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Production of high-purity water by continuous electrodeionization with bipolar membranes: Influence of concentrate and protection compartment

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Abstract

Main advantages of continuous electrodeionization with separated beds of cation- and anion-exchange resins and bipolar membranes are compared with other established electrodeionization concepts. Co-ion leakage from the concentrate into the diluate through ion-exchange membranes of limited permselectivity has been identified as the main reason for increased diluate conductivity. Diluate conductivity can be strongly reduced by either a “protection compartment” between the diluate and the concentrate compartment or by a concentrate compartment filled with an ion-exchange resin. In both cases a part of the diluate produced should be used as rinse for the protection or concentrate compartment. Experimental results with two electrodeionization modules comprising either separated beds with protection compartment or concentrate compartment filled with ion-exchange resin are presented and discussed. The influence of the flow rate through the protection compartment, the flow directions in different compartments, the feed water conductivity, the current density as well as the current density distribution on the process performance is investigated. © 2007 Elsevier B.V. All rights reserved.

Keywords: Electrodeionization; Bipolar membrane; Protection compartment; Concentrate compartment; Permselectivity

1. Introduction

The demand for high-purity industrial process water is rapidly increasing. Large quantities of water of different quality requirements are used as boiler feed water, in the production of semiconductors, and in chemical and biochemical laboratories. Conventional systems for high-purity water production contain several process steps in series such as microfiltration and reverse osmosis. As a final demineralisation step ion-exchange with mixed beds is applied where the ion-exchange resin has to be regenerated or replaced in certain time intervals.

Today, ion-exchange is more often replaced by a process referred to as continuous electrodeionization (CEDI). Compared with ion-exchange the CEDI process provides a product water of equal or better quality and is less costly since no separate regeneration step or replacement of ion-exchange resin is required. Thus, application of CEDI as a final demineralisation step after reverse osmosis desalination is currently a cost-effective alternative to the previously used mixed-bed ion-exchange in

the production of high-purity process water. A number of manufacturers supply a rapidly growing market with water demineralisation systems containing CEDI, where the CEDI stage varies significantly in its basic concept and in stack design.

The first commercially available CEDI modules [1] were similar to a conventional electrodialysis stack with cation- and anion-exchange membranes in alternating series, forming individual diluate and concentrate compartments between two electrodes. In contrast to conventional electrodialysis, the diluate compartment in CEDI stack was filled with a mixed-bed ion-exchange resin.

Several modifications of the original CEDI stack design have meanwhile significantly improved the efficiency of the process [2–5]. The electrical resistance of the stack was substantially reduced by filling also the concentrate compartment with a mixed-bed ion-exchange resin.

The changes applied have lowered the overall process and maintenance costs, the energy consumption and the susceptibility to scaling and fouling, and increased water recovery as well as the ability to remove weakly dissociated contaminants. The main concepts of the CEDI processes are described in detail in the corresponding literature and shall be briefly reviewed in the following section.

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2. Main concepts of CEDI

The most widely applied CEDI concepts utilize diluate compartments filled with ion-exchange resin either as a mixed-bed [1], as clustered beds [6,7], as layered beds [4,8] or as separated beds [9–11]. In the electro-regeneration regime of a CEDI process the ions from the feed water are removed by ion-exchange and the regeneration of ion-exchange resins takes place by H^+ - and OH^- ions which are generated by electrochemically induced water splitting.

In the mixed-bed CEDI, the water splitting takes place mainly at the bipolar boundaries between ion-exchange resin beads and ion-exchange membranes. The presence of so-called reverse junctions between ion-exchange beads of different polarity interrupts the ion migration through the resin. That limits the concept of CEDI with mixed-beds to compartments which are not thicker than a few beads.

The CEDI systems with clustered beds [6] or with layered beds [8] have the diluate compartments filled with alternating clusters or layers of cation-exchange resins (CR) and anion-exchange resins (AR), placed between the membranes. These clusters or layers provide a continuous migration path of ions through the resin of the diluate compartment from one membrane to another. It prevents the formation of reverse junctions and improves deionization performance, especially for the removal of weakly dissociated electrolytes. Such CEDI systems can use substantially thicker cells than mixed beds and are now well established in practice [5,7].

The main drawbacks of the CEDI with clustered or layered beds result from the different water splitting rate and conductance of the AR and CR clusters or layers. This leads to different current densities through the CR and AR and thus to differences in regeneration of both resins.

The CEDI system with separated beds overcomes this disadvantage by placing the AR and the CR in individual com-

partments in series so that the feed water flows sequentially through the CR and the AR while the same current is passing through both resin beds, as shown in Fig. 1.

The continuous regeneration of separated ion-exchange beds is carried out by H^+ - and OH^- -ions, which can be produced in bipolar membranes [11] or in electrode reactions [9]. The use of bipolar membranes has obvious advantages over the concept using electrode reactions, especially for the larger modules containing many repeating units [12,13].

Compared to the CEDI system containing a mixed-bed ion-exchange resin, the system with separated beds provides better removal of weak acids and allows the use of thicker compartments. Thus, for the same module capacity, a lower number of compartments and membranes is required, leading to a reduction in stack costs. However, due to incomplete permselectivity of the ion-exchange membranes, the CEDI processes with separated beds could so far not achieve a complete removal of ions [13], i.e. a product water resistivity of $18.2 M\Omega cm$, which is required in certain applications.

To utilize the above-mentioned advantages of the CEDI system with separated beds and bipolar membranes, the problem of the diluate contamination due to incomplete membrane permselectivity must be overcome. The work described in this contribution is a comparative study of two different modifications of the CEDI system with bipolar membranes (CEDI-BM), which have recently been introduced and which provide product water of extremely low ion content. The first system contains a so-called protection compartment and in the second system the concentrate compartment is filled with an anion-exchange resin.

3. Background of CEDI with bipolar membranes

The design of a CEDI-BM system is illustrated in Fig. 1 which shows a stack with cation- and anion-exchange resin beds (CR and AR) separated by a bipolar membrane (BM).

