

PRESENTATIE BODEMBREEDFORUM

Wim Plaisier

12 december 2019

Safety moment: hoe verantwoordelijke voelen we ons voor dit dossier?



http://www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html?_r=0

Ver van mijn bed, of toch dichterbij dan je denkt?

Kunstmestkorrels

Bedoelde vaten - 857 stuks van elk 1.000 liter, volgens Rutgers - staan nu nog achterop een terrein aan de Voltastraat, op bedrijventerrein De Huet. Aanvankelijk stonden er ruim 1.000. In deze vaten zit brandblusschuim. Dit schuim verwerkte Rutgers tot vorig jaar - de productie is inmiddels gestopt, omdat de enige afnemer is weggefallen - tot kunstmestkorrels.

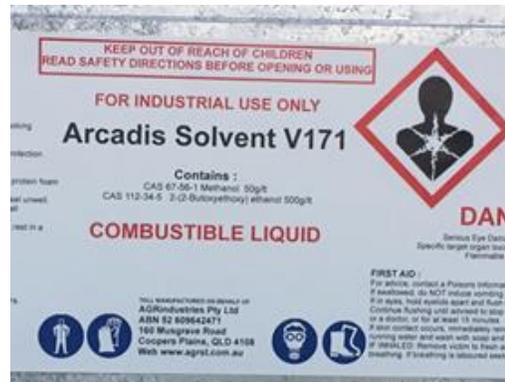


Say what? Premix AFFF verwerkt in kunstmest?

SANEREN EN LEREN

PFAS Treatment and Cleaning Solutions

- ❑ Bundelen van kennis van Arcadis, Boskalis Environmental en Hoelscher Wasserbau.
- ❑ Ontwikkelen en optimaliseren PFAS reinigingstechnieken voor grond, water en systemen.
- ❑ Boskalis Environmental reinigt 500.000 ton grond per jaar
- ❑ Hoelscher Wasserbau is groot in grondwateronttrekking en reiniging. O.a. projecten op Frankfurt Airport, nieuwbouw T3



PFAS Treatment and Cleaning Solutions

Hölscher Wasserbau GmbH

- Water treatment
- Building, operating and maintaining installations
- Treatment techniques and treatment concepts
- Activated carbon regeneration, IX systems

New partners

- Foam transitioning
- Cleaning services
- Concrete sealing



Arcadis Netherlands BV

- Thought leadership
- Research
- Soil and groundwater research
- Project management
- Consultancy
- Design and engineering
- Technical concepts
- In-situ remediations

Boskalis Environmental BV

- Soil cleaning
- Excavation
- Soil washing plants
- Remediation and treatment

WEER EEN NIEUW HANDELINGSKADER...

Aanpassing tijdelijk handelingskader

Ministerie van Infrastructuur
en Waterstaat

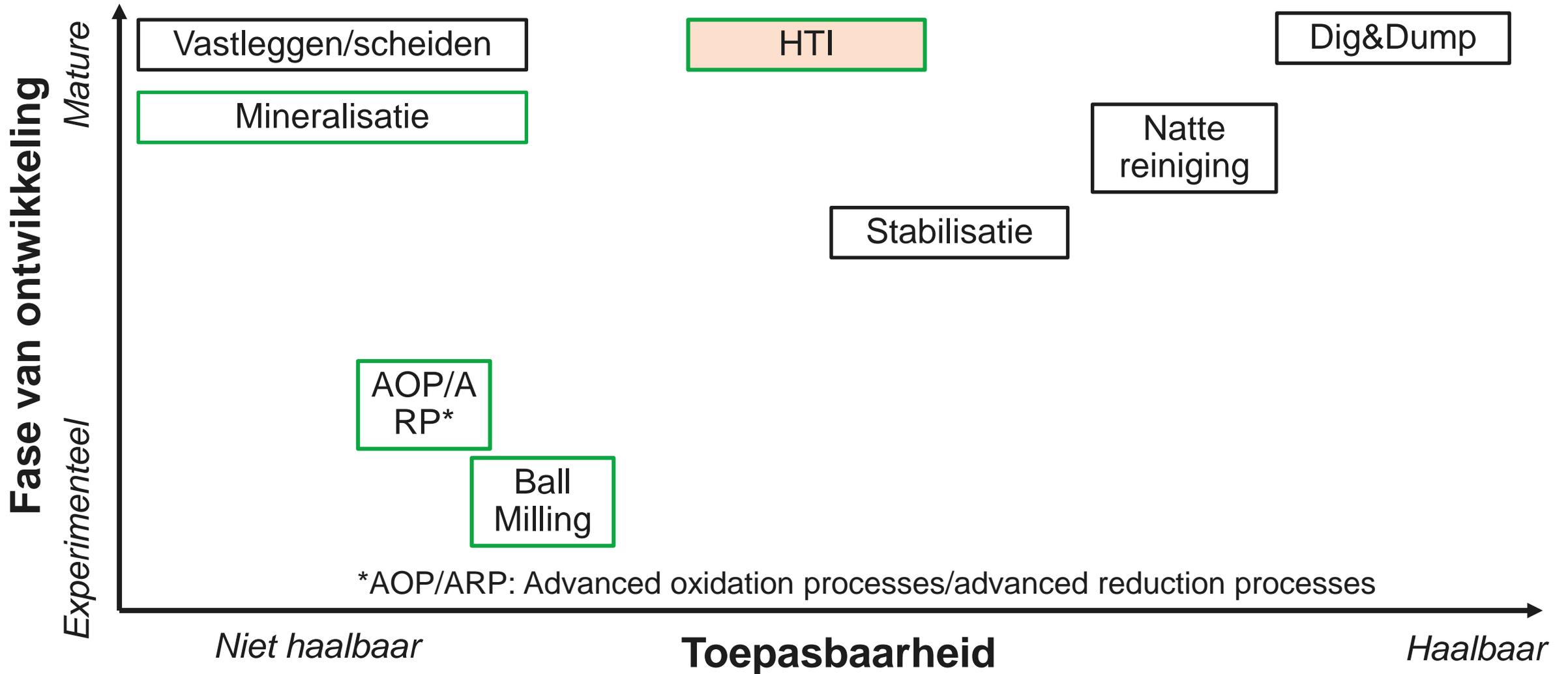
Datum 29 november 2019
Betreft Aanpassing tijdelijk handelingskader PFAS

- partij. Een aantal punten wordt met spoed verder worden uitgewerkt, zoals
- de wijze waarop vergunningverlening kan plaatsvinden van directe en indirecte lozingen van water met PFAS door grondreinigers, grondbanken, stortplaatsen, afvalinzamelaars;
 - het verlenen van een niet-reinigbaarheidsverklaring voor zand met PFAS boven 3-7-3 µg/kg droge stof, zodat stort kan plaatsvinden.

Eerste bullet snap ik, tweede klopt niet (maar staat er wel)

REINIGINGSTECHNIEKEN GROND

Saneringstechnieken voor PFAS (grond)



Extractieve reiniging

- Fysieke reiniging – schone zandfractie wordt uit de grond gewassen. PFAS hoopt op in het waswater en het vrijkomende slib.
- Toepasbaar voor grond met <30-40% fijne fractie
- In vergelijking met normale extractieve reiniging meer aandacht voor waterzuivering en polishing
- Diverse ex-situ installaties in Nederland hebben nog geen vergunning voor reiniging grond boven hergebruiksnorm PFAS.
- Veel discussie over proefreinigingen en/of aanpassing vergunningen....(taak I&W?)
- Diverse reinigers nemen grond tot 3-7-3 norm in voor reiniging
- Tarieven: n.n.t.b.



Foto: Boskalis Engineering

Deze plant in Duitsland draait al twee jaar (vergund) op oliehoudende en PFAS houdende grond.....



Bron: Strabag / Zublin

- Zublin/Strabag plant
- Ingolstadt (Bayern)
- Voormalige raffinaderij locatie
- Zandige / grofzandige bodem
- < 10% afslibbaar
- Strenge norm voor uitloging (Z 1.1.)

2018/2019 Proeven met soil washing (Z 1.1.)

