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SWRO brine reuse by diaphragm-type chlor-alkali electrolysis to produce alkali-activated slag

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HIGHLIGHTS

- SWRO discharge brine was electrolyzed to make mild alkaline solution.
- Maximum 3.3 wt% NaOH solution was obtained through electrolysis of SWRO brine.
- Electrolyzed brine and GGBFS were mixed to make solid alkali-activated product.
- Maximum 15.3 MPa of compressive strength was obtained on day 28 cured specimen.

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ABSTRACT

Seawater desalination generates concentrated brine, which may pose a threat to marine ecosystems upon discharge into the ocean. This study was conducted to evaluate possibility possible novel approach for electrochemical post-treatment of seawater reverse osmosis (SWRO) discharge brine and reuse without further additional brine enrichment processes. A synthetic brine and real brine from a SWRO plant were electrolyzed under controlled conditions to obtain a mild alkaline solution using a diaphragm-type chlor-alkali cell. Under a 100 mA/cm^2 current density and 37.5–45 min of hydraulic retention time (HRT), a maximum NaOH concentration of 3.3 wt% was obtained from real SWRO brine (initially 1.7–1.9 times the salinity of seawater) with 63% chloride removal via electrolysis. In electrolyzed brine reuse, a solid alkali-activated slag (AAS) product resulted from mixing 3.5 and 2.0 wt% NaOH alkali effluents (as an alkaline activator of slag) produced via electrolysis of synthetic brine and ground granulated blast furnace slag (GGBFS) from steelworks. For the specimens cured for 3–28 days, relatively high compressive strengths of 12.9–15.3 MPa and 9.8–11 MPa, respectively, were obtained.

1. Introduction

Seawater desalination is an effective technology for obtaining fresh water and is currently widely used, especially in coastal areas. Concentrated brine is inevitably produced through all desalination processes. Among several brine disposal methods, the ground processing methods such as deep well injection, land applications, and evaporation ponds have inherent limitations of soil and ground water contamination. Although challenging research for brine reuse such as microbial cultivation for nutrient removal in SWRO brine environments [1], process combination between chlor-alkali and fuel cell [2] have been conducted, most of the concentrated brine produced is discharged into seawater or sewers (approximately 80%) [3–4]. However, this discharged concentrated brine is a threat to marine ecosystems because of the higher temperature [5] and salinity compared to natural seawater [6]. Specifically, in reverse osmosis, which is the most common method of fresh water production, the discharge concentration is 1.3–1.7 times that of natural seawater [7–9]. Abdul-Wahab et al. reported that concentrations of discharged brines are usually double or close to double that of natural seawater [10–11].

Because concentrated brine has high electric conductivity in proportion to the salinity, which shows high reuse electrolysis potential, this study used the electrolysis method (chlor-alkali process) to treat and reuse concentrated brine.

The chlor-alkali process is applied via three methods involving a membrane, a diaphragm, and mercury. Among these techniques, the diaphragm method produces a dilute and impure alkaline solution compared to the other methods; however, it offers several advantages in the application of concentrated seawater. The diaphragm method operates at a lower voltage than mercury cells, avoids mercury discharge problems, and requires less pure brine than membrane cells, thus reducing the burden of brine pretreatment, especially if real seawater brine is used. For these reasons, the diaphragm method was applied in this study.

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As an electrolysis product, the alkaline effluent was produced from saline water, and it has meaningful industrial purpose for obtaining NaOH [12]. If a saturated NaCl solution is used in a commercial diaphragm-type chlor-alkali plant, up to 10–12 wt% NaOH can be produced [13].

GGBFS, an industrial byproduct, is a major aluminosilicate material with latent hydraulic properties and is the most frequently studied alkali-activated binder. The possibility of alkali-activated slag (AAS) products was first reported in the 1940s by Purdon [14].

In the field of construction, GGBFS has been used with Portland cement as a sustainable pozzolanic construction material [15]. GGBFS is activated by alkali and calcium components generated by Portland cement hydration [16]. However, when using GGBFS without Portland cement, alkalis (such as NaOH or KOH), aluminates or silicates are generally used to activate aluminosilicate precursors to produce an alternative binder such as cement [14,17], termed AAS. More specifically, alkaline activation of slag produces a calcium-silicate-hydrate, aluminum-modified calcium silicate hydrate, or sodium-alumino-silicate-hydrate gel as the reaction product, with a polymerization process after dissolution of minerals (mainly, SiO_2, CaO, MgO and Al_2O_3) at alkaline environments, commonly 6–12% of NaOH [16,18–24].

This reaction has several advantages including the consumption of industrial by-products (GGBFS) through production of an alkali-activated product without CO_2 emission, reduced expansion and faster curing speed compared to ordinary Portland cement [14,25], which also hardens in an alkaline environment due to the same pozzolanic reaction. If desalination brine is converted to an alkaline solution (as an alkali activator) by electrolysis and used successfully with industrial by-products, it can be utilized as an economical construction material.

