I2 Scrubbing Simulations with Modified SPARC/MELCOR: Influence of Iodine Chemistry

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http://petr.olsak.net/ctustyle.html

OUTLINE

- parametric benchmark calculations with improved, old version of MELCOR/SPARC, to test the tool (within the frame of the IPRESCA project)

- simulations of CRIEPI experiments on I2 scrubbing

NUGENIA IPRESCA Project benchmark with MELCOR/ SPARC

- objectives of the *parametric* benchmark for *gaseous iodine scrubbing*
  - "to clarify important sensitivity parameters for gaseous iodine scrubbing"
  - "to assess current analytical tools" in terms of *qualitative* predictive capabilities
  - additional goal of ours: check the iodine chemistry set (equilibrium) in SPARC (MELCOR/ SPARC) —mainly because of the pH dependence modeling for I2 scrubbing
- only I2 modeled no organic iodide scrubbing looked at in our work —can be done later
- major sensitivity parameters studied
  - influence of iodine chemistry (pH, reaction kinetics, ...)
  - mass transfer parameters (mass transfer coefficients, I2 partition coeff)
  - selected thermalhydraulic variables (bubble dynamics not studied here)

modified SPARC and equilibrium chemistry at the bubble-water interface

- small omissions in the MELCOR_186 implementation of the SPARC I2 treatment corrected
- MELCOR/SPARC implementation of the Eggleton model (for equilibrium iodine chemistry) changed in order to relate it to the original Eggleton's work
  - in principle, Eggleton's model works for "normal" chemistry, thermal (non-radical chemistry), not necessarily for radiochemical interactions (where fast reactions of radicals prevail) —thus works for most of today's experiments with iodine, but ...
  - as an equilibrium model, it implies that the equilibrium on the interface bubble-water would not be just a function of Henry's constant of I2, but also a function of the chemical equilibrium parameters, i.e, most notably, of the water pH

Eggleton's chemistry set

$$\mathrm{I_2\ (gas\text{-}bubbles)} \overset{K_1}{\rightleftharpoons} \mathrm{I_2\ (aqueous)} \qquad K_1 = \frac{[I_2]_{aq}}{[I_2]_{gas}} \tag{1}$$

$$\mathrm{I_2\,(aq) + I^-} \overset{K_2}{\rightleftharpoons} \mathrm{I_3^-} \qquad K_2 = \frac{[I_3^-]}{[I_2]_{aq}\,[I^-]} \tag{2}$$

$$\mathrm{I_2\,(aq) + H_2O} \overset{K_3}{\rightleftharpoons} \mathrm{H^+ + I^- + HOI} \qquad K_3 = \frac{[H^+]\,[I^-]\,[HOI]}{[I_2]_{aq}} \tag{3}$$

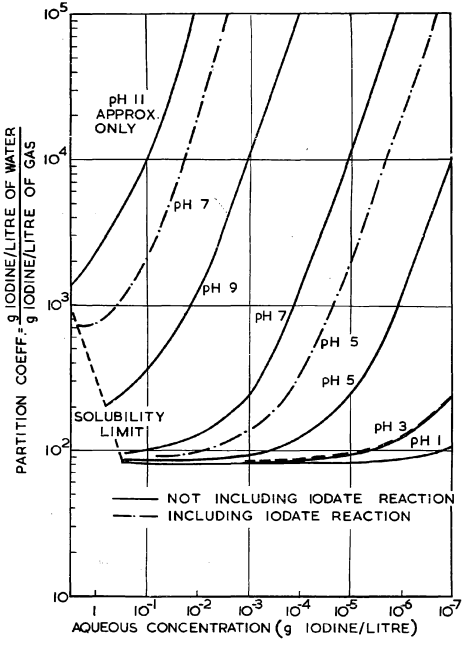
$$\mathrm{I_2\,(aq) + H_2O} \overset{K_4}{\rightleftharpoons} \mathrm{H_2OI^+ + I^-} \qquad K_4 = \frac{[H_2OI^+]\,[I^-]}{[I_2]_{aq}} \tag{4}$$

