Pilot Scale Ball Milling of PFAS Impacted Soil from a Firefighting Training Area – Key Operational Parameters

Nicholas Battye, **David Patch**, Natalia O'Connor, Dylan Roberts, and Kela Weber (Royal Military College of Canada, Kingston, ON, Canada)

Lauren Turner and Bernard Kueper (Queen's University, Kingston, ON, Canada)

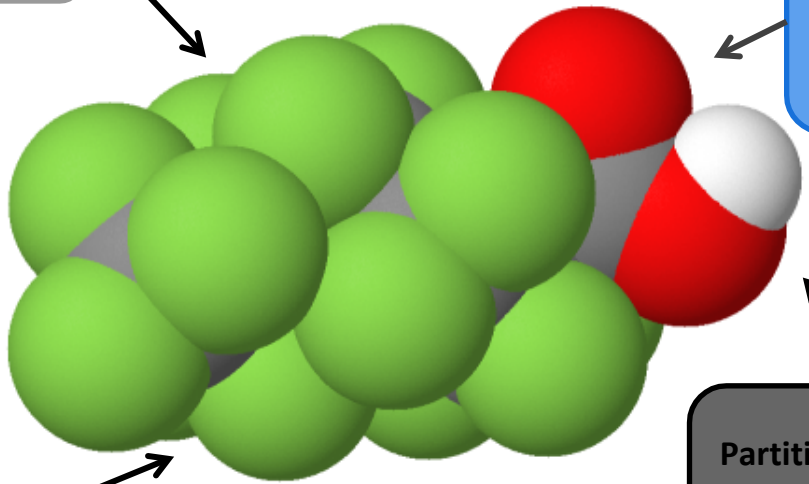
Stefano Marconetto and Tony Lyon (WSP Golder, Ottawa, ON, Canada)

Brenda Harris (Sarnia Technology Applications & Research, Imperial Oil Ltd., Sarnia, ON)

Why Are They Hard to Destroy?

Electron-dense shell resists chemical attack

Variable PFAS chemistry further increases complexity



Partitioning complexities require multi-media applications

Bond energy resists thermal attack

Objective

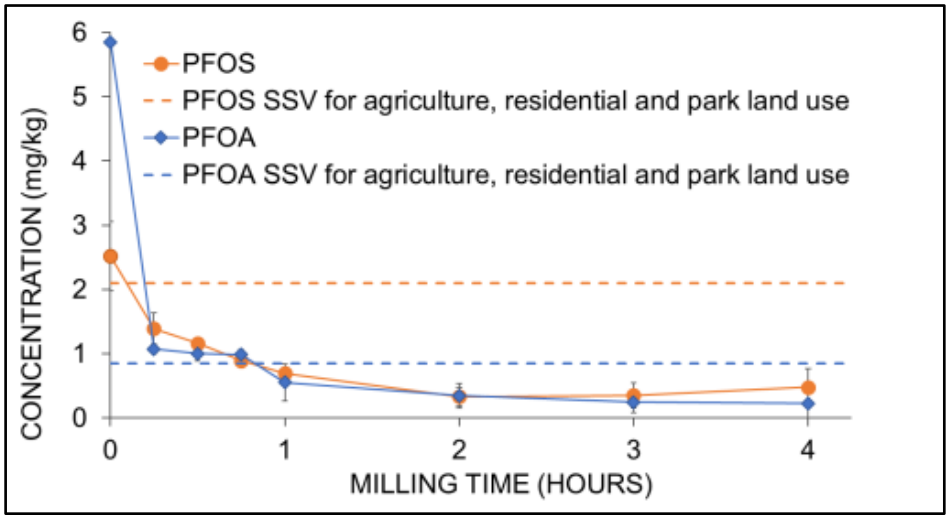
Can PFAS be destroyed by ball milling in environmentally relevant earth materials in realistic site conditions?

PFOS and PFOA Spiked Sands

AFFF Spiked Sands

AFFF impacted soils from a Canadian FFTA

Success at Lab Scale



*SSV = Canadian guidance value 2018

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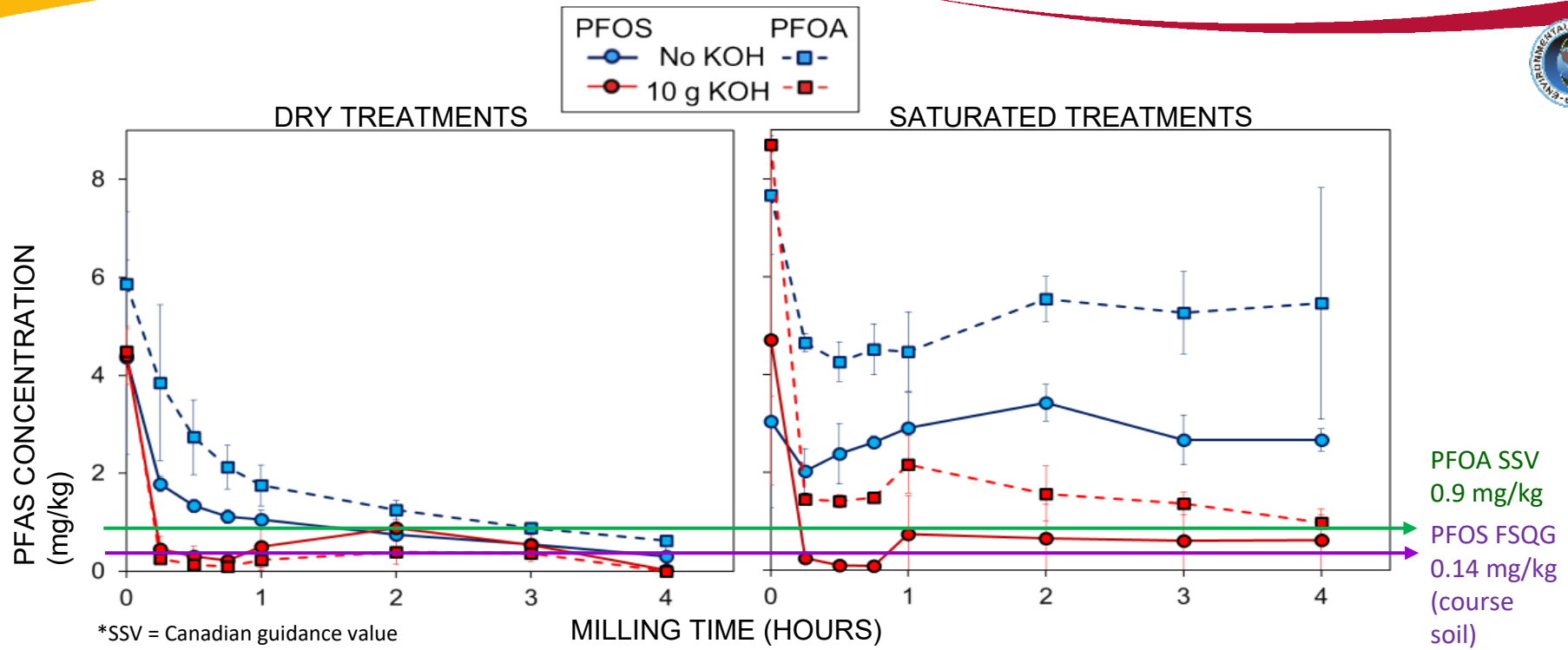
Science of The Total Environment

