Recyling manganese-rich electrolytic residues: a review

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Abstract

Huge amounts of manganese-rich solid residues are yearly produced worldwide by industrial electrolysis, calling for advanced methods of recycling in the context of the circular economy. Here, we review manganese recycling with focus on ore reserves, electrolytic production, residue stockpiling and environmental impact, reducing the amount of residue and improving metal separation, and recycling the residues. Diposal techniques include dry disposal, wet disposal and fire roasting disposal. Residues can be recycled in buildings, functional materials and fertilizers.

Keywords: Electrolytic manganese solid residue; Source reduction; Harmless treatment; Resource utilization; Valuable; Sustainable development; Building materials; Environmental impact; Gradient utilization

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1 Introduction

Electrolytic manganese solid residue, named 'Mn-rich residue', is a by-product of electrolytic manganese metal production (Duan et al. 2010; He et al. 2021a; Yang et al. 2022; Wang et al. 2022a). It contains harmful components such as ammonia nitrogen, soluble manganese and other heavy metals (Chen et al. 2016; Wang et al. 2020; He et al. 2021b). Although numerous treatment methods have been proposed recently, no sustainable and practical industrial process for treating Mn-rich residue exists. Therefore, the review of the existing studies on the extraction, separation and stabilization or solidification of Mn-rich residue harmful substances is imperative for an in-depth investigation. An overview of various disposal technologies and a discussion of existing challenges and prospects are presented. In general, the sustainable development of the electrolytic manganese industry is hampered by the complex associated minerals that limit the quality of Mn-rich residue disposal. The United Nations has proposed seventeen sustainable development goals, many of which focus on developing healthier and more sustainable production systems. Thus, there is an urgent need to develop higher-quality disposal methods for Mn-rich residue. Aiming at this goal, the electrolytic process of manganese and the formation mechanism of Mn-rich residue was first clearly described in this work. This laid a foundation for clarifying the definition of Mn-rich residue and promoting the subsequent disposal of Mn-rich residue.

1.1 World manganese ore reserves and production distribution

The basic properties of manganese elements are essential for understanding manganese mining from the source. Manganese is a group 7 element in the fourth period of the periodic table of chemical elements. It has considerable lithophile properties in the lithosphere and silicate phase meteorites but exhibits strong oxygenophilic properties in the upper lithosphere (Liu et al. 2019). Manganese is a silver-white hard and brittle transition metal with a density of 7.44 $g \cdot cm^{-3}$, a melting point of 1244 °C and a boiling point of 1962 °C. Manganese has II, III, IV, VI and VII valence states in nature, specifically +2 (Mn^{2+} compounds), +3, +4 (MnO_2), +6 (manganates such as K_2MnO_4) and +7 (permanganates such as $KMnO_4$). The +2, +4, +6 and +7 valence states of manganese exhibit high stability (Sorensen et al. 2010; Singh et al. 2020). Manganese is highly susceptible to oxidation under moist air, forming a brown laminated manganese oxide shell with an outer layer of Mn_3O_4 and an inner layer of MnO on its surface. Several common manganese minerals are described as shown in Table 1.

Table 1. The basic properties of common manganese minerals

Types	Crystals	Chemical compositions	Mn (wt.%)	Structure	Density ($g \cdot cm^{-3}$)	Rarity	Metallization
Pyrolusite	Tetragonal	MnO_2	63.2	Loose	5	Common	Sedimentation
Psilomelane	Monoclinic	$mMnO \cdot MnO_2 \cdot nH_2O$	35~60	Granular	4.4~4.7	Common	Sedimentation
Newkirkite	Monoclinic	$Mn_2O_3 \cdot H_2O$	62.4	Column	4.2~4.3	Rare	Sedimentation
Hausmannite	Tetragonal	Mn_3O_4	72	Granular	4.84	Common	Denaturation
Braunite	Tetragonal	Mn_2O_3	69.6	Granular	4.7~5.0	Common	Denaturation
Rhodochrosite	Trigonal	$MnCO_3$	47.8	Granular	3.6~3.7	Common	Sedimentation
Alabandite	Equiaxial	MnS	63.1	Block	3.9~4.1	Common	Sedimentation

As a vital strategic mineral resource, the manganese ore is widely used in steel, non-ferrous metallurgy, chemical, electronics, batteries, agriculture, medicine, and other fields (Figure 1). Based on the latest USGS 2022 data (Figure 2a and Table 2), manganese ore reserves (by metal content) are mainly located in South Africa (about 640 million tons, 43%), Brazil (about 270 million tons, 18%), Australia (about 270 million tons, 18%), Ukraine (about 140 million tons, 9%), Gabon (about 61 million tons, 4%), China (about 54 million tons, 4%), and India (about 34 million tons, 4%) (USGS 2022). The global manganese ore resources are abundant, but the distribution of resources is uneven, and the ore grade varies significantly among these regions. The manganese-rich ore is concentrated in South Africa, Gabon, Brazil, India and Australia, whose grades are generally 35 to 50% (USGS 2022). However, Ukraine, China and Ghana are dominated by low-grade manganese ores, whose grades are mostly below 30%. Regarding manganese ore production (Table 2 and Figure 2b), the global manganese ore production in 2020 was about 18.9 million tons, with South Africa producing 6.5 million tons, accounting for nearly 30% of the total global manganese ore production. The global manganese ore consumption in 2021 once exceeded 20 million tons, of which South Africa produced 7.4 million tons, accounting for 37% of the global production. Gabon and Australia produced 3.6 million tons and 3.3 million tons, respectively, at 18% and 16%. In 2021, China became the fourth largest producer of manganese ore in the world, producing 1.3 million tons and having a 7.5% market share (USGS 2022).

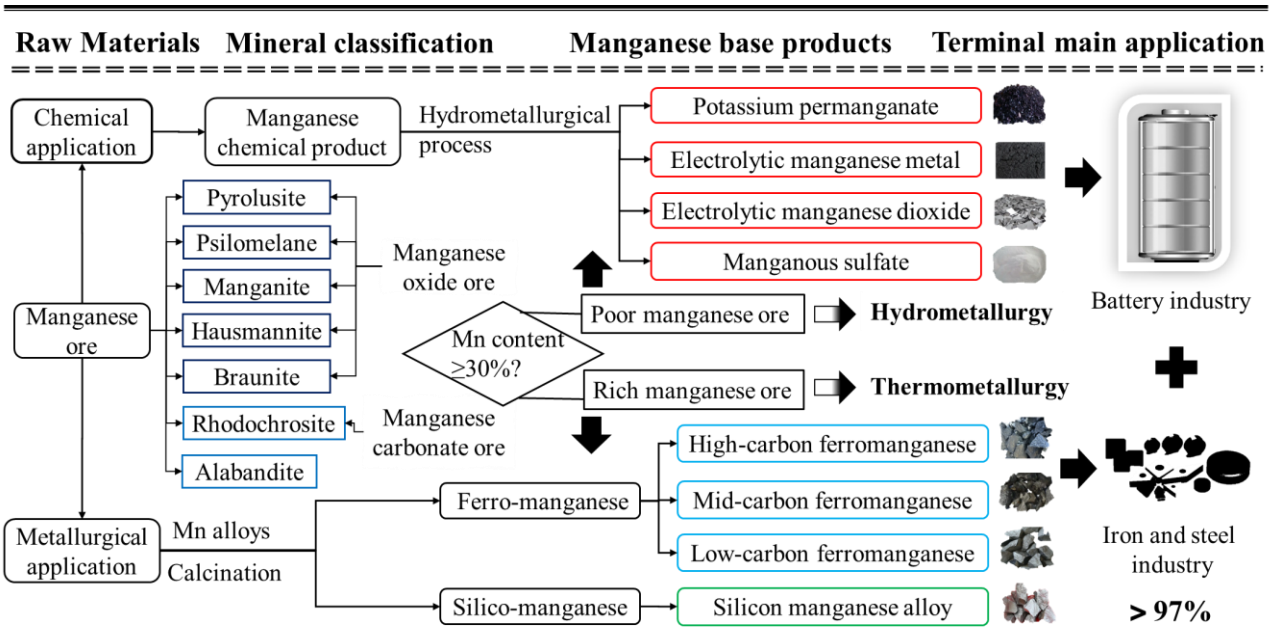

Figure 1. Simplified structure of the manganese industry chain. According to the grade of manganese ore, the formation process of manganese-based products can be recognized clearly. According to the difference in manganese content, different varieties of manganese ore can be divided into poor and rich ore. The differentiated manganese ore is prepared by the thermal and wet methods to achieve high-efficiency utilization of manganese ore. The figure of > 97% indicates that manganese used in iron and steel industry and battery industry accounts for more than 97% of industrial utilization of manganese ore.

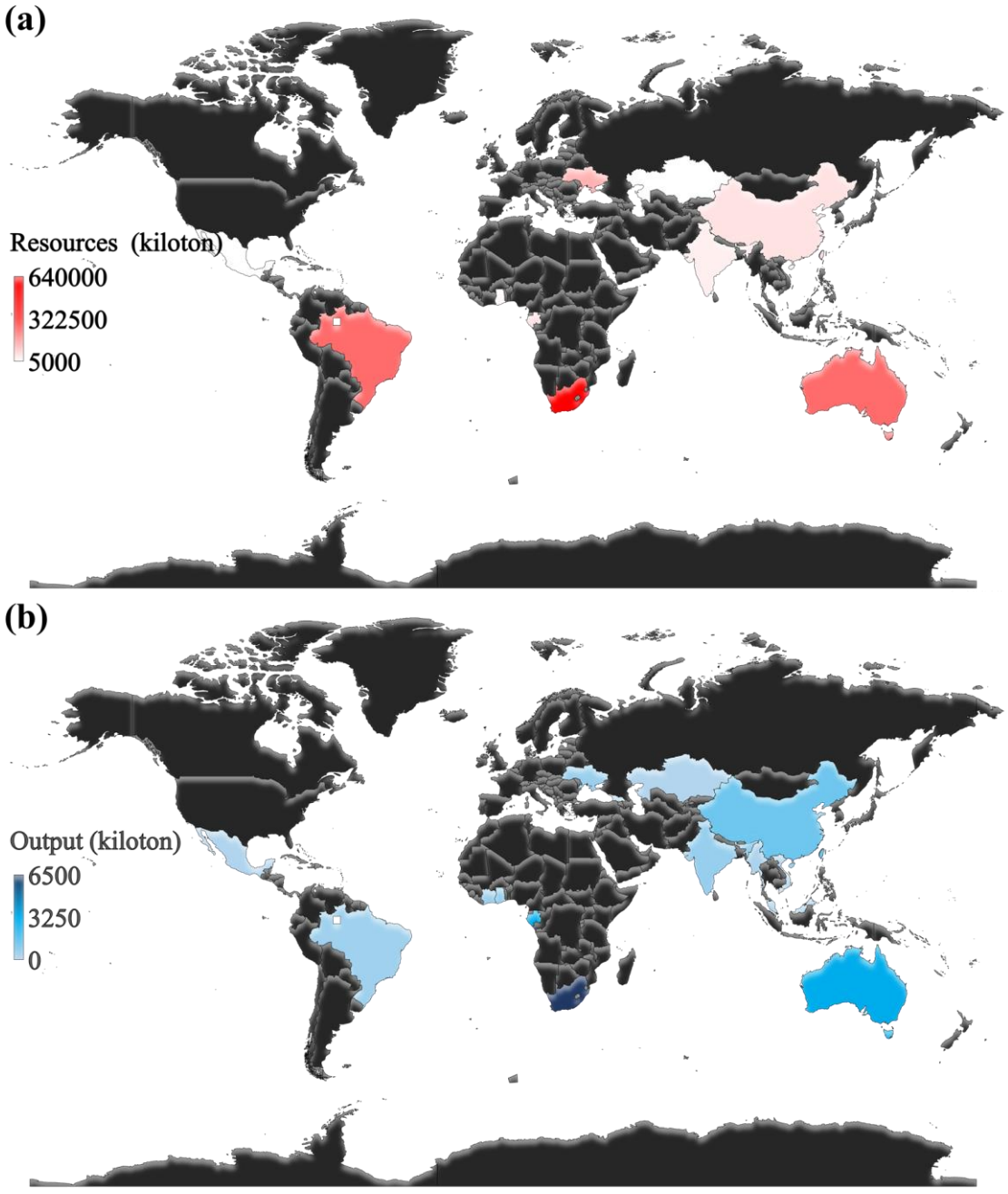

Figure 2. Latest global manganese ore distribution characteristics (a) Reserves distribution in 2022 (b) Production distribution in 2020 (USGS 2022).

Table 2. Mine production and reserves in the world (data from USGS 2022)

Countries	Mine production (kton)								Statistics of reserves (kton)							
	1995	2005	2015	2016	2017	2018	2019	2020	1997	2007	2017	2018	2019	2020	2021	2022
United states	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Australia	1070	1450	2450	2240	2820	3480	3180	3330	30000	73000	91000	94000	99000	100000	230000	270000
Brazil	905	1590	1090	1080	1160	1310	1740	494	21000	25000	116000	120000	110000	140000	270000	270000
Burma	-	-	-	-	-	207	430	254	NA	NA	NA	NA	NA	NA	NA	NA
China	1000	1100	3000	2330	1700	1200	1330	1340	40000	40000	43000	48000	54000	54000	54000	54000
Côte d'Ivoire	-	-	-	-	-	395	482	525	NA	NA	NA	NA	NA	NA	NA	NA
Gabon	895	1290	2020	1620	2190	2330	2510	3310	45000	20000	22000	20000	65000	61000	61000	61000
Georgia	150	-	-	-	-	200	116	186	7000	NA	NA	NA	NA	NA	NA	NA
Ghana	-	-	416	553	810	1360	1550	637	NA	NA	12000	13000	13000	13000	13000	13000
India	627	640	900	745	734	961	801	632	24000	93000	52000	34000	33000	34000	34000	34000
Kazakhstan	-	-	222	212	168	140	140	158	NA	NA	5000	5000	5000	5000	5000	5000
Malaysia	-	-	201	266	478	390	390	347		NA	NA	NA	NA	NA	NA	NA
Mexico	174	180	220	206	212	210	202	198	4000	4000	5000	5000	5000	5000	5000	5000
South Africa	1350	2100	5900	5300	5400	5800	5800	6500	370000	32000	200000	200000	230000	260000	520000	640000
Ukraine	1100	770	410	425	735	517	500	578	135000	140000	140000	140000	140000	140000	140000	140000
Vietnam	-	-	-	-	-	-	158	121	NA	NA	NA	NA	NA	NA	NA	NA
Others	309	1390	678	681	898	397	270	260	Small	Small	Small	Small	Small	Small	Small	Small
Total	7580	10500	17500	15700	17300	18900	19600	18900	680000	440000	690000	680000	760000	810000	1300000	1500000

Note: NA stands for not available.

1.2 Distribution of manganese ore reserves and production in China

China has included manganese in the national strategic reserve during the 11th Five-Year Plan (Duan et al. 2010). In China, manganese ore deposits are primarily concentrated in Guizhou, Guangxi, and Hunan provinces. According to the "China Mineral Resources Report (2021)" released by the Ministry of Natural Resources, China has identified 213 million tons of manganese ore reserves by the end of 2020 (China Mineral Resources, 2021). There are 31.72 million tons more than in 2019, making it the second most valuable metal mineral reserve after bauxite (Figure 3a). The industrialization of manganese-based cathode materials is speeding up due to the rapid advancement of modification technology, which means that the high demand for manganese in the steel industry and the high growth of manganese batteries will cause the dichotomous pattern of the manganese industry. The manganese ore reserves in China are only one-fifth of those in South Africa, which is ranked first in terms of manganese content until 2021, and the average manganese ore grade is only 21.4%, while that of the world's major manganese resource countries is approximately 40% (Figure 3b).

In contrast, the grade of manganese ore in China is much lower than in other major manganese ore resource countries. In the metallurgical industry, manganese ore can be divided into rich and poor according to the high or low manganese content, and the finished ore with manganese content above 30% is called rich manganese ore in China. Low-grade manganese ore resources cannot meet the development demand, and China is highly dependent on manganese ore imports. According to statistics in 2021, the import quantity of manganese ore and its concentrate in China reached 30.03 million tons (Figure 4), with the discovery of four world-class mega manganese deposits and one mega manganese rich deposit in Guizhou in 2021, recording about 60% of all manganese ore resources in China. In addition to promoting Guizhou to become the largest manganese ore deposit in China, this discovery could also alter the pattern of manganese ore deposits in China and worldwide. Although the discovered manganese ore resources are still of low grade, their large reserves make China the country with the largest manganese ore reserves in the world. Therefore, the manganese ore resources in China are characterized by polarization between the rich and the poor regarding mineral grade and rich in quantity (China Mineral Resources, 2021).

