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1 **Strong etching formulation (time and rate) for PADC with deep depth bulk**  
2 **etch rate study**

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17

18 **Abstract**

19           Aqueous NaOH with ethanol (strong) etchant is widely used. It shortens  
20 etching time effectively compared to normal etching conditions (6.25N NaOH at  
21 70 °C). Two equations have been proposed to calculate the etching time with  
22 NaOH molarity and ethanol volume. Another two empirical equations were  
23 introduced for estimating the bulk etch rates of PADC etched in strong etchant. Up  
24 to now, there were no such equations available in the literature that can predict  
25 etching time and  $V_b$  of PADC with etchant molarity and ethanol volumes. The  
26 proposed equations were compared to fundamental  $V_b$  models stemming from  
27 literature. Fast etching enables the follow-up of bulk etch rate variation versus  
28 depth in the detector material up to  $\approx 80 \mu\text{m}$ . In agreement with previous studies,  
29 an equation is given which allows such variations to be expressed under the form  
30 of a reciprocal bulk etch rate normalized to depth (i.e., removed layer).

31

32

33 **Keywords:**

34 PADC; Soft/strong etching; Arrhenius model; Multi-hit model; Bulk etch rate;  
35 Etching time.

36

37

38        **1. Introduction**

39        The standard procedure when using solid-state nuclear track detectors (SSNTD)  
40 is to reveal latent ion tracks by operating a chemical etching which makes them  
41 visible under the optical or atomic force microscope. Commonly used etching  
42 solutions in the literature are alkaline etchant such as NaOH or KOH with  
43 concentration range of 6-7 N at temperatures of 60-70 °C [1-10]. However, a new  
44 etchant solution composed of NaOH with different amounts of alcohols (ethanol  
45 and/or methanol) has been used as a strong and active etchant [11-13]. Such  
46 mixtures are very effective in reducing the time needed to reveal and measure  
47 diameters of alpha tracks. Strong etching was found to provide a quadratic function  
48 of growing alpha particle tracks diameter with etching time. So, the strong etching  
49 can reduce the etching time by factor “4”, and thus enhance the etching time [13].  
50 Processing many detectors can be time-consuming using normal etching compared  
51 to strong one. Therefore, it requires fine-tuned analyses for better understanding  
52 and use in routine work.

53        Poly-allyl-diclycol-carbonate (PADC) is mainly made of the monomer allyl-  
54 diclycol-carbonate (ADC). ADC chemical structure contains two carbonate groups  
55 and one ether function. Its alkaline dissolution results in the loss of the carbonate  
56 groups from the residual molecule (see next section). This process is activated in  
57 the presence of hydroxyl ions available in an alkali solution (alkaline hydrolysis).

58 The reaction is endothermic i.e., the process needs energy to be initiated and its  
59 rate increases with increasing temperature of the solution. In principle, two models  
60 were used to describe chemical etching process. The first one is Arrhenius model,  
61 accounting thermodynamic equilibrium of chemical reaction between educts and  
62 products in homogeneous phase. In this statistical consideration, the bulk etch rate  
63 can be determined as a function of etchant concentration ( $C$ ), temperature ( $T$ ), as  
64 follows [14]:

$$65 \quad V_b(C, T, B, n, \varepsilon) = BC^n e^{\frac{-\varepsilon}{kT}} \quad (1)$$

66 Where,  $B$  is the normalization constant, the power  $n$  (not necessary integer)  
67 indicates the chemical reaction order and the activation energy  $\varepsilon$  (eV) are the  
68 adjustable parameters.  $k$  is Boltzmann's constant. Its results are widely used as  
69 well as accepted [15,16]. From this model, only two important parameters are  
70 deduced: the order of chemical etching ( $n$ ) and the activation energy of etching ( $\varepsilon$ ).