Sample name	C6	GA-03	GA-06	G-42
Sample Depth	0-0.6 m	0.8-1.7 m	0.6-1.1 m	0.2-0.9 m
Colour	Grey	Light orange brown	Black	Dark brown grey
Organic	Not humic	Not humic	Humic	Little humic
Dry matter content	96.2%	94.4%	95.1%	97.9%
Sum PFAS (µg/kg DM)	99	581	3540	170
PFOS (µg/kg DM)	99	560	3500	170
Sum PFAS leaching (µg/l)	7.8	74	160	7.9
PFOS leaching (µg/l)	7.7	72	150	6.6

Table 1 Bavarian criteria used to calculate the maximum PFAS concentration

Stoff	Z 0 in µg/l	Z 1.1 / Z 1.2 in µg/l	Z 2 in µg/l
Perfluoromonansäure PFNA	0,03	$\Sigma (C_n / Z_{0n}) \leq 1$	$\Sigma (C_n / Z_{2n}) \leq 1$
Perfluoroktansulfonsäure PFOS	0,05		
Perfluoroktansäure PFOA	0,05		
Perfluorhexansulfonsäure PFHxS	0,05		
Perfluorhexansäure PFHxA	2,0		
Perfluorbutansulfonsäure PFBS	2,0		
Perfluorbutansäure PFBA	3,0		
Perfluordekansäure PFDA ggf. Summe mit allen PFC > C10	0,1		
H4-Polyfluoroktansulfonsäure H4PFOS	0,1		
Perfluoroktansulfonamid PFOSA	0,1		
Perfluorheptansulfonsäure PFHpS	0,3	0,1	
Perfluorheptansäure PFHpA	0,3		
Perfluorpentansäure PFPeA	3,0		



C6

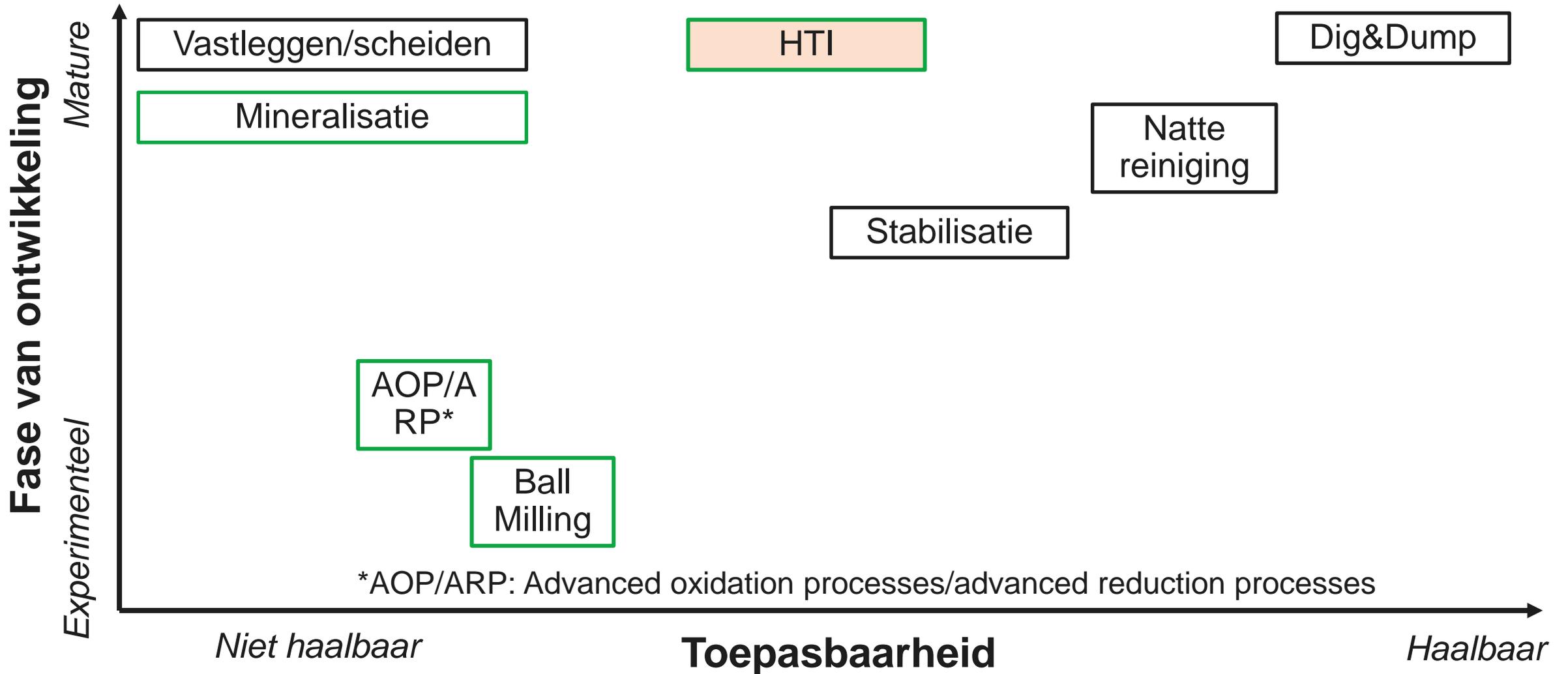
GA-03

GA-06

G-42

Figure 1: Photos of the initial soil samples

Saneringstechnieken voor PFAS (grond)

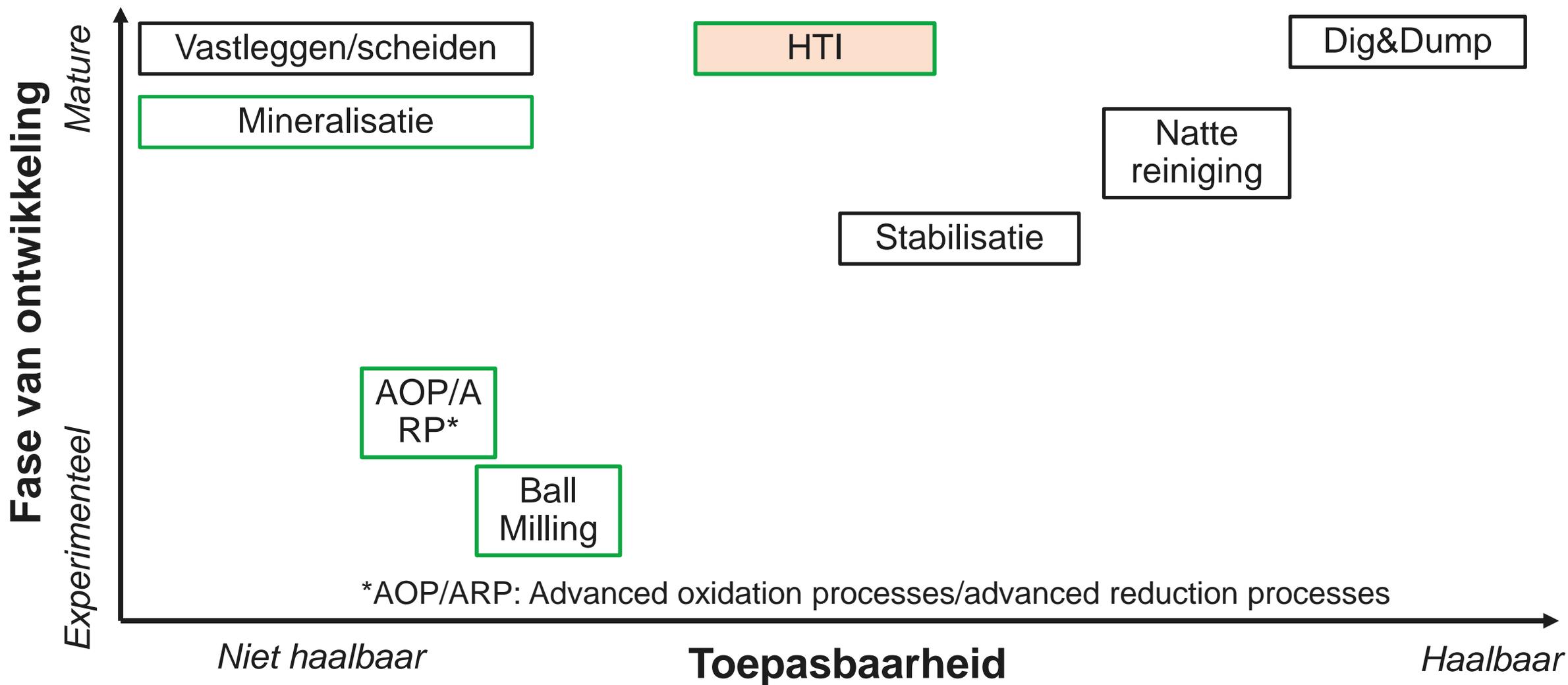


Stabilisatie / Immobilisatie

- Pragmatische oplossing om uitloging te verminderen
- Geluidswal, depot, overig
- Geen afbraak van PFAS, ex-situ of in-situ
- Diverse leveranciers en producten:
 - Ziltek Rembind/+ , MatCARE, CETCO fluorosorb, Osorb
 - Arcadis en GBN hebben eigen producten ontwikkeld
- Doe labtesten, maak commerciële afwegingen op basis van de testresultaten
- US test van Arcadis field: lange duur monitoring – ongoing
- Tarieven:



Saneringstechnieken voor PFAS (grond)

