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A HYBRID ED/RO PROCESS FOR TDS REDUCTION OF PRODUCED WATERS

UN PROCÈS ÉLECTRODIALYSE/OSMOSE INVERSE HYBRIDE POUR REDUCTION DES SELS DISSOUS EN L'EAU "PRODUITE"

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ABSTRACT

Large volumes of produced waters are generated from natural gas production. In the United States the prevailing management practice for produced waters is deep well injection, but this practice is costly. Therefore minimizing the need for deep well injection is desirable. A major treatment issue for produced waters is the reduction of total dissolved solids (TDS), which consist mostly of inorganic salts. A hybrid electrodialysis/reverse-osmosis (ED/RO) treatment process is being developed to concentrate the salts in produced waters and thereby reduce the volume of brine that needs to be managed for disposal. The desalted water can be used beneficially or discharged. In this study, laboratory feasibility experiments were conducted by using produced waters from multiple sites. A novel-membrane configuration approach to prevent fouling and scale formation was developed and demonstrated. Results of laboratory experiments and plans for field demonstration are discussed.

RÉSUMÉ

L'extraction de gas naturel est accompagnée d'une grande quantité d'eau (nommeé l'eau "produite"). Les régulations ne permettent pas la décharge d'eau produite dans l'environment. Aux États-Unis, l'eau produite est reinjecter sous terre, un procès qui est très cher. Il est possible de décharger l'eau produite dans l'environment si les sels inorganiques dissolues sont réduits. Un procès électrodialyse/osmose inverse hybride est étudié qui a comme but de concentrés les sels inorganiques. Ce procès produit une petite quantité de liqueur-mère qui contient la majeur partie des sels. Ensuite, la masse d'eau produite peut être déchargé à l'environment ou être beneficielment utilise. L'encrassment de la membrane est diminuée par une nouvelle configuaration de la membrane utilisée. Ce procès a ete' étudié en laboratoire avec l'eau produite venant de plusieurs emplacements, et des plans de demonstration sous lieu seront présentés.

BACKGROUND

Large volumes of produced waters are generated from natural gas production. An estimated 5.4×10^{10} L of produced water were generated in the United States in 1990 from non-associated gas (NAG) and coal bed methane (CBM) production. Because of the large volume of produced water, the cost of its management could impact the profitability of the natural gas industry. Produced water is not a hazardous waste as defined by the Resource Conservation and Recovery Act (RCRA). Its disposal, nevertheless, is subject to various other regulations, such as those associated with the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA), depending on the method of disposal. Of the 5.4×10^{10} L of produced water generated in 1990, it was reported that 3.4×10^{10} L (63%) were managed by injection (Daly et al. 1992). The prevailing management practice for produced water is class II injection through enhanced oil recovery (EOR) and salt water disposal (SWD) wells. Other management options, including surface discharge, surface evaporation, land application, and off-site commercial disposal, are also practiced, but to a lesser extent. Whereas produced water from oil and associated-gas (AG) production are typically injected to SWD or EOR wells, NAG- and CBM-related produced water are more often injected into SWD wells.

The cost of injecting produced water through SWD wells is high, ranging from U.S. $3.15 to U.S. $11.02 per 1,000 L. Installing new SWD wells costs from U.S. $400,000 to over U.S. $3,000,000 per well and can be time-consuming for technical and regulatory reasons. With more stringent environmental regulations, this management option can be expected to become more difficult and expensive. Therefore, minimizing the need for deep well injection is desirable. Treatment of produced water followed by surface discharge or beneficial reuse of the treated water can be an attractive management approach. The major issue associated with the surface discharge or beneficial reuse of produced water is the reduction of total dissolved solids (TDS), which consist mostly of inorganic salts. The most abundant salt is sodium chloride, but other cations (such as potassium, calcium, magnesium, barium, etc.) and anions (such as sulfate, bicarbonate, etc.) can also be present at considerable concentrations. In addition, produced waters contain volatile and semivolatile organic compounds, including aromatic hydrocarbons and aliphatic petroleum hydrocarbons. These organic compounds may or may not be subject to environmental regulations. However, their presence can affect the feasibility of the technologies selected for TDS reduction, a consideration that needs to be addressed for the development of treatment technologies. The quantities and characteristics of produced waters vary widely. Compared with the NAG-produced water, the CBM-produced water is typically generated at a larger volume per well per day but contains lower concentrations of TDS. Even among the CBM- or NAG-produced waters, wide variations exist. Therefore, the feasibility of any treatment technology is expected to be highly case-specific.

