

Mechanism of Acid Mine Drainage Remediation with Steel Slag: A Review

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Cite This: *ACS Omega* 2021, 6, 30205–30213



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ABSTRACT: Technologies for remediation of wastewater by industrial solid waste have recently attracted interest. Acid mine drainage is an extraordinarily acidic and highly heavy metal ions contaminated leachate which posed some challenges for the environment. Nonetheless, steel slag shows significant potential application prospects in wastewater treatment, due to its excellent physicochemical properties and structures. This paper elaborately reviewed the structure, properties, water treatment applications of steel slags, and the mechanism for removing heavy metal ions from acid mine drainage, discussed the problems existing in industrial wastewater treatment by steel slag, and proposed the solutions for future research, aiming to provide theoretical references for the practical application of steel slag in AMD treatment.



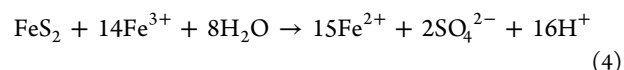
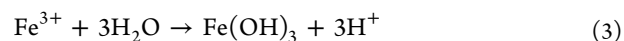
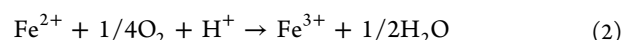
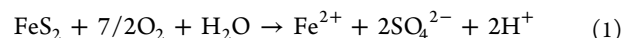
1. INTRODUCTION

As the coal mining industry enters the stage of structural adjustment and transformation, the number of abandoned mines has increased sharply. The legacy of the mining industry in many regions has posed some challenges, such as the threat of groundwater and surface water pollution arising from acid mine drainage (AMD). An abandoned mine containing strong AMD is shown in Figure 1.



Figure 1. An abandoned mine containing strong AMD in the Guizhou region emanating from coal mining activities.

AMD is an extraordinarily acidic and highly contaminated leachate generated from underground workings of closed or abandoned mine sites and accumulations of tailings or mullocks, which is one of the most severe water pollution problems worldwide.¹ The leachate is mainly derived from the oxidation of sulfide mineral ores, which are initially exposed to the environment by intensive mining activities. Notably, among the metal sulfides, pyrite ore (FeS_2) is one of the primary minerals responsible for the generation of AMD owing to the tendency of oxidation when accessed to oxygen, water, and microorganisms. The pyrite oxidation process can be summarized by the following reactions (eqs 1–4):



First, the pyrite is oxidized to ferrous sulfate via the action of excess water and molecular oxygen (eq 1), which is a critical

Received: July 4, 2021

Accepted: October 22, 2021

Published: November 5, 2021



reaction for AMD generation. Subsequently, the Fe^{2+} is oxidized to Fe^{3+} (eq 2); this step is usually a slow process, which is considered a “rate-determining step”. Then a part of Fe^{3+} is precipitated as $\text{Fe}(\text{OH})_3$ (eq 3), while another amount of Fe^{3+} is reduced to Fe^{2+} and forms sulfate by oxidizing pyrite (eq 4). The fourth reaction, where Fe^{3+} acts as the oxidant, shows the complete oxidation of pyrite, and it is also deemed to be faster than the first reaction. All the reactions above are simultaneous processes, which occur and last when there is access to water and oxygen. Therefore, a large number of various toxic trace elements, including Sb, Se, Sn, As, Cd, Co, Zn, Cu, Fe, Ni, and Pb are also released during the oxidation process of minerals and mining water acidification. These high concentrations of toxic heavy metals ions are nonbiodegradable and prone to accumulate in the environment, resulting in various threats in nature ultimately. For example, the direct discharge of untreated AMD may cause toxic effects on organisms in the river; the acidic wastewater can also erode the soil and result in the decay of the plant. Hence, finding effective treatment methods to remove the heavy metal and neutralize the acidity of the AMD will contribute to wastewater treatment and recycling.

In recent years, AMD treatment has been studied through various methods such as constructed wetlands, microorganisms, neutralization, and adsorption. These treatment techniques are described in Table 1. Constructed wetlands

Table 1. Comparison with the Current Method of Remediating AMD

technique	advantage	disadvantage	ref
constructed wetlands	low cost and maintenance	low remediation efficiency	2
	stable effluent and excellent load resistance	poor sustainability	
microorganisms	allows for differential removal of metals	easily affected by the climatic and vegetation environment	1
	no secondary pollution	Remediation efficiency is governed by heavy metal ions.	
neutralization	simple to operate	requires continuous additions of organic substrates	1, 2
	low operating investment	Mo, Cr, and Hg cannot be insolubilized via pH control.	
adsorption	simple to operate	A considerable sludge will be generated.	3
	strong affinity	requires large amounts of neutralizing agents	
	high effectiveness and flexibility	The adsorption capacity of conventional adsorbents is low.	
		Some commercial adsorbents are expensive.	

