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Electrodialytic concentration of NaCl for the chlor-alkali industry

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ABSTRACT

Production of chlorine and sodium hydroxide in the membrane electrolysis plants requires saturated brines, free of calcium, magnesium, and sulfates. On the other hand, desalination plants produce waste brines, which are considered as an environmental hazard. Electrodialysis with univalent permselective membranes can simultaneously preconcentrate the sodium chloride solution up to the level required by the chlor-alkali industry and decrease the salinity of the desalination plant brines. In order to assess the bivalent ions transport across univalent permselective membranes during the NaCl concentration process, a series of batch-scale experiments were performed in an electrodialyzer of 4.5 cm^2 effective membrane area and four membrane pairs. The tested membranes were Neosepta CMS/ACS and Aciplex K-192/A-192, the tested concentration range was 0.3–3.0 g/L in case of Ca^{2+}, 0.6–6.0 g/L in case of Mg^{2+}, 1–20 g/L in case of SO_4^{2-}, and 35–300 g/L in case of NaCl. The results allowed the estimation of empirical mass transport coefficients in the membrane. Based on the estimated parameters and a hydrodynamic model of a single-pass electrodialyzer, an electrodialyzer was designed and the energy consumption of saturated brine production was estimated.

Keywords: Electrodialysis; Brine saturation; Univalent permselective membranes; Mass transfer

1. Introduction

Chemical industry requires chlorine and sodium hydroxide, both of which can be produced electrochemically by the chlor-alkali industry, using diaphragm, amalgam, or membrane electrolysis. Nowadays, membrane electrolysis is considered the best available technology for the chlor-alkali industry [1], as it shows the lowest energy consumption [2] and it is considered to be more environmental friendly than diaphragm and amalgam electrolysis. The main drawback of the membrane electrolysis is that it requires highly concentrated brines (300 g/L as NaCl) with only minimal content of bivalent impurities: sum of magnesium and calcium less than 20 mg/L and sulfate concentration less than 7 g/L [3]. The presence of magnesium in the membrane electrolysis feed can lead to the evolution of hydrogen on the anode, which can react with the chlorine [4]. Typically, the lean brine from the anode compartment of the membrane

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electrolysis cell is resaturated with solid sodium chloride and recirculated. The lean brine is typically resaturated with solid sodium chloride (vacuum crystallized salt from solution-mined brine, rock salt, or solar salt [1,4]). The membrane electrolysis feed usually require two-stage pretreatment [1]: first, sodium carbonate and sodium hydroxide are added to precipitate calcium carbonate and magnesium hydroxide. The precipitates are removed by sedimentation or filtration. The second stage is ion-exchange with chelating resins.

The chemical industry, chlor-alkali industry in particular, is the largest consumer of solid sodium chloride [4]. The search for the alternative sodium chloride sources has become an important issue for the chlor-alkali industry. The salt can, depending on the purity, cost up to \$100/*t* [4]. On the other hand, there are plenty of brines that needs to be treated, i.e. desalination brines or mine drainages; therefore, there is a possibility of cheaper salt source for the chlorine and sodium hydroxide production. Casas et al. [3,5,6] have investigated the electrodialytic concentration of sodium chloride. Although the required sodium chloride concentration (300 g/L) was not reached, the grounds for future development and research goals in terms of energy consumption and concentration were laid down (see Fig. 1). A theoretical work [5] has proved that it is possible to produce saturated brine by electrodialysis at applied current density of 600 A/m^2. In our previous research, a concept of electrodialytic brine concentration for the chlor-alkali industry was presented [7]. Brines from a seawater desalination plant could be used as a sodium chloride source, resulting in simultaneous production of concentrated brine from the lean brine and a waste brine of such salinity, that a safe discharge back to the sea is possible. The concept is presented in Fig. 2. The 300 g/L NaCl concentration was reached, however, the energy consumption was quite high (in case of SWRO brine: 0.28 kWh/kg of transported salt at applied current density of 620 A/m^2). Application of univalent permselective membranes allowed to decrease the amount of bivalent impurities passing to the concentrate compartment of the electrodialyzer. Such membranes owe their permselectivity to the presence of highly crosslinked resin [8] or to the presence of additional, oppositely charged layer, which hinders the mass transfer of bivalent ions [8,9]. Univalent permselective membranes have been used in food processing [10,11], pulp and paper industry [12,13], reverse electrodialysis units and in electrodialytic desalination [14–16].

