WET & DRY ELECTRICAL AGING OF XLPE

A Molecular Approach

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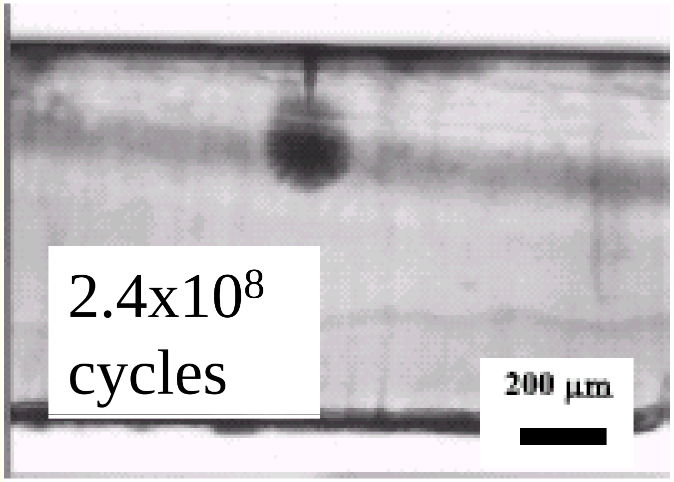
Plan

- 1- Wet aging- water treeing: data, fatigue, electromechanical effects, a comprehensive model
- 2- Dry aging- endurance and breakdown: ac vs. dc, bonds scission, radicals, sample size, a tentative model
- 3- Conclusion: summary and what remains to be done

WATER TREEING

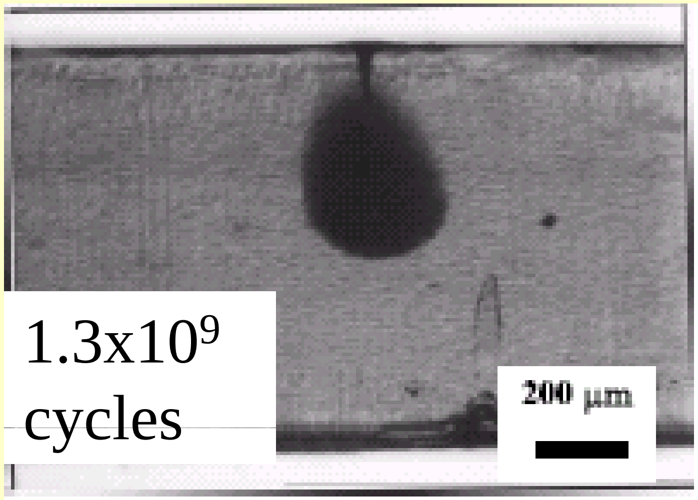
- oxidation is NOT the bad boy !
- the essential role of fatigue
- a simple model
- links with dry aging

Influence of the number of field cycles on water tree length and shape (Maeda et al., ICSD04)



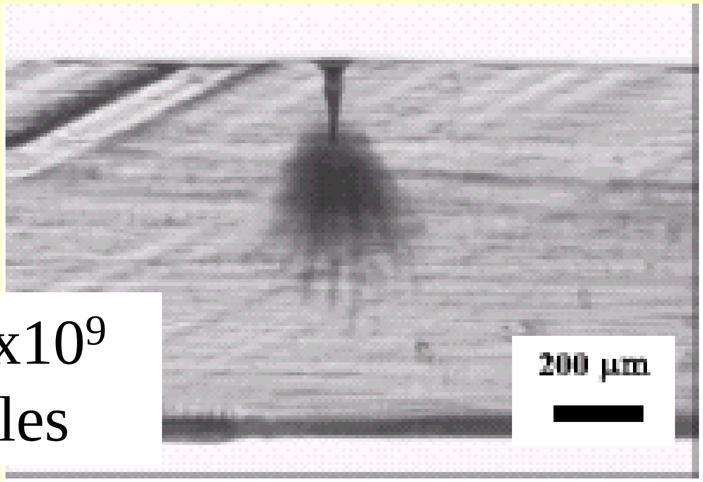
2.4x10^{8} cycles

(15) 50 Hz (10 kV$_{rms}$) + 2 kHz (3.0 kV$_{rms}$)



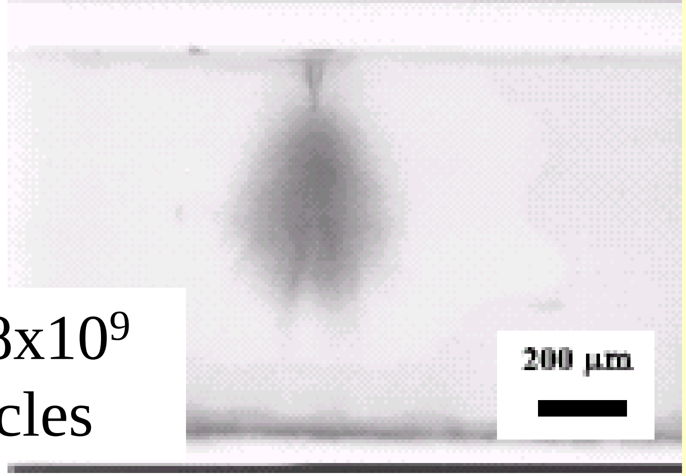
1.3x10^{9} cycles

(18) 50 Hz (4.0 kV$_{rms}$) + 4 kHz (3.0 kV$_{rms}$)



2.4x10^{9} cycles

(1) 2 kHz (3.0 kV$_{rms}$)



4.8x10^{9} cycles

(3) 4 kHz (3.0 kV$_{rms}$)

Parameters related to water tree growth in PE

- Humidity
- Alternating field
- Amplitude of electric field
- Frequency of field
- Nature and concentration of soluble ions
- Temperature
- Possibility that oxidation and residual mechanical stresses might play some role (?)

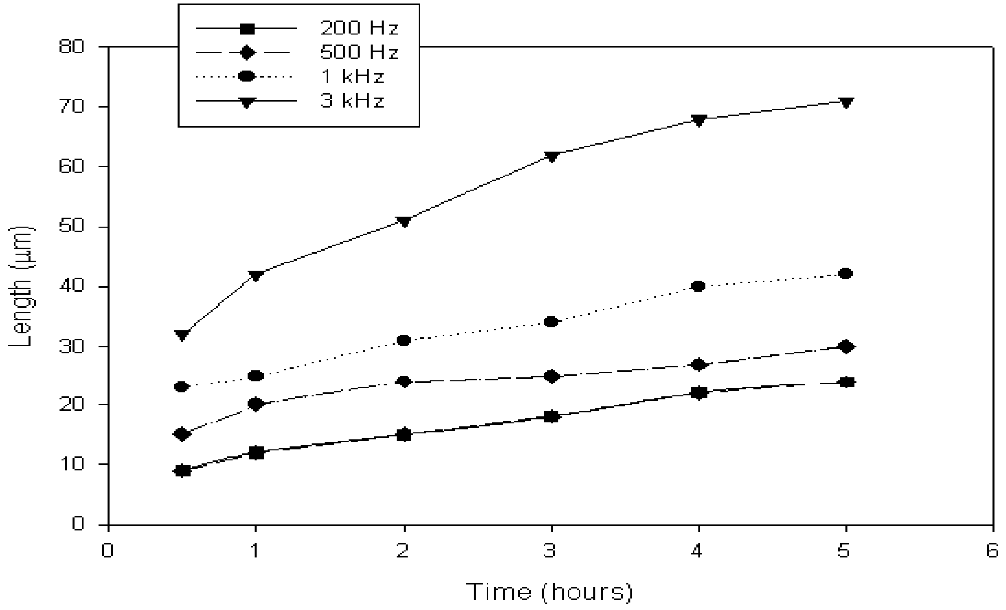
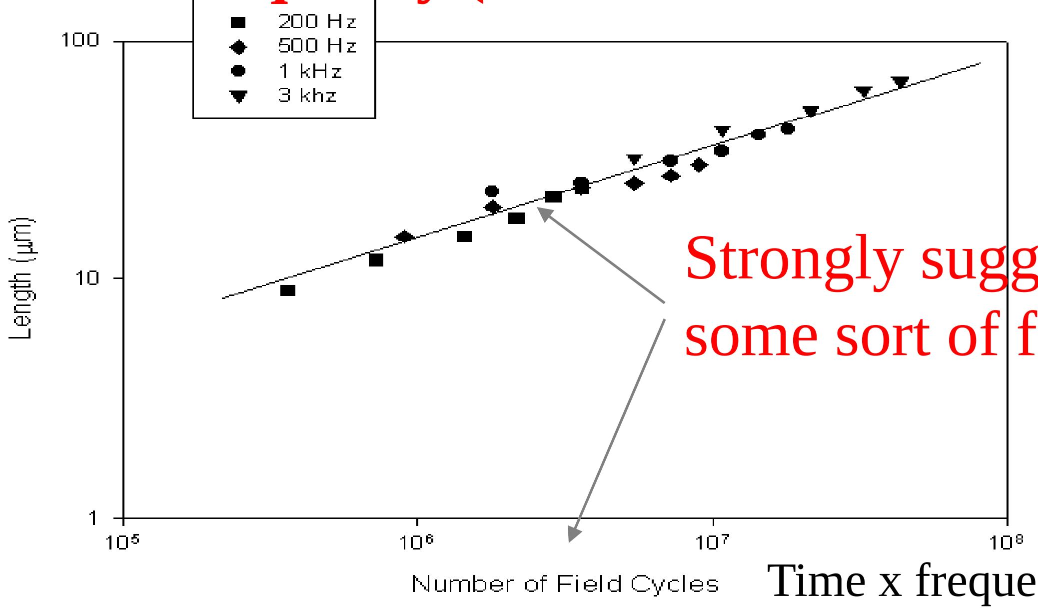


Fig.1

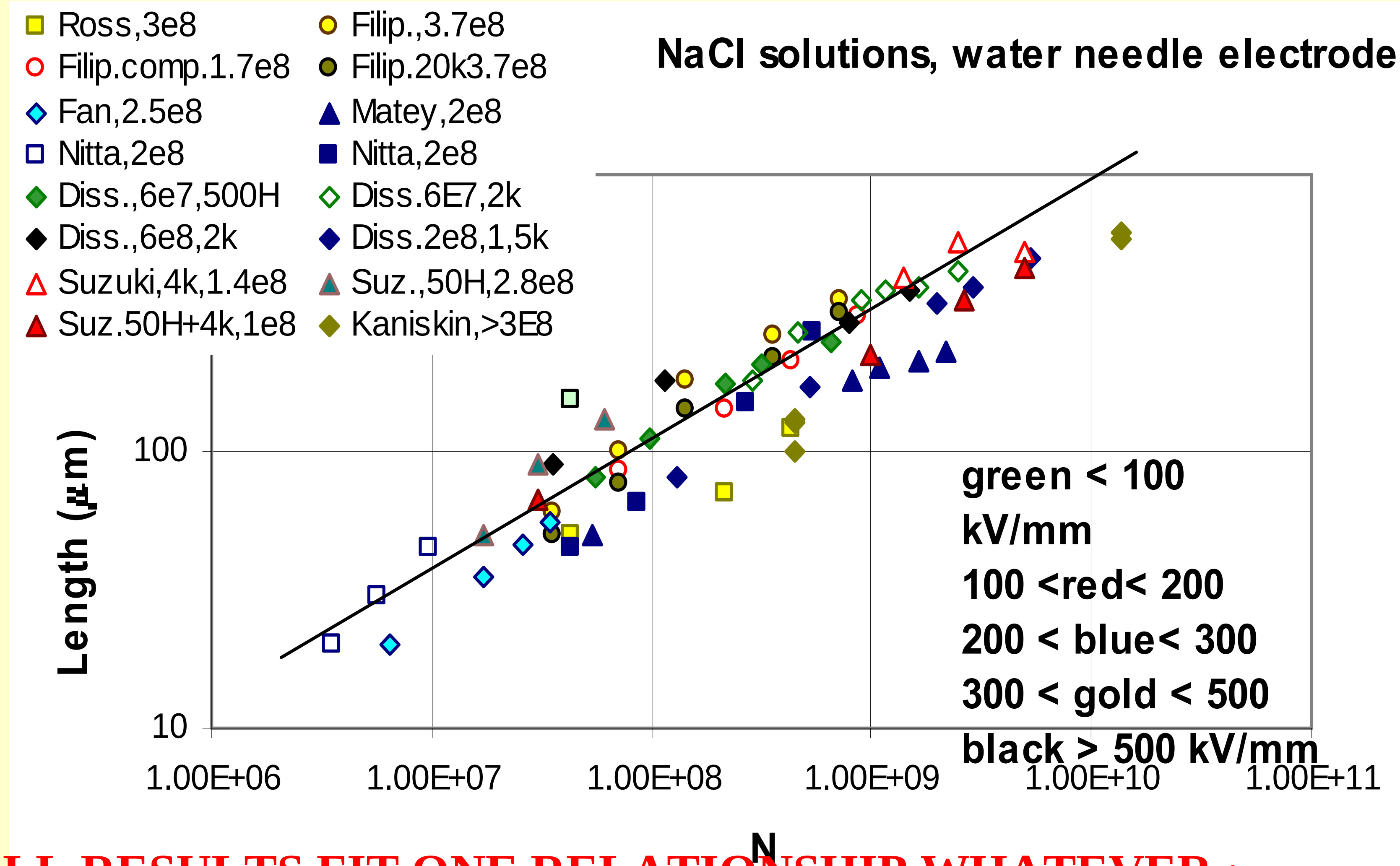
Effect of frequency (constant F & distilled water)



Strongly suggests
some sort of fatigue

Time x frequency

Fig. 2

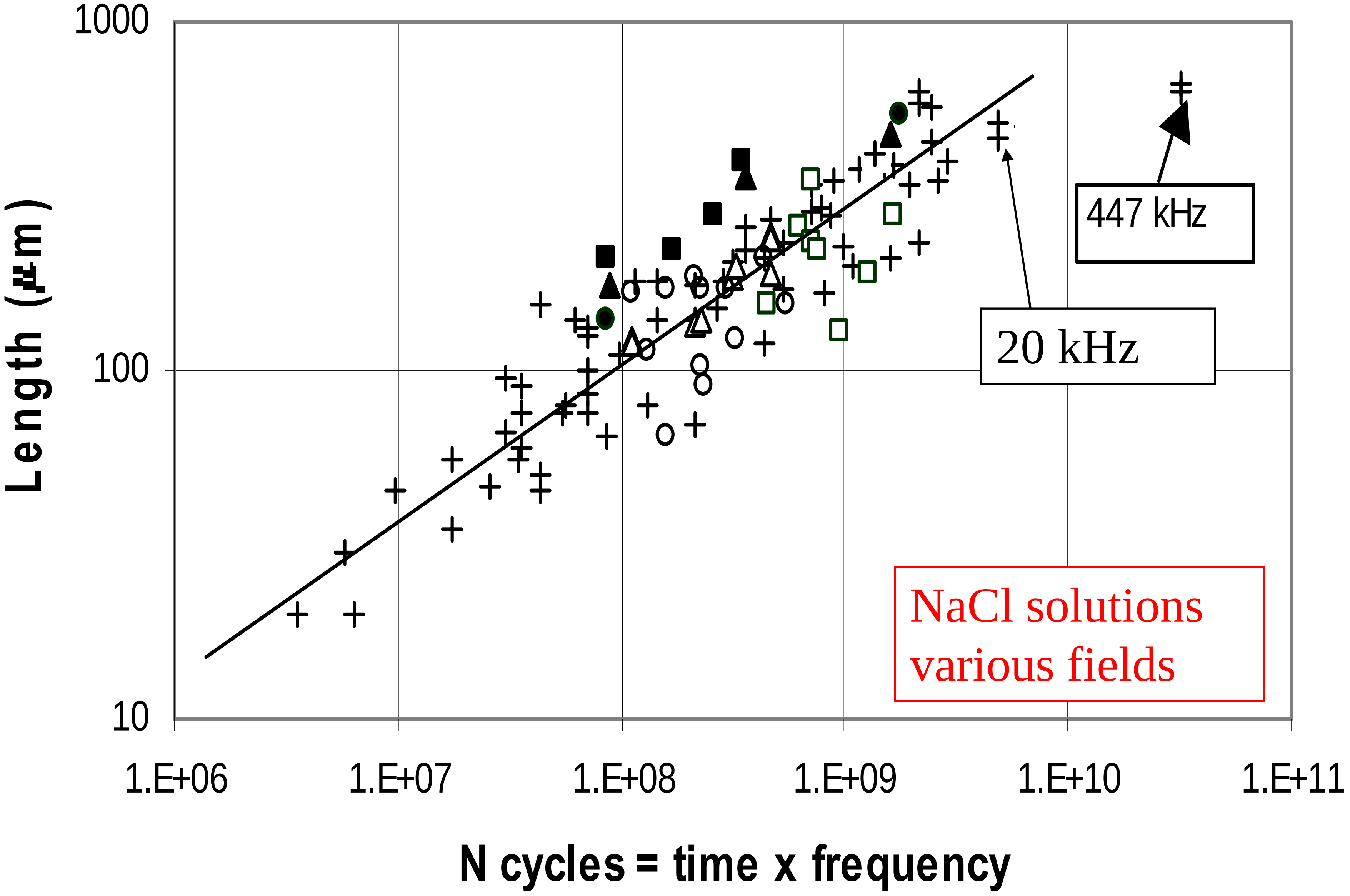


ALL RESULTS FIT ONE RELATIONSHIP WHATEVER :

1. **THE VOLTAGE**
2. **THE ATMOSPHERE**
3. **THE TESTING CELL**

PROVIDED WATER TREE LENGTH IS PLOTTED AS A FUNCTION OF THE NUMBER OF CYCLES.