generally incur low costs and maintenance. However, their remediation efficiency and sustainability largely depend on the climate and vegetation.² Microorganisms are an alternative method to remediate AMD with the advantages of allowing for differential removal of metals and no secondary pollution. Embarrassingly, the remediation efficiency of microorganisms is significantly governed by heavy metal ions. The heavy metal precipitates produced during remediation will be wrapped on the surface of the bacteria, further hindering the substances exchange. Additionally, the growth of microorganisms requires

continuous additions of carbon sources. Neutralization is a quick temporary solution for AMD treatment, with a simple process and low operating investment. Nevertheless, large amounts of neutralizing agents are required in the process and will generate a considerable sludge after remediation of AMD.¹ Notably, adsorption is an essential technique for removing heavy metals from wastewater resulted from its strong affinity and high loading capacity, compared to other approaches. The advantages of adsorption in the purification of wastewaters are its high effectiveness and flexibility. Currently, there is an inevitable trend of finding high-efficiency, low-cost, and readily available adsorbents such as steel slag, fly ash, and kaolin instead of traditional expensive adsorbents for the remediation of AMD.³

China is the largest steel producer in the world. According to statistics, the cumulative production of raw steel in China has gradually increased to 1.053 billion tons as of 2020, where approximately 1 million tons of steel slag have been released. Although steel slag can be used as building materials, the utilization rate is only about 10%.⁴ Notably, as solid wastes produced in the steelmaking process, steel slag, as shown in Figure 2, has excellent adsorption performance and strong

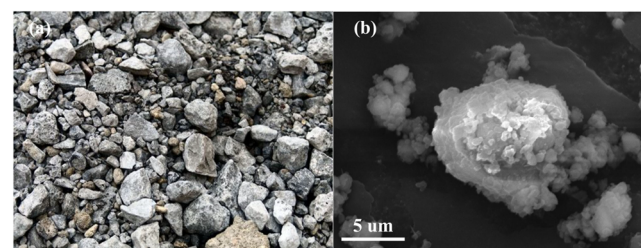


Figure 2. Steel slag from steel-making industry company in China (a) and the SEM image of steel slag (b).

alkali releasing capacity. Thus, the studies of steel slag in removing pollutants from industrial effluents have attracted the attention of many scholars. Name et al.⁵ found basic oxygen slag to be of significant potential as a remediating agent; for simulated AMD with pH 2.5, a sulfate concentration of 5000 mg/L, and an Fe concentration of 1000 mg/L, the slag was capable of increasing its pH to 12.1, removing 99.7% of soluble iron and 75% of sulfate within 30 min. Similarly, Saha et al.⁶ investigated the feasibility of basic oxygen furnace (BOF) slag for AMD treatment; the result showed that steel slag could increase the pH of simulated AMD to 8.6 and remove 99% of heavy metal ions within 24 h under the optimal process parameters. Additionally, Kruse et al.⁷ also observed that the dicalcium silicate (C_2S), tricalcium silicate (C_3S), and free calcium oxide (f-CaO) in steel slag have excellent alkalinity, which is 100–2000 mg/L as CaCO_3 . Moreover, the neutralization ability of steel slag can be as long as ten years. Hence, steel slag could be used as a candidate to replace the traditional expensive adsorbents or alkaline chemicals to remediate AMD.

The development of an inexpensive and available adsorbent has been active in adsorption study. Steel slag as a neutralizing adsorbent shows a good application prospect in wastewater treatment. Herein, the characteristics, mechanism, influencing factors, and application of steel slags in AMD remediation have been reviewed systematically, aiming to provide theoretical references for the practical application of steel slag in AMD treatment.

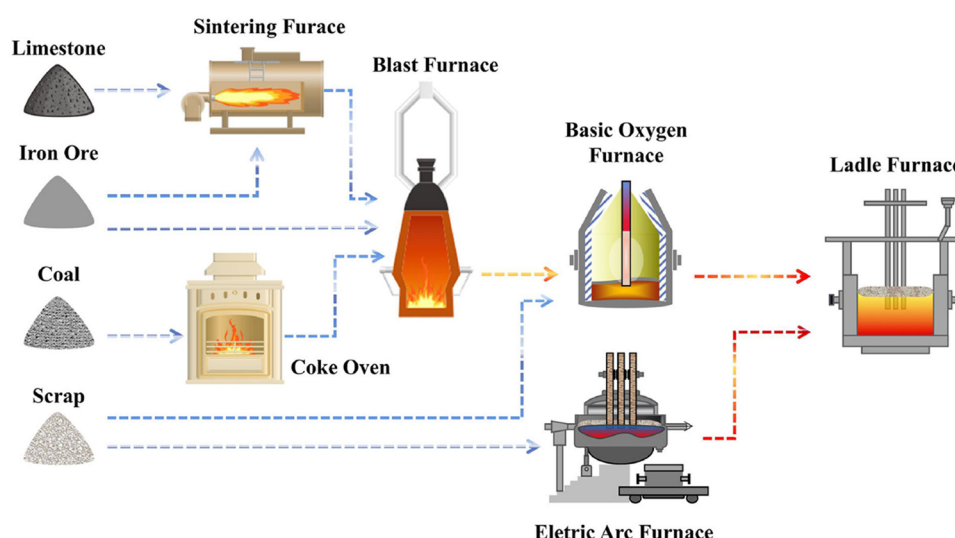


Figure 3. Flow of steelmaking processes. Adapted with permission from ref 8. Copyright 2011 Hindawi.

