

The impact of impurities in brine on the economy of membrane cell electrolyzers

Denis Krude

Electrolysis Division, Krupp Uhde GmbH,
Friedrich-Uhde-Strasse 15, 44141 Dortmund, Germany

This article is dealing with brine impurities mainly originating from the salt used for the electrolysis. Considering the enormous mass transport through the membranes, an economic operation requires extremely low impurity levels in the brine. If these limits are exceeded the performance of a membrane cell plant declines significantly resulting in high energy costs and elevated maintenance efforts.

1. Flux through the membrane

In a membrane cell a cation-exchange membrane separates the anolyte and catholyte, as shown in Figure 1. Saturated brine is fed into the anode compartment, where chlorine gas is evolved at the anode:

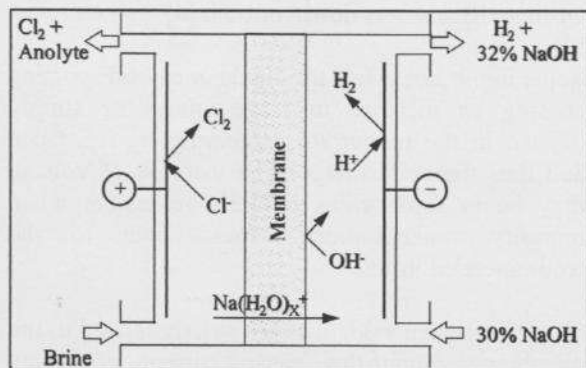
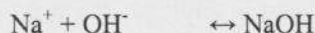
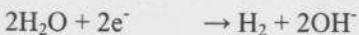


Figure 1. Membrane cell principle.

The anolyte is discharged from the cell. By applying an electrical field hydrated sodium ions migrate through the membrane into the catholyte. In the cathode compartment, hydrogen is evolved at the cathode, leaving hydroxyl ions, which together with the permeating sodium ions constitute the caustic soda:



Liquid and gaseous phases of anolyte/ Cl_2 and catholyte/ H_2 can be separated either in the cell compartment or downstream of the cell outlet. The chlorine saturated anolyte is then treated in a dechlorination unit to regain the chlorine.

The total flux through a membrane can be divided in three parts [1]:

- 1) Migration due to electrical field
- 2) Convection
- 3) Diffusion due to chemical gradients

Migration is the flux of ions through the membrane, driven by electrical force. This includes the wanted transfer of sodium ions to the cathode compartment and the unwanted transfer of hydroxyl ions to the anode compartment. The capacity for selective separation of the cation exchange membrane is determined by the repelling forces of the membrane for hydroxyl ions. This effect determines the current efficiency.

The back migration of hydroxyl ions increases the formation of oxygen, hypochlorites and chlorates in the anode compartment and causes a loss of current efficiency of 3-7 % in caustic production. The evolution of oxygen gas can be depressed by selecting an anode coating with suitable characteristics or by decreasing the pH in the anode compartment by acidifying the inlet brine.

Convection and diffusion determine the flow of uncharged compounds and ions through the membrane. For example chloride anions in the catholyte are excluded by the cation-exchange membrane and repelled by the electrical field, so that the transfer rate of chloride anions from the anolyte to the catholyte is extremely low. As a result, a caustic soda solution of about 32-35 wt. % with a salt content of less than 20 ppm can be obtained. The water transport through the membrane is about 3.5 to 4.5 mols of water per mol of sodium-ion and can be understood as hydrate shell of the migrating sodium-ions. Water flux increases with decreasing anolyte concentration.

Migration, convection and diffusion influence each other and the resulting flux depends on membrane type, current density, temperature and composition of anolyte and catholyte. But in any case, the mass transport through a membrane of only 200 μm thickness during a lifetime of 4 years and more is enormous. At a nowadays usual current density of 5 kA/m^2 approximately 620 tons per square meter of sodium ions and water are passing the membrane. This huge mass transported is the reason for the extremely low impurity limits tolerated in the feed brine. If they are exceeded performance will decline quickly.

2. Performance impact of brine impurities

The introduction of membrane technology into chlor-alkali electrolysis has dramatically increased the demands on the quality of the pure brine [2]. The lifetime of chlor-alkali membrane cells is determined by the operation conditions and the quality and purity of the brine fed into the electrolyzers. Good long-term performance of the cells may be obtained if brine impurities are kept within the limits recommended in Table 1. This chapter deals with a variety of impurities eventually present in the brine, their interactions with each other, common sources and effects on the performance when limits are exceeded and suggests methods of control.