Argonne's proposed treatment process for produced water is an integrated ED/RO process for TDS. A biological fluidized-bed reactor (FBR) that removes organics precedes the ED/RO process. The applications of these two membrane technologies, RO and ED, for produced water treatment, have been investigated by some researchers (Nakles et al. 1992; Simmons 1992; Kok 1993), but only to a limited extent and not as an integrated ED/RO process. RO is a pressure-driven membrane process that can concentrate the TDS from produced water into a retentate stream while producing a permeate stream that is sufficiently clean for discharge or reuse. The performance of RO is affected by the osmotic pressure of the process stream, which is proportional to the total concentration of the ionic and non-ionic solutes. In general, RO can concentrate a salt-laden water to one molar (e.g., 58.45 g NaCl/L) before cost of the treatment becomes prohibitive. ED is an electrical field-driven process that uses ion-exchange membranes for salt removal or concentration. ED is able to produce a highly concentrated salt solution by transporting dissolved salts from a solution on one side of the membranes to a concentrated salt solution on the other side of the membranes. For the production of table salt from sea water, a 20% (3.4 M) sodium chloride solution is generated from the sea water, which contains 3% (0.5 M) sodium chloride. Successful applications of ED are widespread in Japan. The scale of Japanese plants ranges from very large (over 2×10^{8} kg/yr) for table-salt plants to small-scale flavor extraction plants. Long membrane life (4 yr) has been established for several operations. Automated cleaning-in-place (CIP) techniques have been developed for specific applications to extend membrane life and to improve process consistency. Several ED membrane manufacturers have developed desalting ED membranes that are highly efficient and stable, moderately priced, and energy efficient (e.g., Japanese plants for desalting sea water consume 130—150 kWh/ton of NaCl). These new membranes are now available for process development and commercial applications. The biological FBR process developed by EFX uses acclimated microbial culture immobilized on granular activated-carbon support. The system has been demonstrated to be very efficient (capable of removing a high percentage of salt at a hydraulic retention time of several minutes) for treating waters containing aromatic and aliphatic organic compounds commonly associated with gas production operations. The system has also been shown to be effective even at the salt concentrations found in produced waters.

A schematic of the proposed process is shown in Figure 1. The produced water is first pretreated in the biological FBR to remove organics, then fed to the ED system. In the ED step, salt ions are removed from the produced-water feed and are transported through ion-exchange membranes into a concentrated salt stream. This concentrated salt stream is of a much smaller volume than that of the original produced water and, therefore, can be more easily and economically managed by deep well injection, surface evaporation, or off-site commercial disposal. The desalted produced water from ED is fed to the RO unit to generate a permeate that will be suitable for surface discharge or beneficial uses and a retentate that contains a re-concentrated salt stream that is recycled to ED for further concentration. This process combines ED and RO in a synergistic manner.

In field applications of the ED/RO treatment of produced water, it would be desirable to pump the produced water from several production wells to a central treatment site where the treatment system could be operated for long periods with minimal human intervention. Fouling is a potential problem for the long-term operation of all membrane separation processes. Proper integration of ED and RO can reduce the tendency of fouling, and CIP techniques can be practiced, as needed, to restore membrane performance. Long-term, unattended operation of the process can be accomplished by computer-based, on-line monitoring of process parameters, in conjunction with protocols for automated process operation and CIP procedures. Automated processing is common in several small- and large-scale ED plants in Japan and has been widely practiced for RO.