Table 2. Type and Chemical Composition of Various Steel Slag

type	chemical composition (wt %)								ref
	CaO	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	MnO	TiO ₂	
BOF	45–60	7–20	3–9	10–15	1–5	3–13	2–6		10
	47.71		24.36	13.25	3.04	6.37	2.64	0.67	11
	42–55	10–35		8–20	1–6	5–15	2–8	0.4	12
EAF	30–50	8–22	5–6	11–20	10–18	8–13	5–10		10
	45.5	3.3	1.0	32.2	3.7	5.2	2.0	0.13	13
	46.9	1.07	0.36	33.5	2.30	6.22	2.6	0.16	14
LF	30–60	0.1–1.5		2–35	5–35	1–10	0–5		9
	55		2.1	15	12.5	7.5	0.36	0.33	15

2. THE CHARACTERISTICS OF STEEL SLAG

2.1. The Composition of Steel Slag. Steel slag materials, including basic oxygen furnace (BOF) slag, electric arc furnace slag (EAF), and ladle furnace (LF) slag, are the byproducts from steelmaking industries. Figure 3 shows the flow of the steelmaking processes.

The composition of steel slags is governed by the type of steel produced and the quality of starting raw materials. For example, the chemical composition of BOF slags is prone to have a high CaO content (>35%).⁸ The composition of EAF slags varies significantly, which are composed of 22–60% CaO, 10–40% FeO, 6–34% SiO₂, 3–14% Al₂O₃, and 3–13% MgO.⁸ Also, the composition of LF slags varies within a wide region of 30–60% CaO, 2–35% SiO₂, 5–35% Al₂O₃, 1–10% MgO, and 0.1–15% FeO.⁹

The composition of different steel slags listed in Table 2, which indicated that the main components and contents of varying steel slags vary greatly, and the dominant constituents are CaO, FeO, Fe₂O₃, MgO, and SiO₂, accounting for 30–60%, 2–35%, 0–25%, 1–15%, and 0–35%, respectively.

2.2. The Mineralogical Properties of Steel Slag. The adsorptive capacities of steel slag are closely linked to the mineralogical properties. Moreover, the mineralogical properties of steel slags produced are various from the steelmaking process. Table 3 lists the mineralogical phases of steel slag as reported in literature. The primary mineralogical phases in steel slags include dicalcium silicate (2CaO·SiO₂), calcium ferrite (2CaO·Fe₂O₃), CaO, FeO, MgO, and the RO phase (a solid solution of CaO–FeO–MnO–MgO).⁸ Since the high

Table 3. Mineralogical Phases of BOF, EAF, and LF

slag type	mineralogical phases	ref
BOF	C ₂ S, C ₂ F, RO phase (FeO–MgO–CaO–FeO), MgO, CaO	16
	2CaO·Al ₂ O ₃ ·SiO ₂ , Fe ₂ O ₃ , CaO, FeO	17
	Ca ₂ SiO ₄ , Ca ₃ SiO ₅ , FeO, 2CaO·Fe ₂ O ₃	18
EAF	MnO ₂ , MnO, Fe ₂ SiO ₄ , Fe ₇ SiO ₁₀	17
	Ca ₂ Mg(Si ₂ O ₇), Ca ₂ Fe ₂ O ₅ , Ca ₂ SiO ₄ , CaCO ₃ , FeO, SiO ₂	19
	γ-Ca ₂ SiO ₄ , C ₃ MS ₂ , FeO–MnO–MgO solid solution	20
LF	Ca ₁₂ Al ₁₄ O ₃₃ , β-Ca ₂ SiO ₄ , γ-Ca ₂ SiO ₄ , Ca ₂ Al ₂ SiO ₇	12
	γ-Ca ₂ SiO ₄ , C ₃ MS ₂ , MgO	20

content of FeO in BOF and EAF slag, the solid solution of FeO is one of the main mineralogical phases of BOF and EAF. The FeO content of LF slag is relatively low, and thus the polymorphs of C₂S are typically regarded as the primary phase.

