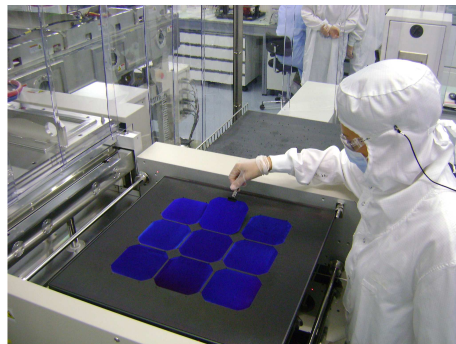
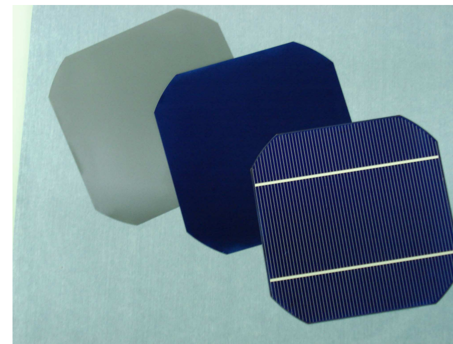
HF last passivation for high efficiency a-Si:H/c-Si heterojunction solar cells

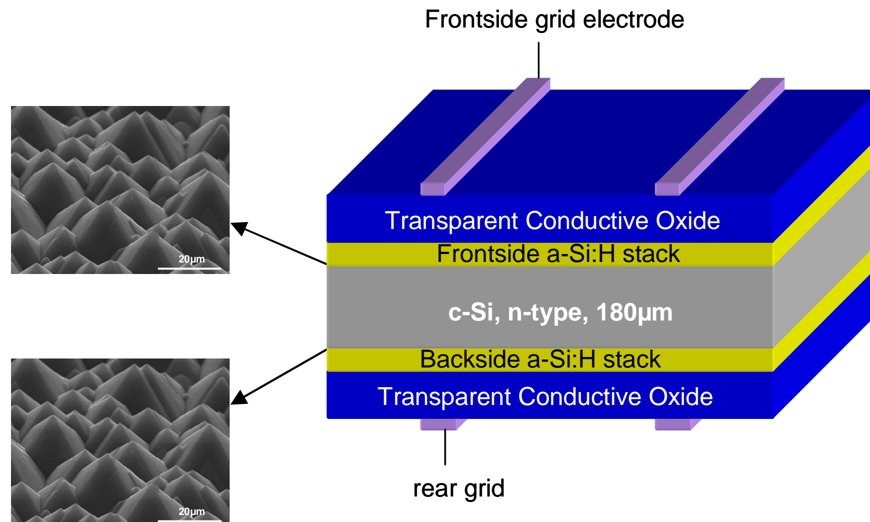
Adrien Danel, F. Souche, PJ. Ribeyron : INES
Y. Le Tiec : LETI
T. Nolan : Akrion Systems





Heterojonction solar cells at INES

- *125 PSQ, CZ or FZ (100), n-type 1-5 Ohm.cm, PV wafers for 148.5 cm^2 cells*



Surface / Interface is (111) oriented pyramid facets

1) Texturing c-Si substrates (KOH & IPA)
- ✓ *Removal of damaged zone*
- ✓ *Good optical confinement*

2) Surface cleaning
- ✓ *Insure good interface quality*

3) HF-last passivation
- ✓ *SiO_2 removal*
- ✓ *As clean, as dense, as stable as possible Si-H termination*

4) a-Si:H low T°deposition (PECVD)
- ✓ *i,p & i,n stacks for emitter and BSF formation*

5) TCO deposition
- ✓ *Antireflective coating, charge collection*

6) Grid electrode (screen printing) and edge isolation (laser cutting)
- ✓ *Electrical tests : cell performance*

Outline

- ***Impact of practical parameters on cell performance***

1) HF concentration
2) Process time
3) Post rinse and drying
4) Delay before deposition steps
5) HF cleanliness and HCl spike
6) HF & NH_4F

