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Modern design of electrochemical reactors

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Industrial electrochemistry started more than a century ago with very simple equipment designed utilizing elementary tools substantially based on practical full scale tests. This pragmatic approach remained and deeply conditioned the structure of the electrochemical reactors until twenty years ago. Since then the design had a progressive evolution including multidisciplinary knowledge and modern techniques to model and describe the complexity of an electrochemical reactor that necessarily has to take into account mechanical, electrical, electro catalytic and hydrodynamic parameters as well as membrane or separators behaviour, mass balance and cost aspects. Even if a full scale testing is still required as a final verification, the modern design allows for a degree of optimization never achieved before. This presentation describes some new techniques and their relevant application in industrial cases made by Gruppo De Nora."

1. Membrane process for C/A industry

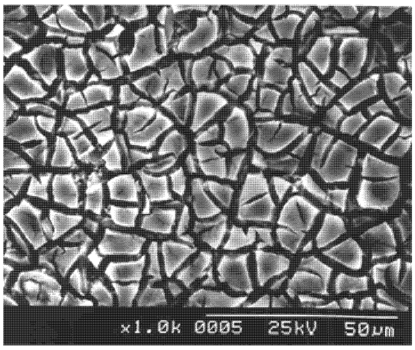
After the 2nd World War with the great development and expansion of inorganic and organic chemistry the C/A electrolysis was expanded by using the diaphragm and mercury cathode technology. Mercury cells have been the preferred in Europe whereas diaphragm cells largely dominated in USA. A really great improvement was achieved when the graphite anodes, that were quickly consumed by the parasitic Oxygen evolution, were progressively substituted by the DSA® anodes made of Titanium activated by noble metal oxides: the DSA anodes were developed and industrialized by dedicated Companies of the De Nora Group which acquired the property rights of the original Beer patents. Thanks to the improvements made possible by the installation of the DSA anodes the two technologies had a large diffusion in the Sixties and Seventies reaching a world total production of about 30 millions of MT of caustic. In the second half of the Seventies DuPont developed and began to commercialise the Nafion® membranes based on perfluorinated polymers that, for their unique chemical stability and ion selectivity, immediately appeared as the ideal separators between the anodic compartment, where brine and chlorine produce a very oxidant and corrosive environment , and the cathodic one where the ambient is strongly hygroscopic and reducing due to the presence of concentrated caustic soda and hydrogen. The membrane electrolysers development started almost at same time in USA, Japan and Europe and since then this process grew steadily winning the competition with the amalgam cells because of the lower power consumptions and with the diaphragm process for the higher caustic quality: the present world caustic soda production is now around 65 millions of MT per year and more than the half is obtained by Membrane Process.

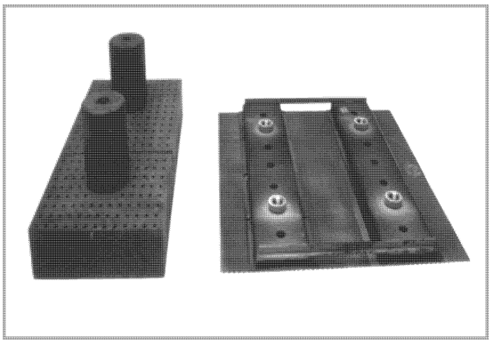
The new technology had to overcome several problems starting from the typical ones of the chemical surface processes like homogeneity of concentrations, temperatures and current density, the reduction of diffusion gradients at the electrodes and the membrane and the correct fluid dynamics of the flows: this talk will be devoted in particular to the current distribution (and the relevant cell voltage optimization) and to the pressure profile in the electrolyser (and the consequent membrane mechanical damages), with a short presentation of the evolution which has characterized the catalytic coating of the DSA anodes.

