



## Ultrapurification of hydrogen peroxide solution from ionic metals impurities to semiconductor grade by reverse osmosis

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### ARTICLE INFO

#### Article history:

Received 21 June 2010

Received in revised form

10 September 2010

Accepted 15 September 2010

#### Keywords:

Ultrapurification

Hydrogen peroxide

Reverse osmosis

High-purity chemicals

Metallic ion traces

### ABSTRACT

The present research is centred upon the application of reverse osmosis to the ultrapurification of aqueous hydrogen peroxide (35%, w/w). Semiconductor Equipment and Materials International (SEMI) organization develops the globally most respected standards to establish the quality requirements for the chemicals used in this sector; one of these standards, SEMI (30 is proposed for hydrogen peroxide. Electronic grade hydrogen peroxide accounts for sub-ppm metallic impurity levels (sub-ppb concentrations are required for the most exigent grades), so various elements present as impurities in technical grade hydrogen peroxide exceed the fixed limits. A preliminary experimental study was carried out with a laboratory-scale facility (flat-sheet membrane unit) with 6 different commercial reverse osmosis membranes in order to choose the most appropriate one for hydrogen peroxide ultrapurification. BE membrane (manufactured by Woongjin (hemical) was selected for further viability study because of its higher permeate flux ( $1.95 \times 10^{-5} \text{ m}^3/\text{m}^2 \text{ s}$  at 40 bar) and metal rejections values (ranging from 0.825 for B to 0.961 for (u). The Kedem-Katchalsky model resulted as the most representative for characterizing the selected membrane behaviour as it achieved a percentage of overall variation explained upper than 94%.

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### 1. Introduction

Hydrogen peroxide is considered a key chemical for the semiconductor industry. The preparation of semiconductor materials and the manufacture of printed circuit boards employ aqueous hydrogen peroxide solutions for cleaning silicon wafers, removing photoresists or etching copper on printed circuit boards. Most usual cleaning baths for silicon wafer surface cleaning (S(1, S(2 or SPM) include hydrogen peroxide in their formulations [1]. The said baths remove particulate, organic and metallic pollutants from silicon surface, avoiding electric inoperativeness and decreased minority carrier lifetime caused by pollution [2]. In order to avoid contamination because of the bath itself, extremely high levels of purity are required for all the components, so strict control about impurity concentration in these chemicals becomes necessary.

Semiconductor Equipment and Materials International (SEMI) organization is the global industry association serving the manufacturing supply chains for the microelectronic, display and photovoltaic industries. This organization facilitates the development of the globally most respected technical standards in this field. Among all the topics regulated, some refer to process chemicals and indicate the requirements to be fulfilled in order to be accepted as

electronic chemicals. For the particular case of hydrogen peroxide, the SEMI (30 document is applicable [3], where six different electronic grades are defined in function of the allowed maximum pollutant concentration, as can be seen in Table 1.

Although typically commercialized grades of aqueous hydrogen peroxide solutions have been treated by traditional purification techniques (L-L extraction, adsorption, membrane technologies, distillation...) for lowering impurity levels [4], hydrogen peroxide for use in electronics demands very low content of pollutants. Hence, ultrapurification processes are needed to achieve electronic grade requirements from standard grade product.

While technical viability of hydrogen peroxide ultrapurification is well solved as commercialization of the different electronic grades demonstrates, scientific papers hinting process fundamentals cannot be found. Therefore, patents become the only available bibliographic source.

As result of the bibliographical review over the last twenty years, more than 25 patents relative to purification of hydrogen peroxide have been found. According to the noticed references, distillation, adsorption, ion exchange and membranes technologies are the most relevant techniques when electronic grade chemical is desired.

Whichever technology is selected, prevention measures to avoid as much as possible contamination from environment and materials are essentials for successful results. The use of cleanroom is a solution for the maintenance of low levels of environmental

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## Nomenclature

A	solvent permeability coefficient in the SO model (m/s bar)
A <sup>I</sup>	solvent permeability coefficient in the SOI model (kg/m <sup>2</sup> s bar)
C <sub>F</sub>	solute feed concentration (mol/m <sup>3</sup> )
C <sub>P</sub>	solute permeate concentration (mol/m <sup>3</sup> )
C <sub>R</sub>	solute reject concentration (mol/m <sup>3</sup> )
(C <sub>S</sub> ) <sub>ln</sub>	logarithmic average solute concentration across the membrane (mol/m <sup>3</sup> )
J <sub>S</sub>	flux of the solute due to the gradient of chemical potential (mol/m <sup>2</sup> s)
J <sub>V</sub>	permeate volume flux (m/s)
J <sub>W</sub>	flux of the solvent due to the gradient of chemical potential (m/s)
K <sub>1</sub>	membrane transport coefficient in SO model (m/s)
K <sub>2</sub>	membrane transport coefficient in SOI model (kg/m <sup>2</sup> s)
K <sub>3</sub>	coupling coefficient due to the membrane imperfections (kg/m <sup>2</sup> s bar)
K <sub>A</sub>	dissociation constant (mol/l)
L <sub>P</sub>	hydraulic permeability coefficient (m/s bar)
N <sub>S</sub>	total solute flux (kg/m <sup>2</sup> s)
N <sub>W</sub>	total solvent flux (kg/m <sup>2</sup> s)
P <sub>h</sub>	local hydraulic permeability in the membrane (m <sup>2</sup> /s bar)
P <sub>M</sub>	local solute permeability (m/s)
R	rejection coefficient
R	gas constant (bar m <sup>3</sup> /K mol)
T	temperature (K)
x <sub>F</sub>	hydrogen peroxide feed concentration (mol/l)
x <sub>P</sub>	hydrogen peroxide permeate concentration (mol/l)
x <sub>P</sub>	solute mass fraction on the permeate
x <sub>S</sub>	solute mass fraction on the upstream side of the membrane
x <sub>W</sub>	solvent mass fraction on the upstream side of the membrane
Greek symbols	
$\tilde{\omega}$	=J <sub>V</sub> (1 - $\alpha$ )/P <sub>M</sub> , Spiegler-Kedem parameter
$\Delta P$	pressure difference across the membrane (bar)
$\Delta x$	total membrane thickness (m)
$\Delta P$	osmotic pressure difference across the membrane (bar)
$\Delta C_S$	difference between the concentration of solute on either side of the membrane (mol/m <sup>3</sup> )
$\nu$	stoichiometric coefficient
$\alpha$	reflection coefficient
$\omega$	coefficient of solute permeability (mol/m <sup>2</sup> s bar)
$\omega^I$	modified coefficient of solute permeability (m/s)

