



Sodium hydroxide production from sodium carbonate and bicarbonate solutions using membrane electrolysis: A feasibility study



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ARTICLE INFO

Article history:

Received 31 October 2013

Received in revised form 14 February 2014

Accepted 15 February 2014

Available online 28 February 2014

Keywords:

Coal seam gas produced water

Brine treatment

Membrane electrolysis

Chlor-alkali

Sodium hydroxide

Sodium bicarbonate

ABSTRACT

This study demonstrates the feasibility of producing NaOH from coal seam gas (CSG) brine by membrane electrolysis. Membrane electrolysis of NaHCO₃, Na₂CO₃, and NaCl, which are the three dominating sources of sodium in CSG brine, were evaluated and compared. Overall, the current efficiency did not change significantly when different brine solutions (i.e. NaCl, NaHCO₃ and Na₂CO₃) were used as feedstock. The counter ions (i.e. Cl⁻, HCO₃⁻ and CO₃²⁻) did not affect the transport of sodium ions (Na⁺) through the membrane. Similarly, no significant variation in NaOH production was observed when the three brine solutions, which contained 100 g/L of the corresponding salt each, were evaluated under the same conditions. It is noteworthy that membrane electrolysis was most effective for desalting a NaHCO₃ brine solution, followed by NaCl and then Na₂CO₃ of equivalent concentration. This is because of the equivalent weights (with respect to Na⁺) of these three salts decreases in the order of NaHCO₃ (84 g/eq) > NaCl (58.5 g/eq) > Na₂CO₃ (53 g/eq). The energy efficiency of the membrane electrolysis process with respect to NaOH production increased as the brine concentration increased. On the other hand, the desalination efficiency (or brine concentration reduction) by membrane electrolysis increased as brine concentration decreased. The results also revealed a drawback of the use of NaHCO₃ as feedstock to the membrane electrolysis process. The produced NaOH solution strength obtained from a 100 g/L NaHCO₃ solution within a specified time was limited to about 12% w/w, whereas that of NaCl was as high as 18% w/w. The lower NaOH strength obtained from NaHCO₃ could be attributed to lower osmotic pressure and electrical conductivity of this salt as compared to NaCl.

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1. Introduction

Recent coal seam gas (CSG) developments have resulted in a major shift in the global energy outlook. CSG is essentially natural gas (primarily methane) that occurs in underground coal seams. Natural gas currently accounts for 21–25% of the global primary energy consumption [1]. With significant reserves in many parts of the world including North America, Europe, and Australia, the contribution of natural gas from coal seams to the global energy mix will continue to rise in the future. It is estimated that 70% of the global liquefied natural gas capacity under construction is taking place in Australia to tap into its vast CSG reserve [2]. Natural gas is a cleaner fuel than coal and oil; with less polluting combustion products and electricity generation can be instantaneously adjusted to match the energy demand. The latter advantage avoids unnecessary energy production and greenhouse gas emission. In

addition, natural gas extraction is essential to reduce the risk of methane outburst and fugitive methane emission, which are critical for any future coal mining activities. However, CSG extraction inevitably requires the co-extraction of water (often referred to as CSG produced water) to the surface to depressurise the coal seams and allow natural gas to flow to the surface. The volume of CSG produced water is very large. For example, a recent study commissioned by the Queensland Government estimates that the volume of CSG produced water from Southern Queensland generated each year may be as much as 175 GL, with a potential accumulative volume of 5100 GL to 2060. This CSG produced water is brackish, due to a rich mixture of salts including sodium chloride, bicarbonate or carbonate. Thus, without appropriate treatment, CSG produced water cannot be put to beneficial use or directly released into the environment due to a significant impact on the environment [3–6]. For this reason and because of the high cost of RO brine discharge, many dedicated studies have prompted the development of suitable treatment technologies for the management of RO brine [7–11]. The current CSG produced water practice consists of pre-treatment (e.g. coagulation, pH adjustment),

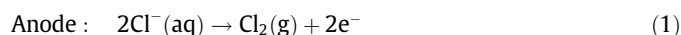
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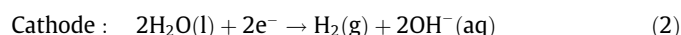
ultra- or microfiltration, followed by reverse osmosis (RO) desalination [12]. A state of the art RO process can produce high quality treated water, suitable for a wide range of uses [6,13]. However, produced water management remains a bottleneck in the otherwise fast growing CSG industry. The RO process can only achieve 70–80% water recovery. Managing CSG RO brine (which is about 20–30% of the initial CSG water volume) and high salinity produced water from the oil and gas industry remains a major technological challenge and only a few studies have been conducted to address this issue [14].

In most, if not all current CSG operations, the RO brine is stored in fully lined brine ponds for future treatment, which can be only considered as a temporary option due to cost and environmental risks. However, the CSG RO brine can be a potential feedstock for the extraction of saleable minerals, which results in the reduction of the volume and salinity of the CSG RO brine. Such techniques involve a further concentration of the brine to near saturation by both well-established and emerging technologies such as multi-effect distillation (MED) or membrane distillation (MD) followed by a mineral recovery step. For example, Penrice (Penrice Soda Holdings Limited, Australia) in collaboration with GE (General Electric, Australia) and QGC (QGC Pty Limited, Australia) has announced a pilot project to demonstrate the recovery of soda ash from CSG brine. Another notable technique is to use the saturated CSG brine as a feedstock for the production of sodium hydroxide using the chlor-alkali membrane electrolysis process.

