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Mathematical modeling of a three-compartment electro-reactor process with ion-exchange membranes for recycling and resource recovery of desulfurization residuals

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ABSTRACT

A mathematical model of a three-compartment electro-reactor process with ion-exchange membranes for recycling and resource recovery of desulfurization residuals was developed. This model describes the electrochemical separation process in the bulk solution and the diffusion boundary layer close to the membrane surfaces with a multiphysics-based approach. This approach considered the following mechanisms: diffusion and migration in different control volumes, the effect of bubbles, the effect of the geometry of the reactor, and the electrochemical reactions of the gases. The analytical solution to the developed model was obtained using a Laplace transformation, and the numerical solution was solved in Wolfram *Mathematica* and COMSOL *Multiphysics*. All analytical solutions exhibit a good agreement with the numerical solutions. The analysis of the model revealed that the following parameters may have a positive effect on the performance of the electro-reactor: (1) a high concentration gradient across the membrane enhances mass transport; (2) the current density is the key controlling parameter for both mass transport and bubble formation; (3) a small gap in the cell spacer may improve the performance of the reactor; (4) appropriate effective areas of the membrane for mass transfer guarantees high performance.

1. Introduction

One of the first air pollutants to be significantly investigated was sulfur dioxide. Sulfur dioxide is linked with a number of adverse effects on the respiratory system, environment, and building materials. The largest anthropogenic sources of sulfur dioxide emissions are from electric utility fuel combustion (69.7%) and industrial fuel combustion (13.6%) [1]. To achieve the effectiveness of the control of SO_2 emissions, precombustion and postcombustion desulfurization technologies have been employed in commercial units. Among these technologies, the methods referred to as flue gas desulfurization (FGD) or scrubbing processes are widely applied to control SO_2 emissions from power plants worldwide [2].

In the FGD processes, one of the greatest challenges is the large amounts of waste sludge after SO_2 absorption. These waste sludges may exist in a wet slurry or dry powders depending on the FGD process used. The sludge generated in the process of wet scrubbing is typically a dewatered mixture of sulfite and sulfate with unreacted sorbent and water, while the dry-FGD sludge is usually composed of three typical components: (1) the desulfurization reaction product, which is usually sulfate; (2) the unreacted sorbent; and (3) coal combustion ash with some undesirable trace elements (e.g. As, Cd, Cr, Ni, Pb, and Se) [3,4]. In China, it is estimated that approximate 530 GW thermal power unit installing FGD facilities will be in service by 2020 and about 90 million tons of waste sludge will be produced per year [5,6]. Thus, the waste sludge, otherwise called FGD residuals or desulfurization residuals, should be disposed or reused in an appropriate way to minimize environmental concerns and enhance beneficial purposes. Generally, desulfurization residuals can be utilized in certain chemical processes such as conserving existing natural resources [7–9] or manufacturing building materials [10,11]. Electrodialysis with membranes, a technology which is based on a concept of green chemistry, can realize new synthesis processes to achieve the reuse and recycling of resources and prevention of pollution [12]. This paper proposes an environmentally friendly method for electrochemically regenerating the alkali-sorbent (NaOH), recovering sulfur from the flue gas as H_2SO_4, and producing H_2 as a clean energy source from FGD residuals in a three-compartment electro-reactor with ion-exchange membranes. This electrochemical process is a feasible method to utilize desulfurization residuals with little or no secondary pollution because the only reagent is electrons [13]. However, a chemical process usually occurs in conjunction with the transfer of mass, heat, and momentum, which behaves differently in the laboratory, pilot plant, and during production (a large scale). For this reason, chemical engineers try to simulate the chemical processes in models which assist in the design and scaling of the reactor [14]. Therefore, a model must be

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developed to gain a deeper understanding of the proposed electrochemical process for the recycling and resource recovery of desulfurization residuals.

In the literature, several models have been developed to describe the behavior of an electromembrane reactor for different chemical processes. Van der Stegen et al. [15] presented a mass transfer model to describe the transport in ion-selective membranes used in a chloralkali electrolysis process based on the Maxwell–Stefan theory. The predictions of this model agreed with the experimental results of a pilot plant electrolyser. However, the main problem in the application of this model is a lack of available diffusivities for the membrane. Chen and Tilak [16] developed a simple model for an electromembrane reactor based on the Nernst–Planck equations, which can be used to describe the effect of the operating conditions on the caustic quality produced. Lu et al. [17] developed a mass transport model by considering the voltage equation across the stack to simulate a modified two-phase electro-electrodialysis process for recovering lactic acid. Although the simulated results closely matched the experimental data, this model is a relatively simple mathematical model without accounting for several physical states of the electrolyser such as emulsion changes during processing. A model that is basically composed of water and solute mass balances coupled with the voltage equation was developed by Fidaleo and Moresi [18] to indicate several critical aspects in the electrodialytic recovery of sodium lactate. This method mainly focuses on the electromigration by neglecting the contribution of solute diffusion and requires many sequential experiments to assess the main engineering parameters. Several additional complicated models based on statistical theory [19,20] and artificial neural networks [21,22] have been presented in recent years.

