

Accepted Manuscript

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PII: S1383-5866(17)33219-7
DOI: <https://doi.org/10.1016/j.seppur.2018.06.023>
Reference: SEPPUR 14677

To appear in: *Separation and Purification Technology*

Received Date: 4 October 2017
Revised Date: 2 June 2018
Accepted Date: 7 June 2018

Please cite this article as: C. Cruz, L.A. Cisternas, A. Kraslawski, Scaling problems and control technologies in industrial operations: Technology Assessment, *Separation and Purification Technology* (2018), doi: <https://doi.org/10.1016/j.seppur.2018.06.023>

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Scaling problems and control technologies in industrial operations: Technology Assessment

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1 ABSTRACT

2 Calcium and magnesium ions are the major components of scaling in different
3 water sources, especially seawater. Calcium and magnesium scale causes problems in
4 various industrial operations such as reverse osmosis unit, heating unit of multi-stage
5 flash distillation, concentration operation of copper-molybdenum mining industry,
6 cooling water system of power generation industry, and water injection operation of
7 oil and gas production. In general terms, scaling affects the operation performance
8 that leads to increased production, as well as maintenance costs. The pH control, scale
9 inhibitors, and nanofiltration membrane have been implemented by industrial
10 operations to control scale. However, the drawbacks of these technologies may force
11 to seek alternative technologies which could be potential alternatives for scale control.

12 This paper discusses the problems of calcium and magnesium scale affecting
13 various industrial operations when seawater is used. It presents current technologies
14 for scale control such as pH control, scale inhibitors, and nanofiltration. Moreover, the
15 technology assessment (TA) was made to evaluate existing and emerging scale control
16 approaches in the case of reverse osmosis (RO) process. The identification of the
17 emerging technologies of scale control has been performed using bibliometric
18 analysis. The comparison of the technologies was made using House of Quality
19 (HOQ) matrix. The identified emerging technologies are: bioelectrochemical system,
20 biomineralization, biosorbent, microbial desalination cells, step by step deposition and
21 extraction technique, carbon dioxide as a precipitator, gas hydrate, ultrasonic
22 crystallization, and capacitive deionization. The comparison of the technologies has
23 shown that nanofiltration, as a common technology, could be an appropriate approach
24 to ensure feasibility and efficiency of RO process, while emerging technology,
25 microbial desalination cells, could become a potential alternative in the future.

26
27 **Keywords:** seawater; technology assessment; scale control technologies; scaling,
28 hardness ions.

29

1 **1. Introduction**

2 Water is a key element for agriculture, urban, and industrial development
3 sector. However, many places in the world are facing water shortages and lack fresh
4 water. Some of the major causes are climate change, rapid population growth, limited
5 natural resources, and unsustainable development (Mahmoud and Obada, 2014). As
6 less than 3% of the world's water is fresh while the rest is seawater (Fry and Martin,
7 2005), the oceans and seas have become potential sources of water supply for
8 industrial, urban, and agriculture sectors in semi-arid, arid, and hyperarid regions. For
9 the industrial sector, quality of water is essential for its operations to achieve expected
10 performance and desired specification of final products. Seawater quality is not
11 suitable because it contains more dissolved ions of all types than fresh water.
12 Nevertheless, it is used in several industrial operations, including reverse osmosis
13 (RO) units, heating units in multi-stage flash distillation (MSF) (Khayet, 2016),
14 cooling water systems in power generation industry (Pugh et al., 2005), water
15 injection in oil and gas production industry (Bader, 2007), and concentration
16 operation in copper-molybdenum mining industry (Jeldres et al., 2017).

17 Industrial operations, in which seawater is used face problems of corrosion,
18 biofouling, and scaling (Demadis et al., 2007). The latter occurs when soluble
19 minerals precipitate from seawater and deposit on surfaces that affect the performance
20 of industrial operations. Scale deposition increases the costs of production linked with
21 maintenance costs that cause losses billions of dollars (Gilron, 2013). Calcium and
22 magnesium are the main ions that cause scaling problem and their scale deposits are
23 calcium sulphate (CaSO_4), calcium carbonate (CaCO_3), calcium fluoride (CaF_2),
24 calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), and magnesium
25 carbonate (MgCO_3) (MacAdam and Jarvis, 2015).

26 The pH control, scale inhibitors and nanofiltration membranes are the most
27 common technologies for scale control (Jwa et al., 2017; Mahmoud et al., 2016).
28 However, these technologies present some disadvantages, e.g. risk of contamination
29 of the marine environment, corrosion and high energy consumption. During the last
30 decades, the technological advances have allowed developing new technologies,
31 which can provide competitive advantages over current scale control technologies.
32 Besides, it has provided many options for designing and improvement current scale
33 control technologies. Technology development offers not only economic benefits, but
34 also could reduce negative impacts on the environment contributing to the sustainable
35 development (Ibáñez-Forés et al., 2014).

36 Technology assessment (TA) in an important field which has evolved over the
37 past four decades (Tran and Daim, 2008). TA is essential for managers and decision
38 makers to understand the circumstances in which a given technology is could be used.
39 We see it being developed increasingly in the industrial sector to improve deficiencies
40 in existing technologies or to introduce new technologies for minimizing the
41 environmental impact of companies. TA can be relevant in determining new
42 technology adoption, research and development direction, incremental improvement
43 of existing technologies, level of technology friendliness, “make or buy” decision,
44 identification market advantage, optimal expenditure of capital equipment fund and
45 market diversification (Henriksen, 1997).