+: water needle, filled symbols: scratched samples,
open symbols: Rogowski cells

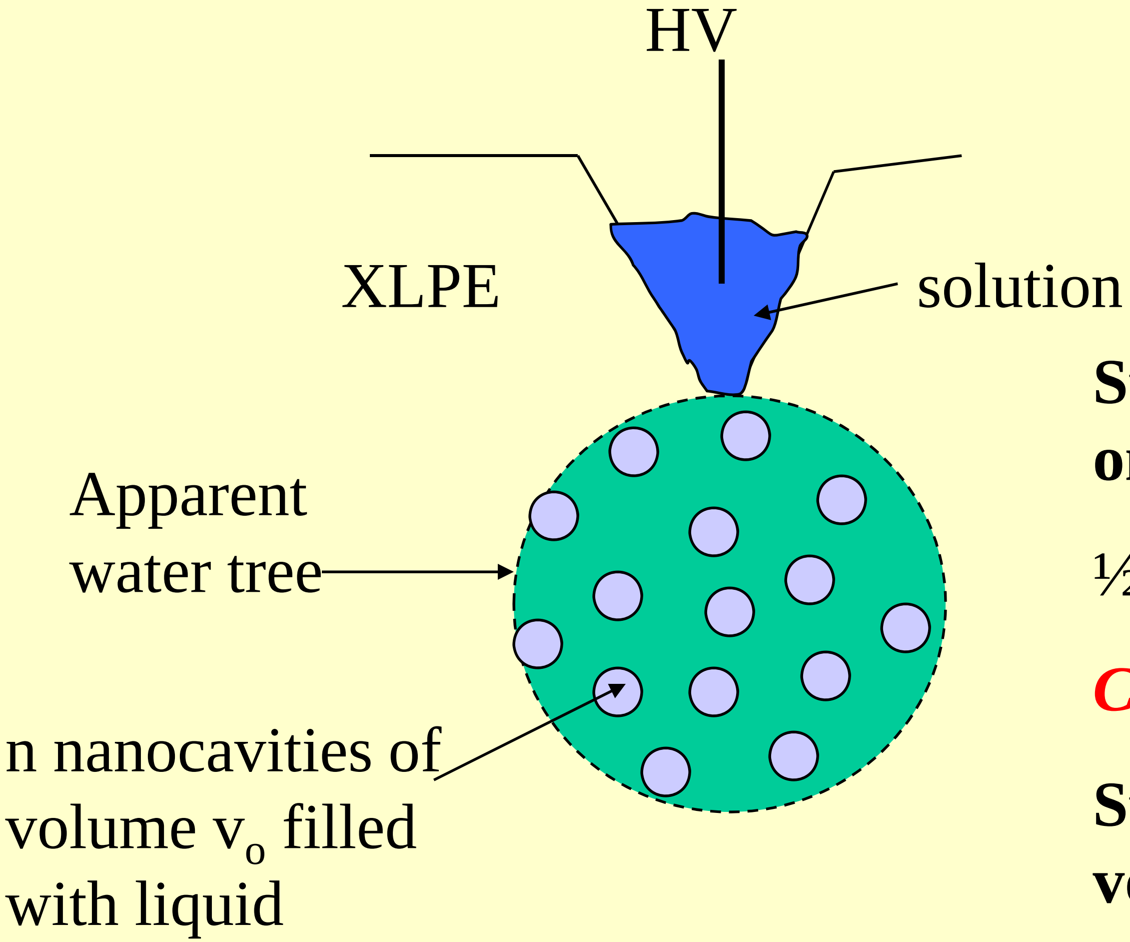


447 kHz

20 kHz

NaCl solutions
various fields

THE MODEL



Stress applied by the field on the nanocavities:

$\frac{1}{2}\,\varepsilon_o\varepsilon' F^2\, n\, v_o$

Criterion for growth:

Stress on water treed volume > yield strength Y

The number of cavities filled with water depends on water diffusion, i.e varies with $t^{1/2}$. Thus, after N field cycles and for a water tree volume V_{wt} we got

$$N\,\frac{1}{2}\,\varepsilon_o\varepsilon' F^2\, n_o\, t^{1/2}\, v_o > Y\, V_{wt}$$

Assuming the water tree has the shape of a sphere

$$V_{wt} = (4\,\pi/3)\,(L/2)^3 \sim L^3/2$$

where L is the length of the water tree; it means

$$L^3 = N\,\varepsilon_o\varepsilon' F^2\,n\,v_o/Y$$

Assuming a conical shape for the water tree with the diameter of the cone equal to half the length L of the water tree gives

$$V_{wt} = (\pi/3)\,L^3/4 \sim L^3/4$$

Thus, the effect is very small and does not change the basic relationship; we have therefore assumed a spherical shape for the sake of simplicity.

There is no growth in absence of a liquid. We may expect that the liquid obeys a diffusion-like process. Thus, we assumed that the concentration of filled nanocavities n was described by

$n = n_o\, t^{½}$

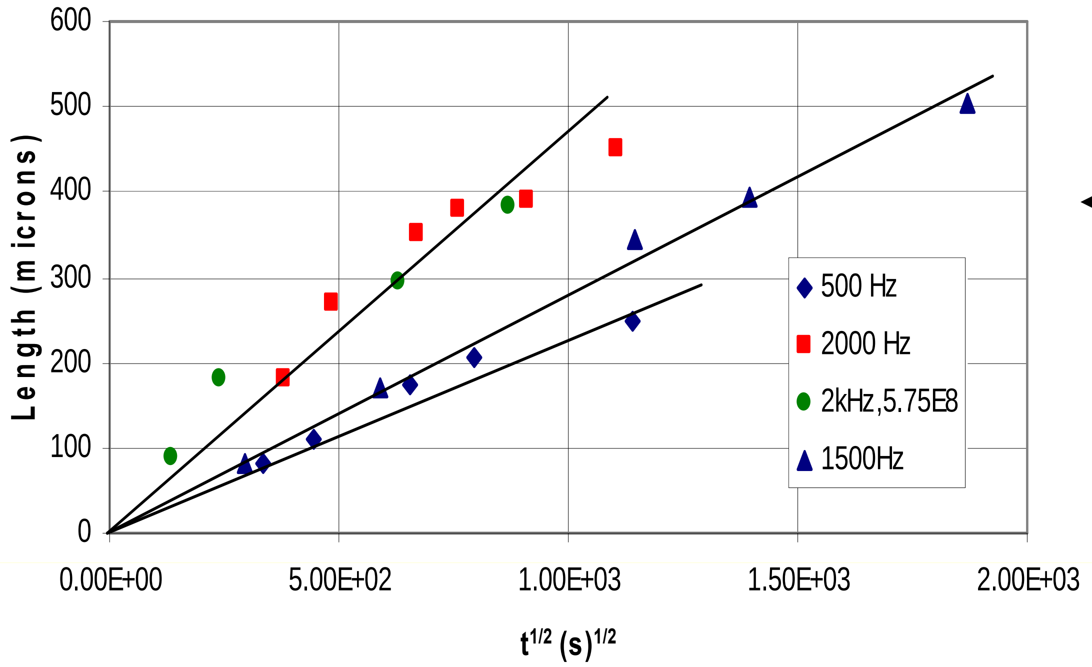
The water tree length L then varies as

$L \sim (N\varepsilon_o\varepsilon'\, n_o t^{½}\, v_o\, F^2/Y)^{1/3}$

Thus, L should varies with $t^{½}$ (under constant frequency) and with $f^{\,1/3}$ (for a given time).

Note that L varies with the field as $F^{2/3}$, i.e. a limited influence of field - as indeed observed.

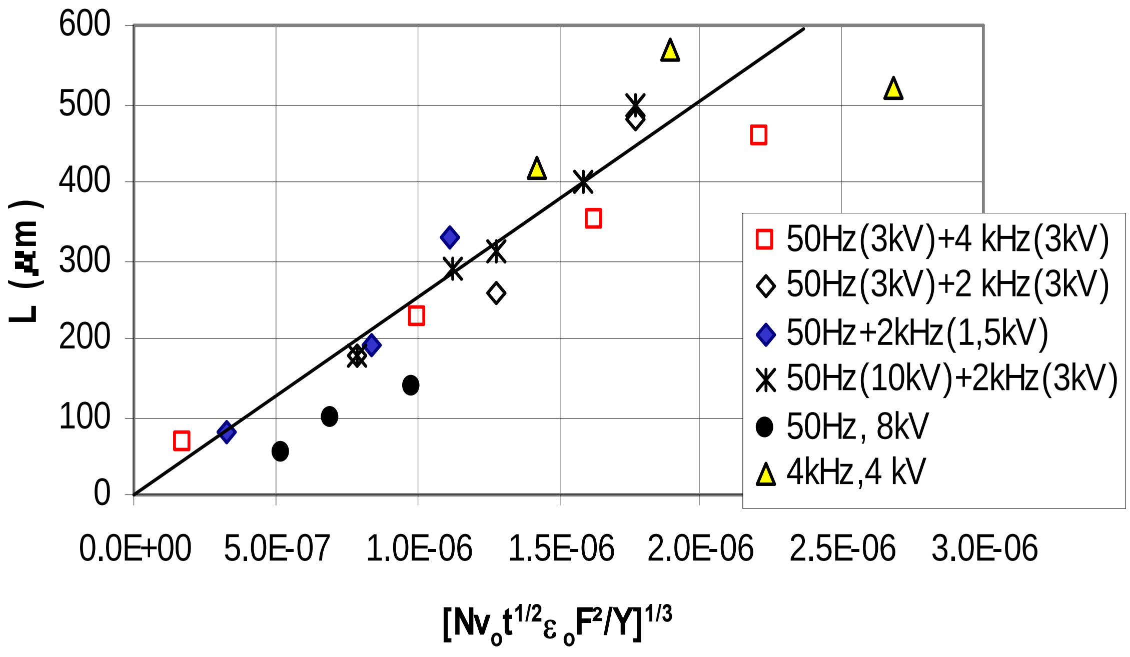
The nature and concentration of the ionic solution affects ε' and the morphology of the polymer affects Y (and ε' to a lesser extent).

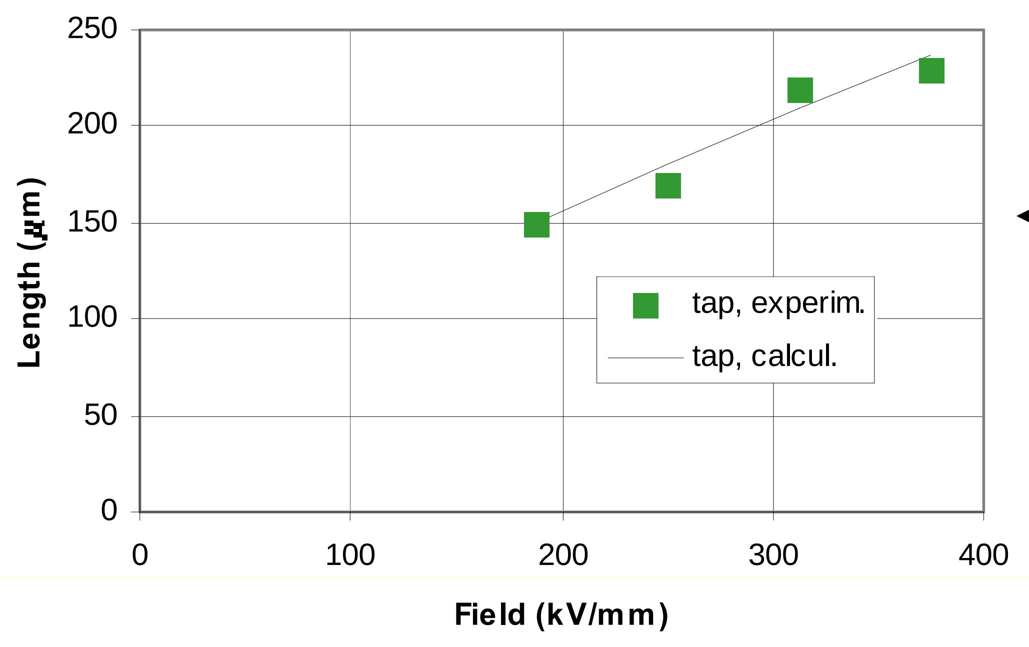


Time dependence in agreement with theoretical prediction (XLPE, NaCl, various frequencies)

Same results plotted according to the model:

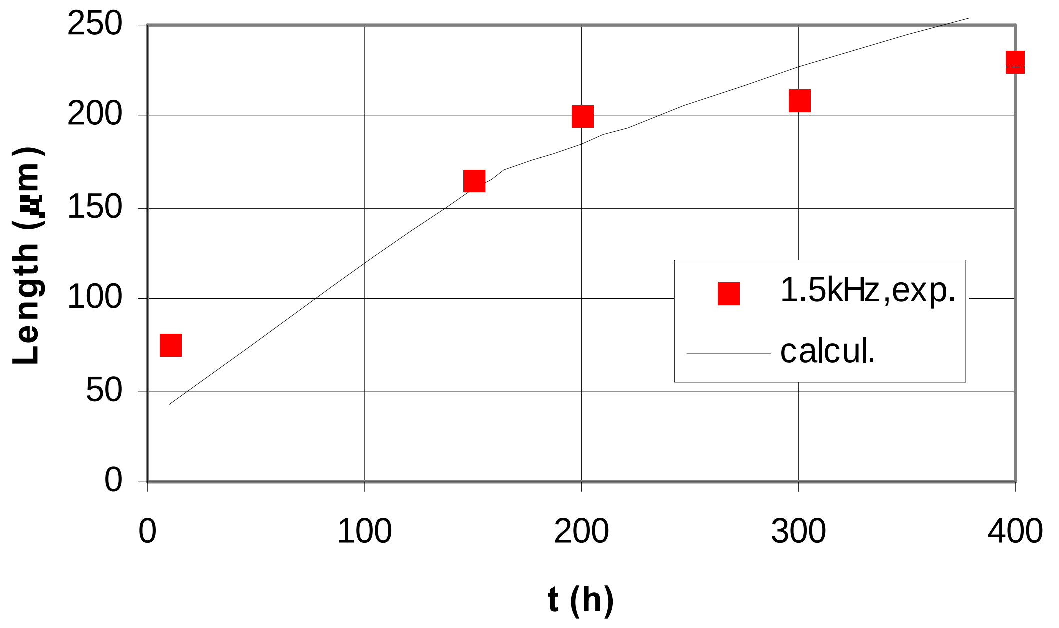
all results fit one general relationship whatever the field or frequency





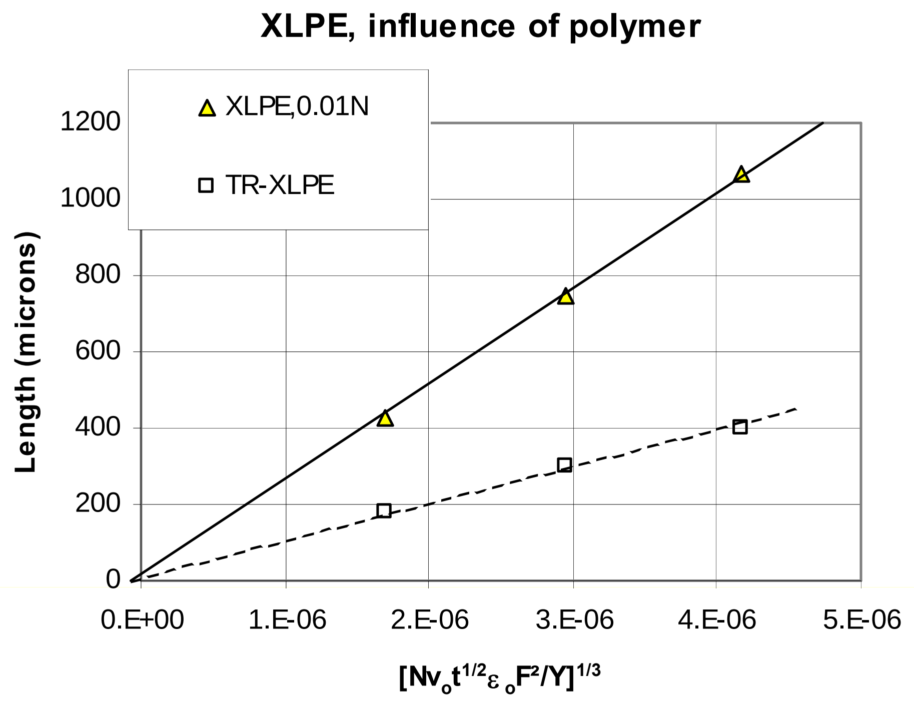
Agreement between theory and experiment (in tap water) for constant frequency

Agreement between theory and experiment (in NaCl) for constant frequency and field



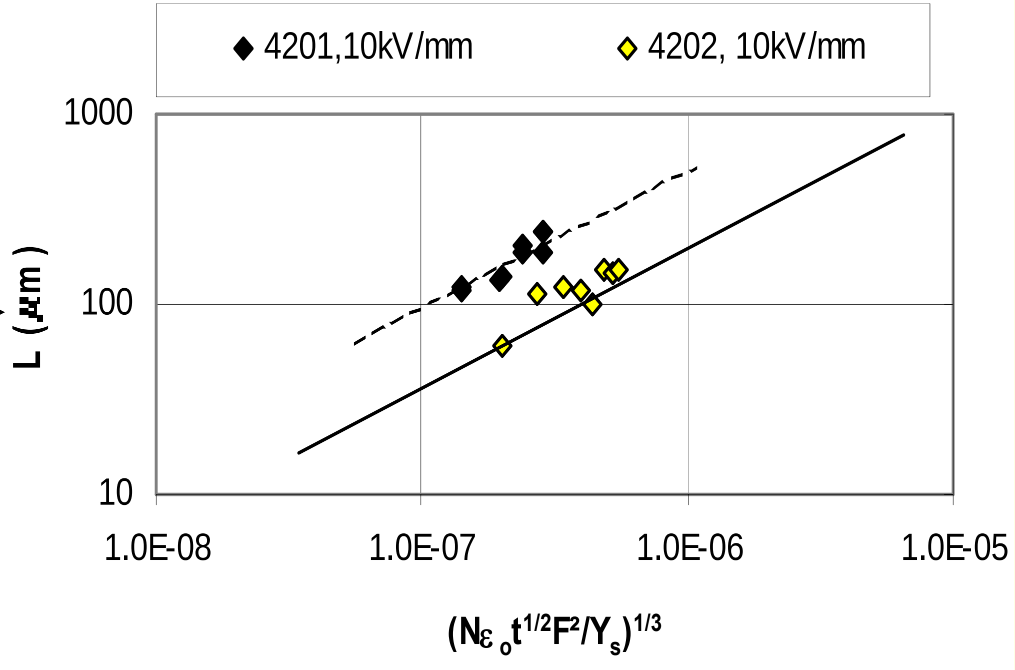
TR-XLPE vs. XLPE

(NaCl solutions)

