An Investigation into the Unexpected Corrosion of Nickel Alloy Vessels with Selectfluor I

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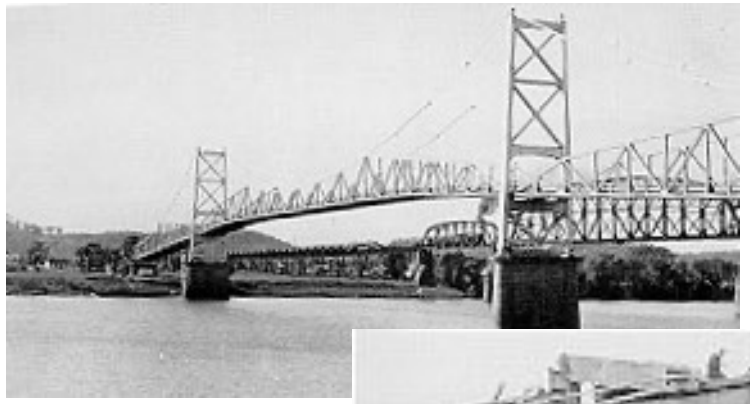
Corrosion Examples



$$M \rightarrow M^{n+} + n\, e^{-}$$

Belzutifan (WELIREG™)

Belzutifan (MK-6482) is a HIF-2α Inhibitor

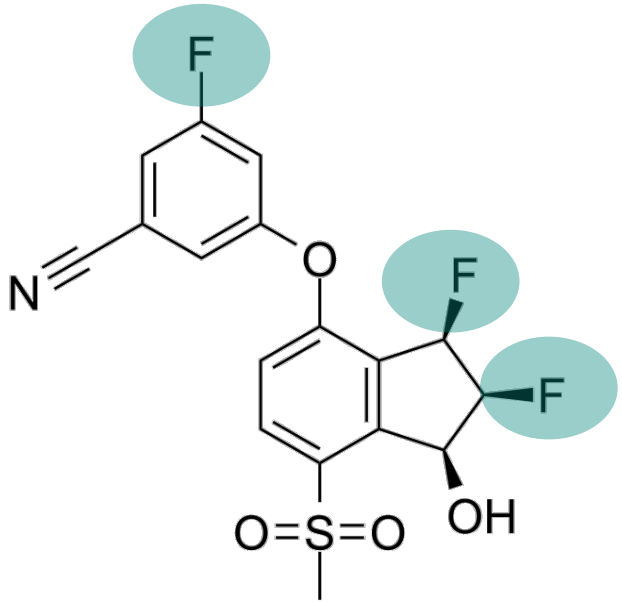
- Approved for treatment of VonHippel-Lindau (VHL) disease (related to several types of cancer) in 2021.

Where may cysts or tumors from VHL disease appear in the body?

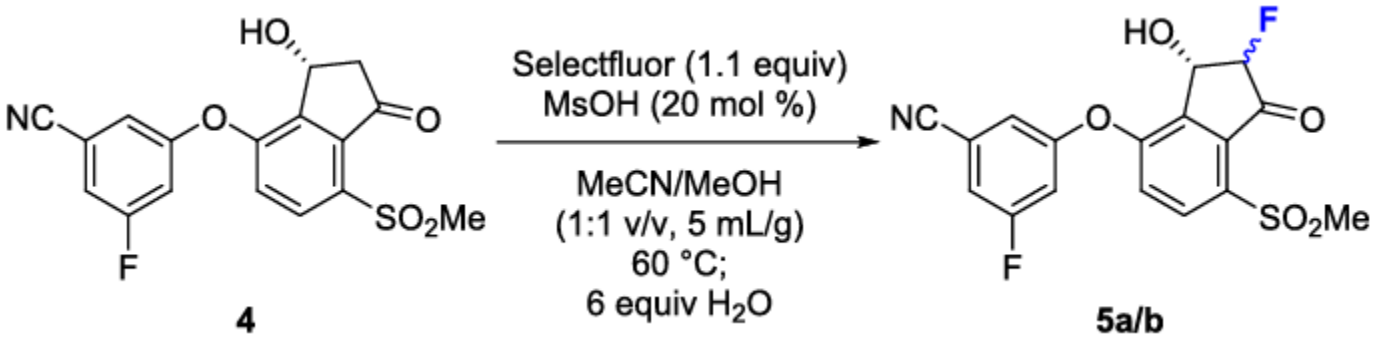
Cysts and tumors caused by VHL disease may appear in multiple organs, and include:

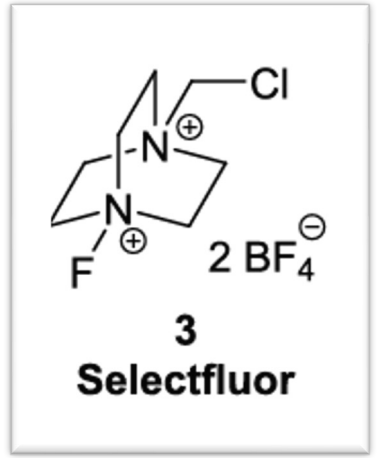
- Brain and spinal cord tumors (central nervous system hemangioblastomas)
- Kidney tumors (renal cell carcinomas)
- Tumors in the pancreas (pancreatic neuroendocrine tumors)

It is very important for people with VHL disease-related tumors to stick with their monitoring schedule. This may help in identifying cancerous tumors before they spread to other parts of the body.



