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Minimization of Energy Consumption for Chemicals Ultrapurification Processes

Ricardo Abejón*, Aurora Garea, Angel Irabien

Universidad de Cantabria, Departamento de Ingeniería Química y Química Inorgánica
Av. Los Castros s/n, 39005 Santander, Spain
abejonr@unican.es

Semiconductor industry requires ultrapure chemicals to manufacture microelectronic devices. Hydrogen peroxide is one of the most demanded chemical by the semiconductor industry and ultrapurification processes are needed to achieve the electronic grade requirements for this chemical. Among all the ultrapurification alternatives, reverse osmosis emerges as the most desirable option according to environmentally friendly criteria. Through modelling based on membrane transport equations and mass balances, different integrated reverse osmosis membrane cascades have been previously optimized. All the optimal solutions were characterized by the maximum allowed values for the applied pressures in the reverse osmosis stages, corresponding to the highest energy consumption and the lowest energy productivity (expressed as economic profit of the process for each unit of energy consumed). In this work, the energy productivity of the process was maximized and the optimal operation conditions were those with minimum applied pressures. However, under those conditions the membrane area required increased and the membrane productivity (expressed as economic profit of the process for each unit of membrane area employed) decreased. Therefore, multi-objective optimization was formulated to maximize simultaneously the productivities of both resources (energy and membranes).

1. Introduction

Semiconductor manufacturing involves a highly complex process and a great variety of high-purity chemicals are required for the different tasks. A typical silicon wafer might spend the equivalent of 2 days immersed in various liquids (specifically called wet chemicals) during the manufacturing process, so the importance of extremely low levels of impurities in these chemicals becomes critical, as trace metallic impurities on the surfaces of silicon wafers adversely affect the electrical characteristics of the silicon microdevices.

Aqueous hydrogen peroxide is among the most commonly used wet chemicals in semiconductor manufacturing. Semiconductor Equipment and Materials International (SEMI) is the global industry association serving the manufacturing supply chains for the microelectronic, display and photovoltaic industries. This entity develops the worldwide most respected technical standards in this manufacturing sector. Among all the topics regulated, some refer to wet chemicals and indicate the requirements to be fulfilled in order to be accepted as electronic grade chemicals. For the particular case of hydrogen peroxide, the SEMI C30-1110 Document is available (Semiconductor Equipment and Material International Association, 2010), where five different electronic grades are defined in function of the allowed maximum concentration of contaminant impurities (Table 1).

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Table 1: Impurity limits for electronic grade hydrogen peroxide according to SEMI standard

SEMI Grade	TOC limit	Anion limit range	Cation limit range
1	20 ppm	2000 - 5000 ppb	10 - 1000 ppb
2	20 ppm	200 - 400 ppb	5 - 10 ppb
3	20 ppm	200 - 400 ppb	1 ppb
4	10 ppm	30 ppb	0.1 ppb
5	10 ppm	30 ppb	0.01 ppb

Hydrogen peroxide is produced on an industrial scale by the anthraquinone oxidation process (Campos-Martin et al., 2006). Although commercial grades of hydrogen peroxide obtained by this process have been treated by traditional purification techniques (L-L extraction, adsorption, membrane technologies, distillation...) for lowering the impurity levels, these levels still exceed the limits of the electronic grades. Hence, ultrapurification processes are needed to achieve electronic grade requirements from standard grade product.

2. Ultrapurification of hydrogen peroxide by reverse osmosis

While technical viability of hydrogen peroxide ultrapurification is well solved as commercialization of the different electronic grades demonstrates, scientific papers describing the process fundamentals are scarce. Therefore, patents become a useful bibliographic source. As result of a bibliographical review over the last twenty years, more than 25 patents relative to purification of hydrogen peroxide can be found (Abejón et al., 2010). According to the patents, distillation, adsorption, ion exchange and membranes technologies, including reverse osmosis, are the most relevant techniques when electronic grade chemical is desired.

