



Guide To Electrochemical Technology

For Synthesis, Separation, and Pollution Control

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Chemical manufacturers and users are daily faced with decisions associated with the need to improve chemical processes (e.g., increase selectivity, separate difficult mixtures, decrease energy consumption, recover the value of chemicals in waste streams, minimize the discharge of a toxic by-product, etc). Sometimes appropriate technology is available, but often it is necessary to evaluate whether an R&D program is likely to provide an economic and timely solution to the needs of the company. A number of technologies may warrant consideration and possible approaches may include electrolysis. Commonly, however, research directors, plant managers, and other technical support providers have relatively little knowledge of and/or experience with electrochemical technology. This **Guide** seeks to show that modern electrochemical technology can offer the preferred solution to a range of problems, and several illustrative examples are described. On the other hand, electrochemistry is not the answer for all situations; therefore the **Guide** also discusses those factors that should be considered to determine whether electrolysis is a viable option.

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WHAT IS ELECTROLYSIS?

Electrolysis is a unit process in which chemical change results from electron transfer reactions across the electrode/solution interfaces. A voltage applied between the two electrodes in an electrolytic cell drives these reactions. A schematic of an electrolytic cell for the manufacture of Cl_2 and NaOH is shown in Figure 1.

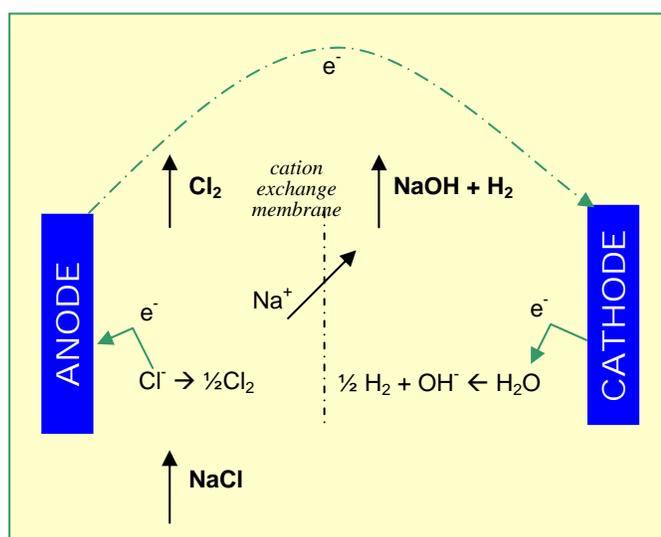


Figure 1. Schematic representation of an electrolysis cell for the manufacture of chlorine and sodium hydroxide.

The feedstock is aqueous NaCl brine, fed to the anolyte compartment between the anode and a cation permeable membrane. Chloride is oxidized to chlorine gas at the anode surface and water is reduced to hydrogen gas and hydroxide ion at the cathode. In order to maintain charge balance, migration of ions must occur, and the membrane is designed to allow the passage of only Na^+ from anolyte to catholyte. As a result, sodium hydroxide is formed in the catholyte compartment. Also, in order to preserve charge balance, the rate of transfer of electrons at the two electrodes must be equal – therefore for

each mole of chlorine formed, two moles of sodium hydroxide must also be produced. Furthermore, it may be seen that the rate of chemical change is proportional to the cell current and the total amount of product may be calculated from the charge passed via Faraday's Law.

Overall, the process objective (the conversion of sodium chloride to chlorine and sodium hydroxide) is achieved through two selective electrode reactions and a selective transport process through the membrane. In common with all processes, a chlor-alkali plant will need several other unit processes to prepare the feedstock for the cell and recover the products. In a chlor-alkali plant, the brine for the cell will be treated to remove hardness and transition ions, and then heated; the products are converted into the appropriate form for sale or downstream use.

The technology for the chlor-alkali process, including the design of the cell and the development of high-performance cell components and the other unit processes in a plant, has been described,¹ while a further series of books cover the fundamental electrochemistry, electrochemical engineering and membrane chemistry.^{2,3,4}

¹ D. Pletcher and F. C. Walsh, *Industrial Electrochemistry*, Chapman and Hall, London 1990.

² D. Pletcher, *A First Course in Electrode Processes*, The Electrochemical Consultancy, Romsey, 1991.

³ F. C. Walsh, *A First Course in Electrochemical Engineering*, The Electrochemical Consultancy, Romsey, 1993.

⁴ T. A. Davis, J.D. Genders and D. Pletcher, *A First Course in Ion Permeable Membranes*, The Electrochemical Consultancy, Romsey, 1997.