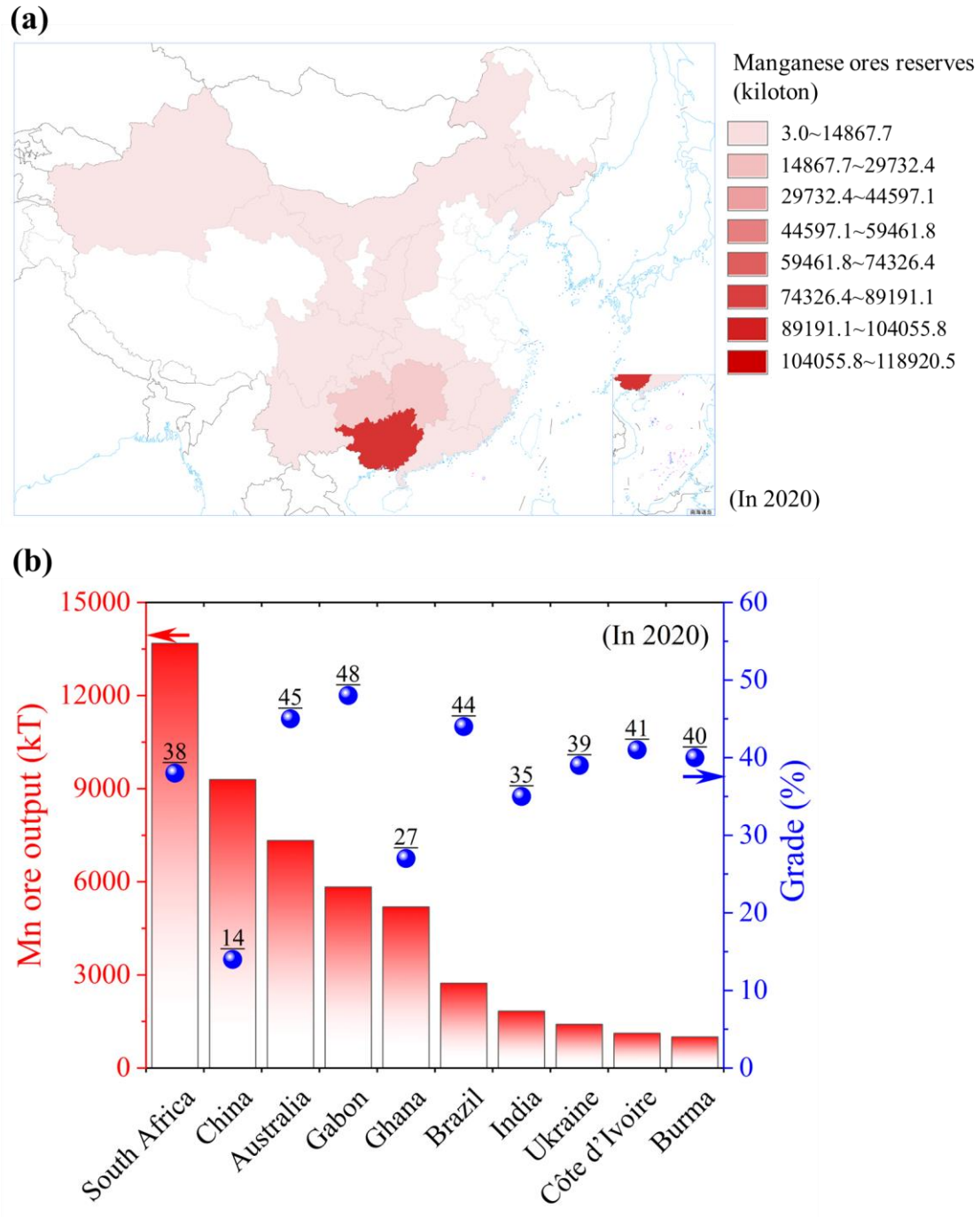

Figure 3. Distribution of manganese ore reserves in 2020 (a) Specific distribution of manganese ore reserves in China. Guangxi, Hunan and Guizhou are the three provinces with the richest distribution of manganese ore. (b) Global output and corresponding grade of manganese ore resources. The manganese ore grade is 14% in China, which is much lower than in other countries with an average grade of about 40% (Data from China Mineral Resources, 2021). The symbol unit of kT stands for kiloton.

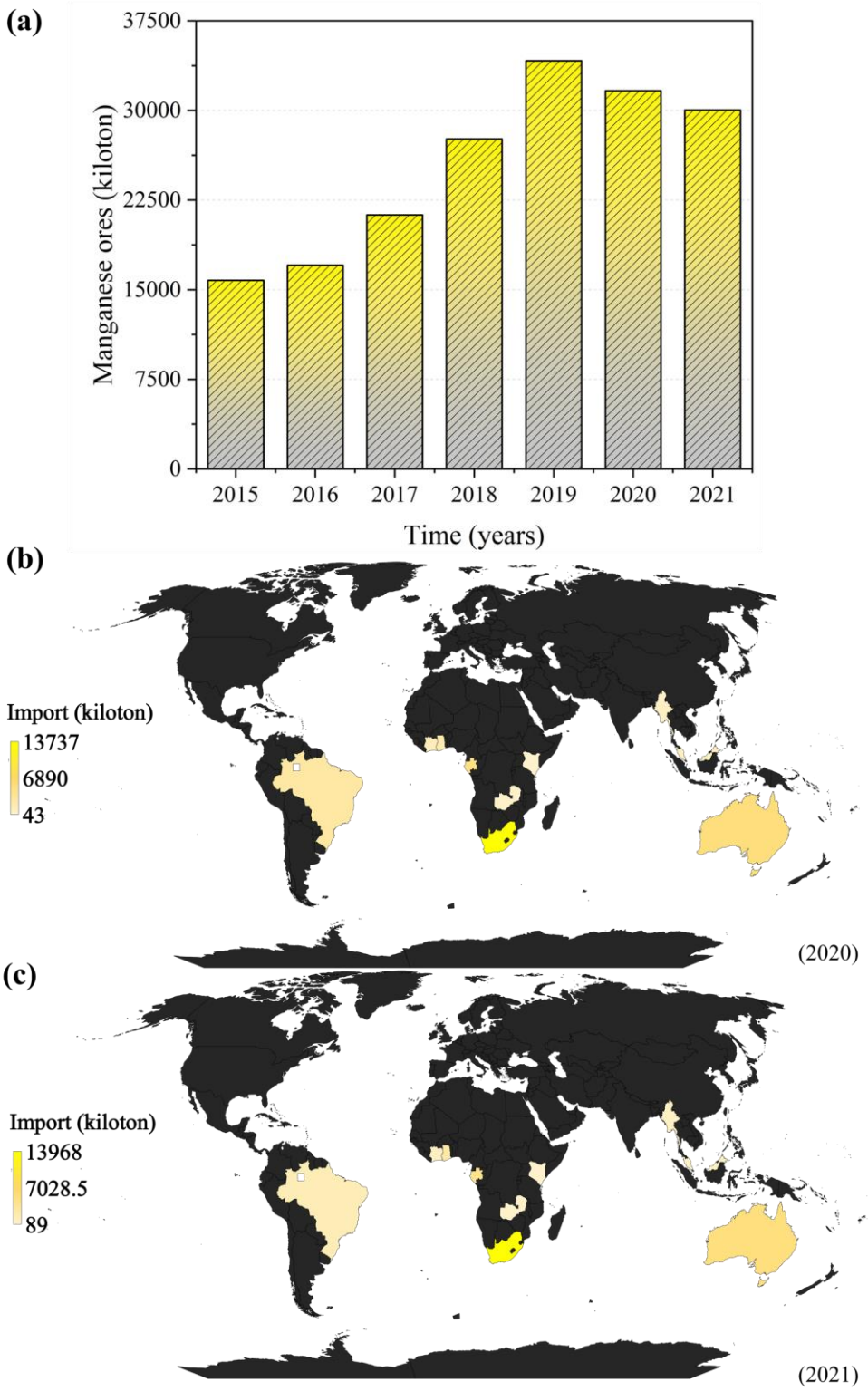

Figure 4. Global import distribution of manganese ore and its concentrates in China. (a) The import quantity of manganese ore resources from 2015 to 2021. The import quantity of manganese ores increased first and then decreased, and the maximum import quantity was the largest in 2019. (b) Global distribution of China's imported manganese ore in 2020 (c) Global distribution of China's imported manganese ore in 2021 (China Mineral Resources, 2021). The manganese ore imports from China are mainly concentrated to East Africa, Australia, Brazil and other countries.

1.3 Production and resource distribution of electrolytic manganese

Over 90% of manganese ores are processed to prepare manganese alloy products, mainly including ferromanganese alloy, silicomanganese alloy and manganese metal. In particular, ferromanganese alloy and silicomanganese alloy are mainly processed by high-grade manganese oxide ore. In 2020, China produced 11.77 million tons of silicomanganese alloy, 1.89 million tons of ferromanganese, and 1.5 million tons of electrolytic manganese (China Mineral Resources, 2021) (Figure 5). Therefore, China is the country with the highest levels of both production and consumption of manganese alloy.

Electrolytic manganese is extracted from manganese ore by acid leaching and is subsequently electrolyzed and precipitated in an electrolytic cell. More precise data show that the output of manganese ore in China was 1.3 million tons in 2021, while the output of electrolytic manganese reached 1.304 million tons in 2021 (Figure 5). As a result, the production of various downstream manganese products depends upon imported high-grade manganese ore owing to the low grade of the manganese ore produced locally. The import dependence of manganese ore in China is consistently above 90%, and the import volume of manganese ore reached 29.968 million tons in 2021, with the external dependence as high as 95.7%. Due to the increase of "double control of energy consumption", the price range of electrolytic manganese and electrolytic manganese dioxide in China was 220% and 90%, respectively, in 2021 (Figure 6).

An essential component of electrolytic manganese is electrolytic manganese dioxide, the production of which has grown significantly since 2020. In 2020, the production of electrolytic manganese dioxide reached 351,000 tons, an increase of 14.3% over the previous year. Driven by the demand of downstream primary battery enterprises, the output of the electrolytic manganese dioxide market increased significantly in 2020 (Figure 5). In addition, the market demand for electrolytic manganese dioxide has grown significantly due to the sustained increase in the shipment of lithium manganate materials. In this regard, Xiangtan Electrochemical Group, the largest producer of electrolytic manganese dioxide, produced 106,000 tons in 2020, accounting for over 30% of the total domestic output with a significant scale advantage (China Mineral Resources, 2021).

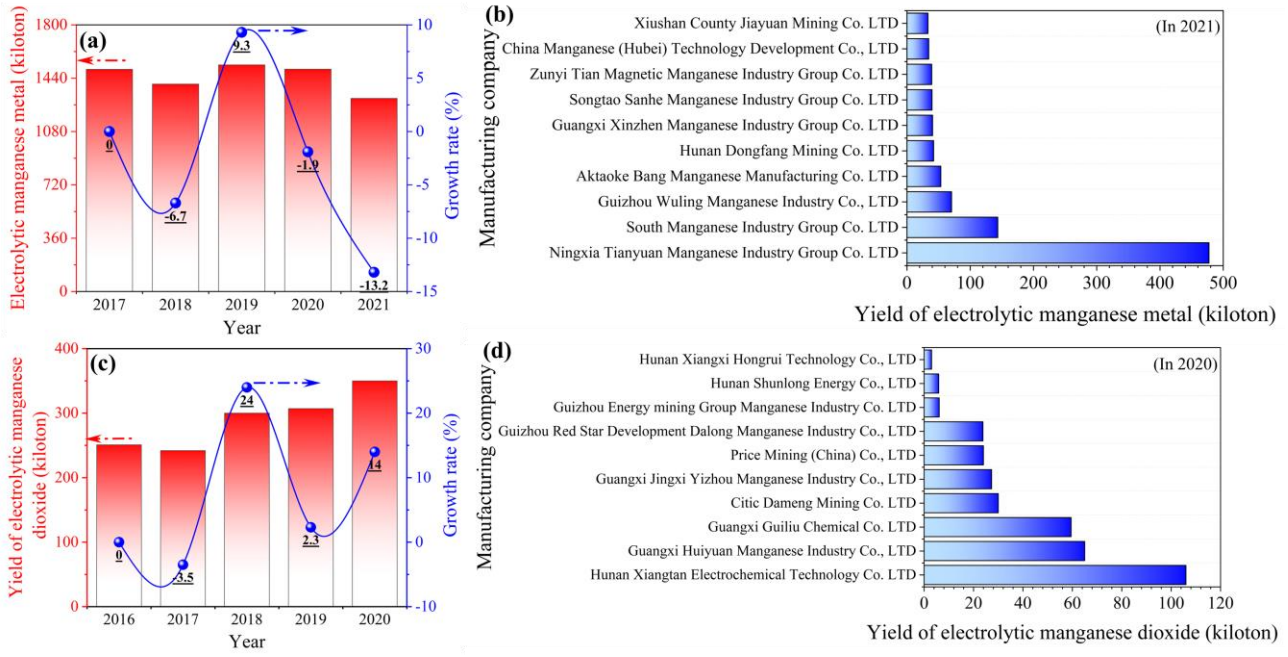

Figure 5. Annual production and main production units of electrolytic manganese in China. (a) Production and growth rate of electrolytic manganese metal from 2017 to 2021. The maximum output of electrolytic manganese metal occurred

in 2019. (b) Top ten electrolytic manganese metal production units in China in 2021. At present, the largest production site of electrolytic manganese metal is Ningxia Tianyuan Manganese Industry Group Co. Ltd. (c) Yield and growth rate of electrolytic manganese dioxide from 2016 to 2020. The maximum output of electrolytic manganese metal occurred in 2020. (d) Top ten electrolytic manganese dioxide production units in China in 2020. Currently, the largest production site of electrolytic manganese dioxide is Hunan Xiangtan Electrochemical Technology Group Co. Ltd.

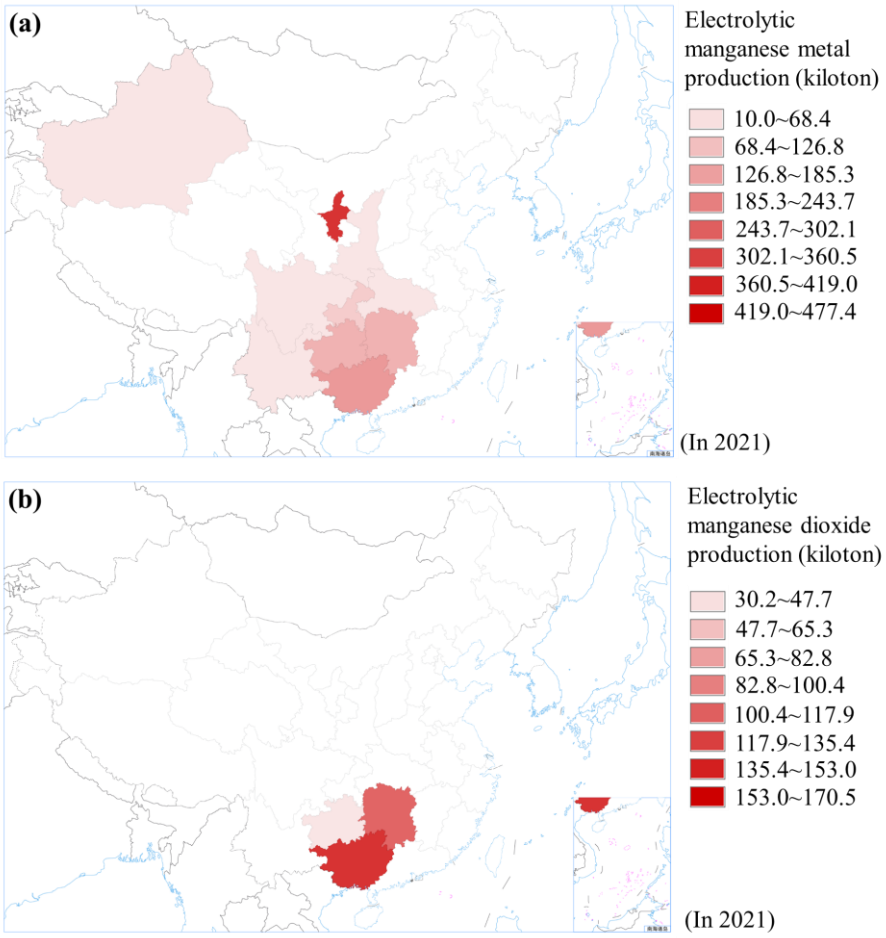

Figure 6. Spatial distribution characteristics of electrolytic manganese in China. (a) Yield spatial distribution of electrolytic manganese metal in 2021. Ningxia, Guangxi and Hunan province have become the main electrolytic manganese metal production. (b) Yield spatial distribution of electrolytic manganese dioxide in 2021. Guangxi, Hunan and Guizhou provinces are the main production areas of electrolytic manganese dioxide.

1.4 Formation and stockpiling of Mn-rich residue

The process from manganese ore to the final manganese product is closely related to the target demand and the grade (manganese content) of the original ore. Most of the rich manganese ores containing at least 30% manganese are smelted by a pyrometallurgical process to be used in the metallurgical industry. The mining of poor manganese ores is often closely linked to the wet smelting process. Among the manganese electrolytic products, electrolytic manganese metal and electrolytic manganese dioxide belong to the manganese chemical processing products. With 93.6% of the manganese ore resources in China classified as poor, electrolytic manganese is the most significant manganese-based target product.

At present, there are two kinds of manganese metal production in the world consisting of wet metallurgy, such as the electrolytic method and pyro smelting, including electric silicon thermal and aluminium thermal

methods (Liu et al. 2019). The aluminium-thermal method consumes more aluminium, has a high cost, and needs to use rich manganese ore as raw material. Meanwhile, the electro-silicon thermal method requires a high grade of manganese ore and obtains manganese metal with low purity and a complicated process. The electrolytic method of manganese sulfate solution is highly manipulable and not limited by low-grade manganese ore resources. However, the electrolytic process known as leaching-separation-electrodeposition can obtain electrolytic manganese ore with purity ≥99.8% using low-grade (8–15%) manganese ore. Thus, it is widely used in the electrolytic manganese ore industry. Therefore, wet metallurgy production has become the primary way of manganese metal production. Almost all electrolytic manganese metal is manufactured in South Africa and China, of which China accounts for more than 97% of the total electrolytic manganese metal.

