Evaluation of a Solidification/Stabilization Process for PFAS Contaminated Soils

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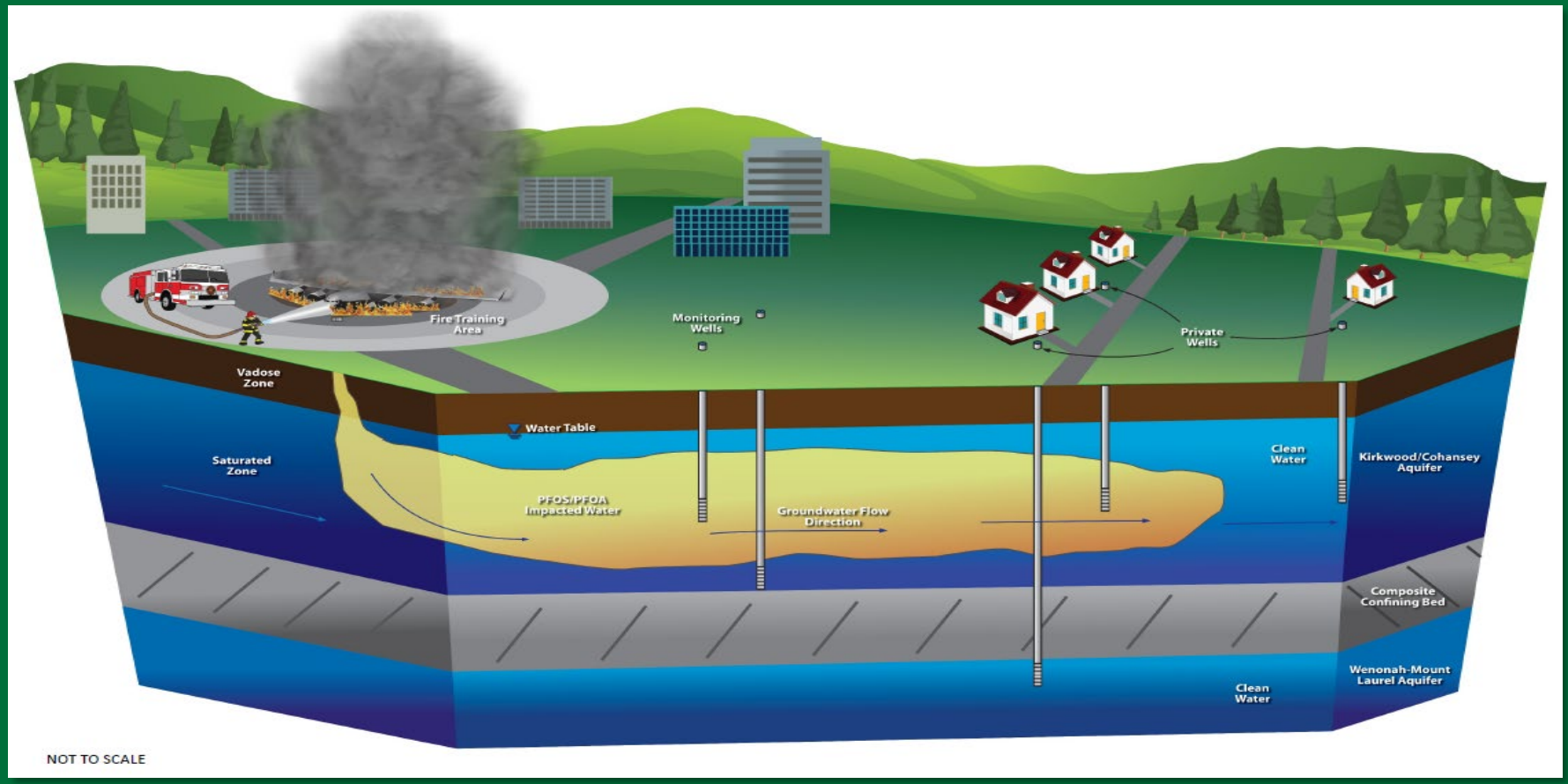
Remedial Action Objective: Minimize PFAS Contaminated Soils Contributing to Groundwater Contamination



Definitions of Solidification/Stabilization

"***stabilization***" – conversion of waste to a less soluble, less mobile, or less toxic form (the physical nature may not change)

