NDA DRP LOT 2:
Integrated Waste Management
WP/B2/7

Solubility Studies in the Presence of Polycarboxylate Ether Superplasticisers

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Preface

This report has been prepared by Loughborough University and NSG Environmental Ltd under contract to the Nuclear Decommissioning Authority (NDA). The views expressed and conclusions drawn are those of the authors and do not necessarily represent those of NDA.

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Abstract

Superplasticisers are chemical admixtures used in the production of concretes and mortars. The use of superplasticisers for the packaging of low heat generating wastes has been proposed due to the operational advantages of reduced water content and increased fluidity of cementitious mixtures. However, concerns have previously been raised over the potential for superplasticisers to enhance the mobility of radionuclides during the post-closure phase of a geological disposal facility.

This report presents the results of experimental studies undertaken to gain greater insight into the likely effect of the latest class of superplasticisers, polycarboxylate ethers. The studies focussed on the effect of superplasticisers on the mobility and leaching of selected radionuclides through intact cement monoliths. The study also included verification of the effect of superplasticisers on radionuclides in cement-equilibrated waters for comparison against existing data available in the literature, the effect of gamma irradiation on the mobility and leaching from crushed superplasticiser-amended cement monoliths and porosity studies on superplasticiser-amended cement monoliths.

Contents

Executive Summary

The use of superplasticiser (SP) amended grouts could offer a range of operational and engineering advantages when packaging Low Heat Generating Wastes, which include Intermediate Level Waste (ILW) and Low Level Waste (LLW) not suitable for disposal at the Low Level Waste Repository. Superplasticiser amended grouts may also be used in the construction of a future Geological Disposal Facility. However, research at Loughborough University and elsewhere has shown that these high molecular weight, water miscible organic polymers have the potential to both enhance radionuclide solubility and inhibit the effective uptake and incorporation of the radionuclides by the cement matrix. If this were to occur, it could have an impact on one of the key safety functions of the engineered barrier system.

The engineering benefits of SP are well known but their impact on the behaviour of encapsulated radioactive material is much less well understood. It has been shown that SP vary substantially in their metal complexation behaviour, even between batches of ostensibly the same product. Commercial formulations may contain a number of adjuncts including anti-foaming agents, biocides, viscosity modifiers, grinding aids and impurities, all of which may affect pore solution chemistry.

The overall aim of the current project is to gain greater insight into the likely effect of commercial polycarboxylate ether (PCE) superplasticisers and associated adjuncts on radionuclide solubility and mobility in relevant cementitious systems. The project was funded under Lot 2 of the Nuclear Decommissioning Authority's Direct Research Portfolio. The specific project objectives were to:

- Verify the effect of a range of cement additives (SP and adjuncts) on the solubility of selected radionuclides in cement-equilibrated waters;
- Improve understanding of the role of SP - modified cements in the migration of key radionuclides through intact monolithic samples;
- Determine the extent to which they affect mobility and leaching of selected radionuclides from crushed samples;
- Determine the effect of gamma irradiation on mobility and leaching of selected radionuclides;
- Measure changes in total and accessible porosity on reference grout formulations.

The cementitious materials tested were 3:1 Pulverised Fuel Ash/Ordinary Portland Cement (PFA:OPC) and 9:1 Ground Granulated Blast Furnace Slag/OPC (GGBS:OPC) grouts. The radioisotopes used were ^{63}Ni, ^{239}Pu, ^{241}Am and U, the latter at natural isotopic abundance. Six SP formulations, including two new products synthesised at Loughborough University, together with three individual adjuncts were trialled in the programme.

The analyses undertaken showed that the SP formulations increase radionuclide solubility in free solution by between one and three orders of magnitude. The defoamer and biocide, when tested in isolation, showed no significant effect on the solubility of the radioisotopes studied. With one exception, this was also true for the viscosity modifiers. Interestingly, one of the bespoke formulations synthesised at Loughborough University tended to produce a less pronounced solubility enhancement than the commercial products. The reason for this has not yet been confirmed, but it is noted that the synthesised SP product had been dialysed prior to use in order to remove lower molecular weight material, including residual monomer.

Leaching and diffusion experiments indicated that the solubility increase observed in aqueous solution did not produce a corresponding increase in the mobility of the

radionuclides from solid grouts within the six month timescale available to the project. In all cases, including irradiated samples, experiments with the SP formulations and adjuncts could not be consistently differentiated from the corresponding blank experiments, indicating that the presence of the SP did not result in the migration of radioisotopes through the cements. A series of digital autoradiographs of the samples used for through-diffusion experiments provided visual confirmation that no significant radioisotope migration had occurred into the grout matrices. Within the constraints of the sample scale and timeframe of the experiments, the leaching and diffusion trials suggest that the mobility of active species would not be increased through the use of an SP amended grout. This was also observed to be the case for gamma irradiated samples.