Fluorination with SelectFluor I





- Due to presence of residual fluoride (and low pH), this chemistry is **corrosive to glass** (34 mil/yr)
- Hastelloy C seems like a good option for vessel construction
  - The reaction had been run successfully in Hastelloy C-22 lab reactors
  - Plant reactors constructed from Hastelloy C-276
    - C-276 (UNS10276) is a solid-solution-strengthened Ni-Mo-Cr alloy with a small amount of W.

element	content in C-276 (wt %)
Ni	57
Mo	15–17
Cr	14.5–16.5
Fe	4–7
W	3–4.5
Co	2.5
Mn	1
V	0.35

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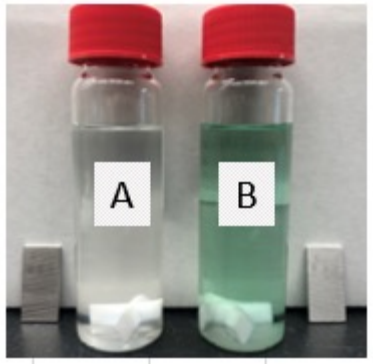
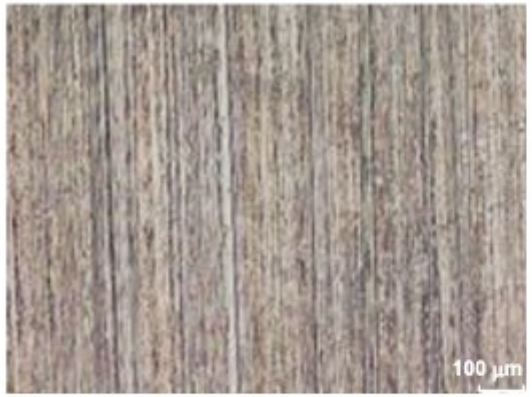
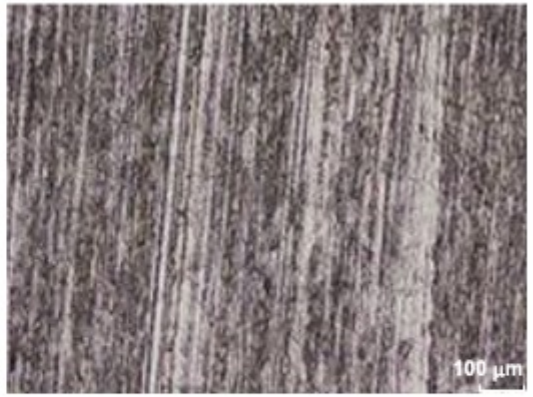
Coupon Immersion Studies – inconsistent results





Entry 5. Lot A
Non-corrosive
Mass loss = 0.6 mg

0 mil/yr



Entry 6. Lot B
Corrosive
Mass loss = 7.6 mg

37 mil/yr

Inconsistent Reaction Performance!

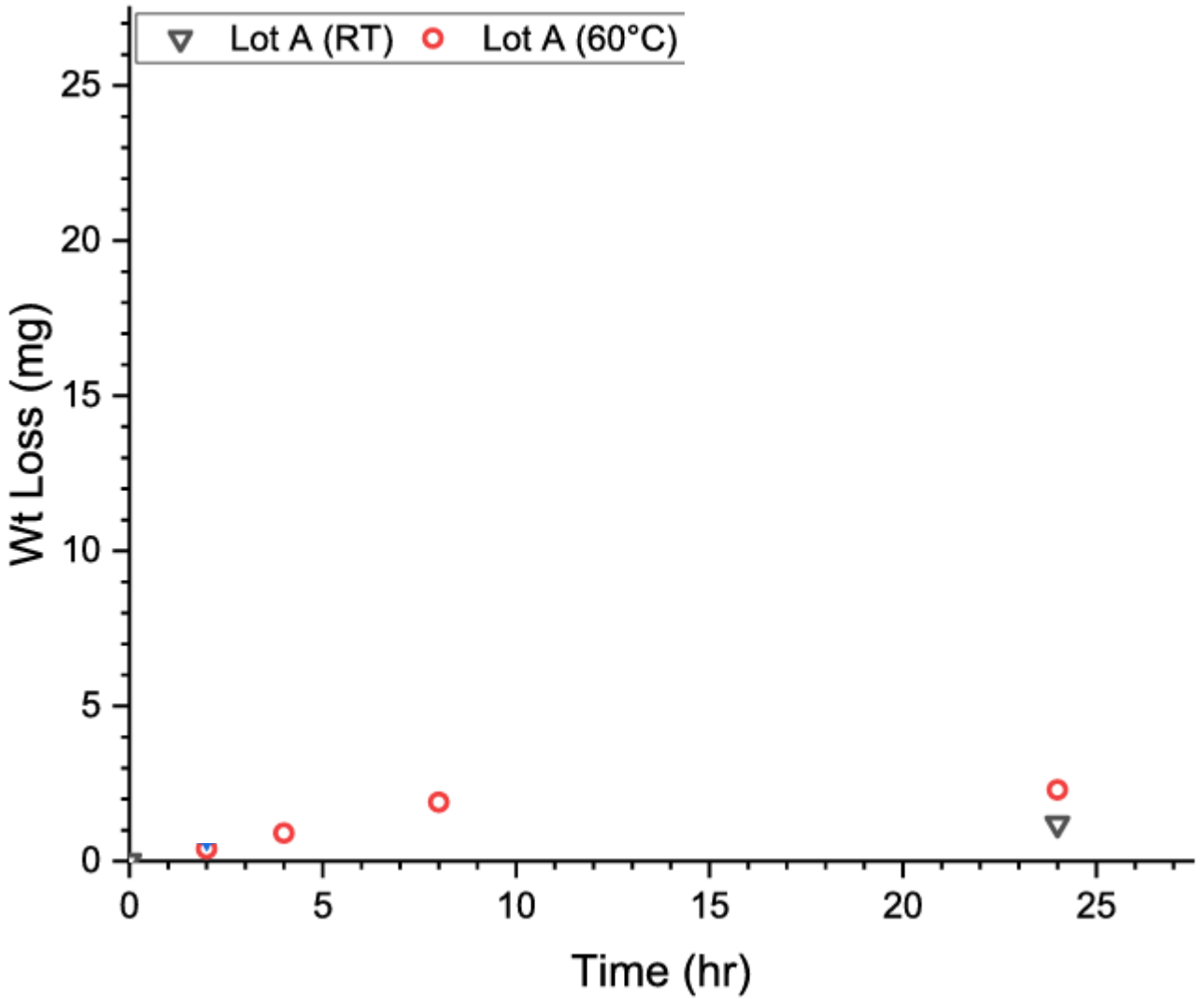
Reactor setup	Conversion (%)
Glass	>99.9
Glass	99.7
Hastelloy C-276	>99.9
Hastelloy C-276	**94.5**
Glass w/ C-276 coupon	99.3
Glass w/ C-276 coupon	98.1

