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Halogen Removal from Tritium Gas Streams

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ISFNT 15

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Outline

- Background
- Experimental approach
- Analytical instrumentation
- HCl results
- Water overlap
- Conclusions

Background

- Halogen impurities are poisonous and/or corrosive
  - Poison for catalysts and equipment
  - Causes pitting in most austenitic stainless steels
  - Minimized to prevent damage over time
  - Prone to appear in certain processes
    - Appear if certain materials degrade (i.e., elastomers, etc.)
    - Present as trace impurities in a large number of metals and zeolites (<200 ppm)

www.materialgrades.com

Background

- Extra precaution for fluoride-salt breeder materials
  - Possible TF formation in the salt
  - Unlikely but possible for TF to migrate to fuel cycle
  - Easy preventative measure, very costly after the fact
- Effective if typical fluorinated polymers begin to decompose
  - Perfluoroelastomers used in most pumps
  - Degradation products would include TF, other fluoride compounds in tritium
- -F or –Cl will deactivate noble metal-based materials
  - Permeator/diffuser, palladium membrane reactor
  - Pd-based hydrogen isotope separation
  - Pt-based water gas-shift catalysts
  - Ru-based ammonia decomposition catalysts

Background

- Halogens typically removed using aqueous KOH
  - Forms KF or KCl salts that precipitate out of solution
- Aqueous KOH not viable in a tritium environment
  - Large amounts of caustic solutions that need to be detritiated and neutralized
- Is gas-phase halogen capture a viable option?

Background

- Several materials have been investigated
  - Alumina, commercial nickel catalyst, activated carbon, NaI*
  - Na and Ca hydroxide/carbide/oxide+
  - Mg-modified alumina++
- Carbon is incompatible with tritium
  - Can also form carbon fluoride, which can deflagrate at >100°C
- Na/Ca require elevated temperatures
  - Typically >400°C, all >100°C
  - Can release water or carbon when exposed to tritium decay
- Mg-modified alumina is promising, but are there metals with higher capacities?

*https://doi.org/10.1007/s11356-023-27322-5 +https://doi.org/10.2172/9286 ++https://doi.org/10.1080/09593330.2022.2026484

Experimental Approach

- Investigate various metals deposited on tritium-compatible substrates
  - Co, Ni, Pt, Cu, Ag, Au metal salts
  - Alumina 4A zeolite binder-free 4A zeolite 5A zeolite




- Determine HF and HCl capacity
  - Compare pre- and post-testing samples for structural and chemical changes

- Down-select materials for optimization trials

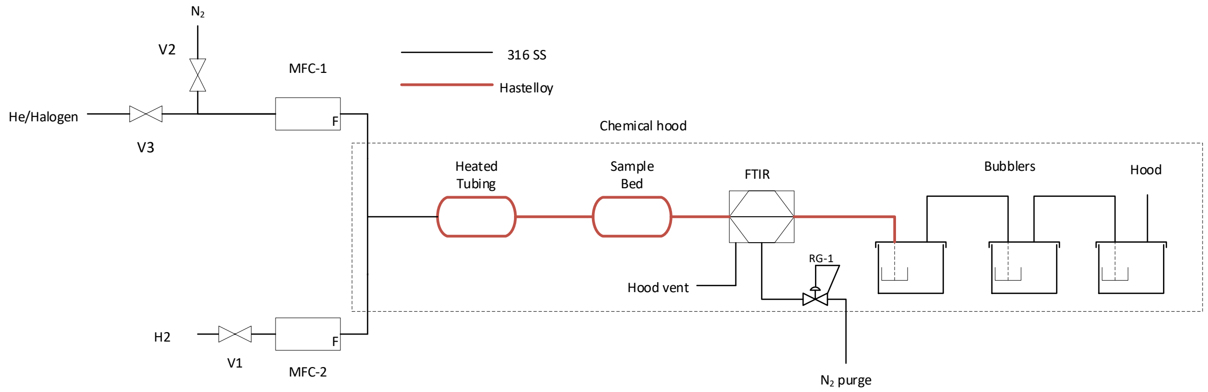
Adsorbent Synthesis

- Substrates dried at 110°C overnight
- Metal salt was added using wet impregnation
  - Nominal 1.0 wt% metal loading, same for all metal salts
- Air dried overnight
- Dried for 2 hours in 110° oven
- Calcined at 550°C for 2 hours