Total (gas) and accessible porosity were determined by argon pycnometry and methyl methacrylate (MMA) impregnation, respectively. Markedly different fracture porosity was shown by the PFA and GGBS blends. These differences were apparent in the results of pore water squeezing tests carried out at pressures up to 4,000 psi. The PFA samples released greater volumes of pore water, particularly at lower pressures, and several SP - modified PFA samples failed completely indicating false set.

Overall, the results indicated significant enhancement of radionuclide solubility caused by PCE superplasticisers in free solution, in accordance with published work. Synthesised products did not increase solubility to the same extent, possibly due to the removal of low molecular weight components. In each case, enhanced solubility in aqueous solution did not manifest itself in terms of increased mobility in the presence of solid grouts, at least on the timescale of these experiments. Leach tests on disaggregated material provide further evidence of immobilisation by the cement matrix. The above appears to be true of both PFA and GGBS grouts, notwithstanding clear differences in microstructure and fracture porosity.

Although the work was undertaken on laboratory scale samples, the results are considered to be indicative of SP amended PFA and GGBS grout behaviour at larger scales and further tests are planned to verify whether this is the case. This work will allow an assessment to be made of the acceptability of SP amended grouts in waste management applications, including waste encapsulation and waste container (‘concrete box’) manufacture.

Introduction

The Radioactive Waste Management (RWM) Limited illustrative concept for geological disposal of Low Heat Generating Wastes (LHGW) in higher strength rock is immobilisation of waste in grouted waste packages surrounded by a cementitious backfill. In a cement-based near-field, the persistence of alkaline conditions during the post-closure phase of the Geological Disposal Facility (GDF) is intended to result in low solubilities of certain key radionuclides, limiting the source term for migration via the groundwater pathway.

The use of cementitious grouts for the treatment of waste is mature and results in passively safe waste packages suitable for long term management prior to disposal. These grouts typically comprise either Pulverised Fuel Ash/Ordinary Portland Cement (PFA:OPC) or Ground Granulated Blast Furnace Slag/OPC (GGBS:OPC) blends.

The addition of superplasticiser (SP) additives to the grouts used for waste packaging has been identified by site licence companies (SLCs) as desirable [1] as they may offer a range of operational advantages e.g. increased grout fluidity, reduced water content. Additionally, they may be of use in the production in ‘concrete box’ waste containers, currently being investigated by the SLCs. Different chemical classes of SP have been developed over several decades for use in the civil construction industry, the latest comprising polycarboxylate ethers (PCE). However, research at Loughborough University and elsewhere (e.g. [2], [3]) has shown that these high molecular weight, water miscible organic polymers have the potential to both enhance radionuclide solubility and inhibit the effective uptake and incorporation of the radionuclides by the cement matrix. If this were to occur it could have an adverse impact on one of the key safety functions of the disposal concept.

Thus, while there are clear benefits to be derived from using SP in terms of improving the workability of cements, it is important to understand their effect on the long term behaviour of the encapsulated radioactive waste inventory; this aspect is, as yet, much less well understood. It has been shown that SPs vary substantially in their metal complexation behaviour. Commercial formulations may also contain a number of adjuncts including anti-foaming agents, biocides, viscosity modifiers, grinding aids and impurities, all of which may affect pore solution chemistry.

Despite recognition of the potential benefits of SP modified cements and several attempts by SLCs to gain endorsement for their use, uncertainties remain over their long term impact on radionuclide solubility and mobility. Owing to the complexity of the subject and the high costs related to developing and delivering a suitable research programme, these uncertainties are unlikely to be resolved by any single SLC.

The Nuclear Decommissioning Authority’s (NDA) Higher Active Waste (HAW) strategy [4] includes the provision for exploring alternative waste treatment options to enable a more cost effective and flexible approach to the management of radioactive waste. Additionally, RWM, a wholly owned subsidiary of the NDA, has the responsibility of implementing the UK Government’s policy on geological disposal of HAW under the framework established by ‘Implementing Geological Disposal: A framework for the long term management of higher activity radioactive waste, 2014’ [5].

