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

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Abstract

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

Keywords:

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

1. Introduction

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

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

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

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

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

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

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

$$P_v(\xi) = 1 - \sum_{k=1}^{v-1} \frac{\xi^k}{k!} e^{-\xi} \quad (2)$$

These centres are etched if they suffer a fluctuating number of hits, v at the nanometre scale by etchant molecules greater than some threshold value of v . Parameter (ξ) represents the average number of hits per sensitive volume. Several functions for bulk etch rate proposed in terms of multi-hit approximation [17]. In the present study, the focus was on the effect of etchant concentration on etching rate. Therefore, two modules were considered (where the concentration effect is dominant) to calculate the detector bulk etch rate. Module 8 of multi-hit, we will 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 it MHM-M15. More information about this model can be found in [18-22] and references therein. MHM-M8 bulk etch rate can be written as:

$$V_b(C, T, B, v, \varepsilon, c_0) = BC e^{\frac{-\varepsilon}{kT}} P_v\left(\frac{C}{C_0}\right)$$

(3)

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

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

(4)

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

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

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

(5)

Where a_1 to a_5 are free adjusting parameters.

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

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

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

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

2. Etching Mechanism

Since its discovery in 1978 [24], PADC (also known as CR-39TM) is considered as one of the most successful SSNTD for detection of charged particles with linear energy transfer greater than 10 keV/ μm (in water) [25]. It is a highly cross-linked thermoset polymer. Soft (NaOH/H₂O) and strong (NaOH/ethanol) etching processes follow the same etching mechanism as illustrated in Figures 1-3. Etching takes place due to scission of the carbonate ester bond by hydroxide ions through basic hydrolysis of ester moiety (see Fig. 1). Electron rich hydroxide ions cause the scission of ester linkage because carbonyl groups (C=O) are electrically polarized

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

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

3. Experiment

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

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

SSNTDs were irradiated to normal incident high energy ions of 7 GeV Si at Bevelac, Berkeley, USA with particles density $\approx 1000\text{-}2000$ particles/cm². The detectors were cut perpendicularly to the detector surface into several pieces of area 1 cm². Each piece was etched in strong etching solution (8 mL of 18 N NaOH+1mL ethanol) at 70°C for different successive etching times. Removed layer, h was determined experimentally by measuring the change in detector thicknesses using the optical microscope after the detector was mounted in its edge. After etching, track cones shaped etch-pits were found by careful polishing of the detector edge to produce ion's nuclear track profile for Si ions. The growth of the cone shaped etch-pits for Si tracks at one side of the detector were followed at different etching times. From the track cone length (L) at every etching step and the corresponding removed layer, the track etch rate V_t was determined directly [30-32]. For normally incident particle, the track etch rate at given removed layer, h can be deduced if the track etching started immediately at the detector surface without delay. Thus, the time dependent track length is available by track profile technique and track etch rate is given as:

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

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

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

4. Data analysis

4.1 Data fitting method

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

4.2 New approximation for etching time

Two different equations are proposed to calculate the etching time. In the first one, the etching time t_{e1} necessary to reveal 18 μm diameter of fission tracks is given in terms of the etchant concentrations as follows:

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

(8)

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

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

(9)

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

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

4.3 New approximation for bulk etch

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

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

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

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

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

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

4.4 New approximation for reciprocal bulk etch rate

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

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

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

5. Results and Discussion

5.1 Etching time

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

5.2 Bulk etch rate

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

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

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

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

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

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

illustrated in Tables 6&7. The different adjusting parameters Q , i , j , U , a_1 , a_2 and a_3 of equations 10&11 are compiled. The adjusting parameters are showing slight dependence on C and x . Of course, the 27 % ethanol content (3 mL) data shows higher χ^2 value compared to the other ethanol volumes. However, it is statistically accepted. This is expected in terms of bulk etch rate has been duplicated compared to the closest ethanol volume of 20%. The best fitting parameters are: $\alpha=0.05$, $DF=4$, $\chi^2 < 9.488$ and $\alpha=0.05$, $DF=10$, $\chi^2 < 18.307$ for the limited and extended concentration ranges. By the goodness of the fitting curves in comparison with the well-known models (Arrhenius and Multi hit) the validity of suggested empirical formula has been determined.

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

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

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

5.3 Reciprocal bulk etch rate

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

Detector sensitivity, V for Si ion was determined and normalized to value achieved at the first etched-off layer of a detector where $V = \frac{V_t}{V_b}$. Variation in normalized sensitivity as a function of the removed layer h is presented in Fig. 12. One can observe that the detector sensitivity decreases with depth and reaches 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 μm 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.

6 Conclusions

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

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

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

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

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

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