- Prior to testing, dried in vacuum oven and calcined similar to synthesis
  - Remove residual moisture before packing in test column

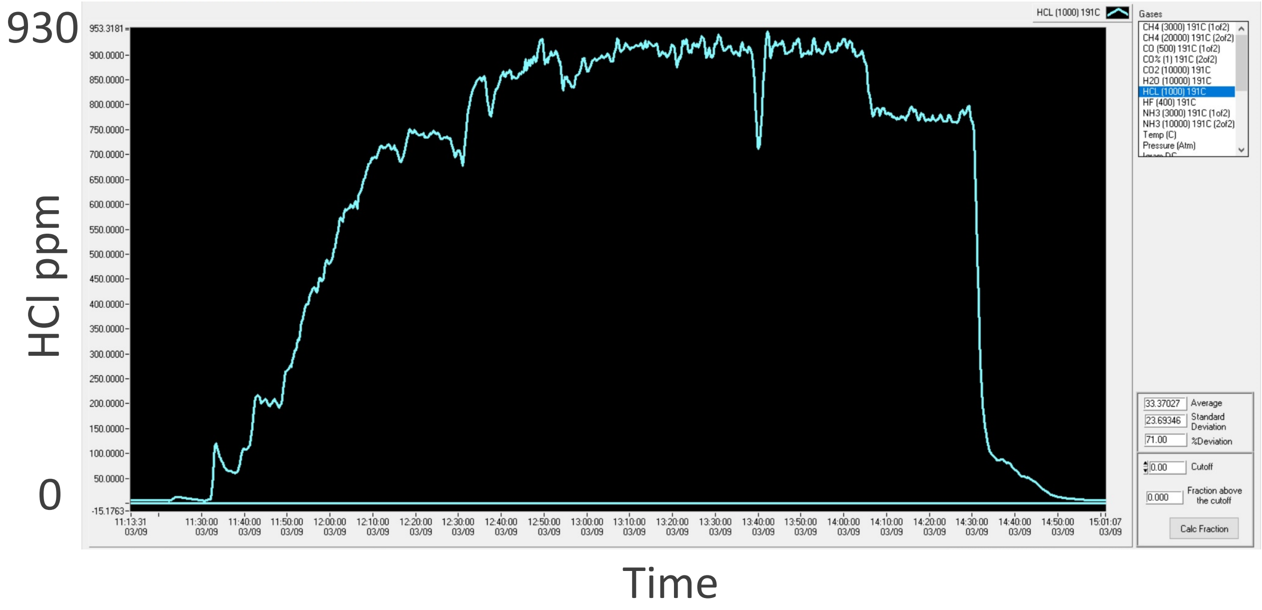
Halogen Generation

- Halogens expected to be trace impurities
- Pre-mixed gas mixtures of 1000 ppm of diatomic halogen (F_2 or Cl_2) in helium
- Combined in-line with H_2, fed through heated Hastelloy C-276 tube
  - Tube heated to 375°C for autocatalytic HCl and HF formation
  - 50 sccm of Cl_2/He mixture, 20 sccm of H_2
- Three 5N KOH bubblers before vent
  - Ensure no HCl/HF are vented



