

## Remediation of PFAS by immobilization – and other options

**Peter Freitag**

Keller Grundbau Ges.mbH, Wien, Austria, [Peter.Freitag@keller.com](mailto:Peter.Freitag@keller.com)

Thomas G. Reichenauer

AIT – Austrian Institute of Technology GmbH, Tulln a.d. Donau, Austria, [Thomas.Reichenauer@ait.ac.at](mailto:Thomas.Reichenauer@ait.ac.at)

Regine Patek, Blanka Kruzslicz-Luque

TERRA Umwelttechnik GmbH, Vienna, Austria, [Regine.Patek@terra.cc](mailto:Regine.Patek@terra.cc), [Blanka.Kruzslicz@terra.cc](mailto:Blanka.Kruzslicz@terra.cc)

**ABSTRACT:** As a group of chemical compounds that is equally useful and harmful to humankind, PFAS, the "forever chemicals", have drawn a lot of attention over the last years. In Austria first sites have been declared as heavily contaminated and an increasing need for applicable remediation methods is already foreseeable. As no practical experience exists in Austria, the federal government funded a research project to determine the best approaches for remediation regarding geology, hydrology, and contaminants found in Austria.

What sets this project aside from others is that, although it can be considered basic research, the applicability has a high priority. Therefore, ground engineering contractors are a part of the consortium to ensure the field suitability of all developed approaches.

When writing this paper, the project is in its second year. Framework conditions such as groundwater chemistry and relevant PFAS species have been determined, and the experimental laboratory work has commenced. This paper presents the first experiments conducted by geotechnicians to investigate immobilization of PFAS by cement and cement-adsorbent mixtures. For this experimental work slurries of cement and other commercially available binders were examined for immobilization of PFAS in soil and groundwater by measuring their concentration in the extract of the hardened mixture. An essential requirement is the availability of binders in Austria. The set-up of experiments and preliminary results as well as further steps and experiments to ensure the suitability in the field will be discussed briefly. We will also give a glimpse at the techniques and approaches which are followed by other teams in the project.

**KEYWORDS:** PFAS, immobilization, extraction, biochar, bacteria.

### 1 INTRODUCTION

In 2022 the Environment Agency Austria declared the Airport Salzburg as the first heavily contaminated site caused by Per- and Polyfluorinated Alkyl Substances (PFAS) (Döberl, 2022). This marks the starting point of various efforts to understand the situation in Austria and react to potential risks.

PFAS are a huge group – between thousands and billions - chemical species - of chemicals, which are aliphates<sup>1</sup>, containing more than one fluoride group. It is this extremely stable C-F coupling which lets them exhibit properties that are favorable in modern applications:

- Hydro- AND Oleophobic
- Extremely stable/non-degrading
- Foam building

They are used in nearly every modern product, e.g. cosmetics, food packaging, clothes, paints and crockery.

The downsides are that they are bioaccumulating, cancerogenic and some even acute toxic (Dickman and Aga, 2022).

Produced since the late 1940ies they can now be found widespread in the environment, even at places far away from human influence/settlements.

#### 1.1 PFASan research project

Behind PFASan is a consortium of three Austrian Research Institutes, which contracted geotechnical experts to ensure the feasibility/applicability of the basic research being done. Four main work packages (WP) are included in the project and the work is ongoing.

#### 1.2 Situation in Austria

WP1 is tasked with providing information about spatial distribution and chemical composition of PFAS-mixtures across Austria. The results indicated a strong correlation between human activity and concentrations found in groundwater. As for the chemicals themselves, foam building agents are the main contaminants. This is backed by the fact that the two actual sites are former fire-fighting training grounds. Figure 1 shows the concentration of perfluorooctanoic acid (PFOA) in groundwater clusters consisting of one or more groundwater bodies (Niemann, 2024). Identified punctual contamination sources have been removed.

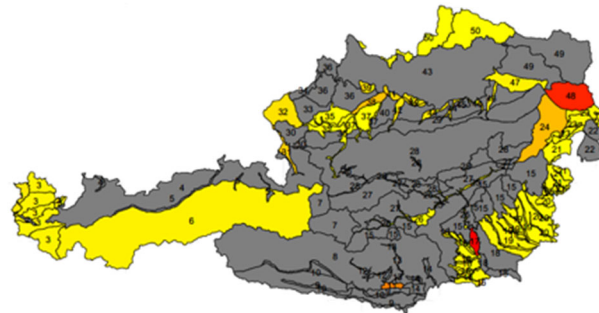


Figure 1 The distribution of PFOA in Austrian groundwaters. Concentrations range from 0.00 ng/L (grey) to 4.00 ng/L (red).

PFOA used as foam forming agent is one of the most often encountered substances, but similar distribution can be found with others as well.