APPLICATIONS OF ELECTROCHEMICAL TECHNOLOGY

The present commercial applications of electrochemical technology are many and diverse. Figure 2 is taken from a recent EPRI report, *Electrolytic Processes, Present and Future Prospects*,⁵ which reviewed applications under the chapter headings:

- The Chlor-Alkali Industry
- Metal Extraction
- The Manufacture of Inorganics
- The Manufacture of Organics
- The Recycle of Chemicals and Materials
- Separation and Purification
- Pulp and Paper
- Water and Effluent Treatment
- Atmosphere Control and Improvement
- Destruction of Toxic Waste
- Soil and Groundwater Remediation

While all this technology is based on the same fundamental principles, its practical manifestations may be quite different with, for example, cell configurations, electrode materials and sizes, electrolytes and separators, which are each designed to meet the particular demands of the application. Even within a particular heading, the processes may be quite different. For example, consider the manufacture of inorganic chemicals:

- The world production of Cl_2 is $\sim 45 \times 10^6$ tons/year at some 700

different sites. The chlor-alkali industry is a major user of electric power, consuming $\sim 125 \times 10^9$ kWh/year, > 1% of the total electricity generated. Not surprisingly, energy consumption is a major consideration in process operation. Also, the scale of the industry warrants the development of highly optimized cell designs and high-performance anodes, cathodes and separators. A modern cell house will be fully automated and will operate continuously without maintenance for several years.

- The world production of potassium permanganate, KMnO_4 , is only $\sim 20,000$ tons/year at a few sites. Energy consumption is a less important consideration in the process economics, and the electrolysis plant is more traditional, without components specifically developed for this process.
- Electrolysis is used for the on-site manufacture of pure arsine, AsH_3 , for the electronics industry. It avoids storage of highly toxic gas since the cells may be switched on/off as the gas is required. Highly automated and safe units are operated on a very small scale.

A similar story could be told with respect to the manufacture of organic chemicals or with respect to the technology for process stream recycle and environmental protection. Thus, electrolysis is used for the manufacture of the polymer intermediate, adiponitrile, at several sites with a total world production of $\sim 300,000$ tons/year. It is also used for the production of a number of fine

⁵ EPRI Report, *Electrolytic Processes, Present and Future Prospects*, Report Number TR-107022, December 1997.

Manufacture of Inorganic Chemicals: e.g., Cl_2/NaOH , KOH , ClO_3^- , ClO_2^- , BrO_3^- , H_2 , O_2 , F_2 , O_3 , H_2O_2 , MnO_2 , Cu_2O , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{S}_2\text{O}_8^{2-}$, N_2O_5 , NH_2OH , SnO_3^{2-} , Ce^{4+} , and AsH_3 .

Synthesis of Organic Compounds: including monomers, fine chemicals, and pharmaceutical and agrochemical intermediates.

Extraction of Metals: e.g., Al, Na, K, Mg, Li, Cu, Zn, and Ga.

Recycle of Chemicals and Process Streams: e.g., metal recovery and refining, recycle of redox reagents, salt splitting, and electrodialysis for stream concentration.

Chemicals Purification and Separation: e.g., the refining of metals, the separation of organics from electrolytes, and purification of amino acids by electrodialysis.

Water and Effluent Treatment: e.g., salt removal; ClO^- , H_2O_2 and O_3 treatment; removal of metal ions to < 1 ppm; and removal of organics, nitrate and radioactive ions.

Total Destruction of Toxic Materials: e.g., destruction of contaminated waste from nuclear industry, and polychlorinated biphenyls.

Soil Remediation: in situ treatment of soils to remove toxic materials.

Atmosphere Control: devices for removing toxic substances or improving the O_2 content of atmospheres.

Metal Finishing: e.g., electroplating, anodizing, electropainting, and surface modification.

Manufacture of Electronic Components: e.g., printed circuit boards, deposition of metal contacts, and semiconductor layers.

Metals Fabrication: e.g., electrochemical machining, electroforming, and electrogrinding.

Corrosion Control: e.g., anodic and cathodic protection and sacrificial anodes.

Batteries and Fuel Cells: e.g., batteries for electronic devices, household and portable devices, and fuel cells for vehicles and on-site power generation.

Sensors: for monitoring atmospheres, warning of toxic hazards, optimization of engine/furnace performance, and monitoring water quality, process streams, medical applications, etc.