71 The second is Multi-hit model (MHM, also known as v-hit) [17], in which  
72 the dissolution of the bulk material described by the number of hits ( $v$ ) between the  
73 molecules of etchant and detector. The model is thus combining hits frequency  
74 with thermodynamic equations for a simultaneous interpretation of chemical  
75 reactions and diffusion processes. The basic idea of this model is to claim that the  
76 processes are initiated by single or repeated interactions or hits of the target

77 (molecules, molecular fragments, emulsion grains and/or living cells). SSNTDs are  
 78 then considered as composed of sensitive nanometric volumes (*SNV*) and such *SNV*  
 79 can switch from the state “*No*” to the etched state “*Yes*” after etching process with  
 80 a certain probability. Poisson’s distribution describes this probability as below:

$$81 \quad P_\nu(\xi) = 1 - \sum_{k=1}^{\nu-1} \frac{\xi^k}{k!} e^{-\xi} \quad (2)$$

82 These centres are etched if they suffer a fluctuating number of hits,  $\nu$  at the  
 83 nanometre scale by etchant molecules greater than some threshold value of  $\nu$ .  
 84 Parameter ( $\xi$ ) represents the average number of hits per sensitive volume. Several  
 85 functions for bulk etch rate proposed in terms of multi-hit approximation [17]. In  
 86 the present study, the focus was on the effect of etchant concentration on etching  
 87 rate. Therefore, two modules were considered (where the concentration effect is  
 88 dominant) to calculate the detector bulk etch rate. Module 8 of multi-hit, we will  
 89 call it MHM-M8, in which  $\xi = \frac{C}{C_0}$  and module 15 in which  $\xi = \frac{C}{C_0} e^{\frac{\varepsilon}{kT}}$ , we will call  
 90 it MHM-M15. More information about this model can be found in [18-22] and  
 91 references therein. MHM-M8 bulk etch rate can be written as:

$$92 \quad V_b(C, T, B, \nu, \varepsilon, c_0) = BC e^{\frac{-\varepsilon}{kT}} P_\nu \left( \frac{C}{C_0} \right)$$

93 (3)

94 While bulk etch rate with MHM-M15 is as follows:

95

96 
$$V_b(C, T, B, \nu, \varepsilon, c_0) = BCe^{\frac{-\varepsilon}{kT}} P_\nu \left( \frac{C}{C_0} e^{\frac{\varepsilon}{kT}} \right)$$

97 (4)

98 Many physical parameters can be deduced from this model,  $n$ ,  $\varepsilon$  and number of hits  
 99 necessary to activate the reaction between etchant molecules and detector  
 100 molecules ( $\nu$ ). Etching process is envisioned as a macroscopic process when  
 101 described by those two models; however, much information about etching  
 102 processes at the microscopic scale were ignored (see etching mechanism section).

103 Many empirical equations have been used to calculate bulk etch rates as  
 104 function of both  $C$  and  $T$  [23], such as for example:

105 
$$V_b(a_1|a_5) = a_1 10^{(a_2 C + a_3 T - a_4 CT - a_5)}$$

106 (5)

107 Where  $a_1$  to  $a_5$  are free adjusting parameters.

108 Recently, another equation assigned in terms of the etchant concentration  
 109 ( $C$ ), and free adjusting ( $a$ ) and ( $b$ ). This equation (referred here as Al-Jubbori-  
 110 2016) was proposed in [5] as follows:

111 
$$V_b = a(e^{bC} - 1) \tag{6}$$

112 Nevertheless, since the involvement of the strong etching (NaOH plus ethanol)  
 113 in 2005 [11] no equation was found to predict such specific bulk etch rates as a

114 function of the etchant concentration  $C$  at different ethanol fractions. Thus, the aim  
115 of the present work is to introduce a new empirical equation that can predict the  
116 etching time and the bulk etch rate in a wide NaOH concentration range (2-22N) of  
117 different ethanol volume of 0, 1, 2 and 3 mL (corresponding to 0, 11, 20 and 27%  
118 volume fraction) that was added to 8 mL of aqueous NaOH solutions.  
119 Additionally, an explanation to the rigorous bulk etch rate mechanism and the  
120 significant reduce in etching time by strong etching is proposed. Strong etching is  
121 used to investigate the bulk etch rate to deeper depth layers up to 80  $\mu\text{m}$  or more.  
122 Besides, a reciprocal bulk etch rate equation is going to be deduced and compared  
123 with those of literature data.

