

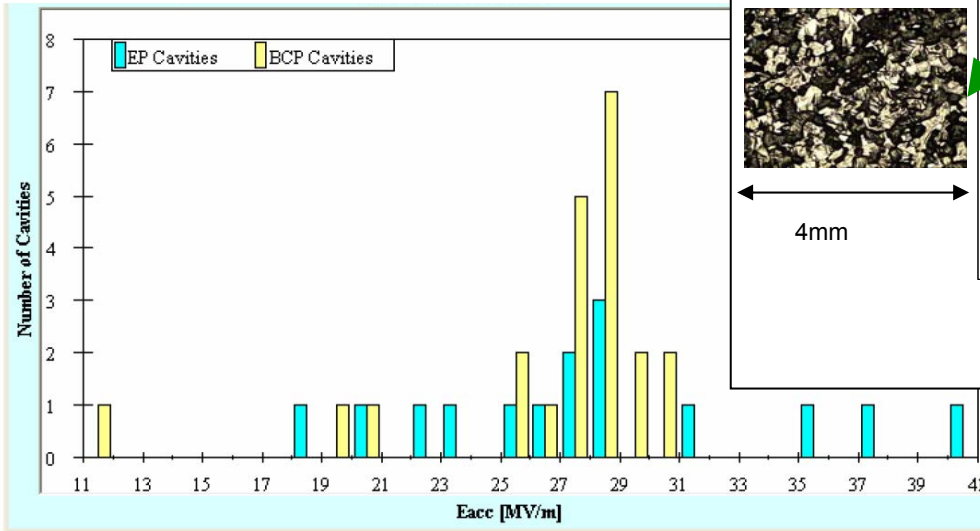
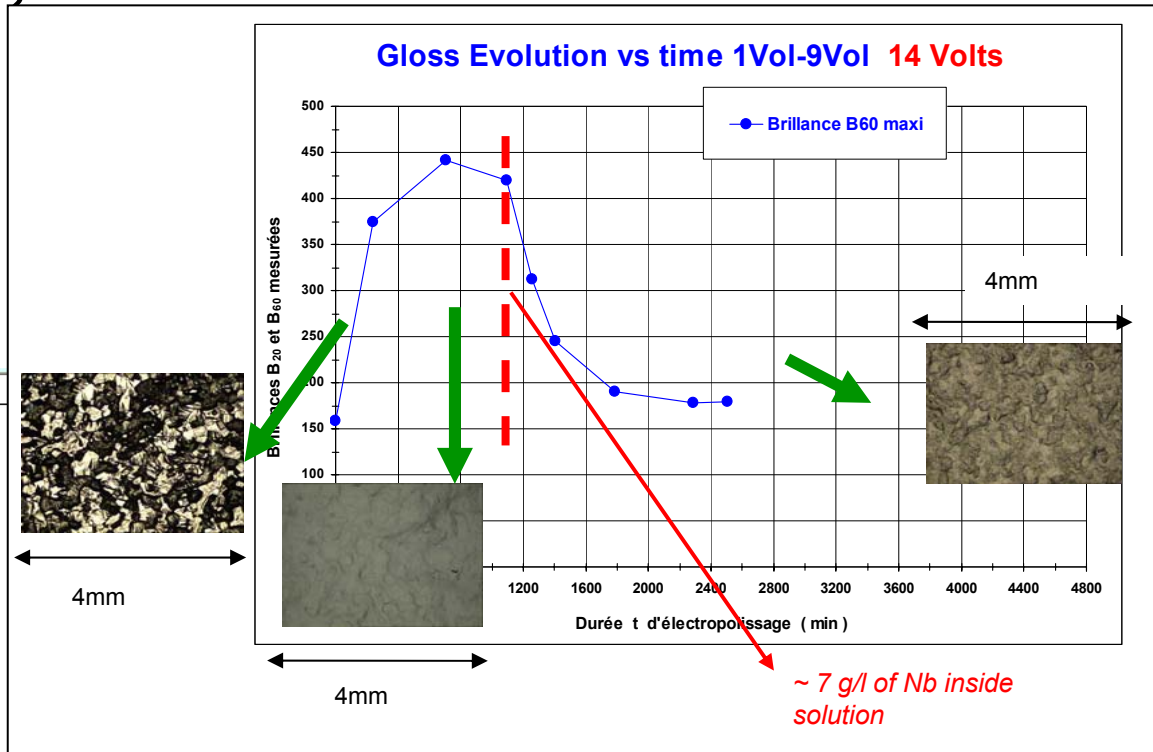


