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Electrodialysis of highly concentrated brines: Effects of calcium

Thomas D. Hayes^a, Blaine F. Severin^{b,*}^a Gas Technology Institute, Des Plaines, IL 60018, United States^b Environmental Process Dynamics, Inc., Okemos, MI 48864, United States

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ABSTRACT

Electrodialysis (ED) is an electrochemically driven membrane technology that is usually used for treating feed water containing several thousand mg/l total dissolved solids (TDS). This research investigated the use of ED for the treatment of flowback water from shale gas hydro fracture. Shale brines contain tens of thousands of mg/l TDS and contain a mixture of multivalent cations, such as calcium, magnesium, barium, strontium, radium, iron, and manganese. This paper covers efforts undertaken to mitigate problems associated with high concentrations of calcium (4000 mg/l) in the presence of 30,000 mg/l NaCl. Eight baseline ED tests were performed with sodium chloride. Seven additional runs were designed to understand the effect of calcium on the electrodialysis process. Initial tests showed strong incursion of calcium into the electrolyte using a CMX barrier membrane. The apparent calcium fouling (in and around) the electrode cells was indicated by a rapid degradation of process efficiency, observed as a decrease in current. The single cathode boundary membrane was replaced with a membrane that was more selective against multivalent cations (CMX-S). Calcium flux into the electrolyte was reduced by 47–73% and the ion flux from the concentrate to the diluate improved by approximately 40% compared to the baseline. Additionally, the replacement of the single cathode boundary membrane imparted an apparent immunity to direct fouling by addition of calcium directly into the electrolyte.

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1. Background

This project was a part of a larger investigation into the quantity and quality of the flowback water and produced water from shale gas hydraulic fracture processes, and the alternatives available to maximize the reuse of recovered water, minimize the volume of deep well disposal, and reduce the cost and environmental impact associated with the disposal of flowback and produced water [5]. As part of this project, we investigated the potential to utilize electrodialysis (ED) for partial treatment of these types of saline waste water [13]. We approached the investigation from the standpoint of providing (1) acceptable power utilization (0.22–0.33 kW h/kg salt) using standard equipment, (2) insights into means of minimizing equipment size (area of membrane), and (3) means of overcoming difficulties, either anticipated or encountered in the field. These goals led the research down one path that included (1) methods to maximize salt transfer by changing the ionic strength and pH of the electrolyte rinse solution [11], (2) mitigation of calcium incursion into the catholyte (this paper), and mitigation of problems associated with other multivalent cations [12]. In follow-

ing this research path, we chose to solve the problems associated with calcium incursion into the electrolyte by using a more selective barrier membrane at the cathode cell boundary.

There has been some discussion in the literature about mitigating fouling by changes to the chemistry utilized as the electrolyte rinse solution. One such alternative is sulfamic acid. Sulfamic acid (HSO_3NH_2) is commonly used as an industrial cleanser and has some application in home cleanser products. Because sulfamic acid is a strong acid and relatively non-corrosive compared to sulfuric or hydrochloric acid, it has been evaluated as a descalant in large electrodialysis plants [10]. Due to the relatively higher solubility of calcium and barium salts of sulfamic acid [2] compared to the sulfate salts, sulfamic acid or its sodium salt has been suggested as an alternative electrolyte rinse solution to mitigate electrolyte fouling. Sodium sulfamate has been used in at least one study [3] instead of sodium chloride to limit corrosion of the electrodes. However, the solution concentration was not mentioned in the article. In another study, 0.05 M sulfamic acid was used as the electrode rinse solution in an ED application to recover Ni and Cu from plating wastes [16]. As part of our overall research effort to improve the ion flux in treating highly concentrated brines [13], we concentrated efforts on the electrolyte system (disodium sulfamate) recommended by the manufacturer of the ED pilot unit.

* Corresponding author.

E-mail address: bfseverin@hotmail.com (B.F. Severin).

Nomenclature

RFI	relative flux index, ratio of flux into electrolyte to flux into concentrate (%)	CBM	coal bed methane
Calcium rejection (%)	% calcium rejected at the cathode membrane (%)	ED	electrodialysis

Due to the relatively low solubility of sodium sulfamate and sulfamic acid and the relatively poor-conductive nature of the sulfamate anion [14] we contend that this would have been a poor choice for our research needs.

1.1. Hydraulic fracture of shale

The hydraulic fracture of shale formations for the capture of natural gas melds decades old hydro fracture technology with new advances in horizontal drilling. Work on North American shale formations, such as the Barnett and the Marcellus, has demonstrated the potential to capture trillions of cubic feet of high value gas. During the fracture process, between 1 and 5 million gallons (4000–19,000 cubic meters) of water and sand are expended “down hole” into each well to aide in the fracture. A portion of this water (termed flowback) is recovered during the initial extraction of the gas. As the well matures, it continues to generate low volumes of concentrated brine (termed produced water). The recovered fluids contain high concentrations of complex mixtures of dissolved salts, plus trace concentrations of residual antioxidants and lubrication fluids. Therefore, recovered flowback water presents a disposal problem, of which there are presently few non-controversial disposal methods.

