NEW WAYS IN CHEMICAL PROCESSING WITH ACID-ED

Patrick Altmeier, of PCA GmbH, discusses how electrodialysis can become a useful tool for intelligent design of closed flow chemical production lines.

The chemical industry produces a wide range of products making modern life possible by using a few simple raw materials such as water, mineral oil and gas, rock salt, oxygen, nitrogen, sulfur and raw phosphate. Countries with small natural resources exhibit a well developed refining industry using some base chemicals such as chlorine, caustic soda, ammonia, sulfuric nitric and phosphoric acid. Beyond these most important base chemicals, there is the group of ionic compounds such as acids, bases and salts, which represent a key substance group for the chemical industry.

TRADITIONAL WASTE WATER TREATMENT

The classical and emerging process techniques for the treatment (winning, recycling, concentrating or purification) of this substance group have an important impact on the design of our process industry. Due to the high energy consumption of these processes (e.g. evaporation, crystallisation, distillation, reverse osmosis, ion exchange, electrodialysis), their use in recycling is limited to situations where the compounds are valuable or legislative restrictions forbid the emission of such compounds.

The direct recycling of valuable compounds is used in new production plants and avoids the emission of substances to the environment (ecological aspect) and reduces raw material input (economic aspect).

To comply with new legislative restrictions for existing production lines the chemical engineer has to add some process steps at the end of the production facility. The result is, for example, an additional neutralisation, oxidation, or adsorption step in the waste water treatment plant of the company. This has only a small or no ecological impact, because the waste streams are changed but not avoided, and has a large negative economic impact. In many Asian countries there is simply no space for the construction of an additional waste water treatment facility. Therefore, a change in thinking is necessary including:

- the more effective use or reuse of our raw materials; and
- the use of new processing technologies for the treatment of wastewater.

ELECTROMEMBRANE PROCESSING

Electromembrane processing is a tool that fulfils both of the above conditions. Electromembranes are small processing units that have the ability to selectively remove ionic compounds from aqueous process streams and concentrate these compounds to a level where their direct reuse becomes possible. As such, both the economic and the ecological aspects are considered.

ELECTRODIALYSIS IN THE PROCESS INDUSTRY

Electrodialysis (ED), as a technique for the enrichment of ionic compounds, has its traditional application in the brackish- and sea water desalination, and table salt production, and has been well established in Japan almost 40 years. Since ED must compete with other desalination processes, like reverse osmosis, it has been most useful in applications where the salt content of the raw material is low or a concentrated brine solution is desired as a coupled product.

In the second case, ED finds its application in instances where the ionic compounds in multi-component mixtures should be removed. Some well established applications are whey desalination, soy bean hydrolyzate desalination or fruit juice conditioning.

In general, the scope and limitation of the use of ED is given by the membrane properties. New membrane types open new application fields, although problems associated with membranes (such as membrane fouling, scale formation, proton leakage) limit the use of this processing alternative.

ED IN THE PRODUCTION OF ACIDS AND BASES

The most promising advances in ED were the introduction of bipolar membranes (EDBM) and gas diffusion electrodes (electro-electrodialysis - EED). Both techniques are the key for decoupling caustic soda production from chlorine production as it is in chloralkali electrolysis. Instead of chlorine, these processes deliver acid as coupled product. This is a very practical coupling, because most caustic soda users also need equivalent amounts of acids, and it meets the ecologic demand of reducing chlorine consumption within the chemical industry.

Market volumes of membrane sales for EDBM were predicted to be more than US$ 200 million each year at a time when bipolar membranes were almost not available, and this technique had not been proven in practice. In the following years, the industrial introduction of these techniques slowed down due to three main reasons:

- First, the product purity of caustic soda produced by EDBM did not fit the technical requirements. As the product is one of the base raw materials of the chemical industry all competitive products have to fit the well established quality standard if it wants to have a wider use. In this case, there is an impurity of about 1 % of salt within the caustic soda, which comes into the product due to some properties of the bipolar membranes. In spite of this, EED promises the production of caustic soda fitting all purity requirements but - depending on the salt used - a corrosion problem of the special anodes arises. This is the main reason why EED was not developed beyond the R&D divisions of companies and universities.