This project, funded under the NDA Direct Research Portfolio, aims to contribute to the body of knowledge regarding SP behaviour in a GDF environment. This will help assess their use in waste packaging operations and concrete waste container production. It could also provide significant benefits to SLCs, should SPs be endorsed for such applications.

This project has been carried out by the Unity team, led by NSG Environmental Ltd. Loughborough University delivered the work, utilising their in-house laboratory facilities and resources with Synergy Health providing use of an irradiation facility. W.R Grace & Co. provided the majority the SP materials tested, with Loughborough University providing two bespoke and well characterised superplasticiser formulations for comparison purposes.

Project Objectives

The overall aim of the project was to gain greater insight into the likely effect of commercial SP and associated adjuncts on radionuclide solubility and mobility in PFA:OPC and GGBS:OPC systems. The results will provide quantitative data which will help RWM in assessing the suitability of SP in both cement encapsulation matrices for the packaging of LHGW and the manufacture of concrete box waste containers. Additionally, the results may provide input into decisions regarding the use of SP in the design of a GDF.

The specific objectives were to:

- Verify the effect of a range of cement additives (SP and adjuncts) on the solubility of selected radionuclides in cement-equilibrated waters;
- Improve understanding of the role of SP - modified cements in the migration of key radionuclides through intact monolithic samples;
- Determine the extent to which they affect mobility and leaching of selected radionuclides from crushed samples;
- Determine the effect of gamma irradiation on mobility and leaching of selected radionuclides;
- Measure changes in total and accessible porosity on reference grout formulations.

This work builds upon research conducted on various SP products (including [2], [6], [7]) by several organisations, and at Loughborough University, utilising commercial products supplied by W.R Grace & Co. (e.g. [3], [8]) together with phenomenological studies into the synthesis of new products specifically designed to minimise radionuclide uptake under a related Lot 1 NDA Direct Research Portfolio project.

Scope

The project investigates the effects of SP products and some of their constituent components both individually and combined in SP formulations, on radionuclide solubility and mobility. The radionuclides chosen were ^{63}Ni, ^{241}Am, ^{239}Pu and U, the latter at natural isotopic abundance covering important waste inventory materials and a range of oxidation states from (II) to (VI).

Nickel and uranium were included in earlier studies on ADVA Cast 551 ([3], [7], [8]) and in similar work with cellulose degradation products [9]. The methodology and results of this previous work provide comparative data on the experimental design utilised for this project. Previous studies used europium as a surrogate for trivalent actinide species; however, in this work, americium was chosen as questions remain over the validity of the former as an actinide analogue [9]. Data obtained for trivalent americium are inherently valuable and can also be used as an indication of the likely behaviour of the heavier transuranics (e.g. Cm [9]). ^{241}Am is relatively easy to detect and quantify by gamma counting; therefore small “spike” concentrations can be used, representative of a trace component. For similar reasons, plutonium was chosen over thorium given the unique chemistry of this element and the relative paucity of data available. Thus, radionuclides and oxidation states considered were ^{63}Ni(II), ^{241}Am(III), ^{239}Pu(IV) and total U(VI).

The programme of work was proposed in response to the areas of interest detailed in a tender provided by the NDA, and further developed following discussion. These were specifically chosen to be consistent with and build upon previous work, encompassing a series of trials in representative cementitious systems.

The programme was divided into eight areas for investigation, as detailed below:

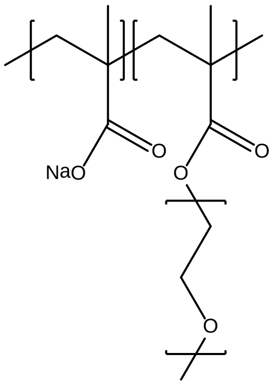
- Formulation Trials – these were carried out to determine the optimal dose of SP, recognising that the manufacturer’s dosing recommendations relate to the production of concretes not cement grouts. Ideally, the dose used would minimise bleed (given the possibility that bleed water might retain some of the radionuclides used in active trials) yet be relevant to likely operational applications;
- Preliminary Leaching Trials – to obtain a baseline for leaching of non-active metals from the chosen formulations and to compare the results against later leaching tests;
- Solubility Experiments – to determine the effect on solubility of the radionuclides in SP amended, cement equilibrated water;
- Through and Intact Leaching Experiments – to determine the radial transport of point radionuclide sources through monolithic SP amended cement samples and to determine the leaching of evenly distributed radionuclides from the surface of SP amended monolithic samples;
- Crushed Sample Leaching – to investigate the leaching of evenly distributed radionuclides from disaggregated samples;
- Performance of Irradiated Materials – to determine the effect on radionuclide mobility when SP amended cement monoliths were subjected to gamma radiation levels taken to be representative of those anticipated in a GDF; these results were compared to those from the (un-irradiated) crushed sample leaching trials;
- Porosity Measurements – to determine the impact on total and accessible porosity of two SPs in PFA:OPC and GGBS:OPC cement monoliths;
- Pore Water Extraction – to determine the volume of extractable pore water and the amount of SP not incorporated into the cement matrix through total organic carbon (TOC) analysis.

