Ex Situ Stabilization and Solidification (S/S) of PFAS-Contaminated Materials

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Why stabilize (sequester) PFAS?

- Landfills are secure PFAS repositories
- No feasible destruction technologies
- Leachates are discharged to POTWs (no treatment!)
- On-site leachate treatment only collects/concentrates PFAS
    - PFAS-laden residuals disposed of in landfill

WE CAN STABILIZE PFAS!

- I've done it for 6 years!
  - ➢Can reduce PFAS concentrations in leachate to below DW standards
- Sörengård et al. (2019) & Hale et al. (2017)
  - ➢Leaching of PFOS & PFOA reduced by 98% by adding 2% AC with cements.
- Sörengård et al. (2021)
  - ➢Pilot- and lab-scale studies: reduced leaching of PFOS & PFOA more than 97%.
- McDonough et al. (2022)
  - ➢Bench- & field-scale data show >99% decrease in total PFAS mass leachability
- Cai et al. (2022)
  - ➢Increasing ***I*** and cation valency enhances PFAS sorption onto solids

Ex Situ (S/S)

In Situ (ISS)

Stabilization/Solidification (S/S)

- Stabilize: transfer from aqueous to solid phase.
- Solidify (encapsulate?):
- Performance criteria:
  - (1) decrease K
  - (2) increase strength (enhance handling)
  - (3) decrease RATES of leaching

Disadvantages of S/S

- Not Permanent!
  - Cement will disintegrate,
  - PFAS will desorb
- S/S Amendments INCREASE VOLUME of waste!

Materials & Methods

Lessons Learned: Sorbents

- Clays and Minerals:
  - Iron oxide (FeO) powder, aluminum hydroxide (Al(OH)), montmorillonite, quaternary ammonium-modified smectite
  - Don’t mix well
    - Clump and form pockets within cementing agents.

- Organic (AC & Biochar):
  - perform the same!

S/S Amendments (Approximate Costs)

Binders/Cements

- Ordinary Portland Cement (PC) ($150/ton)
- Class C Fly Ash (FA) ($150/ton)
- Ground-Granulated Blast-Furnace Slag (GGBS) (140/ton$)

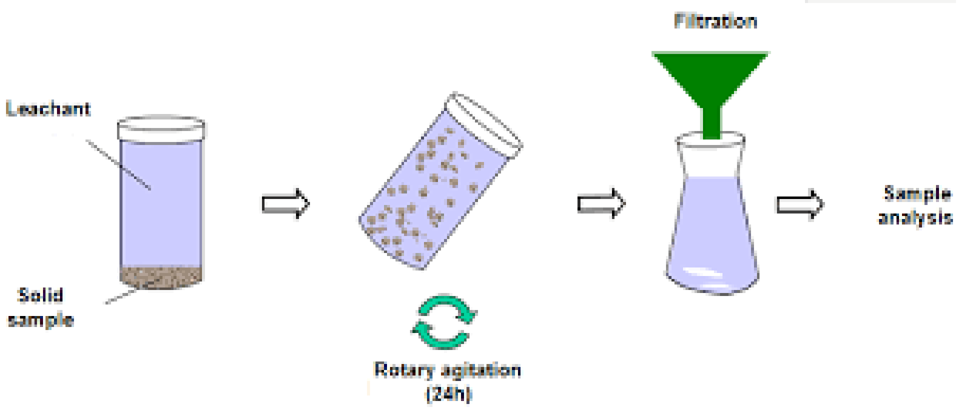
Sorbent

- Biochar & Activated Carbon ($1,500-$2,000/ton)

