Chapter 13
Paper Industry, Construction, and Mining Process Wastes

Abstract Several alkaline wastes are likely to pose a threat to the ambient environment due to their high alkalinity and fine particles, if disposed improperly. These alkaline wastes include paper pulp and mill waste (lime mud), bauxite mining residue (red mud), and cement and demolition wastes. In this chapter, the characteristics of these alkaline solid wastes from paper industry, construction, and mining process are discussed. In addition, the situations and challenges in conventional utilization of the alkaline wastes are illustrated. After appropriate treatment or activation processes, the solid wastes can be utilized in various novel approaches, such as coagulant and adsorbent for water purification process.

13.1 Introduction

The rapid population growth and industrialization have been generating large amount of solid wastes over the world. Throughout the world, since ongoing urbanization prompted massive urban development and renovation activities, a large quantity of alkaline solid wastes has been produced from the following:

- paper industry;
- construction, demolition, and reconstruction sites; and
- mining process

These alkaline wastes are likely to pose a threat to the ambient environment due to their high alkalinity and fine particles, if disposed improperly, including bauxite residue (red mud), paper pulp and mill wastes, and cement wastes. Although the majority of these wastes are materials that could be reused and recycled, they were usually disposed of by landfilling and dumping, triggering serious environmental impacts [1].

To overcome the critical issues, in this chapter, the characteristics and convention utilization of these alkaline solid wastes from paper industry, construction, and mining process are discussed. Moreover, it is noted that there is a high potential for recycling and reuse of solid wastes from accelerated carbonation with positive

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results in base and subbase layers of roadways, which will be discussed in detail in Chaps. 14–16 (in Part IV).

13.2 Paper and Pulping Mill Waste

Paper and pulping mills produced large amounts of pulp annually. Massive inorganic (such as ashes and dregs) and organic residues are generated in bleached kraft pulp, which would potentially lead to adverse environmental pollution. The types of wastes generated from the paper and pulping industry can be categorized as follows:

- White liquor (cooking liquor):
  - It is an acidic mixture of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-).
  - It also contains various inorganic ions such as Mg, NH_3, Na, and Ca.
- Green liquor:
  - It is a solution of carbonate salts, primarily Na_2S and Na_2CO_3.
  - It contains insoluble unburned carbon and inorganic impurities.
- Black liquor:
  - It is a dilute solution with approximately 12–15% solids.
  - It contains wood lignin, organic materials, oxidized inorganic compounds (Na_2SO_4, Na_2CO_3), and white liquor (Na_2S and NaOH).
- Lime mud:
  - It is a waste of the calcinations or conversion of calcium carbonate to lime for causticizing black liquor.
  - The main component of lime mud is calcium carbonate ($CaCO_3$), typically around 65% [2].
  - Approximately 0.47 m^3 of lime mud can be generated for one ton of pulp [2].

Figure 13.1 shows a process flow diagram of pulp and paper manufacturing. The pulp and drying processes are the major energy consumers in the industry. The main production facilities are either pulp mills or integrated paper and pulp mills [3]. The integrated mills can achieve higher energy efficiency by eliminating intermediate pulp drying, compared to a single pulp mill. It is noted that a paper and pulping factory with a unit production capacity for one-ton pulp will generate around 0.5 ton of lime mud [4].

In this section, the physico-chemical properties of paper and pulping mill waste (lime mud) are illustrated. The challenges in convention utilization of lime mud are also provided.

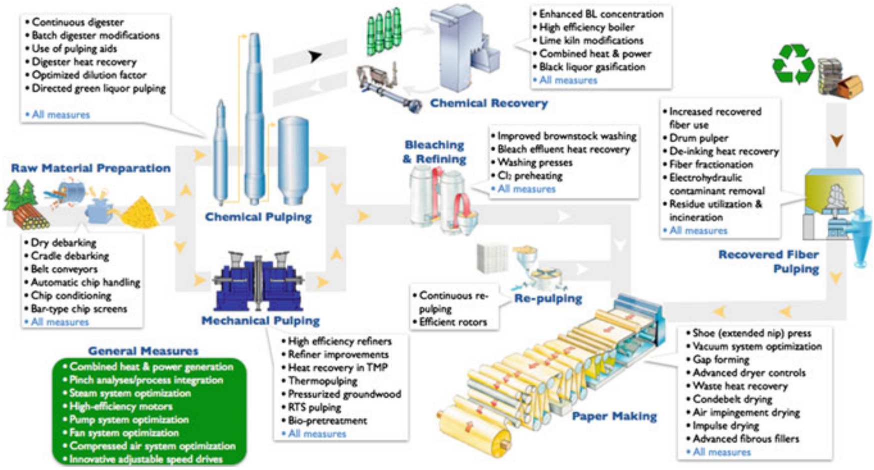

Fig. 13.1 Process flow diagram of pulp and paper manufacturing. Reproduced from Ref. [3] by permission of Institute for Industrial Productivity