Together with PFOA two other carboxylic acids (PFBA, PFHxA), three sulfonic acids (PFBS, PFOS, PFHxS) and one

<sup>1</sup> Non cyclic carbon chains of different length

precursor substance 6:2-fluorotelomersulfonic acid (6:2 FTS) were identified as most relevant (“PF7”) for further investigation.

### 1.3 Project scope

With the data obtained by WP1 (Typology), WP2 (Immobilisation) and WP3 (Degradation) are tasked with the evaluation of existing and the development of new immobilization and treatment techniques respectively.

WP4 will combine the results into synergistic treatment trains. This is also the reason why water treatment techniques are also in the scope of this project. The state of the work will be discussed in the next chapters.

## 2 IMMOBILISATION

Due to the longevity and stability of PFAS solidification/stabilization (S/S) techniques are current state of technology in their remediation. In this project we are looking at them because Austrian soils and locally, commercially available binders (cements, etc.) must be examined as they can vary significantly in composition and therefore differ from published data.

Furthermore, immobilization with cement will serve as a baseline for further investigations and comparisons. This requires the development of an experimental methodology.

### 2.1 Inorganic binders

Replicating geotechnical techniques in a chemical laboratory is a challenging task. Due to the high pressures and shear deformations, installation effects can only be simulated very rudimentary and costly, if at all. For this reason, screening experiments are conducted to identify favorable materials for large scale experiments.

The first step consists of developing a Standard Operating Procedure (SOP) which can be applied for all further experiments. Figure 2 depicts the proposed approach.

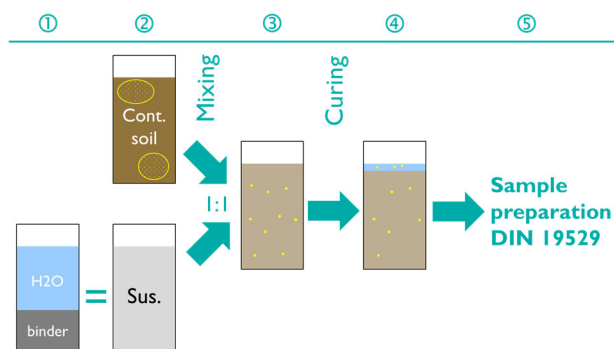


Figure 2 Standard operating procedure for screening tests.

First, a binder slurry is prepared according to experience or manufacturer recommendations (①). For cement mixtures, a water:binder ratio of 1:1 is chosen. This slurry is mixed with contaminated soil in step ②. The resulting test specimen is left to cure for a prescribed time (③,④). To be comparable to other experiments the time steps considered are 1, 8, 28 and 96 days. For longer periods extra samples are prepared. The load with PFAS was specified with 500 ng/kgDM and 2,000 ng/kgDM

The downstream sample preparation acc. to DIN 19529 works with a 1:2 eluate, using deionized water as solvent. Simplified, the sample must be broken down in aggregates smaller than 4 mm (Figure 3). The exact amount of water which must be added depends on the determined water content of the sample. The samples are then placed in an overhead shaker and are shaken for  $24 \pm 0,5h$ . Following this period, the samples are

allowed to sediment for 30 min, after which they are centrifuged for 30 min with 20,000 g at 20 °C. The PFAS concentration in the extract is measured by Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). With the obtained concentration  $c$  and the water content  $\omega$  the release of contamination  $A$  can be calculated according to equation (1).  $M$  and  $V$  being volumes and masses, dry (T) and fresh (F).

$$A = \frac{c \cdot (V_L + M_F \cdot \omega)}{M_T} \quad (1)$$

This parameter will be an important indicator for comparison of different treatment trains.

For the quantification of the extracted PFAS the whole preparation process was played through without binders to identify potential sources of error, i.e. leakages and losses of PFAS due to adsorption.

Additionally, as there is more water in the system than required for the curing of cement ( $w/b \approx 0.42$ ) a supernatant forms in the bottles. PFAS in this liquid phase must be quantified and treated as loss.

For the selection of materials for the laboratory equipment used in the experiments, experience from previous projects could be used.