2. Electro-catalysis

The greatest breakthrough in the area of electro-catalysis was represented by the installation of titanium anodes as the substitute of the previously used graphite electrodes. Titanium is extremely resistant to the aggressive anolyte comprising sodium chloride, dissolved chlorine and hypochlorite thanks to the formation of a thin protective film of titanium dioxide which unfortunately is also an efficient electric insulator. To become an anode Ti has to be covered with a conductive and catalytic coating which provides the catalytic characteristics required for the easy evolution of chlorine. The initial material selected for such catalytic action was platinum which soon demonstrated to be inadequate in view of its tendency to become covered by a surface thin layer of oxide capable to strongly hinder the reaction of chlorine evolution: all the attempts, directed to prevent the passivation, were unsuccessful in long term operation and were in any case too expensive. The real breakthrough took place when Mr. Beer filed in the 1950s a patent application concerning titanium anodes provided with a catalytic coating of ruthenium dioxide: the industrial development of these types of anodes and their final large scale commercialization were carried out by the De Nora Group through dedicated Companies under the Trade name of DSA®. A large number of further patent applications were filed to cover other coating formulations, including the use of other valve metal oxides and other noble metal oxides, which were basically directed to improve the lifetime of operation of the anodes. The DSA anodes, first installed in industrial cells based on the mercury and diaphragm technologies, were provided with coating comprising ruthenium and titanium oxides in a weight ratio around 1 to 2 to reach a sufficient electrical conductivity and in the same time to control the content of oxygen in chlorine. A second step of the development promoted by the data coming from the industrial operation was the optimization of the decomposition temperature which determines many properties such as electric conductivity, wear rate, oxygen content in the chlorine and finally the anode potential that is the major factor for energy consumption. Whereas the Ru based DSA anodes behaved very positively in diaphragm cells, the same anodes when installed in mercury cathode cells were characterized by very short lifetime: the failure analysis based on measurement of the anode potential vs. time and the residual ruthenium content in the coating showed the problems be generated by an increased oxygen evolution caused by the local dilution of the brine due to the high current density that shifts the Ru to high valence states that are soluble or volatile. The problem was effectively overcome by the addition of a further oxide of valence – stable metals of the platinum group: the additional platinum group

metal has been applied with very positive performances in term of life and power consumptions at current densities up to 15 kA/m^2. The penetration of the novel membrane technology introduced a new operation environment for the DSA anodes: as the membrane is supported by the anodes in direct contact they have to cope with the caustic soda which back-diffuses from the cathodic compartment with the consequent increase of the pH of the brine contacting the anode surface to values much higher than those typical of the diaphragm and mercury cathode cells. This situation leads to an increased oxygen evolution and to an accelerated wear rate connected to the easier oxidation of ruthenium in the alkaline environment: both problems could be dealt successfully with the same approach used for the mercury cells that is by the optimized addition of a further oxide of a valence – stable platinum group metal to achieve a reasonably extended lifetime and by the tuning of the decomposition temperature of the precursors to the final oxide, to balance lifetime against oxygen content in chlorine.
A typical “cracked dry mud” DSA anode superficial morphology is reported here below on the left together with a photo of old graphite and equivalent Ti structures.





All accumulated experience of many years of worldwide operation in chlor/alkali plants based on the diaphragm, mercury and membrane technologies has made possible the detailed definition of the today industrial production parameters in terms of preparation of the titanium substrate, that is surface roughness and optional application of protection pre-layers, composition of the coating, type of precursors and thermal levels for their decomposition to the final oxide, and quality assurance procedures such as measurement of the anode potential in standardized conditions, accelerated lifetime tests and resistance to reversing current regime. The membrane technology has also brought about the topic of the activated cathode. In the diaphragm technology the application of a catalytic coating resulted to be extremely difficult for a number of reasons, the most important of them being the very scarce adhesion due to the corrosion of carbon steel substrate and the inactivation caused by the deposition of iron during operation. In the membrane technology the high purity of the produced caustic soda may only be kept if the construction material of both the cathodic compartment and the cathode substrate is nickel: due to the much higher corrosion resistance of the nickel metal even in severe alkaline environments the adhesion depends only on the surface roughness and the process used for the deposition of the catalytic coating. Many types of cathodic activation have to now been proposed: among them the ruthenium – based formulations such as composite RuO_2 – galvanic nickel, mixed $(Ru, Ni)O_x$ oxides and platinum dispersed in ceramic oxides have been particularly successful.

