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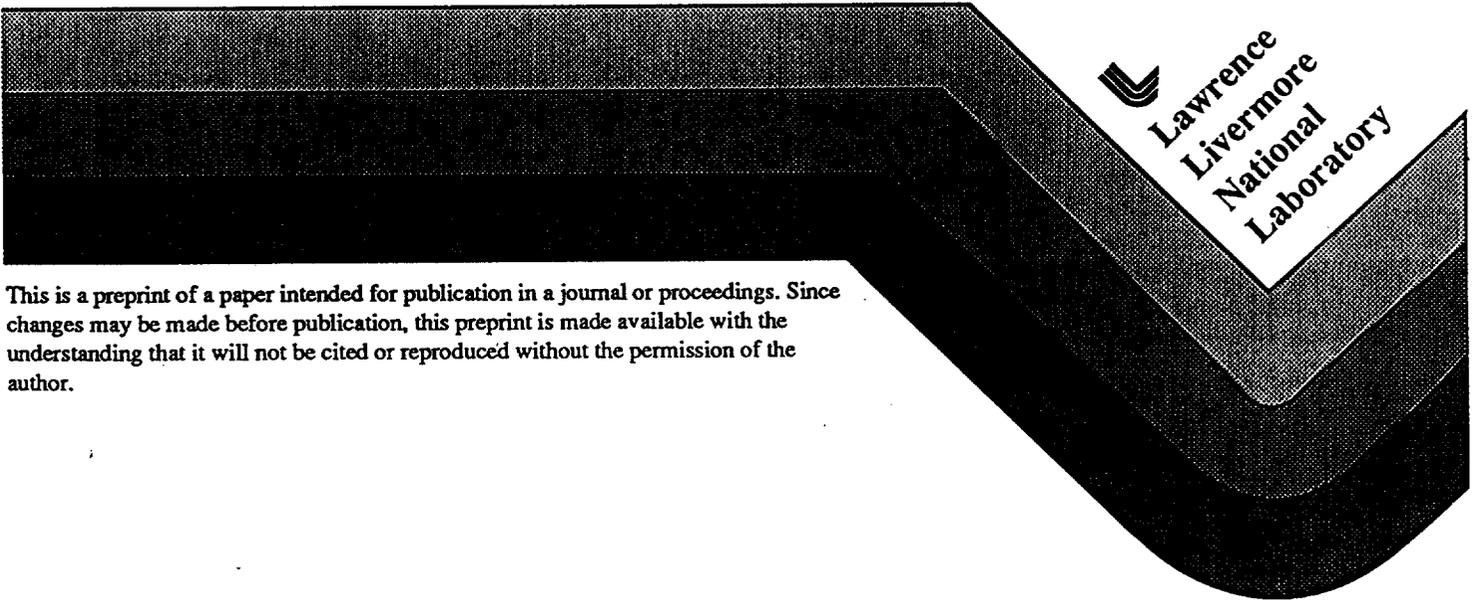
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CAPACITIVE DEIONIZATION SYSTEM

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ABSTRACT

The new capacitive deionization system (CDI) removes ions, contaminants impurities from water and other aqueous process streams, and further selectively places the removed ions back into solution during regeneration. It provides a separation process that does not utilize chemical regeneration processes, and thus significantly reduces or completely eliminates secondary wastes associated with the operation of ion exchange resins. In the CDI, electrolyte flows in open channels formed between adjacent electrodes, and consequently the pressure drop is much lower than conventional separation processes. The fluid flow can be gravity fed through these open channels, and does not require membranes. This feature represents a significant advantage over the conventional reverse osmosis systems which include water permeable cellulose acetate membranes, and over the electrodialysis systems which require expensive and exotic ion exchange membranes. The CDI is adaptable for use in a wide variety of commercial applications, including domestic water softening, industrial water softening, waste water purification, sea water desalination, treatment of nuclear and aqueous wastes, treatment of boiler water in nuclear and fossil power plants, production of high-purity water for semiconductor processing, and removal of salt from water for agricultural irrigation. CDI accomplishes this removal of impurities by a variety of mechanisms, but predominantly by electrostatic removal of organic and inorganic ions from water or any other dielectric solvent.