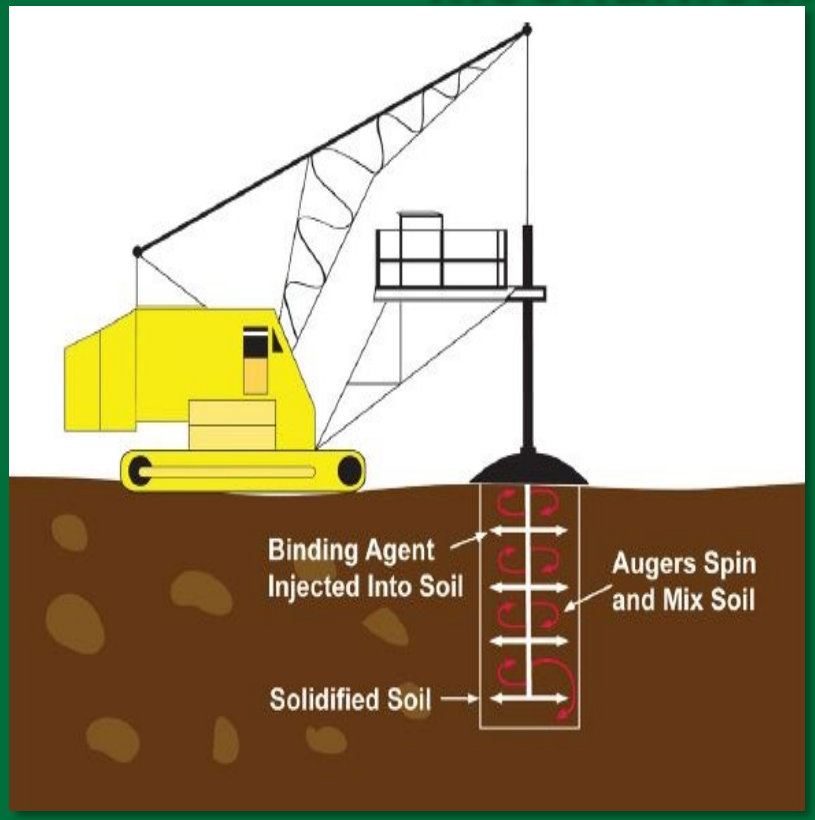
"***solidification***" – encapsulation of the waste into a monolithic solid with structural integrity (micro-encapsulation and macro-encapsulation)

"immobilization" (or "fixation"): either solidification or stabilization (or both)

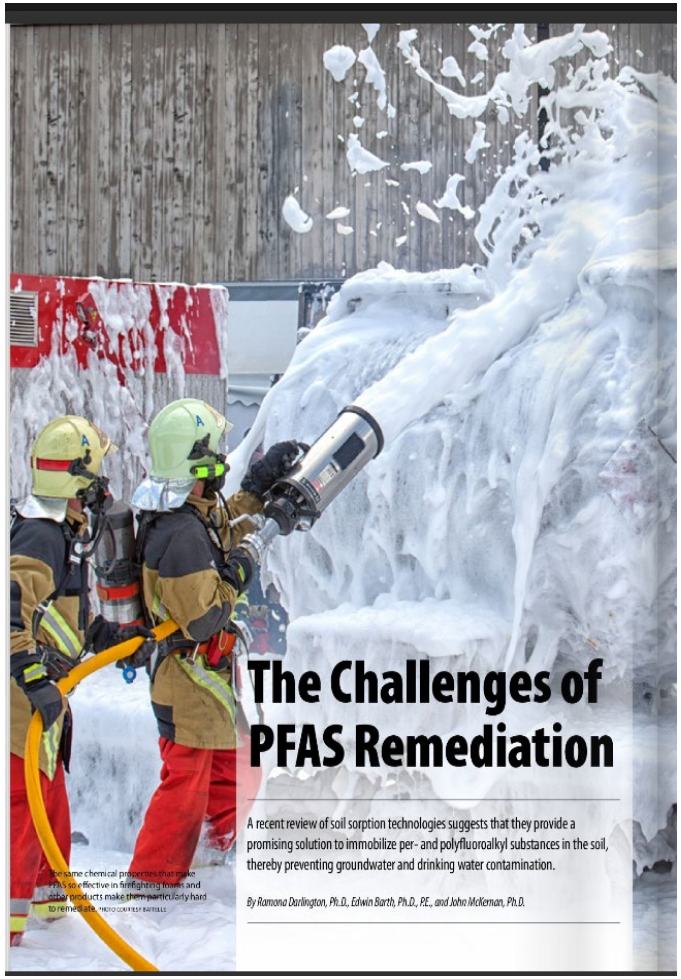
- related remediation processes might fit the term "immobilization"

- *reference:* Barth, E., P. Bishop, P. Colombo, J. Conner, and J. Buelt. 1994. Innovative Site Remediation Technology Monograph Series. Solidification/Stabilization. Volume 4. American Academy of Environmental Engineers and Scientists Monograph on Solidification/Stabilization. (EPA 542-B-94-001)

In-situ Solidification/Stabilization (ISS) Mechanical Delivery System



Literature review/experience



- **Pre-2019:** Limited information on immobilization processes for PFAS contaminated soils

- **Post-2019:** Increase in relevant lab, pilot, and field evaluations; however many articles still are deficient in:
- peer-review
- quality control
- description of chemistry/name of sorbent
- quantity of materials used
- consistency in leaching protocols

- *reference:* Darlington, R., E. Barth, and J. McKernan. 2018. The Challenges of PFAS Remediation. Military Engineer. 110(712): 58-60

Experimental design approach: Phases I and II

- **Phase I:** Compare the sorptive properties of five viable sorbents (plus a control sorbent) for a dilute PFAS solution involving six PFAS compounds
- **Phase II:** Evaluate the best performing sorbent (in Phase I), with and without cement addition, to immobilize two different PFAS contaminated soils (obtained from PFAS contaminated sites).