The mineralogical properties of steel slags are associated with the processes employed for cooling the slags after being tapped from the furnace. Generally, the majority of slag-processing approaches for steelmaking plants are slow-cooling and granulation.²¹ It reported that steel slags, after being slow-cooled or granulated, are prone to form more complex oxides and silicates during solidification, which exist as complicated and heterogeneous phases.^{9,11}

Additionally, the adsorbing performance of slags is also affected by the crystallinity obtained upon the solidification process. Several studies suggested that the adsorptive capacity of cations and anions from solution improved by the number of crystalline phases.^{8,21} These crystalline phases mainly

includes gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), akermanite ($\text{Ca}_2\text{MgSiO}_7$), bredigite ($\text{Ca}_5\text{MgSi}_3\text{O}_{12}$), and merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$).⁸ The vital role of the crystalline phase in the process of heavy metal ions sorption can be ascribed to the presence of active sites appearing during the isomorphous substitution of the type $\text{Al}^{3+} \rightarrow \text{Si}^{4+}$ in the above crystalline phases.²¹

2.3. The Physical Properties of Steel Slag. When steel slag cooled from the molten liquid phase to the solid phase, the Ca_3SiO_4 , CaO , MgO , and other components in steel slag may undergo a series of physical and chemical reactions which will change the volume and pore structure of the slag.⁸ Moreover, the adsorbing performance of steel slag is mainly governed by its pore structure.²¹ Therefore, a porous structure with a large specific surface area is a requisite for the excellent adsorptive performance of steel slag. Xue et al.²² proposed that the BOF slags are mesoporous, with an mean pore diameter between 2 and 50 nm. Liu et al.²³ found the average pore diameter and specific surface area of steel slags with different particle sizes are in the range of 17–27 nm and 0.8–1.9 m^2/g , respectively. The results from various studies in Table 4 affirmed that steel slags could be considered chiefly mesoporous adsorbents.

Table 4. Selected Physical Properties of Steel Slag

type	surface area (m^2/g)	pore volume (cm^3/g)	mean pore diameter (nm)	particle size μm	ref
BOF	7.34	0.028	15.9	0.044–0.149	24
EAF	0.142		12.58	0.05–0.63	25
LF	3.04	0.0026	3.21	0.125–0.063 mm	24

However, steel slags with typical low specific surface areas less than 10 m^2/g may limit the adsorption capacity to pollutants in industrial effluent,^{21,24} even though the relative values of the specific surface area of steel slag up to 32 m^2/g has been reported by Feng et al.²⁶ Therefore, it is advisable that steel slags, which have the typically low specific surface area, can be modified to increase the total porosity and specific surface area, thereby enhancing its ability to adsorb.

3. THE MECHANISM OF STEEL SLAG IN AMD REMEDIATION

The adsorption mechanism of steel slag can be divided into physisorption and chemisorptions. Physisorption mainly relies on the van der Waals force between steel slag and pollutants. Chemisorption involves the transfer of electrons between the adsorbate and adsorbent and the formation and destruction of chemical bonds. Among the previous literature, the pseudo-first-order kinetic model (eq 5) and pseudo-second-order kinetic model (eq 6) are commonly applied to explain the controlling mechanism of AMD remediation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_1 (min^{-1}) and k_2 (min^{-1}) are the pseudo-first-order and pseudo-second-order adsorption rate constants, respectively. q_e (mg/g) and q_t (mg/g) correspond to the heavy metal ions adsorption capacity at equilibrium and at time t (min^{-1}), respectively.

A large number of studies confirmed that the process of removing heavy metals by steel slag conforms to the pseudo-second-order kinetics model, which revealed that chemisorptions plays a leading role in removing heavy metal ions.^{11,23} Particularly, chemisorptions includes chemical precipitation, ion exchange, and surface coordination. The mechanism of steel slag in AMD remediation is shown in Figure 4. The entire adsorption process is completed by multiple mechanisms in cooperation, although the dominant role of each mechanism varies from different stages or conditions.

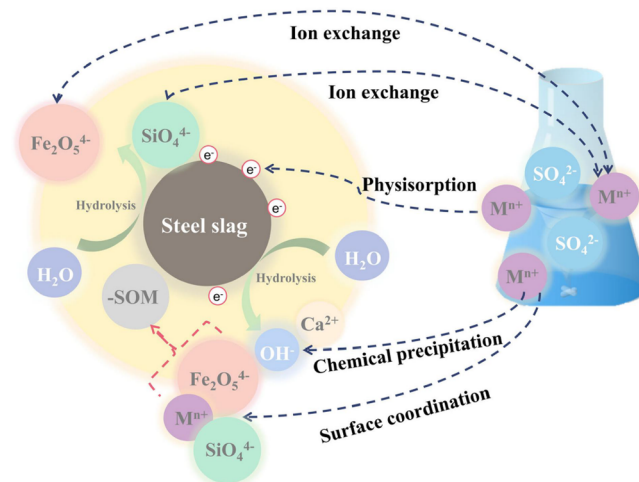
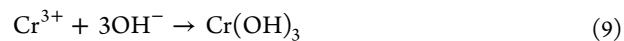
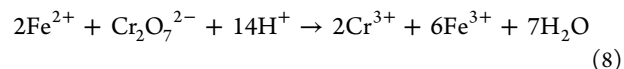
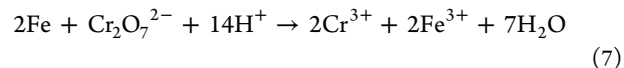


Figure 4. Mechanism of steel slag in AMD remediation.