Some hints about EP mechanism



Aging

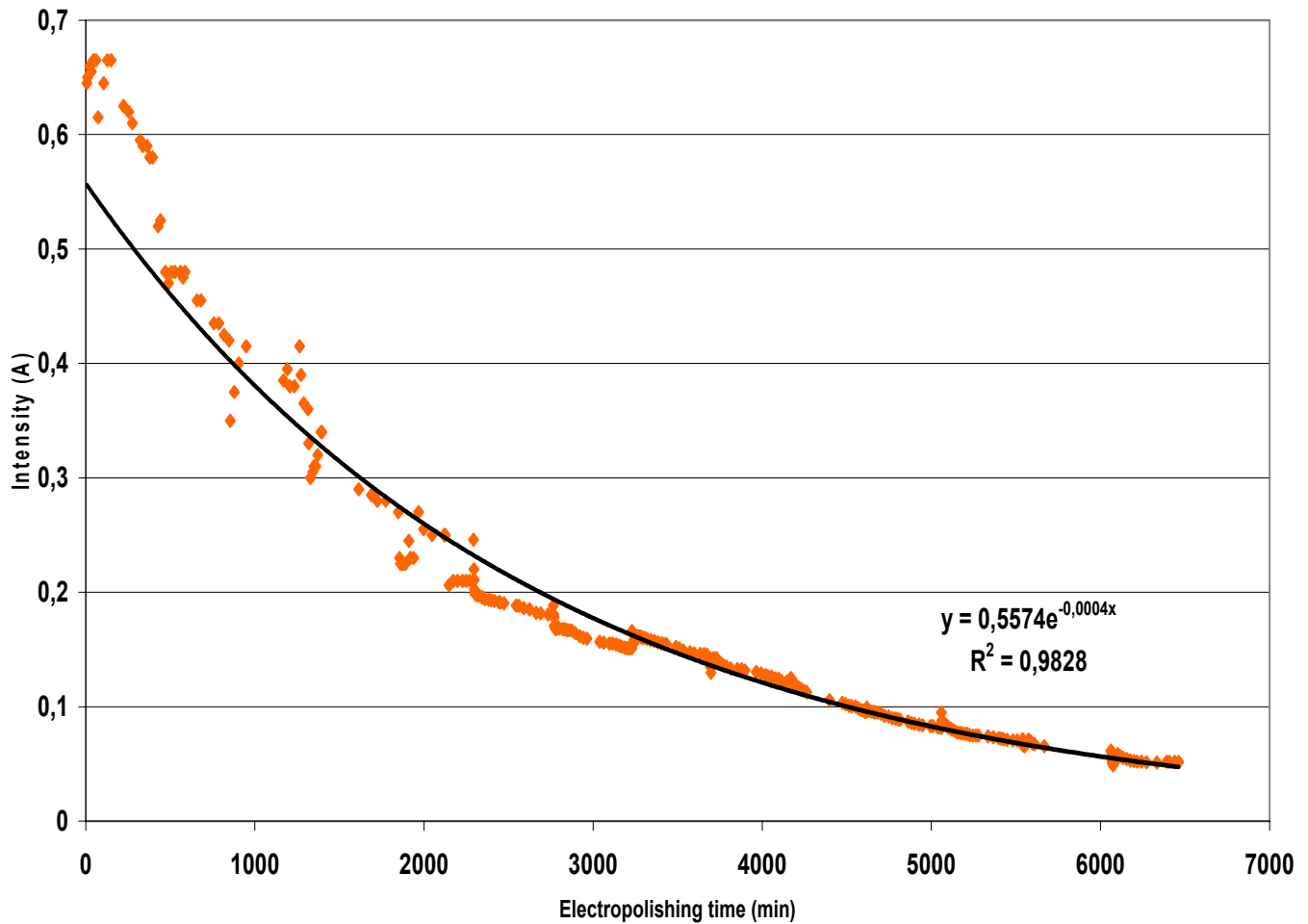
- EP gives very high E_{acc} but large spreading of results
- EP recipe seems very effective for short etching (cf Kek 3 μm last etching)
- Lifetime issues ?





Intensity decreases with time

Intensity Evolution Vs Time 1V-9V mixture 8 Volts



[F. Eozenou et al
Care report XXXXX]



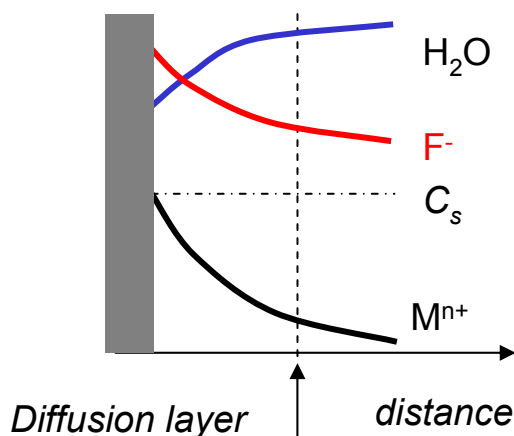
Remind :