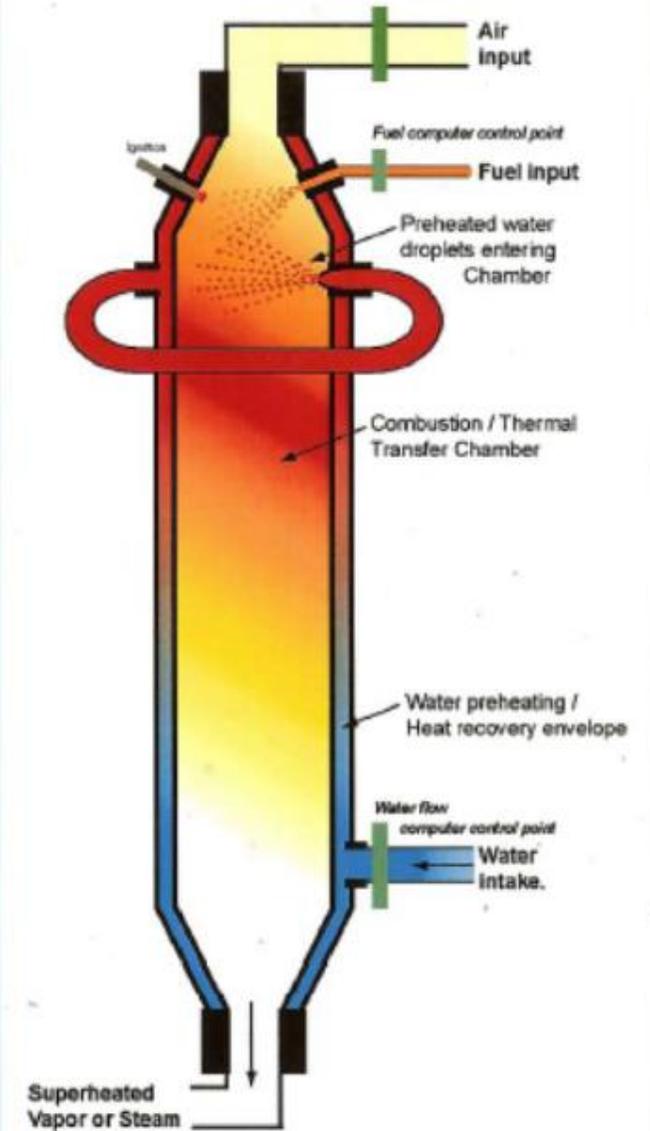


Vapour Energy Generator (VEG) Technology

- Compact, high efficiency steam generator – air, recycled water and propane
- Soil temperatures up to 950°C achieved – PFASs destroyed and desorbed into vapour – successful trial for PFOS completed
- Multi stage vapour treatment – caustic, steam, ZVI, lime
- Treated vapours, condensed water & syngas rerouted to VEG unit – **closed loop**
- ~50 full scale applications but mainly for heavy end hydrocarbons
- Mobile units - patented system (Endpoint US), limited availability in Europe



VEG Internals Diagram

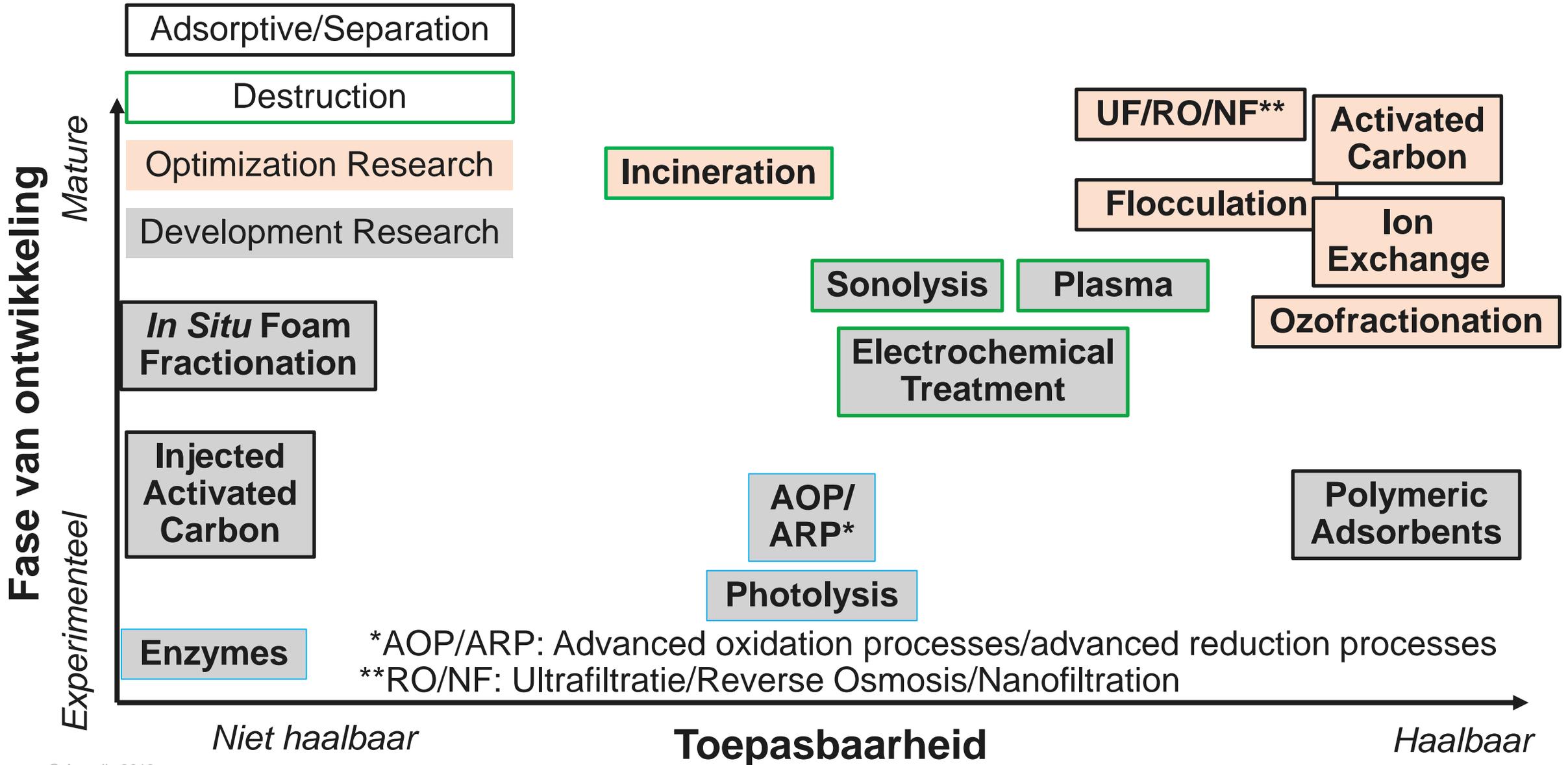


GROUNDWATER REMEDIATION TECHNOLOGIES

**Talk about suitable watertreatment systems is
also talking about applicable discharge levels
and BAT...**



Beschikbare technieken voor water



De bomen en het bos...we werken eraan (mee)

Table 3. PFAS remediation technologies tested in this research

	Groundwater	Firefighting wastewater
Sorption technologies		
Granular activated carbon (GAC)	X	X
Surface modified clay-based (SMC)	X	X
Bio-based or polymeric based adsorbent (PBS)	X	X
Separation technologies		
Flocculant (FLC)	X	X
Nanofiltration (NF)	X	X
Foam (o ₂)fractionation (FOF)	X	X

GAC werkt - Case havengebied Amsterdam (2019)

- Ongeveer 400 m³ bluswater gereinigd over actief kool
- Voorkeursvariant voor RWS
- Concentratie PFAS relatief laag (30 µg/L), rendement van 99,99%
- Extra aandacht voor vermijden cross-contaminatie en personal safety

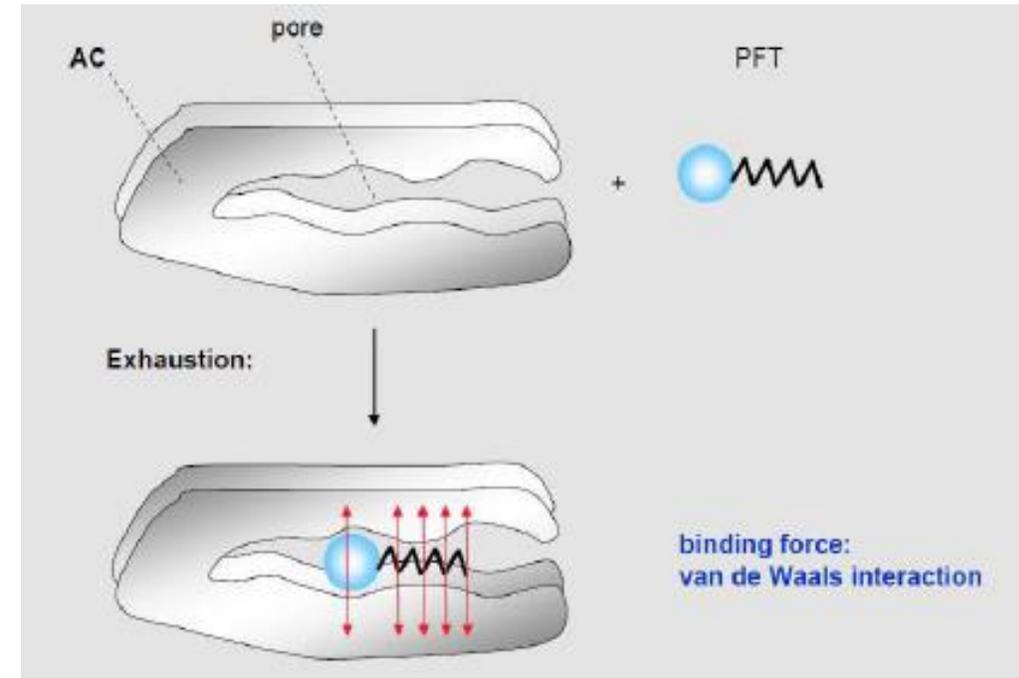
- Verwerking of regenereren van actief kool – gaat dat wel goed?



