In Situ Stabilization and Solidification (ISS) to Reduce PFAS Leaching from Contaminated Soils

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Why ISS for PFAS?

- No <u>feasible</u> technologies mineralize PFAS *in situ*
- ISS treats soils onsite (source treatment)
- Dig and haul? ………Expensive!
- Because we can!

We CAN Stabilize PFAS!

- **I've tested ISS for 6+ years**
- Sörengård et al. (2019) & Hale et al. (2017)
  - ➢Lab Study on AFFF-Contaminated soils using AC and commercial binders
  - ➢Leaching of PFOS & PFOA reduced by 98% by adding 2% AC with cements.
- Sörengård et al. (2021)
  - ➢Pilot- and Lab-scale studies: leaching results well-correlated ($p < 0.001$).
  - ➢Removal rate >97 % for PFOS & PFOA.
- McDonough et al. (2022)
  - ➢Bench-and field-scale data showed >99% decrease in total PFAS mass leachability (mass basis; >98% mole basis) as

Ex Situ (S/S)

In Situ (ISS)

ISS Review*

- <u>Stabilize</u>:
  - ➢transfer from aqueous to solid phase.
- <u>Solidify</u>:
  - ➢encapsulate and/or coat sorbed PFAS
  - ➢decreases surface area
  - ➢improve handling and physical characteristics.

*EPA (2000); ITRC (2011)

Disadvantages of ISS

- <u>Not Permanent!</u>
  - Cement will disintegrate
  - PFAS will desorb
- Amendments <u>INCREASE VOLUME</u>!
  - Requires landfilling

Materials & Methods

Amendments Used (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)

Materials Tested*

- **AFFF-Contaminated Soils**: airports, tank farms
- **Soils, sediments, sludges:** metal platers, leather tanners, etc.

*spent GAC, RO concentrate, AFFF, biosolids

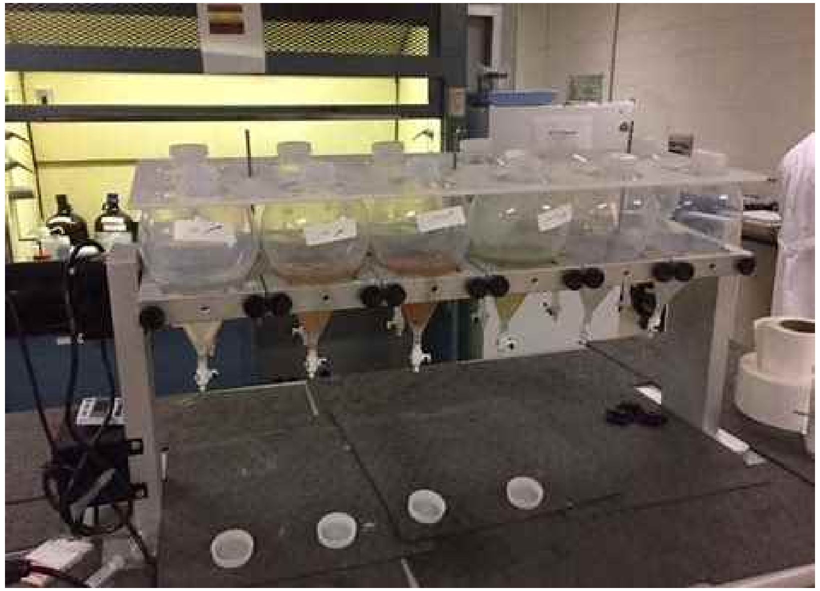
Mix & Cure (28 days)

3 Performance Criteria*

- **Decrease <u>hydraulic conductivity</u> (K)**
  - 10^{-6} cm/sec

- **Increase <u>Compressive Strength</u> (UCS)**
  - 345 kPa (50 psi)
  - Concrete 25,000-50,000 kPa (3,625-7,250 psi)

- **Reduce leaching**
  - Target PFAS concentrations in leachate?
  - Michigan 7 drinking water standards?