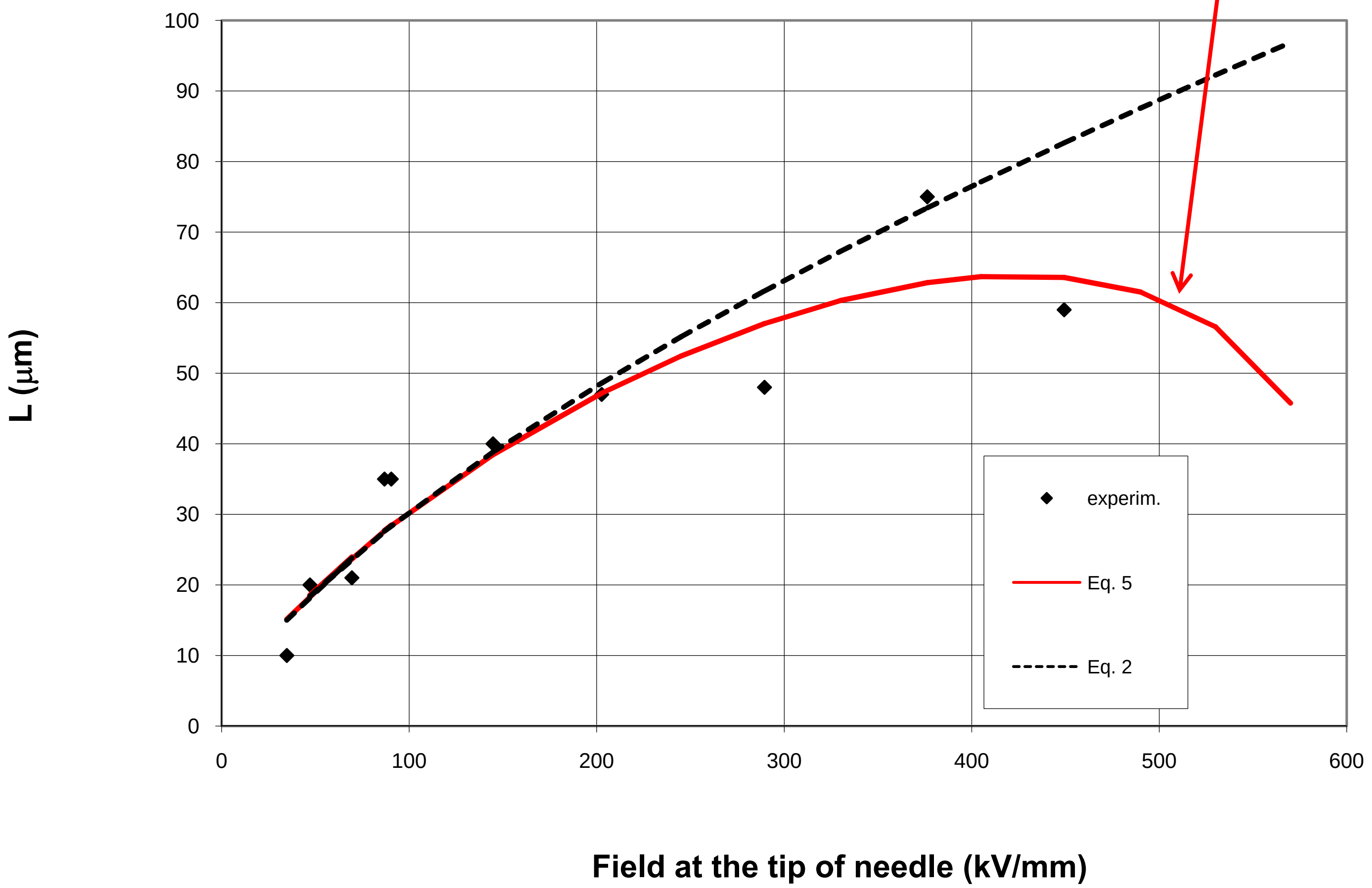


Aschcraft cell (water needle electrode)

Rogowski cell



SLOWER WATER TREE GROWTH AT VERY HIGH FIELDS: influence of the strain energy (dv stress/2E)



Summary for water treeing:

- A model succesfully describing the influence of frequency and field on water trees grown in various laboratory test cells exists.
- It suggests that water trees grow when the pressure exerted on nanocavities filled with liquid is larger than the yield strength of the polymer. Fatigue plays a major role in growth.
- The field dependence is limited and there is possibly a maximum frequency over ~ 20-30 kHz.
- Some work remains to be done to explain the influence of ions and of temperature.

ELECTRICAL TREES ?

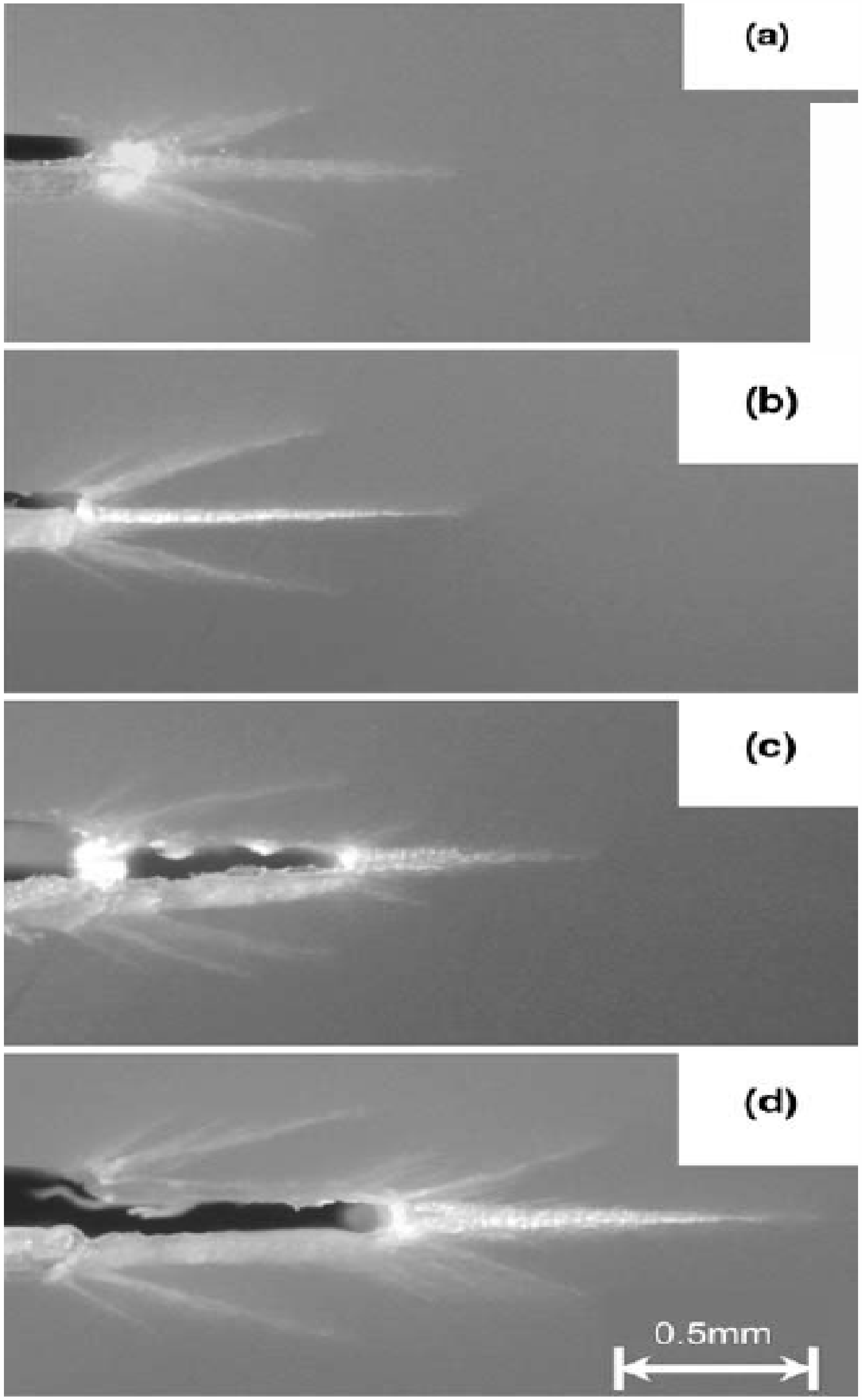


Fig. 4 Light micrographs of the crack tip damage zone showing the periodical formation and fracture of the craze during stepwise fatigue crack propagation at 50 °C: (**a**) 20,000 cycles; (**b**) 58,000 cycles; (**c**) 74,000 cycles; and (**d**) 97,000 cycles. The compact tension specimens were loaded under $K_{I,mean} = 0.65$ MPa $m^{1/2}$ and $R = 0.1$

Of course, high energy kinetic electrons will be "injected" at a point tip and breakdown will end as an electron avalanche lasting 10^{-9} s or less. But if structures like trees can be created without ANY field, is it possible that degradation might be induced without "tons" of free electrons (excepted at the very end)?

LINKS/SIMILARITIES BETWEEN WET AND DRY AGING

-Fatigue should also play a role under ac stress meaning faster aging under ac than under dc,

-The low dielectric constant of the dry polymer means a smaller electrostatic (Maxwell) energy and nearly no strain (electromechanical) energy below ~100 kV/mm (thin films),

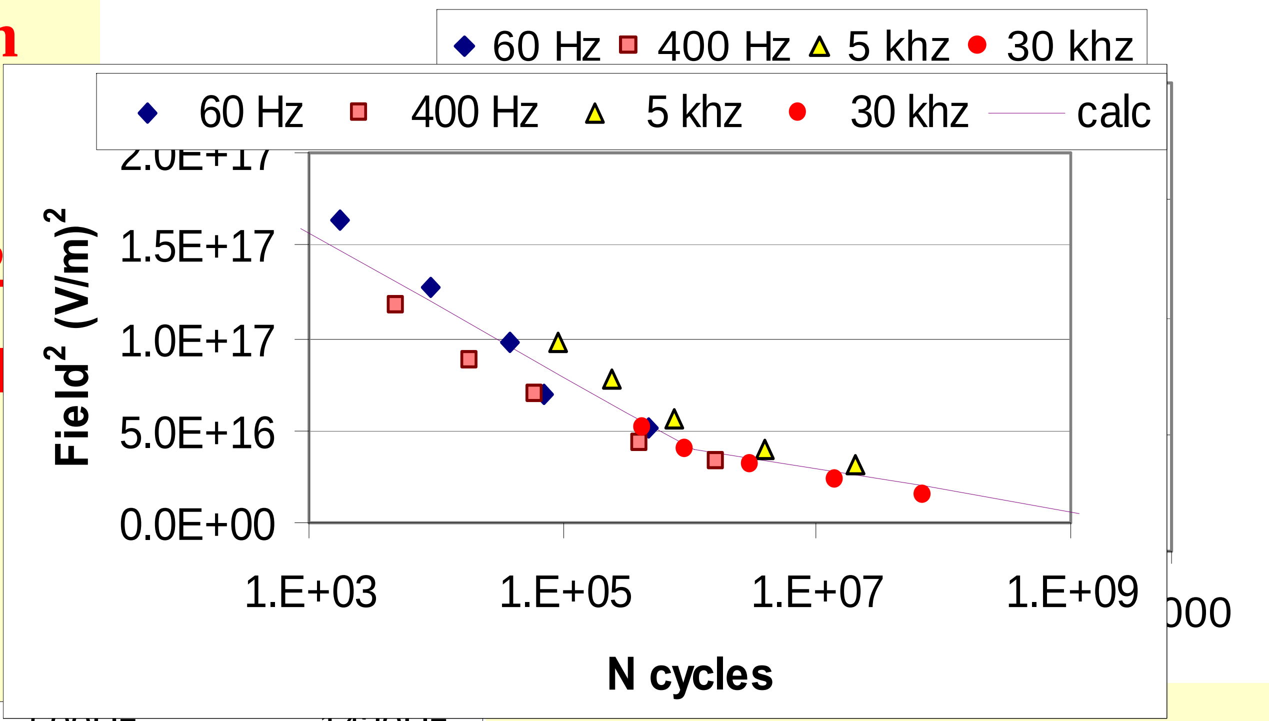
- Electrical aging is an activated process meaning that Eyring equation could be used,

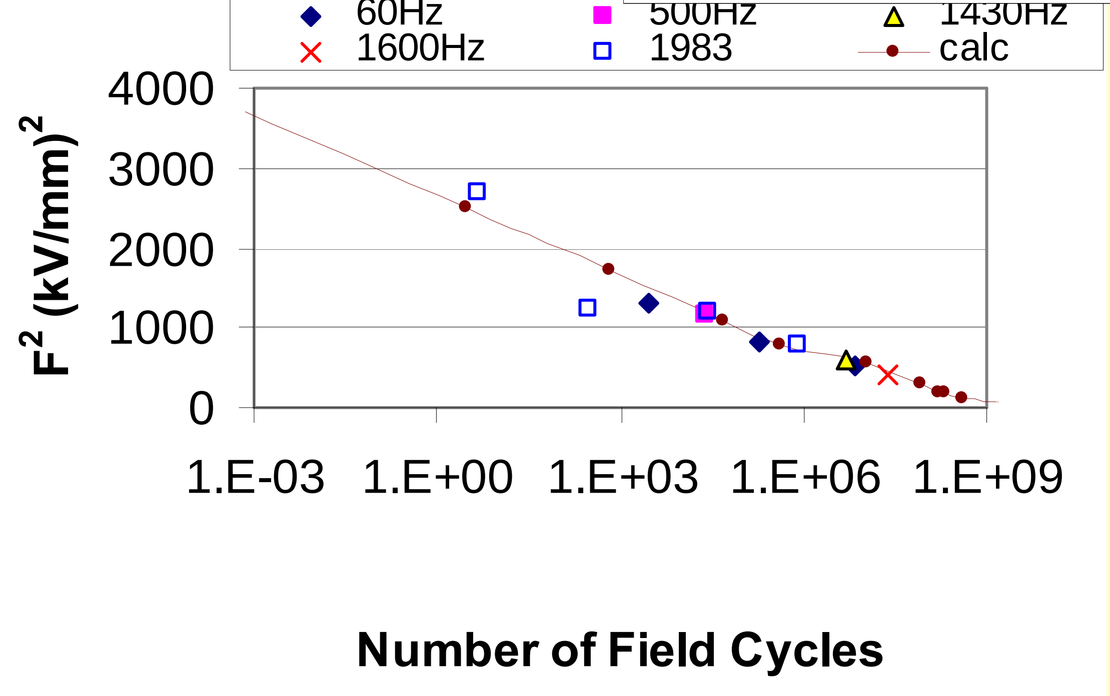
- Molecular and mechanical properties should have a major influence on aging and breakdown characteristics,

- Space charges are present but their local field is not a major factor (as was also the case in water treeing).

ac Aging of a PP film under Various Frequencies (Khachen et al. 1992

Same Results Plotted as a Function of the Number of Field Cycles = f x time





XLPE Example: results of Bahder et al.(1982-3) for XLPE cables aged and broken down under various frequencies.

DRY ELECTRICAL AGING & BREAKDOWN

-Limits of existing models (see CEIDP 2005 and 2007)

- Basic principles of our model

- ac vs. dc: fatigue and amplitude of stress

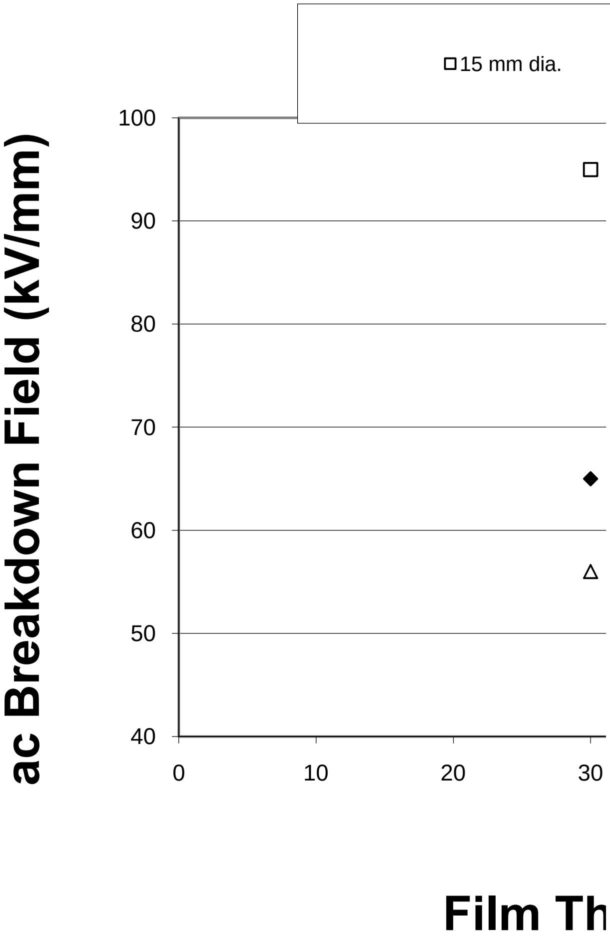
- Nature and significance of ΔG & ΔV: broken bonds and free radicals; influence of sample size

- Summary and what remains to be done

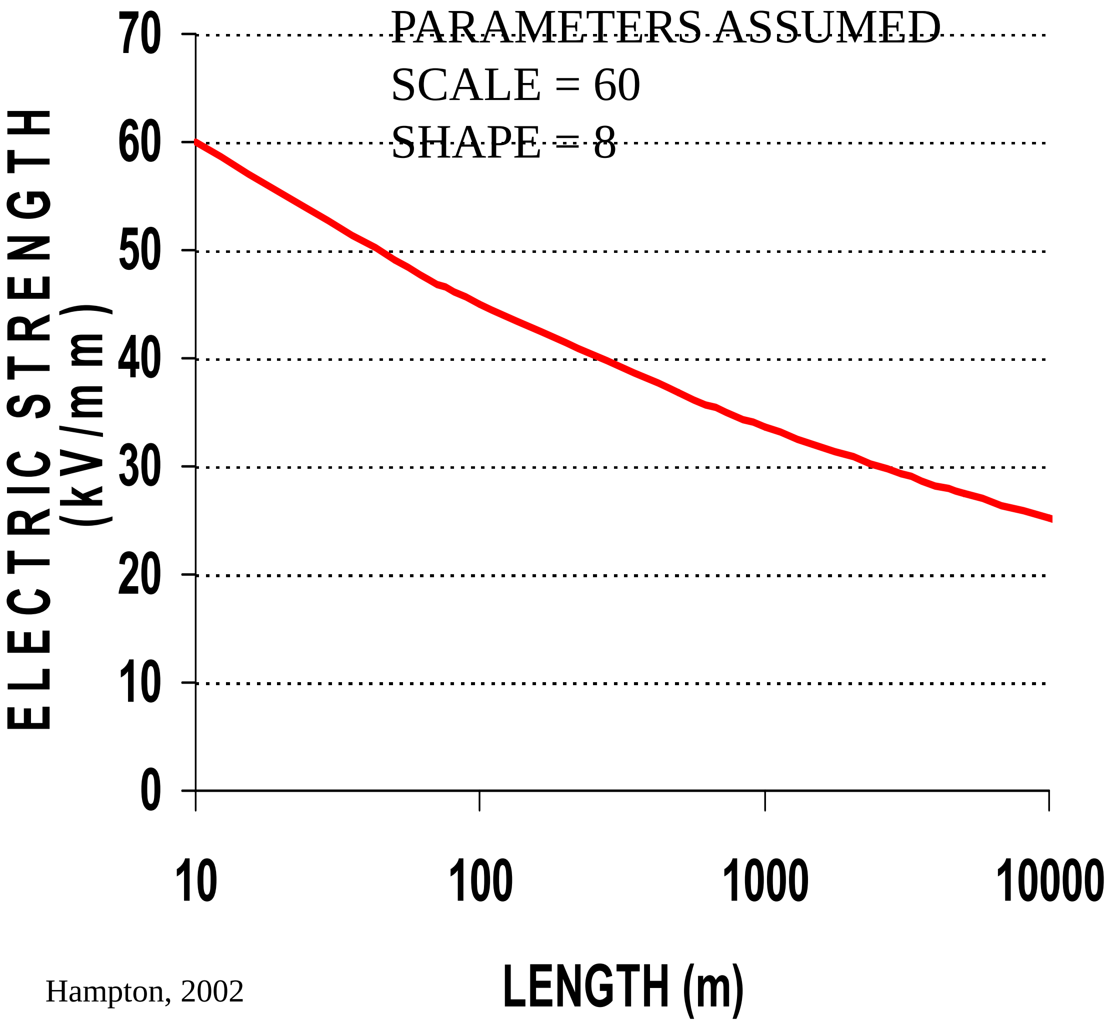
SOME COMMON PITFALLS AND OTHER SOURCES OF DISCREPANCIES

-The real value of the applied field: Laplacian, peak or rms ?
- The influence of the alternating field on fatigue and on some parameters
- Extrapolating life from a log-log plot
- Neglecting statistics !
- Extrapolating life or breakdown values of a full size cable from small lab samples
- Giving too much importance to space charge field as an aging factor
- Assuming that dielectrics are just wide band semiconductors….