RWS geeft voorkeur aan on-site behandeling t.o.v. verwerking via de keten!

GAC werkt, maar...

- **Low efficiency : 0,01% (10 grams of PFAS per 100 kg of GAC)**
- Understand types of GAC available - bituminous, sub-bituminous, anthracite, lignite, coconut shell
- Mesoporous GAC (e.g. coal, lignite) better sorption capacity for PFASs than microporous GAC (e.g. coconut)
- GAC with lower density (sub bituminous) may be more cost effective
- Organic Matter (TOC) can out compete PFOA/PFOS for adsorption site/pore obstruction
- TOC less sorptive as pH increases - slight pH adjustments pre-AC may improve efficiency

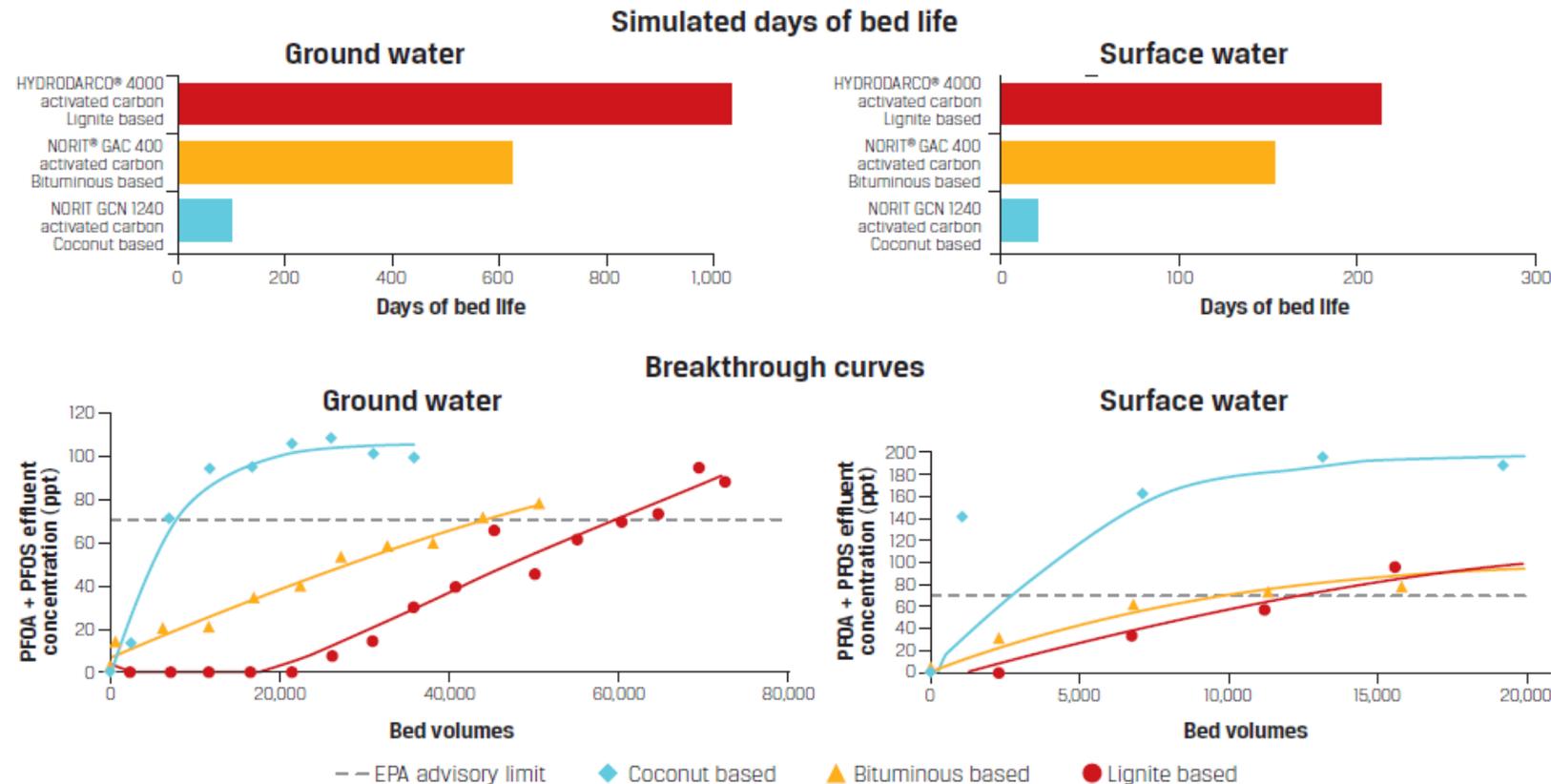


60.000 BV @ 209 ppt = 0,003% belading

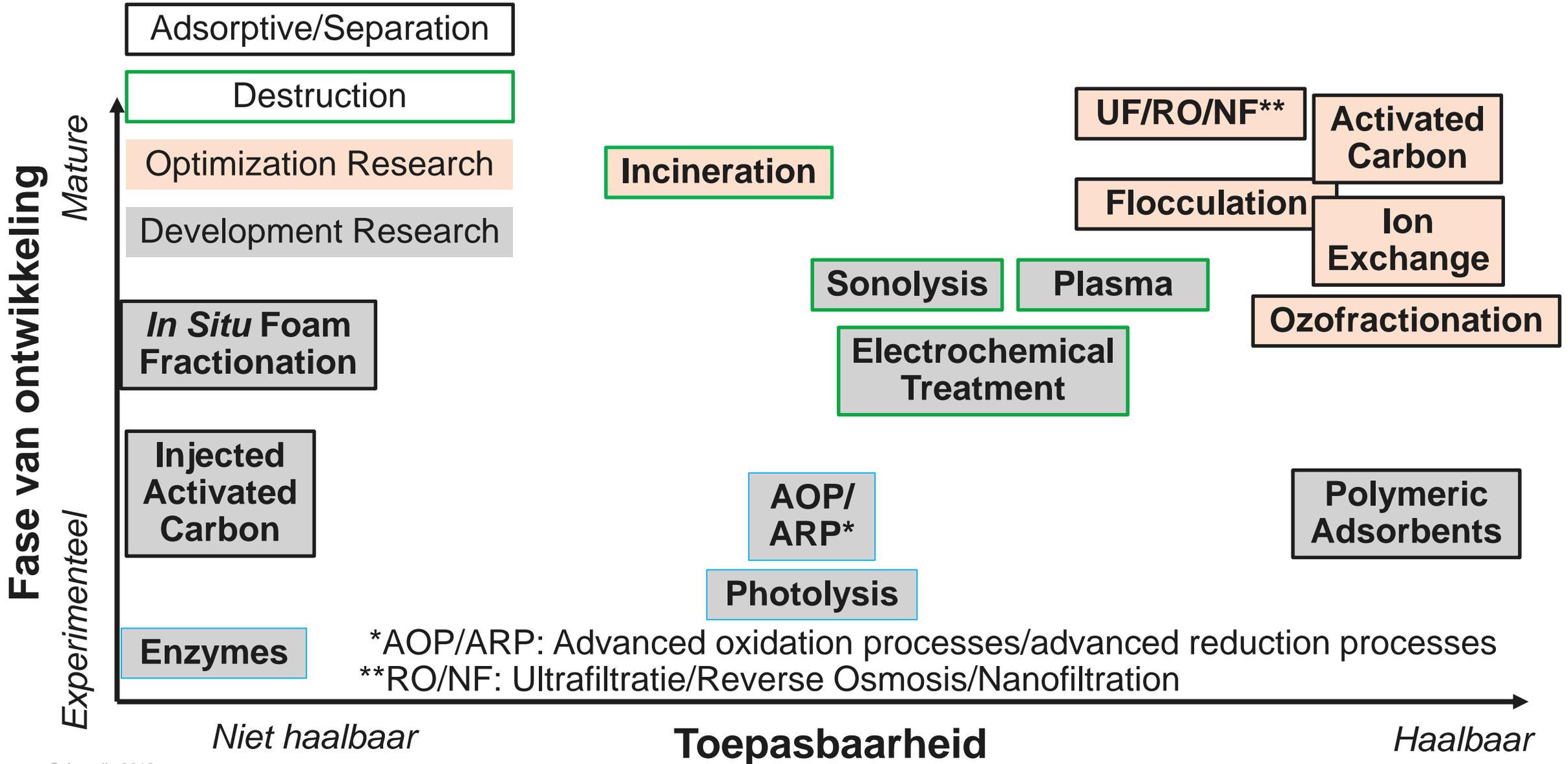
Test results are provided in the following tables.

