



Treatment Technology Considerations at Plating Facilities Comingled with PFAS and Chromium-6

Sophia Nguyen, MS

Sr. Research Associate/Analytical Chemist

Keith M. Gaskill, LPG

Sr. Design Specialist/Technical Services Group Coordinator

Paul Erickson, PhD

Director of Research & Development

Yen-Ling Liu, PhD

Research Scientist

Ryan Moore

Senior District Manager and PFAS Program Manager

Problem Statement and Summary

The number of chrome plating facilities undertaking remedial action on their own or by regulators has seen a noticeable increase in recent years. Many of these facilities are comingled sources of Per- and polyfluoralkyl Substances (PFAS) and hexavalent chromium (Cr(VI)), as both were used in the plating process.

- The remedial approach to this problem is safe, effective, and efficient
- Field scale use of these technologies separately is well documented
- Bench scale testing has been completed to look at the combination of technologies for successful scenarios
- A greater understanding of how to manage both contaminant plumes simultaneously has been obtained and is ready for large-scale field utilization
- But what if you add CVOCs?

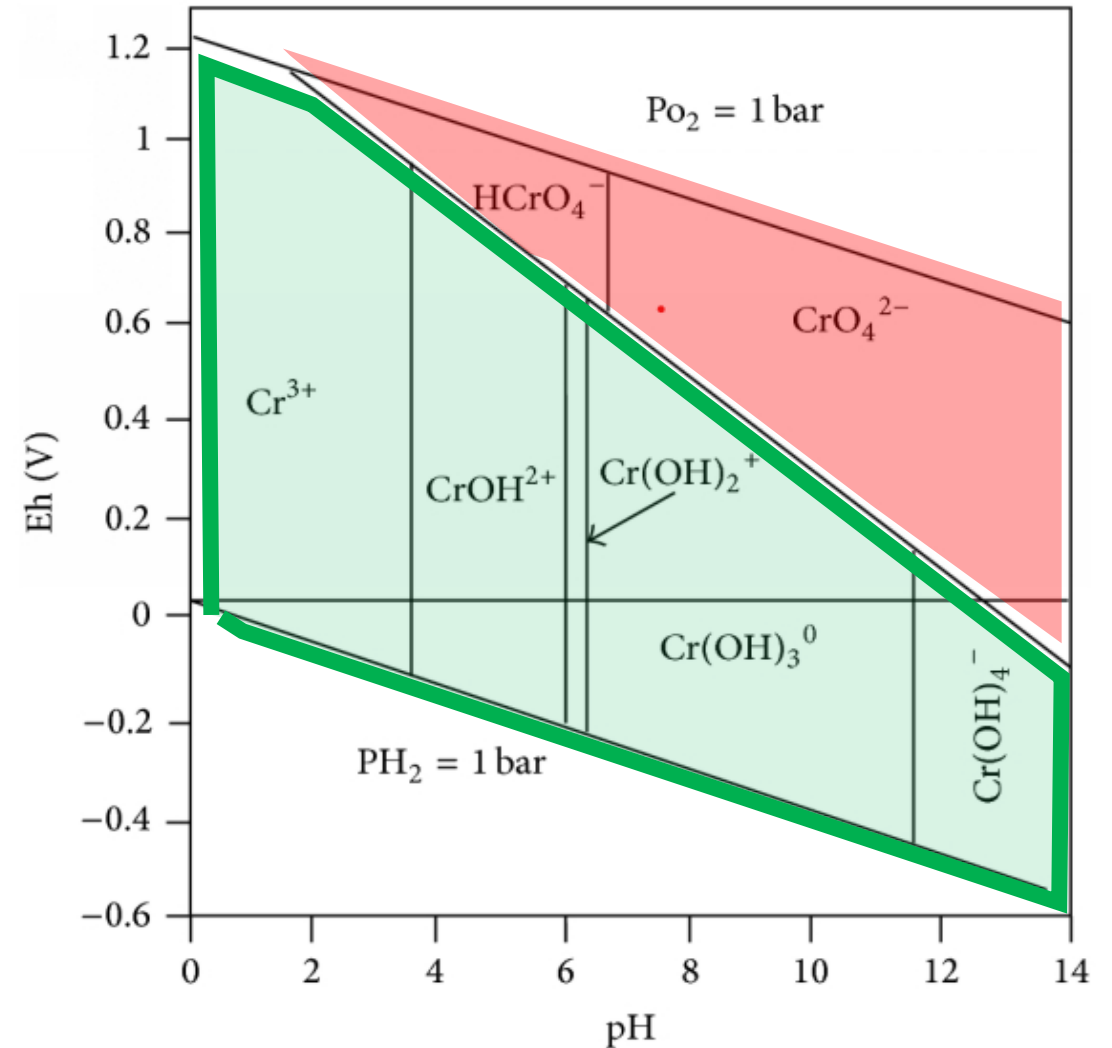
Hexchrome

- **Chromium Geochemistry**

- **Hexavalent** – CrO_4^{2-}
- **Trivalent** – Cr(OH)_2^+ species

- **Phase Diagram**

- **Cr(VI) (oxidized) compounds are not stable under normal environmental conditions**
- **Once Cr(III) (reduced) hydroxide is formed, it remains a stable precipitate that is less toxic than hexchrome**

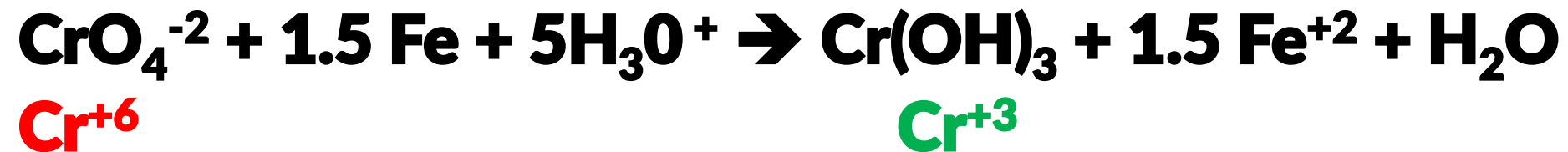


Hexchrome

- **How to Treat Hexchrome?**

- Provide Electrons = Reducing Conditions
- Electron Donors both biological (3DME/AquiFix) and abiological (S-MZVI) preferred for maximum effectiveness and longevity