46 Information monitoring is an important stage of TA. It allows monitoring a
47 technology in question, as well as providing exhausting information to decision
48 makers. One of the methods of information monitoring is bibliometric analysis. It has
49 been used to analyze information in various filed, e.g. medicine, social science,
50 engineering, environmental science (Abejón and Garea, 2015). TA comprises also
51 others stages ranging from the formulation of criteria to a final decision based on the
52 technology comparison (Ibáñez-Forés et al., 2014). One of the methods for
53 technologies comparison is House of Quality (HOQ). It is a tool that allows the
54 translation of customer needs into technical characteristics of a technology or process
55 under evaluation (Ramírez et al., 2017). HOQ is a conceptual matrix that has been
56 used for the development and improvements of technologies or processes in various
57 industries due to its simplicity and effectiveness (Yang et al., 2015).

58 This study seeks to achieve two objectives; first, to present the calcium and
59 magnesium scale problems that affect different industrial operations when seawater is
60 used. The second objective is to assess scale control technologies. Existing and
61 emerging technologies of scale control are presented to conduct the technology
62 assessment. The emerging technologies to control scales were identified through a
63 bibliometric analysis in a subject-specific literature. Next, HOQ matrix is applied to
64 compare scale control technologies for RO process.

65

66 *1.1 Industrial operations affected by scale deposition*

67 Scaling is described as precipitation or crystallization of inorganic salts, such
68 as calcium, magnesium, carbonate, sulphate, phosphate, and silica that allow
69 depositing minerals on the surface (Antony et al., 2011). Precipitation is a process
70 which results in a rapid formation of solids that can produce small crystals at the
71 beginning, which promotes scale formation and its deposit. Supersaturation is the

72 main factor that leads to precipitation; it occurs when the activity of ions in the
73 solution is above their saturation limit (MacAdam and Jarvis, 2015). This condition
74 allows rapid nucleation of scale formation and growth of the crystal. However,
75 temperature and pH of water environment, the presence of impurities, changes in
76 pressure, hydrodynamics, and flow velocity are other factors to trigger precipitation of
77 inorganic salts (El et al., 2011).

78 Scaling can be present in different types depending on operating conditions. In
79 general terms, calcium and magnesium scales, such as CaCO_3 , CaSO_4 , $\text{Ca}_3(\text{PO}_4)_2$,
80 MgOH , MgCO_3 , calcium silicate (Ca_2SiO_4), and calcium hydroxide ($\text{Ca}(\text{OH})_2$) have
81 an inverse solubility, i.e. their solubility decreases with increasing temperature. While,
82 other species are sensitive to pH, where scale formation increases with increasing pH;
83 this is true of CaCO_3 and MgOH (MacAdam and Jarvis, 2015). So, scale deposition
84 depends on the operating conditions of the industry.

85 As was mentioned above, scaling is a common problem in various industrial
86 operation that uses seawater either directly or indirectly. Desalination industry uses
87 seawater directly as feed water to obtain fresh water. In the RO process, concentration
88 polarization takes place in the RO unit and is the main factor that promotes various
89 scales formation on semipermeable membrane surfaces (Gilron, 2013). The
90 phenomenon occurs when solute tends to accumulate on membrane surfaces while the
91 solution passes through the membrane. This way, it increases retention of large
92 molecules on membrane surfaces, while retention of small molecules decreases.
93 Therefore, scale film blocks membrane pores, decreasing permeate flow and
94 efficiency of water recovery as well (Arras et al., 2009). The scales of CaCO_3 , CaSO_4 ,
95 $\text{Ca}_3(\text{PO}_4)_2$, and CaF_2 are the main sources of scale deposits on semipermeable
96 membrane surface (Antony et al., 2011; MacAdam and Jarvis, 2015). On the other
97 hand, MSF is carried out at temperatures as high as 120 °C and scale are formed
98 mainly due to thermal effects of the process because some scales have inverse
99 solubility. Scaling affects mainly the heating unit in the MSF process, depositing on
100 heat exchanger surfaces. Also, the release of carbon dioxide gas (CO_2 (g)) from
101 evaporation brine in heating unit leads to the changes in pH of the solution, which
102 influences the concentration of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), hydrogen
103 (H^+) and hydroxide (OH^-) ions and induces carbonate scale deposition (Al-Anezi and
104 Hilal, 2007). The scale of $\text{Mg}(\text{OH})_2$, CaCO_3 , and CaSO_4 blocks the flow of water on
105 heat exchanger surface reducing heat transfer, as well as decreasing the operation
106 performance (Al-Rawajfeh, 2005). Furthermore, scale deposits increase fuel
107 consumption between 10 and 15% in comparison to free of scale situation (Knudsen,
108 1990). For both, RO and MSF desalination processes, scaling not only reduces water

109 production rate and its quality but also increases the cost of water and shortens the life
110 of components that are in contact with scale (Khayet, 2016).

111 Mining is another industry that uses seawater directly in its operations and its
112 consumption in different metal and non-metallic mining industries have increased
113 across the world (Dreisinger et al., 2008). Some mining industries are more affected
114 than other when using seawater and depend on the type of mineral to be treated and
115 the operating conditions. Concentration operation of copper-molybdenum sulfide ores
116 is especially affected when seawater is used due to the presence of calcium and
117 magnesium ions (Jeldres et al., 2017). Scale formation takes place when the operation
118 is carried out in an alkaline environment to depress non-valuable minerals (Castro,
119 2012). Precipitation of calcium and magnesium species occurs leading to the
120 formation of the scale of $Mg(OH)_2$, $CaCO_3$ and $CaSO_4$ on the surface of valuable
121 ores, mainly on molybdenum ore, at $pH > 10$ (Laskowski and Castro, 2012). Thus,
122 operation performance decreases because scale disposition decreases the recovery of
123 valuable minerals. Also, some concentration operations of copper-molybdenum
124 sulfide ores are conducted in closed water circuits to recycle water into the operation.
125 Recycling of seawater leads to the accumulation of calcium and sulphate ions, which
126 can precipitate on molybdenum surface as $CaSO_4$, reducing their recovery by around
127 20% (Lucay et al., 2015).