INFLUENCE OF SAMPLE (FILMS OR CABLES) SIZE ON BREAKDOWN



Sekii and Kazama, 2004

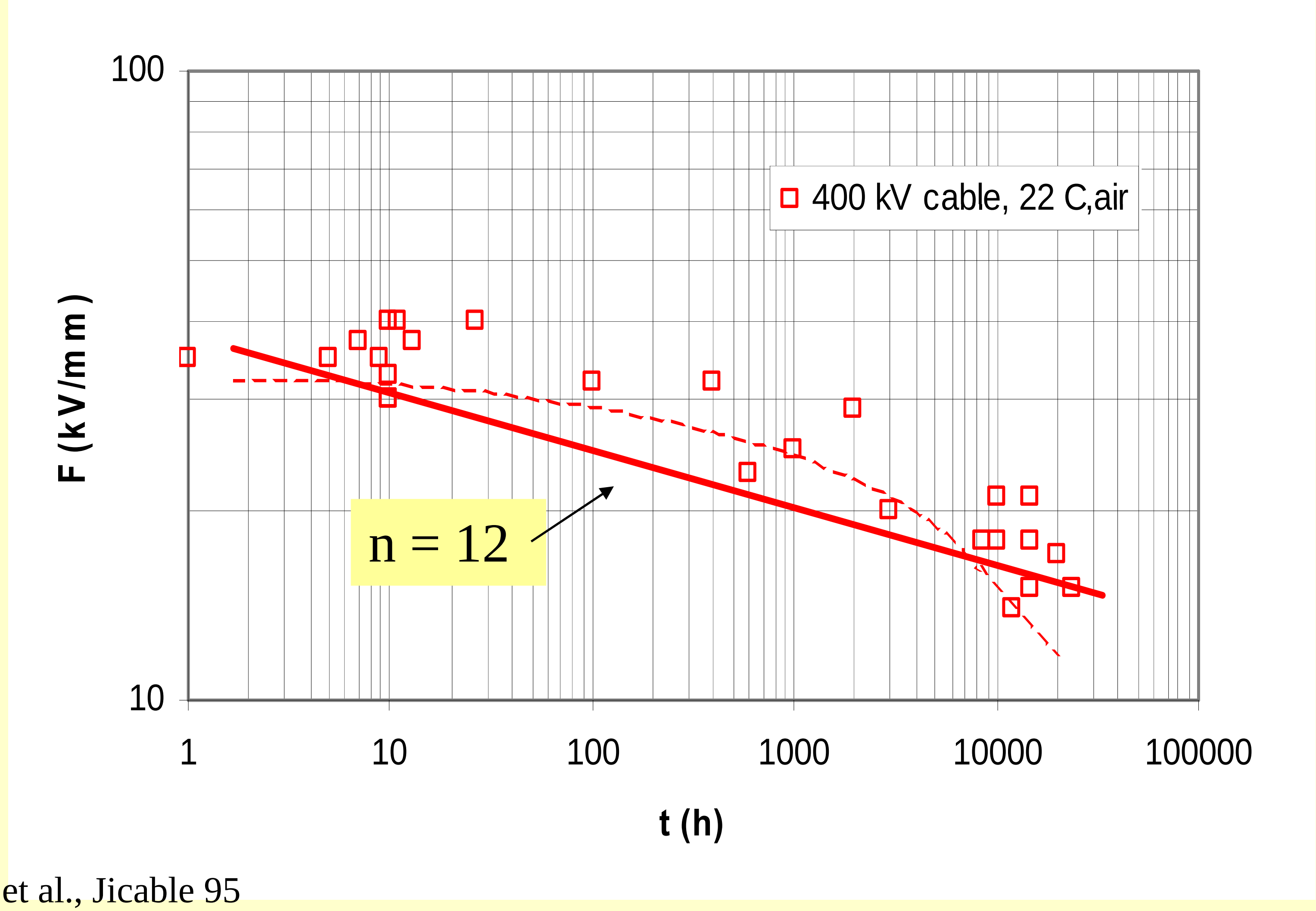


Hampton, 2002

Cable life extrapolated from the inverse power law

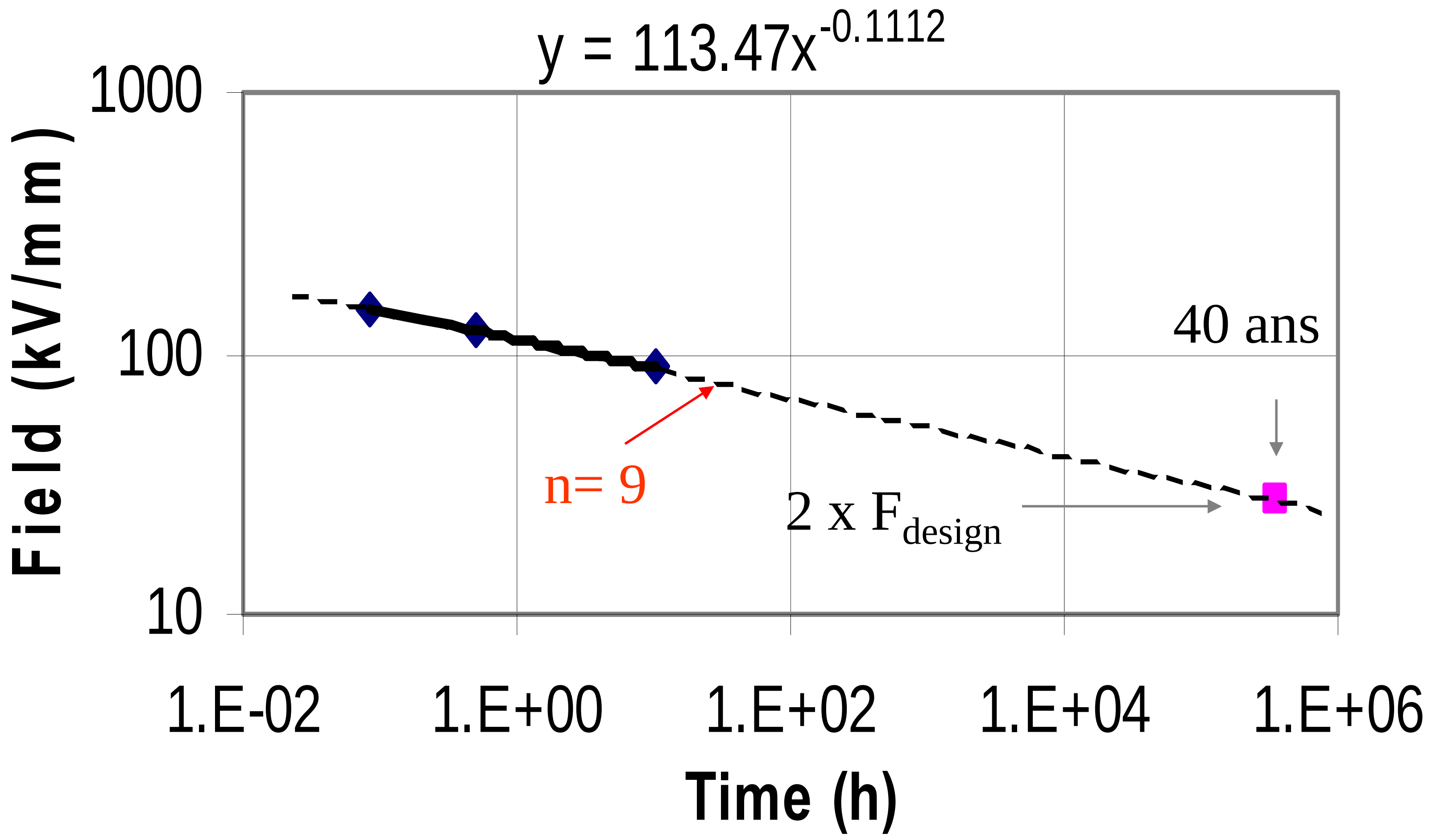
$$t = C\ F^{-n}$$

(an extension of the S-N graph used in mecanics for 150 years)



Peschke et al., Jicable 95

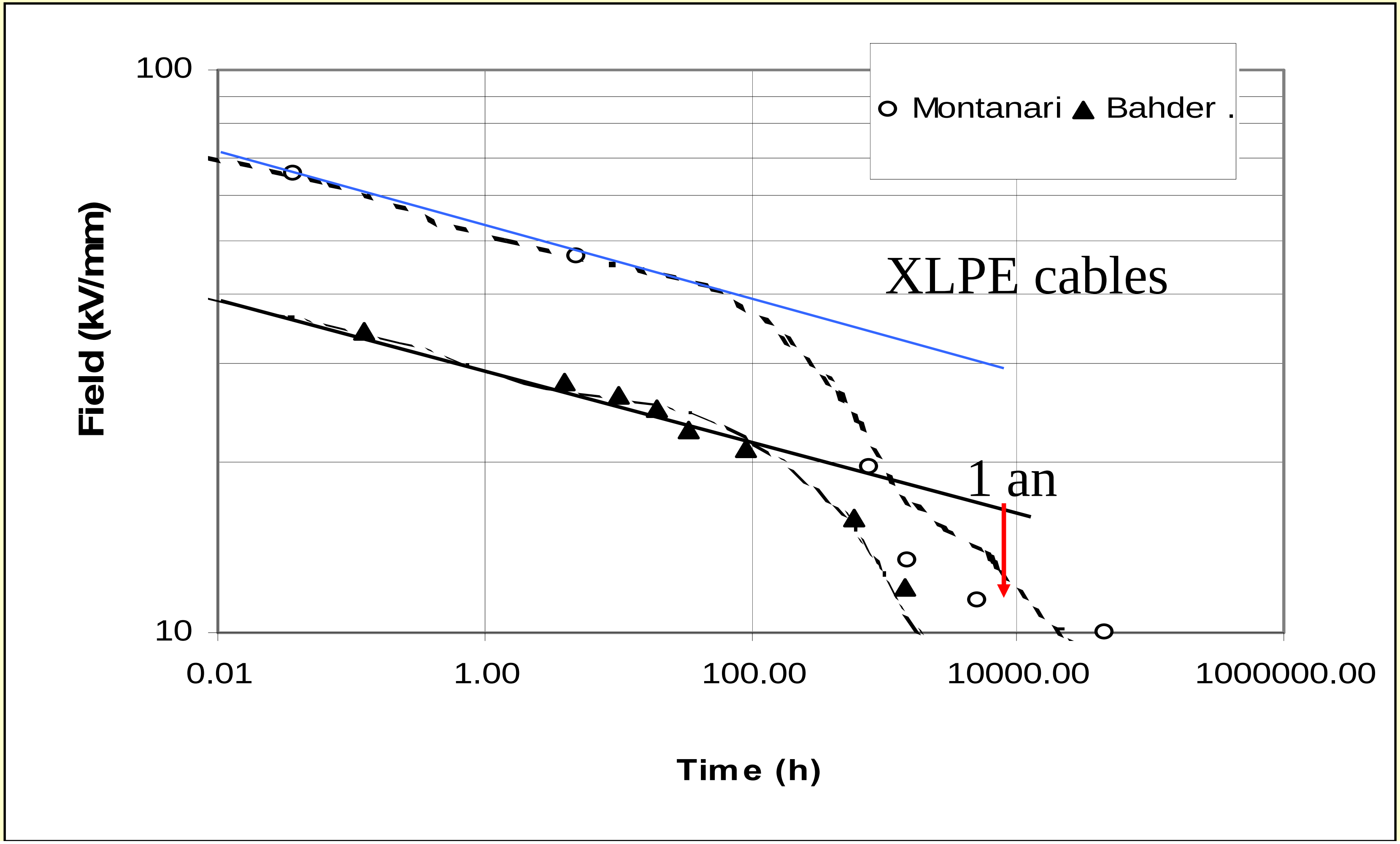
Testing of samples taken in a 345 kV XLPE cable



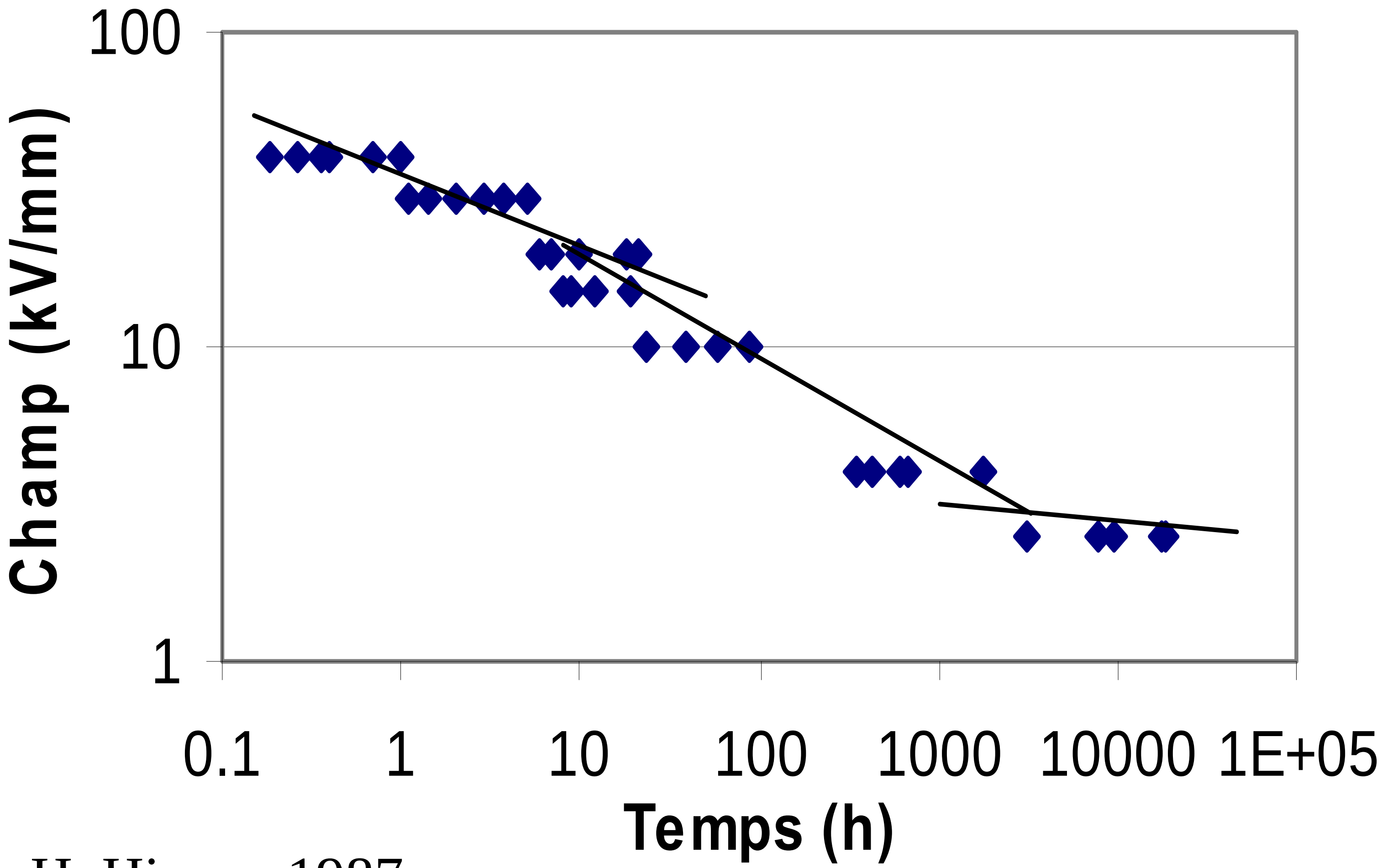
Ref.: B. Gregory, EPRI Workshop on Cables Aging, Detroit, 2002

The linear relation between Log t and Log F is <u>always</u> limited to some period of time:

it is therefore dangerous to extrapolate life in service (low field- long time) from high fields- short times testing



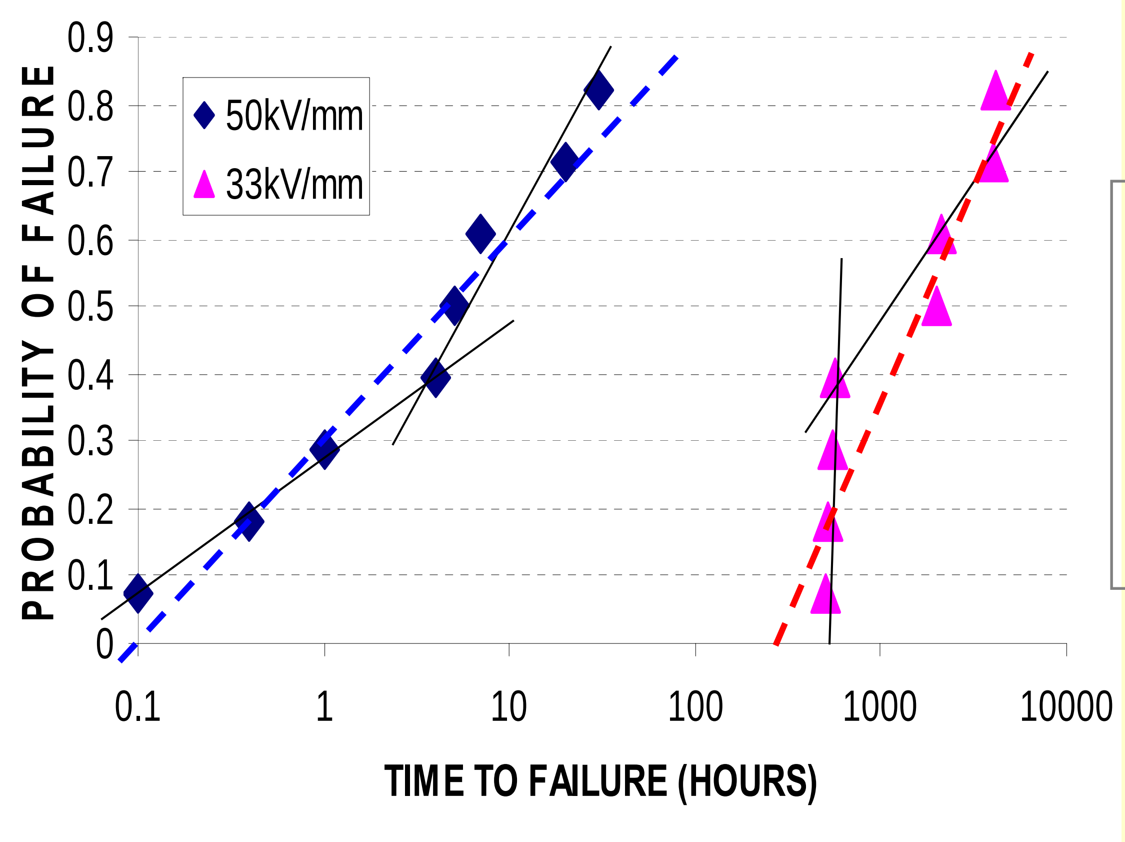
Three regimes for polyimide aged at 80 °C



H. Hirose, 1987

WEIBULL DISTRIBUTION WITH 2 OR 3 PARAMETERS

ONE (---) OR TWO (___) MECHANISMS ?



