Chapter 9
The Utilization of CO_2, Alkaline Solid Waste, and Desalination Reject Brine in Soda Ash Production

Dang Viet Quang, Abdallah Dindi and Mohammad R. M. Abu Zahra

Abstract Conventional Solvay process, which utilizes CO_2 to synthesize sodium carbonate, has been well-known for more than a century, but the only purpose of this process is to produce soda ash. Annually, significant amounts of CO_2 are converted into soda ash using Solvay process; however, this conventional process does not sustain CO_2 and waste cycle. Increasing the awareness of global warming and climate change linking to CO_2 emission has pressured this industry to move for a more eco-friendly process that should exploit its potential for CO_2 utilization and sequestration and thus contribute to both CO_2 emission and waste management. In conventional Solvay process, to produce one mole of Na_2CO_3, at least one mole of CO_2 might be emitted to atmosphere due to the use of CaO. Therefore, a number of studies have been done to explore novel processes or to modify the Solvay process in order for it to engage more in CO_2 mitigation. This chapter introduces the most up-to-date modified Solvay process and novel pathways to produce soda ash and baking soda in the consideration of waste and CO_2 utilization. Simultaneous waste and CO_2 utilization offers a great opportunity for shifting to a green production, not only soda ash industry but others where their exhausted CO_2, alkaline solid wastes, or reject brine can be utilized. However, there are challenges which require further research and technological development initiatives for the idea to be industrially implemented.

Keywords Soda ash · CO_2 utilization · CO_2 emission · Reject brine
Slag · Fly ash · Layered double hydroxide · Hydrotalcite · Solvay process

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Nomenclature

C_3A	$Ca_3Al_2O_6$
H	H_2O
AN	NH_4NO_3
AC	NH_4Cl
AA	CH_3COONH_4
AS	$(NH_4)_2SO_4$
MAE	Methyl aminoethanol
LDH	Al layered double hydroxide
HT	Hydrotalcite-like materials
Cl–HT	Chloride-form hydrotalcite
AOD	Argon oxygen decarburization
BOF	Basic oxygen furnace
BF	Blast furnace
EAF	Electric arc furnace
MW	Municipal solid waste
XRD	X-ray diffraction
EDS	Energy dispersive X-ray spectroscopy

9.1 Potential Contribution of Inorganic Waste in CO_2 Emission Mitigation

9.1.1 Carbon Utilization with Alkaline Solid Waste

Industrial wastes such as slag or fly ash may have composition similar to cement; therefore, they have great potential to use as active additives to replace a certain fraction of cement in concrete [1–3]. Recent study indicated that the strength of cement mortar can be significantly enhanced by adding carbonated slag or fly ash [4, 5]. These wastes contain significant amount of CaO and MgO which has been extensively investigated for CO_2 sequestration [6]. The most effective CO_2 sequestration for those wastes is gas–liquid method in which slag is dispersed in water and then CO_2 gas is introduced into the slurry. Divalent ions such as Ca^{2+} leached from slag react with dissolved CO_2 according to Eqs. 9.1–9.3 to form calcium carbonate [7–9]. The $CaCO_3$ reacts with $Ca_3Al_2O_6$ (C_3A) phase in concrete as shown in Eq. 9.4 that results in the formation of calcium carboaluminate hydrate ($C_3A \cdot CaCO_3 \cdot 11H$, where H stands for H_2O) and ($C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H$). The formation of calcium carboaluminate hydrate could contribute to enhance the mechanical strength of concrete [4]. With an estimated 400 million tonnes of iron and steel slag (for every tonne of steel produced, two tonnes of CO_2 emission, 400 kg of blast and basic oxygen furnace slag, and 200 kg of electric arc furnace slag are generated) [10], 750 million tonnes of fly ash from coal-fired power plant [11], and huge quantity of alkaline waste from other industries' discharges annually, this alternative could contribute to reduce a great amount of CO_2 emission.

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow 2H^{+} + CO_3^{2+} \tag{9.1}$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^{-} \tag{9.2}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{9.3}$$

$$\begin{aligned} 2C_3A + 1.5\ CaCO_3 + 0.5Ca(OH)_2 + 22.5H &\rightarrow C_3A \cdot CaCO_3 \cdot 11H \\ &+ C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H \end{aligned} \tag{9.4}$$

Global phosphate industry, mainly fertilizer producers, discharges approximately over 200 million tonnes of phosphogypsum annually (4.5–5.5 tonnes for one tonne of P_2O_5 produced), and about 85% of this is disposed without any treatment [12, 13]. This waste is dumped in large stockpile causing serious environmental impact. Phosphogypsum has high content of calcium sulfate, about 24–34 wt% as CaO and 48–58 wt% as SO_3. This make it high potential for CO_2 utilization and sequestration [14–20]. However, not only sequestration, this solid waste could be converted to marketable $(NH_4)_2SO_4$ fertilizer [21]. CO_2 utilization and $(NH_4)_2SO_4$ fertilizer production is based on the conventional Merseburg process in which $CaSO_4$ reacts with $(NH_4)_2CO_3$ to form $CaCO_3$ and $(NH_4)_2SO_4$ as Eq. 9.5 [22, 23].

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O \tag{9.5}$$

$$CaSO_4 \cdot 2H_2O + 2NH_4OH + CO_2 \rightarrow (NH_4)_2SO_4 + CaCO_3 + 3H_2O \tag{9.6}$$

Conventionally, $(NH_4)_2CO_3$ that previously produced by bubbling CO_2 into ammonium solution is added into the slurry of gypsum or phosphogypsum. Recent studies reveal that bubbling CO_2 or flue gas directly into ammonium-saturated phosphogypsum solution helps reduce reaction process from two steps to one step which could result in saving expense and lower production cost [8, 24, 25]. This modified Merseburg process is chemically described in Eq. 9.6. Accordingly, for every tonne of $(NH_4)_2SO_4$ produced, 0.9 tonnes of $CaCO_3$ is generated which can permanently sequester 0.4 tonnes of CO_2, and 1.6 tonnes of waste gypsum is consumed [25]. With over 200 million tonnes of phosphogypsum from phosphate industry together with significant amount gypsum from flue gas desulfurization process in power plant [24], its reveals the high potential of gypsum waste and CO_2 utilization to produce marketable products such as $CaCO_3$ and $(NH_4)_2SO_4$.

9.1.2 CO_2 Utilization with Aqueous Inorganic Waste

Beside the solid alkaline wastes that contain mainly Ca^{2+} and Mg^{2+} with the large capacity of CO_2 sequestration, there are also aqueous solution wastes that have high concentration of Na^+, Mg^{2+}, and Ca^{2+} such as reject brine from desalination plant [26, 27], saline brine from CO_2 storage sites [28] or textile industry [29]. High demand on clean water due to the world population growth and scarcity of freshwater has driven the increase in the deployment of desalination plants worldwide. Desalination has become an important source of drinking water production with the capacity of estimated >86 million m^3/day from >18,000 plants in 2015 [28]. Over 15,000 desalination plants were installed in 2009 in which reverse osmosis technology accounted for 80% and global market for reverse osmosis alone is predicted to reach $8.1 billion by 2018 [30–32]. Desalination is the most viable way that can produce enough clean water to meet the high demand. However, this method faces some issues that are high energy consumption and reject brine management and disposal. According to Dawoud and Mulla, every 1 m^3 clean water produced results in 2 m^3 of reject brine [33]. Advanced technologies may enhance the water recovery and reduce the reject flow, but the reject volume still remains very large. Reject brine disposal is a costly process which accounts for 3–33% of the total cost of desalination depending on the selection of disposal method [34]. The major constituents in reject brine comprise of calcium, magnesium, sodium cations, sulfate and chloride anions, and sometime antiscalants. Their concentrations are dependent on the water sources, desalination technologies, and water recovery ratio or concentration factor [27, 34]. Seawater desalination plant recovery is typically limited to 40–65%, and its total dissolved solid concentration usually ranges from 65,000 to 85,000 mg/l [27]. Reject brine disposal either inland or into the sea may result in negative environmental impact due to locally increasing in temperature and salinity; hence, a proper management and treatment procedure is required for the disposal [31, 35]. A number of methods such as solar evaporation, membrane distillation, electrodialysis, forward osmosis, zero liquid discharge, salt recovery have been proposed to reduce and eliminate the brine disposal in which the methods that combine brine treatment with the recovery of valuable component have drawn significant interest [31, 32, 35–37]. Recently, several studies have considered the recovery of salt and minerals from rejected brine in the context of CO_2 capture and utilization [38–42]. Simultaneous CO_2 and brine utilization is based on the reaction between CO_2 and major inorganic cations prevailed in the rejected brine. Generally, CO_2 utilization with brine can be divided into two methods: direct precipitation of earth alkaline cations of Ca^{2+} and Mg^{2+} by CO_2 gas to form $CaCO_3$ and $MgCO_3$ [43–46] and indirect precipitation of Na^+ to form sodium bicarbonate [41]. In the former method, less soluble carbonates removed from water can be value-added products; nevertheless, with the low Ca^{2+} and Mg^{2+} concentrations of several hundred to several thousand ppm, this method is potentially used for brine pre-treatment other than the recovery of $CaCO_3$ for marketing [45], whereas, the latter method makes up a core technology for the industrial production of soda ash (Na_2CO_3) [47]. Soda ash is an important raw material used in many industries such as glass, chemicals, soaps and detergents, metallurgy, water treatment, pulp, and paper. Producing soda ash from rejected brine and CO_2 is an opportunity for at the same time utilizing two waste streams in one product. By producing soda ash, CO_2 can be sequestered in the way that generates the added value for CO_2 captured.