128 The cooling water system is another operation that uses seawater as a coolant,
129 either directly or indirectly, due to high heat capacity that it presents. The operation is
130 used in various industries e.g. in chemical plants, steel mills, and oil refineries,
131 however, power generation industries consume huge amounts of seawater (Pugh et al.,
132 2005). Cooling water system involves seawater circulation through a network of heat
133 exchangers to remove heat from the process. During the operation, changes in
134 temperature and pressure drops are the main factors that cause scale formation of
135 $CaCO_3$, $Mg(OH)_2$, $CaSO_4$ and $Ca_3(PO_4)_2$ on heat exchanger surfaces (MacAdam and
136 Jarvis, 2015, 2015). Scale increases the resistance to heat transfer and decreases
137 thermal efficiency of the equipment (Pugh et al., 2005).

138 On the other hand, seawater is used indirectly in processes for oil and gas
139 production located offshore and near the coast. Seawater is the most common option
140 for water injection operations to obtain oil and gas as in the case of Arabian Gulf
141 (Bader, 2007). Changes in temperature and pressure in the operation promote the
142 formation of $CaCO_3$ scale, while the mix of brine waters with a high content of
143 sulphate and calcium ions promotes $CaSO_4$ scale formation (MacAdam and Jarvis,
144 2015). Therefore, scaling blocks the tubes and flow lines of water injection and
145 deteriorates operating performance (Bader, 2007).

146 1.2 *Common technologies for scale control*

147 Seawater has a complex chemistry profile that inevitable contains some ions
 148 interfering with the performance of industrial operations. In particular, calcium and
 149 magnesium ions from seawater are the common ions that cause scaling problems. To
 150 control scale formation and its deposition, technologies have been implemented: pH
 151 control, scale inhibitors, and nanofiltration membrane (Jwa et al., 2017; Mahmoud et
 152 al., 2016). Table 1 shows the relationship between technologies used by the industrial
 153 operations commented above. Also, a description of these technologies are presented
 154 below.

155

156 **Table 1**

157 Technologies for scaling control used in industrial operations.

Operation affected	Technologies for scale control		
	pH control	Scale inhibitors	Nanofiltration membrane
RO unit	✓	✓	✓
Heating unit of MSF	✓	✓	✓
Concentration operation of copper-molybdenum mining	✓		
Cooling water system of power generation industry	✓		
Water injection operation of oil and gas production		✓	

158

159 1.2.1 *Scale inhibitor*

160 Scale inhibitor or antiscalant is a chemical reagent used to control the
 161 formation and/or deposition of scale. It does not eliminate the components of scale
 162 formation but prevents crystal nucleation and crystal growth (Hasson et al., 2011). To
 163 select a specific antiscalant and its doses, it is necessary to carry out tests to find out
 164 the composition of feed water and identify types and concentration of inorganic salts.
 165 Further, the type and efficiency of antiscalant will depend on the nature of the feed
 166 seawater and the conditions of the industrial operation to which they are applied
 167 (MacAdam and Jarvis, 2015). As shown in Table 1, RO unit, heating unit of MSF, and
 168 water injection operation of oil and gas production use scale inhibitor (Hasson et al.,
 169 2011). Regarding desalination processes, commercial scale inhibitors available to RO
 170 process are phosphates, phosphonate and polycarboxylates, and sodium
 171 hexametaphosphate ((NaPO₃)₆) as the first antiscalant available to the membrane
 172 industry (Antony et al., 2011). Thermal desalination processes use antiscalants of
 173 polycarboxylic acid species and phosphonate as well, being the low-molar-mass
 174 polymers or copolymers of acrylic or maleic acid the commercial antiscalants

175 available (MacAdam and Jarvis, 2015). While, in water injection operation of oil and
176 gas production, the two main categories of antiscalants used are polymers and non-
177 polymers; polymers prevent scaling nucleation, while non-polymers prevent the
178 crystal growth (MacAdam and Jarvis, 2015).

179

180 *1.2.2 pH control*

181 The pH control takes place through the dosing of acid to reduce pH of the feed
182 seawater to 5-7. The acid reacts with carbonate and hydroxide ions present in
183 seawater yielding H_2O and CO_2 and preventing the formation of $CaCO_3$ and $Mg(OH)_2$
184 mainly because ions remain soluble into the solution (Al-Hamzah and Fellows, 2015;
185 MacAdam and Jarvis, 2015). As shown in Table 1, RO unit and MSF heating unit
186 (Greenlee et al., 2009) and cooling water system (Müller-Steinhagen, 1999) use acid
187 for scale control. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are common
188 acids used in these industrial operations. Meanwhile, concentration operation of
189 copper-molybdenum ores uses sodium metabisulfite reagent to avoid operating at pH
190 >10 when scaling occurs on the surface of valuable minerals. The use of sodium
191 metabisulfite allows operating at a slightly acidic pH, which keeps calcium and
192 magnesium ions soluble in seawater (Cisternas et al., 2014). Thus, high recovery of
193 valuable minerals can be obtained.

194

195 *1.2.3 Nanofiltration membrane*

196 Nanofiltration membrane (NF) is a pressure-driven, membrane-based
197 separation process. Membranes are ion-selective and their retention rates are
198 determined according to ions valence. Thus, monovalent ions such as chloride,
199 sodium, and potassium can pass through membranes, while multivalent ions such as
200 calcium, magnesium, carbonate, and sulfate are retained on the membrane (Koyuncu
201 et al., 2015). NF is used as pretreatment for RO and MSF processes (see Table1).
202 When it is introduced in RO process, the osmotic pressure of seawater fed to RO is
203 reduced, which leads to the lower energy consumption of the system by about 25 -
204 30% and higher water recovery rate of more than 70% (Kaya et al., 2015; Llenas et
205 al., 2013). Meanwhile, when NF is introduced to MSF process, it can operate at
206 higher top brine temperature in the range between $120^{\circ}C$ and $160^{\circ}C$, which increases
207 plant production and improves water cost due to the reduction of sulfate, calcium and
208 magnesium and carbonate ions from seawater (Hassan et al., 1998).

