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1 **AN AUTOPSY STUDY OF A FOULED REVERSE OSMOSIS MEMBRANE**
2 **ELEMENT USED IN A BRACKISH WATER TREATMENT PLANT**

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9
10 **Abstract**

11
12 The fouling of a spiral wound RO membrane after nearly one year of service in a brackish
13 water treatment plant was investigated using optical and electron microscopic methods, FTIR
14 and ICP-AES. Both the *top surface* and the *cross-section* of the fouled membrane were
15 analysed to monitor the development of the fouling layer. It has been found that the extent of
16 fouling was uneven across the membrane surface with regions underneath or in the vicinity of
17 the strands of the feed spacer being more severely affected. The fouling appeared to have
18 developed through different stages. In particular, it consisted of an initial thin fouling layer of
19 an amorphous matrix with embedded particulate matter. The amorphous matrix comprised
20 organic–Al–P complexes and the particulate matter was mostly aluminium silicates.
21 Subsequently, as the fouling layer reached a thickness of about 5 to 7 µm, further amorphous
22 material, which is suggested to include extracellular polymeric substances such as
23 polysaccharides, started to deposit on top of the existing fouling layer. This secondary
24 amorphous material did not seem to contain any particulate matter nor any inorganic elements

25 within it, but acted as a substrate upon which aluminium silicate crystals grew exclusively in
26 the absence of other foulants, including natural organic matter (NOM).

27

28 **Key words:** Reverse osmosis, fouling, water treatment, desalination, fouling mechanisms

29

30 **1. Introduction**

31

32 Reverse osmosis (RO) is a commonly used process in desalination and advanced wastewater
33 treatment. However, like other membrane filtration processes, fouling is a major obstacle in
34 the efficient operation of RO systems. Membrane fouling causes deterioration of both the
35 quantity and quality of treated water, and consequently results in higher treatment costs.
36 Foulants may be classed into one of four major categories: sparingly soluble inorganic
37 compounds, colloidal or particulate matter, dissolved organic substances, and microorganisms
38 (Speth *et al.*, 2000). Fouling by sparingly soluble inorganic compounds is governed by
39 concentration polarization and scale layer formation when the product of the concentration of
40 the soluble components exceeds the solubility limit (Boerlage *et al.*, 1999). Particulate and
41 colloidal matter rejected by the membrane may form compact cakes, which introduce an
42 additional resistance barrier to filtration (Gabelich *et al.*, 2002). Organic fouling is governed in
43 part by interactions between the membrane surface and the organic foulants, as well as
44 between the organic foulants themselves (Dalvi *et al.*, 2000). Microbial attachment and growth
45 on the membrane surface leads to the formation of biofilms, which consist of microbial cells
46 embedded in an extracellular polymeric substances matrix produced by the microbes
47 (Ivnitskya *et al.*, 2005). Despite various research efforts, to date the characterization of sea
48 water fouling of RO membranes has not progressed significantly, compared to low-pressure
49 membrane fouling by surface and ground waters (Kumar *et al.*, 2006).

50

51 Although membrane fouling is traditionally measured by flux decline with time, this method is
52 inadequate for characterizing fouling development in a RO process. It has been shown that
53 when the permeate flux is noticeably affected, the membrane is so severely fouled that

54 restoration to its original permeability may become impossible (Tay and Song, 2006).
55 Autopsies of fouled membranes have also been carried out in order to better understand the
56 physico-chemical processes governing the fouling (see, for example, Butt *et al.*, 1997; Speth *et*
57 *al.*, 1998; Sahachaiyunta *et al.*, 2002; Vrouwenvelder and van der Kooij, 2002; Gwona *et al.*,
58 2003). The methods of chemical and structural analyses used in these studies including
59 inductively coupled plasma mass spectrometry (ICP-MS), gas chromatography / mass
60 spectrometry (GC-MS), Fourier transform infra-red spectroscopy (FTIR) and X-ray diffraction
61 (XRD) provide only the *average* composition of the surface deposits. Because these deposits
62 are complex and heterogeneous, information on average composition is of limited value in
63 elucidating the fouling mechanisms. Direct observations using optical and electron
64 microscopic methods, including scanning electron microscope (SEM) and associated energy-
65 dispersive X-ray spectroscopy (EDS), often focus on the *top* surface deposits, but not on the
66 underlying deposit layers. This leads to an incomplete understanding of the deposition kinetics
67 of various foulants, and therefore of the fouling mechanisms, particularly where thicker
68 deposits have been developed.

