Low-energy sodium hydroxide recovery for CO_2 capture from atmospheric air—Thermodynamic analysis

Maryam Mahmoudkhani *, David W. Keith

Energy and Environmental System Group, Institute for Sustainable Energy, Environment, Economy, University of Calgary, T2N 1N4 Calgary, AB, Canada

ARTICLE INFO

ABSTRACT

To reduce the risks of climate change, atmospheric concentrations of greenhouse gases must be lowered. Direct capture of CO_2 from ambient air, "air capture", might be one of the few methods capable of systematically managing dispersed emissions. The most commonly proposed method for air capture is a wet scrubbing technique which absorbs CO_2 in an alkaline absorbent, i.e. sodium hydroxide producing an aqueous solution of sodium hydroxide and sodium carbonate. In most of the previous works it was assumed that the absorbent would be regenerated and CO_2 liberated from the alkaline carbonate solution using a lime and calcium carbonate causticization cycle.

We describe a novel technique for recovering sodium hydroxide from an aqueous alkaline solution of sodium carbonate and present an end-to-end energy and exergy analysis. In the first step of the recovery process, anhydrous sodium carbonate is separated from the concentrated sodium hydroxide solution using a two-step precipitation and crystallization process. The anhydrous sodium carbonate is then causticized using sodium tri-titanate. The titanate direct causticization process has been of interest for the pulp and paper industry and has been tested at lab- and pilot-scale. In the causticization process, sodium hydroxide is regenerated and carbon dioxide is liberated as a pure stream, which is compressed for use or disposal. The technique requires ∼50% less high-grade heat than conventional causticization and the maximum temperature required is reduced by at least 50 °C. This titanate cycle may allow a substantial reduction in the overall cost of direct air capture.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

To avoid dangerous climate change, the growth of atmospheric concentrations of greenhouse gases must be halted, and the concentration may have to be reduced. The concentration of carbon dioxide, the most critical greenhouse gas, has increased from 280 ppm in the pre-industrial age to more than 380 ppm now and is now increasing by more than 2 ppm per year driven by global CO_2 emissions that are now increasing at more than 3.3% per year (Canadell et al., 2007).

Carbon capture and storage (CCS) technologies target CO_2 removal from large fixed-point sources such as power plants. Stationary sources, however, emit approximately half of global CO_2 emissions. Direct capture of CO_2 from ambient air, "air capture", might be one of the few methods capable of systematically managing dispersed emissions. Therefore, while air capture is more expensive than capture from large point sources it remains important as it will primarily compete with emission reductions from dispersed sources such as transportation which can be very expensive to mitigate. The cost of air capture is uncertain and disputed.

1.1. Air capture

Carbon dioxide absorption from atmospheric air using alkaline solution has been explored for half a century (Spector and Dodge, 1946; Tepe and Dodge, 1943) and was used commercially as a pre-treatment before cryogenic air separation. Large-scale scrubbing of CO_2 from ambient air was first suggested by Lackner et al. (1999) in the late 1990s. In wet scrubbing techniques, CO_2 is absorbed into a solution of sodium hydroxide, NaOH, and is leaving behind an aqueous solution of sodium hydroxide and sodium carbonate, Na_2CO_3. For this process, the contactor, as the component of the system that provides the contact between CO_2 and sodium hydroxide, has thus far been a point of contention. Large convective towers (Lackner et al., 1999), and packed scrubbing towers (Baciocchi et al., 2006; Zeman, 2007) have been the most frequently suggested designs. A packed tower equipped with Sulzer Mellapak has been investigated by Baciocchi et al. (2006) to absorb CO_2 from air with an inlet concentration of 500 ppm to an

outlet concentration of 250 ppm using a 2 M NaOH solution. Zeman (2007) however, selected a chamber filled with packing material that provides sufficient surface area for 50% capture rate from air with inlet concentration of 380 ppm with 1 M sodium hydroxide solution.

An alternative strategy, suggested by Storaloff et al. (2008), is to generate a fine spray of the absorbing solution for providing large surface to the air flow through an open tower. This strategy could have the potential to operate with a small pressure drop in air and avoids the capital cost of packing material. Storaloff et al. (2008) studied the feasibility of a NaOH spray-based contactor by estimating the cost and energy requirement per unit CO_2 captured.
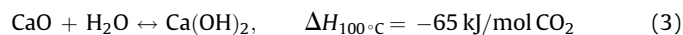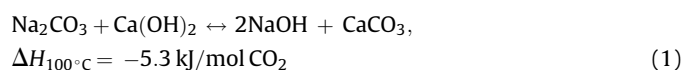
Storaloff et al. (2008) addressed the water loss, as a major concern in any aqueous air capture process and found that the water loss could be managed by adjusting of the NaOH concentration with temperature and humidity of air, i.e. the higher the concentration of sodium hydroxide, the lower is the water loss, e.g. using $\sim$7.2 M NaOH, at 15 °C and 65% relative humidity, water loss is eliminated.

All of these processes produce a sodium carbonate solution which must be converted back to sodium hydroxide solution and carbon dioxide gas in order to close the loop. It should be noted that the contaminants from air might be an issue in air capture and these are the issues that must still be worked out, however, for contaminants like SO_2, the risk might not be so high as the concentration of SO_2 in too low in atmosphere, ranging from 20 ppt to 1 ppb.

1.2. Caustic recovery for air capture

Conversion of sodium carbonate into sodium hydroxide, so-called "causticization" or "caustic recovery", is one of the oldest processes in industrial chemistry. In Kraft Pulping for paper making, wood is digested using sodium hydroxide to liberate cellulose and produce pulp. The remained solution, so-called "black liquor", consists of mainly other organic material originated from wood (e.g. lignin), along with sodium carbonate. To convert sodium carbonate and recover NaOH the conventional causticization using lime has been used for almost a century.

In conventional chemical recovery, Na_2CO_3 is causticized with lime to form NaOH and lime mud ($CaCO_3$), reaction (1). The conversion of Na_2CO_3 to NaOH and regeneration of lime is a series of liquid–solid reactions, reactions (1)–(3), i.e. all involved calcium compounds are solids. Prior works on air capture with NaOH has focused on this recovery cycle (Baciocchi et al., 2006; Storaloff et al., 2008; Zeman, 2007).
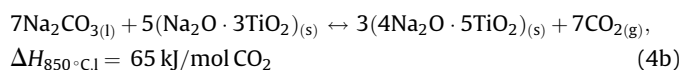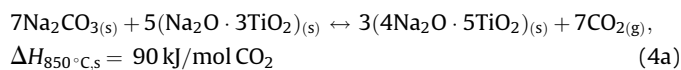
$$Na_2CO_3 + Ca(OH)_2 \leftrightarrow 2NaOH + CaCO_3,$$
$$\Delta H_{100\,°C} = -5.3 \text{ kJ/mol CO}_2 \tag{1}$$

$$CaCO_3 \leftrightarrow CaO + CO_2, \qquad \Delta H_{900\,°C} = 179 \text{ kJ/mol CO}_2 \tag{2}$$

$$CaO + H_2O \leftrightarrow Ca(OH)_2, \qquad \Delta H_{100\,°C} = -65 \text{ kJ/mol CO}_2 \tag{3}$$

