# CHALLENGES IN DEVELOPING A TREATMENT SOLUTION FOR PFAS - AN EMERGING CONTAMINANT

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# ABSTRACT

Per- and poly-fluorinated alkyl substances (PFAS) are a group of emerging contaminants which are present at sites where aqueous film forming foams (AFFF) have been use for firefighting or related training activities. PFAS has been shown to be persistent, bioaccumulative and toxic to some aquatic and land organisms, so there is growing concern and impetus to find a treatment solution for water and soil contamination. The path to finding a treatment solution is complicated by the nature of these chemicals and the concurrent development of our understanding of toxicology, environmental fate and suitable policy.

This paper outlines the challenges confronting the development of a feasible treatment solution for PFAS-impacted wastewater, which were identified and demonstrated during the development and testing of a process for two commercially available products in the treatment of PFAS-impacted firefighting training wastewater. In addition to describing the trial method, results and findings, it discusses the challenges in defining the objectives, designing the trials and dealing with developing understanding during the piloting period.

The two proprietary products trialled, RemBind<sup>®</sup> and MyCelx<sup>™</sup>, were included in a pilotscale treatment process which was developed and deployed to an existing firefighting training ground. The trials were framed in the context of the typical firefighting training site, with irregular contaminant levels, competing contaminants reporting in the wastewater streams and a target residual that was not well defined by regulatory authorities.

The products and processes used in the trials were able to remove at times greater than 99% of PFAS, including the shorter-chain (typically C4) compounds which have not been effectively removed by typical wastewater treatment technologies such as granular activated carbon and reverse osmosis. The trials also demonstrated some of the unique difficulties in design for treatment, sampling and laboratory analysis of this particular group of chemicals and challenges remain in implementing the treatment processes tested on a permanent, full-scale basis.

# **KEYWORDS**

PFAS, PFOS, PFOA, AFFF, wastewater treatment

# **1** INTRODUCTION

Per- and poly-fluorinated alkyl substances (PFAS) are a set of synthesized compounds developed for use in many applications, including consumer goods packaging, textiles and mist suppression in metal plating processes. Two PFAS compounds, Perfluorooctane

sulfonate (PFOS) and perfluorooctanoic acid (PFOA), were primary ingredients in some aqueous film forming foams (AFFF) used historically by firefighting services and in foam deluge systems.

In May 2009, PFOS and PFOA were addressed by the Stockholm Convention on Persistent Organic Pollutants. PFAS are now considered emerging contaminants as they have been shown to be persistent, bioaccumulating, and toxic. Firefighting services globally have since sought to remove or reduce PFAS-containing AFFF from use. At sites where AFFF has been removed from service, legacy contamination from past use often remains on surfaces, in soil and in groundwater.

Firefighting crews need to perform simulated exercises to maintain their experience and competency. This usually involves igniting a mock building or vehicle structure with a fuel such as wood, kerosene/jet fuel or LPG to be extinguished by water, foam (ideally non-fluorinated) or dry chemical powder (DCP). When these exercises are performed, the contaminated equipment, surfaces and infrastructure leach PFAS into the runoff, producing a wastewater stream that can contain PFAS, hydrocarbons, soot, dust and other solids, surfactants from foam and potassium bicarbonate (typically the main ingredient in DCP).

As awareness and regulation develops, there is an increasing need to identify a treatment solution for PFAS-impacted waters and soils. Treatment options explored in various scales include sorption, thermal and chemical oxidation, filtration and ion exchange. Trials of these technologies have often been performed in controlled laboratory environments or in specific site contexts. Each process has limitations which means there is no singular tried and tested process that can be adapted easily for all applications.

In developing a treatment process for wastewater produced by firefighting training, there are various contextual realities that need to be considered, including:

- Firefighting training exercises vary in time, frequency and scale and therefore do not produce a consistent wastewater stream
- Discharge limits for PFAS are gradually being developed and implemented by regulatory bodies, and some jurisdictions are yet to implement a PFAS-specific policy. These often also vary between jurisdictions although in Australia attempts are being made to develop nationally consistent criteria
- Firefighting training grounds are often located in areas where there is no local access to utilities including power, water and sewerage
- Firefighting services do not employ plant operators or have technical wastewater expertise.

A firefighting service provider in Australia engaged Beca to develop, test and assess PFAS treatment processes at a pilot scale based around two commercially available products - RemBind<sup>™</sup> and MyCelx<sup>™</sup>. These products had been shown to be able to remove PFAS from wastewater in the presence of hydrocarbons in prior studies and lab-scale trials, so the client was interested to understand whether these results could be repeated in the field.

This paper describes the methods, results and challenges identified and encountered in developing the treatment processes and undertaking the pilot trials. Considerations for scale up and development of other PFAS treatment processes are also discussed.

