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CHAPTER 5

Chlor-Alkali Membrane Electrolyzer Simulator Fed in Ratio to Its Current

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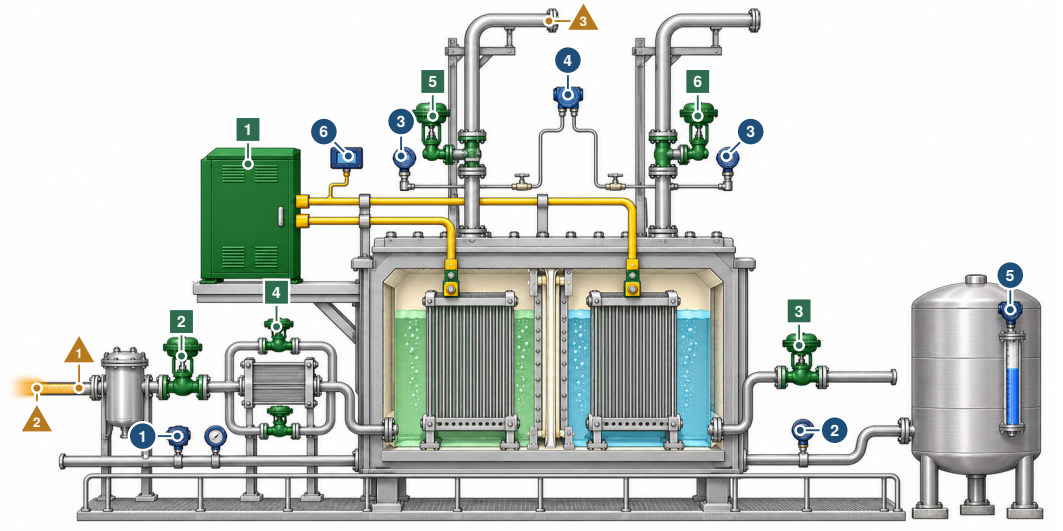
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CHAPTER 5

Chlor-Alkali Membrane Electrolyzer Simulator Fed in Ratio to Its Current



The controller moves 1 rectifier, which sets the current and so the production 2 brine feed valve, in ratio to the current 3 water feed valve, in ratio to the current 4 heater and cooler on the brine 5 chlorine valve to the compressor 6 hydrogen valve

The controller reads 1 brine strength (density) and cell temperature 2 caustic strength (conductivity) 3 chlorine and hydrogen pressures 4 hydrogen-over-chlorine pressure difference 5 caustic tank level 6 voltage of every cell

What disturbs it 1 hardness the ion exchange lets through 2 weaker or colder brine 3 chlorine compressor trip

Notice the two gas pipes and the transmitter between them: the hydrogen must stay a few tens of millibars above the chlorine while every product follows the one current from the rectifier. Illustration, not to scale.

IN PLAIN TERMS **Feeding the Cells in Step With the Current**

The main idea. Electricity splits salt water into chlorine, hydrogen and caustic soda. Every bit of product is made by the electric current, so the salt water and the fresh water must be fed in step with it.

The challenge. A fixed feeding rule is never quite right, so measured strengths must correct it. The hydrogen must also stay a little above the chlorine in pressure, and when the chlorine stops being drawn away, a controller that waits to see the gap shrink acts too late.

Why it matters. Too small a gap stops the plant to protect the thin sheet between the two sides. Some harm to that sheet can never be undone.

THREE WAYS TO READ THIS CHAPTER

Explore	12 min	the first page; the fact box of Section 5.1; the history box of Section 5.2; the fact box of Section 5.5; the try-it boxes of Section 5.6; the key points
Study	50 min	the whole chapter with its pause points and the exercises
Practice	15 min	the first page; Section 5.6 with its result chart; Section 5.7; Section 5.8 with its open challenge

The control question A membrane electrolyzer makes every product in proportion to one current, and its hydrogen must stay a few tens of millibars above its chlorine. What do feeds in ratio to the current, a chlorine pressure feedforward on the hydrogen header and a load plan on the electricity price each buy, and which losses can no controller recover?

Learning objectives

- Compute the products, the oxygen in the chlorine and the specific energy of a membrane electrolyzer from Faraday's law and its current efficiencies.
- Explain why a ratio station needs an analyzer trim, and what the ratio alone and the trim alone each get wrong.
- Estimate how long a feedback-only pressure-difference loop rides through a compressor trip, and explain why a chlorine pressure feedforward removes the race.
- Relate the hydrogen header volume to the fastest rise the hydrogen can make, and find the volume above which no tuning keeps pace.
- Evaluate what a load scheduler saves on an hourly price, what limits it, and what permanent membrane damage costs a day.

Prerequisites Sections 1.4.6 (ratio stations with a trim), 1.6.2 (velocity-form PI) and 1.6.4 (scenarios, scorecard and exported files) of Chapter 1. Chapter 3 holds a second ratio on measured feeds.

The app https://apmonitor.com/apps/chlor-alkali/

See also Volume 3, Chapter 4 for an air-to-fuel ratio trimmed on an oxygen analyzer, Volume 3, Chapter 7 for a ratio blend trimmed on a refractometer, and Volume 3, Chapter 6 for a dose computed from a measured cause. Volume 9, Chapter 11 for a pumping schedule on the electricity price, and Volume 9, Chapter 6 for heat priced across a network. Volume 4, Chapter 2 for a protective loop on a compressor, and Volume 4, Chapter 6 for a safety limit that bounds the throughput.



5.1 Introduction

Chlorine and caustic soda are made together by the electrolysis of brine, in an industry that has run since the nineteenth century on three technologies, the diaphragm cell, the mercury cell and the membrane cell, of which the membrane cell is the most energy efficient and the only one free of asbestos and mercury [1]. Brine electrolysis is the predominant industrial use of ion-selective membranes [2]. The membrane passes sodium from a brine anolyte to a caustic catholyte and keeps the two gases apart, and Faraday's law ties every product to the one current that crosses it. In the electrolyzer of this chapter, 16.2 kA through 150 cells in series makes 3.45 t/h of NaOH, 3.18 t/h of chlorine and 91 kg/h of hydrogen for 7.54 MW of direct current, 2188 kWh/t for every tonne of caustic.

> **DID YOU KNOW? World Chlorine Around 2016**
>
> Around 2016 the world could make roughly 76 million tonnes of chlorine a year, and more than half of it came from membrane electrolysis [2]. Each of those tonnes comes with its caustic soda and hydrogen in the fixed proportions of Faraday's law, which Section 5.3 applies to one electrolyzer.

The simulator is aimed at a common belief about cell rooms, that the plant is under control once its strengths sit on their setpoints. Because the current is the throughput, a feed that is not tied to it drifts whenever the load moves. In case 1 a morning load-up from 5.0 to 6.5 kA/m^2, with the feeds left where they were, takes the anolyte from 210 to 177.9 g/L and sends 81.0 t of the day's 86.8 t of caustic off specification. The gas side is faster than any analyzer. When the chlorine compressor stops, the chlorine header rises 1.11 mbar/s, and a hydrogen loop that learns of it only through the pressure difference loses its 15 mbar margin to the interlock in 20 s. Some losses are permanent. In case 6 three hours of hardness raise the cell voltage by 75.4 mV for the rest of the membrane's life while every loop is back on its setpoint. None of this appears in a transfer function from a brine valve

to a densitometer, which knows nothing of the load, of the race between the two headers, or of a loss that no setpoint recovers.

This class of problem reaches well beyond chlorine. A plant whose production rate is a measured and exactly known quantity can feed its reagents forward in ratio to it and trim the ratios on a composition, which is textbook ratio control [3] and the subject of Section 1.4.6. The fired heater of Volume 3, Chapter 4 trims its air-to-fuel ratio on an oxygen analyzer in the same way. The same electrochemical structure recurs in water electrolysis, fuel cells and the smaller electromembrane processes [2]. Every two-compartment device whose membrane must not see a reversed pressure difference shares the gas-side problem, and every power-intensive process that can move its load within hours is a candidate for demand response [4], as the pumping station of Volume 9, Chapter 11 is. The chemistry sets the limits the controllers work inside. Oxygen evolution competes with chlorine at the anode [5], impurities in the brine degrade the membrane [6], and the cell voltage and current efficiency depend on the process conditions [7].

The published work on the membrane cell relates its voltage and efficiency to the operating conditions [7], and the demand-response studies schedule the plant as a load over hours [8–11]. Neither gives a plant in which the ratio stations, the millibar loop, the interlock, the permanent damage and the price schedule interact, and in which each can be taken away to see what fails. This chapter audits, in tonnes, dollars and millibars, what each feedforward buys in a membrane electrolyzer, on a browser simulator in which every feed follows the current, the hydrogen follows the chlorine and the load follows the price. Faraday's law, ratio control with an analyzer trim, cascade pressure control, an interlock and a scheduling linear program (LP) are established practice. The analysis gives a closed-form estimate of how long the pressure-difference loop can ride through a compressor trip on feedback alone, 21.5 s at the shipped tuning against 20 s on the engine, and a ratio of the two headers' fastest rise rates, 1.207 at every current, which fixes a hydrogen header volume of 301.8 m^3 above which the hydrogen cannot keep pace with the chlorine even with its valve shut. The model has 17 physical states and 33 ledgers that close to 4.0×10^{-13}, and the controls use the framework's shared sampled analyzer, an interlock on its own transmitter and a bounded-variable simplex that plans the day in about a millisecond, all written down so that the model can be rebuilt from this text. The eight cases and the graded day set a ratio apart from its trim, a feedforward from a faster feedback, a loss the loops can correct from one they cannot, and a cheap hour from a tank with no room left.

Section 5.2 traces the industry from mercury and asbestos to the ion-exchange membrane and to load management on the electricity price. Section 5.3 sets out the balances, the voltage and efficiency correlations, the heat balance, the gas headers and the tank. Section 5.4 describes the instruments, the ratio stations and their trims, the pressure cascade with its feedforward, the interlock, the rectifier and the load scheduler. Section 5.5 derives how long the hydrogen can follow a tripped chlorine compressor on feedback alone and checks the estimate on the engine. Section 5.6 measures the eight cases and the graded day, Section 5.7 names the hardware and the practice behind the model, Section 5.8 states where the model stops holding, and Section 5.9 collects the results.

5.2 Mercury, Asbestos and the Ion-Exchange Membrane

Electrolytic chlorine is older than the membrane by most of a century. The diaphragm and mercury processes carried the industry for more than a hundred years and remain the most used worldwide, and both proved the most harmful to the environment through their asbestos and their mercury, while the membrane process was developed within the last sixty years [1]. The history of the industry, its brine preparation and treatment, the design of its cell rooms and their instrumentation and control systems are collected in one handbook [12].

The history box at the end of this section traces the membrane from the first patent to its adoption. The membrane brought constraints of its own. Brine for membrane cells is polished by ion exchange after its primary treatment [13], because the impurities that reach the membrane cost the cell its

performance [6]. The anode evolves some oxygen beside its chlorine, and the selectivity between the two has been reviewed at length [5], while the effects of the process conditions on the cell voltage, the current efficiency and the voltage balance of a membrane cell have been studied in their own right [7]. Oxygen-depolarized cathodes, which reduce oxygen at the cathode instead of evolving hydrogen and so lower the cell voltage, have a history, a present status and prospects of their own [14].

Control reached beyond the cell room through the electricity bill. The electrolytic process is highly energy intensive, and load management under a time-of-use tariff was posed for a caustic-chlorine plant as a mixed-integer nonlinear program that cut its peak demand by about 19 % and its electricity cost by about 3.9 % [15]. Later work treated chemical plants as grid-level batteries that bid into short-term electricity markets [8], built dynamic models of membrane chlor-alkali plants for demand response [9], let a plant switch between operating modes with an oversized cell room [10], and integrated the scheduling with the control under price and demand uncertainty [11], inside a wider literature on industrial demand-side management [4]. Those schedules sit on regulatory loops that the scheduling papers take as given. In the simulator the two layers share one plant, and the true strengths, efficiency and pressure difference are logged beside every instrument that reports them.