The enthalpy of the reaction for absorption of CO_2 from air into sodium hydroxide solution for a nominal 1 M solution and at 298 K and a pressure of 1 bar is -109.4 kJ/mol CO_2 which implies that to go from sodium carbonate to sodium hydroxide the thermo-dynamic minimum required energy is 109.4 kJ/mol CO_2. Conventional causticization using lime requires a minimum of 179 kJ/mol CO_2 at standard T and P for reaction (2). Comparing the high temperature energy required to regenerate NaOH using conventional causticization with the thermodynamic minimum (109.4 kJ/mol CO_2) indicates that the required energy for conventional causticization is far beyond the thermodynamic minimum.

As a tool for air capture, conventional causticization has, several major drawbacks including:

- A comparatively large demand for high temperature heat compared to thermodynamic minimum to go from Na_2CO_3 to NaOH, i.e. 109.4 kJ/mol,
- a causticization efficiency limited to 80–90% in a typical Kraft recovery cycle and
- the alkalinity of the regenerated NaOH solution is limited by the causticization reaction to about 1 mol/L.

Methods introducing alternative causticization processes have been widely investigated in pulp and paper industry. Auto-causticization[1] (using borate), direct causticization[2] (using iron oxide or titanium dioxide) or partially auto- or direct causticization has been addressed in number of literature (Covey, 1982; Hoddenbagh et al., 2002; Kiiskilä, 1979a,b; Nagano et al., 1974; Maddern, 1986; Palm and Theliander, 1997; Sinquefield et al., 2004; Yusuf and Cameron, 2004; Zou, 1991). The titanate causticization process has been studied as an addition to or replacement for the calcination process used in Kraft paper making for a few decades. Titanate process has been tested in small-scale fluidized bed, laboratory conditions and pilot-scale but has not yet been applied to commercial scale. This research has been driven by the needs of the pulp industry; therefore it is focused on titanates reactions in the presence of black liquor. For this reason knowledge of the thermodynamics of the pure state reactions is not systematic.

Studies of the direct causticization of sodium carbonate with titanium dioxide have been carried out by Chen and van Heiningen (2006), Kiiskilä (1979a,b), Nohlgren (2002), Palm and Theliander (1997), Zeng and van Heiningen (1997) and Zou (1991). Depending on the feed molar ratio and temperature, the reaction between Na_2CO_3 and TiO_2 leads to various sodium titanates as products. It has been found that the main decarbonization reaction in the direct causticization based on TiO_2 is the reactions between Na_2CO_3 and $Na_2O\cdot3TiO_2$, i.e. reactions (4a) and (4b) (Kiiskilä, 1979a,b; Nohlgren, 2002; Zou, 1991).

$$7Na_2CO_{3(s)} + 5(Na_2O \cdot 3TiO_2)_{(s)} \leftrightarrow 3(4Na_2O \cdot 5TiO_2)_{(s)} + 7CO_{2(g)},$$
$$\Delta H_{850\,°C,s} = 90 \text{ kJ/mol CO}_2 \tag{4a}$$

$$Na_2CO_{3(s)} \rightarrow Na_2CO_{3(l)}, \qquad \Delta H_{851\,°C,s} = 25 \text{ kJ/mol CO}_2$$

$$7Na_2CO_{3(l)} + 5(Na_2O \cdot 3TiO_2)_{(s)} \leftrightarrow 3(4Na_2O \cdot 5TiO_2)_{(s)} + 7CO_{2(g)},$$
$$\Delta H_{850\,°C,l} = 65 \text{ kJ/mol CO}_2 \tag{4b}$$

Note that the overall reaction enthalpy is 90 kJ/mol CO_2, weather the reaction is performed below or above melting point of Na_2CO_3 (65 + 25 = 90 kJ/mol). Titanate process requires $\sim$50% less high temperature energy than lime process, however in both processes there are issues with moisture contents and heat recovery.

The sodium penta-titanate, $4Na_2O\cdot5TiO_2$, is then hydrolyzed, Eq. (5), in a leaching unit at a temperature of about 100 °C, to

---

[1] The term "auto-causticization" is used when the reaction product is water soluble and the decarbonizing agent is carried out through the entire pulping and recovery cycle as a caustic solution. In this process the caustic solution causticized itself during combustion or gasification.

[2] The term direct causticization is used when the reaction product is insoluble in a caustic solution and the decarbonizing agent is separated from the caustic solution and is not carried through the liquor cycle. In this process the decarbonizing agent is added and subsequently removed.
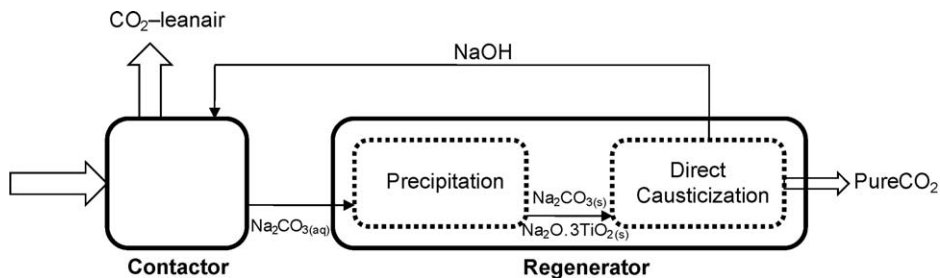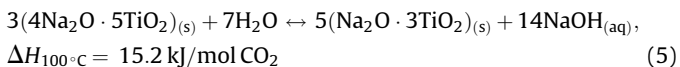
Fig. 1. Block diagram for chemical recovery using titanates in air capture.

sodium hydroxide and sodium tri-titanate, which the latter is recycled to the causticization unit.

$$3(4Na_2O \cdot 5TiO_2)_{(s)} + 7H_2O \leftrightarrow 5(Na_2O \cdot 3TiO_2)_{(s)} + 14NaOH_{(aq)},$$
$$\Delta H_{100\,^{\circ}C} = 15.2\,kJ/mol\,CO_2 \tag{5}$$

The conventional titanate process cannot be directly applied to air capture because it requires pure and dry anhydrous sodium carbonate, and it is not obvious how to extract solid sodium carbonate from the rich solution of sodium hydroxide and sodium carbonate coming from the air capture contactor. This solution would typically have 1–4 M NaOH and less than 1 M of dissolved Na_2CO_3. The major focus of this work, therefore, is on separation of anhydrous sodium carbonate from Na_2CO_3-NaOH feed solution, and preparation of a well-mixed stream of solid sodium carbonate and sodium tri-titanate, the latter used as a reagent for decarbonizing of sodium carbonate via reaction [(4a) and (4b)]. This is the crucial step necessary for applying the titanate process

to air capture. After describing the process for recovering solid Na_2CO_3, we present an end-to-end energy and exergy analysis for the regeneration of NaOH via direct causticization using titanate as an alternative to conventional causticization is assessed.