pollutants. On the other hand, selection of adequate equipment materials is crucial in order to minimize contamination and risk of accidents [5].

The employment of distillation for purifying hydrogen peroxide is oriented to organic pollutant diminution in greater extension than to inorganic impurities [6–8]. Requirements for the least strict electronic grades can be satisfied if metal concentrations in the feed solution do not exceed the low ppm level. The requirement of inert columns made of fluorinated polymers (poor heat conductors) stresses the energy intensiveness of this technique.

Very different adsorbents have been tested with aqueous hydrogen peroxide solutions: stannic oxide [9], zirconium phosphate

Table 1

Concentration and impurity limits for electronic grade hydrogen peroxide according to SEMI standards.

Grade	[H <sub>2</sub> O <sub>2</sub> ]	[Most exigent anion]	[Most exigent cation]
1	30–32%	<2 ppm	<10 ppb
2	30–32%	<200 ppb	<5 ppb
3	30–32%	<200 ppb	<1 ppb
4	30–32%	<30 ppb	<100 ppt
5	30–32%	<30 ppb	<10 ppt
VLSI	30–32% or 34–36%	<500 ppb	<10 ppt

[10] and various non-ionic resins [11,12]. Both organic and inorganic pollutants can be removed from the chemical, but attained maximum efficiencies (below 80%) are not comparable with results reachable by ion exchange or membranes technologies (above 99%). Exhausted adsorbents imply waste production, either directly when substituted with fresh adsorbent or indirectly when regenerated. Besides, in the latter case, toxic and hazardous chemicals could be needed as regenerants.

Ion exchange is the most mentioned ultrapurification technology, covering a wide range of conditions [13–18]. Multiple-pass processes are common when strictest electronic grades are desired. Special caution should be recommended when ion exchange resins contacts with hydrogen peroxide solutions, since hydroxyl groups as functional moieties in anionic resins or cationic resins highly charged with transition metallic ions can catalyze violently hydrogen peroxide decomposition. Again, regeneration of exhausted resins implies waste streams and employment of hazardous chemicals (strong acids and bases).

Membrane technologies appear as adequate options for ultrapurifying aqueous hydrogen peroxide. Reverse osmosis is expected to be the most appropriate membrane technique for elimination of metallic traces and other impurities [19–22] and ultrafiltration has also reported its potentiality when employed jointly with chelating chemicals [23]. These chelating agents sequester metallic ions from feed solution and keep these pollutants away from permeate, since non-permeant chelators must be chosen. Polyamides, polypiperazinamides, polyacronitriles, polysulphones and fluoropolymers are recommended materials for the membranes, although all examples illustrating patents resort to polyamide membranes.

Among all the ultrapurification alternatives, reverse osmosis emerges as the most desirable technology according to environmentally friendly criteria. Auxiliary chemicals are not needed and virtual zero waste generation is achieved (only damaged membranes become residue when replaced after lifetime), since the retentate stream can be recirculated or commercialized as non-electronic grade for other industrial uses. In addition, a great percentage of the energy supplied for increasing the pressure of the feed stream can be recovered from the retentate by different systems [24].

Taking into account the lack of published papers concerning to the fundamentals of membrane technologies applied to the ultrapurification of aqueous hydrogen peroxide, the present work is focused on this objective with the study of reverse osmosis to the further purification of industrial grade hydrogen peroxide solutions in order to achieve electronic specifications. The ionic metal impurities rejections and permeate flux were evaluated, paying special attention to the assessment of the permeation parameters of the membranes.

## 2. Experimental

### 2.1.

#### Chemicals

Interox ST-35 hydrogen peroxide H<sub>2</sub>O<sub>2</sub> was kindly supplied by Solvay Quimica Torrelavega as raw material for the

Table 2  
Main characteristics of the flat-sheet membranes from the supplier.

Designation	Manufacturer	Material	Permeate flow (m <sup>3</sup> /m <sup>2</sup> day)	Rejection (%)
AD	GE Osmonics	Polyamide	0.61	99.5
CE	GE Osmonics	Cellulose acetate	0.96	97
BE	Woongjin Chemical	Polyamide	1.12	99.5
CRM	Woongjin Chemical	Polyamide	0.92	99.5
SW30HR	Filmtec	Polyamide	0.66	99.7
UTC 80 B	Toray	Polyamide	0.57	99.75

ultrapurification process. It is an aqueous 35% (w/w) hydrogen peroxide solution without any type of stabilizers. Preliminary membrane characterization was performed with ultrapure and doped water. Ultrapure water (18.2 MQ cm resistivity) was obtained by a Milli-Q Element (Millipore). Doped water was prepared by adding both sodium chloride NaCl (PA-ACS-ISO from Panreac) as sodium source and aluminium chloride anhydrous AlCl<sub>3</sub> (98% PS from Panreac) as aluminium source to ultrapure water in order to achieve metal concentrations similar to those in Interlox ST-35 hydrogen peroxide. Na and Al were selected for doping the water because these components are the major impurities in Interlox ST-35 technical grade hydrogen peroxide.