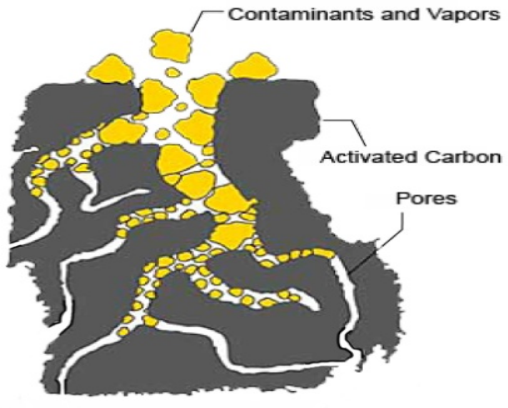
- *reference:* Barth, E., J. McKernan, D. Bless, and K. Dasu. 2021. Investigation of an Immobilization Process for PFAS Contaminated Soils. Journal of Environmental Management 296 113609; https://doi.org/10.1016/j.jenvman.2021.113609

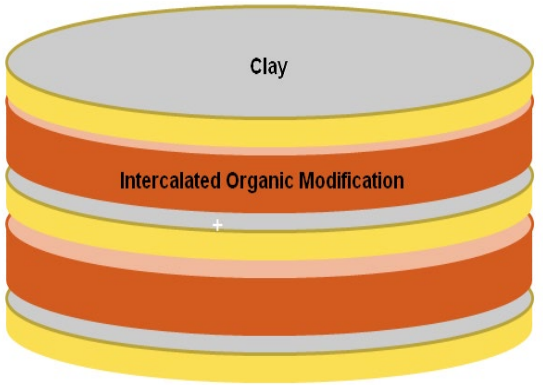
PFAS compound analysis

- Department of Defense (DoD) Quality Systems Manual (QSM) version 5.1 criteria: liquid chromatography tandem mass spectrometry (LC—MS/MS)
- AB Sciex QTRAP 5500 Triple Quadrupole MS
- HPLC equipped with PEEK™ tubing and solvent delay column
- Negative electrospray ionization mode with multiple reaction monitoring (MRM)
- Column: Kinetex 2.6 µm C18 100 A 50 x 4.6 mm
- Run time: 10 minutes
- Quantitation Method: Isotope Dilution
- Detection Limits range (liquids): 0.14 – 1.36 ng/l
- Detection Limits range (soils): 0.19 – 2.31 ng/g
- acceptable surrogate recoveries of spiked samples

Phase I: Sorbents evaluated

- Granular Activated Carbon (GAC)
- Modified Clay
- Activated Carbon/Clay Blend
- Biochar (low temperature)
- Biochar + Iron Blend (low temperature)
- Control (Ottawa sand)





Phase I: Sorbent physical characteristics

Sorbent	BET Surface Area (m^2/g)	Micropore Surface Area (m^2/g)	Pore volume (mL/g)	pH of solution @ day 20 - after sorption kinetic study
GAC	888	601	0.51	6.2
AC/Clay Blend	442	182	0.31	5.2
Modified Clay	0.5	0.1	ND	5.2
Biochar-Fe	0.2	1.4	ND	4.6
Biochar	348	273	0.19	7.0

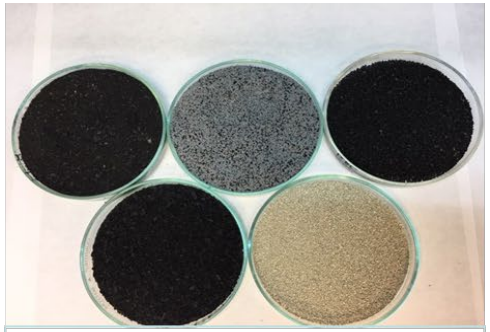
ND: Not Detected

Phase I: Dilute PFAS solution for sorption studies

- non-buffered, dilute PFAS solution (500 ug/L each) for 6 selected short and long chained PFAS compounds (3,000 ug/L total); ranging from chain lengths from C4-C9:
- PFBA (C4-short)[1]
- PFBS (C4-short)
- PFHxA (C6-short/long)
- PFOA (C8-long)
- PFOS (C8-long)
- PFNA (C9-long)