13.2.1 Characterization

Table 13.1 presents the physico-chemical properties of paper and pulping wastes in the literature. The regeneration of the cooking liquor results in the formation of several types of portlandite-rich wastes, collectively referred to as paper mill wastes [5]. For instance, lime mud (or calcium mud) is a solid waste originated from the causticization process. Typically, the presence of high concentrations of portlandite ($Ca(OH)_2$) in calcium mud accounts for the high alkalinity [6]. Moreover, the main component of lime mud was found to be $CaCO_3$ [4].

13.2.2 Utilization

In paper and pulping industries, the alkaline by-products are usually sold for the cement manufacture and as alkaline amendment for agricultural soils. Conventional uses such as soil amendments, landfill, and building materials are continually conducted. Land application is one of the several limited methods available to manage solid wastes, which is more economically and ecologically sound than landfill practice [10]. However, it is limited by the presence of chloride and metals (such as Fe, Mn, Cd, Cr, Cu, Ni, Pb, As, and Zn), and its fine particle size and high alkalinity (pH > 12.1) [6, 9, 11].

The lime mud exhibited a promising potential to improve soil fertility by releasing K, Ca, and Mg into soils as an amendment [9]. In addition, applications of lime mud as adsorbents, ameliorants, and additives for treatment of liquid and solid

Table 13.1 Physico-chemical properties of paper and pulping wastes reported in the literature

Properties	Items	Units	Lime mud		
			A [7][a]	B [8, 9]	C [4]
Physical	Average size	µm	–	15	77
	pH	–	12.1	11.96	–
	Density	g/cm^3	–	2.62–2.66	–
	BET surface area	m^2/g	–	2.3–4.7	7.65
	Porosity	%	–	<5.0	–
XRF	Fe_2O_3	%	0.37	–	0.29
	TiO_2	%	–	–	0.06
	Al_2O_3	%	0.40	0.17	1.49
	SiO_2	%	0.37	0.34	2.52
	CaO	%	36.0	83.2	52.4
	Na_2O	%	0.82	0.88	0.14
	MgO	%	1.30	0.35	0.7
	SO_3	%	0.54	2.0	0.31
	K_2O	%	–	0.13	0.01
	P_2O_5	%	0.35	2.4	–
	Free CaO	%	–	–	–
	(O as element)	%	17.85	N.A.	–
Chemical analysis	$Ca(OH)_2$	%	–	55.0	–
	$CaCO_3$	%	39.0	33.0	–
	$Ca_{10}(PO_4)_6(OH)_2$	%	–	12.0	–
Thermal analysis	LOI	%	–	–	41.2

[a]The chemical compositions are presented in element forms

waste present promising effects [9]. On the other hand, CO_2 is generated at pulp mills in both the recovery boiler and lime kiln, which could be used to carbonate the paper mill wastes to produce $CaCO_3$. By the accelerated carbonation, it is reported that approximately 218 kg of CO_2 per ton of paper mill waste could be successfully sequestered into stable calcite [8].

13.3 Cementitious Waste (Construction and Demolition Waste)

Cement-type solid wastes include (1) construction and demolition waste, (2) cement kiln dust, (3) waste concrete, and (4) anorthosite tailings. The physico-chemical properties of these solid wastes are similar to that of Portland cement. Cement and demolition wastes constitute a major portion of total solid waste production in the world. For example, after urban renewal programs or natural disasters (e.g., earthquakes), demolition of older buildings leads to environmental problems particularly in larger urban areas. However, most of them are currently disposal in landfills [12]. They are generally in highly alkaline characteristics and rich in calcium-bearing components. As a result, the utilization of these cement-type solid wastes is limited because of their great concerns on environmental impacts.

13.3.1 Characterization

In this section, the physico-chemical properties of construction and demolition waste are illustrated. Table 13.2 presents the physico-chemical properties of cement-type wastes in the literature. In general, the cement-type wastes are mainly composed of SiO_2, CaO, Al_2O_3, and Fe_2O_3, along with several trace elements such as SO_3, TiO_2, and Na_2O. The chemical composition of metal oxides with an alkaline character of cement-type wastes could be considered as a suitable material for CO_2 mineralization.