## 2.2. Installation and reverse osmosis membranes

A lab-scale cross-flow flat-sheet configuration test unit SEPA CF II from Osmonics was purchased for reverse osmosis experiments. The membrane cell can accommodate any 19 cm × 14 cm flat-sheet membranes, resulting 140 cm<sup>2</sup> of effective membrane area. Diverse commercially available polymeric flat sheet RO membranes from different manufacturers were preselected for this ultrapurification study. After revision of the patents which employ reverse osmosis [19–22], it was clear that polyamide was the preferred membrane material, so manufacturers were contacted for request of their most appropriate polyamide membrane for the present application. It was also suggested by a manufacturer to include a cellulose acetate membrane among the preselected ones because of its lower susceptibility to degradation by oxidizing agents such as chlorine, hydrogen peroxide or ozone. Information about the preselected membranes is summarized in Table 2.

The membrane cell was fed by a Hydra-Cell G-03 (Wanner Engineering) diaphragm pump equipped with digital variable frequency drive to adjust flowrate. Materials of all the components were chosen to maximize compatibility with concentrated hydrogen peroxide. HP PFA tubing was selected for all the installation except for the tube joining the pump and the cell (which worked under pressure), where a PTFE tube enhanced with braided stainless steel has been preferred; and the feed tank, which is made of polyethylene (PE). A simple scheme of the entire installation is showed in Fig. 1.

To minimize as possible the contamination by metals coming from the laboratory environment, the most critical components of the ultrapurification system were located under cleanroom condi-

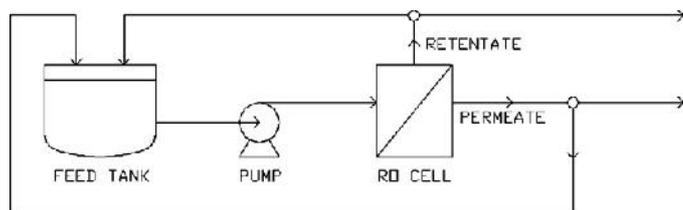


Fig. 1. General schematic of the experimental installation for ultrapurification by reverse osmosis.

tions. A Bio-48-M vertical laminar flow cabinet (Faster) guaranteed ISO Class 5 atmosphere.

## 2.3. Reverse osmosis experiments

Different tests were carried out with ultrapure and doped waters and aqueous hydrogen peroxide. The feed tank (220 l max. volume) was filled with 180 l of the corresponding fluid and a constant feed flow of 3.4 l/min was maintained (corresponding to a cross-flow velocity of 0.5 m/s in the membrane cell, value representative for cross-flow velocities in spiral-wound elements in full-scale RO plants [25]). The different applied pressures were adjusted by the high-pressure concentrate control valve supplied with the membrane cell. The experiments were performed at room temperature (temperature control was not needed as the temperature rise of the chemical in the feed tank during the operation time was negligible taking into account the large volume of this tank) and in total recycling mode; that is, with permeate and retentate streams being continuously recycled to the reservoir vessel, which assured constant characteristics in the feed stream during the whole experiment.

As a first step prior to the experiments, membranes were put in ultrapure water to soak at least 12 h before the start of the experiments. Then, each membrane is flushed with the feed liquid for 5 h at a feed pressure of 40 bar to ensure compaction of the membranes. In the experiments, the applied pressure in the system was varied between 10 and 40 bar. After 15 min of operation under each pressure, time enough for reaching steady state conditions, the permeate flux was measured and, for the cases of doped water and hydrogen peroxide, samples for determining metal concentrations were taken. Triplicate flux measures and samples were performed with 10 min intervals among them. All samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7500ce ICP-MS system for the most exigent SEMI Grade defined metals. A special sample introduction system (ESI Upgrade Kit) made of PFA for resistance to hydrogen peroxide was necessary. Determination of hydrogen peroxide concentration was carried out also for triplicate following the procedure of the supplier [26].

## 3. Results and discussion

### 3.1. Characterization of technical grade hydrogen peroxide

The characterization of technical grade H<sub>2</sub>O<sub>2</sub> 35% (w/w) by ICP-MS for the 21 metals required in SEMI C30 most exigent grade is showed in Table 3. It can be observed a broad range of concentrations of impurities, ranging from more than 20,000 ppb of Na to concentrations below 1 ppb [27].

The technical grade H<sub>2</sub>O<sub>2</sub> exceeds the fixed limits of the less stringent electronic grade (Grade 1) for 3 metals: Na (1000 ppb), Al (1000 ppb) and Fe (100 ppb). When compared with a more demanding grade as Grade 3, the number of elements that fail the specifications (1 ppb for all the metals) increase to 13: B, Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn.

Table 3  
Characterization of technical grade H<sub>2</sub>O<sub>2</sub> by ICP-MS.