Acquisition of Materials

Superplasticiser Products

Seven commercially available SP products identified by NDA in consultation with stakeholders were supplied by W.R Grace & Co for the trials - Table 1. These included four commercial formulations, incorporating PCE SP components along with adjuncts (i.e. defoamer, biocide, viscosity modifier), as well as the three individual adjuncts in isolation, in order to identify which ingredients in the commercial products contribute to any observed increase in radionuclide solubility or mobilisation. The chemical identity of the components and their ratios in the formulations were proprietary and hence, unknown. However, a typical PCE structure is shown below in Figure 1.

Figure 1: General PCE Chemical Structure



For ease of reference, the products will henceforth be referred to by the last letters of the sample identifier, referred to in column one of Table 1, e.g. WRBDP, MPBDP, DEF etc.

Table 1: Superplasticiser Products Supplied by W.R Grace & Co.

Sample Reference	Composition	Water Content %	Suggested Dosage Range % by weight of cement (bwoc)
EXP ADVA 0900 lot. Nr. 143359 WRBDP	Polycarboxylate, carbohydrate, defoamer, biocide	73.5	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 MPBDP	Polycarboxylate, carbohydrate, defoamer, biocide	73.6	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 FWBFP	Polycarboxylate, carbohydrate, defoamer, biocide	73.3	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 WRBP	Polycarboxylate, carbohydrate, biocide	73.8	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 BIO	Biocide in solution	99.6	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 DEF	Defoamer in solution	99.6	0.3 – 1.0
EXP ADVA 0900 lot. Nr. 143359 VMA	Viscosity modifier (VMA) in solution	98.5	0.1 – 1.0

The four superplasticiser formulations detailed in Table 1 contain a range of component concentrations such that they may be used to encompass the properties required for the applications anticipated by W.R Grace & Co.

Cement

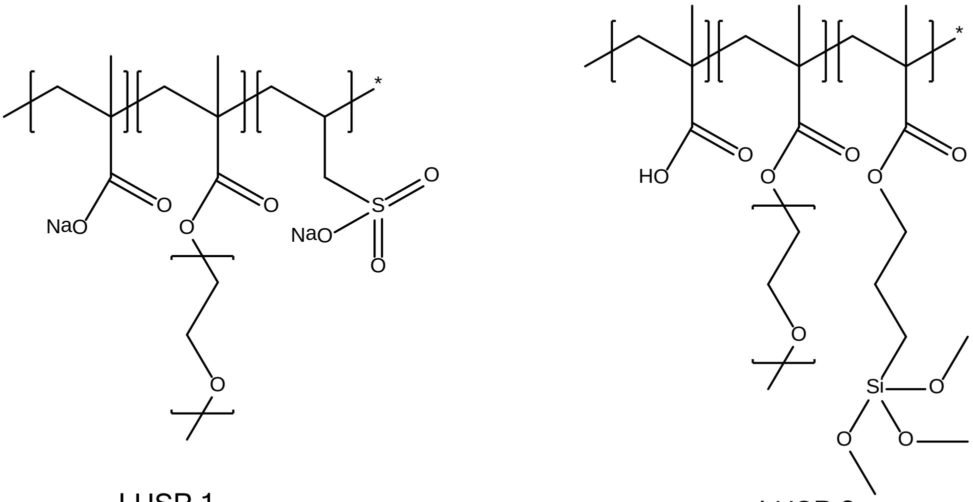
Cement products (PFA:OPC and GGBS:OPC) were supplied by Hanson Cement plc.

Additional SP Materials Developed by Loughborough University

In addition to the commercially available SP products supplied by W.R Grace & Co., two novel SP developed by Loughborough University were also tested. These were:

- A high purity polycarboxylate comb SP with no additional modifiers [10]. This is identified as ‘LUSP 1’ in the report (structure shown in Figure 2) ; and
- A polycarboxylate comb SP with organosilane functional groups which cross-link over time [11]. This is identified as ‘LUSP 2’.