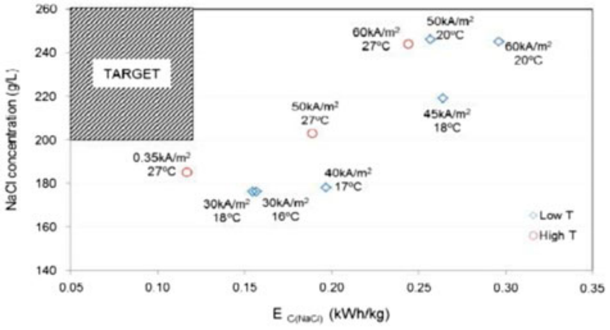

Fig. 1. Energy consumption and brine concentration during brine saturation production [6]. Reprinted from Desalination, 342, M. Reig et al., Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialysis, p. 10, © 2013 Elsevier B.V., with permission from Elsevier.

To integrate electrodialysis into brine saturation loop of chlor-alkali plant and design a pretreatment of saturated brine leaving the concentrate compartment of an electrodialyzer, a detailed information on predicted calcium, magnesium, and sulfate(VI) ions is required. Such information is also important from the point of view of scaling prevention. The gypsum solubility decreases as the sodium chloride concentration in the diluate is decreased down to the sea water level. Moreover, the application of univalent permselective membranes should cause the relative decrease in calcium sulfate concentration to be lower than the decrease in sodium chloride concentration. Combination of these both effects may lead to the appearance of scaling. Previous experience [7] proved that the bivalent ions transport numbers, provided by the membrane manufacturer, may not always describe the observed Ca^{2+} and Mg^{2+} fluxes correctly, therefore, the studies on bivalent ions transport across univalent permselective membranes are required. The Nernst–Planck equation is a standard approach for modeling the mass transfer across the ion-exchange membrane at steady-state conditions. It describes the diffusion driven by the concentration gradient, electromigration driven by potential gradient, and convective mass transfer driven by solvent–solute interactions [17]:

$$J_i = -D_i\left(\nabla C + \frac{z_i F}{RT} C_i \nabla\psi\right) + C_i \sum v_{ij} J_j \tag{1}$$

where J_i is the molar flux of *i*th ion across the membrane, D_i is the diffusion coefficient of the *i*th ion, ∇C is the concentration difference of the *i*th ion between the both sides of the membrane, C_i is the diluate concentration, $\nabla\psi$ is the voltage drop on the membrane, v_{ij} is the convective coupling coefficient between *i*th and *j*th species passing through the membrane, and J_j

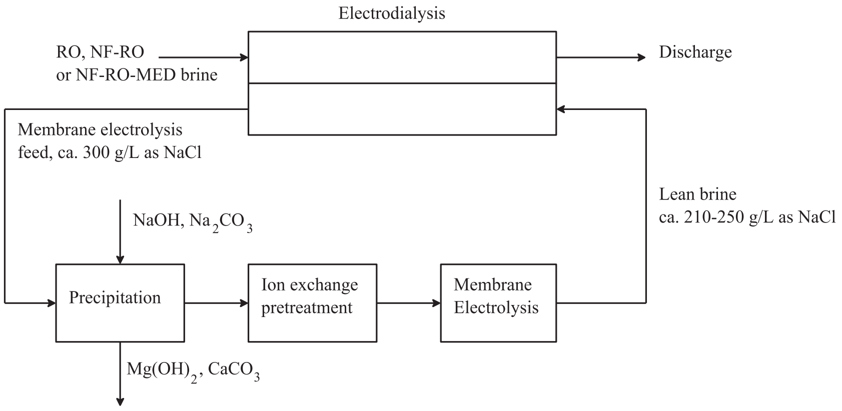

Fig. 2. A scheme of electrodialytic saturation of the lean brine leaving the membrane electrolyzer [7].

is the molar flux of the jth species. The equation has been widely applied for the description of various species transport across the ion-exchange membranes.