	Concentration (ppb)	Element	Concentration (ppb)	Element	Concentration (ppb)
Li	<1	Ti	72	Zn	13
B	6	v	<1	As	<1
Na	20895	Cr	48	Cd	<1
Mg	17	Mn	3	Sn	<1
Al	1067	Fe	161	Sb	<1
K	36	Ni	24	Ba	<1
Ca	89	Cu	2	Pb	<1

### 3.2. Membranes performance with ultrapure and doped water

The preselected membranes were used in preliminary experiments with ultrapure and doped water in order to compare them and choose the most appropriate one for the ultrapurification process. Ultrapure water experiments were useful to establish the dependence of the permeate flux ( $J_v$ ) on the applied pressure ( $\Delta p$ ). As it is showed in Fig. 2 the water fluxes increased with increasing pressures, obtaining a linear relationship with high correlation coefficients. The linear evolution of fluxes shows that Darcy's law is verified. The slope of this straight line is the solvent permeability  $L_p$  which is defined as  $J_v$  divided by  $\Delta p$  [28].

Both membranes manufactured by Woongjin Chemical (BE and CRM) stood out from the rest when their permeate productions were compared. The other polyamide based membranes (UTC 80 B, AD and SW30HR) showed a very similar  $L_p$  value, but it was not comparable with that of the BE membrane, as it was more than double. The cellulose acetate membrane CE permeability was intermediate between Woongjin Chemical membranes and the rest of polyamide membranes.

When experiments with doped water (15,000 ppb of Na and 1,400 ppb of Al) were carried out, the same linear relationship was observed and slopes could be calculated. The values of solvent permeability obtained for ultrapure and doped water are quite similar for both matrixes as shown in Table 4 (this coincidence between both values was expected as osmotic pressure related to these low levels of solute concentrations can be considered negligible), where some information about the solvent permeability values reported in the literature for other flat-sheet reverse osmosis membranes is also included [29–32]. The experiments with doped water were also suitable for the determination of the efficiency of the preselected membranes for metal removal at low ppm concentrations. Their rejection coefficients ( $R$ ) were defined by the equation:

$$R = \frac{C_F - C_P}{C_F} \quad (1)$$

where  $C_F$  and  $C_P$  represent the metal concentrations measured in the feed and permeate streams, respectively. These coefficients for

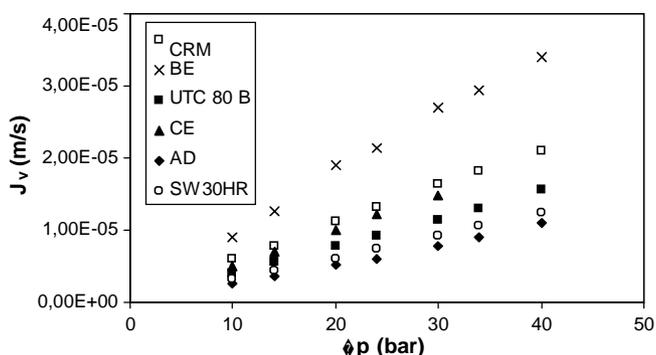


Fig. 2. Determination of the solvent permeability of the membranes for ultrapure water.

Table 4  
Mean membrane solvent permeability values from ultrapure and doped water experiments and comparison with literature References.

Membrane	Solvent permeability, $L_p$ (m/s bar)
AD	$2.86 \pm 0.31 \times 10^{-7}$
SW30HR	$3.11 \pm 0.01 \times 10^{-7}$
UTC 80 B	$3.83 \pm 0.06 \times 10^{-7}$
CE	$5.04 \pm 0.06 \times 10^{-7}$
CRM	$5.64 \pm 0.34 \times 10^{-7}$
BE	$8.29 \pm 0.71 \times 10^{-7}$
Other referenced membranes	
UTC 80 AB [29]	$2.33 \times 10^{-7}$
UTC 80 AB [30]	$2.62 \times 10^{-7}$
LFC1 [31]	$8.20 \times 10^{-7}$
TFC-HR [32]	$9.72 \times 10^{-7}$

Na and Al were determined in the doped water experiments performed with the membranes and the results obtained are plot in Fig. 3.

BE membrane reached the greatest values of rejection coefficients: 0.992 and 0.999 for sodium and aluminium respectively. CRM membrane performance was very close to BE (0.990 and 0.998). As occurred with permeabilities, Woongjin Chemical membranes obtained rejection coefficients were higher than those of the other three polyamide membranes. These three membranes showed again a very similar behaviour except for the UTC 80 B lower values for aluminium. CE was the least effective membrane for sodium removal but exceeded UTC 80 B for aluminium.

As a conclusion of the preliminary experiments carried out with ultrapure and doped with sodium and aluminium water, BE was considered as the most promising membrane for hydrogen peroxide ultrapurification, as showed the highest values for both solvent permeability and rejection coefficients [33].

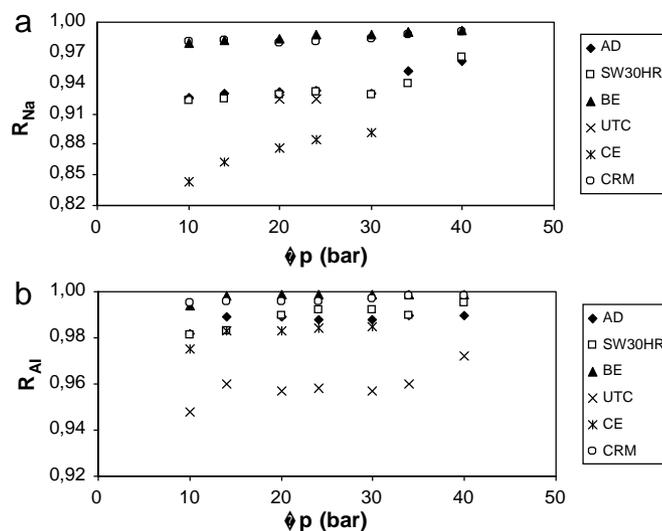


Fig. 3. Influence of the operating pressure on sodium (a) and aluminium (b) rejection coefficients for doped ultrapure water.

