

## The influence of the brine quality on the performance of membrane chlor-alkali cells

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This paper illustrates the effect of feed brine quality on the performance of the membrane chlor-alkali process. In particular attention is given to the working of electrodes and membranes and to mechanism with which impurities in salt affect their behavior. The relation between power usage, product quality and brine quality is also illustrated. A balance between raw material (NaCl) costs on one side and energy consumption, purification and disposal, maintenance costs on the other side decides the most economic solution for a chlorine plant. Stringent requirements to brine purge or the need to operate in a closed loop make salt quality and/or brine treatment and impurities recycling an important issue for the future.

### 1. INTRODUCTION

The basic raw material for the membrane chlor-alkali process is purified feed brine. A typical brine loop (fig. 1) includes of a saturator, where solid NaCl is dissolved with water and depleted brine. The solution enters the purification section and from here the electrolysis cells. Before it is reused in the saturator, brine is de-chlorinated. Eventually, a chlorate destruction unit is also needed. As brine is continuously recycled, all impurities, which are not removed in the purification or with the products, accumulate. In order to regulate their level, a purge is needed.

This paper deals with the influence of feed brine quality on the performance of the electrolysis cell. It is focussed on the specific working of impurities on cell components and on the mechanism that is responsible for the observed effects.

### 2. POWER USAGE, CURRENT EFFICIENCY, PRODUCT QUALITY

The performance of the electrolysis cell is often described in terms of power usage (P), current efficiency (CE) and product quality.

The *current efficiency* is the ratio between the current used to form the desired product and the total current. In chlor-alkali operations CE is

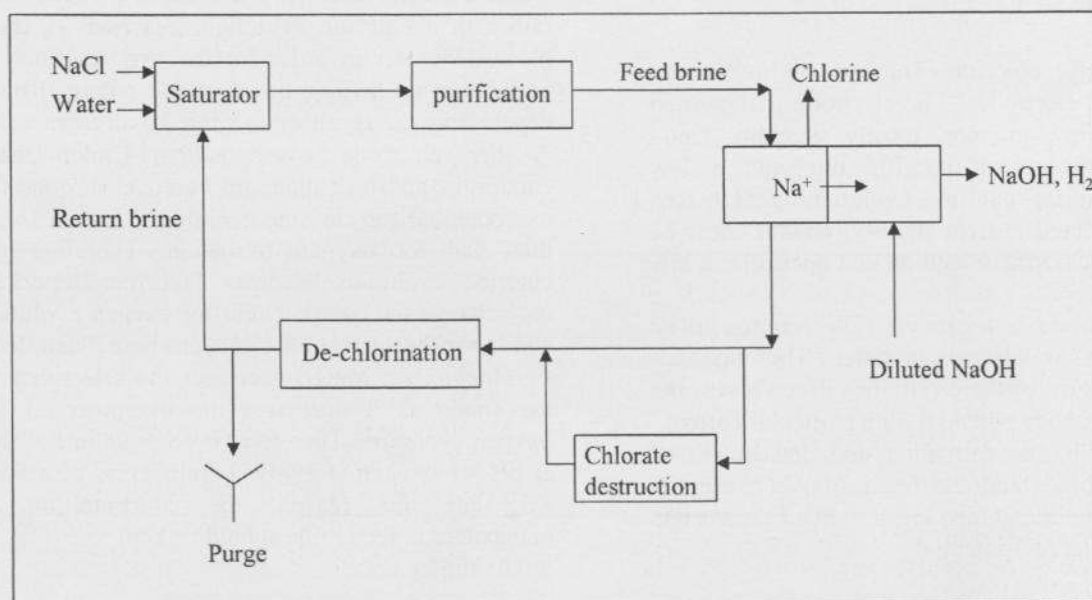


Figure 1. Brine loop

usually  $90 < CE < 98 \%$ .