- EP is a diffusion limited process : the current is limited by the slowest diffusion process;
- How can we test the mechanism ?
- => by changing the concentration of the species in solution and checking $I(V)$ curves
- I is proportional to the diffusion gradient
- => if $C_{\text{surface}} = C_{\text{solution}}$ for the metal ion => $I = 0$

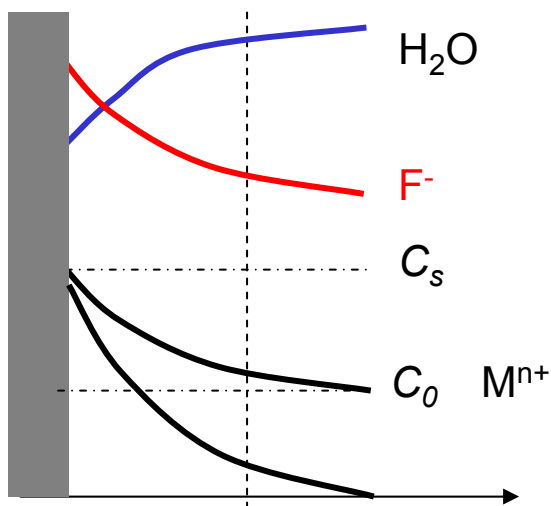


I) If EP is limited by Metal Ions (M^{n+}_{aq}) diffusion

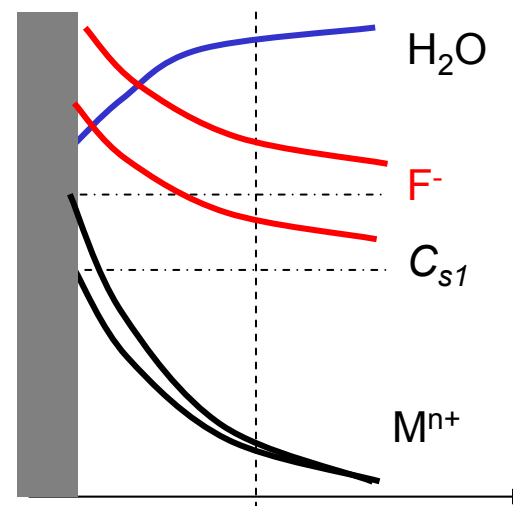


- M^{n+} , in our case = NbF_5
- M^{n+} , is at saturation at the surface
- If you $\uparrow C_0$,
 - Concentration gradient $\downarrow\downarrow$,
 - Diffusion $\downarrow\downarrow$
 - $I \downarrow\downarrow$
- If you $\uparrow [F^-]$,
 - It should not change diffusion
 - It can change solubility: $C_{s2} > C_{s1}$
 - $I \uparrow\uparrow$