Lessons Learned: Leaching procedures

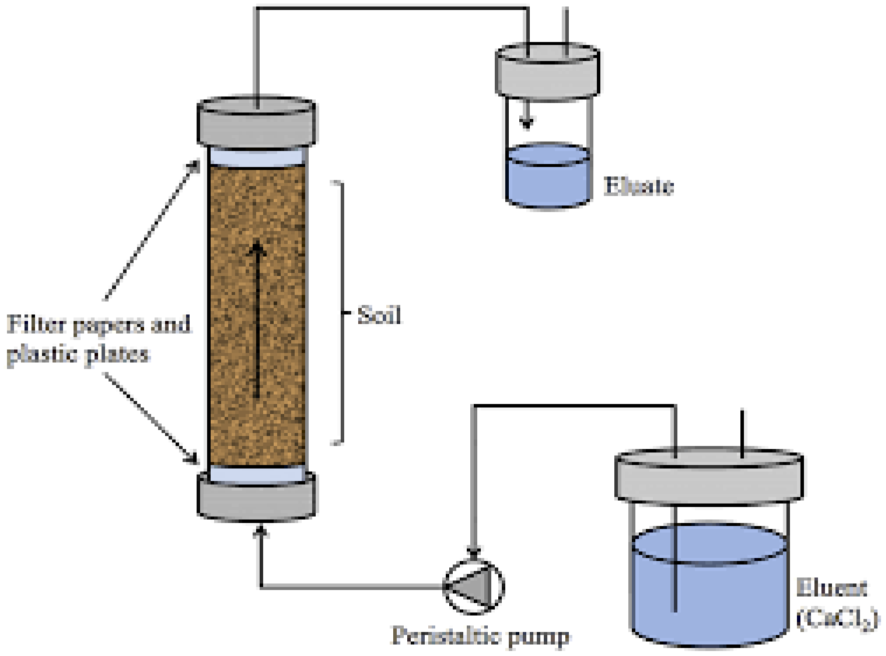
1311 (TCLP)-Toxicity Characteristic Leaching Procedure (CH_3COOH) **Coming Soon……PFOA, PFOS, PFBS, & GenX**

1312 (SPLP)-Synthetic Precipitation Leaching Procedure (H_2SO_4 & HNO_3)