The power usage is proportional to the cell voltage  $E$  (V):

$$(1) \quad P = \frac{nFE}{CE * MW}$$

where  $P$  is expressed in kWh/kg product,  $F$  is the Faraday constant (26.8 kA hr/kg equivalent),  $MW$  is the molecular weight of the product (kg/kmol) and  $n$  the number of electrons required by the concerned oxidation/reduction reaction. Contributions to the cell voltage arise from the thermodynamic components (concentration, temperature, pressure of reactants and products), kinetics components (specific rate of charge transfer reaction at the electrodes), ohmic components (resistance of the anolyte, catholyte membrane and of any other devices through which current is transported). In modern chlor-alkali cells  $P$  is in the order of 2.2-2.5 kWh/kg  $Cl_2$ , depending mainly on the electrochemical cell design and components and on the current density ( $A/m^2$  membrane surface).

Electrical energy costs are a substantial part of the total variable costs. As the brine quality influences both the current efficiency and the cell potential, an optimal balance has to be found between the costs of raw materials, brine purification and power usage costs.

### 3. FEED BRINE QUALITY AND ANODE PERFORMANCE

Anodes for chlorine evolution are ruthenium-based oxide electrodes. The electrode is deposited on a metallic structure, mostly titanium. Good anodes have a high specific rate and a low overpotential for chlorine evolution. This means that, for a fixed current density, anodes must be specific for chlorine evolution and operate at a low potential.

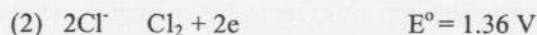
An electrode is a catalyst. The reaction to be promoted is an electron transfer. The physical-chemical nature of the electrode surface settles the value of the anode potential for a particular current.

Next to it, the formation and detachment of chlorine bubbles and the interaction between the anode and the membrane are important parameters in deciding the cell potential.

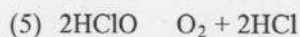
Feed brine quality plays a role on the electrode selectivity, on the active electrode surface and on the rate of formation and detachment of chlorine bubbles. Some components may decrease the electrode life. Each impurity influences the process of chlorine evolution in a different manner. Here some mechanisms are illustrated. Only the working of the anode is taken into account.

#### 3.1 Selectivity

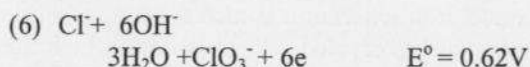
The selectivity of the electrode influences the product quality and the power usage (see: equation 1). The main side reaction is oxygen evolution, i.e. water oxidation:



HClO decomposition may also occur:



or chlorate formation:



If we looked only at the thermodynamic potentials for oxygen and chlorine evolution from brine, we would conclude that oxygen evolution (reaction 3) rather than chlorine evolution (reaction 2) takes place. However in order for the two reactions to occur at a net current, the electrode potential must depart from the equilibrium value by an extra value, the electrode overpotential. Under these conditions and on ruthenium based electrodes the overpotential for chlorine evolution is much lower than that for oxygen formation. Therefore the chlorine evolution becomes favorite. Impurities may change the overpotential for oxygen evolution and lower the current efficiency, as here illustrated.

*Manganese.* Mn(II) decreases the selectivity of the anode as it decreases the overpotential for oxygen evolution. The effect is so pronounced that at pH =1 oxygen is evolved from brine at a 95% CE. For this reason, the concentration of manganese in feed brine should be kept  $< 0.01 \text{ mg/kg}$  brine.

*Sulfate.* Sulfate decreases the activity coefficient of  $\text{Cl}^-$ , i.e. it increases the thermodynamic potential for chlorine evolution. At critical concentrations it alters the kinetics of chlorine evolution as well.

Dotson and others [1] have measured the sulfate solubility algorithms for  $\text{CaSO}_4\text{-NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4\text{-NaCl-H}_2\text{O}$  in chlor-alkali brine at 25, 65, 75 and 85°C. They show that sodium sulfate is very soluble in brine and will displace some NaCl from solution, while calcium sulfate is only slightly soluble. At 85°C the algorithms which describes the relation between sodium sulfate and sodium chloride concentration is:

$$(7) \quad \text{Na}_2\text{SO}_4 = 231 - 0.65 \text{ NaCl}$$

(concentration in g/l).

