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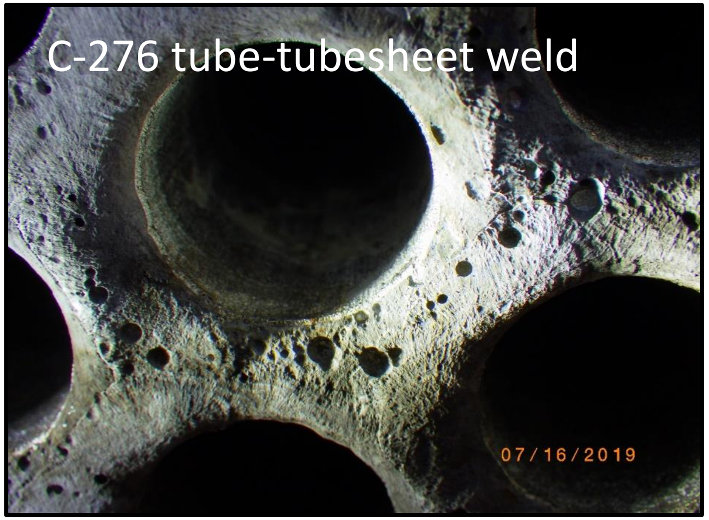
Unexpectedly High Corrosion Rates Caused by Chlorinating Agents in the Presence of Acetonitrile: Importance of Corrosion Testing for Safe Scale-Up

Yamini Krishnan, Jayachandran Devaraj, Paul Speakman, Kelsi Goshinsky, Aaron Shinkle, Ajit Mishra, John Doyle III, Abraham Schuitman

PURDUE PROCESS SAFETY & ASSURANCE CENTER SPRING CONFERENCE
MAY 8, 2024

Applications of Metals/Alloys in the Chemical Industry

Safety Risks Associated with Corrosion

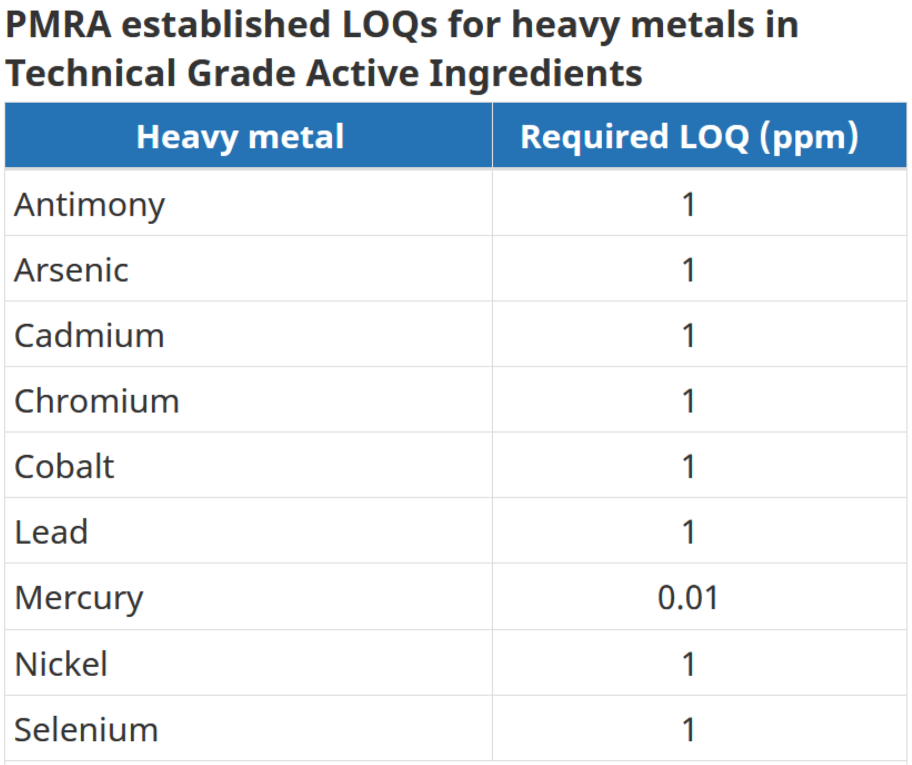


Damage in components can result in product leaks and unexpected shutdowns

Understanding Corrosion Can Be Important to Meet Regulatory Requirements

Canada’s Pest Management Regulatory Agency publishes LOQ values for heavy metals → some are major components in standard equipment metallurgy

Guidance reinforces need for good product stewardship towards corrosion avoidance



PMRA established LOQs for heavy metals in Technical Grade Active Ingredients

Heavy metal	Required LOQ (ppm)
Antimony	1
Arsenic	1
Cadmium	1
Chromium	1
Cobalt	1
Lead	1
Mercury	0.01
Nickel	1
Selenium	1

Found in commonly used alloys

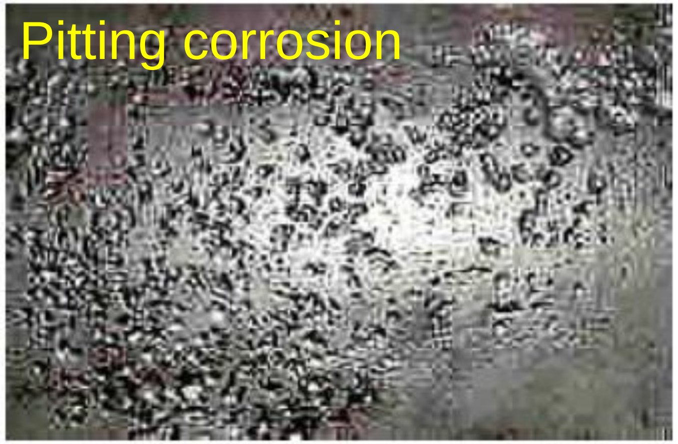
LOQ = limit of quantitation
ppm = parts per million

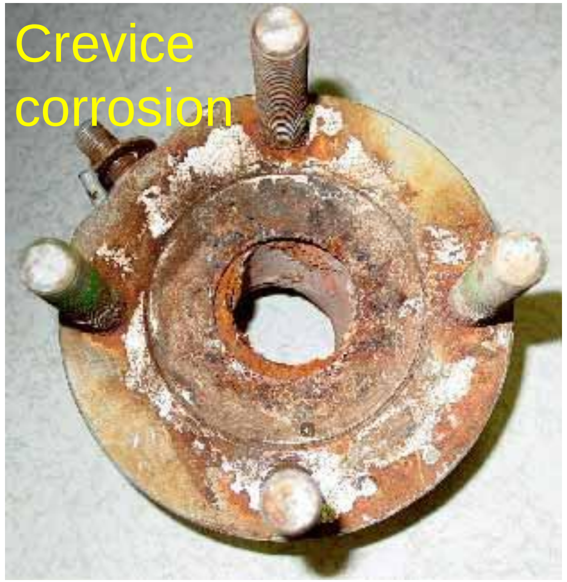
https://www.canada.ca/en/health-canada/services/consumer-product-safety/pesticides-pest-management/registrants-applicants/established-limits-quantitation-heavy-metals-technical-grade-active-ingredients.html

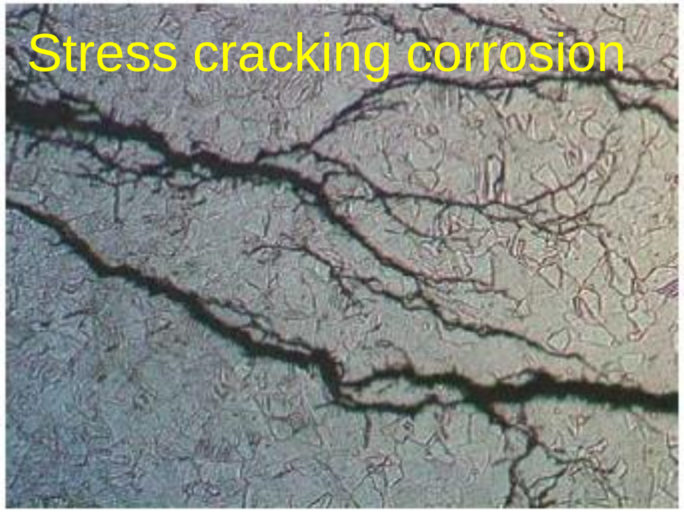
Types of Corrosion

Uniform, localized, and stress cracking corrosion are the 3 main categories


Uniform corrosion


Pitting corrosion


Crevice corrosion

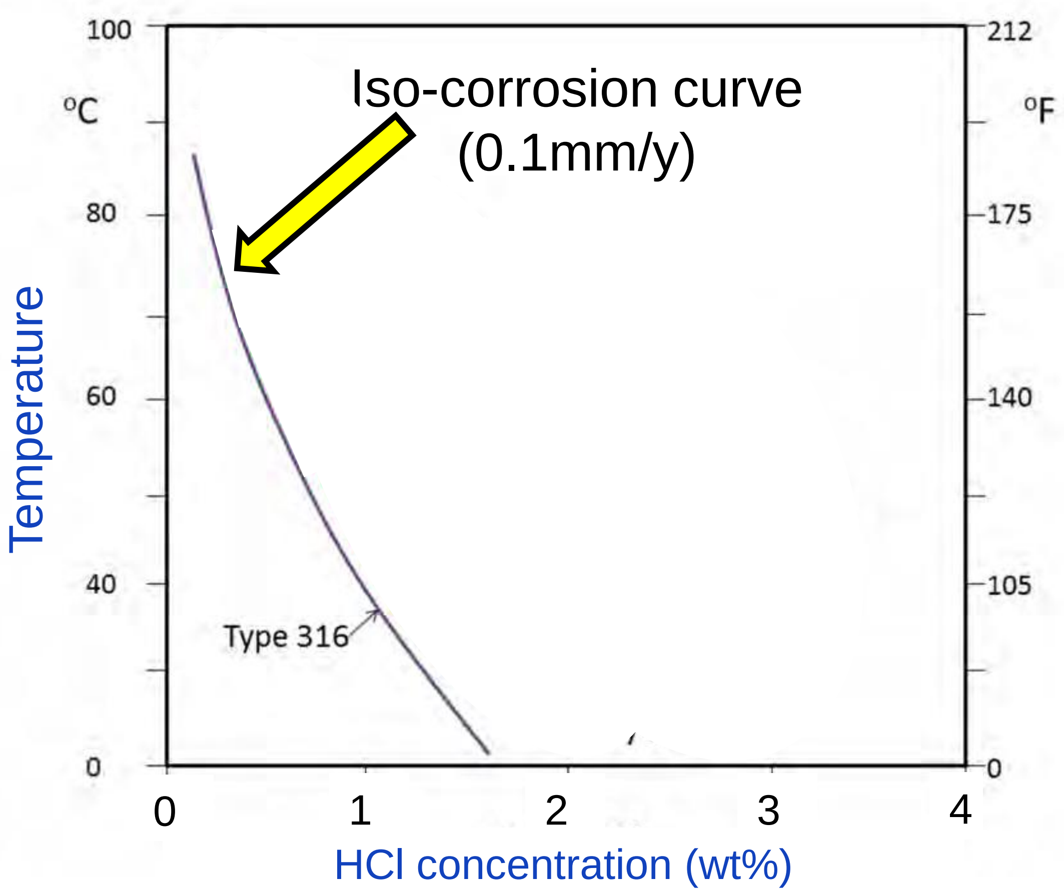

Stress cracking corrosion

Pravitasari +, Springer ISBN 1-85233-758-3,2003
Bardel, E., “Corrosion and Protection”, 2003

Ginzel, R.K., +, 2002

Baig et al., Failure of Control Valves in the Desalination Plants of ADWEA, January 2005, International Corrosion Conference Congress

Corrosion Rates are Concentration and Temperature Dependent



Stainless steel 316 in dilute HCl

Points on the isocorrosion curve: corrosion rate = 0.1 mm/y

Materials Selection in Hydrochloric Acid, MTI Handbook
A.K. Mishra, Acta Metallurgica Sinica, 30 (2017), p. 306