Addition of $[M^{n+}] = C_0$ in the bath

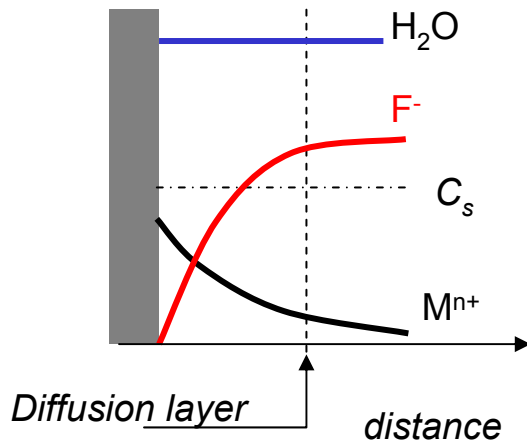


Addition of $[F^-]$ in the bath $C_{s2} > C_{s1}$



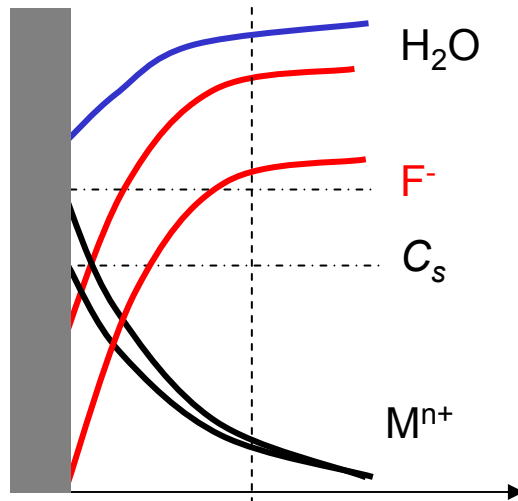


II) If EP limited by Acceptor Ions (F^-/FSO_3^-) diffusion

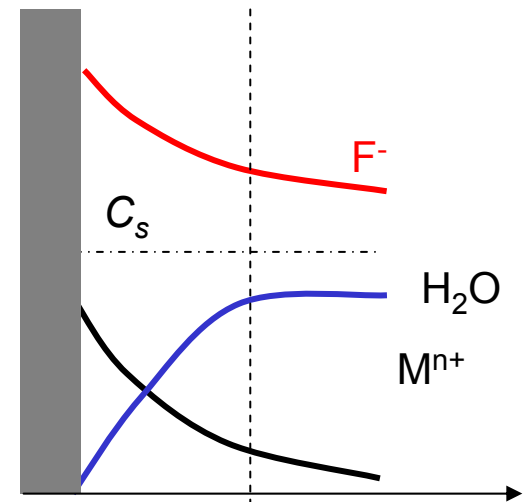


- Acceptor in our case = F^- or FSO_3^- , will be noted $[F^-]$ for simplicity
- $[F^-] = 0$ at the surface
- If you $\uparrow [F^-]$,
 - you are not limited by F^- diffusion anymore
 - $I \uparrow \uparrow$
 - It can also change solubility: $C_{s2} > C_{s1} \Rightarrow I \uparrow \uparrow$ also
- $\uparrow [F^-] \Rightarrow I \uparrow \uparrow$ is not conclusive alone

Addition of $[F^-]$ in the bath



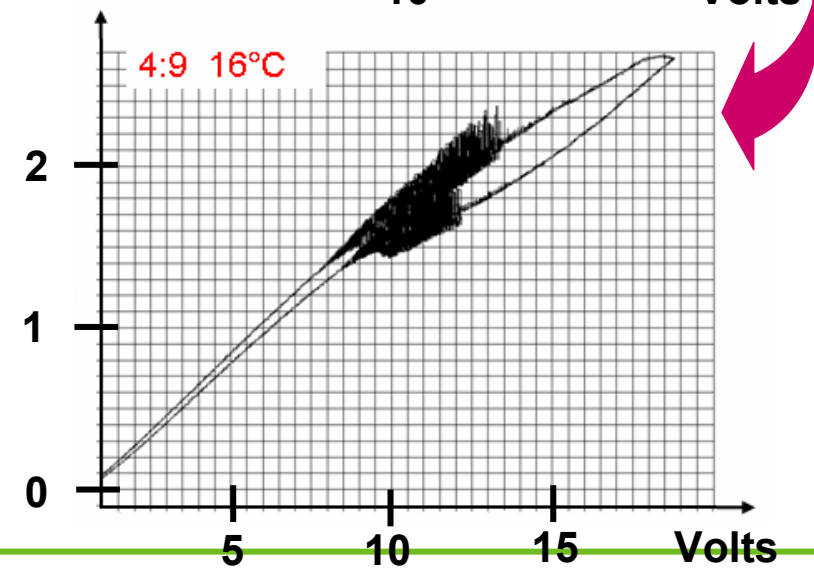
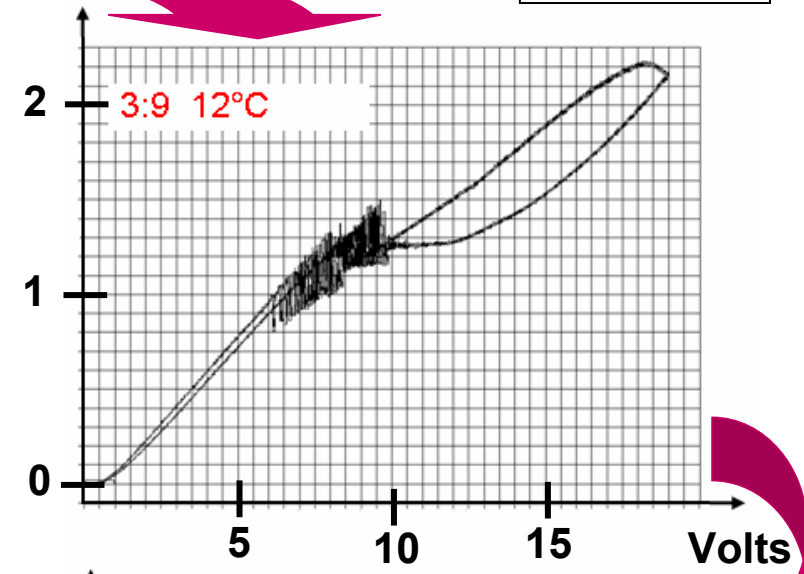
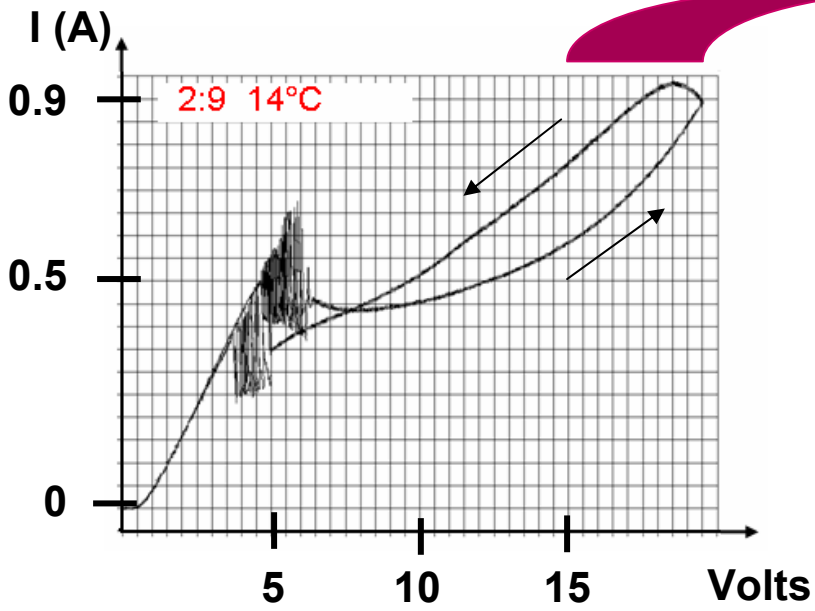
III) Limitation by H_2O