## 124 **2. Etching Mechanism**

125 Since its discovery in 1978 [24], PADC (also known as CR-39<sup>TM</sup>) is considered  
126 as one of the most successful SSNTD for detection of charged particles with linear  
127 energy transfer greater than 10 keV/ $\mu\text{m}$  (in water) [25]. It is a highly cross-linked  
128 thermoset polymer. Soft (NaOH/H<sub>2</sub>O) and strong (NaOH/ethanol) etching  
129 processes follow the same etching mechanism as illustrated in Figures 1-3. Etching  
130 takes place due to scission of the carbonate ester bond by hydroxide ions through  
131 basic hydrolysis of ester moiety (see Fig. 1). Electron rich hydroxide ions cause the  
132 scission of ester linkage because carbonyl groups (C=O) are electrically polarized



133 (the carbon atom site is electron deficient). Electron transfer occurs thus from  
134 electron rich region to electron deficient region, so that, OH groups will attack  
135 electron deficient ones (carbonyl group) as shown in Fig. 2. In PADC there are  
136 four possible positions which are subjected to cleavage by the hydroxide ion [26]  
137 as shown in Fig. 3. Etching of PADC in NaOH/ethanol will fierce bulk etch rate of  
138 the detector compared to NaOH/water. This may likely be due to the better  
139 reactivity during etching and presumably to a better solubilization of organic etch-  
140 products released from PADC. Relative static permittivity (which provides a  
141 measure of polarity) of pure methanol or ethanol are respectively 33 and 24 at  
142 25°C, with quasi-identical dipolar moments of  $\approx 1.70$  debye (D); as water has a  
143 relative static permittivity of typically 75 at 25°C (64 at 70°C) and a slightly higher  
144 dipolar moment of  $\approx 1.85$  D [27]. A decrease of the dielectric constant (i.e., of the  
145 relative static permittivity) of a given medium has a direct consequence on both  
146 reactivity and miscibility. In media containing methanol or ethanol, the dielectric  
147 constant is small, therefore attraction forces between electrical charges are  
148 enhanced in comparison to pure water. It is therefore likely that addition of  
149 alcohols in NaOH aqueous solution may partly lower the relative static permittivity  
150 value of the etchant and thus it can enhance hydroxide ion reactivity on polar  
151 groups (carbonate ester groups).

152 Fig. 3 shows that etch-products are mainly: saturated, unsaturated alcohols and  
153 carbonate ions, the latter being strongly miscible in water. The basic solubility rule  
154 states that "like dissolves like" but when applied to alcohols things become a bit  
155 more complex. Alcohols are sparingly soluble in water; their solubilities decrease  
156 with carbon chain length. Higher alcohols are insoluble in water. Organic alcohols  
157 consist of a carbon chain (always non-polar) and a OH group (which is polar). It is  
158 well-known for example that after 7<sup>th</sup> carbon atoms in a chain (i.e. for homologues  
159 longer or equal to heptanol), alcohols are considered immiscible in pure water. By  
160 mixing water and ethanol (or methanol), solubilities of both higher alcohols and  
161 aromatic hydrocarbons (non-polar in nature) increase in water/ethanol mixtures as  
162 the volume fraction of ethanol increases [27]. PADC etched products are thus more  
163 soluble in ethanol than in water. The decrease in etching time is therefore likely to  
164 be due to both of an enhancement of reactivity of the etchant (hydroxyl ions) and  
165 an increase in solubility of organic etch products resulting in an increase in the  
166 bulk etch rate,  $V_b$ .

167

### 168 **3. Experiment**

169 PADC detector sheet of thickness 650  $\mu\text{m}$ , manufactured by American  
170 Acrylics (US), was used. Detector sheet aging more than 20 years old was cut to  
171 small pieces of area 1  $\text{cm}^2$ . Each piece was irradiated to fission fragments of  $^{252}\text{Cf}$