Figure 2: LUSP 1 and LUSP 2 Chemical Structure



LUSP 1

LUSP 2

LUSP 2 was designed to be short-lived in order to reduce long term reactivity in the wasteform. It needs to be used very soon after manufacture, as it degrades over a period of a few days. As a consequence, it was not possible to include LUSP 2 in all of the experimental work. A single batch of LUSP 2 was manufactured at the appropriate point in the programme when it was needed for addition to the grout mixes. LUSP 2 was not part of the initial formulation trials or solubility determinations.

Experimental Results

Method Uncertainty and Reporting of Results

The analytical techniques used have associated detection limits (Table 2).

Table 2: Analytical Detection Limits

Technique	Minimum Detectable Amount (3σ)
ICP-MS	0.1 ppb (w/w)
ICP-OES	100 ppb (w/w)
Gamma Counting	0.15 Bq in 1 cm^{-3}
LSC	0.2 Bq in 1 cm^{-3}
Ion Chromatography	0.1 ppm (w/w)
Total Organic Carbon	0.5 ppm (w/w)

In the context of this work, an important consideration is the volume of water used in the leaching trials which, when combined with the low radionuclide concentrations, can mean that the detection limit is equivalent to as much as 1% of the radionuclide being leached. Consequently, it is more relevant to make comparisons with the blank experiments and to recognise trends rather than focus on the accuracy of individual measurements.

The analytical data generated in this programme have been reported with varying significant figures, depending on the technique used and data processing techniques employed. Typically, analytical data relating to commercial ‘off the shelf’ instrumentation, operated under a suitable accreditation scheme (e.g. UKAS), are reported to two significant figures. This derives from an assessment by the laboratory of random and systematic errors, precision and accuracy arising from use of the analytical equipment combined with those from any sample preparation procedures used. ^{63}Ni is a low energy beta emitter which can suffer from quenching. As all measurements were performed on comparative solutions quench correcting the counting efficiency of ^{63}Ni was deemed unnecessary.

Formulation Trials

Dosing advice from W.R Grace & Co. was only available for construction concretes, which takes into account aggregate loadings. Consequently, formulation trials were performed to determine a suitable additive dosage for use at laboratory scale for typical waste encapsulation grouts.

Objectives

The objective was to develop a suitable formulation for laboratory use that would eliminate or minimise bleed water. Although desirable operationally, this was also desirable for laboratory tests due to the potential for bleed water to contain the radionuclide of interest and its consequent reduction in the test samples. Any bleed water present would require additional analysis to establish the concentration of radionuclides in the cement samples.

The selected formulation should also be reasonable with respect to the typical dose ranges likely to be used operationally. Once established for both types of cement, it was intended that the agreed formulation would be kept consistent throughout each work package.

Experimental Methodology

Samples of the two grouts were prepared according to the description below. Three dose levels were trialled for the GGBS and four were trialled for the PFA grout (grout compositions detailed in Table 6 and 7). The dose levels were based on the manufacturer's recommended ranges for concretes. In practice, the viscosity modifier (VMA) component is usually added to the SP formulations separately and so a third series of trials at three VMA concentrations was also undertaken on GGBS only, as this showed a greater tendency to bleed [3]. Moulds used for this work package were cylinders with dimensions of diameter 40 mm and height 50 mm. These moulds produced blocks with a mass range of 95 – 110 g. After 24 hours the bleed water was decanted and weighed. The block was then re-weighed and the proportion of bleed water calculated.

Figure 3: Samples Demonstrating Bleed

Results

The results of the formulation trials are presented in Table 3 - 5 below. The bleed water values reported represent the mean of the duplicates for each experiment, expressed as a percentage of the mass of the grout block after 24 hours. NR indicates that the trial was not undertaken because preliminary work had already identified that bleed water was not produced. In general, the bleed from the PFA grouts was lower (< 4%) than the bleed from the GGBS grouts (up to ca. 10%). The results also demonstrate a greater variation in the amount of bleed from the GGBS grouts.