2. Process description

Fig. 1 illustrates a simplified schematic sketch of the proposed process for the regeneration step in capturing CO_2 from air which is viewed as a two step process requiring a precipitation and a decarbonization step. The more detailed flow sheet is illustrated in Fig. 2.

The precipitation unit is a two-stage crystallization/precipitation unit for precipitating anhydrous sodium carbonate from concentrated alkaline aqueous solution. In the first crystallization stage, sodium carbonate decahydrate is crystallized from concentrated alkaline aqueous solution, and in second stage, anhydrous sodium carbonate is precipitated from a saturated sodium carbonate aqueous solution simultaneously as the sodium
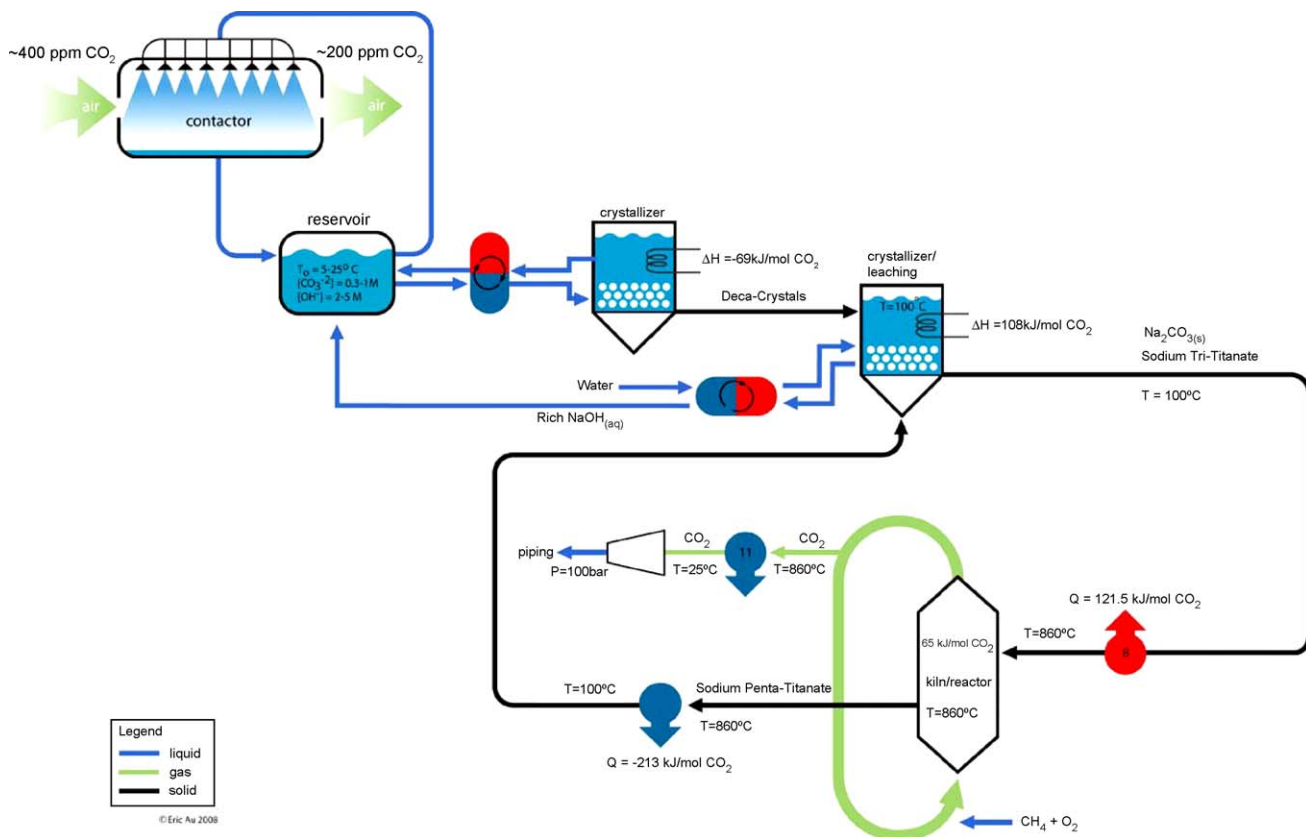

Fig. 2. Process design for air capture using titanate chemical recovery cycle.

penta-titanate is hydrolyzed at elevated temperature. The hydro-lysis of sodium penta-titanate adds aqueous sodium hydroxide to the solution which lowers the solubility of sodium carbonate forcing the precipitation of sodium carbonate.

At temperatures above about 100 °C, the precipitated sodium carbonate is expected to be in the anhydrous form needed for the reaction with tri-titanate reducing the process energy requirements. The sodium hydroxide is regenerated and recycled to the contactor and the solid anhydrous sodium carbonate is then causticized using direct causticization with titanate, in the causticization unit where CO_2 is liberated from sodium carbonated.

2.1. Separation of sodium carbonate from concentrated alkaline feed solution

If sodium carbonate is to be converted to sodium hydroxide via direct causticization process, it must first be separated from concentrated alkaline solution in a pure solid stream. This is necessary because (1) the causticization reaction with titanium dioxide or recycled sodium tri-titanate is a solid state or solid-smelt state reaction and presence of aqueous phase along with sodium carbonate dramatically increases the energy demand due to evaporation, (2) presence of sodium hydroxide along with sodium carbonate in the causticization reactor would cause formation of sticky particles which would lead to corrosion, (3) presence of sodium hydroxide decreases melting point of sodium carbonate (according to $NaOH$–Na_2CO_3 phase diagram).

Before describing the process design, we review the data on the solubility of sodium carbonate in water and in hydroxide and examine the influence of temperature and hydroxide ions concentration on solubility.

2.1.1. Solubility data for sodium carbonate–water system

The solubility data, solid phases and transition temperatures for sodium carbonate–water system were reviewed and collated by Kobe and Sheehy as early as 1948. Sodium carbonate, whose anhydrous and monohydrated forms dissolve exothermically, shows a complex pattern of solubility. In the region in which the equilibrium salt phase is anhydrous, its solubility decreases with increasing temperature, see Fig. 3. Transition points in sodium carbonate–water system are shown in Table 1, in which the temperature at transition point between sodium carbonate monohydrate and sodium anhydrous carbonate is 109 °C.