# 2 THE PROBLEM(S)

Treatment of PFAS-impacted waters is a developing field which has been demonstrated with some success in several contexts (many of which are laboratories). Developing a solution specifically for firefighting training wastewater compounds the complexities by various factors, which are listed below and discussed further in this paper.

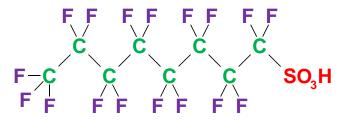
- A complex and varied group of contaminants
- A difficult operating environment
- No well-established treatment process
- No clear discharge limits set by regulatory bodies
- Sampling and laboratory testing sources of error.

# 2.1 PFAS - A LARGE AND COMPLEX GROUP OF CHEMICALS

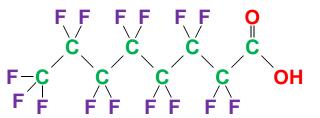
The PFAS group of thousands of chemicals are characterised by a fluorinated carbon chain attached to a functional group such as a sulfonate or carboxylic acid. The strong, thermally stable carbon-fluorine bonds and the hydrophobic / hydrophilic structure of the molecule make the substances very useful in the application of firefighting foams.

Unfortunately, the same properties make these substances a problem for the environment and ecological and human health, being persistent, bioaccumulating and potentially toxic.

Historically PFOS and PFOA were two key PFAS ingredients that have been used in AFFF products. Each consists of an eight-carbon chain with the sulfonate (PFOS) and carboxylic acid (PFOA) functional group (Figure 1). In these historical AFFFs, the compositional proportion of PFAS was greater than current AFFF formulations, meaning that PFOS and PFOA are usually the most abundant PFAS detected. This together with the relative higher toxicity of PFOS and PFOA compared to other PFAS, has meant that these two PFAS have been the focus of measurement, testing and treatment. However, PFAS with variations in chain length and functional group are often present in AFFF-impacted wastewaters and developing environmental and human health research is strengthening the argument that these other compounds can still have a measurable impact and must be considered in a treatment solution.







**PFOA - perfluorooctanoic acid** 

#### Figure 1: Chemical structure of PFOS and PFOA

The various PFAS species exhibit differing properties, e.g. partitioning, hydrophobicity, reactivity, toxicity, mobility and environmental fate. Generally shorter chain PFAS exhibit lower toxicity and lower bioaccumulation, but are more mobile in the environment, equivalently persistent and less studied (Bowles, 2017). Furthermore, some PFAS

chemicals are considered precursors to other more harmful ones, such as some fluorotelomers which can degrade to PFOA.

# 2.2 PFAS AT FIREFIGHTING TRAINING GROUNDS

A firefighting training ground will usually consist of a mock building or structure (e.g. an aircraft) surrounded by a kerbed concrete apron for containment. During a training event, the structure is sprayed with an accelerant such as kerosene or LPG and ignited, to be extinguished by the firefighting crews, with the resulting wastewater draining to a collection tank for removal or treatment.

PFAS typically adsorbs into contacting surfaces such as metal and concrete, and very slowly desorbs with subsequent washdown. After years of use of AFFF use, training ground surfaces have become contaminated with PFAS. So even at sites where the use of PFAS-containing AFFF ceased a decade or more ago, contaminated structures and equipment continue to release legacy PFAS to contaminate the training firewater and stormwater runoff.



Figure 2: A typical firefighting training ground set-up and environment

There are many properties of a typical firefighting training ground which make any form of wastewater treatment difficult, let alone for a relatively untried and tested process. These include:

- A remote site, often within a secure compound (e.g. airport) and unmanned
- Often a lack of utilities available in the training ground area: power, water, sewer
- Varying and irregular wastewater stream, depending on the frequency, number and size of the crews performing training, the duration of the training exercises, how much accelerant is used, the application of foam or DCP in training and rainfall volumes

- The volume of wastewater produced is typically small, up to 20m<sup>3</sup> per week
- Other contaminants, including hydrocarbons (free and emulsified in the presence of foam), DCP, surfactants such as from fluorine-free firefighting foam, grit, ash and soot, metals and vegetation
- No personnel training or capacity to operate and maintain a treatment plant
- A requirement to deploy a system repeatedly at various sites.

# 2.3 EXISTING PFAS TREATMENT TECHNOLOGIES

Like most water treatment, a single unit operation will not be a catch-all solution to a given problem. At the time of this project, a desktop study of available PFAS treatment technologies found that much of the research, trials and implemented systems to date are either focused on a too narrow range of PFAS compounds, were performed in a controlled environment, or were specific to a unique case. And like any wastewater treatment process, the treatment unit operations would need to consider the real-world context of the firefighting training environment.