Small scale column tests for surface and ground water were conducted with different activated carbons. Test water samples contained the following TOC concentrations and PFOA/PFOS influent concentration:

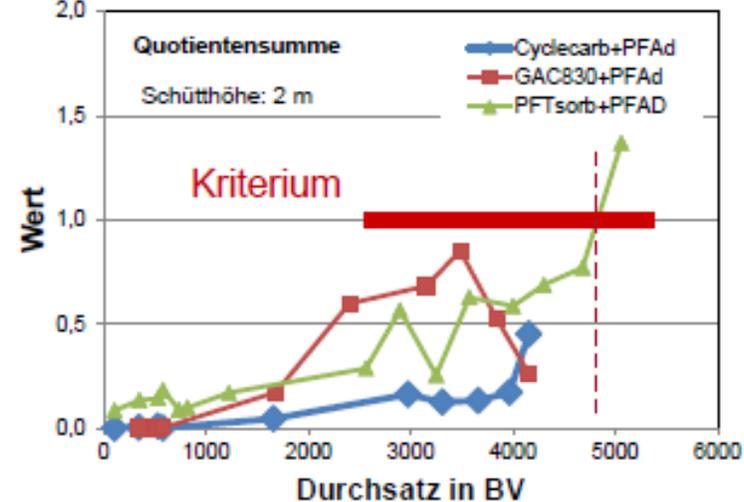
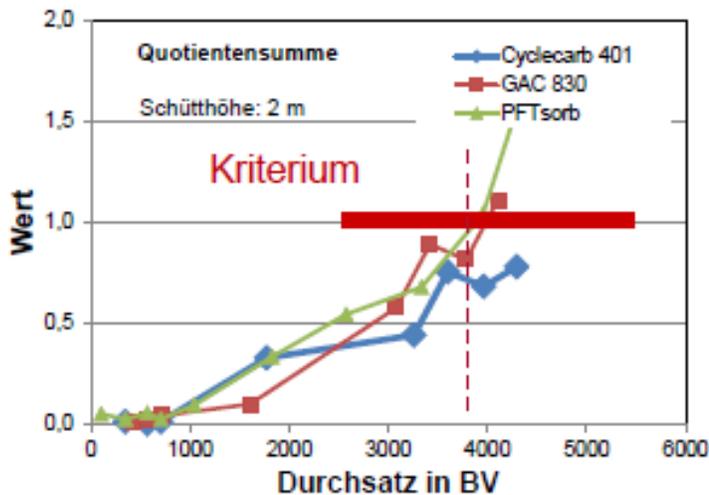
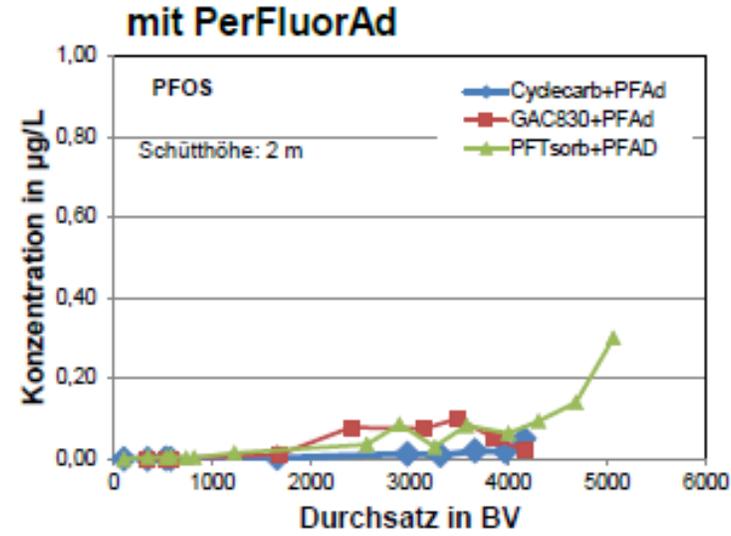
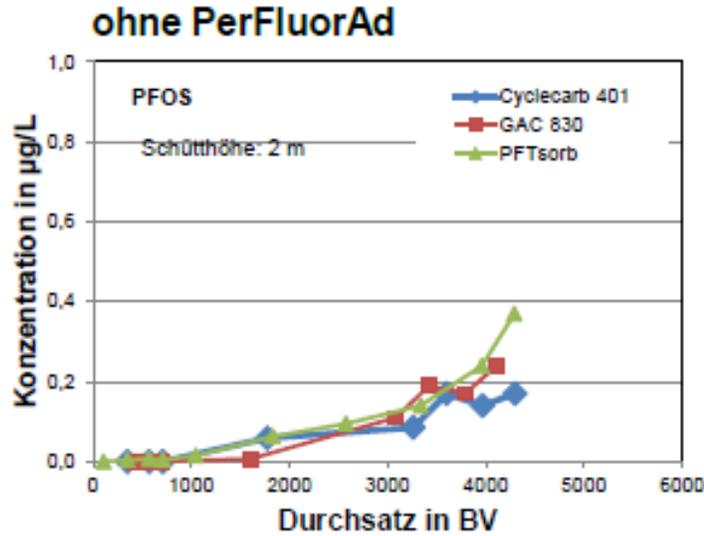
- ◆ Ground water – TOC Concentration of 0.8 ppm
- ◆ Surface water – TOC Concentration of 7.4 ppm
- ◆ PFOA + PFOS Influent Concentration of 209 ppt



GAC met flocculant werkt ook



Vergleich Aktivkohlen mit / ohne PerfluorAd-Vorbehandlung



Diplom Biologe
 Christian Eichelmann
 Berghof Analytik + Umweltengineering GmbH
 Ravensburg / Tübingen

17. Karlsruher Altlastenseminar 2017
 Karlsruhe, 21. Juni 2017



Zusammenfassung (3)

- spezifische Kosten für die Aktivkohle (ohne PerfluorAd-Entsorgung!) für die Reinigung von 1 m³ PFC-kontaminierten Grundwasser:
 - ohne PerfluorAd: 0,13 €/m³
 - mit PerfluorAd: < 0,06 €/m³
 - + Kosten PerfluorAd ca. 0,03 €/m³
 - + Kosten Entsorgung Ausflockungs-Masse

Ersparnis ca. 6-8 % ggü. Linie A ohne Vorbehandlung

Kostenvergleich – $Q_w = 25 \text{ m}^3/\text{h}$, $\Sigma \text{PFC} = 10 \text{ }\mu\text{g/L}$

Reinigungsverfahren	Aktivkohle-adsorption	Ionenaustausch	Flockung	Membranverfahren
Einmalkosten - Montage - Inbetriebnahme	24.000 €	28.000 €	33.000 €	47.000 €
Betriebsmittel	0,07 €/m ³	0,17 €/m ³	0,15 €/m ³	0,63 €/m ³
Betriebsmittel, Anteil Gesamtkosten	14%	22%	18%	34%
Gesamtkosten * - spezifische - jährliche	0,50 €/m ³ 109.500 €/a	0,79 €/m ³ 173.010 €/a	0,82 €/m ³ 179.580 €/a	1,87 €/m ³ 409.530 €/a

* Anlagentechnik (Vorhaltung, Wartung, Reparaturen, Instandhaltung, Überwachung) elektrische Energie, Betriebsmittel inkl. Reaktivierung bzw. Entsorgung

Sigarendoos!

10 ug/L = 10 gram/1000 m³

0,01% max belading komt overeen met 10 gr/100 kg kool

100 kg kool kost minimaal Eur 150,= (levering)

Eur 150,= voor 1000 m³ is 15 ct /m³ en geen 7 ct/m³

CONCLUSIE ADSORBENTS

Doe altijd labtests en een pilot!