Effect of increasing HF in EP solution

HF ↑



- plateau disappear progressively with [HF] ↑.
- I, etching rate ↑
- EP seems to be controlled by F-...!?

... but F effect alone is not conclusive

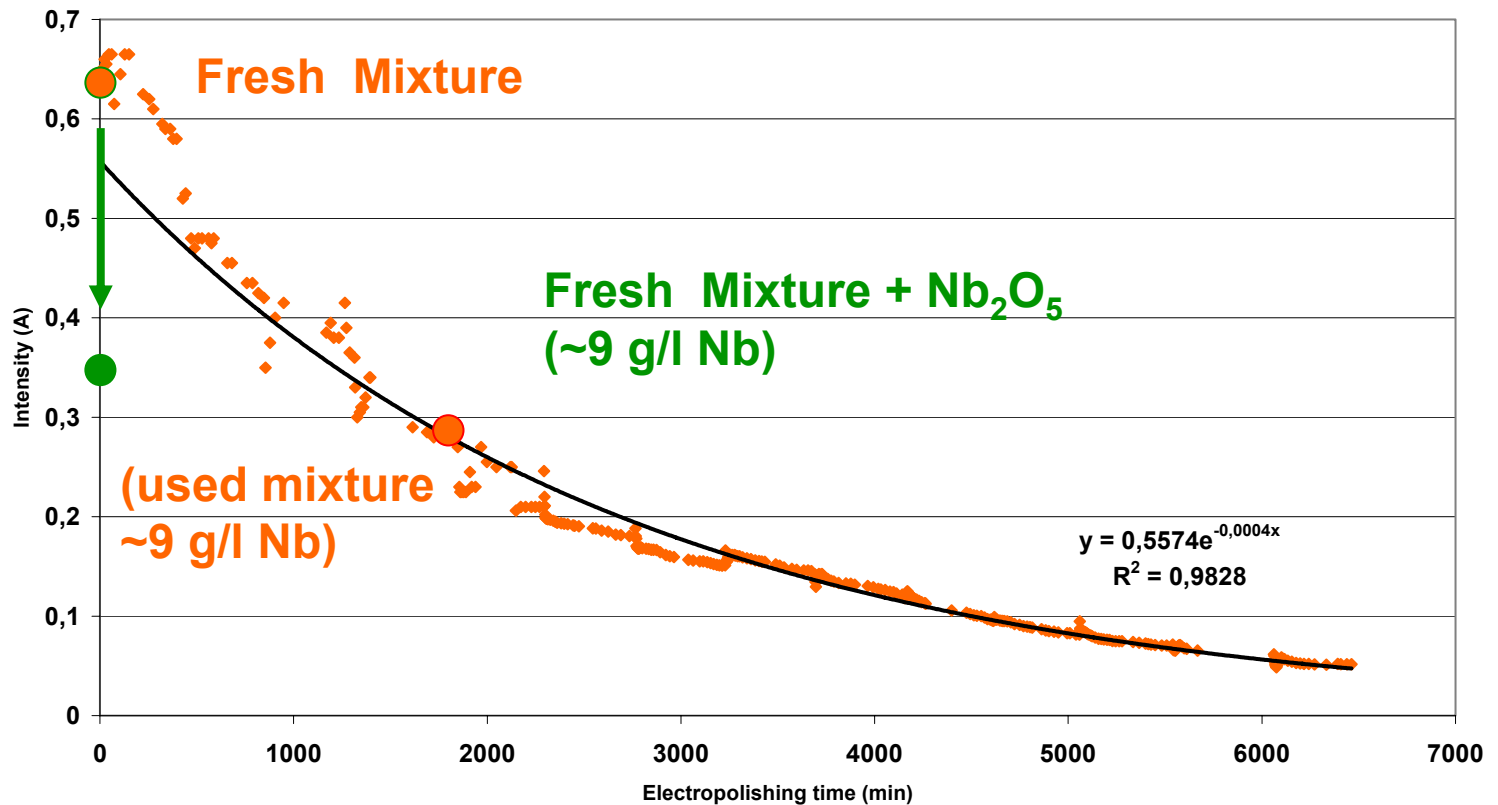