A major source of performance decline is the accumulation of solid material in the membrane [3].

Specific impurity levels are dependent on membrane design, cell design, operating conditions, the impurity itself and other impurities present. The prerequisite requirement for long membrane life is to maintain low levels of for example Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , SO_4^{2-} and SiO_2 in the brine. Traces of these impurities damage the membrane and/or electrodes resulting in irrecoverable current efficiency decrease and/or increased cell voltage. In the case of a closed brine loop with no purge, each impurity brought into or being formed in the system has to be removed in order to remain below its specification level and to prevent accumulation.

The contaminants can be brought into the brine system through the salt, through chemicals used in brine purification steps, through the water for dissolving the salt or through materials of tanks, pipework and cell components or through the process itself [3]. The impurities of the salt depend upon the origin of the raw material. Rock salt, vacuum salt, sea salt, brine from well mining, or salt from waste incinerators serve as supplies of NaCl. The more varied the sources are, the more diversified are the impurities.

Performance is the practical indicator of membrane and electrode damage. Increase in power consumption means that voltage is up or that current efficiency is down, or both [4].

Some impurities affect the anode or cathode coating causing an increase in overvoltage or simply deposit in the membrane increasing its resistance and thus the cell voltage. The increase of voltage may be in some cases partially reversible when impurity concentration comes down to the recommended limits.

Current efficiency declines are strictly related to the membrane. Impurities cause current efficiency decline by reducing the membrane's ability to reject anions, specifically the ability to prevent hydroxyl ions from migrating from the cathode compartment through the membrane to the anode compartment [4]. This is usually a result of physical damage to the membrane caused by precipitation and crystallization of impurities inside the membrane.

Impurities precipitate because the environment in the membrane changes from acidic salt solution (pH 2 - 4) to a caustic solution (pH 14 - 15) over the 100-300 μm thickness of the membrane.

It is important to consider not only the impurities themselves but also their interaction [4]. The solely presence of one impurity may not be harmful but the synergetic combination with others may. The example of silica and aluminum-plus-calcium shows the complex relationship. Silica itself is not a problem in membranes. Only in the presence of calcium and aluminum precipitates form and damage the membrane irreversibly. The concentration of silica and/or the concentration of aluminum-plus-calcium can be adjusted to find the optimum operating conditions. For example, with an effective secondary brine purification, high levels of silica can be tolerated. Similarly, if aluminum concentration is high, calcium or silica concentration can be reduced to maintain acceptable membrane performance. As this example shows, there are many combinations that can be considered when facing problems of brine purity. Further purification is not necessarily the most economic method. Additionally, the benefits of extended membrane life must be balanced against the cost of additional brine purification, including the cost of waste disposal, for each plant location.

In order to meet the strict requirements on brine purity outlined in Table 1 brine treatment system is established [5]. This is accomplished in the following main steps in the brine loop: Saturation, precipitation, clarification, filtration, polishing filtration, ion exchange, electrolysis, chlorate decomposition and dechlorination.

The contaminants, particularly calcium and magnesium are precipitated and separated together with the insolubles from the saturated brine. A sodium carbonate and barium carbonate (barium chloride) solution of approx. 10 wt. % and caustic soda 32 wt. % are used as precipitants.



Alternatively:



All impurities not precipitated, filtered out or extracted by the ion exchangers can only be controlled by purging a part stream of the anolyte to avoid accumulation.