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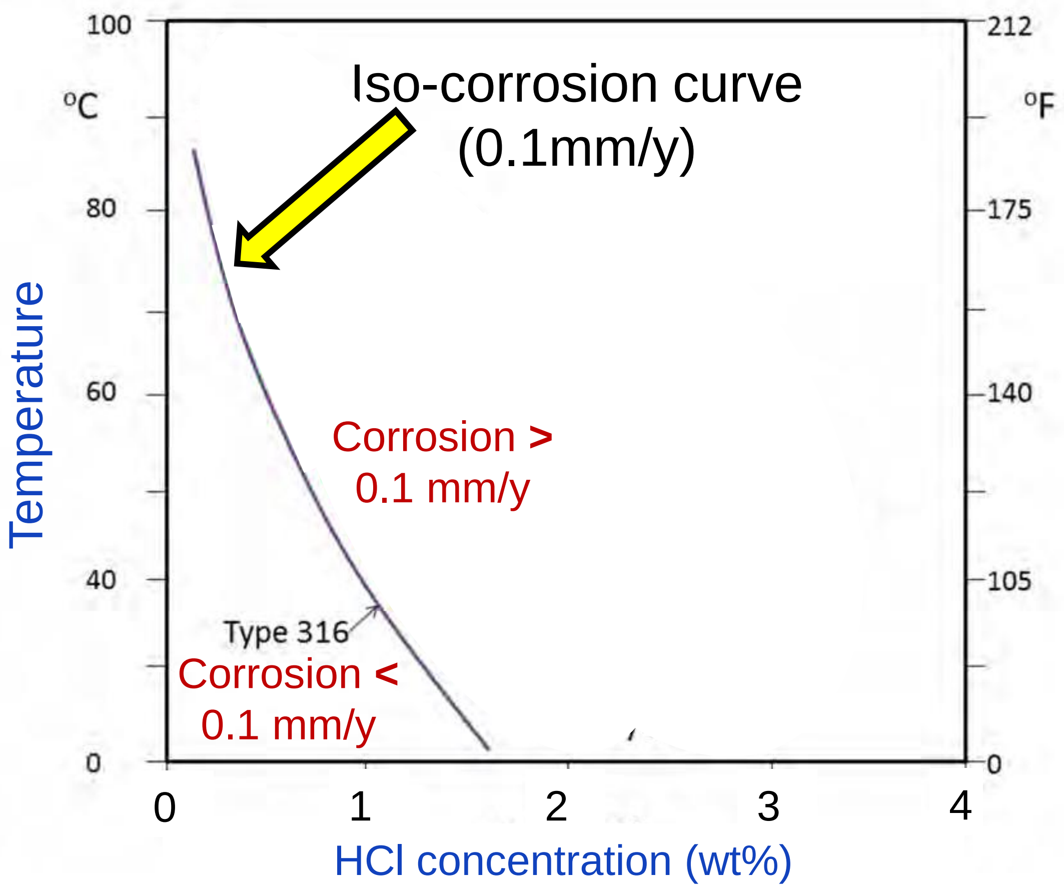

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Corrosion rate is < 0.1 mm/y below curve and > 0.1 mm/y above the curve

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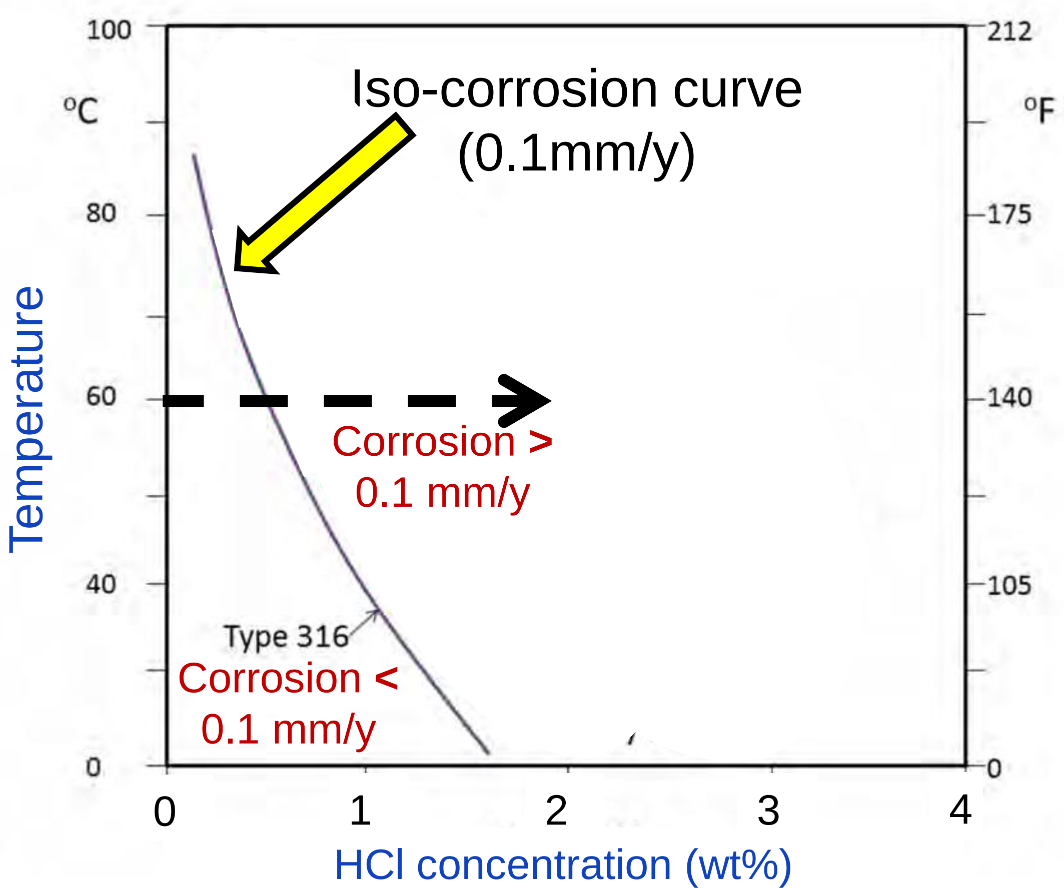

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Corrosion rates increase with HCl concentration

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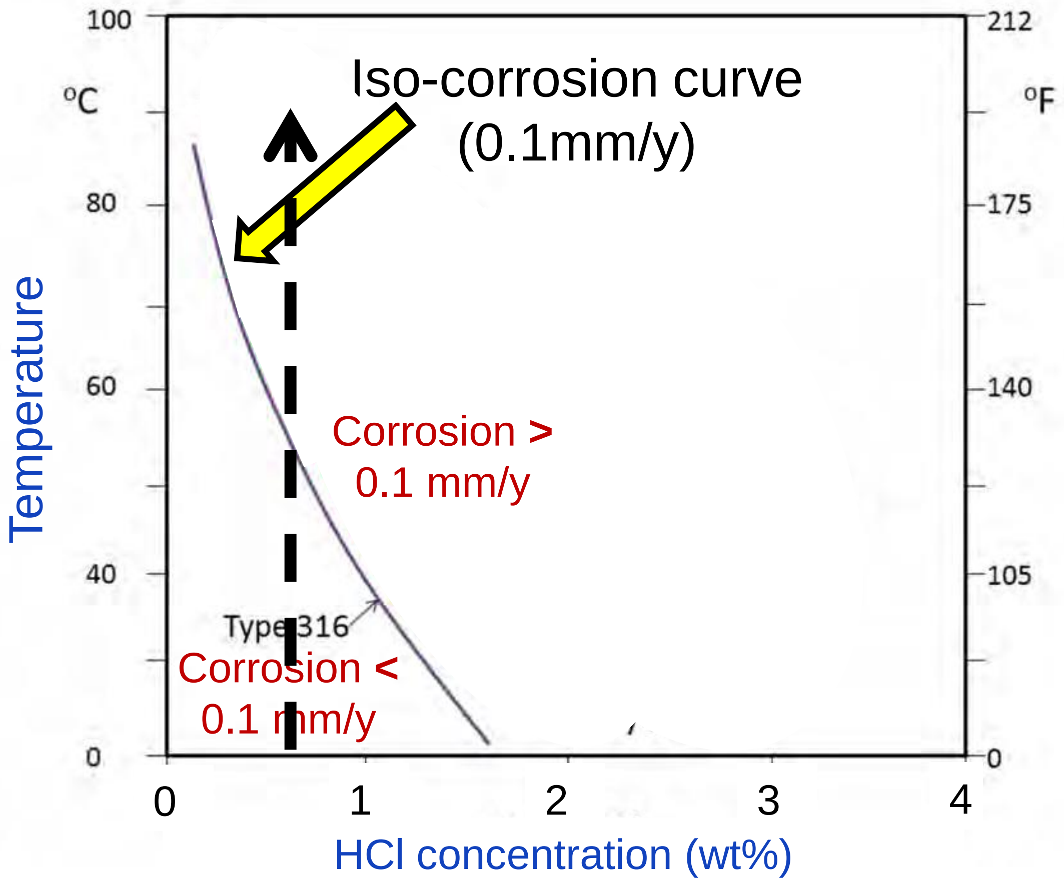

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Points on the isocorrosion curve: corrosion rate = 0.1 mm/y

Corrosion rate is < 0.1 mm/y below curve and > 0.1 mm/y above the curve

Corrosion rates increase with HCl concentration and also with temperature

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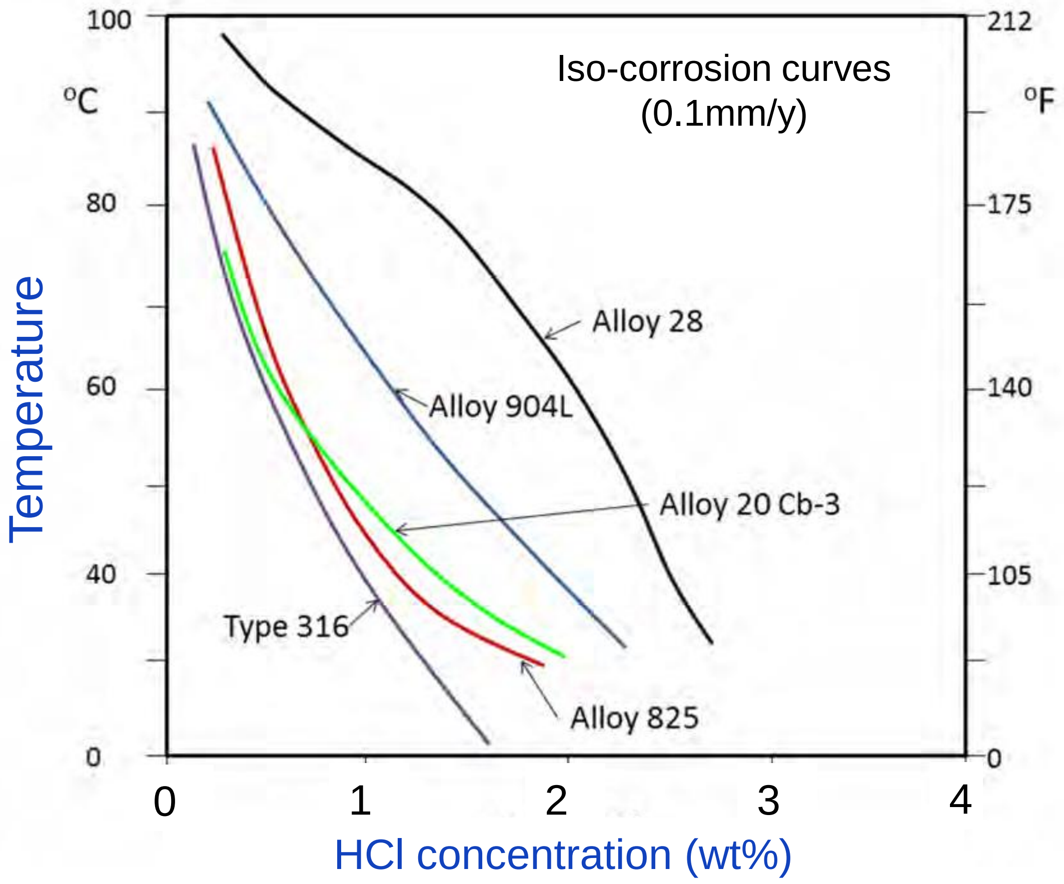
Corrosion Resistant Alloys can Mitigate Risk