> ⧖ HISTORY **From Diaphragms and Mercury to the Membrane, 1851 to 1986**
>
> Making chlorine, caustic soda and hypochlorite by the electrolysis of brine was patented in England by Watt in 1851. In 1890 production began in a cell whose anode and cathode were separated by a porous cement diaphragm, and porous separators, asbestos among them, or a mercury cathode then kept the technology unchanged for decades. In 1970 a safer and more efficient technology was sought. Chemically stable perfluorinated sulfonated membranes of low resistance had appeared at the end of the 1960s, and industrial electrolysis with perfluorinated membranes began in Japan in 1975 [2]. An account of the ion-exchange membrane chlor-alkali process followed in 1976 [16]. In 1986 Japan changed all of its mercury cell production to membranes, and the process spread quickly to other industrial countries. A 2016 review called brine electrolysis the predominant industrial use of ion-selective membranes [2].

5.3 The Electrolyzer as Modeled

The simulated plant is one bipolar electrolyzer of $N = 150$ cells of $A = 2.7\,\mathrm{m}^2$ each at a design current density of $6\,\mathrm{kA/m}^2$, making 32 % caustic at 88 °C from brine of 305 g/L that leaves at 210 g/L. Figure 5.1 shows the loops, the headers, the tank, every instrument and the states and flows used below. Table 5.1 classifies the variables. The application integrates in minutes and quotes flows as a plant quotes them, while the equations below are written in consistent units. Each balance is integrated together with a ledger of what entered and left, so every inventory can be closed from the state itself.

5.3.1 Faraday's Law and the Products

All N cells carry the same current $I = iA$, so the electrons through the stack, $\dot{n}_e = NI/F$, fix every product, as shown in Equation (5.1).

$$\begin{aligned} \dot{n}_{H_2} &= \frac{\dot{n}_e}{2}, \qquad \dot{n}_{Cl_2} = \eta_{Cl}\frac{\dot{n}_e}{2}, \qquad \dot{n}_{O_2} = (1-\eta_{Cl})\frac{\dot{n}_e}{4} \\ \dot{m}_{NaOH} &= \eta\,\dot{n}_e M_{NaOH}, \qquad y_{O_2} = \frac{\dot{n}_{O_2}}{\dot{n}_{Cl_2}+\dot{n}_{O_2}} = \frac{1-\eta_{Cl}}{1+\eta_{Cl}} \end{aligned} \tag{5.1}$$

where $F = 96\,485.332\,\mathrm{C/mol}$ is Faraday's constant, the current efficiency η is the fraction of the current that the membrane gives to sodium, and $1-\eta_{Cl}$ is the fraction of the anode current that oxidizes water to oxygen. The brine is taken as acidified, so the hydroxide that migrates back through the membrane is neutralized in the anolyte and makes no oxygen, which gives chlorine and caustic separate efficiencies. The design point has $\eta = 95.00\,\%$ and $\eta_{Cl} = 98.8\,\%$, which puts 0.60 % oxygen by volume in the dry chlorine, and the stack makes 3.445 t/h of NaOH, 3.18 t/h of chlorine and 91.4 kg/h of hydrogen.

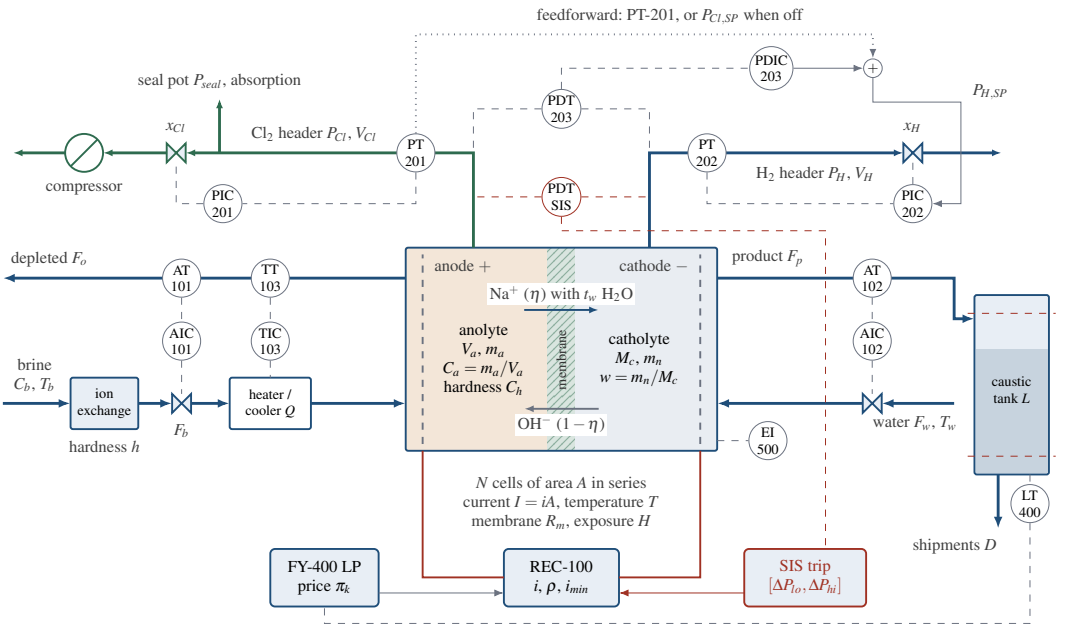


Figure 5.1 Membrane electrolyzer as modeled. Brine of strength C_b and temperature T_b passes the ion exchange, which lets through the hardness h, the brine valve F_b and the heater or cooler Q into the anolyte (V_a, m_a, C_h), and depleted brine F_o overflows past AT-101 and TT-103. Water F_w enters the catholyte (M_c, m_n), whose product F_p overflows past AT-102 to the caustic tank L and its shipments D. The membrane passes a share η of the current as sodium with t_w waters each and returns the rest as hydroxide. Chlorine and its oxygen leave through header P_{Cl} to the compressor's suction valve x_{Cl}, with a seal pot to the emergency absorption, and hydrogen through header P_H and its valve x_H. PDT-203 feeds the master PDIC-203, whose output is added to PT-201 (feedforward on) or to the chlorine setpoint (off) to form the setpoint of PIC-202, while the interlock's own transmitter trips the rectifier REC-100. FY-400 plans the current on the price and the tank gauge LT-400, and EI-500 scans the cell voltages. Measurement lines are dashed.

5.3.2 Anolyte and Catholyte

The anolyte is a well-mixed loop fed with brine and emptied over a weir, as shown in Equation (5.2).

$$\begin{aligned} \frac{dV_a}{dt} &= F_b - F_o - \frac{\dot m_d + \dot m_{v,a}}{\rho_w} - v_s \dot m_{tr} \\ \frac{dm_a}{dt} &= F_b C_b - F_o C_a - \dot m_{tr}, \qquad \frac{d(V_a C_h)}{dt} = F_b h - F_o C_h \\ F_o &= k_{oa} \max(0, V_a - V_{a,0}), \qquad \dot m_{tr} = \eta\, \dot n_e M_{NaCl} \\ \dot m_d &= t_w\, \eta\, \dot n_e M_{H_2O}, \qquad t_w = t_{w,0} + t_{w,a}(C_{ref} - C_a) \end{aligned} \tag{5.2}$$

where $C_a = m_a/V_a$ is the NaCl in kg/m^3 (numerically g/L), $\dot m_{tr}$ is the salt the membrane removes as sodium, counted as NaCl, $\dot m_d$ the water it drags with each sodium ion, $\dot m_{v,a}$ the vapor that leaves with the chlorine, $v_s = 0.33 \times 10^{-3}$ m^3/kg the apparent volume of dissolved salt, $\rho_w = 997$ kg/m^3, and C_h the hardness of the anolyte in ppb. The weir overflows with a 2 min time constant ($k_{oa} = 0.5\,\text{min}^{-1}$), and at the design point the anolyte stands 0.92 m^3 above it. The drag term above $t_{w,0}$ is an illustrative osmotic correction that grows as the anolyte weakens against the strong caustic, and it couples the two loops. The brine density is $\rho_b(C) = \rho_w(1 - v_s C) + C$. The catholyte gains the sodium and its water, loses one water per electron at the cathode, of which only the half hydrogen leaves, and loses

Table 5.1 Variables of the Electrolyzer and Their Design Values

Variable	Role, instrument	Design	Range
C_a	CV, AT-101 (density)	210 g/L SP	170–240
w	CV, AT-102 (conductivity)	32 % SP	28–36
T	CV, TT-103	88 °C SP	80–92
P_{Cl}	CV, PT-201	150 mbar(g) SP	80–250
$\Delta P = P_H - P_{Cl}$	CV, PDT-203	35 mbar SP	22–48
P_H	CV, PT-202 (slave)	185 mbar(g)	0–450
i	CV and MV, REC-100	6.0 kA/m^2	2–7
L	CV of FY-400, LT-400	30 t	10–90 %
F_b, F_w	MVs, feeds (m^3/h)	35.46, 3.869	0–60, 0–8
Q	MV, heater (+), cooler	0.093 MW	±1.5
x_{Cl}, x_H	MVs, header valves	52.6, 50.0 %	0–100
C_b	DV, feed brine	305 g/L	270–315
h	DV, hardness in the feed	10 ppb	0–2000
T_b, T_{cw}	DVs, brine, cooling water	65, 25 °C	30–75, 15–40
π	DV, price, spike ($/MWh)	18–165	+0–500
—	DVs, events	compressor, breakthrough, cell	
V_a, m_a, C_h	states, anolyte	18.92, C_aV_a, 12.9	—
M_c, m_n	states, catholyte	20.36 t, wM_c	—
T, R_m, H	states, cell, membrane	88, 0.06375, 0	—
P_{Cl}, P_H, x_{Cl}, x_H	states, headers, valves	as above	—
F_b, F_w, Q	states, actuator lags	as above	—
L, S	states, tank NaOH, solution	30, 93.75 t	—

Units: m^3 for V_a, ppb for C_h, mΩ m^2 for R_m and ppb h for H. The tank starts at 24 of 30 t in case 8 and the challenge.

the hydroxide that migrates back and the vapor carried by the hydrogen, as shown in Equation (5.3).

$$\begin{aligned}\frac{\mathrm{d}M_c}{\mathrm{d}t} &= \rho_w F_w + \dot{n}_e\left[\eta M_{Na} - (1-\eta)M_{OH} - \tfrac{1}{2}M_{H_2}\right] \\ &\quad + \dot{m}_d - \dot{m}_{v,c} - F_p \\ \frac{\mathrm{d}m_n}{\mathrm{d}t} &= \eta\,\dot{n}_e M_{NaOH} - wF_p \\ F_p &= k_{oc}\max(0, M_c - M_{c,0})\end{aligned} \tag{5.3}$$

where $w = m_n/M_c$. The catholyte's water closes exactly, because $\frac{1}{2}M_{H_2} + M_{OH} = M_{H_2O}$ and $M_{Na} + M_{OH} = M_{NaOH}$. At the design point the membranes carry 5.03 t/h of salt out of the anolyte and drag 5.43 t/h of water with it, the brine feed is 35.46 m^3/h and the depleted brine 27.53 m^3/h, and the catholyte needs 3.869 m^3/h of water to stay at 32 %. The anolyte turns over in 41 min and the catholyte in 113 min, and every one of these flows is proportional to the current. The catholyte weir has the same constant and holds 0.36 t above its level at the design point.

5.3.3 Membrane Resistance and Hardness

Calcium and magnesium above a precipitation threshold damage the membrane in proportion to the exposure and the current, and irreversibly, as shown in Equation (5.4).

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \max(0, C_h - h_{thr})\,\frac{i}{i_{nom}}, \qquad \frac{\mathrm{d}R_m}{\mathrm{d}t} = \frac{r_{age}}{t_{yr}} + k_{HR}\frac{\mathrm{d}H}{\mathrm{d}t} \tag{5.4}$$

where H is the exposure in ppb h, t_{yr} is one year, so that the creep adds only 6.8×10^{-6} mΩm^2 a day, and R_m is the membrane's area resistance referred to 88 °C and 32 %, which starts at $R_{m,0} + r_{age}\,\mathrm{age} = 0.063\,75$ mΩm^2 for an 18-month-old membrane. The threshold and both coefficients are illustrative.