3.1. The Reduction. Steel slag is equipped with certain reducibility since there remains a small amount of Fe and FeO during the slagging process of steelmaking. That reducibility could provide electrons to the aqueous solution, thereby reducing the high-valence heavy metal ions of the solution. Shu et al.²⁷ found that the Cr^{6+} in wastewater could hardly be removed by steel slag directly; the removal of Cr^{6+} was mainly achieved by reducing the ZVI (zerovalent iron) and Fe^{2+} in steel slag to Cr^{3+} . The mechanism as follows eqs 7–9.



However, this reduction occurs only when the adsorbed metal ions, which have multiple valence states, are in the highest valence state, whereas there is no reduction effect on common heavy metal ions such as Pb^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} .

3.2. The Chemical Precipitation. The MgO , CaO , and other alkaline substances in steel slag have hydration reaction activity which can release a large amount of alkalinity after hydrolysis increasing the pH value of acidic wastewater; when the solubility product (K_{sp}) of the contaminant is reached, the precipitate is formed and separated from the wastewater to achieve the purpose of removing the heavy metals. Shao et al.²⁸ applied steel slag-derived CSH-based nanocomposites to remove the heavy metal ions from wastewater with high efficiency. The study confirmed that the heavy metal ions adsorption depend on the release of OH^- and Ca^{2+} from CSH;

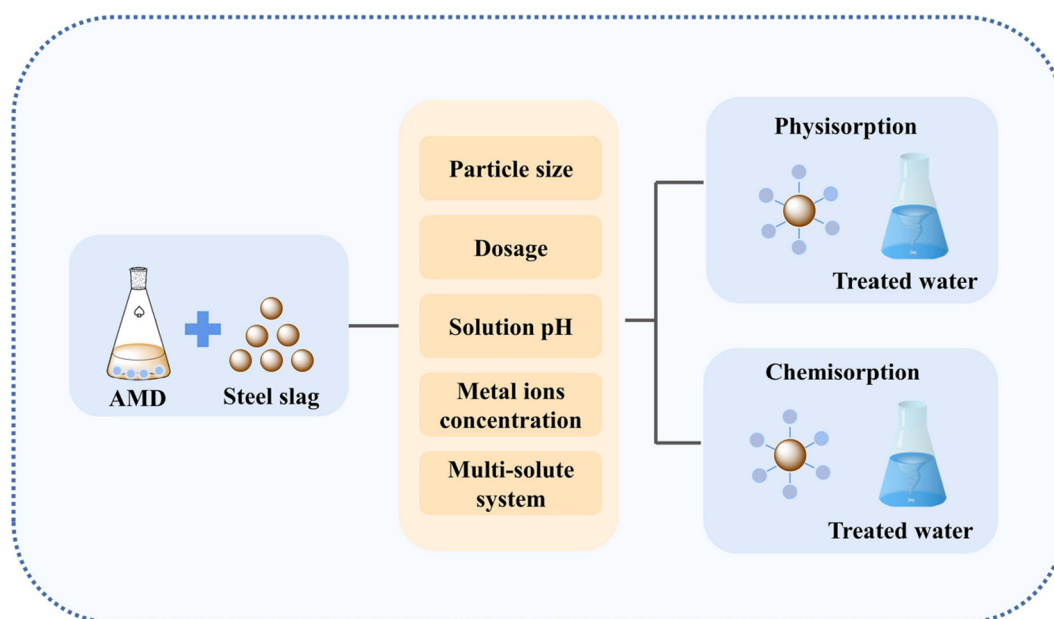
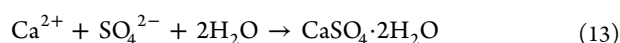
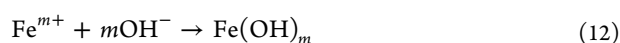
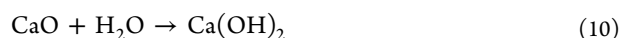
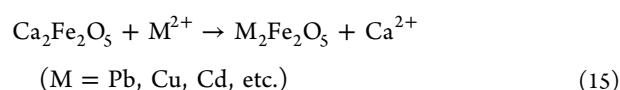
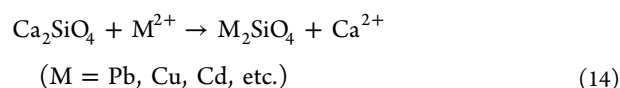


Figure 5. Factors affecting the entrapment of metal ions in AMD by steel slag.

the fast adsorption rate and high adsorption capacity resulted from the weak alkaline environment. Moreover, Name et al.⁵ also confirmed that the removal of Fe^{2+} in AMD by BOF slag was due to the release of alkalinity that leads to precipitation; the reduction of sulfate in AMD could be ascribed to the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). As the pH increases, the reactions involved in removing iron and sulfate are presented as eqs 10–13.