Various grades of **stainless steels** in dilute HCl

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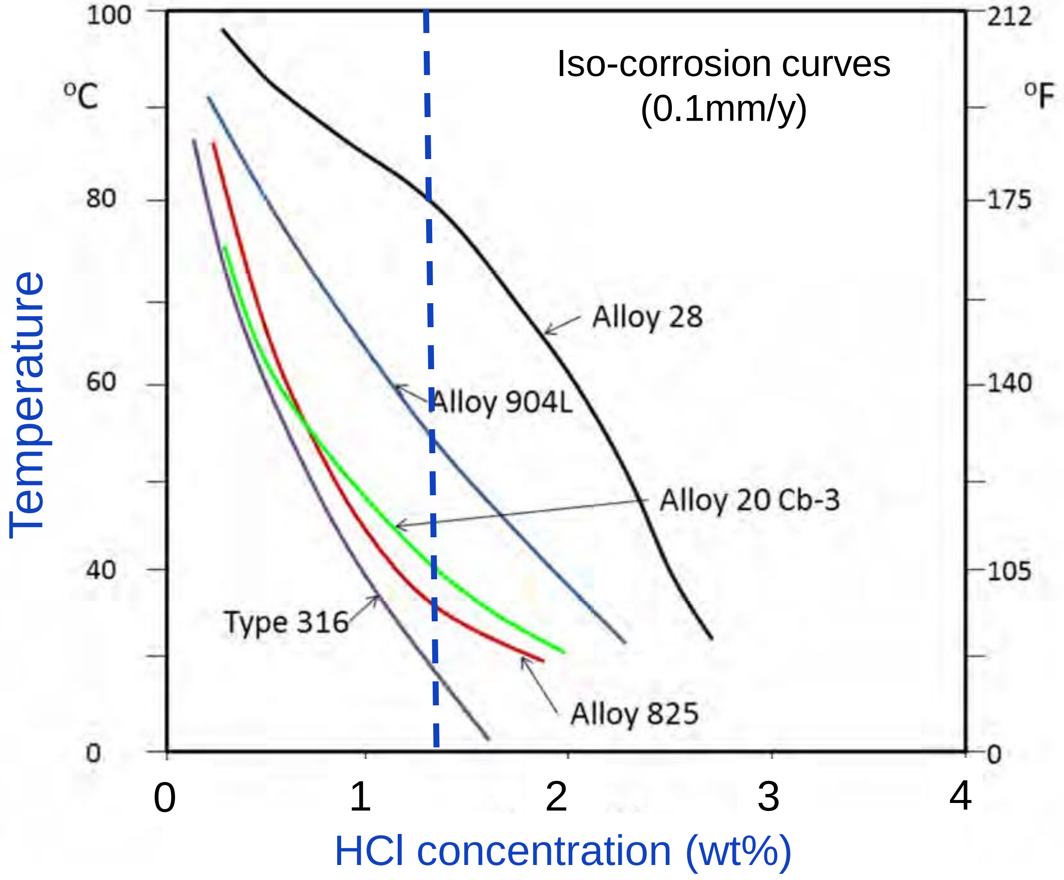

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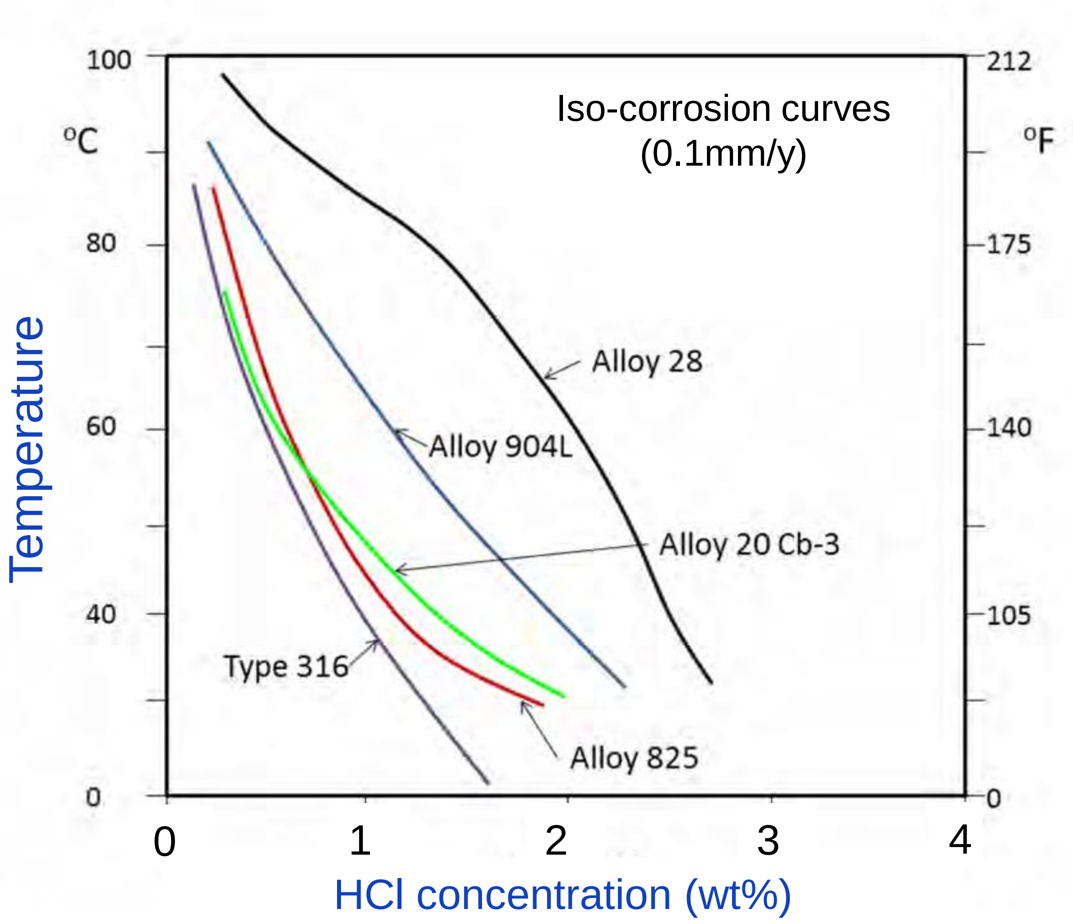

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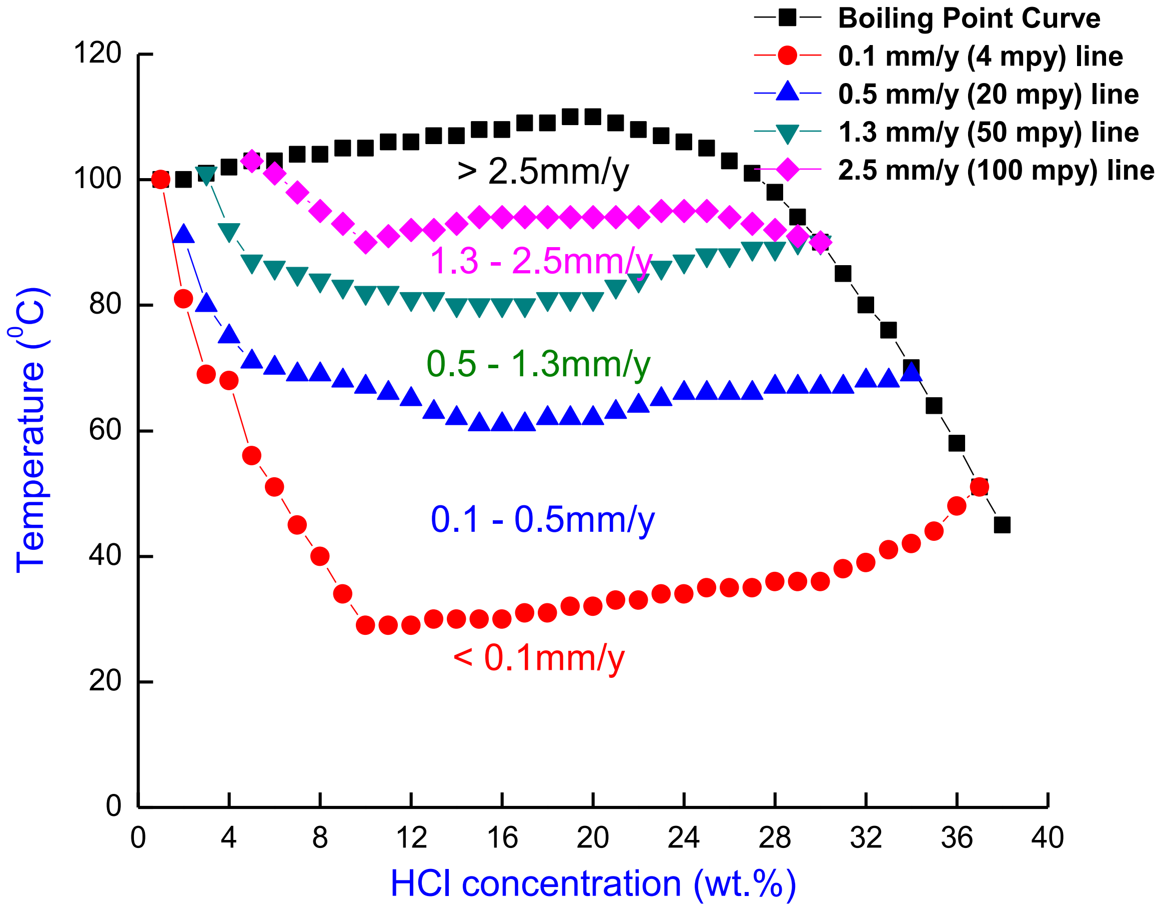

Hastelloy C-276 in reagent grade hydrochloric acid

Higher corrosion-resistant alloys (like Hastelloy C-276, C-22) can provide an extended service life compared to stainless steels in highly corrosive conditions.

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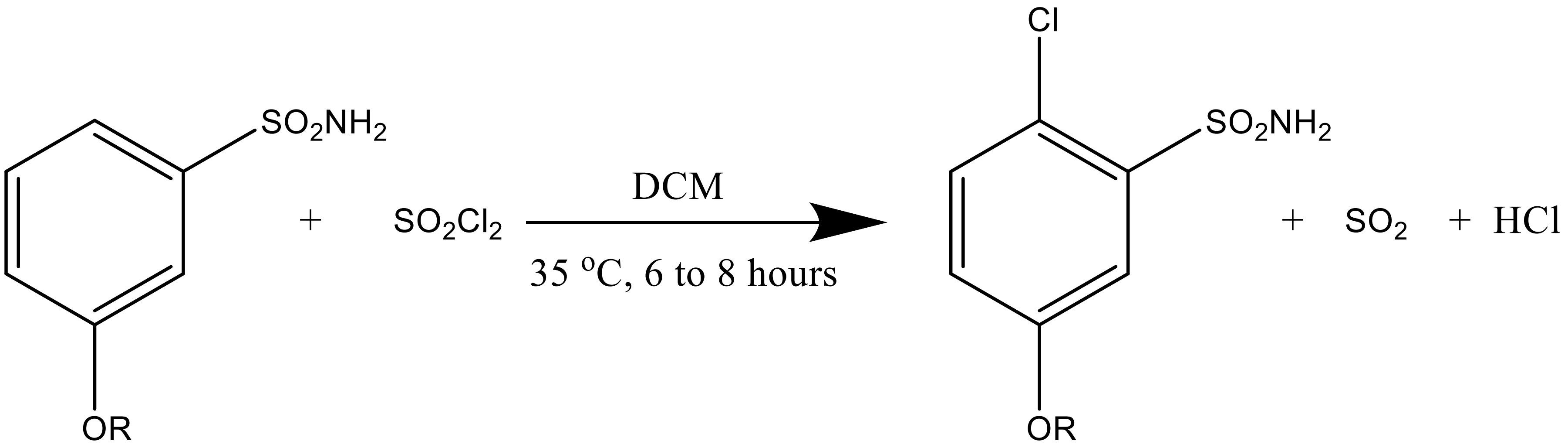
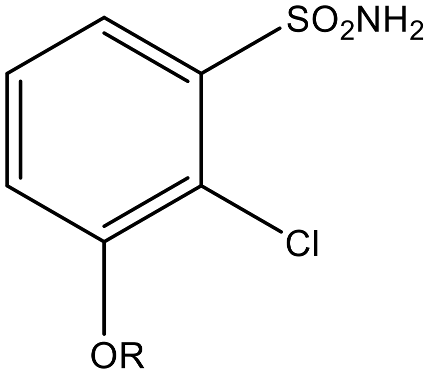
Unexpected Corrosion Surprises with Resistant Alloys:
3 Case Studies

