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Flexible and economical operation of chlor-alkali process with subsequent polyvinyl chloride production

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Abstract

Demand response (DR) can compensate for imbalances in variable renewable energy supplies. This possibility is particularly interesting for electrochemical processes, due to their high energy intensity. To determine the technical feasibility and economic viability of DR, we chose the chlor-alkali process with subsequent polyvinyl chloride production, including intermediate storage for ethylene dichloride. We estimate the maximum possible cost savings of implementing load flexibility measures. A process model is set up to determine the system characteristic. Subsequent optimizations result in the facility's best possible dispatch depending on additional and minimum power load, storage volume, and cost of a load change. Real plant data are used to specify model parameters and validate the system characteristic and the plant dispatch. An economic evaluation reveals the economic advantages of efficiency and flexibility. The approach can be used to analyze the DR potential of other chlorine value chains or facilities with high electricity demand in general.

KEYWORDS
chemical industry, chlor-alkali process, demand response, economic analysis, optimization

1 | INTRODUCTION

As Kondziella and Bruckner[1] noted that “Growing shares of variable renewable energy sources (VRE) in future energy systems necessitate higher levels of flexibility due to spatial and temporal imbalances between supply and demand.” In these energy systems, demand response (DR) of especially 24/7 power requirements can contribute to reducing VRE curtailment, the use of fossil power plants, as well as necessary storage capacity.

Basic material chemistry has the highest demand for electricity in the German manufacturing sector, around 160 PJ/a.[2,3] Based on prior analyses, electrochemical processes are particularly suitable for DR.[4,5] The chlor-alkali electrolysis (CAE) takes a key role within these processes due to the high installed capacity of 1.48 GW in Germany, accounting for 2% of German electricity consumption.[6] Assuming a plant utilization rate of 0.9, an electricity demand of 42 PJ can be estimated.

For the production of organic and inorganic chemicals, both the direct and indirect use of chlorine and sodium hydroxide is possible.[7] The synthesis of both substances is based on the electrolysis of sodium chloride or alternatively of potassium chloride. The CAE is the most important process for the production of chlorine and sodium hydroxide.[8,9] In 2019, a total of 9.416×10^6 tonnes of chlorine was produced in Europe.[10] Assuming a specific electricity consumption of 2.58 MWh to produce 1 tonne of chlorine,[11] the European electricity consumption can be estimated with 87 PJ. Compared with the above-mentioned value, the economic relevance of the German market can be pointed out.

In the last decade, several authors[5,12,13] estimated the DR potential of chlor-alkali processes in Germany. Klaucke et al.[14] reviewed these works and determined the DR potential for chlor-alkali processes, with a maximum of around 590 MW for Germany and 2 GW in the European Union. The recent study of Ausfelder et al.[6] estimates 420 MW as a maximum technical potential for flexibility of the German chlor-alkali processes.

The dispatch and the optimum scheduling or bidding strategies of CAE are addressed in several papers. Babu and Ashok[15] identify DR as a "viable option for industries to reduce their electricity cost." They formulate a mixed-integer nonlinear model to minimize electricity cost and perform a case study for a chlor-alkali process. The daily electricity consumption of the overall plant is about 400 MWh and is modeled with quadratic fits based on operating data of the subprocesses. The optimization under time-dependent tariffs (normal, peak, and off-peak) result in a saving of about 4% in electricity costs. Wang et al.[16] describe a model for a combination of a chlor-alkali process and storage (hydrogen and chlorine) with an energy supply based on renewables (wind and photovoltaic) and a fuel cell. The operation of the grid-connected plant is optimized. Savings in electricity costs are around 25%. Chen et al.[17] link CAE with a fuel cell and other technologies to create a hybrid energy system. The hydrogen from the electrolysis is used as feedstock for the fuel cell. The authors improve the operation and control strategies of the system. Bree et al.[18,19] and Roh et al.[20,21] analyze the DR operation of switchable CAE. The authors use chlorine as intermediate storage and focus their modeling on the cells. Roh et al.[21] investigated the impact of a static electrolyzer lifetime reduction in the capital investment calculation on plant cost and sizing. Otashu and Baldea[22] develop a model for CAE using membrane technology to study the ability for DR of such processes. Again, the authors focus on modeling the electrolysis cells and use chlorine as a storage medium. With their dynamic model of the cell, temperatures and concentrations are predictable. Based on the prior findings, Otashu et al.[23] show the benefits of a cooperative DR management for the case study of a chlor-alkali process and Simkoff and Baldea[24] apply Hammerstein–Wiener models to represent the dynamic of the chlor-alkali process. Richstein and Hosseinioun[25] present a numerical model of the chlor-alkali process. Ethylene dichloride (EDC) is used for the intermediate storage. Their analysis focuses on the impact of network tariffs and regulation on flexibility provision in electricity markets. The linear model represents a storage and the electrolysis with constant specific electricity intensity. Baetens et al.[26] investigate the chlor-alkali process for providing frequency containment reserve and optimize the flexible operation with regard to the day-ahead market. Their process model considers the electrolysis and a chlorine storage.

The review of the scientific literature focusing on CAE reveals that some key points concerning the technical feasibility and economic viability of DR potentials, like the influence of minimum loads, storability, the part-load characteristic, or especially load change costs, are not sufficiently considered. However, this is an essential aspect in particular for electrochemical processes, due to process control and downstream value chain implications. In consequence, a process-wide and detailed analysis of the approach using EDC as a substance to be stored is presented here. This includes a discussion about intermediate storage and process safety, the estimation of the DR potential, and a quantitative analysis of the economic advantages of our proposal. The consideration of the part-load performance, subsequent process units, the power demand of the auxiliaries, and a comprehensive sensitivity analysis on the cost of load change and minimal power load (apart from storage volume and additional capacity) are novelties, which show a significant influence on the results.

Based on the quantitative analysis of Klaucke et al.[11] the chlorine value chain of polyvinyl chloride (PVC) via EDC is of greatest importance for flexibilization. In consequence, this process is investigated here in detail. The entire value chain up to the final product is considered. The study uses real plant data for an overall facility, partly based on detailed modeling already carried out and validated.[27,28] Flexibility and storage capability may be identified for the production of PVC. EDC as an intermediate product can be stored in liquid phase under ambient conditions.[29] Following the idea of DR, the demand for electrolysis from power grid is decoupled from the production of PVC. Depending on storage capacity and part-load capability, the demand may vary between $100\%-x$ at part-load operation and $100\%+y$ with overcapacity installed.

Our goal is to develop a mathematical, physical model of the CAE, which includes downstream process steps. From this model, validated with real plant data, the feasibility of a load management as well as the optimum control strategy for a more flexible operation can be determined. In a second step, the determined technical potentials are evaluated economically. With data from the German electricity market, an economically optimized marketing strategy is being developed. As a result, the maximum possible cost savings of implementing load flexibility measures are determined. For a comprehensive economic analysis, these savings must be compared with the additional investment costs for providing flexibility. According to consultations with the partners from industry, investment cost data published to date are associated with considerable uncertainties. Transferability is not necessarily assured (e.g., for alkaline water electrolysis) or a real-economic reference is missing. Therefore, this study focuses only on examining the savings in the relevant operational costs. Ultimately, the present estimate must already be an indicator of economic viability if the savings achieved are of a magnitude that justifies further consideration of the technology.