2. Experimental

A bench-scale electrodialyzer of active membrane area 4.5 cm^2 was used. The module was equipped in four pairs of univalent permselective ion-exchange membranes, either Neosepta CMS/ACS or Aciplex K-192/A-192. The inter-membrane spacer was 0.26 mm thick. Concentrate was sodium chloride solution, with concentration varying from 220 to 300 g/L as NaCl, with no addition of bivalent ions at the beginning of the experiments. Diluate was sodium chloride of concentration 35–300 g/L as NaCl with the addition of bivalent ion (see Table 1 for the overview of the experimental series): calcium chloride (0.3–3 g/L as Ca^{2+}), magnesium chloride (0.6–6 g/L as Mg^{2+}), or sodium sulfate(VI) (1–20 g/L as SO_4^{2-}). The concentration ranges were chosen to resemble the composition of the typical brines which may be used in NaCl concentration [7]. Ion concentrations were determined by the volumetric titration. Each of the experimental series consisted of 16 experiments with sodium chloride concentration, bivalent ion concentration, and voltage drop per membrane stack as the independent variables; the dependent variable was the bivalent ion molar flux, calculated based on the change in bivalent ion content in the concentration compartment of the electrodialyzer. An example of the plan of the experiment is presented in Table 1. Each experiment was conducted for 30 min. The diluate and concentrate volumes were set to ensure less than 5% concentration change (assuming 100% current efficiency), so that the pseudo-steady state could be assumed and the ion transport could be modeled with the extended Nernst–Planck equation. In case of calcium and magnesium, transport across the cation-exchange membrane was modeled. In case of sulfate, an anion-exchange membrane was investigated.

2.1. Mass transfer modeling

Eq. (1), describing the transport of calcium, magnesium, and sulfate, can be rewritten as:

$$J_{\mathrm{Ca}} = k_{0,\mathrm{Ca}}\Delta C_{\mathrm{Ca}} + k_{1,\mathrm{Ca}}\bar{C}_{\mathrm{Ca}}U_{\mathrm{C}} + k_{2,\mathrm{Ca}}\bar{C}_{\mathrm{Ca}}(J_{\mathrm{Na}} + C_{\mathrm{H_2O}}J_w) \tag{2}$$

$$J_{\mathrm{Mg}} = k_{0,\mathrm{Mg}}\Delta C_{\mathrm{Mg}} + k_{1,\mathrm{Mg}}\bar{C}_{\mathrm{Mg}}U_{\mathrm{C}} + k_{2,\mathrm{Mg}}\bar{C}_{\mathrm{Mg}}(J_{\mathrm{Na}} + C_{\mathrm{H_2O}}J_w) \tag{3}$$

$$J_{\mathrm{SO_4}} = k_{0,\mathrm{SO_4}}\Delta C_{\mathrm{SO_4}} + k_{1,\mathrm{SO_4}}\bar{C}_{\mathrm{SO_4}}U_A + k_{2,\mathrm{SO_4}}\bar{C}_{\mathrm{SO_4}}(J_{\mathrm{Cl}} + C_{\mathrm{H_2O}}J_w) \tag{4}$$

where k_0, k_1, and k_2 denote the empirical mass transport coefficients, describing ion transport in the membrane due to the diffusion, electromigration, and convection, respectively. J denotes the molar flux, calculated based on the concentration change in the concentrate, $\bar{C}$ denotes the mean concentration at the membrane surface in contact with the diluate, ΔC denotes the diffusional mass transfer driving force. Water flux, J_w, was determined by measuring the change in the concentrate and diluate volume, while water concentration at the boundary layer was assumed at 5,560 mol/m^3. Sodium and chloride molar fluxes were calculated based on the electric charge passed during the electrodialysis, assuming 90% current efficiency. The voltage drop on the single membrane was calculated based on the electric resistance