5.3.4 Cell Voltage and Current Efficiency

The cell voltage is an illustrative correlation with area resistances in $\mathrm{m\Omega\,m^2}$, so that i in $\mathrm{kA/m^2}$ times a resistance is volts, as shown in Equation (5.5).

$$\begin{aligned} U &= U_{rev} + b\log_{10}\frac{\max(i,0.05)}{i_0} \\ &\quad + i\big(R_m f_T(1+k_m\Delta w) + R_{el} f_T g_{el} + R_{hw}\big) \\ U_{rev} &= U_0 + \beta_T\Delta T + k_{Uw}\Delta w + k_{Ua}(C_{ref} - C_a) \\ g_{el} &= s_a\Big(\frac{C_{ref}}{\max(50,C_a)}\Big)^{0.9} + (1-s_a)(1+k_{cw}\Delta w) \end{aligned} \tag{5.5}$$

where $\Delta T = T - 88$, $\Delta w = w - 32$ and $f_T = \mathrm{e}^{-\alpha_T\Delta T}$. At the design point the 3.103 V of a cell divide into 2.200 V reversible, 0.180 V at the electrodes, 0.383 V in the membrane, 0.270 V in the electrolyte and bubbles and 0.070 V in the hardware, and the membrane and electrolyte resistances fall about 1.5 % per kelvin. The current efficiency is an illustrative correlation with two knees, as shown in Equation (5.6).

$$\begin{aligned} \eta_{max} &= \eta_0 - a\,\mathrm{age} - k_1\max(0,w-w_k)^2 \\ &\quad - k_2 H - k_3\max(0,C_k - C_a) \\ \eta &= \mathrm{clamp}\big(\eta_{max} - j_d/\max(i,0.1),\ 0.5,\ 0.999\big) \\ \eta_{Cl} &= 1 - \min\big(0.5,\ \phi_0\,\mathrm{e}^{(C_{ref}-C_a)/\phi_s}\big) \end{aligned} \tag{5.6}$$

where the knees sit at $w_k = 32\,\%$ and $C_k = 200\,\mathrm{g/L}$, and j_d/i is hydroxide back-diffusion that does not scale with the current, which makes the efficiency fall at low load, from 95.00 % at 6 $\mathrm{kA/m^2}$ to 94.50 % at 3 $\mathrm{kA/m^2}$. The specific energy follows as $SE = NUI/\dot m_{NaOH} = UF/(\eta M_{NaOH})$, 2188 kWh/t at the design point, 1927 kWh/t at 3 $\mathrm{kA/m^2}$ and 2276 kWh/t at 7 $\mathrm{kA/m^2}$.

5.3.5 Heat Balance

The cells generate heat above the thermoneutral voltage $U_{tn} = \Delta H/2F = 2.31\,\mathrm{V}$, from $\Delta H = 446\,\mathrm{kJ}$ per mole of chlorine, and the feeds, the vapor, the room and the heater or cooler take it away, as shown in Equation (5.7).

$$\begin{aligned} C_{th}\frac{\mathrm{d}T}{\mathrm{d}t} &= I\,(NU - \Delta U_{fs} - NU_{tn}) + F_b\rho_b(C_b)c_{p,b}(T_b - T) \\ &\quad + \rho_w F_w c_{p,w}(T_w - T) - (\dot m_{v,a} + \dot m_{v,c})h_{fg}(T) \\ &\quad - UA\,(T - T_{amb}) + Q \end{aligned} \tag{5.7}$$

where ΔU_{fs} is the voltage a failing cell loses (below), $c_{p,w} = 4.18\,\mathrm{kJ/(kg\,K)}$ and $h_{fg}(T) = 2501 - 2.37T$ in kJ/kg. Both gases leave saturated with water, as shown in Equation (5.8).

$$\begin{aligned} \dot m_{v,a} &= (\dot n_{Cl_2} + \dot n_{O_2})M_{H_2O}\frac{p_a}{P_{Cl}^{abs} - p_a} \\ p_a &= \min\big(a_b\,p^{sat}(T),\ 0.95P_{Cl}^{abs}\big) \\ \log_{10}\frac{p^{sat}}{0.133\,322\,\mathrm{kPa}} &= 8.07131 - \frac{1730.63}{233.426+T} \end{aligned} \tag{5.8}$$

with $\dot m_{v,c}$ likewise from $\dot n_{H_2}$, P_H^{abs} and a_c, the illustrative water activities $a_b = 1 - 0.00047\,C_a$ and $a_c = 1 - 0.0145\,w$ (with w in percent), and absolute pressures from $P_{atm} = 1013.25\,\mathrm{mbar}$. At the design point 1.93 MW of the 7.54 MW, a quarter, is heat, of which the brine takes 0.90 MW, the vapor 0.73 MW, the water 0.26 MW and the room 0.13 MW, while the heater adds 0.09 MW. The vapor is 820 kg/h with the chlorine and 334 kg/h with the hydrogen, and its cooling grows by 51 kW

per kelvin of cell temperature, against 39 for the brine, while the heat generated falls by 26 kW per kelvin as the voltage drops. At fixed strengths these slopes give the heat balance a time constant of 20 min.

5.3.6 Gas Headers

Each header is an ideal-gas volume on a dry basis after the coolers, filled by the cells and emptied through its valve, as shown in Equation (5.9).

$$\begin{aligned} \frac{V_{Cl}}{RT_g}\frac{\mathrm{d}P_{Cl}}{\mathrm{d}t} &= \dot{n}_{Cl_2} + \dot{n}_{O_2} - \kappa C_{v,Cl} x_{Cl}\sqrt{(P_{Cl} - P_s)} \\ &\quad - C_{abs}\max(0, P_{Cl} - P_{seal}) \\ \frac{V_H}{RT_g}\frac{\mathrm{d}P_H}{\mathrm{d}t} &= \dot{n}_{H_2} - C_{v,H} x_H \sqrt{(P_H - P_d)} \\ &\quad - C_{rel}\max(0, P_H - P_{rel}) \end{aligned} \tag{5.9}$$

where the pressures are gauge in mbar, $\sqrt{(d)}$ is $\sqrt{d}$ above 5 mbar, $d/\sqrt{5}$ between 0 and 5 mbar and zero below, and κ is the compressor's share of its suction capacity, zero while it is tripped and recovering linearly to one over 1 min after a restart. At the design point the chlorine header is 150 mbar(g) with its valve at 52.6 %, the hydrogen header 185 mbar(g) with its valve at 50.0 %, and the difference $\Delta P = P_H - P_{Cl}$ is 35 mbar.

5.3.7 Feeds, Actuators, Tank and Events

The brine and water flows respond to their commands as first-order lags of 20 s, the heater duty as one of 1 min and the two valves as lags of 3 s. The caustic tank keeps its NaOH L and its solution S, as shown in Equation (5.10).

$$\frac{\mathrm{d}L}{\mathrm{d}t} = wF_p - D, \qquad \frac{\mathrm{d}S}{\mathrm{d}t} = F_p - \frac{D}{L/S} \tag{5.10}$$

Shipments $D = 3.0\,\mathrm{t/h}$ stop when the tank holds 0.2 t and resume at 1 t, and product reaches the tank on specification while $|w - 32| \le 0.5$ in percent. Hard events are handled after each integration step. The interlock reads its own transmitter, ΔP with 0.2 mbar of noise, once a second, and opens the rectifier when two consecutive scans fall outside $[\Delta P_{lo}, \Delta P_{hi}] = [20, 50]$ mbar. A restart is refused for 30 min and while ΔP is outside the band, and the rectifier then ramps up from zero. The band and its two-scan delay are teaching values that follow the handbook's treatment of the cell room [12]. Real limits come from the electrolyzer's vendor and are implemented as a safety instrumented function designed under IEC 61511. A failing cell, cell 87, opens a pinhole whose severity s grows linearly from 0 to 1 over 120 min. The cell then loses $\Delta U_f s = s \times 0.25\,\mathrm{V}$ and a share $\delta_\eta s = 0.30\,s$ of its efficiency, which lowers the stack's efficiency by $\delta_\eta s/N$, 0.2 % at full failure.

5.3.8 Initial State, Step and Replay

Table 5.2 collects the parameters. Every scenario starts from the explicit steady state of its own configuration, including any setting changed before the run starts. Given the current density, the temperature, both strengths, the brine and the header pressures, the balances give the brine and water flows, the heater duty and the two valve positions that hold the plant still, with no iteration because the temperature and the strengths are given. At that state no derivative of the loop inventories, the temperature, the headers or the actuator lags exceeds 1×10^{-16} relative, where the application's own check asks for 1×10^{-10}. Only the tank, which the cells fill faster than the shipments draw it at the design point, and the slow creep of the membrane with age are not stationary. The ratio stations as shipped are not the ones the steady state needs, 2.15 m³/h of brine and 0.251 m³/h of water per kA against 2.189 and 0.239, errors of −1.8 and +5.1 %, so the trims start out carrying the difference.

Table 5.2 Model Parameters. Class M Entries Can Be Changed in the Show Model Dialog, While Class H Entries Stay Hidden

Symbol	Meaning	Value	Class	Symbol	Meaning	Value	Class
N, A	cells, area per cell	150, 2.7 m^2	H	$V_{a,0}$, k_{va}	anolyte weir holdup, overflow	18 m^3, 0.5 min^{-1}	H
i_{nom}, i_{max}	design, rectifier limit	6.0, 7.0 kA/m^2	H, M	$M_{c,0}$, k_{oc}	catholyte weir holdup, overflow	20 t, 0.5 min^{-1}	H
P_{max}	rectifier rating (trend scale)	10 MW	H	T_w	water temperature	30 °C	H
age	membrane age	18 months	M	$F_{b,max}$, $F_{w,max}$	feed capacities	60, 8 m^3/h	M
U_0, U_{tn}	reversible, thermoneutral	2.20, 2.31 V	M	—	flow, heater, valve lags	20 s, 1 min, 3 s	H
b, i_0	Tafel slope, exchange current	0.080, 0.033 75 kA/m^2	M, H	C_{th}	heat capacity	150 MJ/K	M
$R_{m,0}$, r_{age}	new membrane, creep per year	0.060, 0.0025 mΩ m^2	M	UA, T_{amb}	loss to the room	2 kW/K, 25 °C	H
R_{el}, R_{hw}	electrolyte, hardware	0.045, 0.0117 mΩ m^2	M	$c_{p,b}$	brine heat capacity	3.3 kJ/(kg K)	H
α_T, β_T	temperature coefficients	0.015 K^{-1}, –0.9 mV/K	H	Q_{heat}, Q_{cool}	heater, cooler at 25 °C	1.5, 1.5 MW	M
k_{Uw}, k_{Ua}	U_{rev} per %, per g/L	5, 0.3 mV	H	T_{max}	temperature alarm	92 °C	H
k_m, k_{cw}, s_a	per % caustic, anolyte share	0.03, 0.03, 0.4	H	V_{Cl}, V_H	header gas volumes	300, 250 m^3	M
η_0, a	new efficiency, loss per year	95.8, 0.2 %	M, H	T_g, τ_{comp}	gas temperature, reload	320 K, 1 min	H
k_1, w_k	caustic knee	0.004 $\%^{-2}$, 32 %	M, H	$C_{v,Cl}$, $C_{v,H}$	valves, mol/s per $\sqrt{\text{mbar}}$	1.505, 1.853	H
k_2	loss per exposure	1×10^{-5} $(\text{ppbh})^{-1}$	M	P_s, P_d	suction, hydrogen outlet	−100, 0 mbar(g)	H
k_3, C_k	anolyte knee	0.0006 $(\text{g/L})^{-1}$, 200 g/L	M, H	P_{seal}, C_{abs}	seal pot, mol/s per mbar	300 mbar(g), 0.6	M, H
j_d	back-diffusion	0.03 kA/m^2	M	P_{rel}, C_{rel}	hydrogen relief	450 mbar(g), 0.6	H
ϕ_0, ϕ_s, C_{ref}	oxygen share, scale, reference	1.2 %, 30, 210 g/L	M, H, H	ΔP_{lo}, ΔP_{hi}	interlock band (teaching)	20, 50 mbar	M
$t_{w,0}$, $t_{w,a}$	drag per Na^+, per g/L	3.5, 0.01	M	n_{SIS}, t_{rst}	scans outside, restart	2, 30 min	M
h_{thr}, k_{HR}	threshold, damage per ppb h	30 ppb, 7×10^{-6} mΩ m^2	M	L_{cap}, D	tank capacity, shipments	60 t[a], 3.0 t/h	M
σ_a, σ_w	analyzer repeatability	0.6 g/L, 0.03 %	M	L_{lo}, L_{hi}, L_0	tank band, start	10, 90, 50 %[a]	M
θ_a, Δt_a	sample loops, update	1 min, 30 s	H	δ_L, δ_m	scheduler margins	0.5, 0.3 t	H
—	TT-103 lag, noise	30 s, 0.05 °C	H	ΔU_f, δ_η, τ_f	failing cell 87	0.25 V, 0.30, 120 min	M, H, M
—	PT, PDT, SIS, LT noise	0.1, 0.1, 0.2 mbar, 0.05 t	H	—	EI-500 scan, noise, spread	30 s, 2, 4 mV	H, H, M

[a] 30 t starting at 80 % in case 8 and the challenge. U_0 is taken at 88 °C, 32 % and 210 g/L. Constants: $F = 96\,485.332\,\text{C/mol}$, $R = 8.314\,462\,\text{J/(mol K)}$, and molar masses of NaOH, NaCl, Cl_2, H_2, O_2 and H_2O of 39.997, 58.443, 70.906, 2.016, 31.998 and 18.015 g/mol.