209

210 **2. Methodology**

211 *2.1 Technology assessment*

212 Technology assessment can help in reduction of the inherent risks of the
213 competitive process of technologies by providing information in support of decision
214 making (Henriksen, 1997). TA can be defined, according to Coates (2001) “as a
215 policy study designed to better understand the consequences across society of the
216 extension of the existing technology or the introduction of a new technology with
217 emphasis on the effects that would normally be unplanned and unanticipated”. To
218 achieve this goal, several approaches and a wide range of methods and tools have
219 been utilized e.g. impact analysis, scenario analysis, risk assessment, decision
220 analysis, identification of emerging technologies, cost-benefit analysis methods,
221 information monitoring, roadmapping (Tran and Daim., 2008).

222 Information monitoring is a critical step in TA before the comparison of
223 technologies. It provides information about technologies in question, both existing
224 and emerging, as well as supply valuable information to decision makers. It must be
225 stressed that the final results obtained in TA will depend strongly on the selection
226 criteria. The choice of criteria must be done by the decision maker based on their own
227 opinion, and the rational method can be used to reinforce their selection (Ibáñez-Forés
228 et al., 2014).

229 In this study, a bibliometric analysis is carried out to identify emerging
230 technologies for scale control. Next, HOQ matrix is applied to compare emerging and
231 existing scale control technologies. The selection of criteria used in HOQ matrix is
232 based on the customer needs.

234 *2.2 Bibliometric analysis*

235 Bibliometric is a research method of information monitoring that facilitates the
236 organization and analysis of the topic in question. It measures the data through a
237 quantitative analysis that allows classifying information in given categories. Typical
238 categories include a number of publications and productivity, type of documents
239 published, publication year, collaboration between authors, keywords, citation
240 network, research areas, and so on (Li et al., 2015; Abejon and Garea, 2015).

241 The analysis bibliometric in this study was conducted to find studies related to
242 emerging technologies for calcium and magnesium scale control, mainly from
243 seawater. To do it, the keywords related to seawater, treatment, technology, calcium,
244 magnesium, hardness, and scaling were combined to search relevant papers using the

245 Web of Science database. The timeframe of the searched was between 2000-2017.
246 This period was chosen as after 2000 new laws and regulations have been introduced
247 aiming at the reduction of the environmental impact caused by various technologies.
248 An example of such regulation is European Union through Council Directive 96/61 /
249 EC on prevention and integrated control of pollution (Ibáñez-Forés et al., 2014).

251 2.3 *House of quality*

252 HOQ methodology is a key component of the quality function deployment
253 (QFD) tool for decision making. QFD considers designing a product/service based on
254 customer demands that involve the members of the producer or supplier organization.
255 Basically, it allows that customers and industry think together to produce a quality
256 technology or process that is manageable, attractive, useful, and profitable (Zare,
257 2010). The main purpose of QFD is to consider customer's needs during the design,
258 construction and delivery process to obtain a higher quality product or process in the
259 market (Akao and Mazur, 2003).

260 HOQ methodology is a conceptual matrix that provides the means for the
261 planning and communications between customers and industry (Hauser and Clausing,
262 1988). The development of the HOQ matrix allows to establish priorities for the needs
263 of the customer, identify deficiencies in compared technologies that lead to improving
264 them, fluent communication among customers, engineers, and managers, and better
265 manufacturing decision making (Ramírez et al., 2017; Yang et al., 2015). The HOQ
266 matrix has a defined structure composed of different sections (see Figure 1) which are
267 defined below:

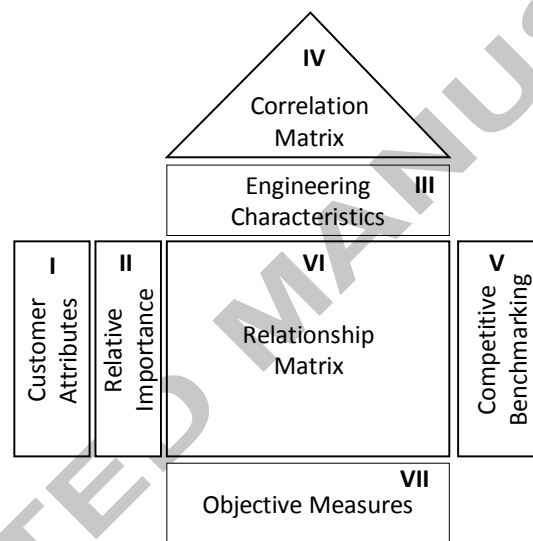
- 268 I. Customer attributes: is the initial input to build HOQ, which is a list of the
269 requirements of the product or service focuses on important needs of the
270 customer in order to express “the voice of the customer”. It can be obtained
271 through focus groups, interviews, existing data in the literature, customer
272 complaints and so on (Ramírez et al., 2017; Zare, 2010).
- 273 II. Relative importance: is a weight established by the customer. It shows how
274 important is every need with respect to the other ones.
- 275 III. Engineering characteristics: is a list of technical parameters about the product
276 or service that can be measured and that should satisfy each customer
277 attribute.
- 278 IV. Correlation matrix: is the roof of HOQ and shows the strength of interaction
279 between engineering characteristics through symbols.
- 280 V. Competitive benchmarking: is customer perception that compares competitors,

281 be it technology or service, against each attribute listed by the customer to
 282 identify opportunities for improvement. In other words, it helps to understand
 283 how customers rate the competition and it is expressed through a scale of
 284 points.