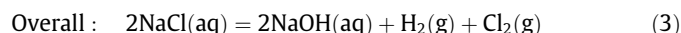
The membrane electrolysis system consists of an anode and a cathode semi-cell. In the current chlor-alkali membrane electrolysis process, NaCl brine is fed into the anode, which produces aqueous NaOH, chlorine and hydrogen gas. Thus, the following reactions occur at the anode and cathode



In the cathode, water is electrolysed into OH^- and hydrogen gas.



A cation-exchange membrane separates the anode and cathode solutions, but is permeable to Na^+ . Thus, Na^+ can migrate across the membrane to combine with OH^- in the cathode to form NaOH. The overall electrolysis reaction of NaCl to NaOH and Cl_2 can be written as:



Membrane electrolysis is a well-established technology for the production of NaOH (or caustic soda), which is an important raw material in many industries. Over 90% of all recently installed sodium hydroxide production capacity is based on the membrane electrolysis process [15]. To date, NaCl brine obtained from sea salts or inland salt lakes has been the only feedstock to the membrane electrolysis. The emergence of seawater desalination as a major source of drinking water supply has presented the chlor-alkali industry with a unique opportunity. In a recent study, Melián-Martel et al. [16], demonstrated that membrane electrolysis is able to use a NaCl rich brine, which is double the concentration of seawater, and also provided a sustainable solution to the management of RO brine disposal from seawater desalination plants. In addition to the brine from seawater desalination applications, CSG brine may also be a suitable feedstock for the membrane electrolysis process. However, to date, all research efforts in membrane electrolysis have focused only on NaCl feedstock. Little is known about the commercial use of NaHCO_3 and Na_2CO_3 , which are two dominating sources of sodium in CSG brine, in membrane electrolysis.

The purpose of this study was to determine the feasibility of producing NaOH by membrane electrolysis using synthetic CSG brine. Current efficiency of the electrolytic process of NaCl,

NaHCO_3 , and Na_2CO_3 , which are usually the dominant species of salts in CSG water, were evaluated and compared. The effects of current density and flow rate upon the current efficiency, NaOH production, decrease in brine concentration, and the energy consumption of the process were systematically investigated.

2. Materials and methods

2.1. Selected cation exchange membrane

A cation exchange membrane (Selemion CMF, AGC Engineering Ltd., Tokyo, Japan) was used in this study. According to the manufacturer, this is a high durability membrane for electrolysis application. The membrane has a thickness of 440 μm and a very low electrical resistance (2.5 Ω/cm^2 at 0.5 M NaCl and 25 °C). The transport number of Na^+ (which is defined as the current carried by the specified ion over the total current of the CMF membrane) is above 0.95.

2.2. Brine solutions

Brine solutions were prepared by dissolving analytical grade NaCl, NaHCO_3 and Na_2CO_3 (supplied by Chem-Supply, Gillman, South Australia) in Milli-Q water. NaHCO_3 and Na_2CO_3 are the two most abundant salts in CSG water reported in the literature [12]. In fact, in a recent pilot study using a combination of RO and MED, we were able to achieve 95% water recovery from CSG produced water from a pilot gas field in northern New South Wales (Australia). The concentrations of Na^+ , HCO_3^- , and Cl^- in the remaining brine were 17.0, 19.7, and 2.2 g/L, respectively. It is noteworthy that NaHCO_3 has the lowest solubility (Table 1). At the same mass concentration of 10%, NaHCO_3 also has the lowest electrical conductivity.

2.3. Membrane electrolysis system and experimental protocol

The membrane electrolysis system (Fig. 1) used consisted of an electrolysis cell (Model E-0, AGC Engineering Ltd., Japan), two peristaltic pumps (Masterflex, John Morris Scientific Pty Ltd., Australia), a programmable power supplier (Model PSH-2018A, GW Instek, Taiwan), and a gas separator connected to the anode outlet. The membrane electrolysis cell included an anode and a cathode semi-cell with an active membrane surface area and channel height of 200 cm^2 and 0.2 cm, respectively. The anode and cathode materials were galvanised titanium and type 316 stainless steel, respectively. The flow rate of the anode (feedstock) and cathode (water) semi-cells can be independently controlled within the range of 18–1200 mL/h by the peristaltic pumps. The programmable power supply is capable to deliver up to 18 A (equivalent to 900 A/m^2) at the maximum voltage of 20 V (DC). The gas separator divided the processed brine solution from the chlorine gas.

At the beginning of each membrane electrolysis experiment, the anode semi-cell was filled with the brine solution and the cathode semi-cell was filled with Milli-Q water. The anode and cathode flow rates as well as the current were then adjusted to

Table 1
Physical properties of selected salts.

Salt	Molecular weight (g/mol)	Solubility at 25 °C (g/L)	Conductivity of 10% (wt/wt) brine at 25 °C (mS/cm)
NaCl	58.44	362	130
NaHCO_3	84	105	55
Na_2CO_3	106	307	79

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