The range of TDS expected in flowback water and produced water encountered in the shale industry is several tens of thousands mg/l [5]. A number of problems were encountered that were systematically addressed as the project proceeded from the treatment of synthetically simulated flowback/produced water containing pure sodium chloride (30,000–60,000 mg/l) to the treatment of solutions with sodium, calcium (up to 4000 mg/l), barium (up to 400 mg/l), iron (up to 50 mg/l), and magnesium (up to 600 mg/l) [13]. This paper addresses some of the problems associated with calcium in the presence of sodium in carbonate poor water.

The ED process is typically operated on brackish water sources that are less concentrated than seawater [15]. Operation of ED under the high salt conditions of flowback and/or produced water places the process in a regime of relatively low electrical resistance, requiring lower voltage and allowing higher amperage (current flow) compared to the normal range of operation. This has led to an understanding of the relation between ion flux and applied voltage that allowed for a number of process improvements for operation in this regime [11]. Another challenge to the desalination of shale flowback water is the potential for process poisoning by soluble calcium and other multivalent cations. This challenge was addressed by other process improvements aimed at mitigating the effects of divalent cations on the electrolyte cell. For this portion of the development program, eight electro dialysis runs were performed with pure sodium chloride. Seven runs were dedicated to understanding the relation of calcium to the electro dialysis process. The effects of other multivalent cations are the topic of another paper [12].

1.2. Effects of calcium on electro dialysis

The adverse role of calcium on the duration of a process run was expected, and demonstrated. The chemical nature of flowback

water from 19 wells in the Marcellus Shale has been reported by Hayes and Severin [5]. The median total dissolved solids was about 67,300 mg/l with a with a median soluble calcium concentration of about 4950 mg/l. Importantly, the median calcium carbonate hardness of 17,700 mg/l as CaCO₃ was balanced against only 122 mg/l alkalinity as CaCO₃, implying that the majority of the hardness was soluble and balanced against the chloride ligand. The waters are typically devoid of carbonate species. Major contributions to this hardness were Mg (559 mg/l), Ba (686), Sr (1080 mg/l), and Ca (4950 mg/l). In these types of brine, the sulfate ion is also usually present in low concentrations. The barium content is dictated (inversely) by the relative concentration of sulfate. The concentrations of the various soluble salts are well above the usual range of operation of ED.

As an example of ED fouling experienced in complex waters, Kaakinen [8] experienced difficulty in treating water from two sources of hydraulic fracture flowback water. One source had a TDS range of 3200–3400 mg/l with calcium (7–18 mg/l) and magnesium (15–30 mg/l). The sulfate concentration was about 980 mg/l balanced against 1160 mg/l chloride. The second source had a TDS range of 9140–9180 mg/l, with calcium (35–60 mg/l) and magnesium (52–55 mg/l). The sulfate concentration was about 2040 mg/l with 3660 mg/l chloride. The author attributed membrane fouling in the concentrate stream to gypsum-like precipitation, and recommended that either the water be pretreated with chemical precipitation to remove divalent cations, or treated in parallel with ion exchange.

Bazinet and Araya-Farias [1] studied the fouling of calcium on cation-selective membranes (CMX-S) in a two cell (three membrane) ED unit in which a model solution containing potassium and calcium at pH 11–12 was desalinated into a solution of sodium chloride at pH 11–12 across a cation selective membrane. The process was meant to mimic application of ED to the food industry (milk purification). They observed no fouling using either 400 or 800 mg/l solutions of calcium chloride in the absence of carbonate in the model solution, but fouling occurred with 400 mg/l calcium chloride in the presence of carbonate (1000 mg/l Na₂CO₃). The fouling material appeared to be calcium hydroxide, which was easily cleaned with an acid rinse. They surmised that the carbonate slowed the treatment time sufficiently to allow increased incursion of calcium across the selective cationic membrane.

Firdaous et al. [7] investigated commercially available monovalent cationic perm-selective membranes for the separation of calcium and magnesium salts from sodium using electro dialysis. They performed systematic research into the ionic competition that can occur at the membrane surfaces due to ionic radii, hydrated radii, and hydration energies. With perm-selective membranes they reported that in solutions with sodium, magnesium, and calcium salts that the relative flux was $J_{Na} > J_{Ca} > J_{Mg}$. However, the presence of calcium abates sodium transport by as much as 33%, whereas, the presence of sodium has little influence on the rate of calcium transport. The interference of calcium and magnesium on sodium transport are attributed to the preferential occupancy of membrane transfer sites on the perm-selective by calcium and magnesium.

Hayes and Moon [4] examined the desalination of coal bed methane (CBM) produced waters using the same ten cell pilot

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