69

70 Another issue is that whilst the distinction between inorganic, colloidal, organic and biological
71 fouling is useful, RO membranes in a typical operation are likely to be exposed to all
72 categories of foulants. Because of the complex nature of fouling, many mechanistic studies on
73 RO membrane fouling have focused on one foulant type for the purpose of simplicity.
74 However, it is very important to understand the effects of interactions between various foulant
75 types on the fouling mechanisms. For instance, it has recently been reported that the enhanced
76 concentration polarization of salt ions within the colloidal cake layer may result in an increase
77 in osmotic pressure and rapid flux decline during cake layer development (Hoek and
78 Elimelech, 2003; Lee *et al.*, 2005). As well, the interactions between colloidal and organic

79 foulants has been found to give rise to considerable synergistic effects, as manifested by a
80 significantly higher flux decline compared to the additive effects of colloidal fouling and
81 organic fouling alone (Li and Elimelech, 2006).

82

83 This paper presents the autopsy results of a spiral wound RO membrane after nearly one year
84 of service in a water treatment facility. Analytical techniques used in the investigation of the
85 surface deposits include inductively coupled plasma atomic emission spectrometer (ICP-AES),
86 FTIR, optical and electron microscopic methods. Both the *top surface* and the *cross-section* of
87 the fouled membrane were analyzed to provide further insights into the development of the
88 fouling layer.

89

90 **2. Materials and Methods**

91

92 ***The fouled spiral wound RO membrane element***

93

94 The fouled RO membrane element (FILMTECH, BW30LE-440DRY) selected for the autopsy
95 study had been in service for nearly one year in a water treatment facility operated by
96 GWMWater in Hopetoun, western Victoria, Australia. The RO desalination plant was
97 integrated into the water treatment facility in response to the increased salinity of surface
98 water in the region due to the extended drought in recent years. The plant was capable of
99 producing 250KL/d of permeate and included a concentrate recycle stream to improve
100 recovery to 80%. A phosphonate-based antiscalant was used in the RO operation and pre-
101 chlorination was not carried out in the treatment process because of the high levels of
102 disinfection by-product precursors.

103

104 Prior to the RO treatment, the raw water from catchments in the Grampians Ranges and stored
105 in open reservoirs had undergone a pre-treatment process including coagulation (aluminium
106 sulphate), flocculation, dissolved air flotation and filtration (DAFF), pH correction and
107 cartridge filtration using 5 and 1 µm pore size filters. The filtered water had pH of 9.1, total
108 dissolved solids of 900 mg/L, total organic carbon (TOC) of 12 mg/L and turbidity of 0.5
109 NTU. Chemical analysis of the filtered water was carried out and the results are presented in
110 Table 1.

111

112 The extended drought created conditions that promoted algal growth in the storage reservoirs
113 and this change had a detrimental effect on the performance of the DAFF process as well as
114 the desalination plant, resulting in a significant decline in production. The algal outbreak
115 required clean-in-place (CIP) events to be scheduled every month, but the flux decline was
116 significant and the original aim of operating at 80% recovery was not possible. Even after the
117 DAFF process was optimised to remove the algal cells and better water was secured from
118 another reservoir, the RO desalination plant could only operate at 75% recovery at best.

119

120 Following the algal outbreak, a fouled RO membrane element was selected for the autopsy
121 study. Surface deposits were scraped from the fouled membrane surface and analysed by ICP-
122 AES and FTIR. [The middle section between the feed end and the concentrate end of the fouled](#)
123 [membrane was also cut into various coupons and prepared for optical and electron](#)
124 [microscopic studies.](#)

125

126 ***ICP-AES analysis***

127

128 The surface deposits were digested in duplicate with 1:1 HNO₃ on a hotplate prior to analysis
129 by using a Varian Vista ICP-AES. A general scan including Al, As, Au, Ba, Be, Bi, Ca, Cd,
130 Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, S, Sb,
131 Se, Si, Sn, Sr, Ta, Th, Ti, U, V, W, Y, Zn and Zr elements were carried out. Only the elements
132 detected in trace levels and above are reported in the results. Chloride concentrations were
133 determined by analysing the sample in duplicate by potentiometric titration with silver nitrate.