The article consists of the following four sections. The next section collects fundamental remarks on DR in chemical industry and describes the process with the conversion steps from sodium chloride to PVC. The two main parts, process and dispatch model, consist of the methodology and model descriptions and collect the results of the analyses. The source code of the models is available via zenodo.[30] Conclusions are given in the last section.

2 | PROCESS

The flexibility of a 24/7 facility typically running at full capacity is strongly connected to the ability to store intermediates. To ensure a constant product feed over time and a flexible operation regarding electricity demand, an intermediate storage and an additional capacity is integrated with the system. The storage decouples product feed and electricity demand. The higher the capacity of the storage, the longer the electricity demand can be reduced. An additional capacity enables electricity demand increasing.

Due to its high toxicity, the storing of chlorine should be avoided.[31] In consequence, the fluctuation of the mass flow should be passed on to the subsequent processes. The more components of the overall production process chain have to adopt the flexible mode of operation, the greater the amount of technical restrictions. Furthermore, up to the point of flexibilization, all components must have overcapacity with related investment costs. The associated component should, therefore, be located as close as possible to the electricity supply. The assessment of the flexibility potential of electrochemical processes, including technical restrictions and process safety requirements, is further described by Hoffmann et al.[32]

EDC is the substance within the investigated chlorine value chains that shows the highest potential for flexibilization and fulfills the process safety requirements.[11] Therefore, it is considered as the medium for intermediate storage in this work.

2.1 | Chlor-alkali electrolysis

Mercury cell, diaphragm, and membrane technologies are available for CAE.[8,31] Since the mercury cell technology has already been phased out in Europe and the use of diaphragm technology is also on the decline,[33] we focus here on the membrane cell process.

The process uses electricity from the power grid. For the operation of CAE, direct current is required (at a voltage of $3\,\mathrm{V/cell}$). Aqueous sodium chloride solution is electrolyzed to generate chlorine, sodium hydroxide, and hydrogen. Assuming $1000\,\mathrm{kg}$ of chlorine as necessary product, the overall reaction of the electrolysis implies a corresponding $1128.3\,\mathrm{kg}$ of sodium hydroxide and $316.3\,\mathrm{m}^3$ of hydrogen as stoichiometric by-products.

$$2\mathrm{NaCl}+2\mathrm{H_2O}\rightarrow 2\mathrm{NaOH}+\mathrm{Cl_2}+\mathrm{H_2} \tag{1}$$

Chlorine and hydrogen are highly reactive. They need to be separated during their formation to avoid explosive reactions. All chlorine manufacturing processes are based on this paradigm. The membrane process uses a $\mathrm{Na^+}$-permeable ion-exchange membrane, see Fig. 1 in Weigert et al.[27] Anions like $\mathrm{OH^-}$ and $\mathrm{Cl^-}$ are only able to pass in small quantities. Consequently, in addition, the chloride contamination of NaOH is kept quite low. The addition of hydrochloric acid to the anolyte compartment ensures the chlorine quality (low oxygen content, less by-products). For its synthesis, chlorine and hydrogen are taken from the product streams. O'Brien et al.[7] give detailed information about the thermodynamics of the CAE.

The CAE is followed by chlorine treatment (CT), which includes cooling, drying, and mist elimination, and compression (CC). Here, a multistage turbocompressor increases the pressure of the dried and filtered chlorine. The resulting heat of compression is dissipated in intermediate coolers and an after-cooler.

2.2 | Ethylene dichloride process

Two alternative methods produce EDC ($\mathrm{C_2H_4Cl_2}$).

Direct chlorination (DC) uses a catalytic addition reaction of chlorine and ethene.

$$\mathrm{C_2H_4}+\mathrm{Cl_2}\rightarrow \mathrm{C_2H_4Cl_2} \tag{2}$$

The exothermic reaction proceeds at a slight overpressure on an iron(III) chloride/sodium chloride catalyst.

Oxychlorination (OXC) uses ethene, hydrogen chloride, and oxygen.

$$2\mathrm{C_2H_4}+4\mathrm{HCl}+\mathrm{O_2}\rightarrow 2\mathrm{C_2H_4Cl_2}+2\mathrm{H_2O} \tag{3}$$

The exothermic reaction is initiated with a copper(II) salt catalyst.[34] In contrast to DC, OXC usually cannot operate with sufficient flexibility. To handle hydrogen chloride resulting from the subsequent cracking, see Equation (4), commonly both processes are used in parallel.

Resulting EDC from DC or oxychlorination can be stored. This storage leads to increased availability and flexibility of the process. The component links EDC production and subsequent processes. Both parts of the process are time-independent.

During thermal cracking (CR), EDC decomposes to vinyl chloride monomer (VCM; $\mathrm{C_2H_3Cl}$) and hydrogen chloride. The reaction is endothermic.

$$\mathrm{C_2H_4Cl_2}\rightarrow \mathrm{C_2H_3Cl}+\mathrm{HCl} \tag{4}$$

Hydrogen from the CAE or natural gas is burned to provide the necessary thermal energy for the endothermic reaction. Most of the hydrogen chloride is used for oxychlorination. In the facility being considered, a side stream of hydrogen chloride leaves this process for the synthesis of other products. The last step to produce PVC $(\mathrm{C_2H_3Cl})_n$ is chain polymerization of the VCM.

3 | PROCESS MODEL

With the information from the process description, a process model is set up. It respects all chemical reactions as well as substance and mandatory energy balances, which allows the chemical and thermodynamic modeling of the process. Including necessary assumptions, simplifications, and parameters, a simulation tool is used to generate the results of the calculation. For this study, the model is implemented with the software Engineering Equation Solver (EES).[35] The access to thermodynamic property libraries is helpful to reduce the model complexity. As a result of EES, the system characteristic of the process is determined. In the present case, it is the production of EDC as a function of electricity demand.

A flow diagram of the simulated CAE and PVC process is shown in Figure 1. All components are grouped to functional units. Since cracker (CR) and polymerization (PM) require constant reactant flows, the focus

