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Introductory Chapter: Metallurgical Solid Waste

Yingyi Zhang

1. Utilization status of metallurgical solid waste resource

The sustainable development of resources and energy is an inevitable trend of social development. With the rapid development of metallurgical industry, a large amount of metallurgical solid waste is produced. However, a lot of metallurgical solid wastes have not been timely and effectively recycled, resulting in serious problems of environmental pollution and resource wastage, such as heavy metal pollution in air, water, soil, and plant system. According to the characteristics of metallurgical industry, this book introduces the main types, sources, and characteristics of metallurgical solid waste. The application and treatment methods of blast furnace slag, converter slag, and electric furnace slag in building materials and ceramics industry are mainly introduced. The comprehensive utilization technology of Bayer process-produced red mud and converter sludge was also investigated.

Blast furnace slag (BFS) is a by-product of iron-making, which is formed by the combination of iron ore with limestone flux. When the molten slag is rapidly cooled by water, a large amount of granulated and amorphous blast furnace slag is produced, and the physical and chemical properties of these slags mainly depend on the production process. It is worth noting that a lot of water and heat are wasted in this process. The main chemical components of these slags are silica (SiO_2), alumina (Al_2O_3), and lime (CaO), which are the main components of cement and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (CAS) glass ceramics [1, 2]. Therefore, the granulated blast furnace slag (GBFS) is usually used as feedstock for cement and glass ceramics manufacturing. The CaO content of blast furnace slag is about 35–56% [3], which can hydrate with water to form cementitious pozzolanic reaction products. When these slags are ground to a finer size, they can be utilized in the production of Portland slag cement [4]. The typical TEM micrograph of hydrated Portland cement (a) and photograph of the glass-ceramics (b) just fabricated from blast furnace slag are shown in **Figure 1**.

Steel slags are by-products of steel production, which are produced during the electric arc furnace process in steel-making, converter steel-making, and the secondary refining of steel, respectively [7]. In the process of steel-making, steel slag production accounts for about 15% of steel output. The steel slag annual production worldwide is about 130 million tons which are mainly electrical arc furnace slag (EAF), basic oxygen furnace (BOF) slags, and ladle furnace basic slag (LFS) [8]. The main chemical components of steel slag include silica (SiO_2), alumina (Al_2O_3), lime (CaO), magnesia (MgO), ferrous oxide (FeO), and hematite (Fe_2O_3), as shown in **Table 1**. The mineral components of steel slag mainly consist of olivine, hydraulic calcium silicate ($\beta\text{-Ca}_2\text{SiO}_4$ (C_2S), Ca_3SiO_5 (C_3S)), non-hydraulic calcium silicate ($\gamma\text{-Ca}_2\text{SiO}_4$ (C_2S), CaSiO_3 (CS)), tetra-calcium aluminoferrite (C_4AF), dicalcium ferrite (C_2F), and free CaO/MgO [15, 16]. As we all know, C_2S and C_3S are the main

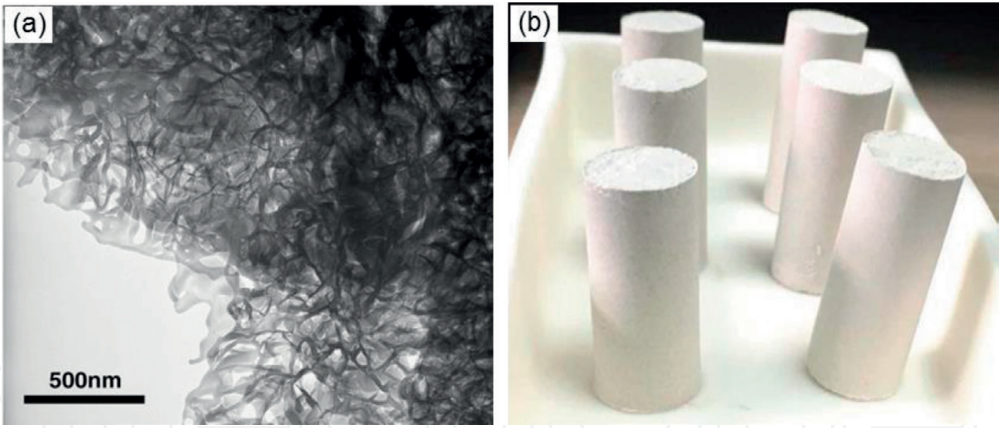


Figure 1. TEM micrograph of hydrated Portland cement (a) and photograph of the glass-ceramics (b) just fabricated from blast furnace slag [5, 6].

Reference	Type	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃
[9]	BOFS	39.08	12.47	6.87	10.57	19.48
[10]		61.21	24.92	1.83	4.89	3.04
[11]		47.7	13.3	3.0	6.4	24.4
[12]	EAFS	38.8	14.1	6.7	3.9	20.3
[13]		24.4	15.4	12.2	2.9	—
[9]	LFS	57.55	6.21	23.17	5.04	3.55
[14]		50.5–57.5	12.6–19.8	4.3–18.6	7.5–11.9	1.6–3.3
[12]		42.5	31.9	22.9	12.6	1.1

Table 1. The main chemical compositions of steel slag (wt%).

components of cement. Therefore, the steel-making slag also has certain cementitious properties and is used as feedstock for cement manufacturing, which is widely used in the construction industry. **Figure 2** shows the application of electric furnace slag concrete in construction.