Presently, most chlor-alkali plants utilize synthetic saturated NaCl solutions. A few researchers have been reported the electrolysis of natural seawater such as Dead Sea brine for electrochemical generation of active chlorine [26], electrolysis of the East-Sea of Gijang, Jumunjun, Gangneung (Korea) for formation of free chlorine, bromate, and chlorate [27–29], electrolysis of Western Australia seawater for biosensor use [30], and Bohai seawater (China) for hardness pretreatment [31]. However, most prior studies used artificial seawater for experimentation and the electrolysis of concentrated brine from a seawater desalination plant including further brine enrichment process has been reported by only a few researchers [9,32–33] because producing a high alkali concentration via electrolysis was not possible due to relatively low salinity and existence of hardness components, which require pretreatment such as hardness removal and brine enrichment process. Nevertheless, proper levels of alkaline solution are expected to yield approximately 3% NaOH, which is adequate for forming the alkali-activated product using GGBFS. Thus, in terms of both industrial waste slag and concentrated brine reuse, the electrolysis method would be effective despite low efficiency compared to commercial chlor-alkali plants due to low brine salinity.

In this study, an alkaline solution was produced using diaphragm-type electrolysis of concentrated brine as an alternative to brine discharge and GGBFS was mixed with the resulting alkaline solution to induce an alkali-activation reaction. Electrolysis cell characteristics of synthetic concentrated brine, which was created using the ASTM D 1141 standard [34], and seawater desalination brine were evaluated to determine the total process feasibility, including the strengths of the AAS product for use in construction materials.

2. Materials and methods

2.1. Brine characteristics and source material for alkali activation

Three types of brine were used in this study. The real seawater brine sample was collected from the SWRO desalination plant of POSCO Gwangyang Steelworks, Korea. The sampled brine represented seawater concentrated 1.7–1.9 times and up to 4.2–4.6 times with respect to the hardness of magnesium and calcium (Table 1). ASTM D 1141 as a standard practice for the preparation of substitute ocean water was referenced to create 2.4-fold concentrated seawater as synthetic brine using guaranteed reagent-grade components (Junsei, Japan). Table 2 shows the chemical composition of the synthetic brine. Specifically, for the alkaline effluent production discussed in Chapter 3.5, 1.14 M of synthetic NaCl solution was used.

Table 1
Characteristics of the seawater brine samples from desalination plant of POSCO Gwangyang steelworks in Korea.

Parameter	Value
pH	7.6
Electric conductivity (mS/cm)	85–86
Chloride (mg/L)	32,600
Sulfate (mg/L)	5050
Magnesium (mg/L)	6100
Calcium (mg/L)	1760

The source material of alkali-activated product was GGBFS obtained from POSCO Steelworks in Korea, which satisfied the micropowder class III requirement according to KS F 2563 of Korean industrial standards [35]. The chemical composition of the GGBFS is shown in Table 3.

2.2. Electrolytic cell configuration

A modified symmetric filter-press type of electrolytic cell (Greentech, Korea) was constructed according to a previous study [12, 36] using a rectangular parallelepiped acrylic resin resulting in an effective total cell volume of 150 to 180 mL. Silicon pads were used at every connecting edge to prevent leakage. Plate-type titanium electrodes (surface area: 47 cm^2, Wookyoung Electrolysis System, Korea), coated by immersion with IrO_2 to a 3 μm thickness, were selected due to ease of supply and price of the platinum-group element. The anode is dimensionally stable and has good electrochemical properties as a transitional metal oxide anode, including excellent thermal stability, corrosion resistance, and low overpotentials for chlorine evolution [37–40].

The electrodes and diaphragm were installed symmetrically in the middle of the cell. The distance between the electrodes was 5 mm. A non-asbestos hydrophilic PTFE filter (JCWP09025, pore size and thickness: 10 and 85 μm, respectively, Merck Millipore, Germany) was used to separate the cell compartments.

A power supply (DCS55-55E, Ametek, USA) was used to simultaneously apply a fixed current to the electrolytic cell and measure the voltage change in each experiment. A peristaltic pump and silicon tubing (Easy-load® II and Masterflex®, Cole-Parmer) were used to feed the brine uniformly to the electrolytic cell. To prevent accidents caused by chlorine leakage, experiments were conducted in a fume hood or using a movable air purifier (TOGA-M01, GTSciEN, Korea). All aqueous solutions were made using deionized water and the experiments were performed at room temperature.

Table 2
Chemical composition of synthetic brine according to the ASTM standard.

Compound	Concentration (mg/L)
NaCl	58,870
$MgCl_2$	12,480
Na_2SO_4	9820
$CaCl_2$	2780
KCl	1670
$NaHCO_3$	480
KBr	240