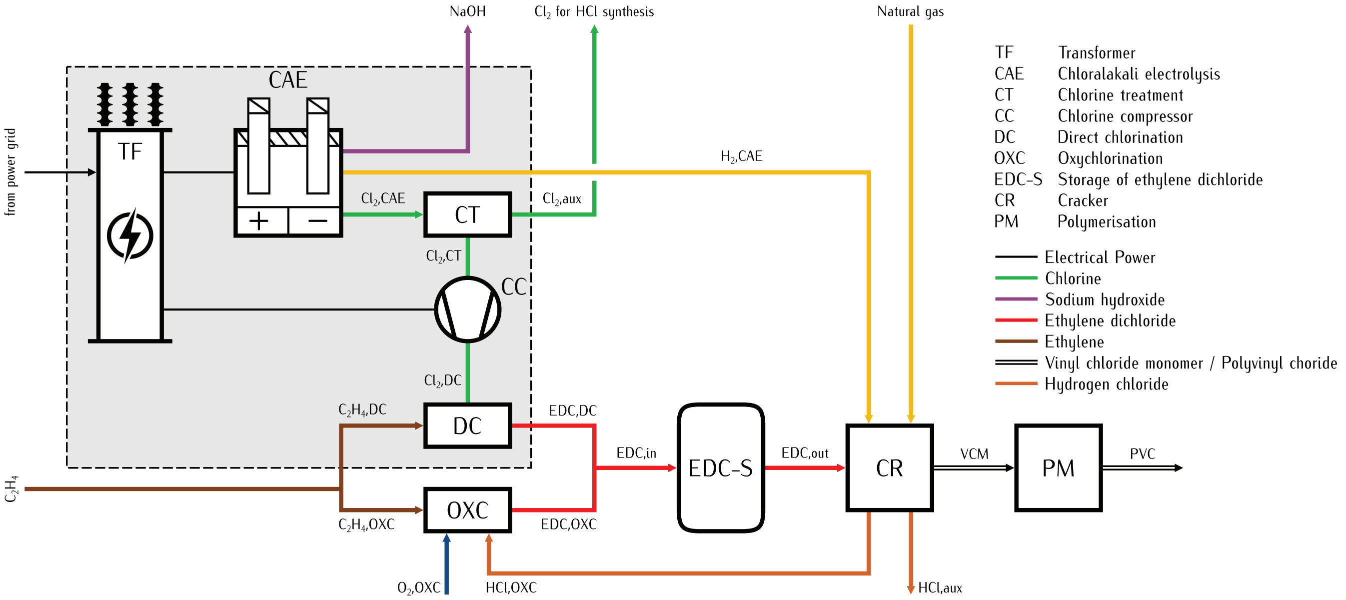

FIGURE 1 Simplified flow diagram of the simulated chlor-alkali process

is on modeling the process from transformer to EDC storage. The shown process diagram is based on a provided structure of a real plant.

3.1 | Model

3.1.1 | General equations

For all substances i, the mass flow rate is given by the molar flow rate and the molar mass of the substance.

$$\dot{m}_i = \dot{n}_i \cdot M_i \tag{5}$$

The volumetric flow rate results from the mass flow rate and the density.

$$\dot{V}_i = \frac{\dot{m}_i}{\rho_i} \tag{6}$$

For all gases, the ideal gas law is used to calculate the volumetric flow rate at standard conditions.

$$\dot{V}_i = \frac{\dot{n}_i \cdot R \cdot T_0}{p_0} \tag{7}$$

3.1.2 | Transformer

The amount of power supplied from the grid $\dot{W}_{\mathrm{Grid}}$ is defined as the product of the nominal power $\dot{W}_{\mathrm{Grid,nom}}$ and the load λ

$$\dot{W}_{\mathrm{Grid}} = \lambda \cdot \dot{W}_{\mathrm{Grid,nom}} \tag{8}$$

The values of λ range mathematically between 0 and 1. The minimum load of the EDC reactor system specifies the technically feasible lower bound for the examined system as substantiated below.

In the model, the supplied power is primarily required for the operation of the CAE and CC, whereby conversion losses should be taken into account by a transformer efficiency factor.

$$\dot{W}_{\mathrm{CAE}} + \dot{W}_{\mathrm{CC}} = \eta_{\mathrm{TF}} \cdot \dot{W}_{\mathrm{Grid}} \tag{9}$$

3.1.3 | Chlor-alkali electrolysis

The overall reaction for the electrolysis is given by Equation (1), which means that the molar flow rates of chlorine and hydrogen are equal.

$$\dot{n}_{\mathrm{Cl_2,CAE}} = \dot{n}_{\mathrm{H_2,CAE}} \tag{10}$$

The produced molar flow of chlorine is given by the Faraday equation multiplied by an electrolysis efficiency factor and the number of electrolysis cells.

$$\dot{n}_{\mathrm{Cl_2,CAE}} = \frac{I_{\mathrm{CAE}}}{2 \cdot F} \cdot \eta_{\mathrm{CAE}} \cdot N_{\mathrm{CAE}} \tag{11}$$

The electrolysis cell exhibits a characteristic relationship between current density, current intensity, and voltage, which are derived from experimental data.[27] Deviations are possible due to the use of preliminary results from the source provided by personal contact with the authors.

$$I_{\mathrm{CAE}} = A_{\mathrm{CAE}} \cdot j \tag{12}$$

$$U_{\mathrm{CAE}} = a_{\mathrm{CAE}} \cdot j + b_{\mathrm{CAE}} \tag{13}$$

$$\dot{W}_{\mathrm{CAE}} = I_{\mathrm{CAE}} \cdot U_{\mathrm{CAE}} \cdot N_{\mathrm{CAE}} \tag{14}$$

Concerning the dynamic evaluation of the temperature in the cells, Weigert et al.[27] carried out detailed dynamic modeling for the plant under consideration based on real plant data. The authors show that for a significant load change of 67%, the temperature decreases by approximately 12 K, while small load changes of approximately 5% cause temperature deviations of less than 1 K. Since the focus of our work is to estimate the economic DR potentials of CAE with downstream EDC production, we do not model the temperature inside the electrolysis cells to keep the optimization problem as simple as possible. Furthermore, no mathematical description of the influence of temperature changes on membrane and electrode aging is known so far. Consequently, we model the load change costs possibly caused by thermal and mechanical stresses in a temperature-independent approach.

3.1.4 | Chlorine treatment

In the CT unit, a certain proportion of the chlorine $r_{\mathrm{aux,CT}}$ is provided for HCl synthesis.

$$\dot{n}_{\mathrm{Cl_2,CAE}} = \dot{n}_{\mathrm{Cl_2,CT}} + \dot{n}_{\mathrm{Cl_2,aux}} \tag{15}$$

$$r_{\mathrm{aux,CT}} = \frac{\dot{n}_{\mathrm{Cl_2,aux}}}{\dot{n}_{\mathrm{Cl_2,CAE}}} \tag{16}$$

3.1.5 | Chlorine compressor

From real plant data, the necessary electrical power of the chlorine compression $\dot{W}_{\mathrm{CC}}$ is known. To determine an isentropic efficiency, a four-stage isentropic compression is modeled first. The inlet temperature and pressure are identical to those at the outlet of the CT, while the outlet pressure is determined by the operating pressure of the DC unit.

$$(p,T)_1 = (p,T)_{\mathrm{Cl_2,CT}} \tag{17}$$

$$p_5 = p_{\mathrm{Cl_2,DC}} \tag{18}$$

The pressure at each step j with $1 \leq j \leq 4$ (stage) is calculated from the overall pressure ratio, which is determined by the inlet and outlet pressure.

$$\frac{p_5}{p_1} = \left(r_{p,\mathrm{stage}}\right)^4 \tag{19}$$

$$\frac{p_{j+1}}{p_j} = r_{p,\mathrm{stage}} \tag{20}$$

The isobaric intercooling lowers the inlet temperature of each stage to the inlet temperature of the first compressor stage. Assuming a stage-wise isentropic compression, as described above, the temperatures at the outlet of each stage can be calculated.

$$s\left(T_{j+1}, p_{j+1}\right) = s\left(T_1, p_j\right) \tag{21}$$

The shaft work of the stage-wise isentropic compression is received using the enthalpy differences between the compressor stages based on the temperatures.

$$w_{s,\mathrm{CC}} = \sum_j w_{s,j} = \sum_{j=1}^{4} \left(h\left(T_{j+1}\right) - h(T_1)\right) \tag{22}$$

Values for enthalpies and entropies are calculated from EES based on NASA ideal gas data and NIST-JANAF tables.[36,37] The necessary electrical power for the real compression is calculated with the determined isentropic efficiency $\eta_{s,\mathrm{CC}}$ and the molar flow rate of chlorine from CT.

$$\dot{W}_{\mathrm{CC}} = \frac{\dot{n}_{\mathrm{Cl_2,CC}} \cdot w_{s,\mathrm{CC}}}{\eta_{s,\mathrm{CC}}} \tag{23}$$

$$\dot{n}_{\mathrm{Cl_2,CC}} = \dot{n}_{\mathrm{Cl_2,CT}} \tag{24}$$

3.1.6 | Direct chlorination

The molar flow rate of chlorine is given from Equation (16). The necessary amount of ethene and the resulting EDC are calculated.

$$\left.\begin{array}{r}\dot{n}_{\mathrm{C_2H_4,DC}} = \\ \dot{n}_{\mathrm{EDC,DC}} = \end{array}\right\} \dot{n}_{\mathrm{Cl_2,DC}} \tag{25}$$

$$\dot{n}_{\mathrm{Cl_2,DC}} = \dot{n}_{\mathrm{Cl_2,CT}} \tag{26}$$

In reality, this process step consists of a main reactor and post-reactor to ensure the total amount of chlorine and a maximum of ethene is converted. As a simplification, both unit operations are modeled together.