Selectivity Challenges for an Agrochemical Intermediate



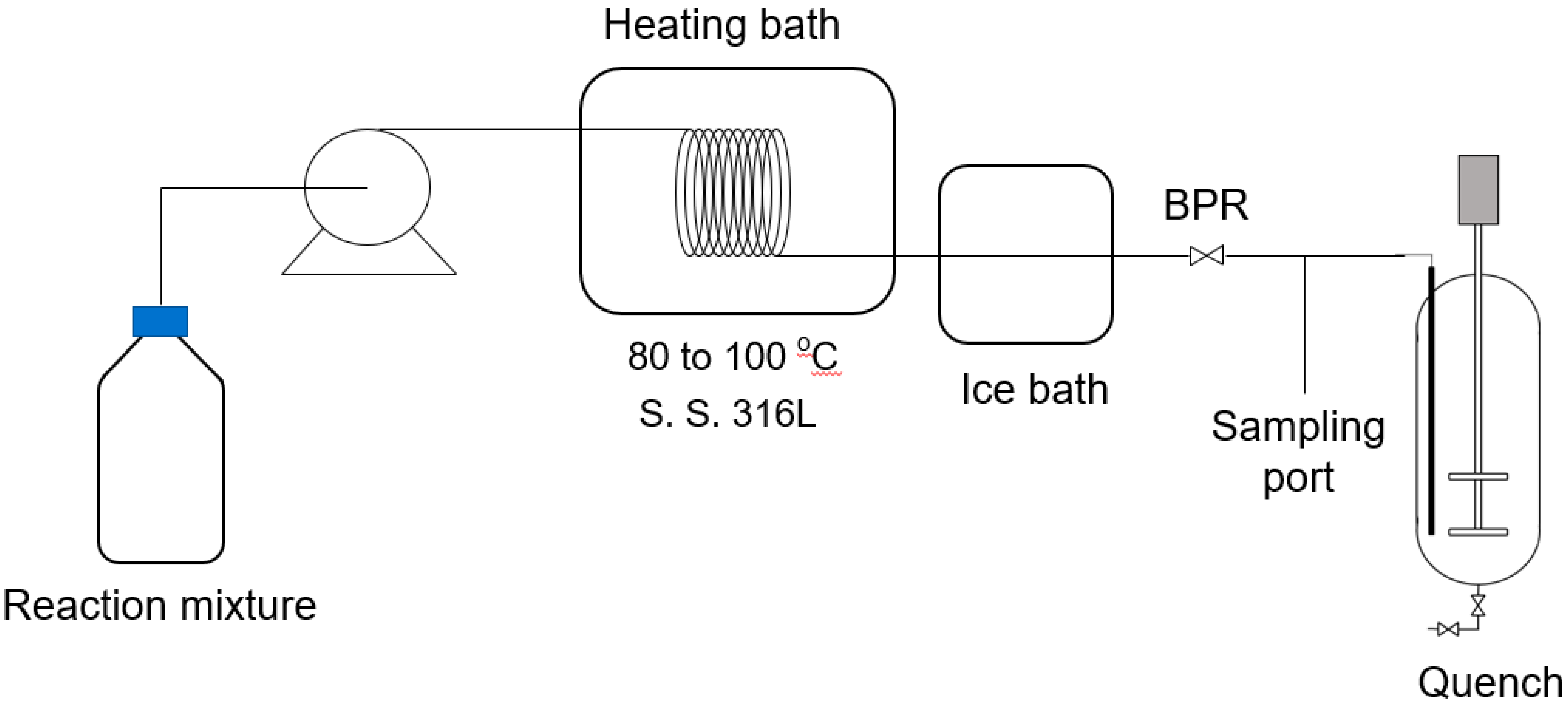
The regioisomer of the desired product was a major impurity



Impurity:Product ratio ~ 10%

Attempts to Improve Selectivity

Run reaction at high temperature in a coiled tube reactor



Challenge: Reaction mixture is a slurry that caused pumping issues

Attempts to Improve Selectivity

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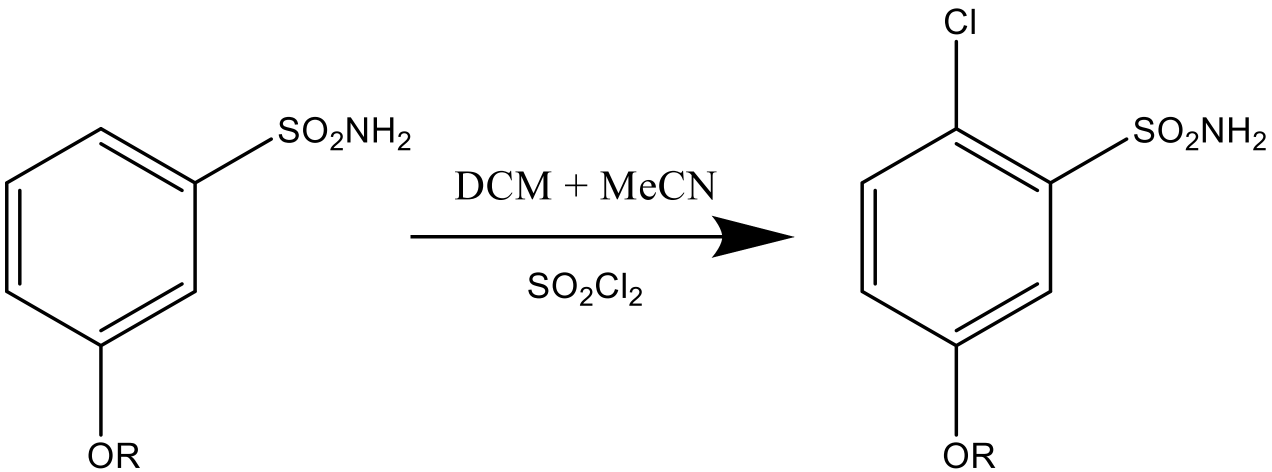
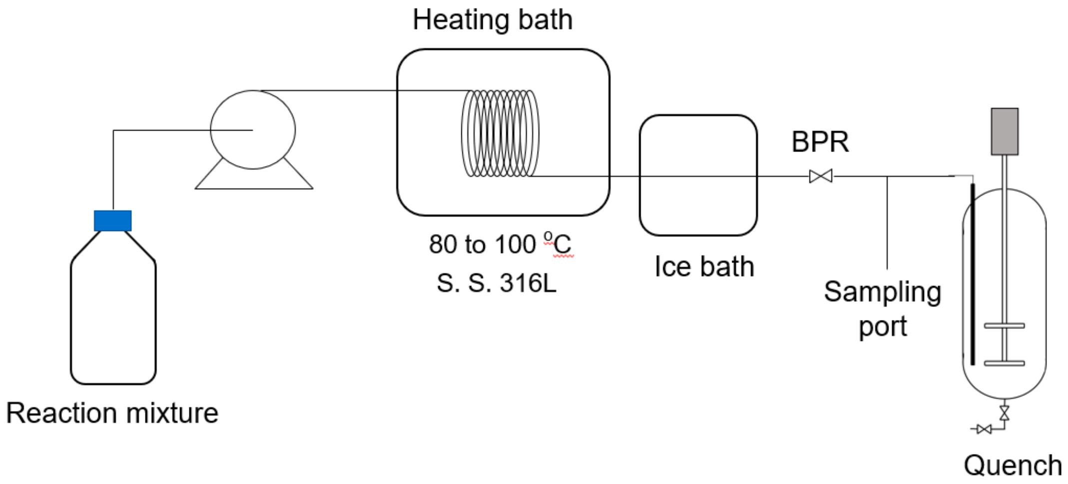




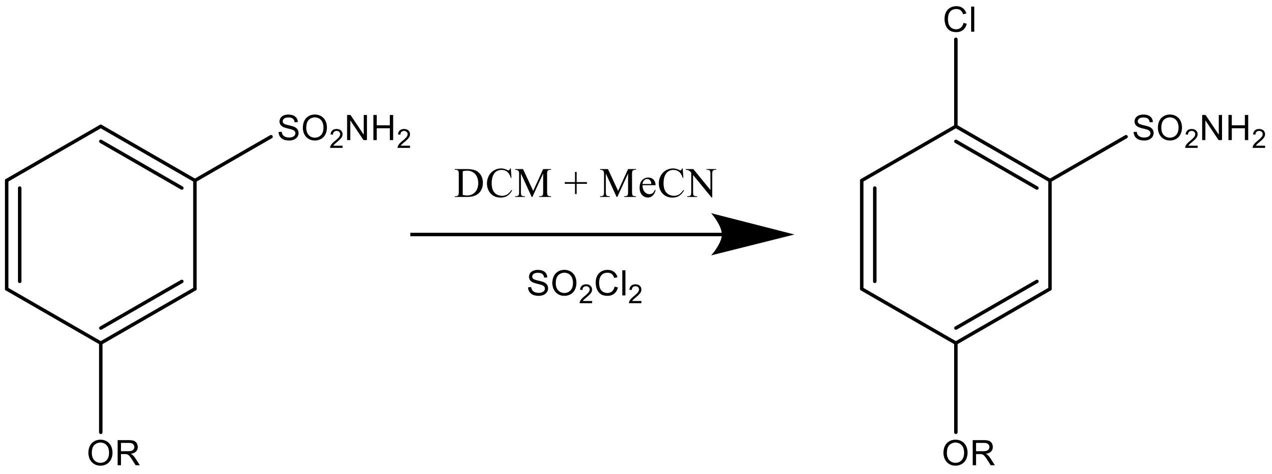
Work-around: Add acetonitrile to improve starting material solubility

Attempts to Improve Selectivity

Reactions were also run at high temperature and pressure in a Parr reactor

Temperature range: 70 to 120 °C

Pressure range: 60 to 400 psi



100mL Parr reactor
Hastelloy C-22

Both Reactor Types Showed Signs of Corrosion

Water was used to quench the mixture at the end of the reaction

Samples from aqueous layer sent for ICP analysis

Samples had high levels of elements found in SS 316L and HC-22

Element	**Coiled Tube Reactor Expt (ppm)**	**Parr Reactor Expt (ppm)**
	Stainless Steel	Hastelloy C-22
Chromium	1880	714
Iron	6500	367
Manganese	148	6.1
Molybdenum	246	404
Nickel	1345	1204

LOQ = 2 µg/g (ppm)

Coupon Testing was Performed to Quantify Corrosion Rate

Hastelloy C-276 and Hastelloy C-2000 coupons were used in a 1L Parr reactor

Coupon	Initial weight (g)
H C-276	8.1130
H C-2000	7.6087

Test conditions:

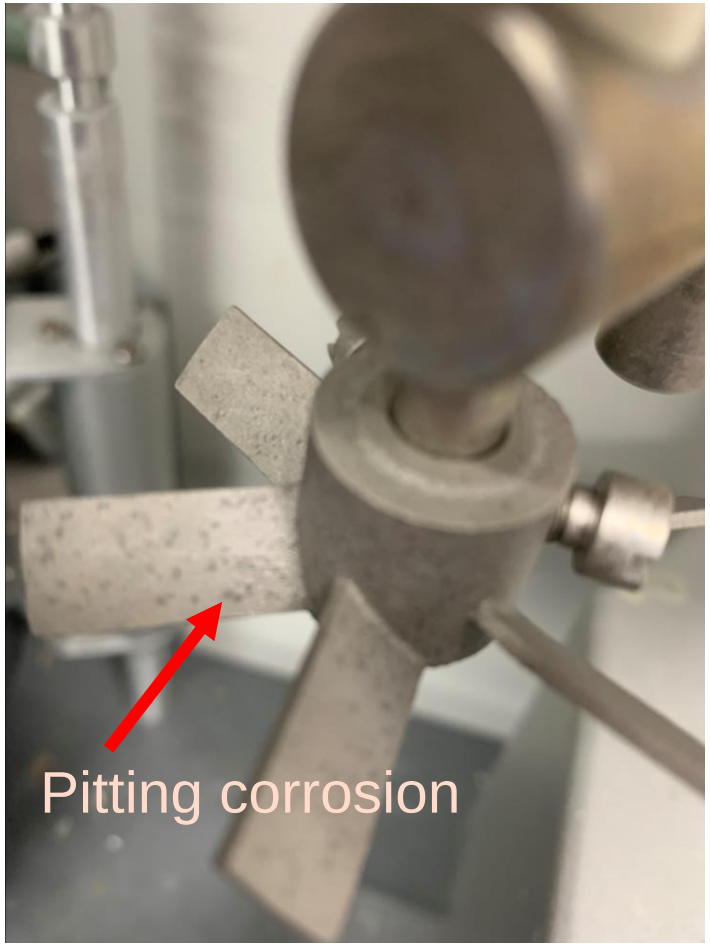
80 °C and 346 psi for 25 hours

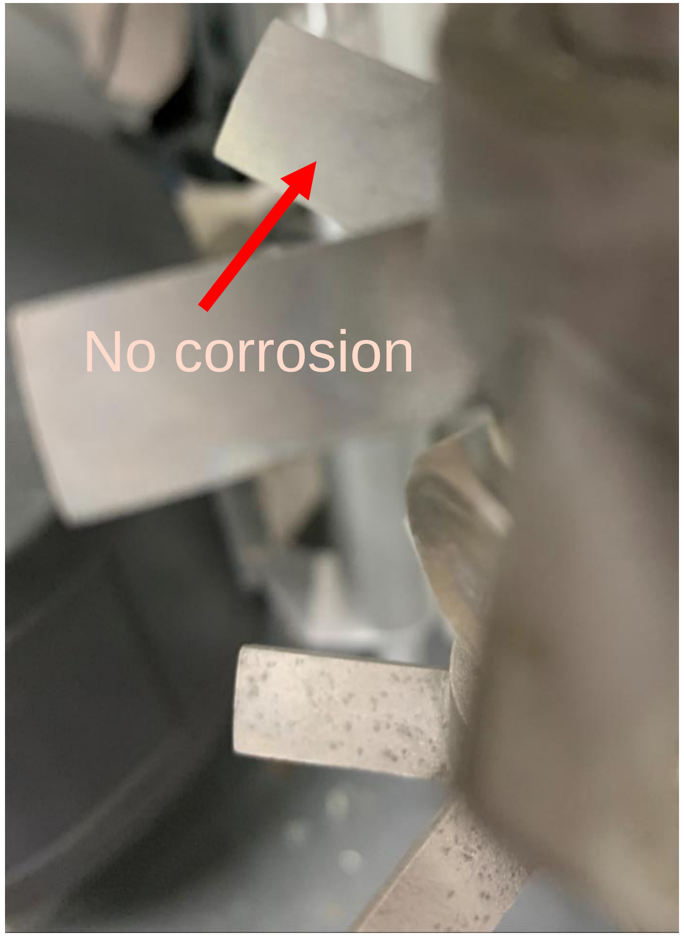
2.5 wt% starting material, 4 eq. SO_2Cl_2, 18 wt% acetonitrile, rest DCM

https://www.parrinst.com/products/stirred-reactors/series-4520-1-2l-bench-top-reactors/

