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Simulation of a 2 MW PEM Fuel Cell Plant for Hydrogen Recovery from Chlor-Alkali Industry

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Abstract

Some chemical processes, like the chlor-alkali production, generate significant amount of hydrogen as byproduct whose recovery within the chemical plant is not always possible. An efficient and attractive use of hydrogen is obtained installing a PEM fuel cell-based cogeneration unit, whose electricity and heat production covers part of plant consumptions. Practical application of this concept requires scaling up the fuel cell plant up to the multi-MW scale, an ongoing process with many open challenges where the development of dedicated modeling tools allows evaluating the plant expected performances and optimizing its operational strategies.

This work presents the results of a the simulation activity modeling of an innovative 2 MW PEM fuel cell power plant, developed within the European project DEMCOPEM-2MW. Simulations are performed with ASPEN Plus®, including a specifically developed lumped model for the stacks in order to investigate their behavior as function of inlet streams conditions and of power set point. The BOP is modeled with particular attention to component expected operating conditions, efficiency, auxiliary consumption, pressure drops. The model is calibrated and validated on data from PEM stacks operated by Nedstack and MTSA in previous installations. Stacks model performs lumped energy and mass balances according to regressed polarization curves; cells decay is modeled through simplified assumptions aiming at evidencing the impact on auxiliaries operation and on global efficiency. Comparison with a different arrangement where excess hydrogen exiting the fuel cell anode is oxidized in a combustor, instead of being recirculated to the fuel cell, is also set up evidencing the possibility to increase the heat to electricity ratio and allow high temperature heat production. The model also allows assessing and optimizing the plant operational strategies (e.g. minimizing the power production and efficiency losses vs. lifetime), evaluating the deviations of real plant behavior from theoretical conditions.

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Nomenclature

BOL   Beginning of Life
BOP   Balance of Plant
EOL   End of Life
GHG   Greenhouse Gases
MEA   Membrane Electrode Assembly
PEM FC   Polymeric Electrolyte Membrane Fuel Cell

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1. Introduction

Chemical industry accounts for approximately 10 % of global energy demand and about 7% of the global GHG emissions [1]. Among different sectors, chlorine and sodium hydroxide production by means of chlor-alkali electrolysis is an energy-intensive process (2.8 MWh_{el}/ton_{Cl}, 27.4 GJ/ton_{Cl} of primary energy), which produces hydrogen as byproduct (340 Nm^3_{H2}/ton_{Cl}) [2]. In Europe, the chlor-alkali industry shows a production of 9612 kton of chlorine in 2014 (+1.7% from 2013, -9.4% from 2007), while the U.S. production is 10776 kton in 2014 (+4.7% from 2013) [3]. China is the largest chlorine producer worldwide, with more than 25000 kton/year production (about 42% of global production) [4] and a stable growth expected for the next years. Membrane technology (Fig. 1a) is the prevalent technology, due to environmental and efficiency issues of classical competitors (mercury and diaphragm cells). Environmental legislation supports this technology and its share is continuously increasing (currently over 60% in Europe [3]). Brine concentration (as well as other products purification) requires a large amount of heat, usually provided by means of high-pressure steam (~0.8 ton/ton_{Cl} at 200°C, 10 bar) [2].
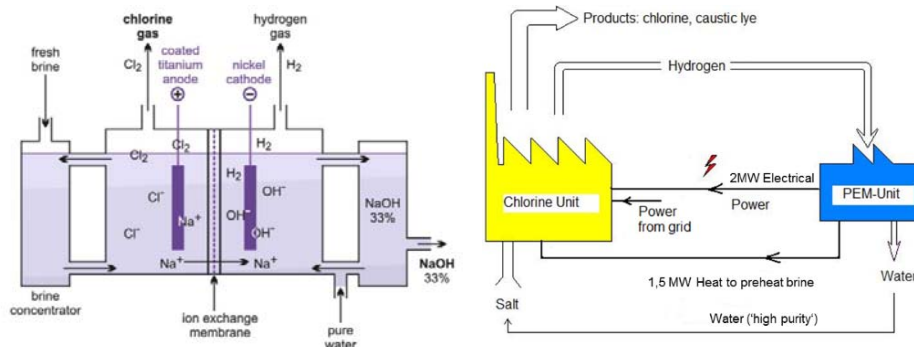