RCA & HF or O_3 & HF –based post texturization clean

+

HF 2%w, HCl 1%w, 5min, 20°C, no rinse & dry

=

reference process of this work

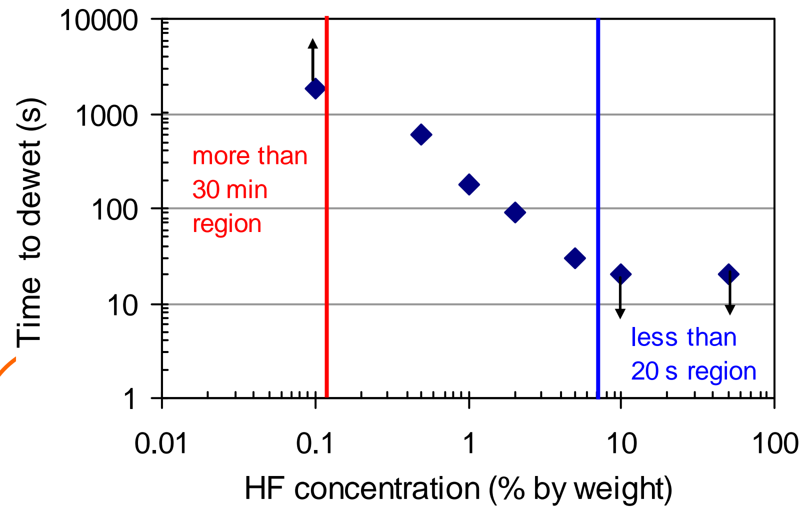
❖ ***Lifetime tests: texturing, cleaning, passivation, intrinsic a-Si:H 40nm***

- **µPCD map (Semilab) and QSSPC (Sinton, transient mode) :**
  - ➔ Effective recombination lifetime (τ_{eff})
  - ➔ Implied Voc and effective surface recombination velocity (S_{eff}) at 1 sun

❖ ***HJ cell: 148.5 cm², full process – module compatible***

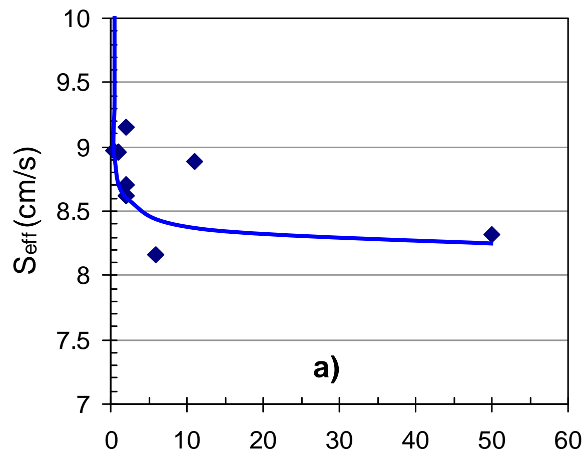
- **I(V) under AM 1.5, 100 mW/cm² condition at 25°C :**
  - ➔ solar energy conversion efficiency (η) with Voc, Jsc, FF

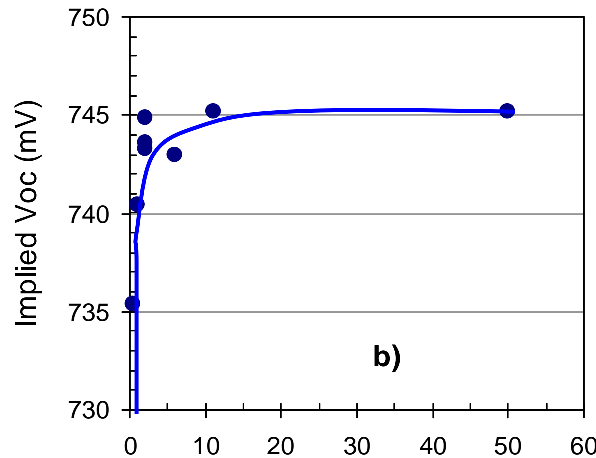
1) HF concentration



- ***For good dewetting, fast and robust process: [HF] ≥ 2% is recommended***

- ***As soon as a good dewet is achieved, only a slight improvement of passivation is seen with [HF] (QSSPC data)***