Coupon Testing was Performed to Quantify Corrosion Rate

End of test → Agitator and reactor surfaces had significant visible corrosion





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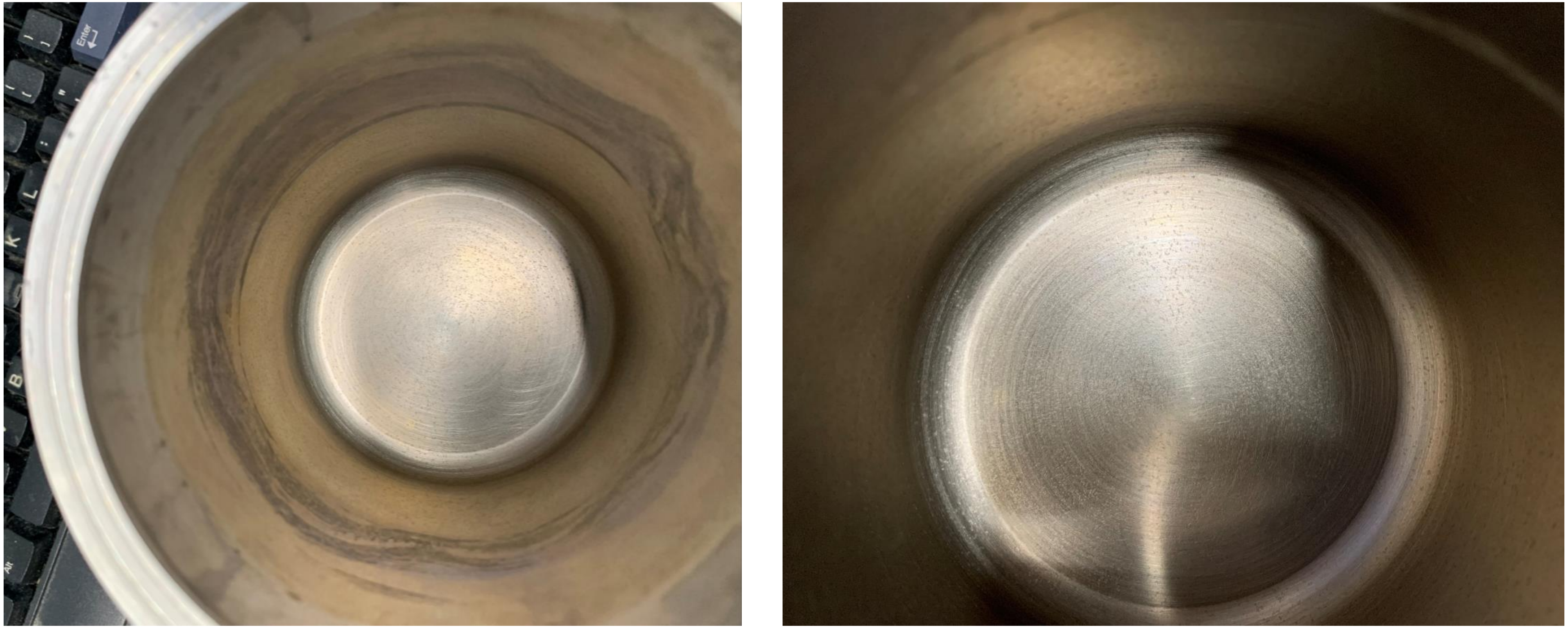
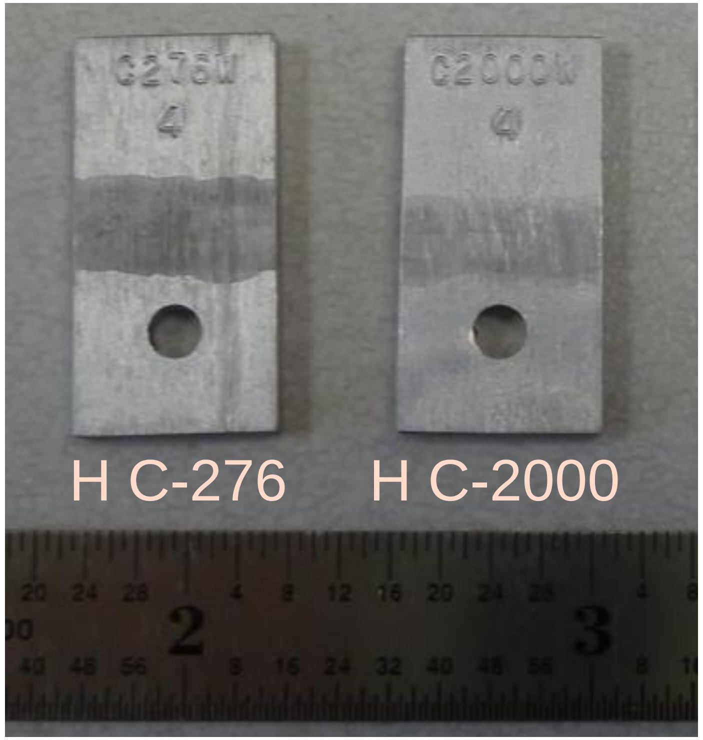


Coupon Testing was Performed to Quantify Corrosion Rate

Coupons had visible surface damage and corrosion rate was extremely high



$$\text{Corrosion Rate} = \frac{\text{Weight Loss}}{\text{Density x Surface Area x Time}}$$

(Calculation assumes uniform corrosion rate)

Coupon	Initial weight (g)	Final weight (g)	% change in weight	**Corrosion rate (MPY)***
H C-276	8.1130	8.0330	0.99%	**144.4**
H C-2000	7.6087	7.5070	1.34%	**193.1**

*5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Coupon Testing Repeated Without Acetonitrile

Test conditions:

2.1 wt% starting material, 4 eq. SO_2Cl_2, rest DCM

80 °C and 370 psi for 25 hours

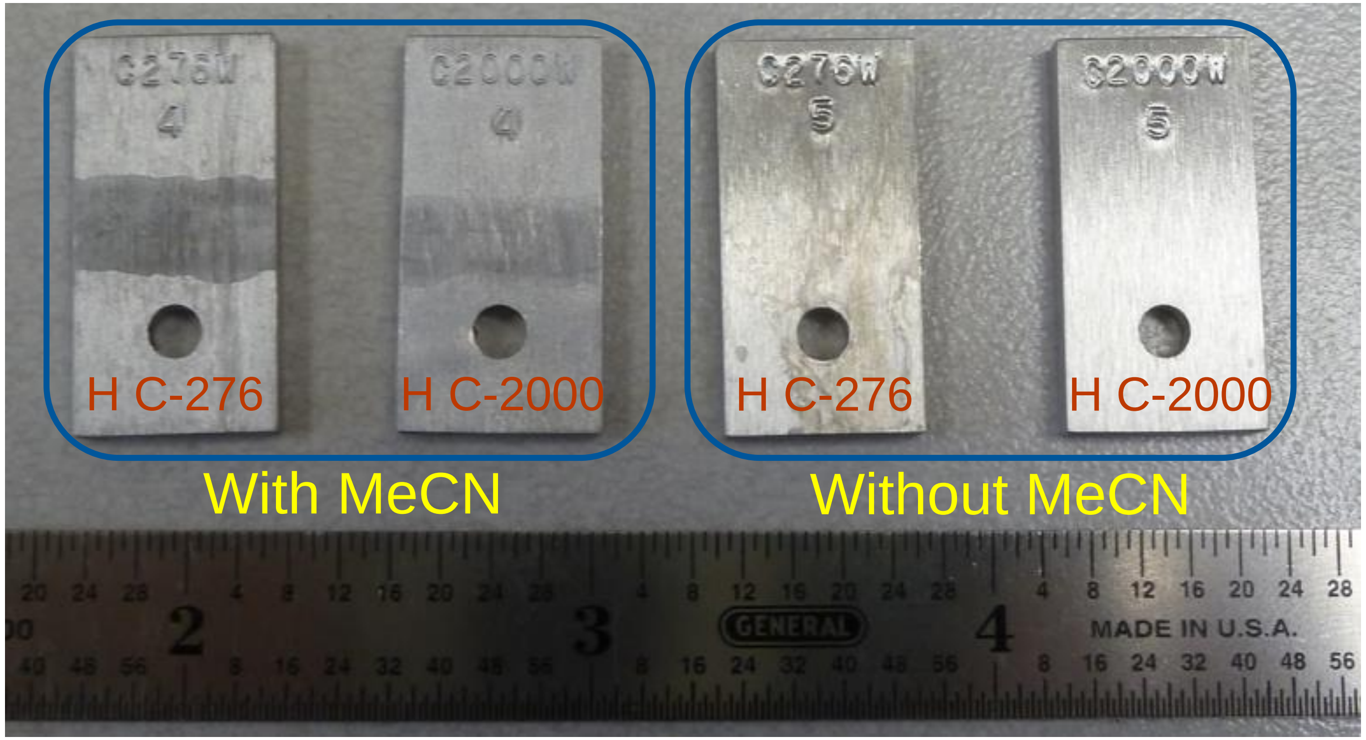
Coupon Testing Repeated Without Acetonitrile

Test conditions:

2.1 wt% starting material, 4 eq. SO_2Cl_2, rest DCM

80 °C and 370 psi for 25 hours

Condition	Coupon	Corrosion rate (MPY)*
No MeCN	H C-276	1.6
No MeCN	H C-2000	1.9
MeCN present	H C-276	144.4
MeCN present	H C-2000	193.1

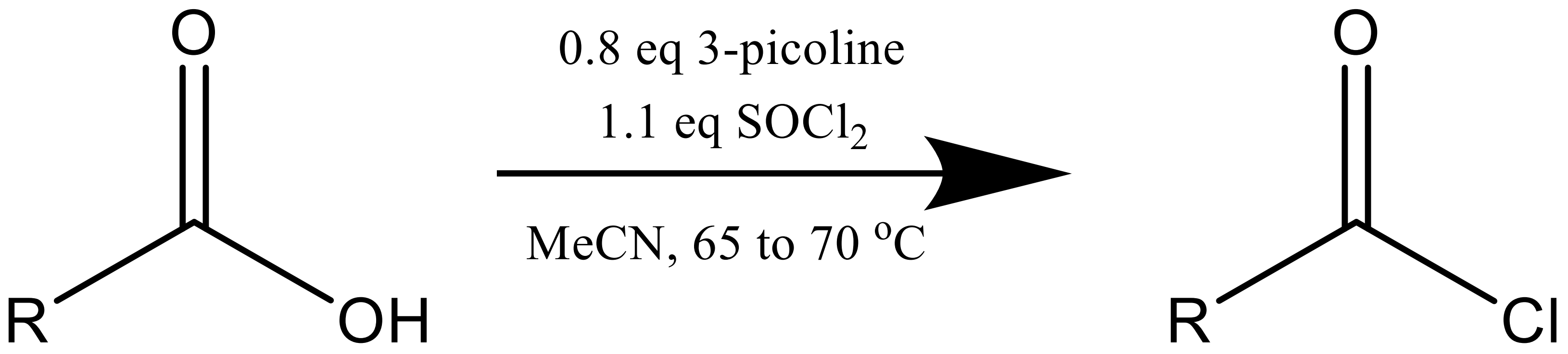


Corrosion rate was ~100x lower; no noticeable damage to reactor

*5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Case Study 2: Another Example of High Corrosion in Chemistry with Acetonitrile