Sodium carbonate can be crystallized as various hydrates. The transition temperature between sodium carbonate monohydrate and anhydrous sodium carbonate is higher than the boiling point of
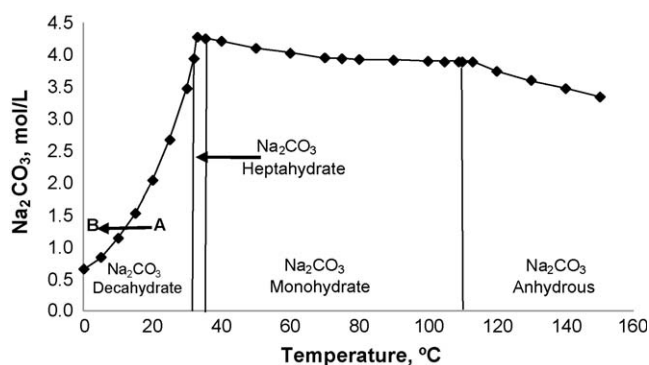

Fig. 3. Solubility of sodium carbonate in water (Kobe and Sheehy, 1948). The two labeled dots provide a schematic indication of the process for separating anhydrous Na_2CO_3 in the method we propose here. A solution of Na_2CO_3 at point 'A', is cooled to point 'B' precipitating decahydrate ($Na_2CO_3 \cdot 10H_2O$). The principal concept for separating Na_2CO_3 from alkaline solution will be similar to what is shown in this figure.

Table 1
Temperature at transit points in Na_2CO_3–H_2O system (Kobe and Sheehy, 1948).

Phases	Temp. (°C)
$Na_2CO_3 \cdot 10H_2O$–ice	−2.1
$Na_2CO_3 \cdot 10H_2O$–$Na_2CO_3 \cdot 7H_2O$	32.00
$Na_2CO_3 \cdot 10H_2O$–$Na_2CO_3 \cdot H_2O$	32.96
$Na_2CO_3 \cdot 7H_2O$–$Na_2CO_3 \cdot H_2O$	35.37
Boiling point	104.8
$Na_2CO_3 \cdot H_2O$–Na_2CO_3	109

a saturated sodium carbonate solution (30 wt%). Crystallization of anhydrous sodium carbonate starts at $T \geq 118$ °C from a 30 wt% (∼2.8 M) sodium carbonate concentration based on solubility data in sodium carbonate–water system (see Fig. 3 and Table 1).

Different methods can be applied to produce anhydrous sodium carbonate from a pure aqueous solution. Operating under pressurized condition is one way to raise the boiling temperature (105.7 °C) above the transition temperature (109 °C). The other way is to crystallize sodium carbonate at lower temperatures either as sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) or monohydrate ($Na_2CO_3 \cdot H_2O$). The hydrates are then calcined at 150–200 °C to obtain the anhydrous form (Oosterhof, 2001). The thermal dehydration of sodium carbonate hydrates is, however, considerably endothermic; the values of 52.67 and 58.77 kJ/mol H_2O has been cited for decahydrate and monohydrate respectively. These values are appreciably greater than the 44 kJ/mol heat of vaporization of liquid water at 298 K. An alternative crystallization method was addressed by Weingaertnet et al. (1991) and Oosterhof et al. (1999, 2001), in which a suitable anti-solvent is used to decrease the solubility of the salt and also to lower the water activity. This means that the transition temperature is lowered and anhydrate can be produced directly at lower temperatures, even below the boiling point of the solution. Addition of ethylene glycol by 25 wt%, for example, would increase the boiling point of the solution from 105.7 to 106.8 °C and lower the transition point from 109 to 105.7 °C (Oosterhof, 2001).

2.1.2. Solubility data for sodium carbonate–sodium hydroxide system

The ternary system of Na_2CO_3–$NaOH$–H_2O has been studied as early as 1923 by Freeth and the solubility of carbonate salts, in general, was found to drop in the presence of hydroxide ions. A number of studies have been done on solubility of sodium carbonate in Na_2CO_3–$NaOH$–H_2O system for which the data is edited and presented by Silcock (1963). Konigsberger (2001) also presented the results of a thermodynamical method which would predict the influence of sodium hydroxide concentration in the solution on the solubility of sodium carbonate. The model was verified for the solubility of monohydrate by experimental data. The result from Konigsberger's work is in agreement with earlier studies on solubility data for sodium carbonate. Fig. 4 illustrates a summary of the literature data on solubility of sodium carbonate at different temperature and concentrations of NaOH solution, 5%, 10% and 17% corresponding to 1.5, 3 and 5 M NaOH.

As it is shown in Fig. 4, in general, the solubility curve for sodium carbonate in presence of sodium hydroxide in the solution follows the same pattern as the solubility curve for Na_2CO_3–water system and approximately the solubility product rule.

The transition temperature of sodium carbonate monohydrate and anhydrous sodium carbonate is influenced by the concentration of sodium hydroxide. Keene and Syracuse (1938) showed that addition of other soluble substances, e.g. sodium hydroxide, to a saturated aqueous solution of sodium carbonate will cause a reduction in its vapor pressure which results in an elevation of its normal boiling point and in reduction of the transition temperature from sodium carbonate monohydrate to anhydrous sodium carbonate, see Fig. 5.
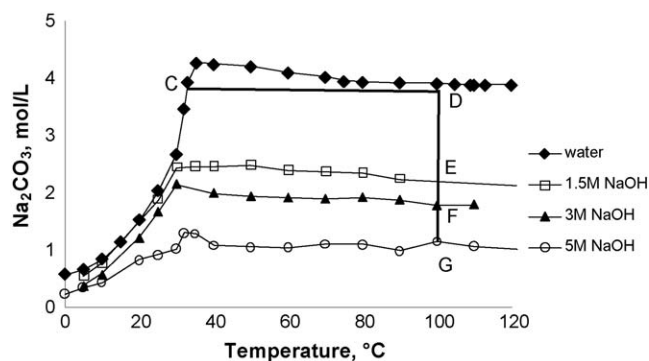
Fig. 4. Solubility of sodium carbonate in water and 1.5, 3 and 5 M NaOH solution. The separated crystals of sodium carbonate decahydrate are dissolved in water at ~30 °C to produce a saturated solution indicated by the point 'C'. The solution is heated to about 100 °C (point 'D') at which due to hydrolysis of added sodium penta-titanate, NaOH is leached out; this would in turn cause the sodium carbonate to be precipitated as anhydrous sodium carbonate. Depending on the concentration of leached NaOH, the solubility of sodium carbonate would drop to points E, F or G.

2.1.3. Process design for the separation of anhydrous sodium carbonate from alkaline solution

Earlier studies on obtaining anhydrous sodium carbonate, deal mostly with separation of anhydrous sodium carbonate from crude sodium sesquicarbonate or brine solution. The precipitation of sodium carbonate from an aqueous solution of sodium carbonate and sodium hydroxide has not been addressed in the literature. In this paper, therefore, we propose a novel method to precipitate a pure anhydrous sodium carbonate from a concentrated alkaline solution, e.g. an aqueous mixture of 1–4 M NaOH and 1–2 M Na_2CO_3.