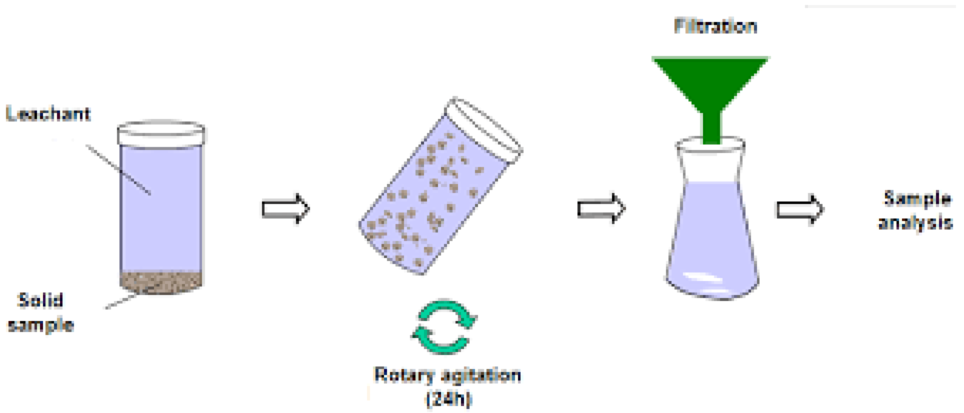
*ITRC (2011)

Leaching Tests (Batch)

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)



PFAS Analyses

- **Soils & sediments - ASTM-D7968 or 537M** with Isotopic Dilution
- **Leachate - ASTM-D7979** with Isotopic Dilution

Results

2 AFFF-Contaminated Soils

	pH	% Water	% SOM	% Sand	% Silt	% Clay
Sand	6.6	3.7	**0.3**	91	8	**1**
Silty Clay	6.4	16.5	**5.5**	14	46	**40**

Untreated Soils

Analyte (MI 7 DW MCLs)	Analyte Abbreviation	# Carbons	Silty Clay Avg. (ng/Kg)	Sand Avg. (ng/Kg)
Perfluorononanoic acid	PFNA	C9	68,000	21,000
Perfluorooctanoic acid	PFOA	C8	130,000	27,000
Perfluorohexanoic acid	PFHxA	C6	55,000	3,200
Perfluorooctanesulfonate	PFOS	C8	3,100,000	1,630,000
Perfluorohexanesulfonate	PFHxS	C6	307,000	6,300
Perfluorobutanesulfonate	PFBS	C4	38,000	830
Hexafluoropropylene oxide dimer acid	HFPO-DA	C6	26,000	3,200
		Σ 28 PFAS (ng/Kg)	**6,250,400**	**3,052,880**