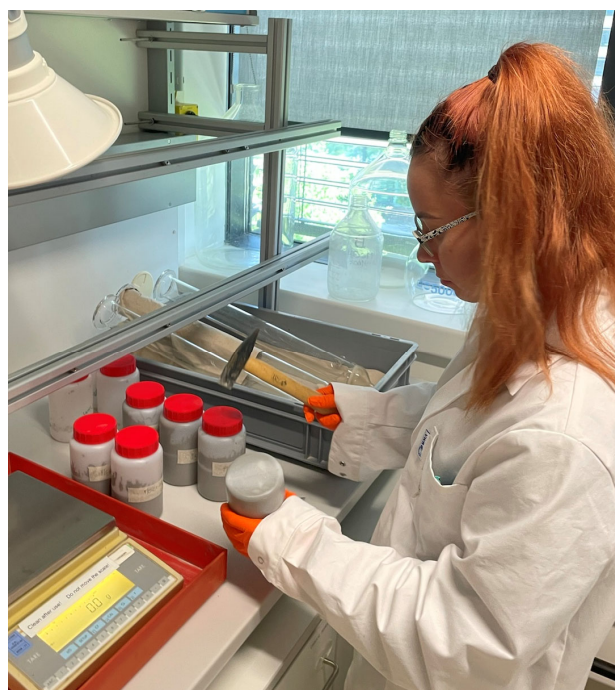


Figure 3 Breaking of samples into aggregates, still in the bottles.

Figure 4 depicts the preliminary results of the first experiments. They were conducted with a binder consisting of Portland cement (OPC, CEM I) and fly ash. As soil matrix an inert quartzite sand was used. All experiments were done in triplicates

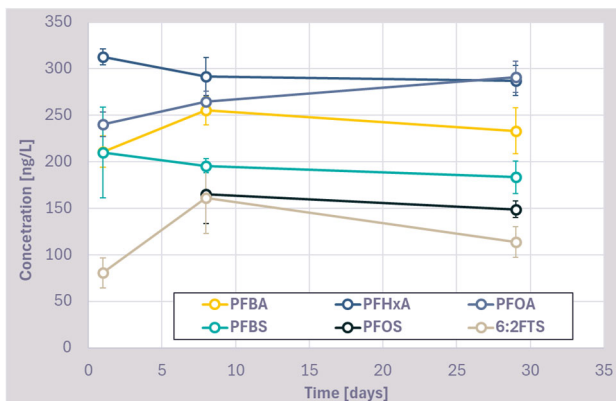


Figure 4 Concentrations of PF7 in eluates.

After 28 days of observation the concentrations in eluates seem stable. For this period, aforementioned, preliminary tests have shown no loss, so it can be assumed that immobilization is working. As for the distribution of PFAS within the S/S system Figure 5 gives an indication.

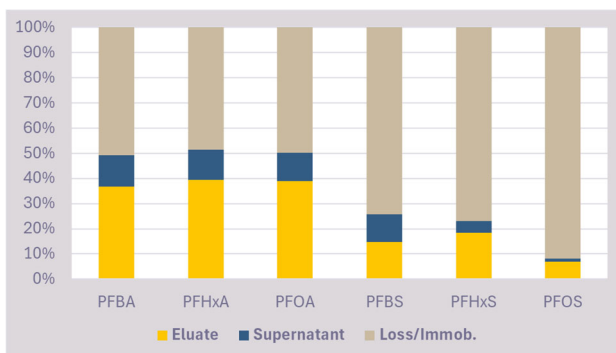


Figure 5 PFAS distribution.

In all cases about 50% of the PFSA were found neither in the eluate, nor in the supernatant, thus they are regarded as immobilized. Assuming that loss effects are equal for all species, sulphonic PFAS are more inclined towards immobilization. This is in line with published data from McDonough et al. (2022) and indicates the feasibility of this approach.

## 2.2 BioChar

Activated carbon has widespread applications in soil remediation. Even for PFAS there are commercial products available (e.g. Söregård, Kleja and Ahrens, 2019). High energy amounts needed during its production have urged researchers to come up with a more sustainable solution leading to various materials, like coconuts and rice husks, being used in so called biochars, which require lower temperatures during production.

Our results so far suggest that biochars are as feasible as an adsorbent but can be challenging in detail. For example, they show a strong dependency on low pH, reducing the possibilities of combined approaches with S/S (cement!).

Another concern is the availability. For example, the most promising candidate identified at the University Vienna, a steam activated biochar, is only available in very small (Gramm!) amounts.

From an application point of view the low density is of concern. A powder with  $\rho=0.30 \text{ g/cm}^3$  which is also electrostatic can be problematic to handle. Therefore, at the moment the focus is to make charcoal more manageable by coating or similar techniques on one hand, and to adapt the

mixing and injection technology so that this new, unusual material can also be used on the other hand.

## 2.3 Biotic Immobilization

Biotic immobilization (MICP, Microbial Induced Calcite Perspiration) has been used for years (Ivanov and Chu, 2008) for example in the field of dam waterproofing. The idea of using microbes instead of mineral binders for sustainability reasons was therefore obvious. The research questions that arise are, can PFAS be trapped by the calcite structures, and which specific microbes should be investigated further.

However, before these questions can be answered, the question arises as to the installation, or the mechanical load of the microbes during introduction into the ground. Working with higher pressures, such as in the jet grouting method, can be ruled out a priori, because survival is not possible. A microbe sample with contained various bacteria that showed good MICP results in the past was selected for testing.