### 3.3. Ultrapurification of commercial grade hydrogen peroxide

#### 3.3.1. Permeation of hydrogen peroxide

The ion exclusion model can be considered for a first approximation to assess the permeation of hydrogen peroxide through reverse osmosis membranes. This model has been applied for estimating permeation of weakly dissociated compounds in ultrapurification processes by membranes technology [34]. The following assumptions are made in its derivation:

- All ions are excluded by the membrane (double layer effect).
- All species in molecular form permeate the membrane completely.
- Perfect mixing conditions prevail on the retentate and permeate sides of the membrane.
- Concentration polarization is ignored.

The final equation for estimating the permeate concentration ( $x_p$ ) from the feed concentration ( $x_f$ ) is:

$$x_p = x_f - \frac{K_A \cdot x_f}{K_A(x_f - K_A \cdot x_p)} \quad (2)$$

where  $K_A$  is the dissociation constant ( $K_A = 1.78 \times 10^{-12}$  M for the particular case of hydrogen peroxide). When the feed concentration is 35% (w/w) (corresponding to  $x_f = 10.3$  M), the rejection coefficient became negligible ( $R < 10^{-6}$ ). This means no theoretical dilution of aqueous hydrogen peroxide solutions when forced to permeate through reverse osmosis membranes. Experimental determination of hydrogen peroxide concentration in both feed and permeate streams confirmed the hypothesis as showed in Fig. 4, so the validity of reverse osmosis for aqueous hydrogen peroxide solutions without dilution or concentration effects was asserted.

The variation of the experimental permeate flux,  $J_v$ , with the increase in the applied pressure for both ultrapure water and 35% hydrogen peroxide is showed in Fig. 5. The linear relationship with high correlation coefficient was also observed for the hydrogen peroxide case and a  $L_p$  value of  $4.92 \times 10^{-7}$  was calculated from the slope, which entailed a decrease of 44% in comparison with ultrapure water. The  $L_p$  parameter can be interpreted based on the Hagen-Poiseuille flow and an inversely proportional relationship between  $L_p$  and the viscosity of the solution is obtained [35]. The values of viscosity of ultrapure water and 35% hydrogen peroxide at 20 °C are 1.00 and 1.11 mPa·s respectively [4], so a decrease of only about 10% can be explained in terms of viscosity variation of the liquid phase. Complex chemical interactions deserving of further investigation between 35% hydrogen peroxide and the membrane could explain the drop of permeate production.

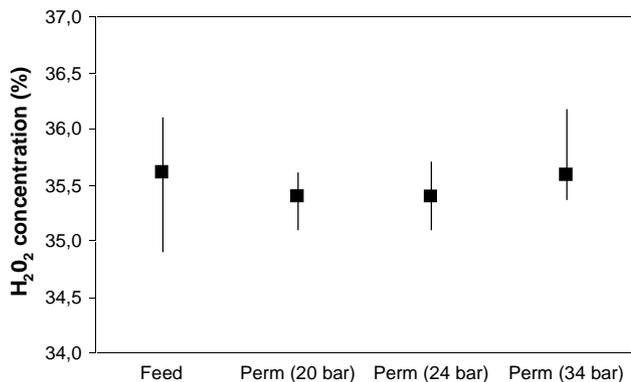


Fig. 4. Hydrogen peroxide concentration on feed and BE membrane permeate streams (maximum, medium and minimum values are plotted)

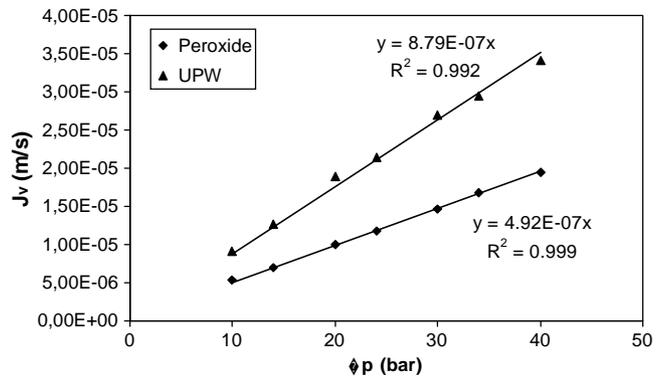


Fig. 5. Comparison of BE membrane solvent permeability for ultrapure water (UPW) and 35% H<sub>2</sub>O<sub>2</sub> (Peroxide).

Experimental tests were designed to investigate the ability of the selected membrane to withstand the highly oxidative environment of H<sub>2</sub>O<sub>2</sub>. Fresh samples of the BE membrane (without previous exposition to H<sub>2</sub>O<sub>2</sub> and designed as Membrane2 and Membrane3) were subjected to 8-hours lasting experiments during several consecutive days until total operation times of at least 64 hours were completed. The applied pressure was maintained at 40 bar except for the characterization intervals when the influence of this operation variable upon permeate flux and metal rejections was studied (8 regularly spaced over time characterization intervals of 2 hours each were fixed).

The evolution of the Membrane2 permeate production through the test when operating at 40 bar is shown in Fig. 6 and a very stable behaviour can be observed. The influence of applied pressure upon permeate flux of the different membrane samples is depicted in Fig. 7: the results of 3 characterization intervals for Membrane2 and a single result for Membrane3 were chosen for representing the performance during the experiment. The permeate flux maintained again a constant performance, as proved by the superposition of the data from different intervals. An assessed standard deviation of 3.17% for the Membrane2 permeability coefficient  $L_p$  confirmed the flux stability.