INTRODUCTION

Technologies for the desalting of water to produce potable water for domestic and agricultural use has been extensively reviewed [1, 2]. Principle approaches have been to separate either water from the solution (e.g., thermal distillation, reverse osmosis) or ions from the water (e.g., electrodialysis, ion exchange). Frequently a separation technique has to be used in conjunction with other techniques, and improvements in materials or energy sources enables the development of new technical solutions which then have to be evaluated on the basis of cost and efficiency. The development of aerogels has recently provided such an enabling impetus, resulting in new developments in the basic technology of capacitive deionization.

Capacitive deionization (CDI) involves the use of porous electrodes to remove dissolved ions through application of an electrostatic field. A process for the capacitive deionization of water with a stack of carbon aerogel electrodes has been developed at Lawrence Livermore National Laboratory. Aqueous solutions of soluble salts are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m²/g). After polarization, non-reducible and non-oxidizable ions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes, as shown in Figure 1. As desired, the effluent from the cell is purified water. A variety of salts have been shown to be removed by CDI: NaCl and NaNO₃, [3], NH₄ClO₄, [4], hexavalent chromium in the form of HCrO₄⁻/CrO₄²⁻/Cr₂O₇²⁻ [5].

This process is also capable of simultaneously removing a variety of other impurities. For example, dissolved heavy metals and suspended colloids can be removed by electrodeposition and electrophoresis, respectively. CDI has several potential advantages over other more conventional technologies. For example, ion exchange is now used as a means for removing anions and cations, including heavy metals and radioisotopes, from process and waste water in various industries. This process generates large volumes of corrosive secondary wastes that must be treated for disposal through regeneration processes. With CDI, unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by electrically discharging the cell. Therefore, no secondary waste is generated. In contrast to thermal processes such as evaporation, CDI is much more energy efficient. Since no membranes or high pressure pumps are required, CDI offers operational advantages over electrodialysis and reverse osmosis (RO). Preliminary data showing selective removal of Cr(VI) from ground water raises the possibility of specific treatment of a number of potential trace water impurities (e.g., B, Se, As). Initial short duration field tests of a pilot scale CDI system are currently being planned. Additional field and laboratory tests are needed to complete demonstrate the potential advantages for specific applications of CDI, but preliminary data to date appears promising.

INTRODUCTION

Conceptually, the CDI process is very simple. After application of a voltage between two adjacent carbon aerogel electrodes, cations and anions are drawn towards the cathode and anode, respectively, as illustrated in Figure 1. These ions are held in the electric double layers formed at the extensive surface of the carbon aerogel electrodes until the voltage is reduced. Double-sided electrodes are made by gluing two sheets of a porous carbon aerogel composite (CAC) to both sides of a titanium plate that serves as both a current collector and a structural support. CAC has an exceptionally high specific surface area of ~500 m²/g.

Early studies on CDI have described flow-through capacitors with porous, activated-carbon electrodes for the desalination of brackish water [6-8]. Several practical problems are encountered with these early CDI systems using activated carbon. For example, significant fractions of the carbon surface may be occluded in electrodes that use polymeric binders; hence, all the surface

area is not available for interaction with the solution. Even though adjacent carbon particles may touch, intimate electrical contact may not exist. Consequently, the electrical resistance is high.

The development of aerogels serve as the enabling technology which makes this CDI system technically and economically attractive. The preparation of resorcinol-formaldehyde (RF) aerogels and their carbonized derivatives has been described previously [9]. Carbon aerogels serve as ideal material for CDI electrodes. The electrical resistance of a carbon aerogel electrode is much lower than a comparable electrode made of activated carbon. Additionally, although other carbon materials may have higher BET surface areas, those materials have much of the surface area located inside pores having diameters less than 1 nm. It is very doubtful that this level of porosity contributes to electrochemical double layer formation since electrolyte penetration and double layer formation are questionable on this scale (i.e., in other carbon materials the electrochemically active area is only a fraction of the measured BET surface area). An electrolytic double-layer capacitor for energy storage based on carbon aerogel has been developed by Lawrence Livermore National Laboratory [10]. This device is based on the same fundamental physics as is CDI.