Several methods for treatment that have been studied and tested at differing scales are outlined in Table 1.

Method	Description	Limitations
Incineration	Wastewater stream fed into a thermal oxidizer or incinerator at temperatures above 1,100°C	There are only a limited number of facilities in Australia with the capability to incinerate contaminated material. These facilities often require the wastes to be relatively 'pure', not mixtures, so the PFAS must be relatively concentrated of even isolated PFAS 'brine'.
Filtration (nanofiltration or reverse osmosis)	Wastewater pumped through a fine filter or RO membrane after pre- treatment	High pressure pumps would require high energy use, sites often have limited or no electricity supply.
		Filters and membranes at risk of becoming clogged or degraded due to varying / emulsified hydrocarbon concentrations (Hodgkiess et al, 2001)
Sorption	Wastewater contacted by activated carbon (powdered or granular) or other sorbtive materials	Activated carbon not effective in removing short chain PFAS (Dudley et al, 2015)
		Susceptible to blinding by other organics and hydrocarbons
Ion Exchange	Wastewater contacted by resins, mineral materials or polymers	Wastewater pre-treatment may be required to prolong the life of the media
		Regeneration may not be possible at site

# Table 1- PFAS Wastewater Treatment Methods

# 2.4 THE REGULATORY ENVIRONMENT

In Australia and New Zealand during the time of this study, there were no regulatory policies in place with discharge limits. Some interim screening levels for soil, surface and groundwater had been developed, but had not been formally accepted.

At the time of project commencement, guideline levels that had generally been referenced by industry included the Minnesota Department of Health, which provided drinking water limits of  $0.3\mu$ g/L for PFOS and  $0.3\mu$ g/L for PFOA. During the period of the study, the US EPA released new drinking water advice, which lowered the limit to  $0.07\mu$ g/L for PFOS or PFOA or a combined total. These limits were acknowledged to being applicable for drinking water quality and therefore limited in their application to environmental discharge levels.

Since completion of the study, several regulatory bodies in Australia and New Zealand have developed and released PFAS environmental and health guidelines and policies. These include:

• The Australian Department of Health (2017), which released health based guidance values for use in site investigations in Australia as provided in Table 2.

Toxicity Reference Value	PFOS/ PFHxS	PFOA
Tolerable daily intake, µg/kg bw/day	0.02	0.16
Drinking water quality value, µg/L	0.07	0.56
Recreational water quality value, µg/L	0.7	5.6

 Table 2: Health based guidance values for site investigations

• DRAFT ANZECC trigger values (Department of Australian Environment and Energy, 2016), a selection of which is provided in Table 3. It is acknowledged in the draft guidance that the 99% species protection level for PFOS is below the limit of reporting offered by most laboratories and a 'detect' threshold could be applied by agencies.

Table 3: Select investigation levels for PFOS and PFOA by exposure scenario

Exposure Scenario	<b>PFOS,</b> μg/L	<b>PFOA,</b> μg/L
99% species protection (Freshwater)	0.00023	19
95% species protection (Freshwater)	0.13	220
99% species protection (Marine water)	0.29	3,000
95% species protection (Marine water)	7.8	8,500

# 2.5 SAMPLING AND TESTING

Due to the properties of PFAS and their abundance in consumer goods, there are many reported sources of environmental sample contamination during PFAS investigations. Some examples include (WA Department of Environment Regulation, 2016):

- PVC and Teflon<sup>®</sup> coated field equipment or container lids, which can be a source of PFAS contamination
- Glass and metals in jars and wrapping can adsorb PFAS and result in underreporting
- Detergents and decontamination solutions such as Decon 90<sup>®</sup> can be a source of contamination

Laboratories are developing experience and methods for PFAS testing and there are many ways in which discrepancies can occur in samples and between laboratories (ALS, 2015), including:

- Matrix interferences in the samples
- Whether linear only or linear and branched standards are used
- Where the lab corrects for recoveries

Laboratories are also developing new techniques that allow them to report results with increasingly lower limits of reporting. As regulatory guideline limits for discharge and investigation are developed, the values are approaching the laboratories' limit of reporting capability. Therefore, sources of error in the field or in the lab can significantly affect the reported success or failure of a treatment system.

# 3 DEVELOPING A TREATMENT PROCESS FOR FIREFIGHTING TRAINING WASTEWATER

Beca were engaged by a firefighting service provider to develop and test a pilot-scale treatment process to remove PFAS from firefighting training ground wastewater based around two commercially-available media: MyCelx<sup>™</sup> and RemBind<sup>®</sup>. These two products had been tested previously by the client and shown promise in removing PFAS.