R&D PROGRESSES AND RESULTS

Scope and Objectives

This ED/RO process development work is being performed at Argonne National Laboratory (ANL) in collaboration with Gas Research Institute (GRI), Remediation Technologies, Inc. (ReTec), and EFX Systems, Inc. (EFX). GRI and ReTec manage the overall project, identify the treatment needs of produced water and potential technological solutions, and develop a knowledge base for the selection of the most promising treatment approaches for the specific situations of each produced water generator (i.e., gas producer). EFX applies its FBR technology for the removal of organics from produced waters. The principal objectives of the ED/RO work at ANL are as follows:

- Evaluate the applicability of the proposed ED/RO process with respect to the varying characteristics of produced waters generated at different gas production sites,
- Determine the technical and economical feasibility of the process with laboratory data,
- Develop and optimize the integrated ED/RO produced water treatment process at the laboratory scale, and
- Demonstrate the long-term process feasibility at selected gas production sites.

Major Technical Parameters

The major technical parameters that can critically affect the technical and economic feasibility of the ED/RO process are as follows.

- Brine volume reduction factor: The objective of the treatment is to reduce the volume of brine. The volume reduction factor is determined by the ratio of achievable TDS level in the concentrated brine to the TDS level of the produced water feed. For sodium chloride solution, the ED process has been shown to be able to generate a 20% brine. For produced waters that contain high levels of multivalent cations and anions, however, the maximum achievable brine concentration is also limited by potential membrane fouling or scale formation, as discussed below.
- Membrane fouling and scale formation: Salts of multivalent cations and anions (e.g., $CaSO_4$ and $CaCO_3$) often have very limited solubility in water. When produced waters are being concentrated, the sparingly soluble salts can precipitate in the brine solution or in the concentration boundary layer near the membrane at a high TDS level and cause scale formation or membrane fouling. In fact, precipitation of inorganic salts has been known to be a major problem for RO applications in produced water treatment. ED is inherently more resistant to salt precipitation. However, care must be taken in selecting the process conditions and cleaning-in-place protocols to prevent membrane fouling and extend membrane life. In addition, intelligent integration of ED and RO can reduce the overall problems of membrane fouling and scale formation.
- ED energy requirement: Besides the cost of replacing the membrane, the electricity cost of the ED step is a major operating cost. At a given current density, the ED energy requirement is proportional to the electrical resistance of the ED membranes and process solutions. The use of low-resistance membranes can significantly reduce the energy requirement.
- ED flux: The flux is proportional to current density and current efficiency. For a given salt removal rate, the size of the ED system required is inversely proportional to the flux. Because the capital cost of the ED system is a significant factor of process economics, it is important that the ED process can be operated at a reasonably high current density and current efficiency.

Laboratory Feasibility Experiments

Produced water samples generated at several sites were tested at ANL. Table 1 shows the characteristics of these samples. They varied widely not only in the TDS concentration, but also with respect to cation and anion profiles. For example, sodium chloride was the predominant salt in Sample C, whereas the sulfate concentration in Sample D was higher than the chloride concentration. Laboratory screening tests were conducted with these samples. Initially, only simple ED feasibility experiments were performed by using the produced water samples as received without biological FBR pretreatment or integration with RO. The experiments were carried out by using a laboratory ED system equipped with a Tokuyama TS-2 stack, which contained several pairs of anion- and cation-exchange membranes (usually 10 pairs) with an effective membrane area of 200 cm^2/sheet. The laboratory system used is a true process development unit (i.e., process data collected with this unit are directly scaleable to full-sized commercial systems). Membranes for each test were selected for their electrical resistance properties, compatibility with the solution to be desalted, and for their capability to separate the ions of interest.

In the batch-desalting mode, the ED process was started with a constant DC current applied to the stack. As dissolved salts were transferred from the produced water feed (diluting stream) to the brine (concentrating stream), the conductivity of the diluting stream decreased and the voltage drop of the stack increased until a preset upper limit was reached. The system was then switched into a constant voltage operation with decreasing current, until a low conductivity of the diluting stream was reached and the run was then stopped. The batch desalting experiments generated such feasibility data as the ED energy requirement, salt removal flux, and the compositions of the desalted water and concentrated brine. In addition to the batch experiments, membrane stability was tested in separate experiments with the recycle of the brine stream to the diluting stream for continuous operation up to 24 h, which is the expected interval for cleaning-in-place techniques.