3 parameters Eq.

$P=1-\exp-[(t-\gamma)/\eta]^{\beta}$

γ: location parameter

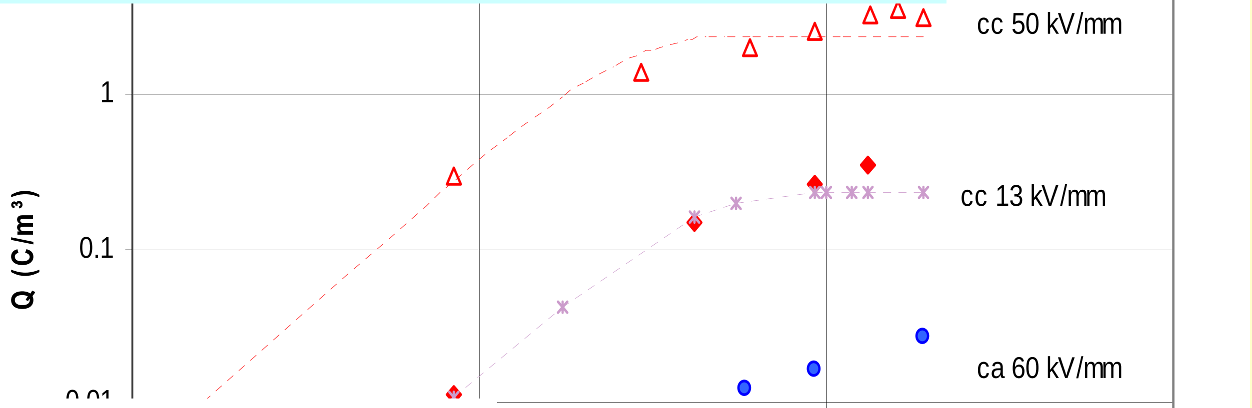
Time to failure of XLPE cables installed in air when tested at two different stresses represented on Weibull plots. Courtesy of N. Hampton.

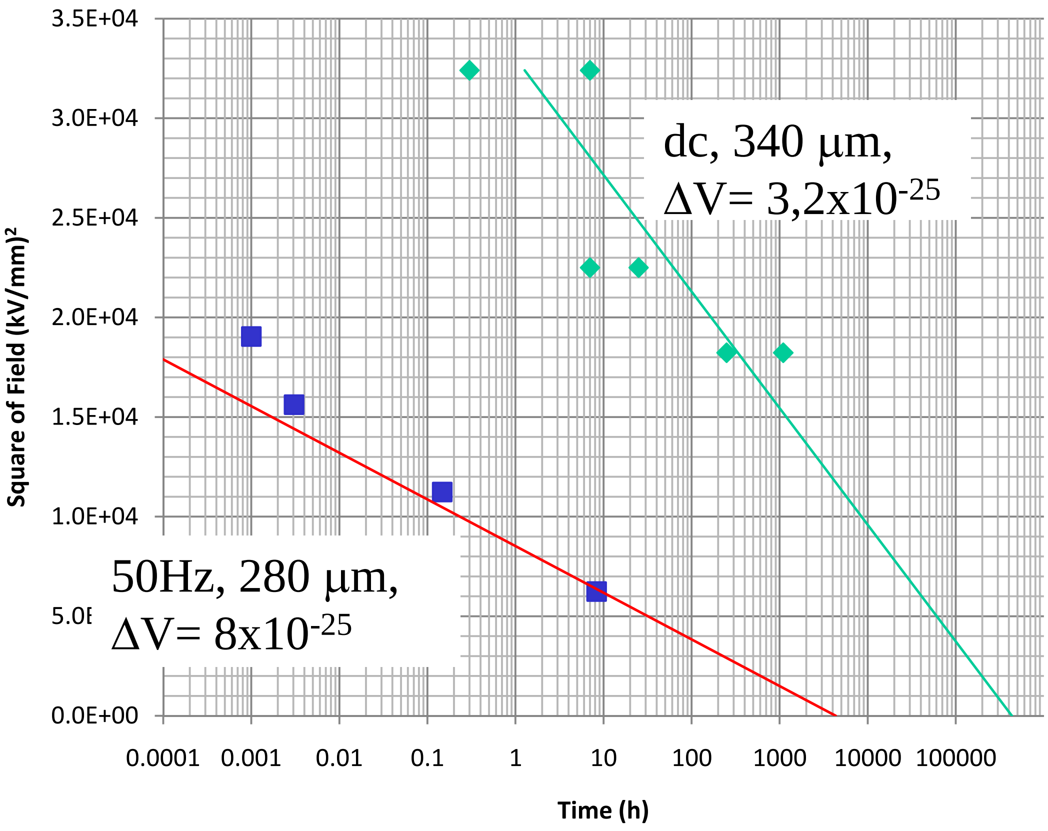
AN EX

LOGIC:

Is it possible that the space charge field has not such a big influence, after all ?...

If space charges are the main cause of aging, more charges should result in





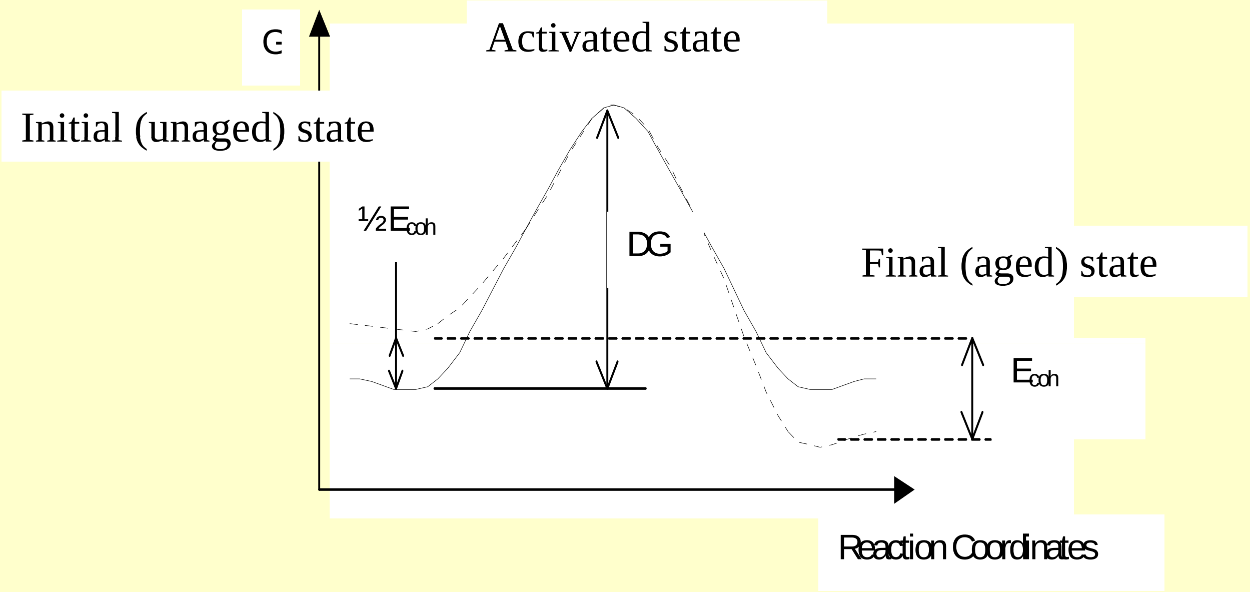
dc, 340 µm,
$\Delta V= 3{,}2\mathrm{x}10^{-25}$

50Hz, 280 µm,
$\Delta V= 8\mathrm{x}10^{-25}$

Then, explain me why life is much much shorter under ac albeit a much much smaller charge concentration than under dc!

Crine Model: rate equation, free radical formation and bonds breaking above a critical field

- **The energy barrier is symmetrical (or nearly symmetrical) and is deformed by the Maxwell stresss σ induced by the field; $\sigma = \frac{1}{2} \varepsilon F^2$.**



The reaction rates (forward and backward) are given by

$K_{forward} = \nu \exp(-(\Delta G - 0.5\varepsilon \Delta V F^2)/kT)$

$K_{backward} = \nu \exp(-(\Delta G + 0.5\varepsilon \Delta V F^2)/kT)$

where ΔG is the Gibbs activation energy of the process and ΔV is the activation volume, i.e. the strained volume and $\nu = h/kT$.

$K_{forward} – K_{backward}$ = (kT/h) exp (-ΔG/kT) [exp(x)-exp(-x)] (1)

where h = Planck constant, k = Boltzmann constant and

x = ½ ♏ ΔV F^2/kT.

By definition,

sinh (x) = [exp(x) – exp (-x)]/2

Hence, Equation (1) becomes

K = 1/t = (kT/h) exp (-ΔG/kT) 2 sinh (x) (2)

And t (for dc fields) is given by

t = (h/2kT) exp (ΔG/kT) csch (½ ♏ ΔV F^2/kT) (3)

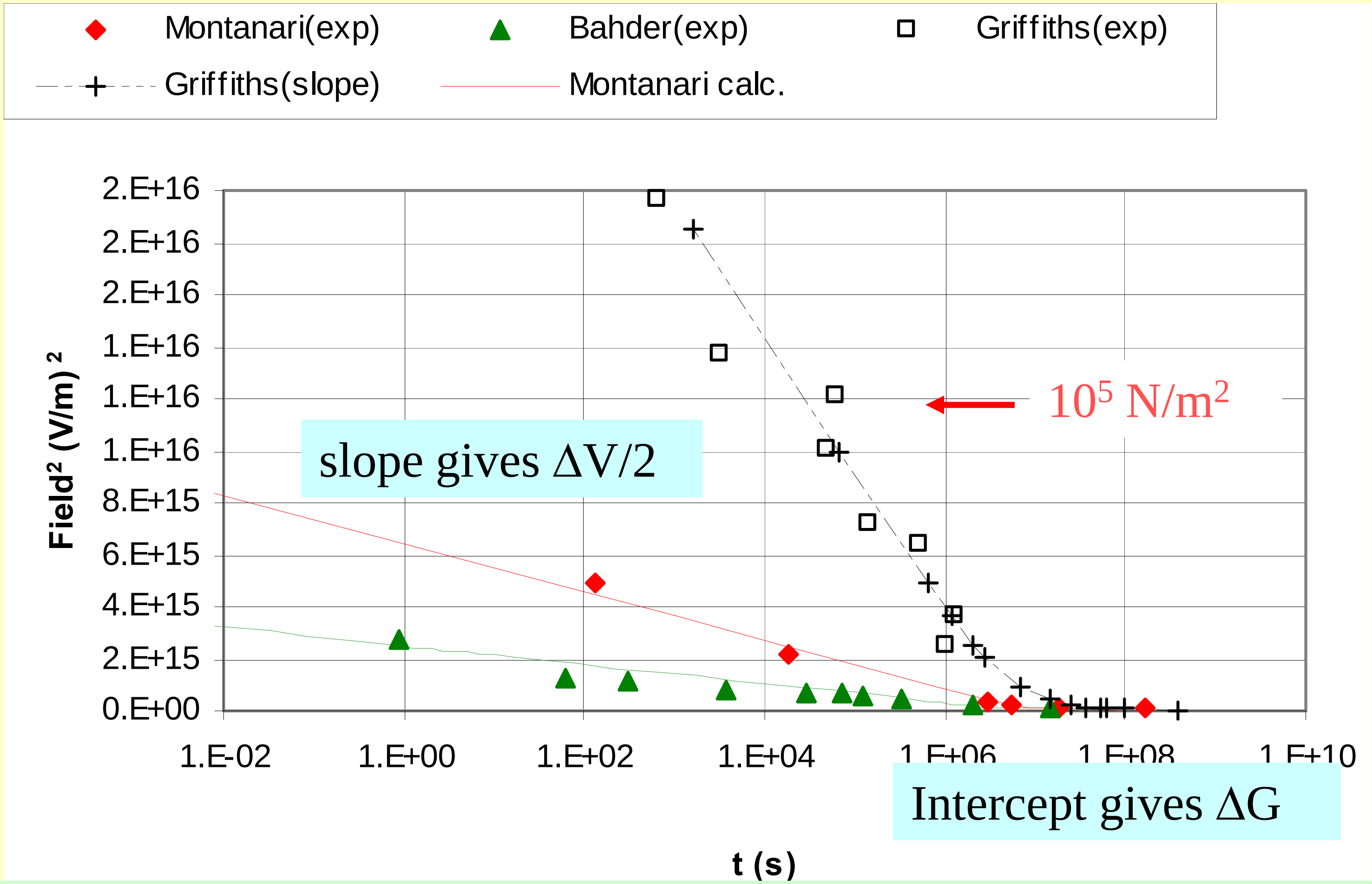
Which means t = infinity for x = 0 (csch (0) = infinity).

At high dc fields, Equation (3) reduces to

t = (h/2kT) exp [{ΔG - (½ ♏ ΔV F^2)}/kT] (4)