In the following section, the CO_2 utilization in the most updated sodium bicarbonate ($NaHCO_3$) and sodium carbonate production process will be introduced; especially, its relevance to CO_2 mitigation strategy and brine and solid waste treatment will be considered.

9.1.3 Conventional Solvay Process and Its Potential for CO_2 Utilization

Solvay process developed in 1861 by Ernest Solvay is the most commercially accepted process for soda ash production due to its low investment and maintenance costs compared to others. This process produces soda ash from brine (NaCl) and limestone ($CaCO_3$) with the overall reaction given in Eq. 9.7 [48]. In fact, it is more complicated and goes through many different steps that are schematically described in Fig. 9.1. Brine after purification is ammoniated and carbonated by passing the CO_2 gas (Eq. 9.8). The carbonation leads to the precipitation of bicarbonate ($NaHCO_3$) that is subsequently filtered and calcined to produce soda ash (Eq. 9.9). Filtrate mainly consisting of NH_4Cl and residual NaCl is mixed with CaO in the distillation process to regenerate NH_3 that is returned to ammoniation process (Eq. 9.10). CaO reacts with NH_4Cl and NaCl in the filtrate to form $CaCl_2$ as a major chemical species in distiller waste (Eqs. 9.10 and 9.11). Limestone is burned to supply CaO for NH_3 regeneration and CO_2 for carbonation process (Eq. 9.12). The conventional Solvay process faces a significant problem of waste management [48–50]. To ease its impact on the environment, the waste utilization is usually added into the traditional Solvay process in which $CaCl_2$ can be converted to $CaCO_3$, calcium phosphate, magnesium phosphate, or gypsum that are commercializable by-products [50–55]. The Solvay process itself does not substantially contribute to reduce CO_2 emission due to the burning fossil fuel for CaO and CO_2. This process consumes a significant amount of CO_2 because of the high demand on soda ash and therefore has high potential for CO_2 utilization and sequestration, but it can become reality only when the whole process is revised with the replacement of CaO and CO_2 sources. These chemicals are abundant in many industrial wastes such as fly ash, slag, and flue gas. Thus, the exploration of those wastes as major sources for CaO and CO_2 instead of burning $CaCO_3$ should be considered. This strategy does not only reduce CO_2 emission but also mitigate other wastes to be discharged to the environment. In the following parts of this chapter, the modified Solvay method and related methods to produce $NaHCO_3$ and Na_2CO_3 in the consideration of waste and CO_2 utilization will be introduced.

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \tag{9.7}$$

$$NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl \tag{9.8}$$

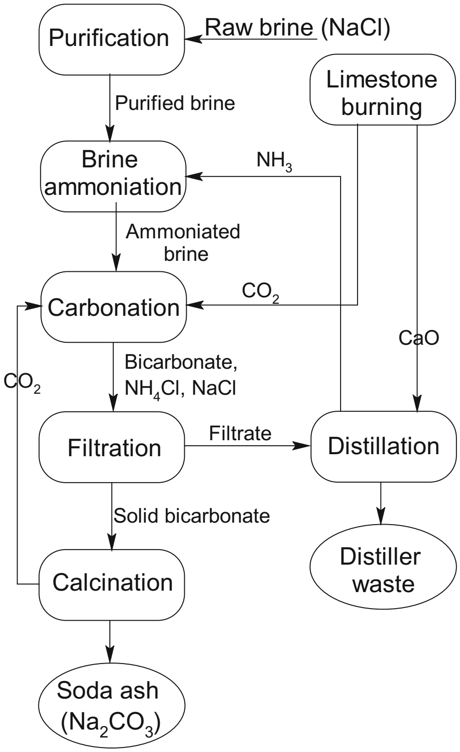

Fig. 9.1 Schematic diagram of a traditional Solvay process

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \tag{9.9}$$

$$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O \tag{9.10}$$

$$2NaCl + CaO + H_2O \rightarrow CaCl_2 + 2NaOH \tag{9.11}$$

$$CaCO_3 \rightarrow CaO + CO_2 \tag{9.12}$$

9.2 Modified Solvay Process and Solid Waste Utilization

9.2.1 Solid Waste Utilization in a Modified Solvay Process

Looking at the Solvay process as shown in Fig. 9.1, we can find a number of precursors or process steps where the traditional sources can be partially or even completely replaced by wastes. First of all, let us analyze the CO_2 cycle in the process; every mole of Na_2CO_3 produced requires one mole of CO_2 from burned $CaCO_3$ fed into system. This process looks like a carbon neutral one emission because CO_2 in a close loop, however, there is a hidden event, i.e., $CaCO_3$ burning process that combusts fossil fuel and generate significant amount of CO_2 [56]. The emission from fossil fuel combustion in lime production may vary with the type of kiln and fuel, but according to Shan et al., an average of 56.55 million tonnes CO_2 emitted for the production of 207.5 million tonnes lime in China in 2012 [56]. This means that every tonne of CaO produced generates 0.27 tonnes CO_2 that are not used in soda ash production. Steinhauser indicated that the production of one tonne of soda ash emits from 0.2 to 0.4 tonnes of CO_2 [48]. This makes the traditional Solvay process not attractive in the term of CO_2 emission. CO_2 is however very abundant in flue gas from power plant or industry that burns fossil fuel as energy source. Flue gas from coal-fired power plant, for example, contains approximately 15 vol.% of CO_2 that can be a viable CO_2 supply for soda ash industry. The issue now lies in the CaO source because burning $CaCO_3$ does not only provide CO_2 but also provide CaO. Stop burning $CaCO_3$ means the alternatives for CaO source must be taken into account. Fortunately, as discussed in earlier section, a variety of alkaline solid wastes such as ash and slag which have high content of CaO are available from coal-fired power plants and other industries that burn coal for energy as well. Depending on industry, technology, and type of coal, chemical composition and alkaline contents of solid wastes can be varied. In the industrial process, e.g., steelmaking illustrated in Fig. 9.2, slag can be collected from different process steps with different quantities and qualities. Table 9.1 shows the chemical composition of major alkaline wastes that are available from the literatures [6, 7, 57, 58]. The slag collected from blast furnace (BF slag) contains about 38–42 wt% CaO, while that collected from basic oxygen furnace (BOF slag) has 46.3–55.9 wt% CaO. As can be seen in this table, there are a number of wastes that have high CaO content with maximum above 50 wt% such as municipal solid waste (MW) incinerator bottom ash (53 wt%), fly ash class C (54.8 wt%), blended hydraulic slag cement (56.9 wt %), air pollution control residue (60 wt%), argon oxygen decarburization (AOD) slag from steel industry (60.7 wt%), and paper sludge incineration ash (69

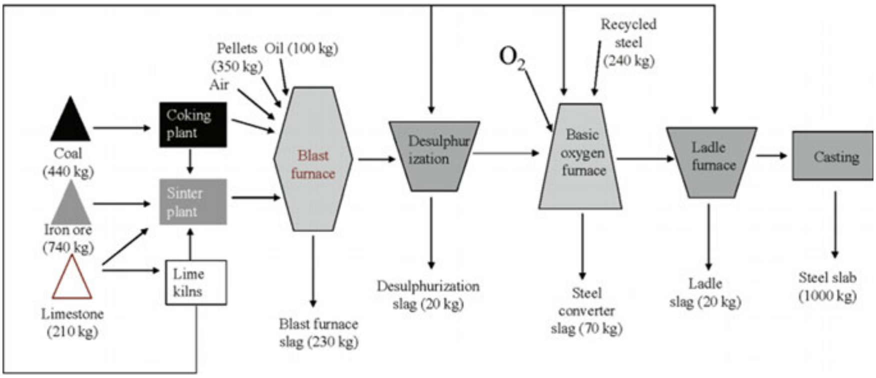

Fig. 9.2 Flowchart of a typical integrated steelmaking process. Reprinted with permission from [59], copyright 2008 American Chemical Society

Table 9.1 Chemical composition of different alkaline solid wastes

Wastes	Chemical composition (wt%)								References
	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	Na_2O	K_2O	LOI	
Fly ash (class C)	15.1–54.8	0.1–6.7	11.8–46.4	1.4–15.6	2.6–20.5	0.2–2.8	0.3–9.3	0.3–11.7	[57]
Fly ash (class F)	0.5–14.0	0.3–5.2	37.0–62.1	2.6–21.2	16.6–35.6	0.1–6.3	0.1–4.1	0.3–32.8	[57]
Blast furnace slag (BF)	38.0–42	5.0–8.2	33.0–36.7	0.2–0.5	13.5–15.5	–	0	–	[58]
Steel slag (BOF)	46.3–55.9	2.1–6.3	9.3–12.9	22.7–25.3	1.1–2.0	0.3	0.1	–	[58]
Steel slag (EAF)	25.0–47.0	4.0–15.0	27.0	1.6	–	–	–	–	[6]
AOD process slag	60.7	5.83	27.6	0.21	–	–	–	–	[6]
Desulfurization and ladle slag	43–58	1.0–6.0	16.0–19.0	10.0–20.0	–	–	–	–	[7]
Cement kiln dust	38.0–50.0	0–2.0	11.0–16.0	1.0–4.0	3.0–6.0	–	–	–	[58]
Biomass and wood ash	24.0–46.0	8.0–9.0	5.17	1.0–1.3	–	0.5	14.0–21.0	–	[6]
Recycled concrete aggregate	15.0–24.0	2.03	–	–	–	0.1	0.2	–	[6]
Incinerator sewage sludge ash	9.0–37.0	3.0	40.0	5.6	–	0.7	2.3	–	[6]
MW incinerator bottom ash	32.0–53.0	2.8	4.0–30.0	1.0–7.9	–	2.2–5.7	0.8–2	–	[6]
Pulverized-fuel ash	1.3–10	1–3	56	13.8	–	0.5	0.1	–	[6]
Oil shale ash	42.0–50.0	5.0–6.5	22.0	4.0	–	–	–	–	[6]
Air pollution control residue	50.0–60.0	8.0	10.0	0.5–1.5	–	–	2.0–6.0	–	[6]
Paper sludge incineration ash	45–69	1.3–5.3	10–25	1–4.7		0–1	0–2		[6]
Blended hydraulic slag cement	51.4–56.9	2.5–5.4	25–28	1.5–3.7	8.4–9.3	–	–		[58]
Waste concrete	35.7	3.0	25.1	1.2	3.4	–	–		[60]

BF Blast furnace; *BOF* Basic oxygen furnace; *EAF* Electric arc furnace; *AOD* Argon oxygen decarburization; *MW* Municipal solid waste wt%). These two waste streams, flue gas and alkaline solid waste, could be perfect alternatives for CO_2 and CaO sources and positive contribution to CO_2 emission and solid waste mitigation.