Table 3: Formulation Trials with GGBS

	[Bleed (g) / Block mass (g)] x 100			
Additive Dosage bwoc %	**0**	**0.1**	**0.3**	**0.5**
WRBDP	ND	0.04	4.91	9.76
MPBDP	ND	0.23	3.85	8.63
FWBFP	ND	1.53	5.35	10.13
WRBP	ND	0.54	4.84	9.66
BIO	ND	NR	NR	0.07
DEF	ND	NR	NR	0.31
VMA	ND	NR	NR	ND
LUSP 1	ND	0.09	0.66	3.30

NR: No result ND: Not detected

Table 4: Formulation Trials with PFA

	[Bleed (g) / Block mass (g)] x 100				
Additive Dosage bwoc %	**0**	**0.1**	**0.2**	**0.3**	**0.5**
WRBDP	1.71	1.49	1.64	1.54	3.82
MPBDP	1.71	1.52	1.64	1.26	0.43
FWBFP	1.71	1.15	1.49	1.72	3.66
WRBP	1.71	1.25	1.16	2.03	3.86
BIO	1.71	NR	NR	3.89	ND
DEF	1.71	NR	NR	1.35	ND
VMA	1.71	NR	NR	0.79	ND
LUSP 1	1.71	0.88	1.29	2.65	ND

NR: No result ND: Not detected

Table 5: Formulation Trials with GGBS and VMA

	[Bleed (g) / Block mass (g)] x 100			
VMA Dosage bwoc %	**0**	**0.1**	**0.5**	**1**
WRBDP 0.5 %	10.67	10.36	4.61	2.41
MPBDP 0.5%	9.43	9.62	4.15	1.34
FWBFP 0.5%	11.02	9.48	4.15	1.81
WRBP 0.5%	10.50	9.97	2.98	0.58
WRBDP 0.3%	5.26	2.24	2.04	0.86
LUSP 1 0.5%	3.60	3.01	0.75	ND

ND: Not detected

Conclusion

It was not possible from the limited trials performed to establish a bleed-free formulation that was suitable for all mixtures of cement or VMA with the SPs. Consequently, an additive dose level of 0.5% bwoc was chosen as being a mid-point for construction concrete based on advice from W.R Grace & Co. (0-1 %) and also having low bleed, particularly for PFA. It was recognised that SLCs would develop formulations based on their own specific operational requirements and that, whichever dose was chosen, it was unlikely to encompass all SLCs' requirements. A decision was also made to add the biocide, defoamer and viscosity modifier adjuncts at the same dosing level.

Preliminary Leach Trials

Objectives

The objective of these trials was to ascertain the baseline leaching of metals and other components from the SP amended PFA:OPC and GGBS:OPC materials. This would allow comparison to the more exhaustive leaching trials detailed below.

Experimental Methodology

Table 6: GGBS Grout Formulation

GGBS: OPC Cement	
GGBS/OPC ratio	9:1
Water/Solids wt. ratio	0.31
SP or adjunct dose (bwoc)	0.50%

Table 7: PFA Grout Formulation

PFA: OPC Cement	
PFA/OPC ratio	3:1
Water/Solids wt. ratio	0.37
SP or adjunct dose (bwoc)	0.50%

The powder ingredients were weighed and mixed for an hour using a Pascal Lab Powder Mixer. The SP mix or adjunct and mains drinking water at room temperature were weighed and added to a stainless steel mixing bowl; the bowl was positioned on a Kenwood KMX54 food mixer. The solution was stirred and the pre-weighed powder added at a constant rate over a five minute period. The paste was allowed to mix for a further 5 minutes before being poured into suitable moulds. Batch sizes were between 1 and 2 kg. The cylinder sample dimensions were 25 mm diameter by ~45 mm height. These moulds produced blocks with a range in mass from 35-55g. They were allowed to harden for a period of 24 hours and the bleed collected. Samples were de-moulded and placed in water to cure for 28 days under a N_2 atmosphere.

After curing, the samples and blanks were crushed for granular HazWAC leaching according to the method in BS EN12457-3:2002 (Part 3, two stage) [12]. This is a two stage leach test, the first stage being a 6 hour leach with a liquid to solid ratio of 2 dm^3/kg and the second stage, an 18 hour leach with a liquid to solid ratio of 8 dm^3 /kg. Leachates were analysed for dissolved metals (Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)) plus anions (ion chromatography). Total Organic Carbon (TOC) was used as an indicator of additive release.

The methodology produces results that are reported as ‘A_2’ and ‘A_{2-10}’. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter gives the total released by combining data obtained for both leachates (i.e. a cumulative liquid/solid ratio of 10:1).

Results

Leaching of Metals (Ni, Se, Cs, Eu, Th and U)

The ICP-MS results are presented in the appendices as Table A1. 1 toTable A1. 4. Nickel and U were analysed to enable comparison with forthcoming experiments. The remaining analytes were selected because RWM and NDA are known to be interested in the behaviour of nuclides of these elements in cementitious media. The leaching procedure was performed following standard in-house protocols and analytical determinations were undertaken in triplicate on two samples (i.e. WRBDP 1 and WRBDP 2 are two samples from the same mix) using an Agilent Technologies 7700 series ICP-MS.