Taking the anorthosite tailings as an example, the anorthosite is a rock containing more than 90% of feldspar plagioclase minerals. Feldspar plagioclase is the most abundant mineral in the earth's crust and is considered a solid solution due to

Table 13.2 Physico-chemical properties of cement-type wastes reported in the literature

Properties	Items	Units	Types of samples		
			Cement wastes [13]	Anorthosite tailings [14]	Concrete waste [14]
Physical	Particle size	µm	–	14.0–18.0	21.4–36.7
	pH	–	–	–	–
	Density	g/cm^3	–	–	–
	BET surface area	m^2/g	–	–	–
	Porosity	%	–	–	–
Chemical	Fe_2O_3	%	1.2–1.7	0.72–0.96	2.1–3.2
	TiO_2	%	0.5	0.11	0.34–0.69
	Al_2O_3	%	3.4–6.0	25.6–34.8	6.23–8.47
	SiO_2	%	12.6–25.1	50.0–66.0	37.9–48.5
	CaO	%	35.7–48.3	8.1–11.2	20.7–26.8
	Na_2O	%	2.0	4.8–6.5	1.39–1.63
	MgO	%	3.0–4.8	0.13–0.17	0.63–1.28
	SO_3	%	6.3	–	0.98–1.12
	K_2O	%	0.9–3.4	0.7–0.9	1.74–2.18
	P_2O_5	%	0.3	0.01–0.03	–
	MnO	%	–	0.01	–
	Free CaO	%	–	–	15.4–21.3

its variable composition between two pure poles: anorthite (calcic pole: $CaAl_2Si_2O_8$) and albite (sodic pole: $NaAlSi_3O_8$) [14]. The general process chemistry of carbonation with anorthite can be expressed as Eq. (13.1):

$$CaAl_2Si_2O_{8(s)} + CO_{2(g)} + 2H_2O_{(l)} \rightarrow 4CaCO_{3(s)} + Al_2Si_2O_5(OH)_{4(s)} \quad (13.1)$$

This reaction could naturally occur (so-called weathering), or it can also be accelerated in laboratory under specific operating conditions. According to the results in the literature [14], a total of 45 g CO_2 per kilogram of sample could be fixed within a reaction time of 15 min. In contrast, the waste concrete was found to be much reactive than anorthosite tailings in the aqueous carbonation. This might be attributed to the presence of susceptible phases to dissolving and reacting with CO_2, mainly portlandite ($Ca(OH)_2$) and calcium silicates [14]. In other words, the lower reactivity of andesine could be associated with its structure in framework, which probably inhibits the availability of calcium.

13.3.2 Utilization

The demolition waste consists mainly of concrete, mortar, brick, metal, timber, and plastic [1]. The major source of demolition wastes in rural areas is wastes from building remodeling and structural removal [12]. Typically, the conventional disposal methods for cement and demolition wastes are time-consuming, expensive, and environmentally unsound. Currently, in the member countries in European Union, about 46% of the construction and demolition waste is recycled [15]. It indicates that the most effective way to eliminate the cement-type waste issue is to reuse and recycle the construction materials in construction activities. Several studies have found that the use of cement-treated recycled wastes in the base (or subbase) is feasible for low-volume roads if the mix design is appropriate [12].

13.4 Mining and Mineral Processing Waste

Alumina is an important basic raw material for national economic development. In the aluminum manufacturing industries, a large amount of bauxite residues, so-called the red mud, can be produced from the digestion of bauxite ores with caustic soda (i.e., Bayer process) under elevated heat and high pressure. In general, the production of 1 ton of alumina could generate 0.3–2.5 tons of red mud, depending on the bauxite source and process efficiency of alumina extraction [16–18]. Therefore, for example, it is estimated that over 70 million tons of red mud was generated per year in China [17].

In this section, the physico-chemical properties of mining and mineral processing waste (red mud) are illustrated. In addition, the challenges in convention utilization of red mud are provided.

13.4.1 Characterization

Table 13.3 presents the physico-chemical properties of red mud in the literature. The results indicated that the chemical composition of red mud varied in a wide range, depending on the location and process of manufacturing. In general, the red mud is largely composed of SiO_2, Al_2O_3, Fe_2O_3, and CaO, along with several trace elements such as TiO_2 and Na_2O. The chemical composition of metal oxides with an alkaline character of red mud (i.e., with an average pH value of 13.3 $\pm$ 1.0 [19]) may contribute to a suitable material for CO_2 mineralization. The particle size distribution of red mud is similar to fly ash, having an average particle size of <10 μm. The specific surface area (BET) is typically 10−25 m^2/g [18]. Besides its high alkalinity, bauxite residues usually exhibit a large specific surface area and a high ion-exchange capacity [17].