134

135 *FTIR analysis*

136

137 Approximately 1.5 mg of dried sample was ground and mixed with approximately 50 mg of
138 anhydrous KBr and subsequently pressed into a disc. FTIR spectra (500–4000 cm⁻¹) of the
139 discs were obtained using a Perkin Elmer 2000 FT-IR spectrophotometer in transmission
140 mode with KBr as the background reference.

141

142 *Optical and electron microscopic analyses*

143

144 An Olympus BHSM Metallographic Optical Microscope was used for general observation of
145 the fouled membrane sections. The microstructures of the surface deposits were analyzed
146 using a Philips XL30 field emission SEM operating at 5-15kV in conjunction with EDS to
147 obtain chemical information. EDS spot analysis using a spot diameter of about 3 nm at
148 selected areas on the samples was carried out. Since the X-ray sampling volume is close to the
149 electron-sample interaction volume, the spot analysis data typically included X-ray signals
150 generated from a sampling volume of about 1 μm³ (Goodhew and Humphreys, 1992).

151

152 Both the *top surface* and the *cross-section* of the fouled membrane coupons were analysed.
153 For the *top surface* analyses, the membrane coupons were mounted on a holder using double-
154 sided carbon tape. For the *cross-section* analyses, the coupons were embedded in a polymeric
155 resin in such a way that their cross-section was oriented perpendicular to the incoming light /
156 electron beam. The samples were then polished with various grades of diamond paste using
157 oil-based lubricant before analyses.

158

159 **3. Results and Discussion**

160

161 ***General observations by optical microscopy***

162

163 Generally, the deposits were distributed unevenly across the membrane surface. Optical
164 images of the membrane surface before and after the feed spacer was removed are shown in
165 Figures 1a and b, respectively. It can be seen that regions underneath or in the vicinity of the
166 spacer strands were covered by brown stains, whereas the extent of staining in regions located
167 further away was generally less severe and varied considerably. Examination of regions near
168 the strands at higher magnifications also revealed the occasional presence of microorganisms,
169 as shown in the inset of Figure 1b.

170

171 The uneven fouling is also evident from the investigation of the cross-sections which showed a
172 considerable variation in the thickness of the surface deposits. In particular, many deposits in
173 regions underneath or close to the spacer strands had a thickness of about 90 μm or more, as
174 illustrated in Figure 2(a), whereas those located further away were thinner and had a thickness
175 ranging from less than 1 to about 25 μm , as shown in Figures 2(b) and (c).

176

177 A major objective of using the feed spacer is to promote eddy mixing which increases mass
178 transfer and reduces concentration polarization (Belfort and Guter, 1972). Whilst turbulence is
179 created between the spacer strands, it is also known that the spacer may promote excessive
180 particle precipitation in regions close to the strands (Gimmelshtein and Semiat, 2005). This
181 undesirable effect is evident in the present study from the observation of the thick deposits in
182 these regions. The presence of the thick deposits could lead to detrimental consequences. In
183 particular, they could act as an effective barrier to prevent water in the local environment from
184 penetrating through the underlying membrane, and therefore could greatly diminish the local
185 water flux. They could also have adverse effects on the feed flow properties, for instance, by
186 distorting the flow path and lowering the cross-flow velocity in the feed channel, which could
187 in turn contribute to the uneven and enhanced fouling across the membrane surface.

188

189 The difficulty in characterizing fouling is often attributed to the complexity of feed water
190 composition and to the different fouling mechanisms of different foulant types. Feed water is
191 usually characterized using common water analysis parameters such as the concentration of
192 each foulant present in the water. The flow properties and rate of fouling are often assumed to
193 be uniform throughout the membrane surface. The observations in the present study highlight
194 the importance of local variations in the hydrodynamic conditions in that they may lead to
195 considerable uneven fouling, and therefore should be featured more prominently in the
196 characterization of RO membrane fouling.