MyCelx is a polymer agent which binds to hydrocarbons and water soluble organics while repelling water. The MyCelx polymer is infused with various substrates to enable contact with the contaminated fluid, such as polypropylene for spun-woven filters or granules for filter media.



# Figure 3: MyCelx Performer column media

RemBind is a powdered reagent which was developed to bind and immobilise contaminants in soil. The product primarily contains powdered activated carbon and aluminium hydroxide (amorphous) in powdered form mixed with kaolin clay.



Figure 4: RemBind powder

The general philosophy adopted for the project was to develop and trial the process trains in the context of the typical firefighting training ground constraints. This included:

- Focusing on developing a simple, robust system that would not require a dedicated and trained operators
- Using actual wastewater collected from the firefighting training grounds rather than spiked waters
- Using basic unit operations and equipment that don't require complex control or other inputs (e.g. chemical dosing).

# 3.1 STUDY OBJECTIVES

The objectives of the study were to:

- 1. Perform trials at a pilot scale using rudimentary components to assess to what extent PFAS can be removed from wastewater using MyCelx and RemBind
- 2. Identify a process that can be trialled using each of MyCelx or RemBind and understand the process operation
- 3. Review the feasibility of each technology at full-scale to inform whether further development and trials of either process could be considered.

# 3.2 DEFINING TRIAL SUCCESS

The primary measure of feasibility for any process train developed for one of the two products is its ability to remove PFAS from the wastewater. In lieu of specific discharge criteria for PFAS in relevant Australian regulations at the time of the trials, different levels of success were nominated ranging from the limit of commercial laboratory capability to available industry guidance. The categories of success for the trials were defined as shown in Table 4.

Ref	Benchmark	Threshold Levels <sup>1</sup>	Outcome
L1	Below the laboratory	$PFOS = 0.002 \mu g/L$	Process train is capable of
	limit of reporting	$PFOA = 0.002 \mu g/L$	removing PFAS and should be assessed against other
		6:2 fts = 0.01µg/L	feasibility criteria
		Other PFASs = $0.002-0.1 \ \mu g/L$	
L2	Below the US EPA	$PFOS = 0.07 \mu g/L$	Process train is capable of
	Drinking Water Health Advisories limit for	$PFOA = 0.07 \mu g/L$	removing PFAS and should be assessed against other
	PFOS and PFOA	Or combined = $0.07 \mu g/L$	feasibility criteria
L3	Below the Minnesota	PFOS = 0.3µg/L	Process train is capable of
	Administrative Rules (2009) drinking water	$PFOA = 0.3 \mu g/L$	removing PFAS and should be assessed against other criteria
	limits	6:2 fts = 0.3µg/L	or may have other applications
L4	Possibly acceptable discharge to sewer	PFOS and PFOA = 3µg/L	Process train might be of use, but in a limited context and the business case may only stack up on a site-by site basis.
L5	Greater than acceptable threshold	PFOS and PFOA > 3µg/L	Process train trial has been unsuccessful and should not be considered for pilot plant

Table 4: Residual PFAS: levels of success

Note: (1) The threshold levels developed for this project were based on guidelines and capabilities available at the time. Since the completion of the study, some regulatory bodies and municipal wastewater treatment plants have developed PFAS discharge policies which differ from these levels.

# 3.3 MYCELX TRIALS

#### 3.3.1 METHODOLOGY

#### PROCESS DESCRIPTION

The MyCelx treatment train was developed in conjunction with the technology vendor based on the client's prior trials and the vendor's past experience in treating other wastewater streams. The general process philosophy was to progressively remove other contaminants before targeting PFAS removal in a polishing stage, so as to maximize the removal capacity of the MyCelx media.

The stages of treatment were as follows. The equipment used in the pilot scale were not intended to be retained in a scaled up version, rather represent a unit operation that would be employed in a full-scale process.

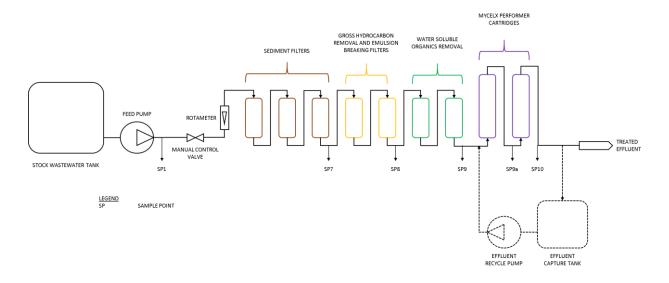
- 1. Solids removal by cartridge filter
- 2. Hydrocarbon removal and emulsion breaking by vendor proprietary filter
- 3. Water soluble organics by vendor proprietary filter
- 4. PFAS removal by MyCelx performer cartridges

The MyCelx process consisted of a series of pre-filters followed by MyCelx Performer cartridges as shown in Figure 5.