In the Solvay process, thermal energy consumption accounts for 30% of production cost and considerable fraction of it comes from firing $CaCO_3$ for CaO [63]. The use of solid waste instead of CaO does not only reduce CO_2 emission but also directly contributes to lower the cost of product thanks to the reduction in energy consumption and low cost of solid waste. In order to improve the input parameters such as energy and material cost and diminish the amount of waste in conventional process, Carvalho Pinto et al. proposed a modified Solvay process as shown in Fig. 9.3 where lime used in the regeneration of ammonia is partially replaced by steel slag milk [63]. The steel slag having 40.1 wt% CaO was utilized in the laboratory investigation. The effect of various conditions such as temperature, time, NH_4Cl concentration, and slag/NH_4Cl ratio on the extraction of Ca^{2+} ions from slag was investigated. The maximum Ca^{2+} extraction efficiency reaches 5 wt% at the optimum condition of NH_4Cl 1.5 mol/L at 90 °C for 60 min with a solid-to-liquid ratio of 2 wt%. The Ca^{2+} leaching is however significantly affected by the $NaHCO_3$ concentration remained in the filtrate from the Solvay process after solid $NaHCO_3$ is separated. For a better Ca^{2+} leaching, it requires a thermal treatment to decompose $NaHCO_3$ prior to the addition of alkaline waste [54, 63]. By thermal treatment, the Ca^{2+} concentration is improved from 192 to 1520 mg/L, which is close to leaching efficiency of pure NH_4Cl (1840 mg/L). NH_3 recovery also varies with reaction conditions and is possible to reach a maximum of 40 wt%. The study at bench scale indicated that the maximum NH_3 recovery of 40 wt% can be reached only when multi-recovery stages is applied.

It is easily understandable that the success of alkaline solid wastes as alternatives to CaO depends on the amount of Ca^{2+} ions that can be extracted as active components. The extraction is controlled by several factors including the type of solid waste, CaO content of waste, the nature of calcium in solid waste, extracting solution, and temperature [7, 59–62, 65, 68–71, 73]. CaO content in solid waste is a primary parameter to evaluate the potential of a waste utilization. The CaO content greatly varies with the type of solid waste. As shown in Table 9.1, CaO contents in

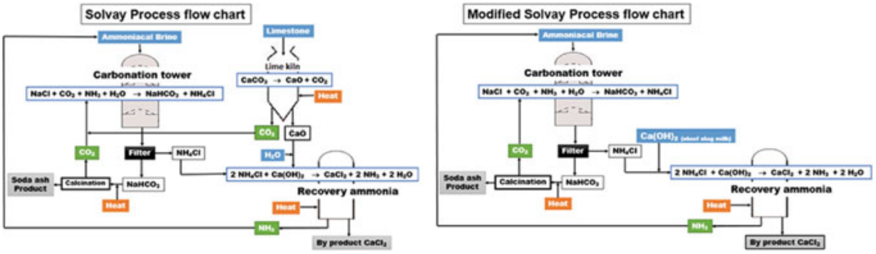

Fig. 9.3 Conventional Solvay process and its modified one by partial replacement of CaO with steel slag. Reprinted with permission from [63], copyright 2015 Springer Nature publisher

different solid wastes are variable, the higher CaO wastes are usually expected to have more amount of Ca^{2+} extracted, but it also depends on which type of crystalline phase existing in the wastes. In a research to extract Ca^{2+} from steel slag containing 40.1 and 30.5 wt% CaO using NH_4Cl solution and the filtrate of the Solvay process conducted by de Carvalho Pinto et al., the maximum Ca^{2+} extraction reached only 22 wt%, much lower compared to many others as shown in Table 9.2 [54, 63]. Even though only 22 wt% calcium was extracted, 84.3 wt% of the NH_3 inlet can be recovered, demonstrating a great potential of solid waste use in a modified Solvay process. Therefore, the key to the success of this process now lies on calcium extraction method. In the following section, the essential parameters for effective calcium extraction using the NH_4Cl solution or the filtrate from the Solvay process will be intensively discussed based on the available literatures.

9.2.2 Calcium Extraction by Extracting Agent

The number of studies has been conducted to extract the calcium from solid waste for a purpose of CO_2 sequestration and calcium carbonate production [6, 7, 58, 61, 65, 67, 70, 73, 74]. The calcium extraction efficiency is used as a major parameter to evaluate the effectiveness of an extraction system. The extraction efficiency is defined as the percentage of Ca extracted by extracting solution to the total calcium in the solid waste used in the test as expressed in Eq. 9.13. Pure water has very poor calcium extraction because it can dissolve only part of free CaO in solid waste. In a research conducted by Said et al. [61], only 0.81 wt% of calcium in steel-converted slag was extracted by pure water. However, in another research, He et al. can extract more than 10 wt% of calcium from fly ash using pure water even though the fly ash contains less CaO, 30.47 wt% (Table 9.2) [62]. The difference in calcium extraction efficiency is probably due to the different contents of free calcium oxide or the waste microstructure that prevents the migration of Ca^{2+} into water phase. The calcium extraction efficiency offered by water is usually far below the requirement for an application, and thus, it needs a more effective method. Various extracting agents such as acids (HCl, HNO_3, CH_3COOH, and CH_3CH_2COOH) [59, 74–76] and ammonium salts (NH_4Cl, NH_4NO_3, CH_3COONH_4, and $(NH_4)_2SO_4$) [59–62, 71] have been used to improve the Ca^{2+} extraction. Recent works have indicated that the addition of these extracting agents helps enhance the Ca^{2+} extraction significantly thanks to their possibility to selectively dissolve some calcium compounds in solid waste, e.g., the dissolution of calcium silicate and calcium ferrite phases given in Eqs. 9.14 and 9.15 [65, 66, 68, 70, 72].

$$\text{Ca extraction efficiency}(\%) = \frac{m_{Ca}(g)}{m_t(g) \times \frac{C_{CaO}(\%)}{100} \times \frac{M_{Ca}\left(\frac{g}{mol}\right)}{M_{CaO}\left(\frac{g}{mol}\right)}} \times 100 \qquad (9.13)$$

Table 9.2 Calcium extraction by NH_4Cl solution in the literature

No.	Waste	CaO (wt%)	Extracted (wt%)	Selectivity (%)	NH_4Cl concentration (mol/L)	Solid–liquid ratio (g/L)	Particle size (micro)	Ca in leachate (g/L)	Temperature (°C)	Time (Min)	References
1	Steel slag	44.9	0.81	–	Water	0.0	0–125	–	30	60	[61]
2	Fly ash	30.47	10	–	Water	50.0	<100	–	40	60	[62]
3	Steel slag	40.1	5.9[a]	–	0.1	20.0	–	0.34	85	45	[63]
4	Steel slag	40.1	3.7[a]	–	0.1	50.0	–	0.53	85	45	[63]
5	Steel slag	40.1	2.1[a]	–	0.1	100.0	–	0.61	85	45	[63]
6	Steel slag	40.1	0.8[a]	–	0.1	300.0	–	0.69	85	45	[63]
7	Steel slag	41.1	0.5[a]	–	0.1	500.0	–	0.75	85	45	[63]
8	Steel slag	40.1	4.8[a]	–	1	400.0	–	5.52	85	45	[63]
9	Steel slag	30.5	22.1	93.9[a]	2.8	50.0	–	1.28	85	45	[54]
10	Steel slag (BOF)	40	52.5[a]	75.38[a]	2	100.0	–	15.00	60	120	[64]
11	Steel slag (BOF)	44.9	56	–	1	20.0	0–125	–	30	60	[61]
12	Steel slag (BOF)	51.4	78	–	1	100.0	<250	–	20	30	[65]
13	Steel slag (BOF)	36	62.1[a]	–	1.8	83.3	250–500	13.30	53	68	[66]
14	Steel slag (BOF)	45.9	about 70	–	2	20.0	74–125	–	20	60	[67]
15	Desulphurization slag	58	50	–	2	20.0	–	–	20	60	[67]
16	Ladle slag	49.4	about 15	–	2	20.0	–	–	20	60	[67]
17	Steel slag (BF)	34.5	<10	–	2	20.0	–	–	20	60	[67]
18	Steel slag (BOF)	34.4	20.4[a]	97.0	2	100.0	150–500	5.01	–	120	[68]
19	Steel slag (BOF)	34.4	34.4[a]	97.0	2	100.0	<150	8.46	–	120	[68]
20	Ladle slag	38.2	15.4[a]	97.0	2	100.0	150–500	4.21	–	120	[68]
21	Ladle slag	38.2	30.7[a]	96.0	2	100.0	<150	8.37	–	120	[68]