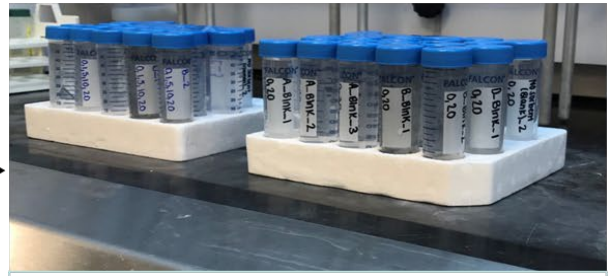
[1]data later excluded due to background contamination

Phase I: Sorbent screening isotherm studies



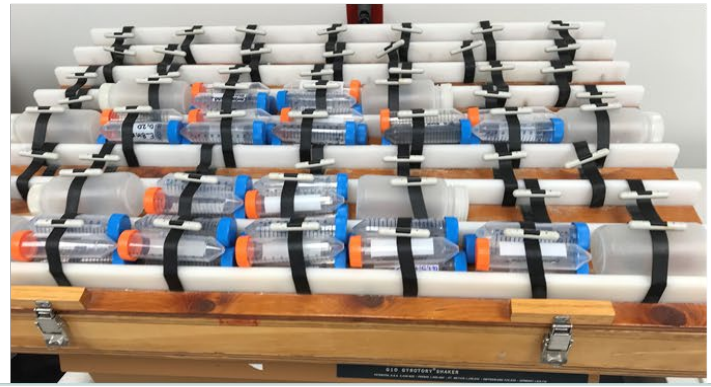
5 sorbents selected

5.0 mg: 50 mL sorbent to solution
0.01 M NaCl background electrolyte



Triplicates for all treatments including blanks and controls

Spike PFAS target analytes
Initial conc. 500 µg L^{-1}



Shaked at 125 rpm, 23±1ºC and sampled over 0-20 d

Sample dilution
Surrogates & Internal standard spiked

Analysis on LC-MS/MS

Phase I: Sorption kinetic and partitioning parameters

- Pseudo second order kinetic model: $\frac{t}{C_S} = \frac{1}{kC_e^2} + \frac{t}{C_e} = \frac{1}{v_0} + \frac{t}{C_e}$
- C_s: analyte sorbent concentration at time t
- C_e: analyte sorbent concentration at equilibrium
- K: rate constant
- V_0: initial adsorption rate

- C_e: GAC relatively higher values for PFBS (C4), PFHxA (6C), PFOS (C8); similar to carbon/clay blend and modified clay values for PFOA (C8) and PFNA (C9); two biochars and control exhibited much lower values

- V_o: activated carbon/clay blend higher for all the PFAS compounds in solution

Phase I: Partitioning coefficients (log Kd in L/Kg)

Sorbents	PFHxA	PFOA	PFNA	PFBS	PFOS
GAC	5.8	7.4	NC	6.0	NC
Activated carbon-clay blend	4.1	5.6	5.5	4.0	5.1
Modified clay	4.0	5.3	6.4	4.7	6.1
Biochar	3.5	3.8	4.4	2.6	4.4
Fe amended Biochar	3.2	3.1	3.2	3.1	2.8
Ottawa Sand (control)	2.9	3.1	2.9	2.7	3.5

NC: Not calculated due to non-detect concentration of analyte in the solution

Phase II: Contaminated soil properties

Properties	Soil 2	Soil 8
Textural Classification	Sand	Sandy/Clay Loam
Soil pH	5.7	8.1
% Moisture	7.8	6.5
% Organic matter	0.3	1.0
Cation Exchange Capacity (CEC) meq/100g	2.6	71.6
Ca (in ppm)	250	13,150
Mg (in ppm)	15	650

Phase II: Soil concentrations (ng/g dry weight)

Analytes	Soil 2	Soil 8	Analytes	Soil 2	Soil 8
PFBA	ND	91	NEtFOSAA	ND	ND
PFPeA	ND	296 D	PFOSA	979 D	907 D
PFHxA	ND	650 D	PFBS	ND	137 D
PFHpA	ND	109	PFPeS	ND	210 D
PFOA	20	751 D	PFHxS	10	2,363 D
PFNA	ND	11	PFHpS	ND	177 D
PFDA	31	6	PFOS	2,282 D	13,676 D
PFUnA	21	ND	PFNS	100	26
PFDoA	17	ND	PFDS	87	7
PFTrDA	5	ND	4:2FTS	ND	118 D
PFTeDA	ND	ND	6:2FTS	7	3,839 D
NMeFOSAA	37	ND	8:2FTS	431 D	1,009 D