Compared to those models mentioned above, a multi-physics model allows for a better understanding of the mechanisms of a certain chemical process and would give an appropriate solution to a better design of the reactor under different operating conditions [23]. A mathematical model is also a powerful method to obtain optimal operating parameters and analyze their effects on the performance of the reactor since it can reduce operating costs for experimental trials. In order to represent the electrochemical process in this study, a model that corresponds to the key characteristics of the designed electro-reactor was developed. The numerical solutions were obtained using the commercial software packages *Mathematica* and *Comsol*, and were subsequently validated for a wide range of operating parameters by comparing with the analytical solutions and experimental data, which verified the capability of the developed model. The approach presented in this work is more general and accounts for electrochemical, geometrical and bubble formation phenomena.

2. Model development

2.1. Principle of the electro-reactor process

As an efficient and environmental friendly method for the disposal of desulfurization residuals, a three-compartment electro-reactor with ion-exchange membranes was designed to electrochemically regenerate the alkali sorbent recycled in FGD processes, simultaneously producing sulfuric acid, hydrogen, and oxygen as profitable byproducts. Fig. 1 shows a schematic diagram of the designed reactor consisting of a titanium cathode and a Ti based dimensionally stable anode (DSA). The catholyte and anolyte are separated by ion-exchange membranes (IEMs). As shown in Fig. 1, the Na^+ and SO_4^{2-} in the middle compartment migrated through the cation-exchange membrane (CEM) and anion-exchange membrane (AEM), respectively, when a constant current density was applied by a DC power supply. The hydrogen and oxygen evolution reactions are the main electrochemical reactions occurring on the cathode and anode, respectively, as shown in Eqs. (1) and (2). The overall reaction, shown in Eq. (3), is the electrolysis of water.

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow \quad (1)$$

$$\text{Anode}: 2H_2O \rightarrow 4H^+ + O_2\uparrow + 4e^- \quad (2)$$

$$\text{Overall reaction}: 2H_2O \rightarrow 2H_2\uparrow + O_2\uparrow \quad (3)$$

For this electrochemical process, a number of critical aspects should be considered to achieve a high performance in the reactor. These aspects include the voltage distribution linking with the electrical resistances, activation barriers of the electrochemical reactions occurring on the surfaces of the electrodes, availability of the electrode surface area that is partially covered by bubbles formed by hydrogen and oxygen evolution reactions, and operating parameters. Therefore, a complete description of this electromembrane reactor requests a multi-physics model to better comprehend the process. However, the developed model should not be too simple (neglecting detailed behavior of the electromembrane reactor) nor too complicated (requiring complex computations) [24]. A model that corresponds to all characteristics of

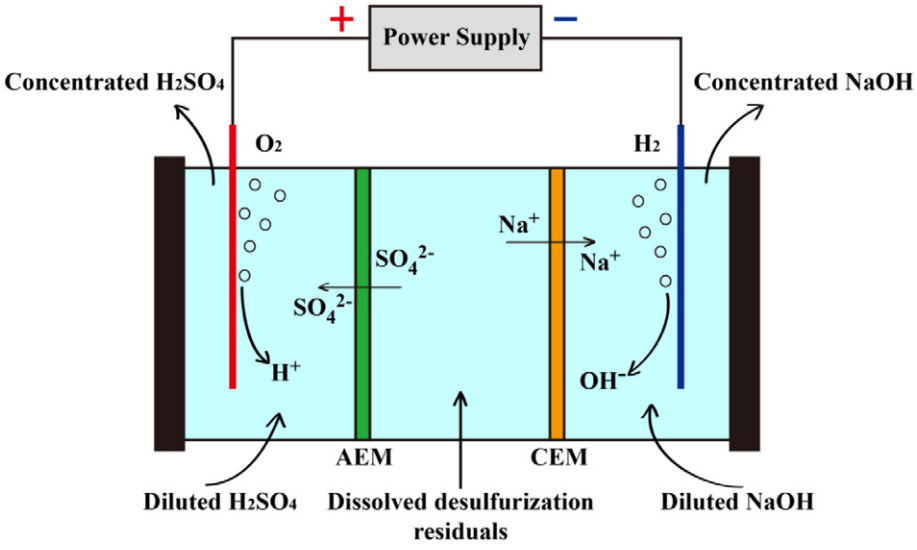

Fig. 1. Schematic diagram of the electromembrane reactor.