3. Electrodes design and optimization by means of Finite Elements modelling

The choice of the shape of the electrodes is mainly driven by the reduction of the cell voltage by respecting the correct conditions to achieve a high current efficiency for long term operation. The old design started with a selection of the few easily available shapes based only on the mechanical and electrical properties, followed by both tests on Lab scale to choose the best geometry and a final test at industrial scale. Thanks to the consolidated past experience, today we can take into consideration a high number of possible shapes, even the ones that could be manufactured by a dedicated tool. Modelling its behaviour by FE, each single geometric parameter can be examined and optimised so to obtain a precise definition of the most promising candidates for the final anode and cathode geometries. The practical example that we are now presenting is the process for the substitution of the traditional Louver anode on the UhdeNora Single Element 2,7m2 BM cell by an electrode able to obtain a more homogeneous current distribution on the membrane even if the "Gap" is reduced almost to zero. The membrane is usually mechanically supported by the anode and the "Gap" is the distance between the Membrane and the cathode: this distance is the most important component of the current ohmic drops in the caustic and represents the major field of development for the never ending efforts towards the reduction of power consumptions. The development started with the creation of some FE models of the Louver with different levels of complexity to reproduce its behaviour both in 2D and 3D.

First a Pseudo tertiary model was defined. It takes into account:

a. A primary current distribution model (Ohm's law for ionic conduction in the electrolyte domain)
b. Full electrode kinetic expressions (Butler-Volmer expressions including the influence of both activation and concentration over-potential, where concentration over-potential depends only on an input parameter, the boundary layer thickness, and not on a real chloride distribution).

This model was then implemented both in the anolyte and catholyte by the addition of a

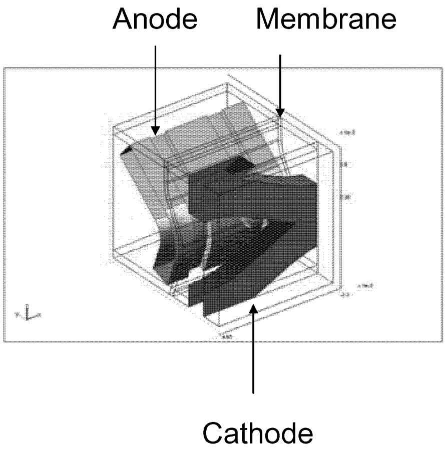
c. full hydrodynamic description using a so-called mixture model that accounts of
    - Buoyancy effect from the gas content
    - Viscosity effects due to gas content
    - Relative velocity between the gas phase and the liquid phase

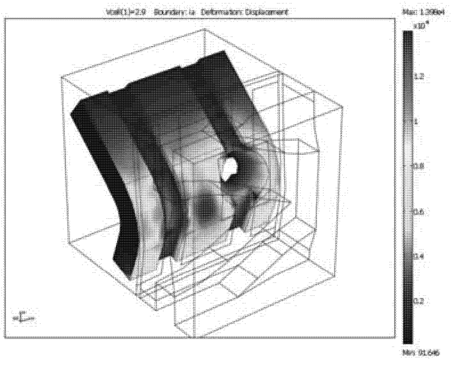
As a further step the Fully Coupled Model was defined by adding

d. Chloride transport using a diffusion-convection equation (full tertiary current distribution).

For a complete description of the current distribution and the relevant cell voltage over all the possible operating ranges many simulations had to be performed: the last developed 3D Fully Coupled Model is quite heavy to run so it has been used mainly to verify the reliability of the results and to compare the different models. To speed up

calculation time an approximated method (pseudo 3D Fully Coupled model) that gives sufficiently precise results has been developed: the results of simulations related to different 2D cross-sections are summed up on the basis of geometric weight factors.
Drawing of the Louver anode, membrane and cathode mesh and an example of Current Distribution on the Louver is reported here below.