Fig. 1 - (a) Working principle of chlor-alkali membrane cells and (b) integration of PEM FC plant in chlorine production unit (DEMCOPEM-2MW concept [5]).

Hydrogen recovery is about 90% (usually as feedstock for nearby industries), while the remaining is currently vented [3]. In the past, several companies bottled and marketed the co-produced hydrogen; however most of them progressively sold the activity to specialized companies [2] because of the additional investment and effort required for this 'non-core' business, not justified by the limited amount of product.

In this framework, the solution of feeding excess hydrogen to an on-site cogeneration plant –where electricity and heat are utilized in the chemical plant itself - spontaneously points to PEM high efficiency fuel cell technology (see Fig. 1b). Energy saving and emissions reduction allowed by a PEM plant could contribute to both plant economics and environmental goals. Owing to the large scale of these industries (hundreds thousands tons of chlorine per year, with tens-to-hundreds MW of electric power required overall), this type of application requires large energy systems, calling for the scale-up and demonstration

of MW-scale fuel cell plants. The European Project DEMCOPEM-2MW [5], led by AkzoNobel (NL), aims at demonstration of PEM FC technology scale-up, integrated in a chlorine production facility. Project objectives include high system efficiency (over 50% electrical and 85% total with cogeneration) and improvement of lifetime. Economical design is supported by development of specific MEA production processes and fully automated remote operation. The resulting demonstration plant has been installed in 2016 at the site of Ynnovate Sanzheng Fine Chemicals Co. Ltd in Yingkou, Liaoning province, China. The high electricity prices (up to 2 times higher than in Europe and rising) in most geographical areas, together with the availability of waste hydrogen by many of the ca. 180 chlor-alkali plants currently in operation, makes the perspective adoption of this technology particularly attractive for this country. In this work, a model of the plant is set up in order to assess the plant energy balances, optimize the plant operational strategies (e.g. minimizing the power production and efficiency losses vs. lifetime) and evaluate possible deviations of real plant behavior from theoretical conditions.

2. Plant modeling

The simulation tool is Aspen PLUS® [6], a software specifically designed for energy and chemical plant process design and rating. The code includes standard component libraries and allows the definition of custom components – as done here for the fuel cell modeling; it includes libraries for thermochemical properties of several fluids.
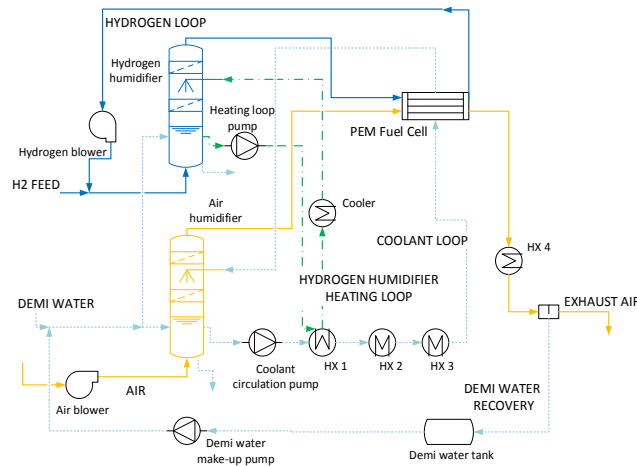

Fig. 2 - System layout and material streams.