The method requires two precipitation steps, in the first sodium carbonate is precipitated as sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$, from a saturated solution of Na_2CO_3–NaOH by means of a temperature swing. The concentration of dissolved Na_2CO_3 in the reservoir is a critical operational parameter; Table 2 shows a practical range of carbonate concentration in the solution as a function of temperature. Running the reservoir with carbonate close to saturation minimizes the energy required for the temperature swing, but if the concentration is too close to saturation, carbonate may precipitate in the reservoir tank. The two labeled dots, A to B, in Fig. 3 illustrate the schematic indication of sodium carbonate decahydrate precipitation. Although, the separation process is sketched for Na_2CO_3–water system, the separation process for Na_2CO_3 from Na_2CO_3–NaOH–H_2O would follow the same concept.
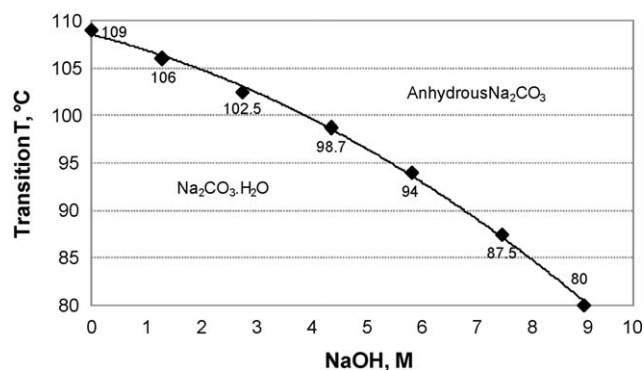

Fig. 5. Dependency of transition T between monohydrate and anhydrous on NaOH concentration. Note: the figure is redrawn from Fig. 1 in Keene and Syracuse (1938).

While crystallization of sodium carbonate decahydrate can be assured by imposing a sufficiently large temperature swing, a practical large-scale process requires that crystals be grown to a large enough size that they can be cost effectively removed from solution with a minimum of solution carry-over. Different crystallizer designs via cooling process are available. A draft tube baffle (DTB) crystallizer from Swenson Crystallization Equipment has proven to be very useful for crystallizing sodium carbonate decahydrate from aqueous sodium carbonate. The same kind of crystallizer might efficiently crystallize sodium carbonate dec-ahydrate from the reservoir, e.g. aqueous sodium carbonate and sodium hydroxide. The DTB crystallizer includes a baffle section surrounding a suspended magma of growing crystals from which a stream of mother liquor is removed containing excess fine crystals. These fines can be destroyed by adding heat (as in an evaporative crystallizer) or by adding water or unsaturated feed solution. The magma is suspended by means of a large, slow-moving propeller circulator which fluidizes the suspension and maintains relatively uniform growth zone conditions. Another design by DHV Water AB is a pellet reactor type crystallizer which is called "crystalactor". The crystalactor is filled with suitable seeding material to provide nuclei for the crystallization of sodium carbonate decahydrate. The crystalactor has successfully been in operation for metal and anion recovery from waste water (Giensen and van der Moldeh, 1996). This type of crystallizer has also been studied for precipitation of other metal-carbonates. Damien and Lewis (2001) studied the carbonate precipitation of nickel in pellet reactor and Lewis (2006) investigated the precipitation of nickel hydroxyl-carbonate using the fluidized pellet reactor. The fluidized bed provides a very large crystallization surface and in a fast controlled reaction almost all the anion crystallizes directly from the solution into the crystal lattice. Therefore, pure, almost moisture-free (moisture content of only 5–10%) salt are produced after atmospheric drying. The crystalactor has not been tested for crystallization of sodium carbonate decahydrate.

The next step in our process, is to dissolve pure crystals of $Na_2CO_3 \cdot 10H_2O$ in warm water (at temperature above 30 °C) to a total concentration of ~2.8 M (30 wt%) providing a pH level of about 12. It should be mentioned that the pH level is all the process units in our study is high enough to prevent co-crystallization of any sodium bicarbonate crystals during the process (i.e. sodium bicarbonate precipitates at pH between 6 and 9, while the pH level for all the process is always above 12). In order to precipitate anhydrous sodium carbonate from this aqueous solution, the solution should be heated to temperatures above 118 °C. However, as stated earlier, the boiling point of a 30 wt% sodium carbonate solution is 105.7 °C. To avoid boiling the system might be pressurized. Crystallization of anhydrous sodium carbonate can be accomplished by removing water using and evaporative process or reverse osmosis. Alternatively, it might be achieved by use of anti-solvents; however, the addition of anti-solvents is probably not applicable to air capture process because of hazardous organic vapors emissions in air via entering a few percent of organic anti-solvents into alkaline solution which is sprayed in the contactor.

The alternative process is to introduce sodium hydroxide into the solution when the solution is heated to temperature close but below the boiling point. This would significantly drop the solubility and anhydrous or a mixture of anhydrous and monohydrate Na_2CO_3 would precipitate, e.g. dropping the solubility from point D to G in Fig. 4, when concentration of NaOH in the solution increases to 5 M at temperature of about 100 °C. Based on Keene and Syracuse's studies, the transition temperature between sodium carbonate monohydrate and anhydrous sodium carbonate would shift from 109 °C in Na_2CO_3–water solution to about 97 °C in a Na_2CO_3–NaOH–water system with a final concentration of about 5 M of NaOH. The phase boundary of sodium carbonate would,

Table 2
The changes in concentrations of carbonate when NaOH is present at different concentrations.

Ambient T (°C)	NaOH concentration in reservoir (mol/L)	Maximum carbonate concentration in (mol/L)	T swing ΔT (°C)	Carbonate concentration out (mol/L)	Precipitated carbonate, ΔC
30	5	0.9	20	0.42	0.48
25	5	0.85	15	0.42	0.43
20	3	1		0.55	0.45
	5	0.75	10	0.42	0.33
15	3	0.75		0.55	0.2
	5	0.55	5	0.42	0.13

therefore, shift to permit the crystallization to be carried out at atmospheric pressure while still growing crystals of anhydrous sodium carbonate.

To provide a high concentration of NaOH in a saturated solution of sodium carbonate at elevated temperature, we describe a novel process in which anhydrous sodium carbonate is precipitated simultaneously as the sodium penta-titanate from decarbonization unit is hydrolyzed to leach sodium hydroxide out, reaction (5). The leaching of sodium hydroxide from sodium penta-titanate has been studied by Richards and Theliander (1999) and the influence of temperature and initial concentration on leaching rate was addressed. It was found that the leaching reaction, reaction (5), is an endothermic reaction, $\Delta H = 15.2$ kJ/mol CO_2, and that by presenting experimental data at temperatures of 70 and 100 °C, it was shown that leaching rate at about 100 °C and for the studied experimental time, can be high enough to produce a maximum 5 M aqueous solution of sodium hydroxide. The influence of other soluble compounds, e.g. carbonate ions on the hydrolysis of sodium penta-titanate, has, however, not been studied in the literature.