Inconsistent Reaction Performance!

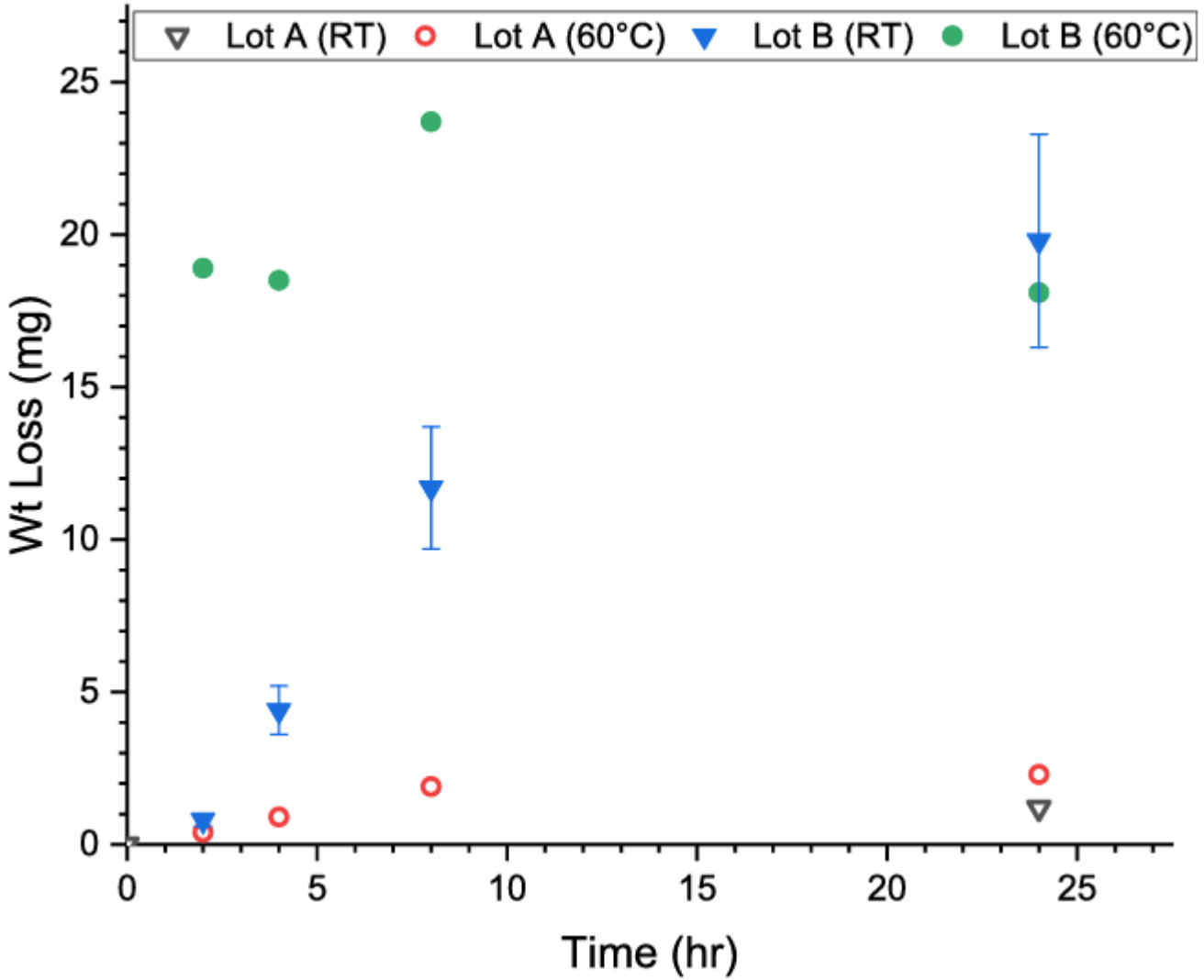
Selectfluor lot	Reactor setup	Conversion (%)
A	Glass	>99.9
B	Glass	99.7
A	Hastelloy C-276	>99.9
B	Hastelloy C-276	**94.5**
A	Glass w/ C-276 coupon	99.3
B	Glass w/ C-276 coupon	98.1