When compared with the sample used during the preliminary experiments (designed as Membrane1 in Fig. 7), the Membranes 2 and 3 were noted for its slightly lower permeate flux. In terms of  $L_p$  values, this difference is below 5% in the case of Membrane3 ( $L_p = 4.68 \times 10^{-7}$  mls bar) and is lesser than 22% for Membrane2 ( $L_p = 3.86 \times 10^{-7}$  mls bar) and the discrepancy can be explained by the intrinsic variability among samples of the reverse osmosis membranes. Woongjin Chemical, the manufacturer of BE membrane, informs about this small uncertainty as permeate flow rate

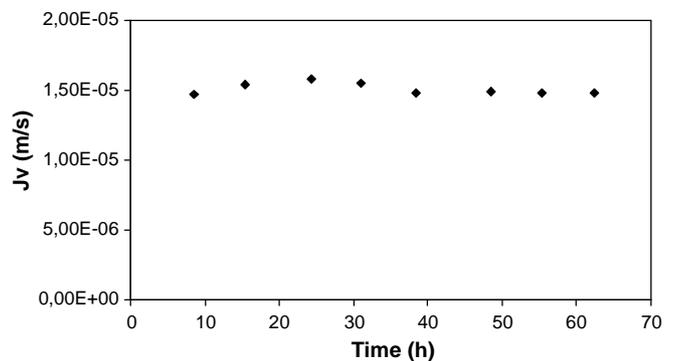


Fig. 6. Measured permeate fluxes through the hydrogen peroxide ultrapurification process by Membrane2 sample at 40 bar.

Table 5  
Metal concentrations on BE membrane permeate and corresponding rejection coefficients operating at 40 bar.

	Concentration (ppb)									
	B	Na	Al	Ti	Cr	Mn	Fe	Ni	Cu	Zn
Feed	6	>20000	>1000	72	48	3	161	24	2	13
Permeate (at 40 bar)	1.0	1565	87	6.7	4.6	0.3	19	2.2	0.1	1.0
Rejection coefficients (R)	0.825	0.925	0.919	0.906	0.903	0.912	0.883	0.909	0.961	0.920

for each element may vary but will be no more than 10% below the specified value [36], but there is no notice about the percentage that can typically exceeds the specification. On the other hand, another membrane manufacturer such as Filmtec accepts 15% of uncertainty over the permeate flux both by excess or defect [37]. These margins can accommodate relative differences greater than 25% between the maximum and minimum values of the range, so the variability found in this experimental case lies within the expected interval.

### 3.3.2. Rejection of metallic components

The concentrations of metals in the permeated hydrogen peroxide stream obtained with the maximum tested applied pressure (40 bar) are shown in Table 5, also including the metal rejection coefficients. High rejections were found for all the studied elements, with values around 0.9 except for the case of boron, which reached a value of 0.825. As occurred with ultrapure water, better rejections were obtained at higher applied pressures and quite similar performance could be observed for whichever chosen metal but boron, with no discrimination because of atomic mass, ionic charge or feed concentration. The rejection coefficients corresponding to the characterizations for Membrane2 during the 64 hours lasted experiment are tabulated (Table 6). Highly stable values were obtained for all the metals through the tested time. Further investigation is planned in order to study the membrane behaviour for longer time periods (more than 64 hours) in both permeate production and rejection terms.

The permeated hydrogen peroxide solution comply with SEMI Grade 1 requirements for all the metals but sodium (1565 ppm is above the 1000 ppm fixed limit). Based on a value of rejection coefficient of 0.9 as representative of the metal rejections, and taking

into account the requirements of metal traces in electronic grades of hydrogen peroxide (SEMI C30, Table 1), an estimation of the multistage membrane process was calculated based on the reverse osmosis results: 2 stages required for Grade 1 quality, 4 stages for Grade 2, and 5 stages for Grade 3, which is the aim of further experimental work in the H<sub>2</sub>O<sub>2</sub> ultrapurification: multistage operation for flat membranes and spiral-wound configuration in module for

intensification [38] and integrated reverse osmosis membrane cascades [39].

### 3.4. Transport equations

Four frequent reverse osmosis models [40] that relate permeate fluxes and rejection coefficients with applied pressure were chosen as approximations to represent the behaviour of the hydrogen peroxide ultrapurification process:

Solution-Oiffusion (SO) model, two parameters (A, K<sub>1</sub>)

$$J_W = A(\phi P - \phi^{\sim}) \quad (3)$$

$$J_S = K_1 (C_R - C_P) \quad (4)$$

$$\frac{1}{R} = 1 + \frac{K_1}{J_W} \quad (5)$$

Solution-Oiffusion-Imperfections (SOI) model, three parameters (A<sup>I</sup>, K<sub>2</sub>, K<sub>3</sub>)

$$N_W = A^I(\phi P - \phi^{\sim}) + K_3 \phi P X_W \quad (6)$$

$$N_S = K_2 (X_R - X_P) + K_3 \phi P X_R \quad (7)$$

Spiegler-Kedem (SK) model, three parameters (p<sub>n</sub> l<sub>0</sub>x, a, P<sub>M</sub>)

$$J_V = \frac{P_h}{\phi X} (\phi P - a \phi^{\sim}) \quad (8)$$

$$R = \frac{a(e^{-1} - 1)}{e - a} \quad (9)$$

$$\begin{aligned} \sim J &= \frac{1}{a} \\ &= v \frac{1}{P_M} \end{aligned} \quad (10)$$