The proposed process works as follows: penta-titanate is added to the ~2.8 M saturated sodium carbonate solution at temperatures of ~100 °C. The sodium penta-titanate hydrolyzes releasing NaOH which drives the sodium carbonate out of solution. The leaching of sodium hydroxide would shift the solubility curve of sodium carbonate as well as the transition temperature of sodium carbonate monohydrate and anhydrous sodium carbonate. We performed a preliminary laboratory studies for the simultaneous leaching and precipitation reactions and found that the sodium hydroxide can be leached out from sodium penta-titanate, and drive the anhydrous sodium carbonate to precipitate out from the solution. The concentration of sodium hydroxide was controlled so that a 3 M hydroxide solution is produced and the anhydrous sodium carbonate was precipitated at temperature of ~103 °C. The crystalline structure of the precipitates, i.e. anhydrous sodium carbonate and sodium tri-titanate was analyzed by means of XRD. More detailed experimental data will be discussed in a separate paper.

2.2. Decarbonation of sodium carbonate via direct causticization

Thermodynamics of titanate reaction has been widely studied as early as 1979 by Kiiskilä. Zou (1991) showed that the lower limit for reaction temperature is 840 °C in order to achieve sufficiently high reaction rates due to reaction (4a) under the applied experimental conditions in that study. At temperatures above the melting point of sodium carbonate, the enthalpy of reaction (4b) was reported to be ~65 kJ/mol CO_2 (Nohlgren, 2002), whereas at temperatures below melting point and above 840 °C, the enthalpy of reaction (4a) is 90 kJ/mol CO_2. The enthalpy of fusion for Na_2CO_3 is 25.7 kJ/mol, which is approximately equal to the difference between the enthalpy of reaction (4a) and (4b), above

and below the melting point. So the net enthalpy of reaction is about the same in either case.

After a thorough thermodynamical analysis, we found that although the reaction can be carried out in solid state, but at temperatures slightly above the melting point (~860 °C), the total energy requirement for heating the reactant and the reaction is 3% less than for temperatures below melting point. Moreover, at temperatures slightly above the melting point, the total energy that can be recovered from cooling of the products is ~3% more than for the temperatures below melting point. This would, in turn, lead to 6% more energy efficiency when causticization is carried out at temperatures slightly above the melting point. The reaction rate is also higher at temperature slightly above melting point, which is of great importance for the residence time in the fluidized bed reactor.

The parameters influencing the kinetics of reaction (5) are addressed to be the particle size of both sodium carbonate and titanium dioxide and molar ratio of titanium dioxide and sodium carbonate (TiO_2/Na_2CO_3). Zou (1991) found that all of the sodium carbonate is converted below its melting point (858 °C) within a few minutes for particle sizes of sodium carbonate and $TiO_2 < 25$ μm and for $TiO_2/Na_2CO_3 = 1.25$, indicating that the reaction can be carried out successfully in the solid state, this was also confirmed by Nohlgren (2002). However, when larger particle sizes of sodium carbonate and TiO_2, e.g. 63 μm (Kiiskilä, 1979), or smaller molar ratio, e.g. $TiO_2/Na_2CO_3 = 1$ (Zou, 1991), was used, the causticization reaction was slower than the previous cases at temperatures below sodium carbonate melting point.

Besides the parameters discussed above, the partial pressure of CO_2 in the reaction atmosphere seems to influence the reaction kinetics of (4a) and (4b) too. The mechanism is not yet clearly understood. Nohlgren and Sinquefield (2004), Nohlgren et al. (2004) and Sinquefield (2005) reported a retarding effect of CO_2 partial pressure on reaction rate. A thorough investigation of the mechanism for the influence of CO_2 partial pressure on titanate reaction is required, because for the purpose of this paper, we would rather to separate a CO_2 stream at partial pressure of about 15 bar from the fluidized bed reactor. This would simplify the compression of separated CO_2 to higher pressure of about 1005 bar.

Design and process engineering of the system for heating the mixed carbonate/titanate particles is beyond the scope of this paper. In this section we provide speculation about two possible design alternatives that provide for heat and CO_2 recovery.

Highly efficient kilns for heating fine particles to temperatures above that required here have been developed for lime production. The so-called 'D' kilns developed by the Italian lime kiln manufacturer, Cimprogetti, for example have demonstrated thermal efficiencies above 90% in large-scale applications. The efficiency comes from a counter flow design in which the particles drop through upward flowing gas. In the upper section of the kiln the cool particles are heated by the hot exhaust gases creating a

counter current heat exchanger. The calcination reaction proceeds in the middle of the kiln. In the lower section of the kiln the hot particles fall through the incoming air preheating it. It seems plausible that similar kiln designs could be readily adapted to drive the tri-titanate to penta-titanate reaction, although this design would not be directly applicable to particles in the size range discussed above.

The most conservative approach would be to use natural gas fired in air as a heat source and then to capture the CO_2 using a post-combustion process such as amines or chilled ammonia from the exhaust gases. This approach would require minimal adaptation of existing kiln designs, and would presumably, carry the minimum technical risk. However the use of post-combustion capture would demand an efficiency penalty and would add capital cost.

Alternatively, the energy demands of the titanate process are sufficiently low that it might make sense to use a natural gas fired, indirectly heated kiln in which the CO_2 from the gas combustion was not recovered. This is feasible because, for an efficient kiln, five times less CO_2 is produced by combustion of the gas than is extracted from air.

A more advanced and perhaps more cost-effective design would use recirculating CO_2 into which heat introduced by an "oxyfuel" mixture of oxygen and natural gas or syngas. The design of such systems could be adapted from the many design studies for oxyfuel coal fired power plants which are now being applied at scales of greater than 30 MW (Vattenfall). In this case the primary operating gas would be CO_2 at a pressure of atmospheric or above. The presence of CO_2 at atmospheric pressure might, however, cause problems in the titanate kinetics. At this step of research on titanate process, this is not yet fully understood.

A still more advanced design would use indirect heat provided by a high temperature gas cooled reactor (HTGR). The second generation of HTGR reactors is currently being developed by several companies including PBMR, AREVA, and General Atomics. The first commercial scale passively safe PBRM reactor is expected to start construction in 2009. In these reactors the primary loop helium temperature is ~900 °C, and the secondary loop temperature can be above 850 °C. It might therefore be practical to drive the titanate reactions using indirect heat provided by the secondary

helium loop from an HTGR. In this design essentially the only gas inside the kiln would be CO_2 since no water would introduced by combustion as is the case for oxyfuel.