- ❑ Zeker bij langjarige grondwatersaneringen
- ❑ Ieder type water heeft ander adsorptie gedrag
- ❑ Ieder type kool of resin moet je in de praktijk testen
- ❑ Voorbehandeling essentieel

- ❖ Ongoing proefsanering nabij Düsseldorf
- ❖ Influent wordt gesplitst in vier stromen
- ❖ Verschillende adsorbents worden getest



ARCADIS Design & Consultancy for natural and built assets

PFAS TREATMENT WITH GRANULAR ACTIVATED CARBON – USING RAPID SMALL-SCALE COLUMN TESTS TO PREDICT FULL-SCALE PERFORMANCE

Using granular activated carbon (GAC) to remove perfluoroalkyl substances (PFAS) from water is a widely applicable, reliable treatment method. GAC can serve as a stand-alone process or be combined with other treatment technologies. For example, it can be used by itself to remediate water from soil washing, or as an additional step to enhance the performance of a treatment system including other (less effective) processes. GAC is seen as the 'base-line' for PFAS treatment, and new PFAS treatment methods are often measured against activated carbon performance. The key advantages and limitations of PFAS removal with GAC are listed below:

Advantages:

- Applicable at different scales (household to industrial)
- Efficiency PFOS removal of > 99%
- Effective at low concentrations
- Reactivation of activated carbon
- Proven, well understood method

Limitations:

- Not as effective for short-chain PFAS and precursors
- Competition of PFAS with other constituents
- Reactivation Costs

Because soil properties and remediation goals vary per case, rapid small-scale column tests (RSSCT) should be done prior to remediation. With these tests applicability of activated carbon can be determined and the most suitable activated carbon can be selected.

Design of the test (materials, scale of the test, etc.) is highly dependent on the target contaminant and the goal of the tests. The designs should not be interfering with the test and expertise is needed to make sure the tests give the most reliable results. Arcadis has multiple experts who worked on PFAS RSSCT all over the world. We executed these tests for multiple clients in amongst others the USA, Germany and the Netherlands. The remediation can be tested using RSSCT, but exact procedures for these tests are dependent on national standards and regulations and on the task at hand.

Many people within Arcadis have employed RSSCT's to evaluate GAC performance, for clients all over the world. Several Arcadians with RSSCT experience are identified below.



Carolin Klauer (D)
Team Leader Environment
Expert in water remediation technologies
Carolin.Klauer@arcadis.com
+49 15117143410



Kirk Nowack (USA)
Technical Expert – Drinking Water
Subject matter expert - RSSCTs
Kirk.nowack@arcadis.com
+1 3028946937



Laura Sloot (NL)
Specialist soil and toxicology
PFAS remediation advisor Arcadis EMU
Laura.sloot@arcadis.com
+31 614382245

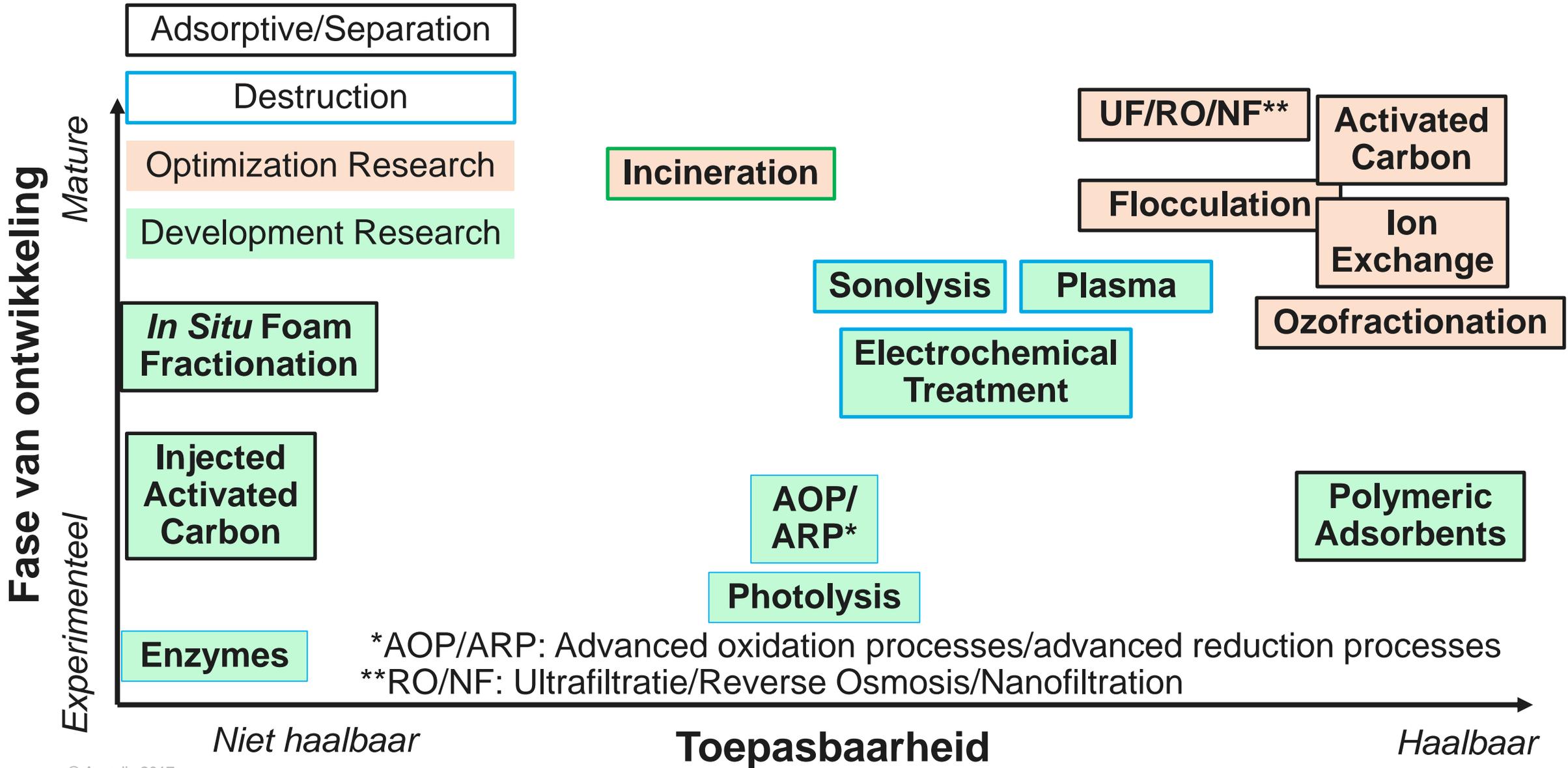


Typical RSSCT apparatus (source: Engineering Performance Solutions, USA)

© Arcadis 2019

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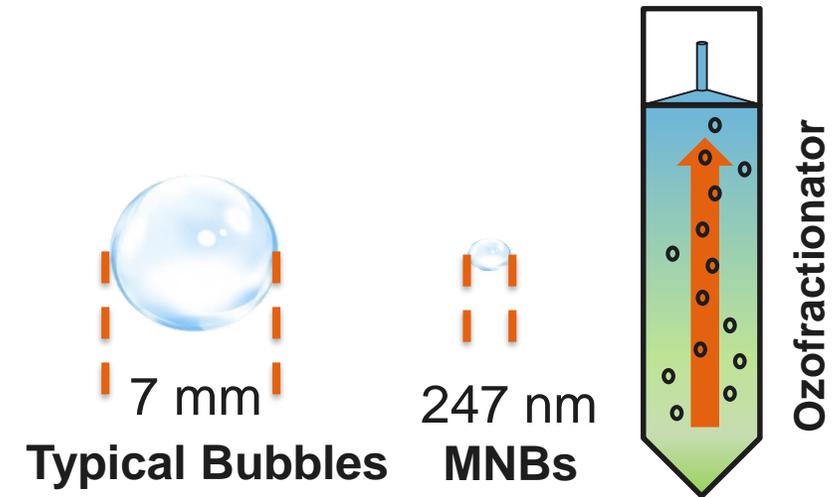
Beschikbare technieken voor water



Ozofractionation in de kern

- Techniek ooit ontwikkeld als oplossing voor AMD
- PFAS (surfactants!) worden uit geschuimd en in restfractie geconcentreerd (factor 1000-2000 minder volume)
- Efficiënt door micro-bubbels met lading!!!
- Geschikt voor complex water (afvalwater ed)
- Geschikt voor hoge vrachten aan PFAS (nu tot 20 mg/L)
- Beter in het verwijderen van de kort ketenige PFAS verbindingen
- Overige BOD of COD wordt geoxideerd of gemineraliseerd
- Minerale delen worden afgescheiden

- Nog niet geschikt voor foam concentrates (g/L niveau)