285 VI. Relationship matrix: is the body of HOQ and indicates the relationship
 286 between customer attributes and engineering characteristics. It is represented
 287 by symbols or numerical value.

288 VII. Objective measure: is a target value for each engineering characteristics and
 289 can then act as a baseline to compare.

290



291

292 **Fig. 1.** Structure of HOQ. Adapted from Adiano and Roth, 1994.

293

294 **3. Results and discussion**

295 *3.1 Potential future technologies for scale control*

296 Biosorption (Mahmoud et al., 2013), biomineralization (Arias et al., 2017),
 297 bioelectrochemical system (Nam et al., 2015), microbial desalination cells (Brastad
 298 and He, 2013), gas hydrate (Park et al., 2011), carbon dioxide as a precipitator (Zhao
 299 et al., 2013), capacitive deionization (Seo et al., 2010), ultrasonic crystallization (Su et
 300 al., 2015; Chen et al., 2016) and layer by layer chemical deposition technique
 301 (Mahmoud and Obada, 2014) are emerging technologies as a potential alternatives to
 302 calcium and magnesium scale control identified from bibliometric analysis.

303 Biosorption is a physicochemical process that uses microorganisms as
 304 biosorbent. It involves the interaction of ionic species and functional groups present

305 on the surface of the cell of a microorganism able to adsorb ionic species according to
306 their size and specific charge. Meanwhile, biomineralization is a process by which
307 living organisms produce minerals as a result of their cellular activity that promotes
308 physicochemical conditions necessary for the formation and growth of minerals. In
309 other words, bacteria have the ability to induce minerals formation (Achal, 2015).
310 Bio-electrochemical system and microbial desalination cells (MDC) can generate
311 electricity from chemical energy produced by microorganisms as biocatalysts and
312 remove several ions from aqueous solutions (Subramani and Jacangelo, 2015). The
313 difference between both technologies is their system design. MDC is composed of
314 three chambers; anode, cathode and a desalination chamber in the middle separated
315 with an anion-exchange membrane and a cation-exchange membrane. Bacteria
316 growing on the electrode in the anode chamber oxidize organic substrate generating
317 bioelectricity due to the potential difference across the electrode chambers. In
318 addition, positively charged ionic species move to the cathode through a specific
319 cationic membrane, where they combine with electrons and oxygen species to
320 produce soft water (Saeed et al., 2015; Sophia et al., 2016). Meanwhile, the bio-
321 electrochemical system is composed of two chambers (cathode and anode) separated
322 with an anion-exchange membrane only. The microorganisms convert organic matter
323 into electrical current in the anode chamber, while in the cathode chamber electrons
324 and protons catalytically combine by reducing oxygen to water. Proton consumption
325 at the cathode increases pH (at the cathode surface) inducing precipitation of metal
326 ions (Nancharaiah et al., 2015; Chen et al., 2013).

327 Gas hydrate is a technology based on the crystallization of salts. It consists of
328 a long column pressurized with saline solution and gas such as ethane, propane, and
329 butane under specific conditions of temperature and pressure (Kang et al., 2014;
330 Karamoddin and Varaminian, 2014). Gas is introduced into the column to react and
331 form complex hydrates in the form of crystals, which float on the top of the column.
332 These complex hydrates can store large amounts of crystallization water, so they are
333 washed and dehydrated by adding heat to obtain water free of ions. The technology of
334 carbon dioxide acting as precipitator is based on the dissolution of CO_2 (g) in
335 seawater. It is done to provide a rich source of CO_3^{2-} and HCO_3^- ions which react with
336 divalent ions to precipitate different species of calcium and magnesium (Al-Anezi and
337 Hilal, 2007). This technology is attractive from an environmental perspective because
338 it could mitigate greenhouse gas emissions related to CO_2 (g). Chemical absorption
339 process with aqueous amine solvent is a widely technique used to separate CO_2 (g)
340 from fuel gas (Nagy and Mizsey, 2015). Thus, it could support emerging technology
341 by providing CO_2 (g) as a raw material.

342 On the other hand, capacitive deionization is an energy-effective and low-
343 pressure technology. The ions are removed from saline solutions with the use of
344 electrodes, which have a specific surface area and low electrical resistivity
345 (Subramani et al., 2015). In this technology, positively charged electrode captures
346 negatively charged anions from seawater while negatively charged electrode captures
347 positively charged cations. Meanwhile, ultrasonic crystallization is a physical
348 treatment in which acoustic waves are applied to the frequency higher than 20 kHz,
349 i.e. within the range beyond human perception (Chen et al., 2016). The treatment is an
350 effective way of achieving faster and uniform primary nucleation of crystal, and
351 relatively easy nucleation of particles at lower supersaturation levels (Chen et al.,
352 2012). Layer by layer chemical deposition is a simple and inexpensive technique,
353 which has allowed developing new concepts, new materials, and applications through
354 the fabrication of multilayer films (Ariga et al., 2014). For this technique, it is
355 necessary to select appropriate species for interaction deposition, which can react and
356 deposit a particular compound on the surface of solid substrates for the formation of
357 deposited materials without the possibility of back-dissolution in the aqueous solution
358 (Mahmoud and Haggag, 2011; Mahmoud and Obada, 2014).

359 Emerging technologies show superior performance over existing scale control
360 technologies in terms of energy generation from microorganisms, biological waste
361 generation, use of a limited number of reagents and creation of opportunities for use
362 of CO₂ (g) as a raw material. However, most of those technologies are still under
363 research or in the early development stage. Therefore, further studies and large-scale
364 evaluations are needed to determine their commercialization potential.