Acid chloride formation reaction:



Coupon testing was performed over 2 weeks at 20 °C and 70 °C as part of scale-up preparations

Case Study 2: Another Example of High Corrosion in Chemistry with Acetonitrile

H C-276 at 20 °C

Before

Mass: 17.9738 g

After

Mass: 17.7754 g

Coupon cleaning

Corrosion rate = 11.8 mpy

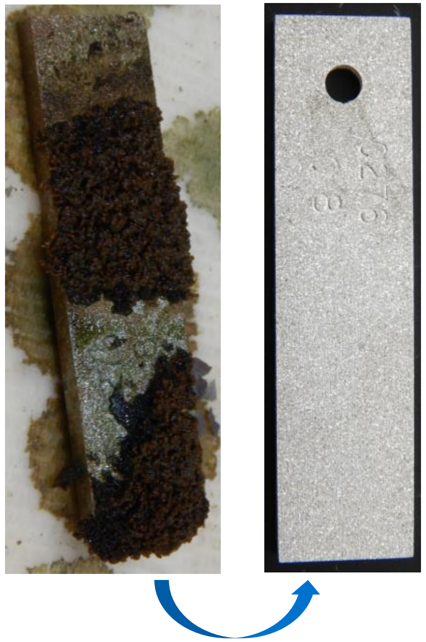
H C-276 at 70 °C

Before

Mass: 17.9969 g

After

Mass: 17.1059 g



Coupon cleaning

Corrosion rate = 59.1 mpy

5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Case Study 2: Another Example of High Corrosion in Chemistry with Acetonitrile

H C-22 at 20 °C

Before

Mass: 17.8526 g

After

Mass: 17.6497 g

Coupon cleaning

Corrosion rate = 15.8 mpy

H C-22 at 70 °C

Before

Mass: 17.9969 g

After

Mass: 17.1059 g

Coupon cleaning

Corrosion rate = 74.8 mpy

5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Evidence for Acetonitrile being the Root Cause of Corrosivity

Coupon tests were performed with mixtures of chlorinating agents and solvents

No other reagents (including ag intermediates) were included

Coupons:

1) Hastelloy B3
2) Hastelloy C-2000
3) Hastelloy C-276
4) Inconel 600
5) Monel 400
6) Nickel 200
7) Stainless Steel 316

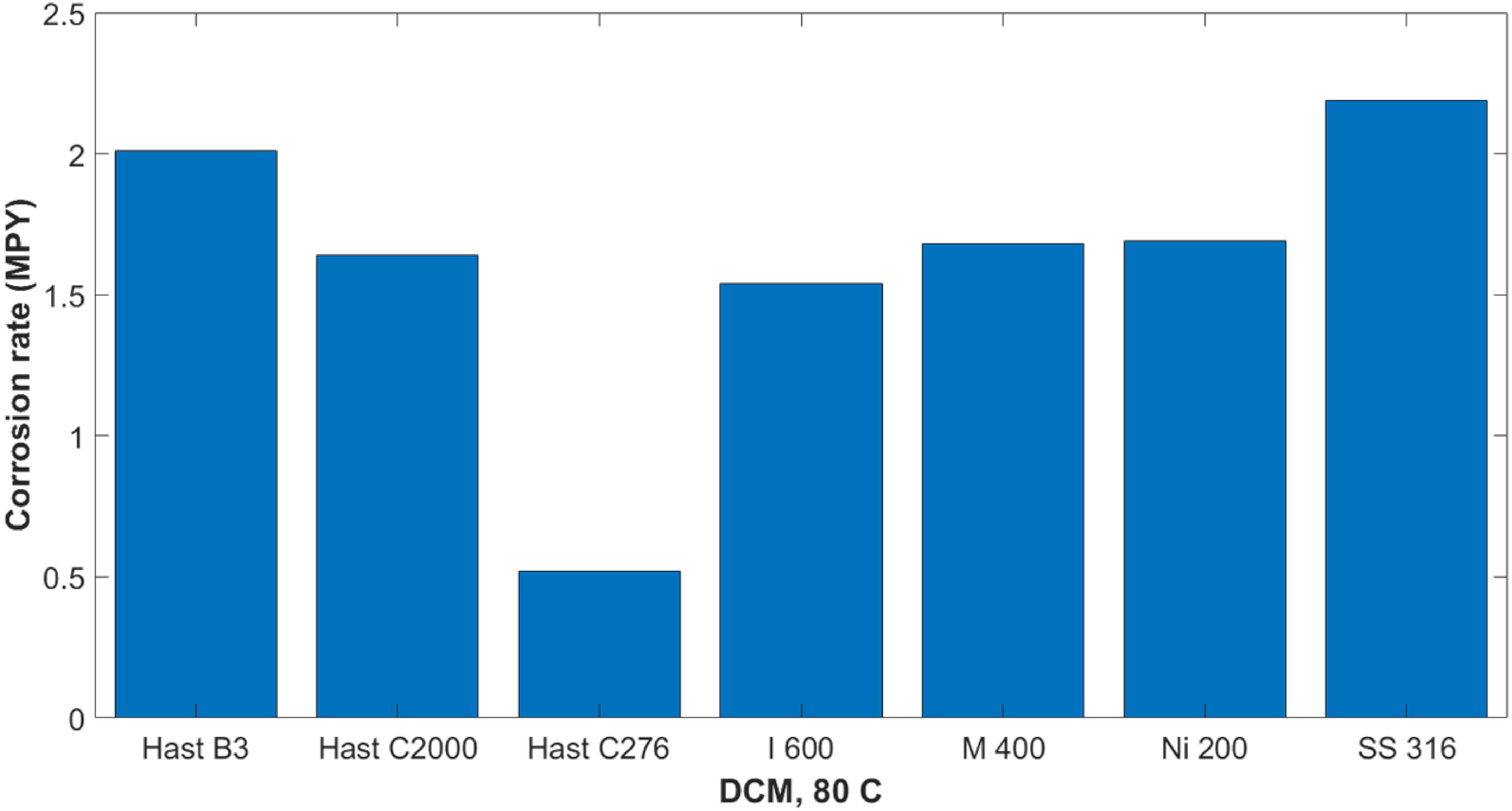
Chlorinating agents:

1) Sulfuryl Chloride
2) Thionyl Chloride
3) Oxalyl Chloride

Solvents:

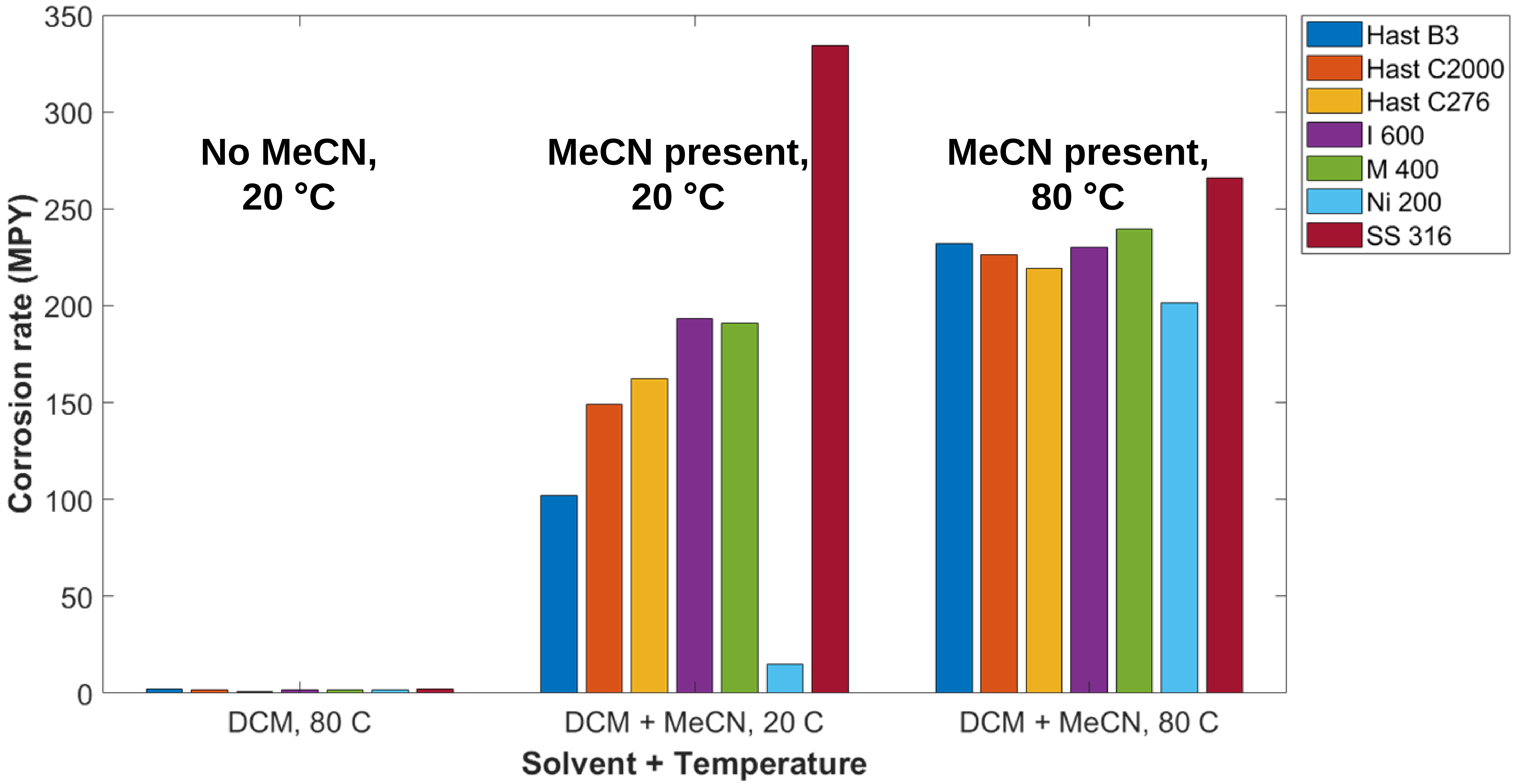
1) Dichloromethane (DCM)
2) DCM:MeCN 4:1 mix

Corrosion Rates for Sulfuryl Chloride + DCM (80 °C)



5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Corrosion Rates for Sulfuryl Chloride



