ELECTRODIALYSIS OF SALTS, ACIDS AND BASES

Jakob Johannes Schoeman

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ELECTRODIALYSIS OF SALTS, ACIDS AND BASES BY ELECTRO-OSMOTIC PUMPING

Jakob Johannes Schoeman

Promoter: Professor Jacobus F van Staden

Department of Chemistry, University of Pretoria

Degree: Doctor of Philosophy

SYNOPSIS

Salts, acids and bases frequently occur in industrial effluents and usually have considerable pollution potential. Preliminary work has indicated that electro-osmotic pumping electrodialysis (EOP·ED) has the potential to recover chemicals and water for reuse and to reduce effluent volumes significantly. However, with respect to this technology, the following needs were identified:

a) consider and fully document the relevant EOP·ED and ED theory;
b) study the EOP·ED characteristics (transport numbers, brine concentration, current efficiency, current density, electro-osmotic coefficients, etc.) of commercially available and other membranes in a single cell pair (cp) with the aim of identifying membranes suitable for EOP·ED;
c) evaluate a simple method and existing models with which membrane performance for concentration by EOP·ED can be predicted and described;
d) evaluate EOP·ED for industrial effluent treatment in a conventional ED and in a sealed-cell ED (SCED) membrane stack.

A conventional ED membrane stack which was converted into an EOP·ED stack performed satisfactorily for concentration/desalination of sodium chloride, hydrochloric acid and caustic soda solutions. Dialysate concentrations of less than 500 mg/ℓ could be obtained in the feed water and cell pair voltage ranges from 1 000 to 10 000 mg/ℓ and 0,5 to 4,0 V/cp. Small brine volumes were obtained. Brine volume varied between 1,5 and 4,0%; 2,4 and 7,8%; and between 2,3 and 7,3% in the case of sodium chloride, hydrochloric acid and caustic soda solutions (1 000 to 5 000 mg/ℓ feed). Current efficiency was high. Current efficiency varied between 75,2 and 93,6%; 29,2 and 46,3%; and between 68,9 and 81,2% when sodium chloride, hydrochloric acid and caustic soda solutions were electrodialyzed, respectively. Low electrical energy consumptions were obtained. Electrical energy consumption was less than 2,5 kWh/m^3 product for sodium chloride solutions in the 1 000 to

3 000 mg/ℓ feed concentration range; between 0,2 and 3,2 kWh/m^3 product at 1 000 mg/ℓ hydrochloric acid feed concentration; and between 0,4 and 2,2 kWh/m^3 product for caustic soda in the 1 000 to 3 000 mg/ℓ feed concentration range. Water yield increased with increasing cell pair voltage and increasing linear flow velocity through the stack and decreased with decreasing feed water concentration. It would be advantageous to operate an EOP-ED stack at the highest possible linear flow velocity.

Sealed-cell ED should be very effectively applied for concentration/desalination of relatively dilute (500 to 3 000 mg/ℓ TDS) non-scale-forming salt solutions. Product water with a TDS of less than 300 mg/ℓ could be produced in the feed water concentration range from 500 to 10 000 mg/ℓ TDS. Electrical energy consumption of 0,27 to 5,9 kWh/m^3 product was obtained (500 to 3 000 mg/ℓ feed water concentration range). Brine volume comprised approximately 2% of the initial feed water volume. Therefore, brine disposal cost should be reduced significantly with this technology. Sealed-cell ED became less efficient in the 5 000 to 10 000 mg/ℓ TDS feed water concentration range due to high electrical energy consumption (3,3 to 13,0 kWh/m^3 product). However, SCED may be applied in this TDS range depending on the value of the product that can be recovered.