The engine of Section 1.6.1 advances the electrolyzer by fourth-order Runge-Kutta in steps of one second. The controllers run every 5 s and the historian writes a row every 30 s, while a ring buffer keeps the true ΔP once a second for the scene's scope. The speed selector spans 1 to 1200 minutes of plant time per second, with 10 as the default, and the seed is 20261127. With every instrument noise-free, halving the step moves the lowest ΔP of the compressor trip with the feedforward on by 0.064 mbar and the challenge's electricity cost by less than 1×10^{-6} %. Over the challenge day the salt, volume, hardness, catholyte mass, NaOH, water, tank and header ledgers close to 4.0×10^{-13} relative, far inside the 1×10^{-9} that one of the application's 42 checks demands.

5.3.9 Assumptions

One lumped cell stands for all 150, with the same current, strengths and temperature, so end cells, gradients along the stack and uneven flows are absent, and only the monitor sees the cells apart, through a fixed cell-to-cell fingerprint of 4 mV and the one failing cell. The voltage, efficiency, water-activity, oxygen and hardness correlations are illustrative teaching choices fitted to one design point, valid between about 2 and 8 kA/m^2, 80 and 92 °C, 28 and 36 % and 150 and 240 g/L. The application itself notes that real damage depends on calcium, magnesium, strontium, barium, iodide and silica together and on the membrane type, and the impurities of the brine set the performance of a membrane cell in general [6]. The brine is acidified without the hydrochloric acid dosing being modeled, and chlorate, hypochlorite, dechlorination and resaturation are left out, so the saturators appear only as the strength and temperature of the brine they deliver.

The heat balance uses the thermoneutral voltage at 25 °C without a heat-capacity correction and one lumped heat capacity. The headers are ideal gases on a dry basis, the compressor is a suction capacity, and the emergency absorption has no limit. Chlorine and hydrogen are taken by their consumers without limit, so the caustic tank is the only storage the scheduler sees, while in many real plants the chlorine outlets limit flexibility more than the caustic does. Electricity is priced on the direct current with rectifier losses neglected, and the steam is not priced. The price profiles are synthetic.

Table 5.3 Loops, Directions and Shipped Tunings

Tag	CV → MV	γ	K_c	τ_I	Output
AIC-101	$C_a \to F_b$, bias $r_b I$	+1	1.0	30 min	0–60 m³/h
AIC-102	$w \to F_w$, bias $r_w I$	−1	2.0	60 min	0–8 m³/h
TIC-103	$T \to Q$	+1	0.25	20 min	$-Q_{cool}(T_{cw})$–1.5 MW
PIC-201	$P_{Cl} \to x_{Cl}$	−1	2	2 min	0–100 %
PDIC-203	$\Delta P \to u_{\Delta P}$	+1	0.5	1 min	0–150 mbar
PIC-202	$P_H \to x_H$	−1	6	1 min	0–100 %

Gains in m³/h per g/L, m³/h per %, MW/K, % per mbar, mbar per mbar and % per mbar, in the order of the rows.

5.4 Instruments and Implemented Controllers

5.4.1 Instruments

No controller reads the plant's state. AT-101 reports the anolyte strength that a densitometer infers from $\rho_b(C_a)$, and AT-102 the caustic strength from conductivity, through the framework's shared sampled analyzer, each with a 1 min sample loop, a result every 30 s describing a sample that left the cell at least 1.5 min earlier, repeatabilities of 0.6 g/L and 0.03 %, and a STALE flag when a result has not been refreshed for four cycles. TT-103 lags the cell by 30 s with 0.05 °C of noise, the two header transmitters and PDT-203 carry 0.1 mbar of noise, LT-400 carries 0.05 t, and the rectifier knows its own current exactly and measures the stack voltage. EI-500 scans every cell every 30 s with 2 mV of noise.

5.4.2 The Shared PI Law

All six loops run the framework's velocity-form PI of Section 1.6.2, written for this chapter as Equation (5.11).

$$\begin{aligned} e_k &= \gamma(\mathrm{SP}_k - \mathrm{PV}_k), \quad P_k = K_c e_k, \quad D_k = -K_d \gamma \dot{\mathrm{PV}}_k \\ S_k &= S_{k-1} + (P_k - P_{k-1}) + (D_k - D_{k-1}) \\ v_k &= b_k + S_k + I_{k-1}, \qquad u_k = \mathrm{clamp}(v_k, u_{min}, u_{max}) \\ I_k &= I_{k-1} + \left[\frac{K_c}{\tau_I} e_k + \frac{u_k - v_k}{\tau_I}\right]\Delta t_c \end{aligned} \tag{5.11}$$

where $\gamma = \pm 1$ is the loop's direction, b_k an output bias and $\Delta t_c = 5$ s. Derivative action is switched off in every loop of the cell room ($K_d = 0$), so $S_k = P_k$. The back-calculation corrects the integral alone, with τ_I as the tracking time, and the clamp bounds nothing but the emitted value. No PI output is rate limited, and the only slew in the cell room is the rectifier's ramp of Equation (5.14). A loop in MANUAL recomputes its integral as $I_k = u_{op} - b_k - S_k$ at every scan, so the return to AUTO starts from wherever the operator left the actuator. Table 5.3 lists what each loop measures and moves, its direction and its shipped tuning.

5.4.3 Ratio Stations and Trims

AIC-101 and AIC-102 are ratio stations whose bias is the feedforward, the station with a feedback trim of Equation (1.10), as shown in Equation (5.12).

$$\begin{aligned} F_{b,cmd} &= \mathrm{clamp}\big(r_b I + u_a,\ 0,\ F_{b,max}\big) \\ F_{w,cmd} &= \mathrm{clamp}\big(r_w I + u_w,\ 0,\ F_{w,max}\big) \end{aligned} \tag{5.12}$$

where I is the stack current in kA and u_a, u_w are the PI trims of Equation (5.11) on AT-101 and AT-102. The ratio moves the flow the instant the rectifier does, and the integral carries the correction. Each loop has three strategies. Ratio plus trim is Equation (5.12), ratio only sends $r_b I$ with the trim tracking, and trim only drops the bias so that feedback sets the whole flow. A switch of strategy moves

the integral by exactly the feedforward that appears or disappears, which keeps the flow continuous. While its analyzer is out of service or STALE, a trim holds what it has learned and the ratio carries on alone. More brine raises the anolyte, so AIC-101 is direct acting, and more water dilutes the caustic, so AIC-102 is reverse acting. TIC-103 is one PI over a split range, the steam heater up to 1.5 MW and the cooler down to $-Q_{cool}(T_{cw}) = -1.5(78 - T_{cw})/53$ MW, whose capacity shrinks as the cooling water warms.

5.4.4 The Gas Side and the Interlock

PIC-201 holds the chlorine header with the compressor's suction valve. PDIC-203 is the master of a cascade, and its output $u_{\Delta P}$ is the difference it asks the hydrogen slave for, as shown in Equation (5.13).

$$P_{H,SP} = \mathrm{clamp}(B + u_{\Delta P},\, 0,\, 450), \quad B = \begin{cases} \text{PT-201} & \text{FF on} \\ P_{Cl,SP} & \text{FF off} \end{cases} \tag{5.13}$$

in mbar(g), with $u_{\Delta P}$ between 0 and 150 mbar and FF the chlorine pressure feedforward. With the feedforward on, the hydrogen setpoint follows the chlorine header as PT-201 measures it, and the master only trims the difference. With it off, the setpoint is built on the chlorine setpoint and every rise of the chlorine header has to appear as a PDIC-203 error first. With PIC-202 on its local setpoint or in MANUAL the cascade is open and the master tracks. The interlock of Section 5.3 sits behind the cascade on its own transmitter, so a controller that is too slow loses the day's production but not the membrane.

5.4.5 Rectifier

REC-100 takes the scheduler's plan when FY-400 is on and the plant is in AUTO, and the operator's setpoint otherwise, as shown in Equation (5.14).

$$\begin{aligned} i_{tgt} &= \mathrm{clamp}(i_{want},\, i_{min},\, i_{max}) \\ i_{tgt} &\leftarrow \max(i_{min},\, i_{sh}) \quad \text{if } L \geq 0.97 L_{cap} \text{ and } i_{tgt} > i_{sh} \\ i_k &= \mathrm{slew}(i_{tgt},\, i_{k-1},\, \rho,\, \Delta t_c) \end{aligned} \tag{5.14}$$

where the ramp limit is $\rho = 0.03\,\mathrm{kA/m^2}$ per minute, the minimum load is $i_{min} = 3.0\,\mathrm{kA/m^2}$, and $i_{sh} = (D/c + j_d)/0.95$ is about the current density whose production matches the shipments, with $c = NA\,M_{NaOH}/F = 0.6044\,\mathrm{t/h}$ per kA/m^2 at full efficiency. After a trip the current is zero until the interlock is reset. The I key requests an interlock reset; R keeps its shared simulation Reset action.

5.4.6 The Load Scheduler

FY-400 plans the current density v_k at every hour boundary from now to midnight with a linear program, and between boundaries the rectifier ramps linearly, so a plan that respects the ramp row is executed exactly. The day's electricity cost is minimized subject to the ramp, the load limits, the tank band and the target, as shown in Equation (5.15).

$$\begin{aligned} \min\ & \textstyle\sum_{k=1}^{K} \pi_k \tfrac{1}{2}\big(\hat{P}(v_{k-1}) + \hat{P}(v_k)\big)\Delta t_k \\ & \quad + M_T\,\sigma + M_L(\zeta_{lo} + \zeta_{hi}) \\ \text{s.t. } & |v_k - v_{k-1}| \leq \rho\,\Delta t_k, \qquad i_{min} \leq v_k \leq i_{max} \\ & L_{lo} + \delta_L \leq \hat{L}_k + \zeta_{lo} - \zeta_{hi} \leq L_{hi} - \delta_L \\ & \textstyle\sum_k \hat{m}_k + \sigma \geq m_{day} + \delta_m - m_{made} \\ & \hat{m}_k = c\,\big(\hat{\eta}\,\tfrac{1}{2}(v_{k-1} + v_k) - j_d\big)\Delta t_k \\ & \hat{L}_k = L_0 + \textstyle\sum_{j \leq k}(\hat{m}_j - D\,\Delta t_j) \end{aligned} \tag{5.15}$$

where v_0 is the present current, π_k the price of hour k, $m_{day} = 72\,\mathrm{t}$ the daily target, m_{made} the NaOH made since midnight as the tank gauge and the shipments' meter measure it, and L_0 the tank gauge.

The power $\hat{P}(v) = NAv\hat{U}(v)$ uses the voltage correlation with a new membrane at the measured temperature and strengths, shifted by a bias so that it passes through the measured stack voltage, so a damaged membrane raises the price of every tonne the scheduler plans. $\hat{P}$ is convex, and it is replaced by its chords over four equal segments between i_{min} and i_{max}, whose slopes rise from 1.312 to 1.613 MW per kA/m^2, so the LP fills the cheap segments first without integer variables and overstates the power by at most 12.7 kW. The efficiency $\hat{\eta}$ is the model's η_{max} at the measured strengths with no hardness loss, and the back-diffusion term enters exactly, because j_d/i times the current is a constant. The margins $\delta_L = 0.5$ t and $\delta_m = 0.3$ t absorb the model's error and the gauge's noise, and the slacks σ, ζ_{lo} and ζ_{hi} carry prices of $M_T = \$10^5$ and $M_L = \$10^6$ per tonne, so the LP always returns a plan and reports a shortfall rather than relaxing a limit. With four segment variables per hour the full day has 99 variables and 49 rows. A bounded-variable simplex solves it, pricing by the largest reduced cost and falling back to Bland's rule [17] after 30 pivots without progress, in 172 pivots and bound flips and about 1 ms in Node.js. The plan is re-solved on the hour, when the present hour's price moves by more than 20 %, at a new day, after a restart and whenever a limit or the target changes. The day-ahead price is known and a real-time spike is seen only once it has begun.