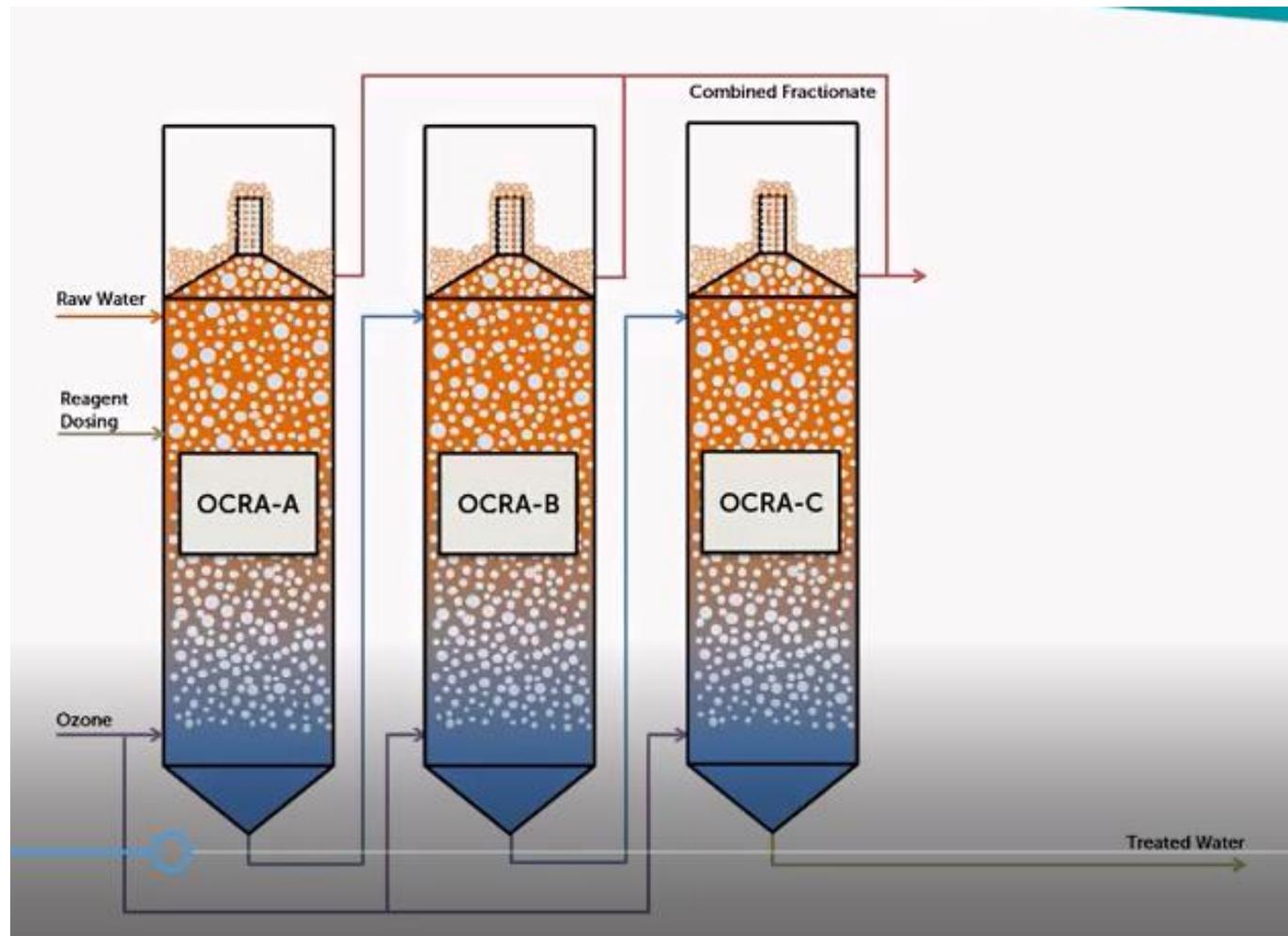


Bench- en Pilottests in Nederland: vanaf Q1 2020

Ozofractionation – Process Flow Diagram

EVOGRA Pty Ltd,
UNITED STATES
PATENT No.
2014/0190896.

EVOGRA Pty Ltd,
AUSTRALIAN PATENT
No. 2012289835.



In detail

Ozon microbubble generator schuimt de PFAS uit de waterstroom af

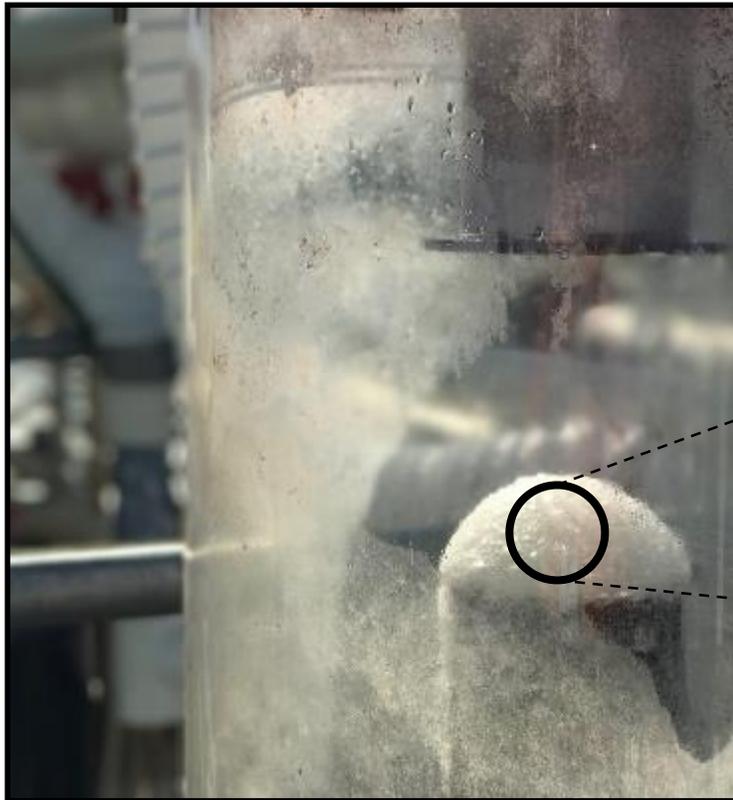


Photo Source: Evocra 2017



***EVOGRA 2nd Generation PFAS Water Treatment Plant
Hobart Airport***



***PFAS removed in foam concentrate
(re-concentrated to approximately 0.05% of original volume)***





Hobart Airport HFTG - Sample of results (ppb)

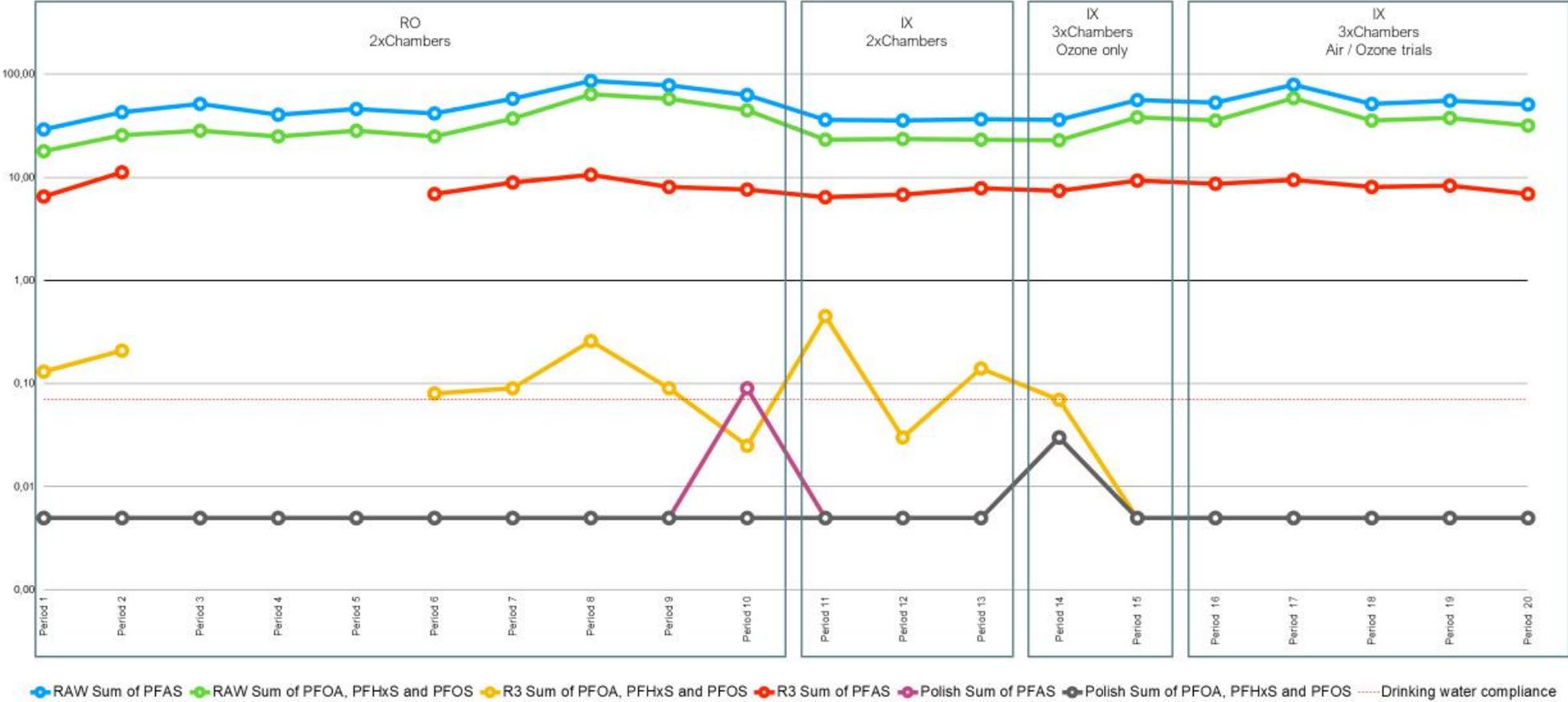


Table 1

A Select Summary of a Larger Poly and Perfluoroalkyl Substances (PFASs) Data Set (Ross et al. 2017) Demonstrating the Separation Effectiveness of the Ozofractionative Catalyzed Reagent Addition (OCRA) Process