- Not always necessary for both to be used simultaneously
- Recall phase diagram – once formed Cr (III) is stable precipitate
- Reversibility of the process is unlikely

- **Treatment Chemistry Example (abiotic)**



Hexchrome

How effective is treatment in practice?

- Midwestern site
- Pilot used 3DME/CRS
- Full-Scale optimized by substituting CRS with S-MZVI

Site Granted NFA

...Not so Fast!

Closure for hexchrome only
Former Plating Facility with PFAS impact found after Cr(VI) treatment

Monitoring Well Identification	Screen Interval	Remediation Status	Sample Date	Dissolved Metals			Field Parameters					
				Chromium	Manganese	Iron	Temperature	pH	Specific Conductance	Oxidation Reduction Potential	Turbidity	Dissolved Oxygen
Reporting Units				µg/L	µg/L	µg/L	Celsius	S.U.	mS/cm	mV	NTU	mg/L
NR 140 Enforcement Standard (ES)				100	300	300*						
NR 140 Preventative Action Limit (PAL)				10	60	150*						
MW-20/20R	5.1 - 15.1	Pre	06/28/17	265,000	NA	NA	NA	NA	NA	NA	NA	NA
			08/31/17	331,000	NA	NA	NA	NA	NA	NA	NA	NA
			04/23/18	296,000	<11.3	<155	15.73	7.21	2.70	282	50.4	NA
		Post Pilot Test	07/16/18	161,000	99.1	929 J	20.33	7.10	2.73	78	47.8	8.76
			08/20/18	174,000	73.1	156	19.93	7.54	2.52	103	0.0	10.05
			01/21/19	179,000	37.1	<35.4	17.09	8.20	2.55	126	1.9	5.02
		Post Full-Scale	04/10/20	7.0	114	9,250	17.90	7.48	1.41	-114	149	1.47
			06/30/20	10.9	166	23,000	20.62	6.98	2.25	-102.7	934	1.01
			09/29/20	16.7	178	17,800	20.36	7.09	2.15	-78.4	57.8	0.69
			09/29/20	22.8	179	17,200	NA	NA	NA	NA	NA	NA
DUP-1	MW-20R	12/29/20	<3.9	160	1,950	15.24	7.02	2.41	-81.9	235.4	4.09	
03/17/21		145	328	23,100	16.41	7.14	2.17	-51.2	59.96	2.58		
07/07/21		4.9 J	130	10,700	20.68	7.14	2.10	-80.6	36.16	4.60		

