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A critical review on approaches for electrolytic manganese residue treatment and disposal technology: Reduction, pretreatment, and reuse

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ARTICLE INFO	A B S T R A C T
Editor: Dr. L. Haizhou	Electrolytic manganese residue (EMR) has become a barrier to the sustainable development of the electrolytic metallic manganese (FMM) industry. FMR has a great potential to harm local ecosystems and human health due
Keywords: Electrolytic manganese residue	to it contains high concentrations of soluble pollutant, especially NH [‡] and Mn ²⁺ , and also the possible dam break risk because of its huge storage. There seems to be not a mature and stable industrial solution for EMR, though a
Environmental pollution Ammonia nitrogen	lot of researches have been done in this area. Hence, by fully considering the EMM ecosystem, we analyzed the
Manganese Treatment and disposal technology	tion, pretreatment, and reuse; indicated the factors that block EMR treatment and disposal; and proposed

1. Introduction

1.1. Current status of the EMM industry

Manganese is one of the most strategic metals. Manganese and its compounds are widely used in metallurgy, chemistry, batteries, fertilizers, feed additives, especially, the ferroalloy industry, which consumes for more than 90% (Banerjee et al., 2017; Camargo et al., 2018; Ghosh et al., 2016). Steel cannot be produced without manganese since it could significantly improve the strength, hardness, and toughness of steel with limited quantities, generally 0.3 wt%–0.8 wt% (Matlock and Speer, 2010; Lee and Han, 2014; Elliott et al., 2018; Benzing et al., 2019; Pierce et al., 2015).

Manganese mainly exists as manganese ores in nature, and manganese ores are geographically varied (Li et al., 2018; Zhan and Zhang, 2019). South Africa, Ukraine, Brazil, Australia, India, China, Gabon, and Mexico account for almost 97.39% of the global reserves (690,000 kt) with a grade of 15%–50% (Fig. 1a). China only takes 6.23% (43,000 kt) manganese ore reserve of the global, and it could be widely found all over the country with a low grade (15–30%), as shown in Fig. 1b. There are many manganese ores, mainly pyrolusite (MnO₂), pink rhodochrosite (MnCO₃), rhodonite ((Mn, Ca)SiO₃), black manganite (MnO·OH) and alabandite (MnS), while the dominant raw materials of the electrolytic metallic manganese (EMM) industry are pyrolusite and rhodochrosite (Du et al., 2013b; He et al., 2016; Singh and Biswas, 2017; Zhang and Cheng, 2007).

plausible and feasible suggestions to solve this problem. We hope that the results of this review could help solve

the problem of EMR and thus promote the sustainable development of EMM industry.

Metallic manganese can be produced by the aluminothermic method (Kavitha and McDermid, 2012), the electro-silicon thermic method (Randhawa et al., 2018; Heo and Park, 2018), and the electrolytic method (Xu et al., 2014; Lan et al., 2019b; Shu et al., 2018a), which are comparatively analyzed in Table S1. The electrolytic method, also known as the "leaching-purification-electrodeposition" process, is widely applied in EMM industry because it could adopt comparatively low-grade manganese ores (8%–15%) and yield EMM with a purity higher than 99.8%. Currently, almost all EMM is produced in China and South Africa, of which China accounts for over 97% of the total EMM (Zhang et al., 2020).

Fig. 2 presents the flowchart of EMM production by the electrolytic

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Received 22 December 2020; Received in revised form 10 May 2021; Accepted 24 May 2021 Available online 2 June 2021 0304-3894/© 2021 Elsevier B.V. All rights reserved. method (Shu et al., 2018a). After grinding to powders, H_2SO_4 is used to leach Mn^{2+} . At the same time, impurities such as Fe^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} are also leached out into the liquid from the manganese ores.

These impurities would significantly influence the following processes, reducing the current efficiency and EMM purity. Therefore, Fe²⁺ in the leaching liquid is removed as Fe(OH)₃ precipitate first by adding pyrolusite to oxidize it to Fe³⁺, and then adjusting the liquid pH with NH₃·H₂O. Meanwhile, NH₃·H₂O is also used to maintain leaching liquid pH at 6.5–7.0 to ensure the electrolysis process. After that, sodium dimethyl dithiocarbamate (SDD) is used to remove other heavy metal ions, mainly Cu²⁺, Ni²⁺, and Co²⁺. Consecutively the liquid and the residues are filtrated and the filter cake are called as electrolytic manganese residue (EMR). After that, SeO₂ is added into the liquid to

improve the current efficiency before final electrolysis. In this way, the purity of the resulting EMM is higher than 99.8% after passivation, washing, drying, and stripping. Related reaction equations can be presented as:

$$(Mn, Fe, Mg)CO_3 + 2H^+ \rightarrow (Mn^{2+}, Fe^{2+}, Mg^{2+}) + H_2O + CO_2\uparrow$$
 (1)

$$2Fe^{2+} + MnO_2 + 2H^+ \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$
 (2)

$$2Fe^{3+} + 3NH_3 \cdot H_2O \rightarrow 3NH_4^+ + Fe(OH)_3\downarrow$$
(3)

$$(\mathrm{Cu}^{2+}, \mathrm{Ni}^{2+}, \mathrm{Co}^{2+}) + 2(\mathrm{CH}_3)_2 \mathrm{NCSS}^{-} \rightarrow ((\mathrm{CH}_3)_2 \mathrm{NCSS})_2 (\mathrm{Cu}, \mathrm{Ni}, \mathrm{Co}) \downarrow \qquad (4)$$

As described previously, 8–12 tons of EMR will be generated for each one ton of EMM (Duan et al., 2011a; Zhang et al., 2017d). Currently,





Fig. 1. Manganese ore reserves of the world and China (kt metallic manganese): (a) World manganese ore reserves (kt metallic manganese) and distribution in 2016, (b) China manganese ore reserves (kt metallic manganese) and distribution in 2018 (Shanghai Metals Market, 2018).

over 150 million tons of EMR have been generated in China, with an increase rate of 10 million tons per year (Shu et al., 2018a, 2019c).

EMM production enterprises in China primarily located in Ningxia, Guangxi, Guizhou, Hunan, and Chongqing (Fig. 3). As shown in Table S2, China had an EMM production capacity of 2.64 million tons, with an annual output of around 1.5 million tons (Shanghai Metals Market, 2018). In addition, production capacities in South Africa and Indonesia are respectively 43,000 tons and 16,425 tons per year. As shown in Fig. S1, the EMM production in China is 1.01–1.6 million tons, with an average annual output of 1.32 million tons in the year of 2010 – 2018. The mainly export countries for China in 2018 are Korea, Japan, Netherlands, Russian Federation, and India, accounting for 74% of the total (Fig. S2).