The test rig that was finally used consisted of a pump (Grako Ultramax II) that injected into glass bottles. The glass bottles were either empty, filled with sand or gravel or mixed material from it. In this way soil conditions could be taken into considerations very simplified. One control sample was not injected and used to provide a baseline regarding transport and general handling.

The setup also contained various standard installation parts such as fittings and filters. In sum 16m of injection hose, inner diameter 3.00 mm, were used. The pressure applied was about 5.0 bar which represents the standard working pressure of this rig.



Figure 6 Injection test rig. Test with clear water. Insert shows a gravel filled bottle.

After the injection, the bottles were transported to the laboratory, samples were taken and, after a dyeing process, microscopically examined for live and dead bacteria.

Figure 7 suggests an even distribution between living and dead microbes. Simple statistical analysis could show this for all, except the gravel, samples taken (Figure 8). Whether gravel was a singular incident or a systemic effect needs to be investigated further.

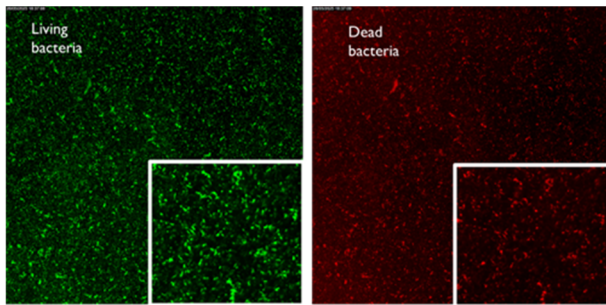


Figure 7 Visualization with microscope, same area of sample.

The results of these first tests provide a good basis for further experiments. Further research will address the question of how microbes can be supplied with nutrients that they need for the conversion of calcium. This appears to be challenging at greater depths, since the permeability decreases steadily due to bacterial activity close to the injection point.

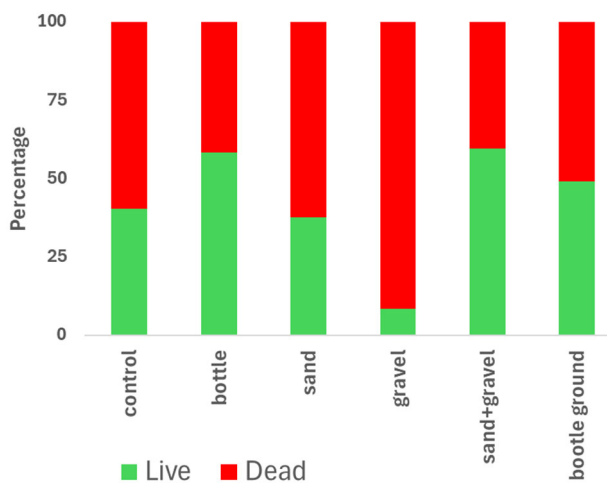


Figure 8 Percental distribution of living and dead microbes.

### 3 TREATMENT

Both treatment methods pursued in the project are on a technical readiness level (TRL) from 3 to 4 .and can be considered basic research.

#### 3.1.1 Biological

Fluor-carbon compounds are very rare in nature. Nevertheless, there is hope to find microbes that can use these rare compounds as a source of energy and/or carbon. Therefore, at AIT a high-throughput environment that can be used to screen quickly a high number of bacterial isolated was developed.

It is used to examine soils from contaminated sites in Austria. In this setup formation fluoride is used as an indicator for breaking the C-F-bond by bacterial activity. Work is underway.

#### 3.1.2 Advanced oxidation techniques

These novel techniques could be used for ex-situ treatment of contaminated water. They are proposed for the elimination of residual concentrations in water effluent from treated sites.

### 4 CONCLUSIONS

Right now, the research project PFASan is in its second year. So far, the experiments have shown promising results giving hope that a novel remediation treatment train can be

established. The geotechnical experts have advised and developed experiments that can simulate the installation on a very basic level and can be used to compare results across working packages/groups.

Open questions mainly revolve around the topic of replicability of the experiments, especially with regard to the quantification of the substances. A mass balance must also be determined for the entire experimental procedure, which requires some additional investigations. The experiments will then be conducted with specialized binders and a natural soil from a contaminated site will be used.

Regarding the application on site, challenges that need to be addressed are the materials themselves (Biochar) and the installation procedures (microbes).

It is clear to those involved in the project that all these questions may not be answered in a three-year research project. For this reason, PFASan was designed in such a way that pilot plants and large-scale trials were not planned in the first place, but are to be executed in a follow-up project, building up on PFASan.

### 5 ACKNOWLEDGEMENTS

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