LOD: 0.5 – 2.5 ng/g
LOQ: 5 ng/g
Data Qualifiers:
ND– Analyte not detected
D - Dilution run

Phase II: Immobilization Mix "Recipe"

Treatment	Sorbent	Cement	Water
Sorbent only	4%	0%	0%
Sorbent + cement	4%	15%	30%

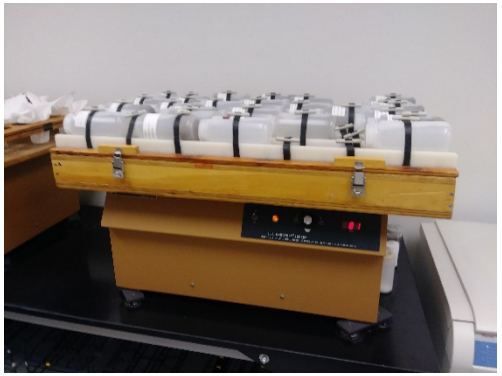
Phase II Leaching protocol: EPA Method 1312

Soil/Sorbent/Binder Treatments in triplicates

Soil/Binder:
Soil + Sorbent(4%)

Soil/Sorbent/Binder:
Soil + Sorbent(4%) + Binder(15%) + Millipore water (30%)

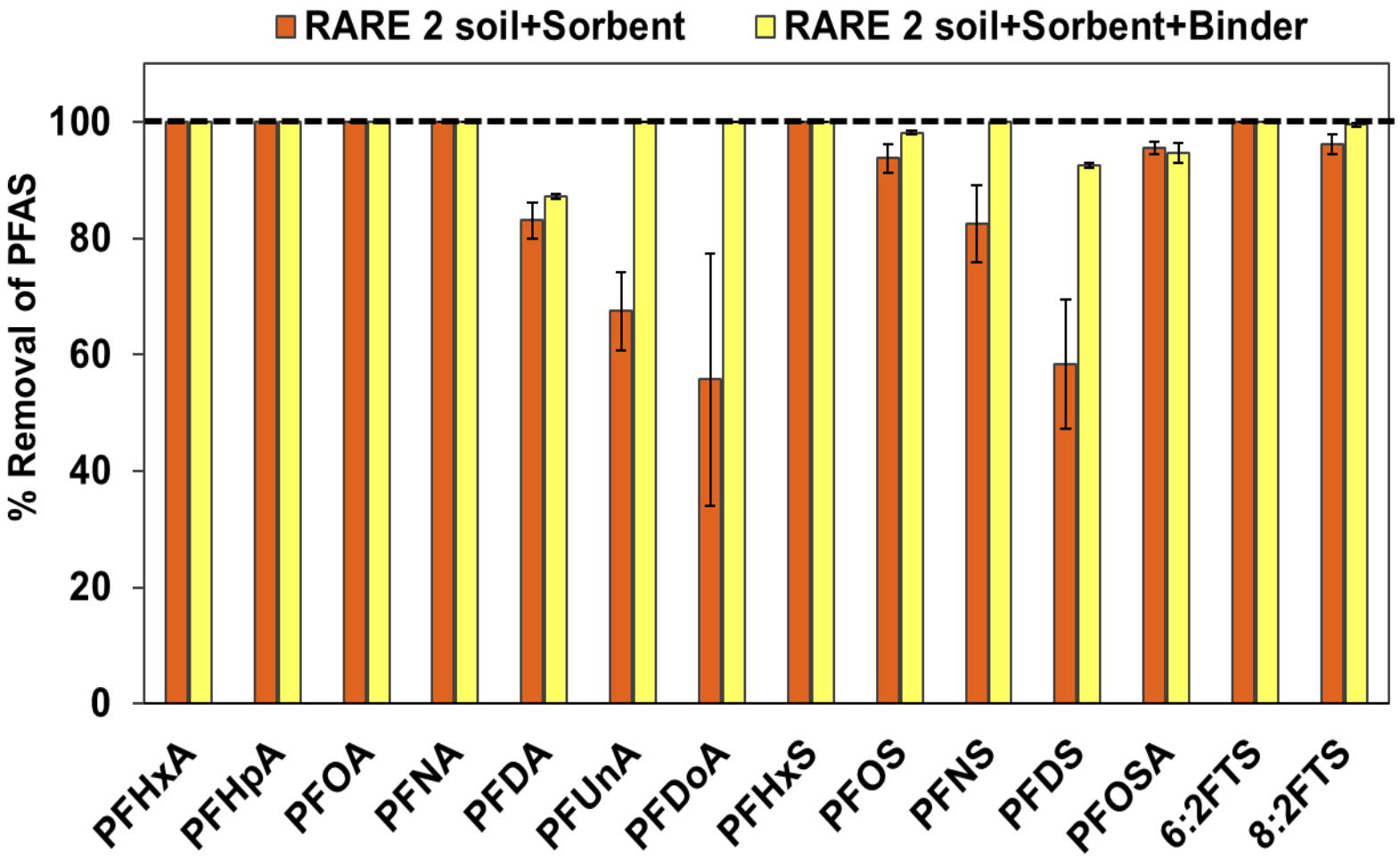
1:20 dilution, stationary incubation for 21 days; temperature 22 ± 3 ° C