Volume 765, 15 April 2021, 142722

Mechanochemical remediation of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) amended sand and aqueous film-forming foam (AFFF) impacted soil by planetary ball milling

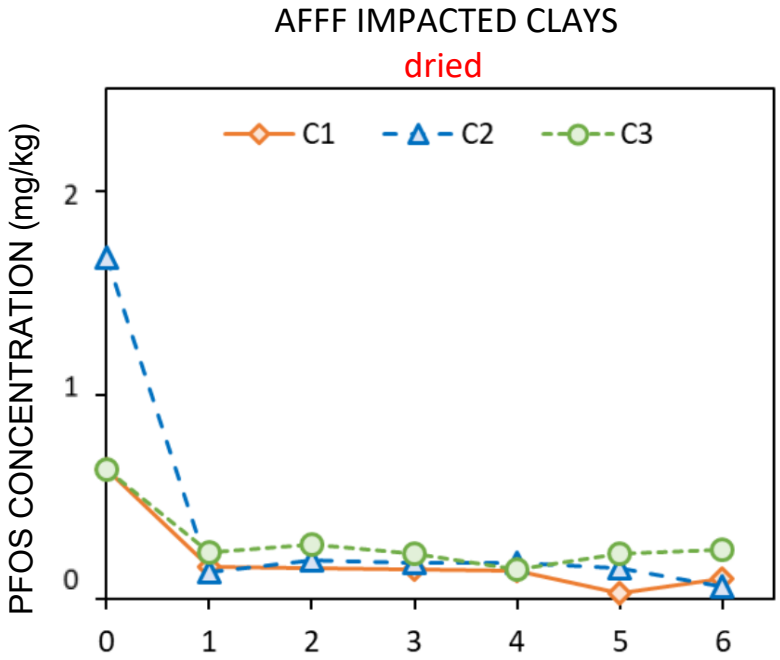
Lauren P. Turner [a], Bernard H. Kueper [a], Kevin M. Jaansalu [b, 1], David J. Patch [b], Nick Battye [b], Omneya El-Sharnouby [a, 2], Kevin G. Mumford [a], Kela P. Weber [a, b]

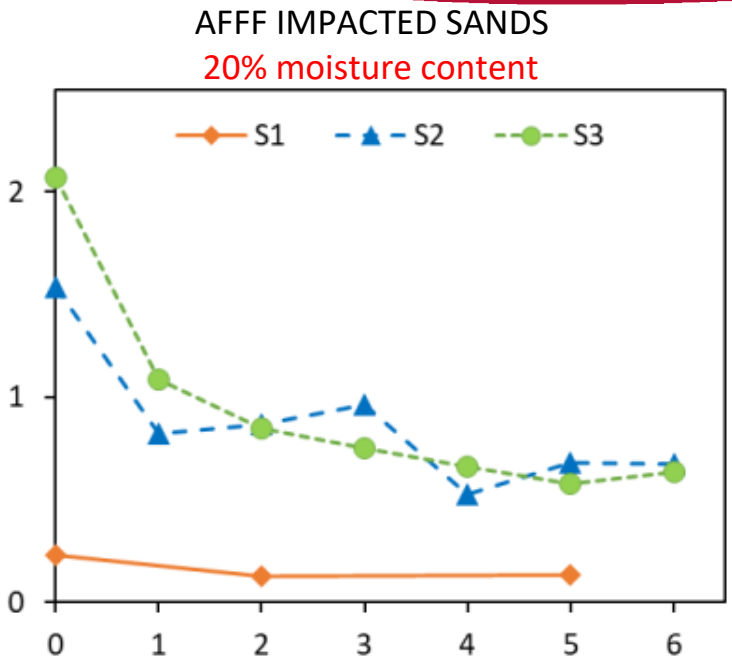
Success at Lab Scale



*SSV = Canadian guidance value

Success at Lab Scale





Lab Scale Fluoride Recovery

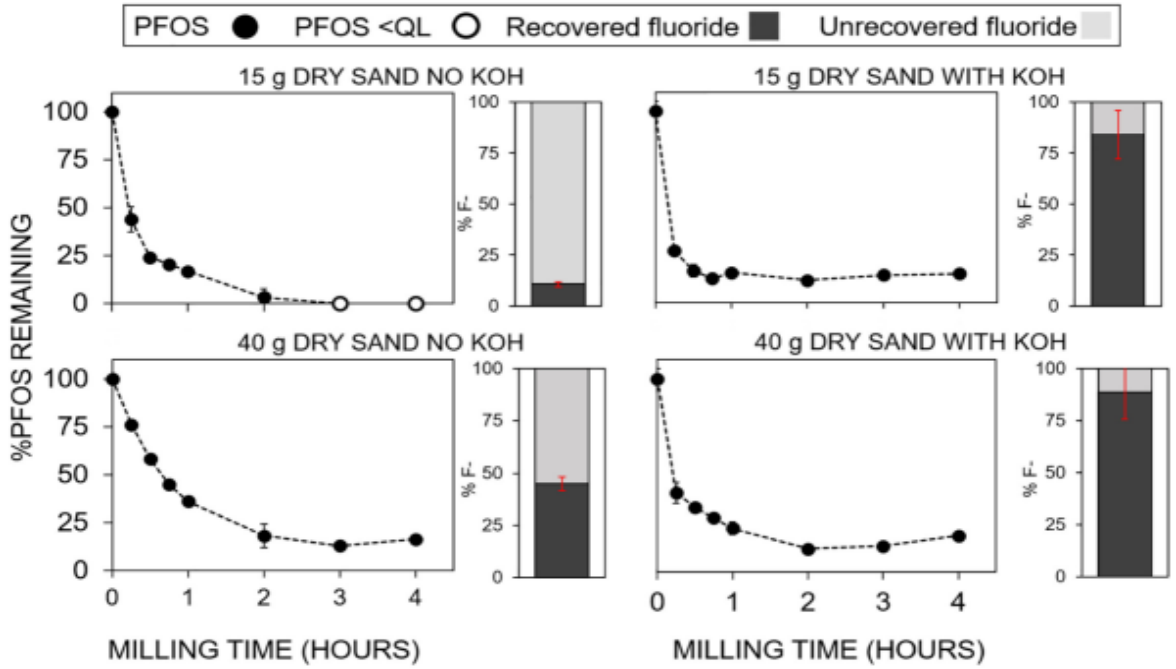
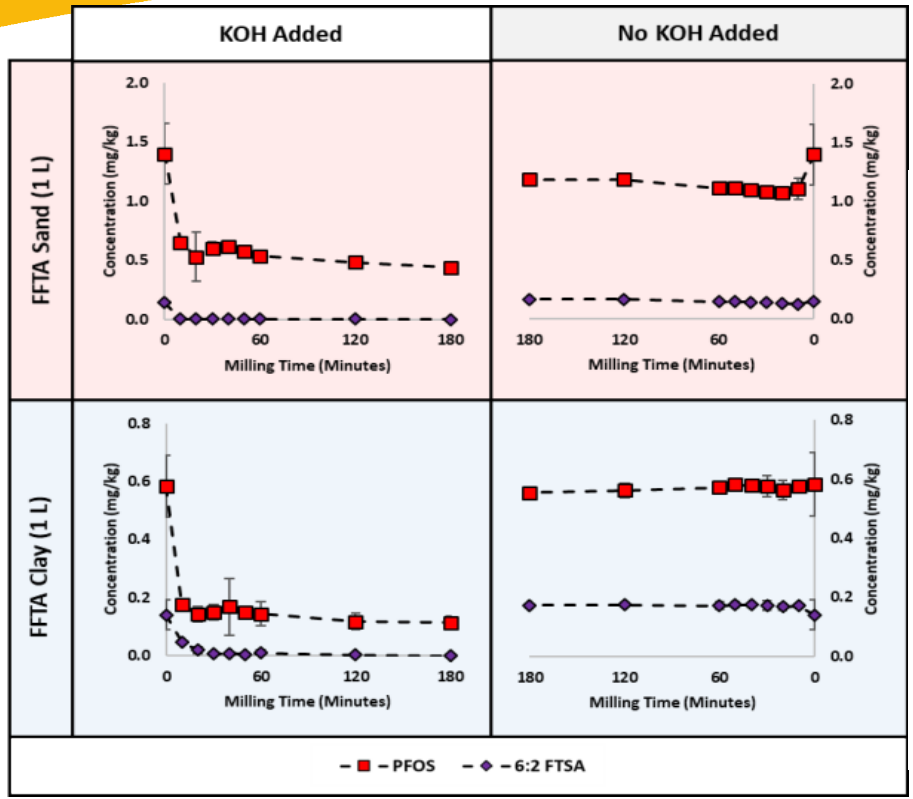