172 for 30 min. Aqueous solution of 8 ml fresh NaOH with concentrations 2, 4, 6.25, 8,  
173 10, 12, 14, 16, 18, 20, 22, 25, 27 and 30N were prepared, and different ethanol  
174 volumes of 0, 1, 2 and 3 ml (equivalent to 0, 11, 20 and 27 % volume fractions)  
175 were added to the NaOH solutions. The suggested equations (9 and 10) have tested  
176 in both a limited NaOH concentration range (2-10N) where most applications are  
177 carried out and in an extended NaOH concentration (2-22N) to show the capability  
178 of the proposed equation. The etchant was kept at 70 °C by a water bath to avoid  
179 ethanol evaporation noting that pure ethanol boils and evaporates at 78 °C and in a  
180 mixture of water and NaOH at 95 °C. For more details about the experiment, please  
181 refer to Awad et al., [8]. Etching time was varied for different etching conditions  
182 to keep the removed bulk etch layer for each case close to  $\approx 10 \mu\text{m}$ . It was done due  
183 to the limited range ( $\sim 20\text{-}25 \mu\text{m}$ ) of fission fragments in PADC detectors. After  
184 etching of exposed detectors, diameters of fission fragment tracks were manually  
185 measured using an optical microscope (OPTIKA B-1000BF-ALC, Italy).  
186 Measurement resolution of track diameters was  $\pm 0.5 \mu\text{m}$ . The etching time  
187 necessary to obtain fission track diameter  $\approx 18 \mu\text{m}$  was determined at the different  
188 etching conditions. Largest diameter of 40 almost circular fission fragment tracks,  
189  $D_{\text{ff}}$  were manually selected as much as possible and drawn as a function of the  
190 etching time,  $t_e$  to determine the bulk etch rate [28] if the linear dependence of  $D_{\text{ff}}$   
191 ( $t_e$ ) is applicable for all etching conditions [29].

192 SSNTDs were irradiated to normal incident high energy ions of 7 GeV Si at  
193 Bevelac, Berkeley, USA with particles density  $\approx 1000$ -2000 particles/cm<sup>2</sup>. The  
194 detectors were cut perpendicularly to the detector surface into several pieces of  
195 area 1 cm<sup>2</sup>. Each piece was etched in strong etching solution (8 mL of 18 N  
196 NaOH+1mL ethanol) at 70°C for different successive etching times. Removed  
197 layer, h was determined experimentally by measuring the change in detector  
198 thicknesses using the optical microscope after the detector was mounted in its  
199 edge. After etching, track cones shaped etch-pits were found by careful polishing  
200 of the detector edge to produce ion's nuclear track profile for Si ions. The growth  
201 of the cone shaped etch-pits for Si tracks at one side of the detector were followed  
202 at different etching times. From the track cone length (L) at every etching step and  
203 the corresponding removed layer, the track etch rate  $V_t$  was determined directly  
204 [30-32]. For normally incident particle, the track etch rate at given removed layer,  
205 h can be deduced if the track etching started immediately at the detector surface  
206 without delay. Thus, the time dependent track length is available by track profile  
207 technique and track etch rate is given as:

$$208 \quad V_t(h) = \frac{dL(h)}{dt} + V_b \quad (7)$$

209 Aging effect for PADC detectors was previously studied for samples stored for  
210 8 and 12 years [33]. Polymer degradation for PADC detectors was investigated

211 microscopically using FTIR for new, medium age, and old detectors. It was proved  
212 that aging effect is not dominant and has minor effect on PADC specially for bulk  
213 and low  $\gamma$ -ray doses samples. Bulk etch rate of PADC (type PM-355) was found  
214 almost constant even after storage for a long time (about ten years) in air at room  
215 temperature in the absence of light in another study [34]. However, for a sample of  
216 age more than 12 years, the forecasted loss of sensitivity is about 2% per year.

217

## 218 **4. Data analysis**

### 219 *4.1 Data fitting method*

220 The non-linear fitting procedure was carried out by minimizing the  $\chi^2$   
221 distribution iteratively for all the considered equations. Iteration process is repeated  
222 many times using many seed numbers for the adjusted parameters till the lowest  $\chi^2$   
223 is achieved [8]. Try and error method was used to obtain the global minimization  
224 as much as possible.  $\chi^2$  values depend on degree of freedom, DF, which refers to  
225 the maximum number of the logically independent values that have the freedom to  
226 vary in the data sample (equals the number of the experimental data points minus  
227 1). In the present work, the significant levels  $\alpha$  was taken as 0.05. The fitting of the  
228 two models and the two equations are discussed accordingly.

229

230 *4.2 New approximation for etching time*

231 Two different equations are proposed to calculate the etching time. In the  
232 first one, the etching time  $t_{e1}$  necessary to reveal 18  $\mu\text{m}$  diameter of fission tracks is  
233 given in terms of the etchant concentrations as follows:

$$234 \quad t_{e1} = \frac{G}{C^q}$$

235 (8)

236 Where  $q$  is a dimensionless adjusting parameter and  $G$  is a normalization etching  
237 time factor of dimension  $[\text{min mol}^q \text{L}^{-q}]$ . In the second one, the etching time  $t_{e2}$  is  
238 given as a function of NaOH molarity and ethanol fraction,  $x$  as follows:

$$239 \quad t_{e2} = K \frac{a+x}{C^b}$$

240 (9)

241 Where  $x$  is the amount of ethanol volume, thus  $a$  and  $x$  are in L (litre) and  $C$  is the  
242 molar concentration  $\frac{\text{mol}}{\text{L}}$  with  $b \neq 1$ , then  $K$  has the following unit  $[\frac{\text{min}}{\text{L}} \cdot (\frac{\text{mol}}{\text{L}})^b]$ .