5.4.7 Cell-Voltage Monitor

EI-500 subtracts the stack mean from each cell's scan, and a cell whose deviation exceeds ±40 mV for two consecutive scans raises a cell fault. The fingerprint is a fixed, zero-mean draw of 4 mV standard deviation, the same in every case, so the monitor must find a failing cell against a stack that is never uniform.

5.4.8 Three Models Kept Apart

Section 5.3 describes the simulated plant. The application fits no control model, and manual steps from the design point with the instrument noise switched off show instead the plants the loops act on. A 1 m^3/h step of brine raises the anolyte by 2.97 g/L, 63 % of the way in 36 min. A 0.1 m^3/h step of water lowers the caustic by 0.28 %, 63 % in 108 min. A 0.1 MW step of the heater warms the cells by 0.82 K, 63 % in 22 min. A one-percent closure of either header valve raises its header by 7.6 (hydrogen) or 9.8 mbar (chlorine), 63 % in 289 s or 469 s, because a root-law valve makes each header self-regulating. Linearized, a header at P above a downstream pressure P_o (P_d or P_s) rises by $2(P - P_o)/x$ per percent of closure, with x in percent, and responds with the time constant $2(P - P_o)/r$, with r the fill rate of Equation (5.16), which gives 7.4 and 9.5 mbar and 276 and 450 s for the two headers. The controllers' internal models are the ratio coefficients, which approximate the stoichiometry in m^3/h per kA, the unit-gain chlorine feedforward of Equation (5.13), and the scheduler's voltage correlation, efficiency, chords and tank integrator of Equation (5.15). The PI trims carry no model at all.

5.5 Riding Through a Compressor Trip

When the chlorine compressor stops, its suction valve can draw nothing and the chlorine header fills with everything the anodes make. Both header rates follow from Equations (5.1) and (5.9), as shown in Equation (5.16).

$$r_{Cl} = \frac{(1+\eta_{Cl})\,NIRT_g}{4FV_{Cl}}, \qquad r_H = \frac{NIRT_g}{2FV_H}$$
$$\frac{r_H}{r_{Cl}} = \frac{2V_{Cl}}{(1+\eta_{Cl})V_H} \tag{5.16}$$

where r_{Cl} is the chlorine header's rise with the compressor stopped and r_H the fastest the hydrogen header can rise, with its valve shut. At 6 kA/m^2 they are 1.110 mbar/s and 1.340 mbar/s. Both scale with the current, so their ratio, 1.207, is the same at every load, and the hydrogen can outrun the chlorine by only 21 % however it is controlled. A hydrogen header larger than $2V_{Cl}/(1+\eta_{Cl}) = 301.8$ m^3 could not keep pace at all. The engine agrees. With the feedforward on, a 300 m^3 hydrogen

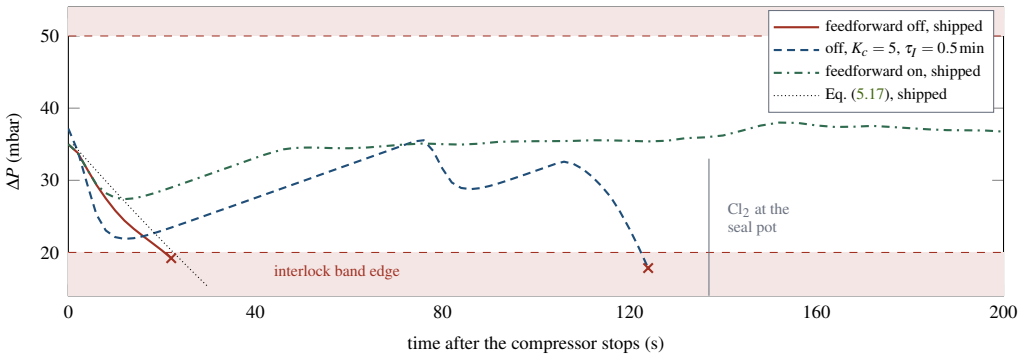


Figure 5.2 Hydrogen-over-chlorine difference after the chlorine compressor stops in case 5, true values from the engine. The shipped tuning without the feedforward (solid) trips at 22 s, ten times its gain with half its integral time ($K_c = 5$, $\tau_I = 0.5$ min, dashed) holds until the master's output limit and trips at 124 s, and the shipped tuning with the feedforward (dash-dotted) never leaves 27.4 to 38.9 mbar. The dotted curve is Equation (5.17) for the shipped tuning, the shaded bands lie outside the interlock band, and crosses mark the trips.

header rides through case 5 with ΔP no lower than 26.1 mbar, while 320 m^3 trips the rectifier 108 s after the compressor stops with the hydrogen valve fully shut, and 400 and 500 m^3 trip after 32 and 24 s.

With the feedforward off and a slave fast enough to hold $P_H = P_{Cl,SP} + u_{\Delta P}$, a chlorine header that starts to rise at r_{Cl} from equilibrium gives the master an error $e = \Delta P_{SP} - \Delta P = r_{Cl}t - (u_{\Delta P} - u_0)$, with $u_{\Delta P} - u_0 = K_c e + (K_c/\tau_I)\int e\,dt$. Differentiating gives Equation (5.17).

$$(1 + K_c)\frac{de}{dt} + \frac{K_c}{\tau_I}e = r_{Cl}$$
$$e(t) = \frac{r_{Cl}\tau_I}{K_c}\left(1 - e^{-t/\tau_e}\right), \qquad \tau_e = \frac{(1 + K_c)\tau_I}{K_c} \tag{5.17}$$

The error settles toward $r_{Cl}\tau_I/K_c$, and the margin $m = \Delta P_{SP} - \Delta P_{lo} = 15$ mbar is gone after the time given by Equation (5.18).

$$t_m = -\tau_e \ln\left(1 - \frac{K_c m}{r_{Cl}\tau_I}\right), \qquad K_c m < r_{Cl}\tau_I \tag{5.18}$$

At the shipped tuning $\tau_e = 180$ s and the settled error would be 133.2 mbar, nearly nine times the margin, so $t_m = 21.5$ s. On the engine the header starts to rise 1 s after the scheduled event, once the integration step in which the compressor stops is complete, the true difference crosses 20 mbar 20 s later, and the interlock opens the rectifier 22 s after the compressor stopped, as shown in Figure 5.2. The estimate assumes a perfect slave and a continuous master, so it overstates the ride-through, by 1.5 s at 6 kA/m^2. On the challenge's day, where the trip comes at 5.3 or 7.0 kA/m^2, it predicts 24.7 and 18.3 s against 23 and 15 s on the engine, whose interlock trips 25 and 17 s after the compressor stops.

Equation (5.18) says the loop holds on feedback alone only if $K_c/\tau_I > r_{Cl}/m$, 4.44 min^{-1} at 6 kA/m^2. A second limit then binds. The master may ask for at most 150 mbar above the chlorine setpoint, so the hydrogen setpoint stops at 300 mbar(g) while the chlorine climbs toward its seal pot at the same pressure, and the difference falls through 20 mbar once the chlorine passes about 280 mbar(g), 117 s after the rise begins. The two runs with $K_c/\tau_I = 10$ min^{-1} cross at 122 and 123 s and trip at 124 and 125 s, their hydrogen header coasting 4 to 5 mbar above the capped setpoint, as Table 5.4 shows. Faster feedback also costs noise. In normal operation the standard deviation of

Table 5.4 PDIC-203 Tuning Against the Compressor Trip of Case 5

			Feedforward off			FF on
K_c	τ_I (min)	t_m, Eq. (5.18) (s)	crossing (s)	trip (s)	σ (mbar)	lowest ΔP
0.5	1	21.5	20	22	0.09	27.4
1	1	30.6	28	30	0.12	28.3
2	1	53.9	48	50	0.29	28.5
2	0.5	104.0	93	95	0.35	28.4
5	0.5	holds	122	124	2.81	22.5
10	1	holds	123	125	2.82	24.0
10	0.1	holds	11	13	6.99	trips

Crossing: true ΔP below 20 mbar, seconds after the chlorine header starts to rise. Trip: seconds after the compressor stops. σ: standard deviation of the true ΔP from 20 to 60 min, before the trip. Lowest: the least ΔP from 1:00 to 2:00 with the feedforward (FF) on, where the last tuning trips at 13 s, inside its limit cycle.

ΔP grows from 0.09 mbar at the shipped tuning to 2.8 mbar at 10 min^{-1}, and at the extreme of the tuning range, $K_c = 10$ and $\tau_I = 0.1$ min, the cascade limit-cycles with a 40 s period between 24.9 and 47.9 mbar, close to both trip limits, with the hydrogen valve commanded to one of its stops 97 % of the time. The compressor trip then catches a swing near its bottom, and that tuning trips the rectifier 13 s after the compressor stops with the feedforward on or off.

> **DID YOU KNOW? Faster Feedback Trips Sooner**
>
> From the simulator: the fastest pressure-difference tuning of Table 5.4, a gain of 10 with an integral time of 0.1 min, trips the rectifier 13 s after the compressor stops, sooner than the 22 s of the shipped tuning without the feedforward, and with the feedforward on or off. Before the trip it already swings between 24.9 and 47.9 mbar.

The feedforward removes the ramp from the master's error, because the hydrogen setpoint now moves with PT-201 from the first second. What is left is the slave's transient and the master's 5 s cycle. The difference dips to 27.4 mbar 12 s after the trip, the chlorine reaches its seal pot 137 s after it, 1.48 t of chlorine go to the emergency absorption before the restarted compressor has reloaded, and the difference stays between 27.4 and 38.9 mbar through the restart. A feedback loop acts on an error it has already seen, while the feedforward acts on the cause, which is measured, and that is the whole lesson of the gas side.

Pause. Try Exercise 5.2 before reading on.

5.6 Measured Cases

The nine scenarios are summarized in Table 5.5, and the Exercises at the end of the chapter work through them. Every case lasts 24 h and starts from the shipped tunings of Table 5.3, with the chlorine feedforward on, both feeds at ratio plus trim and the scheduler off, except for the items its row names, which are set before the run starts. Each number was read from the engine, stepped without the browser through the same step function at the default seed, and a run that trips is continued to midnight. Table 5.6 gathers each day's scorecard, which is kept on the truth at every physics step.

5.6.1 The Current Is the Load

Case 1 starts steady at 5.0 kA/m^2 with 29.51 $\text{m}^3\text{/h}$ of brine and 3.222 $\text{m}^3\text{/h}$ of water set by hand. At 1:00 the rectifier ramps to 6.5 kA/m^2 and reaches it at 1:50, so the membranes carry 5.46 t/h of salt out of the anolyte against 4.19 t/h before, and the brine does not follow. The anolyte passes 200 g/L at 1:43 and 190 g/L at 2:09 and reaches 177.9 g/L by 8:00. The caustic leaves its specification at 1:52 and rises from 32.00 to 33.11 %, less than the current alone would make it because the weaker anolyte

Table 5.5 The Cases, Their Upsets and Their Lessons

#	Scenario and events	Teaching point
1	feeds in MANUAL, 5.0 to 6.5 kA/m^2 at 1:00	the current is the load
2	6.0 to 4.0 at 2:00, to 6.5 kA/m^2 at 12:00	a ratio and its trim
3	caustic SP 33, 34, 35 % at 2:00, 8:00, 14:00	an optimum on a curve
4	ratio only, brine 305 to 285 g/L at 1:00	depletion, oxygen
5	compressor trip 1:00 to 1:30, feedforward off	feedforward, interlock
6	500 ppb hardness 2:00 to 5:00	damage no loop undoes
7	brine 65 to 45 °C at 1:00, heater held	the heat balance
8	FY-400 on, 30 t tank from 24 t	load following on price
9	graded day, three upsets	challenge