3.1.7 | Oxychlorination

According to Equation (3), the molar flow rates of ethene, oxygen, water, and EDC in the OXC unit are dependent on the molar flow rate of hydrogen chloride provided from the CR.

$$\left.\begin{array}{r}\dot{n}_{\mathrm{C_2H_4,OXC}} = \\ \dot{n}_{\mathrm{EDC,OXC}} = \\ \dot{n}_{\mathrm{H_2O,OXC}} = \end{array}\right\} \frac{\dot{n}_{\mathrm{HCl,OXC}}}{2} \tag{27}$$

$$\dot{n}_{\mathrm{O_2,OXC}} = \frac{\dot{n}_{\mathrm{HCl,OXC}}}{4} \tag{28}$$

3.1.8 | Storage of ethylene dichloride

The EDC storage is filled by the streams from the DC and the OXC, while the outgoing stream is determined by the constant reactant feed of the CR.

$$\dot{n}_{\mathrm{EDC,in}} = \dot{n}_{\mathrm{EDC,DC}} + \dot{n}_{\mathrm{EDC,OXC}} \tag{29}$$

$$\dot{n}_{\mathrm{EDC,out}} = \dot{n}_{\mathrm{EDC,CR}} \tag{30}$$

The change in storage amount is given by the difference between inlet and outlet streams of the storage of ethylene dichloride (EDC-S).

$$\dot{n}_{\mathrm{EDC,stored}} = \dot{n}_{\mathrm{EDC,in}} - \dot{n}_{\mathrm{EDC,out}} \tag{31}$$

3.1.9 | Cracker

The cracker (CR) group provides the hydrogen chloride stream, which must be known to determine the amount of EDC produced in the OXC unit. The ratio between the outgoing auxiliary hydrogen chloride and the EDC inlet stream $r_{\mathrm{aux,CR}}$ is kept constant.

$$\dot{n}_{\mathrm{EDC,CR}} = \dot{n}_{\mathrm{VCM}} \tag{32}$$

$$\dot{n}_{\mathrm{EDC,CR}} = \dot{n}_{\mathrm{HCl,OXC}} + \dot{n}_{\mathrm{HCl,aux}} \tag{33}$$

$$r_{\mathrm{aux,CR}} = \frac{\dot{n}_{\mathrm{HCl,aux}}}{\dot{n}_{\mathrm{EDC,CR}}} \tag{34}$$

3.2 | Assumptions, simplifications, and parameters

During the development of the EES model, several assumptions are applied, which are briefly summarized here:

- steady-state process,
- process components are grouped into functional units,
- negligible heat losses, and
- mass flow rates of ethene and natural gas inlets are sufficiently flexible.

The process parameters are given in Table 1. For the molar gas constant R and the Faraday constant F, the recommended values of CODATA[38] are used. The values of the molar mass are taken from NIST Database.[39]

TABLE 1 Parameters used in the process model

Parameter	Symbol	Unit	Value
Standard conditions	T_0	°C	0
	p_0	bar	1.01325
Nominal power load	$\dot{W}_{\mathrm{Grid,nom}}$	MW	100
Storage outlet flow rate	$\dot{n}_{\mathrm{EDC,out}}$	mol/s	237.1
Density, EDC	ρ_{EDC}	kg/m^3	1270
Temperature, CT	$T_{\mathrm{Cl_2,CT}}$	°C	30
Pressures	$p_{\mathrm{Cl_2,CT}}$	bar	1.036
	$p_{\mathrm{Cl_2,DC}}$	bar	3.2
Number of CAE cells	N_{CAE}	–	1800
Membrane surface area	A_{CAE}	m^2	2.72
Linear U/I-parameter	a_{CAE}	Vm^2/kA	0.142
	b_{CAE}	V	2.423
Auxiliary stream ratios	$r_{\mathrm{aux,CT}}$	–	0.0333
	$r_{\mathrm{aux,CR}}$	–	0.2
Efficiencies	η_{TF}	–	0.97
	η_{CAE}	–	0.968
	$\eta_{\mathrm{s,CC}}$	–	0.45

Abbreviations: CAE, chlor-alkali electrolysis; CC, chlorine compression; CR, cracker; CT, chlorine treatment; DC, direct chlorination; EDC, ethylene dichloride; TF, transformer.

3.3 | Results

The purpose of the EES model is to examine the dependency of the EDC production on the applied grid load. Therefore, the current EDC production, which is similar to the molar flow rate that enters the storage, is related to the nominal EDC production at full load.

$$\phi = \frac{\dot{n}_{\mathrm{EDC,in}}}{\dot{n}_{\mathrm{EDC,in,nom}}} \tag{35}$$

In Figure 2, the EDC production load is shown as a function of the grid load. It appears that the OXC provides 40% of the overall nominal EDC production. While the EDC generation by OXC is constant as long as the hydrogen chloride supply by the CR is maintained, the EDC production by DC shows a slightly nonlinear dependency on the grid load. This is due to the fact that the electrolysis cells show a decreased specific energy consumption per tonne of chlorine under part-load conditions, see Equations (11) and (13). In detail, all ohmic losses (e.g., resistance of the conducting parts) increase with the current density, $a_{\mathrm{CAE}} \cdot j$ in Equation (13), while the basic reaction voltage, parameter b_{CAE}, stays constant.

Due to this "advantage of efficiency," stack operation during load reduction always takes place in parallel. If an additional power capacity is installed, that is, increasing $\dot{W}_{\mathrm{Grid,nom}}$, see Equation (38), the qualitative load characteristic remains the same as seen in Figure 2. However, if the EDC demand of the CR is kept constant, the steady-state operating point with $n_{\mathrm{EDC,in}} = n_{\mathrm{EDC,out}}$ is in this case not at $\phi = \lambda = 1$, but it is shifted to the left. Thus, the steady-state CAE efficiency increases with increasing nominal electrical work rate $\dot{W}_{\mathrm{Grid,nom}}$.