- Four, fast reactions (i.e., equilibrium) with corresponding equilibrium constants. One more reaction typically considered in similar analyses, formation of iodate, but not here, because it's relatively slow

$$\mathrm{3\,I_2\,(aq) + 3\,H_2O} \overset{K_5}{\rightleftharpoons} \mathrm{IO_3^- + 5\,I^- + 6\,H^+} \qquad K_5 = \frac{[IO_3^-]\,[I^-]^5\,[H^+]^6}{[I_2]_{aq}^{\,3}} \tag{5}$$

Eggleton's equilibrium model evaluation

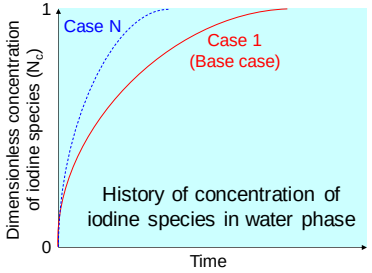
$$P = \frac{[I_2]_{aq} + (1/2)\{[HOI] + [H_2OI^+] + [I^-] + 3[I_3^-]\}}{[I_2]_{gas}}$$



- P is *overall* partition coeff of iodine
- solving analytically for $[I^-]$, the dependence of P on $[I_2]_{(aq)}$ obtained by Eggleton, with temperature dependent K_1–K_4 as parameters
- results of the analysis (here for 25°C) show **very strong pH impact**
- **this wouldn't be the case with standard SPARC nor with standard MELCOR/SPARC**

definition of the benchmark and our base_case

- benchmark defined (nicely:) in Maruyama "Proposed Program Work for IPRESCA WP3.4 on Iodine Modeling", July 2020
  - 1 m height water column, 500 L water volume, injection of air at the bottom, 1 cm diameter injection nozzle (1.6 g/s air injection rate and ~16.5 m/s injection velocity), air and water temp 20°C
  - proposed way of presenting the results



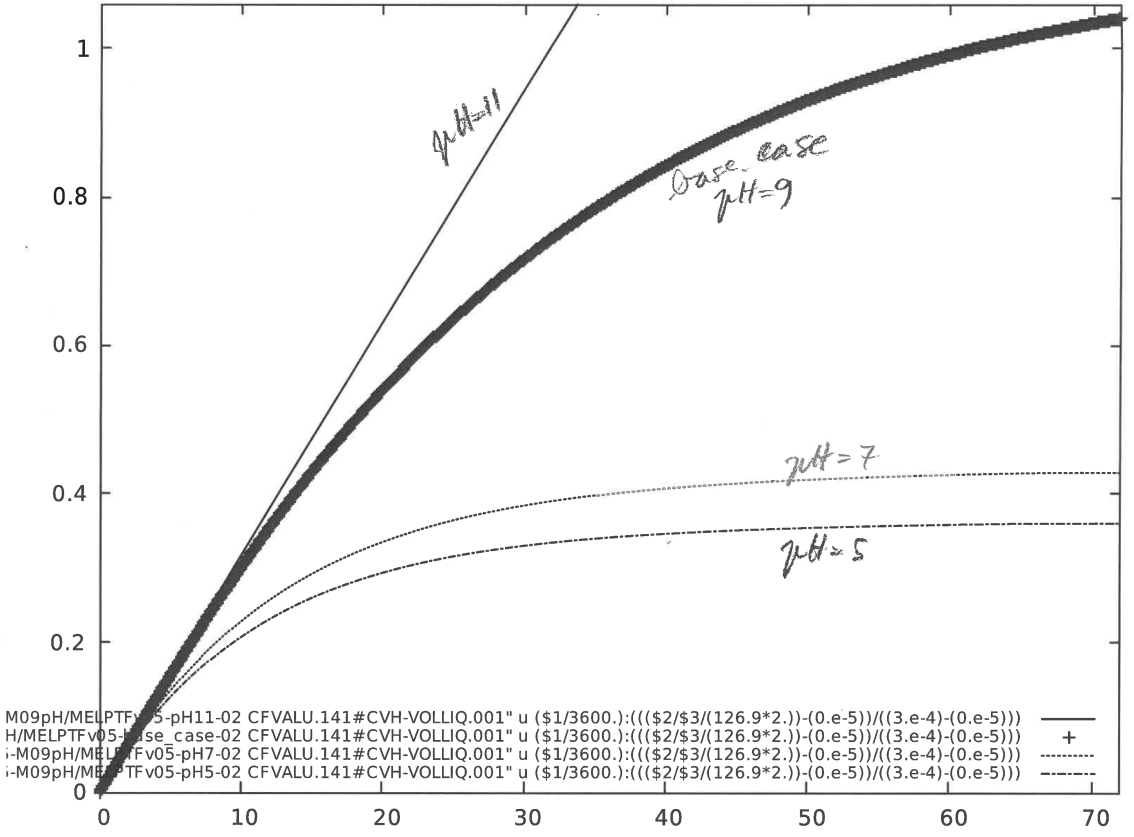
$$N_c(t) = \frac{c_l(t) - c_l^{init}}{c_l^{final} - c_l^{init}}$$