CAC electrodes are assembled into stacks using a lower stainless steel header with a rubber gasket and threaded rods, the array of CAC electrodes, gaskets, and spacers, and an upper stainless steel header. Even electrodes serve as cathodes while odd electrodes serve as anodes. The pressure drop across a stack of 48 electrode pairs is only 0.35 kg/cm² (5 psi) at 1.7 L/min. Electrical conductivity, pH, individual ion concentrations, and temperature are continuously monitored. The CDI system in the laboratory consists of two stacks of CAC electrodes in parallel. This system enables one stack to be regenerated while the other deionizes (i.e., potential-swing electrosorption). During potential-swing operation, a portion of the current produced during regeneration could be used for purification so the overall energy efficiency of the process is improved.

Solutions of NaCl, NaNO₃, and NH₄ClO₄ were used over a range of conductivities (typically 10 to 1000 μ S cm⁻¹) at potentials of 0.6, 0.8, 1.0 and 1.2 V. Batch-mode experiments were done by continuously recycling electrolyte at a flow rate of 1.0 liter/min. Single-pass experiments without were done at a flow rate of 25 ml/min. Chromium removal was investigated using contaminated ground water at the LLNL Treatment Facility C. The TDS of the ground water used is about 530 ppm, with inlet total Cr content of about 35 ppb. A slip stream was taken to provide a feed rate of 100 ml/min.

RESULTS AND DISCUSSION

Overall, tests demonstrated that CDI with carbon aerogel can effectively remove dissolved salts from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity of a typical salt solutions was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, i.e., the electrosorption capacity, had a strong

dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.4 V. No severe irreversible degradation in performance was observed after cycling the stacks several months. Breakthrough was observed during single-pass experiments without recycle. Rejuvenation of aged electrodes can be almost completely recovered repeatedly by voltage reversal.

Typical results are illustrated with NaCl in Figure 2 for the CDI system operated in the recycle mode. Qualitatively, the time to breakthrough increases proportionally with the number of electrode pairs. Under similar conditions, the capacity of the electrodes is anion limited, and comparison with Cl^- with ClO_4^- indicates that the CAC electrode capacity for large monovalent anions is less than for smaller anions. Higher electrode voltages result in greater deionization.

The loss of electrosorption capacity of carbon aerogel electrodes has been observed during prolonged operation [3,4]. Fortunately, such losses can be substantially recovered by reversal of the cell voltage. It is believed that the voltage reversal drives chemically bound ions from the surface of the carbon aerogel by imposing a significant repulsive electrostatic force. Rejuvenation can be used to increase the electrosorption capacity of aged electrodes to levels approaching those achieved initially. It appears that such rejuvenation can be repeated numerous times with essentially the same desirable result.

CDI has been used to continuously remove trivalent and hexavalent chromium from raw, untreated ground water at 530 ppm TDS. Figure 3 shows a plot of the concentrations of both Cr(VI) and Cr(III) in the outlet stream during the first 28 h of operation. Essentially all of the chromium in the inlet stream was Cr(VI), because the total Cr measured by AAS was nearly the same as the Cr(VI) measured by colorimetry. Immediately following polarization at 0.9 V, the total concentration of chromium in the outlet stream dropped from 30-35 ppb to less than 10 ppb. The concentration then started to trend upward. After operating the cells at 0.9 V for 8 h, the polarization was increased to 1.2 V. The additional polarization lowered the total concentration of chromium in the outlet stream from 15 to 8 ppb, while the concentration of Cr(VI) in the outlet dropped from 12 to 5 ppb. The concentration of Cr(VI) remained below 7 ppb during the 28 h shown in the figure, whereas the total concentration of chromium remained below 10 ppb. This selective removal continued for several days, even though the carbon aerogel electrodes were saturated with other ionic species. This selectivity is very encouraging, and suggests similar selectivity might be achieved for other ions.

The minimum energy requirements of the CDI process have been estimated [4]. The minimum theoretical work required by an isothermal process to separate a 1000 ppm NH_4ClO_4 solution into a 1 ppm product stream and a 95,000 ppm concentrate stream is approximately 1.6 J mol^{-1} (0.1 Wh gal^{-1}), assuming that the NH_4ClO_4 obeys the Debye-Huckel activity coefficient model. The minimum electrical energy required for charging a CDI cell with NH_4^+ and ClO_4^- is 4.5 J mol^{-1} (0.26 Wh gal^{-1}) at 0.6 V and 9.0 J mol^{-1} (0.52 Wh gal^{-1}) at 1.2 V. These values correspond to $QV/2$ where Q is the stored electrical charge and V is the cell voltage. In real systems, ohmic losses and finite pressure drops lead to energy requirements above these limiting values.