The requirement of inert columns made of fluorinated polymers (poor heat conductors) stresses the energy intensiveness of distillation when applied to hydrogen peroxide ultrapurification. The attained maximum efficiencies by adsorption are not comparable with results reachable by other alternatives and exhausted adsorbents imply waste production, either directly when substituted with fresh adsorbent or indirectly when regenerated (usually with toxic and hazardous regenerants). Despite the fact that ion exchange is the most mentioned ultrapurification technology, once again regeneration of exhausted resins implies waste streams and employment of hazardous chemicals.

Therefore, reverse osmosis can be considered as the most desirable technology according to environmentally friendly criteria: auxiliary chemicals are not needed and zero waste generation can be achieved since the retentate stream can be commercialized as non-electronic grade hydrogen peroxide for other industrial purposes.

The technical viability of multi-pass reverse osmosis processes without auxiliary techniques applied to the ultrapurification of technical grade hydrogen peroxide to electronic grade chemical has been demonstrated (Abejón el al., 2012a). A simulation model for the process was developed and the economic viability of integrated counter-current reverse osmosis cascades for industrial-scale ultrapurification installations was also demonstrated.

3. Optimization of reverse osmosis networks

The complete optimization of a reverse osmosis network has to include the optimal design of both individual modules and the network configuration. The problem of the design of reverse osmosis networks has been considered from the optimization techniques by the generation of the configurations and their optimization with mass and energy integration and multi-objective optimization, mainly for desalination units of seawater in order to minimize costs and energy consumption or to maximize permeate production and economic profit (Sassi and Mujtaba, 2011).

In most cases, reverse osmosis networks can only compete with alternative separation processes in terms of specific costs under some defined conditions. Therefore, optimising the specific operation costs in multi-stage filtration plants is a necessary objective for economic reasons (Noronha et al., 2002). Energy consumption is usually a major fraction of the total cost of the reverse osmosis networks since the specific energy consumption (energy consumption per volume of produced permeate) is significant in this type of membrane separations because of the high pressure requirements (Zhu et al., 2009). Therefore, research is needed to reduce the specific energy consumption in order to make these systems more affordable and competitive and considerable efforts have been made to reduce the specific energy consumption by enhancing the membrane transport properties and designing effective network configurations (Li, 2010).

An integrated counter-current reverse osmosis cascade can be considered as a particular case of a membrane network (Caus et al., 2009). Membrane cascades for ultrapurification have been subject of optimization, but only focused on the maximization of the economic profit or the minimization of the costs under different conditions and scenarios (Abejón et al., 2011, 2012c). The present work is orientated to the optimization of reverse osmosis cascades for hydrogen peroxide ultrapurification in order to minimize the energy consumption of the process.

4. Ultrapurification process modeling

The proposed simulation model for a n-stage membrane cascade (Figure 1) is based on overall and component mass balances [Eqs (1)-(4)] and the Kedem-Katchalsky equations for solvent [Eq. (5)] and solute [Eq. (6)] transport through reverse osmosis membranes (Abejón et al., 2012b):

$$P(i-1) + R(i+1) = F(i) \tag{1}$$

$$P(i-1)C_{P(i-1)}^{metal} + R(i+1)C_{R(i+1)}^{metal} = F(i)C_{F(i)}^{metal} \tag{2}$$

$$F(i) = P(i) + R(i) \tag{3}$$

$$F(i)\, C_{F(i)}^{metal} = P(i)C_{P(i)}^{metal} + R(i)C_{R(i)}^{metal} \tag{4}$$

$$J_{V(i)} = L_P^{'}\, \Delta P_{(i)} \tag{5}$$

$$R_{(i)}^{metal} = \frac{\sigma^{metal}\, J_{V(i)}}{J_{V(i)} + \omega^{'\, metal}} \tag{6}$$