(continued)

Table 9.2 (continued)

No.	Waste	CaO (wt%)	Extracted (wt%)	Selectivity (%)	NH_4Cl concentration (mol/L)	Solid–liquid ratio (g/L)	Particle size (micro)	Ca in leachate (g/L)	Temperature (°C)	Time (Min)	References
22	Desulphurization slag	39.3	22.2[a]	97.0	2	100.0	150–500	6.24	–	120	[68]
23	Desulphurization slag	39.3	39.9[a]	95.0	2	100.0	<150	11.19	–	120	[68]
24	Hazelwood fly ash	32.4	32	–	4	166.7	<150	–	80	30	[69]
25	Yallourn fly ash	9.4	37	–	4	166.7	<150	–	80	30	[69]
26	Fly ash	30.47	35	–	1	50.0	<100	–	25	120	[62]
27	Steel slag	47	35.0[a]	96.1[a]	2	100.0	–	11.75	45	30	[70]
28	Granulated slag (BF)	22.5	49.0	–	1	10.0	–	–	30	30	[71]
29	Granulated slag (BF)	22.5	52	–	2	10.0	–	–	30	60	[71]
30	Air-cooled slag (BF)	32.9	11	–	1	10	–	–	30	30	[71]
31	Air-cooled slag (BF)	32.9	13.7	–	2	10.0	–	–	30	60	[71]
32	Steel slag (EAF)	39	75[b]	–	2	50.0	–	–	100	60	[72]
33	Steel slag (EAF)	39	85[b]	–	2	50.0	–	–	100	60	[72]
34	Steel slag (EAF)	39	95[b]	–	2	50.0	–	–	100	60	[72]
35	Concrete	35.7	19.4[a]	95.3[a]	0.5	50.0	<149	2.48	20	240	[60]
36	Concrete	35.7	32.0[a]	98.0[a]	1	50.0	<149	4.08	20	240	[60]

[a] Estimation based on the ion concentration in the leachate,

[b] Estimation from the figure of corresponding references. The concept basic oxygen furnace slag (BOF) and steel converter slag are unified as steel slag (BOF) in this table

where m_{Ca} is the mass of Ca extracted by the extracting solution (g), m_t is the mass of solid waste used (g), C_{CaO} is the CaO content in solid waste (wt%), M_{Ca} is molecular weight of calcium (g/mol), and M_{CaO} is molecular weight of CaO (g/mol).

$$2CaO_{(S)} \cdot SiO_{2(s)} + 4NH_4Cl_{(aq)} \leftrightarrow 2CaCl_{2(aq)} + SiO_{2(s)} + 4NH_{3(g)} + 2H_2O_{(l)} \tag{9.14}$$

$$Ca_2Fe_2O_{5(s)} + 2NH_4Cl_{(aq)} \leftrightarrow 2Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + 2NH_{3(g)} + Fe_2O_{3(s)} + H_2O_{(l)} \tag{9.15}$$

The calcium extraction from fly ash by water and ammonium salts at different temperatures was reported by He et al. [62] (Fig. 9.4). It is evident that the calcium extraction improves significantly by adding those extracting agents. Temperature also contributes to the improvement, but it should be controlled in a moderate range. The higher temperatures do not significantly improve the extraction but incur the water vaporization that causes the loss of solvent, difficult process control, and energy intensiveness. In another research, Lee et al. showed the effect of ammonium salts on two types of slag, granulated slag and air-cooled slag [71]. They again confirm the extraction efficiency caused by the type of both extracting solvent and solid waste. NH_4NO_3, NH_4Cl, and CH_3COONH_4 have a comparable extraction efficiency, approximately 49–52 wt% for granulated slag and 11–17 wt% for air-cooled slag (Fig. 9.5). $(NH_4)_2SO_4$ has worse extraction among four ammonium salts due to the formation of less soluble $CaSO_4$ on the outer layer of slag granules that prevents the dissolution of Ca^{2+} into liquid phase. Using 2 mol/L of NH_4Cl, NH_4NO_3, and CH_3COONH_4, Said et al. can extract from 45 to 54% calcium from BOF slag that has the particle size of 74–125 µm. Similar results were observed by

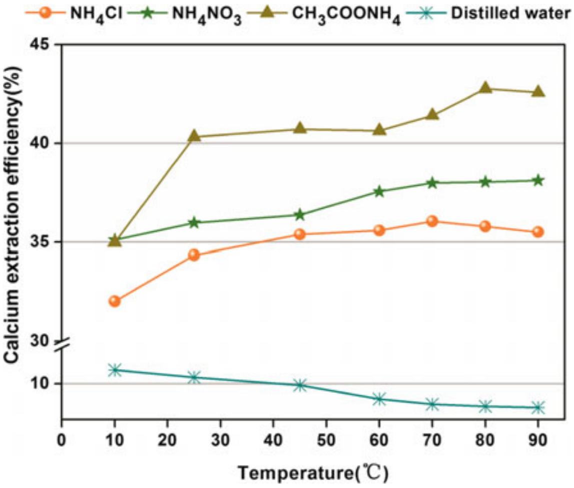

Fig. 9.4 Influence of temperature and the type of extraction solution on Ca^{2+} extraction efficiency (ammonium salt concentration: 1 mol/L, solid-to-liquid ratio: 50 g/L, mixing rate: 500 rpm, time: 60 min). Reprinted with permission from [62], copyright 2013 American Chemical Society

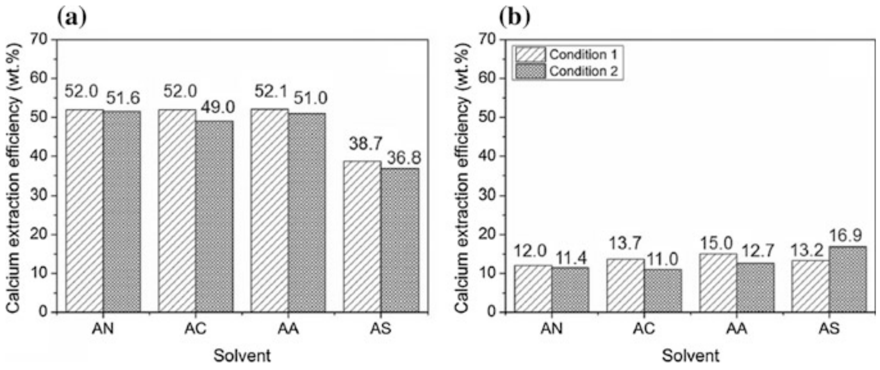

Fig. 9.5 Calcium extraction efficiency of (**a**) granulated slag, and **b** air-cooled slag when different ammonium salts are used. Solvent concentration (mol/L), reaction temperature (°C), reaction time (min), and solid-to-liquid ratio are 2 mol/L, 30 °C, 60 min, and 10 for the condition 9.1 and 1 mol/L, 30 °C, 30 min, and 10 for the condition 9.2, respectively. Further detail on the condition 9.1 and 9.2 can be found in Table 9.2. Abbreviations for the solvents: AN: NH_4NO_3, AC: NH_4Cl, AA: CH_3COONH_4, and AS: $(NH_4)_2SO_4$. Reprinted with permission from [71], copyright 2016 Elsevier

Sanni et al. in which acids that form soluble salts with calcium such as CH_3COOH, HNO_3, and CH_3CH_2COOH possess the highest extraction efficiency (85–100%) followed by ammonium salts (NH_4NO_3, NH_4Cl, and CH_3COONH_4) with the efficiency ranging from 50 to 80%, while $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, and $NH_4H_2PO_4$ showed a poor extraction [67]. For cement waste, 1 mol/L solution of NH_4NO_3 and CH_3COONH_4 has the extraction efficiency of ~69% that is better than NH_4Cl and $(NH_4)SO_4$ with only 32 and 4%, respectively [60]. Generally, ammonium salts of NH_4Cl, NH_4NO_3, and CH_3COONH_4 were recognized as the best solution for extracting calcium from solid waste thanks to their high extraction efficiency and NH_3 recyclability.