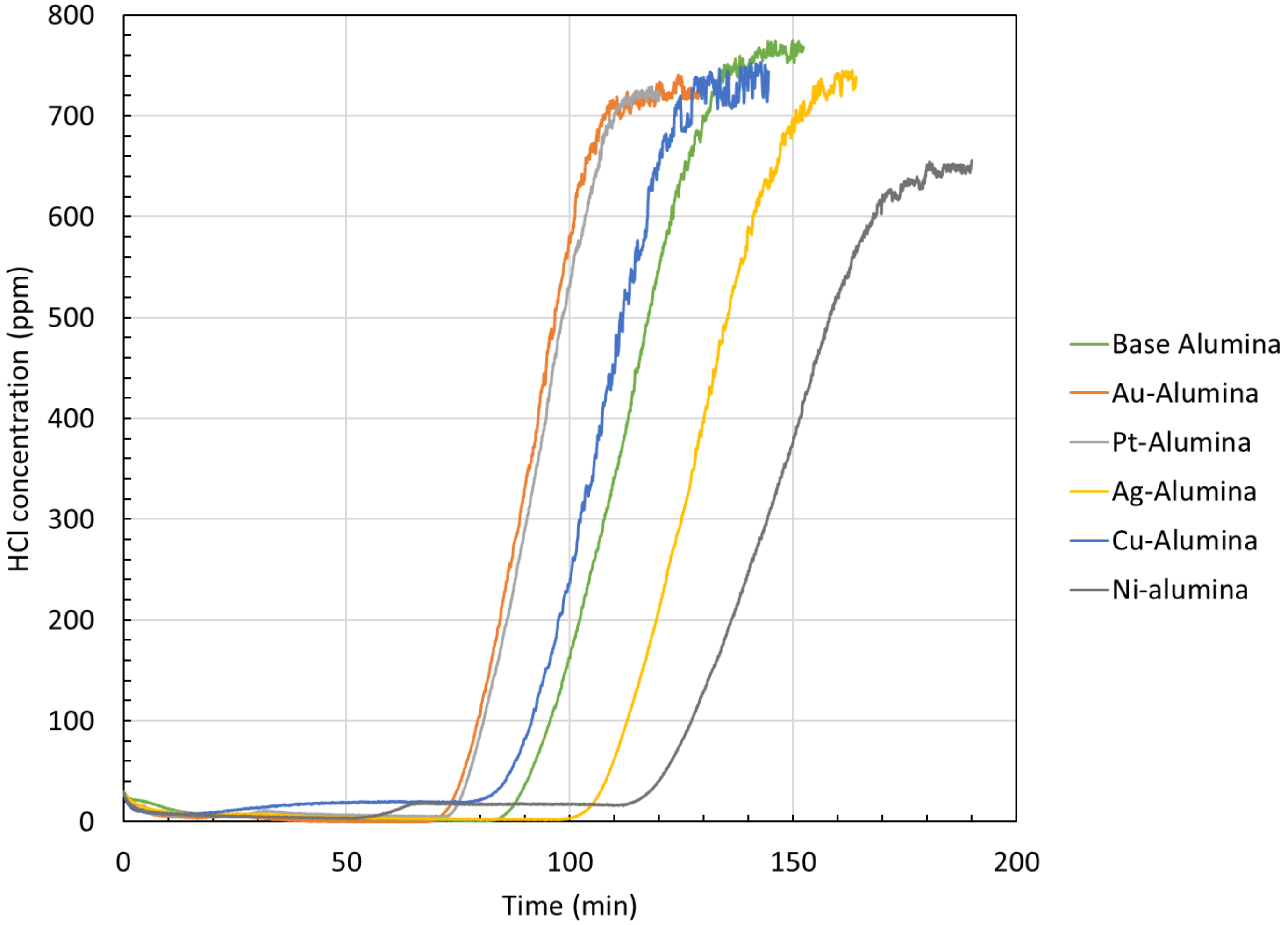
Analytical Instrumentation

- MKS 2030G FTIR
  - LN2 cooled MCT
  - Calibrated for 1000 ppm HCl and 1000 ppm HF
  - Built to withstand test concentrations of HCl and HF
  - Extended 12-hour external dewar

