植物生物量<sup>[54,58-59]</sup>。除此之外,一些其他微生物在煤矸石基质中氮等营养元素循环中也起着潜在的作用<sup>[60]</sup>。

### 3 煤矸石生态修复利用中重金属污染防控

#### 3.1 煤矸石重金属污染

如前所述,尽管大部分煤矸石中重金属含量未超过农田土壤风险筛选值<sup>①</sup>,但是煤矸石中常含有黄

铁矿等硫化物,其在雨水淋溶和铁硫杆菌的共同作用下会产生酸水(式(1)~式(4)),导致重金属释放并在土壤中累积<sup>[61]</sup>。同时,部分煤矸石中迁移能力较强的可氧化态(有机质结合态)和弱酸提取态(离子交换态和碳酸盐结合态)重金属占比较高,也增加了煤矸石中重金属的释放风险。对山西省污染场地煤矸石重金属形态的研究发现,Cu、Ni 和 Zn 以可还原态和可氧化态为主;Mn 以可还原态和酸可提取态(25.38%~44.67%)为主<sup>[62]</sup>。当煤矸石周边环境条件发生变化时,这些形态重金属可释放进入环境,表现出较强的潜在重金属释放风险<sup>[28,63-64]</sup>。



煤矸石堆场周边土壤和地下水重金属污染相关研究也报道较多。YAO 等<sup>[65]</sup>选择重庆市的一个煤矸石堆放区作为研究对象,发现土壤中 Cd 平均含量为 1.23 mg/kg,大多数土壤 Cd 超过了《土壤环境质量标准》(GB 15618—2018)规定的风险筛选值,污染程度为中度~重度。贵州省普安县一煤矸石淋滤液污染农用地,土壤 Cu、Cr、Ni、Zn 和 Hg 含量均值均有不同程度的超标<sup>[66]</sup>。在河南省辉县市龙田煤业程村矿区,以区域背景耕地小麦籽粒重金属含量为评价标准,煤矸石复垦耕地小麦 Cd 污染风险等级达到中度风险<sup>[67]</sup>。雨水冲刷露天煤矸石还会使煤矸石中的重金属及 F<sup>-</sup>、Cl<sup>-</sup>、SO<sub>4</sub><sup>2-</sup>等有害物质随雨水进入土壤,渗入地下水,从而污染地下水(图 2)<sup>[68-69]</sup>。

#### 3.2 煤矸石中重金属释放影响因素

pH 值、有机酸、Fe<sup>3+</sup>、氧化还原条件、煤矸石粒径等均可显著影响煤矸石中重金属的释放。pH 值降低可导致重金属活性升高,煤矸石堆存环境的 pH 值与部分重金属释放存在显著正相关<sup>[62]</sup>。淋溶实验表明煤中 Cu、Zn、As 等随着 pH 值的增大,其从煤中溶出的量减小;而 F、Cr 随着 pH 值的升高,其溶出浓度也随之增大;Pb、Hg 的溶出量与 pH 值的关系不明显<sup>[70]</sup>。根系分泌有机酸可降低环境 pH 值,提高重金属溶出速率,同时有机酸还可以与重金属形成螯合物影响煤矸石中重金属的释放。罗有发等<sup>[71]</sup>向煤矸石中添加少量外源有机酸,如腐殖酸、柠檬酸、草酸、水杨酸等,发现有机酸对煤矸石中重金属元素 Fe、Mn、

①《土壤环境质量 农用地土壤污染风险管控标准(试行)》(GB 15618—2018)。

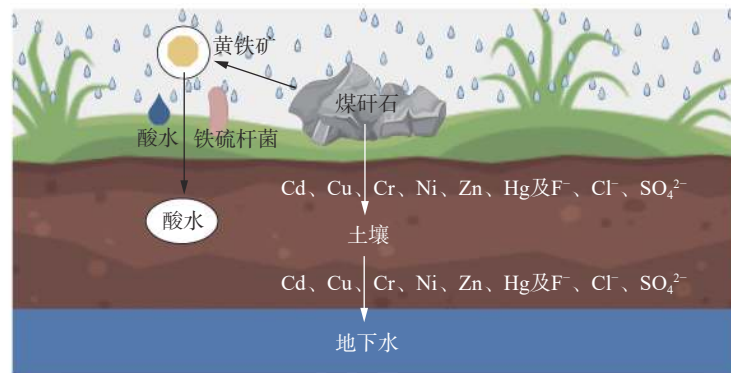


图 2 煤矸石重金属的污染途径

Fig. 2 Pathways of heavy metal pollution caused by coal gangue

Cu、Zn 的溶出具有促进作用,但能有效抑制 Pb 的溶出。煤矸石周边环境中 Fe<sup>3+</sup>浓度可促进煤矸石中黄铁矿的氧化,显著提高 Mn、Cu、Zn、Ni、Cr 等重金属的释放速率<sup>[62]</sup>。付天岭等<sup>[72]</sup>研究发现还原环境下煤矸石堆场浸出液的 pH 值降低不明显,Fe、Mn、Zn、Cu 等污染物质释放显著降低。另外,有研究发现高硫煤矸石的粒径越小,比表面积越大,浸出液的酸性越强,重金属的释放量就越大<sup>[62,73]</sup>。