Electrolytic manganese, including electrolytic manganese metal and electrolytic manganese dioxide, uses raw manganese ore via acid leaching to form manganese-contained salt and then electrolytic precipitation (He et al. 2021b). The production process of electrolytic manganese is shown in Figure 7, with further elaboration as follows:

1) Taking manganese carbonate ore as an example, the block manganese ore is crushed and ball-milled into manganese powder with a particle size of about 100 mesh. About 9 tons of manganese ore with 14% purity are consumed to produce one ton of electrolytic manganese. However, manganese dioxide ores and reducing substances are mixed in closed heating to reduce the tetravalent manganese to bivalent manganese to prepare electrolytic manganese. The divalent manganese obtained from the reduction is crushed and prepared into the above manganese powder for subsequent disposal.

2) Preparation of manganese sulfate solution. The electrolytic anode solution (H_2SO_4, 40 g·L^{-1}) from the reflux plant is introduced into the leaching tank. Then, a certain amount of sulfuric acid solution is added and mixed with the prepared manganese ore powder. The manganese ore powder in the mixture reacts with sulfuric acid to produce a manganese sulfate solution (Equation 1). Different from the process of preparing manganese sulfate from manganese carbonate ore, manganese dioxide ore can prepare manganese sulfate solution by reacting the prepared manganese dioxide powder with sulfuric acid. The other method for preparing sulfate solution is through the redox reaction between manganese dioxide ore powder and sulfuric iron ore under the action of sulfuric acid, which is usually defined as one-step mining of two ores.

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

3) The next step for electrolyte regulation. Due to the low potential of manganese, the electrolyte must maintain a higher ammonium sulfate content to improve its hydrolysis pH and current efficiency. Specifically, the mineral-to-acid ratio (mass ratio) for manganese carbonate ore powder leaching is 1: (0.55 ~ 0.6). The potential effect is generating manganese ammonia ligand ions, which raises the hydrolysis pH of manganese ions and improves the difficulty of hydrolysis. On the other hand, the added ammonium sulfate increases the solution electrical conductivity and plays an excellent buffering role. Adding ammonium sulfate has a non-negligible role in maintaining normal electrolysis operations. It is important to note that the amount of ammonium sulfate added is related to the type of antioxidant used in electrolysis. In the case of selenium dioxide, the content of

ammonium sulfate is usually 100-120 g·L^{-1}. As the selenium dioxide is replaced by sulfur dioxide, the content of ammonium sulfate reaches 130-140 g·L^{-1}.

4) The part of electrolyte purification. A certain amount of soft manganese ore powder is added to the leaching tank to oxidize the divalent iron in the manganese sulfate solution into trivalent iron (Equation 2). Then ammonia is added to adjust the pH to 6.5–7.0. Therefore, the trivalent iron hydrolyzes to iron hydroxide precipitates are removed (Equation 3). Most silica impurities also enter the leaching residues with the iron hydroxide precipitation. A small amount of divalent manganese ions is also hydrolyzed and precipitated.

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

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

5) Solid-liquid separation of Mn-contained electrolyte. The solution delivered from the leaching tank is divided into filtrates and residues after multiple pressure filtrations. The filtrates, also known as manganese sulfate solution, are transferred to the sulfurization tank for deep impurity removal treatment. The residues as the manganese sulfate acid leaching residues that is mostly disposed of by direct storage.

6) The treated step for heavy metals sulfurization and solid-liquid separation. The process is mainly completed in the sulfurization tank. By adding sodium fumarate in the sulfurization tank, it generates sulfide precipitation with copper, nickel, and other heavy metal ions in the manganese sulfate solution (Equation 4). Subsequently, the sulfide precipitate generated in the sulfidation stage is passed by the filter press to complete solid-liquid separation. The separated filtrate enters the settling tank, and the separated solid residues are sent to the residue storage.

$$(Cu^{2+}, Ni^{2+}, Co^{2+}) + 2(CH_3)_2NCSS^- \rightarrow ((CH_3)_2NCSS)_2(Cu, Ni, Co) \downarrow \quad (4)$$

7) Static and fine filtration of the separated filtrate. The filtrate is finely filtered again by filtering equipment, and then the selenium dioxide is added to the filtrate to prepare a qualified electrolyte. As described above, the separated filtrate enters the electrolyzed tank and the separated solid filtrate is sent to the residue storage.

8) Electrolysis and post-treatment. In the electrolyzed tank, the electrolytic manganese metal and electrolytic manganese dioxide will be deposited and precipitated from the cathode rod of the electrolyzed tank. Besides precipitating oxygen on the anode, a certain amount of anode sludge will be generated. The residual manganese ions and sulfuric acid in the anode solution are returned to the leaching tank for reuse. The manufactured Mn-rich residue must undergo various processes once electrolysis is completed, including passivating, washing, drying, and stripping. Specifically, 3% potassium dichromate is used for passivation to prevent the electrolytic manganese from being oxidized in the air. The post-treatment process generates a certain amount of wastewater containing manganese and chromium, which needs to be further treated.

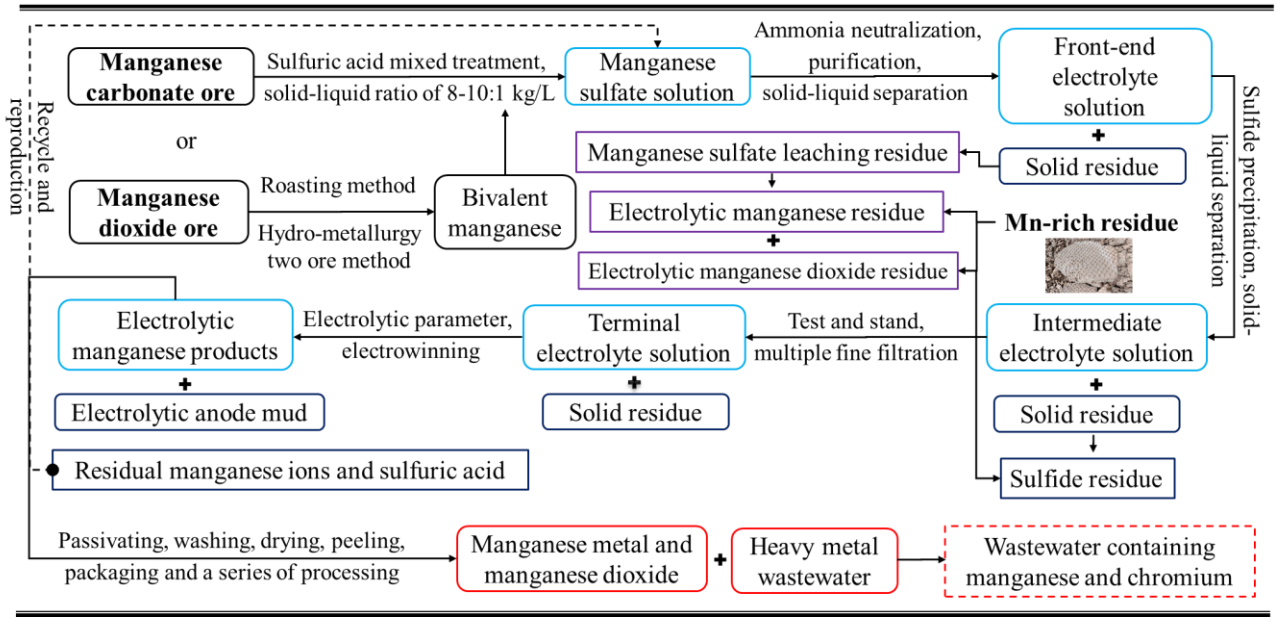

Figure 7. The hydrometallurgical preparation process of electrolytic manganese. Through the detailed preparation process, the formation mechanism of Mn-rich residue can be obtained, thus providing necessary guidance for reduction. Both manganese carbonate and manganese dioxide ores need to be prepared into a manganese sulfate solution. Mn-rich residue is an aggregate of filter residues, which provides a source explanation for its complexity.

Both electrolytic manganese dioxide and metal residue are classified as the residues generated while producing manganese-based electrolytic products. The grade and leaching method cause a large amount of Mn-rich residue to be stockpiled. Due to the low-grade manganese ore, the electrolytic manganese enterprises in China produce an average of 10–12 tons of Mn-rich residue for one ton of electrolytic manganese (He et al. 2021a; Yang et al. 2022; Wang et al. 2022a). Meanwhile, as the grade of manganese ore used in the manufacture of electrolytic manganese industries gradually declines, the amount of Mn-rich residue generated per unit of electrolytic manganese likewise grows. Currently, the stockpile of Mn-rich residue in China has reached more than 160 million tons, with a growing rate of 10 million tons per year. In addition, the low-grade manganese carbonate ore not only increases the difficulty of the production process but also relatively increases the emission of waste residue in the production process. As a result, the manganese electrolysis industry in China is witnessing a more critical circumstance concerning the comprehensive usage of Mn-rich residue resources.

1.5 Characteristics and environmental impact of Mn-rich residue

There are many significant differences between Mn-rich residue and natural minerals, mainly in the uncertainty of Mn-rich residue chemical components caused by regional and process variability. In addition, due to the production process of electrolytic manganese, the content of sulfate, ammonia nitrogen and manganese in manganese residue is severely exceeded. The concentrations of arsenic, mercury, and selenium are also not negligible (Wang et al. 2022b). Based on Figure 8, the specific surface area of Mn-rich residue is 4.2 m^2 g^{-1}, and the moisture content is 31.2%. The particle size D_{50} and pH of the Mn-rich residue are 11.84 μm and 6.2, respectively (Wang et al. 2022a). The existing results indicate that the pH of common Mn-rich residue is 4.00–7.00 and the specific surface area is 3.00–10.00 m^2 g^{-1}. The particle size is 10.00–80.00 μm and the water content is about 20–35%. Meanwhile, the total content of SiO_2, Al_2O_3, Fe_2O_3 and CaO in Mn-

rich residue can generally reach 43–73% (Table 3), and these ingredients are the main chemical components of building materials. Therefore, Mn-rich residue is a potential raw resource for construction materials. However, due to the employed hydrometallurgical process, Mn-rich residue contains many soluble harmful ions in addition to Mn^{2+} and NH_4^+-N.

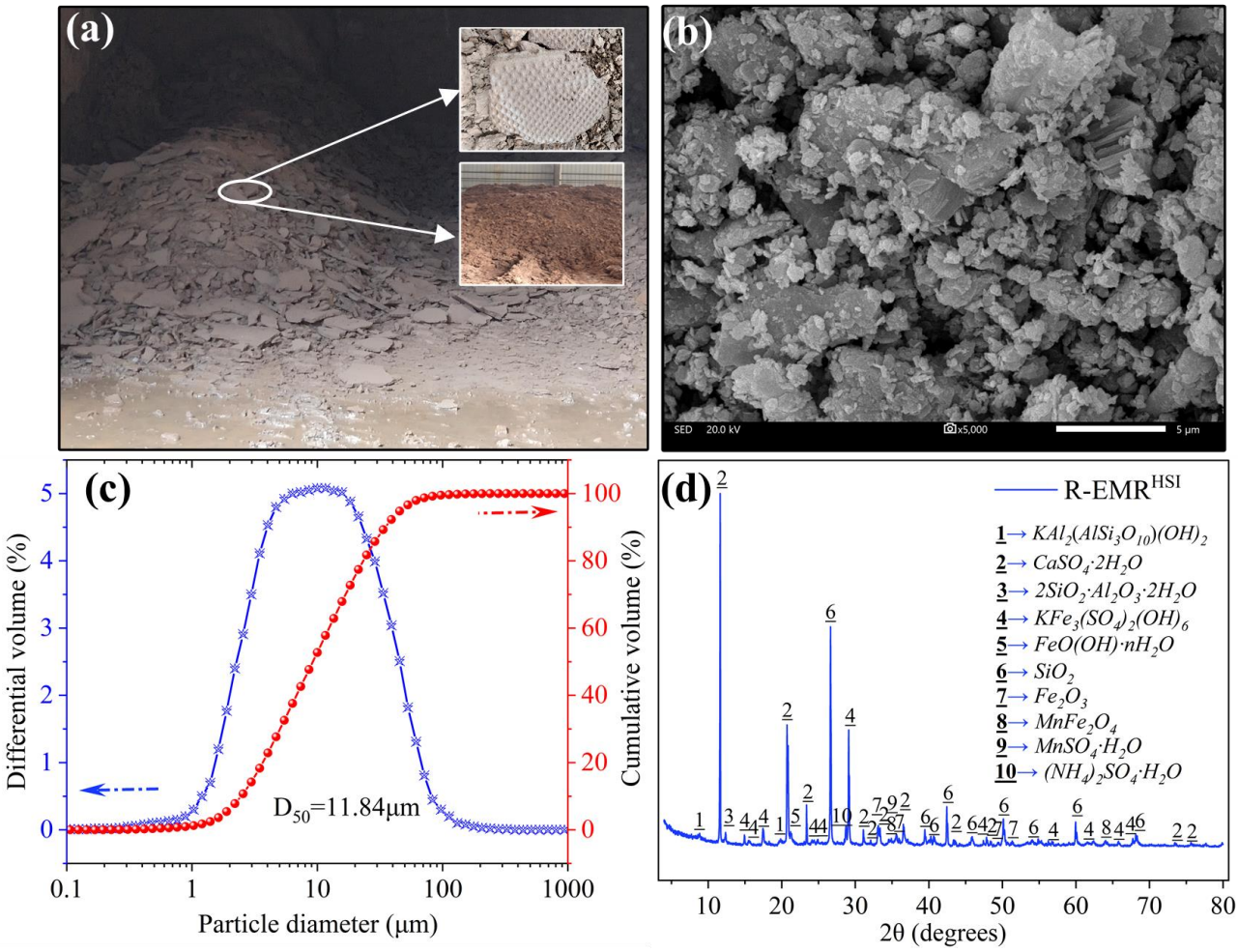

Figure 8. Characteristics of Mn-rich residue. (a) A large amount of Mn-rich residue tailing is deposited in tailings ponds, (b) the image of Mn-rich residue morphology obtained by 5000 times microscopic test. (c) particle size distribution curve of Mn-rich residue obtained by particle size analysis. The particle size D_{50} of Mn-rich residue after drying and sifting is 11.84 μm. (d) mineral composition of Mn-rich residue obtained by diffraction technique. The label of R-EMR^{HSI} stands for the raw Mn-rich residue with high ferrum and silicon. The X-Ray Diffraction test result indicates that the main mineral phases of Mn-rich residue are gypsum, jarosite, and kaolin. Reprinted with permission of Elsevier from Wang et al. (2022a).

Meanwhile, the treatment method of Mn-rich residue is still mainly simple and crude, usually using a mulch landfill and building a reservoir or dam for disposal of stockpiling (He et al. 2021b). Despite establishing dumps or dams, Mn-rich residue poses significant environmental risks to the surrounding soil and water resources due to imperfect impermeability measures. Specifically, 1) On the open Mn-rich residue stockpiling, many abandoned Mn-rich residues occupy valuable land resources. The Mn-rich residue-based dumps are primarily adjacent to residential areas, encroaching on land for farming, forestry, industrial and mining purposes. Stockpiling of Mn-rich residues for a prolonged period may pose several hazards, including

environmental pollution, dam breakage, restrictions on regular production and the long-term development of industries. 2) The harmful Mn-rich residue pollutes the atmosphere and the surrounding water-soil environment as the treatment of Mn-rich residue relies on open stockpiling. Sunlight and wind will make Mn-rich residue with fine particles enter the atmosphere, seriously impacting the surrounding ecological environment. 3) The vast scale Mn-rich residue dissolved by rainwater leaching to produce the leachate pollutants, including sulfate, ammonia nitrogen, manganese, arsenic, mercury and selenium. The formed pollutants cause severe environmental risks, leading to gas, water, and soil hazards. In addition, organic matter is scarce in Mn-rich residue, mainly composed of minerals like calcium and magnesium. There is a negative impact on the significant biodiversity of the area as a result of this. It is challenging for the injured ecosystem to recover when biodiversity is lost. 4) Many abandoned Mn-rich residues are not further integrated and utilized, which causes a waste of resources. The above results show again that a large amount of stockpiled Mn-rich residue causes a huge environmental burden. Therefore, targeting the harmless treatment and resources high value-added utilization of Mn-rich residue is urgent. Notably, reducing the total amount of Mn-rich residue by improving the production efficiency of Mn-rich residue is the primary front-end treatment for Mn-rich residue disposal. Harmless pretreatment of Mn-rich residue is a vital prerequisite for its resource-based reuse. Therefore, the reduction, pretreatment and high-value-added utilization of Mn-rich residue can solve the current issue of manganese resource shortage and bring great environmental and economic benefits to society. China's government has forced all electrolytic manganese companies to deal with Mn-rich residue. There has been some effort to address this issue since the late 1990s, but there has not yet been a mature and reliable industrial application (Duan et al. 2010). Mn-rich residue has thus grown to be a critical challenge in China since it prevents the electrolytic manganese industry from developing sustainably.