A simple economic model based on revenues (sales of permeate product and valuable retentate by-product) and costs (sum of the capital and operation costs) to assess the economic profit of the process is proposed to evaluate the profitability of the process (Abejón et al., 2012b). The capital costs, attributable to membranes and the rest of installation, CC_{memb} and CC_{ins}, are based on the membrane area required; while the operation costs are itemized into raw materials, labour, energy, and maintenance costs, OC_{raw}, OC_{lab}, OC_{en}, OC_{m} :

$$Z = (P\, Y_{EG} + R1 Y_{by}) - (CC_{memb} + CC_{ins} + OC_{raw} + OC_{lab} + OC_{en} + OC_{m}) \tag{7}$$

$$CC_{memb} = \frac{Y_{memb} \sum A_i}{LT_{memb}} \tag{8}$$

$$OC_{en} = \frac{\sum (F(i)\, \Delta P_i)}{36 \eta} Y_{elec} \tag{9}$$

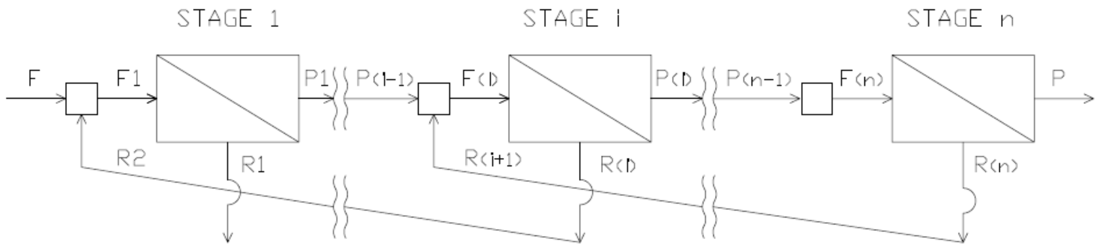

Figure 1: Schematic representation of n-stage membrane cascade with integration of retentate streams

5. Optimization problem formulation and case study

The optimization problem was formulated as a nonlinear programming (NLP) problem and GAMS software was selected as optimization tool to solve it using CONOPT3 solver. The optimum design parameters and operation conditions (recovery rates and applied pressures) that would maximize the energy productivity were obtained by this way. The energy productivity is defined as the ratio between the profit of the process and the energy consumption: $Z / (OC_{en} / Y_{elec})$.

For the case study, a two-stage ultrapurification installation (SEMI Grade 1 as product) was coupled to a manufacturing plant with a target annual production of 9000 tons of technical grade hydrogen peroxide. Table 2 shows the results of the optimization, including the optimal values for the recovery rates of both stages (defined as the percentage of the feed stream that leaves the stage as permeate stream) and the applied pressures. The optimal recovery rates are equal to 90 %, that is, the upper limit fixed for these design variables. On the other hand, the optimal applied pressures are limited by the lower bound of their defined range (10-40 bar).

When the obtained results are compared with the ones corresponding with an optimization problem targeted to maximize the economic profit of the process (Abejón et al., 2012b), the main difference can be found in the operation conditions. The maximum profit situation requires maximum applied pressures in contrast to the minimum applied pressures obtained for maximum energy productivity. Anyway, the profit of the process for energy minimization is 4% lower than the maximum profit case while the energy consumptions are reduced by 75 %. The economic drawback can be explained by the fact that maximum energy productivity can be only obtained by higher total membrane area in the system and the consequent reduction in the energy costs cannot compensate the increase in the cost terms related with the membranes (directly the capital costs attributable to membranes and indirectly the costs of the rest of the installation and maintenance).This way, it is obvious the existence of a counterbalance between the two main operative resources of the installation (energy and membrane area), since low consuming energy systems need high membrane investment and vice versa.