Table 5.6 Truth-Log Scorecard of Each Case and Variant Over Its 24 h Day

Case and configuration	Made (t)	On spec (t)	Off spec (t)	Electricity ($)	*SE* (kWh/t)	ΔP (mbar)	Anolyte lowest (g/L)	η lowest (%)	Other
1 feeds in MANUAL (shipped)	86.8	5.6	81.0	13 724	2300	34.5–35.6	177.9	93.22	O_2 1.78 %
1 both feed loops in AUTO	88.4	88.4	0.0	13 508	2226	34.5–35.6	209.7	94.90	
2 ratio plus trim (shipped)	74.2	74.2	0.0	11 318	2157	34.5–35.6	209.7	94.75	caustic 31.98–32.02 %
2 trim only	74.2	74.2	0.0	11 319	2158	34.5–35.6	205.0	94.75	caustic 31.64–32.40 %
2 ratio only	74.2	9.4	65.0	11 278	2150	34.5–35.6	208.0	94.75	caustic 31.36–32.00 %
3 caustic 33 to 35 %[a]	81.0	7.5	72.9	12 557	2265	34.5–35.6	209.7	91.24	
4 ratio only (shipped)	82.0	82.0	0.0	12 447	2220	34.5–35.6	185.8	94.15	O_2 1.36 %
4 ratio plus trim	82.7	82.7	0.0	12 373	2189	34.5–35.6	205.0	95.00	
5 feedforward off (shipped)	3.5	3.6	0.0	394	2189	19.8–35.3	210.0	95.00	trip, dry 772 min
5 feedforward on	82.7	82.7	0.0	12 373	2189	27.4–38.9	209.6	95.00	1.48 t Cl_2 absorbed
6 breakthrough (shipped)	81.4	81.4	0.0	12 636	2268	34.5–35.6	209.7	93.21	$534/day lasting
6 with cell 87 failing at 12:00	81.3	81.3	0.0	12 633	2270	34.5–35.6	209.7	93.01	flagged 12:22
7 heater held (shipped)	82.7	82.7	0.0	12 684	2243	34.5–35.6	209.5	95.00	80.7 °C
7 TIC-103 in AUTO	82.7	82.7	0.0	12 374	2189	34.5–35.6	209.7	95.00	
8 scheduler (shipped)	72.3	72.3	0.0	9 008	2163	34.5–35.6	209.7	94.50	tank 21.4–26.7 t
8 constant 5.3 kA/m^2	73.0	73.0	0.0	10 617	2127	34.5–35.6	209.7	94.93	tank 24.0–25.0 t

All cases are priced on the sunny profile. Made is NaOH at the membrane, on and off specification are what reached the tank inside and outside 32 ± 0.5 %, and after the trip of case 5 the catholyte above its weir still drains to the tank, so more reaches it than the membranes made. [a] Case 3 moves the caustic off the 32 ± 0.5 % specification on purpose, to trace the efficiency curve.

pushes more water through the membrane. The efficiency falls from 94.90 to 93.22 %, the oxygen in the chlorine rises from 0.60 to 1.78 %, the specific energy climbs from 2101 to 2314 kWh/t, and 81.0 t of the day's 86.8 t reach the tank off specification. With both feed loops in AUTO the anolyte stays within 0.28 g/L and the caustic within 0.016 % of their setpoints all day.

Case 2 turns the load down to 4.0 kA/m^2 at 2:00 and up to 6.5 kA/m^2 at 12:00, which asks the brine for 35.46, 23.57 and 38.43 m^3/h in turn. With ratio plus trim the anolyte stays within 0.28 g/L of 210 and the caustic within 0.022 % of 32. With the trims alone the flows move only after the analyzers have seen the strengths move, and the anolyte swings 4.88 g/L after the turndown and the caustic 0.40 % after the load-up, inside the specification only because the 0.03 kA/m^2 per minute ramp stretches each step over more than an hour. With the ratios alone the flows follow at once but keep the stations' own errors, the anolyte settles 2.0 g/L low and the caustic 0.64 % weak, off specification from 2:47, and 65.0 t of 74.2 t go off specification. Feedforward does the known part at once, and feedback does the part nobody knew.

🕮 **Pause.** Try Exercise 5.1 before reading on.

5.6.2 Two Curves in the Efficiency

Case 3 raises the caustic setpoint one point at a time. Averaged over the hour before each step, the efficiency is 95.00, 94.60, 93.40 and 91.40 % at 32, 33, 34 and 35 %, losses of 0.40, 1.20 and 2.00 points, so the third point costs five times the first. The cell voltage rises 64 mV over the three steps and the specific energy climbs from 2188 to 2213, 2257 and 2322 kWh/t, 6.1 % in all, for 1.00 m^3/h

less water to evaporate downstream (the water added falls from 3.87 to 3.52, 3.18 and 2.87 m^3/h). In case 4 the brine weakens from 305 to 285 g/L under the ratio alone. The anolyte, at 208.4 g/L from the station's own error, falls through 190 g/L at 2:00 and reaches 185.8 g/L by 8:00, the dry chlorine carries 1.36 instead of 0.64 % oxygen, and below the 200 g/L knee the efficiency falls to 94.15 %, while the caustic trim holds 32 % by cutting the water from 3.86 to 3.48 m^3/h. With the densitometer trim the brine rises from 35.5 to 44.9 m^3/h, the anolyte dips only to 205.0 g/L and is back within 1 g/L of 210 by 2:26. A ratio is a model of the feed's strength, and only a measurement can tell it that the strength has changed.

> **TRY IT IN THE APP** **4 · A Weak Brine and Oxygen in the Chlorine**
>
> Load scenario 4 and press Run. At 1:00 the brine weakens from 305 to 285 g/L while its feed follows the current by the ratio alone. Watch the anolyte strip on the Cell view fall through 190 g/L at 2:00 to 185.8 g/L by 8:00. Reset, set the Brine feed strategy to Ratio + trim, and run again: the anolyte dips only to 205.0 g/L.

5.6.3 Damage No Loop Undoes

In case 6, 500 ppb of hardness reaches the cells from 2:00 until a fresh ion-exchange column comes on line at 5:00. The anolyte passes the 30 ppb threshold at 2:01, peaks at 636 ppb at 5:00 and falls back below it at 7:31, an exposure of 1794 ppb h. The cell voltage rises from 3.103 to 3.178 V, 75.4 mV, and the efficiency falls from 95.00 to 93.21 %, so the specific energy is 2285 kWh/t instead of 2188 while the anolyte, the caustic and the temperature are back on their setpoints. At the profile's average price of $68.38/MWh the scorecard prices the damage at $534 a day for as long as this membrane stays in. The monitor stays silent, because hardness raises every cell alike, and the worst of the 150 cells never reads more than 17.2 mV from the mean, against a threshold of 40 mV. In the variant with cell 87 failing from 12:00, the monitor flags cell 87 after 22.1 min, 42 mV below the mean, while the stack mean has moved by 0.3 mV. A threshold of 20 mV flags it after 11.1 min and one of 100 mV after 50.1 min, while 10 mV raises a false alarm on a healthy cell 35 s into the day, at its second scan, inside the stack's own spread.

Pause. Try Exercise 5.3 before reading on.

5.6.4 Cold Brine and the Heat Balance

In case 7 the brine arrives at 45 °C instead of 65 from 1:00 with the heater held at 0.09 MW. The cells cool 63 % of the way in 24.5 min and reach 80.7 °C, the voltage rises by 82 mV to 3.185 V by 8:00, and the specific energy goes from 2188 to 2246 kWh/t, 0.199 MW or 2.6 % more electricity for the same caustic. With TIC-103 in AUTO the heater rises from 0.09 to 0.87 MW, the temperature dips by 1.70 K and is back within 0.3 K of 88 °C by 1:58. The 0.78 MW of steam buys back 0.199 MW of electricity, a trade the price decides, while keeping the membrane at its design temperature keeps it where its correlations were fitted.

5.6.5 Load Following on the Price

Case 8 gives the scheduler a sunny day's price from $18 to $165/MWh, a 30 t tank starting at 24 t, customers drawing 3.0 t/h and a 72 t target. Its first plan, solved at midnight, reaches the rectifier limit at 3:00, from 12:00 to 15:00 and from 23:00, and the minimum load through both price peaks. The rectifier runs within 0.01 kA/m^2 of 7.0 kA/m^2 from 2:59 to 3:06, from 11:59 to 15:01 and after 22:59, and of 3.0 kA/m^2 from 6:58 to 8:09 and from 18:00 to 20:00. What stops it running harder in the cheap hours is the tank, which reaches the scheduler's ceiling of 26.5 t, 0.5 t inside the tank's own 90 %, by 5:00 and again at 16:00, and never leaves 21.4 to 26.7 t. No hourly re-solve plans to pass that ceiling by more than 0.01 t, and the tank still passes it by up to 0.16 t from 16:05 to 17:11, an error of the scheduler's model that its margin absorbs. The day makes 72.3 t for $9 008 at 2163 kWh/t, buying its 156.3 MWh at an average of $57.63/MWh. A constant 5.3 kA/m^2, which starts the day steady at that current, makes 73.0 t for $10 617, 18 % more, although each of its tonnes takes 1.6 % less energy

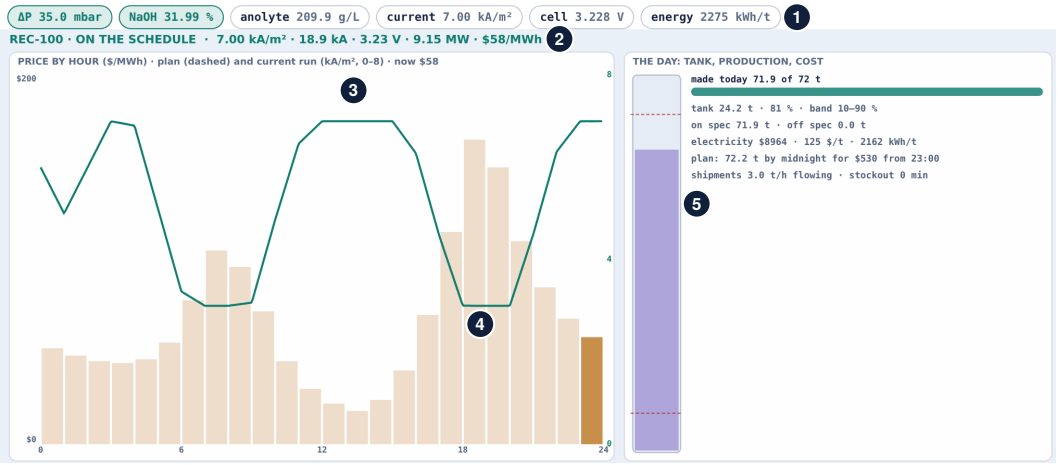


Figure 5.3 The electrolyzer in case 8, load following on the price, at $t = 23.92$ h (1435 min) in the Plant view, with every control as shipped, cropped to the plant view. Numbered callouts mark (1) the badges, (2) the rectifier's status line, (3) the current at the rectifier's limit through the midday dip in price, (4) the minimum load through the evening peak and (5) the tank and the day's tally. The price panel shows the sunny day's hourly price with the present hour at $58/MWh highlighted, and on its right-hand scale the current density actually run, 5.0 kA/m^2 at 1:00, close to the rectifier's 7.0 kA/m^2 at 3:00 and at it from 12:00 to 15:00 and from 23:00, and the 3.0 kA/m^2 minimum load through both price peaks. The plan for the last hour (dashed) lies under the run at 7.0 kA/m^2. The day panel gives 71.9 of the 72 t target made, the tank at 24.2 t (81 %) inside its 10 to 90 % band, 71.9 t on specification and none off, $8964 of electricity at $125/t and 2162 kWh/t, a plan of 72.2 t by midnight, and shipments of 3.0 t/h with no stockout. The header reads REC-100 on the schedule at 7.00 kA/m^2, 18.9 kA, 3.23 V and 9.15 MW, and the badges read 35.0 mbar, 31.99 % NaOH, 209.9 g/L of anolyte and 2275 kWh/t.

(2127 kWh/t), because it pays the profile's average of $68.38/MWh. On the scheduler's own model the marginal energy of one more tonne is 2185 kWh/t at the minimum load and 2881 kWh/t at the rectifier limit, a ratio of 1.32 against a price ratio of 9.2 between the dearest and cheapest hours, which is why the plan sits on its limits. The flexibility is bought with storage. A 60 t tank starting at 24 t, set before the day is restarted, saves another $220 and a 15 t tank starting at 12 t costs $158 more, while a ramp limit of 0.1 kA/m^2 per minute saves $40 and a minimum load of 2.0 kA/m^2 saves $164. A two-hour spike of $250/MWh at 17:00 adds $1 900 to the scheduled day and $3 235 to the constant one. The last minutes of the day are shown in Figure 5.3.