The membrane shape under usual operating conditions (90°C, 210 gpl NaCl as anolyte, 32% NaOH as catholyte, 20–50 mbar of differential cathode to anode pressure) is calculated by a FE mechanical model and automatically embedded in the main model. In that way we succeeded in correctly reproducing the Louver behaviour even with the pseudo 3D simplified model all over the complete operating range. As a further verification of model predictions we have also developed a new lab test using a pollutant (Calcium) as the tracer of the current intensity on the membrane.
After all these verification we could start the new design task by substituting the Louver with other geometries and comparing the results. After a screening among several different shapes the preferred ones have been optimised in their geometrical and mechanical parameters and three candidates to be tested on field on industrial BM 2,7m^2 elements have been defined. Two of them have been already manufactured and they are presently under testing: the results are in line with modelling predictions.
The calculated cell voltages have a precision in the range of few tens of milli-Volts and so are sufficient to predict the correct ranking of the different shapes.
The method has proved to be valid and helpful for saving time and resources.

3. Two phases flow in the electrolyser

The C/A electrolysis is a surface process: the surface of the electrodes is active and even the two surfaces of the membrane play a main role.
This fact leads to the necessity of keeping homogeneous and suitable conditions all over the cell for temperatures and concentrations avoiding the local stagnation of gases and electrolytes:

- the chlorides are consumed at the anode and have to be continuously fed because a too low concentration will result in a dangerous increase of the parasitic Oxygen evolution and consequent local pH decrease at the membrane;
- the Chlorine gas stagnation causes irreversible damages to the Membrane;
- a high Caustic concentration results in higher cell Voltage and even irreversible damages;
- local different temperatures and concentrations will lead to a local different membrane conductivity, unbalanced current distribution and increase of power consumptions.

To keep homogeneous conditions internal or external re-circulations are applied both by natural convection or by pumping: the UhdeNora cell has adopted an internal "gas lift" re-circulation created by a down-comer that divides in two vertical partitions the anodic compartment, the first, close to the anode and full of gas, where Chlorine and brine flow upwards and the second where a large flow of brine, after the separation from the gas, is recycled to the bottom of the cell to be mixed with the fresh feed. The down-comer is interrupted below the top of the compartment to create a region for gas disengaging and then allowing the discharge. The two-phase hydrodynamics presents special characteristics due to the specific flow that is realized: the conditions to obtain a steady flow are very far from what happens in the electrolyser so the discharge is characterized by "slug" or "plug" pattern with heavy pressure pulsations. The membrane is kept against the anode by a differential pressure, 20 – 40 mbar, between Hydrogen and Chlorine gas: this choice is directed to avoid the formation of a gap between anode and membrane which would be characterized by a very high Cell voltage increase; instead the gap between Membrane and cathode does not penalize so much because of the high conductivity of the caustic. This differential pressure has limits, connected to the anode shape, beyond which permanent damages to the membrane are caused and unfortunately these limits are in the same range of the pressure pulsations resulting from the discharge of the two phases. Since the force pushing the membrane against the anode is even reversed by the pressure pulsations, the membrane starts fluttering and, being just a reinforced plastic film, is mechanically damaged by abrasion against the metallic electrodes. The optimization of the design of the natural "gas lift" internal re-circulation of the SE BM2,7m2 cell has been realized through the following steps:

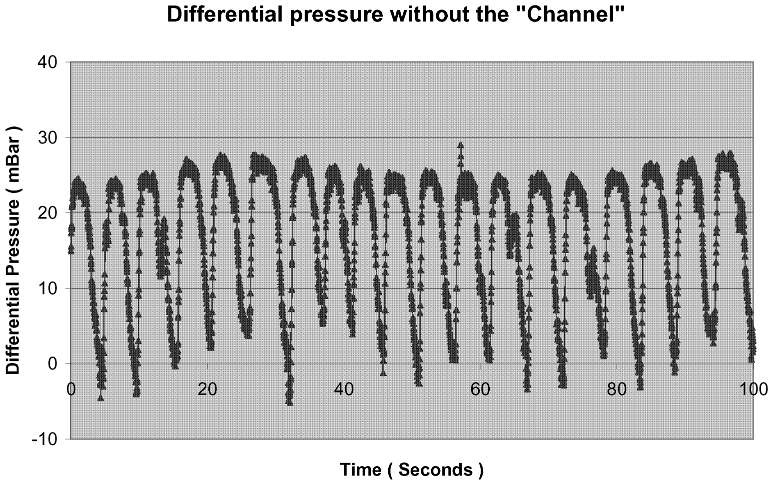
- Verification of the flow rate of anolyte re-cycle in an industrial pilot electrolyser where a terminal cell has been equipped with three glass windows that allow to look inside between the pan and the down-comer and to measure the flow rate by a laser Doppler effect instrument;
- Realization of a full scale mock-up where the new proposals have been introduced and tested artificially by water and air ; the flow rate have been measured by the motion of small filter paper pieces revealed by a fast movie;
- Measurement with the same method of the recirculation in a one compartment Lab cell provided with a movable down-comer the position of which has been optimised;
- Final testing of the best design in full industrial scale, with the same apparatus used for the initial verification, implemented with the addition of a sampling

system that by collecting anolyte samples from 12 different positions allowed the description of the concentration profile all over the surface of the element.

We arrived to increase more than twice the flow rate of the recirculation, reducing the gradients between inlet-bottom and top-exit regions to less than 5 gpl.

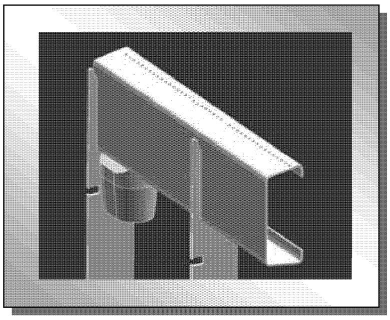
The study for reducing pressure pulsations have been done almost in the same period and used partially the same apparatuses. The UhdeNora cell with the unique “down flow” discharge by vertical Teflon stand-pipes had since the first models a smooth pressure situation that assured a long life to the membrane, up to 7 years at Tofte plant in Norway, at low current densities. The pressure pulsations are function of the current density and when the industrial figures increased more than 4,5 kA/m2 the usual differential pressure of 30 mbar became not sufficient to balance pressure fluctuations and consequently we started the development of a new discharge device capable of reducing significantly the pulsations.

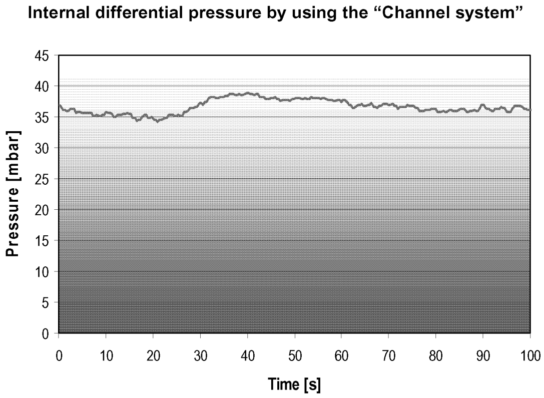
First we realized a reliable method to measure the pressure pulsations: the old methods have been found completely imprecise and un-reliable. New piezo-resistive pressure transmitters, made of suitable materials to be inserted directly in the cell, have been selected and tested; a data logger with a sampling period of 2,5 µs connected with a PC has been procured; special pressure measuring nozzles have been installed on some cells of a large plant. So we realized a series of measurements that demonstrated that the reversing of the differential pressure may happens with a frequency that increases with the CD and the membrane abrasion velocity is directly proportional to that frequency.



We have to point out that a damage in the membrane as an hole or a small cut does not only decrease the Current Efficiency but causes a devastating corrosion of the Titanium that can perforate the pan getting even external leakages of chlorinated brine.

Some different devices have been tested in the mock-up in Milano Lab restricting the choice to two models that have been inserted in real cells in the industrial pilot plant c/o CABB in Gersthofen in Germany: in this plant, under real operation conditions with current densities up to 8 kA/m2 we realized the final selection of the so called ”Channel” that reduces the pressure pulsations to less that 5 mbar assuring a very quiet discharge of gases and liquid and long life to the membranes.





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