Figure 2: Some industrial applications of electrochemistry.

chemicals (total productions 1,000 - 10,000 tons/year) as well as some pharmaceutical and agrochemical intermediates on a smaller scale. Quite different approaches are available for process stream recycle. These will include electrolysis, electrolytic salt splitting, electrodialysis, and salt splitting with a special bipolar membrane, and the choice will depend on the nature of the problem to be tackled and the specification for the product streams. The same technology can provide routes for the separation and purification of products. In effluent treatment and water purification, the objective may be the removal of salts, heavy or transition metals, toxic organics or inorganics, or a reduction of chemical oxygen demand (COD).

With such a variety of applications, it is impossible to make generalizations that will stand detailed examinations.

However, there are certainly several myths about electrolytic processes that should be refuted. For example:

Myth #1: Electrolytic processes are very large consumers of electrical energy. This is only true for very large-scale processes such as Cl_2/NaOH and Al production. In the manufacture of fine and specialty chemicals, the cost of electric power is a minor part of the process cost. More commonly, the economics are dominated by the cost of the feedstock, and the process will be designed to give the highest product selectivity.

Myth #2: Electrolysis cells are unreliable and expensive. Modern electrolysis plants can be fully sealed, automated, and computer-controlled and operate continuously for many months, even years. Moreover, cells need not be expensive, particularly if precious metal electrodes and perfluorinated membranes can be avoided.

Myth #3: Electrolysis cells are difficult to obtain. No! A number of companies, including Electrosynthesis Company, Inc., now market electrolytic cells, and there are also many companies which supply electrode materials and coatings, membranes and separators, etc. Moreover, the understanding of cell design has matured significantly during the last 20 years, and implementing a new cell design to meet the needs of a particular process is much simpler.

WHY CONSIDER ELECTROLYSIS NOW?

As you evaluate conventional processing methods, we suggest that you should be including consideration of electrolysis for the following reasons:

- Electrolysis can be a selective, convenient and cost-effective technology for synthesis, separations, and pollution control.
- Electrodes bring about chemical change without the use of toxic reagents and usually in conditions close to ambient temperature and pressure.
- Electrons are cheap reagents. The cost of a mole of electrons is

< \$0.01 compared to \$0.03 - \$3.00 for common redox reagents.

- Conditions for a wide range of highly selective transformations are known.
- Methods are available for chiral synthesis.
- Suitable electrolytic cells are available off-the-shelf, and these may be combined with other necessary unit processes to construct fully integrated and compact production systems, which may be batch or continuous. Also, electrolytic processes are easily computer-controlled.
- A wide range of modern cell components is now available, providing answers to problems that previously limited process performance.

Electrolysis should be selected as the preferred method because it has advantages over competitive chemical routes.

There are limitations on electrochemical technology, and there are unique solutions that overcome many of these limitations. For example, in a direct electrolysis, the maximum rate of chemical change per unit area of electrode (the current density) is proportional to the concentration of reactant in solution. An economically viable current density often requires a high solubility of reactant. Since many reactants are often relatively insoluble in aqueous electrolytes (the preferred medium for commercial electrolysis), it has been necessary to develop strategies to minimize this limitation. One widely successful approach is indirect

electrolysis, where a redox mediator (a redox couple soluble in water) is used to transfer the electrons between the electrode and the reactant. Essentially the active oxidation state (for oxidation or reduction) is continuously generated at the electrode and allowed to react with the substrate away from the electrode, either in-cell or ex-cell. Many indirect electrolyses employ multiphase conditions. Couples used successfully for oxidation include $\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Cr}^{3+}/\text{Cr}_2\text{O}_7^{2-}$, $\text{Mn}^{2+}/\text{Mn}^{3+}$, and $\text{Os(VI)}/\text{Os(VIII)}$ couples with chiral ligands. The redox species are always recycled; hence, only small amounts of redox reagents are used and there is no stoichiometric by-product stream from the redox reagent. Other approaches include three-dimensional electrodes and the use of gas diffusion electrodes for gaseous reagents.

Many kinds of electrochemical applications are now commercial realities for process stream recycle, product isolation, and water and effluent treatment, including:

- Removal of heavy, transition, and precious metals from effluent to levels $\ll 1$ ppm.
- The removal of many organics, commonly to a COD < 10 ppm.
- The decolorization or detoxification of effluent streams by selective oxidation/reduction.
- Removal of salinity from water to < 200 ppm (by electrodialysis, ED).
- The selective removal of ions – e.g., NO_3^- from aqueous solutions using special membranes (ED).

