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TOWARDS ELECTRIFYING CEMENT PRODUCTION BY ELECTROCHEMICALLY-ENHANCED DISSOLUTION OF CACO3 DURING WATER ELECTROLYSIS UNDER A PH-GRADIENT

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ABSTRACT

The cement industry, which accounts for 7-8% of worldwide CO_2 emissions, is essential to decarbonize but challenging especially due to its high process emissions, high temperature heat requirements and low maturity of decarbonization solutions. A new electrochemical path to produce calcium hydroxide, a precursor of cement, has been proposed recently. This technology is based on a new design of a water electrolyser working in tri-phase environment. It has the potential to electrify cement production while at the same time producing valuable gases, but is still at a very early stage of development (TRL-3). In this paper, lab-scale experiments in a 200mL cell were performed to have a better understanding of the electrochemical system. The development of a pH gradient between the anode and the cathode has been quantified for different electric charges applied. Due to acidification of the anode side, the dissolution of calcium carbonate is enhanced. A solubility ten times higher than at neutral pH has been observed. At the same time, the migration of Ca^{2+} and OH^- ions to respectively the cathodic and anodic side has been demonstrated as well, thereby opening the way for an electrochemically-enhanced $Ca(OH)_2$ precipitation.

Keywords: electrolysis, electrification, cement, hydrogen

INTRODUCTION

In the race to decarbonize our society, reducing emissions from the industrial sector (32% of total greenhouse gas emissions [1]) appears as one of the major challenges to take on. The industry is known as a “hard-to-abate emission” sector due to high-temperature heat requirements, process emissions, long-lived capital assets and trade considerations [2]. This paper focuses on the decarbonization of cement production - one of the three main industries along with steel and chemicals. The cement sector accounts alone for about 7-8% of total CO_2 emissions, so that cutting these emissions is essential to tackle climate change [3-5,7]. Among these emissions, around two third are due to the calcination reaction of limestone. These process emissions make it more challenging to achieve carbon neutrality [4-7]. Several decarbonization technologies are being studied such as carbon capture, electrification, fuel and raw material substitution [2-4].

In 2019, Ellis *et al.* proposed a new electrochemical path for cement synthesis. By taking advantage of the pH gradient established during water electrolysis in an initially neutral medium, limestone ($CaCO_3$) can be decarbonated and the dissolved Ca^{2+} further precipitated as hydrated lime ($Ca(OH)_2$). This calcium hydroxide can then be used directly for its own industrial applications or to produce alite, the major phase of conventional cement. The concentrated gaseous carbon dioxide produced can be easily collected at the outlet while hydrogen and oxygen can be used to generate power for other steps or valued in their respective markets. With the emergence of low-cost renewable energy, this new technology could allow for the production of calcium hydroxide and cement with nearly zero emissions and at a competitive cost [8].

The aim of the current paper is to go further in the understanding and optimization of this new electrolyser design in a triphase environment in order to evaluate its potential on an industrial scale.

ELECTROCHEMICAL SYSTEM

The electrolyser is divided into three compartments. At the anode, the oxidation of water (reaction 1 in Fig.1A) produces oxygen and H^+ ions. Solid calcium carbonate inserted at the anode has a low solubility (14.31mg/L at 25°C [9]). Its decomposition (reaction 4) in neutral water is weak. Thanks to the generated H^+ ions in the anodic environment, the carbonate dissolution equilibrium is modified (cf Fig.1B) and CO_3^{2-} ions react to stabilize as CO_2 (reaction 5) for a pH lower than 6.4 [10]. The chemical dissolution of $CaCO_3$ is thereby further enhanced by the release of gaseous CO_2 and by the migration of Ca^{2+} ions towards the cathode. Besides CO_2, also O_2 is being collected at the anodic side. At the cathode, hydrogen gas and hydroxide ions are produced by water reduction (reaction 2). The hydroxide ions will make the medium alkaline and will naturally migrate towards the anode. In the central compartment, the different migrated ions (H^+, Ca^{2+} and OH^-) react together (reaction 3 and 6),calcium hydroxide precipitation being favoured at pH >12.5 [8].