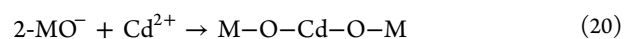
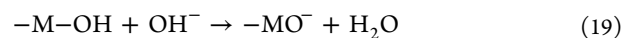
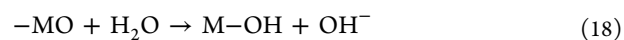
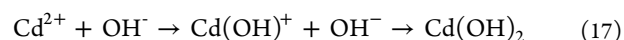
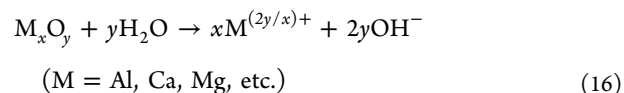


3.3. The Ion Exchange. Most of the Ca^{2+} in steel slag derived from Ca_2SiO_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ is in the crystalline phase, and the Ca^{2+} can be exchanged with the metal cations in the solution. These cations can be adsorbed to the surface of steel slag mainly through electrostatic attraction. The process where the Ca^{2+} in the lattice of Ca_2SiO_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ is replaced by the heavy metal ions is described as eqs 14 and 15.



The above reactions are consistent with the findings of Feng et al.,²⁶ who confirmed that the removal of heavy metal ions was achieved by the ion exchange between the Ca^{2+} in steel slag and heavy metal ions. Additionally, the cation-exchange selectivity is related to the ion valence state, effective hydration radius, and other factors. In particular, the higher the ion valence state, the smaller the hydration radius, the easier it is for ion exchange to occur.²⁴

3.4. The Coordination. Because steel slag is mainly composed of silicon, aluminum, calcium, iron, and other oxides, the ion coordination on the surface of these oxides is not saturated. With access to metal ions, the active site will be occupied by heavy metal ions, forming insoluble or soluble salts on the surface, thereby being fixed in steel slag.²⁹ Besides, steel slag will contact water to form a hydroxylated M–OH group, which can react with the heavy metal cations to develop further complexes, removing the heavy metal ions in the wastewater.²⁸ Duan et al.²⁹ experimented on the removal of Cd^{2+} in acidic aqueous solutions by alkali-modified steel slag. The results showed that the removal mechanism of Cd^{2+} by modified steel slag is related to surface coordination. The process follows eqs 16–20:



4. INFLUENCING FACTORS OF AMD TREATMENT BY STEEL SLAG

The physicochemical and surface properties determined the performance and mechanism of steel slag in removing heavy metal ions in AMD. Notably, as indicated in Figure 5, the initial pH, the dosage, and particle size of steel slag, the initial concentration of heavy metal ions, and other factors also affecting the entrapment of metal ions in AMD by steel slag. Therefore, this section discussed detailed the influence of different parameters on remediating AMD by steel slag.

4.1. Effect of Particle Size. The mass transfer kinetics of a heterogeneous system is governed by particle pore structure, including specific surface area, particle porosity, specific pore

volume, and particle size distribution. That means the particle size has a significant influence on the adsorbing performance by steel slags.

For steel slag with a mesoporous structure, the dispersion force enhanced with the decrease in pore radius; the adsorption force field existing in the pore space and the adsorption potential of van der Waals force in the pore also improved. Furthermore, since the surface area of steel slag increased with the decrease in particle size, the probability of metal ions being adsorbed through Emre diffusion and intraparticle diffusion enhanced. Consequently, the adsorption capacity and removal efficiency of steel slags for metal ions increased accordingly.²⁰ Moreover, the diffusion resistance of mass transfer is more remarkable for steel slag with a large particle size because of the longer diffusion path length and the blockage of surface sites. Abd El-Azim et al.³ confirmed that the removal performance of Cd^{2+} and Mn^{2+} by WS-EAF slag was related to particle size; the removal efficiency of Cd^{2+} and Mn^{2+} increased with a decrease in particle size of WS-EAF slag. Additionally, the reduction of particle size is also conducive to releasing alkaline components in steel slag. Meanwhile, the rate of the ion-exchange process is also negatively correlated with the particle size of steel slag. However, in porous materials, the pores with small particle sizes might be crushed, resulting in a reduction in adsorption capacity.⁶ For instance, Liu et al.²³ found that the adsorptive efficiency of Pb^{2+} was improved from 46.5% to 96% as the granularity of steel slag decreased from 25 to 18 mm to 0.125–0.09 mm, whereas further reduction of the granularity was not conducive to the adsorption.

4.2. Effect of Steel Slag Dosage. Although steel slag has the excellent ability to decontaminate AMD, the percentage removal for the heavy metals is related to the optimum doses of the adsorbing material.

Generally, increasing the dosage of steel slag will improve the number of total available active binding sites at any given solution volume, thereby promoting its adsorption efficiency. Dimitrova et al.³⁰ confirmed the positive correlation between the dosage of g-BFS (modified steel slag) and the adsorptive efficiency of Pb^{2+} , and the adsorption mechanism of Pb^{2+} was mainly related to the ion exchange, where the Ca^{2+} released from g-BFS to create the active binding sites for Pb^{2+} . Hence, promoting the dosage of steel slag will increase the amounts of adsorption sites and facilitate the adsorption equilibrium for metal ions. Similarly, Han et al.³¹ found the adsorption efficiency and rapid kinetics of Cr^{6+} improved with an increase in dosage of BOF slag at the initial stage of the adsorption. Because the removal of Cr^{6+} was through the redox process involving Fe^{2+} , the concentration of solubilized Fe^{2+} available for the redox reaction and the removal efficiency of Cr^{6+} increased with the increase in slag mass.