197

198 *Analyses of surface deposits by ICP-AES and FTIR*

199

200 The results from ICP-AES analysis are shown in Table 2. The major elements detected
201 included Al (2570 ppm), Ca (2760 ppm) and P (1225 ppm). Lesser amounts of Fe (590 ppm),
202 S (865 ppm), Si (410 ppm), Mg (320 ppm), K (110 ppm) and Na (190 ppm) were also present.
203 A relatively high level of Cl was detected (1430 ppm). Low levels of Ba, Cr, Cu, Ni, Sr, Ti, Zn
204 and Zr were also identified in the deposits.

205

206 Generally, the presence of negative ions, including bicarbonate, silicate and sulphate, in the
207 RO feed is important for the precipitation of various compounds. Common deposits found on
208 fouled RO membranes include aluminium silicates, carbonate compounds of Ca and Mg, and
209 sulphate compounds of Ca, Sr and Ba (see, for example, Yiantios *et al.*, 2005; Butt *et al.*,
210 1997). Metal ions, most notably Ca^{2+} , may also form complexes with natural organic matter
211 (NOM), giving rise to subsequent formation of intermolecular bridges amongst organic foulant
212 molecules and enhanced membrane fouling (Li and Elimelech, 2004). As well, where a
213 fouling layer has developed on the membrane surface, the layer may entrap and hinder back-
214 diffusion of dissolved salt ions, resulting in an increase in concentrations of the salt ions near
215 the membrane surface (Herzberg and Elimelech, 2007; Hoek and Elimelech, 2003).

216

217 These deposition mechanisms could operate during the development of the fouling layer in the
218 current case, resulting in various types of deposits detected on the fouled membrane surface. It
219 is noted that the use of aluminium sulphate coagulant and phosphonate-based antiscalant prior
220 to the RO treatment could also raise the levels of Al, S and P in the feed and contribute to the
221 relatively high levels of these elements in the deposits. This issue will be discussed further in a
222 later section. As well, while only trace amount of Fe was detected in the RO feed, a relatively
223 high level of Fe was present on the fouled membrane deposits. A similar finding was also

224 reported in a previous study by Gwona *et al.* (2003), who attributed the high residual Fe levels
225 on the fouled membranes, even after all cleanings, to irreversible fouling.

226

227 A typical FTIR spectrum of the fouled membrane extract is shown in Figure 3. The main
228 absorption bands were in the vicinity of 3428 cm^{-1} (O–H stretching and N–H stretching), 2920
229 cm^{-1} (aliphatic C–H stretching), 1631 cm^{-1} (C=O stretching of amide I, quinone, and ketones),
230 1563 cm^{-1} (N–H deformation + C–N stretching of amide II, symmetric stretching of COO–),
231 and 1078 cm^{-1} (C–O stretching of polysaccharides). The band in the vicinity of 1400 cm^{-1}
232 could be due to aliphatic C–H deformation, C–O stretching and O–H deformation of phenol.
233 The band in the range $600 - 800\text{ cm}^{-1}$ could be due to aromatic compounds. These results
234 suggest that the constituents of the membrane fouling matter included proteins,
235 polysaccharides, and aliphatic and aromatic compounds derived from humic substances.

236

237 ***Investigation of the membrane surface and cross-sections by SEM/EDS***

238

239 Generally, the SEM/EDS investigation confirms the variation in the extent of fouling across
240 the membrane surface as observed by optical microscopy, and gives further insights into the
241 development and the nature of the fouling layer. As shown in Figure 4, a typical fouled
242 membrane surface consisted of particulate matter embedded in an apparently amorphous
243 matrix. Associated EDS analyses indicate that the particulate matter had relatively high levels
244 of C, O, Al and Si, whereas the matrix had high levels of C, O, Al and P. Quite low levels of
245 Ca, Mg, Cl and S were also present. Scales containing high levels of Si and Al, as shown in
246 Figure 5, were often observed.