Effect of dissolution of Nb₂O₅ in EP solution

Addition of NbF₅ : ↑ Nb⁵⁺, but F⁻ also ↓



Intensity Evolution Vs Time 1V-9V mixture 8 Volts

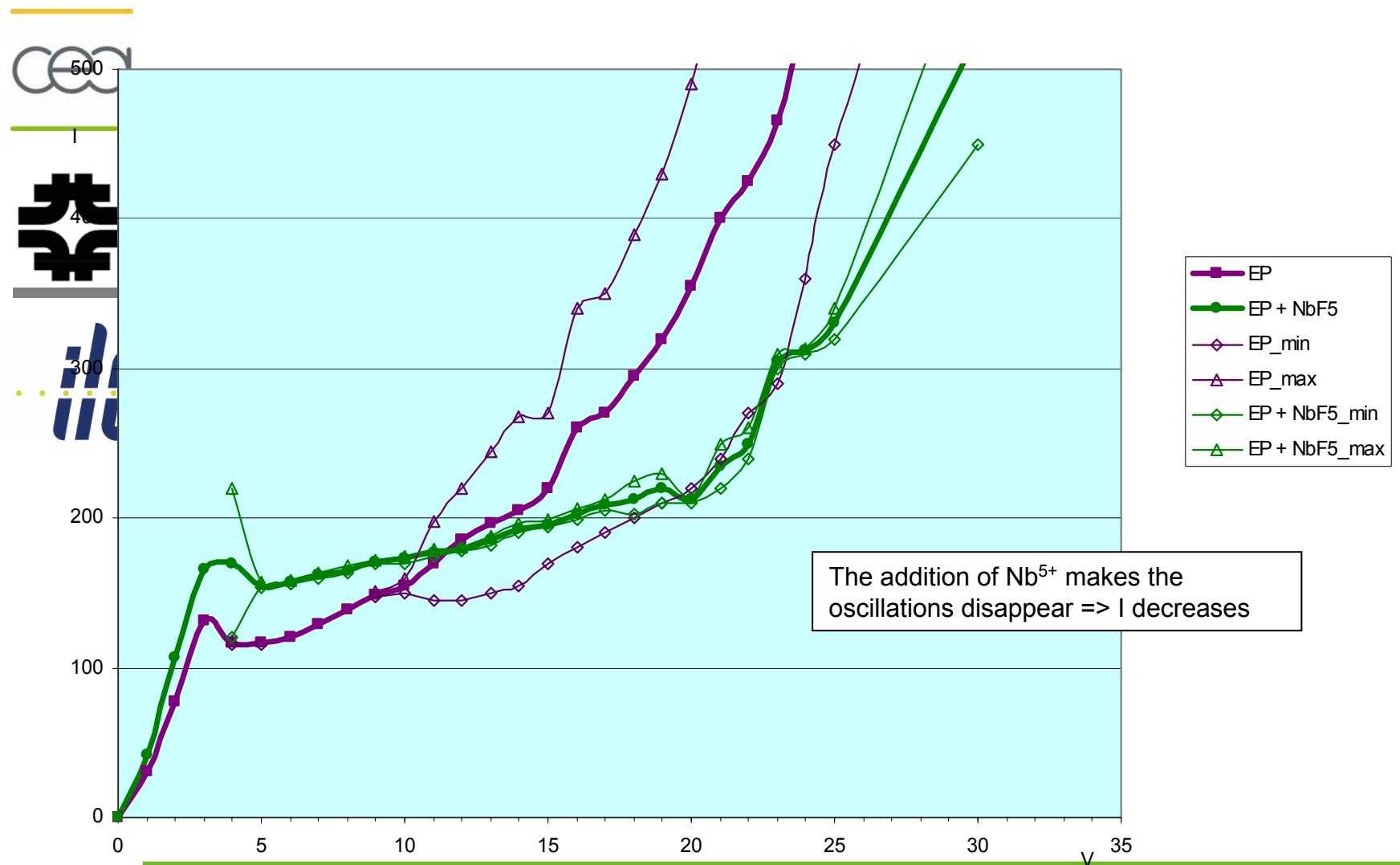


[Fabien Eozenou at Kek TTC meeting]