A relatively concentrated ammonium nitrate effluent (TDS 3 600 mg/ℓ) could be successfully treated with SCED. Brine volume comprised only 2,8% of the treated water volume. Electrical energy consumption was determined at 2,7 kWh/m^3 product. It should be possible to reuse the brine and the treated water in the process. Membrane fouling, however, may affect the process adversely and this matter needs further investigation. Treatment of scale forming waters will affect the process adversely because scale will precipitate in the membrane bags, which cannot be opened for cleaning. Membrane scaling may be removed by current reversal or with cleaning solutions. However, this matter needs further investigation. Scale forming waters, however, should be avoided or treated with ion-exchange or nanofiltration prior to SCED treatment.

Sealed-cell ED has potential for treatment of relatively dilute (< 3 000 mg/ℓ TDS) non-scaling waters for chemical and water recovery for reuse. However, high TDS waters (up to approximately 16 000 mg/ℓ) may also be worth treating, depending on the value of the product that can be recovered. The successful application of SCED technology seems to depend on the need to apply this technology in preference to conventional ED for specific applications where high brine concentrations and small brine volumes are required. Capital cost of SCED equipment should be less than that of conventional ED due to the simpler design of the SCED stack. The membrane utilization factor of 95% is much higher than in conventional ED (approximately 80%).

Electro-osmotic pumping studies in a single cell pair have shown the following:

Brine concentration increased with increasing current density and increasing feed water concentration and levels off at high current density dependent on the electro-osmotic coefficients of the membranes. Current efficiency was nearly constant in a wide range of current densities and feed water concentrations in the case of the *Selemion* (salt and acid concentration) and *Raipore* membranes (salt concentration). However, all the other membranes showed a slight decrease in current efficiency indicating that the limiting current density was exceeded. Water flow through the membranes (salt and base concentration) increased with increasing current density and increasing feed water concentration. Increasing water flow increased current efficiency significantly, especially in the case of the more porous heterogeneous membranes. It will therefore not be necessary for membranes to have very high permselectivities (> 0,9) for use in EOP·ED because efficiency will be increased by water flow through the membranes. Consequently, water flow through ED membranes also has a positive effect in ED and this effect is often neglected. The electro-osmotic coefficients decreased with increasing feed water concentration until a constant value was obtained at high current density. Osmotic flow in EOP·ED decreased relative to the total flow with increasing current density while the electro-osmotic flow increased relative to the osmotic flow. Osmotic flow contributes significantly to the total water flow in EOP·ED. Membrane permselectivity decreased with increasing brine and feed concentration and increasing concentration gradient across the membranes.

Selemion AMV and CMV and *Ionac* membranes; *Selemion* AAV and CHV and the newly developed Israeli ABM membranes; and *Selemion* AMV and CMV, *Selemion* AMP and CMV and *Ionac* membranes performed well for salt, acid and base concentration, respectively. Current efficiencies varied between 62 and 91% (*Selemion* AMV and CMV); 34 and 60% (ABM-3 and *Selemion* CHV); and between 47 and 76% (*Selemion* AMV and CMV) for salt, acid and base concentration, respectively, in the feed water concentration range from 0,05 to 1,0 mol/ℓ.

A simple membrane potential measurement has been demonstrated to function satisfactory to predict membrane performance for salt, acid and base concentration. Membrane performance could be predicted with an accuracy of 10; 20 and 20% and better for salt, acid and base concentration, respectively. Brine concentration could be predicted satisfactorily from apparent transport numbers and water flows. Maximum brine concentration, c_b^{max}, could be predicted satisfactorily from two simple models.

The correct Onsager relationships to be used for potential measurements and for the transport number are at zero current and zero volume flow, and at zero concentration gradient and zero volume flow, respectively. In practical ED, measurements are conducted at zero pressure and in the presence of concentration gradients and volume flows. These factors will influence the results considerably in all systems in which volume flow is important and where the concentration factor is high as encountered in EOP·ED. In measurement of membrane potential, the volume flow is against the concentration potential and in general will decrease potential. In ED water flow helps to increase current efficiency, but the concentration gradient is against current efficiency.