PFAS Overview

PFAS have been used in the metal finishing industry since the 1950s for a variety of purposes. PFAS, particularly PFOS, have been used as mist suppressants that are added to metal plating and finishing baths to prevent air emissions of toxic metal fumes.

- **EPA estimated >4,000 chromium plating facilities**
- **Based on 1999 survey, likely much, much more**

PFAS: The Elephant in The Room

- Forever Chemicals
- Very difficult to break C-F bonds
- **Many methods to manage risk ex-situ**
 - pump and treat
 - supercritical oxidation
 - plasma
 - foam fractionation

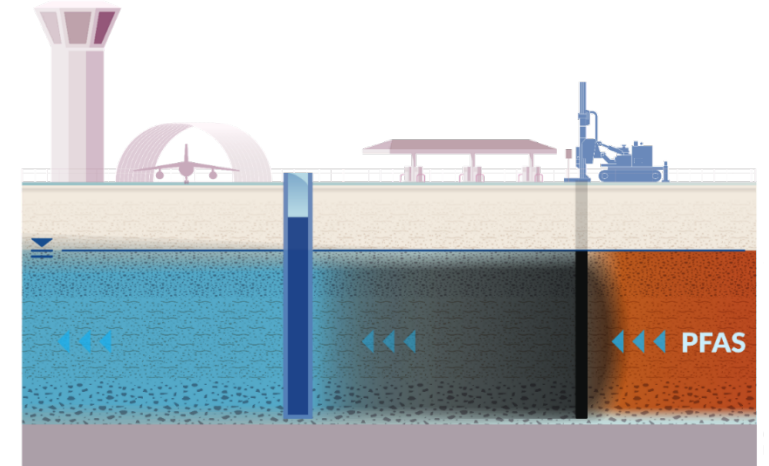


PFAS: The Elephant in The Room

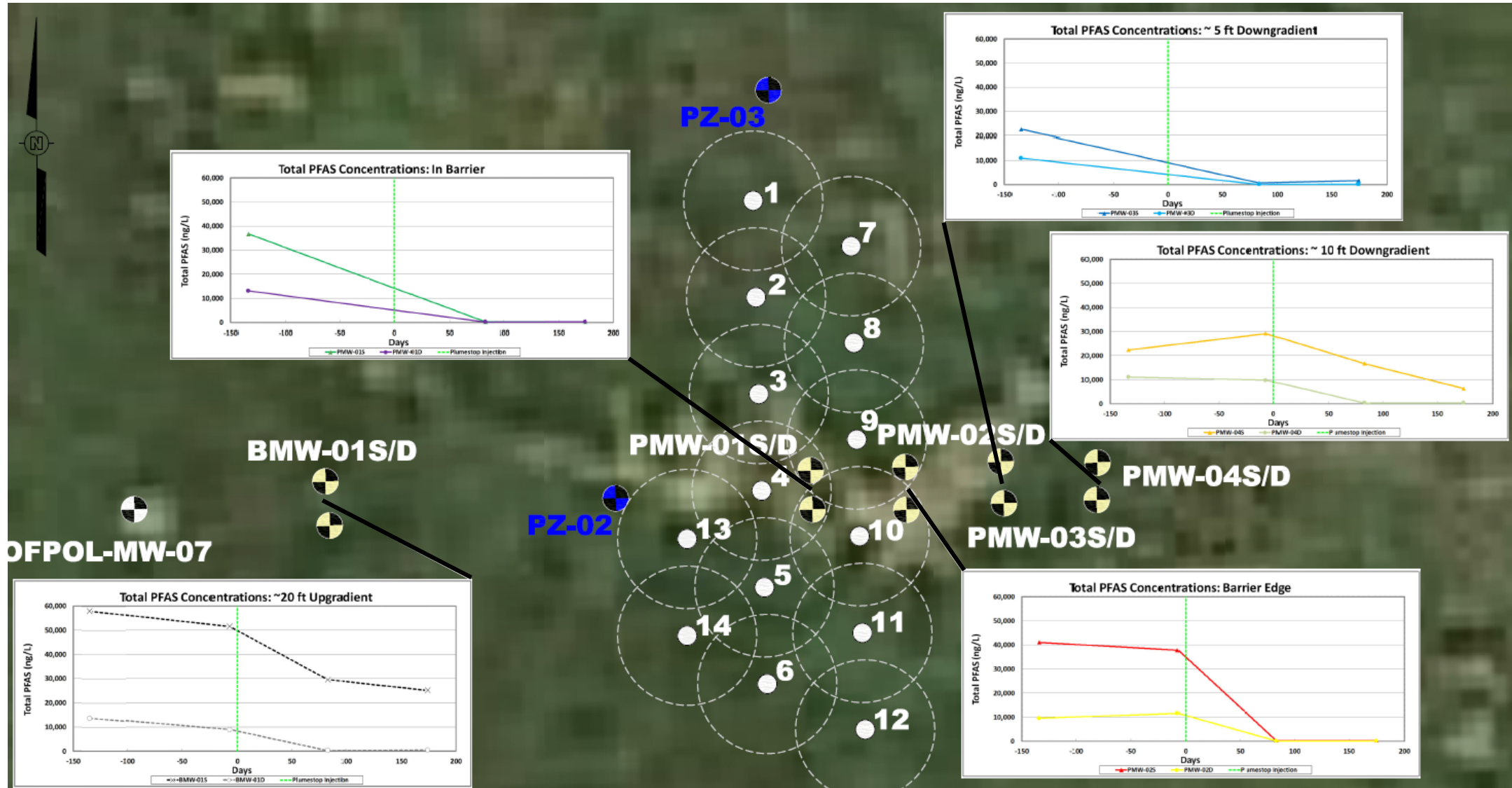
- **REGENESIS manages PFAS risk in-situ** through use of colloidal activated carbon (CAC) injections and chemical adsorption to the carbon matrix from PFAS compounds
- Most responsible parties need a way to manage offsite migration and legal/ecological risk downgradient
- Property line and/or near source barriers of colloidal activated carbon is the most cost-effective method for this task



- **Colloidal activated carbon formulated for subsurface distribution**
 - 1-2 microns (μm) in size
- Mode of action with PFAS
 - Effect: Increases retardation of PFAS plume
 - Natural retardation factors for PFAS: 3-20x
 - Retardation factors achievable with CAC: Orders of Magnitude Higher
 - Sequester for decades



CAC for PFAS



Will They Play Well Together?

Can these technology groups be mixed?

- CAC and S-MZVI have been mixed and co-injected at dozens of sites with a very high success rate for CVOCs and similar chemical groups
- The hexchrome and PFAS mix of contaminants is a more recent issue and due to PFAS, more complicated
- **Need for treatment of comingled Cr(VI) and PFAS**
- **May be accomplished by combined S-MZVI/CAC treatment**
 - Cr (VI) reduced/(co)precipitated by S-MZVI
 - PFAS adsorption by CAC

What potential for interactions do the treatments have?