- The concentration of transition metal ions from plating wash waters (ED).
- The conversion of waste salt streams to acid and base (either by electrolysis or bipolar membranes).
- Recovery of pure NaCl from seawater (ED).
- Isolation of pure organic acids from chemical streams (ED).
- On-site electrogeneration of ClO_2^- , H_2O_2 , and ozone for effluent treatment.

WILL ELECTROCHEMICAL TECHNOLOGY SOLVE YOUR PROBLEM?

Of course, there can be no general answer to this question. It will depend on your specific requirements and the ability of both electrochemical technology and competing approaches to meet your challenge. Clearly, for electrochemical technology to be your chosen route, there must be a reasonable match between the capabilities of the technology and your technical needs. We have already cautioned about generalizations and myths about electrolytic processes. Furthermore, we would reiterate that there have been significant advances in the availability and performance of cells and cell components as well as in knowledge of electrode reactions and electrochemical engineering; overall, it is now easier to take a process through to commercial operation. The key to success in an R&D program is to select an appropriate approach and to identify how modern components and concepts can be

applied. If you or your colleagues are unfamiliar with the field, we would strongly recommend that you talk to a suitable consultant or approach an organization with knowledge and experience in developing electrolytic processes.

Below, you will find several examples of successful electrochemical processes developed in recent years.

We have deliberately stressed the key features that make them successful and also tried to give you some idea of what the plants might look like. We hope that you will find them interesting, although we would not necessarily expect there to be close analogies between the examples and your requirements. They are intended only to illustrate the possibilities.

EXAMPLES OF ELECTROLYTIC PROCESSES

(a) *The Synthesis of an Intermediate for the Cephalosporin Antibiotic, Ceftibuten⁶*

The reaction in Figure 3 was identified as a step in the conversion of the readily available cephalosporin C and the third

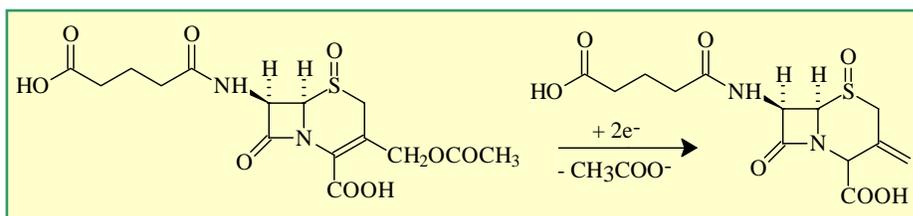


Figure 3. A step in the conversion of cephalosporin C to third generation cephalosporin antibiotics.

generation cephalosporin antibiotics. Preliminary studies showed that the highest yields of the product from the electrochemical reduction were obtained with an aqueous phosphate buffer, pH 7 - 8, and a temperature ~ 280 K. The reduction was always accompanied by significant H₂ evolution, which lowered the current efficiency. The preferred cathode material was tin, and it was found advantageous to use an extended area tin cathode fabricated from tin mesh since this gave improved mass transport of the reactant to the cathode in a flow cell. A compact and convenient pilot plant was built based on a commercial electrolyzer, the FM21-SP (marketed by ICI). It had a cathode made by welding expanded Sn mesh to both sides of a Sn plate, giving a nominal cathode area of 0.42 m². The

⁶ G. D. Zappi, 12th International Forum on Electrolysis in the Chemical Industry - Clean and Efficient Processing, Sheraton Sand Key, Clearwater Beach, Florida, October 1998.

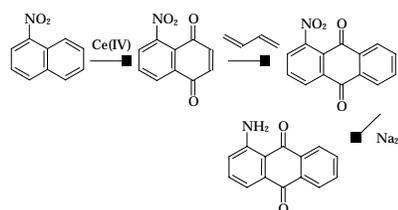
unit had DuPont's stable perfluorinated cation exchange membranes and catalyst-coated titanium anodes suitable for O₂ evolution placed on either side of the cathode. The flow circuit was based on one 100-gallon fiberglass anolyte (0.5 M H₂SO₄) tank, a 30-gallon polyethylene catholyte tank, a heat exchanger, and a recirculating cooler. The system used a 1000 A power supply and a number of safety devices and sensors to allow automatic shutdown in the event of process malfunctions. The pilot plant was operated batchwise but unattended during electrolysis; each batch converted ~ 3 kg of starting material. With current densities of 1.2 - 2.0 kA m⁻², the batch time was 10 - 12 hours; the conversion was 99% and the chemical yield ~ 95%. The development of this process from very preliminary laboratory scale to completion of the pilot plant trials took ~ 20 man months.