Leaching of Na and K

The ICP-OES results are presented in Table A1. 5 andTable A1. 6. The leaching procedure was performed and analytical determinations were undertaken in triplicate on two samples (i.e. WRBDP 1 and WRBDP 2 are two samples from the same mix) using a Thermo Fisher iCAP 6000 Series ICP-OES. Magnesium was also determined but all samples gave results below the blank used for calibration.

Leaching of Anions

The results from ion chromatography are presented in Table A1. 7 toTable A1. 9. The leaching procedure was performed and analytical determinations were undertaken in duplicate on two samples (i.e. WRBDP 1 and WRBDP 2 are two samples from the same mix and A2(1) and A2(2) are duplicate chromatography runs) using a Dionex DX-100 with AS4A column and carbonate/bicarbonate eluent.

Determinations of F, Cl, NO_3 and SO_4 also showed a late, small and inconsistent peak, tentatively attributed to thiosulphate. This was noted but not quantified in the chromatograms from the GGBS:OPC samples.

Determination of pH values

The pH values were determined using a Fisher pH electrode calibrated at pH 7, 10 and 13. The pH of leachates from samples at each liquid/solid ratio was determined for two cement samples from each mix. The results are provided in Table A1. 11.

Total Organic Carbon (TOC)

TOC was determined using a Sievers Innovox online analyser. Leachate samples for each cement and additive combination were analysed along with deionised water blanks. Organic carbon was not detected in any leachate solution or the blanks. TOC analysis requires a relatively large sample volume (~40 cm^3) and consequently, some samples were diluted and/or combined with the appropriate duplicate to ensure that sufficient sample volume was available for analysis. Dilution resulted in an increase of the typical detection limit from 0.5 ppm to values in the 2-5 ppm range (and potentially higher for a few samples where leachate volumes were particularly limited).

Conclusion

The results from the leaching tests show no significant change in the leaching of metals or TOC from the cement mixtures after the addition of superplasticiser or adjunct.

Solubility Experiments

Objectives

The aim was to determine the effect of the SP formulations and adjuncts on the solubility of Ni(II), Am(III), Pu(IV) and U(VI) in cement equilibrated water samples. In addition, the experiments were designed to investigate whether the traces of SP and adjuncts already in the water equilibrated with the cement samples were capable of affecting the solubility of the metals in the absence of further additions. The results of these trials were intended to provide information on the solubility of the radionuclides once released from waste packages.

Experimental Methodology

Cement equilibrated water was prepared by filtering the curing water of the cement blocks produced for the preliminary leach trials. Duplicate analysis of pH and ions in solution was carried out, whereas the TOC analyses were undertaken in triplicate. Compositional information relating to the individual equilibrated water is provided in Table 8 toTable 11. All data are reported to two significant figures. Note that the blank samples were manufactured using the same methodology but without SP or adjuncts.

Table 8: TOC Concentrations in GGBS and PFA Equilibrated Water

Sample	GGBS	PFA
	TOC (ppm)	TOC (ppm)
MPBDP	0.4	4.2
WRBP	1.0	6.2
WRBDP	2.7	8.5
FWBFP	2.1	5.2
BIO	1.8	0.7
VMA	1.1	8.9
DEF	0.8	1.4
LUSP 1	0.8	1.2
LUSP 2	1.1	8.9
Blank	1.0	0.1

Table 9: pH of GGBS and PFA Equilibrated Water

Sample	GGBS pH	PFA pH
MPBDP	12.9	12.3
WRBP	12.8	12.3
WRBDP	12.9	12.3
FWBFP	12.8	12.3
BIO	12.9	12.3
VMA	12.8	12.3
DEF	12.9	12.3
LUSP 1	12.9	12.3
LUSP 2	12.8	12.3
Blank	12.8	12.3