Variety of agents have proved to be effective for calcium extraction, however, to apply in the Solvay process, and only NH_4Cl is a suitable candidate because it is the main component in the filtrate that will react with CaO for NH_3 recovery. In a typical Solvay process, NH_4Cl concentration in the filtrate is around 3.6–4.9 mol/L, but it could not directly apply for calcium extraction because of the presence of HCO_3^+ in the filtrate that reacts with Ca^{2+} to form insoluble $CaCO_3$ [54, 55, 63]. The $CaCO_3$ may form the less soluble carbonated shell around slag particles that prevents the dissolution of Ca^{2+} ions [7, 9, 58]. Thermal treatment can decompose the HCO_3^+ to release CO_2, but also remove NH_4^+ as NH_3 in the gas phase; this causes the decrease in the NH_4Cl concentration. The reduction in NH_4Cl concentration may influence the extraction capacity of the filtrate. Recent researches have indicated that NH_4Cl concentration plays a very important role in the calcium extraction [60–63, 65, 67, 70, 72]. Table 9.2 shows the calcium extraction from various solid wastes using NH_4Cl in the literatures. In this table, numerous parameters including NH_4Cl concentration, solid-to-liquid ratio, particle size,

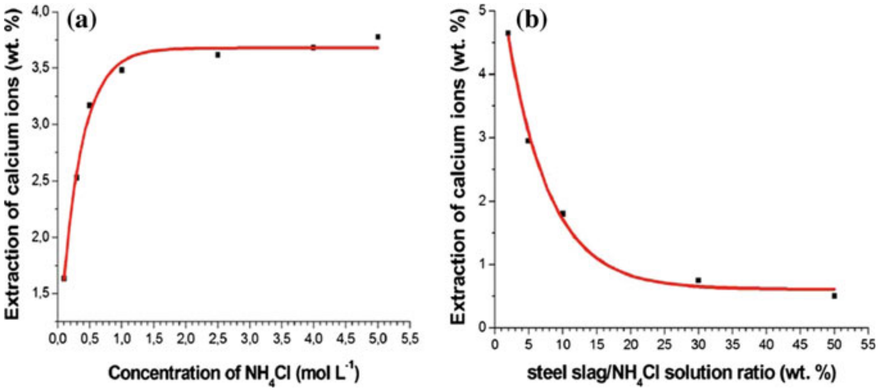

Fig. 9.6 Effect of NH_4Cl concentration (**a**) and solid-to-liquid ratio (**b**) on the calcium extraction efficiency. Reprinted with permission from [63], Springer Nature publisher

temperature, and extraction time and their influence on the extraction efficiency, calcium selectivity, and calcium concentration in leachate are introduced. A good agreement among published works is that the extraction efficiency improved with the increase in NH_4Cl concentration; however, its concentration above 1 mol/L would be preferable. A rapid increase in the extraction efficiency was observed at the NH_4Cl ranging from 0 to 1 mol/L. Above 1 mol/L, the increase is not significant (Fig. 9.6a). The decrease in NH_4^+ concentration due to thermal treatment of the filtrate has been verified by de Carvalho Pinto et al. [54, 63]. By boiling the filtrate containing NH_4Cl 4.2 mol/L for 30 min, they can recover 16.7% NH_3 which causes the NH_4Cl concentration decrease to 3.5 mol/L [63]. In another study, the reduction on the NH_4Cl concentration from 3.6 to 2.8 mol/L was found by boiling the filtrate [54]. These suggest that a fraction of NH_3 can be recovered by thermal treatment, but it does not influence on the following extraction activity because the NH_4Cl concentration is remained in preferable range. By boiling the filtrate for 30 min prior to the addition of slag, de Carvalho Pinto et al. can enhance the calcium extracted into filtrate solution from 192 to 1520 mg/L [63] confirming the effectiveness of the thermal treatment.

9.2.3 *Type of Solid Waste*

Types of solid waste and the crystalline phases existing in solid waste are the most influent factors that decide the success of extraction using NH_4Cl. CaO content and its compounds in waste vary with the waste sources and directly affect the extraction efficiency. The calcium extraction from different wastes under various conditions is provided in Table 9.2. In general, BOF slag has a high extraction efficiency. Most of BOF slag samples show the extraction efficiency above 50 wt%, while only few samples of desulphurization lag and BF slag attain 50 wt% calcium extraction. Investigating on the calcium extraction from different slags, Sanni et al. recognized that free lime in BOF and desulphurization slags contributes to high extraction with about 70 and 50%, respectively, while all calcium in BF and ladle slags exists in silicate form that explains for a poor extraction with a efficiency below 15% [67]. According to Lee et al., air-cooled slag contains higher CaO content (32.9 wt%) compared to granular slag (22.5 wt%) but the extraction efficiency is much lower, 11–17 wt% compared to 49–52 wt%, respectively [71]. The differences are attributed to the crystallinity of these two slags caused by collecting methods. Granular slag is generated by rapid cooling using water produced about 50% amorphous phase and 50% crystalline phases including mainly wustite (15.23%), $Ca_2Fe_2O_5$ (13.32%), beta-Ca_2SiO_4 (13.10%), and magnetite (10.96%), whereas air-cooled slag is obtained by slow cooling under an ambient atmosphere containing mostly crystalline phases, which account for the poor extraction from this slag. To demonstrate the high extraction contributed by free CaO in solid waste, the comparison between MgO + CaO mixture and fly ashes was made by Hosseini et al. [69]. Two fly ashes collected from electrostatic precipitator of coal power plant that are Hazelwood fly ash (32.4 wt% CaO) containing mainly $CaSO_4$, CaO, calcium ferrite ($CaFe_2O_4$), and silicate and Yallourn fly ash (9.4 wt% CaO) containing mostly magnesia ferrite, quartz, and amorphous CaO were tested. As shown in Fig. 9.7, above 80 wt% of calcium in MgO + CaO mixture can be extracted, while only 32 and 37 wt% of calcium was leached from Hazelwood and Yallourn fly ash in the first cycle using NH_4Cl, respectively.

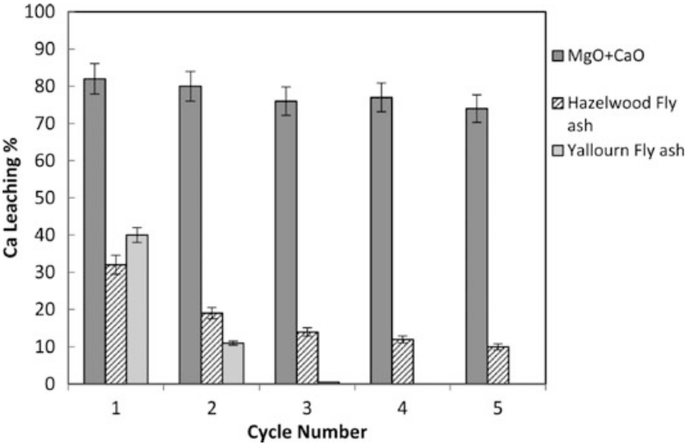

Fig. 9.7 Calcium extraction efficiency for five leaching-carbonation cycles at optimum conditions (80 °C and 30 min) using MgO + CaO mixture, Hazelwood and Yallourn fly ash. Reprinted with permission of [69], copyright 2014 American Chemical Society

9.2.4 Particle Size and Microwave Treatment

Particle size distribution is another crucial characteristic that influences on the calcium extraction. Data on the effect of size on the calcium extraction can be found in Table 9.2. Investigating the calcium leaching from various slags with size <150 and 150–500 µm by Hall et al. indicated an impressive increase in extraction efficiency by size reduction with a maximum 50% higher in small size samples [68]. By reducing the size of slag from 250–500 to 0–125 µm, Said et al. can improve almost 50% of the extraction efficiency of a steel converter slag which contains the majority of $CaSiO_4$, $Ca_2Fe_2O_5$, $Fe_{0.925}O$, and Fe_3O_4 without free CaO (Fig. 9.8) [61]. Further extraction improvement can be executed by the application of microwave [72], ball milling, and heat treatment [70]. Tong et al. found that the calcium leaching can be improved about 10% by the combination of NH_4Cl extracting agent with microwave treatment on electric arc furnace slag [72]. The research indicated that Ca_2SiO_3, Ca_2SiO_4, and Ca_3SiO_5 can be dissolved by NH_4Cl solution generating leaching Ca^{2+} and SiO_2. Lee et al. showed a calcium extraction improvement by combining NH_4Cl extracting agent with ball milling [70]. The improvement is attributed to the particle size reduction that decreased from <10 to 1–5 µm by ball milling.

9.2.5 Solid-to-Liquid Ratio

Solid-to-liquid ratio (g/L) for extraction is another key parameter. Most of studies agree that lower solid-to-liquid ratio offers better extraction efficiency (Table 9.2) [61–63, 65]. The relation was clarified by de Carvalho Pinto et al. as shown in Fig. 9.6b; the extraction efficiency drastically declines as the slag concentration increases [63]. This is in congruence with the observation by Said et al. where the

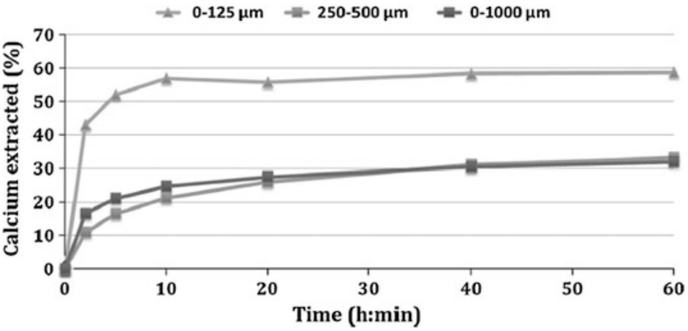

Fig. 9.8 Effect of particle size on calcium extraction from steel converter slag in NH_4Cl solution 1 mol/L (solid-to-liquid ratio: 20 g/l). Reprinted with permission from [61], copyright 2012 Elsevier

calcium extraction from BOF slag by ammonium salts reached a maximum (73%) at the lowest solid concentration (5 g/L) and the lowest extraction (6%) by the highest solid concentration (100 g/L) [61]. The analogous effect was also observed when calcium was extracted from fly ash [62]. The reason for this reduction in the extraction efficiency is most likely due to the high viscosity causing the low mobility of solution that prevents proper mixing and consequently reducing calcium extraction. It is also believed that the higher buffer effect of the NH_4^+/NH_3 couple is attained at pH = 9.25. At this pH, NH_4^+ and NH_3 concentrations are equal and their interconversion occurs that prevents the further Ca^{2+} extraction [63]. In contrast to the extraction efficiency, the Ca^+ concentration in the liquid increased a long with the increase in solid-to-liquid ratio; this relation is illustrated by He et al. in Fig. 9.9. In a practical application, an optimum solid-to-liquid ratio must be determined to balance the extraction efficiency, Ca^{2+} concentration, and water consumption for efficient production.