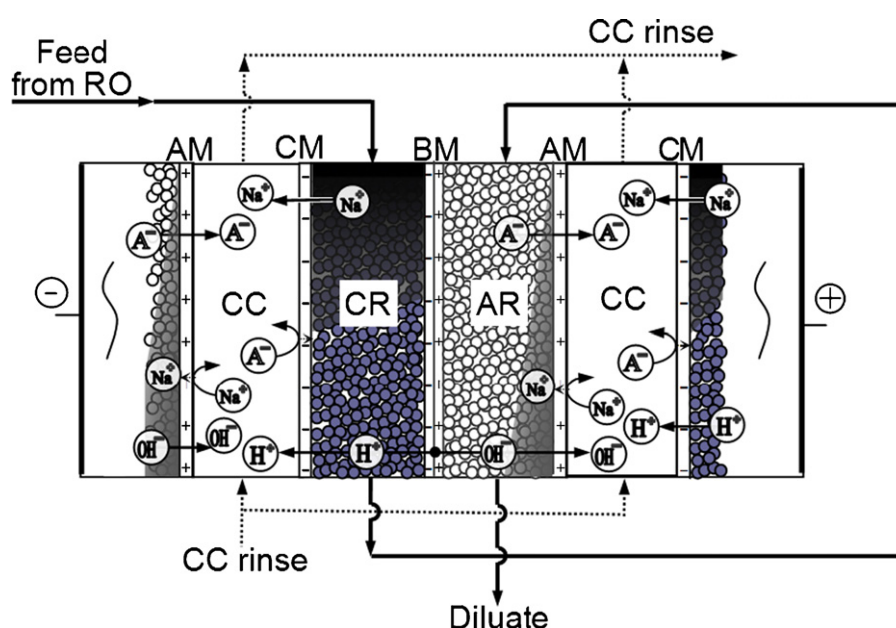


Fig. 1. Flow scheme of a CEDI-BM stack with separated cation- and anion-exchange resin beds (CR and AR) in the compartments on both sides of a bipolar membrane (BM), separated from the concentrate compartments (CC) by cation- and anion-exchange membranes (CM and AM) according to Ref. [11].

The resin beds are separated from the concentrate compartments (CC) by cation- and anion-exchange membranes (CM and AM). The resin beds (CR and AR), the bipolar membrane (BM), the ion-exchange membranes (CM and AM), and the concentrate compartment (CC) form a repeating unit, stacked between two electrodes. The applied voltage causes the generation of H^+ - and OH^- -ions in the BM and their subsequent transport into the CR and into the AR, respectively.

Permeate of a reverse osmosis unit (RO) is used as feed water. It is first passed through the compartment filled with the CR. Here the salt cations of the feed water are taken up by the resin, releasing H^+ -ions. The cations migrate through the resin and through the CM into the CC. The now slightly acidic feed water is passed through the compartment containing the AR where the salt anions of the feed water are taken up and the OH^- -ions released, while anions migrate through the AM into the CC. Thus, all ionic contaminants can be removed from the feed. The H^+ - and OH^- -ions exchanged from CR and AR are replenished by the ions generated in the BM. When feed water of low conductivity such as RO permeate is used, the current is almost completely conducted through the ion-exchange resins, which have a much higher conductivity than the feed water. The process is then operated in the so-called electro-regeneration regime.

The CC is usually filled with an inert mesh spacer and rinsed by a solution with an ion concentration providing sufficient conductivity. The electrical current in the CC is transported by the ions in the solution. Due to concentration polarization their concentration is increased at the surfaces of the ion-exchange membranes facing the CC.

A contamination of the diluate is mainly caused by the leakage of ions from the CC through the AM facing the diluate compartment. This leakage could occur by the electromigration of salt ions such as Na^+ -ions in the AM. A second cause of product water contamination is the diffusion of neutral molecules of weakly dissociated electrolytes through the membrane from the

compartment with higher concentration and lower dissociation degree into the diluate compartment with lower concentration and higher dissociation degree. The main process parameters effecting the diluate contamination are the electrical field strength which is proportional to the current density and the concentration of the CC rinse at the AM surface, which is effected by the rinse flow velocity. In Fig. 1 the progress of leaking Na^+ -ions into the diluate of AR compartment is schematically indicated by the grey color.

The transport of the Na^+ -ions from the CC into the diluate compartment can be eliminated by a stack design which includes a protection compartment (PC) filled with an AR and placed between the diluate and the concentrate compartment [14]. The concept of a CEDI-BM-Pro stack with a protection compartment (CEDI-BM-Pro) is illustrated in Fig. 2. The flow scheme here is identical to the one shown in Fig. 1 with the exception of the PC, which separates the AM of the diluate compartment from the CC. The PC is filled with an AR and rinsed with low-conductivity water, such as a part of the diluate. Cations from the CC penetrating the anion-exchange membrane of the protection compartment (^{PC}AM) are rinsed from the PC before reaching the AM which separates the PC from the diluate compartment. In Fig. 2 the profile of co-ions leaking from the CC into the PC is again indicated by the grey color.

The concentration of co-ions which penetrated into the rinse water of the PC is a function of the rinse flow velocity, the electrical field strength, and the concentration of these ions in the CC close to ^{PC}AM . At sufficient PC rinse flow rates most of the ions entering the PC are rinsed out of the PC. But with increasing electrolyte concentration in the PC the flux of ions through the water of the PC from ^{PC}AM to the AM surface increases, increasing the risk of diluate contamination. Therefore, low-conductivity water with sufficient flow rate should be used as PC rinse.