243 The physical meaning of the adjusting parameters could be deduced from their  
244 physical dimensions. However, due to their phenomenological nature, the physical  
245 meaning of the current parameters is not straightforward. At least a meaning could  
246 be deduced from their physical dimensions; such an attribution remains  
247 nevertheless hypothetically.  $K$  is thus simply a scaling time constant.

248

249 *4.3 New approximation for bulk etch*

250 The present work is suggesting two bulk etch rate equations. In the first one,  
251 bulk etch rate ( $V_{b1}$ ) was treated as a bulk quantity without considering the added  
252 ethanol fraction, like literature ones.  $V_{b1}$  can be determined in terms of the etchant  
253 concentration, C as follows:

254 
$$V_{b1} = Qe^{\left(\frac{C-i}{j}\right)^2} \quad (10)$$

255 Where Q is the bulk etch rate normalization factor of dimension  $\left[\frac{\mu\text{m}}{\text{h}}\right]$ , while i and j  
256 are two adjusting parameters have concentration dimension,  $\left[\frac{\text{mol}}{\text{L}}\right]$ .

257 As stated before, no formula has been suggested by researchers to predict the  
258 bulk etch rate as a function of NaOH concentration, C and amount of ethanol  
259 volume, x in the etchant. Therefore, a second bulk etch rate formula,  $V_{b2}$  is  
260 suggested as a function of C and x simultaneously as follows:

261 
$$V_{b2} = U (a_1 + x) \exp\left(\frac{C-a_2}{a_3}\right)^2 \quad (11)$$

262 Where U is a conversion adjusting factor of dimension  $\left[\frac{\mu\text{m}}{\text{h L}}\right]$ , x is amount of  
263 added ethanol in L, C is NaOH concentration. The free parameter  $a_1$  has dimension  
264 of [L] while both of  $a_2$  and  $a_3$  have concentration dimension  $\left[\frac{\text{mol}}{\text{L}}\right]$ .

265

266 *4.4 New approximation for reciprocal bulk etch rate*

267 The reciprocal bulk etch rate using strong etching normalized to depth (by  
268 taking the whole removed layer as  $z=1$ ) was obtained as follows:

$$269 \quad \frac{1}{v_b(z)} = f + ge^{-z} \quad (12)$$

270 Where  $f$  and  $g$  are the reciprocal bulk etch rate factors of dimension of  $\frac{h}{\mu m}$ .

271

## 272 **5. Results and Discussion**

### 273 *5.1 Etching time*

274 Fig. 4 shows the variation of etching time with the different NaOH molarity for  
275 soft and strong etching, respectively. Tables 1 and 2 compile the adjusting  
276 parameters  $G$  and  $q$  of Eq. 8 and  $K$ ,  $a$  and  $b$  of Eq. 9, respectively. From Fig. 4 and  
277 Table 1&2, one can observe that the suggested two equations produce the etching  
278 time with exactly same accuracy. However, Eq. 9 has the advantage of  
279 incorporating the ethanol volume,  $x$ .

280

### 281 *5.2 Bulk etch rate*

282 Experimental bulk etch rates for PADC SSNTD in the extended  
283 concentrations range of NaOH (2-22N) and added ethanol volumes of (0, 1, 2 and  
284 3 mL) in 8 mL of NaOH aqueous solutions are illustrated in Fig. 5. Experimental



285 uncertainty or error bars ( $\approx 15\%$ ) is relatively high. It represents the standard  
286 deviation of the measured fission fragment diameters,  $D_{ff}$ . This higher uncertainty  
287 may be accepted in terms of the manual track diameter measurements, extended  
288 concentration range, highly active and strong etching process implemented.