  - we modified slightly to $N'_c(t) = \frac{c_l(t) - c_l^{init}}{c_l^*(\text{const}) - c_l^{init}}$ —we never really got to any equilibria

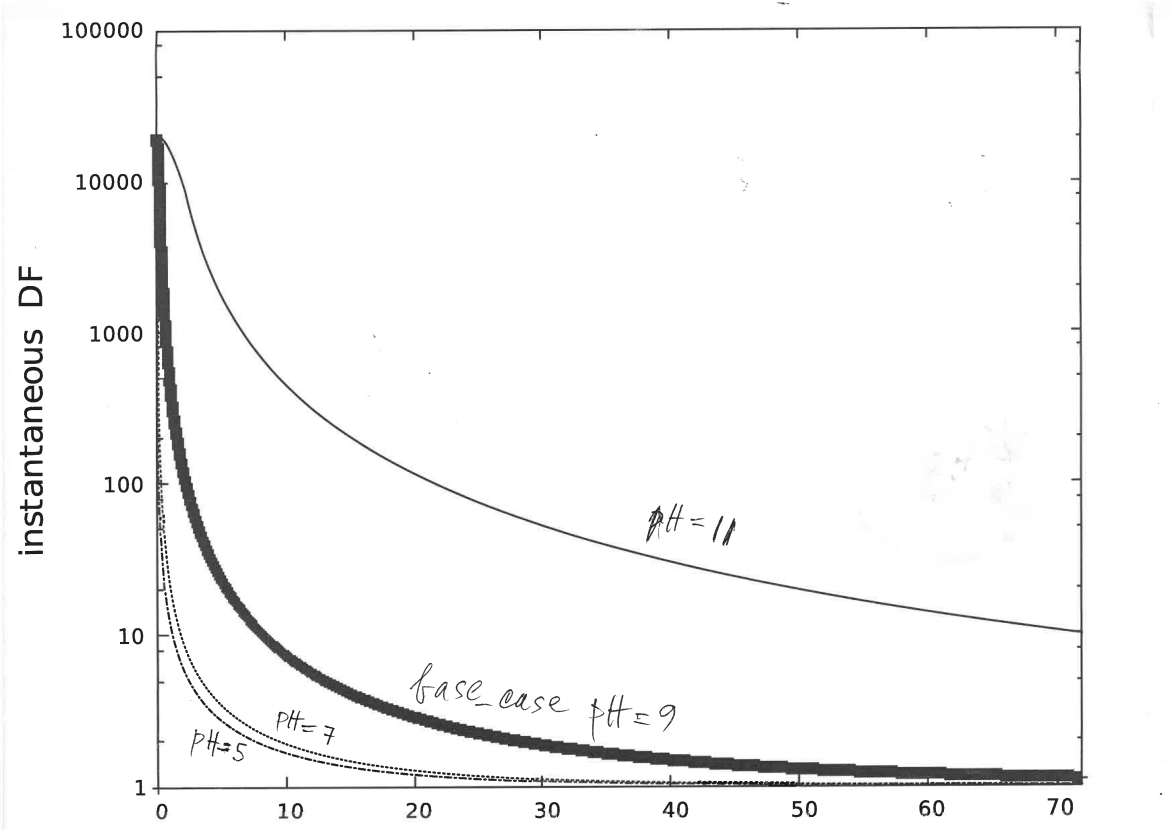
- the chosen I2 concentration in the bubbles 1×10^{-6} M (1×10^{-6} mol of I_2/dm^3), and for pH=9 and 20°C is $c_l^*/c_g^* \approx 300 \Rightarrow c_l^*(\text{const}) = 300 \times 1 \times 10^{-6}\,\text{M} = 3 \times 10^{-4}\,\text{M}$