It is valuable to point out two further features of this process. First, it would have been preferable to carry out the reduction with equivalent substrate with the cephalosporin ring structure itself, but the reduction of the substrate then gives a significant amount of by-product. It was therefore worthwhile to carry out a peracid oxidation to form the sulfoxide prior to cathodic reduction (a type of decision familiar to synthetic chemists). Second, although the current efficiency was reasonable at low conversions, it became low at full conversion. It was, however, advantageous to the downstream processing to ensure full conversion. The low current efficiency was acceptable because the energy consumption was not at all significant to the process economics. The economic

drivers were high selectivity at full conversion (reflecting the high cost of starting material) and high product purity; both requirements were achieved in the electrochemical process.

(b) The Production of Aminoanthraquinone⁷

For some years, Hydro Quebec has been developing indirect electrolytic processes for the manufacture of organic compounds where the electrochemical step is the oxidation of Ce(III) to Ce(IV) in aqueous methanesulfonic acid. This medium is advantageous because of the high solubility of the cerium salts which allows a higher current density and gives higher rates for the reaction between Ce(IV) and the organic substrate. An early target was the production of anthraquinone where the Ce(IV) was reacted with naphthalene. More recently, a process for the production of aminoanthraquinone has been described. The route envisaged was:



The electrochemical regeneration of the Ce(IV) oxidant has been carried out in three different commercial electrolyzers,

⁷ S. Harrison, *10th International Forum on Electrolysis in the Chemical Industry - The Power of Electrochemistry*, Sheraton Sand Key, Clearwater Beach, Florida, November 1996.

and in each it was possible to achieve a current efficiency of 92 - 95% for a 70% conversion of a 1 M solution of Ce(III) at a current density of 4 kA m⁻². Again, the cost of the nitronaphthalene was the largest factor in the process economics; therefore, it was critical to optimize the chemical yield of the reaction sequence. Two-phase conditions were identified for conversion of the nitronaphthalene to nitronaphthoquinone in a chemical yield of ~ 95% at a conversion of 99%. The Diels-Alder reaction and final reduction were also shown to give high chemical yield.

A pilot plant was built and operated. The regeneration of Ce(IV) and the coupled oxidation of nitronaphthalene were carried out continuously over a period of 750 hours, and the yield of nitronaphthoquinone was maintained at 90%. The other chemical steps were carried out batchwise in 600 - 750 liter reactors, and high-quality aminoanthraquinone was isolated.

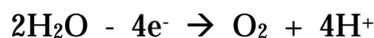
A plant with an annual production of 3,300 tons was designed and costed. The electrolyzer required a total anode area of 120 m² which could be constructed as a "black box" unit, ca 1 m x 1 m x 2 m. Raw materials represented 70% of the production costs, and the total direct manufacturing cost \$3,370/ton of aminoanthraquinone (assuming that the cost of nitronaphthalene as \$2,200/ton). The total equipment (electrochemical + chemical) cost was estimated as \$11 million.

(c) *The Manufacture of Hydriodic Acid*⁸

The requirement was for very high purity 57% HI. The conventional chemical process employed reduction of iodine with red phosphorus, a difficult technology with effluent problems. Some years ago, an electrochemical process was described. Iodine was made soluble in the catholyte by complexation with HI, and the cathode reaction was



and the anode reaction was



in a cell with a perfluorinated cation exchange membrane and a sulfuric acid anolyte so that H⁺ migrated through the membrane. The process, however, had problems associated with shortcomings in membrane performance. Some sulfate passed through the membrane, leading to unacceptable sulfate contamination of the HI product. In addition, some iodide passed from catholyte to anolyte where its oxidation led to insoluble iodine and fouling of the membrane. A recent development overcame these problems. The key change was to the anolyte, which became iodic acid; the major anode reaction remained the evolution of oxygen but some oxidation



also occurred. As a result, any iodide reaching the anolyte was consumed



⁸ J. D. Genders, *10th International Forum on Electrolysis in the Chemical Industry - The Power of Electrochemistry*, Sheraton Sand Key, Clearwater Beach, Florida, November 1996.

before it was oxidized at the anode. Therefore, the fouling problems were overcome. With no sulfate in the cell, it cannot contaminate the HI product while any iodate or periodate passing through the membrane into the catholyte would react with iodide to reform iodine, leading only to a slight loss in current efficiency.