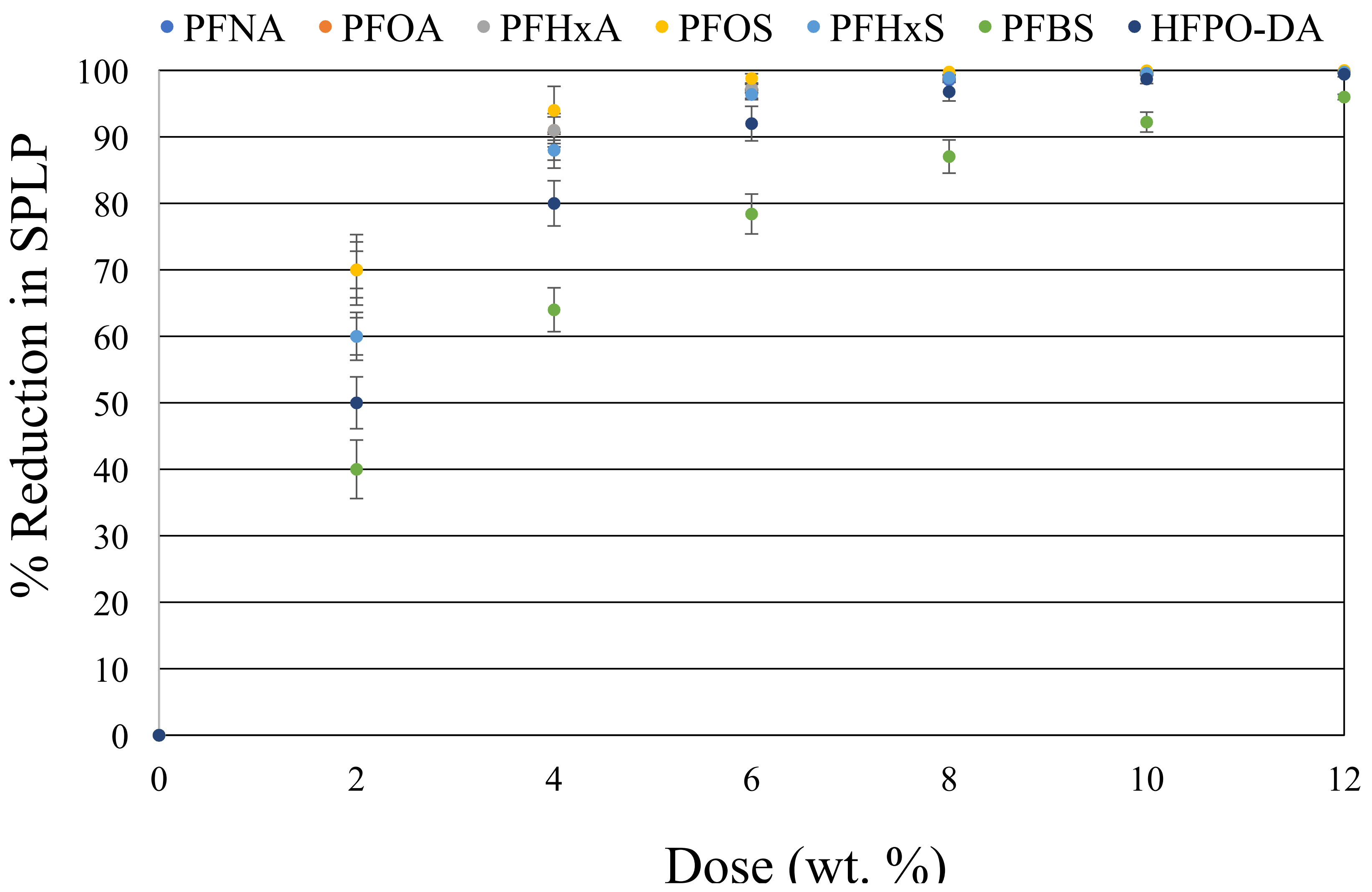
SPLP: Silty Clay (dose=10%)

Analyte	Abbreviation	Avg. SPLP Untreated (ng/L)	Avg. SPLP (ng/L)	MI DW MCLs (ng/L)
Perfluorononanoic acid	PFNA	1,900	3.6	6
Perfluorooctanoic acid	PFOA	3,700	5.2	8
Perfluorohexanoic acid	PFHxA	3,400	7.0	400,000
Perfluorooctanesulfonate	PFOS	99,400	12	16
Perfluorohexanesulfonate	PFHxS	13,600	34	51
Perfluorobutanesulfonate	PFBS	1,300	52	420
Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA	6,900	39	370
	Σ 28 PFAS (ng/L)	**212,060**	**253**	