Table 3. Major chemical compositions of Mn-rich residue from different Mn-rich residue stockpiling sites

No.	Country	Sites	Major composition (wt%)						Reference
			SiO_2	SO_3	CaO	Fe_2O_3	Al_2O_3	MnO	
1	China	Guizhou	26.22	36.63	18.97	7.79	3.00	5.21	Tian et al. 2019
2	China	Guizhou	33.75	20.61	14.03	5.07	8.99	3.94	Tang et al. 2019
3	China	Guizhou	31.38	18.58	9.45	7.35	10.71	4.82	Zhang et al. 2019
4	China	Guizhou	29.74	29.59	14.71	5.85	6.86	6.47	Chang et al. 2020
5	China	Guizhou	31.49	25.6	12.85	4.09	7.07	3.51	Huang and Zhang, 2022
6	China	Guizhou	27.60	33.97	18.90	3.58	8.21	2.34	He et al. 2022a
7	China	Guizhou	20.27	26.64	11.48	2.50	6.38	1.92	He et al. 2022b
8	China	Guizhou	29.63	29.54	14.82	5.41	8.32	2.02	Wang et al. 2022a
9	China	Guizhou	25.17	35.87	16.99	3.81	7.30	3.32	Duan et al. 2021
10	China	Guizhou	23.14	33.06	21.54	5.25	6.88	5.90	Shu et al. 2021
11	China	Guizhou	39.97	23.39	10.43	5.30	12.32	3.05	Shu et al. 2020a
12	China	Guizhou	37.56	22.95	16.93	4.78	12.14	3.12	Shu et al. 2020b
13	China	Guizhou	32.15	31.78	12.56	5.36	7.68	N.D	Chen et al. 2020a
14	China	Guizhou	32.32	30.77	14.27	6.32	7.63	3.00	Shu et al. 2018a
15	China	Guizhou	35.52	19.84	10.09	8.04	11.43	5.15	Xu et al. 2019
16	China	Guangxi	38.75	10.80	1.30	14.94	8.12	6.40	Li et al. 2018

17	China	Guangxi	30.79	18.24	7.68	3.13	9.18	N.D	Hou et al. 2019
18	China	Guangxi	27.62	28.07	16.52	10.97	2.89	10.41	Zhou et al. 2021
19	China	Guangxi	23.40	24.70	13.20	9.10	3.10	4.20	Lan et al. 2021a
20	China	Guangxi	35.20	9.38	1.19	15.17	7.85	6.14	Li et al. 2021
21	China	Guangxi	23.99	25.92	10.53	7.24	2.56	4.67	Lan et al. 2021b
22	China	Guangxi	22.30	36.88	13.22	9.40	3.20	4.65	Li et al. 2020a
23	China	Guangxi	23.41	34.22	15.45	10.79	2.60	9.60	Xue et al. 2020
24	China	Guangxi	23.99	n.d.	10.53	7.24	2.56	4.67	Lv et al. 201
25	China	Guangxi	24.80	25.70	16.20	13.10	5.10	4.75	Lan et al. 2019a
26	China	Guangxi	23.40	27.60	15.00	8.60	6.50	4.80	Li et al. 2019a)
27	China	Guangxi	23.41	27.58	14.96	8.57	2.46	4.80	Li et al. 2019b
28	China	Guangxi	38.75	10.80	1.32	14.94	8.12	6.40	Li et al. 2018
29	China	Hunan	34.67	20.53	5.58	21.21	9.01	3.94	Wang et al. 2022
30	China	Hunan	35.04	21.37	8.67	20.54	5.97	N.D	Li et al. 2016
31	China	Hunan	31.80	32.20	12.60	5.80	7.60	2.30	Liu et al. 2013
32	China	Hunan	24.60	37.80	8.60	7.90	12.20	4.60	Li and Zhang, 2020
33	China	Hunan	44.10	5.54	6.05	2.81	23.74	12.00	Yu et al. 2019
35	China	Hunan	24.60	N.D	8.60	7.90	12.20	4.60	Li et al. 2015a
36	China	Hunan	24.60	22.00	8.59	7.87	12.15	10.90	Wu et al. 2015
37	China	Chongqing	32.32	32.77	15.10	5.62	7.01	2.42	Shu et al. 2019a
38	China	Chongqing	40.08	22.72	7.34	5.58	13.78	2.99	Wang et al. 2020
39	China	Chongqing	34.65	26.40	14.78	7.01	8.21	3.02	Shu et al. 2016
40	China	Chongqing	27.93	37.31	15.39	5.29	5.78	5.05	Du et al. 2015
41	China	Chongqing	61.24	3.86	11.57	3.97	11.36	0.82	Chen et al. 2021
42	China	Chongqing	36.40	19.60	13.10	5.83	9.37	N.D	Zhan et al. 2020
43	China	Chongqing	34.40	26.80	13.00	6.12	7.85	N.D	Zhan et al. 2018
44	China	Chongqing	32.32	30.77	14.27	6.32	7.63	3.00	Shu et al. 2017
45	China	Chongqing	17.17	19.89	8.85	3.89	5.03	3.05	Wang et al. 2016
46	China	Chongqing	22.03	31.37	19.16	8.83	3.09	8.54	Du et al. 2014a

Note: N.D stands for not detected.

1.6 Potential of resource utilization of Mn-rich residue as building materials

The entire society has progressively agreed that environmental conservation is necessary to ensure human living standards and advance the resource - efficient development of the national economy and society (Rodrigues et al. 2022; He et al. 2022b; Wang et al. 2022a). As the main environmental protection content, the tri-wastes treatment and comprehensive utilization is a vital pivot to purify the living environment and protect the ecological balance. Given the huge amount of Mn-rich residue, a high efficiency and low environmental impact approach for utilizing and disposing of Mn-rich residue is urgently needed. However, the over-quantification of harmful substances and low reactivity of Mn-rich residue have caused adverse effects, which hinder the development of the resource utilization of building materials. The existing results indicate that the cycle usage amount of Mn-rich residue is small and the properties of cement cementitious materials made by Mn-rich residue are dissatisfactory. The requirements of the current rapid industrialization cannot be fulfilled

in the existing context. Therefore, the cyclic utilization of Mn-rich residue is the top priority in its treatment procedure.

Due to the electrolysis, purification and deposition process, Mn-rich residue contains many aluminosilicate, hematite, quartz, gypsum, jarosite and kaolin for potential development into a construction material (Duan et al. 2011; He et al. 2021a). Therefore, how to turn Mn-rich residue into treasure and realize the high value-added resource utilization of Mn-rich residue-based building materials is worth further investigation. As far as we know, most of the current reviews and studies focus on the direct or indirect resource utilization of Mn-rich residue, which promotes the treatment of Mn-rich residue to a certain extent. The Mn-rich residue is rich in silicon, aluminium, iron, calcium, sulfur, and other chemicals, which means that Mn-rich residue, as a misplaced resource, is also a promising artificial mineral material. Meanwhile, the building materials industry is experiencing a mineral resource shortage, causing it to struggle to find suitable and alternative mineral resources. The current treatment of Mn-rich residue still presents some concerns, including high costs, low efficiency, limited resource utilization, and disposal method. The benefits of the substantial amounts of aluminosilicate, quartz, hematite, gypsum, and other components in Mn-rich residue are not fully exploited by the existing resource exploitation. The misplaced resources will likely be wasted again if the value of waste to wealth is low. Therefore, Mn-rich residue still has substantial utilization potential and disposal value in China. It is urgent for Mn-rich residue to be utilized in a harmless and high-value-added manner. As of yet, there has not been a systematic review of Mn-rich residues that are utilized in high-value-added applications. This paper comprehensively compares and analyses the most advanced technologies of Mn-rich residue in fountainhead reduction, pretreatment and high value-added utilization. In conjunction with current Mn-rich residue production and treatment technology, the industrial application reveals the barriers to recycling and reusing Mn-rich residue. The benefits and drawbacks of the existing Mn-rich residue processing and disposal technologies are discussed, along with practical solutions for achieving high value-added resource utilization of Mn-rich residue. This work supports realizing the sustainable development and environmental protection strategy of Mn-rich residue.

2. Mn-rich residue reduction and safe storage technology

This section primarily focuses on the fountainhead reduction of Mn-rich residue, which is the first premise of its effective long-term management. Mn-rich residue fountainhead reduction mainly refers to reducing the initial production of Mn-rich residue as much as possible, thereby reducing its impact on the ecosystem at the source. Specifically, the reduction of Mn-rich residue is mainly reflected in optimising the hydrometallurgical process and purifying the original manganese ore.

2.1 Improvement of manganese ore grade

The impurities such as phosphate, silica-aluminium phase and iron and associated metals such as nickel, zinc, and copper, which are difficult to separate, cause the significant difference between the reserves of manganese ore and the amount of manganese resources. Therefore, reducing the impurity of manganese ore and realizing the enrichment of manganese resources can effectively decrease the yield of Mn-rich residue. The main challenge is to improve the manganese richness of manganese ore and reduce the impurities in manganese ore. Meanwhile, the methods to improve manganese ore grade mainly focus on physical enrichment, such as water washing, gravity separation, magnetic separation, flotation, and microwave heating (Xie et al.

2021a). The coupled methods also can be formed to improve its enrichment efficiency. Table 5 lists the fountainhead reduction results of Mn-rich residue using the physical method to improve manganese ore grade. As the initial procedure, the water washing removes clay minerals from manganese ore, which provides a prerequisite for the subsequent operations. Gravity separation screens manganese minerals based on mineral density difference and the reported maximum enrichment rate of MnO reached 91.1% (Muriana, 2015). However, due to the negligible density difference between the Fe-Mn minerals (Table 4), the gravity separation for iron and manganese minerals is insignificant. Therefore, high-intensity magnetic separation has become a wall-breaking technology for sorting Fe-Mn minerals.

After high-intensity magnetic separation, manganese can be concentrated to more than 45% and Mn sorting index is close to 90% (Tripathy et al. 2015). However, the single magnetic separation for manganese and iron is still not ideal. Therefore, the flotation method consisting of some chemical substances is provided to achieve the manganese from Fe-Mn ores separation to some extent. The manganese grade can be raised from 10.7 to 18.3% and the sorting index can reach 97% using linoleic acid (Zhou et al. 2015). However, the slurry formed by flotation is overly complex with the dissolution of Mn^{2+}, Mn^{3+}, Fe^{2+} and Fe^{3+} ions. The oxidation-reduction and hydration of dissolved ions on the mineral surface deteriorate the flotation. In addition, the microwave heating method increased the manganese grade from 30 to 40% (Chen et al. 2017).

In conclusion, a single-treated method cannot deal with more and more complex manganese ore resources. In other words, this means that the multi-coupling method has great potential. When the combined treatment of high-gradient magnetic separation and wet- beneficiation, the manganese recovery efficiency can reach 64% and a purity of 97.9% $MnCO_3$ can be obtained (Zhang et al. 2017a).

Table 4. The density of various manganese-bearing minerals

Manganese-bearing minerals	Density (g cm^{-3})	Manganese-bearing minerals	Density (g cm^{-3})
Pyrolusite	4.7–4.8	Hematite	4.9–5.3
Psilomelane	4.4–4.7	Magnetite	4.9–5.2
Rhodochrosite	3.6–4.7	Siderite	3.7–4.0
Braunite	4.7–5.0	Limonite	4.0–4.3

Table 5. Summary of results of direct physical methods to improve the grade of manganese ore

Mn ores	Separation methods	Feed (wt.%)	Concentrates (wt.%)	Recovery (wt.%)	Reference
Nigeria	Gravity	25.36	56.13	95.18	Oyelola 2020
Nigeria	Wet gravity	NA	NA	91.11	Muriana 2015
Hunan, China	High-intensity magnetic	10.39	22.75	89.88	Wu et al. 2015
India	Two-stage magnetic	22.40	42.10	44.70	Tripathy et al. 2015
India	Single dry magnetic	27.33	35.52	44.00	Bhoja et al. 2021
Canada	Direct dry magnetic	26.00	49.00	69.00	Elliott 2020
India	Direct wet magnetic	32.42	42.00	47.00–49.00	Singh 2011
South Africa	High-intensity magnetic	29.80	29.72	59.90	Mpho et al. 2013

Note: NA stands for information not available. Mn recovery (wt.%) =Product weight (wt.%) × Product Mn grade (wt.%)/ Feed Mn grade (wt.%)

2.2 Leachate enhancement by Mn^{2+}

After enhancing the manganese ore grade to reduce the final Mn-rich residue yield, the further operation to achieve Mn-rich residue reduction is to improve the Mn^{2+} leaching efficiency in the leachate. The improvement of leaching efficiency is closely related to the type of manganese ore. Manganese carbonate ore, such as rhodochrosite, can be obtained directly by H_2SO_4 with a leaching efficiency of over 96% for Mn^{2+} during the hydrometallurgical process (Liu et al. 2014). With the gradual depletion of manganese carbonate ores with high grades, the recovery of manganese oxide ores, such as soft manganese ore, has become a matter of concern. Therefore, mining low-grade soft manganese ore and low-grade manganese carbonate ore can boost the amount of raw materials for electrolytic manganese metal production, and much attention has been conducted to this territory. As stated above, soft manganese ores need to be converted from tetravalent to divalent form before leaching by the introduced reducing substances to enhance the formation efficiency of manganese sulfate solution.

The critical point for improving Mn^{2+} leachate is the selection of reducing and leaching agents. All reducing agents in acidic environments effectively reduce tetravalent Mn to a divalent state, achieving the Mn leaching value of over 90%. The addition of calcium sulfide can reach 95% Mn leaching efficiency by converting MnO_2 to Mn_3O_4 (Li et al. 2015a). The sulfur dioxide translates Mn^{4+} into Mn^{2+} to realize the Mn leaching rate of 95% (Sun et al. 2013). The Mn^{2+} leaching rate reached 96.6% as the SeO_2 was the reducing agent (Ding et al. 2016). When using H_2O_2 as a reducing agent to improve the reducibility of acid-leaching environment, the leaching rate of Mn^{2+} from low-grade manganese ores reaches 97%. The leaching rate of divalent Mn from manganese ores can reach 95.6% using H_2SO_4 as leachate (Zhang et al. 2013). Introducting lignin can realize the Mn leaching rate of 91% by reducing Mn^{4+} to Mn^{2+} via H_2SO_4 (Xiong et al. 2018). It is noted that reducing agents, such as pyrite, must be utilized carefully with iron-bearing Mn ores because they might introduce a lot of Fe ions into the leachate and dramatically raise the post-treatment cost. The electric field has an excellent leaching efficiency but is seldom employed in production due to the problematic leaching conditions, limited application, and expensive costs (Zhang et al. 2017b). In addition, the bioleaching method is another good option for Mn^{2+} leaching because of its simple operation and low cost. The 99% Mn^{2+} leaching rate can be obtained using microorganisms (Xin et al. 2015). Electrolytic manganese is not widely used in bioleaching because it is time-consuming and more complex than other processes.

2.3 Improvement of the mineral separation degree and water content regulation

The following enhancement measure is to remove other impurities, such as iron from the manganese sulfate solution, which is the main impurity in manganese ore. Since iron has similar chemical properties to manganese, the iron phase needs to be eliminated before electrolysis to improve the purity of the manganese sulfate solution (Liu et al. 2019). Iron ions are removed by adjusting the pH and forming $Fe(OH)_3$ to separate them from the leach solution. Most impurity silica also precipitates with $Fe(OH)_3$ to constitute the leaching residue during the iron deposition and separation. Some manganese ions are also partially precipitated into the leaching residue. Therefore, stepwise graded filtration can remove heavy metals from Mn-rich residue by leaching the residue. It is debatable that the huge added disposal costs directly limit the broad application of this disposal process. However, this issue can be solved more effectively by directly separating the mineral phase using chemical products or supplementary building materials as target products.

Based on the hydrometallurgy process of electrolytic manganese, finer manganese powder is used to

improve the leaching efficiency. It means that the particle size of the leaching residue is around 10–50 μm (Wang et al. 2022a). The clay mineral contained in fine power has a multitude of interlayer waters. Meanwhile, H_2SO_4 interacts with calcareous minerals to create extremely hydrophilic gypsum during leaching. The $Fe(OH)_3$ colloid deposited and separated during the leaching process also contains a lot of water. Therefore, the above substances cause Mn-rich residue to have an extremely high moisture content of 20 to 35%. A large amount of soluble manganese ions (2.0–5.0%), $(NH_4)_2SO_4$ (2.5–5.0%) and heavy metals such as Ni^{2+}, Co^{2+}, Cr^{6+}) are also stored in the water solution. The leading cause that makes Mn-rich residue capable of causing significant contamination with these dangerous compounds. A point of concern is that nearly 10% of the manganese is lost in the contamination process by soluble substances. Hence, the water content of Mn-rich residue is relatively high in the case of direct disposal due to the storage of rainwater. Although the air-dried Mn-rich residue is lumpy, it still contains a significant amount of chemically bound water. Since Mn-rich residue contains a high amount of water, it is difficult to recover and recycle, while its high viscosity and tendency to harden after evaporation prevents it from being readily mixed with other materials. In this manner, controlling Mn-rich residue water content reduces the amount of Mn-rich residue and the potential ecological risk as well as saving land resources. It has been reported that the use of surfactants such as dodecyl amine can change the hydrophilicity of the Mn-rich residue particle surface and form a semi-micellar Mn-rich residue surface, resulting in a significant reduction of water content. In addition, innovative filtration devices are developed to facilitate the control of moisture content.

2.4 Limitations and future direction

There are several restrictions on the above-mentioned disposal methods, notwithstanding their ability to decrease the volume of the Mn-rich residue stockpile. 1) First, due to the gradually increased complexity of associated minerals in manganese ores, reducing the Mn-rich residue stockpile volume is challenging using simple methods. There are relatively few works to develop coupled-composite beneficiation processes for this issue. 2) In addition, due to the high-water content of Mn-rich residue and the residual of soluble materials, it is necessary to innovate new preparation processes to reduce the stockpile volume of Mn-rich residue. As a result, the cost of production is inevitably increased, which is unfavourable for business. In addition, the use of foreign high-grade manganese ore also provides a potential option for Mn-rich residue fountainhead reduction. However, the fountainhead reduction treatment of Mn-rich residue will become more prominent with the increasing emphasis on the natural environment and the shortage of manganese ore resources with high-grade. Mn-rich residue fountainhead reduction should be characterized as a complicated task, requiring reduction of the water content in the Mn-rich residue, improvement of the manganese leachate purity, and constant process control of the electrolytic manganese production. In addition, it is critical to ensure the Mn-rich residue fountainhead reduction is conducted without contributing to secondary environmental damage.