The layout of the plant is shown in Fig. 2. The central component of the system is the PEM FC, made up of several stacks; the model of this component is discussed in a specific section. Chlorine unit provides pure hydrogen at a sufficiently high pressure, directly humidified and fed to the stacks. Excess hydrogen is then recirculated and mixed (after compression) with the fresh feed. Compressed air is humidified and fed to the stacks; exhaust air is cooled down (HX4) in order to recover demineralized water. Overall water production is higher than humidification requirement, yielding a positive contribution to chlorine plant consumptions. A closed water loop provides cooling power to fuel cell modules. Heat is removed by two heat exchangers, one recovering useful heat for brine pre-heating in the chlorine plant (HX2), the other dissipating heat for accurate temperature control (HX3). Another heat exchanger (HX1) supplies heat to a separate water loop feeding the hydrogen humidifier; the latter loop, depending on plant operating conditions, could also require removing heat through a dedicated cooler. Counter-current spray humidification is modeled through lumped mass and energy balances in order to match the relative humidity

requirements of the cell; gas streams saturation is avoided to keep a margin vs. possible condensation in the pipe distribution system due to thermal losses. Characteristic curves of both air and hydrogen blowers are included, in order to catch the influence on plant performances of an operation with different reactant excess and/or additional hydrogen and air requirements due to the changes of cell performances during lifetime. Cooling heat exchangers are modeled assuming fixed temperatures, considering that the auxiliaries of the industrial plant are always able to provide the required cooling power and to modify flows in order to match design temperatures. The main heat recovery exchanger (HX2), due to its importance in terms of plant cogeneration performances, is modeled considering the global heat exchange coefficient U variation with volumetric flowrate according to:

$$U = U_{nom} \left(\frac{\dot{V}}{\dot{V}_{nom}} \right)^{4/5} \tag{1}$$

where nominal values are calculated in design conditions from datasheets. The influence of volumetric flowrate on pressure drops is also included in the model as:

$$\Delta p = k \cdot \dot{V}^2 \tag{2}$$

where coefficients k are design data for heat exchangers and calculated from hydrodynamics models for piping.

3. PEM Fuel Cell Modeling

The correct description of plant performances requires including an effective model of fuel cell behavior, able to catch both operating conditions and decay effects. Anyway, the size of the problem (thousands of cell assembled in several stacks and groups) advise against a high level of detail in the description of internal structure of the electrochemical device. Moreover, it is not required by the final goal of the model, focused on a larger scale. So, the choice is a lumped 0D stack model, whose operating parameters (power and current) can be set individually for groups of stacks (see Fig. 3a), while thermal and reactants conditions are defined by distribution system (hydrogen, air and coolant water). A customized model is developed in Aspen Custom Modeler®, designed also to analyze the off-design operation, taking into account variations in the cell stoichiometry as well as the influence of cell performance decay. The analytical formulation of the polarization curve [7] adopted for single cells can be summarized in the voltage (V) vs. current density (i, A/cm^2) expression:

$$V(i, x_{H2}, x_{O2}) = A + B \ln\left(\frac{x_{H2}}{x_{H2,st}}\right) + C \ln\left(\frac{x_{O2}}{x_{O2,st}}\right) + Di + E \ln\left(\frac{i}{i_0} + 1\right) + F \ln\left(1 - \frac{i}{i_L(x_{H2}, x_{O2})}\right) \tag{3}$$

where stoichiometry effects are taken into account through species molar fractions x_i. Due to the lumped approach, hydrogen and oxygen concentrations are estimated as average between inlet and outlet of the cell, leading to:

$$\frac{x_{H2}}{x_{H2,st}} = 1 + \frac{S_H - 1}{S_H - 1 - x_{sat} \cdot RH_H} \tag{4}$$

$$\frac{x_{O2}}{x_{O2,st}} = 1 + \frac{S_O - 1}{S_O + 0.21(1 - x_{sat} \cdot RH_O)} \tag{5}$$