The sulfate concentration that is advised in membrane chlor-alkali is around 5-8 g/kg brine. Sulfate ions may still move to the NaOH compartment, lowering the NaOH quality (see: paragraph 5). In combination with cations, insoluble sulfates may precipitate on several cell components lowering their performance.

*Calcium.* As it will be shown in the next paragraph, some impurities make the selectivity of a membrane decrease. Calcium is among those. The consequence of the decreased membrane selectivity is that hydroxide ions leak from the cathodic to the anodic compartment. As the membrane is usually pressed on the anode, the pH in the proximity of the anode feels the effect of the hydroxide leakage. As the pH increases, the selectivity for chlorine evolution decreases.

### 3.2 Active surface

*Barium.* Barium may precipitate on the anode surface as sulfate and make the active electrode surface decrease. The maximum allowed level is related to the concentration of sulfate. Usually it is recommended to keep the concentration < 0.5 mg/kg brine.

*Organic components.* All those impurities that modify the surface tension of the anode surface by adsorbing on it influence the rate of formation and of detachment of chlorine bubbles. Large chlorine bubbles provoke a decrease in the active electrode surface, an increase in the electrical resistance of brine (chlorine gas is an insulator) and a perturbation of the current distribution. The limit of

the total organic concentration is a few mg/kg brine.

### 3.3 Anode life time

*Fluoride.* Fluoride attacks  $\text{TiO}_2$  that is one of the components of common anodes for chlorine evolution. The reaction is:



The dissolution rate of  $\text{TiO}_2$  depends on the brine pH and on the fluoride concentration. Fluoride should be kept as low as < 0.1 mg/kg brine. It should be mentioned that fluoride could be present in rock salt but also arise from the dissolution of the saturator, in case its is made out of concrete, or from acidification with HCl contaminated with HF.

## 4. FEED BRINE QUALITY AND MEMBRANE PERFORMANCE

A membrane has the function to separate brine and chlorine from caustic soda and hydrogen and to allow the transport of sodium ions. There are two parameters of importance in a membrane: the selectivity and the electrical resistance.

Selectivity is the ratio between the charge transported through the membrane by sodium ions and the total charge through the cell. In principle only positive ions and neutral molecules can be transported through an ion selective membrane. Nevertheless also the transport of anions is observed, especially hydroxide, chloride, sulfate ions.

Membranes are responsible for somewhat 10-20% of the total energy consumption in the electrolysis cell. The lower the resistance to the transport of ions, the lower the energy costs.

A chlor-alkali membrane consists of two or more polymer layers and a reinforcement. The polymer layer facing the cathode is designed to impart selectivity to the membrane. A damage to this layer (the "carboxylic layer") means a decrease in the selectivity. A second layer, which has a lower resistance but also a lower selectivity, is added to the carboxylic (the "sulfonic layer"). A damage to this layer means an increase in the resistance of the membrane.

*Calcium and magnesium.* Calcium and magnesium are the most common and most harmful



impurities in brine. Fig. 2 shows the effect of the presence in brine of Ca(II) 1 mg/kg brine and Mg(II) 0.6 mg/kg brine.

Their hydroxides precipitate in the membrane. This is not surprising, as the membrane separates the feed brine with an acid-neutral pH from concentrated caustic soda. Therefore through the membrane there must be a large pH variation. When the  $\text{OH}^-$  and the Mg(II) or Ca(II) concentration reach the solubility product of the respective hydroxides, the precipitation of the hydroxide takes place. Calcium and magnesium hydroxide have a different solubility product [3], the solubility product of calcium hydroxide being larger. Magnesium hydroxide reaches its solubility product in the sulfonic layer [2]. The effect of the precipitation of this specie in the sulfonic layer is an increase in the resistance of the membrane. Calcium hydroxide, on the other hand, precipitates in the carboxylic layer. When its concentration in brine is around 1 mg/kg, the precipitation of the hydroxide provokes an irreversible damage at the carboxylic polymer. The current efficiency decreases drastically. The concentration of calcium and magnesium should be kept  $< 0.02$  mg/kg brine.