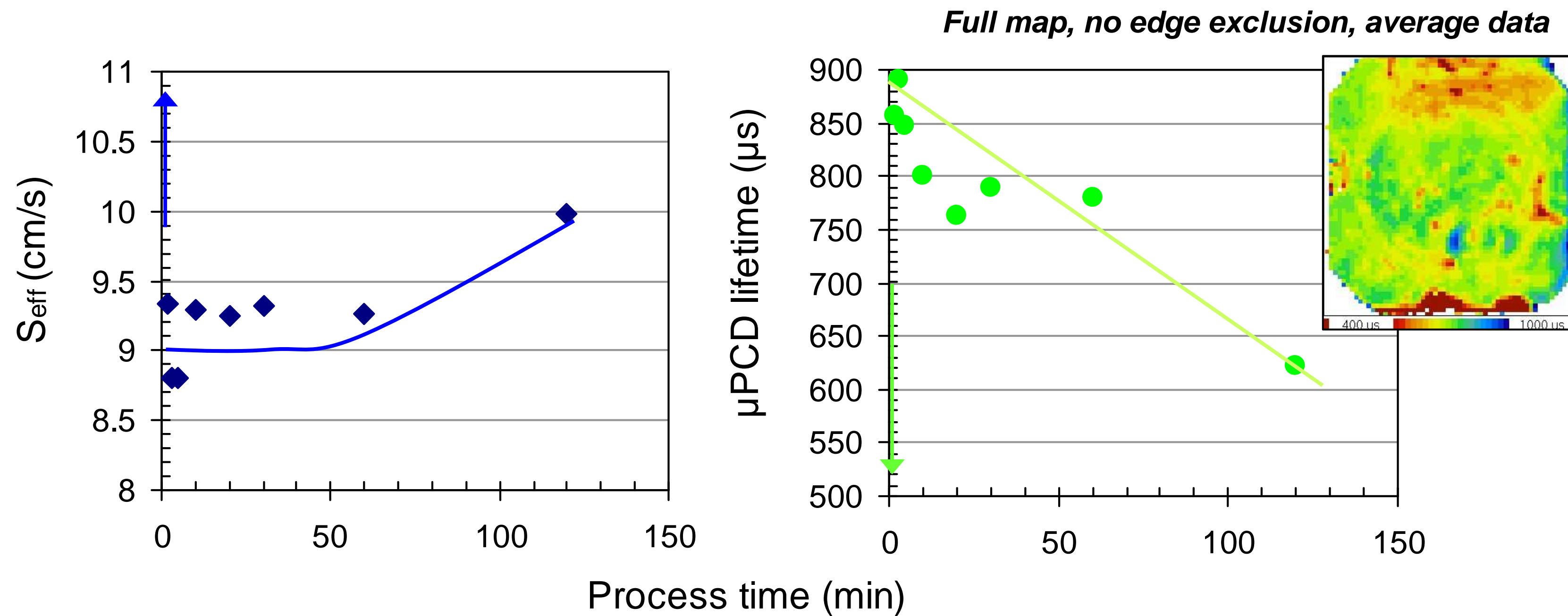


HF concentration (% by weight)

Confirmation on cells

	η (%) & (sigma)	Jsc (mA /cm^2)	Voc (mV)	FF (%)
HF 2%	18.4 (0.05)	35.1	686	76.4
HF 20%	18.5 (0.10)	35.1	689	76.5

2) Process time



- *A **slight degradation** is seen, mostly on data taken from the complete full wafer : likely time dependent roughening and contamination issues*

- *As soon as the deox is achieved, the shorter the better: with **HF ≥ 2%, 2 – 5 min long process** is recommended*

3) Post rinse and drying

- ***For safety reasons, post HF rinse & drying is mandatory in industrial application***

❖ ***Rinse**: dump HF-HCl + overflow UPW rinse varied from 5min to 2h*

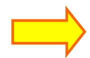
S_{eff} stable

Si (100): 2h stable Si-H_x passivation in UPW reported by H. Morita et al, JAP 68, 1272 (1990)

❖ ***Drying**: 5min UPW*
→ *10min hot N2 flow*
→ *6min slow drain with IPA vapor + 5min hot N2 (LUCID®)*

	η (%)	Jsc (mA /cm²)	Voc (mV)	FF (%)
No rinse & dry	16.9 (0.3)	34.2	678	73.0
Hot N2	17.0 (0.2)	34.1	683	73.3