Fig. 3. Dry PFOS-amended sand treatment combinations destruction profiles and percent fluoride recovery. Error bars indicate ±one standard deviation. Concentrations below quantification limit (<QL).

Success at Horizontal Ball Mill (HBM) Scale



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Science of The Total Environment

Volume 835, 20 August 2022, 155506

Use of a horizontal ball mill to remediate per- and polyfluoroalkyl substances in soil

Nicholas J. Battye [a], David J. Patch [a], Dylan M.D. Roberts [a], Natalia M. O'Connor [a], Lauren P. Turner [c], Bernard H. Kueper [c], Michael E. Hulley [b], Kela P. Weber [a, c]

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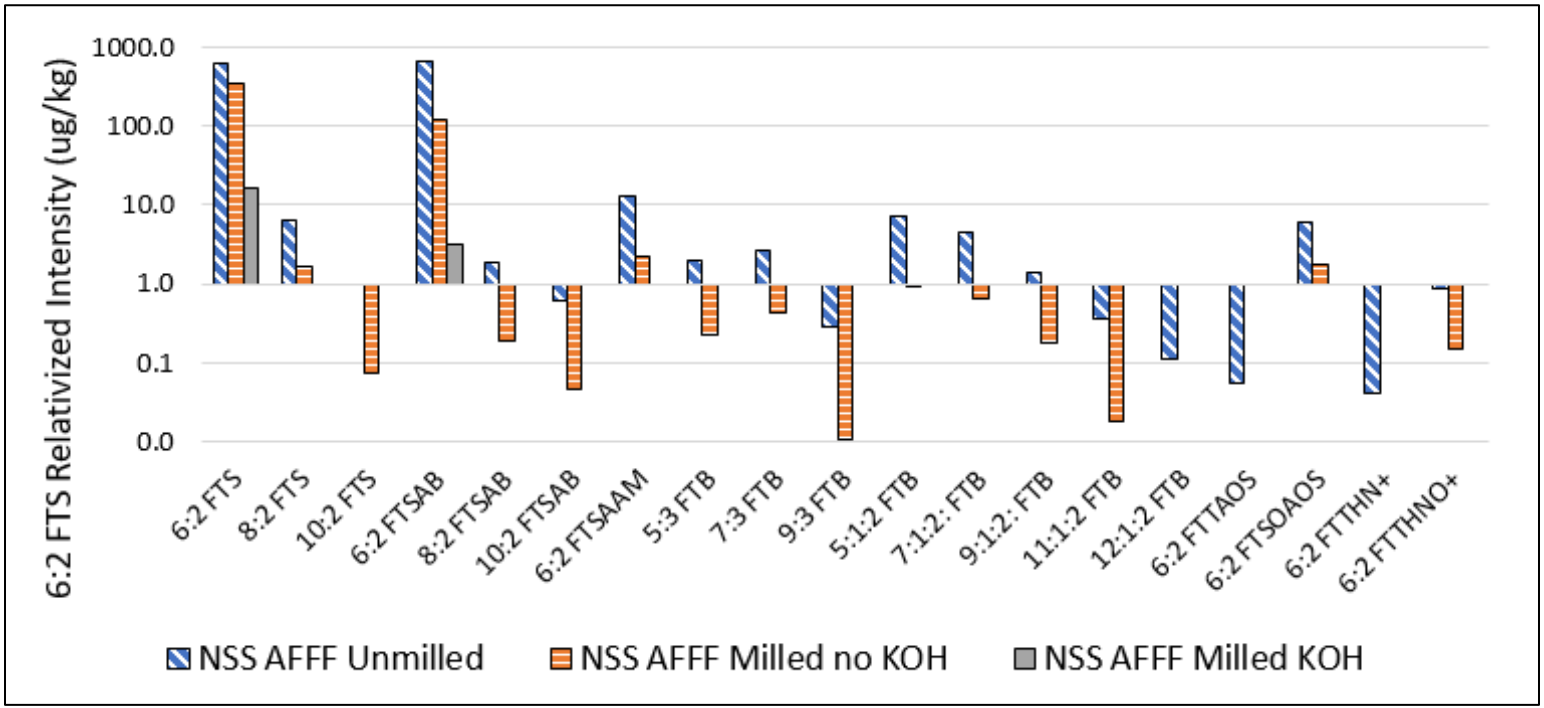
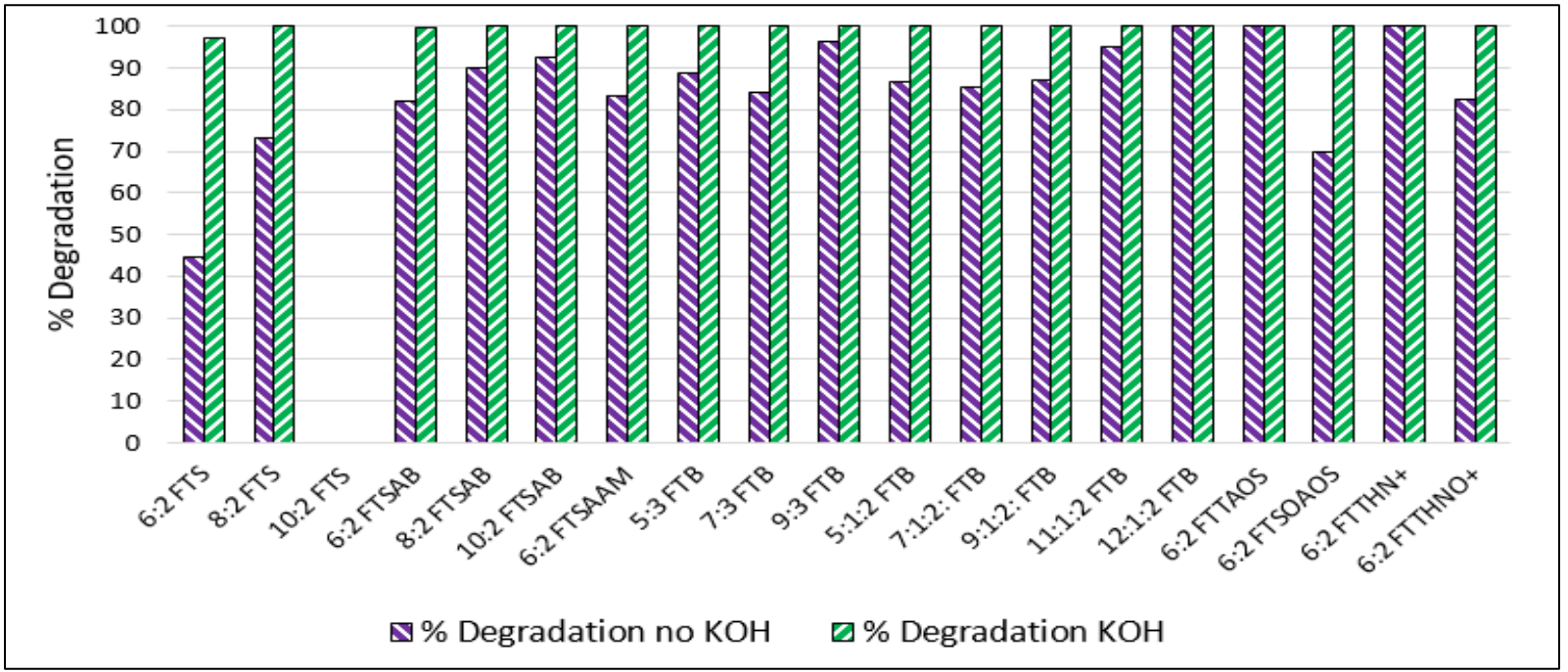
https://doi.org/10.1016/j.scitotenv.2022.155506