> **TRY IT IN THE APP** **8 · Load Following on the Price**
>
> Load scenario 8 and press Run on the Plant view. Watch the current against the price bars: it runs at the rectifier's 7.0 kA/m^2 from 12:00 to 15:00 and at the 3.0 kA/m^2 minimum through both price peaks. The tank reaches the scheduler's ceiling of 26.5 t by 5:00, which is what stops the plan running harder in the cheap hours.

5.6.6 The Graded Day

The challenge runs case 8's day with three upsets, brine at 290 g/L from 6:00, a compressor trip at 14:00 for 15 min, and a $250/MWh spike at 17:00 for two hours. The target asks for at most $11 500 of electricity, at least 71.5 t of NaOH at 32 ± 0.5 %, an anolyte never below 190 g/L, an efficiency never below 94 %, ΔP always inside the band, no trip and no stockout. The cost ceiling

Table 5.7 Challenge Configurations Over the 24 h Day

Configuration	On spec (t)	Off (t)	Cost ($)	ΔP (mbar)	Fails on
shipped[a]	9.8	33.0	4 880	19.9–35.4	trip, ΔP, short, dry
suggested[b]	72.3	0.0	10 908	26.4–39.0	passes
constant, trims, FF	73.0	0.0	13 853	28.5–38.7	cost
sched., FF, ratios	10.8	61.4	10 868	26.5–38.9	short, η
sched., trims, no FF	42.8	0.0	4 288	19.98–35.4	trip, ΔP, short, dry

[a] constant 5.3 kA/m^2, ratio-only feeds, feedforward (FF) off.
[b] ratio plus trim on both feeds, scheduler on, feedforward on.
Sched.: scheduler. Short: less than 71.5 t on specification.

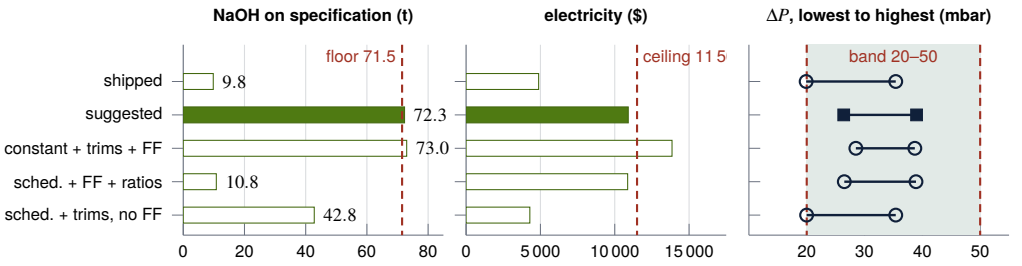


Figure 5.4 Table 5.7 as bars and ranges, digit for digit: the NaOH on specification against the 71.5 t floor, the electricity cost against the $11 500 ceiling, and the lowest to highest true ΔP against the 20 to 50 mbar band. The rows are the table's, and the filled bar and squares mark the one configuration that passes. Notice that the two cheapest days are the two that trip, and that the constant current fails on cost, the ratio-only feeds on tonnage, and the day without the feedforward on ΔP.

is the suggested configuration's cost plus 5.4 %, and the tonnage floor its tonnage less 1.0 %, so the suggested configuration passes with margins of $592 and 0.76 t. Changing a model parameter or a disturbance voids an attempt, so a larger tank, which case 8 prices, cannot be bought here. Table 5.7 compares the measured configurations, and Figure 5.4 draws three of its columns against the targets.

As shipped the caustic leaves its specification at 3:12 and falls to 30.65 %, the anolyte falls to 191.3 g/L, the interlock opens the rectifier 25 s after the compressor stops, and the tank runs dry for 107 min from 22:13, so of 42.5 t made only 9.8 t reach the tank on specification. The suggested configuration holds every limit, with 72.3 t on specification for $10 908, the anolyte never below 207.7 g/L, the efficiency never below 94.50 %, ΔP between 26.4 and 39.0 mbar through a compressor trip at the full 7.0 kA/m^2, and the tank between 21.5 and 26.7 t. Leaving out any one element fails a different line of the scorecard. A constant current with the trims and the feedforward is safe and on specification but costs $13 853. The scheduler and the feedforward on ratio-only feeds cost $10 868 but put 61.4 t off specification with the caustic down to 30.60 % and the efficiency down to 93.998 %, just under its floor. The trims and the scheduler without the feedforward trip 17 s after the compressor stops and run the tank dry for 109 min.

5.7 Technology in Practice

What Measures It

Figure 5.5 draws the loops of Section 5.4 with their devices. The two strengths are read on the liquids leaving the cells, the anolyte by a densitometer and the caustic by conductivity. An electrodeless conductivity cell induces a current in the liquid with one toroidal coil and measures it with a second, a voltage in proportion to the conductivity, and such cells are preferred wherever they can be used for

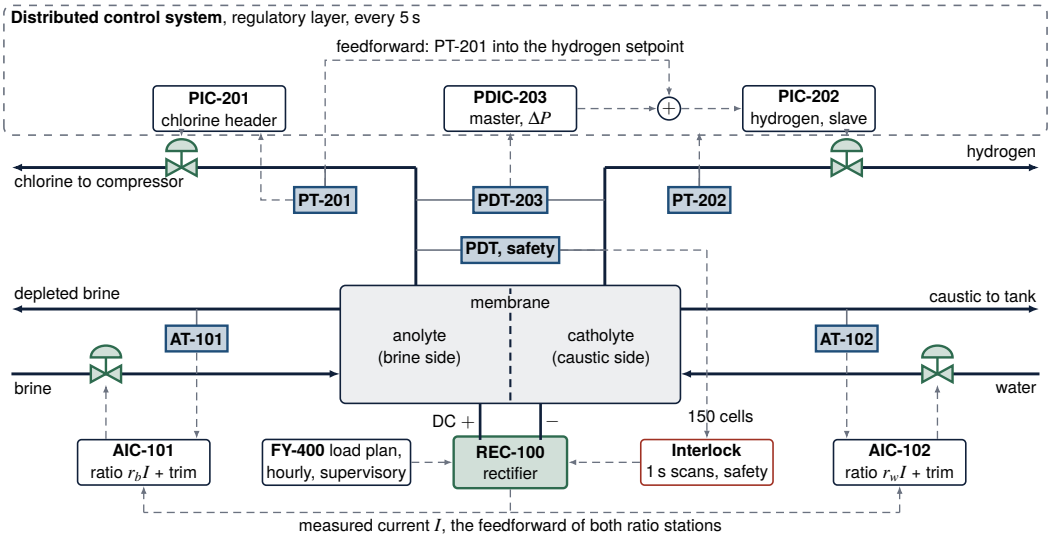


Figure 5.5 The loops of the electrolyzer with their hardware. Lettered boxes are sensing devices: the densitometer (AT-101) on the depleted brine, the conductivity analyzer (AT-102) on the caustic, the two header transmitters (PT), the difference transmitter of the loop (PDT-203) and the interlock's own transmitter (PDT, safety). Valve symbols and the rectifier are final elements, dashed arrows are signals. Notice that the measured current enters both ratio stations before any analyzer has seen a change, that PT-201 enters the hydrogen setpoint in the same way, and that the interlock reaches the rectifier by a path of its own. The temperature loop, the tank gauge and the cell-voltage monitor are left out. Not to scale, and not a piping diagram.

their ruggedness and near immunity to fouling [18]. The gas side, the lesson of Section 5.5, is read by difference transmitters, one for the loop and one for the interlock, of the kind shown in Figure 5.6.

> **TECHNOLOGY Sensor: A Differential Pressure Transmitter**
>
> A differential pressure transmitter has two ports, high and low, and a diaphragm between them that flexes with any difference of pressure. It ignores the pressure common to both ports and sends a standard signal, such as 4 to 20 mA or a digital code, for the difference alone. Where the process fluid is corrosive, isolating diaphragms and a filled capillary, a chemical seal, keep it out of the instrument, and on a gas service a bleed fitting lets condensed liquid out. An impulse line that plugs makes the transmitter respond too slowly, or not at all, so its trend turns sluggish or flat while the process moves [18]. The model's PDT-203 carries 0.1 mbar of noise and the interlock's own transmitter 0.2 mbar, and neither ever plugs.

What Moves It

The rectifier moves everything at once: the chapter's REC-100 sets the current, and Faraday's law turns it into chlorine, hydrogen and caustic. The design point matches a typical bipolar membrane plant of a 2014 European reference document, 2.70 m^2 membranes at 6.0 kA/m^2 and 16.2 kA per electrolyzer [19]. The brine and water flows follow their ratio stations as first-order lags of 20 s, and the two header valves follow their controllers as lags of 3 s.

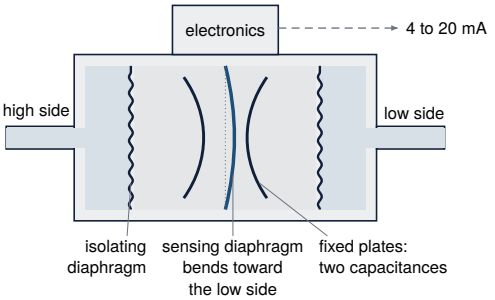


Figure 5.6 A differential pressure transmitter, the device behind PDT-203 and the interlock's transmitter. Notice that the sensing diaphragm responds to the difference between its two sides and ignores the pressure common to both [18].

> **TECHNOLOGY** **Final Element: The Rectifier**
>
> A cell room needs huge quantities of direct current, usually taken from a high-voltage alternating supply. Step-down transformers lower the voltage, silicon diode or thyristor rectifiers convert it to direct current, and busbars carry it to the cells. In 2010 a rectifier and transformer unit had an efficiency between about 94 percent (older units) and 98 percent, and the units are cooled by air or by water circuits [19]. A controlled rectifier sets its output by timing the trigger pulses of its silicon-controlled rectifiers against the alternating cycle: the earlier each one fires, the longer it passes current [18]. The model's REC-100 knows its current exactly, ramps at 0.03 kA/m^2 per minute, and after a trip stays at zero until the interlock is reset.

Where the Controller Runs

A plant runs such loops in a distributed control system, in which a supervisory level sends set points to local controllers, loops are sometimes nested, and cycle times range from milliseconds to minutes [20]. The app executes its six PI loops every 5 s, inside that range. The ratio stations and the pressure cascade with its feedforward belong to the regulatory layer, the load scheduler is supervisory and writes the rectifier's target at every hour, and the interlock scans its own transmitter once a second, apart from both.

> **IN PRACTICE** **A Trip With Its Own Transmitter**
>
> When a mercury cell room is converted to membranes, the main concern is gas pressure control: the membrane needs a steady differential pressure of hydrogen over chlorine, so a differential pressure controller is added. Behind it a chlorine absorption unit is sized to take the full cell-room production in an emergency [19]. A safety instrumented system reads its own transmitters and decides in its own logic solver, apart from the regulatory controls, and a plant built for automatic shutdown will probably shut down more often than it needs to [18]. IEC 61511-1 sets its requirements from specification to maintenance [21]. The chapter's interlock reads its own transmitter and waits for two scans.

What Is Modernizing It

Three developments bear on this cell room. Oxygen-depolarized cathodes reduce oxygen to hydroxide instead of making hydrogen, which lowers the cell voltage by about 1 V at 4 kA/m^2 and the electricity by about 30 %, and the first industrial installation went into operation in 2011 [19]. Plants already run at varying current densities to follow product demand and the electricity price [19], and a 2023 study used a digital model of a cell room to shift its load on the day-ahead and balancing markets, finding that the flexibility depends largely on intermediate storage or on downstream processes [22], as the tank of case 8 shows. And bipolar electrolyzers make faulty cells easier to find by monitoring every cell voltage [19], the job of EI-500.

5.8 Limitations

One lumped cell stands for all 150, and the voltage, efficiency, water transport, oxygen and hardness correlations are illustrative fits through one design point rather than a vendor's data. The damage law is a threshold and a linear exposure that knows nothing of the individual impurities [6]. The brine circuit stops at the cells, with no acid dosing, chlorate, dechlorination or resaturation, and the gases leave for consumers that never limit the plant.

The analyzers are sampled, delayed and noisy but never biased, and the scheduler knows the day-ahead price exactly. The interlock band of 20 to 50 mbar and its two-scan delay are teaching values. The scheduler plans on hourly boundaries with one lumped tank and a fixed customer draw, where a real plant would also schedule its chlorine consumers [10]. The heater's steam is never weighed against the electricity it saves.