289 Arrhenius-like model successfully reproduce the experimental data in the  
290 extended molarity range, as shown in Fig. 5. The best fitting parameters are:  
291  $\alpha=0.05$ ,  $DF=10$ , and  $\chi^2 < 18.307$ . Table 3 compiles the fitting parameters of the  
292 Arrhenius-like model. The degree of fitting is slightly degraded with increasing  
293 amount of ethanol and NaOH concentration. Considering physical data of bulk  
294 etch rates and Arrhenius fitting, the bulk etch kinetics can be explained chemically  
295 based on collision theory. During etching process, etching species in the etching  
296 solution collide with the molecules and atoms of the PADC detector with a range  
297 of energies which is dependent on the etching temperature. Etching reaction would  
298 take place if energies of colliding species are greater than activation energy of  
299 etching ( $\epsilon$ ). The evaluated activation energies ( $\epsilon$ ) are given in Table 3. The mean  
300 value 0.676 eV (with deviation  $\pm 0.023$  eV, i.e.,  $< 3.5\%$ ) remains in agreement with  
301 previous resulted, reported in [15]. The activation energy of etching is weakly  
302 dependent (or almost independent) on the amount of ethanol added to the solution.  
303 This proves that etching process and chemical reaction rate within such extended  
304 concentration range is still at equilibrium.

305 Fig. 6 illustrated the two multi-hit models (MHM-M8 & MHM-M15)  
306 prediction to bulk etch rates of the extended concentration range incorporated with  
307 the experimental data. Fitting parameters of multi-hit models are given in Table 4.  
308 Inspecting Fig. 6 and Table 4 one can conclude that multi-hit model can reproduce  
309 bulk etch rate with good accuracy. Activation energy,  $\varepsilon$  deduced by multi-hit  
310 model is less than previously reported value ( $\approx 0.70$  eV) [2, 15, 19] however, still  
311 have the same order of magnitude. Values of number of hits,  $\nu$  required for  
312 activating the sensitive volume of the polymer were 2 for 0 ethanol and 1 in the  
313 presence of ethanol as expected. This is one advantage for the multi-hit model  
314 where this number of hits,  $\nu$  is another indicator about the etchant activity. As  $\nu$   
315 decreases ( $=1$ ) for ethanol solution, as the etchant activity probably increases  
316 compared to  $\nu=2$  for soft etching.

317 Bulk etch rates can also be predicted using an equation with only two  
318 adjusting parameters [5]. This simple equation can reproduce the bulk etch rate  
319 with accuracy where the best fitting parameters are:  $\alpha=0.05$ ,  $DF=10$ , and  $\chi^2 <$   
320  $18.307$  as given in Table 5 and illustrated in Fig. 7.

321 Experimental bulk etch rate and the non-linear fit using Eq. 10&11 for the limited  
322 (2-10N) and extended molarity are shown in Fig. 8 and 9, respectively. The new  
323 equations are predicting the bulk etch rate with the same high accuracy as

324 illustrated in Tables 6&7. The different adjusting parameters Q, i, j, U, a<sub>1</sub>, a<sub>2</sub> and  
325 a<sub>3</sub> of equations 10&11 are compiled. The adjusting parameters are showing slight  
326 dependence on C and x. Of course, the 27 % ethanol content (3 mL) data shows  
327 higher  $\chi^2$  value compared to the other ethanol volumes. However, it is statistically  
328 accepted. This is expected in terms of bulk etch rate has been duplicated compared  
329 to the closest ethanol volume of 20%. The best fitting parameters are:  $\alpha=0.05$ ,  
330 DF=4,  $\chi^2 < 9.488$  and  $\alpha=0.05$ , DF=10,  $\chi^2 < 18.307$  for the limited and extended  
331 concentration ranges. By the goodness of the fitting curves in comparison with the  
332 well-known models (Arrhenius and Multi hit) the validity of suggested empirical  
333 formula has been determined.

334 In the previous paragraphs, the different equations for bulk etch rate were  
335 studied individually. All the equations were succeeded to reproduce the bulk etch  
336 rate as depicted in Fig. 10 but with different accuracy Tables 3-7. However, Eq. 11  
337 is more advantageous since it adds both NaOH molarity and ethanol fraction as  
338 etching parameter. Eventually, this equation can be applied to other SSNTDs and  
339 chemical etchants, such as KOH.