THUS, PLOTTING RESULTS AS F^2 (or σ) vs. Log t
SHOULD YIELD A STRAIGHT LINE

GRAPHICAL VALIDATION



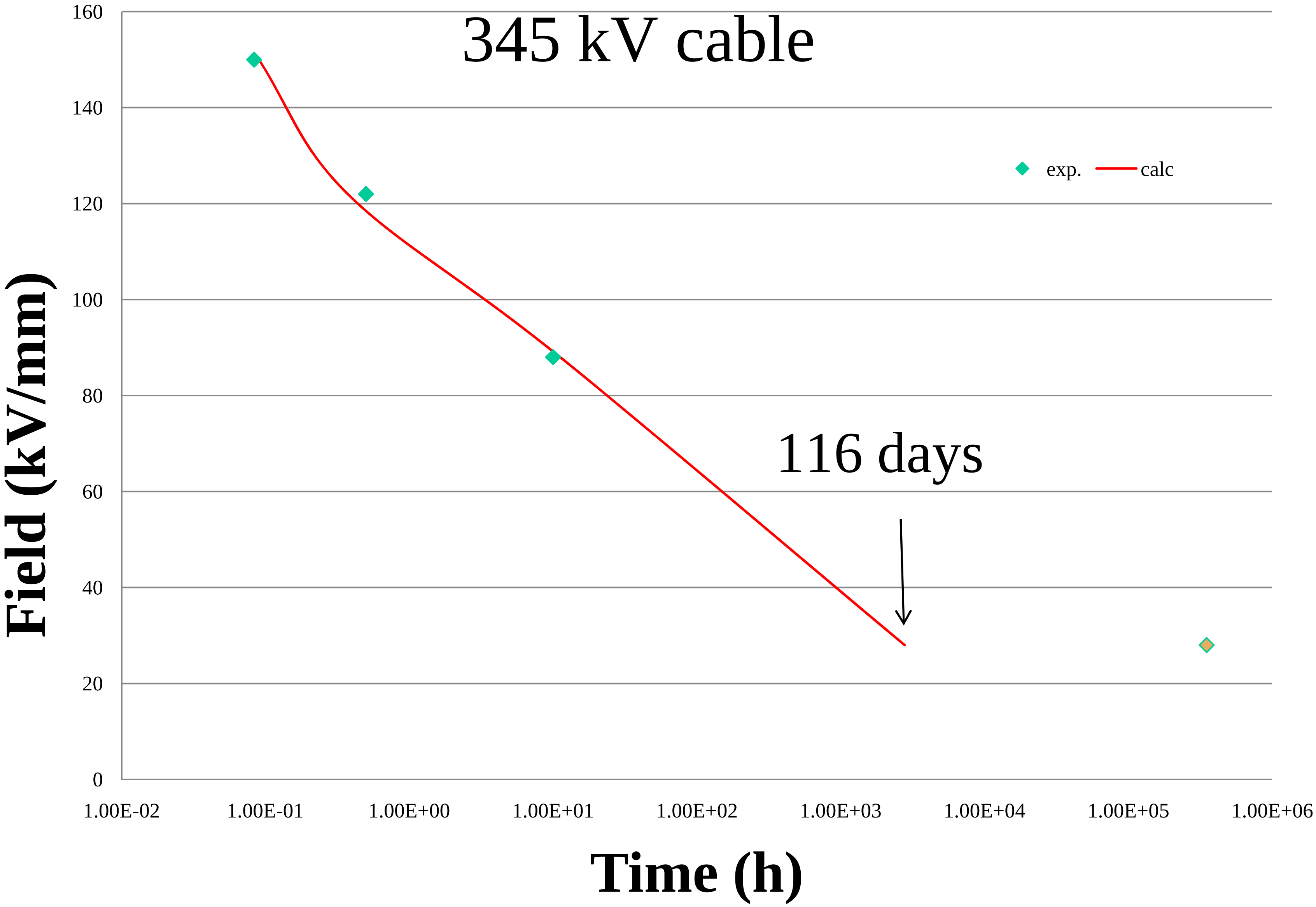
10^5 N/m^2

slope gives ΔV/2

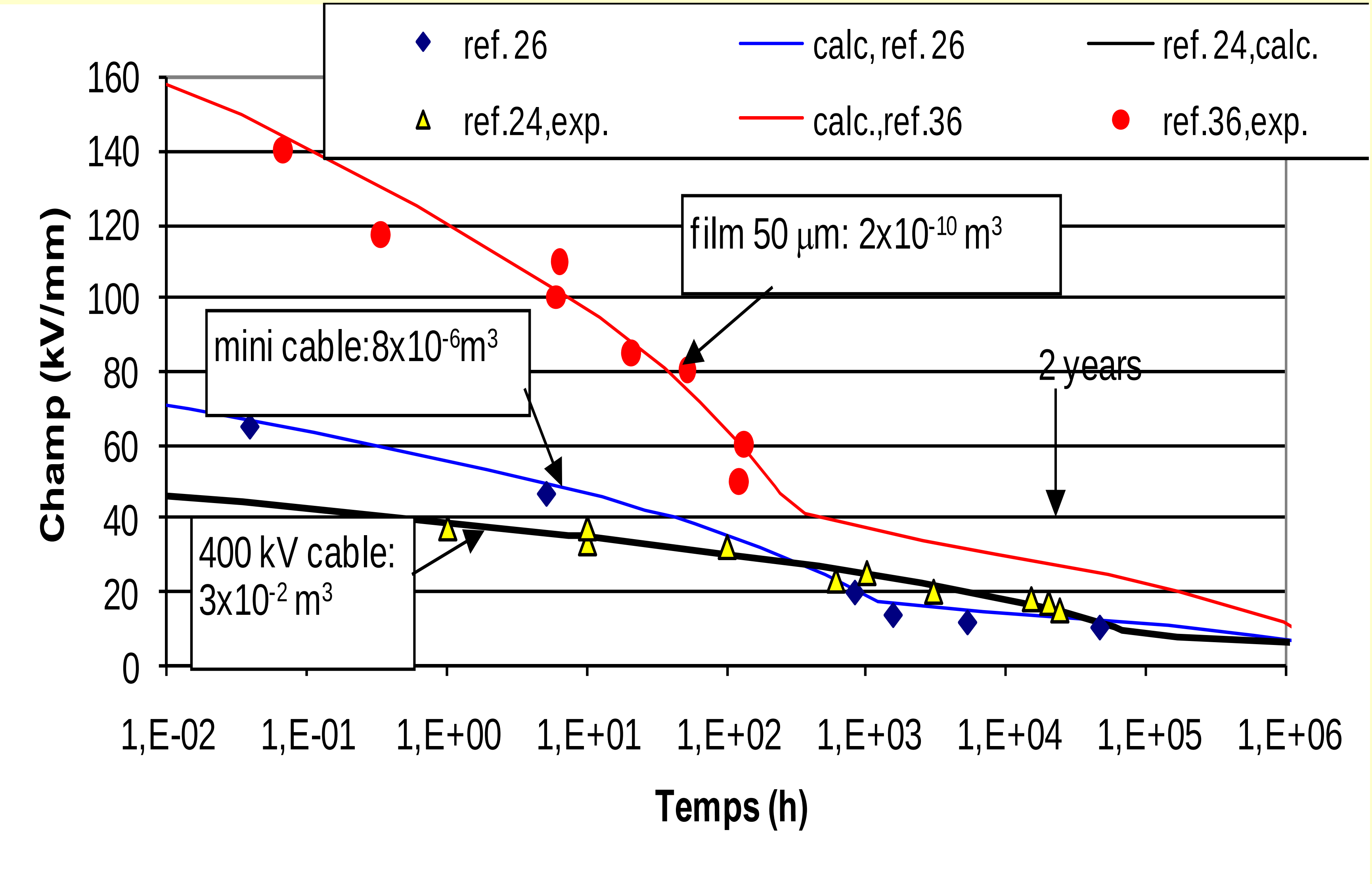
Intercept gives ΔG

QUESTION: how the very modest Maxwell stress (10^5 N/m^2 – 1 atmosphere- for100 kV/mm) can break C-C or C-H bonds whose strength is of the order of 3.5-4 eV ?

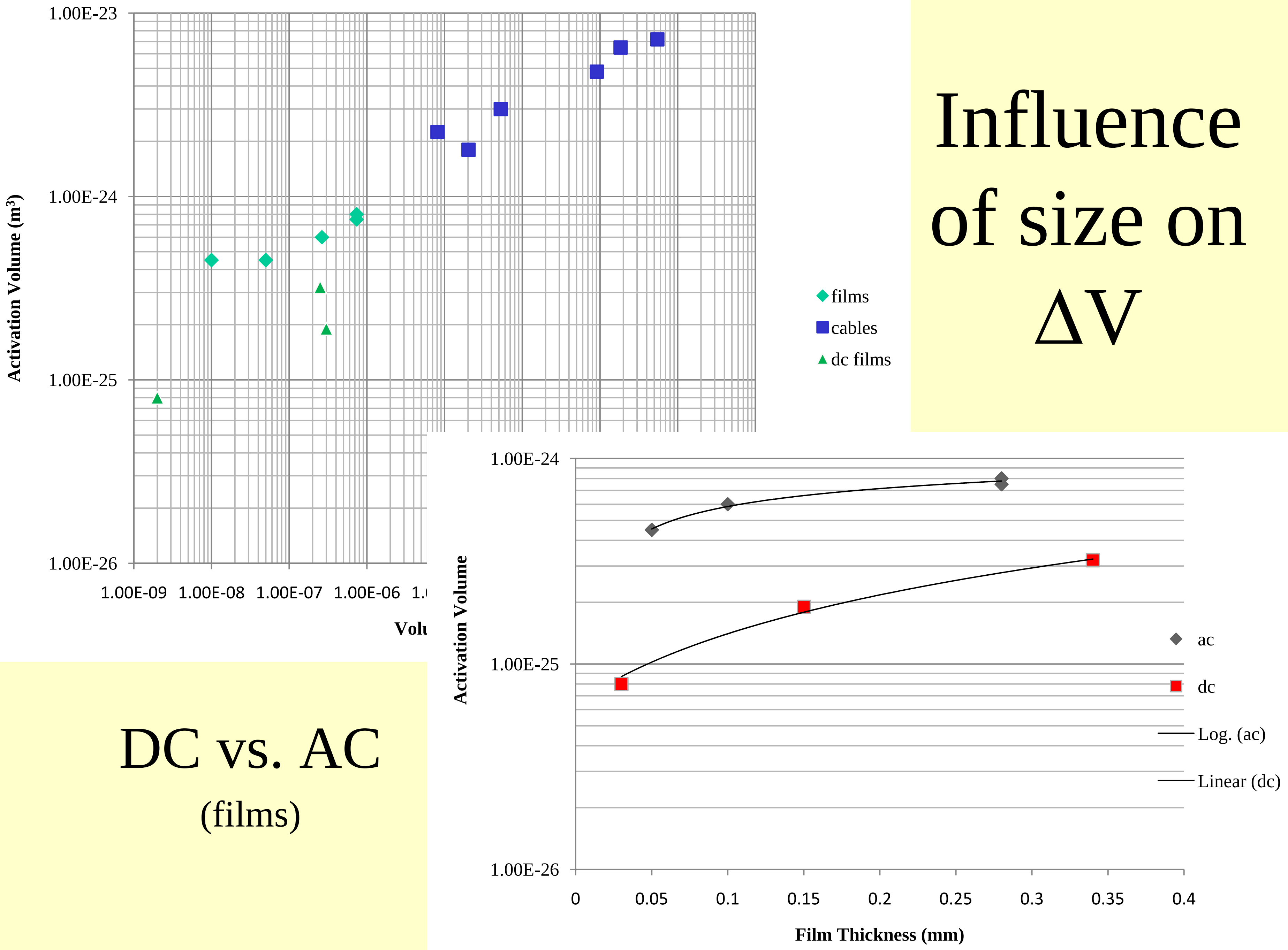
NB: the elastic limit of PE at 22^{o}C is ~ 1.5x10^7 N/m^2


345 kV cable
116 days
exp.
calc
Field (kV/mm)
Time (h)
160
140
120
100
80
60
40
20
0
1.00E-02
1.00E-01
1.00E+00
1.00E+01
1.00E+02
1.00E+03
1.00E+04
1.00E+05
1.00E+06

INFLUENCE OF SAMPLE SIZE ON ΔV



Influence of size on ΔV



DC vs. AC

(films)

Thus, there is a significant difference between ac and dc aging due to:

- the different activation volumes,
- the fatigue factor (2f, i.e. the change of polarity of the field per second) in the pre-exponential term of our life equation.

The activation volume increases with sample size (whatever the type of field and the shape of samples).

The theoretical estimation of the ΔV value and its relationship with sample size remains to be done. But it can be easily determined from experimental data.

WHAT IS THE SIGNIFICANCE OF THE ACTIVATION ENERGY?

Aging of XLPE at 22^{o}C in air yields ΔG values in the 2-2.08x10^{-19} J (1.28 eV), that is 2-3 times lower than the strength of C-C bonds.

HOWEVER, THERE IS NOW AMPLE EVIDENCE THAT C-C BONDS ARE INDEED BROKEN EVEN UNDER MODERATE STRAINS AND STRESSES.

It was shown by Kao that free radicals (a fact indicating bonds breaking) are indeed formed during electrical aging of PP supporting the bonds breaking process.

SECONDARY (stable) FREE RADICALS IN PP: they were measured 20 h AFTER the formation of the primary (highly reactive) free radicals; Kao et al., 2003

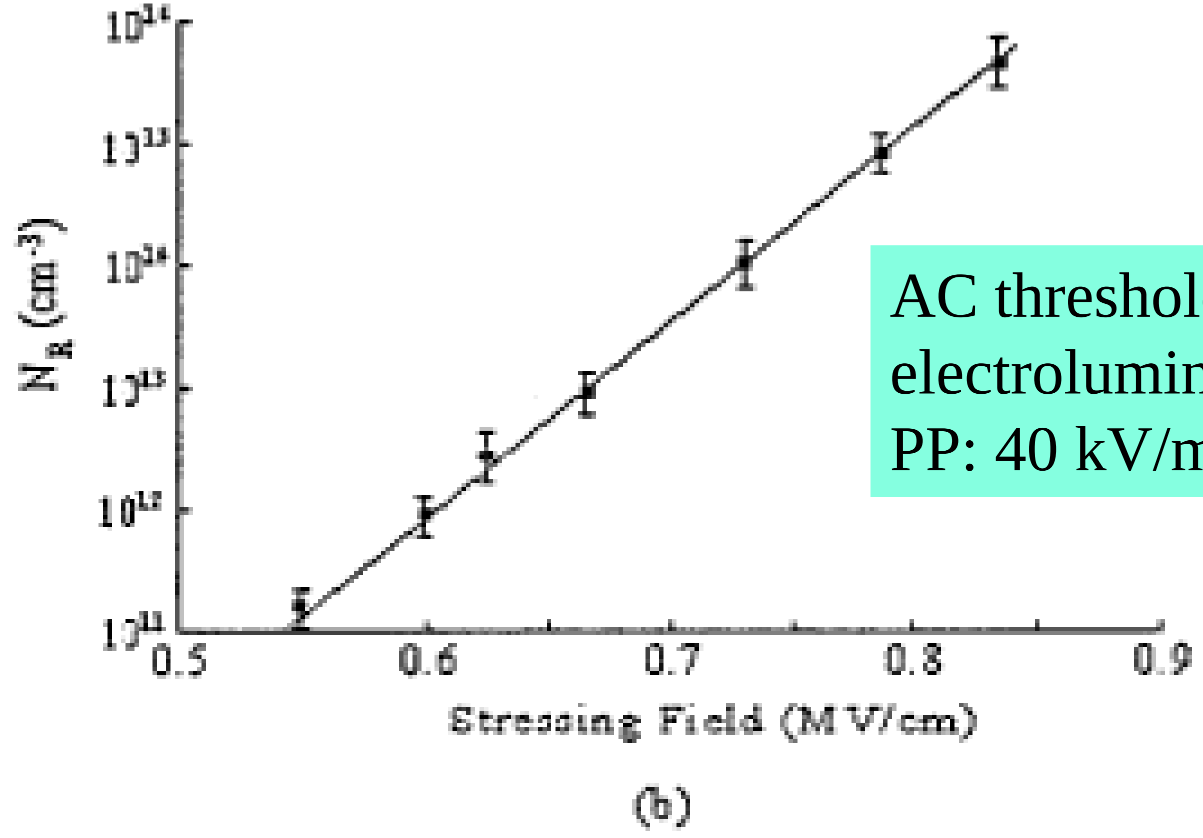


Figure 1 The concentration of free radicals (N_R) in PP specimens after being subjected to electrical stressing (a) at a fixed ac field of 833 kV cm^{-1} as a function of the stressing time and (b) for a fixed stressing time of 250 h as a function of the stressing field.

AC threshold for electroluminescence of PP: 40 kV/mm (Laurent et al.)

Adding piperidine (a radical scavenger) to PE, improves the breakdown strength and reduces the space charge content: an indirect evidence supporting the formation of free radicals during aging of PE.

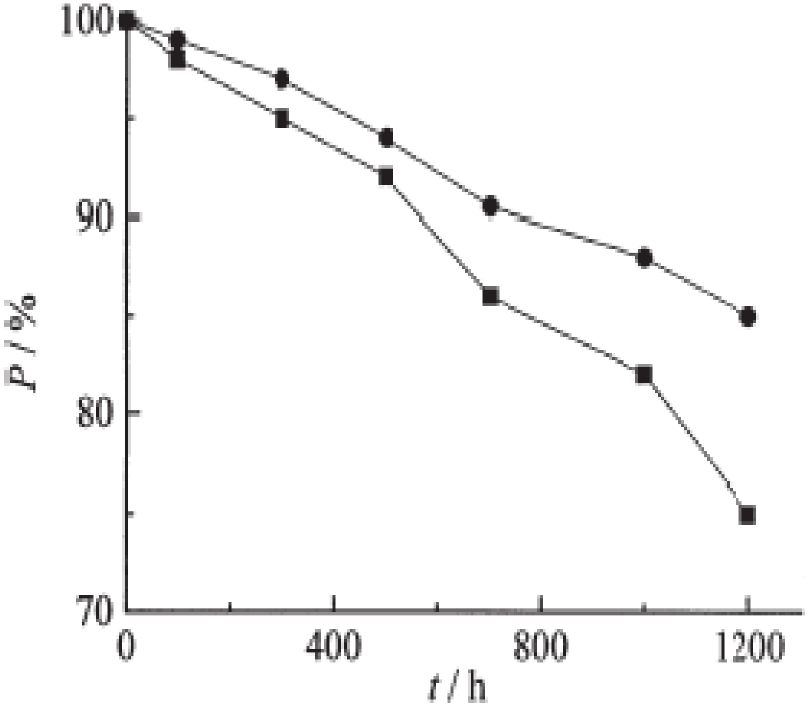


Fig. 2. Relationship between breakdown strength and aging time (●: LDPE + 0.5% FRS); ■: pure LDPE).