1.2. Characterizations and ecoenvironmental impact of EMR

EMR characterizations, presented in Fig. S3, showed that pH value of EMR was 4.00–6.40, with a specific surface area of 3.00–9.66 m²/g. Its particle size was 17.37–80.00 μ m, with a moisture content of 18.6%–30% (Du et al., 2013a; Hou et al., 2012; Zhou et al., 2013). EMR chemical compositions are given in Table S3, mainly examined by XRF. The total content of SiO₂, Al₂O₃, Fe₂O₃, and CaO in EMR is 43.31%–72.85%, and these four are the primary chemical components of building materials. Therefore, EMR is a potential raw material for building materials. EMR contains many soluble hazardous ions, including Cu²⁺, Zn²⁺, Cr⁶⁺, Cd²⁺, Se⁴⁺, Pb²⁺ and Ni²⁺, beside those are Mn²⁺ and NH⁴ (Table S4).

Although yards or dams are established, EMR still posing a significant ecoenvironmental risk to the surrounding soil and water due to imperfect anti-seepage measures. In open EMR yards, EMR may occupy a great deal of land, and soluble ions (especially Mn^{2+} and NH_{4}^{+}) could move with rains, leading to severe ecoenvironmental issues (Yang et al., 2012; Duan, 2009; Jiang et al., 2011; Luo et al., 2019; Li et al., 2014). EMR is harmful to plant growth (Lu et al., 2018; Wang et al., 2019a), human health (Xu et al., 2011; Frisbie et al., 2012; Shu et al., 2019; Abu Hasan et al., 2014; Liu et al., 2017), and aquatic animals and plants (Niu et al., 2013). It has been reported that, from 2009 to 2012, more than

four dam-break accidents occurred in Hunan and Guizhou, killing nine people, causing significant property losses and pollution. All these influences caused by EMR are summarized in Fig. 4.

EMR reduction can reduce the total amount of EMR from the beginning, and the pollutants in EMR can be removed by pretreatment. EMR reuse could adopt EMR as secondary materials either for valuable resource recovery or directly for preparing products. Therefore, EMR reduction, pretreatment and reuse can not only solve the current shortage of manganese resources, but also bring huge environmental and economic benefits to the society.

Over the past few years, China is devastating in ecoenvironmental protection (Cai and Ye, 2020; Chen et al., 2020). The government forced EMM enterprises to dispose of EMR. Although many EMM plants and researchers have tried to do so since late 1990s, there seems to be no mature and stable industrial application. Thus, in China, EMR has become a significant issue since it is blocking the sustainable development of the EMM industry. To the best of our knowledge, there seems to be no systematic review on how to treat EMR.

Herein, we comprehensively investigated the state-of-the-art technologies and their corresponding industrial implementations for EMR reduction, pretreatment, and reuse, highlighted the factors that hinder pollution control and circular utilization for EMR. Analyzed the advantages and limitations of the existed EMR treatment and disposal technologies, proposed plausible and feasible suggestions to solve the EMR issue.

2. EMR reduction

EMR reduction, means to minimize EMR's volume and mass, and thus to reduce its impact on the ecosystem. Generally, EMR reduction refers to reduce the generated EMR, while this could be expanded to EMR source reduction which includes improving the manganese ore grade (beneficiation and enrichment), increasing the leaching efficiency of Mn^{2+} , separation of iron from leaching solution before final filtration, and reducing its moisture content (Table 1).



Fig. 2. Technical flow chart of EMM.



Fig. 3. EMM production enterprises of China in 2019.



Fig. 4. Influence of EMR on the environment and fauna.

2.1. Beneficiation and enrichment

Manganese ore beneficiation and enrichment is a global problem, because impurities such as phosphate, iron, and associated metals (Cu, Ni, Zn, and Pb) are difficult to separate. Beneficiation and enrichment, or in other words, reducing the impurities of manganese ore, could effectively reduce the amount of EMR.

Beneficiation and enrichment methods for manganese ores include physical beneficiation, such as wet gravity separation, high-intensity magnetic separation, flotation, microwave heating, and combined with those methods. Wet gravity separation is used to enrich manganese-containing minerals from manganese raw ores based on the density difference of minerals, and the maximum recovery efficiency of MnO could be 91.1% (Muriana, 2015). However, this method is not effective enough to separate iron minerals from manganese minerals due to their ignorable density difference. High-intensity magnetic separation is a common technology to separate iron minerals and manganese minerals because of their differences in magnetic susceptibility. Manganese could be concentrated to over 45% after high-intensity magnetic separation with a recovery efficiency of Mn almost 90% (Fig. S4a) (Wu et al., 2014a; Tripathy et al., 2015; Mishra et al., 2009). Manganese grade can be increased from 30% to 40% by microwave heating (Fig. S4b) (Chen et al., 2017). Mn recovery efficiency could be 64% by a combined process with high-gradient magnetic separation and hydrometallurgical method, and MnCO₃ with a purity of 97.9% can be obtained (Fig. S4c) (Zhang et al., 2017c). By flotation with linoleate hydroxamic acid, manganese grade can be increased from 10.7% to 18.3% with a recovery efficiency of 97% (Fig. S4d) (Zhou et al., 2015). Although the mentioned methods are able to beneficiate and enrich manganese grade, it was too tricky to enrich low-grade manganese ore

Table 1

Overview of EMR reduction.