Selectfluor lot	purity (wt %)	F^- level (ppm)	Cl^- level (ppm)	Fe level (ppm)
A	97.9	47613	673	48
B	98.0	48781	2610	252

HC276 Coupon Studies



HC276 Coupon Studies - Kinetics

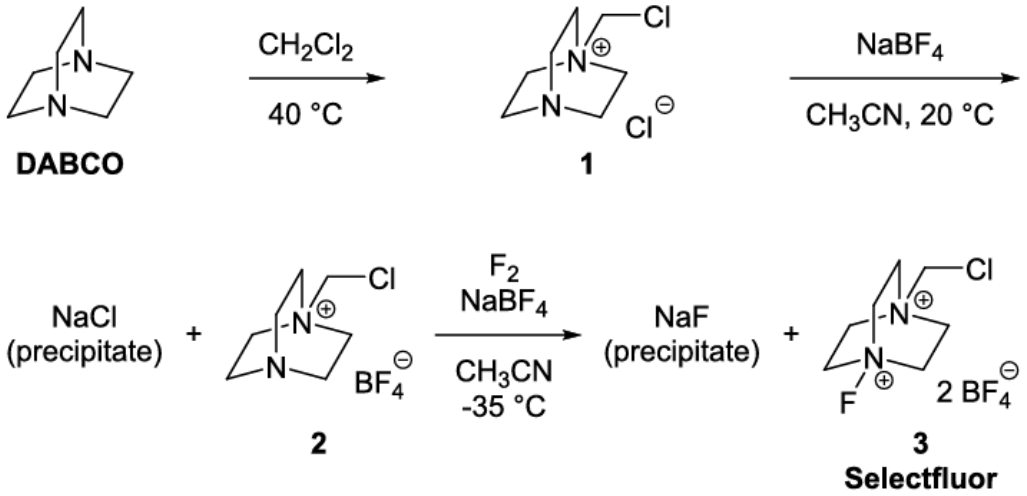


We conclude that the corrosion is not due to the Selectfluor per se, **something else** must be playing a role

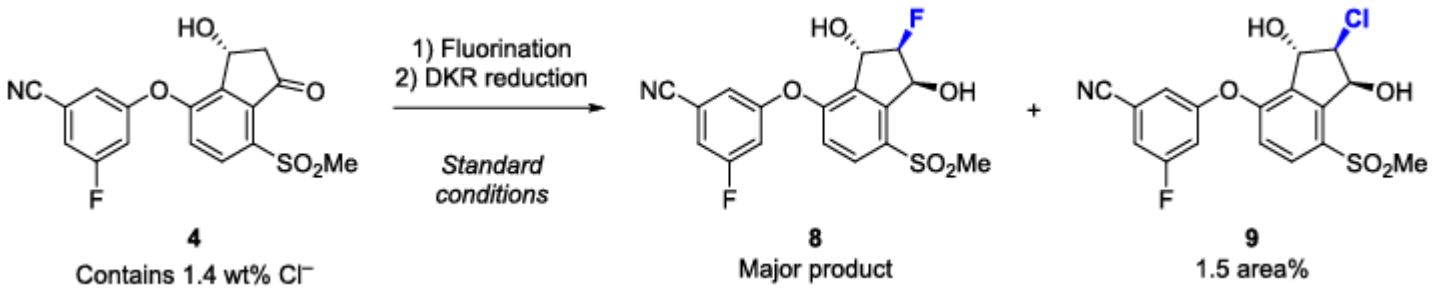
Kinetics show a rapid plateau

The Culprit: Chloride?

How is Selectfluor manufactured?