Table 1
Impurities and effects

Impurity	Max. Limit in w/w	Reagents	Mechanism	Negative Effect on Performance					
				Voltage Increase			CE	PQu	Methods of Control
				An.	Cath.	Mem.			
Ca ²⁺	Ca ²⁺ +Mg ²⁺ < 20 ppb	Ca ²⁺ +OH ⁻	precipitation on the cathode				++		precipitation with Na ₂ CO ₃ plus ion exchange
		Ca ²⁺ +SO ₃ ²⁻	side of the membrane, forming				++		
		Ca ²⁺ +SO ₃ ²⁻	of large crystals				++		
		+Al ³⁺							
		Ca ²⁺ +I ⁻	very fine precipitation in the membrane						
Mg ²⁺	Ca ²⁺ +Mg ²⁺ < 20 ppb	Mg ²⁺ +OH ⁻	fine precipitation on the anode side of the membrane			++			precipitation with NaOH plus ion exchange
Sr ²⁺	< 0.4 ppm	Sr ²⁺ +OH ⁻	precipitation on the cathode side of the membrane, forming of crystals			+	++		coprecipitation with Na ₂ CO ₃ plus ion exchange
Ba ²⁺	< 0.5 ppm	Ba ²⁺ +OH ⁻							purge, control of Na ₂ SO ₄ -content in brine > 4 g/l, precipitation with NaHSO ₃
		Ba ²⁺ +I ⁻	very fine precipitation in the membrane			+	+		
		Ba ²⁺ +SO ₄ ²⁻	coating of the anode	+					
Al ³⁺	< 0.1 ppm	Al ³⁺	precipitation on anode side of the membrane,			++			precipitation as hydroxide at pH 7-9, ion exchange in acid condition
		Al ³⁺ +SiO ₃ ²⁻	forming of crystals (aluminosilicate) in the cathode side of the membrane				++		

SiO ₂	< 5 ppm	SiO ₃ ²⁻ +Ca ²⁺ SiO ₃ ²⁻ +Al ³⁺	precipitation on the cathode side of the membrane and crystalization	++	
Fe ³⁺	< 0.1 ppm	Fe ³⁺	if brine acidified, penetration into anode side of membrane	++	precipitation with NaOH
I ⁻	< 0.2 ppm	I ⁻ +Na ⁺ I ⁻ +Ca ²⁺ , I ⁻ +Ba ²⁺ I ⁻ +K ⁺	precipitation on the cathode side of the membrane, forming of crystals very fine precipitation in the membrane	++	purge
F ⁻	< 0.5 ppm		destruction of the anode coat.	++	purge
SO ₄ ²⁻	< 4-8 g/l Na ₂ SO ₄	SO ₄ ²⁻ +Na ⁺ SO ₄ ²⁻ +Ba ²⁺	precipitation on the cathode surface of the membrane coating of the anode	++ +	purge, precipitation with BaCO ₃ or BaCl ₂
TOC	< 1 ppm		increased foaming, overplating	+ + +	activated carbon
K ₄ (Fe(CN) ₆)	< 0.1 ppm	Fe ³⁺ Fe ³⁺	see under Fe ³⁺ evolution of N ₂ and formation of NCl ₃ in Cl ₂ (danger of explosive concentrations, if Cl ₂ liquefied)	++	oxidation with active chlorine ++ plus precipitation with NaOH

An.: Anode, Cath.: Cathode, Mem.: Membrane, CE: Current Efficiency, PQu: Product Quality
+: small effect, ++: large effect

3. Costs of declined performance

Any voltage rise of the cell elements originating from the membrane, the cathode coating or anode coating and any current efficiency decline will directly increase the production cost represented by the specific power consumption in kWh/t 100% NaOH.

$$PC = u / (F * CE) * 1000$$

with

PC	specific power consumption in kWh/t 100% NaOH
u	single element voltage in V
F	Faraday constant for NaOH 1.4923 kg/kAh
CE	current efficiency.

At start-up of a membrane cell electrolysis operating at 5 kA/m² the initial specific power consumption is around 2,150 kWh/t 100% NaOH. A voltage rise of 100 mV per cell element results in a consumption rise of 70 kWh/t, a decline of 1% current efficiency yields a loss of 20 to 25 kWh/t. If impurity limits are exceeded a voltage rise of 200 mV and a current efficiency drop from 96% to 92% are easily achieved in a few days or weeks. Depending on the energy costs, this loss is more or less severe. However, energy costs are not the only impact. The lifetime of a membrane – at proper operating conditions 4 years and more – will be shortened significantly (i.e. 2 instead of 4 years). The consequences are elevated maintenance efforts and inevitably a premature remembraning campaign which causes not only material costs – approx. 1,000 \$/m² including membranes, gaskets, bolts, etc. – but also labor efforts, element repair works and production losses.

Therefore it is highly profitable to select the appropriate salt source and to monitor and control carefully the brine and salt quality in order to prevent a membrane cell electrolysis from upsets in early stage and to extend its lifetime.

References

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