340 Rigorous bulk etch rate  $V_b$  of PADC in NaOH/ethanol compared to  
341 NaOH/water and lowering etching time,  $t_e$  can be attributed to the fact that media  
342 containing methanol or ethanol has smaller dielectric constant. Attraction forces  
343 between electrical charges are enhanced in comparison to pure water. Therefore, it

344 is likely that addition of alcohols in NaOH aqueous solution may partly lower the  
345 relative static permittivity of the etchant and thus enhances hydroxide ion reactivity  
346 on polar groups (carbonate ester groups).

347

### 348 *5.3 Reciprocal bulk etch rate*

349 PADC bulk and track etch rate variation with depth up to  $\approx 80 \mu\text{m}$  was  
350 intensively investigated where strong etching allows successive etching effectively  
351 with reasonable etching time. The variation in  $V_b$  and  $V_t$  with depth for swift Si ion  
352 are illustrated in Fig. 11. It was found that bulk etch rate is slightly increasing with  
353 depth in agreement with Fujii and Nishimura, 1986 [35]. Simultaneously, the track  
354 shaped etch-pits were measured for limited number of cones, and the  
355 corresponding track etch rate  $V_t$  was determined. The track etch rate  $V_t$  is found to  
356 be almost constant as expected for swift heavy ions passes through the bulk of  
357 SSNTD.

358 Detector sensitivity,  $V$  for Si ion was determined and normalized to value  
359 achieved at the first etched-off layer of a detector where  $V = \frac{V_t}{V_b}$ . Variation in  
360 normalized sensitivity as a function of the removed layer  $h$  is presented in Fig. 12.  
361 One can observe that the detector sensitivity decreases with depth and reaches  
362 between 60-80% and becomes more stable at depth  $25 \mu\text{m}$  inwards. This reduced

363 sensitivity with depth is due to the slight increase in  $V_b$  while  $V_t$  is almost constant.  
364 The variation of  $V_b$  is an effect, probably specific for long etching time periods as  
365 already mentioned in literature [35] (and references therein) in the case of a 2  
366 GeV/nucleon iron nucleus track etched for more than 20 hours. The reasons for  $V_b$   
367 (and hence  $V$ ) variation with depth may be due to a property of used plastic,  
368 structural inhomogeneity in the detector material linked with its curing process  
369 during fabrication and finally the successive etching process that follows heating  
370 and drying of the detector sample many times. It was mentioned by Fujii and  
371 Nishimura [35] that "most of the thick CR-39 sheets commercially available show  
372 the depth dependence". However, this phenomenon deserves further investigation.

373 Experimental and calculated reciprocal bulk etch rate with normalized depth  
374 (total depth,  $z=1$ ) are illustrated in Fig. 13 where the best fitting of Eq. 12 was  
375 obtained at  $f=0.04$  and  $g=0.07$ . Prolonged etching with the amount of bulk-etch  
376 exceeding  $80\ \mu\text{m}$  is necessary for producing swift heavy ions thick track membrane  
377 [36] and study the track wall curvature development with removed layer through  
378 the entire detector depth. Eq. 12 is fundamental for simulating the etched track  
379 profiles and the shape of the track curvature developed with depth inside the  
380 polymer and it can describe the reciprocal  $V_b$  as a function of ( $z$ ) for soft etching  
381 conditions as well.

382

## 383 **6 Conclusions**

384 Two empirical equations were proposed for bulk etch rate estimation. Both  
385 equations were applied to soft and strong etching. A reasonable reproduction of  
386 bulk etch rate was found at both limited and extended concentration range with  
387 different ethanol volumes. Validity of suggested empirical formula has been  
388 proved by goodness of the curves compared to Arrhenius and Multi-hits models.  
389 Eq. 10 is using etchant concentration like literature equations. Eq. 11 has the  
390 advantage that it reproduces the bulk etch rate as a function of both NaOH  
391 concentration and ethanol fraction simultaneously. This equation can be extended  
392 to other SSNTDs, and another etchant as well.

393 Two equations were suggested to calculate the etching time as a function of  
394 molarity and molarity with ethanol volume. The reduction in etching time can save  
395 considerable time in many applications.

396 Higher  $V_b$  and lower  $t_e$  of PADC can be explained by better solubility of etch  
397 product in ethanol than in water. Ethanol medium provides smaller dielectric  
398 constant and thus improves the attraction forces between electrical charges. Lower  
399 static permittivity of ethanol etchant enhances hydroxide reactivity on carbonate  
400 ester groups.