Actually, the amount of adsorbent has a significant impact on the design size of the reactor and the overall [processing cost](#) for wastewater treatment. Considering the limited adsorption capacities of steel slag, large quantities of slag would be a requisition for attaining the effluent discharge standards in China,²¹ which essentially poses a challenge in terms of reactor size. Thus, it is necessary to develop some promising methods to improve the adsorptive capacities of steel slags.

4.3. Effect of Solution pH. The solution pH has a distinct impact on the treatment of AMD by steel slag. One objective to remediate AMD is to increase the pH level from acidic to neutral or basic. Researchers have used various waste materials to enhance the pH of the AMD. Fly ash, metallurgical slag, and

cement kiln dust can improve the pH of AMD from 2 to the range of 8–12.⁵ Among the various alkaline industrial wastes, BOF slag has more potential to enhance the pH from 2.5 to 12.1.²⁹

Meanwhile, it has been observed that with the increase in solution pH, the removal of metal ions in AMD is more significant. The influence of pH on the process of AMD remediation is chiefly by the functional groups, the surface-active sites, and the precipitation process from the release of OH^- .²² Moreover, the removal performance of steel slag on cations has relations with the OH^- and H^+ concentration in the solution; the solution with a high OH^- concentration is favorable for the adsorption or precipitation of cations.

On the other hand, the pH value is affiliated with the zero point of charge (pHzpc), and the adsorption of anions and cations is affected by the pHzpc of the solution. The surface of steel slag is positively charged at $\text{pH} < \text{pHzpc}$ and neutral at $\text{pH} = \text{pHzpc}$. Notably, the surface of steel slag is negatively charged when $\text{pH} > \text{pHzpc}$, which is conducive to the adsorptive uptake of metal ions. Zahar et al.³² found that the removal performance of Mn^{2+} by steel slag strengthened by the increase of pH, and the percentage removal of Mn^{2+} exceeded 93% at pH 3.0–8.0. Duan et al.²⁹ also observed a similar tendency; with an increase in solution pH, the competition of H^+ attenuated, and large amounts of positively charged Cd^{2+} hook up the free binding sites. Therefore, the amount of Cd^{2+} adsorbed on the surface of steel slag increased, and the removal efficiency of Cd^{2+} was more than 99.0% at pH 4.0.

4.4. Effect of Metal Ion Concentration. The metal ion concentration in solution is one of the critical parameters affecting the removal characteristics of steel slag. Several studies have investigated the factors of the metal ion concentration in solution on the adsorptive performance of steel slag. The authors found that the adsorbing performance of steel slag was promoted by the increase in initial metal ion concentration because of the strengthened driving force that overcomes the mass transfer resistance between the liquid and solid phases. For instance, Abd El-Azim et al.³ found that the adsorptive efficiency of steel slag increased with the increase of the initial concentration of Cd^{2+} in the solution. Since the external diffusion is considered a rate-controlling step, a higher solute concentration is beneficial to strengthen the driving force and weaken the resistance of external diffusion for metal ions.³³ Xue et al.³⁴ also observed a similar trend, as the metal ion concentration increase, the removal efficiency of Pb^{2+} by BOF slag increased. Notably, other researchers have found diametrically opposite results. Wang et al.³⁵ argued that the metal ions tend to be adsorbed and removed at low initial metal ion concentration because of the high availability of free adsorption sites and surface area, whereas the total available active sites are limited by the higher initial concentration, causing a reduction in adsorption to metal ions. For instance, Han et al.³¹ also reported that in the adsorption system where the initial concentration of up to 100 mg/L Cr^{6+} , the slag wholly adsorbed. Whereas with the concentration of Cr^{6+} improved to 150 mg/L, the adsorption efficiency of steel slag dropped to 65%.

4.5. Effect of Multisolute System. Since AMD generally contains multiple solutes, there is the synergistic or antagonistic competitive effect between ions in multisolute industrial effluents, which is not conducive to the ability to remove metal ions. Although several studies have proposed that multisolute adsorption involved a synergistic combination

of multiple mechanisms such as surface complexation, ion exchange, and chemical precipitation. However, the relative contribution of these mechanisms is still unclear, which is mainly due to the heterogeneity of the slag and the complexity caused by the interaction of metal ions in the multi-ion system.²¹ Besides, the interpretations of experimental data for multisolute adsorption seems inconsistent, and the mechanisms are yet to be further investigated. Some researchers have attempted to clarify the selectivity sequence of multi-ion competitive adsorption. For instance, Dimitrova³³ experimented with competitive adsorption in AMD containing Cu^{2+} , Ni^{2+} , and Zn^{2+} and reported that the adsorption sequence followed the selectivity sequence $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$.