The Culprit: Chloride

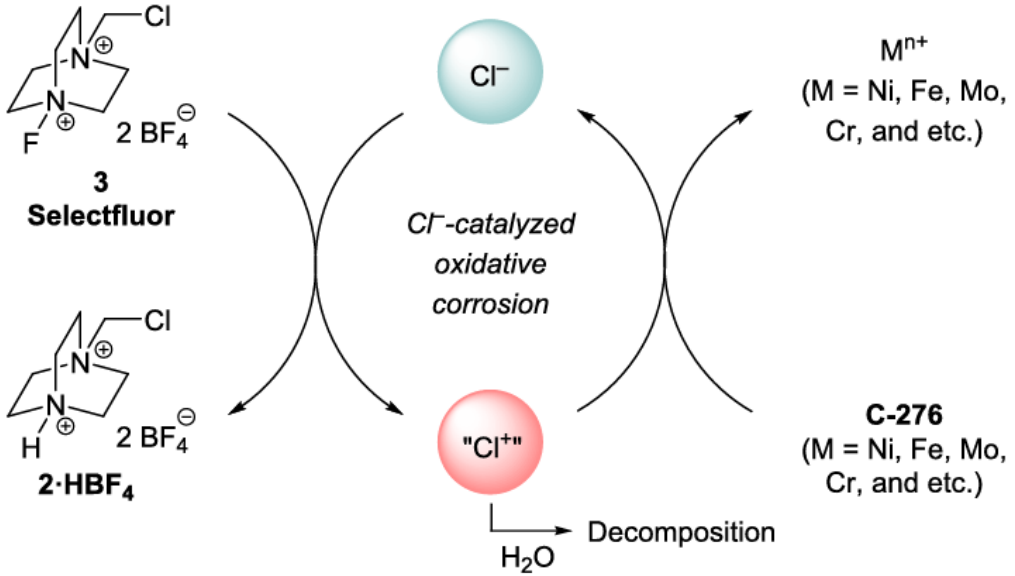


4
Contains 1.4 wt% Cl^-

8
Major product

9
1.5 area%

A chlorinated impurity



"Cl^+" (chloronium) species (Cl-F?)
Likely oxidizes M to M^+ and is regenerated by Selectfluor

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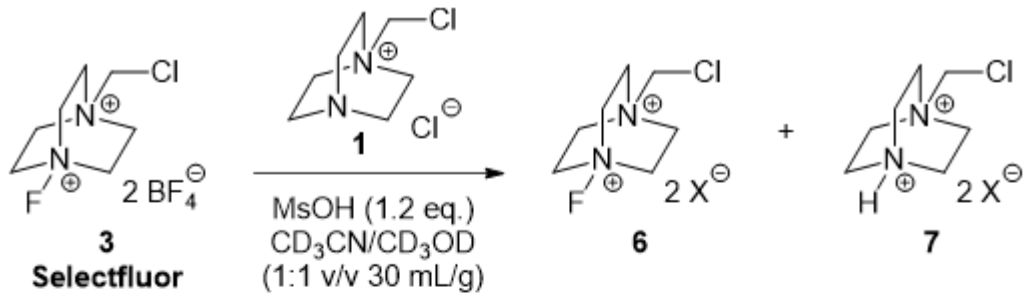
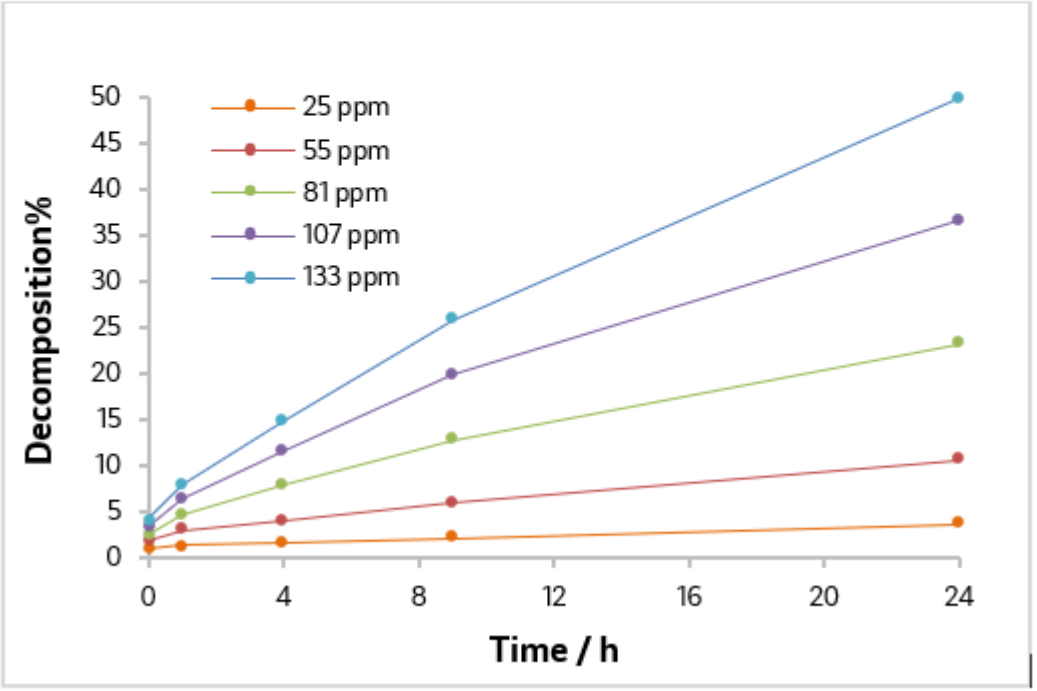
Selectfluor stability vs. Cl^-