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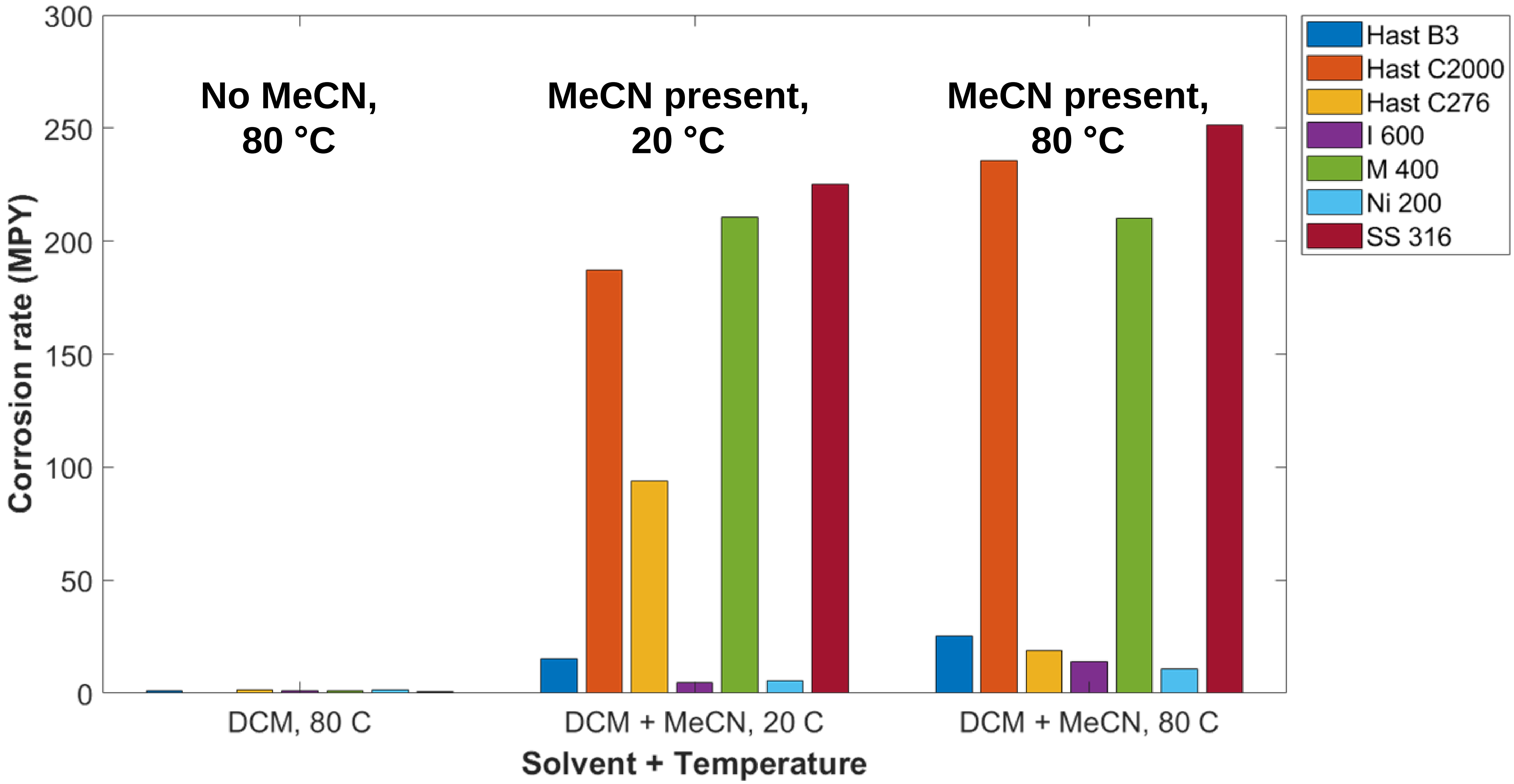
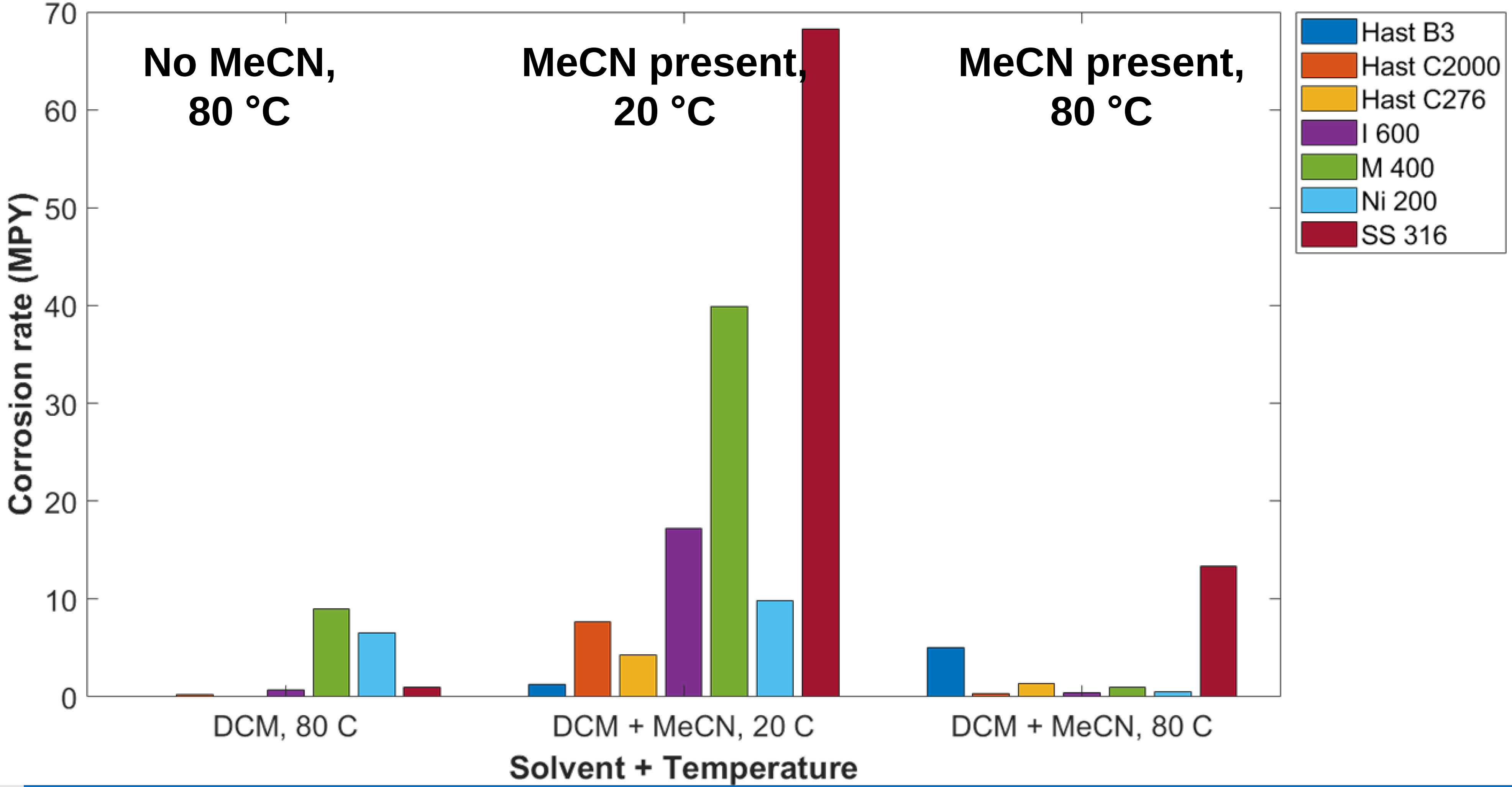
Corrosion Rates for Thionyl Chloride



5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Corrosion Rates for Oxalyl Chloride

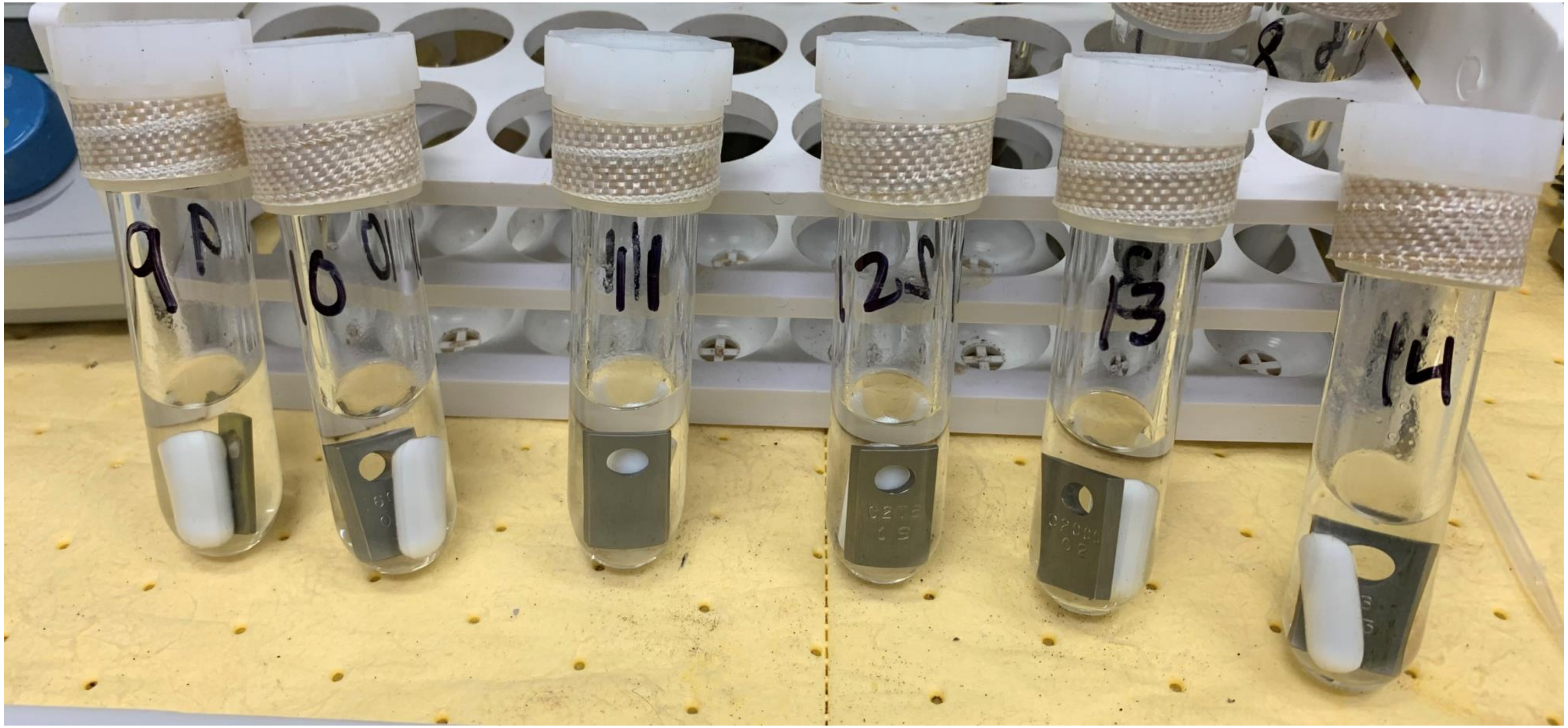
Oxalyl chloride behaves differently from sulfuryl or thionyl chloride
Further investigation needed to understand mechanism



5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

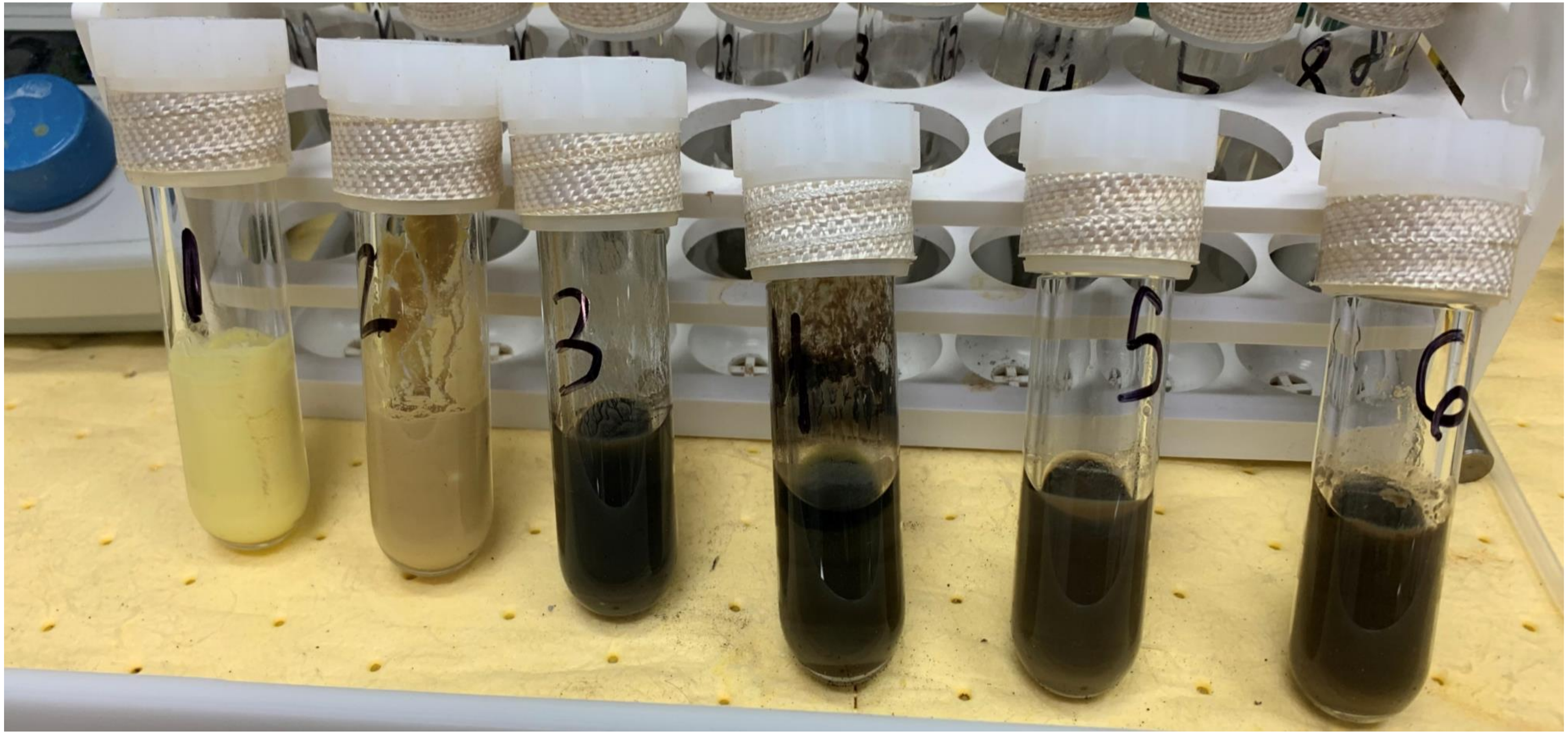
Representative Images at End of Coupon Tests