Kedem-Katchalsky (KK) model, three parameters (L<sub>p</sub>, ω<sup>I</sup>, a)

$$J_V = L_p(\phi P - a \phi^{\sim}) \quad (11)$$

$$J_S = \omega \phi^{\sim} + (1 - a) J_V (C_S)_h \quad (12)$$

$$\frac{1}{R} = \frac{1}{a} + \frac{\omega^I}{a} \frac{1}{J_V} \quad (13)$$

$$\omega^I = \omega v R T \quad (14)$$

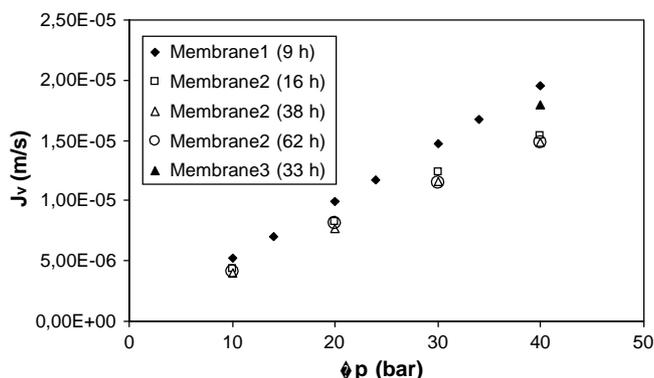


Fig. 7. Evolution of permeated hydrogen peroxide flux at different times for the different BE membrane samples.

Table 6  
Calculated rejection coefficients for Membrane2 (mean values ± experimental standard deviation calculated from samples taken during operation up to 64 h).

Element	Rejections coefficients (R)			
	ϕ P (bar)			
	10	20	30	40
B	0.504 ± 0.010	0.663 ± 0.024	0.725 ± 0.024	0.769 ± 0.008
Na	0.930 ± 0.024	0.954 ± 0.012	0.960 ± 0.007	0.966 ± 0.005
Al	0.973 ± 0.004	0.979 ± 0.002	0.979 ± 0.003	0.981 ± 0.004
Ti	0.968 ± 0.005	0.977 ± 0.003	0.978 ± 0.005	0.980 ± 0.006
Cr	0.942 ± 0.013	0.962 ± 0.005	0.967 ± 0.006	0.971 ± 0.007
Mn	0.899 ± 0.015	0.939 ± 0.008	0.948 ± 0.006	0.955 ± 0.009
Fe	0.906 ± 0.023	0.936 ± 0.016	0.940 ± 0.025	0.952 ± 0.021
Ni	0.926 ± 0.007	0.949 ± 0.007	0.951 ± 0.005	0.955 ± 0.005
Cu	0.900 ± 0.057	0.951 ± 0.012	0.961 ± 0.013	0.972 ± 0.010
Zn	0.852 ± 0.059	0.912 ± 0.045	0.928 ± 0.020	0.954 ± 0.017

Table 7  
Evaluation of the fitting of the experimental data by the proposed osmosis reverse models.

Model	SD	SDI	KK	SK
Percentage of overall variation explained (%)	79.0	88.8	94.4	94.1

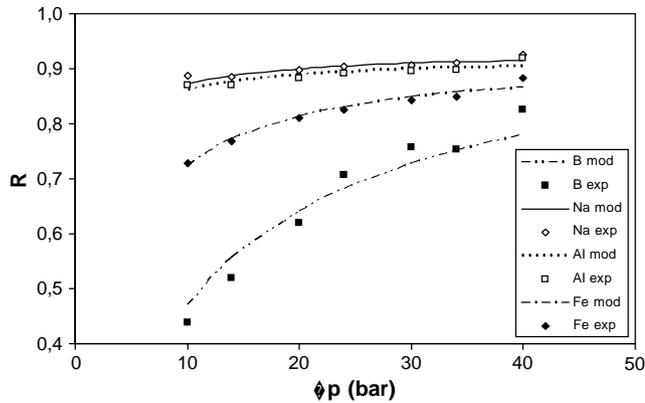


Fig. 8. Kedem-Katchalsky model applied to the experimental rejection coefficients of the main metallic impurities.

With the experimentally obtained values for permeate flux ( $I_v$ ) and metal rejections ( $R$ ) as functions of the applied pressure, the estimation of the parameters in these models was performed by a software tool (Aspen Custom Modeler). The osmotic pressure related term in the equations describing the solvent flux was considered as negligible (as suggested by the agreement between the values of solvent permeability for ultrapure and doped water) for all the models. The agreement of the models to the experimental data was quantified as the percentage of variation explained for the overall system. As reported in Table 7, best results were obtained with the Kedem-Katchalsky model, which obtained parameters are summarized in Table 8. In the pressure operation range, the model adequately describes the experimental data permeate flux and metal rejections (see Fig. 8).

Related to the transport parameters in the Kedem-Katchalsky model, Eqs. (11)-(14), three practical parameters are required to characterize each membrane + solution system:  $L_p$ , is the hydraulic permeability of the membrane;  $\omega$ , is called the solute mobility (or solute permeability); and  $\alpha$ , the reflection coefficient. The parameters  $L_p$  and  $\omega$  depend strongly on the thickness of the selective membrane and correlations between the practical parameters in order to compare different membranes are valid only when the results are normalized to layers of the same thickness. Moreover,  $\alpha$  and  $\omega$  depend strongly on the nature of each solute and they may be used to relate the ability of the separation respect to the solute or solutes (also expressed in the values of rejection coefficients,  $R$ ).

Table 8  
Assessment of the Kedem-Katchalsky model parameters: transports coefficients  $\omega^l$ ,  $\alpha$  and  $L_p$  for both hydrogen peroxide solution and doped ultrapure water.