Stock wastewater was collected from runoff produced over a week of firefighting training and weather events. The stock was tested and was shown to have relatively high levels of PFAS, in the range of  $800\mu g/L$  to  $1,000\mu g/L$ .

Wastewater was pumped from a stock wastewater tank through the filter bank via a ball valve and rotameter. The ball valve was manually adjusted against the rotameter reading to achieve the target flow rate for each run.

Sample points were located at various stages in the process as shown in Figure 5 to determine if PFAS was being removed in prior stages. Each sample was analysed in a laboratory using the LC/MS/MS method with 20 PFAS analytes tested.



#### TRIAL RUNS

The proposed process train was tested by conducting a series of trials altering the following process variables.

- Flow rate / bed contacting time
  - Trial runs were conducted at two flow rate set points using the vendor standard size MyCelx Performer cartridges
- MyCelx bed depth
  - Trial runs were conducted at a fixed flow rate with multiple MyCelx cartridges in series
  - Samples were collected in between the cartridges across a time frame to determine breakthrough rates and hence cartridge capacity

During each trial run, samples were collected at various points throughout the process and sent to a laboratory for testing and analysis. In between runs, all the media was changed and the rig flushed with clean water.

# 3.3.2 KEY RESULTS AND FINDINGS

Figure 6 provides the results of trial runs performed using the best-performing process variables. The results showed that under these conditions:

- The L3 success threshold could be met for total PFAS.
- For individual PFAS the Mean residual was below the L2 threshold, with PFOS being present in the highest concentration in the wastewater and achieving a final effluent of  $0.061 \mu g/L$
- The MyCelx system was able to achieve significant reductions for the range of PFAS compounds tested

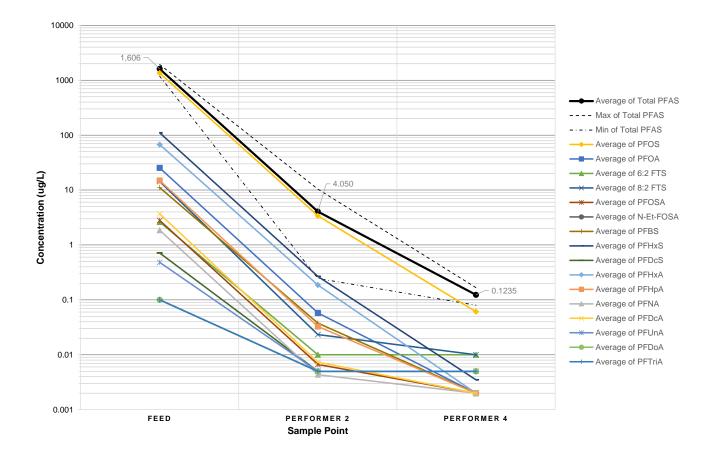


Figure 6: Mean results of samples from runs performed using optimised MyCelx process parameters (undetected PFAS compounds omitted)

# 3.4 REMBIND TRIALS

# 3.4.1 METHODOLOGY

RemBind is a mixture that primarily contains powdered activated carbon, which is widely used in water treatment processes. In developing a process for RemBind, both batch addition and a fixed column bed were considered.

Batch addition followed by filtration was preferred over a fixed column due to:

- Likely caking or channeling issues during the trial and at full scale, since RemBind exists as a fine powder
- Handling and disposal issues. A RemBind Plus column had been trialled at a pilot scale in Germany (Ziltek 2015), which used a sand/RemBind mix to treat groundwater. However, this approach would add to the total disposal cost and volume and may make thermal destruction more difficult.
- Available contact time might be restricted in a column set-up.

# 3.4.2 PROCESS DESCRIPTION

Stock wastewater was pumped into a batch contact tank where a quantity of RemBind was manually dosed and mixed for a given contact time.

At the end of the contact time, the mixture was pumped through a bank of three filters of decreasing pore size to produce the treated effluent.

In some experiments, treated effluent was captured in a second batch mixing tank. RemBind was re-dosed into the tank, mixed for the designated time and pumped through the filter bank.

Sample points were installed at various points within rig, as shown in Figure 7.