pH dependence

N_c' versus $time$ in hours



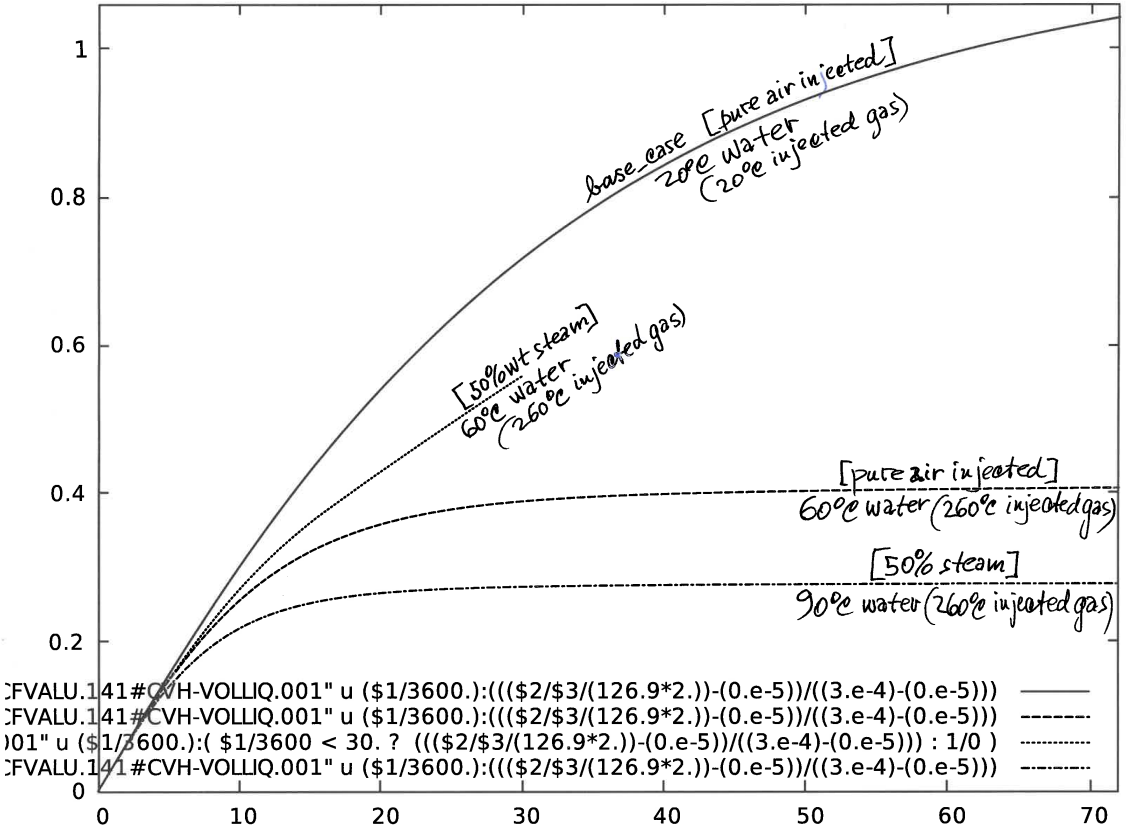
pH dependence in terms of instantaneous DF



* A.Rýdl: IPRESCA Benchmark: I2 Scrubbing and Modified Approach to its pH Dependence Modeling in SPARC (*NURETH-19, 2022*)

temperature dependence and steam content

N_c' versus $time$ in hours



simulations of the CRIEPI I2 scrubbing tests

- so we believed that chemistry —manifesting itself mostly as the water pH effect— plays a role

  and we believed that the necessary adjustments had been made to our tool

- hence, among CRIEPI I2 scrubbing tests we tried to pick up some where the pH influence had been studied

  - series of tests to study the effect of submergence simulated too —this was utter failure :)