Table 1
The overview of the experimental series

Series	Membrane	Bivalent ion	Bivalent ion concentration range (g/L)
1	Neosepta CMS	Ca^{2+}	0.3–3.0
2	Neosepta CMS	Mg^{2+}	0.6–6.0
3	Neosepta ACS	SO_4^{2-}	1.0–20.0
4	Aciplex K-192	Ca^{2+}	0.3–3.0
5	Aciplex K-192	Mg^{2+}	0.6–6.0
6	Aciplex A-192	SO_4^{2-}	1.0–20.0

of both cation-exchange and anion-exchange membranes. For instance, for a cation-exchange membrane the voltage drop was calculated as:

$$U_C = \frac{R_C}{R_C + R_A}\frac{U}{4} \tag{5}$$

where U denotes the voltage drop measured on the whole membrane stack. The assumed electrical resistances of the membranes were: $R_C = 1.75\,\Omega\,\text{cm}^2$ and $R_C = 1.75\,\Omega\,\text{cm}^2$ for Aciplex membranes [18]; $R_C = 1.8\,\Omega\,\text{cm}^2$ and $R_C = 3.8\,\Omega\ \text{cm}^2$ for Neosepta membranes, as claimed by the manufacturer [19].

To estimate mass transport parameters of ions in the membrane, first the concentration at the membrane surface was calculated. Since, the sodium chloride concentration is higher than the concentration of calcium, magnesium, and sulfate, the viscosity, η, and density, ρ, of diluate and concentrate were calculated based on the mean NaCl concentration, according to data available in the literature [20,21]. The diffusion coefficients of ions at 25°C were taken from the data provided by Yuan-Hui and Gregory [22]. The mass transport coefficient in the diluate boundary layer was calculated based on the equation [23]:

$$\text{Sh}_d = \frac{k_d d_h}{D} = 1.85\left(\text{Re}_d \text{Sc}_d \frac{d_h}{L}\right)^{\frac{1}{3}} \tag{6}$$

where Sh_d is the Sherwood number of diluate, k_d is the mass transport coefficient in the boundary layer [m/s], d_h is the hydraulic diameter of the compartment (5.191×10^{-4} m), Re_d and Sc_d are the Reynolds and Schmidt numbers of the diluate, calculated as:

$$\text{Re}_d = \frac{u_d \rho_d d_h}{\eta_d} \tag{7}$$

$$\text{Sc}_d = \frac{\eta_d}{\rho_d D} \tag{8}$$

where ρ_d is the diluate density [kg/m^3], η_d is the diluate viscosity [Pa s], u_d is the linear flow velocity of the diluate [m/s]. The mass transport coefficient in the concentrate boundary layer was calculated in the same manner. Assuming linear profile in the boundary layer, the bivalent ion concentrations at the membrane surface were calculated. For instance, the calcium concentration at the membrane surface in touch with diluate and concentrate was calculated, respectively:

$$\bar{C}_{d,\text{Ca}^{2+}} = \frac{C_{d,\text{Ca}^{2+}}(t=0) + C_{d,\text{Ca}^{2+}}(t=30)}{2} - \frac{J_{\text{Ca}^{2+}}}{4k_d} \tag{9}$$

$$\bar{C}_{k,\text{Ca}^{2+}} = \frac{C_{k,\text{Ca}^{2+}}(t=0) + C_{k,\text{Ca}^{2+}}(t=30)}{2} + \frac{J_{\text{Ca}^{2+}}}{4k_k} \tag{10}$$

where $C(t = 0)$ denotes the initial bulk concentration, before the start of the experiment, and $C(t = 30)$ denotes the final bulk concentration, after the end of 30 min long electrodialysis. The diffusional mass transfer driving force, ΔC, was calculated as:

$$\Delta C_{\text{Ca}^{2+}} = \bar{C}_{k,\text{Ca}^{2+}} - \bar{C}_{d,\text{Ca}^{2+}} \tag{11}$$

3. Results

The estimated transport parameters for each of the bivalent ions are presented in Table 2. Some general conclusions can be drawn, although the model is far from satisfactory, as it can be seen when comparing experimentally observed fluxes to the predicted ones (see Fig. 3). Bivalent ion fluxes were lower through the Aciplex K-192 membrane than through Neosepta CMS membrane, which suggests the former should be applied in electrodialytic production of membrane electrolysis feed.