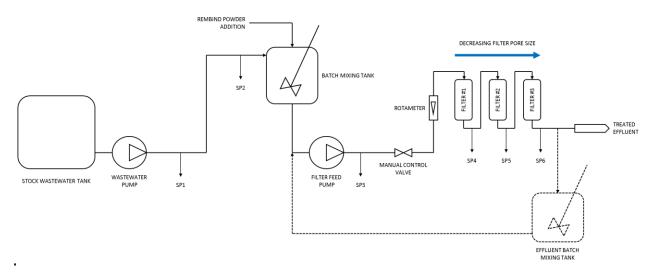


Figure 7: Pilot RemBind Process

# TRIAL RUNS

The proposed process train was tested by conducting a series of trials, altering the following process variables:

- RemBind dose rate, ranging from 0.005g/L to 50g/L
- $_{\odot}$   $\,$  Filter type (bag vs cartridge) and pore size (from 50  $\mu m$  to 0.35  $\mu m)$
- $\circ$   $\,$  Contact time, ranging from 10min to 1hr  $\,$
- Inclusion of a second dose of RemBind

During each trial run, samples were collected at various points and sent to the laboratory for testing and analysis.

# 3.4.3 KEY RESULTS AND FINDINGS

Figure 8, Figure 9 and Figure 10 provide the mean PFAS results measured for trial runs conducted using a secondary batch dose of RemBind with varying dose rates. The results suggest that the RemBind process is effective in removing the PFAS down to the L3 threshold and close to the L2 measure of success.

It was postulated that the secondary dose of RemBind was required as the presence of hydrocarbons and other organics adsorb to the media and potentially blind it from further PFAS adsorption.

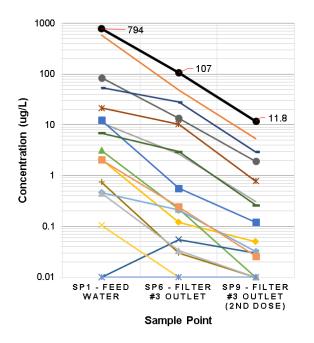


Figure 8: Mean PFAS results for trials conducted with a two lots of 5mg/L RemBind doses

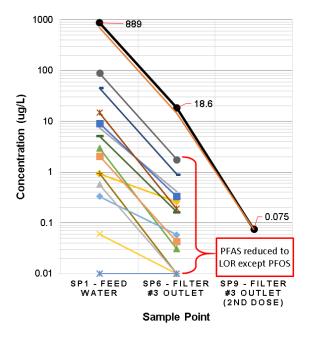


Figure 10: Mean PFAS results for trials conducted with two lots of 20mg/L RemBind doses

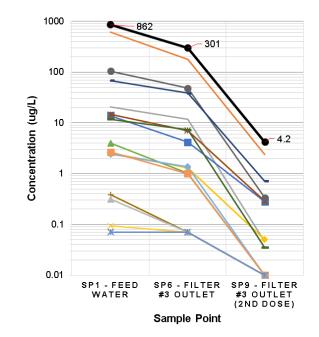
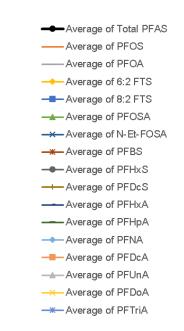


Figure 9: Mean PFAS results for trials conducted with two lots of 10mg/L RemBind doses

Legend:



# 3.5 INTERFERENCES

# 3.5.1 FIELD CONTAMINATION

During the trials several control samples were collected and tested for PFAS. This included:

- Clean water used for equipment rinses, which was supplied from a fire truck as there was no local water supply
- Samples taken of clean water pumped through the equipment before a trial run to validate the equipment flushing
- Sampling equipment after being rinsed thoroughly with clean water.

Equipment flushing and cleaning was deliberately performed to replicate what a typical cleaning cycle which would be performed under the operation restrictions. That is, it would be impractical to provide a dedicated chemical clean-in-place system.

Table 5 provides the results of field control samples collected during the trials. Generally, both pilot rigs were made from polypropylene or polyethylene components, with the exception of some piping in the MyCelx trial rig being mild steel and the Performer filter housings made from stainless steel.

Sample	Clean Water	Clean Water	MyCelx Rinse Blank	MyCelx Rinse Blank	RemBind Rinse Blank	RemBind Rinse Blank	Sample Equipment Rinse Blank
PFOS	0.048	0.292	0.201	0.592	4.44	0.865	0.477
PFOA	<0.002	<0.002	<0.002	<0.002	0.141	0.024	<0.002
6:2 FtS	<0.01	<0.01	<0.01	<0.01	<0.10	<0.01	<0.01
8:2 FtS	<0.01	<0.01	<0.01	<0.01	<0.10	<0.01	<0.01
PFOSA	<0.002	<0.002	0.004	0.015	0.022	<0.002	<0.002
N-Me-FOSA	<0.05	<0.05	<0.05	<0.05	<0.10	<0.05	<0.05
N-Et-FOSA	<0.005	<0.005	<0.005	<0.005	<0.020	<0.005	<0.005
N-Me-FOSE	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
N-Et-FOSE	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PFBS	<0.002	<0.002	0.002	<0.002	0.076	0.009	<0.002
PFHxS	0.005	0.006	0.013	0.012	0.657	0.08	0.007
PFDcS	<0.005	<0.005	<0.005	<0.005	<0.020	<0.005	<0.005
PFHxA	<0.002	<0.002	0.005	<0.002	0.366	0.02	<0.002
PFHpA	<0.002	<0.002	<0.002	<0.002	0.1	0.006	<0.002
PFNA	<0.002	<0.002	<0.002	<0.002	0.02	<0.002	<0.002
PFDcA	<0.002	<0.002	<0.002	<0.002	<0.020	<0.002	<0.002
PFUnA	<0.005	<0.005	<0.005	<0.005	<0.020	<0.005	<0.005
PFDoA	<0.005	<0.005	<0.005	<0.005	<0.020	<0.005	<0.005
PFTriA	<0.005	<0.005	<0.005	<0.005	<0.020	<0.005	<0.005
PFTeA	<0.05	<0.05	<0.05	<0.05	<0.10	<0.05	<0.05