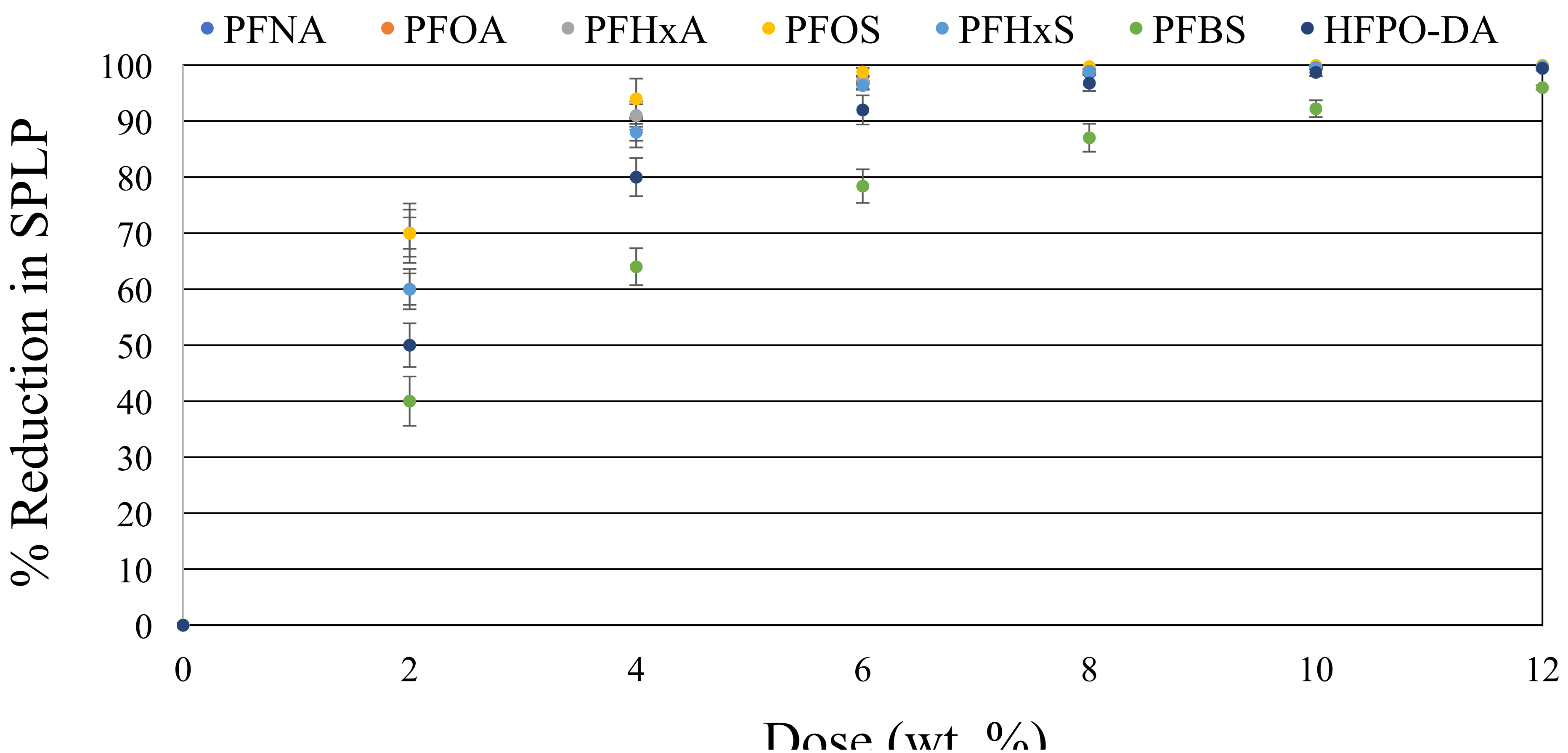
SPLP: Sand (dose=10%)

Analyte	Abbreviation	Avg. SPLP Untreated (ng/L)	Avg. SPLP (ng/L)	MI DW MCLs (ng/L)
Perfluorononanoic acid	PFNA	610	ND	6
Perfluorooctanoic acid	PFOA	1,000	4.8	8
Perfluorohexanoic acid	PFHxA	200	ND	400,000
Perfluorooctanesulfonate	PFOS	52,300	12	16
Perfluorohexanesulfonate	PFHxS	280	ND	51
Perfluorobutanesulfonate	PFBS	44	ND	420
Hexafluoropropylene oxide dimer acid (GenX)	HFPO-DA	980	ND	370
	Σ 28 PFAS (ng/L)	**70,123**	**38**	