Initial Work (2022-2023) REGENESIS R&D

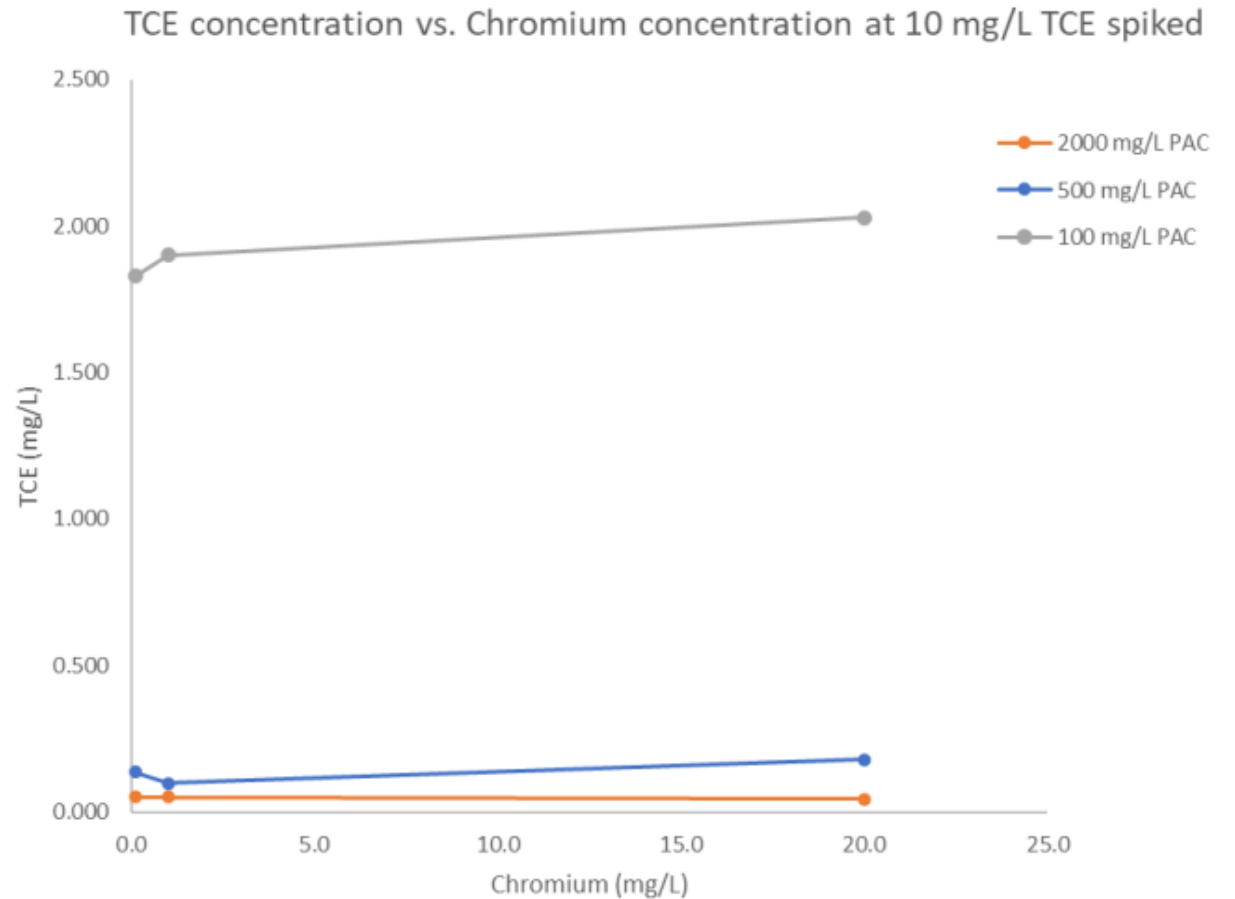
Experimental Questions

- Will Cr(VI) affect PFAS adsorption on AC?
- Will ZVI (or conditions induced by it) impact PFAS sorption?
- Do Cr(VI) treatment technologies affect AC adsorption capability?