- Secondly, the energy requirements of this process were found to be higher than expected. The process uses only electrical power for the conversion of the salt and water to the acid and bases, the amount of which is given by the voltage drop of the production cell and their current efficiency. No problems occurred with the voltage drop of the process, but the current efficiency was found to be low depending on the concentration of the produced acid. The reason for this problem was found in the so called "proton leakage" of the anion exchange membranes - another membrane type used in this process. It is also the job of membrane developers to solve this problem as it has such a negative impact on the process. Since a current efficiency of more than 90 % is possible in principal, the current efficiency drops - depending on the acid concentration - to less than 50 % resulting in almost double the energy requirements and plant investments.

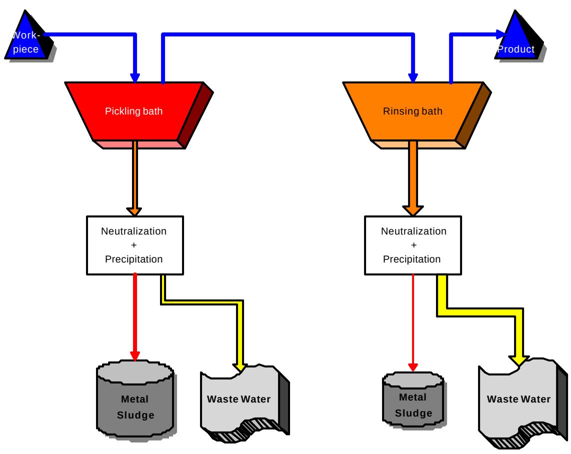
- Finally, caustic soda prices have dropped dramatically within the last 10 years due to changes in the structure of chloralkali industry. Ten years ago, the old diaphragm and amalgam based chloralkali electrolysis installations in Europe produced energetically expensive caustic soda which competed successfully - due to the low amortisation costs of the old production facilities - with the more efficiently produced caustic soda from the new membrane installations based in the Far East and the United States. It was clear that the installation of modern plants would be necessary in Europe.

However, the race to develop the new EDBM technique, which would have given the European industry the necessary tool to unburdened itself from coupled chlorine production, was lost to the well established membrane based chloralkali electrolysis technique due to the problems mentioned above.

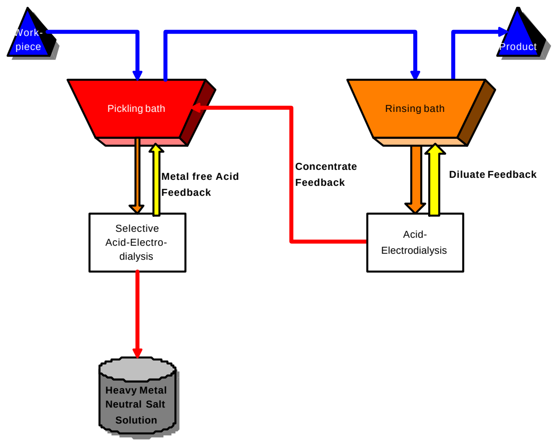
In spite of these disappointing trends, EDBM developed to be an important tool as a process unit in the production of specialty chemicals and in the integrated workup of process solutions within the chemical industry. Furthermore, encouraging efforts concerning proton leakage have been made within the last few years, which have had a direct influence on the product cost.

To summarise, these techniques for the production of caustic soda can be very advantageous. A partial substitution of chlorine coupled caustic production by acid coupled caustic production will arise slowly in the future. Such developments depend, however, on political developments because the main chlorine consuming product today is polyvinylchloride, which has advantageous properties on the one hand but ecological problems on the other.

Figure: 1: Processing Scheme for the Pickling of Stainless Steel Parts



1a) Conventional pickling and rinsing solution management.