The high-electrical conductivity of ion-exchange resins compared to that of water allows the use of pure water to rinse the

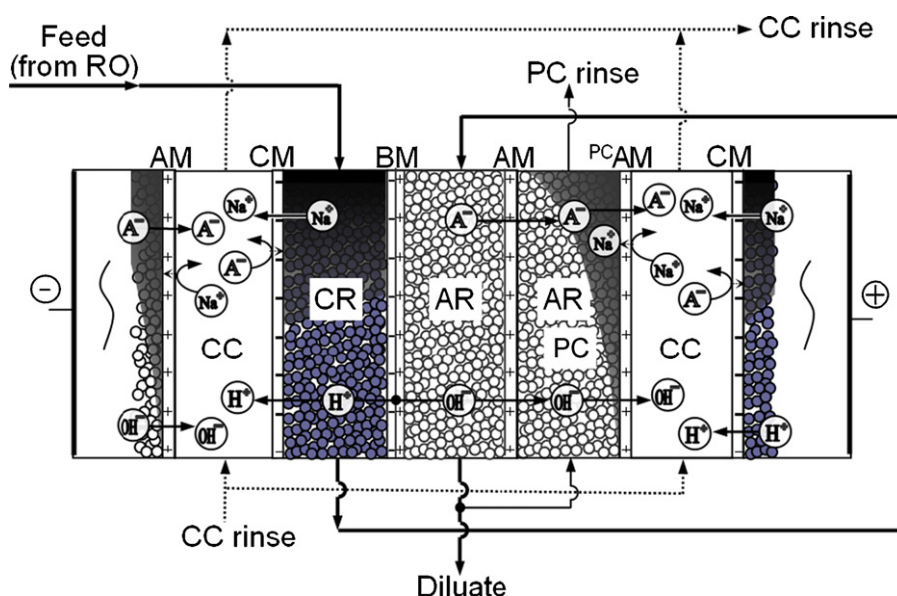


Fig. 2. Flow scheme of a CEDI-BM-Pro stack with separated cation- and anion-exchange resin beds (CR and AR) in the compartments on both sides of a bipolar membrane (BM) exhibiting a protection compartment (PC) filled with an AR, between the concentrate compartment (CC) and the AR-filled diluate compartment.

PC without a significant increase of the stack resistance. Since the current is transported almost completely through the anion-exchange resin phase, the migration of cations across the PC and through the AM is negligibly low and product water with conductivity close to that of ultrapure water can be obtained [14]. However, the use of a PC increases the number of compartments in one repeating unit of a stack and results in higher capital and operating costs.

Another possibility to decrease the cation transport through the AM into the diluate of CEDI-BM (Fig. 2) is to fill the CC with an AR [13]. When the CC is rinsed with low-conductivity water the part of the current carried by ions in the solution of the CC will be substantially decreased. This diminishes the concentration of cations in the CC near the AM and thus their transport into the diluate.

In order to compare the two options under identical conditions, a CEDI-BM stack containing one unit with PC and one unit with CC filled with AR has been set up and tested with the objective to obtain almost completely demineralised product water.

4. Experimental

In a first series of experiments the effect of flow rate and of the flow scheme in the PC of a single-unit CEDI-BM-Pro stack was investigated. A second series of experiments was carried out in a CEDI-BM stack containing one unit with a PC and one unit with an AR-filled CC. The performance of both units was studied under identical test conditions at different current densities and feed water conductivities.

4.1. Tests of CEDI-BM-Pro stack

The stack used in the first series of experiments is identical to a repeating unit of the stack shown in the schematic draw-

ing of Fig. 2 where the electrode compartments act as the CC. Every compartment is 1 cm thick, 10 cm wide and 30 cm long. Compartments are separated by NEOSEPTA® ion-exchange membranes and filled with DOWEX™ strong basic and strong acidic resins. The details of materials and construction of the CEDI-BM-Pro stack are described elsewhere [14].

Softened tap water with a conductivity of $335 \pm 3 \mu\text{S}/\text{cm}$ was used to rinse the electrode compartments with a flow rate of 15 L/h. The RO-permeate containing Na^+ -cations and different anions (mostly hydrocarbonate ions) was used to feed the CEDI with a flow rate of 48 L/h. A part of the diluate was used to rinse the PC. The tests were carried out at $20 \pm 2^\circ\text{C}$.

4.2. Comparison of CEDI-BM units with a PC and with an AR-filled CC

The stack used in the second series of experiments is schematically shown in Fig. 3. It is composed of two units, one unit containing the PC and the other one containing the AR-filled CC.

The geometry and materials used in this assembly, the flow rates of feed and electrode rinse are identical to those given above. A part of the diluate was used to rinse the PC or the CC with a flow rate 2.5 L/h each, corresponding to a water recovery of about 95% for a repeating unit.

The current efficiency (η) is calculated for the removal of Na^+ as the main exchangeable cation in the feed water. Since the concentration of Na^+ in the feed water is significantly higher than in the diluate, $C_{\text{Na}^+}^{\text{F}} \gg C_{\text{Na}^+}^{\text{D}}$, the following simplified equation for the calculation of the current efficiency is obtained:

$$\eta = \frac{FQ_{\text{F}}(C_{\text{Na}^+}^{\text{F}} - C_{\text{Na}^+}^{\text{D}})}{A} \frac{1}{i} \approx \frac{FQ_{\text{F}}C_{\text{Na}^+}^{\text{F}}}{I} \quad (1)$$