where S_H and S_O are the ratio to stoichiometry of hydrogen and oxygen respectively, while RH is relative humidity that takes into account real operating conditions with respect to water fraction in saturation conditions $x_{sat}(T)$. Pure hydrogen feeds the anode, while standard air (21%$_{vol}$ oxygen) is considered at the cathode.
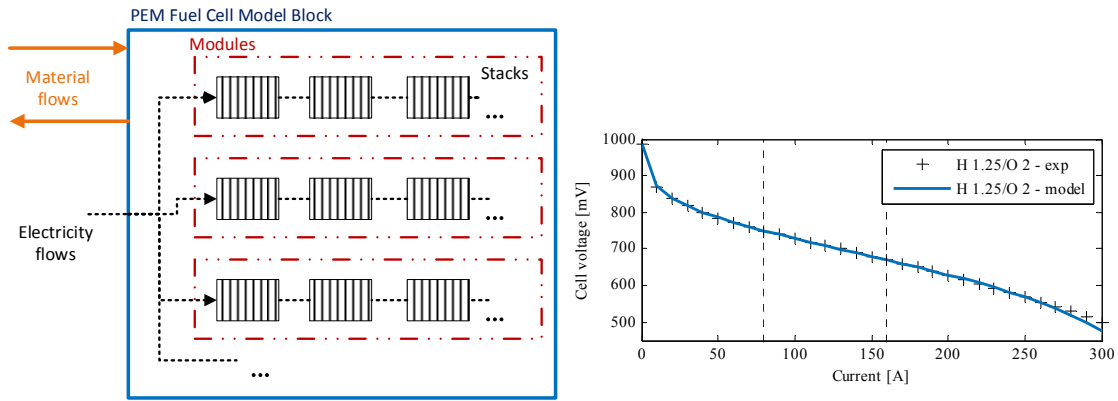
Fig. 3 - (a) Generic modular structure of a large PEM fuel cell system and (b) Example of regressed polarization curve for a given stoichiometry at BOL

Coefficients A,B,C,D,E and F, as well as exchange and limiting current densities i_o and i_L are regressed on experimental data from stacks [8, 9] previously operated by Nedstack. An example is shown in Fig. 3b. Because of a dependence of exchange i_0 and limiting current i_L on stoichiometry when going towards EOL, they are calculated as linear functions of reactants molar fractions. Moreover, linear decay of cell performance is considered between the available datasets. This assumption is justified by experimental evidences with similar stacks [8, 9]. Fig. 4 shows the resulting operating map for a given stoichiometry. Accordingly, it is possible to evaluate the performances and optimize the plant operating point during lifetime, while maintaining the required electric output.
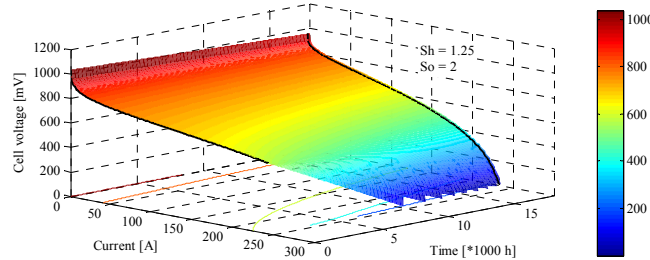

Fig. 4 - Regressed polarization curves as function of current and time

Contribution of stacks to pressure drops are also included according to equation (2) where coefficient k is regressed and validated against experimental data for different reactants excesses and current densities.

4. Model validation

Due to the large number of assumptions regarding interactions between components, the model has been validated against data from (i) a 70 kW PEM stack installation operating in AkzoNobel's plant in Delfzijl [9], where Nedstack PEM fuel cell stacks of the same class used in the projected plant are being tested; and from (ii) a 1 MW PEM plant which has been run in 2010-2015 in Lillo (Belgium), developed by Nedstack and MTSA with a layout similar to the design of DEMCOPEM-2MW plant.