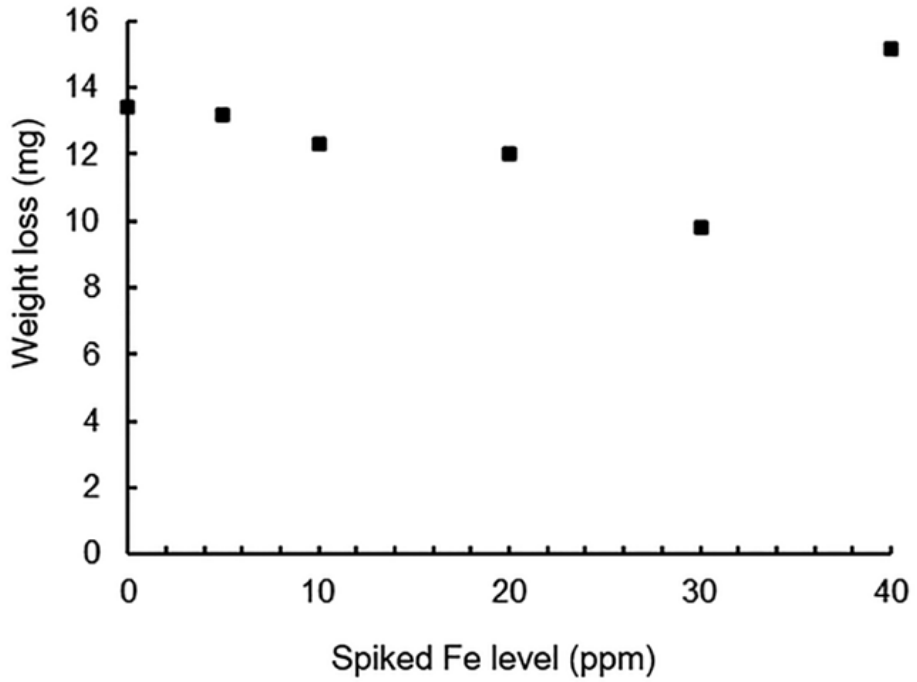
[a] Cl^- concentration of the solution in ppm (or µg/g)

Impact of metal ions?

As Hastelloy corrodes, metal ions (Ni, Mo, Cr, Fe) are released into solution.

Metal salts were spiked into coupon immersion tests to assess their impact on corrosion.

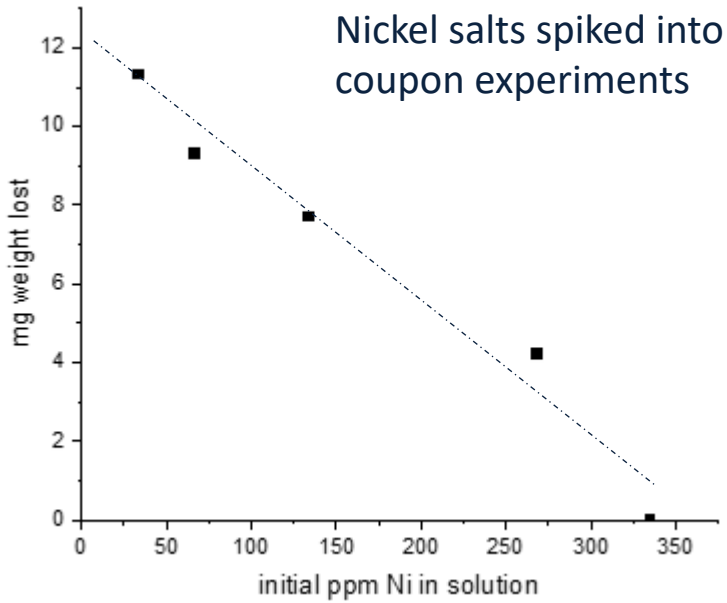
Fe



element	content in C-276 (wt %)	concentration in EOR (ug/g)	relative ratio in EOR by weight (%)
Ni	57	390	58
Mo	15–17	102	16
Cr	14.5–16.5	108	15
Fe	4–7	43	6
W	3–4.5	22	3
Co	2.5	10	1
Mn	1	N.D.	NA
V	0.35	N.D.	NA
total	NA	675	NA

Impact of metal ions?

Ni



Nickel salts spiked into Selectfluor coupon experiments

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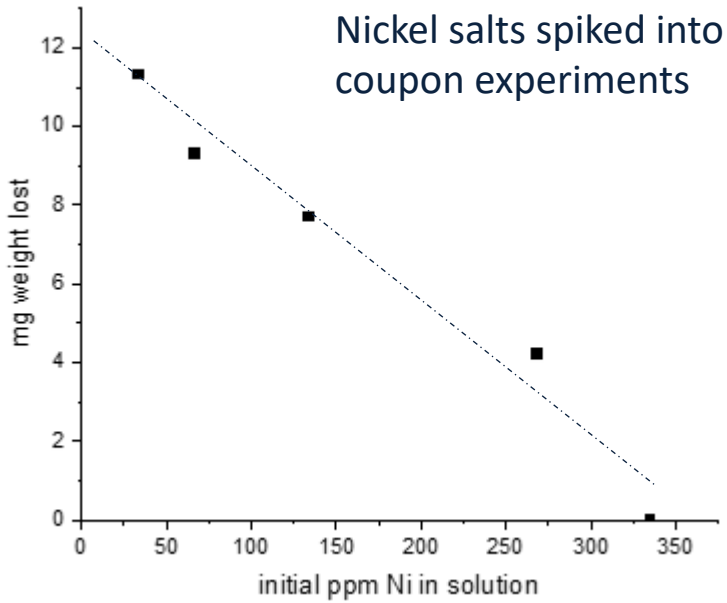
Co	2.5	10	1
Mn	1	N.D.	NA
V	0.35	N.D.	NA
total	NA	675	NA

Nickel appears to suppress corrosion!