247

248 The C and O peaks are likely due in part to organic and/or biological materials. The high
249 levels of Al and Si in the particulate matter suggest that it was mainly aluminium silicates,
250 which are common foulants in RO operations. Given that cartridge filtration with 5 and 1 μm
251 pore size filters had been used to pre-treat the water, the RO feed was likely to be free from
252 larger size silt/clay particles. However, finer particles might remain in the feed and
253 subsequently form part of the fouling layer. The use of aluminium sulphate as coagulant prior
254 to the RO treatment could also elevate the Al concentration in the RO feed and contribute to
255 the formation of aluminium silicates (Gabelich, 2005). It is noted that phosphonate-based
256 antiscalants, as used in the present case, have been reported to be ineffective for suppressing
257 the precipitation of aluminum silicates (Gabelich, 2005; Butt *et al.*, 1995). The use of
258 phosphonate-based antiscalant in the present case could also contribute to the relatively high
259 levels of P observed in the matrix. It is possible that in the presence of metal ions such as Al^{3+}
260 that act as cationic “anchors”, there would be strong interactions between anionic humates and
261 phosphates (Riggle and von Wandruszka, 2005). A previous study has also suggested that
262 phosphorus from phosphonate-based antiscalants can react with aluminium to form
263 precipitates on RO membrane surfaces (Gabelich, 2005). Another possibility is that calcium
264 phosphate, which has a low solubility, could precipitate and form part of the matrix. However,
265 given the relatively low levels of Ca compared to those of P, the possible presence of calcium
266 phosphate in the matrix would not be a major factor contributing to the high levels of P in the
267 matrix.

268

269 The SEM/EDS investigation of the cross-sections of the membrane gives further insights into
270 the development of the fouling layer. Micrographs of a thin fouling layer at different
271 magnifications and associated EDS analyses are shown in Figure 6. Note the similarity
272 between Figure 6 and the optical image of the same section at similar magnification presented

273 in Figure 2c. EDS analysis of the microporous support layer showed S and Cl. The presence of
274 S is likely due to polysulphone, whereas Cl ions could have diffused through the polyamide
275 skin layer with some retained in the microporous support. In contrast, Cl was absent in the
276 fabric layer. It is possible that once Cl reached this layer, mass transport would be more
277 efficient and most Cl would diffuse into the bulk of the permeate.

278

279 The fouling layer presented in Figure 6 had a thickness of less than 1 μm and consisted of
280 particulate matter embedded in an apparently amorphous matrix. These features are similar to
281 those observed on the top surface of the fouled membrane. EDS analysis of this layer also
282 showed the presence of Al, Si, P, S and Cl. As discussed above, aluminium silicates and the
283 association of organic–Al–P could contribute to the Al, Si and P peaks, whereas the Cl peak is
284 likely due to the entrapment of dissolved chloride ions in the fouling layer as discussed
285 previously. Although it is possible that parts of the underlying polysulphone membrane could
286 be lifted together with the fouling layer and thus contributed to the S peak, the analyses of the
287 thicker fouling layer, as will be shown below, suggest that sulphur is part of the fouling layer.

288

289 Similar features were also observed in the thicker fouling layer. A typical example is shown in
290 Figure 7 with associated EDS analyses. In this case, the fouling layer was about 3 μm thick
291 and, similar to the case of thinner fouling layer, consisted of an amorphous organic–Al–P
292 matrix embedded with aluminium silicates. Sulphur was present in regions located away from
293 the surface of the microporous support (area 1 in Figure 7). A range of elements including Ca,
294 Mg, Na, Fe, Cl and Ti were also present in lesser amounts.

295

296 For fouling layer with a thickness greater than about 10 μm , additional features were observed.
297 A typical micrograph and associated EDS analyses of such a layer are shown in Figure 8. It
298 can be seen that the layer consisted of two distinct Regions. Region 1 had a thickness ranging
299 from about 5 to 7 μm and was similar to the thinner fouling layer shown in Figure 7 in that it
300 had an amorphous organic–Al–P matrix with aluminium silicates embedded within (EDS
301 analysis is not presented here).