The existing high-temperature reduction-smelting separation process is the most promising pyrometallurgical process for separating ferromanganese from ores (He et al. 2021a; Wang et al. 2022a). The difference in fusibility between silicate and ferrofluid or iron carbide is the key to manganese and iron separation. In decades of successful manufacturing operations, the method has proven suitable for fully utilizing ferromanganese ores. In addition, the separation process of carbon thermal reduction roasting is better for the separation of manganese and iron in ferromanganese-based minerals. Alkaline additions can accelerate

the development of metallic iron during direct reduction thermal treatment and disassemble the structure of irreducible silicates, which further enhances the reduction of ferromanganese oxides. Since the combined reaction of manganese dioxide and sulfur is thermodynamically feasible, sulfate roasting or sulfur leaching is a promising method for selective extraction from ferromanganese ores. Overall, it is recommended to use a combination of various physicochemical approaches and thermal treatment processes to achieve a high-quality realization of the fountainhead reduction of Mn-rich residue.

3. Harmless pretreatments of Mn-rich residue

The optimization of the metallurgical process and purification of the acid leachate can initially realize Mn-rich residue fountainhead reduction. In practice, it is not feasible to interrupt the production of Mn-rich residue by the filter-pressing operation, which entails that the subsequent disposal of the Mn-rich residue stockpiled will require a new technology for disposal. As mentioned earlier, stockpile based Mn-rich residue depletes land resources and causes environmental damage. The harmfulness of Mn-rich residue is attributed to the heavy metal ions and ammonia nitrogen contained in the high-water content with high migration rates. Therefore, in-situ Mn-rich residue pretreatment or synergistic control of the harmless and resource utilization is required regardless of resource utilization or disposal in stockpiles.

The pretreated Mn-rich residue has the potential to construct building and industrial materials rather than being a dangerous industrial solid waste material that endangers environmental safety. As such, the harmless pretreatment of Mn-rich residue is an essential prerequisite to ensuring the efficient use of resources which is often closely related to its utilization. Mn-rich residue treatment techniques can be classified into dry, thermal, and wet disposal technologies according to their physicochemical characteristics.

3.1 Direct dry disposal technology of Mn-rich residue

The direct dry disposal technology of Mn-rich residue benefits from the introduction of additional chemicals. The addition of chemical substances to the Mn-rich residue can achieve the immobilization of harmful substances, but also improve its own chemical composition, and thus improve the reactivity. As part of the stabilization-solidification process, soluble hazardous substances are transformed into insoluble and chemically stable hazardous substances to reduce migration and diffusion (Kim and Lee, 2017; Salami et al. 2022). This method has the potential for the environmentally friendly disposal of solid waste in landfills, providing a focused guide for direct dry disposal of Mn-rich residue. The stockpiled Mn-rich residue is mixed with cementitious materials or selected chemical reagents to stimulate reactivity while providing long-term safety and optimizing resource utilization. In addition, the effective stabilization of soluble heavy metal ions in Mn-rich residue also somewhat reduces environmental pollution.

Currently, quicklime, magnesium oxide, silicate, phosphate, and cement are used as common curing agents (Qiao et al. 2010; Silva et al. 2011; Cho et al. 2014; Zhang et al. 2018; Ouhadi et al. 2021; Hossain et al. 2022). The main results are summarized as follows: 1) The alkaline environment provided by alkaline curing agents such as quick lime and magnesium oxide allows the rapid removal of NH_4^+-N, while the soluble Mn is cured to MnOOH and $Mn(OH)_2$ (Chen et al. 2019). 2) Intensive stabilisation of Mn^{2+} and removal of NH_4^+-N from Mn-rich residue can be achieved using strong alkaline solutions such as sodium hydroxide. However, the expensive treatment costs limit the widespread use of this technology. 3) Introducing low-grade chemical reagents provides a more economical solution to the above limitation. Shu et al. (2020b) prepared a phosphate-

based binder to stabilize Mn^{2+} and NH_4^+-N in Mn-rich residue using a low-cost, low-grade MgO and calcium super-phosphate. The leachate of phosphorite by-product as an inexpensive phosphate source was employed to achieve high-quality stabilization of NH_4^+-N and Mn^{2+} in collaboration with MgO or CaO (Chen et al. 2020a). Although the economics and stabilization efficiencies were improved, the long-term service stability of the formed condensation products and the optimal design of the disposal process continue to impede the long-term development of this technology. In this regard, a stepwise stabilization and solidification strategy was adapted for the high-quality disposal of Mn^{2+} and NH_4^+-N in Mn-rich residue (Shu et al. 2019b). Despite the excellent removal efficiency of Mn^{2+} and NH_4^+-N, the long-life durability of the final products was not effectively expressed. 4) The CaO-based solidification products were prevented from ageing owing to the application of $CaCO_3$ and Na_3PO_4. Additionally, carbon dioxide and alkaline additives were used to achieve manganese carbonation fixation while reducing carbon emissions in the form of carbon capture (Chen et al. 2016; Baena-Moreno et al. 2022; Ho et al. 2022). The added CaO solidified the soluble manganese in Mn-rich residue to $MnCO_3$, and the addition of $MgCl_2{\cdot}6H_2O$ and $Na_3PO_4{\cdot}12H_2O$ solidified NH_4^+-N in Mn-rich residue to $MgNH_4PO_4{\cdot}6H_2O$.

In summary, the main principle of typical chemical reagent disposal for Mn-rich residue is to use the selected alkaline oxides to regulate the pH value during the solidifying process and transforms soluble manganese into insoluble manganese-based hydroxide and high-valent manganese oxide. The remaining soluble manganese was solidified using different phosphorus-containing compounds, and magnesium ions in Mn-rich residue hardened the NH_4^+-N into an insoluble phosphate. The adequate solidification of soluble Mn^{2+} and NH_4^+-N can be achieved by modulating the molar ratios of compounds such as CaO, MgO, and P, as well as the dissolution degree, thus providing a significant contribution to the improvement of the site safety index of Mn-rich residue.

In addition, cement as a hydraulic cementitious material forms a dense microstructure by cement hydration reaction, while the constructed microstructure enables high-quality curing of solid waste (Wang et al. 2022b). The C-S-H gel phase generated during the cement hydration can adsorb and encapsulate Mn^{2+}. In addition, $Ca(OH)_2$ formed from cement hydration reacts with Mn^{2+} to form $Mn(OH)_2$ precipitate. Since the ammonium salts can be translated to dissociated ammonia in alkaline cement-based pastes or mortars, the hydration heat release can accelerate the change of the dissociated ammonia to gaseous ammonia, which is eventually released in the form of ammonia gas (Zhan et al. 2022). When the cement mass fraction was 25–45%, the leaching concentration of manganese was still within the safe range under acidic conditions at a pH of 2, even if the cement curing body was damaged during employing (Wang et al. 2022a). Li et al. (2016) found that the soluble Mn content was reduced to 0.515 mg L^{-1}, attributed to the prepared cementitious material with encapsulation properties by mixing cement with Mn-rich residue. Cement, synergistic quicklime and waste fly ash were used to solidify Mn-rich residue, and the final toxic leachate Mn^{2+} concentration was only 0.022 mg L^{-1} (Zhan et al. 2018). In addition, red mud, calcium carbide slag, and furnace slag were also used as coagulants to solidify soluble Mn in Mn-rich residue with a 99% solidification rate (Zhang et al. 2020), resulting the solidified Mn including MnO_2, Mn_2SiO_4 and $Ca_4Mn_4Si_8O_{24}$. In addition, He et al. (2022b) successfully stabilized Mn-rich residue using alkaline burning material, a by-product of the cement industry. The high-activity substances form C-S-H gel and ettringite with good ionic substitution and encapsulation on

heavy metal ions.

In short, the co-curing of cement and other chemicals can further improve the curing effect of Mn^{2+} and NH_4^+-N in Mn-rich residue. Unfortunately, the high disposal costs and strength losses present a significant obstacle to the development and application of co-curing technology. Although industrial byproduct substitutes have reduced the cost of Mn-rich residue processing, the additional ions carried by the byproducts increase the complexity of the curing system. In response to the decline in the grade of Mn ore resources, the components of Mn-rich residue become increasingly complex. The complex environment in which Mn-rich residue products are cured severely challenges their long-term durability. As the chemicals introduced into the Mn-rich residue curing body become more complex, the stability of the product is also being challenged. Consequently, the more complex phase composition creates an ever-present environmental risk for the curing environment. While this was taking place, the project focused primarily on the safe and stable development of the Mn-rich residue stockpile site and did not fully consider the potential application of Mn-rich residue due to a lack of consideration for the use of resources.

3.2 Wet disposal technology of Mn-rich residue

The wet disposal technology does not conflict with the extraction of iron and manganese elements in Mn-rich residue fountainhead reduction but is a win-win strategy that complements each other. The main difference between Mn-rich residue fountainhead reduction and the wet disposal process for Mn-rich residue harmless disposal lies in the disposal goal. The former is to minimize the final Mn-rich residue yield, while the latter mainly serves for safe stockpile disposal and resource utilization. With the decline in mineral storage and grades, re-leaching recovery and electroremediation technology have emerged as a new hotspot for Mn-rich residue development to reach sustainable development and reduce tailings waste (He et al. 2021c). Re-leaching recovery disposal is mainly focused on water leaching, acid leaching, alkaline leaching and bioleaching. The content of Mn^{2+} and NH_4^+-N decreases with increasing stockpile time, which indicates that these soluble compounds are leached out by dissolving with rainwater flushing (Velusamy et al. 2021).

The water leaching technology is mainly used to recover Mn^{2+} ions and NH_4^+-N through water or enhanced water washing (Huang et al. 2022). It has been shown that 1) Water leaching can recover soluble manganese from Mn-rich residue. The kinetic leaching process is controlled by the diffusion of Mn ions in Mn-rich residue with crystalline phases such as SiO_2 and $CaSO_4 \cdot nH_2O$ (n=0.5 and 2). The temperature and liquid-solid ratio boost can enhance extractive efficiency (Zheng et al. 2020). 2) The primary water leaching efficiency is only near 80%, and multiple water leaching can increase the leaching efficiency again to more than 90%. The total recovery of soluble ions increases significantly with an increasing number of washes (Wang et al. 2018). 3) The traditional mixed water washing method was changed to mixed water with filter cake and the manganese recovery reached 95.82% after six times water-washing. 4) Enhanced water leaching can significantly improve leaching efficiency. A combination of calcination and multiple water washing was used by He et al. (2020) to achieve high-efficiency disposal of Mn^{2+} ions and NH_4^+-N, resulting in an Mn^{2+} concentration of 0.005 mg L^{-1}.

In contrast to water leaching, acid leaching is also an environmentally safe common wet disposal technology (Chen et al. 2022). In particular, acid leaching involves the application of sulfuric acid, hydrochloric acid, nitric acid, and some organic acids to destroy the mineral structure of an ore material under

specific conditions. By converting the target matter into acid-soluble ions, this method enables the efficient extraction of valuable elements from the ore. The results of existing Mn-rich residue acid leaching shown that 1) a single acid leaching can achieve efficient leaching and recovery of Mn. About 20 wt% H_2SO_4 was used at 90 ℃ for 3 h to leach manganese with a leaching efficiency of 96% (Peng et al. 2013). This indicates that acid leaching helps to enhance the recovery of Mn^{2+} and NH_4^+-N. 2) Enhanced acid leaching technique can further improve the leaching efficiency of Mn-rich residue. The 1.67 M H_2SO_4 solution at 85 ℃ in conjunction with 0.2 M $H_2C_2O_4$ was performed to finish the leach and the leaching efficiency of Mn under this effect achieved 99.9%. However, Mn-rich residue could not be recovered in large quantities using the water and acid leaching techniques due to the low solubility of silica and silicate in acidic environments.

Alkaline leaching can be used to recover silica resources for secondary use. The alkaline leaching studies show that 1) silicon resources can be leached from Mn-rich residue using a common sodium hydroxide solution at 130 ℃ for 5 h, achieving a leaching efficiency of 82.04%. 2) The leaching behavior of silicon in Mn-rich residue in an alkaline environment follows the contraction nucleation model controlled by interfacial chemical reactions. It was determined that the problem could be addressed by leaching the washed Mn-rich residue with 40 wt% NaOH at 140 ℃ for 12 h and adding the synthesized polyamide to form mesoporous silica (Zhang et al. 2017c).

Bioleaching has more potential for using industrial solid waste due to its mild reaction conditions, feedstock adaptability and high target selectivity (Lv et al. 2021a). The bioleaching results show that: 1) The suitable microorganisms can achieve high leaching efficiency while accomplishing the target elements. Sulfur-oxygen and iron-oxygen microorganisms were used to leach Mn-rich residue. The combined leaching efficiency of Mn attained 99.7% (Duan et al. 2011; Lan et al. 2021c). 2) Bioleaching technology has different differentiation and decomposition abilities for minerals and can be recovered into regulated phases by acid-base adjustment. 3) Bioleaching technology contributes well to enriching and extracting silicon resources (Chen et al. 2021). The bacteria were isolated from Mn-rich residue and stored in residue yards, with molasses being used as the carbon or nitrogen source for bacterial growth. The pH of the solution was adjusted to 8.5-9.0, which resulted in complete bioleaching that can achieve leaching and recovery of S, Mn, Mg, Fe, and NH_4^+-N (Lan et al. 2019). However, the leaching technology is accompanied by the intervention of a large amount of solution, which means there is a risk of secondary contamination of the leachate. The high disposal cost and low disposal efficiency hinder the further advancement of leaching technology.

Electroremediation technology is widely used as a more desirable physical remediation method for disposing of contaminated soils and industrial wastes. The target contaminants are transferred into unique solutions by electro-migration and electro-osmosis to achieve contaminant remediation (Chen et al. 2020b). In contrast to the extraction of valuable materials, this technology is primarily concerned with removing and disposing of hazardous waste. Shu et al. (2019c) used deionized water and H_2SO_4 solution as the anode electrolyte and cathode electrolyte and added sodium dodecylbenzene sulfonate and oxalic acid as electric field enhancers in Mn-rich residue. The removal efficiency of Mn^{2+} and NH_4^+-N reached 94.74% and 88.20%, respectively. The electroremediation promoted the decomposition of complex salts such as $(NH_4)_2$(Mg, Mn, Fe)$(SO_4)_2 \cdot 6H_2O$. The Mn^{2+} ions moved from the cathode to the anode region, eventually forming $Mn(OH)_2$ and MnOOH, while NH_4^+-N transported from the cathode to the anode region, respectively, where they

eventually solidified as $(NH_4)_2SO_4$ on the Mn-rich residue surface. As a result, the utilization of electric field disposal has significantly improved the distribution of ions on the surface of Mn-rich residue particles and promoted the dissolution of phases containing Mn^{2+} and NH_4^+-N (Yang et al. 2021; Li et al. 2022a; Deng et al. 2021). Shu et al. (2016a) employed a 9.2 wt% H_2SO_4 solution with $FeSO_4·7H_2O$ to leach the Mn-rich residue by an enhanced electric field, resulting in an Mn leaching rate of 96.2%. Other literature indicated that: 1) The Fe^{2+} added and improved electric field might boost Mn leaching efficiency by more than 50%. 2) Optimizing the electric field parameters, including increasing H_2SO_4 concentration, decreasing the reacted intensity, extending the reacted time, and synergistically adding a surfactant, may improve the final leaching rates of Mn^{2+} and NH_4^+-N. In addition, the multi-step collaboration wet disposal of Mn-rich residue can improve the leaching efficiency of detrimental substances. The physicochemical synergies promote the high-quality disposal of Mn-rich residue. However, the complexity of the process reduces the universality of disposal and increases the cost of disposal. The development of multifield coupling processing technology with high adaptability, low cost, and low power consumption requires further exploration and research.

3.3 Fire roasting disposal of Mn-rich residue

Fire roasting technology is one of the most metallurgically mature extraction techniques compared to other disposal methods that still need further development. It provides a high-temperature environment where other chemicals are mixed in a given atmosphere. The target minerals can be efficiently extracted by converting the difficult-to-separate raw materials into easily separable or soluble raw minerals. Table 6 shows the equations and required temperatures for the sulfate calcination and reduction roasting reactions in Mn-rich residue. It can be seen that calcination above 600 ℃ decomposes the sulfate into SO_2 and oxidizes Mn^{2+} to Mn_3O_4, Mn_2O_3 and MnO_2.

The decomposition temperature of common sulfate in the Mn-rich residue can be reduced by adding an appropriate amount of reducing carbon powder. When high-temperature calcination or roasting is performed, the Mn-rich residue can be stimulated to improve the feasibility and availability of resource utilization. Currently, fire roasting technology has been widely used to treat sub-stable industrial solid waste. For Mn-rich residue, 90.75% of Mn elements can be recovered by a two-step roasting operation. Mn-rich residue also exhibits high pozzolanic activity after calcination due to the continuous generation of glassy materials. This offers infinite possibilities for utilizing Mn-rich residue as a high-valued resource (Wang et al. 2022a). Notably, the undue energy consumption and increased carbon emission caused by fire roasting technology significantly limit its popularization in the harmless stage of Mn-rich residue. Harmless disposal caused by fire roasting does not involve high value-added stimulation of resource utilization because it can realize both harmless and resource utilization. Compared with harmless treatment, fire roasting contributes more to effectively utilizing Mn-rich residue resources. The Mn-rich residue resource utilization part further elaborates the specific summary and analysis.