365

366 3.2 *House of quality*

367 In this study, HOQ matrix is applied to RO process and assessing existing and
368 emerging technologies of scale control technologies. The technologies under
369 evaluation to RO process are the pH control, scale inhibitors and nanofiltration
370 membrane as common technologies and microbial desalination cells as emerging
371 technology. The reason for choosing the microbial desalination cells over the other
372 emerging technologies is MDC offers a new cutting-edge solution that integrates scale
373 removal and energy recovery in a single reactor. In addition, Sophia et al (2016)
374 suggested that the introduction of MDC into RO process can reduce the overall load
375 on RO membrane and to reduce water cost of desalination.

376 Edraw Max Software was used to build the HOQ matrix to evaluate scale
377 control technologies for RO process. The HOQ was built considering customer

378 attributes, relative importance, engineering characteristics, correlation matrix,
379 competitive benchmarking, relationship matrix and objective measure as shown in
380 Figure 2.

381 Customer attributes were identified from the literature using the Website
382 Science Direct. A bibliographic research was performed to search the principal
383 characteristics of the four scale control technologies. The analysis was performed
384 considering the problems, advantage, drawbacks, and challenges of each technology.

385 Relative importance was obtained by counting the number of scientific
386 publications on Science Direct website that mentions each customer attributes.

387 Engineering characteristics were identified from literature addressing technical
388 information of scale control technologies that are under evaluation.

389 The relationship of the correlation matrix is denoted by positive (+) or
390 negative (-) symbols. The negative symbol indicates that when an engineering
391 characteristic increases it is accompanied by a decrease of another characteristic. In
392 contrast, the positive symbol indicates that both characteristics decrease or increase
393 simultaneously. However, there are engineering characteristics that do not interact
394 with each other, so it is denoted by a blank space.

395 Competitive benchmarking was done using the results given by customer
396 attributes. The customer perception is expressed by a 5-point scale; 1 is very poor, 2 is
397 poor, 3 is neutral, 4 is good, and 5 is very good.

398 Relation matrix is represented by the symbols; ● denoted strong, ■ medium,
399 and ▲ weak

400 The values of objective measure were obtained from the literature of “state of
401 the art of RO desalination” (Fritzmann et al., 2007).

402 As mentioned before the customers attributes were obtained from
403 bibliographic research to each scale control technology under evaluation. The
404 customer attributes identified are presented below.

405 • Corrosion: The pH control leads to corrosion problems when pH value falls below
406 4.5 (Al-Hamzah and Fellows, 2015). Scale inhibitor causes minimal corrosion
407 problems (Al-Hamzah and Fellows, 2015). In addition, there are scale inhibitors
408 designed to prevent corrosion and scale formation at the same time (Hasson et al.,
409 2011). The NF has a more dilute concentrated waste stream, and product water
410 requiring less stabilization to minimize distribution system corrosion
411 (Shahmansouri and Bellona, 2015). In MDC, one of the main problems is the short
412 life of the electrode due to the highly corrosive electrolytes that are in the system
413 as is the case of seawater (Bebelis et al., 2013).

414

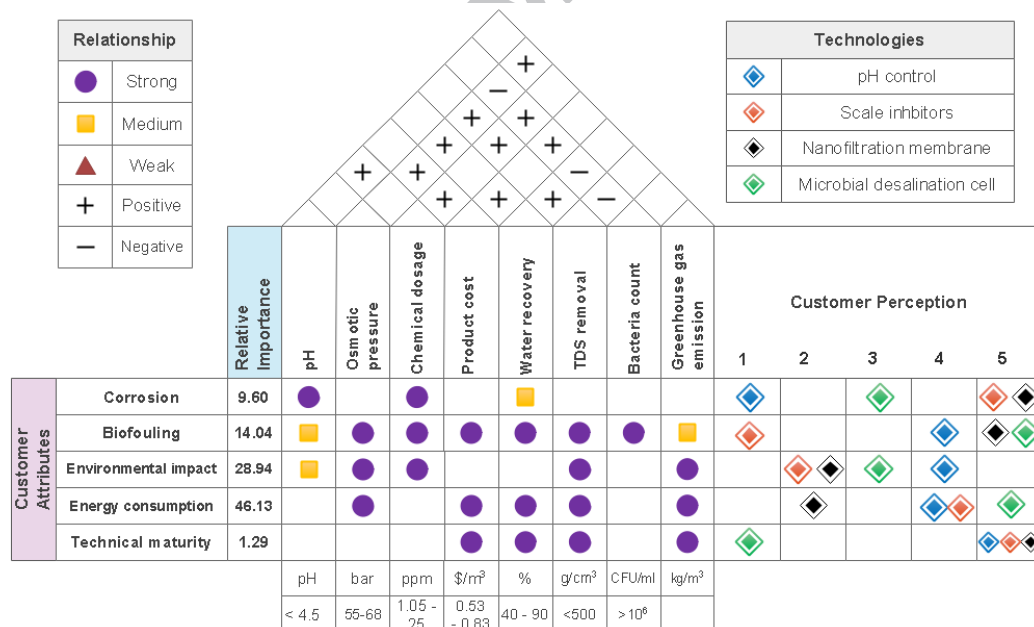
- 415 • Biofouling: It is significant when the bacterial count is higher than 10^6 CFU/ml
416 (Fritzmann et al., 2007). The pH control does not affect the growth of
417 microorganisms, however, chlorine is the most effective disinfectant for the
418 deactivation of microorganisms in pretreatment stage for RO process (Jiang et al.,
419 2017). Antiscalants, mainly polyphosphonate-based, induce biofouling formation
420 due to an additional source of phosphorous in seawater which enhances microbial
421 population (Sweity et al., 2013). The biofouling is not a specific problem for NF as
422 it can remove bacteria and turbidity from seawater (Llenas et al., 2013; Koyuncu et
423 al., 2015). In addition, bacterias are too large and will remain as a biofilm on the
424 surface and not inside the membrane pores (Van der Bruggen et al., 2008). The
425 MDC has a separator which is a piece of glass fiber attached to the water-facing
426 side of the cathode to prevent the occurrence of biofouling on the cathode (Saeed
427 et al., 2015).
- 428
- 429 • Environmental impact: The acidity of pH control is consumed by naturally alkaline
430 seawater, therefore the discharge pH to seawater is typically similar or slightly
431 lower than that of seawater (Gude, 2016). Conventional polymeric antiscalants
432 have a long lifespan and persist for several years after their disposal. However,
433 polyphosphonate-based antiscalants are a concern as they can become nutrients
434 leading to eutrophication problems in seawater (Hasson et al., 2011). NF
435 technology discharges brine into seawater at ambient temperature and it has a
436 salinity of 70 g/l (Pontié et al., 2013), being about double the normal salinity of
437 seawater. Besides, the technology releases 2.1 kg/m^3 of CO_2 to the environment
438 (Youssef et al., 2014). Instead, the MDC is considered as an environmentally
439 friendly technology because it can generate electricity from microorganisms
440 (Brastad and He, 2013; Sophia et al., 2016). So it could generate less impact on the
441 environment
- 442
- 443 • Energy consumption: The acid for pH control and antiscalant are added by
444 chemical dosing pumps, where energy consumption of H_2SO_4 dosing pump is
445 $1.51\text{E-}05 \text{ kWh/m}^3$ of permeate, while antiscalant dosing pump uses $1.27\text{E-}06$
446 kWh/m^3 of permeate (Al-Malek, 2005). For dual stage NF process with feed water
447 of 35,000 and 39,000 mg/l of salinity, energy consumptions were 3.35 and 3.84
448 kWh/m^3 , respectively, and the permeate stream were of 254 and 295 mg/l,
449 respectively (AlTae and Sharif, 2011). In contrast, the MDC can generate
450 electricity from chemical energy produced by microorganisms. Although it is a
451 growing technology yet, it can produce 180 to 231% energy in the form of