Overnight extraction using pH 4.2 ± 0.05 H_2SO_4/HNO_3 (60:40) extraction solution

Sample dilution
Surrogates & Internal standard spiked

Phase II: % Immobilization results (Soil 2)

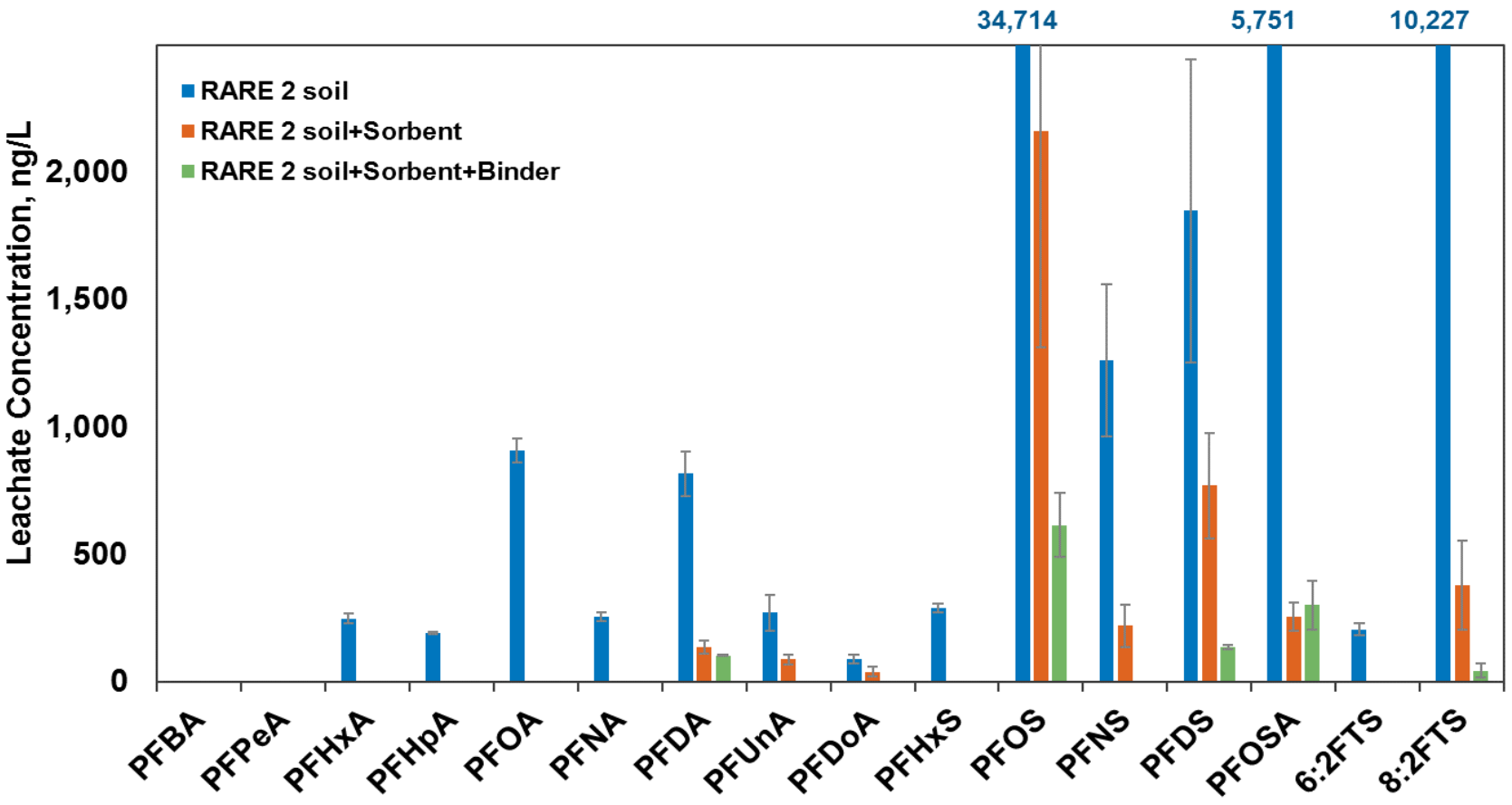


Phase II: % Immobilization results (Soil 2)