Table 6 The sulfate calcination and reduction roasting reactions in Mn-rich residue

Direct high-temperature calcination disposal process	
$2(NH_4)_2SO_4 = 4NH_3\ (g) + 2SO_2\ (g) + 2H_2O\ (g) + O_2\ (g)$	T≥600 ℃
$4MnSO_4 = 2Mn_2O_3 + 4SO_2\ (g) + O_2\ (g)$	T≥970 ℃
$3MnSO_4 = Mn_3O_4 + 3SO_2\ (g) + O_2\ (g)$	T≥980 ℃

$MnSO_4 = MnO_2 + SO_2$ (g)	T≥1120 ℃
$2MgSO_4 = 2MgO + 2SO_2$ (g) + O_2 (g)	T≥1040 ℃
$2CaSO_4 = 2CaO + 2SO_2$ (g) + O_2 (g)	T≥1670 ℃
The process of high temperature calcination of reductive substances	
$2(NH_4)2SO_4 + C = 4NH_3$ (g) + $2SO_2$ (g) + $2H_2O$(g) + CO_2 (g)	T≥240 ℃
$4MnSO_4 + C = 2Mn_2O_3 + 4SO_2$ (g) + CO_2 (g)	T≥420 ℃
$3MnSO_4 + C = Mn_3O_4 + 3SO_2$ (g) + CO_2 (g)	T≥530 ℃
$2MgSO_4 + C = 2MgO + 2SO_2$ (g) + CO_2 (g)	T≥310 ℃
$2CaSO_4 + C = 2CaO + 2SO_2$ (g) + CO_2 (g)	T≥850 ℃

3.4 Constraints and future directions for the harmless disposal of Mn-rich residue

The harmless treatment of Mn-rich residue is a prerequisite for resource utilization that mainly involves the extraction of valuable elements and the high-quality elimination of hazardous elements. Some studies have proposed relatively suitable solutions for the environmentally friendly treatment of Mn-rich residue, but the current disposal methods are still limited due to the increase of Mn-rich residue emissions caused by the mineral complexity of Mn-rich residue and the reduction of manganese ore grade. The harmless treatment of Mn-rich residue is closely related to its reduction and resource utilization. There is a limited way in which direct dry disposal can fully utilize the value-added of Mn-rich residue since it is usually restricted to the consumption of highly hazardous elements. This means that Mn-rich residue is often disposed of as worthless waste. Mn-rich residue contains a large amount of calcium, aluminium, silicon, iron, sulfur and other elements and their oxides and minerals based on the mineral composition. Therefore, in the hazardous-free disposal of Mn-rich residue, harmful elements should be selectively absorbed and other harmless mineral elements should be retained to contribute to the high-value resource utilization of Mn-rich residue.

The wet disposal technology can realize the high-efficiency extraction of valuable elements in Mn-rich residue through the dissolution-leaching-filtration process. The use of high-efficiency extraction is closely linked to the regulation of the leaching parameters, which in turn results in an excessive quantity of leaching liquid and a significant risk of secondary contamination. In spite of the fact that electroremediation offers a reasonable solution to these problems, its continued development is limited by the efficiency of this technology, the secondary treatment of electrolytes, and the economic feasibility. The calcination technique can activate Mn-rich residue while achieving harmless disposal, which implies that Mn-rich residue can be subjected to resource utilization rather than inert waste. Despite this, the release of gas and the consumption of energy during the calcination process inhibit the promotion of this technique. In order to resolve this issue, co-calcination technology could be adopted in the development of Mn-rich residue calcination. Specifically, the exhaust gas from calcined Mn-rich residue can be collected using a gas collection device and transformed into chemicals or reducing gases for demand. Physicochemical excitation is applied before the Mn-rich residue is calcined to maximize its activity. The utilization of Mn-rich residue will be maximized when it is processed into high-active resource minerals such as fly ash and slag. Therefore, the development of an evaluation system between Mn-rich residue activity and energy consumption, economic cost and disposal efficiency would significantly impact the progression of environmentally sound disposal of Mn-rich residue.

4. Resource utilization of Mn-rich residue

The resource utilization of Mn-rich residue after harmless disposal is the key procedure to realize the transformation of waste into treasure. The Chinese government supports using industrial waste residues in manufacturing construction materials such as brick, cement clinker, concrete skeleton, and ceramsite as long as they adhere to national regulations to promote the holistic reuse of waste resources (Figure 9). Mn-rich residue has much potential for use in construction materials since its main phases, quartz, aluminium silicate, iron phase, and gypsum, where all of these belong to the CaO-SiO_2-Al_2O_3-Fe_2O_3-$CaSO_4$ compositions (Wang et al. 2023). This section mainly summarizes and critically analyzes the specific components of Mn-rich residue resource utilization, which will help improve the efficiency of Mn-rich residue.

4.1 Building materials resource utilization of Mn-rich residue based on chemical component regulation

4.1.1 Aluminosilicate phase

Following the 11th Five-Year Plan national circular economy development goals in China, the "Notice of the General Office of the State Council on further promoting wall material innovation and energy-saving Buildings" was issued. The use of non-clay bricks based mainly on industrial solid waste has been considerably encouraged. However, with economic development and living standard improvement, public awareness of environmental protection has become increasingly widespread. In addition, clay brick has some insurmountable defects such as high energy consumption, high pollution, and waste of cultivated land. Therefore, using solid waste to prepare wall materials effectively realizes resource utilization, brings economic benefits, and substantially reduces environmental pollution. The Mn-rich residue contains many silicon and aluminium elements, promoting the stable development of its resource utilization. The resource utilization in building materials of the aluminosilicate phase from Mn-rich residue mainly focuses on brick and roadbed materials. Previous studies have shown that Mn-rich residue can be mixed with lime to achieve manganese fixation and ammonia removal, and then the treated Mn-rich residue is combined with cementitious material and sand aggregate to produce baking-free bricks under high-pressure steam (Zhou et al. 2014; Du et al. 2014a and 2014b). All the indexes and toxic leaching test results meet the requirements when the Mn-rich residue content is 30%, the cement content is 10.5%, the sand and stone aggregate content is 59.5%, the forming pressure and vapor pressure are 25 MPa and 1.2 MPa, respectively. When the proportion of Mn-rich residue, cement, aggregate and water is 25%, 20%, 30% and 25%, respectively, the compressive and flexural strength properties of the non-burning brick are 16.40 MPa and 3.19 MPa, respectively. Li et al. (2020b) mixed calcium hydroxide, heat-activated feldspar powder and Mn-rich residue to make a billet and treated it for 2 h under forming pressure of 20 MPa and steam temperature of 160 °C. The maximum compressive strength of the steam brick was 23.5 MPa. The above studies showed that SiO_2 in Mn-rich residue reacted with calcium hydroxide to form hydrated calcium silicate under high-temperature steam conditions.

The Mn-rich residue, cement and slag were also mixed to form non-firing permeable bricks (Wang et al. 2019). After 28 days, the strength of 3.53 MPa and the permeability of 3.2×10^{-2} cm s^{-1} were higher than the demand for standard. The inside hole morphology of the Mn-rich residue-based porous brick was examined utilizing industrial computer tomography (Tang et al. 2019). The results showed that its optimum permeability coefficient prepared with 6 MPa forming pressure was 3.3×10^{-2} cm s^{-1}. Unlike non-burning bricks, the calcinated Mn-rich residue has excellent pozzolanic activity and can be used as a brick-making base material. As sintering temperatures increase, brick loss on ignition and shrinkage rates increase, but porosity and water

absorption decline while brick strength and density increase significantly. The compressive strength of sintered bricks prepared by mixing Mn-rich residue with shale and fly ash can reach 22.64 MPa, and the manganese concentration in leachate decreases from 451.08 to 0.68 mg L^{-1} (Zhang et al. 2011). Roadbed material has excellent raw material adaptability since it is used as an infrastructure material (Qiao et al. 2010). Zhang et al. (2019) used Mn-rich residue, calcium carbide slag and red mud to prepare the subgrade materials with 7 days of unconfined compressive strength up to 5–7 MPa. The concentration of NH_4^+-N and Mn^{2+} in the leaching solution collected from subgrade materials was lower than the threshold of groundwater quality standard. In conclusion, the above studies were focused on the resource reuse of the Mn-rich residue aluminosilicate phase in building materials. The use of aluminosilicate in Mn-rich residue as a wall and roadbed material expands the scope of Mn-rich residue applications and improves its utilization efficiency.

4.1.2 Resource utilization of sulfate phase in Mn-rich residue

The Mn-rich residue is rich in sulfate, which is as high as 15~25% in the SO_3 state. When Mn-rich residue is added to cement concrete as a mixture or admixture, its sulfate-rich properties cannot be fully exploited. The pozzolanic activity of sulfate-activated fly ash is defined as a fly ash-lime-sulfate system. Sulfate can change the arrangement structure of fly ash particles and activate the active SiO_2 and Al_2O_3 in fly ash effectively (Nandhini et al. 2022; Priyadarshi et al. 2023). By increasing its solubility, the activity of pozzolanic ash can be stimulated. The soluble sulfate in Mn-rich residue can better stimulate the pozzolanic activity of fly ash and lime and can be used as the mixture or admixture by taking full advantage of its sulfate-rich property. Calcium oxide was used to dissolve and dehydrate Mn-rich residue to prepare the fly ash activator, which could stimulate the hydration activity of low-grade fly ash and produce the concrete composite admixture. The adverse effects of manganese slag can be minimized by adding the appropriate amount of waste stone powder.

In addition, Mn-rich residue can also be employed to enhance the pozzolanic properties of the calcined slag. The roasting-activated Mn-rich residue, calcium hydroxide and cement clinker were mixed as an activator to prepare slag-based cement (Wang et al. 2013). The carbide slag also can be employed to prepare cement binding material by mixing it with Mn-rich residue and blast furnace slag (Xu et al. 2019). With the increased calcium hydroxide dosing in the formed binding materials, the sulfate in Mn-rich residue contributes to the depolymerization and hydration of blast slag. The pore refinement enhances the structural compactness of the product and significantly reduces heavy metals in Mn-rich residue. In a crystalline structure of silico-oxygen and alumina-oxygen bonds, a portion of silicon is substituted by heavy metal ions. The PI 32.5 cement threshold was attained by the composite cementitious material created.

The strength of the composite made by Mn-rich residue is also better than that of PI 42.5 cement after activating Mn-rich residue with an alkaline activator. The prepared sample remarkably cures Cd, Pb, Mn, Zn and other heavy metals in Mn-rich residue. The Mn-rich residue was also utilized as a sulfate activator to promote the pozzolanic properties of steel slag. When mixed Mn-rich residue with steel slag instead of 40% cement, the strength of the formed cement samples was significantly higher than that of the non-Mn-rich residue activated materials. Additionally, the cement based on Mn-rich residue can achieve the strength requirements of PI 42.5 when the replacement content of cement is increased to 50% with 14% Mn-rich residue. As a means to further reduce cement content, the ground Mn-rich residue, alkali metal hydroxides, and furnace

slag were mixed to produce composite binding materials (Wang et al. 2020). Cementing material prepared with 45% Mn-rich residue has a 28-day strength property of 30 MPa and an excellent Mn curing property.

In the process of cement production, gypsum can be employed to regulate the serviceability of products. Due to the hydrometallurgy processing, the Mn-rich residue contains a certain amount of gypsum dihydrate phase and shows a remarkable effect as retarding agent. For Mn-rich residue without calcination, it belongs to inert silica-aluminium material with extremely rich sulfate content and inactive SiO_2 (about 20–40%). As a result, the early mechanical properties of Mn-rich residue-doped cement are lower than those of natural gypsum dihydrate cement produced by the abundant SO_3 and additional parts of inactive substances. Based on the small differences in the late strength between Mn-rich residue-doped cement and natural gypsum dihydrate, it is apparent that the overall effect of Mn-rich residue is similar to natural gypsum dihydrate as a cement retarder. In addition, the sulfate in Mn-rich residue mainly exists in various forms, such as gypsum dihydrate, ammonium sulfate, and manganese sulfate. Adding a certain amount of quick lime in Mn-rich residue is conducive to converting other forms of sulfate into gypsum dihydrate to provide more favourable conditions for its use as a cement retarder.

In conclusion, the resource utilization of sulfate in Mn-rich residue is due to the excitation effect of sulfate. Therefore, adding activated Mn-rich residue as high-activity sulfate activators in cooperation with other active materials can prepare low-carbon and high-powered supplementary cementitious materials. As a result, the utilization efficiency of sulfate in Mn-rich residue is improved, and the amount of recycles disposed of in Mn-rich residue is increased. As a result of reduced cement usage, carbon emissions from cement are diminished.

4.1.3 Resource utilization on multiple-phase oxides in Mn-rich residue

Ceramics are more commonly used in construction than cement because of their superior mechanical properties, outstanding acid and alkali resistance, and workability. Since Mn-rich residue contains the main components for the preparation of ceramics (CaO, SiO_2, Al_2O_3, and Fe_2O_3), Na, K, Mg and other alkali metal ions, it can be used as a flux during the production to reduce the sintering temperature of the prepared ceramics. Qian et al. (2012) melted Mn-rich residue and ground it into less than 150 mm particle size powder with water quenching and cooling to prepare matrix glass powder. The ceramics with excellent crystallization activation energy were then obtained by mixing the matrix glass powder with a polyethylene glycol solution. Jiang et al. (2020) successfully prepared Mn-rich residue-based glass ceramics with 1% porosity, 40% sintering shrinkage and 425 MPa micro-hardness by high-temperature calcination. The prepared glass-ceramics have a good immobilization effect on manganese ions in Mn-rich residue, and the toxic concentration of the leaching solution is much less than the prescribed limits.

The combination of Mn-rich residue with carbonite, kaolin, and dolomite at 1100 ℃ and 3 MPa forming pressure produced porous ceramics with a porosity of 69.7%, a strength of 6.97 MPa, and good pH tolerance (Wu et al. 2016). As a result of using Mn-rich residue and talc as the primary processing materials and then adding suitable bauxite and quartz, it is possible to prepare ceramics with a high bending strength of 105 MPa when heated at 1100~1200 ℃ (Wu et al. 2013). Ceramic bricks with low water absorption, high volume density and good performance were prepared by sintering Mn-rich residue and waste glass at 900 ℃. The water absorption rate and compressive strength of reclaimed ceramic wall brick prepared by Mn-rich residue and

waste ceramic grinding powder are 0.75% and 25.2 MPa (Wang et al. 2013). The mechanical properties of the porous materials decrease with the increase in silicon carbide content. Zhan et al. (2021) produced lightweight ceramide by sintering the mixture of Mn-rich residue, fly ash, and cleaned fly ash at 1160 ℃, plus a holding time of 12 min. The product possesses a good curing effect on heavy metal elements in raw materials (Zhan et al. 2021).

Cement-based cementitious materials are the main infrastructure construction material, and their preparation involves a certain amount of clay minerals and other ore resources. With the development of urbanization, increasing infrastructure construction has put forward higher requirements for producing necessary cement-based cementitious materials. However, large raw material ore consumption limits cement-based cementitious material output development. The use of industrial waste residue to replace clay, sand and ore in part or whole realizes the effective utilization of industrial waste residue as resources. Additionally, it lessens the usage and waste of these resources as well as the harm caused by ore mining to the environment. Mn-rich residue contains rich elements such as silicon, iron, aluminium, calcium and sulfur, which are consistent with the elemental composition of cement-based cementitious materials. The similar element composition lays a solid foundation for preparing Mn-rich residue-based cementitious materials. However, the presence of harmful components in Mn-rich residue, low activity of raw materials and high-water absorption significantly limit the direct utilization of Mn-rich residue. Therefore, the preparation of Mn-rich residue-based cementitious materials needs to benefit from the excitation of reprocessing technology. As for the application of Mn-rich residue in cementing materials (Wang et al. 2022a), the existing research results show that: 1) As a result of the decomposition of poor crystallinity, calcination can significantly enhance the pozzolanic activity of Mn-rich residue. This is due to the release of calcium oxide as well as the activation of amorphous active aluminium silicates. 2) There is a suitable range of calcination temperature of 800–900 ℃ in which low temperature limits the dehydration of gypsum and iron phase and then changes the solubility of gypsum followed by Mn-rich residue activity. Moreover, the high-temperature treatment limits the decomposition of heavy metal-containing minerals in Mn-rich residue to form inert and complex oxides such as spinel. 3) The calcination treatment of Mn-rich residue can improve the solidification effect of heavy metal ions.

The quasi-sulphoaluminate cementitious materials with the 56-d mechanical properties of 35-65 MPa might also be manufactured utilizing Mn-rich residue, kaolin, and limestone to sinter clinker at 1200 ℃, in accordance with the ternary phase diagram of SiO_2-Al_2O_3-CaO (Hou et al. 2012). The quasi-sulfoaluminate cementitious material with 5% gypsum increased its early and long-term strength by about 50% and 30% than that without gypsum, respectively. However, the utilization path is still debatable in terms of the improvement of Mn-rich residue consumption efficiency and the examination of the durability of the product. He et al. (2022a) used Mn-rich residue, barium slag, limestone and bauxite to prepare belite-ye'elimite-alite cement at 1350 ℃ for 1.5 h. The results show that introducing Mn-rich residue can decrease the clinker formation temperature, resulting in cement with 5% gypsum in preparing 28 d compressive strength of 30 MPa. The Mn-rich residue used to fabricate the belite-ye'elimite-ferrite-overfired gypsum cement clinker has excellent mechanical properties. The prepared cement clinker can cure heavy metals (Wang et al. 2023), suggesting the potential realization of high value-added resource reuse of Mn-rich residue. The sintered temperature of this clinker phase is 50~150 ℃ which is lower than that of traditional sulfoaluminate cement clinker (Wang et al.