Beneficiation and enrichment Methods	Concentrate grade of	Recovery	Notes	References
	Mn	efficiency		
Wet gravity separation	NA	91.1%	1. It is extremely hard to enrich low-grade manganese ore better with a single method.2. The combined beneficiation processes and automatic	(Muriana, 2015)
High-intensity magnetic separation	22.8%	89.9%	equipment with large-scale and high-efficiency need to be developed.	(Wu et al., 2014a)
Two-stage magnetic separation	22.4%	44.7%		(Tripathy et al. 2015)
Dry belt type magnetic separator	45%	69%		(Mishra et al., 2009)
Microwave heating	40%	NA		(Chen et al., 2017)
High-gradient magnetic separation	30%	64%		(Zhang et al., 2017c)
Flotation with linoleate hydroxamic acid	18.3%	97%		(Zhou et al., 2015)
Leaching Mn ²⁺ with high efficiency				
Raw materials	Methods	Mn ²⁺ leaching efficiency	Notes	References
Manganese carbonate ores	H ₂ SO ₄	96.2%	1. Acid leaching is proven and simple, but the equipment is easily eroded, and easy to cause pollution.2. Traditional processes rarely used in industrial	(Liu et al., 2014)
Manganese oxide ores	SO ₂	95.5%	production due to their complicated leaching conditions and poor applicability.3. It is difficult to break through the water balance problem,	(Li et al., 2015a)
Manganese oxide ores	CaS	> 95%	and the soluble salt is easy to enrich.	(Sun et al., 2013)
Manganese oxide ores	HCl	97.1%		(Ding et al., 2016)
Low-grade pyrolusite	Lignin and H_2SO_4	91%		(Xiong et al., 2018)
Low-grade pyrolusite	Microwave pyrolysis	92%		(Li et al., 2019b)
Manganese dioxide ore	Alicyclobacillus sp. and Sulfobacillus sp.	99%		(Xin et al., 2015)
Low-grade manganese dioxide	Electric field enhancement	98.2%		(Zhang et al., 2017b)
Separate iron from leaching solution				
Methods	Notes			References
Ammonium hydroxide and MnO ₂	Fe^{3+} removed as $\mathrm{Fe}(\mathrm{OH})_3$.	Fe ²⁺ was oxidized	to Fe^{3+} by MnO ₂ , and then removed as Fe(OH) ₃ .	(Yan and Qiu, 2014)
$CaCO_3$ in a wet stirred ball mill	Ball milling increased the n	reactivity of CaCO ₃	, and increased the reaction efficiency of \mbox{CaCO}_3 and iron.	(Wang et al., 2019b)
EMR moisture content control				
Methods	EMR moisture content	Notes		References
Dodecylamine	It decreased from 41.1% to 34.1%.	It can effectively r	educe the moisture content of EMR.	(Hao and Qiu, 2015)
Sodium dodecyl benzene sulfonate	It decreased from 29.5% to 26.3%.			(Sun, 2018)

NA: Information not available.

to a satisfied one just by one single method.

2.2. Leaching Mn^{2+} with a high efficiency

After increasing manganese grade in its ores to reduce the final amount of EMR, the second step to reduce EMR is try to improve the leaching efficiency of Mn^{2+} .

Manganese carbonate ore (rhodochrosite) could be leached directly via H_2SO_4 , and Mn^{2+} leaching efficiency over 96% in EMM production (Liu et al., 2014). Meanwhile, with the increasing consumption of rhodochrosite, its reserves is also decreased. Hence, researches in this area are limited. Manganese oxide ore (pyrolusite) and low-grade pyrolusite can expand the available raw materials for EMM production, and a number of studies has been devoted on this area. Pyrolusite needs be inverted from tetravalent Mn to divalent form before leaching. CaS can improve Mn leaching efficiency of pyrolusite to over 95%, because MnO₂ in pyrolusite can be reduced to Mn_3O_4 by CaS (Li et al., 2015a). When SO₂ is pumped into the grinding manganese ore solution, Mn^{4+} could be reduced to Mn^{2+} , with a leaching efficiency over 95% (Fig. 5d) (Sun et al., 2013). Mn^{2+} leach efficiency from pyrolusite could be 96.6%

when bismuthinite is used as reductant in the hydrochloric acid (Ding et al., 2016). For low-grade manganese ores, H_2O_2 is applied as reductant to improve the reducibility of the hydrochloric acid leaching system, and Mn^{2+} leaching efficiency could reach above 97% (Fig. 5a) (El Hazek et al., 2006). By roasting with sulfur, a leaching efficiency of 95.6% for manganese oxide ores can be reached using H_2SO_4 as the leaching (Zhang et al., 2013). Using lignin, a low-cost and environmentally friendly reductant, to reduce Mn^{4+} to Mn^{2+} by H_2SO_4 , 91% of manganese could be leaching out from manganese oxide ores (Fig. 5b) (Xiong et al., 2018). There are also reports on using electric field to increase Mn^{2+} leaching efficiency (Fig. 5c) (Zhang et al., 2017b).

However, the above methods are rarely used in industry due to complicated leaching conditions, poor suitability and high leaching cost. Bioleaching is another choice for Mn^{2+} leaching since its process is simple and the cost is low. Mn^{2+} leaching efficiency reached 99% using *Alicyclobacillus* sp. and *Sulfobacillus* sp. simultaneously (Xin et al., 2015). However, compared with other approaches, bioleaching needs more time, and it is still in the lab and not applied in EMM industry.



Fig. 5. Flowchart, effect and mechanism of high efficiency leaching of Mn^{2+} : (a) Effect of H_2O_2 (El Hazek et al., 2006), (b) Effect of lignin (Xiong et al., 2018), (c) Effect of electric field enhancement (Xin et al., 2015) and (d) Flowchart of EMM production with low pyrolusite and SO₂ (Sun et al., 2013).

2.3. Separate iron from leaching solution

The next step after leaching is removing impurities, like iron, which is the main one in the manganese ores, usually around 2.93%-24.2%. It needs to be removed before electrolysis since it has similar chemical properties as Mn (Liu et al., 2019). Generally, EMM industry separates iron from the leaching liquid by adjusting its pH to form Fe(OH)₃ and they do not filtrate it immediately (Zhang and Cheng, 2007). They usually precipitate other heavy metal next to iron and then filtrate the liquid and leaching liquid. Thus, EMR is a mixture of manganese ore leaching residues, the precipitations of iron and other heavy metals (Yan and Qiu, 2014; Wang et al., 2019b). Therefore, filtrate step by step could reduce the volume of EMM and also reduce EMR complexity. Regrettably, hardly EMM conducts this process.

2.4. EMR moisture content control

After precipitating the impurities, the mixture is filtrated and EMR is generated. Because the manganese ores are grounded, after leaching, the radius of the leaching residues is around $30-50 \ \mu$ m. Fe(OH)₃ is also a colloid. Meanwhile, gypsum will also be generated during the leaching by H₂SO₄, which is strong hydrophilicity. Therefore, the moisture content of EMR is extremely high, around 22%–35%. One thing should be pointed out is that a large amount of soluble MnSO₄ (2.0%–3.5%), (NH₄)₂SO₄ (2.5%–5.0%) and heavy metals (such as Co²⁺, Ni²⁺, and Cr⁶⁺) are carried in this part of water. This is the reason why EMR would cause a serious pollution (Du et al., 2013; Hou et al., 2012; Zhou et al., 2013; Yang et al., 2012; Duan, 2009; Jiang et al., 2011; Luo et al., 2019; Li et al., 2014). Moreover, almost 10% of manganese will be loss because of this. Therefore, EMR moisture control is significantly important.