Clearly, it was desirable to carry out the reduction of HI_3 to complete conversion, and this was achieved in a two-cell system. The major part of the conversion (I_2 concentration decreased from 4.6 M to 0.4 M) was carried out in the "production cell," a conventional plate and frame cell with graphite plate electrodes. The catholyte from this cell then passed to a "polishing cell" with a three-dimensional cathode fabricated from graphite felt. Overall, the two-cell process led to 57% HI with a very high specification including an iodine content < 10 mM. The yield based on iodine was close to 100%, and the overall current efficiency was 90%. Note that the process has no unwanted effluents. A pilot plant was operated for 1000 hours without any significant drop in performance, and a full-size plant was then designed.

(d) The Selective Removal of Nitrate from Water^{4,9}

A major development of the past twenty years has been the introduction of large-scale electro dialysis plants for the

production of drinking water. These can be very large plants producing several thousand cubic meters of high-quality water per day from brackish feedstock and tens of thousands of square meters of membranes with up to 500 membrane pairs in each cell unit.

A further interesting development has been the introduction of membranes with some selectivity of ion transport. One such membrane is Neosepta ACS (Tokuyama Corp.) which gives selectivity for NO_3^- with respect to SO_4^{2-} . Eurodia Industrie S.A. has employed these membranes in its units for removing nitrate from drinking water (nitrate in drinking water is an increasing problem, especially in Europe). Eurodia Industrie has also sought to advance cell component design and has incorporated optimized designs into the electro dialysis stacks for 5 commercial plants around Europe. These produce 250 - 4000 m^3 of treated water per day and contain 200 - 4000 m^2 of membrane, usually in 2 - 4 stacks. Typically, they reduce the nitrate level from 100 - 150 ppm to 10 - 30 ppm. Based on EUR 20 electro dialysis stacks, the investment cost varies between \$150 - 300 m^{-3} per day depending on plant size (500 - 4000 m^3 treated water per day) and the fraction of nitrate removed (0.65 - 0.85). The total operating cost, including membrane replacement and electric power consumption, lies in the range of \$0.05 - 0.10 m^{-3} .

⁹ B. Gillery, *12th International Forum on Electrolysis in the Chemical Industry - Clean and Efficient Processing*, Sheraton Sand Key, Clearwater Beach, Florida, October 1998.

(f) The Recovery of Copper from Effluent in the Scottish Whiskey Industry^{1,10}

A number of companies market electrochemical technology for the removal of transition, precious, and heavy metal ions from effluents. Moreover, the electrolytic cells are based on quite different cell concepts, and the process objectives may either be the recovery of metal value or for the effluent to meet legal requirements for discharge. Here, we will illustrate this technology with an example that employs the Renocell™ (formerly known as Porocell™).

Renocell is based on a three-dimensional cathode fabricated from graphite felt with a very high surface area/unit volume. It has cylindrical geometry and is usually undivided; it is shown schematically in Figure 4. Cylindrical, carbon felt cathode is surrounded by a cylindrical mesh anode, usually an expanded Ti mesh with a precious metal oxide coating catalytic for O₂ evolution. The effluent flow is directed through the cathode by the solid polymer disc at the top. This flow through the cathode gives uniform mass transport throughout the cathode surface and a reasonable mass transfer coefficient. The cell is fitted into a polypropylene pipe whose inlet/outlet have quick-release couplings so that the cathode, designed as a cartridge, may be changed rapidly when it is fully loaded with metal. The cartridges are a simple,

robust, and inexpensive design and these are sold as a complete unit. The size of a typical unit is 1 m long and 0.18 m in diameter.

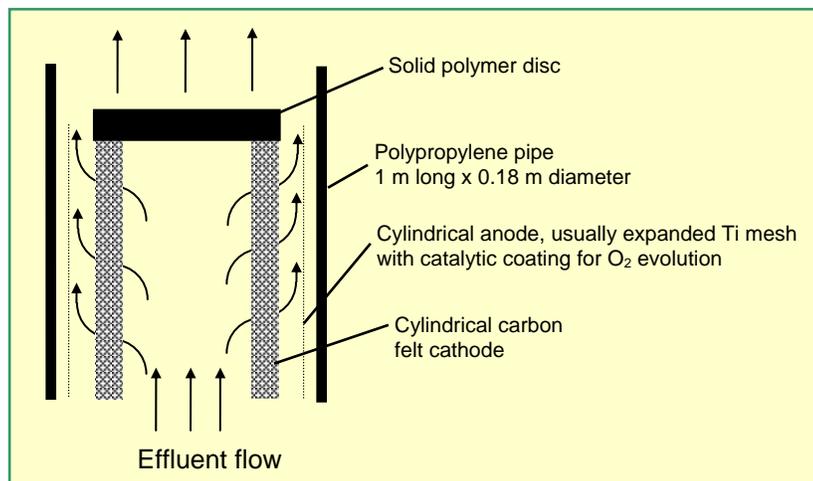


Figure 4. Schematic of the Renocell metal recovery cell.