Success at HBM Scale



Success at HBM Scale



Industrial Scale Remediation

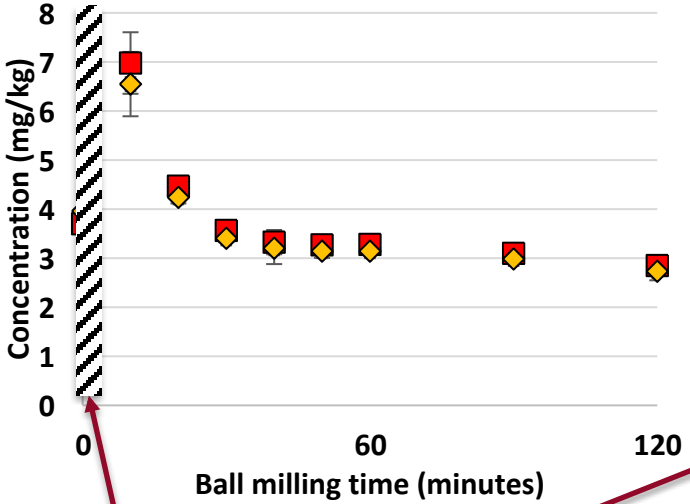
- Ball milling has been shown to successfully destroy PFAS at the <1L, 1L, and 25L scales
- Industrial scale remediation tested using 267L horizontal ball mill

Grinding media: mild steel balls (1.3 to 3.8 cm diameter).

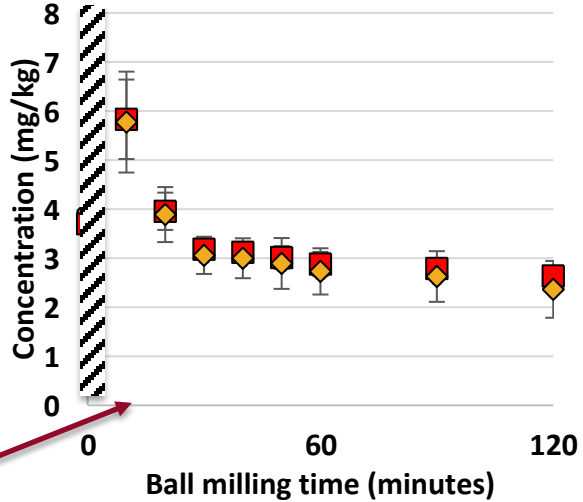
RPMs: 42 (75% of the critical speed).