2023). In addition, the modified Mn-rich residue calcined at 350 °C was used to activate the granulating furnace slag to prepare Mn-rich residue-based slag cement (Wang et al. 2020). Mn-rich residue and modified sulfur can be mixed to produce an acid and alkali-resistant sulfur cement. When the content of sulfur is 45–55%, Mn-rich residue is 20–35%, and the content of sand is 15–30%, the compressive and flexural strength of the cement can reach 48.89–63.17 MPa and 7.12–9.47 MPa, respectively, which are higher than that of ordinary portland cement (Yang et al. 2014). The manufactured sulfur concrete effectively stabilizes the heavy metals in the Mn-rich residue, and the leaching solution is within permissible limits of heavy metals.

In a word, calcination provides a new perspective for high value-added resource utilization of Mn-rich residue. The high-temperature treatment of Mn-rich residue to prepare ceramics and clinker reduces the consumption of ore resources and realizes the resource reuse of Mn-rich residue. The prepared Mn-rich residue-based cement clinker makes full use of the oxide of Mn-rich residue, and the presence of heavy metals reduces the calcination temperature, contributing to the carbon emission reduction and carbon peak.

4.2 Preparation of Mn-rich residue-based functional materials

Mn-rich residue can meet the chemical composition requirements of zeolite preparation (Ma et al. 2023). Using Mn-rich residue as raw material, Li et al. (2015c) prepared the zeolite material at high temperatures using a two-step method with NaOH and $NaAlO_2$. The zeolite adsorbent with a specific surface area of 35.38 $m^2\ g^{-1}$ was successfully prepared at the Si to Al ratio of 1.5. The maximum adsorption capacities of Ni^{2+} and Mn^{2+} were 128.70 mg g^{-1} and 66.93 mg g^{-1}, respectively. The synthesized Mn-rich residue-based zeolite can be employed as a promising low-cost adsorbent. Zeolite is often prepared using Mn-rich residue as raw material by microwave alkali fusion activation method heated at 500 °C for 60 min and then crystallized at 100 °C for 7 h. The maximum manganese adsorption capacity of the zeolite reached 79.18 mg g^{-1} (Chang et al. 2019).

Depending on their physicochemical characteristics, Mn-rich residue can be utilized directly as adsorbed materials for treating wastewater with simple or without additional operation. Therefore, Mn-rich residue was effectively employed as a raw material towards the hydrothermal method at 100 °C and pH 12 to manufacture an Mn-rich residue- calcium silicate hydrate (C-S-H) adsorption material with a high specific surface area of 205 $m^2\ g^{-1}$ (Li et al. 2015b). The synthesized adsorbent may effectively adsorb the manganese and phosphoric acid ions in the solution. The Mn-rich residue was added to the Na_2SiO_3 solution and then obtained the suspension by adding $MgCl_2$ drop-by-drop (Shu et al. 2018b). After a hydrothermal reaction for 24 h, the prepared material with a specific surface area of 500.8 $m^2\ g^{-1}$ was obtained from the obtained suspension. The adsorption capacity of the synthesized Mn-rich residue-based adsorption material achieved 548.15 mg g^{-1} after fifty cycles. In addition, Mn-rich residue was put into EDTA-2Na/NaOH solution for ultrasonic etching treatment (Lan et al. 2019a). The nano-sheet structure with 100–200 nm size and a new type of high-activity Fe-Mn oxide nano-composite catalyst was obtained. The prepared material has a high dye removal capacity in a wide pH range of 1~8.5 and a temperature range from 25 to 45 °C, indicating that the process has broad application potential in wastewater treatment. The sieved Mn-rich residue was mixed with the deionized water and oscillated at 13500 rad min^{-1} for 15 min to form hydrogel (Ma et al. 2020). Thermal activation of Mn-rich residue was achieved by incubating the synthesized hydrogel for 120 min at 800 °C. Pb^{2+} and Cd^{2+} exhibited the highest adsorption capacities of 119.88 mg g^{-1} and 35.97 mg g^{-1}, respectively. A thermal-activated Mn-rich residue is primarily based on ion exchange, electrostatic attraction, and surface precipitation as its adsorption

principle. As a result of electrostatic attraction, the heavy metals in the treated Mn-rich residue are adsorbed on iron-manganese oxides and silicate minerals. Therefore, the Mn-rich residue prepared by thermal activation is an environmentally friendly and effective adsorption material, which can be employed to eliminate heavy metals in the solution.

The transited metal oxides can also be used as functional materials (Li et al. 2022b). Due to the abundance of manganese and iron phases within Mn-rich residue could be exploited as a raw material or precursor to prepare functional products (Xie et al. 2021b). The Mn-Zn ferrite precursor was prepared by adding the corresponding sulfate and ammonia water according to the proportion of various metal elements. Mn-Zn ferrite was synthesized by burning the precursor at 1200 ℃ for 5 h while combining it with 0.45% SiO_2 powder. When the doping amount of SiO_2 is 0.45%, the obtained Mn-Zn ferrite has a saturation magnetization of 71.95 emu g^{-1}. Therefore, the preparation of Mn-rich residue-based functional materials helps realize the resource reuse of Mn-rich residue.

4.3 Preparation of Mn-rich residue-based soil fertilizer

The presence of significant amounts of soluble NH_4^+-N, sulfate, calcium, iron, and silicon in Mn-rich residue suggested that it may have fertilizer-like positive attributes. The compound fertiliser can be prepared by mixing Mn-rich residue with commercial nitrogen, phosphorus and potassium. The application of mixed fertilizer was more fertile than that of Mn-rich residue alone, which was reflected in the significant increase in grain yield. The Mn-rich residue mixed with inorganic fertilizer significantly enhanced pepper growth compared to fertilization alone. For the preparation of silicomanganese fertilizer containing 6.94% soluble silicon, Mn-rich residue was mixed with $CaCO_3$, Na_2CO_3 and NaOH and calcined at 400 ℃. The mixed Na_2CO_3 with Mn-rich residue increased the active silica content from 0.19 to 12.59% after ball milling activation and calcination (Li et al. 2018a). These results infer that the calcined Mn-rich residue-based material can be employed as silicon fertilizer. In addition, silicate bacteria can be used to activate silica in Mn-rich residue. Since the bioleached solution contained a silicon concentration of 163.27 mg L^{-1}, hence making it a useful source of silicon fertilizer (Lv et al. 2021b).

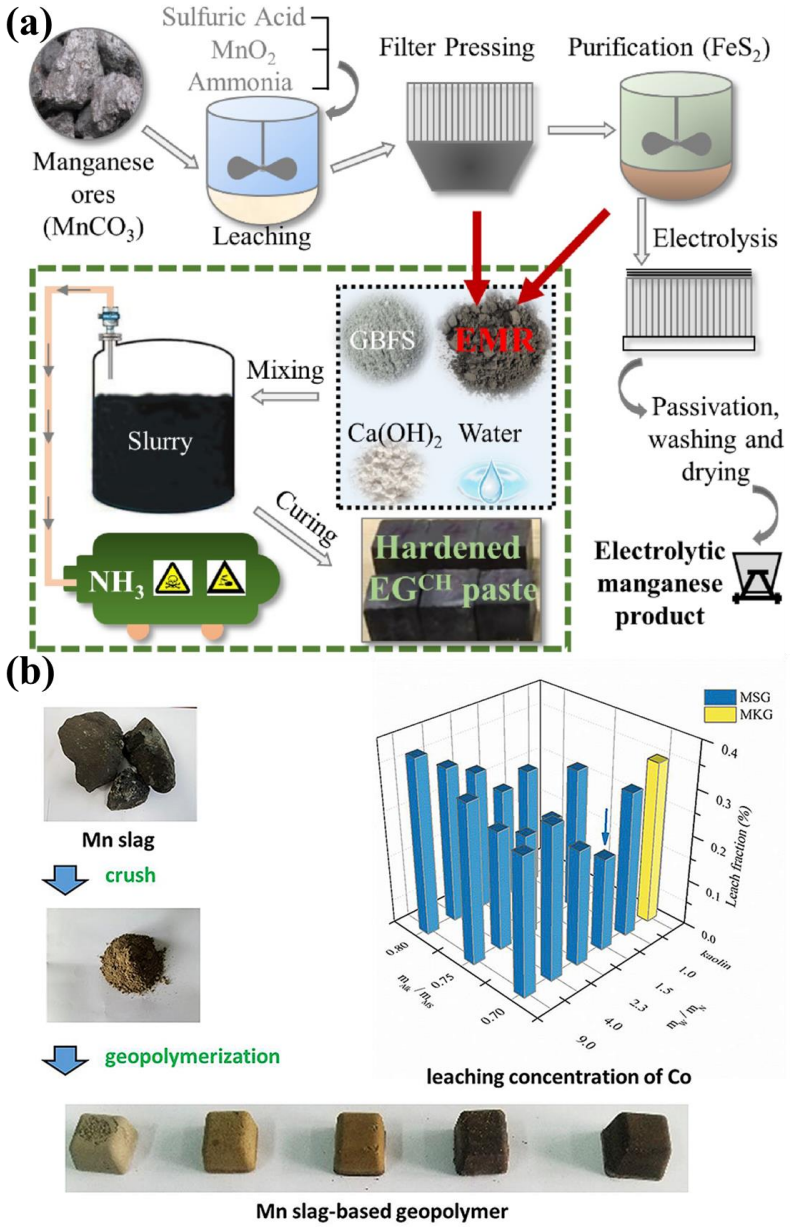

Figure 9. Resource utilization results of Mn-rich residue. (a) Mn-rich residue-based cementitious material using activating blast slag. The labels of GBFS and EMR refer to granulated blast furnace slag and electrolytic manganese residues, respectively. The mark of EG^{CH} stands for the composite material consisting of GBFS, EMR and calcium hydroxide. The 28-d hardened samples achieved 30 MPa at 45 wt.% of Mn-rich residue dosage. The Mn^{2+} and NH_4^+-N can be well treated by encapsulation and strong alkaline environment. Reprinted with permission of Elsevier from Wang et al. (2020). (b) Mn-rich residue-based geopolymer by alkali-activation. The MSG and MKG refer to the Mn slag-based geopolymer and metakaolin-based geopolymer, respectively. The prepared Mn-rich residue geopolymer exhibited a better nuclear waste immobilization capability. The oxidation environment of the waste material is instrumental in fixation. Reprinted with permission of Elsevier from Yu et al. (2019).

5. High-value resource utilization of Mn-rich residue

Mn-rich residue is the main solid waste powder produced in electrolytic manganese and electrolytic manganese dioxide production. Due to the hydrometallurgical production process, Mn-rich residue contains a

lot of sulfates and heavy metals, as well as a lot of quartz, calcium sulfate and aluminosilicate (Duan et al. 2011). The existing works on the harmless treatment and resource reuse of Mn-rich residue are mainly based on the chemical composition and mineral properties of Mn-rich residue. As mentioned above, the work in the field of harmless treatment and resource utilization is mainly conducted in the following aspects, including recovery of valuable elements in Mn-rich residue, direct stabilization or solidification and electric restoration of piled Mn-rich residue, resource disposal of building materials, adsorption materials, fertilizers and other functional materials. Implementing these works provides solutions for the hazard-free disposal and resource utilization of Mn-rich residue. However, there are obvious advantages and disadvantages to these approaches.

Additionally, due to the complex mineral and chemical compositions of Mn-rich residue, it is more difficult for these resources to be utilized and the breadth of their use. Solid waste is also a misplaced resource that fundamentally attaches the greatest importance to solid waste resources by achieving high-value resource utilization rather than simple consumption and treatment. Although direct and simple disposal can absorb the accumulated reserves of Mn-rich residue, abundant minerals are not exploited and utilized with maximum efficiency, which is also a resource waste to a certain extent. Therefore, by comparing the advantages and disadvantages of various technologies and combining them with the development law of Mn-rich residue, it is worthy of expectation and affirmation to sum up and put forward the efficient, green and high-value resource utilization way of Mn-rich residue.

In terms of re-leaching in Mn-rich residue, both water and acid leaching can achieve high-efficiency recovery of Mn^{2+} and NH_4^+-N under the enhanced treatment process. However, water leaching has superior results in handling expenses and environmental safety compared to other techniques since Mn-rich residue would still result in more substantial secondary pollutants and a larger cost of raw materials after acid leaching. Nevertheless, water filtration caused by leaching increases the risk of secondary pollution and disposal costs. The major purpose of the alkaline environment produced by alkaline leaching is to recover silicon. However, acid and base neutralization reactions are generated in the provided alkaline environment, resulting in secondary waste pollution caused by gas overflow. Bioleaching is highly targeted, and the presence of microorganisms will not cause serious secondary pollution. However, bioleaching needs to provide a suitable growth environment for microorganisms to stimulate their reactivity, which increases the burden of economic costs. In addition, severe and unregulated high reactivity limits the widespread use of this technology.

The calcination process concentrates and removes Mn^{2+} and NH_4^+-N from Mn-rich residue. On the one hand, the Mn-rich residue can realize the recovery and utilization of sulfur resources after calcination; on the other hand, the thermal activation effect of Mn-rich residue significantly improves the reactivity of Mn-rich residue. It is noteworthy that calcination will increase energy consumption and cause a large amount of greenhouse gas emissions. Direct calcination is widely used to re-extract valuable elements in Mn-rich residue due to energy consumption and gas emission limitations. As it stands now, when economic costs and secondary environmental pollution are considered, the prospect of re-extracting valuable elements from accumulated Mn-rich residue is poor. Compared with the reduction of Mn-rich residue and the resource utilization of Mn-rich residue, the re-extraction of valuable elements of Mn-rich residue should fully consider the coordinated development of economic applicability, environmental friendliness and activity excitation degree.

For stabilization or solidification disposal and electric restoration, the technology focuses on harmless

disposal of the Mn-rich residue storage site rather than recycling the disposed Mn-rich residue. Therefore, the main application fields of this part of technology are closely related to the soil environment. The stabilization or immobilization of Mn-rich residue mainly reflects that a single chemical (NaOH, CaO or MgO) acts as a curing agent to promote the elimination of Mn^{2+} and NH_4^+-N through an acid-base neutralization reaction. The soluble Mn in Mn-rich residue precipitated and solidified as $Mn(OH)_2$, MnO_2, and $MnCO_3$, among other insoluble compounds. The treatment mechanism of a single solidified agent is the neutralization reaction between the alkaline environment provided by an alkaline solidified agent and acidic Mn-rich residue to remove Mn^{2+} and NH_4^+-N. Initial Mn-rich residue may require further chemical or physical treatment, resulting in additional disposal costs.

Meanwhile, curing Mn-rich residue with chemical reagents increases Mn-rich residue volume. After curing, Mn-rich residue still needs to be treated safely to ensure the long-term stability of the landfill. In addition, the chemical bonding ceramics were formed by acid-base neutralization reaction between magnesium salts such as MgO, $MgSO_4$, $MgCl_2$ and phosphates such as Na_3PO_4, Na_2HPO_4 and NaH_2PO_4 to realize harmless disposal of Mn-rich residue. However, the development of this technology for Mn-rich residue disposal is limited by the solubility and high economic cost of magnesium materials. As opposed to chemically bonded ceramics, cement may be able to reduce economic costs to a certain extent. The hydration products formed by the cement hydration stabilize the soluble salt and heavy metal in the Mn-rich residue via the aluminosilicate structure, indicating that the effective solidifying of a certain amount of Mn-rich residue can be achieved. However, the durability and long-term stability of the cured body prepared by acidic Mn-rich residue and cement are still hidden dangers. Unlike extracting valuable elements, stabilization or solidification can incorporate other alkaline wastes into the Mn-rich residue disposal system.

Further, the addition of fly ash, furnace slag, steel slag and other solid wastes with potential pozzolanic properties, phosphate by-products, and other solid wastes for physico-chemical composite curing treatment can realize harmless disposal of Mn-rich residue and ensure the environmental safety of the storage site. The synergic solidification or stabilization mechanism of Mn-rich residue and phosphate by-product is mainly attributed to the interaction of many ions in the two solid wastes to form insoluble substances. Mn-rich residue co-solidification or stabilization with other wastes significantly decreases costs and enables multi-layer collaborative treatment of multiple solid wastes. However, the current research results still have pollution risks due to the lack of long-term durability evaluation systems for cured products. Suppose the solidified cost is effectively controlled and the durability of the cured product is effectively guaranteed. In that case, collaborative stabilization or solidification can be employed as a high-efficiency method for the harmless treatment of Mn-rich residue.

Unlike the solidification or stabilization treatment of Mn-rich residue, electric remediation involves transferring Mn^{2+} and NH_4^+-N in Mn-rich residue. The migration of unstable soluble ions was changed and evaluated by adding an electric field enhancer. With the periodic electrolyte replacement, most Mn^{2+} and NH_4^+-N in Mn-rich residue can be removed. Therefore, electrical repair technology requires a large amount of electricity to provide continuous electric drive and continuous consumption of electric field enhancers. The process produces a large amount of waste electrolyte and the secondary pollution caused by the enhancers still needs further disposal. In short, harmless disposal is imperative. However, the harmless process of Mn-rich

residue is closely related to the economic cost, disposal efficiency and secondary pollution caused by disposal. Notably, the harmless disposal of Mn-rich residue is the basis of resource utilization. Therefore, the harmless disposal and resource utilization of Mn-rich residue is intricately linked to building more economical, high utilization efficient and high-value resource utilization of Mn-rich residue-based materials.