**Iodide.** When the concentration of  $\text{I}^- > 0.2$  mg/kg brine, iodide produces a loss of current efficiency. Iodide may precipitate in both

the sulfonic layer and in the carboxylic layer as paraperiodate ( $\text{Na}_x\text{H}_y\text{IO}_6$ ;  $x+y = 5$ ). Also a synergic effect between barium and iodide has been observed, even if the mechanism of the interaction between the two is controversial.

**Iron.** Some ions form amphoteric hydroxides with a different solubility at different pH. Iron is one of those. The behavior of iron in chlor-alkali cells has been extensively described [4]. When evaporated salt is used as raw material, the main source of iron is the anti-caking agent: potassium ferrocyanide. Ferrocyanide decomposes in contact with chlorine and Fe(III) is formed. Fe(III) oxide may precipitate on the surface of the membrane, provoking an increase of the cell potential. In [4] an increase of 400 mV in 18 months has been reported for a plant that shifted from rock to evaporated salt. If the acidity of the feed brine decreases to  $\text{pH} < 5$ , iron enters the membrane [5]. If the pH profile in the membrane is such to allow the precipitation of iron in the carboxylic layer, also a decrease in the current efficiency may be expected. Iron in feed brine should be  $< 0.02$  mg/kg.

**Silica.** Silica ( $\text{SiO}_2$ ) may accumulate in the membrane as silicate [6]. If the silicate and calcium concentration reach the solubility product, calcium silicate will precipitate. Also aluminum forms aluminosilicates, which damage the membrane.

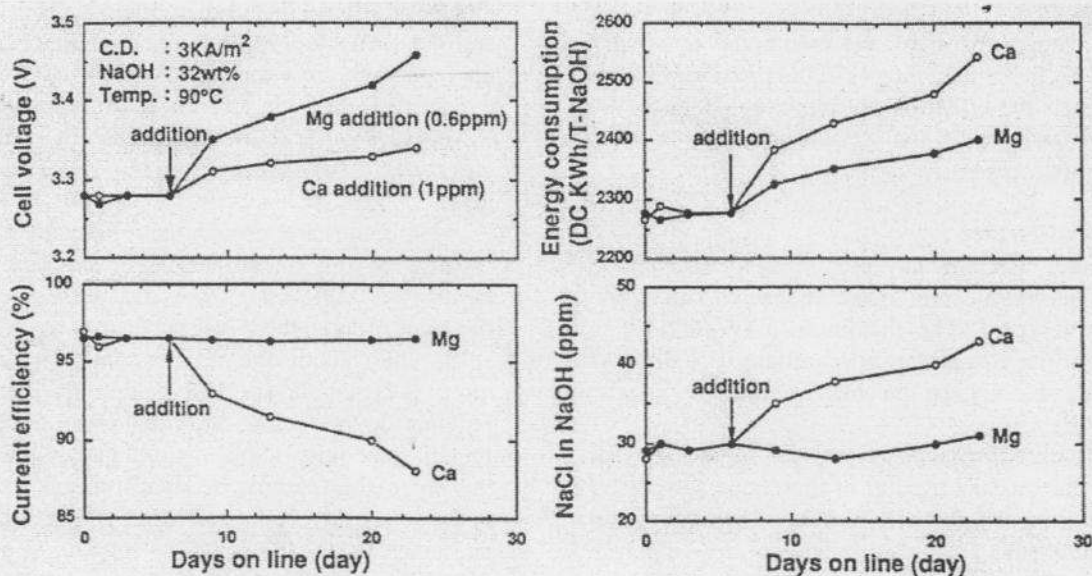


Figure 2 Effects of calcium and magnesium in feed brine on cell performance. CD = 3 kA/m<sup>2</sup>; T = 90°C; NaCl = 200 kg/m<sup>3</sup>; NaOH = 32%. Figure from [2]: "Effects of low concentration levels of calcium and magnesium in the feed brine on the performance of a membrane chlor-alkali cell" reproduced by permission of The Electrochemical Society, Inc.