452 hydrogen during the desalination of sodium chloride solution from 30g/l to 5g/l
 453 (Saeed et al., 2015). Also, osmotic MDC, which integrates forward osmosis into
 454 MDC, can produce 0.16 kWh/m³ of the energy of treated saline water. (Zhang and
 455 He, 2013).

456

457 • Technical maturity: The pH control is an ancient technology that was widely used
 458 during the 1960s and the 1970s as the only practical technology for scale control
 459 (Al-Shammiri., 2000). Regarding a survey of 47 commercial RO plants in 2000,
 460 about 42.6% still use pH control whereas antiscalant alone represent 17% of
 461 surveyed plants (Al-Shammiri., 2000). Several studies have shown the evolution of
 462 NF as pretreatment technology in the desalination industry; moving from pilot to
 463 commercial/industrial scale (Llenas et al., 2013). In contrast, MDC is a new
 464 technology, in fact, it has been developed for less than a decade (Sophia et al.,
 465 2016). The technology is still used at laboratory scale and has high capital
 466 investment.

467



468

469

Fig. 2. House of Quality of the scale control technologies.

470

471 By analyzing the information provided by the HOQ matrix (see Figure 2),
 472 energy consumption is a big challenge in customer attributes because RO process is
 473 an energy-intensive process. Typically, the RO process requires about 4 - 7 kWh/m³ of
 474 energy, including pre and post- treatment, however, the value depends on the size of
 475 plant and energy recovery system installed (Subramani and Jacangelo, 2015;

476 Lattemann and Höpner, 2008). When scale control technologies are not efficient in
477 reducing the ions to prevent scale formation, the efficiency of RO process is reduced
478 due to the increase in osmotic pressure, which leads to a higher total energy
479 consumption. The MDC is the suitable technology to reduce energy consumption in
480 comparison with its competitors. The MDC can generate electricity from chemical
481 energy produced by microorganisms, being a competitive advantage over other
482 technologies. Therefore, there is no need to improve MDC to address this customer
483 need. In contrast, NF is not the suitable technology to reduce energy in the RO as it is
484 a pressure-driven process that requires energy for ions separation.

485 The production of water through the RO process involves environmental
486 impacts. This is the second concern for customers due to the discharges of brine or
487 chemicals to the environment, which could affect marine life as well as air pollutant
488 emissions attributed to the energy demand of the process. The pH control technology
489 has a less environmental impact than other technologies because acidity is consumed
490 by naturally alkaline seawater. Therefore, the discharge pH to seawater is typically
491 similar or slightly lower than that of seawater (Gude, 2016). While scale inhibitors
492 and NF have a greater impact on the marine environment: the polyphosphonate-based
493 antiscalants lead to eutrophication problems in seawater, whereas NF discharge brine
494 into the environment which could affect the marine environment. So, to mitigate these
495 problems, green scale inhibitors that readily biodegrade and have a minimum
496 environmental impact have been developed (Hasson et al., 2011). In addition, brine
497 should be pre-diluted with seawater to minimize the effect of high salt concentration
498 into the marine environment, as well as salts recovery and selection of outfall location
499 for maximum mixing and dispersion have been conducted (Gude, 2016; Fritzmann et
500 al., 2007).