However, energy recovery by a second device operating in parallel can be used to substantially reduce the overall requirement, allowing CDI systems to more closely approach the theoretical minimum based on thermodynamics.

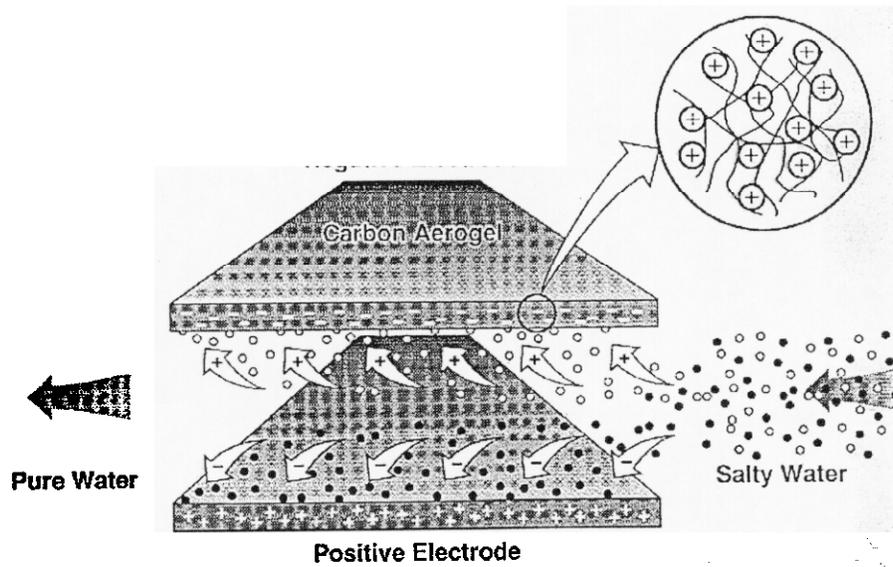
While a more detailed study should and is being done, it appears that in many cases CDI compares favorably with the energy requirements for other desalting technologies (e.g., reverse osmosis, thermal distillation). Additionally, the virtually infinite shelf life plus the robustness of carbon electrodes under service conditions suggest an operational advantage with respect to material durability for CDI; some of the CAC electrodes have been operated for nearly 2 years continuously with no significant degradation in performance. These potential attributes of CDI are being more closely evaluated. Additionally, systems are being assembled with 50-100 times the aerogel electrode surface area. It is intended that these systems will be applied to pilot- and field-scale evaluations of CDI.

REFERENCES

1. K.S. Spiegler, (Ed.), Principles of Desalination, Academic Press, New York, 1966.
2. A. Delyannis and E.-E. Delyannis (Ed.), Seawater and Desalting. Springer-Verlag, Berlin, 1980.
3. J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, and J. F. Poco, J. Electrochem. Soc. 143 (1996) 159-169.
4. J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, and J. F. Poco, J. Appl. Electrochem. 26 (1996) in press.
5. J. C. Farmer, D. V. Fix, G. V. Mack, R. W. Pekala, and J. F. Poco, UCRL-JC-124565 (1996).
6. D. , J. H. Tucker, J. L. Cooper, B. B. Arnold, and A. Papastamataki, Electrochemical Demineralization of Water with Carbon Electrodes, Research and Development Progress Report No. 188, United States Department of Interior, May 1966, 190 p.
7. A. M. Johnson and J. Newman, J. Electrochem. Soc. 118 (1971) 510-517.
8. Y. Oren, A. Soffer, J. Appl. Electrochem. 13 (1983) 489-505.
9. R. W. Pekala, S. T. Mayer, J. F. Poco, and J. L. Kaschmitter, Structure and Performance of Carbon Aerogel Electrodes. In: Novel Forms of Carbon II, C. L. Renschler, D. M. Cox, J. J. Pouch, and Y. Achiba (Eds.), Materials Research Society Symposium Proceedings 349 (1994) 79-85.
10. S. T. Mayer, R. W. Pekala J. L. Kaschmitter, J. Electrochemical Soc. 140 (1993) 446-451.

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A single cube of carbon aerogel, one inch on a side, has an effective surface area of more than twenty million square inches. This unusually high effective surface area makes it possible to adsorb large numbers of ions.