Stack performances at BOL are compared with data from individual groups of stacks in the plant, leading to power values within a 1% tolerance. Air humidification temperature and coolant flow are assumed as indicative of accuracy in modeling thermal balance, because of the availability of field data for comparison. They respectively exhibit errors below 0.5% and 1.5%, comparable with measurement uncertainties. Hydrogen inlet flow and air excess are in the expected nominal ranges, validating the global

mass balance. Table 1 reports stream results and general performances of the simulated 1MW plant. Humidified hydrogen and air feed the stacks in a quantity higher than the stoichiometric (2.0 and 2.4 respectively). Heat recovery from FCs to the chlor-alkali plant is about 500 kW. Gross efficiency of the FCs is close to 60% on H_2 LHV. Auxiliary consumption is ~67 kW, mostly concentrated on air and hydrogen blowers, followed by coolant pumps and inverter systems. The share of energy losses is detailed in Fig. 5, yielding a net plant efficiency of 54%, while the chemical plant can recover 29% of the heat.

Table 1 – Simulated streams conditions and modelling results for the reference plant used for model validation.

	T	Flow rate
	°C	Nm³/hr
Hydrogen to stacks (dry)	50	1200
Recirculated hydrogen (dry)	65	600
Air to stacks (dry)	63	3450
Coolant (FC inlet/outlet)	60/65	165
Water loop (Hum inlet)	50	60
Gross DC electric power	kW	1040
Gross DC efficiency (H_2 LHV basis)	%	57.7
Recovered heat	kW	522
Auxiliaries consumption	kW	67

A significant fraction of heat is then rejected to the environment (13%) because of cooling requirements and temperature control; consequently, there is room for further improvements in plants integration. Among the auxiliaries, the air blower plays a major role, together with electrical losses in the inverter. By this point of view, the direct coupling with chlor-alkali process electrolysers could allow part of the electrical losses, although requiring specific equipment (DC/DC converter) and control systems.
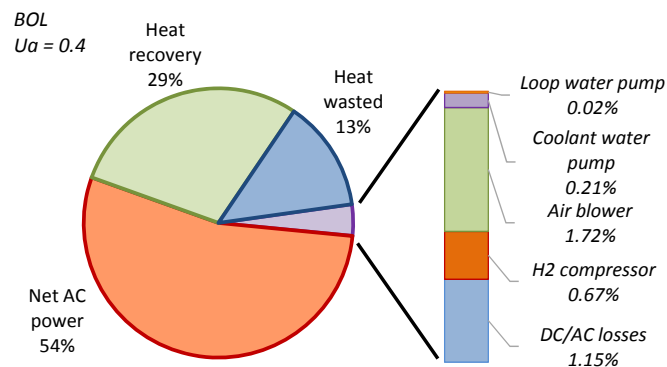

Fig. 5 - System energy balance of the reference plant used for model validation (1 MW$_{el}$, U$_a$ = 0.4, constant gross power).

The results of components simulation have been compared with preliminary data of operating conditions from Factory Acceptance Tests (FAT). Due to reduced load during tests and lower operating temperature, performances of stacks are lower than nominal; nevertheless, they show compatibility with expected results. Moreover, hydrogen and air blowers performances were confirmed, validating the assumed performance maps.

5. Simulation results

First, the expected impact of decay on performances is evaluated, as shown in Fig. 6a. About 6 percentage points of efficiency are lost due to the lower stack efficiency at EOL. In order to match the gross