The nickel source spiked was a hydrate: $Ni(BF_4)_2.6H2O$

Impact of metal ions?

Ni



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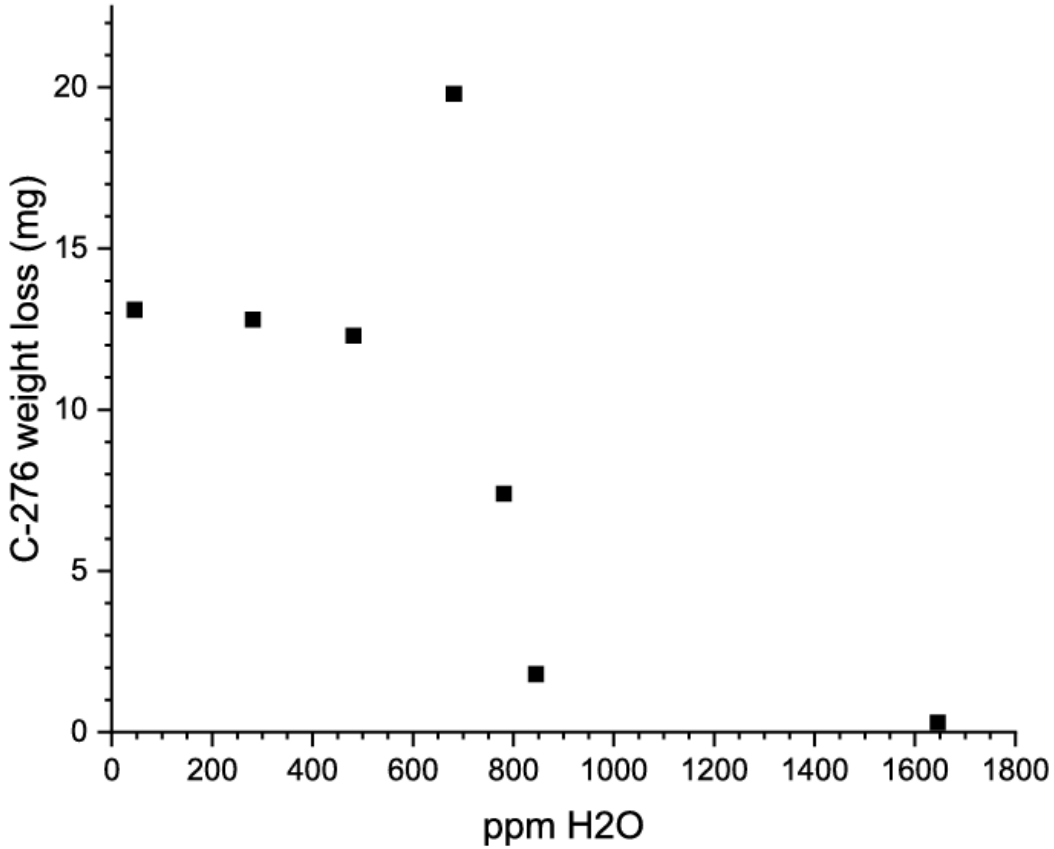
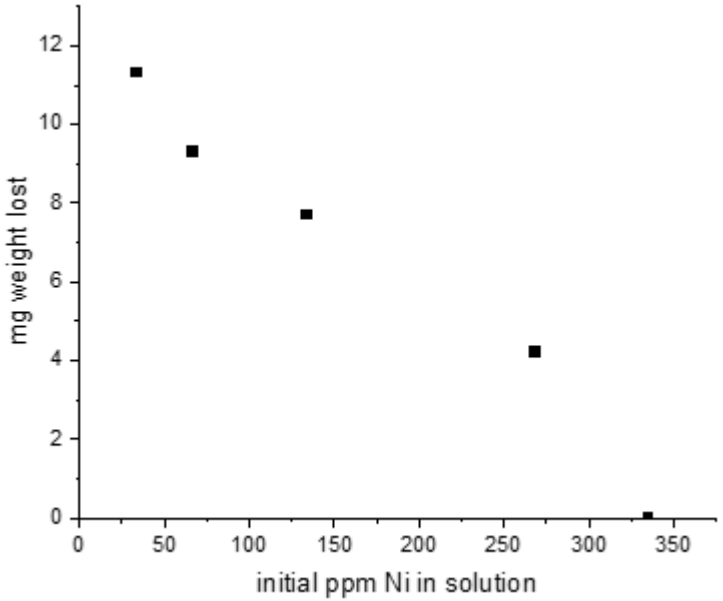
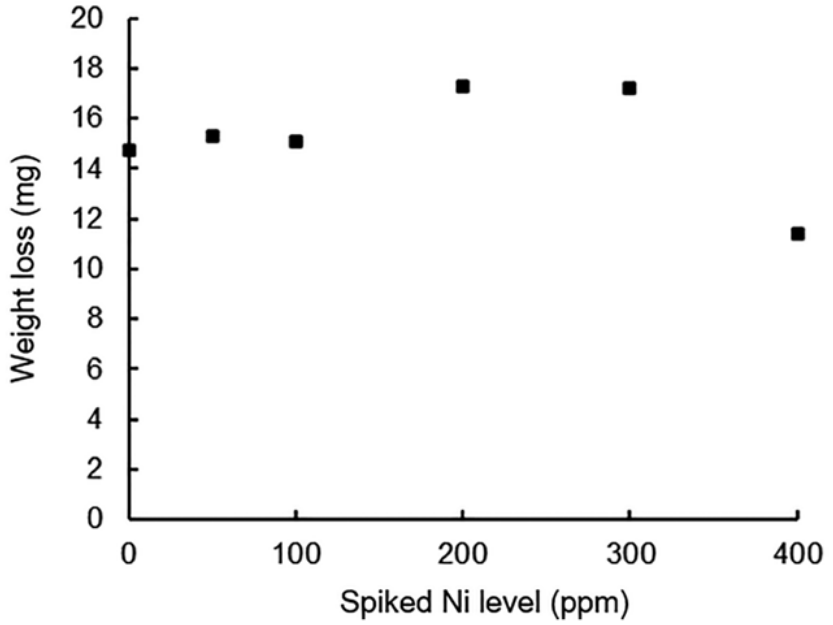