Initial Work (2022-2023) REGENESIS R&D

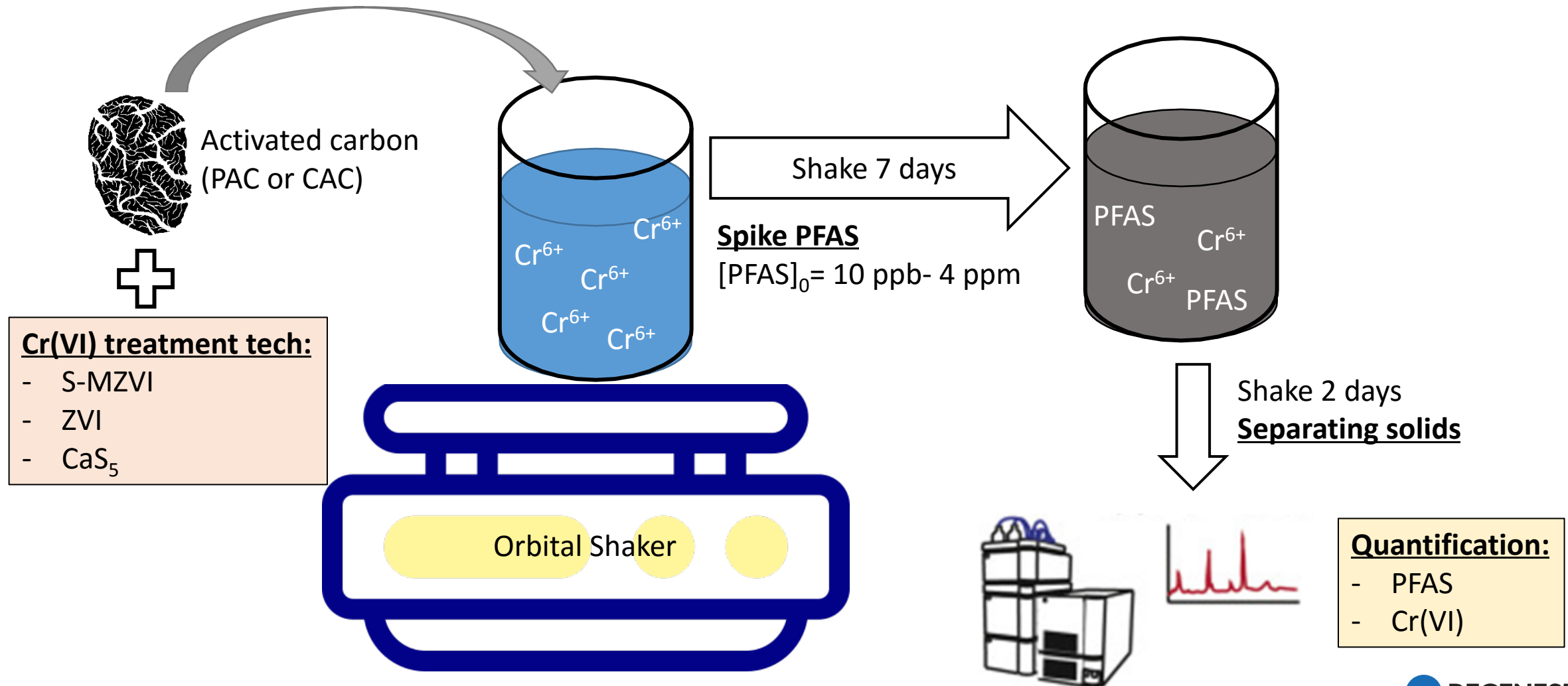
Affect of Cr(VI) on TCE Adsorption

- **TCE adsorption unaffected by Cr(VI)**
- **Cr(VI) has little affinity for AC at relevant pHs**



Cr(VI) and PFAS Bench Scale Study Setup

REGENESIS R&D (2023)



Bench Scale Study Results

Would the presence/conc. of Cr(VI) impact the sorption of PFAS to AC?