Results – PFOS/PFOA

No KOH



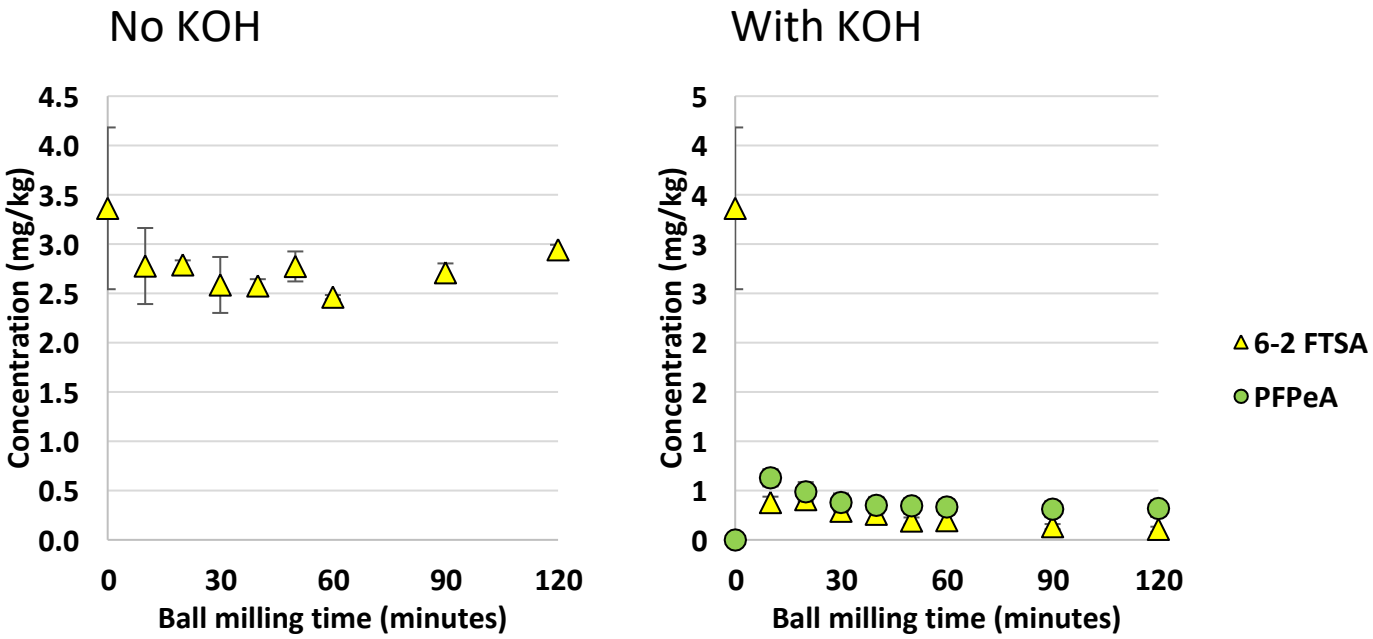
With KOH



- Similar destruction of both PFOS and PFOA, with *and without* KOH
- Destruction of both linear and branched PFOS isomers

Mixing period, high heterogeneity, ongoing work to establish accurate T=0 concentration

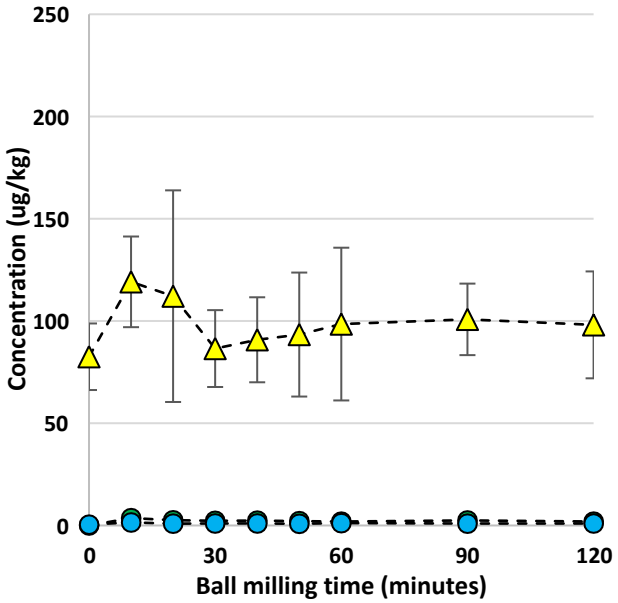
Results – 6:2 FTS



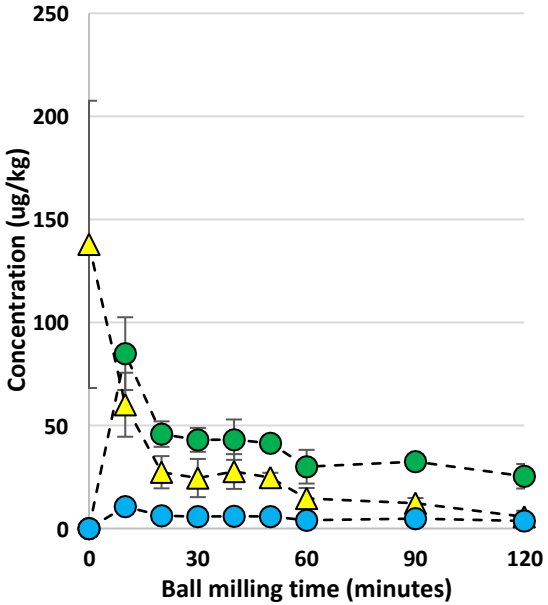
- Without KOH no destruction of 6:2 FTS occurs
- Addition of KOH allows for degradation of 6:2 FTS, with minor formation of PFPeA
- PFPeA is in turn destroyed by ball milling

Results – National Foam

No KOH



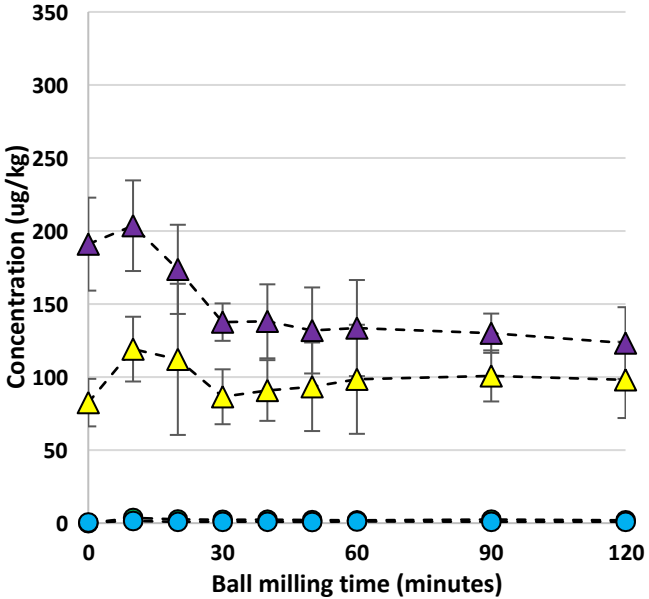
With KOH



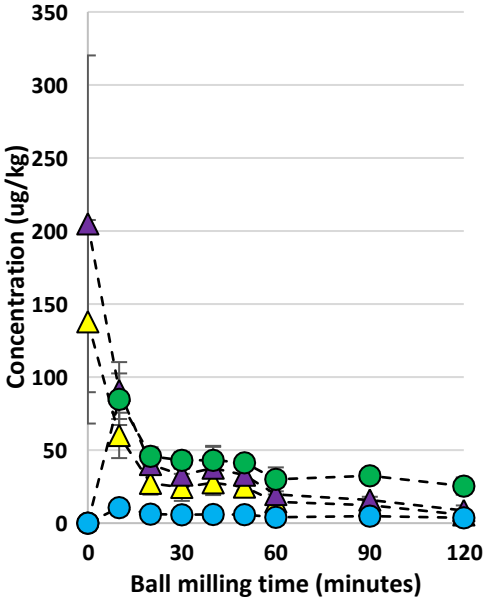
- Targeted LC-MS analysis only reveals 6:2 FTS
- Addition of KOH with ball milling results in degradation of 6:2 FTS, with formation of PFPeA
- Formation of PFPeA is substantially higher than 6:2 FTS, indicating substantial precursor load

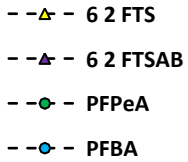
Results – National Foam High Resolution Analysis