The resource utilization of building materials in Mn-rich residue is because Mn-rich residue contains a lot of aluminium silicate, hematite, quartz, gypsum, and other potential components which can be used as construction materials. Cement-based cementitious material, ceramics, roadbed material and brick can be prepared by Mn-rich residue. It is necessary to monitor the long-term safety risk of the prepared Mn-rich residue-based material. Currently, the utilization rate of Mn-rich residue in this part is 10~45%. The utilization efficiency of Mn-rich residue is an important index of the resource disposal of Mn-rich residue, and the utilization rate of Mn-rich residue-based ceramics can be close to 100%. The prepared Mn-rich residue-based ceramic can be used as the framework of building materials, providing excellent mechanical properties and heavy metal solidified effects. However, its main disadvantage is that it requires high-temperature calcination, which causes energy consumption and greenhouse gas emissions. Hard ceramic frames require more crushing energy to achieve the target size. In addition, sintering brick can also realize the consumption of a large amount of Mn-rich residue, but the unbalanced development between energy consumption and the high-value degree of Mn-rich residue limits the production and use of sintering brick. The development of non-burning bricks has somewhat improved the above shortcomings because of the rapid reduction of energy consumption. However, the preparation of Mn-rich residue-based unfired brick often requires the addition of chemicals to motivate the reactivity of Mn-rich residue and other additives to improve the mechanical properties of the finished product. Because Mn^{2+} and NH_4^+-N are not treated properly, the prepared Mn-rich residue-based non-burning bricks have long-term performance and safety risks. For roadbed materials based on Mn-rich residue, the stable removal of Mn^{2+} and NH_4^+-N and the stability of long-term mechanical properties and toxicity are prerequisites for its wide application. In addition, the huge demand potential for roadbed materials means a broad application prospect. Therefore, the harmless disposal of Mn-rich residue has imperative significance.

For Mn-rich residue-based adsorption functional materials, the main target is to translate the aluminosilicate phase in Mn-rich residue into soluble aluminosilicate under the action of specific activation and then add aluminate or silicate for secondary treatment to fabricate porous adsorption materials with an excellent adsorption activity. Therefore, the realization of Mn-rich residue functionalization mainly stimulates its properties of aluminosilicate, quartz and hematite by physical and chemical methods such as alkaline additions, hydrothermal method or calcination method to form adsorptive materials such as zeolite. It is of concern that the secondary waste generated by the prepared adsorbent and its dissolving hazard and durability still need to be monitored over time for further evaluation. A soil fertilizer developed based on Mn-rich residue has an improved fertility and growth promotion effect on the growth of specific plants since it contains a large amount of soluble Mn^{2+}, NH_4^+-N and other micronutrients required for crop growth. However, heavy metal elements carried by Mn-rich residue migrate into the soil environment with hydraulic power, posing risks to human health and soil. For the preparation of other functional materials by Mn-rich residue, Mn and Fe equivalent metals in Mn-rich residue can be developed into infrared radiation or magnetic materials. However, the use efficiency of Mn-rich residue in preparing such Mn-rich residue-based materials is extremely low,

which means that Mn-rich residue-based functional materials are highly inefficient for eliminating Mn-rich residue. In addition, secondary pollutants produced during the production process put forward more demanding requirements for the durability of the final product prepared. Similar to the other materials described above, the long-time safety and chemical stability of Mn-rich residue-based products must be evaluated and monitored in long-term tests.

6. Current deficiencies and further prospects

The complexity of Mn-rich residue components increases with the hydrometallurgical treatment process caused by reducing manganese ore grade. Therefore, many soluble sulfates, heavy metals, and components left over from chemical disposal reagents constitute the main chemical components of Mn-rich residue. The yield of Mn-rich residue also increases with the decrease in manganese ore grade, which means that the amount of Mn-rich residue stored in an open pit is difficult to decrease significantly in a short period. Due to this, the accumulated Mn-rich residue significantly affects the physiological well-being of the public, as well as polluting and destroying the environment.

From the perspective of soil resources, environmental protection and life health, the harmless treatment and resource utilization of Mn-rich residue is urgent. It can be seen from the formation process of Mn-rich residue that the activity of hydrometallurgical Mn-rich residue is lower than that of pyrometallurgical waste. The presence of inter-layer water, capillary water and chemically bound water further hindered the expansion of Mn-rich residue activity. Acidic Mn-rich residue affects its application in cement alkaline environments because it reduces the hydration pH environment of the cementitious materials. There is no way to achieve efficient, low-cost, and low environmental impact recycling disposal of Mn-rich residue simultaneously by reducing the harmfulness or recycling.

All the above treatment processes can be divided into heating and non-heating treatment. Specifically, the physical and chemical disposal of Mn-rich residue without heating mainly aims to recover valuable elements and cannot achieve good economic benefits, also the formation of potential secondary wastes deteriorates the environment. Chemical reagents and cementitious materials such as cement were used for harmless curing treatment of accumulated Mn-rich residue, focusing on the optimal safety control of the Mn-rich residue storage site. However, this technique requires a large amount of stabilization or solidification agent consumption, which leads to high disposal costs and low overall disposal efficiency. Moreover, the long-term durability of solidified products and the long-term environmental impact must be continuously monitored and evaluated due to the erosion and washing effect of rain during site restoration.

The use of Mn-rich residue as building materials has better progression due to the large demand, which releases the accumulation pressure of Mn-rich residue to a large extent. The influence of long-term stability and durability of Mn-rich residue-based building materials is still the biggest obstacle to the resource utilization of Mn-rich residue building materials. In addition, Mn-rich residue is defined as hazardous solid waste due to the presence of Mn^{2+} and NH_4^+-N. Therefore, giving full play to the complex components value of Mn-rich residue, turning waste into treasure and transforming Mn-rich residue into high-value resources are the most potential disposal solutions for resource utilization in building materials. When Mn-rich residue is prepared into adsorbent materials, the purpose of waste treatment can be achieved. Mn-rich residue-based adsorption materials mainly depend on the adsorption potential of SiO_2. However, the low consumption, secondary

environment and water resources pollution limit its popularization significantly. The same issue occurs when Mn-rich residue is used to develop soil fertilizers. When Mn-rich residue is used to prepare other functional materials, its effective utilization rate is low, and secondary solid waste is generated in the production process. The special characteristics of the low-purity materials that have been manufactured cannot be adequately guaranteed, and it is necessary to monitor and assess their chemical stability and leaching toxicity over an extended time.

In conclusion, compared with the single absorption treatment, the collaborative disposal of other solid wastes or building materials stabilized or immobilized by Mn-rich residue has a better prospect of harmless disposal and resource utilization. As opposed to other consumption types, the use of building materials is an effective way to maximize Mn-rich residue consumption. The abundant oxides in Mn-rich residue can be used as effective substitutes for cementitious materials and mineral admixtures in building materials, thus helping to reduce the consumption of building materials. However, the effective removal of Mn^{2+} and NH_4^+-N from Mn-rich residue is the prerequisite for resource reuse. In light of the continual consumption of mineral resources, the exploitation and utilization of solid wastes containing rich mineral resources have a good prospect. As part of a sustainable development strategy, maximising the utilization of Mn-rich residue resources and realising their maximum value is imperative. The realization of maximum high-value resource utilization of Mn-rich residue is due to the synergistic regulation and maximization among disposal efficiency, harmless degree, environmental disturbance degree and common properties ratio of materials. In other words, it is necessary to develop and progress toward high disposal efficiency, non-toxicity, no environmental pollution, high performance, and good long-term stability to maximize the high value-added utilization of Mn-rich residue in building materials.

All factors coordinate and improve the performance and unit absorption efficiency of Mn-rich residue-based products to ensure the harmfulness before using Mn-rich residue and the long-term durability of Mn-rich residue-based products. In this way, the waste can be turned into treasure in a real sense, the disadvantages of Mn-rich residue can be overcome, the advantages of Mn-rich residue can be highlighted, the misplaced resources can be reused to the greatest extent, and a high feasibility, high stability and low-cost solution can be provided for the sustainable development of the building material field with high energy consumption, high carbon emission and high resource consumption. The high value of Mn-rich residue resource utilization must fully stimulate the activity advantage of Mn-rich residue mineral components. Currently, the activation pathways of Mn-rich residue mainly come from physics, chemistry and heat treatment, and relevant research finding are also shown in the previous studies.

In general, the physical method mainly uses the collision caused by mechanical force to regulate the particle morphology of Mn-rich residue to change the specific surface area and particle size of Mn-rich residue. In resource utilization of building materials, finer Mn-rich residue tends to play a more significant role in micro-powder filling, while Mn-rich residue with larger specific surface areas shows higher activity after the water absorption characteristics are well treated. In addition, increased work by mechanical forces may lead to defects in the crystalline mineral lattices of Mn-rich residue, and these defective crystals may exhibit higher reactivity. The chemical mode is to form new reaction products conducive to resource utilization by introducing specific chemical substances and chemical reactions with the minerals in Mn-rich residue. The addition of

chemicals can regulate the mineral phase composition of the Mn-rich residue and adjust the water absorption characteristics and pH degree of the Mn-rich residue. However, specific and high-purity chemicals often mean high disposal costs and the introduction of low-purity chemicals poses a risk of secondary contamination.

At specific temperatures, thermal disposal differs from the previously discussed two treatment methods and provides a suitable high-temperature environment where certain Mn-rich residue mineral phases can undergo phase transformations (Figure 10). The amorphous mineral phases also significantly improve the reactivity of Mn-rich residue. Under high temperatures, Mn-rich residue can cooperate with other solid wastes or other chemicals to prepare the clinker phase of cementitious materials. Different Mn-rich residue-based cementitious materials can be prepared under specific temperature conditions with different proportions of Mn-rich residue and other substances. Mn-rich residue treated at different temperatures must also form high-value-added materials according to their component advantages. Therefore, further research should be conducted on the evaluation system and the performance safety of sintered Mn-rich residue-based products to achieve high value-added utilization and transform waste into wealth.

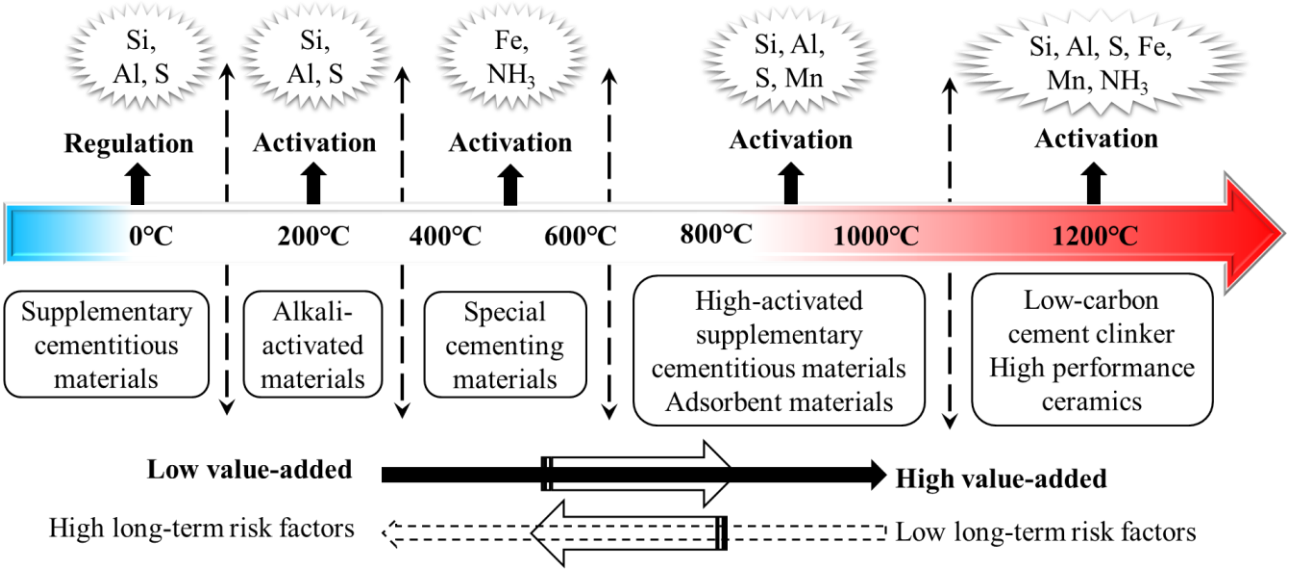

Figure 10. The consideration of high value-added resource utilization of Mn-rich residue in thermal treatment. Different heat treatment temperatures emphatically change the specific mineral and oxide components of Mn-rich residue. This means that different construction materials can be developed for the temperature-modified Mn-rich residue to realize the high-value cascade utilization of Mn-rich residue. High energy consumption brought by high temperature can also realize the high added value of Mn-rich residue utilization to realize the transformation of waste into wealth. Parameterized control of Mn-rich residue at specific temperatures provides a guarantee for high efficiency.

7. Conclusions

The disposal of Mn-rich residue has become an obstacle to the sustainable development of the Mn-rich residue industry. Therefore, the source reduction, process safety and high value-added reuse of Mn-rich residue have become the most important steps in the disposal of Mn-rich residue. However, the fountainhead reduction is limited by the increasing Mn-rich residue production, high-water content, and added chemical agents. For harmless disposal of Mn-rich residue, the existing methods are difficult to improve the disposal efficiency, meaning the large-scale disposal of Mn-rich residue is difficult to realize. In addition, disposal costs, secondary

contamination, and long-term stability are all barriers that limit their development. Resource utilization is important for Mn-rich residue, from waste to wealth. The main limitations of Mn-rich residue reuse are uncertain long-term stability, durability, low value-added, low disposal efficiency and low active utilization. In addition, the lack of utilization standards, disposal policies and evaluation systems for Mn-rich residue-based high-value use products severely restricts the pretreatment and reuse of Mn-rich residue. Meanwhile, the use of Mn-rich residue should not only be the direct disposal of low-activity, low-efficiency and low value-added; more importantly, the Mn-rich residue resources should be recovered. Several key recommendations are as follows:

1) The use of chemical additives in the preparation process of electrolytic manganese should be controlled, such as SO_2 instead of SeO_2 as an antioxidant, rather than artificially increasing the complexity of Mn-rich residue. Adding a separate sulfide precipitation process enriches and recovers Cu, Ni, Co and other valuable metals to reduce their entry into Mn-rich residue. Filter or wash the Mn-rich residue before storage or direct resource utilization, and the washed Mn-rich residue can be directly employed as raw materials of low-value-added constructed materials.

2) Heat treatment can be used throughout the whole process of reduction, harmless and resource utilization of Mn-rich residue. Thermal disposal is utilized for ferromanganese enrichment and separation in the Mn-rich residue reduction, dehydration and NH_4^+-N removal and Mn^{2+} enrichment in the harmless and activating Mn-rich residue mineral activity and sintering cementitious materials during resource utilization.

3) Low-temperature calcination can realize the dehydration and conversion of gypsum in Mn-rich residue to prepare sulfate activator and slag-based cementitious material. The formation of an amorphous phase can prepare high-activity supplementary cementitious materials and mineral admixtures during high-temperature calcination. Mn-rich residue can be combined with other solid wastes and minerals to build new cementitious materials with specific clinker phase proportions by rising the calcination temperature to the sintering interval of cement clinker.

4) Silicon dioxide in Mn-rich residue is converted to C_2S and C_3S, alumina and sulfate are used for conversion to calcium sulphoaluminate clinker phases, and the iron phase can be used to prepare ferrite phase solid solutions such as C_4AF. Other heavy metals, iron and manganese, and sulfur dioxide could be used to construct a feasible calcining atmosphere, which lowers the sintering temperature and improves the sintering efficiency. However, the environmental and equipment effects of ammonia and sulfur losses in Mn-rich residue still require further understanding.

5) The existence forms and release behaviors of Mn^{2+} and NH_4^+-N in Mn-rich residue under different conditions need to be monitored and evaluated for a long time. In the process of Mn-rich residue formation, the source and destination of various chemicals and their effects on soil, ecological environment and human health need to be deeply scrutinized.

6) Efficient dispersion of Mn-rich residue, reduced moisture content, stabilization or solidification of Mn^{2+} and NH_4^+-N, and reactive activation techniques should be strengthened. The evolution behavior of water absorption and water content of Mn-rich residue in the process of harmless disposal and resource utilization needs to be quantitatively evaluated.

7) Establish an evaluation system among the process performance, economy and environment of harmless

disposal and resource utilization of Mn-rich residue to standardize the quantitative standard between resource-based and high-value utilization of Mn-rich residue. The evaluation indexes among carbon emission, mechanical properties, durability and environmental impact factors were constructed to provide parametric guidance for the high-value resource utilization of Mn-rich residue.

Acknowledgements

The authors thank the Hunan Province Key Field R&D Program (Grant No.2020wk2005), and Central South University's autonomous Graduate students' Exploration and Innovation Project 2022ZZTS0619 (grant # 506021744).

Conflict of interest:

The authors declare no conflict of interest in this paper.

Ethics approval:

Not applicable.

Consent to participate:

Not applicable.

Consent for publication:

Not applicable.

Availability of data and material:

Not applicable.

Code availability:

Not applicable.

Author contributions

Fan Wang, Guangcheng Long,·Kunlin Ma, Xiaohui Zeng,· Zhuo Tang, Rongzhen Dong, Jionghuang He,· Minghui Shangguan, Qingchun Hu, Rock Keey Liew, Yang Li, John Zhou were involved in writing-review and editing. Fan Wang and Guangcheng Long were involved in supervision and funding acquisition. Fan Wang, Guangcheng Long, Qingchun Hu, Rock Keey Liew, Yang Li and John Zhou were involved in figure drawing. Fan Wang, Guangcheng Long, and John Zhou were involved in conceptualization. Fan Wang and Guangcheng Long were involved in scope planning.

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