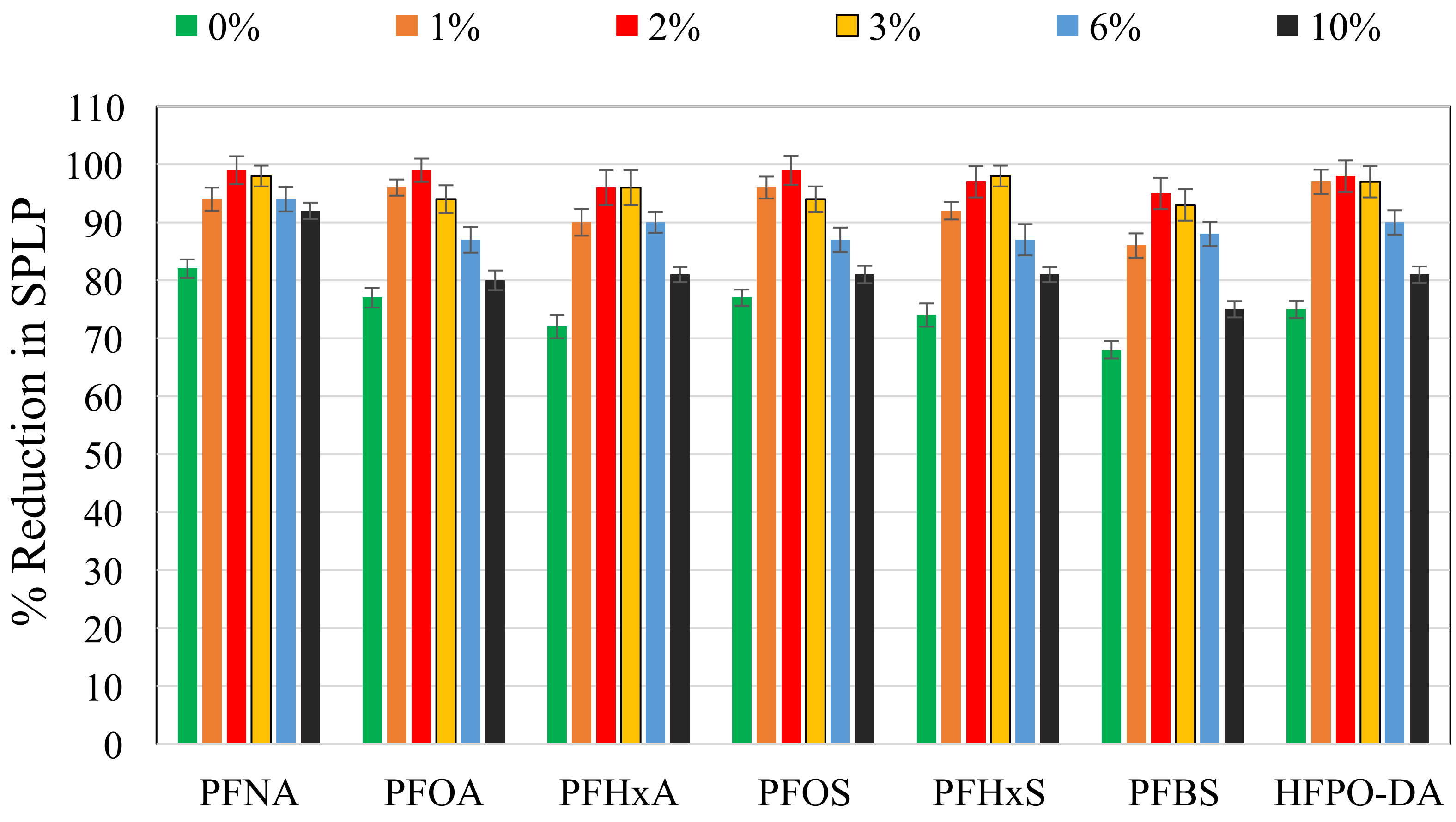
Dose-Response: Silty Clay



Dose-Response: Sand



Varying PAC dose (sand)



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

Varying PAC dose (sand)

% PAC/cement	Unconfined Compressive Strength (psi)
0	820
1	1,230
2	1,410
3	1060
6	830
10	420

1% to 3% AC or Biochar increases strength (Na et al., 2021)

Miscellaneous Observations

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

2. Small amounts of AC & Biochar (1% to 3%) increases strength and decreases PFAS leaching

3. 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

- ISS is effective for PFAS-contaminated soils
  - Decreases RATES of PFAS leaching
  - Decreases K
  - Increases strength

- Recipes and doses should be determined for each soil.

Literature

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Questions

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