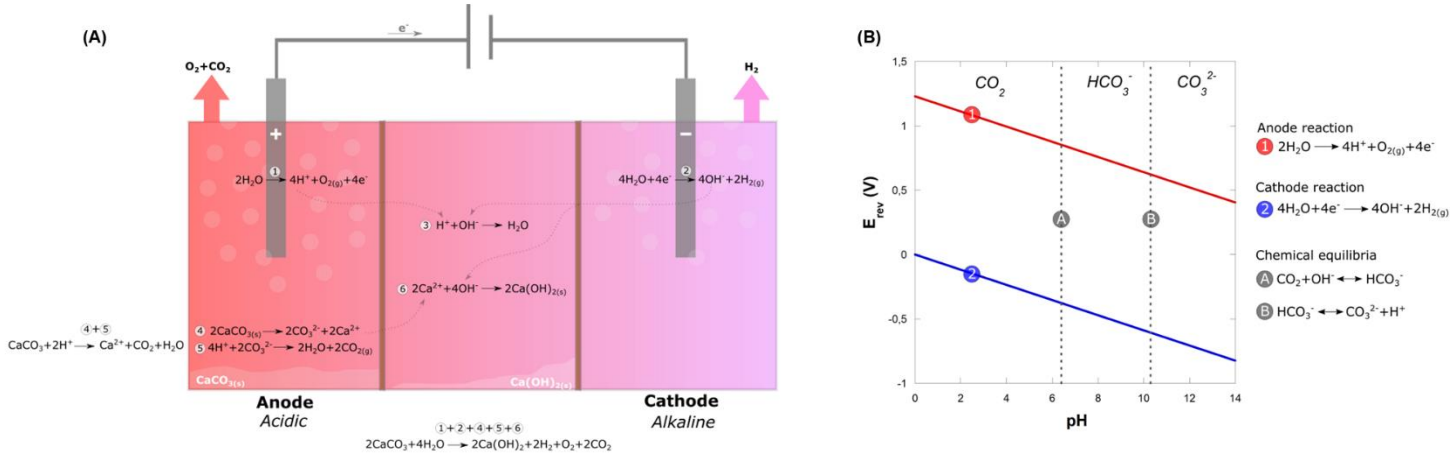

Figure 1. (A) Electrochemical system and chemical reactions (B) Pourbaix diagram for water electrolysis and carbonate equilibria

MATERIALS AND METHODS

Experiments were performed in a H-type cell (200mL, Adams & Chittenden Scientific Glass) at room temperature. The electrolyte used is a 1M $NaNO_3$ (Sigma-Aldrich BioXtra, >99%) solution in ultra pure water (18.2MΩ/cm). The physical separations used to divide the three compartments are paper filters (VWR, 516-0818). Electrodes are platinum foils. The potentiostat used (AUTOLAB, Methrom) is equipped with a booster (allowing to go up to 10A) and two continuous pH readers. Two types of one-hour experiments have been carried out: a galvanostatic set of 6 experiments between 2.5-4.5V and a potentiostatic set of 7 experiments between 0.007-0.06A. For each experiment, 50mg of calcium carbonate (Sigma-Aldrich BioXtra, <99%) are initially inserted on the anodic side. ICP-AES analysis were performed to quantify the Ca^{2+} ions in solution.

RESULTS AND DISCUSSION

Figure 2A clearly illustrates the establishment of a pH gradient between the anodic and cathodic compartments. The higher the electric charge, the more the gradient becomes important. The theoretical pH value shown in Figure 2B is obtained as the value for which all the current applied is converted into H^+/OH^- while assuming that none of these ions will react or move from their respective compartments. As it can been seen, the difference between the theoretical and real pH is more pronounced on the anode side, essentially since H^+ are being consumed by reaction with CO_3^{2-} (reaction 5 in Fig. 1A).