Table 2: Optimization results for maximum energy productivity

Variable	Optimal value
Energy productivity ($/kWh)	1672
Economic profit Z ($/d)	33,512
Recovery rates (%)	
Stage 1	90
Stage 2	90
Applied pressures (bar)	
Stage 1	10
Stage 2	10
Membrane area (m^2)	
Stage 1	56.3
Stage 2	50.7
Product stream P (m^3/d)	21.5
By-product stream R1 (m^3/d)	2.7

Table 3: Optimization results for maximum membrane productivity

Variable	Optimal value
Energy productivity ($/kWh)	3919
Economic profit Z ($/d)	34,928
Recovery rates (%)	
Stage 1	90
Stage 2	90
Applied pressures (bar)	
Stage 1	40
Stage 2	40
Membrane area (m^2)	
Stage 1	14.0
Stage 2	12.7
Product stream P (m^3/d)	21.5
By-product stream R1 (m^3/d)	2.7

Therefore, the membrane productivity was defined, in an equivalent way to the energy productivity, as the ratio between the profit of the process and the membrane investment: $Z / (CC_{memb} / Y_{memb})$. A new optimization problem was formulated in order to maximize the membrane productivity of the installation. The resulting configuration is the same obtained when the maximization of the economic profit was proposed, that is, maximum allowed values for the applied pressures (Table 3).
Once this new productivity has been defined, multi-objective optimization can be formulated to maximize simultaneously the productivities of both resources (energy and membranes). The multi-objective optimization is carried out by application of the epsilon constraint method. This method tackles multi-objective optimization problems by solving a series of single objective subproblems, where all but one objectives are transformed into constraints. (Bérubé et al., 2009). Figure 2 shows the resultant Pareto set of solutions for the two-stage installation obtained by bi-objective simultaneous optimization. A point in the Pareto frontier corresponds to the maximum feasible energy productivity for a fixed membrane productivity and vice versa (the maximum feasible membrane productivity for a fixed energy productivity). The lowest bound on the right side represents the maximum membrane productivity solution and in an analogous way, the highest point on the left side the maximum energy productivity.

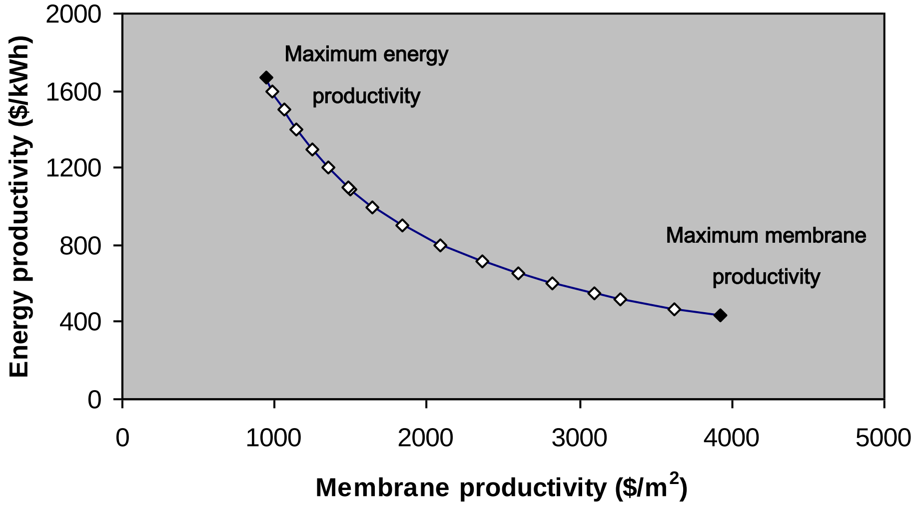

Figure 2: Pareto set of solutions for the two-stage (SEMI Grade 1 production) reverse osmosis system

6. Conclusions

This study develops a useful tool to estimate the maximum achievable energy productivity for a chemicals ultrapurification process by reverse osmosis. Minimization of energy consumption in such type of installations imply an increase of the total membrane area required by the system and, in fact, the process economy favours the configurations focused to maximization of membrane productivity instead of energy productivity. The multi-objective optimization of the process is able to represent as a Pareto frontier all the possible situations that simultaneously optimize both resources productivities.

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