Effect of dissolution of NbF_5 in EP solution

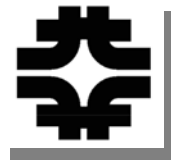
Addition of NbF_5 : Same quantity of fluoride, $\uparrow \text{Nb}^{5+}$



The addition of Nb^{5+} makes the oscillations disappear => I decreases



What have we observed ?



- If we \uparrow $[F^-]$, by adding HF or by using HF 48% instead of 40%
 - $I \uparrow\uparrow$

- If we \uparrow $[M^{n+}]$, by adding Nb_2O_5 in EP 1-9

- $I \downarrow\downarrow$

Note: When adding Nb_2O_5 in EP 1-9, $[F^-] \downarrow$, (5 F per Nb).

It could affect the Nb solubility. This experiment needs to be confirmed with NbF_5

- If we \uparrow $[M^{n+}]$, by adding NbF_5 in EP 1-9

- $I \downarrow\downarrow$, but only for $V > 10-12$ Volts !

Note: I has been observed to decrease at V as low as 8 Volts

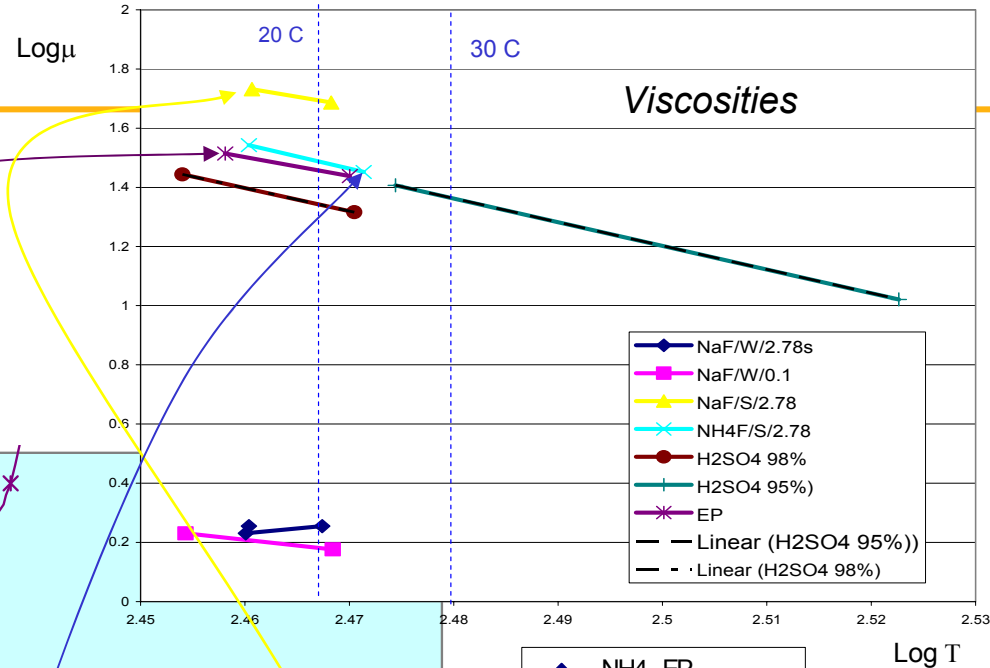
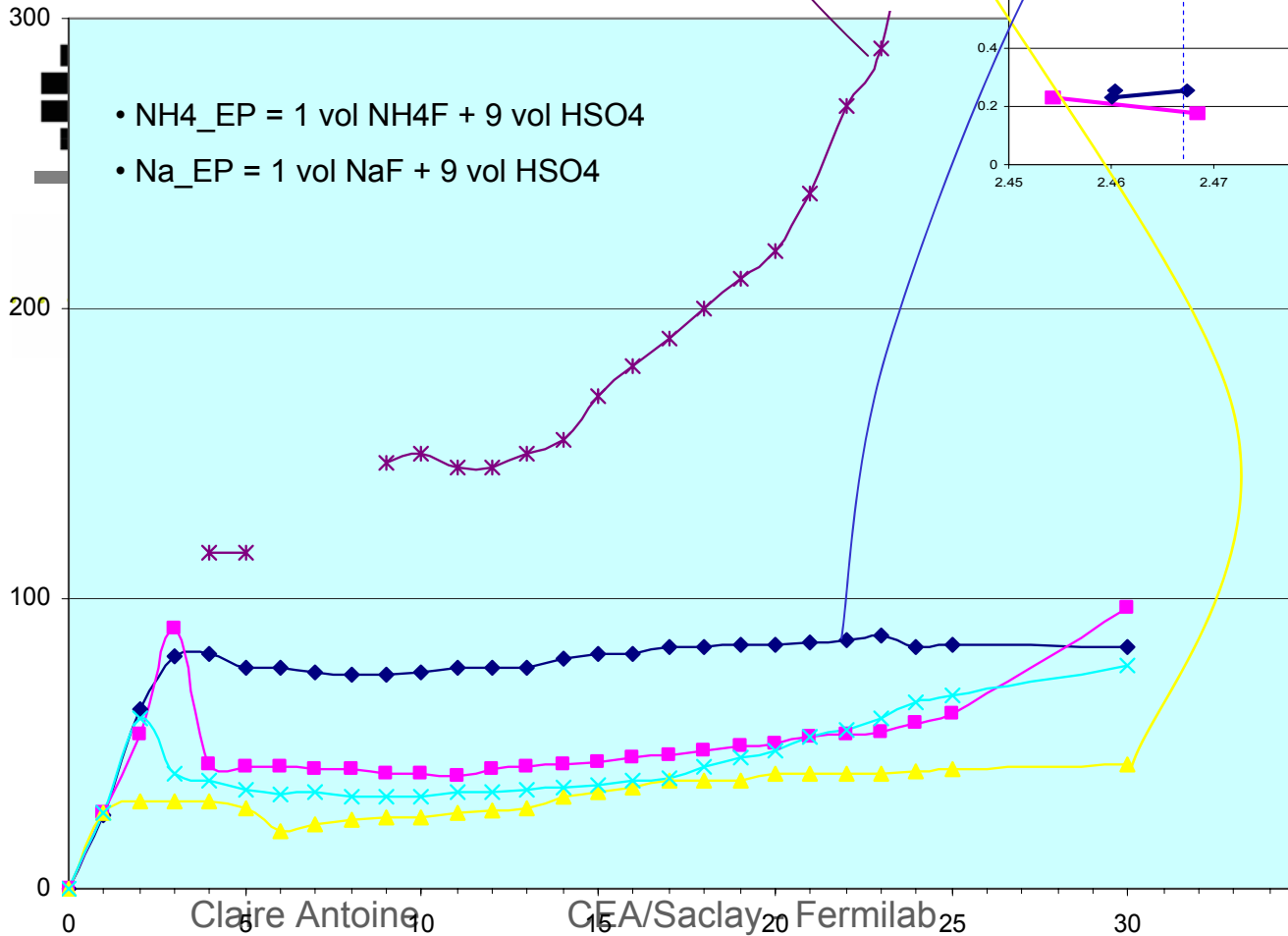
Although we have strong indication for type I mechanism, the aging process cannot be related to the saturation of the solution in Nb^{5+} .