design power required by the plant, current has to be increased, yielding an additional contribution to performances reduction with respect to stacks aging alone. This behavior conditions electric and thermal production (see Fig. 6b), with a net decrease of the ratio electricity/heat from 2.1 to 1.9.
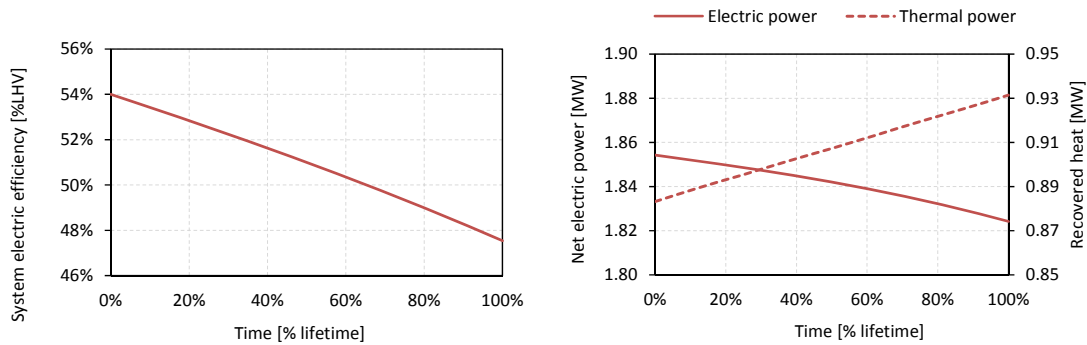

Fig. 6 - (a) System efficiency and (b) Electric and thermal power production as function of time for a reference air excess (Ua = 0.4, constant gross power)

The impact of performances decay can be evaluated by comparing Fig. 7a and Fig. 7b, evidencing the share of losses. The figures are calculated considering the point of view of a system at constant electrical output (2 MWel gross power). The lower EOL net electrical efficiency (48%) yields an additional hydrogen requirement (+12%) that is assumed available from the chlor-alkali plant since only a fraction of available hydrogen is used in nominal conditions. In relative terms, the recovered heat decreases because it is calculated assuming that the operating conditions of the heat load circuit (flow and temperature) are constant. Consequently, the wasted heat increases because of additional thermal losses in the cells; auxiliary consumption also increases because of additional feeding flow and increase of cooling requirements.
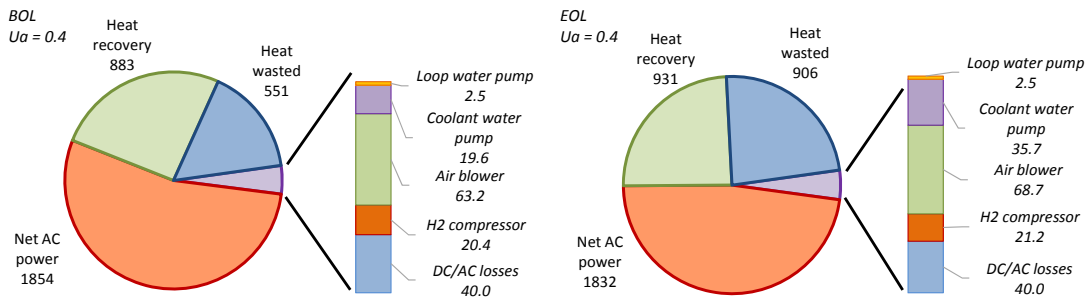

Fig. 7 - (a) System energy balance (BOL, 2MWel, Ua = 0.4, constant gross power) and (b) system energy balance (EOL, 2MWel, Ua = 0.4, constant gross power). Numbers are in kW.

6. Alternative layout with catalytic combustion

We consider here an alternative plant layout, designed to produce low temperature steam (assumed at 200 °C and 10 bar) [2] as alternative heat recovery solution, based on the plant layout shown in Fig. 8. Hydrogen fueled boilers are already a solution in some chlor-alkali plants, as an alternative to hydrogen vent [2]; the additional PEM FC could increase the effectiveness of the solution with electricity production. This solution avoids the necessity of the H_2 recycling compressor as well as of a H_2 blower (provided that the hydrogen feeding is available at a sufficient pressure). On the other hand, it requires an additional blower to provide fresh air to the combustor, since exhaust air from cathode does not provide a sufficient amount of oxygen. Excess air is set in order to match a $3\%_{vol}$ of oxygen in the flue gases, according to common

industrial burners operation; the exhaust stream is cooled down to 100 °C avoiding water condensation. Nevertheless, due to the absence of CO_2, sulphur compounds and contaminants in the flue gases (feed is pure hydrogen), the risk of acid compounds formation is extremely low and this temperature could be lowered, where allowed by the heat recovery circuit, substantially increasing the recovered heat.