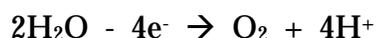
In the Scotch whiskey industry, distillation is carried out in copper pot stills, and this leads to an effluent stream contaminated with Cu(II). At Invergordon Distillers, this leads to 7 m³/hour of an effluent stream known as “spent lees” containing 10 - 30 ppm of Cu(II). The “spent lees” contains a high concentration of organics but little electrolyte, and it exits the distillation unit at 85° C. Despite low conductivity, the Cu(II) concentration is decreased to < 1 ppm by a Renocell unit. The unit has 5 cells in parallel, and has a footprint of 0.5 m x 0.75 m. The unit continuously operates, removing ~ 2 kg/day of copper, and cartridges are replaced every month. Cathodes are then loaded with some 10 - 20 kg of copper and are sent away for copper recovery. Renocell units operate in many countries on a wide range of metals including precious, transition, and heavy metals, producing exit streams that are acceptable to the local environment.

¹⁰ G. Sunderland at *The 8th International Forum of Electrolysis in the Chemical Industry - Applied Electrochemical Technology*, Lake Buena Vista, Florida, November 1994.

(g) The Recovery of 32% Sodium Hydroxide from a Waste Aqueous Sodium Sulfate Stream¹¹

Many processes produce an effluent stream, which is essentially an aqueous solution of a pure salt in high concentration. Even when the stream is sodium sulfate, it often cannot be discharged, and an attractive option can be to convert the stream back to acid and alkali. In principle, this can be achieved with either electrolysis or bipolar membranes, although with the latter approach, the concentration of acid and alkali

which can be produced is limited to ~ 5%. One electrolytic approach is based on a three-compartment cell with both anion and cation permeable membranes (see Figure 6). The salt stream is fed to the central compartment between the anion and cation permeable membranes. Proton and hydroxide ions are produced at the anode and cathode respectively by the reactions



and the acid, HX, and base, MOH, are formed by migration of X^- and M^+ through the anion and cation permeable membranes under the influence of the potential field between the electrodes. The limitation of this approach is the characteristics of the anion permeable membrane. Such membranes do not have a high transport number when contacted by a high proton