No KOH



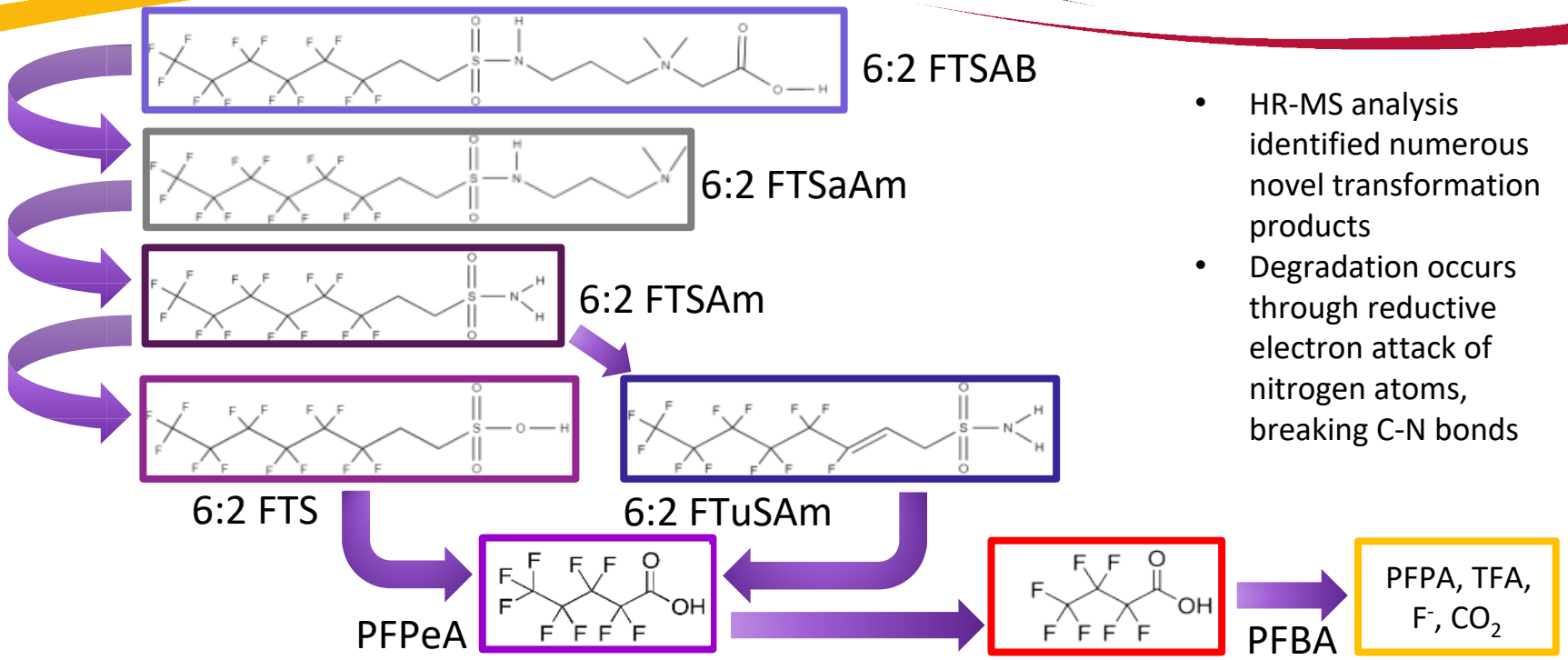
With KOH





- HR-MS analysis identified the presence of 6:2 FTSAB and smaller quantities of other fluorotelomers
- 6:2 FTSAB follows similar degradation trends to 6:2 FTS

Results – National Foam Degradation Mechanism



- HR-MS analysis identified numerous novel transformation products
- Degradation occurs through reductive electron attack of nitrogen atoms, breaking C-N bonds

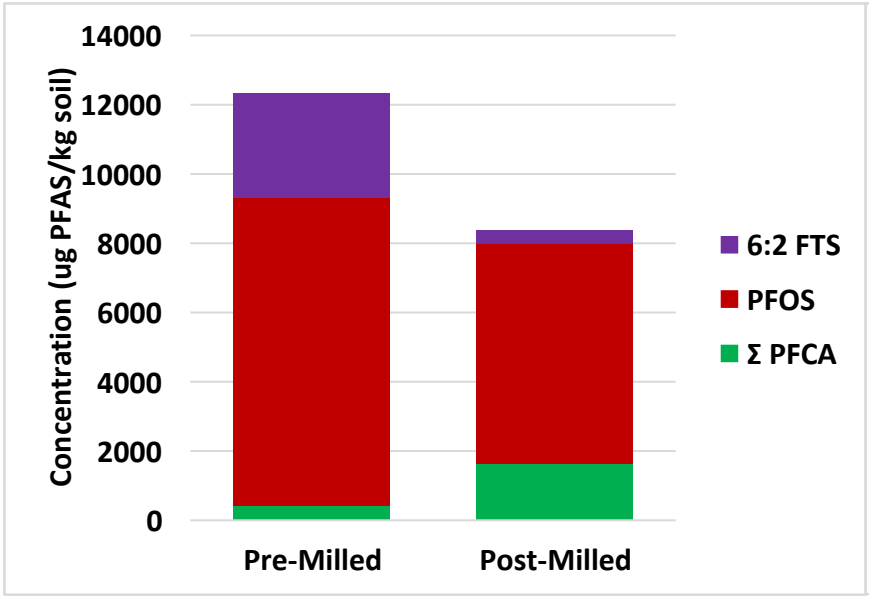
Industrial Scale FFTA Soils

	Planetary Mill Scale (<1 L, Lab)	Horizontal Mill Scale (25 L, Lab)	Horizontal Mill Scale (265 L, Industrial)
PFAS Spiked Sands	Success	Success	Success
AFFF Spiked Sands	In Progress	Success	Success
AFFF Impacted FFTA Soils	Success	Success	?