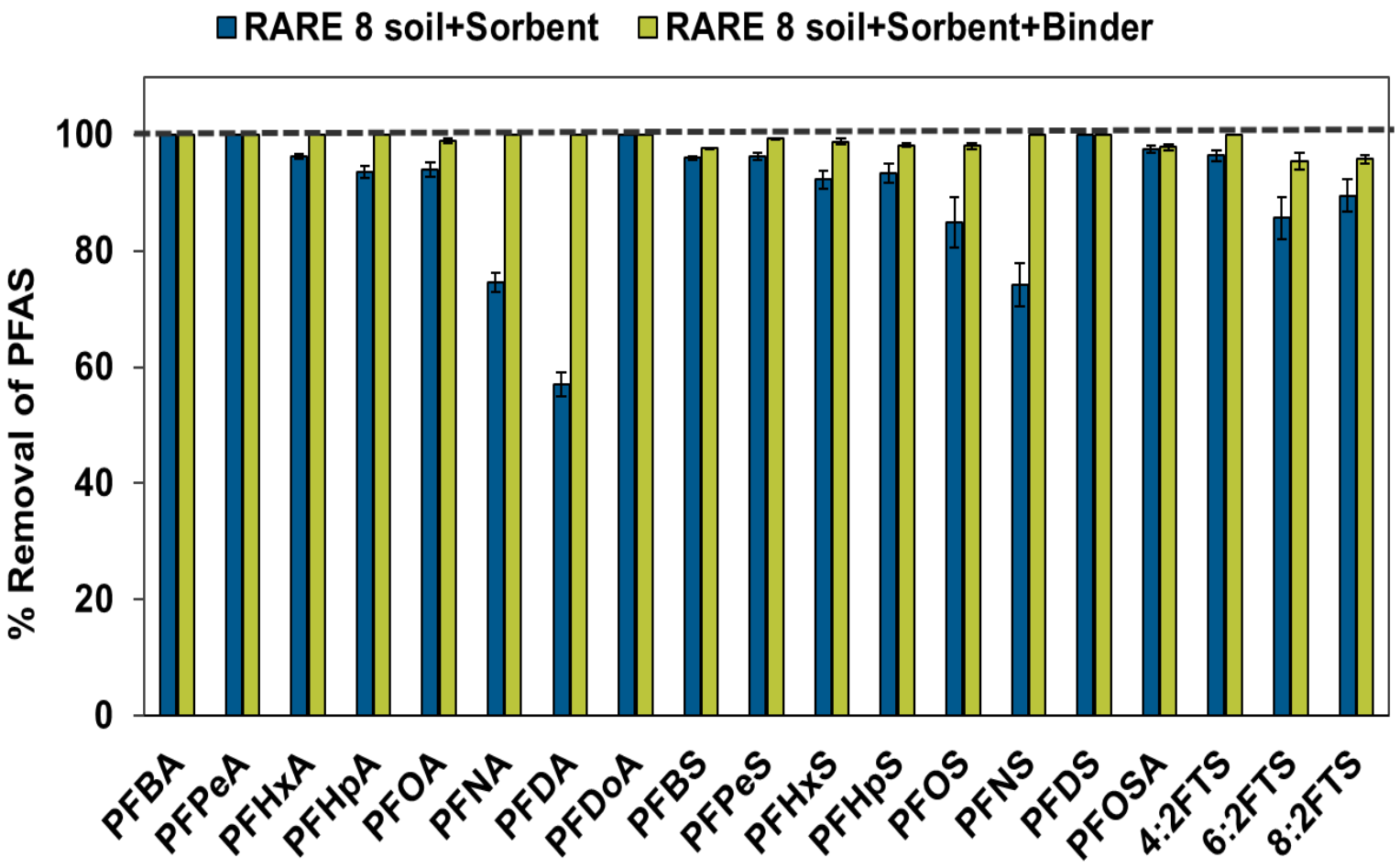
- 99.9% SPLP reduction: PFHxA, PFHpA, PFOA, PFNA, PFUnA, PFDoA, PFHxS, PFNS, 6:2 FTS

- <99.9% SPLP reduction: 8:2 FTS (99.5%), PFOS (98.2%), PFOSA (94.7%), PFDS (92.5%), PFDA (87.1%)

Phase II: SPLP leaching results (Soil 2)



Phase II: % Immobilization results (Soil 8)