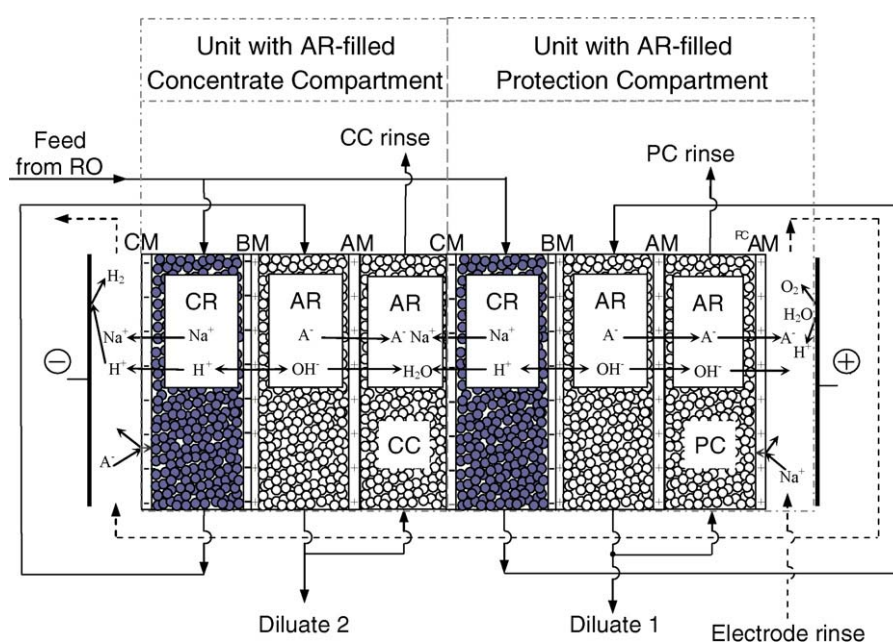


Fig. 3. Experimental stack assembly of CEDI-BM with one unit containing a PC and one unit containing a CC filled with AR (abbreviations in text).

Here F is the Faraday constant, Q_F the feed water flow rate, I the current, i the current density and A is the active surface area of the membranes. The sodium concentration in the feed water was measured by atomic absorption spectrometry.

It should be noted that often in practical CEDI applications not the concentration of total exchangeable cations but the concentration of total exchangeable anions is used for the calculation of the current efficiency [2]. Since the total exchangeable anions include non-dissociated CO_2 dissolved in water, higher values of calculated current efficiency result. For the used feed water with a conductivity in the range of 2.3–20 $\mu\text{S}/\text{cm}$ the pH values were in the range of 5.8–6.6, indicating that a significant part of inorganic carbon is present in non-dissociated form. The current efficiency calculated from the sodium ion concentration, on the other hand, is independent of pH and more accurately to define, but yields values which are lower than those calculated from anion concentrations.

5. Results and discussion

5.1. Investigation of CEDI-BM-Pro stack

5.1.1. Influence of the flow rate through the PC

The diluate conductivities (κ_D) and PC-rinse conductivities (κ_{PC}) obtained in experiments with different PC-rinse flow rates (Q_{PC}) and current densities (i) are presented in Figs. 4 and 5.

It can be seen from Figs. 4 and 5 that for the current densities of 3.3 mA/cm^2 and 5.0 mA/cm^2 the conductivity of the diluate (κ_D) and of the PC rinse (κ_{PC}) increases with the decreasing PC-rinse flow rate (Q_{PC}). But even if the Q_{PC} is down to 1.25 L/h, which relates only to 2.5% of the diluate used to rinse

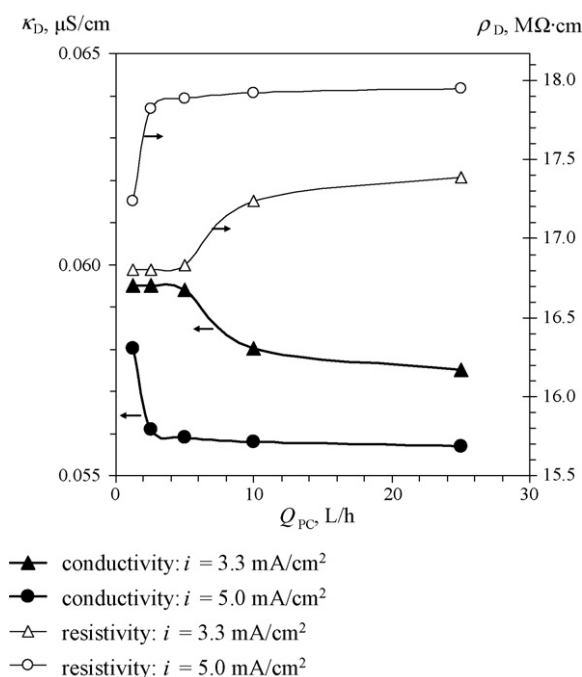


Fig. 4. Effect of the flow rate in the PC on the conductivity and resistivity of the diluate, determined at two different current densities for a constant feed conductivity of $\kappa_F = 2.3 \mu\text{S}/\text{cm}$.

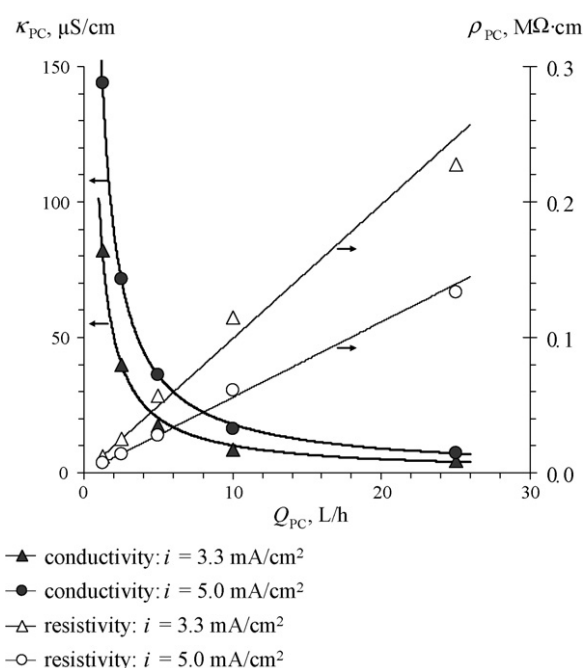


Fig. 5. Effect of the flow rate in the PC on the conductivity and resistivity in the outlet of the PC-rinse, determined at two different current densities for a constant feed conductivity of $\kappa_F = 2.3 \mu\text{S}/\text{cm}$.

the PC, κ_D can be kept as low as 0.060 $\mu\text{S}/\text{cm}$ and 0.058 $\mu\text{S}/\text{cm}$, respectively.

The higher conductivity of the PC rinse at a current density of $i = 5.0 \text{ mA}/\text{cm}^2$ compared to $i = 3.3 \text{ mA}/\text{cm}^2$ can be explained by the higher leakage rate of Na^+ -ions from the CC into the PC through the PC AM at higher current density.