4 | DISPATCH MODEL

In order to examine the economic value of the flexible operation of the chlor-alkali process, a dispatch model is set up. For every time

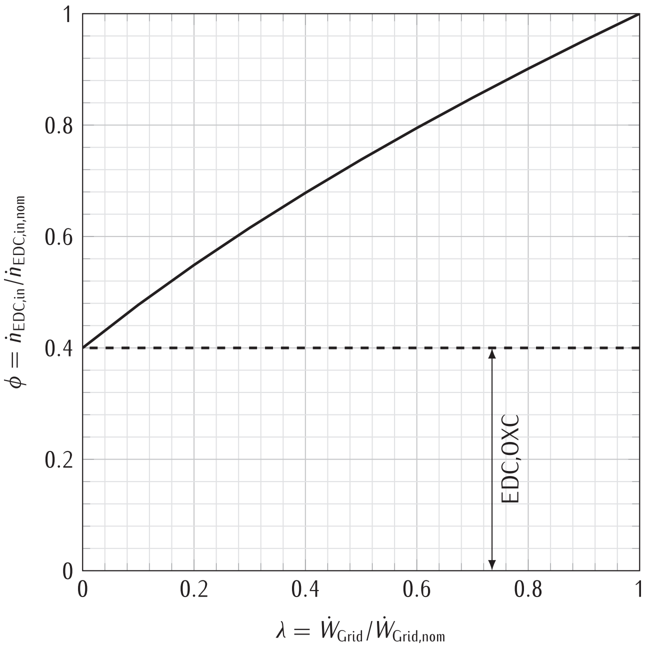

FIGURE 2 ϕ,λ-diagram showing EDC production as a function of the grid load of the CAE based on EES modeling. CAE, chlor-alkali electrolysis; EDC, ethylene dichloride; EES, Engineering Equation Solver

step, we obtain the production of the facility, the power load, and storage fill level. The model is implemented in GAMS.[40] The problem is solved using CPLEX.[41] The objective is cost minimization.

In a sensitivity analysis, the impacts of four different parameters are discussed:

- additional power load k_{add},
- minimum power load $\lambda_{\min}$,
- additional storage volume s_{add},
- cost of a load change c_{LC}.

4.1 | Model

A dispatch model should show the use of the process over a certain period of time. By the definition of a given number of time steps

$$t = 1 \ldots n, \tag{36}$$

every variable becomes time-dependent.

As a result of the EES model, we can describe the EDC production load

$$\phi(t) = \frac{\dot{n}_{\mathrm{EDC,in}}(t)}{\dot{n}_{\mathrm{EDC,in,nom}}}, \tag{37}$$

based on the power load

$$\lambda(t) = \frac{\dot{W}_{\mathrm{Grid}}(t)}{\dot{W}_{\mathrm{Grid,nom}}} \quad \text{with} \quad \dot{W}_{\mathrm{Grid,nom}} = (1 + k_{\mathrm{add}})\dot{W}_{\mathrm{Grid,ref}}, \tag{38}$$

which is the actual electrical work rate necessary for the CAE in relation to the nominal value at full load. In the reference case, the factor of the additional available installed capacity is $k_{\mathrm{add}} = 0$. This factor may be varied to carry out a sensitivity analysis. The actual power load can never exceed the nominal value. The lower bound represents the minimum load, which is technically or economically acceptable.

$$\lambda_{\min} < \lambda(t) < 1 \tag{39}$$

The technically feasible lower bound for the examined system amounts to a value of 0.25, respectively, 0.75 due to the minimum load of the EDC reactor system. The lower bound of 0.75 is already feasible in the plant under consideration. The minimum load of 0.25 is technically feasible but involves more significant interventions in the operation of the plant. The impact of the minimum load on the flexibility of the system and the reduction of electricity purchase costs is considered in the sensitivity analysis.

Analogous to production and power load, the dimensionless fill level of the EDC storage is described.

$$\psi(t) = \frac{FL_{\mathrm{EDC\text{-}S}}(t)}{FL_{\mathrm{EDC\text{-}S,nom}}} \quad \text{with} \quad FL_{\mathrm{EDC\text{-}S,nom}} = s_{\mathrm{add}} \cdot FL_{\mathrm{EDC\text{-}S,ref}} \tag{40}$$

The factor s_{add} expresses an additional accessible storage volume, which is used for the sensitivity analysis described below. The capacity of EDC-S is expressed as a volume with a value of $FL_{\mathrm{EDC\text{-}S,ref}} = 39.1\,\mathrm{m}^3$ corresponding to 1 h of full electrolysis operation at $\dot{W}_{\mathrm{Grid,ref}} = 100\,\mathrm{MW}$.

To express the nonlinear function shown in Figure 2 for optimization purposes, we use a piecewise linearization based on binary decision variables to obtain an Mixed-integer linear programming (MILP) formulation. The EDC production rate $\dot{n}_{\mathrm{EDC,in}}$ is approximated by $i = 10$ linear segments to reduce the error to a negligible level.

$$\dot{n}_{\mathrm{EDC,in}}(t) = \sum_i l_i \dot{W}_{\mathrm{Grid},i}(t) + Y_i\Big((m_i - m_{10})\dot{W}_{\mathrm{Grid,nom}} + m_{10}\dot{W}_{\mathrm{Grid,ref}}\Big) \quad \forall\ i = 1 \ldots 10. \tag{41}$$

The time-independent term on the right side of Equation (41) consists of a sum containing $\dot{W}_{\mathrm{Grid,nom}}$ and $\dot{W}_{\mathrm{Grid,ref}}$. This takes into account that when an electrolysis overcapacity is installed, the DC unit is expanded but not the OXC unit, see Figure 1. The values for the linear equation parameters l_i and m_i can be found in Table 2.

The binary decision variable Y_i is set to 1 if the respective linear segment of the EDC function is active. Since only one linear segment can be active at a time, the remaining binary decision variables are set to 0 by Equation (42).

TABLE 2 Coefficients for the EDC production function

i	l_i	m_i
1	0.316186	0.3354686
2	0.327405	0.3253715
3	0.339913	0.3153651
4	0.353970	0.3055252
5	0.369932	0.2959480
6	0.388270	0.2867790
7	0.409640	0.2782310
8	0.434983	0.2706281
9	0.465708	0.2644831
10	0.504034	0.2606505

Abbreviation: EDC, ethylene dichloride.

$$\sum_i Y_i(t) = 1 \tag{42}$$

The constraints of the linear sections and the actual electrical work rate are defined as follows:

$$\dot{W}_{\mathrm{Grid},i}(t) \le Y_i(t) \cdot \dot{W}^u_{\mathrm{Grid},i} \tag{43}$$

$$\dot{W}_{\mathrm{Grid},i}(t) \ge Y_i(t) \cdot \dot{W}^l_{\mathrm{Grid},i} \tag{44}$$

$$\dot{W}_{\mathrm{Grid}}(t) = \sum_i \dot{W}_{\mathrm{Grid},i}(t) \tag{45}$$

The upper and lower bounds of the linear segments $\dot{W}^u_{\mathrm{Grid},i}$ and $\dot{W}^l_{\mathrm{Grid},i}$ are calculated by equating the respective linear expressions from Equation (41).

The modeling of the EDC production load represents the results from the EES model. As described, the CAE technology used shows an "advantage of efficiency" in the case of part-load operation. The efficiency of the CAE is higher in such cases. In consequence, for an identical power rate $\dot{W}_{\mathrm{Grid}}(t)$ the EDC production rate $\dot{n}_{\mathrm{EDC,in}}(t)$ is higher for $k_{\mathrm{add}} > 0$ compared with the reference case. The results section includes a further evaluation of this effect.