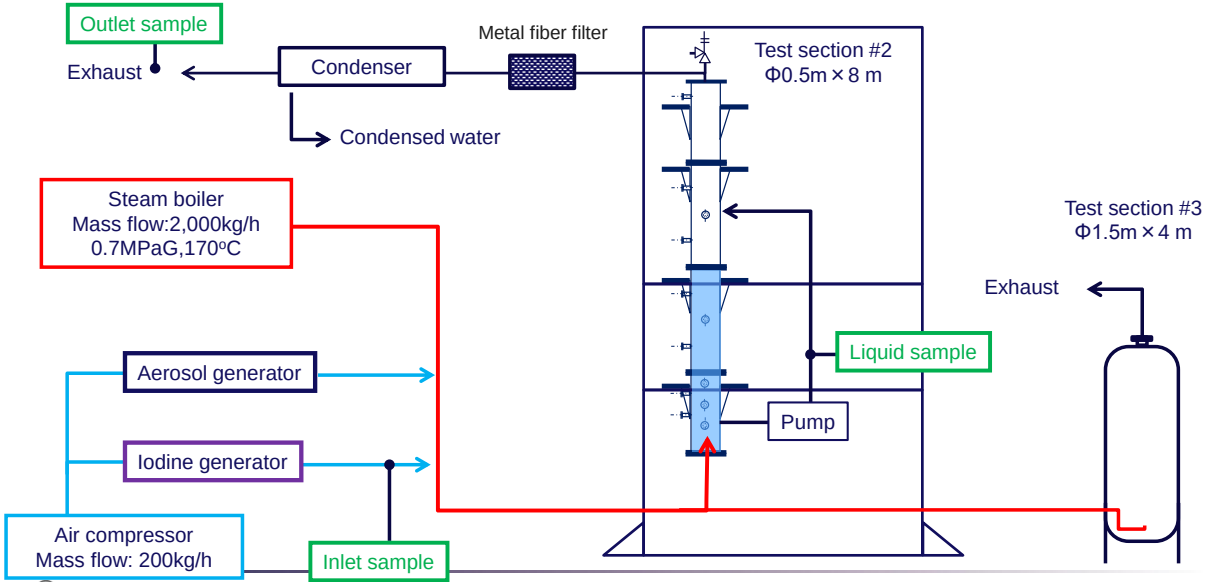
- however, we found out that in order to capture —at least **qualitatively**— the pH dependence, the (relatively slow) **chemical changes in water had to be modeled too** (in addition to the bubble-water interface equilibria, solely calculated by SPARC, as in the parametric calculations)

  - complex aqueous interactions, with the overall scheme $I^- \rightleftharpoons I_2$

- MELCOR is capable —in its Iodine Package— of modeling water (radio)chemical reactions (more than 200 elemental reactions, INSPECT database)

- debug version of MELCOR_1.8.6 employed, some small changes to the coding necessary (e.g. pH tables)

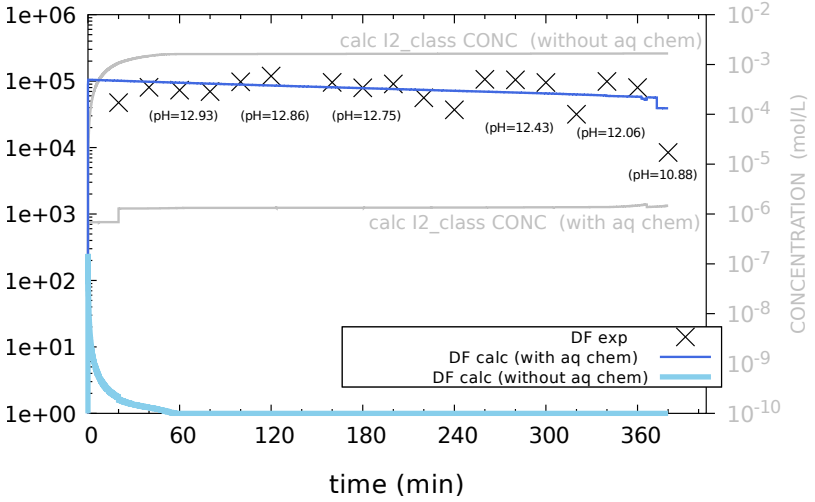
CRIEPI experiments

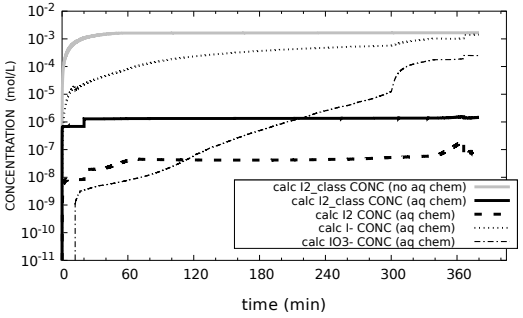


- in the tests selected for this work : submergence of 2 m, highly alkaline pool with no chemically interacting additives (e.g. thiosulphate), ∼30–40°C
  - 1000 L/min air (∼60°C), with about 1000 ppm iodine (volumetric) —relatively high concentration