Assuming that at constant current density the flux of Na^+ -ions through the PC AM into the PC is constant and independent of flow rate in the PC, the concentration of these ions at the outlet of PC rinse is inversely proportional to Q_{PC} . Due to the direct proportionality between the concentration and the conductivity of strong electrolytes in dilute solutions, the conductivity of the PC-rinse solution decreases hyperbolically and the resistivity increases linearly with increasing Q_{PC} as shown in Fig. 5.

In the PC, the increase of Q_{PC} results in a higher dilution of Na^+ -ions having penetrated the PC AM . This reduces the flux of Na^+ -ions across the PC and the flux through the AM into the diluate compartment. It can be assumed that the regeneration degree of the ion-exchange resins in the diluate compartments is hardly changed at constant current density. Thus, the decrease in the κ_D with the increasing Q_{PC} as shown in Fig. 4 can be related directly to the decrease of the Na^+ -ions transport from the PC through the AM into the diluate.

On the other hand, the lower diluate conductivity obtained at a current density of $i = 5.0 \text{ mA}/\text{cm}^2$ compared to $i = 3.3 \text{ mA}/\text{cm}^2$ is the result of the better regeneration of the ion-exchange resins in the diluate compartments, causing a better removal of weak acid residuals.

It is evident from Fig. 4 that at very low Q_{PC} the conductivity in the PC-rinse solution can reach comparatively high values. Thus, depending on the membrane permselectivity and the current density, the flow rate in the PC should be above a certain

Table 1
Comparison of different flow directions in the CEDI-BM-Pro stack^a

Type of the flow direction	Flow direction in the compartment			Diluate		κ_{PC} ($\mu\text{S}/\text{cm}$)	U (V)
	Diluate CR	Diluate AR	PC	κ_D ($\mu\text{S}/\text{cm}$)	ρ_D ($\text{M}\Omega\text{ cm}$)		
Type-1	↓	↓	↓	0.0578	17.30	83.2	16
Type-2	↓	↓	↑	0.0571	17.51	48.5	16
Type-3	↓	↑	↓	0.0557	17.95	24.4	29

^a The flow rates of feed and PC-rinse solution are 48 L/h and 2.5 L/h, respectively; the overall current density is 5.0 mA/cm² and the feed conductivity is 2.3 $\mu\text{S}/\text{cm}$.

minimum value to prevent a possible contamination of the diluate. However, higher flow rates in the PC require larger amounts of diluate used as rinse solution and thus lower product yields. An optimal Q_{PC} depends on the stack geometry, the operating conditions, and the costs of energy and water.

5.1.2. Effect of different flow directions in the CEDI-BM-Pro stack

To study the effect of the flow directions in the feed, in the concentrate and in the PC compartments on the overall performance of the CEDI-BM-Pro, three different types of flow configurations are compared experimentally. The flow directions in the respective compartments are indicated by arrows in Table 1. Type-1 flow configuration relates to the flow directions as given in Fig. 2, i.e. all flows are in the same direction from the top to the bottom of the compartments. In the type-2 flow configuration the flow in the PC is in opposite direction to the flows in the CR and AR diluate compartment. In the flow configuration of type-3 the flows in the CR compartment and the PC are in the same direction, i.e. from top to bottom, but the flow in the AR diluate compartment is in opposite direction.

In all experiments about 5% of the diluate is used to rinse the PC with a flow rate of $Q_{PC} = 2.5$ L/h. The applied overall current density is $i = 5.0$ mA/cm², and the other conditions are the same as in previous experiments. The current density distribution was measured with a segmented anode, consisting of 10 equal size segments along the compartment. The measured conductivities of diluate and PC rinse, as well as the voltage (U) applied to the electrodes are summarised in Table 1 and Fig. 6.

It can be seen from Table 1 that among the tested flow directions, the type-2 configuration shows a lower diluate conductivity than type-1, while the type-3 configuration shows the lowest diluate conductivity. The same sequence is even more obvious from the conductivities in the PC-rinse solution with a maximum in the type-1 configuration and a minimum in the type-3 configuration.

The experiments with different PC-rinse solution flow rates and the experiments with different flow directions in the stack show that at the same current density the diluate conductivity increases with increasing PC-rinse conductivity. This again supports the assumption of Na⁺-ions leaking from the PC into the diluate through the AM. Although this leakage is extremely small, it will not be acceptable in ultrapure water production. Thus, to obtain the low-product water conductivity, the conductivity in the PC-rinse solution should be as low as possible.

The influence of the different flow schemes can be rationalized by considering the current density distribution along the

compartment length, measured from the top to the bottom of the compartment.

The results presented in Fig. 6 show large differences in the local current densities along the 30 cm long flow path. Since the distance between an electrode and the membrane (0.6 mm) is sufficiently short, the influence of electrode compartments on the current distribution can be neglected. From the small difference between type-1 and type-2 profiles in Fig. 6 it is evident that the flow direction in the PC has also little effect on the current density distribution.

The main factor influencing the current density distribution has therefore to be found in local difference of the conductivity of the resins along the diluate compartments. These conductivities differ strongly whether the CR and the AR are either in the H⁺-ion and in the OH[−]-ion form or in a salt ion form. Since both diluate compartments, CR and AR, are at the feed inlet in the salt ion form and at the outlet in the H⁺-ion and OH[−]-ion form, respectively, the observed differences can be easily explained. For flow type-1 and type-2 configuration, where the flow in the CR and the AR diluate compartment is both downward, a higher current passes through the stack in the bottom part, where the CR and the AR are in H⁺- and OH[−]-ion form. In the type-3 flow configuration the flow in the CR is from top to bottom and in the AR diluate compartment from bottom to top, i.e. in opposite direction. Therefore, the conductivity in the CR will be lower at the top side and higher at the bottom side, while in