The plant also features a different operation of heat exchanger HX1 that provides heat to evaporate water for the H_2 humidifier. Being the enthalpy contribution of the recirculated hydrogen no longer available, all the evaporation heat is provided by the water heating loop, requiring a different design.
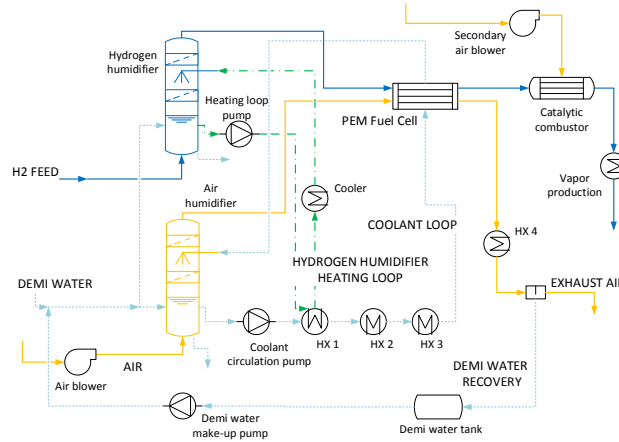

Fig. 8 - System layout and material streams for catalytic combustion option.

Two strategies are then available: (i) constant DC gross power production (2 MWel) or (ii) constant hydrogen input. In the first case, the hydrogen input should be doubled, leading to a net useful heat production of about 4.3 MW_{th}. Steam production is 4.3 ton/h. In the second case, the same H2 consumption allows a lower electric production (1 MW_{el}), whereas about 2.4 MW_{th} are recovered with 2.2 ton/h of steam production. In both cases the net electric efficiency is reduced to 28÷31%, but the solution at constant hydrogen input leads to a total energy recovery up to 98% vs. about 88% for the constant electric production case.

7. Conclusions

The use of a cogenerative PEM FC system is a suitable solution for hydrogen recovery in chlor-alkali plants, where energy consumptions are high and high purity hydrogen is available as byproduct. Modeling of large PEM FC systems (at MW scale) is possible considering the appropriate detail level; we adopted here a lumped approach for cells modeling as well as for other main components (blowers, humidification). All the interactions between components and the influence of operating conditions (load, temperature, reactants excess) are taken into account. A constant decay is also assumed for the FC, allowing to investigate performances trends during lifetime. Comparison with measurements from on-field data from similar plants yields errors around 1%, validating the approach and components modelling. Electric efficiency lost during lifetime (about 6% at EOL) is partially recovered as additional recovered heat. Most of the additional heat would be anyway lost to the environment in absence of a flexible operation of the industrial plant heat recovery loop, suggesting room for further integration between the chemical plant and the PEM plant. Anyway, it should be considered that a more integrated design is feasible for new plants, while is difficult in case of efficiency improvement actions on existing plants. In order to match the electricity requirements, an additional 12% hydrogen flow has to be fed to the plant at EOL. The model allows also investigating alternative layouts. For instance, hydrogen catalytic combustion without recirculation on anode side is a

possible solution, suggested by the current strategy of some chlor-alkali plants where excess hydrogen is burned for industrial steam production. Additional heat recovery in this case would allow a very good total efficiency (i.e. over 98%), but with lower electric efficiency (~30%); therefore, this solution is competitive only in case of high temperature steam requirement otherwise obtained with external combustion systems. In case of plants that already include the hydrogen boilers for steam generation, the PEM FC system could help valorizing the hydrogen byproduct by producing high value electricity as intermediate step in the process.

Acknowledgements

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