Characterization of representative samples of red mud by XRD suggests that the mineral phases in red mud include hematite (Fe_2O_3), goethite (α−FeOOH), gibbsite ($Al(OH)_3$), limonite, boehmite, cancrinite, gismondine, goosecreekite, anatase, rutile, and quartz (SiO_2) [16–18,21]. Cancrinite and chantalite are the main calcium-bearing phases in red mud [16]. Since the abundant amount of metals (such as Al, Fe, Ti, and Ga) in red mud, the recycling of the metallic components has been gained great interests, such as metal extraction by using oxalic acid [23].

Table 13.3 Physico-chemical properties of red mud in the literature

Properties	Items	Units	Samples				
			A [16]	B [20]	C [21]	D [22]	E [19]
Physical	Average size	μm	5–50	–	–	–	1.9
	pH	–	7–8	–	–	–	13.3
	density	g/cm^3	1.5–2.2	2.8	2.2	–	2.93
	BET surface area	m^2/g	10.8	22.6	–	–	–
	Porosity	%	0.45	–	–	–	–
Chemical	Fe_2O_3	%	31.9	22.6	2.85	13.7	17.3
	TiO_2	%	21.2	3.37	2.03	2.10	3.43
	Al_2O_3	%	20.1	25.0	40.7	7.02	15.1
	SiO_2	%	8.5	20.2	45.8	18.1	22.8
	CaO	%	2.99	3.83	4.98	42.2	12.2
	Na_2O	%	6.0	8.78	N.D.	2.38	4.37
	MgO	%	–	<0.1	N.D.	2.06	0.27
	SO_3	%	–	N.D.	2.15	–	–
	K_2O	%	–	2.26	0.45	0.24	1.19
	P_2O_5	%	–	–	1.10	–	2.43
	Free CaO	%	–	N.D.	–	–	–

13.4.2 Utilization

The disposal of red mud remains a worldwide issue, in terms of environmental concerns, due to its high alkalinity and leachability of pollutant components. Therefore, utilization of red mud would provide significant benefits in terms of environmental and economic by reducing landfill volume and contamination of soil and groundwater. Great interests have been devoted to various types of utilization pathway for red mud, such as the following:

- coagulant [18],
- adsorbent [18],
- supplementary cementitious materials [20],
- self-compacting concrete [21],
- lightweight aggregate [24],
- soil mixture [25],
- glass-ceramics [22], and
- geopolymers [19].

Table 13.4 presents the performance of various types of utilization pathway for red mud in the literature. The details of the key performance indicators for cement materials can be referred in Chap. 15. For example, coagulants are widely utilized in water purification process, where the commonly used coagulants are Fe^{3+}- and Al^{3+}-based compounds. Due to the high contents of Fe and Al in red mud, it is considered as a promising material for coagulant production. Moreover, red mud can be used as a low-cost adsorbent for phosphorus, fluoride and nitrate ions, and trace heavy metals [18]. However, raw red mud generally presents low adsorption capacity and catalyst sintering. Therefore, several methods are proposed to activate red mud, including acidification, thermal treatment, and carbonation.

Table 13.4 Various types of utilization pathway of red mud in the literature

Pathways	Features	Performance	Reference
Self-compacting concrete	Blended with fly ash	• Pozzolanic activity: 76.6% at 7 d • Pozzolanic activity: 88.5% at 28 d • Reduced drying shrinkage due to internal curing effect	[21]
Soil mixture	Mixed with soil	• No adverse effect on test organisms for at least 10 months • There is an active microflora	[25]
Geopolymers	Mixed with fly ash and alkali activator	• Excellent long-term performance in field engineering applications • Successful formation of amorphous geopolymer gels	[19]
Cement paste	Blended with 3% fresh red mud	• Delayed chloride diffusion and CO_2 penetration in paste • Exhibit good pore refinement	[26]

Several benefits have been associated with the use of carbonated red mud, including soil amendment (removing nitrogen and phosphorus from sewage effluent), fertilizer additive in solid, fillers for plastics, and cement additive. The pozzolanic activity of fresh red mud, i.e., strength activity index (SAI), blended with fly ash in concrete was found to be 76.6 and 88.5% at 7 and 28 d, respectively, indicating that the red mud is roughly equivalent to those of fly ash [21].

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