The technical feasibility of ED desalting was demonstrated for all the produced waters tested. The significant findings are as follows:

- The ED process was shown to concentrate sodium chloride, the predominant salt in most produced waters, to about 18%, suggesting the potential of a significant volume reduction of the brine.

- There was no evidence of rapid fouling of the ED membranes, even without pretreatment for organic removal.

- Some migration of organics into the brine stream was observed. This observation suggests that some organics were able to enter the matrix of the ED membranes. Although this did not cause membrane fouling, the use of a biological FBR as a pretreatment to remove organics from the produced water before it enters the ED/RO system will prevent potential fouling of ED and RO membranes. The presence of organics in the concentrate should not be a problem, however, if brine disposal is managed by reinjection.

- The ED energy requirement was strongly affected by the selection of membranes. A membrane configuration using low-resistance membrane was found to reduce the energy consumption of ED by 20%.

- A novel approach to preventing membrane fouling of the ED/RO process was developed an demonstrated.

Process Simulation

A spreadsheet computer program is being developed to simulate the material balance of this ED/RO proces and to predict the potential of membrane fouling and scale formation. For a given composition of the produced wate feed, the program calculates the composition of each process stream on the basis of the TDS concentration factor an the membrane selectivity and compares these valves with the solubility of sparingly soluble salts to predict th potential of scale formation. Taking into account concentration polarization near the membrane surface, the prograr also predicts the potential for membrane fouling.

Process Economics and Sensitivity Analysis

In addition, a process costing model is being developed. The ED module of the model has been complete and used to calculate the ED processing costs, including the costs of the system depreciation, electricity consumptic (for stack and pumping), and membrane replacement. Sensitivity analyses were performed to predict the effects (technical parameters and process conditions (e.g., current efficiency, plant size, and salinity of the produced water fe and the desalted water) on the process economics. For a model system that has 5% TDS in the produced water fee the ED processing cost was estimated to be about U.S. $2.33/1,000 L. This cost compares favorably with the cos of alternative methods of produced-water management. The model is being expanded to perform cost estimation the integrated ED/RO process. The total costs of the ED/RO-based management method, including the costs

ED/RO, pre-treatment, and final disposal costs, should still be lower than or comparable with the cost of SWD well injection. However, the flexibility and reliability of this aboveground treatment process should it more attractive than injection, considering the intensive capital investment and uncertainties related to establishing new injection wells.

CONCLUSIONS

The laboratory experiments and economic analyses to date have demonstrated the technical and economic feasibility of ED desalting of produced waters. The characteristics of produced waters varies widely, and the optimal process conditions and membrane configuration will need to be selected accordingly. The laboratory work is being continued to integrate the ED process with the biological FBR and RO and to determine the long-term performance of the integrated ED/RO process. Cleaning-in-place techniques and automation protocols will be developed. A field demonstration is being planned to perform a slip-stream operation of the integrated FBR-ED/RO process at a gas production site, starting fall 1995 or spring 1996.

ACKNOWLEDGMENT

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Table 1. Characteristics of Various Produced-Water Samples

Analyses	Site A	Site B	Site C	Site D	Site E
pH, SU	6.4	7.6	7.2	7.2	7.4
Conductivity, mS/cm	67.0	12.6	18.6	33.7	75.4
Total Suspended Solids, mg/L	195	18.0	14	24	318
Fixed Suspended Solids, mg/L	–	12.0	8	15	110
Volatile Suspended Solids, mg/L	–	6.0	6	9	208
Total Dissolved Solids, mg/L	–	8,000	14,700	28,900	83,400
Oil & Grease, mg/L	–	98.4	< 5	< 5	< 5
Total Recoverable Petroleum Hydrocarbons, mg/L	–	243.0	1.1	73.5	695
TOC, mg/L	–	143.0	22.2	383	40.7
Chloride, mg/L	29,930	3,630	1,920	8,400	61,600
Sulfate, mg/L	1,500	6.9	10.6	9,290	6
Sulfide, mg/L	900	3.5	1.8	6.1	2.2
Fluoride, mg/L	–	2.4	0.92	0.77	0.88
Sodium, mg/L	15,400	2,640	6,200	8,600	23,600
Potassium, mg/L	306	48.2	24.0	66.0	146
Calcium, mg/L	2,010	18.9	22.10	284.0	1,900
Magnesium, mg/L	575	< 5	17.4	52.9	264
Barium, mg/L	–	10.1	27.2	< 0.2	21.5
Iron, mg/L	0.1	3.87	3.16	5.34	4.76
Total Alkalinity, mg/L	–	1,620	9,590	1,000	128
Carbonate Alkalinity, mg/L	–	0	0	0	0
Bicarbonate Alkalinity, mg/L	–	1,620	9,590	1,000	128
Total BTEX, mg/L	4.6	9.5	0.0326	41.4	161.5
Total TPH, mg/L	12.2	215.2	< 0.8	29.33	123.5