OPEN CHALLENGE **Caustic at the Strength Customers Buy**

A membrane cell makes caustic of up to about 35 weight percent, a limit set by the water each sodium ion carries through the membrane, close to four molecules, and hydroxide leaking back costs about five percent of the charge [2]. Membranes that would make the commercial 50 percent directly were abandoned around 2000 for technical problems, and their higher cell voltage made them pay only where steam is dear and electricity cheap [19]. Cutting the back-migration of hydroxide to raise the current efficiency remains a target [2]. Progress would be a membrane that keeps its efficiency in stronger caustic, moving the knee that case 3 steps into.

5.9 Conclusion

A membrane chlor-alkali electrolyzer is a plant whose throughput is a current, and this simulator shows what follows from that at each layer. Feeds tied to the current hold the anolyte within 0.28 g/L and the caustic within 0.022 % through two load steps, feeds left in MANUAL send 81.0 t of a day's 86.8 t off specification, and each ratio needs its trim because a station 1.8 % wrong or a brine 20 g/L weak leaves an offset no feedforward can see. On the gas side a chlorine header rising 1.110 mbar/s takes the margin from a feedback-only hydrogen loop in 20 s, against the 21.5 s of the closed-form estimate, and the rectifier trips 22 s after the compressor stops, while the chlorine pressure feedforward holds the difference above 27.4 mbar. The two headers' fastest rise rates stand in a ratio of 1.207 at every current. Hardness costs 75.4 mV and $534 a day that no controller recovers, and the scheduler makes the day's caustic for $9 008 against $10 617 at a constant current, limited mainly by its tank. The model is one lumped cell with illustrative correlations and teaching limits. A fuller model would add stack gradients and individual membranes, the brine's acid dosing and chlorate, a limited chlorine outlet, analyzer bias and an uncertain price. The application needs only a browser, and its lesson is that a measured cause, fed forward, does in time what no feedback can.

KEY POINTS

- In an electrolyzer the current is the production rate, so a feed that is not tied to it drifts whenever the load moves.
- Feeds tied to the current hold both strengths through two load steps, and each ratio still needs its analyzer trim.
- A chlorine header rising 1.110 mbar/s takes the margin from a feedback-only hydrogen loop in 20 s, while the chlorine pressure feedforward holds the difference above 27.4 mbar.
- Hardness costs 75.4 mV and $534 a day that no controller recovers, and the scheduler makes the day's caustic for $9 008 against $10 617 at a constant current, limited mainly by its tank.

Where else this applies. Volume 3, Chapter 4 trims an air-to-fuel ratio on an oxygen analyzer in the same way, and Volume 9, Chapter 11 schedules its load on the electricity price.

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5.10 Exercises

5.1 Concept check · 2 min

In case 2 both feeds are set to Ratio only before Run, and the load is turned down from 6.0 to 4.0 kA/m^2 at 2:00. The stations send 2.15 m^3/h of brine and 0.251 m^3/h of water per kA, where the design point needs 2.189 and 0.239. What does the anolyte do?

(a) It settles about 2 g/L below its setpoint and stays there, since nothing corrects the station's own error
(b) It returns to 210 g/L after the turndown, since the ratio moves the brine in proportion to the current
(c) It keeps falling while the load stays low, since the anolyte integrates the brine shortfall
(d) It swings about 5 g/L after the turndown and then recovers, as the analyzer catches up

5.2 Concept check · 2 min

In case 5 the chlorine compressor stops and the chlorine header rises about 1.1 mbar/s. With the chlorine pressure feedforward off, ten times the shipped PDIC-203 gain with half its integral time holds the difference for about two minutes and then trips the rectifier, while the shipped tuning with the feedforward on never leaves 27.4 to 38.9 mbar. Why does the feedforward succeed?

(a) It doubles the master's gain while the chlorine header rises, so the hydrogen reacts faster
(b) The hydrogen setpoint follows the measured chlorine pressure, so the rise never becomes an error
(c) It throttles the chlorine suction valve less, so the chlorine header rises more slowly
(d) It widens the interlock band while the compressor is stopped, so a lower difference is allowed

5.3 Concept check · 1 min

In case 6 a hardness breakthrough raises the cell voltage by 75.4 mV for the rest of the membrane's life. Why does the cell-voltage monitor EI-500 raise no alarm?

(a) The rise takes three hours, slower than the monitor's two-scan delay can follow
(b) The monitor watches only cell 87, the one cell the model allows to fail
(c) It compares each cell with the stack mean, and hardness raises every cell alike
(d) The trims return the anolyte and caustic to setpoint, which takes the rise back out

5.4 Theory and calculation · 6 min

The electrolyzer has 150 cells of 2.7 m^2 in series at 6.0 kA/m^2, with $F = 96\,485.332\,\mathrm{C/mol}$, $\eta = 0.950$ and $\eta_{Cl} = 0.988$. Molar masses are 39.997 (NaOH), 70.906 (Cl_2) and 2.016 g/mol (H_2). Give each answer to three significant figures.

(a) Find the moles of electrons through the stack per second and the NaOH made in t/h. *Checkpoint:* 25.2 mol/s and 3.45 t/h.

(b) Find the chlorine in t/h, the hydrogen in kg/h and the oxygen as a percentage by volume of the dry chlorine. *Checkpoint:* 3.18 t/h, 91.4 kg/h and 0.604 %.

(c) The cell voltage is 3.103 V. Find the DC power and the specific energy in kWh per tonne of NaOH. *Checkpoint:* 7.54 MW and 2190 kWh/t.

5.5 Theory and calculation · 7 min

With the feedforward off and a perfect slave, the PDIC-203 error after a compressor trip follows Equation (5.17). At 6.0 kA/m^2 the chlorine header rises at $r_{Cl} = 1.110\,\mathrm{mbar/s}$, the setpoint is 35 mbar and the interlock acts at 20 mbar. Give times to 0.1 s.

(a) For the shipped $K_c = 0.5$ and $\tau_I = 1\,\mathrm{min}$, find τ_e, the error the master would settle at, and the time t_m until the margin is gone. *Checkpoint:* 180 s, 133.2 mbar and 21.5 s.

(b) Find t_m for $K_c = 2$ and $\tau_I = 1\,\text{min}$, and the smallest K_c/τ_I for which the loop holds on feedback alone. *Checkpoint:* 53.9 s, and $4.44\,\text{min}^{-1}$.

(c) The rise scales with the current. Find r_{Cl} and t_m at the shipped tuning when the compressor trips at $7.0\,\text{kA/m}^2$, and say why the engine's crossing, 15 s after the rise begins, comes earlier. *Checkpoint:* 1.295 mbar/s and 18.3 s.

5.6 Theory and calculation · 6 min

Use Equation (5.16) with $R = 8.314\,\text{J/(mol K)}$, $T_g = 320\,\text{K}$, 150 cells, $I = 16.2\,\text{kA}$, $\eta_{Cl} = 0.988$, $V_{Cl} = 300\,\text{m}^3$ and $V_H = 250\,\text{m}^3$. Give rates to 0.001 mbar/s.

(a) Find the chlorine header's rise with the compressor stopped and the fastest rise of the hydrogen header, with its valve shut. *Checkpoint:* 1.110 mbar/s and 1.340 mbar/s.

(b) Find their ratio, and the largest hydrogen header volume that can still keep pace with the chlorine. *Checkpoint:* 1.207, and $301.8\,\text{m}^3$.

(c) Find both rates and their ratio at $3.0\,\text{kA/m}^2$. Then estimate how long the chlorine header takes at $6.0\,\text{kA/m}^2$ to climb from its 150 mbar(g) setpoint to the seal pot at 300 mbar(g), and compare with the 137 s measured after the compressor stops. *Checkpoint:* 0.555 mbar/s, 0.670 mbar/s, 1.207, and about 135 s.

5.7 App challenge · 8 min

Load case 1, Manual feeds: the electrolyzer starts at $5.0\,\text{kA/m}^2$ with the Anolyte loop and the Catholyte loop in Manual, and the current is raised to $6.5\,\text{kA/m}^2$ at 1:00. Keep the default seed, run at 300x and let the run pause at 24:00. Read the scorecard tiles NaOH made, Off-spec caustic, Anolyte lowest and Efficiency lowest.

(a) Report the four tiles for the day as shipped. *Checkpoint:* 86.8 t made with 5.6 t on specification, 81.0 t off, anolyte at least 177.9 g/L, efficiency at least 93.22 %.

(b) Press Reset, set the Anolyte loop and the Catholyte loop to Auto on the AIC-101 and AIC-102 cards before pressing Run, and run the day again. Report the same tiles. *Checkpoint:* 88.4 t made, all on specification, anolyte at least 209.7 g/L, efficiency at least 94.90 %.

(c) Both days run the same current. Explain why the second makes 1.6 t more caustic. *Checkpoint:* The efficiency stays near 94.90 %.

5.8 App challenge · 8 min

Load case 5, Chlorine compressor trip, which opens with Chlorine pressure feedforward Off on the PDIC-203 card. The compressor stops at 1:00 and restarts at 1:30. Keep the default seed and run at 60x. Read the scorecard tiles ΔP worst and Trips · stockout.

(a) Run as shipped. The run pauses when the interlock opens the rectifier. Report the two tiles. *Checkpoint:* 19.8 to 35.3 mbar, 1 trip.

(b) Press Reset, set the feedforward On before pressing Run, run to 1:40 and export the CSV file, whose time column is in hours. Report the ΔP worst tile and the chlorine sent to the emergency absorption, column `cl2_absorbed_t`, in the last row, within 0.01 t. *Checkpoint:* 27.4 to 38.9 mbar, no trip, 1.48 t.

(c) Press Reset, set the feedforward back to Off, the ΔP gain to 5.00 and the ΔP integral time to 0.5 min, and run until the run pauses. Report the two tiles, and say why this tuning holds the ramp and still trips. *Checkpoint:* 19.3 to 40.0 mbar, 1 trip.

5.9 App challenge · 9 min

Load the challenge, a day on the price, which starts at a constant $5.3\,\text{kA/m}^2$ on ratio-only feeds with the chlorine pressure feedforward Off. Keep the default seed and run each day to 24:00 at 1200x,

pressing Run again if the run pauses at a trip. Read the tiles Electricity, NaOH made, ΔP worst, Trips · stockout and Day target.

(a) Run as shipped. Which parts of the target fail? *Checkpoint:* \$4880, 9.8 t on specification of 42.5 t, ΔP 19.9 to 35.4 mbar, 1 trip, 107 min of stockout: not met.

(b) Press Reset, set Brine feed strategy and Water addition strategy to Ratio + trim, the Load scheduler On and the Chlorine pressure feedforward On, all before pressing Run, and run the day. *Checkpoint:* \$10 908, 72.3 t on specification, ΔP 26.4 to 39.0 mbar, no trip or stockout: met.

(c) Press Reset, set only the feedforward back to Off and run the day. Which parts fail, and why does the ΔP worst tile turn red although its lowest value reads 20.0 mbar? *Checkpoint:* \$4288, 42.8 t on specification, ΔP 20.0 to 35.4 mbar, 1 trip, 109 min of stockout.

5.10 Application area · 4 min

In case 7 the brine arrives at 45 °C instead of 65 from 1:00. With the heater held at 0.09 MW the cells settle near 80.7 °C and draw 0.199 MW more electricity for the same caustic. With TIC-103 in Auto the heater rises to 0.87 MW and holds 88 °C. The sunny profile averages \$68.38/MWh.

(a) What does the extra electricity cost a day, and at what price of heat, in dollars per MWh, would the steam cost the same? *Checkpoint:* About \$327 a day, and about \$17.4/MWh of heat.

(b) Give one reason from the chapter to hold 88 °C even when the steam costs more than that.

5.11 Application area · 4 min

In case 6, three hours of 500 ppb hardness leave the membranes with a lasting cost of \$534 a day, priced at the sunny profile's average. The membranes are 18 months old. A plant manager asks what one breakthrough costs if the membranes are replaced at four years of age, and whether the cell-voltage monitor will warn of the next one. Answer both, and recommend how to catch a breakthrough.

5.12 Review the agent · 5 min

An AI assistant is asked how to keep case 5 from tripping and writes: "A larger hydrogen header buffers its pressure. Raise V_H from 250 to 500 m^3 in the Show Model dialog. Twice the gas volume halves how fast the difference can change after the trip, so the interlock has twice the time, with or without the feedforward." Find the flaw, and say how you would check the claim.