# Table 5: Field Control Samples

The clean water used to rinse both systems carried some PFAS contamination, mainly from PFOS. PFHxS was also consistently present in all blank samples, though usually in trace amounts just above the limit of reporting. This suggests contamination by an AFFF product that was phased out of use on site in 2003 and it was not determined whether it is a result of site or source contamination, field error or laboratory error.

The post-rinse results suggest that the RemBind equipment did not rinse as clean as the MyCelx rig and therefore carried a greater degree of interference. The level of PFOS contamination observed through the MyCelx rig is in the range of that observed in the clean water, so it can be deduced that very little of the MyCelx surfaces carried residual contamination after a clean.

The RemBind system possibly carried more contamination due to the larger filter housings used in the rig (10 inch housings as opposed to the 4 inch housings used for the MyCelx pre-filters), where a larger dead zone was created in the empty housing and therefore did not flush as completely.

This difference between the MyCelx and RemBind systems is not inherent in the relative processes themselves – contamination would likely occur in both cases. However, a key difference of the MyCelx system is that the PFOS adsorption stage occurs in the most downstream unit. That means, any cross contamination picked up in the system by flushing water, wastewater or stormwater will pass through the Performer cartridge (and possibly be adsorbed) before discharge.

With the RemBind process, the RemBind addition and adsorption occurs upstream of the filtration stages, so any downstream contamination (which is likely to occur in an unattended plant) will carry through to the effluent stream.

# 3.5.2 SAMPLING ERROR

Throughout the trials, duplicate samples were taken and tested for PFASs to assess the level of sampling error. A key sources of error could be a heterogeneous mixture, either in the feed water or in the sample from which lab sub-samples were drawn. To collect the duplicate samples, a separate bucket of sample water was collected approximately 30 seconds after the primary sample was taken.

All duplicate samples were taken from treated effluent streams. In this set of duplicates, the coefficient of variance was generally 20% or lower, except for sample with the lowest PFOS concentration. Although the coefficient of variance was relatively high (75%), the small standard deviation (0.034 $\mu$ g/L) suggests that the variability would not have a significant effect and therefore the results can be used with confidence.

Field Sample (µg/L)	Duplicate (µg/L)	Standard Deviation (µg/L)	Coefficient of Variance
0.078	0.011	0.034	75%
0.095	0.085	0.0050	6%
1.1	0.74	0.19	20%
633	497	68	12%

Table 6: PFOS results from duplicate samples

# 4 RISKS AND OPPORTUNITIES FOR SCALE UP

While the trials identified a process that could be built around each technology that was effective in significantly reducing PFAS levels in the wastewater, there are many considerations that need to be explored further in order for a full-scale system to be feasible.

Risk	Consequence	Mitigation Measures / Opportunities
Capital and operational costs:	<ul> <li>Project costs are prohibitive for treatment on site. Removal and disposal by third party favourable</li> </ul>	<ul> <li>RemBind cost of treatment was low, but more capital intensive to handle, dose and dewater</li> <li>MyCelx process equipment relatively low cost, but frequency of media replacement meant operating cost was high</li> <li>Opportunity for technology vendors to modify offering to reduce costs e.g. pre- wetted RemBind or larger MyCelx columns</li> <li>Consider combining processes to have RemBind (lower cost) most of the PFAS and other organics prior to a polishing stage by MyCelx.</li> </ul>
Effluent quality requirement is lower than that demonstrated	<ul> <li>Process can't meet effluent quality target</li> </ul>	<ul> <li>Consider combining the two technologies where RemBind (lower cost) removes most of the PFAS and other organics prior to a polishing stage by MyCelx.</li> </ul>
Varying concentrations in feed water – PFAS or hydrocarbons	<ul> <li>Downstream treatment stages blinded by temporary spike</li> <li>Temporary high PFAS levels may not be able to be treated to desired residual concentration</li> <li>Cost of treatment significant</li> <li>If PFAS lower than expected, equipment may be being replaced before saturation</li> </ul>	<ul> <li>Install buffering at the feed end of the system</li> <li>Consider procuring under a Design / Build / Operate / Maintain (DBOM) contract with performance guarantees</li> <li>Develop seasonal characterisation and implement a regular monitoring and testing scheme</li> </ul>
Uncertainty in PFAS discharge limits	<ul> <li>Plant design cannot achieve compliance</li> <li>Damage to the environment or human health in long run</li> </ul>	<ul> <li>Design to allow for addition of treatment modules (e.g. additional banks of MyCelx cartridges)</li> <li>Consider procuring under a DBOM contract with the ability to renew performance criteria</li> </ul>