The water is shutting down the corrosion, not the nickel!

Impact of metal ions?



$Ni(BF_4)_2.6H2O$



$Ni(BF_4)_2$
(dried over 3A mol sieves)

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Conclusions

Selectfluor is not inherently corrosive towards HC-276

Chloride impurities from the reagent's manufacture can be corrosive to HC and can impact the desired chemistry (chlorinated impurities, degradation of the Selectfluor, reduced conversion)

The purity of the reagent is critical, and should be tested for Cl^- before use in a HC reactor

If the desired chemistry is tolerant to water, water can be used to suppress corrosion of HC

A footnote…

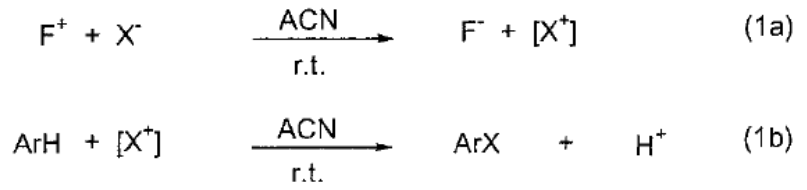
A few months after publication, we received an email from Bob Syvret (Principal/Owner, Fluorine Chemistry and Technology, LLC, Allentown PA):

"As the person who first scaled and developed commercial processes for both Selectfluor® (I) and (II), I have observed similar variances in the past…

"Hastelloy … can create significant problems with Selectfluor® (I) owing to its reactivity with Ni alloys.

"I agree fully with your assessment that the corrosion is due to Cl+ formation. We studied this extensively insofar as it can cause a real problem with by-products formed due to electrophilic chlorination (due to oxidation of residual Cl-) that are observed in addition to the expect electrophilic fluorination products."

J. Org. Chem. (2002) 67(13) 4487-4493.pdf



Electrophilic nitration can be accomplished using a variety of reagents, some of which include nitronium salts,[34–38] methyl nitrate,[39] and sodium nitrite mediated by trifluoroacetic acid.[40]

In the present work, we describe a new process for generating electrophiles Cl^+, Br^+, SCN^+, and NO_2^+ and have applied these in electrophilic aromatic substitution reactions of various substrates.

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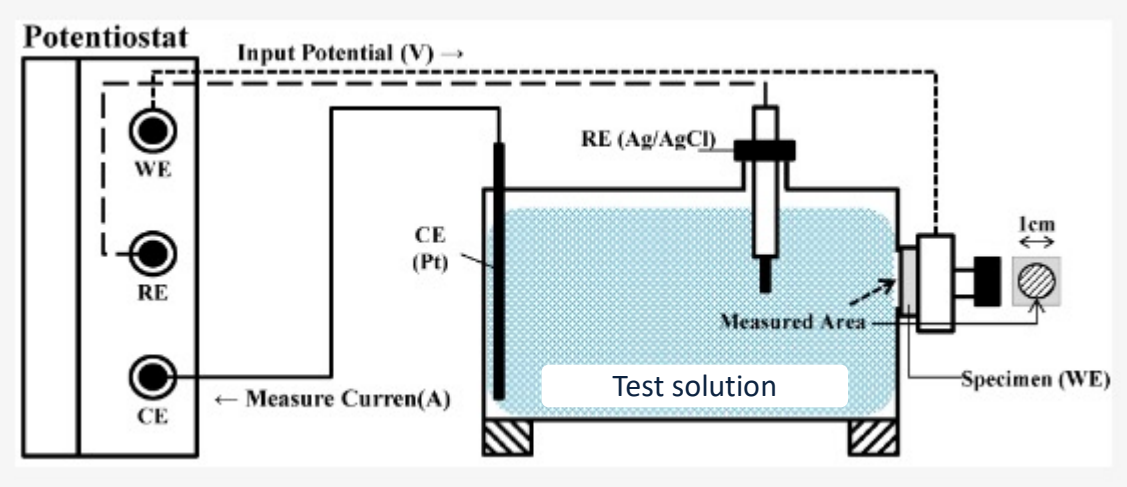
Future work…

Increase speed and precision:

Electrochemical measurements of corrosion in non-aqueous media



Materials **2014**, *7*(12), 7722-7736

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