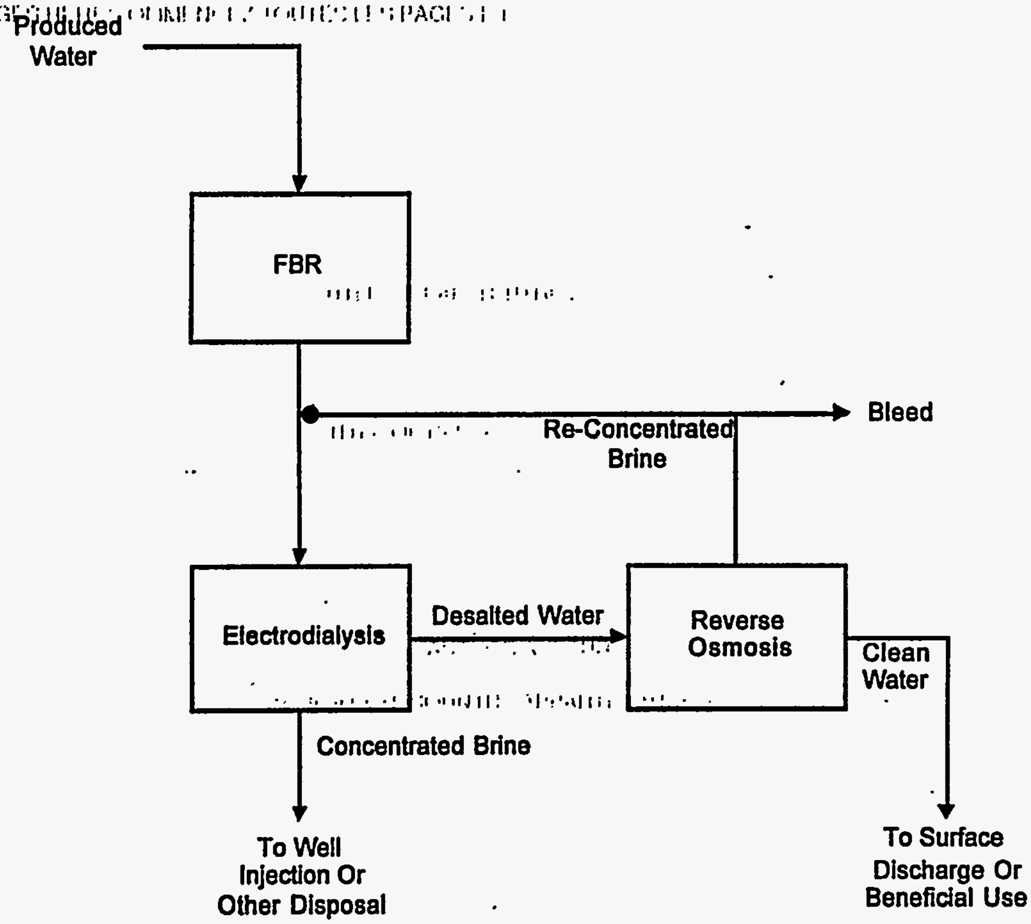

Figure 1. Schematic of the Integrated ED/RO Process for Produced-Water Treatment

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