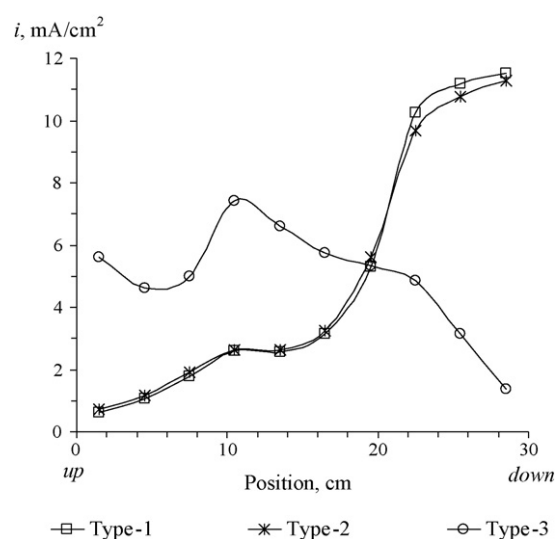


Fig. 6. Current density distribution at the anode over the stack length for different flow directions as defined in Table 1 ($\kappa_F = 2.3$ $\mu\text{S}/\text{cm}$; $Q_{PC} = 2.5$ L/h; $i = 5.0$ mA/cm²).

the AR diluate compartment the situation is reversed. This may cause some deviation of the current stream lines from the more conductive regions in the CR into the more conductive regions of the AR and results in the more uniform current distribution as compared to the type-1 and type-2 flow schemes, but also in a substantially higher voltage drop.

Table 1 shows the lowest diluate conductivity for the type-3 flow configuration. This is mainly caused by the more uniform current density distribution and following decrease of PC-rinse solution conductivity. As already stated, the PC-rinse solution conductivity results from the leakage of sodium ions, which is locally enhanced by high-current density. Since for type-3 the current density is comparatively uniform, co-ion leakage is minimized. Comparing type-1 and type-2, the latter shows a lower PC rinse conductivity and hence a slightly lower diluate conductivity. Since the PC rinse flow is upward, the highest co-ion concentration is at the upper rinse flow outlet, where the current density is low, as shown schematically by the shaded profile in the PC of Fig. 2. This prevents the co-ions to penetrate into the diluate while the opposite is true for the type-1 flow configuration.

Because of the lower diluate conductivity of the type-2 flow configuration compared to type-1 and the substantially higher voltage drop of type-3, type-2 has been used in the further tests, where a repeating unit with PC is compared with a repeating unit containing an AR-filled CC in the same stack.

5.2. Comparison of CEDI-BM units with PC and with AR-filled CC

5.2.1. The influence of feed conductivity

In a first set of experiments the diluate conductivity was measured as a function of the feed conductivity. The conductivity of RO-permeate used as feed for CEDI-BM was varied between 2.3 $\mu\text{S}/\text{cm}$ and 20 $\mu\text{S}/\text{cm}$ by changing the RO recovery. Test results are presented in Fig. 7 in which the diluate conductivity (κ_D) and the current efficiency (η) obtained at various current densities are shown as a function of the feed conductivity (κ_F). The test results show that the conductivity of the diluate can be kept below 0.065 $\mu\text{S}/\text{cm}$ when κ_F is below 15 $\mu\text{S}/\text{cm}$ in both tested units. This demonstrates the possibility to obtain high-purity water with CEDI-BM using either PC or CC filled with AR.

The increase of κ_D with increasing κ_F or with decreasing i , indicates a reduction in the regeneration degree of the ion-exchange resins in the diluate compartment. Most important is the reduced regeneration of the AR, resulting in an excess of weak acids anions in the AR. At the lowest i and highest κ_F tested, the breakthrough of incompletely removed ions through the AR bed becomes more significant and a rapid increase of the κ_D with increasing κ_F is observed. However, an increase of i from 5.0 mA/cm^2 to 6.7 mA/cm^2 at $\kappa_F = 20 \mu\text{S}/\text{cm}$, increases the regeneration degree of the resins substantially and leads to a decrease of κ_D from about 0.1 $\mu\text{S}/\text{cm}$ to less than 0.065 $\mu\text{S}/\text{cm}$.

In most experiments the diluate conductivity of the unit with a PC is slightly lower than that of the unit containing an AR-filled CC. This indicates a better prevention of co-ions, leaking

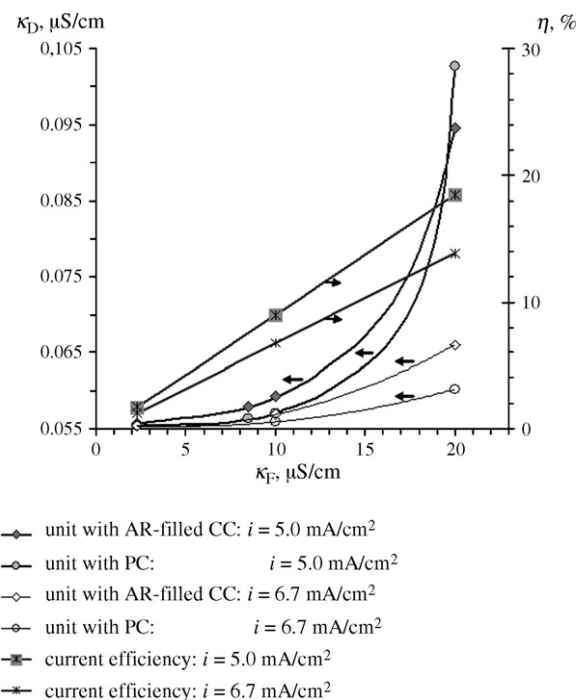


Fig. 7. Diluate conductivity and current efficiency as function of the feed conductivity and current density.

through the AM into the diluate. Only in the experiment with the lowest current density ($i = 5.0 \text{ mA}/\text{cm}^2$) and highest feed conductivity ($\kappa_F = 20 \mu\text{S}/\text{cm}$) the diluate conductivity in the unit with the PC is slightly higher than in the unit containing the AR-filled CC. This result indicates that the incomplete regeneration of the AR at low-current densities and high-feed conductivities is the crucial item, while the co-ions leakage under these condi-