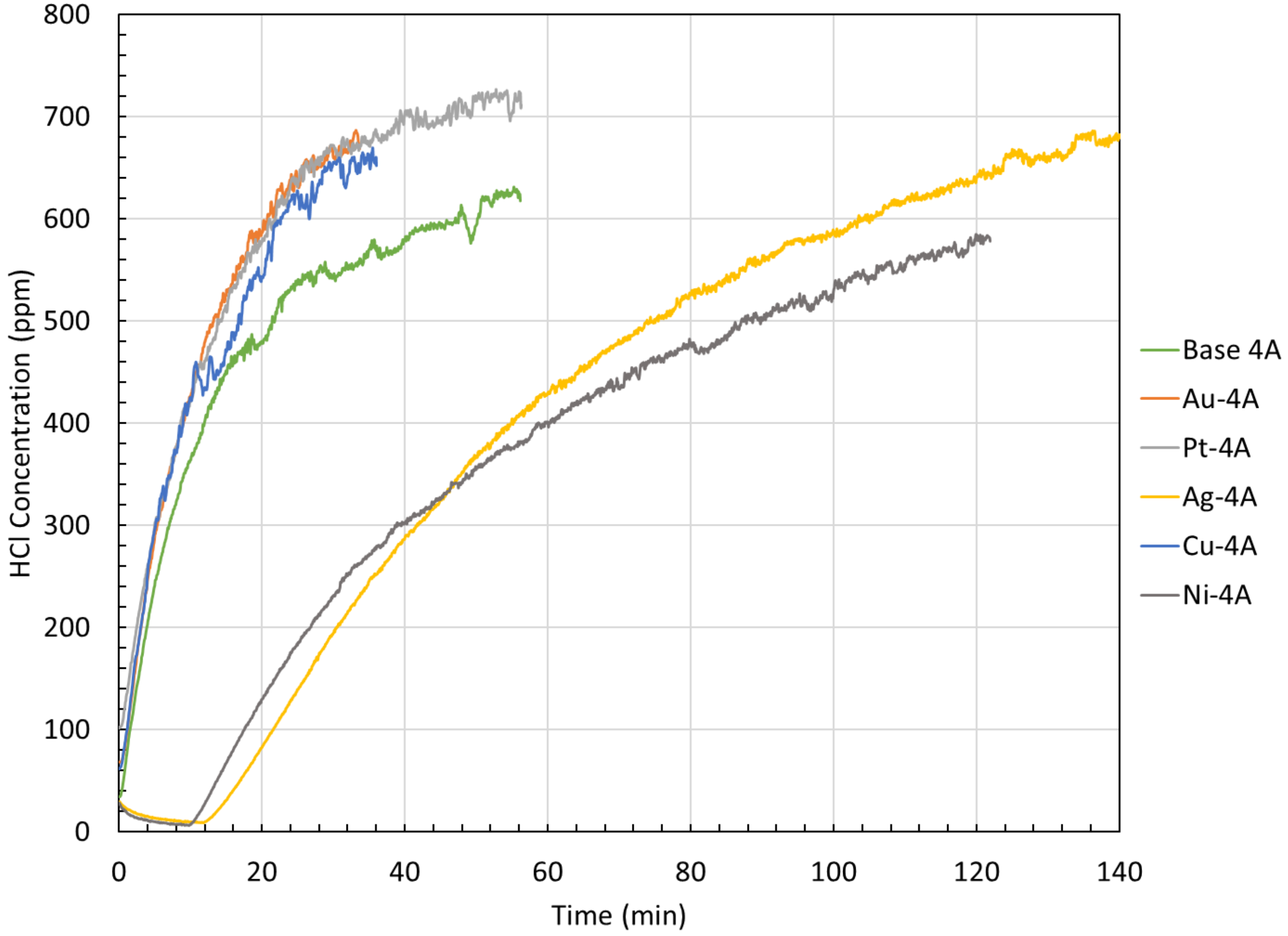


Average: 33.37027
Standard Deviation: 23.69346
%Deviation: 71.00
Cutoff: 0.00
Fraction above the cutoff: 0.000