9.2.6 Extraction Selectivity

Since solid waste has a diverse chemical composition, the extraction may simultaneously leach various metal ions into solution. Selectivity of a metal is a fraction of its concentration to total metal concentration in the leachate. A good solid waste should generate high selectivity for Ca over others. Impurity leached into the filtrate does not impact on the quality of resulting $NaHCO_3$ or Na_2CO_3 product, but it may affect the NH_3 recovery efficiency and relate to the strategy for later waste management. High selectivity of unreactive species toward NH_4Cl or metal ions that form stable complexes with NH_3 will result in low NH_3 recovery. In general, ammonium salt solution shows a good selectivity for calcium against undesired

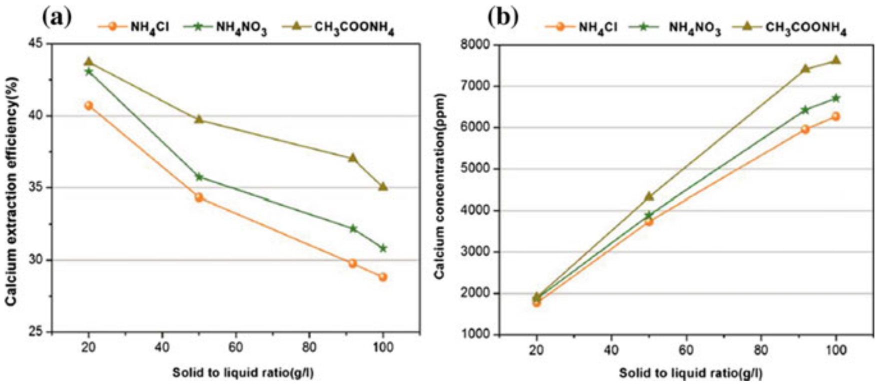

Fig. 9.9 Effect of solid-to-liquid ratio on calcium extraction efficiency (**a**) and Ca^{2+} concentration in leachate (**b**) at 25 °C for 60 min with the NH_4Cl concentration of 1 mol/L and mixing rate 500 rpm. Reprinted with permission from [62], copyright 2013 American Chemical Society

species (Table 9.2) [54, 60, 65, 68, 70]. Relatively small quantity of undesired metals, e.g., Mn, Fe, Ni, Al, Si are detected in the leachate. A study by Jo et al. on the calcium extraction from cement waste using ammonium salts showed that most of ammonium salts have a good selectivity for calcium, which is greater at higher salt concentration, reached above 98% at the salt concentration of 1.0 mol/L (Fig. 9.10) [60]. Other studies on steel slag by Hall et al. and Lee et al. show that the calcium extraction can attain more than 95% selectivity [68, 70]. Sun et al. found only 75.7% Ca selectivity when extracting it with NH_4Cl 2 mol/L from oxy furnace steel slag; however, total selectivity for two alkaline metals of Ca and Mg reached 96% [64]. Since magnesium could contribute well for NH_3 recovery in the Solvay process, the high selectivity for these two elements is acceptable.

9.3 Modified Solvay Process with Amines and Reject Brine Utilization

Finding a way to prevent or mitigate sea disposal of concentrated brine wastes has huge environmental benefits. The idea to combine CO_2 utilization with waste brine treatment derives from the unique opportunity provided by the availability of vast amounts of brine wastes from desalination plant. Due to its ability to treat two environmental wastes, CO_2 utilization with brine is a promising technology for solving the problem of desalination brine wastes [36]. Over the years, different ideas have been proposed to accomplish this kind of process, most of which are based on the Solvay process first developed by Ernst Solvay in 1861 [77]. Recently, methods involving the use of CaO and layered double hydroxides have also been

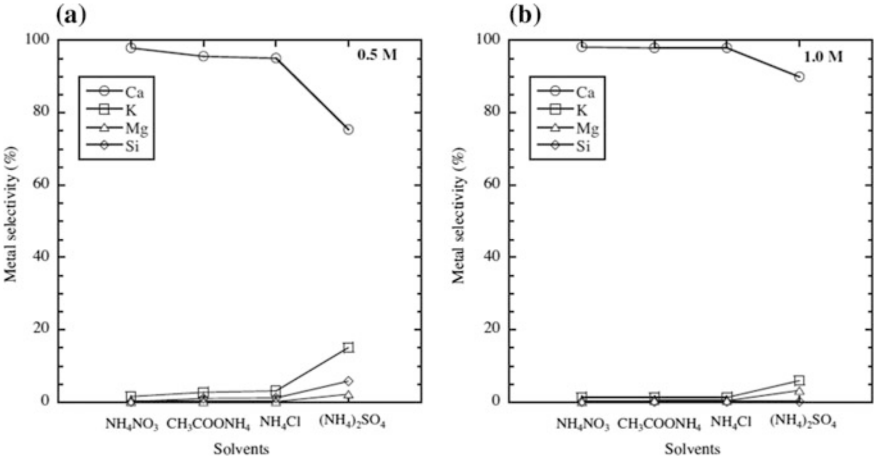

Fig. 9.10 Selectivity of major metal ions in different ammonium salts at the concentration of **a** 0.5 mol/L and **b** 1.0 mol/L. Reprinted with permission from [60], copyright 2014 Elsevier

shown to give promising results with regard to this process. The goal of the following sections is to provide a more detailed description of these processes and their performances with respect CO_2 utilization and reject brine treatment.

The conventional Solvay process involves reacting CO_2 with ammonia/brine solution to produce $NaHCO_3$ and ammonium chloride (Fig. 9.1). The $NaHCO_3$ is precipitated and separated, while the ammonium chloride solution (filtrate) is reacted with lime to produce ammonia, which is recycled, and $CaCl_2$ as a waste product. While this process scheme can be applied directly for CO_2 utilization and brine treatment as demonstrated by El-Naas [78, 79], it is not very appropriate for the processes where sodium removal is the main goal due to its low sodium conversion. This, in addition to the volatility of ammonia at the temperatures at which CO_2 capture processes operate, poses a problem for the application of Solvay process for CO_2 utilization and brine treatment [80, 81]. Also, Solvay process applies CaO for the regeneration of ammonia. This is counterproductive for the CO_2 capture process due to the fact the production of CaO is CO_2 intensive. For every two moles of CO_2 from power plants captured, one mole of CO_2 from calcination of limestone is released [82].

Modifications of the Solvay process for CO_2 capture and utilization processes have been mostly focused on the replacement of volatile ammonia with alcohol amines which are stable at the temperature range of CO_2 capture processes. Alcohol amines also tend to give better performance results (Na conversion/removal) than ammonia with dilute CO_2 streams such as flues gas as shown in Table 9.3.

Huang et al. used a sterically hindered alcohol amine and methyl aminoethanol (MAE), in the place of ammonia, and reported a CO_2 capacity of 0.9 mol/mol MAE and a $NaHCO_3$ yield of 14.3 g $NaHCO_3$/mole MAE ($\sim$17.14 g/kg solution) at MAE and NaCl concentration of 1.2 and 3.4 M, respectively [82]. In similar vein, Dindi et al. investigated the use of different classes of alcohol amines as replacement for ammonia and found that secondary or sterically hindered amines such as 2-amino, 2-propanol-amine gave the best performance [83, 86]. The reaction of amines with CO_2 could follow either a carbamate or the bicarbonate route depending on the class of the amine. Primary and secondary amines react with CO_2 to form carbamates following the zwitterion mechanism Eq. 9.16, while tertiary and sterically hindered amines react with CO_2 to form bicarbonates according to Eq. 9.17 [87].

Table 9.3 Na conversion in brine treatment with the Solvay process

Alkali	NaCl conc.	Alkali/NaCl	Na conversion (%)	References
AMP	0.6	0.57	60	[83]
AMP	1.8	1.87	85	[83]
NH3	Actual brine	2	42	[79]
NH3	4.5	1.74	82.2	[84]
NH3	Actual brine	2	75.8	[85]

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$$2R_1R_2NH + CO_{2(aq)} \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (9.16)$$

$$R_1R_2R_3N + CO_{2(aq)} + H_2O \leftrightarrow R_1R_2R_3NH^+ \cdot HCO_3^- \quad (9.17)$$

$$R_1R_2NCOO^- + R_1R_2NH_2^+ + H_2O \rightarrow R_1R_2NH_2^+ \cdot HCO_3^- + R_1R_2NH \quad (9.18)$$

$$R_1R_2NH_2^+ \cdot HCO_3^- + NaCl \rightarrow NaHCO_3 + R_1R_2NH_2^+ \cdot Cl^- \quad (9.19)$$

$$R_1R_2R_3NH^+ \cdot HCO_3^- + NaCl \rightarrow NaHCO_3 + R_1R_2R_3NH^+ \cdot Cl^- \quad (9.20)$$

Primary or secondary amines react with CO_2 to form carbamate (Eq. 9.16) accordingly, two molecules of amine are needed to capture one mole of CO_2. For this reason, the CO_2 absorption capacity of such amines cannot exceed 0.5 mol CO_2 per mole of amine theoretically. Meanwhile, the tertiary or sterically hindered amines which follow the bicarbonate pathway have the potential of reaching a capacity of 1 mol CO_2 per mol amine as shown in Eq. 9.17, although they may be prevented from reaching this capacity due to kinetic limitations of the bicarbonate pathway. Sometimes, the capacity of primary or secondary amines exceeds the theoretical limit due to the carbamate hydrolysis (Eq. 9.18) which releases an amine to react with more CO_2, thereby increasing the CO_2 absorption capacity beyond the theoretical limit. This effect is even more pronounced in the presence of brine.