EMR moisture content control can not only reduce EMR amount and its ecoenvironmental risks but also reduce its yards or dams, and thus save land. Surfactants, such as dodecylamine and sodium dodecylbenzene sulfonate can decrease EMR particle surface hydrophilic and thus reducing the moisture content by 7.03% and 3.18%, respectively (Hao and Qiu, 2015; Sun, 2018). Another reason could be ascribed to that these surfactants may form semimicelles on EMR surface, increasing its hydrophobic. On the other hand, researches also focused on the research of developing innovative filtering equipment, instead of the mechanisms to promote the moisture content control (Liu et al., 2010, 2019).

2.5. Limiting factors and future development

Although the previously mentioned methods were capable to reduce EMR volume, there are also some limits. For example, one single method is hard to reduce EMR due to the complexity of manganese ores and also its high moisture content. There were relatively few studies on researching and developing combined beneficiation processes and automatic equipment. In practice, to ensure the water balance of EMM production, a constant production process and low production costs, EMM enterprises are unwilling to change the production process. Now, enterprises prefer to import high-grade manganese ores (Mn>40%) from other countries to pursuit profits, and this is also a good choice for EMR reduction. EMR reduction is not a single process, and the EMM production process should be combined with a reduction in the EMR water content. Moreover, EMR reduction should ensure the continuity of the EMM production process, with a low disposal cost and without secondary pollution.

3. EMR pretreatment

After filtration, it is hard to reduce the generation of EMR. And as discussed previously, EMR is harmful to the eco-environment and human health because of the high mobility of Mn^{2+} and NH_4^+ carried by the high moisture content. Therefore, before EMR reuse, these high mobility ions should be removed or solidified/immobilized. After pretreatment, EMR is no longer a "harmful industrial solid waste" that

would harms the ecoenvironment and human health, but rather an available resource for industrial production. Representative studies on EMR pretreatment are summarized in Table 2.

3.1. Mn^{2+} and NH_4^+ removal

Washing, leaching, electric field enhancement leaching, electrokinetic remediation, and bioleaching are used to remove Mn^{2+} and NH_4^+ from EMR. Washing includes traditional slurry washing, slurry-cake washing and combining filtration with washing. The elution efficiencies for soluble Mn²⁺ and (NH₄)₂SO₄ could be up to 95.8% and 90.9%, and the soluble Mn^{2+} and NH_4^+ concentrations in the discarded EMR are lower to 0.25 g/L and 0.87 g/L, respectively (Fang, 2014; Zhao et al., 2017). Washing can wash soluble Mn^{2+} and NH_4^+ out from EMR, while it is not suitable for insoluble substances. Moreover, washing would also bring water balance problem, which may cause additional investment for treating the generated washing liquid. By leaching with 10% H₂SO₄, the elution efficiency of Mn^{2+} could be 97.3%, with a Mn^{2+} residue concentration of about 0.32 mg/L, meeting the limits (2 mg/L) of GB 8978-1996 (Integrated wastewater discharge standard) (Wang et al., 2012). Electric field enhancement leaching and electrokinetic remediation can remove Mn²⁺ and NH⁴ from EMR, and the leaching efficiencies reached 99.5% and 99.7%, respectively (Fig. 6a, b). NH₄+ concentration in the discarded EMR decreases to 1.17 mg/L, meeting the limits of GB 8978-1996 (15 mg/L), while Mn²⁺ concentration cannot meet the limits of GB 8978-1996 (Tian et al., 2019; Shu et al., 2019e; Liu et al., 2020). The main reason is the increase of mutual repulsion between the charged silicate and sulfate particles (Hou et al., 2012; Shu et al., 2016a). The removal efficiencies of Mn^{2+} and NH_4^+ are 98% and 99% by bioleaching, and the leaching concentrations were reduced to 39.95 mg/L and 22.38 mg/L, respectively (Fig. 7c) (Lan et al., 2019b).

3.2. Mn^{2+} and NH_4^+ stabilization/solidification

Stabilization/solidification is one of the primary methods to dispose of toxic or hazardous solid waste. The basic mechanism is to encapsulate

Table 2

Overview of EMR pretreatment.

the toxic pollutants or hazardous substances in solid waste by adding cement materials, adhesives, and inert materials, so that the pollutants or hazardous substances cannot be leached out. The stabilization/solidification materials for EMR includes alkaline materials, phosphate, and other chemical agents.

Using alkaline materials, Mn^{2+} in EMR would change to insoluble precipitates such as $Mn(OH)_2$, MnO_2 , Mn_3O_4 and $MnO \cdot OH$, and NH_4^+ would escape as NH_3 . The reaction equations are as follows:

$$Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_{2} \downarrow$$
(6)

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO \cdot OH + 2OH^-$$
(7)

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO_2 + 2H_2O \tag{8}$$

$$6Mn(OH)_2 + O_2 \rightarrow 2Mn_3O_4 + 6H_2O \tag{9}$$

$$\mathrm{NH}_{4}^{+} + \mathrm{OH}^{-} \rightarrow \mathrm{NH}_{3} \uparrow + \mathrm{H}_{2}\mathrm{O} \tag{10}$$

The United States and Japan pretreat EMR with hydrated lime and then buried them. When quicklime was applied for EMR disposal, Mn²⁺ solidification efficiency reaches 99.8% and NH₄⁺ removal efficiency was 97%. Mn^{2+} and NH_4^+ leaching concentrations in the discarded EMR after pretreated by quicklime are 2.60 mg/L and 19.53 mg/L, respectively (Luo et al., 2017). Mn²⁺ solidification efficiency is 99.98%, and NH₄ removal efficiency is 99.2% when the mass ratio of CaO and EMR is 1:8. Meanwhile, Mn^{2+} and NH_4^+ leaching concentrations in discarded EMR met the relevant regulations of GB 8978-1996 (Zhou et al., 2013). Combining CaO with NaHCO3 can solidify soluble Mn²⁺ more completely since they could form insoluble substances, such as Mn₃O₄ and MnCO₃, and here NaHCO₃ also used to form a buffer system with EMR. In our previous study, the basic burning raw material, an intermediate product pre-decomposed by suspension preheater, can remove NH₄⁺ in EMR completely, and the NH₄⁺ concentration of EMR after treated by this basic burning raw material meets the limits of GB 8978–1996 (Fig. 8a) (Shu et al., 2020a). The above methods can realize the Mn²⁺ stabilization/solidification, while the released NH₃ may cause secondary pollution, which should be further disposed.