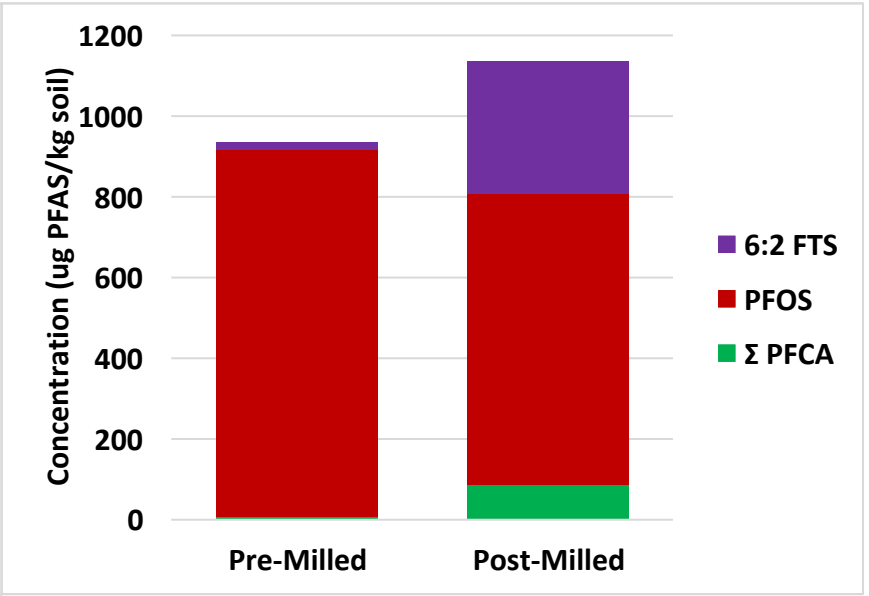
Initial Evaluation of Degradation

Made conclusive remarks difficult based on standard targeted analysis only

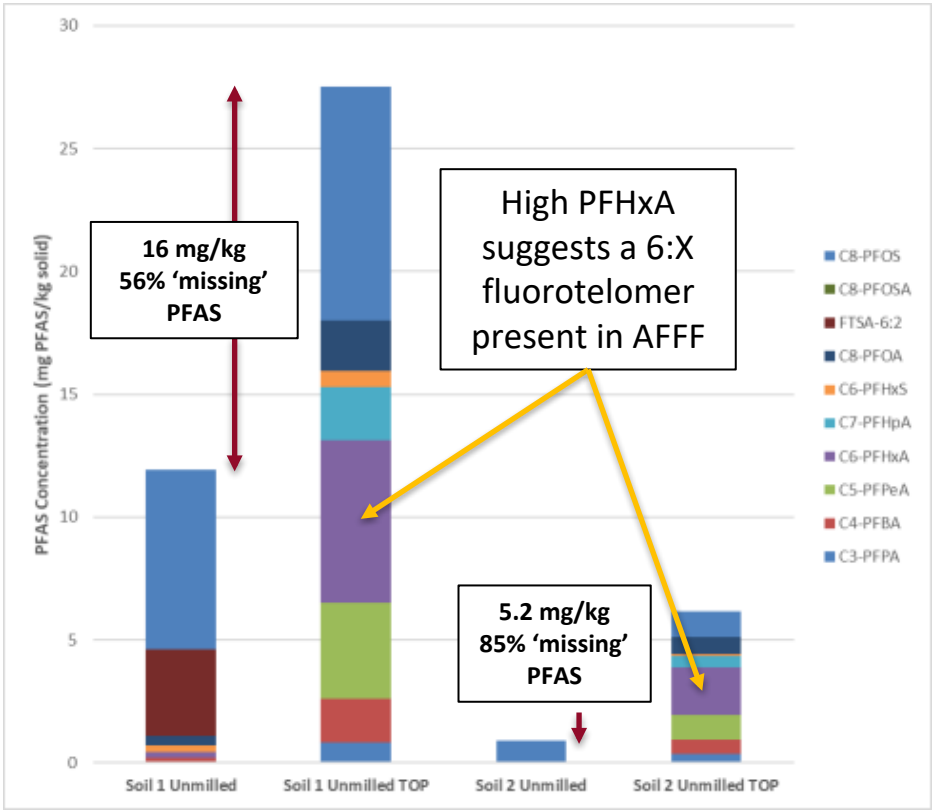
Soil 1: 31% PFAS Degradation



Soil 2: +18% PFAS 'Creation'



Characterization of PFAS on FFTA Soils



- PFAA precursors present in both types of soil

Total PFAS destruction estimates

- Free fluoride analysis – best evidence of PFAS destruction.

Trial	Fluoride (mg/kg)	Equivalent PFOS destruction (mg/kg)	Targetted analysis PFOS destruction (mg/kg)
Soil 1, dry, spiked, 100:1 KOH (1)	12	19	35
Soil 1, dry, spiked, 100:1 KOH (2)	12	19	13

Discrepancies in mass balance imply hidden PFAS transformations and/or destruction.

Targeted analysis alone cannot be used to judge remedial effectiveness for these two soils.

Leachability and Soil Quality Health

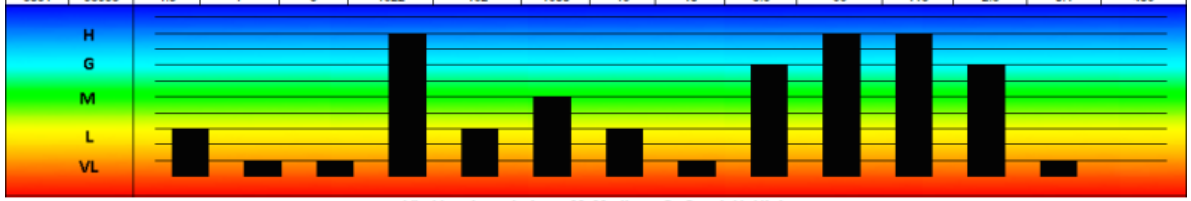
- Soil health testing performed by A&L Canada Laboratories
- Synthetic precipitation leachability procedure (SPLP) performed by ESG

Reported Date:
Printed Date:2021-02-09

VitTellus Soil Health Report

Page: 3 / 6

Sample ID	Lab Number	Organic Matter %	Phosphorous-P ppm		Potasssium K ppm	Magnesium Mg ppm	Calcium Ca ppm	Sodium Na ppm	Sulfur S ppm	Zinc Zn ppm	Manganese Mn ppm	Iron Fe ppm	Copper Cu ppm	Boron B ppm	Aluminum Al ppm
			Bicarb	Bray-P1											
3031	58553	1.3	7	8	1622	162	1600	19	10	8.8	66	118	2.8	0.1	406



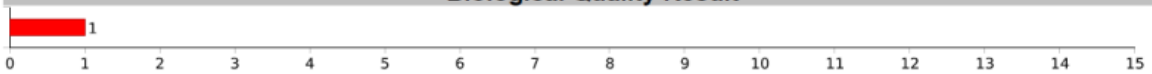
VL=Very Low, L=Low, M=Medium, G=Good, H=High

Parameter	Result	Optimum Level
CEC, meq/100g	13.6	
K/Mg Ratio	3.09	0.25-0.35
GFI	46	L
%K	30.6	3-5
%Mg	9.9	10-20
%Ca	58.9	65-72
%H	0	5-15
%Na	0.6	<1

Parameter	Result	Rating
pH	9.2	VH
Buffer pH		
EC, ms/cm	0.18	VL
Saturation %P	3	L
Saturation % Al	0	G
Nitrate-N, ppm	1	VL
Chloride, ppm	7	VL
PMN, ppm	6	

Parameter	Result	Rating
Solvita CO2-C, ppm	5	
Reactive C, ppm	151	
Soil Health Index	23	VL L M G H

Biological Quality Result



0-1: Very Low Soil Microbial Activity- Associated with dry sandy soils and little to no organic matter.
1-2.5: Low Soil Microbial Activity- Soil is marginal in terms of biological activity and organic matter.
2.5-3.5: Medium Soil Microbial Activity- Soil is in moderately balanced condition.
3.5-4: Ideal Soil Microbial Activity- Soil is well supplied with organic matter and has an active population of microorganisms.
>4: Unusually High Soil Microbial Activity- Soil has very high level of microbial activity. May have excessive organic matter.