Table 2
The estimated transport parameters k_0, k_1, and k_2

Series	Membrane and ion	$k_0 \times 10^5$ (m/s)	$k_1 \times 10^5$ (m/(Vs))	$k_2 \times 10^5$ (m^3/mol)
1	CMS, Ca^{2+}	1.68	1.47	4.26
2	CMS, Mg^{2+}	8.24	1.67	2.11
3	ACS, SO_4^{2-}	4.74	6.47	8.30
4	K-192, Ca^{2+}	0.14	0.67	0.95
5	K-192, Mg^{2+}	0.39	1.03	−1.79
6	A-192, SO_4^{2-}	6.96	0.64	25.1

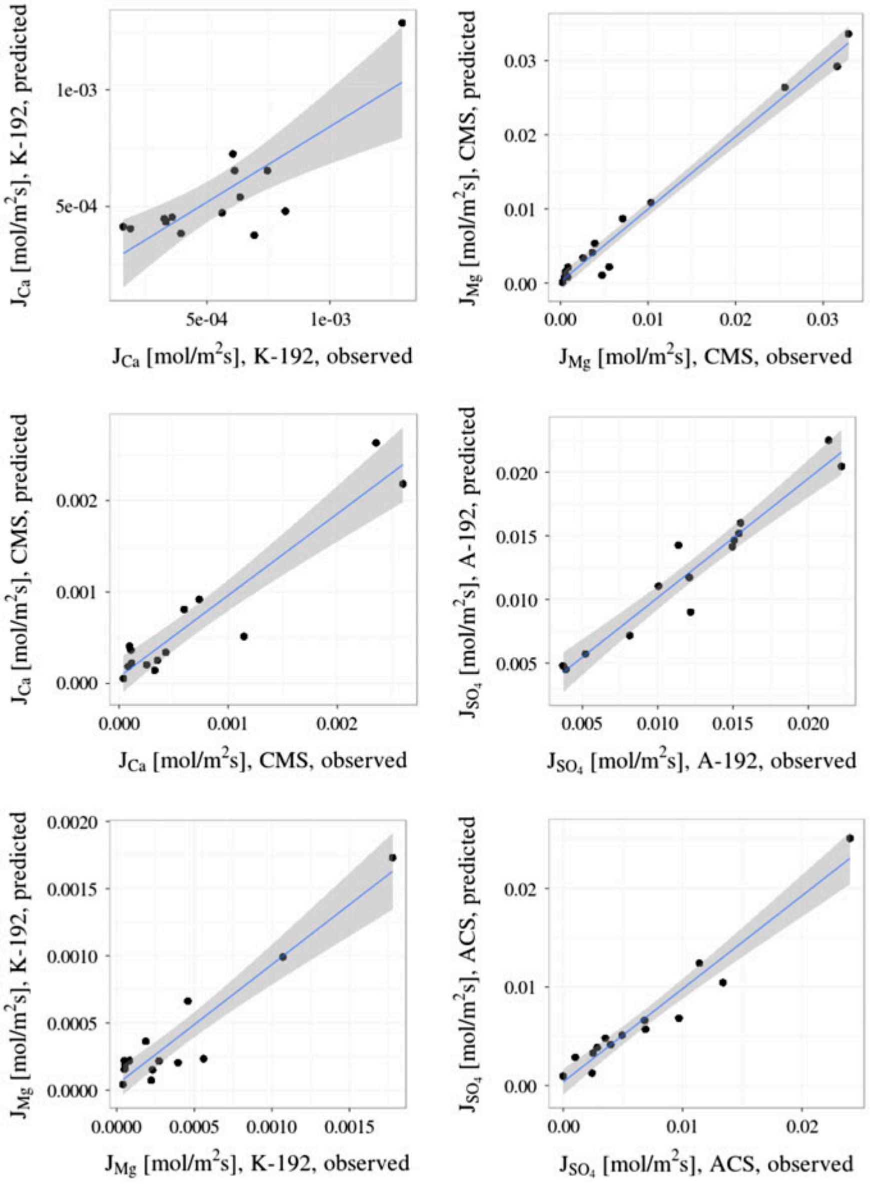

Fig. 3. Comparison of the bivalent ion fluxes observed experimentally with the ones predicted by the model.