302

303 Region 2 was structurally and chemically different from Region 1 and had two distinct zones:
304 an inner amorphous layer and an outer crystalline layer. It can be seen in Figure 8 that the
305 outer crystalline layer consisted of mainly aluminium silicate crystals. In contrast, there was
306 no particulate matter embedded within the inner amorphous layer and the EDS analysis of this
307 layer did not detect any elements except carbon and oxygen. NOM is unlikely to be a major
308 constituent of this layer, given the tendency of NOM to incorporate inorganic matter within its
309 matrix as is the case for Region 1. One possibility is that this layer was proteinaceous in nature
310 and included extracellular polymeric substances such as polysaccharides produced by
311 microbes. This hypothesis is consistent with the detection of polysaccharides in the fouling
312 layer by FTIR. Their late appearance in the fouling development may reflect the biofouling
313 episodes due to the algal outbreak which occurred at the later phase of the RO operation. It is
314 interesting that whilst there was no particulate matter, nor inorganic element, associated with
315 the inner amorphous layer, the layer acted as a substrate upon which aluminium silicate
316 crystals grew exclusively in the absence of other foulants including NOM. It is noted that a
317 variety of polysaccharides have been used to reduce biological fouling of surfaces due to their
318 ability to provide steric barrier and electrostatic repulsion which hinder adsorption (Hartley *et*
319 *al.*, 2002). In the present case, these properties of polysaccharides could play a role in

320 facilitating the crystal growth, but had the effect of preventing the deposition of larger
321 foulants.

322

323 **4. Conclusions**

324

325 This paper presents the autopsy results of a spiral wound RO membrane after nearly one year
326 of service in a brackish water treatment plant using optical and electron microscopic methods,
327 FTIR and ICP-AES. Both the *top surface* and the *cross-section* of the fouled membrane were
328 analysed to provide further insights into the development of the fouling layer. The results
329 obtained from different techniques are consistent and complementary to each other. A number
330 of conclusions are made:

331

332 1. The extent of fouling was uneven across the membrane surface with regions underneath or
333 in the vicinity of the feed spacer strands being most affected. The fouling in regions located
334 further away from the strands was generally less severe, but varied considerably. These results
335 highlight the importance of local variations in the hydrodynamic conditions in characterizing
336 RO fouling.

337

338 2. The major inorganic elements in the fouling layer included Al, Ca and P. The use of
339 aluminium sulphate as coagulant and phosphonate-based as antiscalant could contribute to the
340 high levels of Al and P. Lesser amounts of Fe, S, Si, Mg, K and Na were also present. Other
341 constituents of the fouling layer included proteins, polysaccharides, and aliphatic and aromatic
342 compounds derived from humic substances.

343

344 3. The fouling appeared to have developed through different stages as reflected in the
345 differences in composition and structure of the fouling layer depending on its thickness. In
346 particular, it consisted of an initial thin fouling layer of an amorphous matrix with embedded
347 particulate matter. The amorphous matrix comprised organic–Al–P complexes and the
348 particulate matter was mostly aluminium silicates. Subsequently, as the fouling layer reached a
349 thickness of about 5 to 7 μm , a secondary amorphous material, which is suggested to be
350 proteinaceous in nature and could include extracellular polymeric substances such as
351 polysaccharides, started to deposit on top of the existing fouling layer. This secondary
352 amorphous material did not seem to contain any particulate matter nor any inorganic elements
353 within it, but acted as a substrate upon which aluminium silicate crystals grew exclusively in
354 the absence of other foulants including NOM.

355

356 A key difference between the approach adopted in the current study and those applied in
357 previous autopsy studies is that the current study investigates not only the *top surface*, but also
358 the *cross-section* of the fouled membrane. As can be seen in this study, the information
359 obtained from the cross-section investigation provides insights into deposition kinetics which
360 are important for the development of a more complete understanding of the fouling
361 mechanisms. Such information would not be readily available from the traditional approach of
362 analysing the top surface. In this study, the absence of NOM and inorganic particulate matter
363 in the secondary fouling layer and the exclusive growth of aluminium silicates on top of this
364 layer are particularly interesting. Work is already underway to identify the nature of this layer,
365 which, as suggested, could include extracellular polymeric substances. This information,
366 together with the identification and isolation of bacterial strains responsible for the production
367 of these extracellular polymeric substances, may have implications in the development of anti-

368 fouling strategies aimed at preventing the deposition of NOM and particulate matter on RO
369 membranes.

370

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372

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376

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378

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