Models describe the system satisfactorily for concentration of salt, acid and base solutions. Brine concentration approached a limiting value (plateau) at high current density dependent on the electro-osmotic coefficients of the membranes. A constant slope (electro-osmotic coefficient) was obtained when water flow was plotted against current density. Straight lines were obtained when cell pair resistance was plotted against the specific resistance of the dialysate. Current efficiency increased with increasing flow of water through the membranes, decreased when the concentration gradient was high and the apparent transport numbers were low.

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ELEKTRODIALISE VAN SOUTE, SURE EN BASISSE DEUR MIDDEL VAN ELEKTRO-OSMOTIESE POMPING

deur

Jakob Johannes Schoeman
Promoter: Professor Jacobus F van Staden
Departement Chemie, Universiteit van Pretoria
Graad: Philosophia Doctor

SAMEVATTING

Soute, sure en basisse kom dikwels in industriële uitvloeisels voor en het gewoonlik 'n aansienlike besoedelingspotensiaal. Voorlopige werk het aangedui dat elekto-osmotiese pomping elektrodialise (EOP·ED) die potensiaal het om chemikalieë en water vir hergebruik te herwin en om uitvloeiselvolumes betekenisvol te verminder. Daar is egter geïdentifiseer dat behoeftes bestaan om:

a) EOP·ED- en ED-teorie deeglik in oënskou te neem en om die relevante teorie ten volle te dokumenteer;
b) EOP·ED eienskappe (transportgetalle, loogkonsentrasie, stroomdoeltreffendheid, stroomdigtheid, elektro-osmotiese koeffisiënte, ens.) van kommersieël beskikbare en ander membrane in 'n enkelselpaar (sp) te bestudeer met die doel om membrane wat vir EOP·ED geskik is, te identifiseer;
c) 'n eenvoudige metode en bestaande modelle te evalueer waarmee membraanwerkverrigting vir konsentrasie met EOP·ED voorspel en beskryf kan word;
d) EOP·ED vir industriële uitvloeiselbehandeling in 'n konvensionele ED en in 'n geseëldesel ED (GSED) membraanpak te evalueer.

'n Konvensionele ED-membraanpak wat na 'n EOP·ED membraanpak omgeskakel is, het bevredigende werkverrigting vir die konsentrering/ontsouting van natriumchloried-, soutsuur- en bytsodaoplossings gelewer. Produkwaterkonsentrasies van minder as 500 mg/ℓ kon in die toevoerwater- en selpaarspanninggebiede van 1 000 tot 10 000 mg/ℓ en 0,5 tot 4,0 V/sp verkry word. Klein loogvolumes is verkry. Loogvolumes het tussen 1,5 en 4,0%; 2,4 en 7,8%; en 2,3 en 7,3% in die geval van natriumchloried-, soutsuur- en bytsodaoplossings, gewissel. Stroomdoeltreffendhede was hoog. Stroomdoeltreffendhede het tussen 75,2 en 93,6%; 28,2 en 46,3%; en tussen 68,9 en 81,2% gewissel toe natriumchloried-, soutsuur- en bytsodaoplossings respektiewelik, geëlektrodialiseer

is. Lae elektriese energieverbruike is verkry. Elektriese energieverbruik was minder as 2,5 kWh/m^3 produk vir natriumchloriedoplossings in die 1 000 tot 3 000 mg/ℓ toevoerwaterkonsentrasiegebied; tussen 0,2 en 3,2 kWh/m^3 produk vir soutsuur by 1 000 mg/ℓ toevoerkonsentrasie; en tussen 0,4 en 2,2 kWh/m^3 produk vir bytsodaoplossings in die 1 000 tot 3 000 mg/ℓ toevoerwaterkonsentrasiegebied. Wateropbrengs het met toenemende selpaarspanning en toenemende liniêre vloeisnelheid deur die membraanpak toegeneem en met afnemende toevoerkonsentrasie afgeneem. Dit sal dus voordelig wees om 'n EOP-ED membraanpak by die hoogste moontlike liniêre vloeisnelheid te bedryf.