Mn ²⁺ and NH ⁺ removal						
Methods	Removal efficiency		Concentrations after disposed		Notes	References
	Mn^{2+}	NH_4^+	Mn ²⁺	NH_4^+		
Clear water for washing EMR	92%	90.9%	0.25 g/L	0.87 g/L	The water balance problem is difficult to overcome.	(Fang, 2014)
Slurrying-cake washing	95.8%	NA	NA	NA	NH ₄ ⁺ was not studied.	(Zhao et al., 2017)
Combining filtration with washing	>93.6%	NA	>1.23 g/L	NA	Including three processes.	(Liu et al., 2019)
H ₂ SO ₄ used in water-acid solution	97.3%	NA	0.32 mg/L	NA	NH ₄ ⁺ was not studied.	(Wang et al., 2012)
Electric field enhancement leaching	98.6%	99.8%	32.10 mg/L	1.17 mg/L	Mn ²⁺ cannot meet the limits of GB 8978–1996.	(Tian et al., 2019)
Electrokinetic remediation	99.5%	99.7%	0–6.15 mg/ L	0–2.26 mg/ L	Powered by solar-cell and eco-friendly.	(Shu et al., 2019e; Liu et al., 2020)
Bioleaching (isolation indigenous bacteria (Y1))	98%	99%	39.95 mg/L	22.38 mg/L	Long disposal period.	(Lan et al., 2019b)
Mn ²⁺ and NH ₄ ⁺ stabilization/solidified	cation					
Methods	Solidification		Concentration after disposed		Notes	References
	efficiency Mn ²⁺	NH ⁺	Mn ²⁺	NH [±]		
Quicklime	99.8%	97%	2.60 mg/L	19.53 mg/L	Mn ²⁺ and NH ⁺ stabilization/solidification	(Luo et al. 2017)
CaO	99.98%	99.2%	0.32 mg/L	5.35 mg/L	NH ⁺ recovery device and process	(Zhou et al. 2013)
CaO and NaHCO ₂	>99.99%	NA	0.05 mg/L	NA	Modest pH was obtained.	(Du et al., 2015a, 2015b)
Basic burning raw material	99.99%	99.3%	0.10 mg/L	12.80 mg/L	Low disposal cost.	(Shu et al., 2020a)
Phosphate and magnesium	99.9%	92.4%	1.30 mg/L	98.00 mg/L	NH_4^+ and Mn^{2+} were immobilized simultaneously.	(Chen et al., 2019)
MgO, CaO and phosphate	>99.99%	84.9%	0.59 mg/L	76.60 mg/L	Modest pH.	(Shu et al., 2016a)
Phosphogypsum (PG)	99.9%	96.4%	0.80 mg/L	55.50 mg/L	Synergistic disposal of EMR and PG.	(Shu et al., 2019d)
PG leachate $+$ MgO $+$ CaO	99.99%	93.7%	0.50 mg/L	80.00 mg/L	Synergistic disposal of EMR and	(Chen et al., 2020)
			-	-	phosphogypsum leachate.	
Ozone	>99.9%	NA	< 0.10 mg/L	NA	NH_4^+ was not studied.	(Yang et al., 2014b)

NA: Information not available.



Fig. 6. Methods and mechanism of Mn^{2+} and NH_4^+ recovery: (a) Mechanism of electric field enhancement leaching (Tian et al., 2019), (b) Mechanism of electrokinetic remediation (Liu et al., 2020), and (c) Leaching mechanism of bio-leaching (Lan et al., 2019b).



Fig. 7. EMR stabilization/solidification mechanism: (a) Basic burning raw material (Shu et al., 2020a), (b) Phosphate resource and low-grade MgO/CaO (Shu et al., 2016b), (c) Phosphate and magnesium sources (Chen et al., 2019), and (d) Phosphogypsum (Shu et al., 2019d).

In phosphate systems, Mn^{2+} and NH_4^+ could be solidified/stabilized as $Mn(OH)_2$, $Mn_5(PO_4)_2(OH)_4$, $Mn_3(PO_4)_2.3 H_2O$ and $NH_4MgPO_4.6 H_2O$. The reaction are proposed as follows:

$$5Mn^{2+} + 2PO_4^{3-} + 4OH^- \rightarrow Mn_5(PO_4)_2(OH)_4 \downarrow$$
 (11)

$$3\mathrm{Mn}^{2+} + 2\mathrm{PO}_4^{3-} + 3\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Mn3}(\mathrm{PO}_4)_2 \cdot 3\mathrm{H}_2\mathrm{O} \downarrow \tag{12}$$

 $NH_{4}^{+} + Mg^{2+} + PO_{4}^{3-} + 6H_{2}O \rightarrow NH_{4}MgPO_{4} \cdot 6H_{2}O\downarrow$ (13)

Using MgSO₄·7H₂O, Na₃PO₄·12H₂O and CaO simultaneously, the



Fig. 8. Flowchart and mechanism of valuable resource recovery from EMR: (a) Mn^{2+} dissolution and migration by pure water (Zheng et al., 2020), (b) Scheme for Mn^{2+} and NH_4^+ recovery with NH_3 ·H₂O and bubbling CO₂ (Wang et al., 2016), (c) Schematic diagram of microwave reactor (Chang and Srinivasakannan, 2020), and (d) Electro-reduction (Shu et al., 2020a).

solidification efficiencies of Mn^{2+} and NH_4^+ in EMR are 99.9% and 92.4%, respectively (Fig. 8c) (Chen et al., 2019). NH_4^+ and Mn^{2+} immobilization efficiencies for EMR are 93.7% and 99.99% when using phosphogypsum leachate and MgO/CaO (Chen et al., 2020). This process has low disposal costs, and the discarded EMR has better stability. In our previous studies, low-grade MgO, $NaH_2PO_4.2H_2O$, MgO, CaO, and phosphogypsum were used for the stabilization/solidification of Mn^{2+} and NH_4^+ (Fig. 8b, d) (Shu et al., 2016a, 2019d). The results showed that the immobilization efficiencies of NH_4^+ and Mn^{2+} in EMR could reach 99.99% and 96.4%. Mn^{2+} concentration was only 0.05 mg/L, meeting the limits of GB 8978–1996.

In addition, ozone is an intense oxidant, and it can convert divalent manganese to high valence states, which then from as insoluble manganese oxides. The results indicated that Mn^{2+} solidification efficiency exceeded 99.9% and its concentration in solution was lower than 0.10 mg/L, meeting the limits of GB 8978–1996 (Yang et al., 2014b). In a system containing ground granulated blast furnace slag (60%), EMR (18%), clinker (16%), and lime (6%), the heavy metal ions in EMR can self-solidify/stabilize (Xue et al., 2020).

3.3. Limiting factors and future development

Using one or several substances among quicklime, CaO, ozone, phosphate, MgO and NaHCO₃ to dispose of EMR, Mn^{2+} and NH⁴ leaching concentrations would be greatly reduced. However, it is difficult for Mn^{2+} and NH⁴ in pretreated EMR to meet GB 8978–1996 simultaneously. Moreover, owing to high viscosity, poor dispersibility, and uneven particle distribution, it is tough to mix EMR with other agents evenly. In addition, the cost of EMR pretreatment is high. In practice, quicklime is generally used for EMR pretreatment, but the pretreatment is not complete since EMM companies do not add enough dose because of the cost. It is necessary to investigate and develop an efficient, cost-effective alkaline agent for EMR pretreatment which could provide a long-term stable storage of EMR without secondary pollution. In addition, the disposal processes or technologies should ensure the subsequent EMR reuse.