The CO_2 absorption capacity of amines increases as a result of precipitation of $NaHCO_3$. Na in the brine reacts with HCO_3^- generated in Eq. 9.17 (tertiary amines) and Eq. 9.18 (primary/secondary amines), thereby shifting the equilibrium to the right and causing more CO_2 to be absorbed and more $NaHCO_3$ to be precipitated in Eqs. 9.19 and 9.20 [88]. The process continues until the solution pH reduces below 9 in which case $NaHCO_3$ cannot be precipitated and equilibrium is reached or until all the amine is consumed to form an amine chloride. This explains why amines give better CO_2 absorption results in the presence of NaCl [82, 83].

Although amines give better results during the carbonation stage, a major drawback of the use of amines in the Solvay process is the difficulty of regenerating the free amine from the amine chloride by-product produced during the carbonation step. Although Huang proposed a method for regenerating ammonia from NH_4Cl using activated carbon as a means of avoiding the use of CaO for ammonia regeneration, no method was proposed for regenerating the MAE chloride [82]. The activated carbon was used to remove HCl from a solution of NH_4Cl with the liberation of ammonia according to Eq. 9.21.

$$NH_4Cl + AC \leftrightarrow NH_3 + AC \cdot HCl \quad (9.21)$$

The HCl-loaded activated carbon was then regenerated with water and used repeatedly to produce about 0.0012 mol HCl per cycle. In addition, the ultra-high lime with aluminum (UHLA) method was proposed by Dindi et al. to recover AMP from the AMP-HCl formed during the carbonation step. However, the efficiency of this process was limited by increasing amine concentration and by the presence CO_2 in the solution [83]. No other method for regenerating amines from amine chlorides has been reported in the literature. Hence, this constitutes a major obstacle in the application of the amine-based Solvay process for brine treatment and CO_2 capture and utilization

Recently, El-Naas proposed a process in which the CaO was used to replace NH_3 in the Solvay process. The CaO is dispersed in brine to increase its pH and then applied for CO_2 capture. The higher pH facilitates absorption of CO_2 into the brine and subsequently the precipitation of $NaHCO_3$. The system was effective for CO_2 capture and Na removal with an optimum temperature of 10 °C and CaO concentration of 20 g/L. Beyond this concentration, Na removal was reduced due to competitive formation of $CaCO_3$. The modified process had a maximum CO_2 capture capacity of 1.44 mol/L and sodium removal efficiency of 35%, while the conventional process had a maximum CO_2 capacity of 1.14 mol/L and a 29% sodium removal efficiency. The modified process is also potentially less costly than the conventional process due to the elimination of energy-intensive ammonia regeneration, fewer unit operations, and lower costs of CaO relative to the cost of ammonia [89].

9.4 Layered Double Hydroxide Process

Due to the shortcomings of the modified Solvay processes for the simultaneous treatment of desalination brines and CO_2 utilization, a new, layered double hydroxide (LDH)-based process has been recently proposed which has the potential to perform better than modified Solvay processes [90]. LDHs, also known as hydrotalcite, are clay materials consisting of alternating layers of mixed metal hydroxides and anion-bearing interlayers, similar to structure of the hydrotalcite mineral as shown in Fig. 9.11 [46]. The mixed metal hydroxides layer are made up of positively charged di or trivalent cations, while the anion layer contains negatively charged balancing anions which combine to give the formula $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]_x + (A^-)\ x/n \cdot mH_2O$. M^{2+} represents divalent cations like Mg, Fe, Co, Cu, Ni, or Zn, M^{3+} represents trivalent cations like Al, Cr, Ga, Mn or Fe, and A^- is the interlayer anion such as CO_3^{-2}, HCO_3^-, SO_4^{-2}, Cl^-, or OH^-. The value of x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$ and is generally in the range 0.2–0.33.

Carbonate LDHs, in which a CO_3^{2-} ion exists within the layers, are the most common LDH forms due to the strong affinity of the LDHs for the CO_3^{2-} ion. While LDHs can exchange their interlayer ions with other ions present in a solution, this is not always possible depending on the relative affinity of the anion to the LDH. However, when calcined, they release the interlayer anion and OH groups to produce mixed metal oxides, which can reconvert to the original LDH structure when being dispersed in an aqueous solution of the appropriate anion, making them

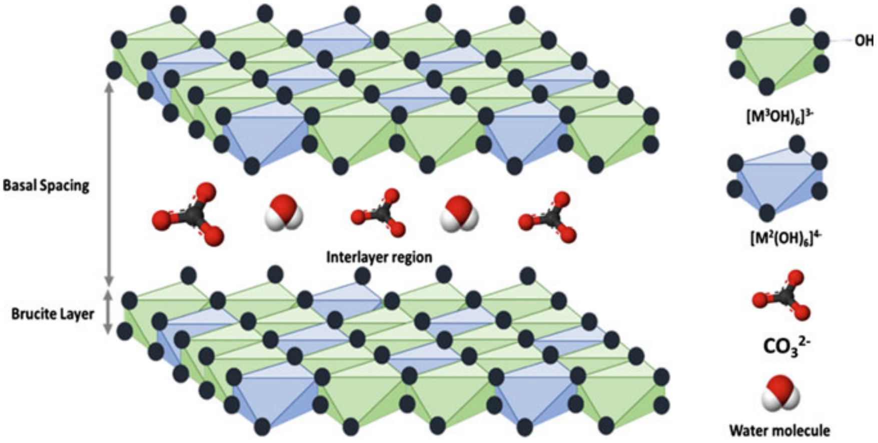

Fig. 9.11 Hydrotalcite structure. Reprinted with permission from [90], copyright 2018 Elsevier

excellent materials for the sorption anions. This property of LDHs has been harnessed for the removal of different kinds of contaminants from wastewater like iodide [91], silicate [92], chlorides [93], heavy metals [94], and rare earth elements [95].

In the case of reject brine treatment, the objective is to reduce chloride and sodium concentrations to levels that are safe for disposal. LDHs can be used to remove chloride from brine as shown in several studies by Kameda and co-workers [93, 96, 97]. Given that the removal of chlorides from brines by Mg–Al–O also results in the increase in OH^- ions in the solution leading to a rise in solution pH, this increased alkalinity can then be employed for CO_2 absorption and precipitation of $NaHCO_3$ which ultimately leads to sodium removal from the brine. In this way, CO_2 capture/utilization and reject brine treatment are combined in one single process as further described in the following section.

9.4.1 Process Description

The process consists of three major stages which are the chloride removal, carbonation, and regeneration stages as shown in Fig. 9.12. In the chloride removal stage, Mg–Al mixed metal oxide, derived from Mg–Al hydrotalcite, is dispersed in the brine to remove the chloride ions via an ion exchange process. Chloride moves from the liquid phase to the solid phase, while the solution is enriched in OH^- ions due to the solvation of the mixed metal oxide. When the slurry is separated, the brine solution becomes more alkaline while mixed metal oxide is transformed to a chloride-form hydrotalcite, Cl^-–HT, according to Eq. 9.22. The resulting alkaline brine solution, a mixture of NaOH and NaCl, is then sent to the carbonation stage

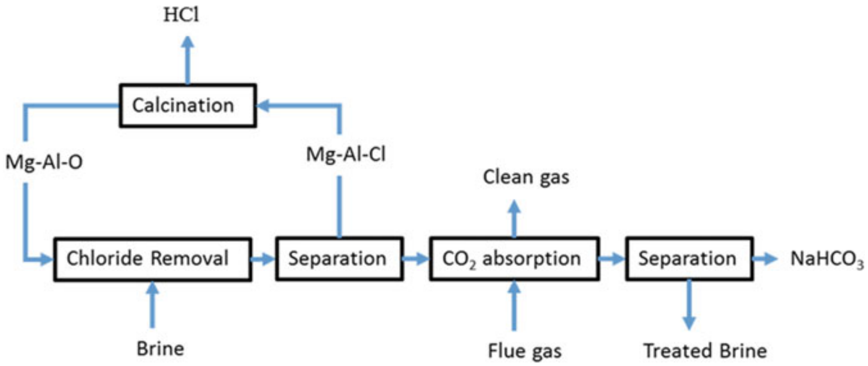

Fig. 9.12 Schematic diagram of the proposed process

for the precipitation of $NaHCO_3$. Depending on the initial concentration of the brine and the extent of chloride removal, a concentration step may be required to bring this solution to a concentration high enough to precipitate NaHCO3.

In the carbonation stage, the CO_2 captured from flue gas reacts with the alkaline solution to precipitate $NaHCO_3$, removing the Na^+ from the brine in the process as described in Eqs. 9.23–9.28. The liquid effluent from this stage has reduced salinity and can therefore be disposed as treated brine, while the $NaHCO_3$ can be dried and packaged for sale. To ensure efficiency of the process, the spent Cl–HT must be reused. This is done thermally in the regeneration stage.