PFAS	Influent (ppt)	Ozofractionation % Removal	Filtration % Removal	Treated Water (ppt)	Total % Removal
PFOS + PFHxS	535	98.13	—	<2	99.63
PFOA	341	97.07	—	<2	99.41
6:2 FtS	18,400	99.14	96.84	<5	99.97
PFPeA	1140	82.46	99.00	<2	99.82
PFHxA	1050	96.19	95.00	<2	99.81
Sum PFAS	7480	96.87	99.15	<2	99.97
Total PFAS, TOP assay	28,800	98.58	99.51	<2	99.99

The influent concentration of two long-chain perfluoroalkyl acids (PFAAs; PFOS and PFOA), two short-chain PFAAs (PFPeA and PFHxA), and one polyfluorinated precursor (6:2 FtS) are presented with subsequent removal during ozofractionation and polishing treatment. Noteworthy is the final entry in the table that presents an accurate reflection of total PFASs as confirmed by the total oxidizable precursor (TOP) assay showing >99.99% removal. OCRA is a patented process by EVO CRA (Dickson 2013, 2014). PFOS, Perfluorooctane sulfonate; PFPeA, Perfluoropentanoic acid; PFHxA, Perfluorohexanoic acid.

GROUNDWATER REMEDIATION TECHNOLOGIES

OVERIGE AL DAN NIET UNDER DEVELOPMENT

Sonolysis

Applicability:

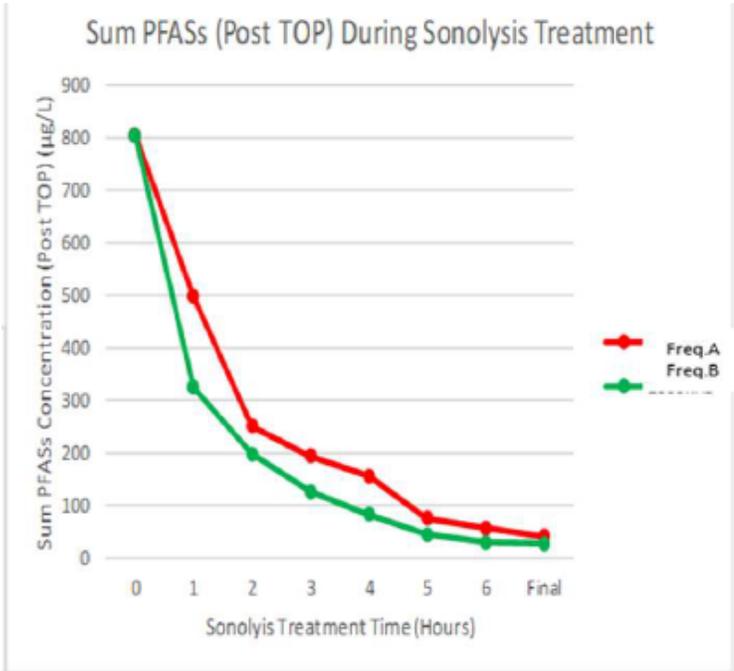
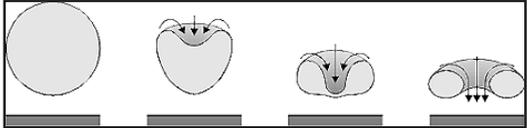
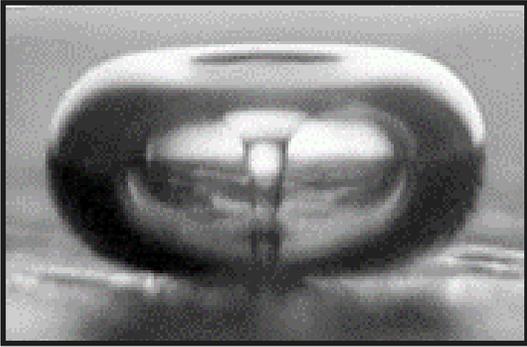
- Ultrasound applied to water results in successive rarefaction/compression of microbubbles ultimately yielding cavitation with extremely high temperatures on the surfaces of the bubbles resulting in pyrolysis of PFASs.

Benefits:

- Can reliably destroy concentrated PFAS waste streams with literature/laboratory supported fluoride mass balance.
- Opportunities to use green energy sources as technology develops (i.e., solar power).

Limitations:

- PFOA rate > PFOS rate. PFOS will require longer residence times and/or more energy.
- Requires specialized equipment and skilled implementation.
- Need high concentrations (mg/L)
- Capital expense of large scale sonolysis units



Electrochemical flow cells (Colorado School of Mines and Aecom)

The researchers are offering a better solution. Tong, a leading expert in membrane filtration and desalination methods for environmental hazards, employed a nanofiltration membrane with appropriate pore sizes to filter out 99.5% of dissolved GenX compounds. Once that concentrated waste stream is generated, the researchers showed that electrochemical oxidation, which Blotevogel considers one of the most viable technologies for destructive PFAS cleanup, can then break down the waste into harmless products.

Table 2 Summary of DE-FLUORO™ treatment results

Trial / Sample #	Client Sector	Sample Description	Initial total PFAS concentration (µg/l)	% Mass Reduction (total PFAS) DE-FLUORO™	Initial 'regulated' PFAS concentration (µg/l)	% Mass Reduction (regulated PFAS) - DE-FLUORO™
1	New Zealand Government	Source area groundwater	27	84%	13	98%
2	Chemical Manufacturer	Industrial wastewater	354	100%	310	100%
3	Australian Government	Source area groundwater	455	99%	445	98%
4	Remediation Contractor	IX R – soft wash recipe	1,570	63.6%	54.9	100%
5	Aviation	Remediation derived wastewater	1,590	90%	1088	98%
6	Oil & Gas	Spent C6 AFFF solution	4,620	83%	6	71%
7	Remediation Contractor	Remediation derived wastewater	10,700	99%	6,572	100%
8	Oil & Gas	3M AFFF Concentrate / Product	6,380,000	58%	5,837,000	62%

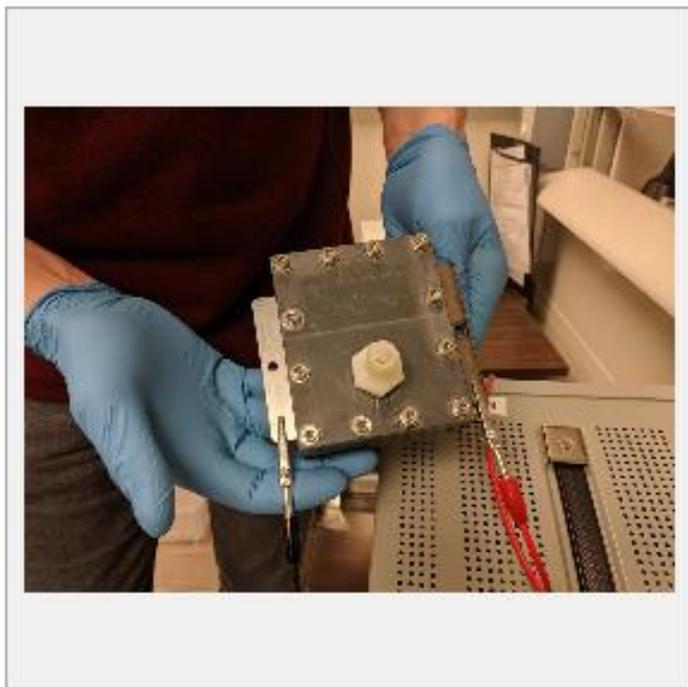


IMAGE: AN ELECTROCHEMICAL FLOW CELL WITH A STAINLESS STEEL CATHODE AND A BORON-DOPED DIAMOND ANODE IS USED TO TREAT A CONCENTRATED WASTE STREAM OF GENX. [view more >](#)

Activated Carbon Injection

- Is carbon distribution sufficient ? **Particles size 1-10 μ m – limited by geology**
- Is the carbon mass sufficient ? **Long term mass flux of PFASs & DOC**
- Is reinjection of AC possible? **Reduced permeability**
- Is there a need to treat short chains & precursors? **Poorer sorption**
- Sorption is reversible, are the PFAS concentrations in the desorption phase low enough to keep remediation targets ?
- Are PFAS displaced by high DOC concentrations ?
- PFASs are not degradable – biodegradation on AC surface not applicable
- Is this concept approvable by the regulators ?

Just turns a plume into a source?



Source: Regenesis, US

Arcadis.
Improving quality of life.