4. EMR reuse

EMR reduction and pretreatment can alleviate EMR pollution, while the discarded EMR still occupies a large amount of land and poses secondary pollution risks. To solve EMR pollution more completely, it must be reutilized. EMR reuse includes recycling valuable resource from EMR, using it in construction engineering and others applications, summarized in Table 3.

4.1. Valuable resource recovery from EMR

Recycling valuable substances such as Mn²⁺, Mg²⁺, Fe²⁺, NH₄⁺, from EMR is an essential part of EMR reuse. MnO content in EMR is 2.42%-6.84%, the total value is 4.69-16.86 billion dollars for the 150 million tons of EMR pilled around the world if Mn is 1700 dollar/t. Water leaching (Fig. 9a) (Zheng et al., 2020), ultrasonic-assisted leaching with additive (Ouyang et al., 2007), ammonia/CO₂ leaching (Fig. 9b) (Wang et al., 2016) and microwave-assisted extraction (Fig. 9c) (Chang and Srinivasakannan, 2020) are the main methods to leach soluble Mn²⁺ from EMR. And the leaching efficiencies are 83.4%, 57.3%, 94.2% and 90%, respectively. Mn^{2+} and Fe^{2+} can be recycled simultaneously by roasting and magnetic separating, with recovery efficiencies of 90.8% and 70.3% (Peng et al., 2018). Ammonium carbonate and polyacrylamide are efficient enough to recycle soluble Mn²⁺ and NH₄⁺ from EMR, about 99.5% and 94.5%, respectively (Tao et al., 2009). Surfactant with electric field enhancement was a new method for leaching Mn^{2+} and NH₄⁺, by which the recovery efficiencies are 97.1% and 98.4% for Mn²⁺ and NH₄⁺, respectively (Fig. 9d) (Shu et al., 2020b). Microbes such as silicate bacteria, sulfur-oxidizing bacteria, pyrite-leaching bacteria, and Paenibacillus mucilaginosus can also leach Mn^{2+} , NH_4^+ and other ions from EMR. The recovery efficiency of Mn^{2+} reached 99.7%, and the silicon available in the leaching solution reached 514.00 mg/L (Xin et al., 2011; Duan et al., 2011b; Cao et al., 2012; Lv et al., 2020). Bioleaching has the advantages of low cost, simple operations, and almost no secondary pollution. However, the treatment time for microbes are long.

Table 3

Overview of EMR reuse.

Valuable resource recovery from	EMR		
Methods	Mn ²⁺ recovery efficiency	Notes	References
Water leaching	83.4%	An economical way to recover Mn.	(Zheng et al., 2020)
Water washing residue-twice	99.5%	94.5% NH ₄ ⁺ was recovered.	(Tao et al., 2009)
precipitation			
Ammonia/CO ₂ leaching	94.2%	Effecitively recover Mn ²⁺ .	(Wang et al., 2016)
Ultrasonic and additive	57.3%	Low Mn ²⁺ recovery efficiency.	(Ouyang et al., 2007)
Magnetic separation	90.8%	Mn ²⁺ and Fe ²⁺ were recycled.	(Peng et al., 2018)
Microwave-assisted leaching	> 90%	The leaching solution contains organic matter.	(Chang and Srinivasakannan, 2020)
Surfactant and electric field	97.1%	98.4% NH ₄ ⁺ was recovered, and it provided a new idea for EMR	(Shu et al., 2020b)
enhancement		disposal.	
Bacteria	98.1%	Sulfur-oxidizing bacteria and pyrite-leaching bacteria were used.	(Xin et al., 2011)
Acidithiobacillus	99.7%	Sulfur-oxidizing bacteria and iron-oxidizing bacteria were used.	(Duan et al., 2011b)
Fusarium sp.	71.6%	Low cost and environment friendliness.	(Cao et al., 2012)
Silicate bacteria	NA	Simultaneous recovered Si and stabilization/solidification of	(Lv et al., 2019)
		heavy metals.	
Paenibacillus mucilaginosus	NA	The leaching concentration of Si reached up to 514.00 mg/L.	(Lv et al., 2020)
Construction engineering materi	als	NY .	
Materials	Content of EMR	Notes	References
Cement mineralizer	2%-8%	Clinkering eutectic temperature was reduced, and C ₃ S content	(Wang, 2010)
		was increased.	
Quasi-sulphoaluminate cement	10%-40%	Compressive strength at 56 d was 36–65 MPa.	(Hou et al., 2012)
EMR-GGBS cement	30%	Reaching P·S 52.5 class.	(Wang et al., 2013b)
Cement clinker	25%	3 d compressive strength reached 49.8 MPa. Mn^{2+} and NH_4^+	(Lei et al., 2013)
		were not studied.	
TiO ₂ -coating cement	8%	The maximum methyl orange degradation was 94.2%. Low	(Li et al., 2016)
		content of EMR.	
Filler in sulfur concrete	30%	The mechanical properties were good.	(Yang et al., 2014a)
Concrete	5%-10%	The dosage should be increased.	(Chousidis et al., 2018)
EMR-activated cementitious	45%	28 d compressive strength reached 30 MPa.	(Wang et al., 2020)
material			
Autoclaved brick	30%-71%	Compressive strength >50 MPa. Pore size distribution and	(Du et al., 2013a, 2014; Li et al.,
		porosity were not studied.	2020a)
Road base	30%-100%	Compressive strength was up to 6.1 MPa.	(Zhang et al., 2020, 2019a, 2019b)
Baking-free brick	50%	Compressive strength in 28d was up to 19 MPa.	(Wang and Liu, 2013)
Non-sintered permeable brick	30%-60%	It can be used as pavement materials.	(Wang et al., 2019c)
Non-burnt permeable brick	15%	The maximum pore and average surface porosity reached	(Tang et al., 2019)
		10.46 mm and 3.68-21.11%.	
Glass-ceramic	100%	Low crystallization activation energy, but the solidification	(Qian et al., 2012)
		theories was not studied.	
Recycled ceramic tile	10%	Compression strength and bulk density reached 25.2 MPa and	(Wang et al., 2013a)
		2.88 g/cm^3 .	
Ceramics	35%	Bulk density and bending strength reached 2.38 g/cm ³ and	(Wu et al., 2013)
		105 MPa.	
Porous ceramic	55%-68%	Apparent porosity and compressive strength reached 69.7% and	(Wang et al., 2016)
		6.97 MPa.	
Ceramisite	42%	Synergistic disposal with MSWI fly ash, and met the requirement	(Hu et al., 2019, 2018; Huang et al.,
		of 700 grade light aggregate.	2013)
Adsorption			
Materials	Specific surface & Sorption capacity	Notes	References
Zeolite	35.38 m ² /g; 66.93 mg/g Mn ²⁺ ,	Low production cost.	(Li et al., 2015a, 2015b, 2015c,
	128.70 mg/g Ni ²⁺		2015d, 2019a)
Modified EMR	500.80 m²/g; 548.15 m²/g ethylene	Low cost and potential eco-friendly adsorbent.	(Shu et al., 2018b)
	blue		
Modified EMR	23.96 mg/g As(V) and 19.98 mg/g	Low cost.	(Lan et al., 2019a; Sun et al., 2019)
	As(III)		
Mesoporous Silica	451.34 m ² /g	Used as catalyst supports.	(Zhang et al., 2017a)
Nanocomposite catalysts	Sizes of 100-200 nm.	About 99.99% of azo dyes can be removed.	(Lan et al., 2020)
Geopolymer			
Materials	Content of EMR	Notes	References
Geopolymer	80%	Compressive and rupture strengths were 8.89 MPa and 1.22 MPa	(Zhao and Han, 2013)
	050/	at 28 d.	
EMR-based geopolymer	25%	MSWI FA and EMR were co-disposed, and the solidification of	(Zhan et al., 2018., 2019a)
		heavy metal ions was good.	
Geopolymer gel	NA	Compressive strength was 96.3 MPa, and manganese	(Han et al., 2018)
		stabilization efficiency was 95.4%.	
EMR-fly ash based geopolymer	60%	Compressive strength was 16 MPa, and it reached the	(L1 et al., 2020b)
		solidification of heavy metal ions.	
Agriculture			
Methods	Notes		Beferences
Rich selenium fertilizer	Improve soil and make agricultural pr	oducts more productive, especially for corp	(Lan and Test 2006; Lan 2005)
Manganese fertilizer	High temperature hurning method ar	id the effective silicon content in to 8 08%	(Sun et al 2019)
Mechanical grinding-reasting	Active silicon in FMR can be increased	(Sinch and Biewae 2017)	
Composting	Ni^{2+} and Zn^{2+} reduced to 106.25 mg/	L and 9.78 mg/L	(Lan et al., 2019b)
			(