Besides, several studies confirmed that for typical cations in AMD, the sequence of selectivity in multisolute systems is associated with the interaction of intricate factors, including the hydration energy, electronegativity, cationic radii, first-order hydrolysis constant, and solubility constant.³⁴ Xue et al.³⁴ conducted a competitive adsorption study in AMD consisting of Pb^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+} and proposed that the selectivity sequence followed $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The preference for adsorbing performance of Pb^{2+} could be ascribed to the lower hydrate ion radius, lower hydration energy, and higher electronegativity that contribute to more intense electrostatic interaction with the active functional groups on the surface of slag.

5. THE APPLICATION AND PERFORMANCE OF STEEL SLAG IN AMD

Steel slag has unique advantages in the treatment of AMD compared with other industrial wastes, not only because it can release large amounts of alkaline substances, raising the pH of a solution and neutralizing the hydrogen ion in AMD, but also because it has excellent removal performance for heavy metal ions and sulfate. Zvimba et al.³⁶ confirmed that the removal of acidity, Fe^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} , was characterized by rapid kinetics. And the fast removal kinetics of acidity was attributed to the quick release of alkalinity from steel slags under mildly acidic conditions. Oh et al.³⁷ employed steel slag as an adsorbent to remove As^{3+} and As^{5+} in acidic aqueous solutions. The study showed that a part of the Ca^{2+} in steel slag could form amorphous CaCO_3 under alkaline conditions; the As^{3+} and As^{5+} in the aqueous solution would be removed by being coprecipitated or adsorbed with amorphous CaCO_3 . According to the research of Abd El-Azim et al.,³ WS-EAF slag could remove large amounts of Cd^{2+} and Mn^{2+} from aqueous solutions, showing great potential in the remediation of industrial effluent. Therefore, the WS-EAF slag with long-term stability could be used as an excellent recyclable adsorbent for Mn^{2+} and Cd^{2+} .

However, several minor components present in steel slag tend to concentrate on the slag surface during crystallization, affecting the adsorption to pollutants. Moreover, due to the limited pore structure of steel slag, the internal components are unavailable for utilization efficiently, resulting in a limited adsorption efficiency of steel slag. Several researchers have employed various activation technologies to improve the adsorbing performance of steel slag.^{29,38,39} Duan et al.²⁹ tested the ability of the modified steel slag to remove Cd^{2+} from AMD. It confirmed that the adsorption of Cd^{2+} by modified steel slag is enhanced since the active site in the slag modified with aluminum hydroxide increased significantly, promoting the Cd^{2+} to diffuse to the surface of the slag. Chen et al.³⁸

prepared acid-modified steel slag as a new type of adsorbent to remove U^{6+} in an aqueous solution. The study found that steel slag modified with sulfuric acid has a rich pore structure and a larger specific surface area. Meanwhile, it also has more functional groups (such as $-\text{OH}$), resulting in the adsorption efficiency of uranium significantly improved. Owing to the relatively stable composition in steel slag, high-temperature treatment of steel slag would crack the dense surface of steel slag and release internal energy, making the surface area more loose and porous, increasing the specific surface area of steel slag, thereby improving the adsorption capacity. Zhan et al.³⁹ employed bentonite-steel slag composite particles (BSC) as an adsorbent to treat AMD containing Pb^{2+} . Due to the strong alkali release capacity of steel slag and the excellent adsorption potential of bentonite for heavy metal cations, the adsorbent can effectively neutralize acidic substances from AMD and achieve complete removal of heavy metal ions Pb^{2+} . All these technologies utilized may modify the morphology and structure of steel slag, the types and amounts of surface functional group, and other properties, thereby improving the adsorption of pollutants through steel slag.

6. CONCLUSIONS

The performance of steel slag is governed by specific properties such as physical, chemical, and mineralogical characterization. Thus, the limited pore structure potentially hindered the application of steel slag in industrial wastewater. Nevertheless, the morphology and structure of steel slag, the types and amounts of surface functional group, and other properties can be significantly improved by purposefully performing activation, thereby enhancing the efficacy of the slag-based adsorbent.

Indeed, the adsorption mechanism is relatively intricate because of the complex chemical composition and mineralogical phase of steel slag and the complexity of multisolute adsorption. Although some researchers have attempted to investigate the adsorption mechanisms of the multisolute system detailed, the interpretations of experimental data seem inconsistent. Hence, in-depth studies in multisolute adsorption of industrial effluent are requisite for understanding the synergistic or antagonistic competitive effects in adsorption phenomena.

Steel slag employed to remediate the AMD is the waste that accumulates high concentrations of the heavy metal ion, and only a few studies have attempted to explore the other application of spent-slag after wastewater treatment. Therefore, to alleviate the environmental challenges related to steel slag loaded with high concentrations of toxic metal ions, improving the reuse, recycling, regeneration, and immobilization treatment of the spent slag is one option for future research.

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Notes

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from the Graduate Student Innovation Program of Chongqing University of Technology (No. clycx 20203064) and the Project of Guizhou science and Technology Department (No. 20204Y007).

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