Exp conditions			Removal efficiency					
PAC	S-MZVI	Cr(VI)	PFPeA	PFHpA	PFOA	PFHxS	PFOS	Cr(VI)
500 mg/L	0 g/L	0.1 mg/L	36.1%	98.8%	99.9%	99.9%	> 99.9%	45.0%
500 mg/L	0 g/L	20 mg/L	54.2%	99.0%	99.9%	99.9%	> 99.9%	55.9%

1. **No**, increasing Cr(VI) conc did not impact PFAS sorption to AC.
2. Loss of Cr(VI) likely due to conversion to Cr(III)
3. Increasing Cr(VI) conc seems enhanced PFPeA sorption.

Bench Scale Study Results

When S-MZVI reduces Cr(VI), will PFAS sorption be impacted?

Exp conditions			Removal efficiency					
PAC	S-MZVI	Cr(VI)	PFPeA	PFHpA	PFOA	PFHxS	PFOS	Cr(VI)
500 mg/L	0 g/L	20 mg/L	54.2%	99.0%	99.9%	99.9%	> 99.9%	55.9%
500 mg/L	4 g/L	20 mg/L	90.3%	98.7%	99.4%	99.6%	99.1	99.8%

1. **No**, reducing Cr(VI) by S-MZVI did not impact PFAS sorption to AC.
2. Over 99% Cr(VI) got removed when applying S-MZVI.
3. Reducing Cr(VI) by S-MZVI improved PFPeA sorption.

Bench Scale Study Results

Would Cr(VI) treatment tech impact the performance of CAC on removing PFAS?

Exp conditions				Removal efficiency					
CAC	ZVI	CaS ₅	Cr(VI)	PFPeA	PFHpA	PFOA	PFBS	PFHxS	PFOS
500 mg/L	0 g/L	0 g/L	0 mg/L	68.1%	99.3%	99.7%	95.7%	99.0%	>99.9%
500 mg/L	4 g/L	0 g/L	20 mg/L	74.3%	98.6%	98.1%	95.8%	99.6%	99.7
500 mg/L	0 g/L	350 mg/L	20 mg/L	23.9%	89.9%	95.9%	16.3%	95.7%	99.6

1. We added PFBS in this test.
2. In ZVI system, **No!** No significant impact on CAC removing PFAS.
3. In CaS₅ system, **Maybe**. It might reduce PFAS sorption to CAC. But it could be analytical bias.

Can it be Applied at Full Scale?

- Current designs generally separate the components
- Next steps include pilot work, modeling for field setting assessment
- Likely that approach can be coapplied in the same barrier
- No current approach available to remediate PFAS and Cr(VI) in-situ simultaneously to save both time and money for a client. REGENESIS is resolving that issue.



What if CVOCs are Present as Well?

For Cr(VI), we would suggest co-injecting sulfidated micro ZVI (SMZVI) with an ERD electron donor component, for complete and sustained longevity in Cr transformation. This is a common mix for many contaminants with a high level of success.

But... co-injection of an oil-based electron donor doesn't work with colloidal activated carbon needed for PFAS treatment. A new product has been developed by REGENESIS to allow colloidal activated carbon, sulfidated micro ZVI, and colloidal solid electron donor in the same site or locale. Bioaugmentation can be added as well.



AquiFix is a colloidal organic remediation amendment engineered to produce in-situ anaerobic degradation of contaminants

AquiFix contains both fast and slow-release organic compounds

The slow-release solid component degrades to produce fatty acids and molecular hydrogen that sustain long-term (10+ years) bioremediation

AquiFix is fully compatible with, and does not interfere with the performance of complementary remediation amendments including PlumeStop and S-MZVI

Conclusions

- Clearly an emerging problem related to and within an emerging problem group
- Internal goals are to further the understanding of the relationship between Cr(VI), PFAS, ZVI, and CAC
- Field application is a next logical step, several options on the horizon



Acknowledgement



Questions?



Sophia Nguyen, MS

Sr. Research Associate/Analytical Chemist

REGENESIS