NA: Information not available.



Fig. 9. EMR related cement and concrete: (a) Photocatalytic degradation of EMR-cement (Li et al., 2016) and (b) EG^{CH} (EMR-activated cementitious material) preparation with EMR (Wang et al., 2020).

4.2. Application in construction engineering

4.2.1. Cement and concrete

C₃S (3CaO·SiO₂, tricalcium silicate), C₂S (2CaO·SiO₂, dicalcium silicate), C3A (3CaO·Al2O3, dicalcium aluminate), and C4AF (4CaO·Al₂O₃·Fe₂O₃, tetracalcium aluminoferrite) are the primary minerals of Portland cement, and they can be formed by calcining EMR, clay, limestone, and other raw materials. Portland cement (Wang, 2010), quasi-sulfoaluminate cement (Du et al., 2013a), EMR-ground slag cement (Wang et al., 2013b), ferro-aluminate cement clinker (Lei et al., 2013) and TiO₂-coating cement (Fig. 10b) (Li et al., 2016) can be manufactured with 2%-40% EMR. EMR reuse in cement is severely restricted by its high NH_4^+ and SO_4^{2-} contents. When mixed with EMR without any deamination and desulfurization or even incompletely, the intense alkaline environment (pH=12-13) formed by cement hydration would cause the NH⁺₄ in EMR to escape as NH₃, which would pollute the environment. To prevent cement sulfur oxides exceeding the standard (<3.5%), which would reduce cement stability, EMR content should not be too high (3%-5%).

EMR is an alternative raw material for producing concrete and sulfur concrete because of its high Al_2O_3 , SiO_2 , and CaO content. C25/C30 concrete with good compressive strength, Young's modulus and resistance to chloride ion attack could be produced with 5%–10% EMR (Chousidis et al., 2018). The compressive and flexural strengths of sulfur concrete reached 63.17 MPa and 9.47 MPa when 30% EMR is used as a filler, and the product leaching toxicity met GB 8978–1996 (Yang et al.,

2014a). Unfortunately, due to the high price of sulfur, the difficulty of supplying polysulfide rubber and the high production cost, this method is difficult in large scale application. In addition, EMR-activated cementitious with a compressive strength of 30 MPa at 28 d can be manufactured with 45% EMR, which could stabilize of Mn^{2+} and NH_4^+ (Fig. 10a) (Wang et al., 2020). The reasons for limiting EMR reuse in concrete are its low activity, cost, and the lack of efficient activation technology.

4.2.2. Bricks and road base

Producing building bricks and road base with waste materials as a substitute for clay has gradually become a hot topic. Autoclaved brick (Fig. S5a) (Zhou et al., 2013; Li et al., 2020a; Du et al., 2014; Wu et al., 2013), baking-free brick (Wang and Liu, 2013), non-sintered permeable brick (Wang et al., 2019c) and non-burnt permeable brick (Fig. S5c) (Tang et al., 2019) have good compressive strength (19–50 MPa), splitting tensile strength and permeability coefficient which can be manufactured with 15%–71% EMR. Road base can be prepared with 30% EMR, red mud, carbide slag and blast furnace slag, and the compressive strength reached 6.1 MPa (Fig. S5b,d) (Zhang et al., 2020, 2019a, 2019b). However, these technologies had not achieved industrialization because the use of NH₃ receiving facilities will lead to high costs and the local building materials market was not sufficient to consume the resulting products.



Fig. 10. Other application of EMR: (a) Mesoporous silica preparation with EMR (Zhang et al., 2017a) and (b) Adsorption mechanism of M-EMRs (Lan et al., 2019a).