The aluminum level in feed brine should be kept < 0.2 mg/kg brine. Silica in feed brine should be < 5 g/kg brine.

## 5. FEED BRINE QUALITY AND PRODUCT QUALITY

*Potassium ferrocyanide.* The anti-caking agent decomposes in contact with chlorine. Next to Fe(III), also oxidation products of cyanide are formed. In particular ammonia can be formed via cyanate:



Ammonia reacts with chlorine and forms chloramines ( $\text{NH}_x\text{Cl}_y$ ), nitrogen or nitrate. The product ratio depends on the brine pH, the chlorine concentration and the time of reaction. Ammonia and chloramines leaves the electrolysis cells with chlorine and are precursor of  $\text{NCl}_3$ . Pure  $\text{NCl}_3$  can decompose violently or even denote. Its maximum allowed concentration in liquid chlorine is 2-20 mg/kg. A special unit for its removal is required, at least in plants producing liquid chlorine.

*Organic components.* All organic components that in contact with chlorine decompose to  $\text{CH}_x\text{Cl}_y$  are undesired as they lower the chlorine quality.

*Sulfate.* Sulfate ions can move through the membrane and end up in NaOH. The passage of sulfate ions is influenced by the quality of the membrane and by the process conditions[7].

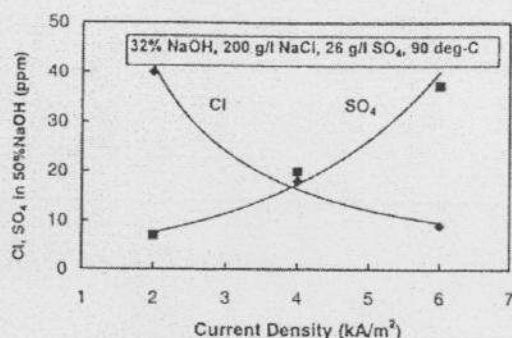


Figure 3 Sulfate transport in caustic soda. Figure from: [7] "High performance operation with Flemion membranes and the AZEC-B1 electrolyzer" © 1998 Society of Chemical Industry (SCI). Reproduced with permission.

*Calcium, iodide.* All those impurities that decrease the selectivity of a membrane, also provoke an increase in the feed brine pH, at the anode surface. As a consequence oxygen and/or chlorate is formed (see reactions 3, 5 and 6). Oxygen is often an undesired component in chlorine. Chlorate may cross the membrane and lower caustic quality. Plants that operate without feed brine acidification have a dedicated unit for the chlorate decomposition.

*Bromine.* The presence of bromide in salt leads to the formation of bromine that ends up in chlorine. Some sequential processes and products are sensitive to high bromine contents.

## 6. CONCLUSIONS

In tab.1 the maximum allowed level of some impurities in feed brine is summarized:

Table 1

$\text{SO}_4^{--}$	< 5-8 g/ kg brine
$\text{SiO}_2$	< 5 mg/kg brine
Ca(II), Mg(II)	< 0.01 mg/kg brine
Fe(II or III)	< 0.02 mg/kg brine
Al(III)	< 0.2 ppm

The requirements to brine quality become more and more extreme as the electrolysis cell is operated at higher current density, a trend of improved electrolysis cells. A balance between raw material (NaCl) costs on one side and energy consumption, purification and disposal, maintenance costs on the other side decides the most economic solution for a particular plant.

Not only variable costs but also investments are related to the salt quality. What for operation units, of which dimension and of which construction material depends on the kind of brine purification requested by a particular salt quality.

In some regions closed-loop operation is a requirement. This makes it particular important to increase the salt quality or to develop alternative processes to separate and recycle brine impurities.

## REFERENCES

1. R.L. Dotson, H.L. Loftis, H.B. Cochran J. Appl. Electrochem. 29, 1999, pg. 525.