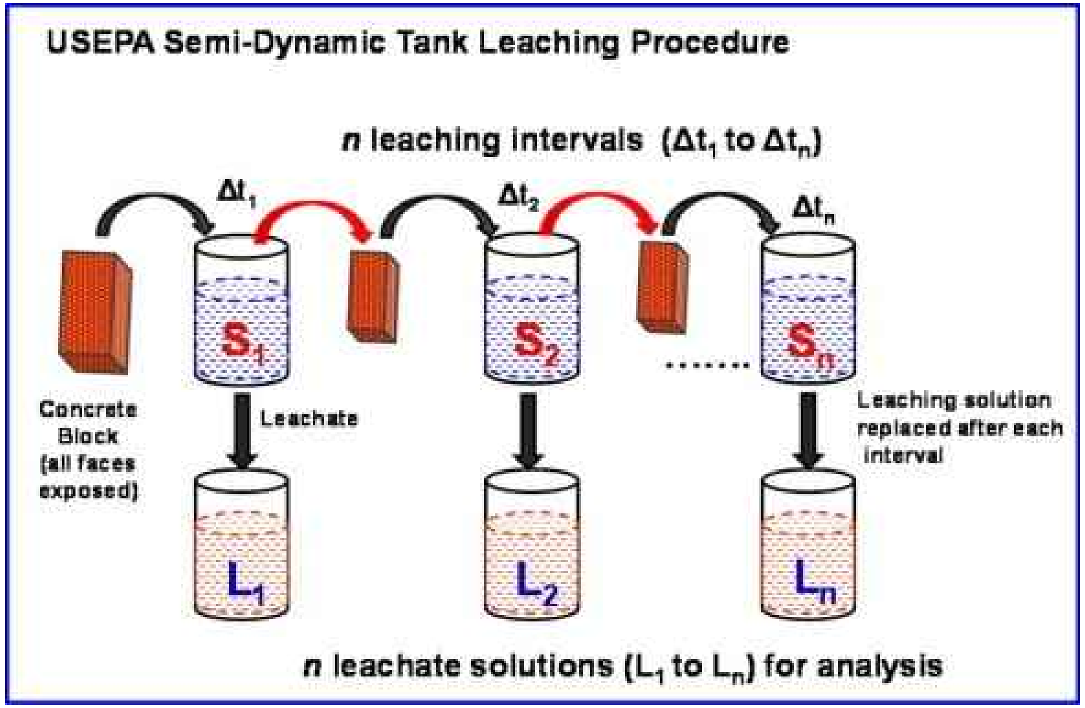


LEAF Methods

1314 – **Vary Liquid:Solid Ratio in Using an Up-Flow Percolation <u>Column</u> Procedure**



1315 – **<u>Monolith</u> or Compacted Materials with a Semi-Dynamic Tank Leaching Procedure (similar to ANSI/ANS-16.1 (ANS, 2003).**



PFAS Wastes

- SOLID wastes:
  - Spent activated carbon
  - Biosolids