1b) Improved management by two Acid-ED steps: continuous removal of metal salts from pickling acid by selective Acid-ED and continuous removal of pickling acid components from rinsing solution.

CONVENTIONAL ED TREATING ACID STREAMS

Beside proton leakage, a key problem with caustic soda production using the anion exchange membrane is the problem of conventional ED of mineral acids. As ED of salts is used for sea water and brackish water (0.2 % to more than 3 % salinity) demineralisation to drinking water (less than 0.05 % salt) and concentration to brine solutions (about 15 % to 30 % salt), Acid-ED is designed to work in the same concentration ranges. Therefore a concentrated acid in this context refers to an acid with a brine concentration in the range of 15 % to 30 %, although this is a more diluted acid in the vocabulary of the chemical process industry.

As aqueous mineral acid solutions in a concentration of between 1 % to 5 % often occur in processing chains, as waste or rinsing solutions up to now to be neutralised and wasted, there is the reasonable demand to deacidify these solutions and recover the acid in a higher concentration range. This is the traditional capability of ED except that we talk of an ionic solution where the cation is not a metal ion (as it is the case in the treatment of salts) but a proton (as it is this peculiarity of a acid that differentiates it from a salt).

As discussed before, traditional used ion exchange membranes show a proton leakage making a concentration of the acid uneconomical. The development of special membranes within the last years open this technique the way to solve problems in this special field.

LEGISLATIVE DEMANDS FOR RECYCLING ACID WASTES

The normative trend towards more stringent regulations as regards acid disposal, makes the use of such processes attractive for the acid recovery and reconcentration from industrial waste streams. Moreover, the highly diversified metal, chemical and pharmaceutical industry mandates to reduce waste that confront us today are applicable at many different processing points. The metal finishing industry within the EU is particulary affected since the new PARCOM limits require an optimised wastewater management. For example, the lower concentration limit for heavy metals may require a change in wastewater treatment technology. This may require a large EU grant to help develop electromembrane processes for the treatment of this kind of waste stream. Indeed, there are currently 5 Brite-Euram III projects effected this way.

ACID-ED IN THE RECYCLING OF WASTE STREAMS

In the following, the possibilities of the introduction of electromembrane processes are illustrated in the example of the treatment of pickling baths of the stainless steel industry:

Stainless steel parts have to be pickled in an acid solution (mainly nitric acid - hydrofluoric acid mixtures) as a finishing step to give a protective dense oxide layer. The product is washed from the acid (which also contains iron, chromium, nickel etc., ions from the steel) before delivery. Once a certain concentration limit has been reached within the aqueous rinsing bath, the acid is neutralised, the metals precipitated and the remaining solution wasted. When a critical metal concentration within the pickling bath is reached, the bath is considered spent and has also to be replaced. This is shown in Figure 1a.

The total consumption of pickling baths within the EU is estimated by European steel producers to be 300,000 m^3 a year for a total stainless steel production of about 6 million tons per year. The annual treatment and replacing costs are estimated to a total amount of about euro 120 million a year.

With Acid-ED, it is possible to hold the concentration of acid and salt within the rinsing solution beyond the limit and concentrate the pickling components up to a level maintained in the pickling bath as it is possible to recycle them to the pickling bath. By this technique, the rinsing solution lifetime is enlarged very much and the emission of toxic heavy metal ions is drastically reduced, because the neutralised and precipitated rinsing solution still contains low concentrations of ecological active heavy metal ions.

The pickling bath itself is replaced when a critical metal concentration is reached because some kinds of fluoride precipitation could appear. With a special kind of Acid-ED (using proton selective cation exchange membranes) a selective removal of metal ions is possible. Using such a technique would lengthen the life of the pickling bath, with the acid being used by the metal ion uptake.

This processing scheme is shown in Figure 1b.

Although such processing is not realised by the industry yet, this example illustrates the new ways in which chemical processing could progress given the development and introduction of new technologies. In summary, it can be seen that new ion exchange membranes are allowing chemical engineers to attack old problems for the benefit of the environment.