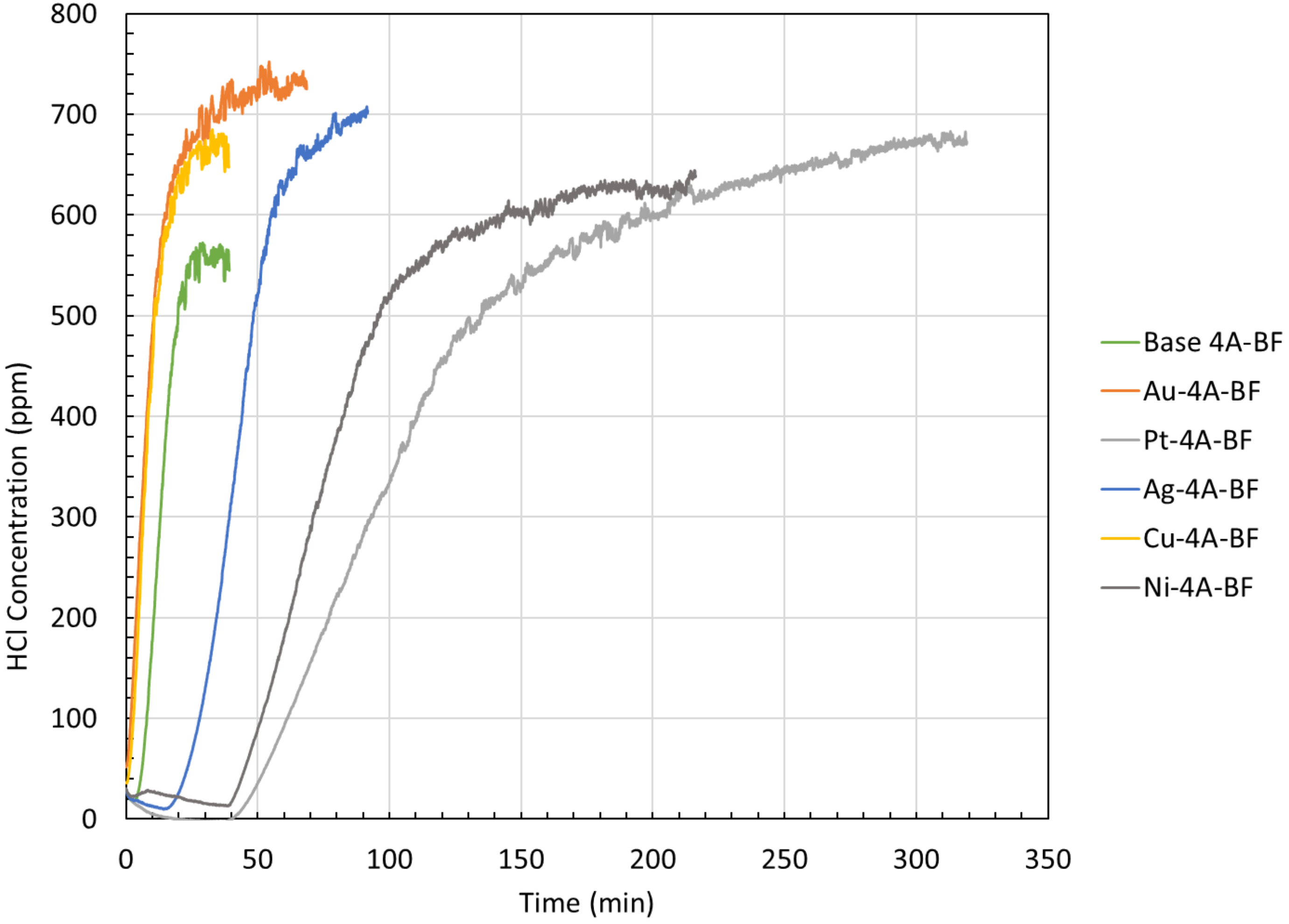
HCl Results


800
700
600
500
400
300
200
100
0
HCl concentration (ppm)
0
50
100
150
200
Time (min)
Base Alumina
Au-Alumina
Pt-Alumina
Ag-Alumina
Cu-Alumina
Ni-alumina