Flexibility must be evaluated economically. Load changes should only be implemented if their costs (higher stress, material fatigue) can be compensated for by the additional revenues. Load change means a temporal change of the power consumption of the CAE.

$$LC_{\mathrm{up}}(t+1) - LC_{\mathrm{dwn}}(t+1) = \lambda(t+1) - \lambda(t)$$
$$\text{with } 0 \le \begin{Bmatrix} LC_{\mathrm{up}}(t) \\ LC_{\mathrm{dwn}}(t) \end{Bmatrix} \le 1 \tag{46}$$

The absolute value of a load change C_{LC} is combined with its specific cost. The specific cost of a load change c_{LC} is a given parameter and has an influence on the operation of the system. The higher the value, the lower the frequency and amplitude of load changes.

$$C_{\mathrm{LC}}(t) = c_{\mathrm{LC}}(LC_{\mathrm{up}}(t) + LC_{\mathrm{dwn}}(t)) \tag{47}$$

If the objective function respects the costs of load changes, they are reduced to the necessary economic minimum.[42]

If the molar flow rate of EDC from DC and OXC is higher than the nominal flow rate necessary for PVC production, the storage can be charged. For $t = 1$ and n, the fill level of storage $FL_{\mathrm{EDC\text{-}S}}$ must be identical. To ensure a constant PVC production, the molar flow rate from storage is time-independent.

$$FL_{\mathrm{EDC\text{-}S}}(t+1) - FL_{\mathrm{EDC\text{-}S}}(t) = (\dot{n}_{\mathrm{EDC,in}}(t) - \dot{n}_{\mathrm{EDC,out}}) \frac{M_{\mathrm{EDC}}}{\rho_{\mathrm{EDC}}} \Delta t$$
$$\text{with } 0 \le FL_{\mathrm{EDC\text{-}S}}(t) \le FL_{\mathrm{EDC\text{-}S,nom}} \tag{48}$$

The objective function represents the minimization of cost of electrical energy and cost of load changes. Auxiliary costs like grid utilization fees are not considered.

$$OBJ = \min\left(\sum_t c_{\mathrm{epex}}(t) \dot{W}_{\mathrm{Grid}}(t) \Delta t + \sum_t C_{\mathrm{LC}}(t) \right) \tag{49}$$

4.2 | Assumptions, simplifications, and parameters

The main cost driver for the operation of the plant considered here are the electricity supply costs. It is assumed that the entire amount of required power is purchased at the day-ahead market of the EPEX SPOT.[43] Furthermore, a perfect forecast for the specific costs of electricity c_{epex} is assumed.

As an additional cost factor, the costs of load changes should be considered. This requires the definition of the specific cost of a load change c_{LC}. To the best of our knowledge, no further studies on this issue are available in the literature in the context of CAE. Therefore, the following considerations are made:

Based on approximate procurement and installation costs for a single membrane of €3000, membrane costs of $€5 \times 10^6$ for a 100 MW plant are assumed. According to information from CAE-operators, an average membrane lifespan is 4 years. This leads to annual costs of $€1.25 \times 10^6$.

Concerning the number of load changes, it is initially assumed that the nationwide power consumption during the day is higher than at night. Furthermore, in an energy system with a significant share of VRE, photovoltaic electricity may often be available during the day. It is therefore supposed, for the sake of simplicity, that there is an increased need for load reduction in the morning and evening hours, while at midday and especially at night, an increase in load is possible. This leads to four load changes per day, while it is further assumed that the load changes are half of the nominal power $P_{\mathrm{Grid,nom}}$. If the membranes under these circumstances are destroyed within 1 year, this results in specific load changes of approximately €5000 per full load change cycle.

However, it should be emphasized that these are highly simplified considerations to give an idea of the magnitude of possible costs

TABLE 3 Parameters used in dispatch model

Parameter	Symbol	Unit	Value
Time step	Δt	h	1
Number of time steps	N	–	8760
Reference case			
Power load	$\dot{W}_{\mathrm{Grid,ref}}$	MW	100
Fill level of storage	$FL_{\mathrm{EDC\text{-}S,ref}}$	m^3	39.1
Factors of the sensitivity analysis			
Additional power load	k_{add}	–	0.05, 0.1, 0.2, 0.4
Minimum power load	λ_{min}	–	0.25, 0.5, 0.75
Additional storage volume	s_{add}	–	0, 1, 2, 4, 8, 16, 32
Cost of a load change	c_{LC}	10^3€/cycle	0, 1, 5, 10, 50

Abbreviations: EDC-S, storage of ethylene dichloride; LC, load change.

resulting from load changes. Therefore, a parameter study with variation of the specific load change cost is conducted on this basis. The values as well as all other variable and constant parameters used can be found in Table 3.

It is also required that load shifting is applied, and thus the annual production volume must be identical in all cases. Furthermore, external purchase of EDC is excluded.

4.3 | Results

The analysis is based on system parameters of an existing facility for PVC production. The determination of the economic potential of DR is a result of the dispatch model. For this purpose, optimal marketing strategies for the system operating as a consumer on the electricity market (day-ahead) are developed.

The objective of the dynamic dispatch model is to minimize electricity purchase costs for a specific year. The time step length is 1h. Due to a given storage volume and an additional available capacity, a flexible operation of CAE is possible. The result of the optimization depends on the given values for k_{add}, s_{add}, λ_{min}, as well as c_{LC}. As part of a sensitivity analysis, the results are discussed.

Assuming k_{add} and s_{add} equal zero while buying at day-ahead market (EPEX SPOT), the electricity procurement costs for a facility with a nominal demand of 100 MW_{el} operating in 2018 are approximately € 39×10^6, representing point (0,0) in Figure 3.

In case of an additional available capacity of 10% ($k_{\mathrm{add}} = 0.1$) the electricity purchase costs are reduced by €0.9×10^6. Note that this saving results only from the "advantage of efficiency" at part-load operation as there is no EDC storage, $s_{\mathrm{add}} = 0$. A further decrease in the electricity purchase costs is possible by installing an EDC storage. In the case of $s_{\mathrm{add}} = 4$, which corresponds to a production period of 4h of nominal operation of CR or a storage capacity of approximately 200 tonnes of EDC, the "advantage of flexibility" leads to an additional decrease of €1.4×10^6. Both effects are marked in Figure 3.

Figure 3 also shows that a further increase in storage capacity does not lead to significantly larger cost reductions. In addition, the results indicate that, e.g., doubling the additional available capacity is not equivalent to doubling the cost savings. For example, doubling k_{add} from $k_{\mathrm{add}} = 0.1$ to $k_{\mathrm{add}} = 0.2$ only leads to a 1.6-fold reduction in costs from €2.3×10^6 to €3.6×10^6. Since increasing storage and power capacities are associated with increasing investment costs, these findings are likely to have relevant implications for potential investment decisions.