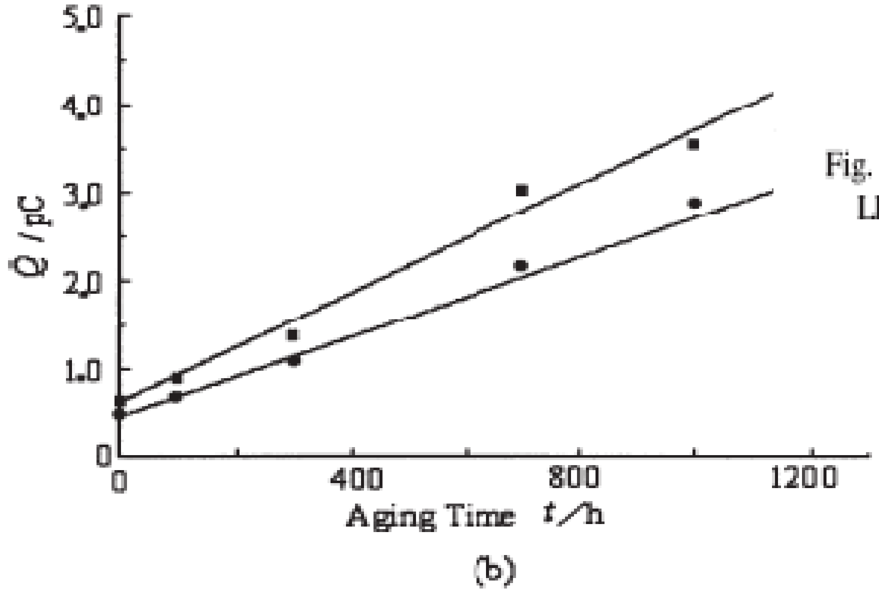
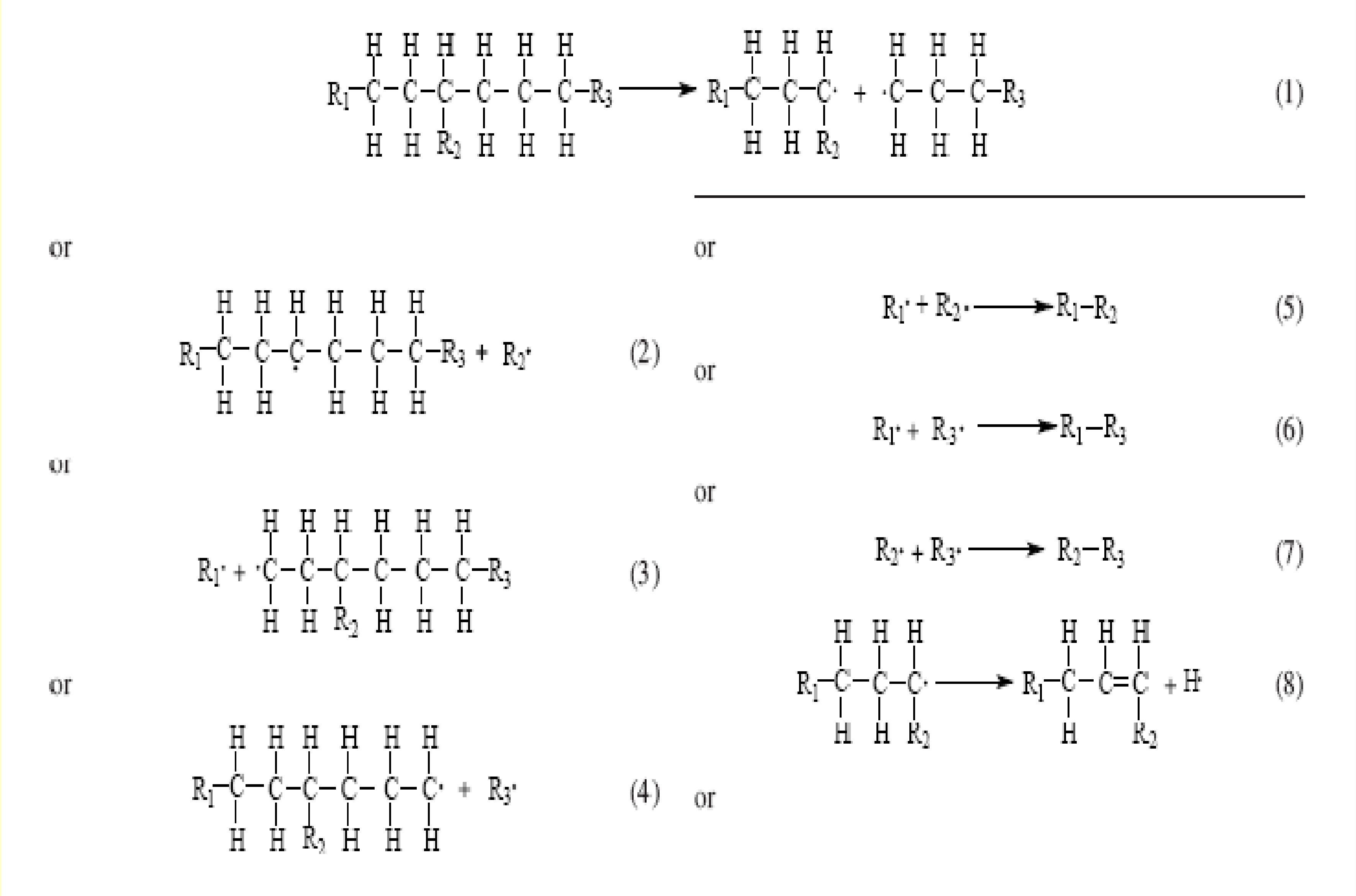


Fig. 9. Relationship between the aging time and the total amount of space charge in polyethylene samples with and without FRS after short-circuiting the samples for 1 min and 60 min, respectively: (a) After short-circuiting for 1 min; (b) after short-circuiting for 60 min (■: Pure LDPE; ●: LDPE + 0.5%FRS).

Y. Yin et al., Jap. J. Appl. Phys., 2002

VARIOUS FREE RADICALS SCHEMES

proposed by Kao (2003)



HAGEMAN et al. HAVE RECENTLY SHOWN THAT FREE RADICALS AND BONDS BREAKING CAN BE INDUCED IN PE UNDER MODEST MECHANICAL STRESSES ASSUMING THAT THE BONDS ORIGINALLY STRETCHED BY THE APPLIED STRAIN RELAX DOWN TO THE FINAL BREAKDOWN.

IN AGREEMENT WITH THE THEORY OF CRIST, THEY ASSUME THAT THE DISSOCIATION ENERGY D OF THE STRAINED C-C BONDS VARY WITH TIME AS

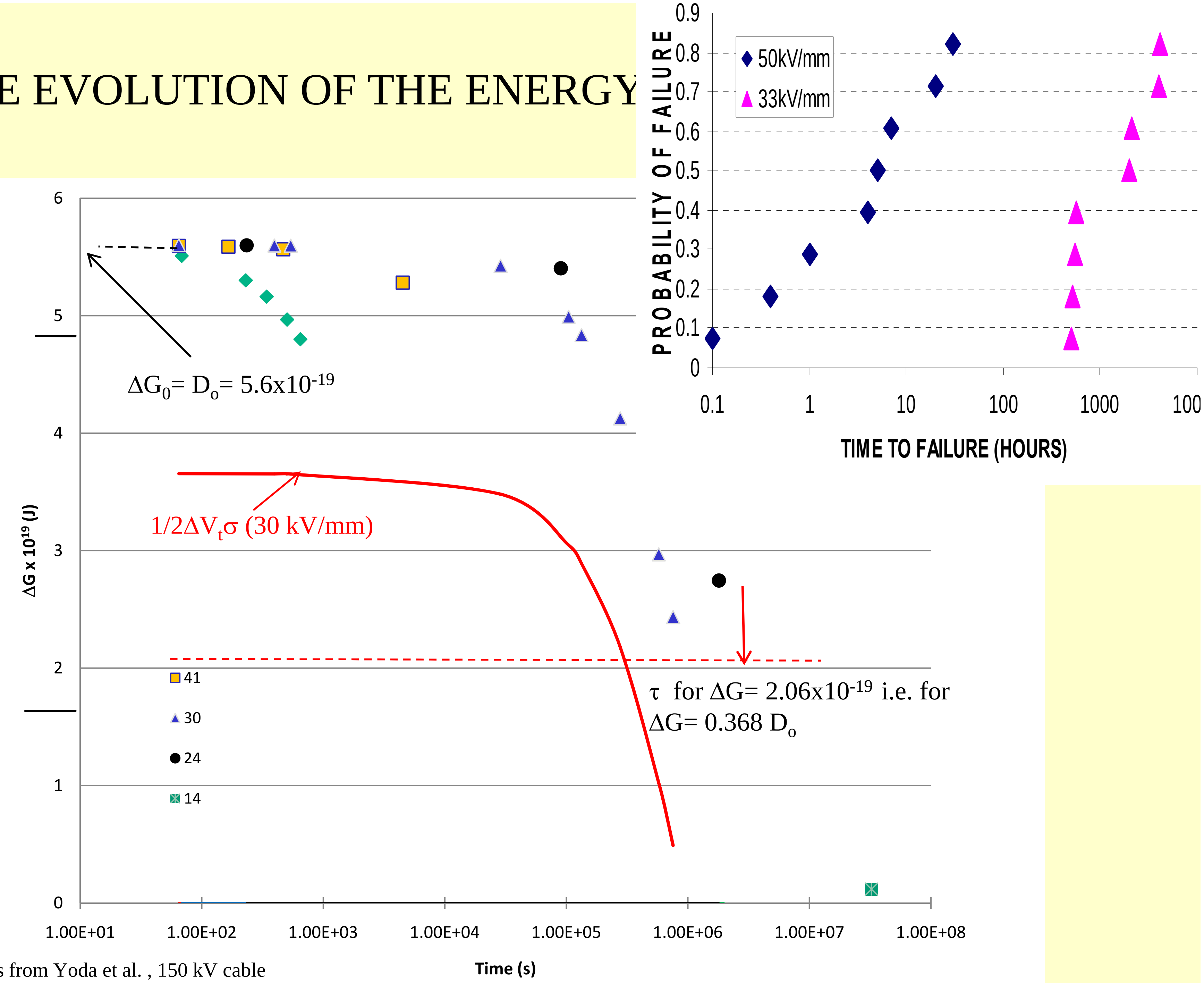
$D = D_0 \exp(-t/\tau)$ with $D_{o(C\text{-}C)} = 5.6\text{x}10^{-19}$ J (3.8 eV)

where τ is the lifetime defined as **$\tau = (h/2kT) \exp(\Delta G/kT) \operatorname{csch}(½\, \varepsilon\, \Delta V\, F^2/kT)$** .

When $t = \tau$, $D = 0.368\, D_0 = 2.06\text{x}10^{-19}$ J

THAT IS RIGHT IN THE RANGE OF THE ACTIVATION ENERGY VALUE DEDUCED FROM EXPERIMENTS !

TIME EVOLUTION OF THE ENERGY



3 eV

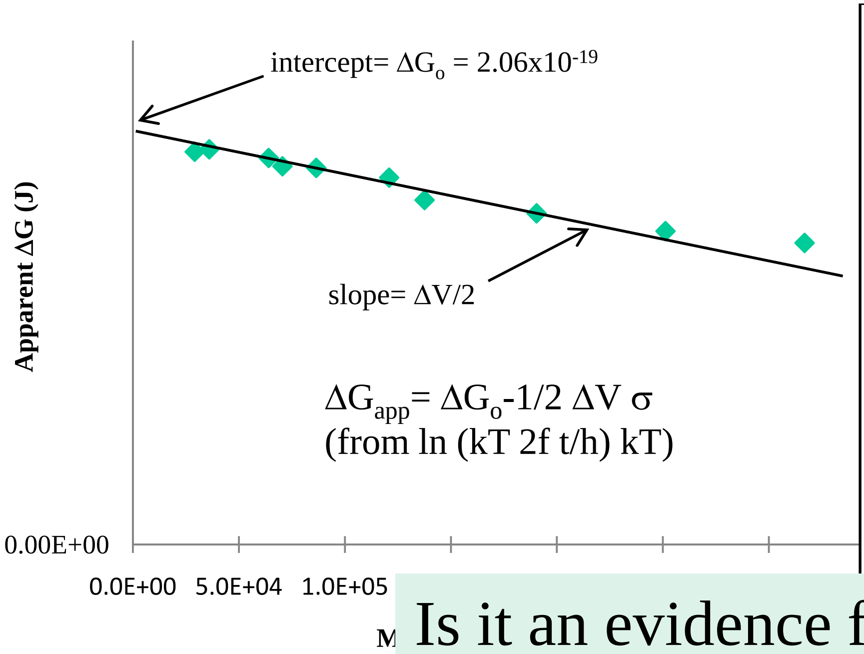
1 eV

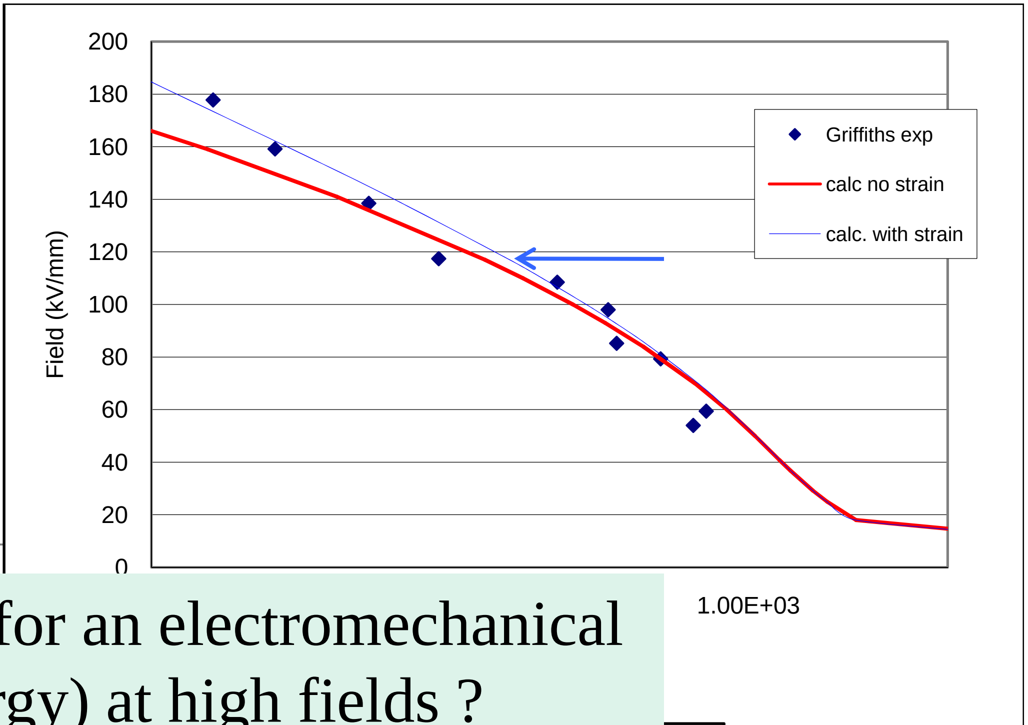
$\Delta G_0 = D_o = 5.6\text{x}10^{-19}$

$1/2\Delta V_t\sigma$ (30 kV/mm)

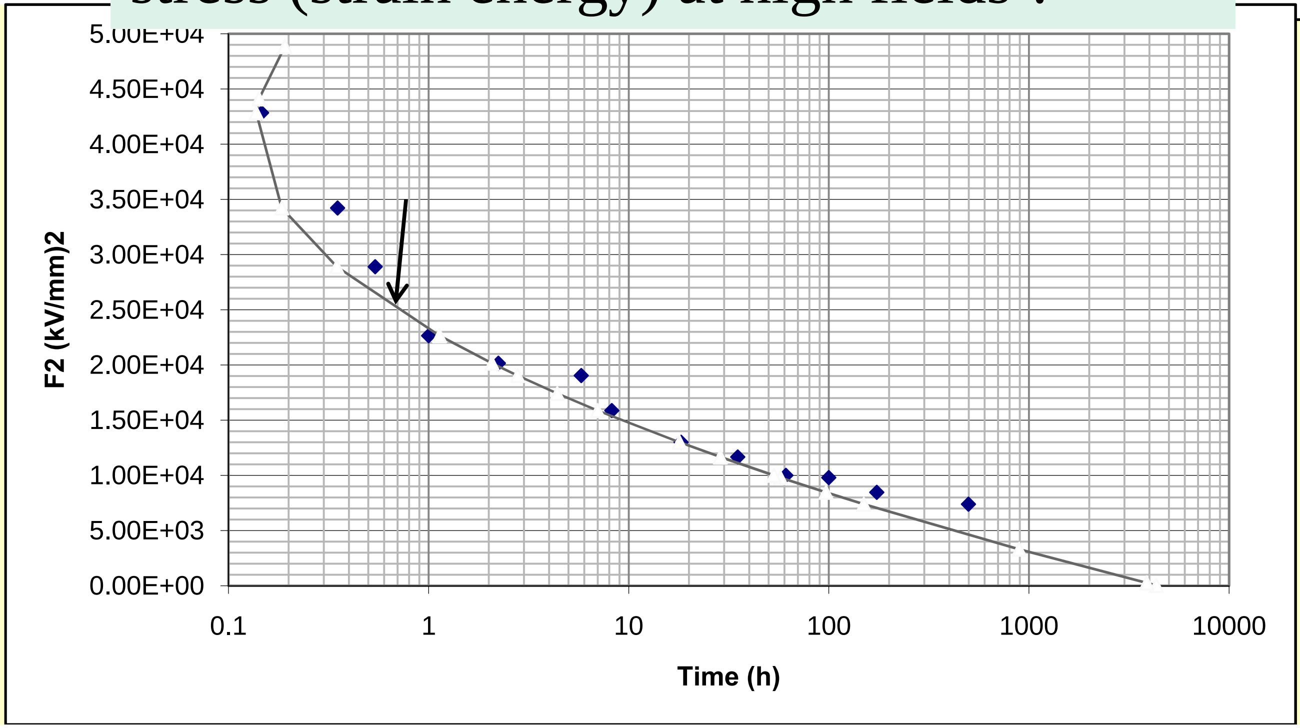
τ for $\Delta G = 2.06\text{x}10^{-19}$ i.e. for $\Delta G = 0.368\ D_o$

Results from Yoda et al. , 150 kV cable





Is it an evidence for an electromechanical stress (strain energy) at high fields ?



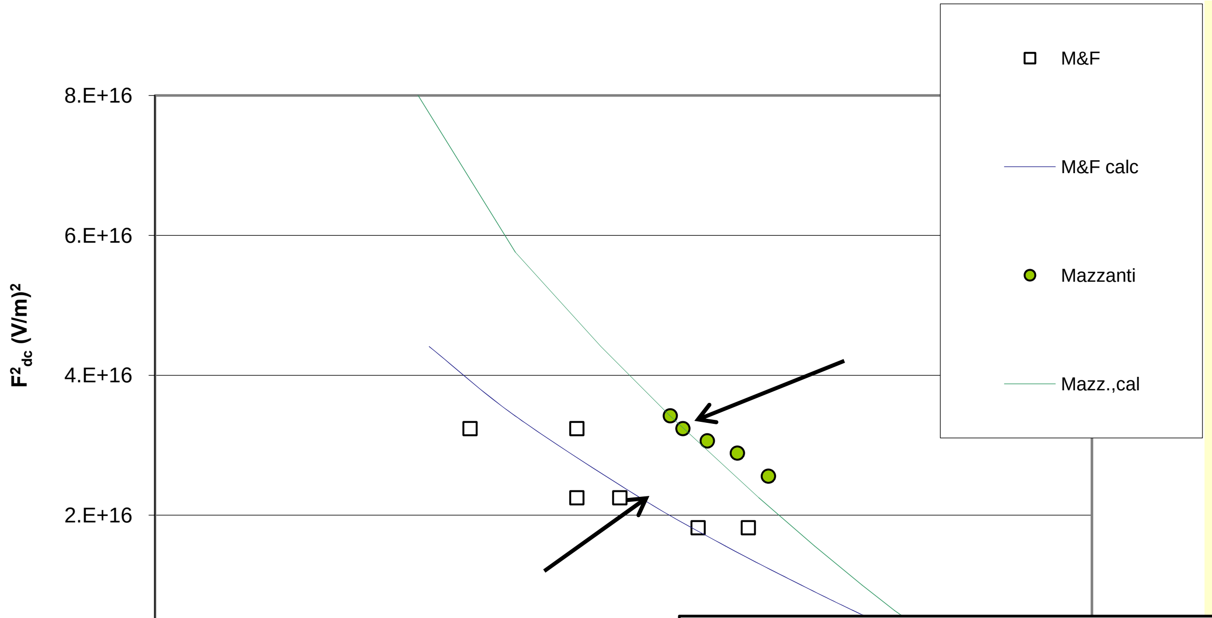
At very high fields, the molecules are already highly deformed but as long as there was enough free volume they were able to extend/ rotate, etc…Increasing the applied stress above a given value, results in a compression of the chains because they have no other opportunity to relax. This additional stress (almost hydrostatic) leads to an energy term called the strain energy that is added to ΔG_{app} as

$\Delta G_{app} = \Delta G_o – (1/2\Delta V\sigma) + (dv\ \sigma^2/2E)$

where E is the eleastic modulus and dv is the compression activated volume (different from ΔV).