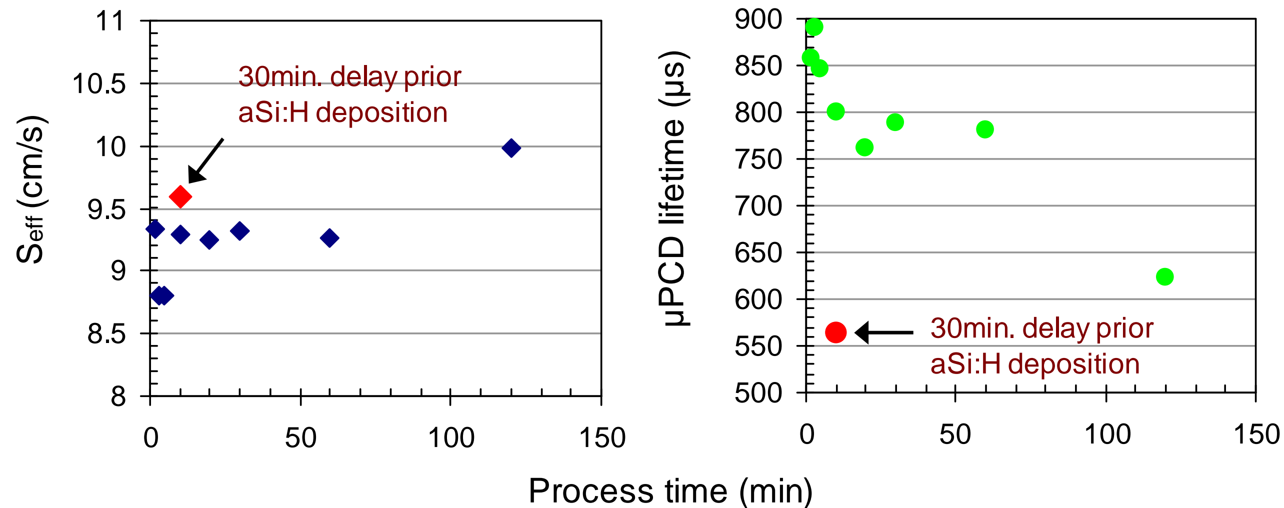
	η (%)	Jsc (mA /cm²)	Voc (mV)	FF (%)
Run #1				
No rinse & dry	17.2 (0.07)	34.9	677	73.0
IPA & hot N2	17.2 (0.16)	33.4	676	76.6
Run #2				
No rinse & dry	18.4 (0.08)	35.1	695	75.4
IPA & hot N2	18.3 (0.30)	35.3	696	74.5



✓ No critical issue
✓ More data needed for precise numbers

4) Delay before deposition steps

- ***Passivation tests (QSSPC) : q-time degradation starts at about 30 min***



✓ Effect is more visible on data from the complete full wafer

- ***Cell performance :*** ❖ ***5 min to 30 min q-time = no visible impact***

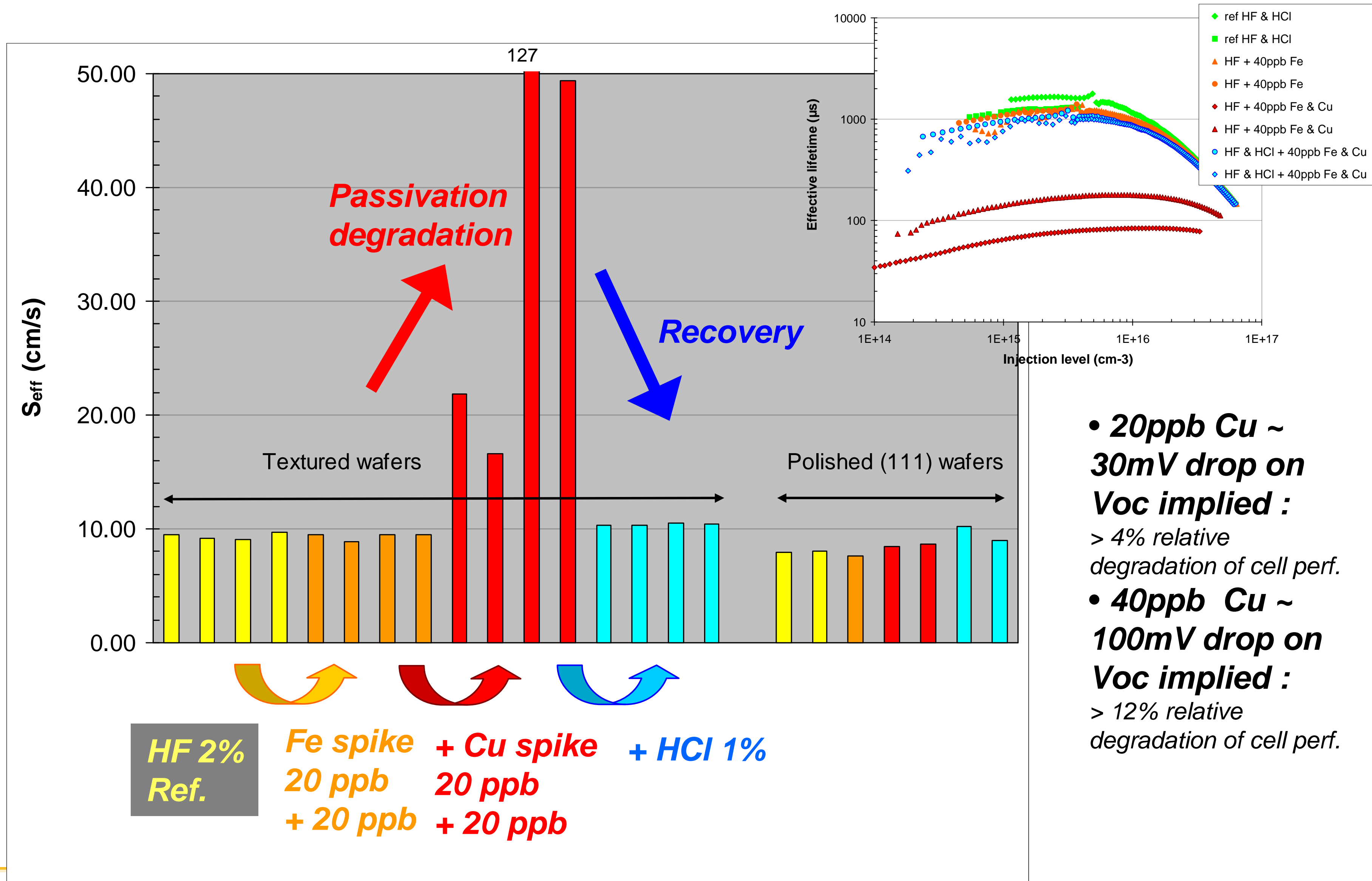
❖ ***90 min q-time in clean room air = about 5% relative degradation***