Table 3
Results of electrodialyzer design

Diluate feed		NF–RO brine (51.4 g/L as Cl^-)	Coal-mine brine (32.8 g/L as Cl^-)
Concentrate volumetric flow (outlet)		0.075 m^3/h	
Concentrate volumetric flow (inlet)		0.063 m^3/h	
Concentrate composition (g/L)	NaCl	300	
	Ca^{2+}	1.23	0.92
	Mg^{2+}	1.18	0.52
Energy consumption (kWh/kg of transported salt)		0.27	0.29

3.1. Electrodialysis design

Based on previously proposed compartmental model of a single-pass, counter current electrodialysis [24], a 1 m long electrodialyzer was designed. Since, the calcium and magnesium are far more problematic from the point of view of membrane electrodialysis, the calculations focused on their content in the produced brine of salinity of 300 g/L as NaCl. Following assumptions have been made:

- effective membrane length 1 m, membrane stack consists of 100 pairs of Aciplex K-192/A-192 membranes,
- elementary unit length of 5×10^{-4} m and height of 0.02 m (totaling 2,001 elementary units), intermembrane distance is 0.26 mm,
- elementary units treated as continuous stirred tank reactors, connected in series,
- current density 722 A/m^2, quadratic current density distribution, as shown previously [24], each elementary unit is a parallel connected resistor,
- two diluate feeds considered: a NF-RO brine [7]: 51.4 g/L as Cl^-, 1.20 g/L as Mg^{2+}, and 0.62 g/L as Ca^{2+}; a coal-mine brine [16]: 32.8 g/L as Cl^-, 0.383 g/L as Mg^{2+}, and 0.462 g/L as Ca^{2+}, in both cases linear flow velocity is 0.02 m/s,
- concentrate outlet: 300 g/L as NaCl, linear flow velocity of 0.01 m/s, bivalent ions content to be calculated,
- concentrate inlet [7]: 220 g/L NaCl, 5.4 mg/L Mg^{2+}, 1.2 mg/L Ca^{2+}, linear flow velocity to be calculated,
- electric resistance of diluate and concentrate solution depends only on NaCl concentration.

The content of bivalent ions in the concentrate outlet was determined by consecutive iterations. The calculated parameters of the produced brine are presented in Table 3. The calculations show that it should be possible to produce 300 g/L NaCl solution with energy consumption of 0.27 and 0.29 kWh/kg of transported salt; however, the total cost of brine production would have to include the cost of removing calcium and magnesium impurities. The estimated energy consumption is quite high, but it is most likely caused by the high current density required to reach the level of salinity needed by membrane electrolysis plants. The energy consumption shown by Reig et al. [6] is much lower; however, the concentrate NaCl content they reached is much lower (less than 260 g/L). The ratio of magnesium to calcium in the NF–RO brine (diluate feed) is 3.2:1 (mol/mol), whereas in the concentrate the ratio is 1.6:1. In case of coal-mine brine, the diluate feed Mg/Ca ratio is 1.4:1, the concentrate Mg/Ca ratio is 0.94:1. The decrease in Mg/Ca ratio has been observed previously [7], and could be beneficial from the point of view of further brine purification; however, the relatively high content of bivalent impurities in the produced brine may hinder the usage of electrodialysis in the chlor-alkali industry. The high concentration of Ca^{2+} and Mg^{2+} in the concentrate stream indicate that univalent permselective membranes are not selective enough to produce high quality brine.

4. Conclusions

Transport of the bivalent ions across the univalent permselective membranes has been investigated. Although the results were not completely satisfactory, empirical transport parameters of Ca^{2+}, Mg^{2+} ions across Neosepta CMS and Aciplex K-192 membranes, as empirical transport parameters of SO_4^{2-} across Neosepta ACS and Aciplex A-192 membranes. Although theoretical scaling might appear in the diluate—gypsum solubility decreases as the NaCl concentration decreases from 140 to 35 g/L, while Ca^{2+} and SO_4^{2-} should decrease slower than NaCl or even slightly increase due to volume changes [7]—the observed low selectivity of univalent permselective membranes suggests that in practice the scaling risk is negligible. Using the estimated transport parameters and previously described model of a single-pass, counter-current electrodialyzer, it was possible to design an electromembrane module for the concentrated brine production, calculate the expected content of bivalent impurities in the produced 300 g/L sodium chloride solution and estimate the energy consumption of the brine concentration process. Preliminary calculations show that it may be possible to produce 300 g/L as NaCl brine with energy consumption of 0.27–0.29 kWh/kg of transported salt.

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