It means that at very high fields (above 60-80 kV/mm), an additional term must be added to the life equation.

Presently, we can determine the two activation volume values only from trial and error.



DC aging of XLPE films

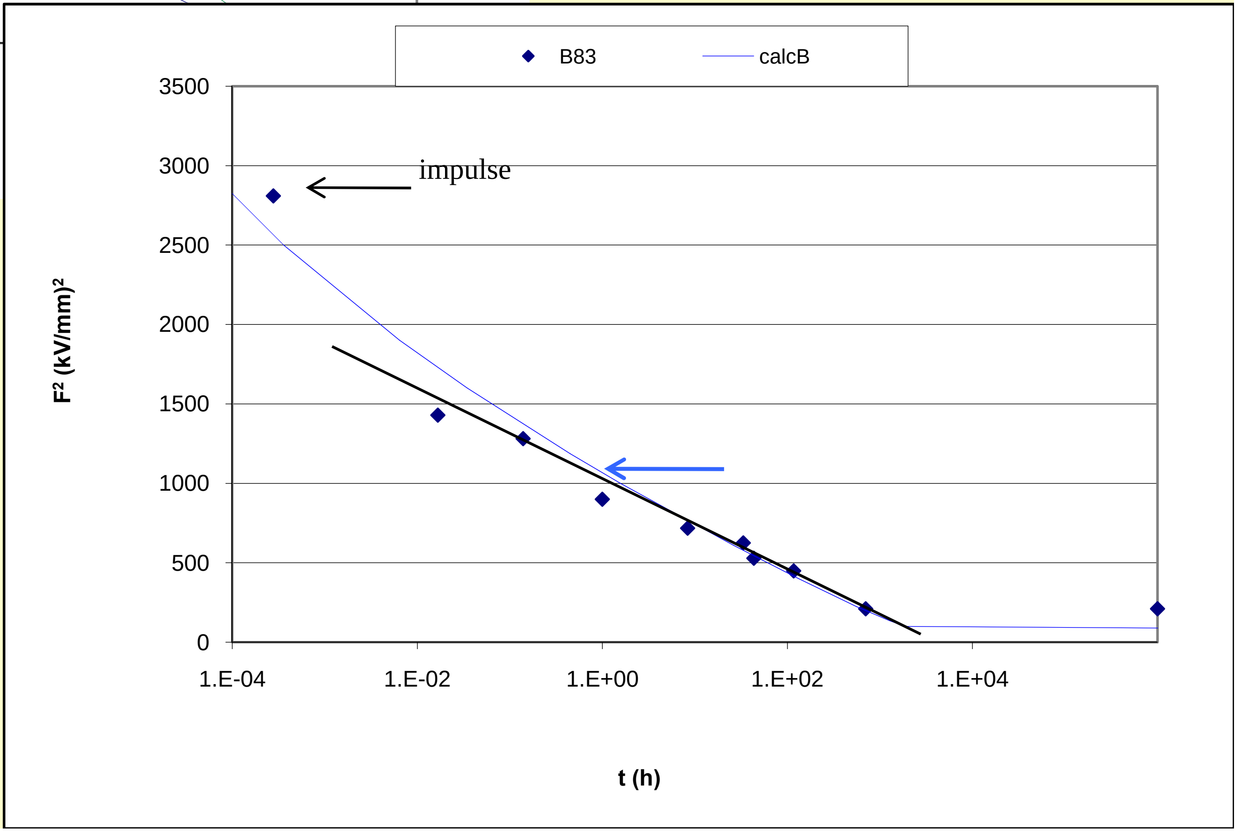
For AC aging under different frequencies and impulse bkdwn;

Bahder et al., mini cable

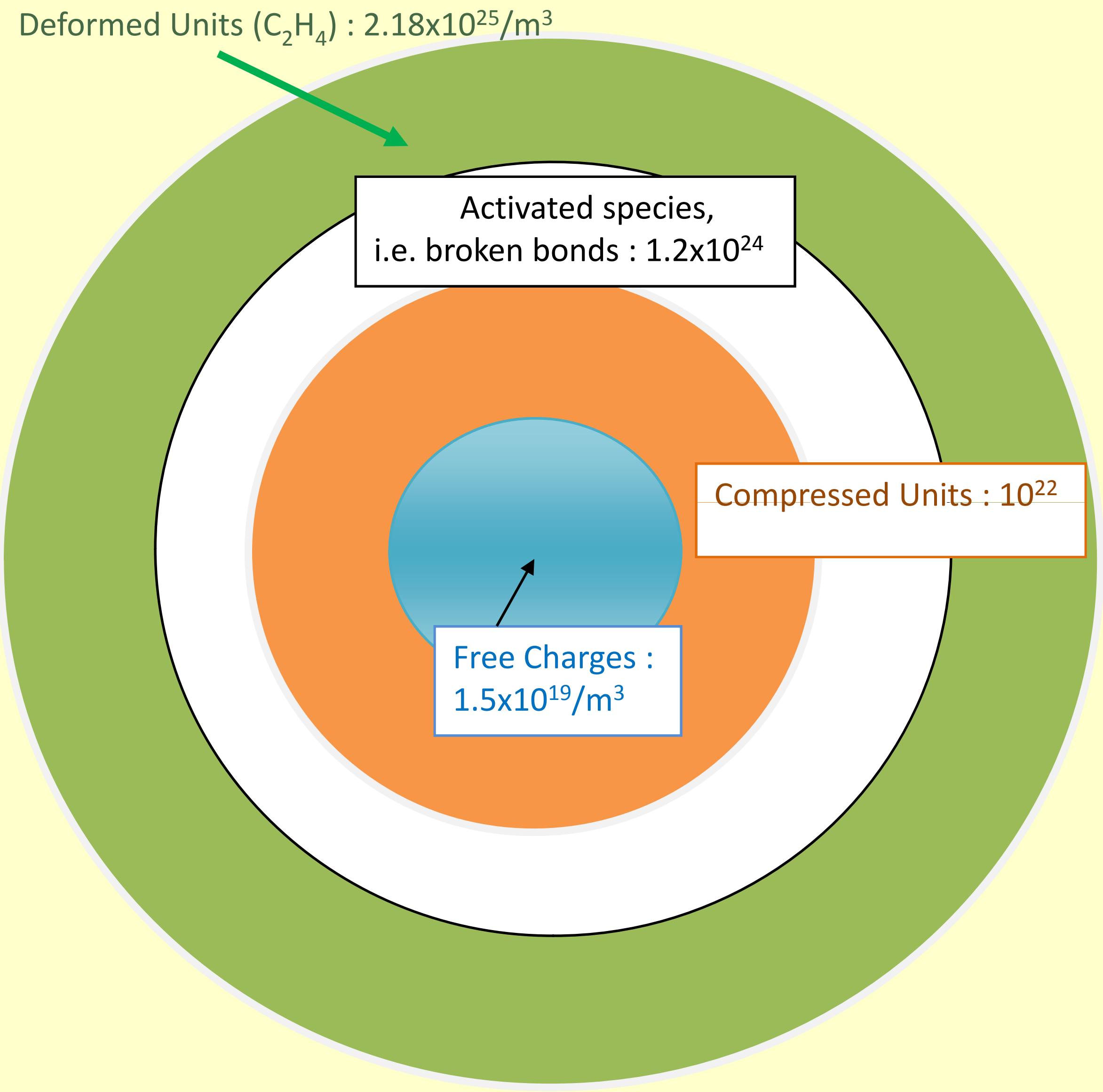
Compression becomes significant when

$(\Delta V/0.368)\ \sigma = B\ v$

where B is the bulk modulus and v is the molar volume



Typical Concentrations at Ultimate Breakdown



Deformed Units (C_2H_4) : $2.18\text{x}10^{25}/m^3$

Activated species,
i.e. broken bonds : $1.2\text{x}10^{24}$

Compressed Units : 10^{22}

Free Charges :
$1.5\text{x}10^{19}/m^3$

Deduced from:

$\sigma/(Ev)$, v= molar volume

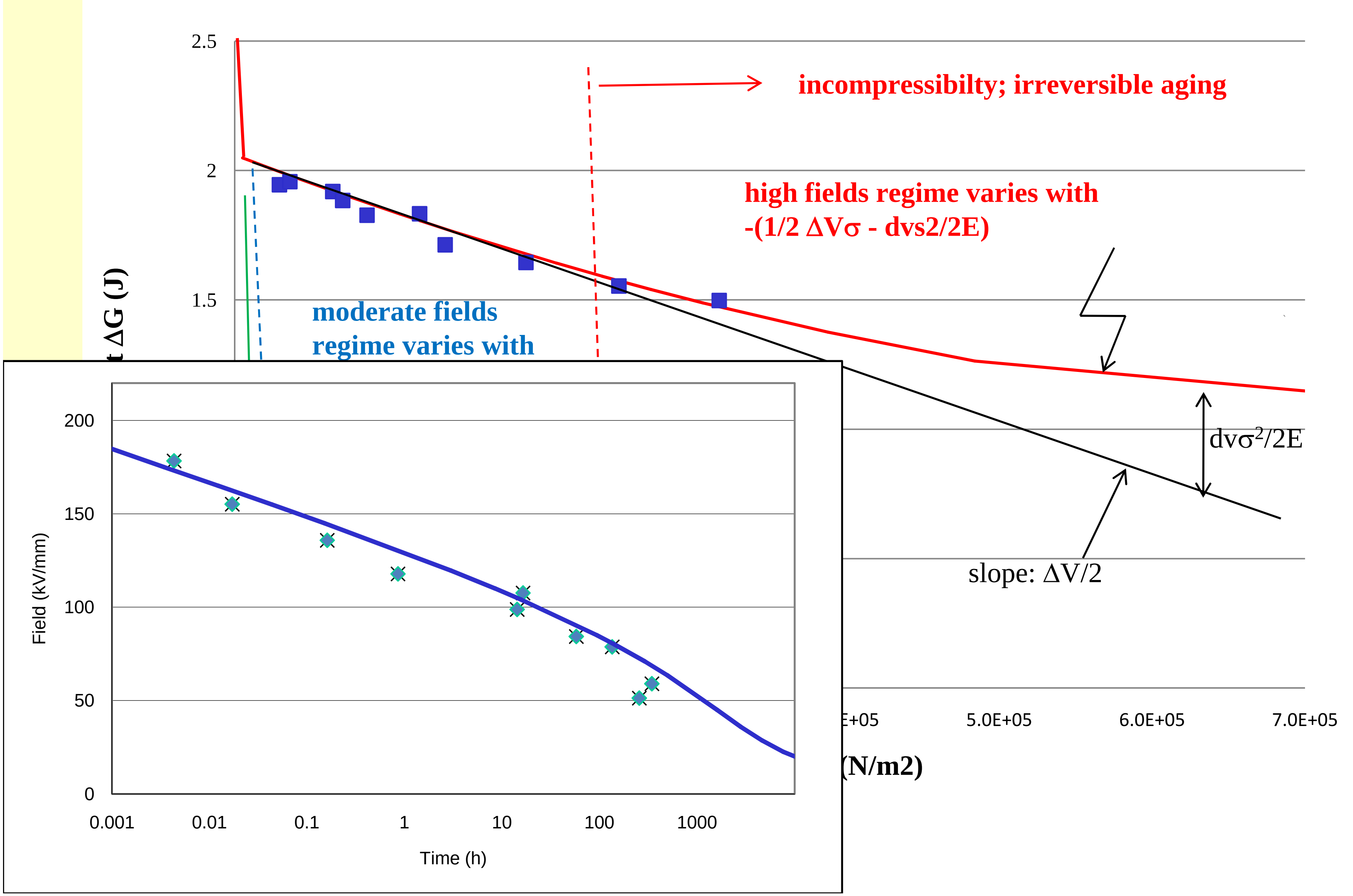
Slope of σ vs. Log t (moderate fields)

Empirical fit between the time calculation (with the above value of ΔV) and the experimental data

CU/(e x sample volume)

XLPE Sample: 280 μm film, aged under 50 Hz, in air, 22°C

ELECTRICAL AGING IS MADE OF 3 REGIMES
(under constant temperature and in air)



CONCLUSION

- **A model based on molecular concepts appears to describe the electrical life of XLPE under constant temperature and a wide range of fields (ac and dc).**
- **The activation energy for electrical aging seems related to the dissociation energy of C-C bonds.**
- **Aging is limited at low fields below a critical/threshold field. We predict that fast aging occurs when C-C bonds are broken above that critical field. Free radicals accelerate the bonds breaking process.**
- **Irreversible aging corresponds to severe compressibility of the molecular chains at a stress predicted by the model.**
- **Electrical aging is thus composed of 3 regimes.**

From a fundamental angle…

– ΔG and ΔV are decreasing exponentially with time; the breakdown values are (1/0.368) time the values at t = 0.

- This implies that at low fields, the energy barrier remains high and very little change would occur.
- Below the critical field (in the 10 kV/mm range) few- if any- bonds are broken, i.e. few radicals are generated, and life will be very long.
- The model can be easily applied to any polymer as long as the value of the basic molecular parameters are known.
- Space charges appear in large content when C-C bonds are broken and their amount vary with the amount of broken bonds: in other words, they are a consequence and a marker of aging, not a cause.

From a practical point of view…

- Comparisons and predictions should be made only from the moderate fields regime.

- Extrapolating life from breakdown data (i.e. very high fields regime) might induce some errors unless the specific value of dv is known.

- Adding a free radical scavenger will improve the breakdown strength, reduce the amount of charges and increase life; the adequate concentration remains to be determined.

- But the MAJOR conclusion is that <u>predicting cable life in service condition from accelerated testing under constant temperature </u>is a total LOSS OF TIME AND $.

INFLUENCE OF TEMPERATURE CYCLES ON CABLE LIFE

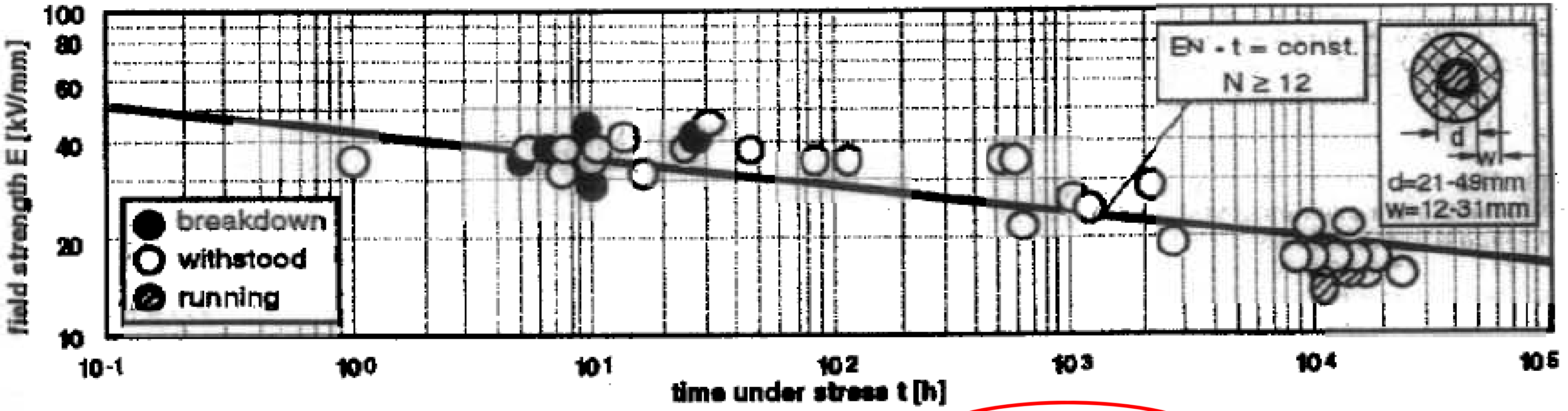


Figure 1: ac voltage life tests on HV and EHV XLPE cable lengths (l = 100 m) at ambient temperature.

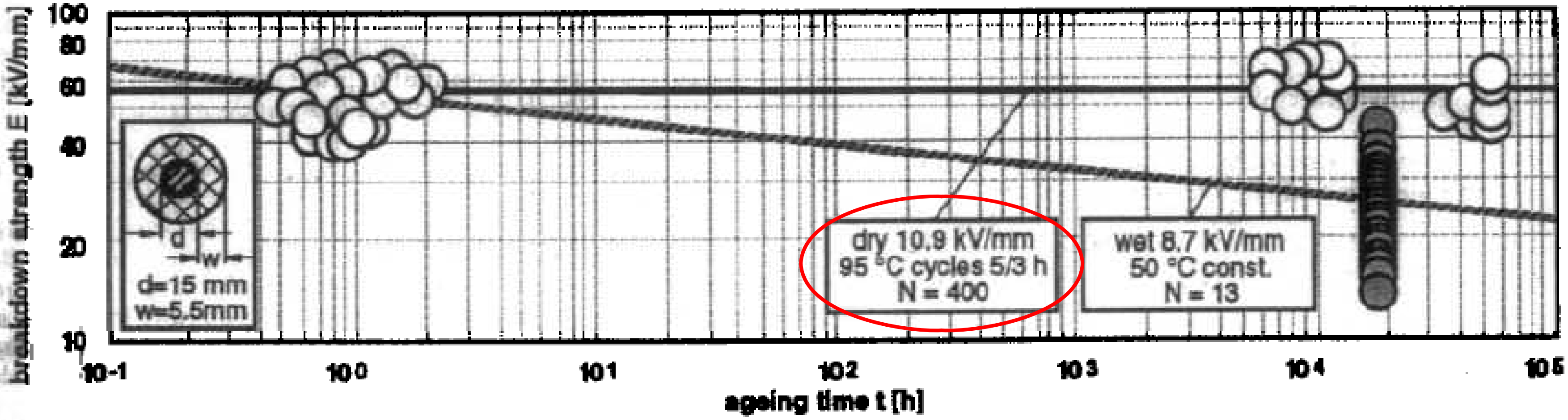


Figure 2: ac voltage ageing tests on 20 kV XLPE cable lengths (l = 15 m). Evaluation by short time ac step tests until breakdown.

Peschke et al., Jicable 95

What Remains to be Done

- **Aging performed under temperature cycles.**

- **Determination of the ΔV value and relation with sample size; Aging and breakdown data obtained with samples of different sizes.**

- **More precise estimation of the critical field value below which there is very little aging.**

- **Measurement of free radicals concentration during electrical aging; Effect of radical scavengers on XLPE Life.**

THANK YOU FOR YOUR ATTENTION. ANY QUESTIONS ?