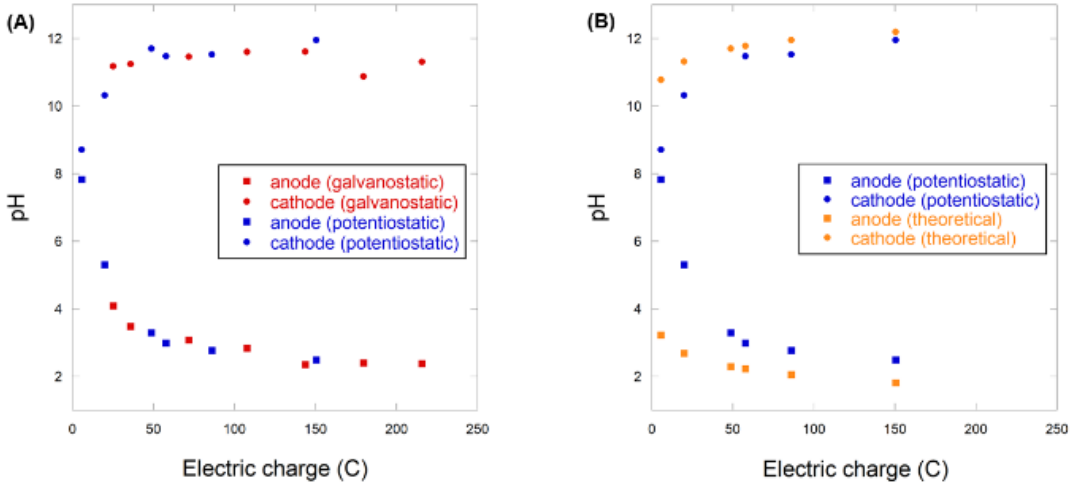

Figure 2. (A) Final pH obtained in anodic and cathodic compartments for a defined electric charge applied in one hour (B) Comparison between final pH obtained and theoretical value expected (potentiostatic experiments only)

Figure 3A shows the amount of Ca^{2+} in solution at the end of the experiments as a function of electric charge. Although all calcium is initially inserted at the anode as $CaCO_3$, a small quantity is found at the cathode as well due to its electrical field induced migration. The total amount increases as a function of the applied electric charge until it reaches a plateau. Indeed, the higher the charge, the lower the pH will be at the anode (cf Fig. 2A). A lower pH will ease the dissolution of $CaCO_3$ due to carbonate equilibrium modification as explained previously. This is illustrated on Figure 3B. The maximum amount found in solution is 13 mg out of a total of 20mg initially inserted. This amount corresponds to a solubility of 126mg/L in the anodic side, which is almost ten times higher than the solubility at neutral pH [9]. The remaining 7mg can be either in the form of undissolved $CaCO_3$ or in the form of $Ca(OH)_2$.

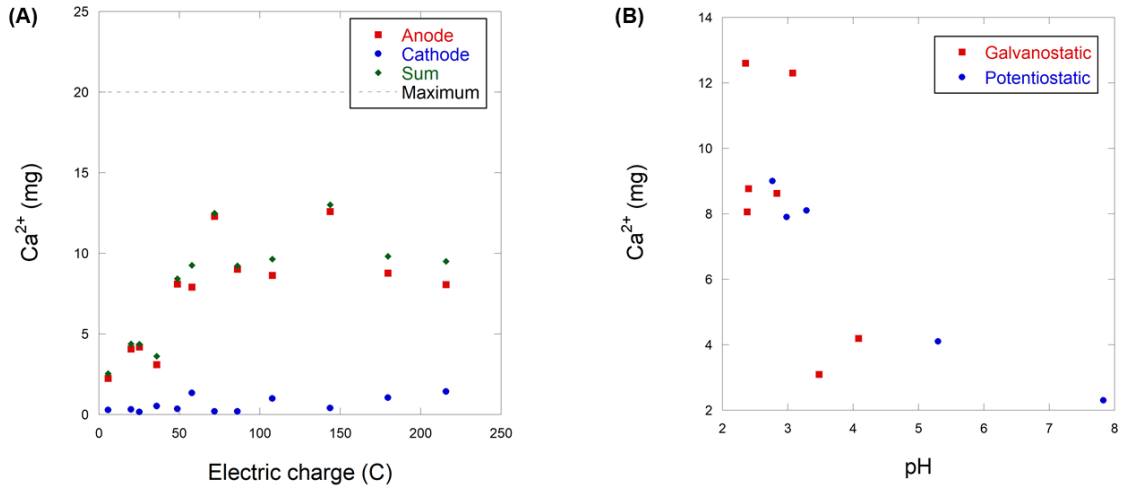

Figure 3. (A) Final mass of Ca^{2+} ions in solution in anodic and cathodic compartments for a defined electric charge applied in one hour (B) Final mass of Ca^{2+} ions in solution in anodic side vs anodic final pH

CONCLUSIONS

During neutral water electrolysis, the development of a pH gradient between anode and cathode has been demonstrated and quantified. This gradient increases with the electric charge applied. The gradient observed is lower than expected due to ion migration, reaction between H^+ and CO_3^{2-} and other potential side reactions. Due to acidification of the anodic compartment, the dissolution of calcium carbonate is favored until a maximum observed solubility of 126mg/L, ten times the value in neutral water at 25°C [9]. The migration of Ca^{2+} and OH^- ions towards the central compartment has been demonstrated as well. This migration is necessary for the production of calcium hydroxide.

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