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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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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 ε (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 (ε).

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, ν at the
 83 nanometre scale by etchant molecules greater than some threshold value of ν .
 84 Parameter (ξ) 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 , ε and number of hits
 99 necessary to activate the reaction between etchant molecules and detector
 100 molecules (ν). 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 μm 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-39TM) is considered
126 as one of the most successful SSNTD for detection of charged particles with linear
127 energy transfer greater than 10 keV/ μm (in water) [25]. It is a highly cross-linked
128 thermoset polymer. Soft (NaOH/H₂O) 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 ≈ 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 ≈ 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 7th 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 μm , 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 cm^2 . Each piece was irradiated to fission fragments of ^{252}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_{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_{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 ≈ 1000 -2000 particles/cm². The
194 detectors were cut perpendicularly to the detector surface into several pieces of
195 area 1 cm². 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 γ -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 χ^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 χ^2
223 is achieved [8]. Try and error method was used to obtain the global minimization
224 as much as possible. χ^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 α 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 μm diameter of fission tracks is
233 given in terms of the etchant concentrations as follows:

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

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

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 (ϵ). The evaluated activation energies (ϵ) are given in Table 3. The mean
300 value 0.676 eV (with deviation ± 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, ε deduced by multi-hit
310 model is less than previously reported value (≈ 0.70 eV) [2, 15, 19] however, still
311 have the same order of magnitude. Values of number of hits, ν 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, ν is another indicator about the etchant activity. As ν
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, a₁, a₂ and
325 a₃ 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 χ^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 μm) 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 μm
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 μm 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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