  - Sludge from leachate pre-treatment
  - Soils, sediments, sludges (source removal)

- LIQUID wastes:
  - AFFF
  - Foam Fractionation concentrate
  - Concentrate from RO, NF, UF
  - Condensate from thermal desorption of soils

PFAS Analyses

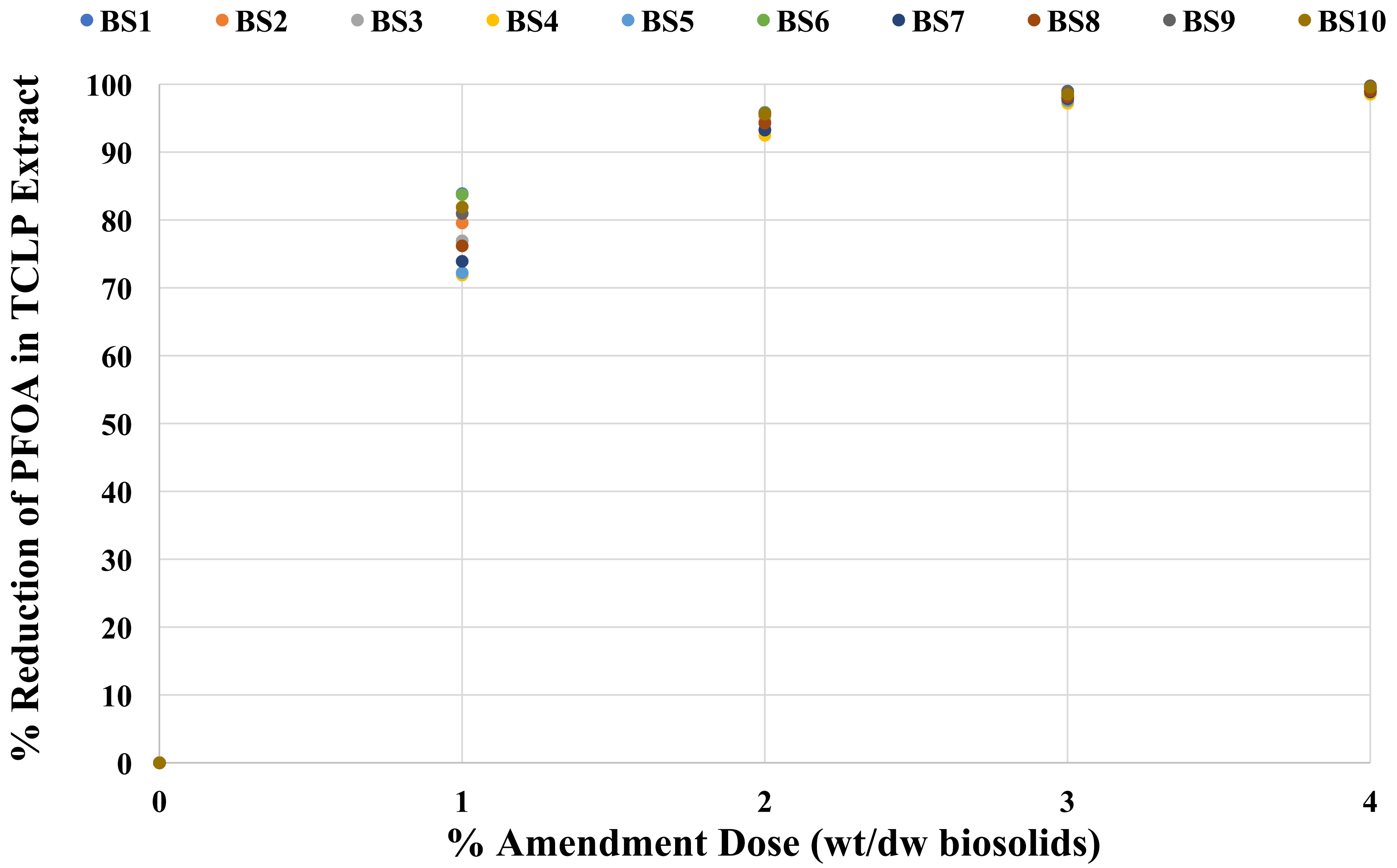
- **ASTM-D7968** for Soils, Sludges & Biosolids:
- **ASTM-D7979** for TCLP & SPLP Leachate