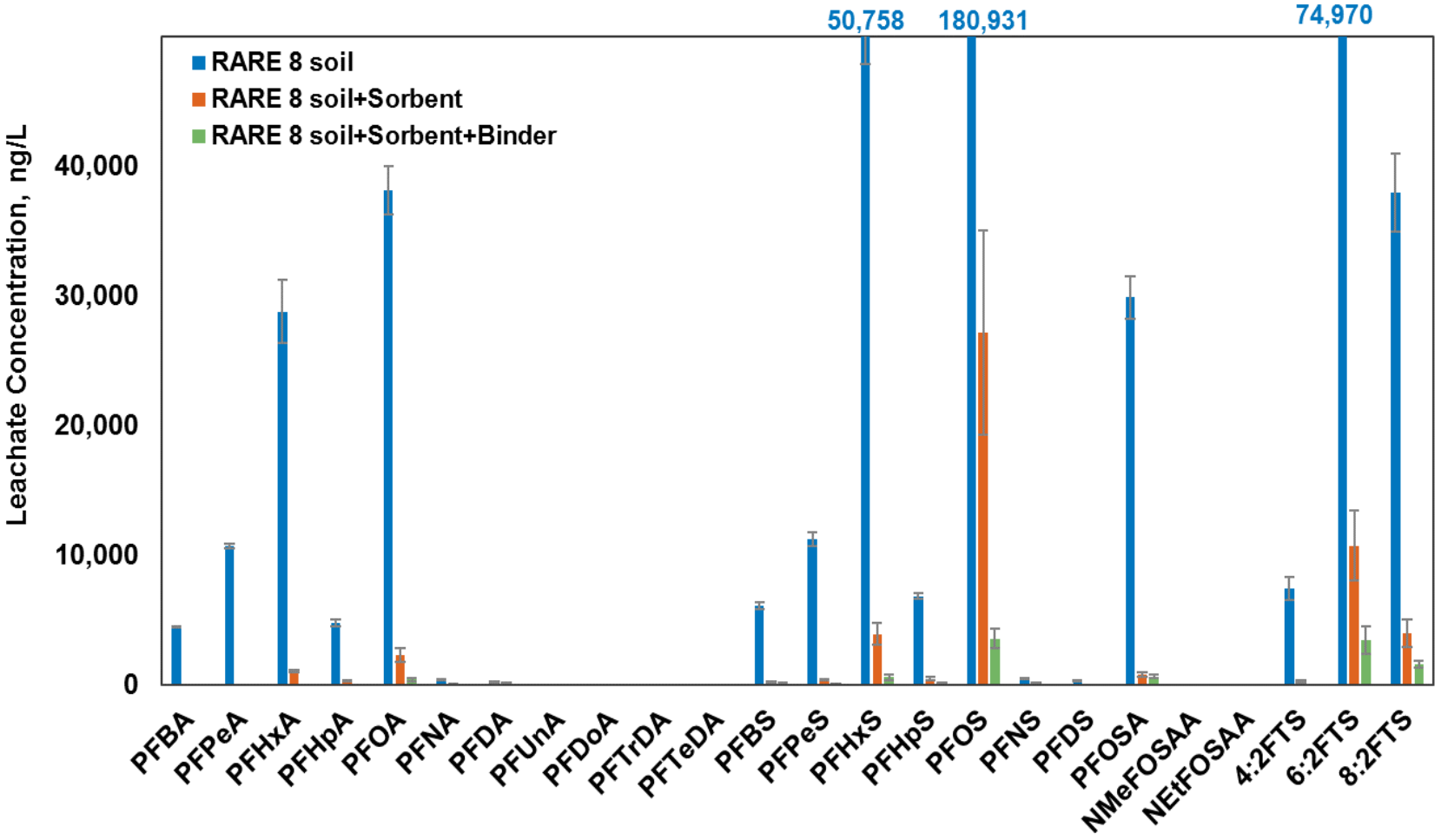


Phase II: % Immobilization results (Soil 8)

- 99.9% SPLP reduction: PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFDoA, PFNS, PFDS, 4:2 FTS

- <99.9% SPLP reduction: PFPeS (99.3%), PFOA (98.9%), PFHxS (98.8%), PFHpS (98.2%), PFOS (98.0%), PFOSA (97.8%), PFBS (97.7%), 8:2 FTS (95.7%), 6:2 FTS (95.4%)

Phase II: SPLP leaching results (Soil 8)



Conclusions from limited, laboratory-scale study

- GAC was slightly more effective than either the modified clay and the activated carbon/clay blend in the sorption studies involving a dilute solution of six selected PFAS (C4-C9) compounds, using the amount sorbed as the only deciding factor (not the kinetics)
- A treatment process involving GAC sorbent and cement binder (stabilization/solidification) resulted in an overall % immobilization range for detected (SPLP) leachable PFAS compounds: 87.1% -99.9%; as the addition of cement (binder) to the soil and sorbent mixture further reduced SPLP leaching concentrations for many of the PFAS compounds in the contaminated soils
- Although there was a substantial % immobilization of PFAS compounds, PFAS concentrations in the post-treatment (detectable) SPLP leachate values were greater than proposed health-based criteria
- In general, PFAS compounds are not intended to be destructed or modified in immobilization processes (effects of specific binders, pH, and elevated temperature are not known)

Acknowledgements

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