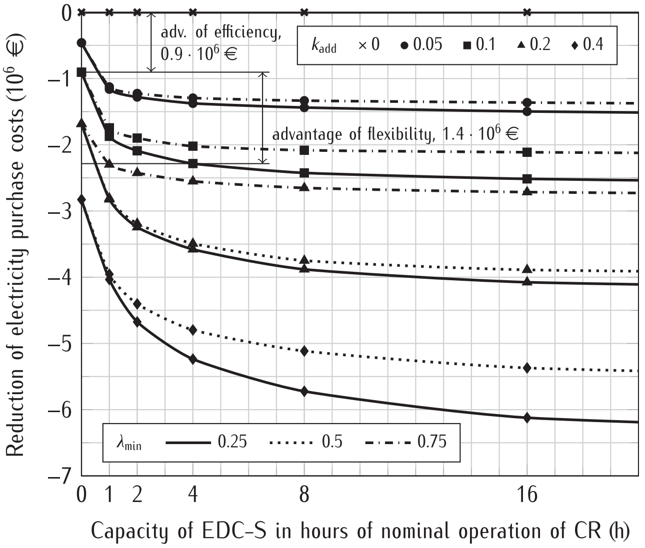

FIGURE 3 Electricity purchase costs depending on volume of EDC storage $s_{\mathrm{add}} = 0\ldots16$ and additional available capacity $k_{\mathrm{add}} = 0\ldots0.4$ with $\lambda_{\mathrm{min}} = 0.25\ldots0.75$ and $c_{\mathrm{LC}} = 0$. The case $k_{\mathrm{add}} = 0.4$ and $\lambda_{\mathrm{min}} = 0.75$ is not considered. The constraint of a constant production of PVC cannot be fulfilled. For every time step $\dot{W}_{\mathrm{Grid}}(t)$ is greater than $\dot{W}_{\mathrm{grid,ref}}$, which leads to a higher annual production of PVC. EDC, ethylene dichloride; PVC, polyvinyl chloride

Based on this analysis, variations are made to the minimum load. Three cases are considered for λ_{min}. As reported in Figure 3, the additional savings between 0.25 and 0.5 are minimal. In the case of an additional available capacity of 5% or 10%, it is not possible to see a difference in the chart. Only in the case of $k_{\mathrm{add}} = 0.4$ and $s_{\mathrm{add}} > 4$ does a recognizable difference appear. It is more relevant to discuss the difference between 0.5 and 0.75 for $\lambda_{\min}$, which becomes even more relevant with increasing additional available capacity and increasing storage volume. Decreasing minimum load leads to a higher flexibility. Especially from 0.75 to 0.5, the economic effect should be sufficient to implement this technical feature for $k_{\text{add}} > 0.05$. A further decrease $\lambda_{\min} < 0.5$ has a relevant economic effect for cases of $k_{\text{add}} > 0.2$ only. Additional technical efforts for minimum load reduction should, therefore, hardly be economically viable.

The observed significant decrease in cost savings at a minimum load of $\lambda_{\min} = 0.75$ in the case of $k_{\text{add}} = 0.2$ is mainly due to the definition of the minimum load by combining Equations (38) and (39). An increase of $\dot{W}_{\text{Grid,nom}}$ results in an increase of the minimum electrical power $\dot{W}_{\text{Grid,min}}$ related to the minimum load $\lambda_{\min}$. For a nominal value of 120 MW at $k_{\text{add}} = 0.2$ this implies a minimum electrical power of 90 MW at $\lambda_{\min} = 0.75$. Consequently, with increasing nominal power, there is a decreasing difference between minimum electrical power and the steady-state value required to maintain a constant storage level. This reduces the flexibility to conduct load reductions and thus the cost advantage. Depending on the type of process design, it may be argued that the minimum load can instead be related to the steady-state power. Therefore, it would seem reasonable to examine this in further work.

In our investigation, determining the cost of load changes is one of the outstanding challenges. The value has an influence on the dispatch of the facility. Furthermore, a high degree of uncertainty is associated with determining the value. Thus, a sensitivity analysis was conducted for this parameter.

It is comprehensible, with increasing cost of load changes the load profile of the system is smoothed, the dispatch is less flexible. The storage intervals become longer and the number of full load change cycles decreases. Depending on the capacity of EDC storage and the cost of load changes, the number of full load change cycles is shown in Figure 4, which is higher for a more flexible system. The lengths of storage intervals (decreasing number of full load change cycles) depending on an increasing storage volume are smoothed by increasing cost of load changes. In other words, with increasing cost of load change, the number of full load change cycles is less influenced by changing the storage volume. The advantage of flexibility shown in Figure 3 is reduced by $€0.3 \times 10^6$ in case of the assumed cost of load changes of $c_{\text{LC}} = 5 \times 10^3\,€/\text{cycle}$, see Figure 5. For the case of very high cost of load changes $50 \times 10^3\,€/\text{cycle}$, the advantage of flexibility is decreased to a minimum of $€0.4 \times 10^6$.

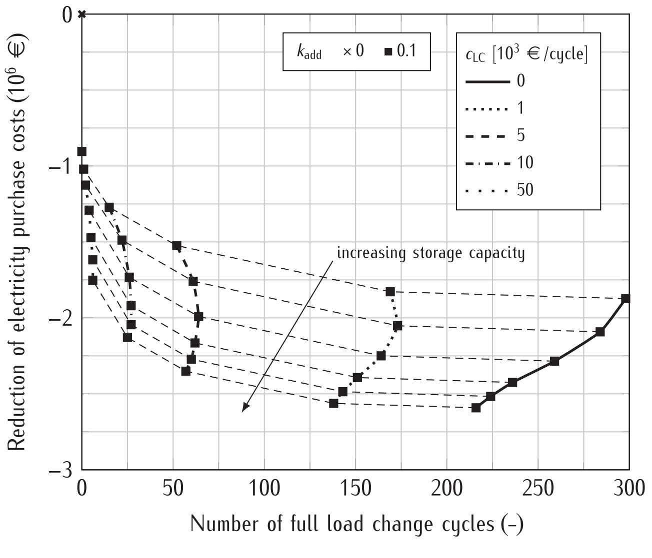

FIGURE 4 Dispatch of the facility and electricity purchase costs depending on the cost of load changes $c_{\text{LC}} = 0 \ldots 50$ for $s_{\text{add}} = 0 \ldots 16$ and $\lambda_{\min} = 0.25$

Assuming increasing price differences for the future development of wholesale prices of the electricity market (day-ahead), the operation of the storage becomes more lucrative, as shown in Figure 6. The figure shows the differences for the given year based on the

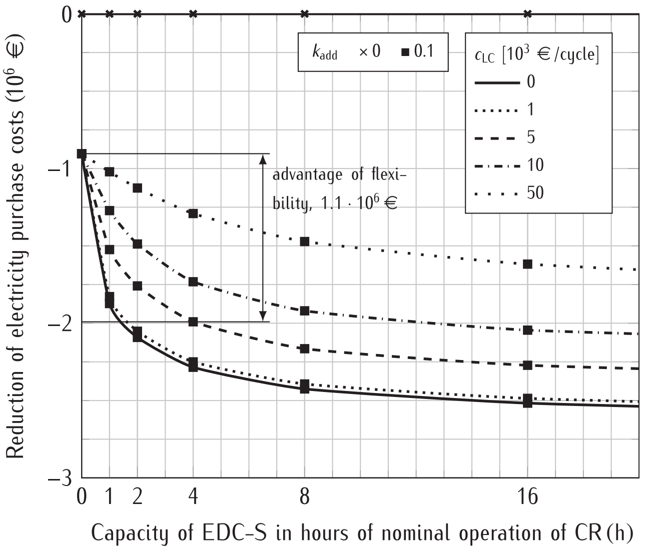

FIGURE 5 Electricity purchase costs depending on volume of EDC storage $s_{\text{add}} = 0 \ldots 16$, $\lambda_{\min} = 0.25$ and cost of load changes $c_{\text{LC}} = 0 \ldots 50$. EDC, ethylene dichloride