Red mud (bauxite residue) is an alkaline solid waste residue generated from the Bayer process [17]. Presently, when producing a ton of alumina via Bayer process, about 0.8–2.0 t of red mud residues are produced, which mainly depends on the properties of raw material and production process conditions [18]. The global annual production of high-alkalinity red mud is about 120 million tons, and the global accumulation of red mud is about 2.7 billion tons [19]. The typical chemical compositions and mineralogical components of red mud are shown in **Table 2**. It can be seen that the red mud has a high pH or alkalinity, the aluminum compounds mainly consist of gibbsite (Al(OH)₃), aluminous goethite (α-(Fe,Al)OOH), boehmite (AlOOH) or diaspor (AlOOH), and the iron oxide mainly consists of hematite (Fe₂O₃) and aluminous goethite (α-(Fe,Al)OOH). However, large quantities of red mud are discarded as waste, and have not been effectively developed and utilized. This leads to serious soil, air, and water pollution and takes up a lot of space [20]. At present, most of the red mud is directly placed in landfill, deep sea, and storage in settling ponds, as shown in **Figure 3**. Despite the harmful impact that these methods pose on our environment, the risks of failure of a poorly engineered storage dam can result in even greater social and economic damage. In addition, the



Figure 2.
The application of EAF slag concrete in pavements [7].

Chemical name	Composition/ wt%	Mineralogical name	Chemical formula	Composition/ wt%
Fe ₂ O ₃	5–60%	Sodalite	3Na ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·Na ₂ SO ₄	4–40%
Al ₂ O ₃	5–30%	Aluminous goethite	α-(Fe,Al)OOH	10–30%
TiO ₂	0.3–15%	Hematite (iron oxide)	Fe ₂ O ₃	10–30%
CaO	2–20%	Silica	SiO ₂	5–20%
SiO ₂	3–50%	Tricalcium aluminate	3CaO·Al ₂ O ₃ ·6H ₂ O	2–20%
Na ₂ O	1–10%	Boehmite	AlO(OH)	0–20%
		Titanium dioxide	TiO ₂	2–15%
		Muscovite	K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·2H ₂ O	0–15%
		Calcium carbonate	CaCO ₃	2–10%
		Gibbsite	Al(OH) ₃	0–5%
		Kaolinite	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	0–5%

Table 2.
Chemical composition and mineralogical components of red mud (wt%).

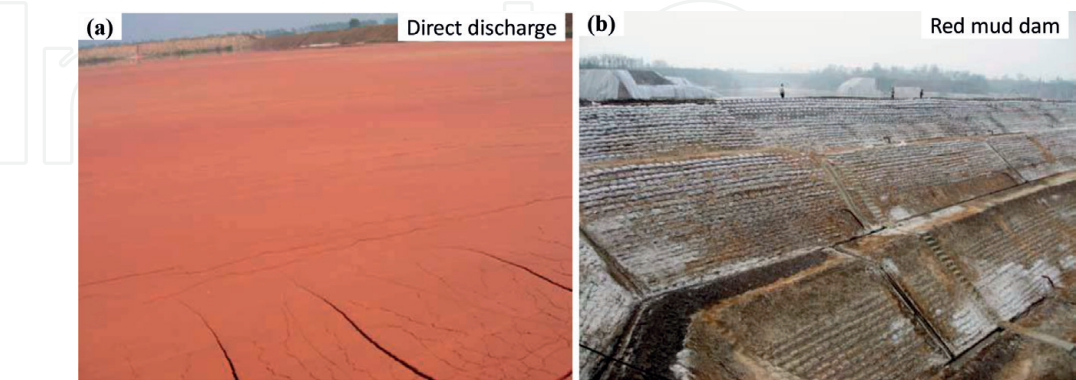


Figure 3.
Typical views of the red mud (a) and red mud dam (b).

red mud has a high concentration of aluminum compound, sodium aluminate, and iron oxide sodium, which limits the application of red mud in cement and ceramic industry (**Tables 2 and 3**). Therefore, the comprehensive utilization of red mud residue is an urgent problem in alumina industry.

Reference	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	TiO ₂	Na ₂ O	MgO	Cr ₂ O ₃	V ₂ O ₅	LOI
[21]	43.59	18.45	11.38	6.0	5.54	1.82	0.35	0.27	0.17	11.7
[22]	28.30	17.67	20.88	8.34	7.34	2.29	0.65	—	—	13.88
[17]	54.8	14.8	2.5	6.4	3.7	4.8	—	—	0.38	9.5
[23]	32.52	18.42	16.74	8.34	6.75	3.59	—	—	—	13.64

Table 3.
The chemical composition of red mud (wt%).

2. Conclusions

The sustainable development of resources and energy is an inevitable trend of social development. The comprehensive utilization of metallurgical solid waste is still a worldwide problem. Because of the limitations of current technology and consumption levels, a large amount of metallurgical solid waste has not been exploited effectively. The granulated blast furnace slag and steel slags are usually used as feedstock for cement and glass ceramics manufacturing. However, the traditional water quenching slag process wastes a lot heat of slag, polluted environment, and consumed water resources. Therefore, it is very important to develop technology for the utilization of waste heat from blast furnace slag and steel slag. Industrial storage is not the only way to solve the problem of comprehensive utilization and pollution of red mud. The recovery of valuable metals from red mud faces many technical problems, which seriously hinder the development of the metallurgical industry. In addition, applying red mud as construction material like cement or soil ameliorant faces the problem of Na, Cr, and As leaching into the environment. So, we must reduce the recycling process costs and energy consumption, promote the recovery of valuable metals, optimize complex processes, and develop new processes.

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