Chloride removal step:

$$Mg_{0.8}Al_{0.2}O_{1.10} + 0.2NaCl + 1.1H_2O \rightarrow Mg_{0.8}Al_{0.2}(OH)_2Cl_{0.2} + 0.2NaOH \quad (9.22)$$

Carbonation step:

$$CO_{2(g)} \leftrightarrow CO_2(aq) \quad (9.23)$$

$$CO_{2(aq)} + OH^- \leftrightarrow HCO_3^-(aq) \quad (9.24)$$

$$HCO_3^- + OH^- \leftrightarrow H_2O(l) + CO_3^{2-}(aq) \quad (9.25)$$

At high pH,

$$Na^+(aq) + CO_3^{2-}(aq) \rightarrow Na_2CO_3(aq) \quad (9.26)$$

At low pH when OH^- has been depleted by reaction 9.24,

$$\mathrm{Na}^{+}(\mathrm{aq}) + \mathrm{HCO}_3^{-}(\mathrm{aq}) \rightarrow \mathrm{NaHCO}_3(\mathrm{aq}) \tag{9.27}$$

$$\mathrm{NaHCO}_3(\mathrm{aq}) \rightarrow \mathrm{NaHCO}_3(s) \downarrow \tag{9.28}$$

During the regeneration, the Cl–HT is calcined at above 450 °C to produce the original Mg–Al mixed metal oxide (Mg–Al–O) by releasing Cl, OH, and CO_2 present in the Cl–HT structure. The mixed metal oxide is then returned to the chloride removal stage and the process loop continues, while the released chloride, on the other hand, provides opportunity for the production of Cl-based products which brings additional value to the process. Overall, the process results in a more extensive treatment of the brine because of the removal of both Na and Cl ions while creating more potential for revenue through the sale of CO_2- and Cl^--based chemical products.

9.4.2 Process Evaluation and Performance

A detailed assessment of the proposed process has been presented in [90]. The process was evaluated based on its ability to accomplish the two process objectives of brine treatment and CO_2 utilization. The performance indices for the evaluation of brine treatment were expressed as overall chloride and sodium removal efficiencies, and for CO_2 capture and utilization, as CO_2 absorption capacity and yield of $NaHCO_3$, respectively. Firstly, hydrotalcite and mixed metal oxide were synthesized; thereafter, cyclic tests were carried out to determine the performance indices. Conversion between hydrotalcite and the mixed metal oxide in a process cycle can be demonstrated by XRD investigation (Fig. 9.13).

The Mg–Al–O was found to be effective for the removal chloride from the brine across the six cycles tested as shown in Fig. 9.14. Chloride removal efficiencies

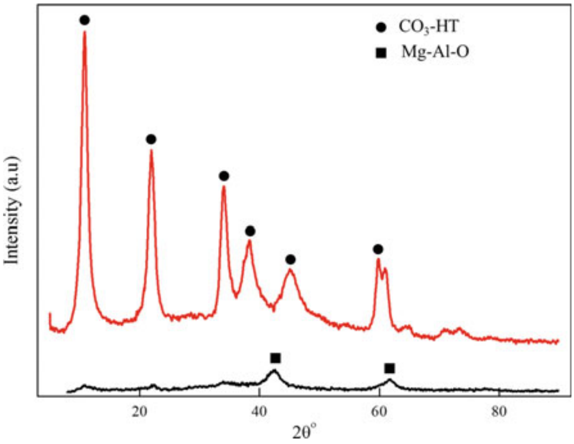

Fig. 9.13 XRD spectra and of the synthesized CO_3–HT and Mg–Al–O. Reprinted with permission from [90], copyright 2018 Elsevier

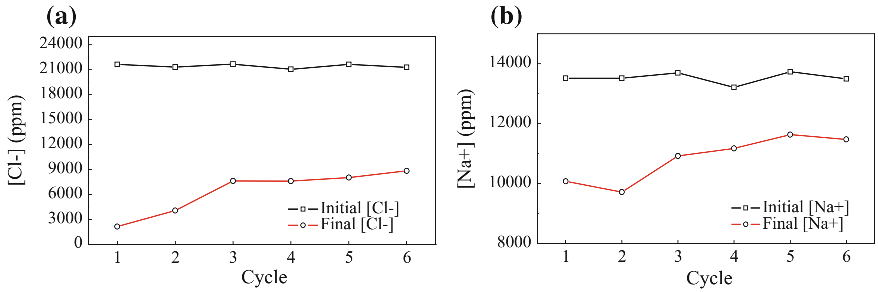

Fig. 9.14 Initial and final concentrations of Cl^- (**a**) and Na^+ (**b**) in brine. Reprinted with permission from [90], copyright 2018 Elsevier

varied from 90 to 58%, from the first cycle to the sixth cycle, with an average of 70% across six cycles. The extent of sodium removal from the brine, due to precipitation of $NaHCO_3$, varied from 26 to 17% from the first cycle to the sixth cycle, with an average of 20% across six cycles, while an average $NaHCO_3$ yield of 44 g/kg carbonated solution was also obtained over six cycles of the process. The characterization of the produced $NaHCO_3$ confirmed that a pure $NaHCO_3$ product can be obtained from the process as presented in Fig. 9.15. Based on these results,

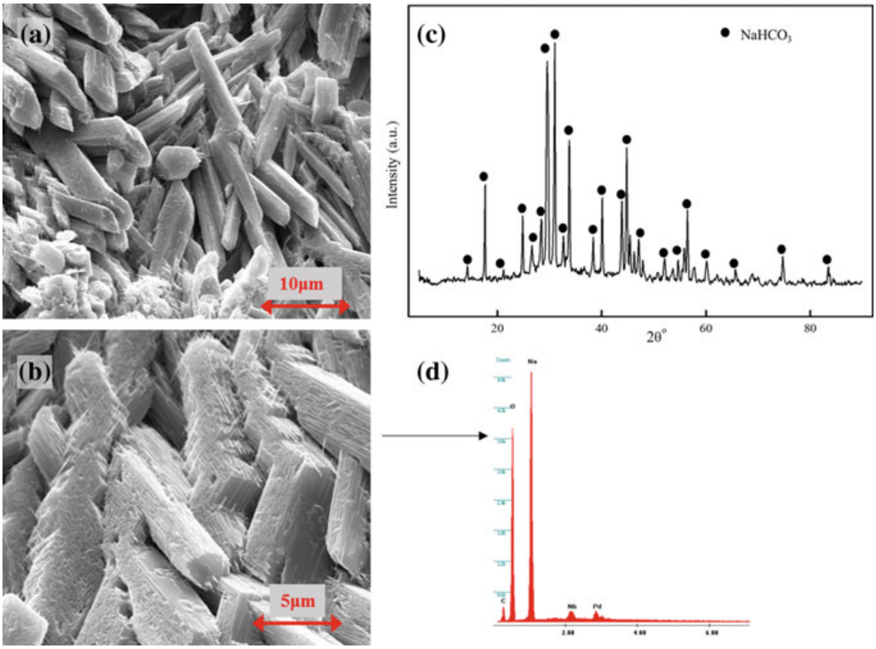

Fig. 9.15 SEM images at different magnifications (**a**, **b**), XRD spectra (**c**), and EDS spectra (**d**) of precipitated $NaHCO_3$. Reprinted with permission from [90], copyright 2018 Elsevier

the proposed process was found to be feasible for the simultaneous treatment of the reject brine and CO_2 utilization.

The proposed process concept is an important contribution to research efforts on brine treatment and CO_2 utilization. It promises to be more effective than earlier processes because it is able to remove both Na and Cl ions from brine, whereas other proposed processes remove only Na ions. Also, in many regions where reject brines are generated in large volumes, desalination plants are usually integrated with power plants; hence, there will be little logistical constraint to the implementation of this process and the potential cost savings from the combined treatment of two industrial wastes as well as the revenue from the sale of two chemical products might justify the investment in this technology. Nonetheless, a detailed techno-economic study is required to determine the economic viability of the proposed process concept.

9.5 Conclusion

Current progress has been demonstrated promising outcomes from solid waste, reject brine, and CO_2 utilization for greener soda ash production. No doubt that the waste and CO_2 utilization in an integrated process has huge potential on the mitigation of CO_2 emission and waste management. Instead of burning $CaCO_3$ for CO_2 and CaO in the conventional Solvay process, those agents can be extracted from the waste streams of power plant or steel plant in a modified Solvay process. The process can further integrate with reject brine treatment from desalination plant to create process that completely consumes wastes as raw materials. This process is suitable to combine with other industries such as power plant or steel plant so that it can at the same exploit both waste material and waste heat for a marketable product production. The revenue received may be partially offset the cost of waste treatment and CO_2 capture that will encourage the effort toward waste and CO_2 emission mitigation.

The calcium extraction from solid waste is influenced by multiple parameters including CaO content and its crystalline phase, particle size distribution, extracting agent concentration (NH_4Cl), and solid-to-liquid ratio. CaO content, particularly free CaO, and the size of solid waste has the most decisive role for an efficient extraction. While the NH_4Cl concentration in the filtrate of the Solvay process is usually in the range of optimum concentration for extraction (>1 mol/L), the solid-to-liquid ratio becomes a very important parameter for balancing Ca^{2+} concentration in the filtrate and extraction efficiency. Recent initiative reveals that steel slag can partly replace CaO in the Solvay process to recover 40% NH_3 [63]; however, it could be significantly improved with a more suitable solid waste (high CaO content with low crystallinity and small particle size).

The modified Solvay process by replacing NH_3 with alcohol amine may render high soda ash recovery, but it faces the critical problem of amine recyclability. The layered double hydroxide process using Al_2O_3–MgO mixture to adsorb Cl^- ions generating NaOH solution that can capture CO_2 for soda ash production is novel and promising route, but it is still in the research stage.

To accelerate the waste and CO_2 utilization in the soda ash production, several challenges must be solved in future research, i.e., (1) to recognize the waste sources that are most suitable for NH_4Cl extraction and NH_3 recovery, (2) to find calcium extraction assistant method to effectively boost the extraction, (3) to revise the extractor, e.g., using multiple stage or combine mixing with microwave, (4) to look for an efficient way to recycle alcohol amine in modified Solvay process, (5) to prevent the formation of spinel phase during calcination of the layered double hydroxide for the long recyclability of Al_2O_3–MgO system, and finally, an economic evaluation for the proposed process is necessary.

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