Results….

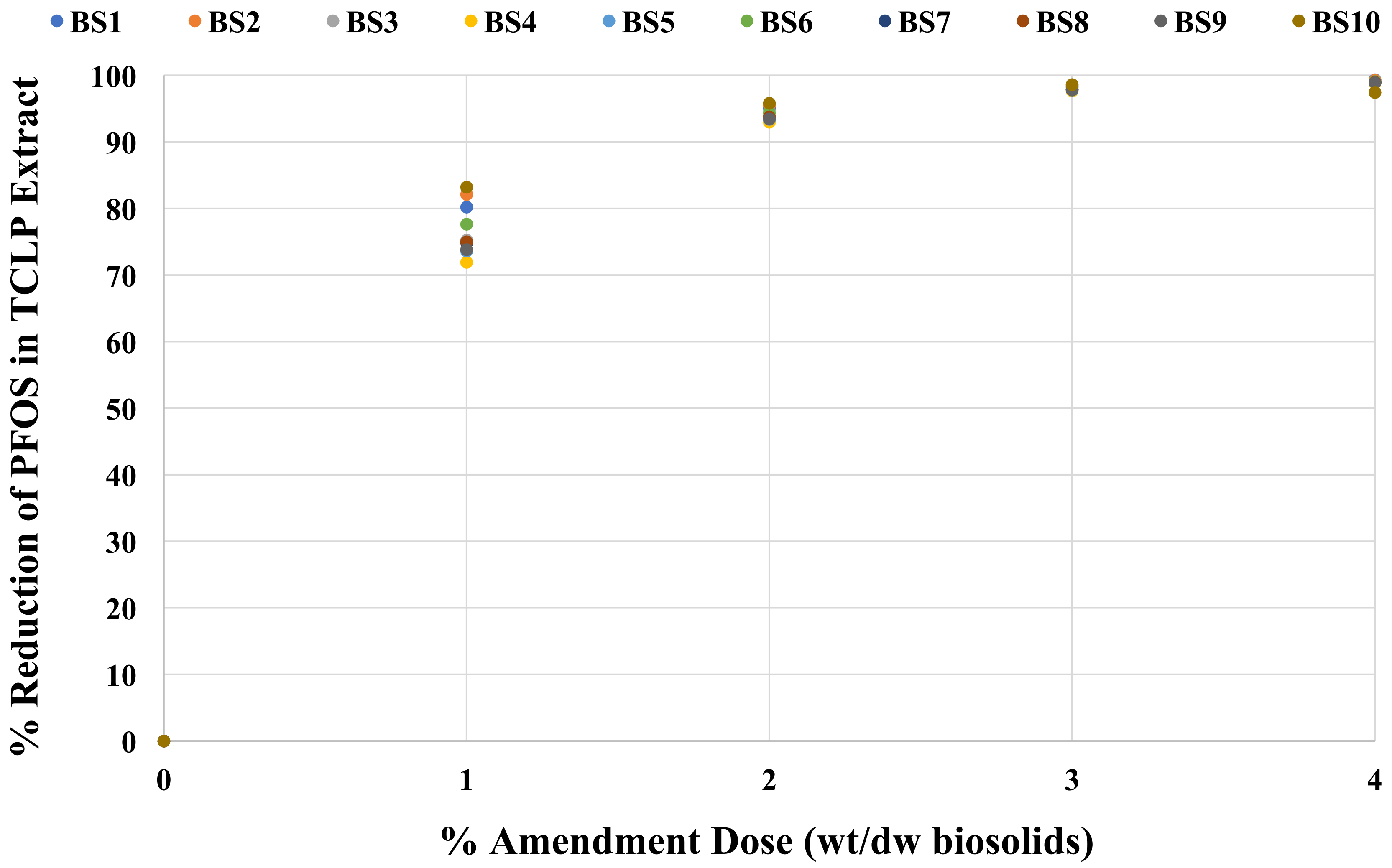
Baseline Properties: Biosolids

Biosolid	PFOA (ng/Kg)	PFOS (ng/Kg)
BS1	0.0083	0.0414
BS2	0.0069	0.0433
BS3	0.0143	0.038
BS4	0.0046	0.0272
BS5	0.0078	0.0321
BS6	0.0122	0.0338
BS7	0.00088	0.0057
BS8	0.00054	0.0026
BS9	0.0057	0.0379
BS10	0.0027	0.0142