HTGRs arguably could provide the lowest cost source of carbon neutral high-grade heat (MIT Report, 2003). If HTGRs are the power source, then the titanate process described here has another advantage, others in energy efficiency, over the calcination process because that titanate process can be operated at temperatures as low as 800 °C, whereas the calcination process requires temperatures of ~950 °C (assuming atmospheric pressure CO_2). Current HTGR designs cannot practically supply heat at 950 °C.

3. Energy and exergy analysis

Richards et al (2004) and Richards et al. (2007) performed a thermodynamical evaluation for the conventional causticization and the direct causticization using titanates and found that the process with highest potential from both energy and energy equality perspective is the titanate process. It should be mentioned that in their studies solid sodium carbonate was used to perform a fair comparison between the two processes.

In this section, we show the results of the energy and exergy analysis for the recovery cycle using titanate in which sodium carbonate and lean sodium hydroxide enters the cycle and carbon dioxide and rich sodium hydroxide leaves the cycle as the products. The other substances are subjected to be recycled between the different units. Note that the starting point for sodium carbonate is the aqueous alkaline solution of Na_2CO_3–NaOH from the feed solution. The energy analysis for the CO_2 absorption section, "contactor", can be found elsewhere (Storaloff et al., 2008).

In this paper, a total energy requirement of ~150 kJ/mol CO_2 is estimated for the recovery cycle using titanate. As shown in Table 3, the highest exergy levels correspond to the decarbonation reaction, heating of reactants and cooling of products.

The amount of energy required by titanate process is compared with the energy requirement in lime cycle in Fig. 6 where enthalpy of change, ΔH, for titanate and lime process at corresponding temperatures is illustrated. In Fig. 6, the lime cycle is presented as dashed line, labeled by numbers, and whereas, the titanate cycle is shown in solid line labeled by letters. As illustrated, the minimum

Table 3
Energy and exergy analysis[a].

	Enthalpy change ΔH (kJ/mol CO_2)	Temperature range T (°C)	Exergy change ΔE (kJ/mol CO_2)
Crystallizer			
Crystallization for $Na_2CO_3 \cdot 10H_2O$	−68.8	10	1.7
Combined crystallizer/leaching unit			
Heating $Na_2CO_3 \cdot 10H_2O$	8.8	10 → 31	1.9
Dissolution for $Na_2CO_3 \cdot 10H_2O$ to 30 wt%	67.9	31	−1.2
Crystallization for Na_2CO_3	45.3	103	−8.3
Leaching reaction	15.2	100	−1.3
Heater			
Heating Na_2CO_3	123.4	100 → 860	93.4
Heating sodium tri-titanate	146.9	100 → 860	84.0
Fluidized bed reactor			
Reaction	65	860	−33.8
Cooler			
Cooling CO_2	−40.7	860 → 25	−22.1
Cooler			
Cooling sodium penta-titanate	−213	860 → 100	−129.1
Total	150	–	–

[a] Data of enthalpy and entropy is taken from thermochemical database software HSC Chemistry v.6.12. Outotec research (www.outotec.com), and exery is calculated as: $E = \Delta H - T_0 \Delta S$ where ΔH and ΔS represent the enthalpy and entropy differences between the stream at the current temperature and the environment at the defined temperature (298.15 K).
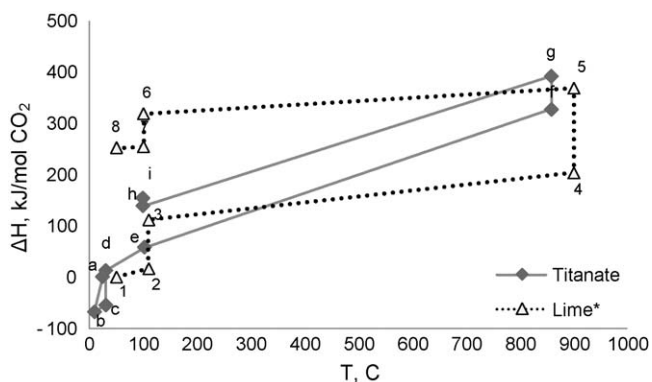
Fig. 6. Enthalpy change for titanate and lime process. *The moisture content of 30 wt% was assumed for CaCO3. (a-b) Crystallization of $Na_2CO_3 \cdot 10H_2O$; (b-c) heating $Na_2CO_3 \cdot 10H_2O$ and water to ~ 30 °C; (c-d) dissolution of $Na_2CO_3 \cdot 10H_2O$; (d-e) crystallization of $Na_2CO_{3(s)}$; (e-f) heating $Na_2CO_{3(s)}$ and $Na_2O \cdot 3TiO_2$; (f-g) decarbonation reaction; (g-h) cooling $CO_{2(g)}$ and $4Na_2O \cdot 5TiO_2$; (h-i) leaching reaction. (1-2) Heating wet $CaCO_3$; (2-3) vaporizing moisture; (3-4) heating $CaCO_{3(s)}$; (4-5) calcination reaction; (5-6) cooling $CaO_{(s)}$ and $CO_{2(g)}$; (6-7) slaking reaction; (7-8) cooling $CO_{2(g)}$.

required energy for titanate process is about half of the required energy for lime process (~ 135 as oppose to ~ 250 kJ/mol CO_2). In lime cycle, the calcinations reaction consumes the most energy, and heat recovery from the calcination reaction products is poor. In titanate cycle, however, most of the energy consumed for heating the reactants can theoretically be recovered by cooling of reaction products. It should however be mentioned that because the energy requirement for heating and cooling of reactants and products are larger in the titanate process, the requirement for efficient heat transfer is more stringent.

The titanate process supplies rather high concentration of regenerated sodium hydroxide solution (190 g/L) compared to conventional causticization (maximum 140 g/L). This is because in conventional causticization using lime, the alkalinity of the NaOH solution produced due to reaction (1) is limited by the causticization reaction to 1 M. For air capture system, proposed by Storaloff et al. (2008), however, a more concentrated hydroxide solution, e.g. 3 or 5 M, might be required depending on relative humidity (RH) and ambient temperature. Another issue with causticizing concentrated alkaline feed solution with lime is the co-precipitation of calcium hydroxide with calcium carbonate. For these reasons, the conventional causticization using lime might not be as efficient as it is for causticizing sodium carbonate from a more dilute solution compared to the concentrated feed solution.

4. Conclusion

We assess a novel energy efficient process for recovering sodium hydroxide for capturing CO_2 from ambient air. The proposed process potentially requires about half of the energy requirement for the conventional causticization process using lime. The heat requirement of the proposed process is similar to the heat requirement for the sorbent regeneration for an amine-based CO_2 (MEA) capture system (for which an average of ~ 130 kJ/mol CO_2 was reported by Rao et al., 2006) for power plants, although the heat required for our proposed process must be supplied at high temperature. Another potential advantage of this process over the conventional causticization process is the lower temperature level, ~ 50–100 °C, which would allow the heat integration between a high temperature gas cooled reactor from nuclear plants and the decarbonation reactor. Moreover, regeneration of concentrated sodium hydroxide would allow the contactor to significantly minimize the water loss.