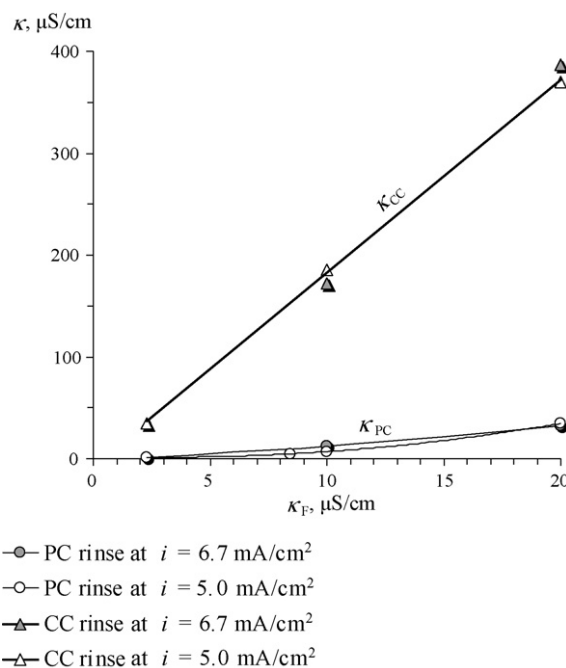


Fig. 8. Conductivity in the PC- and the CC-rinse solution as function of feed conductivity.

tions seems to be of minor importance. Some small variations in current or flow may influence the ions breakthrough under these conditions stronger than the differences in the co-ions transport.

The influence in the co-ions leakage in both units becomes more evident, when the conductivities of the rinse water from the PC and from the CC are compared. The dependence of the conductivities of the PC (κ_{PC}) and the CC (κ_{CC}) rinse solutions on κ_F have been determined at two different current densities and are presented in Fig. 8. Under the given test conditions κ_{CC} is about one order of magnitude higher than κ_{PC} and is directly proportional to the κ_F . As a result of a higher electrolyte concentration in the rinse solution of AR-filled CC, more cations can reach the surface of the AM and permeate through the AM into the diluate, than in the unit with PC. This is also the reason for the lower κ_D obtained in the unit with PC than that in the unit with CC filled with AR as shown in Fig. 7.

Fig. 7 shows that a higher current density as well as a lower feed conductivity leads to a lower current efficiency. Such behaviour is typically for all CEDI applications. When the desalination degree is approaching 100% all mineral ions are efficiently removed from the feed and excess current will be carried by the H^+ - and OH^- -ions which will recombine in the CC to H_2O . Therefore, the current efficiency is increasing linearly with the feed conductivity, which is evident from Eq. (1).

The slope of the κ_{CC} versus κ_F curve in Fig. 8 is proportional to the ratio of the feed flow rate to the CC-rinse solution flow rate and indicates that κ_{CC} is practically independent of the current density. The fact that almost all ions from the feed are collected in the CC-rinse solution but only the co-ions penetrating the ^{PC}AM are present in the PC-rinse solution explains the much higher values of κ_{CC} compared to κ_{PC} .

While the current density in the investigated range has almost no effect on κ_{CC} , it influences the leakage rate of cations from the CC through the AM. The exchange of cations in the CR and its transport into the CC occurs at the top part of the stack. With rinsing the CC from bottom to top, the residence time of these removed cations in the CC is shorter than by rinsing the CC in opposite direction. With increasing current density the profile of removed cations in the CR will shift upwards, which leads to further shortening of the cations residence time in the CC and thus to a reduction of the Na^+ -ions leakage through the AM.

5.2.2. Influence of the current density

The influence of the current density is shown in Fig. 9, where the diluate conductivity and the current efficiency is plotted versus the current density at a constant feed conductivity of $20 \mu S/cm$. At low current densities the diluate conductivity is quite high in both units and decreases very rapidly with increasing current density until κ_D of less than $0.065 \mu S/cm$ is reached at current density above $7 mA/cm^2$. A further increase in the current density results in a much slower decrease of κ_D . The rapid decrease of κ_D over i at low current densities is the result of the subsequent removal of all strongly dissociated electrolytes and the majority of the weakly dissociated feed components. At higher current densities the remaining weakly dissociated electrolytes will be removed.

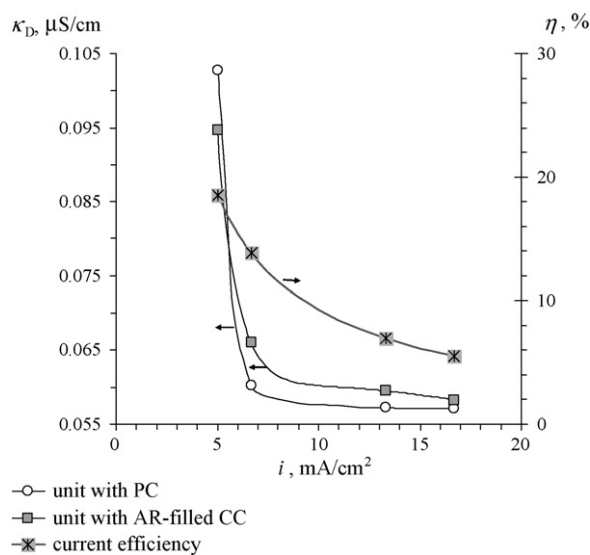


Fig. 9. Diluate conductivity and current efficiency as function of current density determined at $\kappa_F = 20 \mu S/cm$.

The decrease in κ_D with increasing current density is accompanied by a hyperbolic decrease in the current efficiency of the process, which is also evident from the Eq. (1). Since both units show nearly the same salt removal, the current efficiency at different current densities is also nearly identical.

Due to a monotonous decrease of the diluate conductivity with increasing current density, in practical applications the required quality of product water can be adjusted to some extent by the applied current density.