Q-time	η (%)	Jsc (mA /cm^2)	Voc (mV)	FF (%)
< 10 min (ref.)	17.8 (0.2)	34.6	691	74.4
90 min	17.0 (0.2)	34.1	683	73.3

✓ Impact depends on RH and on the effectiveness of the previous clean step

D. Graf et al, J. Appl. Phys. 69, 7620 (1991)
H. Angerman et al, Solid State Phen. 92, 179 (2003)

5) HF cleanliness (1/2) …. Metals



5) HF cleanliness (2/2)

- ***Surface contamination by VPD-DC-ICPMS*** *(H. Fontaine, leti)*

E10 at/cm²

	Na	Mg	Al	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn	Sum
as-textured												
ctl #1	54	2900	370	220	1100	630	95	30080	10	11760	30	**47 300**
ctl #2	27	1300	26	630	64	200	300	4600	2	1200	21	**8 400**
ctl #3	65	1100	59	85	69	510	870	13000	8	8400	16	**24 200**
Texturization + SPM - HF - RCA + HF/HCl last												
ctl #1	4.3	0.8	4.2	11	5.2	<0.1	0.2	16	0.1	<0.5	13	**54.8**
ctl #2	2	0.3	1	5	2	0.2	0.1	0.3	< 0.1	0.6	0.5	**12**
Texturization + O3 & HF -based INES clean + HF/HCl last												
HF 2%	<1	<0.2	<1	4.3	<1	1.2	1.5	**4.2**	<0.1	**<0.5**	0.2	**11.4**
HF 2%, 40ppb Fe	<1	<0.2	<1	<1	<1	<0.1	<0.1	**7.2**	<0.1	**<0.5**	<0.1	**7.2**
HF 2%, 40ppb Fe & Cu	<1	<0.2	<1	<1	<1	<0.1	<0.1	**0**	<0.1	**31**	<0.1	**31**
HF 2% & HCl 1%, 40ppb Fe & Cu	<1	<02	<1	<1	<1	<0.1	<0.1	**1.4**	<0.1	**<0.5**	<0.1	**1.4**

As expected from deposition mechanisms:
- *No impact of Fe in HF (verified @ 40ppb)*
- *Strong impact of Cu (20 and 40ppb)*
- *HCl 1% allows safe process (complexation of Cu)*

6) HF & NH_4F

	η (%)	Jsc (mA /cm²)	Voc (mV)	FF (%)
HF 2% - HCl 1%	18.4 (0.05)	35.1	686	76.4
BOE "2%"	18.0 (0.12)	35.2	680	75.7

- ***HF alternative might be possible but couple of trials with NH_4F (BOE, post HF dip in NH_4F) always showed detrimental impact on our HJ technology***

Conclusion

- More extensive runs are needed for consolidation of the performance numbers, but this work allows some recommendations:
  - ✓ *HF concentration: ≥ 2%*
  - ✓ *Process time: 2 to 5 min*
  - ✓ *Contamination (metals): HCl spike helps*
  - ✓ *Rinse and Dry: no critical issue using industrial equipment*
  - ✓ *Q-time: ≤ 30 min OK if the cleaning steps are reliable … might be critical if poor*

- HF 2%-HCl 1% 5min step was OK for INES HJ ramp up