4.2.3. Glass-ceramics and ceramisite

Aluminosilicate-based glass-ceramic is a widely used solution in industrial solid waste reuse. Calcining EMR without any composition adjustment could yield CaO-MgO-Al2O3-SiO2 series glass-ceramics, and the crystallization activation energy was only 429.00 kJ/mol (Qian et al., 2012). Anorthite/enstatite multiphase ceramics, recycled ceramic tile, porous ceramics have good bulk density, bending strength, compressive strength and apparent porosity which can be produced with 10%-35% EMR (Wang et al., 2016, 2013a; Wu et al., 2014b). Producing ceramisite with EMR is also a topic of interest in EMR reuse. Ceramisite that meets GB/T 17,431.2-2010 standard (Lightweight aggregates and its test methods Part 2: Test methods for lightweight aggregates) can be manufactured with 42.02%-49.19% EMR, and the ceramisite is not hazardous to the environment (Hu et al., 2019, 2018; Huang et al., 2013). These studies provided new ideas for reusing large amount of EMR, while little attention has been devoted to the leaching toxicity, micro-properties, durability, and also the solidification mechanism of heavy metal ions in materials containing EMR.

4.3. Other applications

EMR contains 22.03%–41.24% SiO₂ and 2.27%–8.54% Al₂O₃, and it can be used to synthesize adsorption such as zeolite (Li et al., 2015a, 2015b, 2015c, 2015d, 2019a), mesoporous silica (Fig. 10a) (Zhang et al., 2017a), and others (Fig. 10b) (Lan et al., 2019a; Sun et al., 2019; Su et al., 2018b), used for disposing of wastewater or as catalyst supports (Lan et al., 2020), and geopolymer (Li et al., 2020b; Han et al., 2018; Zhan et al., 2018, 2019b; Zhao and Han, 2013). Nevertheless, due to the low EMR dosage and the complicated production process as well as the limited research on the solidification mechanism of other heavy metal ions, the promotion and application of these technologies are limited. In addition, the market demand is insufficient for the product and secondary pollution may be associated with these products.

EMR contains Si, Fe, Ca, Mg, K, organic compounds, and NH₄⁺, thus it has a potential value for using as fertilizer. EMR could be used to produce selenium rich fertilizer, manganese fertilizer and silicon fertilizer, which was suitable for soil improvement and increased agricultural products, especially corn (Zhan and Zhang, 2019; Lan and Test, 2006; Lan, 2005; Ren, 2017). The bio-availability of heavy metal ions in EMR can be reduced by composting, and the leaching concentrations of Ni²⁺ and Zn^{2+} decreased from 145.23 mg/L and 11.77 mg/L to 106.25 mg/L and 9.78 mg/L, respectively (Lan et al., 2019b). Manufacturing biological organic fertilizer from EMR and biomass solid waste through synthetic fermentation is also an EMR reuse approach. During the multi-stage fermentation process, sugar, cellulose, and lignin are decomposed to form organic matter by microorganisms. In addition, the metabolic assimilation of bacteria and the metal elements in EMR formed a bio-conjugated complex, which reduced the toxicity of free heavy metal ions and increased their availability to crops. These researches had not been industrialized. The primary reason is that the fertilizer effect on crops is lower than that of ordinary fertilizers since EMR has a low active silicon content. Owing to the sulfide formed by heavy metal ions in EMR, the roots of plants may be corroded when fertilizers produced with EMR are used. Furthermore, plants could accumulate heavy metal ions in the fertilizer, which are harm to human body and the ecosystem, a reason to limit its industrialization.

5. Conclusions and future development

5.1. Conclusions

The disposal of EMR has become a barrier to the sustainable development of EMM industry in China because of EMR's serious ecoenvironmental hazards. For EMR reduction, the economy and technique feasibility cannot be reached simultaneously. The primary limitations associated with EMR reduction include the high amount of EMR caused by the low grade of manganese ore and its high moisture content by low efficiency filtering equipment. For EMR pretreatment and reuse, the existing method is difficult to achieve industrial and large-scale EMR disposal or reuse. The primary reasons limiting EMR pretreatment include the high disposal cost, secondary pollution, the high pH value of EMR after stabilization/solidification, the weaken of long-term stability caused by the high concentrations of Mn^{2+} and NH^{\pm} . The main reasons restricting EMR reuse include secondary pollution, incomplete pretreatment, insufficient policies, low activity of EMR, low added value and insufficient product market for EMR-related products, as well as long transportation distances. Notably, the lack of standards for EMR pretreatment and related products also seriously restricts EMR pretreatment and reuse.

5.2. Future development

Although researchers have paid a great deal of attention to EMR reduction, pretreatment, and reuse, there are some drawbacks. Combined with the research status of EMR and with market factors, our suggestions for EMR disposal are as follows.

5.2.1. Thinking revolution

For EMR disposal, we should form a new life cycle of "manganese ore-EMM-EMR-disposal-resource" based on the framework of the EMM ecosystem rather than EMR itself. Considering the relevant regulations of integrated solid waste management, EMR large-scale reuse should combine EMM production process, the characterizations of EMR with EMR reduction and pretreatment, technologies. EMR reduction, or EMM cleaner production, is quite necessary to EMR pretreatment and reuse, and EMR reuse should be based on its pretreatment. Moreover, the ecoenvironmental impact of the resulting products should be no greater than those of EMR, and EMR without reuse should pretreat.

5.2.2. Technological innovation

EMR disposal should combine a set of technologies, because one single disposal technology cannot solve the problems associated with EMR. For the EMM industry, accelerating the research and introduction of technologies and equipment on beneficiation, clean production and high-efficiency presses filter to reduce the total amount and toxicity of EMR. We can also improve the automation and information level on the disposal process through multiple-process integration innovation. Considering the EMM-related industry chain, it is necessary to explore new markets for large-scale comprehensive reuse of EMR, accelerating the research and development of key technologies for EMR industrialization, such as efficient dispersion, moisture content reduction, Mn^{2+} and NH_{+}^{4} stabilization/solidification, deamination, desulfurization, and activation technologies of EMR.

5.2.3. Policy support

EMR reduction, pretreatment, and reuse should be combined consistent with each regulatory level. The yield of EMM should be based on the EMR consumption. In combination with local conditions, EMRrelated policies and laws as well as regulations on comprehensive EMR utilization and pollution prevention should be more complete and comprehensive. Improving EMR toxicity identification and evaluation standards, formulating EMR disposal technical specifications, EMRrelated products standards, and technical feasibility guidelines are all important. Local governments in various regions could combine their own economic and industrial structure plans to publish EMR emission standards and establish special funds and taxation incentives to support the development and implementation of EMR reduction, pretreatment and reuse.

5.2.4. Market regulation

Taking multiple measures to stimulate market potential of EMRrelated products in line with local conditions. It is necessary to accelerate the research and promotion of EMR-related products based on the region of EMR production, and the market demand of these products can be encouraged by improving investments. It is also important to develop and promote EMR's large-volume, high-value-added and multichannel disposal patterns through a comprehensive service platform. Through the introduction of domestic and foreign advanced technology and specialized institutions, it should be possible to guide companies towards engaging in EMR disposal and promoting EMR-related products to users.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126235.

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