	B	Na	Al	Ti	Cr	Mn	Fe	Ni	Cu	Zn
Hydrogen peroxide										
$\omega^l$ (m/s)	$5.58 \times 10^{-6}$	$2.60 \times 10^{-7}$	$3.38 \times 10^{-7}$	$5.11 \times 10^{-7}$	$7.19 \times 10^{-7}$	$2.50 \times 10^{-6}$	$1.40 \times 10^{-6}$	$4.03 \times 10^{-7}$	$1.17 \times 10^{-6}$	$1.53 \times 10^{-6}$
$\alpha$	1.000	0.926	0.920	0.917	0.925	1.000	0.928	0.920	1.000	0.964
$L_p$ (m/s bar)	$4.92 \times 10^{-7}$									
Percentage of overall variation explained (%) = 94.4										
Doped ultrapure water										
$\omega^l$ (m/s)		$1.36 \times 10^{-7}$	$3.15 \times 10^{-8}$							
$\alpha$		0.995	1.000							
$L_p$ (m/s bar)	$7.79 \times 10^{-7}$									
Percentage of overall variation explained (%) = 89.4										

Table 9  
Percentage contribution of the diffusive term to the total solute fluxes.

$\Delta P$	Diffusive contribution to total solute flux (%)									
	Element									
	B	Na	Al	Ti	Cr	Mn	Fe	Ni	Cu	Zn
10	100	59	62	68	75	100	83	65	100	92
14	100	52	55	62	71	100	80	59	100	90
20	100	45	48	55	66	100	76	52	100	89
24	100	41	44	52	63	100	74	49	100	88
30	100	36	39	47	58	100	71	43	100	85
34	100	34	37	45	55	100	69	40	100	84
40	100	32	35	43	53	100	68	38	100	85

The physical meaning of  $\omega$  can be clearly seen by applying Eq. (12) to a situation in which  $I_v$  is zero or no net volume flux. Keeping in mind the van't Hoff equation for the osmotic pressure of an ideal solution ( $\pi = vRTc_S$ ) and setting  $I_v$  equal to zero in Eq. (12) gives

$$(J_s)_{I_v=0} = v\omega RT \Delta c_S \tag{15}$$

where  $\Delta c_S$  is the difference between the concentration of solute on either side of the membrane.

Comparing Eq. (15) with Fick's law of diffusion, it is seen that  $\omega$  gives a measure of the diffusion mobility of each solute across the membrane.

Eq. (13), which relates the rejection coefficient of each solute,  $R$ , to the transport parameters can be rearranged as

$$R = \frac{\alpha J_v}{J_v + \omega^l} \tag{16}$$

showing that the rejection increases with increasing solution flux and reaches a limiting value  $\alpha$  at infinitely high  $I_v$ . As the diffusive flux of the solutes can be neglected in the range of high  $I_v$  (operation at high pressures), the reflection coefficient  $\alpha$  is a characteristic of the convective transport of the each solute; a value of 1 means that no transport by convection takes place at all. This may be the case for ideal RO membranes where the membranes have dense structure and no pores are available for convective transport.

As can be seen in Eq. (12), also expressed as follows

$$J_s = \omega^l \Delta c_S + (1 - \alpha) I_v (C_S)_{in} \tag{17}$$

the flux of each solute across the membrane is the sum of diffusive and convective terms: a concentration difference on both sides of the membrane causes diffusive transport, and solute transport by convection takes place because of an applied pressure gradient across the membrane.

In order to quantify these convective and diffusive terms [41] for the case of the metal components present in the hydrogen peroxide RO system under study, the contribution of both terms has been calculated from the experimental data and the transport parameters; and it is shown in Table 9 as the percentage of solute flux due to diffusion for each metal and pressure related to the total solute flux  $I_s$ . At low pressures, when  $I_v$  is low, the first term of the solute flux

(diffusive term) is dominant, while at high pressures the second term (convective) increases to be dominant.

The obtained results of the contribution of the diffusive term to each total solute flux (Table 9), show that the elements B, Mn and Cu are controlled totally by diffusive transport (in concordance with the value of the parameter  $\zeta = 1$  obtained for these components). Components as Zn, Fe, and Cr show diffusional contributions higher than 50% to their total flux in the range of pressure operation, while for the rest of the components: Na, Al, Ti and Ni, the convective transport contributes significantly (values of diffusive term lower than 50%) when the system operates at pressures higher than 20 bar.

Related to the application of the selected transport model through the membrane lifetime, satisfactory results were obtained in terms of percentage of overall variation explained by the Kedem-Katchalsky model as a mean value of 93.4% was obtained for the different characterization intervals of the experiment.

#### 4. Conclusions

Commercially available RO polyamide membrane BE (manufactured by Woongjin Chemical) has been successfully applied to the diminution of metallic contents of 35% Technical Grade hydrogen peroxide in the pressure range between 10 and 40 bar for exposition time up to 64 h. Rejection coefficients above 0.9 were obtained for most metals.

The Kedem-Katchalsky model can be considered suitable for representing the performance of the reverse osmosis process when employed in the ultrapurification of aqueous hydrogen peroxide solutions from technical to electronic grade, as 94.4% of the overall variation of the system was explained by the proposed model.

#### Acknowledgements

This research has been financially supported by the Ministry of Science and Innovation of Spain (MICINN) through CTM2006-00317 Project. R. Abejón acknowledges also the assistance of MICINN for the award of a FPI grant (BES-2008-003622). We gratefully thank Dow Filmtec and Woongjin Chemicals for the supplied membranes and Solvay Torrelavega for the industrial grade hydrogen peroxide.

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