DF values and calculated concentrations of selected iodine species in water

- Test#3-2: measured and calculated values of I2 Decontamination Factors as a function of pH (all in highly alkaline range —challenge to the code)
  - Iodine Package model very complex —overall balances of all iodine species still somewhat messy in our calculations

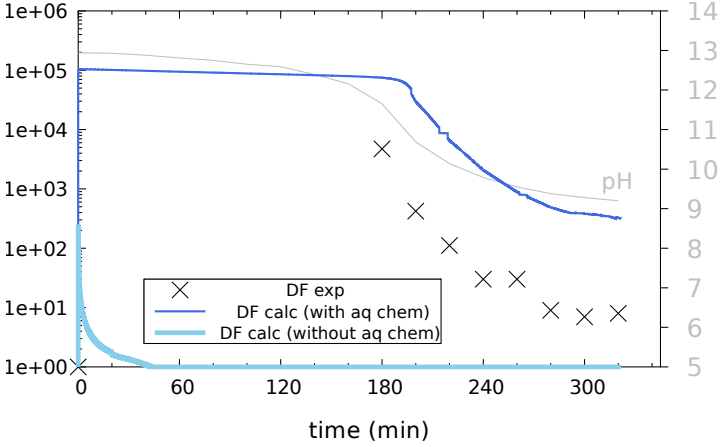




* A.Rýdl & T.Kanai: "Influence of Iodine Chemistry in I 2 Scrubbing Modeling", Nuclear Technology 2024

DF values and calculated concentrations of selected iodine species in water

- Test#3-3 : Measured and calculated values of I2 Decontamination Factors as a function of pH (in alkaline range) .
  And sensitivity calculation for pH dropping to acidic values



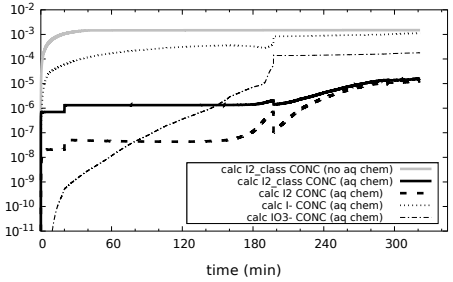


Figure 5. Test#3-3 : Concentrations of selected iodine forms in water calculated by MELCOR

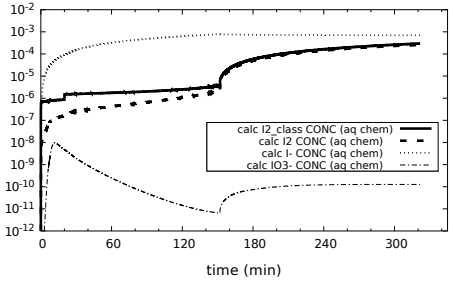


Figure 6. Sensitivity calculation (with boundary conditions taken from Test#3-3) : Concentrations of selected iodine forms in water calculated by MELCOR ("with chemistry"), for linear decrease of pH from pH=9 to 5 during the test

Conclusions

- for IPRESCA benchmark, modified SPARC code in MELCOR_186 employed for calculations of I2 scrubbing
- modifications primarily dealt with iodine equilibrium chemistry (pH dependent) at the bubble-water interface in this respect, modified version of the code is profoundly different from standard version of MELCOR/SPARC
- sensitivity analyses showed the expected patterns in most calculations, *qualitative* influence on iodine DF
  - typically for pH: higher water pH gives significantly higher DF —checked experimentally with CRIEPI tests
- for sensible qualitative simulations of experiments **aqueous chemistry modeling needs to be included** for bulk water phase
  - longer-term changes in water have profound effect on I2 scrubbing: I2 concentration gradients changing
- MELCOR/SPARC (slightly adapted) can be used for I2 scrubbing modeling —**numerous issues still to be tackled**
  (and thermalhydraulics aside:)
- planning to incorporate CH3I (Org I) scrubbing too —problems perhaps mainly with the relevant organic aqueous chemistry as such

Děkuji za pozornost

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Thank you!