Figure 1. Schematic diagram illustrating the principal of capacitive deionization with carbon aerogel electrodes. Cations and anions are held in the electric double layers formed at the cathode and anode, respectively. The high specific surface area of the carbon aerogel enables the process to remove a significant amount of dissolved ions from the water passing between the electrodes.

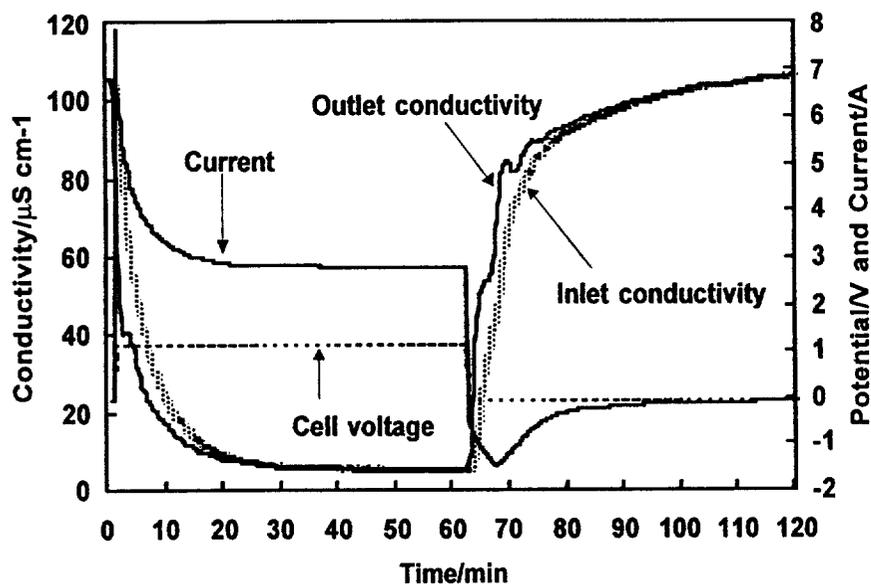


Figure 2. Deionization of a fixed volume of $100 \mu\text{S cm}^{-1}$ NaCl solution. Complete recycle of 4.0 liters at a rate of 1.0 liter / min. The apparatus included 384 aged electrode pairs operated at a cell voltage of 1.2 V.

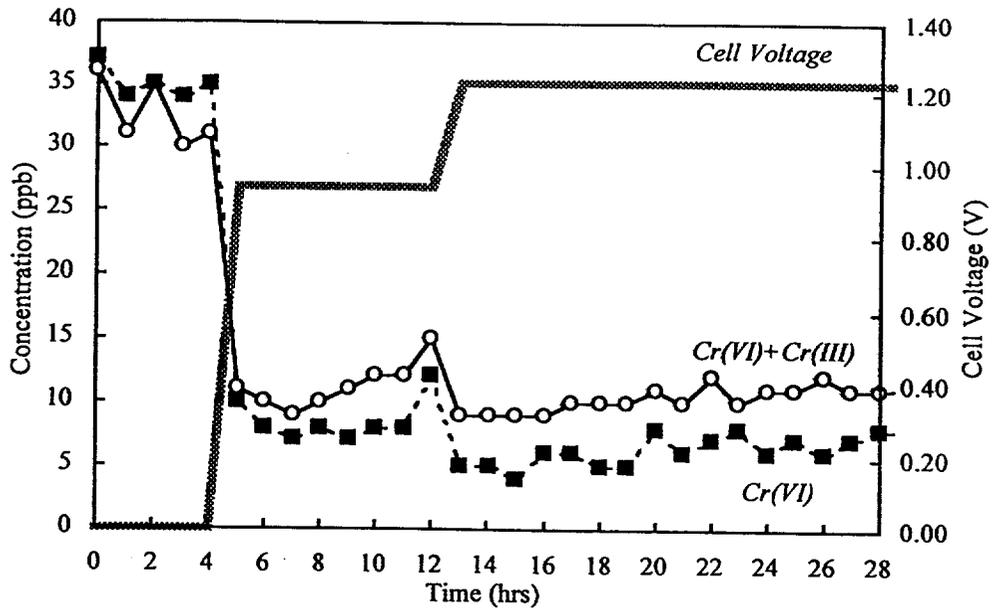


Figure 3. Selective removal of 35 ppb Cr(VI) from brackish LLNL ground water (530 ppm TDS).

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