401 Deep (up to 80  $\mu\text{m}$ ) bulk etch rate and deep detector sensitivity were  
402 investigated.  $V_b$  shows slight increase while  $V$  show slight decrease with depth.  
403 Detector sensitivity is slightly decreasing with depth reaching 60-80 % after 25  $\mu\text{m}$   
404 were removed. The SSNTD sensitivity may become quite stable at depth  $>25 \mu\text{m}$ ,  
405 so more accurate identification of swift heavy ion is possible with long etching  
406 plan.

407 Reciprocal bulk etch rate equation was given with the normalized depth.  
408 This equation is necessary for simulating etched track profiles. Deep-depth-effect  
409 is a subject of particular concern for producing thick nuclear track membranes and  
410 deep profile track curvature study.

411 In progress, etching time ( $t_e$ ) for a given etching conditions will be estimated  
412 in terms of the Multi-hit model. Using geometric considerations, it is possible to  
413 estimate the frequency of collisions of ethanol molecules with the sensitive link of  
414 the detector molecules and obtain the release time of a given thickness in  
415 connection with the etching time.

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## 429 **Figures Caption**

430 Fig. 1 Ester group hydrolysis in PADC CR-39 and the cleavage of ester  
431 linkage caused by hydroxide ion.

432 Fig. 2 Stages of the hydroxyl attack on the carbonyl during the etching  
433 process.

434 Fig. 3 The possible positions of the cleavage and the yielded etching outputs.

435 Fig. 4 Eqs. 8 and 9 prediction to the etching time necessary to obtain  $D_{ff} \approx 18$   
436  $\mu\text{m}$  using different NaOH molarity for soft and strong etching,



437 respectively. Eq. 9 has the advantage of incorporating the ethanol  
438 volume,  $x$ .

439 Fig. 5 Arrhenius equation fit of bulk etch rate in extended NaOH/ethanol  
440 concentration range.

441 Fig. 6 Multi hit model of MHM-M8 and MHM-M15 fit of bulk etch rate in  
442 extended NaOH/ethanol concentration range.

443 Fig. 7 Al-Jubbori-2016 equation fit of bulk etch rate in extended  
444 NaOH/ethanol concentration range.

445 Fig. 8 Prediction of the newly suggested equations (Eq. 10 and Eq. 11) to  
446 bulk etch rate for the limited (2-10N) NaOH concentration range  
447 mixed with different ethanol volume.

448 Fig. 9 Prediction of the newly suggested equations (Eq. 10 and Eq. 11) to  
449 bulk etch rate for the extended (2-22N) NaOH concentration range  
450 mixed with different ethanol volume.

451 Fig. 10 Experimental bulk etch rate and the corresponding calculated ones  
452 using Arrhenius, MHM-M8, Al-Jubbori-2016 and the new suggested  
453 Eq. 11 as a function of NaOH concentration and different ethanol  
454 volumes.

455 Fig. 11 The variation in the bulk and track etch rate with removed layer  
456 (depth) for Si swift heavy ion.

457 Fig. 12 PADC sensitivity (V) normalized to value, achieved at the first  
458 etched-off layer of a detector for Si swift heavy ion variation with  
459 detector depth.

460 Fig. 13 Experimental and calculated reciprocal bulk etch rate with normalized  
461 depth (total removed layer,  $z=1$ ).

462

### 463 **Tables Caption**

464 Table 1 Fitting parameters for etch time formula (Eq. 8).

465 Table 2 Fitting parameters for etch time formula (Eq. 9).

466 Table 3 Arrhenius equation fitting parameters for the extended NaOH  
467 concentration and different ethanol volume at  $B=1.25 \times 10^9$ .

468 Table 4 MHM-M8 and MHM-M15 fitting parameters for the extended NaOH  
469 concentration and different ethanol volume at  $B=1.25 \times 10^9$ .

470 Table 5 Al-Jubbori-2016 equation fitting parameters for the extended NaOH  
471 concentration and different ethanol volume.

472 Table 6 New equation (Eq. 10) fitting parameters for limited and extended  
473 NaOH concentration range at different ethanol volume.

474 Table 7 New equation (Eq. 11) fitting parameters for limited and extended  
475 NaOH concentration range at different ethanol volume.

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