In Fig. 10 the experimentally determined conductivities of the PC- and in the CC-rinse solutions are shown as function of the current density. As expected, the conductivity in the PC-rinse solution increases with increasing current, because of the increasing amount of co-ions leaking through the ^{PC}AM into the PC. The conductivity of the CC-rinse solution remains practically constant and is determined mainly by the amount

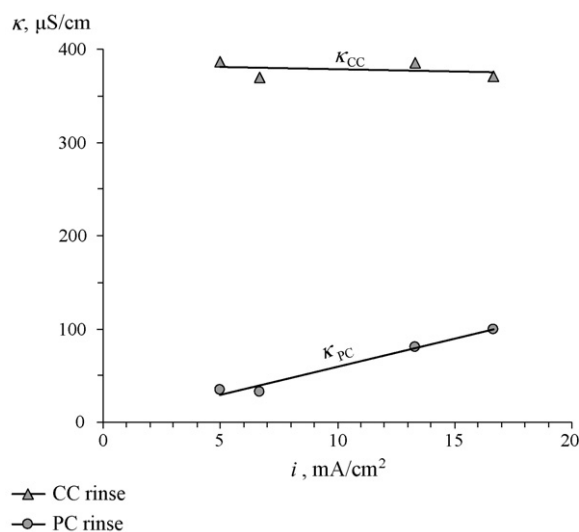


Fig. 10. Conductivity in the PC- and CC-rinse solution as function of current density determined at $\kappa_F = 20 \mu S/cm$.

Table 2
Si removal at 5.0 mA/cm² current density

		κ (μ S/cm)	ρ (M Ω cm)	Si (ppb)
	Feed	5.5	0.2	285
Unit with AR-filled PC	Diluate	0.0556	18.0	0.64
Unit with AR-filled CC	Diluate	0.0563	17.8	2.7

of ions removed from the feed solution into the concentrate. Thus, at nearly complete deionization, κ_{CC} is directly proportional to the feed concentration as already indicated in Fig. 8 and is almost independent of current. The transport of co-ions, however, is directly proportional to the current and thus κ_{PC} is increasing almost linearly with the current as shown in Fig. 10.

5.2.3. Silica removal

Silica is a typical RO water contaminant and silicic acid has a very low-dissociation constant ($pK_1 = 9$ – 10). To estimate the silica removal in the tested CEDI-BM stack, the concentration of total silica (Si) in the diluate of the two units was measured by atomic absorption spectrometry. The experiments were carried out with a feed conductivity of 5.5 μ S/cm and a current density of 5.0 mA/cm². The results are summarised in Table 2.

Table 2 shows that both units provide a good Si removal, which is a result of using separated beds in the CEDI-BM. The diluate from the unit with a PC has a Si concentration below 1 ppb whereas that of the unit with the AR-filled CC has a Si concentration of 2.7 ppb. At higher current density and lower feed concentration the Si removal will be enhanced. For example, at a current density of 13.3 mA/cm² using a feed with a Si concentration of 135 ppb and a conductivity of 2.3 μ S/cm, the unit with AR-filled CC produces a diluate with a Si concentration of 0.24 ppb and a conductivity of 0.0553 μ S/cm.

Weak acids removal in CEDI-BM is the result of a complex interplay of different effects: during their passage through the CR compartment the cations from the feed will be exchanged by H⁺-ions from the CR while a big part of H⁺-ions will react with hydrocarbonate ions, shifting the equilibrium to the formation of the non-dissociated form of inorganic carbon (hydrocarbonic acid and dissolved CO₂). As a result the pH will slightly decrease and the conductivity increases. In experiments using RO feed water with a conductivity of 2.3 μ S/cm and a pH of 5.8, the water leaving the diluate compartment filled with CR has a conductivity of about 3.2 μ S/cm and pH 5.1. These values remain the same at $i = 5$ mA/cm² and at $i = 13.3$ mA/cm² if the same feed is used. At such slightly acidic pH, silica present in the feed water is almost completely in the non-dissociated acid form. When it passes into the AR bed it can only be absorbed if the AR is in the OH[−] form. The increase of the current density increases the regeneration degree of the AR (shifts the OH[−] form of the AR upstream), which improves the removal of weakly dissociated acids, like silicic acid.

Some of the silica however penetrates into the diluate from the CC or PC compartment through the AM in non-dissociated form. The higher Si-content in the diluate of the unit with AR-

filled CC compared to the PC is obviously the result of the higher concentration in the CC-rinse than in the PC-rinse and thus, the higher diffusion rate of non-dissociated Si from the CC into the diluate through the AM.

Since in the CEDI-BM systems with a PC and with an AR-filled CC the leakage of co-ions is significantly reduced, the removal of weakly dissociated substances like Si from the feed can be enhanced by increasing of the current density without a risk of increasing the conductivity of the diluate due to co-ions leakage.

6. Conclusions

The continuous production of high-quality demineralised water, which is almost completely free of weakly dissociated acids, from RO permeate as feed can be achieved either by a CEDI-BM unit with separate CR and AR beds and a protection compartment between the concentrate and the diluate compartment, or with a CEDI-BM unit with separate CR and AR beds and an AR-filled concentrate compartment, if part of the diluate is used as either PC- or CC-rinse.

The effect of the current density, of the flow rate in the PC, and of different types of flow directions in the compartments have been studied experimentally in the CEDI-BM-Pro stack. It has been shown that the flow direction has a strong influence on the local distribution of the current density and on the diluate conductivity. By optimizing the flow directions and flow velocities and the applied current density, a diluate resistivity of ca. 18 M Ω cm can be reproducibly achieved.

In a comparative study where a CEDI-BM unit with a PC and a CEDI-BM unit with an AR-filled CC were simultaneously operated in the same stack, it was shown that a reliable demineralisation can be achieved with both units. However, the diluate conductivity and the Si concentration in the unit with the PC were somewhat lower under most experimental conditions. The difference in the diluate conductivities of the two systems is related to the higher electrolyte concentration in the CC-rinse solution compared to the PC-rinse solution.

The small difference between the diluate conductivity achieved in both units and the theoretical conductivity of pure water is caused by residuals of weak acids or/and by the penetration of some contaminations from the PC or CC through the AM into the diluate.

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