HCl Results

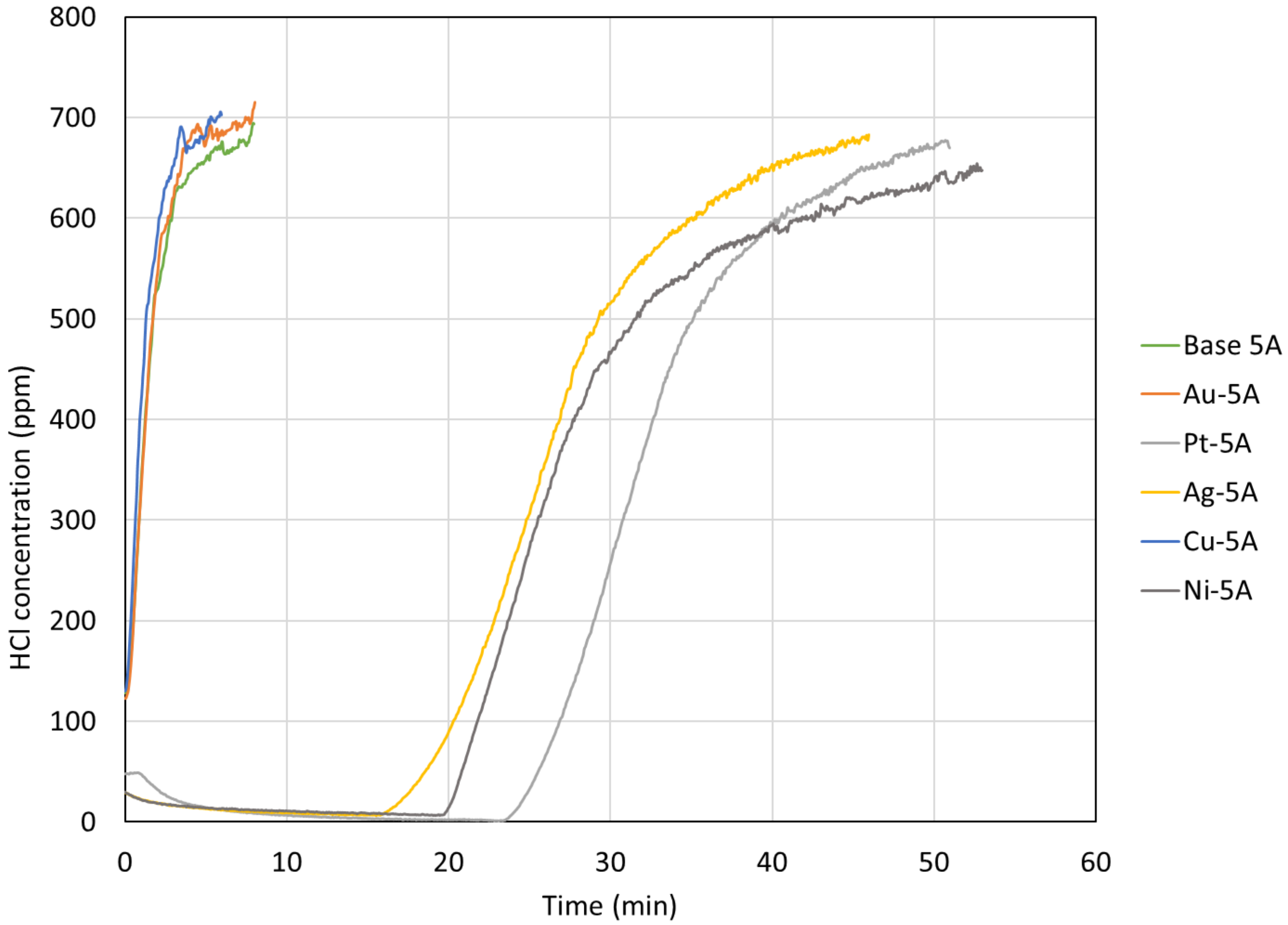

HCl Concentration (ppm)
0
100
200
300
400
500
600
700
800
Time (min)
0
20
40
60
80
100
120
140
Base 4A
Au-4A
Pt-4A
Ag-4A
Cu-4A
Ni-4A

HCl Results



HCl Concentration (ppm)
0
100
200
300
400
500
600
700
800
Time (min)
0
50
100
150
200
250
300
350
Base 4A-BF
Au-4A-BF
Pt-4A-BF
Ag-4A-BF
Cu-4A-BF
Ni-4A-BF

HCl Results


800
700
600
500
400
300
200
100
0
HCl concentration (ppm)
0
10
20
30
40
50
60
Time (min)
Base 5A
Au-5A
Pt-5A
Ag-5A
Cu-5A
Ni-5A