### 3.3 煤矸石重金属污染防控

煤矸石产酸可导致煤矸石中重金属的释放。目前,煤矸石生态修复利用的重金属污染和酸化防控主要通过接种微生物(硫酸还原性菌)抑制硫铁矿还原产酸或矿化重金属、施加杀菌剂抑制氧化菌和添加重金属钝化剂实现。

#### 3.3.1 微生物技术

寡养单胞菌等微生物可使煤矸石基质中重金属矿化,使之形成磷酸盐、碳酸盐等不溶物,抑制重金属的释放<sup>[74]</sup>。微生物如硫酸还原性菌通过在厌氧环境下还原煤矸石氧化后产生的硫酸盐,提高 pH 值,产生 S<sup>2-</sup>与溶液中重金属离子反应生成难溶性沉淀物<sup>[75]</sup>。硫酸还原性菌可以从煤矸石堆场周边土壤中分离出来,应用于煤矿产生的酸性废水和煤矿酸性废石堆的酸化污染修复中<sup>[76-78]</sup>。朱琦<sup>[1]</sup>还从风化煤矸石中分离出了兼性厌氧的硫酸还原性菌,以解决硫酸还原性菌因厌氧特性限制的在煤矸石山等露天场地的应用。马道之<sup>[79]</sup>研究发现乳酸钠、磷酸氢二钾和碳酸氢钙均有利于硫酸还原菌对煤矸石中重金属的固化。

#### 3.3.2 氧化菌抑制技术

杀菌剂能够在短期内影响氧化菌生物对含硫化化合物的氧化过程,降低氧化速率<sup>[75]</sup>。十二烷基硫酸钠、洗涤剂、丙酮酸等都可作为杀菌剂抑制氧化菌生物活性<sup>[80-82]</sup>。最近,有研究开始选择食品防腐剂和阴离子表面活性剂等环境友好型杀菌剂作为煤矸石的氧

化抑制试剂<sup>[83]</sup>。除此之外,化学-微生物技术常协同使用,可有效抑制煤矸石产酸,降低重金属释放风险,且可以弥补两种方法的缺点<sup>[75,79]</sup>。有研究采用兼性厌氧性硫酸还原性菌 SRB 与十二烷基硫酸钠作为杀菌剂联合使用<sup>[84]</sup>,结果表明煤矸石淋溶液 pH 值显著提高,重金属释放风险显著降低。

#### 3.3.3 重金属钝化技术

向煤矸石基质中加入一定比例的碱性土壤调理剂钝化重金属,也是煤矸石生态修复过程中重金属污染防控的有效手段。重金属钝化剂可通过吸附、沉淀、络合等作用与重金属发生作用,降低煤矸石基质中重金属释放风险,改善煤矸石基质理化性质<sup>[85]</sup>。一些黏土矿物、磷酸盐类、生物炭等重金属钝化剂可于煤矸石生态修复中重金属防控。张悦等<sup>[86]</sup>向煤矸石中添加麦饭石和沸石,发现麦饭石和沸石分别对煤矸石中 Ni 和 Cr 表现出较好的钝化效果。MUNIR 等<sup>[87]</sup>在煤矸石中添加生物炭,发现 Cu、Cd、Pb 和 Zn 的可交换态减少,残渣态升高,煤矸石重金属浸出和生物可利用性的大幅降低。HUANG 等<sup>[88]</sup>发现向煤矸石基质中添加粉煤灰可以有效降低重金属的活性。CaO 和方解石可与煤矸石中重金属形成难溶的羟基化合物沉淀和碳酸盐沉淀,起到钝化煤矸石中重金属的作用<sup>[89]</sup>。

## 4 结论及建议

煤矸石生态修复利用是煤矸石综合利用的有效途径,但其受到产酸和重金属释放的制约。本文综述了国内外煤矸石元素和矿物组分、煤矸石生态修复利用技术和煤矸石中重金属释放和防控技术,得到以下结论,并提出建议。

1)煤矸石以石英和黏土矿物为主,并富含氮、磷、钾和有机质等植物生长需要的营养元素和物质,为煤矸石生态利用提供了物质基础。煤矸石生态修复利用主要包括填沟造地、煤矸石植生基质制备。但

煤矸石生态修复利用需尽可能地大规模使用煤矸石,同时降低成本和环境风险,寻求“基于自然”的大宗工业固废综合利用方案。

2)煤矸石中常含有一定量的重金属,且因煤矸石产酸可导致重金属释放,带来一定的环境风险。煤矸石中重金属的释放受到环境pH值、有机酸、 $Fe^{3+}$ 、氧化还原条件及煤矸石粒径等多种因素影响。但煤矸石中重金属的赋存及其在大规模生态修复利用过程中的环境行为尚不清楚,需要重点关注,从而指导煤矸石生态修复安全利用。

3)微生物技术、氧化菌抑制技术及重金属钝化技术可实现煤矸石生态修复利用中重金属的污染防控。微生物技术需额外碳源成本较高,氧化菌抑制技术存在二次污染风险,重金属钝化技术存在长效性等问题,这些因素限制了相关技术大规模的应用。因此,今后需结合不同煤矸石的性质,研发物理、化学、微生物的联用技术,实现经济可行、二次环境污染风险可控、重金属污染防控效果好的煤矸石生态修复安全利用。同时要加强煤矸石生态修复过程中的重金属污染监测,评价重金属释放环境风险。

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