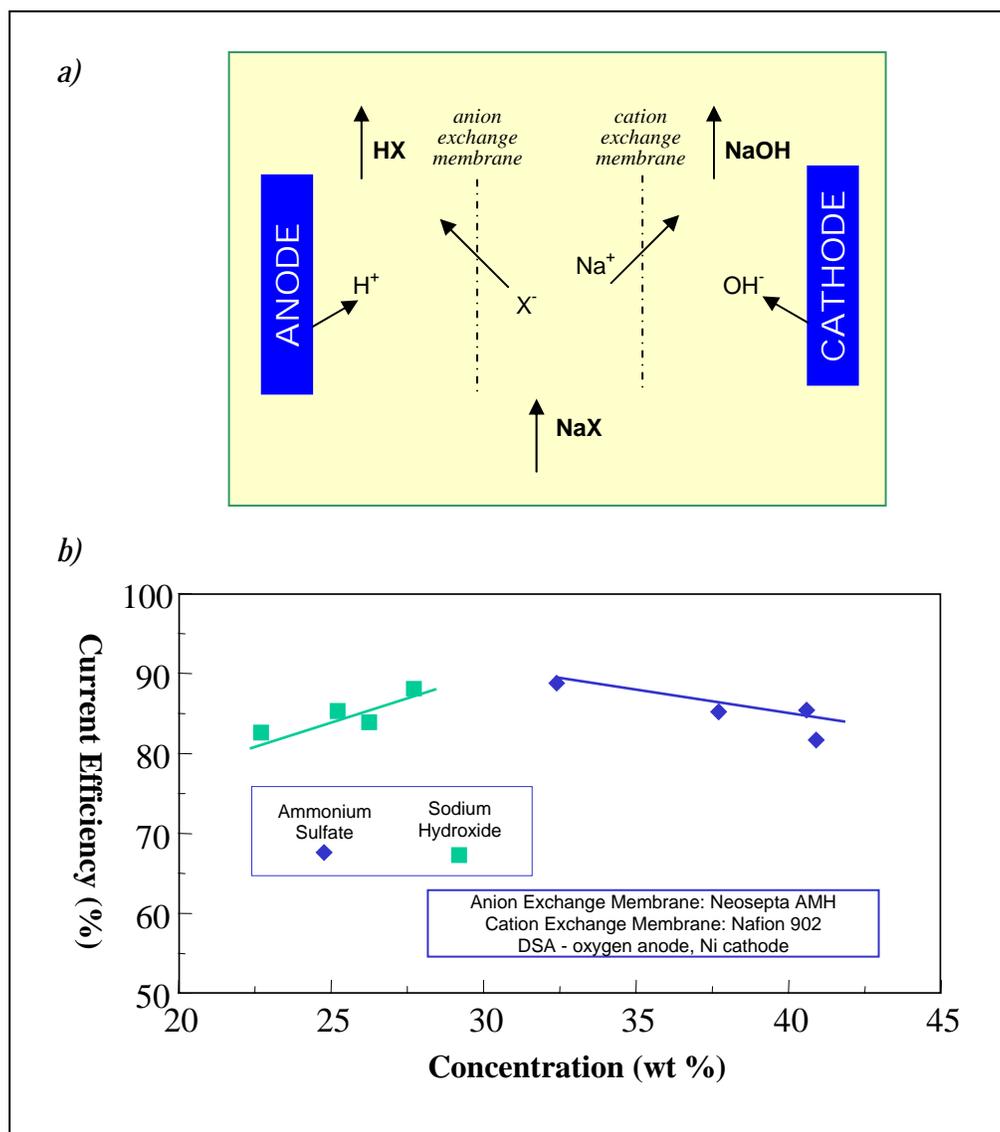
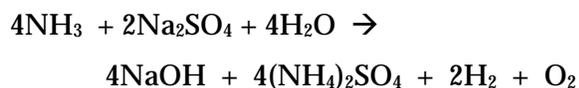


Figure 6 (a) A common cell configuration for salt splitting; i.e., converting a salt to acid and base. (b) Current efficiency as a function of product concentrations for the ElectroSynthesis Co/Ormiston Mining process.

¹¹ J. D. Genders and J. Thompson, US Patent (1992) 5098532.

concentration. Therefore, while a good current efficiency for the process is possible initially, once the acid concentration in the anolyte begins to build up, back-migration of protons occurs (i.e., protons transfer from the anolyte into the center compartment instead of sulfate transporting in the opposite direction). Only a limited acid concentration can be formed, and as protons build up in the center compartment, they start to pass through the cation permeable membrane as well and this limits even the caustic soda concentration.

The Electrosynthesis Company, Inc., in conjunction with Ormiston Mining in Saskatchewan, found a convenient solution to this limitation. Ammonia was added continuously to the anolyte tank so as to maintain the anolyte at pH 2. The overall process then becomes



and in these conditions, a good current efficiency is maintained to high concentrations of both ammonium sulfate and sodium hydroxide. The process was scaled up in a cell designed by the Swedish company ElectroCell, with electrode areas of 0.4 m². The electrodes were plates, the cathode was nickel, and the anode was an O₂-evolving coated titanium. The process was operated at 2.5 kA m⁻². Good performance was achieved over extended trials, and it was possible to manufacture 35% sodium hydroxide. Clearly, the process is only appropriate where cheap ammonia is available and there is also a market for ammonium

sulfate. These conditions prevail in the Canadian Midwest.

Conclusion

Electrochemical technology has become an important processing tool for synthesis, separations, and pollution control. Electrochemical cells and sophisticated cell components are readily available, as is the technical expertise to assist you. Many examples are now well-documented commercial realities, and many more are advancing through piloting toward commercialization. We hope this **Guide** has been useful in presenting the importance of considering electrochemical technology, along with conventional processing options, from the earliest stages of your product or process development analysis.

Electrosynthesis Company, Inc. has performed contract R&D with over 200 groups within companies, government institutions, and independent laboratories since 1977.

Our internationally recognized expertise in electrochemistry gives our clients fast-track technology development and competitive advantage at affordable cost.

*We welcome your comments on this **Guide** and look forward to working together with you on your next electrochemical R&D project.*