HCl Results

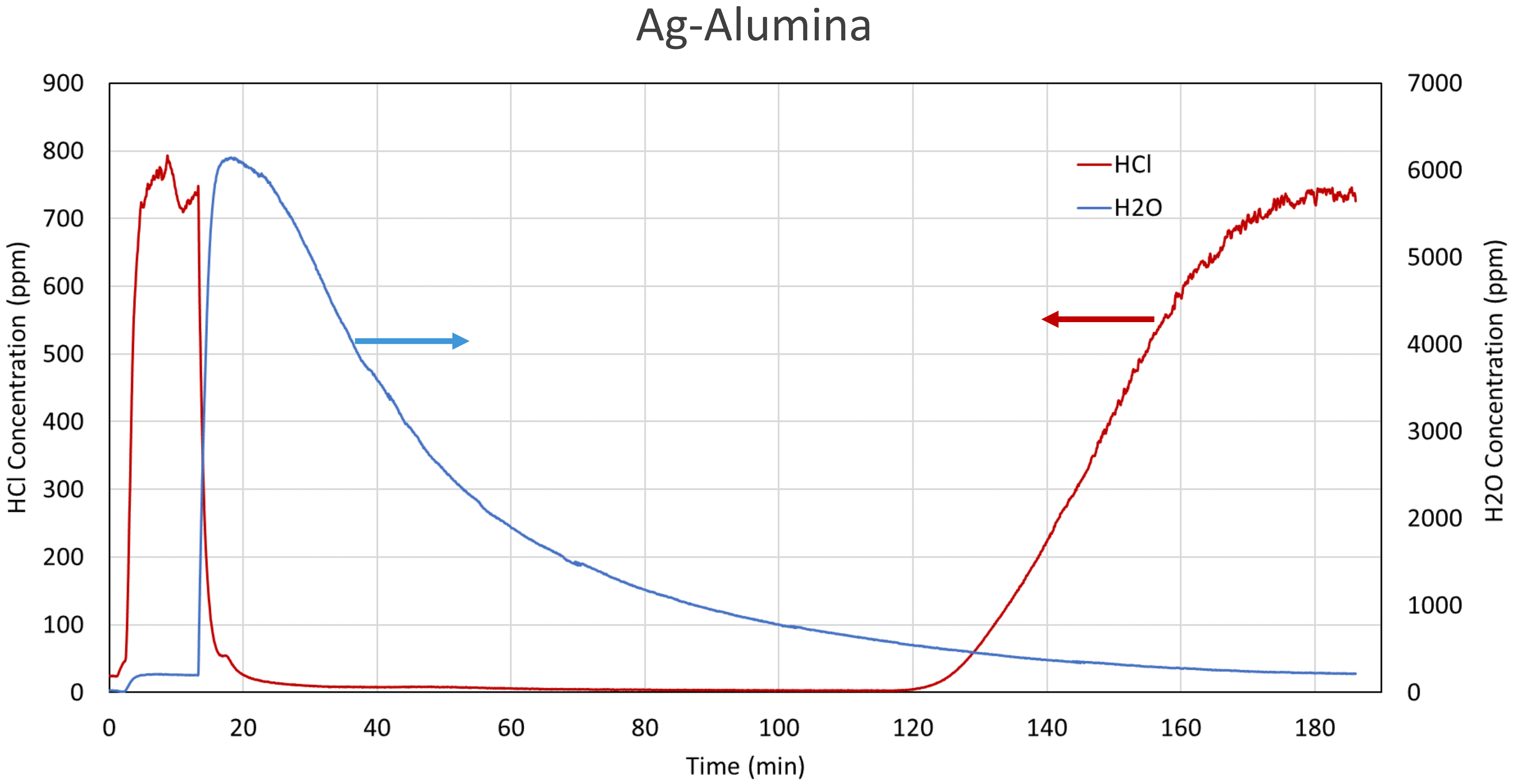
Saturated HCl Uptake

	Alumina	4A	Binder-Free 4A	5A
Bare	2.44	0.460	0.261	0.05
Co				
Ni	2.69	0.994	1.38	0.547
Pt	2.63	0.232	2.56	0.643
Cu	2.24	0.198	0.242	0.038
Ag	2.75	0.970	0.790	0.588
Au	1.92	0.189	0.214	0.048