=> need for other mechanism ; e.g. change of solubility with F decrease ? F evaporation ?



Other tests

cea
I / V curves

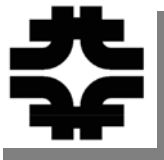


- Variation of viscosity
 - Variation of acidity
- => Evaluation of the modeling
- e.g. NH4_EP and EP have the same viscosity but not the same acidity => different Iplateau*

Try EP + saturated NH4F



Ion Selective Electrode for F monitoring



- Not expensive
- Once the exact procedure is known : very quick, systematic
- Dilution is needed (x100 to x1000 compare to x10 000 for Ionic Chromatography or EPhoresis)
- In principle, it is sensitive to $[F^-] \sim 10^{-6} - 10^{-5}$ Mol/l, in practice rather 10^{-4} Mol/l



Ion Selective Electrode for F⁻ monitoring

ISSUES: F⁻ can be measured only if dissociated

- F⁻ is not dissociated
 - If highly concentrated. Initial [F⁻] ~ 2.78 M, too high !
 - If the solution is highly acidic (oops ! [H₂SO₄] > 16 M)
- => dilution x100 to x 1000 + use a buffer (e.g. pH 7.2)
- => decouple standard measure from sample measure with “known addition” technique (so we can calibrate the ion-meter with standards with a different ionic strength*).
- Feasibility of the technique is demonstrated with ~ 15% sensitivity (in Δ[F])
- Careful adjustment of the dilution and buffer quantities are still needed to gain sensitivity

**Accurate direct measurement of the concentration needs that the standard solutions and the sample solution should be at the same ionic strength... Impossible here*



Next steps



- Monitor F content during long EP operation
- Measure viscosities more carefully other extended temp range
- Input viscosities data in modeling and check if the plateaus of I / V curves are accurately predicted
- Suggestions ?