References

Baciocchi, R., Storti, G., Mazzotti, M., 2006. Process design and energy requirement for the capture of carbon dioxide from air. Chem. Eng. Process. 45, 1047–1058.

Canadell, J.G., et al., 2007. Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity and efficiency of natural sinks. Proc. Natl. Acad. Sci. U.S.A. 104 (47), 18866–18870.

Chen, X., van Heiningen, A.R.P., 2006. Kinetics of the direct causticizing reaction between sodium carbonate and titanium dioxide or sodium tri-titanate. J. Pulp Pap. Sci. 32 (4), 245–251.

Covey, G.H., 1982. Development of the direct alkali recovery system and potential application. Pulp Pap. Canada 83 (12), T350–T354.

Giensen, A., van der Moldeh, J.G., 1996. The crystalactor: wastewater treatment by crystallization without waste production. Technical Report, DHV Water BV. Amersfoort, The Netherlands.

Hoddenbagh, J., Wilfing, K., Miller, D., Harman, D., Tran, H., Bair, C., 2002. Borate causticizing: a cost effective technology. Pulp Pap. Canada 103 (11), T283–T289.

Keene, P.A., Syracuse, A.P.J., 1938. Production of dense soda ash. US Patent 2,133,455.

Kiiskilä, E., 1979a. Recovery of sodium hydroxide from alkaline pulping liquors by smelt causticizing. Part II. Recations between sodium carbonate and titanium dioxide. Paperi ja Puu, Papper och Trä 5, 394–401.

Kiiskilä, E., 1979b. Recovery of sodium hydroxide from alkaline pulping liquors by smelt causticizing. Part III. Alkali distribution in titanium dioxide causticizing. Paperi ja Puu, Papper och Trä 6, 453–464.

Kobe, K., Sheehy, T., 1948. Thermochemistry of sodium carbonate and its solutions. Ind. Eng. Chem. 40 (1), 99–102.

Konigsberger, E., 2001. Solubility equilibria—from data optimization to process simulation. Pure Appl. Chem. J. 74 (10), 1831–1841.

Lackner, K.S., Grimes, P., Ziock, H.J., 1999. Capturing carbon dioxide from air. In: 24th Annual Technical Conference on Coal Utilization, Clearwater, FL.

Lewis, A.E., 2006. Fines formation and prevention in seeded precipitation processes. KONA 24, 119–125.

Maddern, K.N., 1986. Mill-scale development of the DARS direct causticization process. Pulp Pap. Canada 87 (10), T395–T399.

MIT Report, 2003. The future of nuclear power. An interdisciplinary MIT study. Massachusetts Institute of Technology. http://web.mit.edu/nuclearpower/.

Nagano, T., Miyao, S., Niimi, N., 1974. Method of recovering sodium hydroxide from sulfur free pulping or bleaching waste liquor by mixing ferric oxide with condensed waste liquor prior to burning. US Patent 4,000,264.

Nohlgren, I., 2002. Recovery of kraft black liquor with direct causticization using titanates. Ph.D. Thesis. Lulea University of Technology, Lulea, Sweden.

Nohlgren, I., Sinquefield, S., 2004. Black liquor gasification with direct causticization using titanates: equilibrium calculations. Ind. Eng. Chem. Res. 43, 5996–6000.

Nohlgren, I., Sinquefield, S., Ball, A., Zeng, Z., Empie, H., 2004. Direct causticization for low and high temperature black liquor gasification. In: International Chemical Recovery Conference, June 6–10, Charleston, SC, USA.

Oosterhof, H., Witkamp, G.J., van Rosmalen, G.M., 1999. Some antisolvents for crystallization of sodium carbonate. Fluid Phase Equilib. 155, 219–227.

Oosterhof, H., Witkamp, G.J., van Rosmalen, G.M., 2001. Evaporative crystallization of anhydrous sodium carbonate at atmospheric conditions. AIChE J. 47 (10), 602–608.

Palm, M., Theliander, H., 1997. Kinetic study of the direct causticization reaction involving titanates and titanium dioxide. Chem. Eng. J. 68, 87–94.

Rao, A.B., Rubin, E.S., Keith, D.W., Morgan, M.G., 2006. Evaluation of potential cost reductions from improved amine-based CO_2 capture systems. Energy Policy 34 (18), 3765–3772.

Richards, T., Theliander, H., 1999. The leaching of NaOH from 4:5 sodium titanate produced in an autocausticization process: kinetics and equilibrium. Nordic Pulp Pap. Res. 14 (3), 184–192.

Richards, T., Pavletic, C., Pettersson, J., 2007. Efficiencies of different methods of producing NaOH—implications in a Kraft pulp mill. In: International Chemical Recovery Conference, May 29–June 01, Quebec City, QC, Canada.

Silcock, H.L., 1963. Solubilities of Inorganic and Organic Compounds. Part 2, vol. 3. Pergamon Press, New York, pp. 470–485.

Sinquefield, S., 2005. In situ causticizing for black liquor gasification. Phase 2 Topical Report, US DOE Award#DE-FC26-00NT41492. Institute of Paper and Technology at Georgia Tech, Atlanta.

Sinquefield, S., Ball, A., Zeng, Z., 2004. Borate auto-causticization for low and high temperature black liquor gasification. In: International Chemical Recovery Conference, June 6–10, Charleston, SC, USA.

Spector, N.A., Dodge, B.F., 1946. Removal of carbon dioxide from atmospheric air. Trans. Am. Inst. Chem. Eng. 42, 827–848.

Storaloff, J., Keith, D.W., Lowry, G., 2008. Carbon dioxide capture from atmospheric air using hydroxide spray. Environ. Sci. Technol. 42, 2728–2735.

Tepe, J.B., Dodge, B.F., 1943. Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. Trans. Am. Inst. Chem. Eng. 39, 255–276., In: www.vattenfall.com.

Weingaertnet, D., Lynn, S., Hanson, D.N., 1991. Extractive crystallization of salts from concentrated aqueous solution. Ind. Eng. Chem. Res. 30 (3), 490–501.

Yusuf, Z., Cameron, J., 2004. Decarbonization reactions between sodium metaborate and sodium carbonate. Ind. Eng. Chem. Res. 43, 8148–8154.

Zeman, F., 2007. Energy and material balance of CO_2 capture from ambient air. Environ. Sci. Technol. 41, 7558–7563.

Zeng, L., van Heiningen, A.R.P., 1997. Pilot fluidized-bed testing of kraft black liquor gasification and its direct causticization with TiO_2. J. Pulp Pap. Sci. 23 (11), J511–J516.

Zou, X., 1991. Recovery of kraft black liquor including direct causticization. Ph.D. Thesis. McGill University, Montreal, Quebec.