#### Table 7: Considerations for full scape systems

Risk Consequence		Mitigation Measures / Opportunities		
Equipment contamination	<ul> <li>Contamination of equipment internals limits the ability of the process to achieve low residual PFAS</li> </ul>	<ul> <li>Include a polishing stage (e.g. MyCelx after RemBind) and design to limit the amount of wetted surfaces downstream</li> <li>Specify materials which have less affinity to adsorb PFAS (e.g. polyethylene, polypropylene)</li> </ul>		
Disposal of PFAS- impacted consumables and equipment – limited approved providers of	<ul> <li>High cost of disposal by 3<sup>rd</sup> party</li> <li>No practical/feasible means of discarding waste materials</li> <li>Stockpile generated</li> </ul>	<ul> <li>Technologies tested are limited in this sense <ul> <li>opportunity for a process that includes</li> <li>PFAS destruction to be developed</li> </ul> </li> <li>Opportunity for further study of adsorbed material e.g. leachate studies on spent RemBind/MyCelx</li> </ul>		
containment / incineration facility operators	• Stockpile generated	<ul> <li>Opportunity to explore where adsorbent media can be regenerated</li> <li>Opportunity to further optimise the process to reduce waste streams</li> </ul>		
Plant operation	<ul> <li>Treatment system downtime</li> <li>Discharge of PFAS-laden water to the environment</li> </ul>	<ul> <li>Consider procuring under a DBOM contract with performance guarantees</li> <li>Consider remote-monitoring in full-scale plants</li> <li>Opportunity for vendor to develop media column that reduces change-out frequency</li> </ul>		
RemBind Dust	<ul> <li>Housekeeping effort required</li> <li>Respiratory risk</li> </ul>	<ul> <li>Segregated and enclosed (with ventilation) area required for RemBind dosing</li> </ul>		
PFAS discharge limits not determined	<ul> <li>New discharge limits cannot be met by the selected process/equipment</li> <li>Equipment may be over specified</li> </ul>	<ul> <li>Design full scale system to be modular to allow addition of polishing stages</li> </ul>		
Atypical characterisation in wastewater of other pollutants	<ul> <li>PFASs can't be treated effectively</li> </ul>	Use skid-mounted pilot system to trial and test before implementing full-scale solution		

# **5** CONCLUSIONS

PFAS are a group of emerging contaminants that present a legacy issue at many firefighting training facilities due to historic use of firefighting foams containing primarily PFOS and PFOA. As the global understanding of the environmental risks, health effects and behaviours of PFAS develops, so too does the demand for a treatment solution for contaminated wastewater, groundwater and soil.

Currently, there is not a well-established process design for PFAS treatment and of the ones identified, there are limitations when trying to adapt them to different situations. Furthermore, discharge limits for PFAS in treated effluent are only recently being implemented by relevant authorities so the performance criteria required of any proposed treatment process is a risk to implementation.

Developing a treatment solution for PFAS-contaminated firefighting training wastewater adds further complexity to the challenge. The sites are often remote and have limited access to utilities and operational support for a wastewater treatment plant, and have a variable influent quality.

Process designs for two commercially available products, MyCelx and RemBind, were developed and trialled at a pilot scale for their efficacy in treating wastewater produced by firefighting training.

Both MyCelx and RemBind processes were able to reduce PFAS in firefighting wastewater from levels above  $800\mu g/L$  down to below  $0.1\mu g/L$ . This is a significant concentration reduction of >99%, from what is a high starting concentration, however draft policies indicate that residual levels may need to be orders of magnitude below this. The ability to achieve and prove such low levels consistently is also risk, particularly at sites where there is a likely source of interference from contaminated equipment.

To develop these pilot findings into a full-scale, repeatable and robust system, additional barriers will need to be overcome. These vary from technological risks, capital and operating costs and particularly the management and destruction of waste streams.

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