501 Biofouling is the third concern to the customer. It is a dynamic process that
502 involves the formation and growth of a bio-film attached to the RO membrane, which
503 influences the performance of the process due to increased pressure loss along feed
504 channel and reduction of the flux (Fritzmann et al., 2007). The MDC and NF
505 technologies are the suitable alternatives to prevent biofouling in comparison to its
506 competitors. The MDC has a separator in the cathode that prevents the growth of
507 bacteria, while the NF can remove bacteria and turbidity from seawater. Therefore,
508 both technologies meet the customer' demand and no improvements are needed. In
509 contrast, scale inhibitors, mainly polyphosphonate-based, contribute to membrane
510 biofouling reducing the performance of RO process. To struggle this problem efforts
511 are being made to replace polyphosphonate-based antiscalants by polymeric
512 compounds and green antiscalants (Fritzmann et al., 2007).

513 For the last customer attributes, corrosion and technical maturity are less
514 worrying needs of the customer. Regarding corrosion, the pH control is the worst
515 technology in comparison with its competitors as it can induce corrosion into RO
516 process due to low pH values, so correct doses of acid are crucial. To avoid corrosion
517 is needed a proper design with equipment made of corrosion resistant materials and
518 anticorrosive additives (Fritzmann et al., 2007). Thus, this customer need should be
519 better addressed. In contrast, NF and scale inhibitor are the suitable technologies to
520 prevent corrosion. The concentrate waste stream from NF is more dilute. In
521 consequence less effort to stabilization the corrosion in the distribution system is
522 needed. In addition, scale inhibitors can solve scale and corrosion problems
523 simultaneously. In relation to MDC technology, limited information on corrosion is
524 available. So, further studies are needed in order to satisfy this need. Regarding
525 technical maturity, the attribute with less relative importance, the pH control,
526 antiscalants, and NF are mature technologies with commercial applications as
527 pretreatment to RO process to prevent scale formation. Instead, the MDC is a young
528 technology, still at the stage of research and development. However, many studies
529 mention that this could be an environmental friendly technology of the future due to
530 its characteristics: it can remove ions from aqueous solutions and can generate
531 electricity (Subramani and Jacangelo, 2015).

532 In particular, NF technology could be the suitable current option to RO process
533 because it does not cause corrosion problems, it can remove bacteria, turbidity and
534 prevent biofouling on the membrane. Also, it is selective for the retention of ions
535 according to their valence. The technology can remove 89.6% of calcium, 94.0% of
536 magnesium, 97.8% of sulfate and 76.6% of bicarbonate, and 39.3% of total hardness
537 from seawater, and also can remove more than 50% of TDS (Hassan et al., 1998). In
538 fact, by the introduction of NF before RO process, the RO permeate increases because
539 the osmotic pressure of seawater fed to the RO unit is reduced, which leads to higher
540 water recovery rate of more than 70% (Kaya et al., 2015; Llenas et al., 2013). Also,
541 nowadays NF is a mature technology with several commercial and industrial
542 applications. However, it is necessary to improve the energy system to reduce energy
543 consumption as this is a pressure- driven technology, as well as to reduce
544 environmental impact produced by the discharge of brine into the marine
545 environment. On the other hand, the MDC technology could become a potential
546 alternative for scale control in the future due to its energy efficiency and
547 environmental advantages. At laboratory scale for seawater desalination, the
548 technology can remove 98% of salt from synthetic seawater (Sophia et al., 2016).
549 However, to improve the efficiency of MDC more compact reactor design is

550 necessary (Subramani et al., 2015). Also, future work is needed to scale-up the system
551 for practical applications.

552 **4. Conclusions**

553 In this paper calcium and magnesium scale problems occurring in different
554 industrial processes which use seawater were presented. The RO unit, heating unit of
555 MSF, concentration operation of the copper-molybdenum mining industry, cooling
556 water system of power generation industry, and water injection operation in oil and
557 gas production are industrial operations affected by scale formation. The CaSO_4 ,
558 CaCO_3 , CaF_2 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{Mg}(\text{OH})_2$ and MgCO_3 salts are the main components of
559 scale present, with calcium and magnesium ions as the most common species in
560 scaling problems when seawater is used. Independently of industrial operations
561 affected, the scale is formed because operating conditions generate an environment
562 that favours initiating scale formation and its growth.

563 Moreover, a technology assessment to evaluate existing and emerging scale
564 control technologies was performed based on a bibliometric analysis and HOQ matrix
565 for RO process. The pH control, scale inhibitors and nanofiltration membrane are the
566 current technologies used to control calcium and magnesium scale. Whereas, the layer
567 by layer chemical deposition technique, biosorption, carbon dioxide as a precipitator,
568 bioelectrochemical system, microbial desalination cells, gas hydrate,
569 biomineralization, ultrasonic crystallization, and capacitive deionization are emerging
570 scale control technologies.

571 The pH control, scale inhibitors, nanofiltration membrane and microbial
572 desalination cells were the technologies evaluated applied the HOQ matrix. The
573 corrosion, biofouling, environmental impact, energy consumption and technical
574 maturity were customer attributes evaluated for each technology, with energy
575 consumption and environmental impact being the main challenges for RO process. NF
576 technology could be the suitable current option to RO process because it meets with
577 almost all customer needs such as corrosion, biofouling and technical maturity.
578 However, it is necessary to implements solutions to reduce energy consumption and to
579 mitigate the discharge of brine into the marine environment. Whereas, microbial
580 desalination cells could become a potential alternative for scale control in the future
581 due to its energy efficiency and environmental advantages. However, further studies
582 are needed as well as full-scale to evaluate its performance into RO process.

583 .

1 **Acknowledgements**

2 The authors thank CONICYT (PIA program) for financial support through the
3 Project Anillo ACM 170005 and CICITEM for funding through the project
4 R15A10002.

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Highlights

Current and emerging technologies to remove calcium and magnesium ions are discussed

☐ A technology assessment to compare scale control technologies was conducted

☐ The energy consumption is the main challenge in technologies of scale control

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