Dose-Response: PFOA in Biosolids



Dose-Response: PFOS in Biosolids

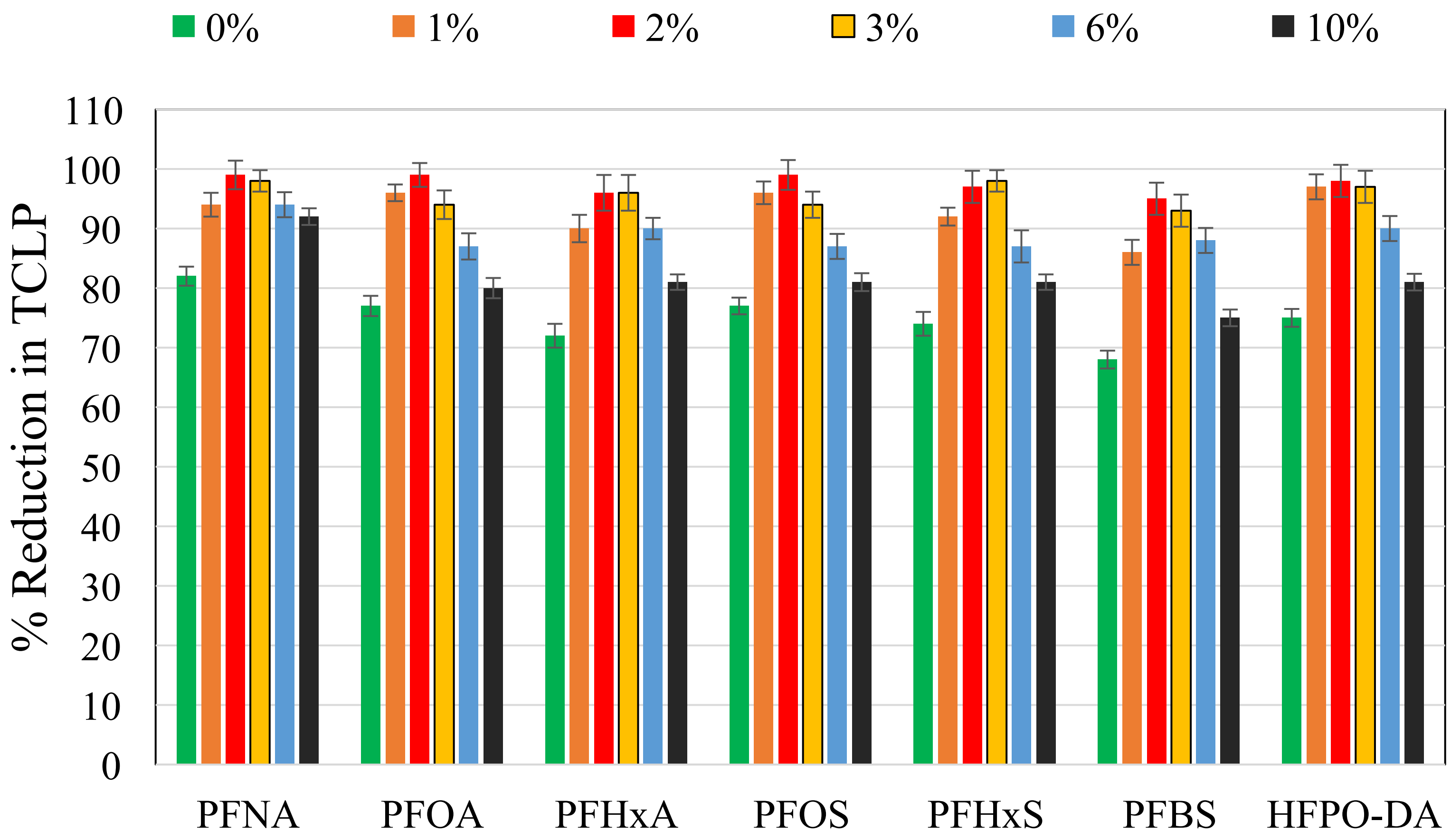


RO Concentrate: PAC Dose vs. Strength

%PAC/cement*	UCS (psi)
0	820
1	1,030
2	1,210
3	730
6	420
10	170

2% to 3% activated carbon increases strength (Na et al., 2021).

RO Concentrate: varying PAC dose



>2% PAC/cement increases leaching (Crane et al., 2014; Srivastava et al., 2016)

Spent GAC

Analyte	Abbreviation	Perfluorinated Carbon #	Avg. TCLP Untreated (ng/L)	Avg. TCLP 15% Dose (ng/L)	MI DW MCLs (ng/L)
Perfluorononanoic acid	PFNA	C9	4,135	4	6
Perfluorooctanoic acid	PFOA	C8	8,105	**11**	**8**
Perfluorohexanoic acid	PFHxA	C6	5,610	210	400,000
Perfluorooctanesulfonate	PFOS	C8	134,100	12	16
Perfluorohexanesulfonate	PFHxS	C6	22,440	32	51
Perfluorobutanesulfonate	PFBS	C4	3,145	41	420
Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA	C6	14,385	88	370
		Σ 28 PFAS (ng/L)	**349,899**	**673**	

Miscellaneous Observations

1. Lime converts precursors to PFAAs
   - $CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)}$ + Heat + High pH
   - Confirmed with TOP assays

2. Higher PFAS concentrations in SPLP than TCLP
   - Sulfate anion (SO_4^{2-}) forms complexes with cured cement, which increases porosity and surface available for leaching.

Conclusions

- S/S is effective for PFAS-contaminated materials (solid & liquid)
  - Decreases RATES of PFAS leaching
  - Decreases K
  - Increases strength
- Adding small amounts of carbon enhances treatment.
- SPLP leaches more PFAS than TCLP.
- Recipes and appropriate doses should be determined for each individual waste and/or material.

Literature

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Questions

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