Geseëldeselelektrodialise behoort effektief vir die konsentrering/ontsouting van relatief verdunde (500 tot 3 000 mg/ℓ TOVS) nie-skaalvormende soutoplossings toegepas te kan word. Produkwater met 'n TOVS inhoud van minder as 300 mg/ℓ kan geproduseer word in die toevoerwaterkonsentrasiegebied van 500 tot 10 000 mg/ℓ TOVS. Elektriese energieverbruik van 0,29 tot 5,9 kWh/m^3 produkwater is verkry (500 tot 3 000 mg/ℓ toevoerwaterkonsentrasiegebied). Loogvolume het ongeveer 2% van die aanvanklike toevoervolume beslaan. Loogwegdoenkoste behoort dus betekenisvol met hierdie tegnologie verminder te kan word. Geseëldeselelektrodialise het minder doeltreffend in die 5 000 tot 10 000 mg/ℓ TOVS toevoerkonsentrasiegebied geword as gevolg van hoë elektriese energieverbruik (3,3 tot 13,0 kWh/m^3). Geseëldeselelektrodialise kan egter in hierdie TOVS gebied toegepas word afhangende van die waarde van die produk wat herwin kan word.

'n Relatief gekonsentreerde ammoniumnitraatoplossing (TOVS 3 600 mg/ℓ) kon suksesvol met GSED behandel word. Loogvolume het slegs 2,8% van die behandelde water volume beslaan. Elektriese energieverbruik is as 2,7 kWh/m^3 produk bepaal. Beide die loog- en die behandelde water behoort in die proses hergebruik te kan word. Membraanbevuiling mag egter die proses nadelig affekteer en hierdie saak behoort verdere aandag te geniet. Behandeling van skaalvormende waters sal die proses nadelig beïnvloed omdat skalie in die membraansakkies kan neerslaan wat nie vir skoonmaakdoeleindes oopgemaak kan word nie. Skalie kan met stroomruiling of met skoonmaakmiddels verwyder word. Hierdie saak vereis egter verdere ondersoek. Skaalvormende waters behoort egter vermy te word of met ioonuitruiling of nanofiltrasie voor GSED behandel te word.

Geseëldesel ED het potensiaal om vir die behandeling van relatief verdunde ($<$ 3 000 mg/ℓ TOVS) nie-skaalvormende waters vir chemiekalieë- en waterherwinning vir hergebruik aangewend te word. Waters met hoë TOVS-vlakke (tot ongeveer 16 000 mg/ℓ) behoort egter ook behandel te kan word afhangende van die waarde van die produk wat herwin kan word. Die suksesvolle toepassing van GSED-tegnologie blyk om van die behoefte af te hang om hierdie tegnologie in voorkeur bo konvensionele ED vir spesifieke toepassings aan te wend waar hoë loogkonsentrasies en klein loogvolumes vereis word. Kapitaalkoste van GSED-toerusting behoort minder te wees as die van konvensionele ED as gevolg van 'n meer eenvoudige ontwerp van die GSED-membraanpak. Die membraanbenuttingsfaktor van 95%

in GSED is baie hoër as wat in konvensionele ED verkry word (ongeveer 80%).

Elektro-osmotiesepompingstudies in 'n enkelselpaar het die volgende aangetoon:

Loogkonsentrasie neem met toenemende stroomdigtheid en toenemende toevoerwaterkonsentrasie toe en plat af by hoë stroomdigthede afhanklik van die elekto-osmotiese koeffisiënte van die membrane. Stroomdoeltreffendheid was bykans konstant oor 'n groot gebied van stroomdigthede en toevoerwaterkonsentrasies in die geval van *Selemion-* (sout- en suurkonsentrasie) en *Raipore* membrane (soutkonsentrasie). Al die ander membrane het egter 'n geringe afname in stroomdoeltreffendheid getoon wat daarop dui dat die beperkende stroomdigtheid oorskry is. Watervloei deur die membrane (sout- en basiskonsentrasie) het met toenemende stroomdigtheid en toenemende toevoerwaterkonsentrasie toegeneem. Toenemende watervloei het stroomdoeltreffendheid aansienlik laat toeneem veral in die geval van die meer poreuse heterogene membrane. Dit sal dus nie nodig vir membrane wees om 'n baie hoë permselektiwiteit (> 0,9) vir gebruik in EOP-ED te hê nie omdat watervloei deur die membrane doeltreffend sal verhoog. Watervloei deur ED-membrane het gevolglik ook 'n positiewe effek, wat dikwels nie in ag geneem word nie. Die elektro-osmotiese koeffisiënte van die membrane neem met toenemende toevoerkonsentrasie af totdat 'n konstante waarde by hoë stroomdigtheid verkry word. Osmotiese vloei in EOP-ED neem met toenemende stroomdigtheid relatief tot die totale vloei af terwyl die elektro-osmotiese vloei relatief tot die osmotiese vloei toeneem. Osmotiese vloei dra betekenisvol by tot die totale watervloei in EOP-ED. Membraanpermselektiwiteit neem met toenemende loog-, toevoerkonsentrasie en toenemende konsentrasiegradiënt oor die membrane af.

Selemion AMV- en CMV- en *Ionac*-membrane; *Selemion* AAV- en CHV- en die nuut ontwikkelde Israeli ABM membrane; *Selemion* AMV- en CMV-, *Selemion* AMP- en CMV- en *Ionac* membrane het respektiewelik goeie werkverrigting vir sout-, suur- en basiskonsentrasie gelewer. Stroomdoeltreffendhede het tussen 62 en 91% (*Selemion* AMV en CMV); 34 en 60% (ABM-3 en *Selemion* CHV); en tussen 47 en 76% (*Selemion* AMV en CMV) respektiewelik vir sout-, suur- en basis-konsentrasie in die toevoerwaterkonsentrasiegebied van 0,05 tot 1 mol/ℓ, gewissel.

Daar is gedemonstreer dat 'n eenvoudige membraanpotensiaalmeting suksesvol gebruik kan word om membraanwerkverrigting vir sout-, suur- en basiskonsentrasie te voorspel. Membraanwerkverrigting kan met 'n akkuraatheid van respektiewelik 10, 20 en 20% en beter voorspel word vir sout-, suur- en basiskonsentrasie. Loogkonsentrasie kan bevredigend met oënskynlike transportgetalle en watervloeie voorspel word. Maksimum loogkonsentrasie; c_b^{mak}, kan bevredigend met twee eenvoudige modelle voorspel word.

Die korrekte Onsager verwantskappe wat respektiewelik vir potensiaalmetings en vir transportgetalle gebruik moet word is by zero stroom en zero volumevloei, en by zero konsentrasiegradiënt en zero volumevloei. In praktiese ED word metings egter by zero druk in die teenwoordigheid van konsentrasiegradiënte en volumevloeie uitgevoer. Hierdie faktore sal die resultate aansienlik beïnvloed in alle sisteme waar volumevloeie belangrik is en waar die konsentrasiefaktor hoog is soos wat in EOP-ED aangetref word. In die meting van membraanpotensiaal werk volumevloei teen die konsentrasiepotensiaal en sal in die algemeen die potensiaal verlaag. In ED help watervloei om die stroomdoeltreffendheid te verhoog maar die konsentrasiegradiënt sal die stroomdoeltreffendheid verlaag.

Modelle beskryf die sisteem vir konsentrering van sout-, suur- en basisoplossings bevredigend. Loogkonsentrasie bereik 'n limietwaarde (plato) by hoë stroomdigtheid afhanklik van die elektro-osmotiese koeffisiënte van die membrane. 'n Konstante helling (elektro-osmotiese koeffisiënt) is verkry toe watervloeie teen stroomdigtheid geplot is. Reguit lyne is verkry toe selpaarweerstand teen die spesifieke weerstand van die produkwater geplot is. Stroomdoeltreffendheid het met toenemende watervloei deur die membrane toegeneem, afgeneem toe die konsentrasie-gradiënt hoog en die oënskynlike transportgetalle laag was.

To my wife Deliana

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