Low corrosion conditions



Representative Images at End of Coupon Tests

High corrosion conditions



Acetonitrile is not the only reagent that can cause unexpectedly high corrosion in resistant alloys

Case Study 3: $POCl_3$ Chlorination

Molecule X + 2 $POCl_3$ + 2 TEA $\longrightarrow$ **Molecule Y** + 2 $N(CH_2CH_3)_3.HOPOCl_2$

The base, triethylamine (TEA), catalyzes $POCl_3$ chlorinations

TEA also suppresses over-chlorination of Molecule X

Both $POCl_3$ and TEA are regenerated at the end of the reaction

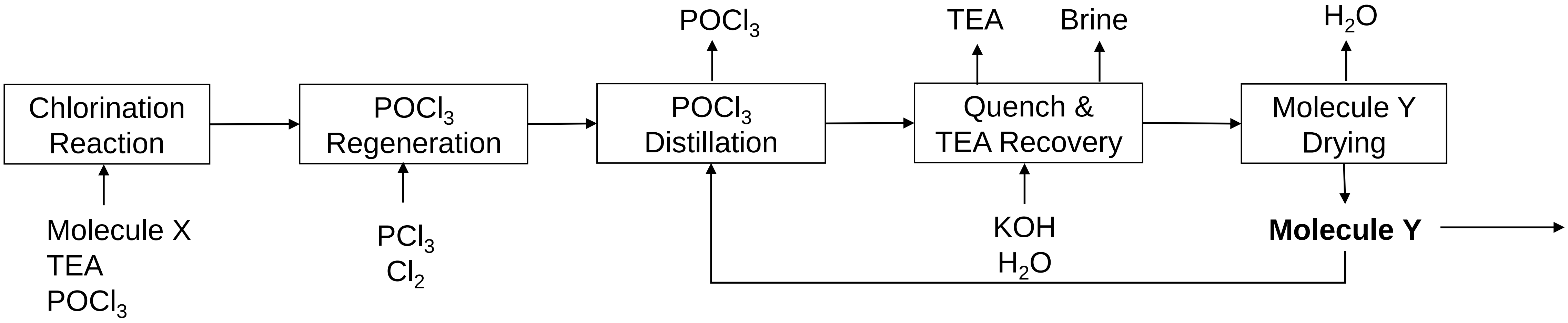
Case Study 3: $POCl_3$ Chlorination

$POCl_3$ Chlorination

Molecule X + 2 $POCl_3$ + 2 TEA $\longrightarrow$ **Molecule Y** + 2 $N(CH_2CH_3)_3.HOPOCl_2$

$POCl_3$ Regeneration

$$2\ PCl_3 + 2\ Cl_2 + 2\ N(CH_2CH_3)_3.HOPOCl_2 \longrightarrow 4\ POCl_3 + 2\ TEA{\bullet}HCl$$



Chlorination Reaction

$POCl_3$ Regeneration

$POCl_3$ Distillation

Quench & TEA Recovery

Molecule Y Drying

Molecule X
TEA
$POCl_3$

PCl_3
Cl_2

$POCl_3$

TEA

Brine

KOH
H_2O

H_2O

Molecule Y

Materials of Construction Surprise

Process was planned to be scaled up in a Hastelloy C reactor in pilot plant

- Reactor had been used for similar $POCl_3$ reaction with good results

*5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Materials of Construction Surprise

Process was planned to be scaled up in a Hastelloy C reactor in pilot plant

- Reactor had been used for similar $POCl_3$ reaction with good results

Coupon testing performed at 75 °C few months before startup

Reaction	Corrosion Rate (MPY)*
$POCl_3$ Chlorination	27
$POCl_3$ regeneration	482
$POCl_3$ Chlorination w/o TEA	< 1

TEA•HCl presumably formed “super acid” in $POCl_3$ → attacked Hastelloy C

*5 to 20 mpy is corrosive; > 20 mpy is severely corrosive

Conclusions

Acetonitrile combined with certain chlorinating agents can severely corrode resistant alloys, even at room temperature

Other reagents can also form “super-acids” that can corrode resistant alloys

Mechanism of severe corrosion is not completely understood → Difficult to predict when it will occur

Perform thorough corrosion testing before scale-up to avoid unpleasant surprises

Acknowledgements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Ajit Mishra


John Doyle


Abraham Schuitman


Greg Whiteker

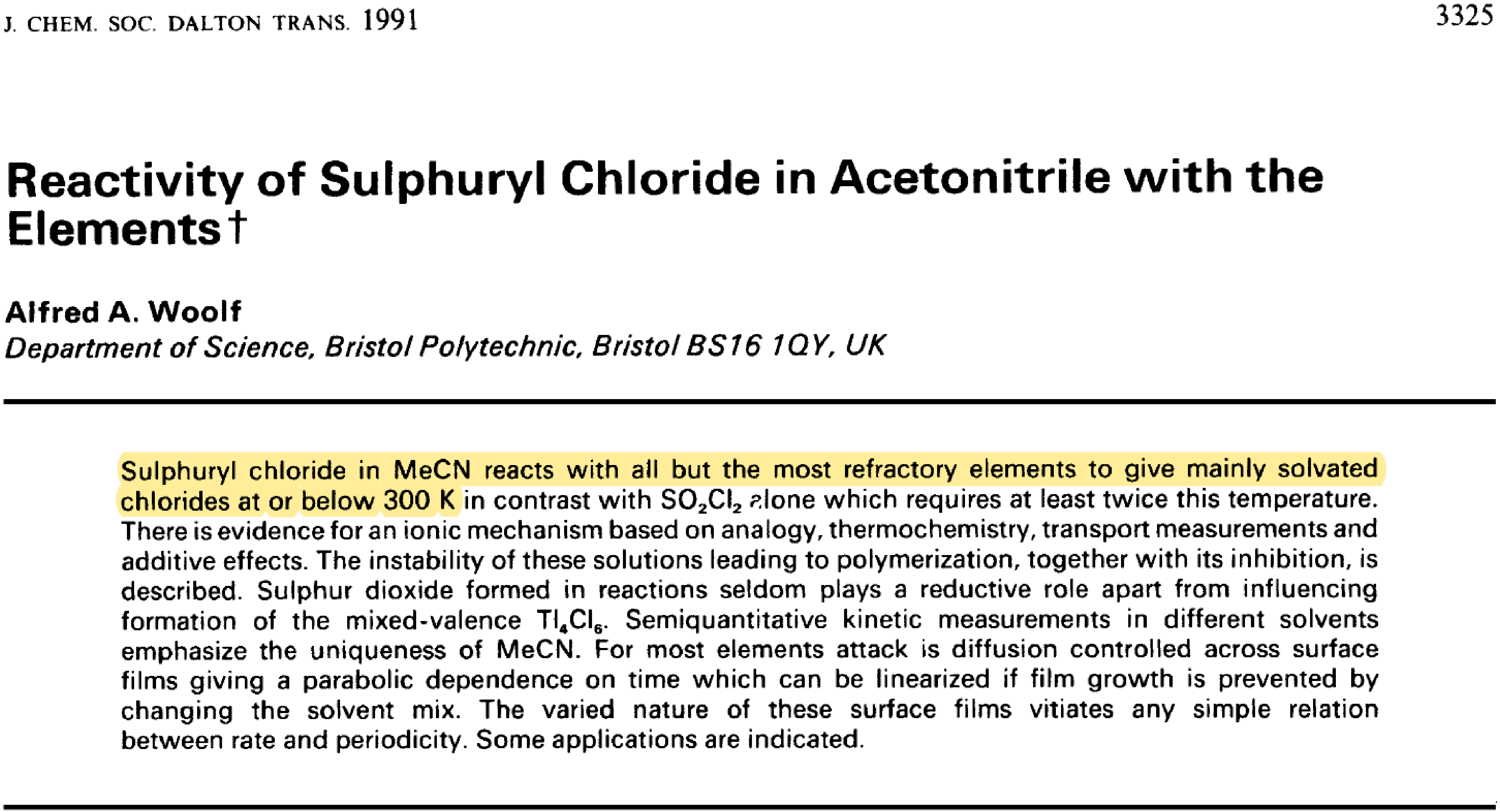

Ron Leng


David Clouse


Matthias Ober


Matthew Bolten

Additional Slides



J. CHEM. SOC. DALTON TRANS. 1991 3325

Reactivity of Sulphuryl Chloride in Acetonitrile with the Elements†

Alfred A. Woolf
Department of Science, Bristol Polytechnic, Bristol BS16 1QY, UK

Sulphuryl chloride in MeCN reacts with all but the most refractory elements to give mainly solvated chlorides at or below 300 K in contrast with SO_2Cl_2 alone which requires at least twice this temperature. There is evidence for an ionic mechanism based on analogy, thermochemistry, transport measurements and additive effects. The instability of these solutions leading to polymerization, together with its inhibition, is described. Sulphur dioxide formed in reactions seldom plays a reductive role apart from influencing formation of the mixed-valence Tl_4Cl_6. Semiquantitative kinetic measurements in different solvents emphasize the uniqueness of MeCN. For most elements attack is diffusion controlled across surface films giving a parabolic dependence on time which can be linearized if film growth is prevented by changing the solvent mix. The varied nature of these surface films vitiates any simple relation between rate and periodicity. Some applications are indicated.

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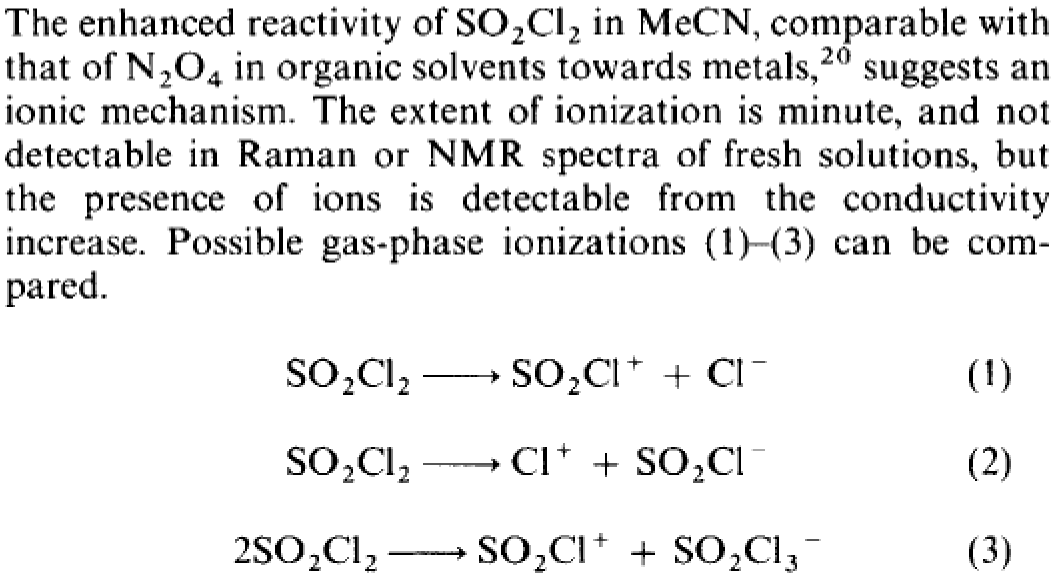

The enhanced reactivity of SO_2Cl_2 in MeCN, comparable with that of N_2O_4 in organic solvents towards metals,[20] suggests an ionic mechanism. The extent of ionization is minute, and not detectable in Raman or NMR spectra of fresh solutions, but the presence of ions is detectable from the conductivity increase. Possible gas-phase ionizations (1)–(3) can be compared.

$$SO_2Cl_2 \longrightarrow SO_2Cl^+ + Cl^- \qquad (1)$$

$$SO_2Cl_2 \longrightarrow Cl^+ + SO_2Cl^- \qquad (2)$$

$$2SO_2Cl_2 \longrightarrow SO_2Cl^+ + SO_2Cl_3^- \qquad (3)$$

J. CHEM. SOC. DALTON TRANS. 1991