Leachability and Soil Quality Health

Soil Health Values	Soil 1 Unmilled	Soil 1 Milled	Soil 1 KOH Milled	Soil 2 Unmilled	Soil 2 Milled	Soil 2 KOH Milled
Potassium (ppm)	1622	2032	6409	442	1010	5878
Calcium (ppm)	1600	3370	2750	350	770	740
Sodium (ppm)	19	107	156	6	140	79
Iron (ppm)	118	216	192	54	156	140
Aluminum (ppm)	406	835	907	1747	1986	2119
Chloride (ppm)	7	43	118	7	53	254
Cation Exchange Capacity (meq/ 100g)	14	26	34	4	9	20
pH	9.2	9.0	10.4	7.1	8.0	10.2
Soil Health Index	23 (Low)	24 (Low)	17 (V. Low)	16 (V. Low)	16 (V. Low)	10 (V. Low)
Biological Quality	1 (V. Low)	1 (V. Low)	0 (None)	3 Medium	1 (V. Low)	0 (None)
Organic Matter	5 (Low)	5 (Low)	2 (Low)	20 (Moderate)	7 (Low)	2 (Low)
Mineralizable Nitrogen (lbs/ac)	12	12	6	36	16	6
PFAS Leachability (%)	91	93	93	100	100	96

Legend

INCREASE
DECREASE

Key Operational Parameters

- Evaluation of success across multiple scales (PBM, HBM, industrial) has allowed for identification of key parameters
- PFAS destruction and fluoride recovery is highest with:
  - Dry soil
  - KOH amendment
- Upcoming work is being performed to optimize additional operational parameters

Conclusions

- Success at the industrial scale more conclusively confirmed on simpler samples.
- Results identify KOH plays a key role in enabling destruction of polyfluorinated (fluorotelomer) PFAS
- Enhanced analytical protocols, including free fluoride analysis, TOP assay, and high resolution mass spectrometry is critical to understand extent of degradation, transformation, and destruction
- Ball milling has shown potential to be a promising technology for destruction of PFAS

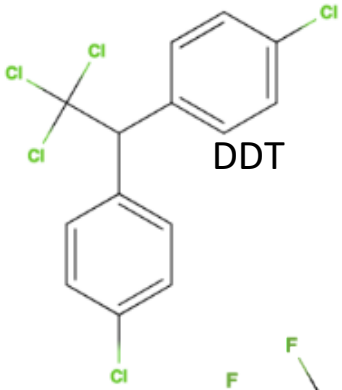
Next Steps

- Develop and implement enhanced analytical protocols for ongoing ball milling work
- Optimize operational parameters
- Conduct on-site pilot-scale testing

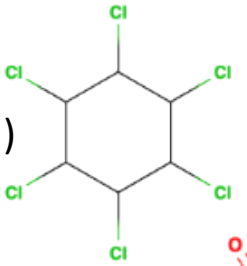
Questions

Mechanochemical Destruction via Ball Milling

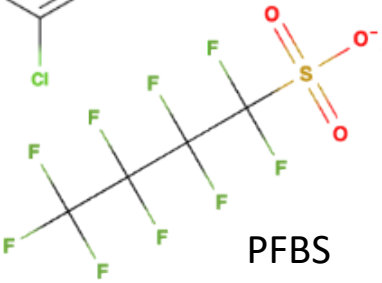
- Literature reports the destruction of several halogenated organic chemicals by planetary ball milling with a co-milling reagent



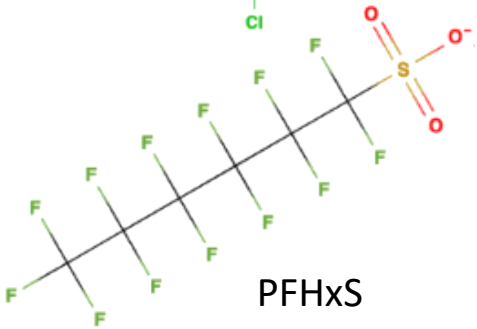
DDT



Lindane (HCH)

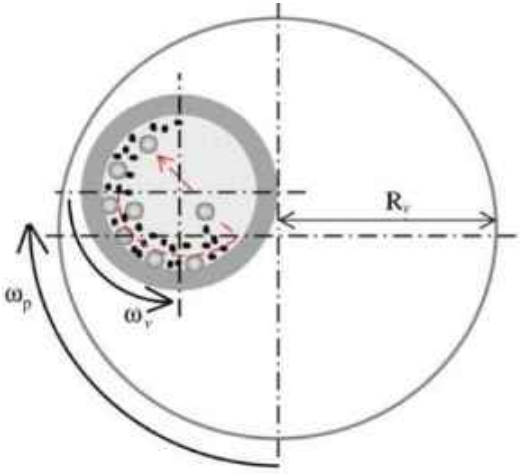


PFBS



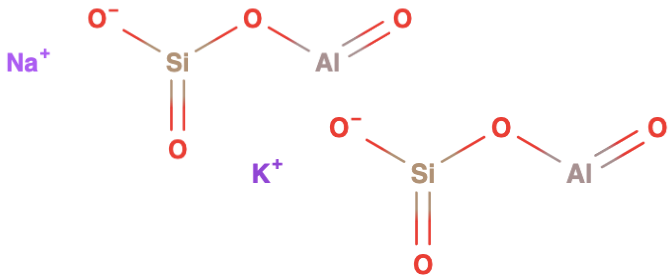
PFHxS

Planetary ball mill



Mechanochemical reactions

$Al_2KNaO_8Si_2$



- Mechanical action promotes reactivity and surface chemistry states that are not attainable in ambient conditions

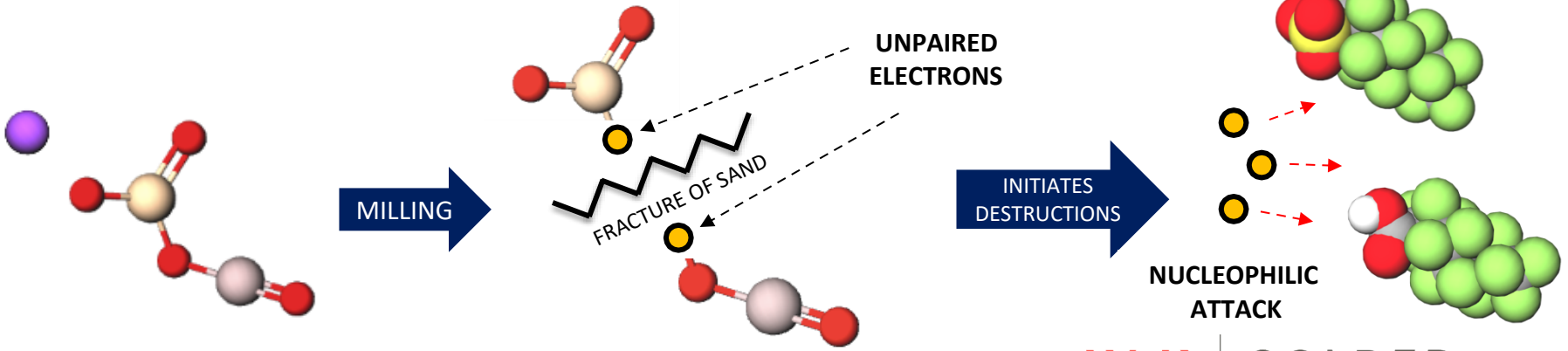


Figure modified from Cagnetta, Huang and Yu (2018)