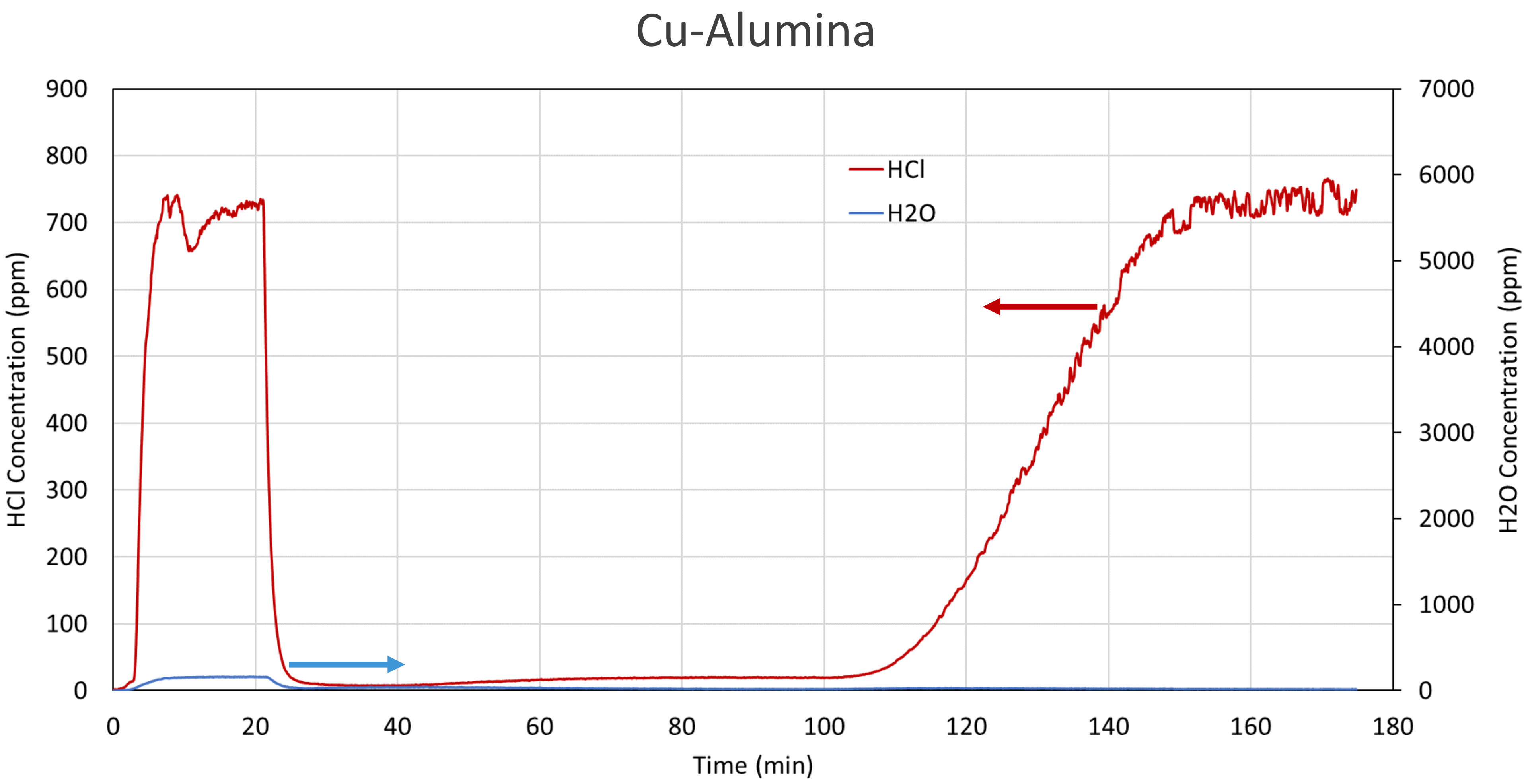
***all in mmol HCl/g sorbent**

- Co-loaded samples currently being measured

Water Overlap



Water Overlap



Water Overlap

- Hypothesized the -Cl displaces any –O or –OH bound to the added metal sites
  - More in Ag, Pt, and Ni across all substrates
  - Less prominent in Cu and Au across all substrates
- All samples given same loading and experimental treatment
  - Rules out environmental/experimental effects
- ICP-MS is planned for metal weight % determination
  - Laser ablation system currently being installed
  - Will be used to help determine if metal loading differences is responsible

Conclusions

- Synthesized metal-impregnated adsorbents
    - 6 metal salts
    - 4 substrates
- HCl generation *in-situ* was successful
- HCl was successfully removed
    - Identified metal/substrate combinations for further study
- Water evolution was observed on specific metals when binding -Cl
- Reduction *in-situ* tests will help clarify unknowns
    - Water evolution cause
    - -Cl capacity for synthesized vs reduced metals

Acknowledgements

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NNSA

National Nuclear Security Administration

Questions?