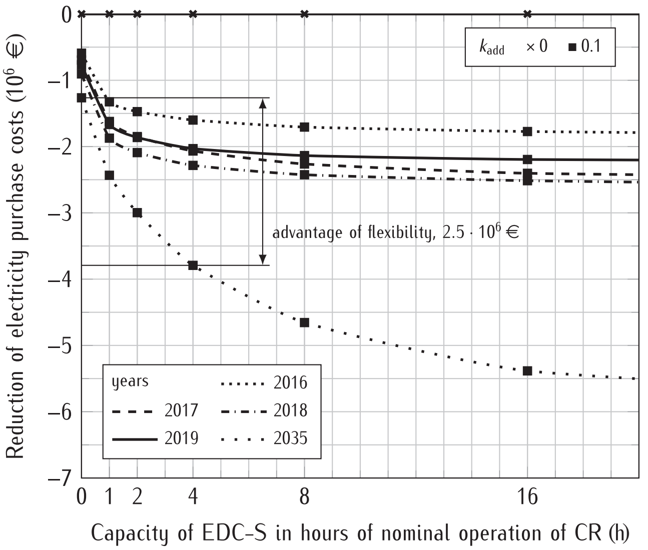

FIGURE 6 Electricity purchase costs depending on volume of EDC storage $s_{\text{add}} = 0 \ldots 16$, $\lambda_{\min} = 0.25$, and $c_{\text{LC}} = 0$ for different years past and present as well as for a future scenario of the year 2035 based on Kopiske et al.[44] EDC, ethylene dichloride

TABLE 4 Average values and standard deviations of wholesale electricity prices from 2016 to 2019 and of 2035 both based on data[43,44] as well as electricity procurement costs with nonflexible operation ($k_{add} = s_{add} = 0$)

		Year				
Value	Unit	2016	2017	2018	2019	2035
Average price	€/MWh	28.98	34.20	44.47	37.67	62.14
Standard deviation	€/MWh	12.48	17.61	17.77	15.52	36.08
Electricity purchase cost, nonflexible operation	10^6€	25.46	29.96	38.96	33.00	54.43

electricity purchased costs of that year. Past, present, and future cases are depicted. The above-described advantage of efficiency is approximately the same for the past and present cases. The advantage of flexibility resulting from the operation of the storages differs by approximately €0.7×10^6 for the case of $s_{add} = 4$ from 2016 to 2019. In a future scenario for the year 2035[44] and the case of $s_{add} = 4$, the advantage of efficiency and flexibility leads to an additional decrease of €3.8×10^6. With nonflexible operation, that is, k_{add} and s_{add} equal zero, the electricity procurement costs would rise to approximately €54×10^6 in 2035. This is explained by the increased average electricity price, as shown in Table 4. Comparison of Figure 6 with Table 4 shows that the possible savings due to flexible operation increase with increasing standard deviations of the electricity price, that is, increasing price fluctuations.

5 | CONCLUSIONS

We have studied DR in PVC production via the EDC route as a feasible option to reduce VRE curtailment, the use of fossil fuels, and storage capacity in future energy systems. Load management potentials are evaluated based on a combined simulation and optimization approach for a chlor-alkali process regarding an entire chemical facility.

The development of a process model based on real plant data results in a system characteristic for the flexible operation of the chlor-alkali process. Taking into account a sufficient storage capacity for EDC, the production of PVC remains constant. A dynamic model is used to optimize the plant dispatch to ensure minimum cost of energy demand. Based on mixed-integer linear programming approaches, sensitivity analyses are carried out to identify the economic impact of several parameters, for example, the cost of load changes.

For all scenarios considered, a flexible plant dispatch (using CAE for DR) is more economical than conventional operation (constant load of CAE) in terms of variable operational costs. Assuming a plant with $100\,\mathrm{MW_{el}}$ nominal power, the reduction of annual electricity purchase cost is at least €0.9×10^6. Increasing the volume of the EDC storage and the additional available capacity increases the cost reduction to around €6×10^6. The reduction of electricity purchase cost is based on efficiency and flexibility effects. For a given additional available capacity, the advantage of efficiency is fixed. The advantage of flexibility increases with increasing volume of EDC storage and the additional available capacity. However, we also showed that increasing the storage and power capacity or reducing the minimum load only seems reasonable up to a certain extent. This is considered a relevant circumstance for potential investment decisions. Considering the cost of load changes decreases the reduction of annual electricity purchase cost. This parameter highly affects the dispatch of the plant. With increasing cost of load changes, the number of full load change cycles decreases. In future scenarios with higher or more volatile wholesale electricity prices a more flexible plant operation leads to higher reduction of electricity purchase cost.

The results summarized in this article are the basis for a feasibility study in a chemical plant and the investigation of other chlorine value chains. The developed model will also be supplemented by the possibility to operate with the plant on balancing markets. Future work may further include more detailed validation studies of individual process elements such as the DC unit. A limitation of this study is the restriction to the investigation of the operational expenditure. Increasing the power load $k_{add} > 0$ or storage volume s_{add} is associated with capital expenditure, which must be determined more reliably for a comprehensive economic analysis. Estimating these costs will be a future task too. In general, DR is considered suitable to reduce CO_2 emissions. A quantitative analysis will also be carried out.

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AUTHOR CONTRIBUTIONS

Mathias Hofmann: Data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); software (equal); validation (equal); visualization (lead); writing – original draft (lead); writing – review and editing (lead). **Robert Müller:** Data curation (equal); formal analysis (equal); investigation (equal); software (equal); validation (equal); writing – original draft (equal); writing – review and editing (equal). **Andreas Christidis:** Conceptualization (lead); formal analysis (equal); investigation (equal); methodology (equal); software (equal); validation (equal); writing – review and editing (supporting). **Peter Fischer:** Data curation (equal); funding acquisition (supporting); resources (equal); writing – review and editing (supporting). **Franziska Klaucke:** Funding acquisition (equal); project administration (lead); writing – review and editing (supporting). **Sebastian Vomberg:** Funding acquisition (supporting); supervision (equal). **George**

Tsatsaronis: Funding acquisition (lead); supervision (equal); writing – review and editing (supporting).

NOMENCLATURE

Latin symbols

a	linear U/I-parameter, Vm^2/kA
A	area, m^2
b	linear U/I-parameter, V
c_{epex}	specific cost of electricity, €/Wh
c_{LC}	specific cost of a load change, cycle, €/cycle
C_{LC}	cost of load change, €
F	Faraday constant, see Ref. 38, A s/mol
FL	fill level, m^3
h	specific enthalpy, J/kg
I	current intensity, A
j	current density, A/m^2
k_{add}	additional power load, –
l	coefficient for EDC production function, mol/Ws
LC	load change, –
m	coefficient for EDC production function, mol/Ws
$\dot{m}$	mass flow rate, kg/s
M	molar mass, kg/mol
$\dot{n}$	molar flow rate, mol/s
N	number, quantity, –
p	pressure, bar
OBJ	objective, €
r	ratio, –
R	molar gas constant, see Ref. 38, J/molK
s_{add}	additional storage volume, –
s	specific entropy, J/kgK
t	time, s
T	temperature, °C
U	voltage, V
$\dot{V}$	volume flow rate, m^3/s
w	specific work, J/kg
$\dot{W}$	work rate, power, W
Y	binary variable, 0 or 1

Greek symbols

ρ	density, kg/m^3
λ	power load, –
η	energetic efficiency
ϕ	production load, –

Subscripts and superscripts

0	reference state
add	additional
aux	auxilliary
ref	reference
i	substance
j	stream
min	minimum
nom	nominal
p	pressure
s	isentropic

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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