Table 10: Major Cations in Cement Equilibrated Water

Sample	mol dm^{-3}			
	Ca	K	Mg	Na
PFA MPBDP	1.9E-03	2.6E-03	1.5E-04	2.7E-03
PFA WRBP	1.3E-03	2.5E-03	1.2E-04	2.7E-03
PFA WRBDP	2.1E-03	2.3E-03	5.5E-04	2.5E-03
PFA FWBFP	2.0E-03	2.4E-03	1.4E-04	2.7E-03
PFA BIO	5.8E-04	1.8E-03	9.3E-05	1.9E-03
PFA VMA	1.1E-03	2.1E-03	1.1E-04	2.2E-03
PFA DEF	1.3E-03	1.9E-03	8.6E-05	2.1E-03
PFA LUSP 1	1.2E-03	2.1E-03	1.2E-04	2.4E-03
PFA LUSP 2	8.4E-04	2.3E-03	1.4E-04	2.3E-03
PFA Blank	4.7E-04	1.9E-03	5.8E-05	2.1E-03
GGBS MPBDP	7.2E-04	8.0E-04	6.0E-05	8.6E-04
GGBS WRBP	5.3E-04	6.3E-04	1.0E-04	8.1E-04
GGBS WRBDP	8.1E-04	7.0E-04	6.4E-05	7.5E-04
GGBS FWBFP	6.1E-04	8.6E-04	5.8E-05	9.6E-04
GGBS BIO	4.9E-04	9.1E-04	5.6E-05	9.5E-04
GGBS VMA	4.4E-04	6.6E-04	4.9E-05	6.4E-04
GGBS DEF	3.4E-04	9.9E-04	4.1E-05	9.4E-04
GGBS LUSP 1	4.3E-04	7.8E-04	3.1E-05	7.4E-04
GGBS LUSP 2	6.8E-04	7.1E-04	8.0E-05	8.5E-04
GGBS Blank	5.6E-04	9.6E-04	5.9E-05	1.0E-03

Table 11: Trace Elements in Cement Equilibrated Water

	mol dm^{-3}					
Sample	**Ni**	**Se**	**Cs**	**Eu**	**Th**	**U**
PFA MPBDP	1.6E-06	4.6E-09	1.6E-07	2.4E-09	1.2E-08	1.6E-06
PFA WRBP	1.5E-06	6.8E-08	1.9E-07	2.3E-09	4.2E-09	1.5E-06
PFA WRBDP	1.5E-06	4.5E-08	1.6E-07	2.4E-09	3.7E-08	1.5E-06
PFA FWBFP	1.8E-06	8.1E-08	1.6E-07	2.4E-09	7.6E-09	1.8E-06
PFA BIO	1.6E-06	1.8E-08	2.4E-07	2.4E-09	2.0E-09	1.6E-06
PFA VMA	1.7E-06	1.9E-08	2.3E-07	2.4E-09	2.6E-09	1.7E-06
PFA DEF	1.5E-06	2.6E-08	2.6E-07	2.4E-09	1.9E-09	1.5E-06
PFA LUSP 1	1.7E-06	2.0E-08	1.3E-07	2.4E-09	3.4E-09	1.7E-06
PFA LUSP 2	1.6E-06	3.4E-08	1.4E-07	2.3E-09	2.8E-09	1.6E-06
PFA Blank	1.6E-06	3.9E-08	1.4E-07	2.4E-09	1.7E-09	1.6E-06
GGBS MPBDP	1.6E-06	1.1E-08	1.6E-07	2.3E-09	1.4E-09	1.6E-06
GGBS WRBP	1.8E-06	1.4E-08	8.2E-08	2.4E-09	1.7E-09	1.8E-06
GGBS WRBDP	1.7E-06	4.3E-08	1.3E-07	2.4E-09	1.5E-09	1.7E-06
GGBS FWBFP	1.6E-06	4.3E-08	1.5E-07	2.2E-09	1.3E-09	1.6E-06
GGBS BIO	1.7E-06	2.2E-08	1.2E-07	2.3E-09	1.6E-09	1.7E-06
GGBS VMA	1.8E-06	ND	9.9E-08	2.5E-09	1.6E-09	1.8E-06
GGBS DEF	1.6E-06	4.1E-09	1.3E-07	2.3E-09	1.6E-09	1.6E-06
GGBS LUSP 1	1.6E-06	3.6E-08	1.0E-07	2.3E-09	1.3E-09	1.6E-06
GGBS LUSP 2	1.7E-06	3.4E-08	5.6E-08	2.3E-09	1.6E-09	1.7E-06
GGBS Blank	1.8E-06	9.3E-09	1.9E-07	2.4E-09	1.7E-09	1.80E-06

The solubility experiments were undertaken in water equilibrated with samples of the PFA and GGBS grouts manufactured with the SP and adjuncts at 0.5% bwoc. It was suspected that the equilibrated water could contain traces of the SP, adjuncts and potentially other organic substances that may influence solubility. The TOC results in Table 8 indicate that measurable quantities of organics are present in the equilibrated waters and, as a result, the following method was developed.

10 cm^3 of each type of equilibrated water (with the exception of LUSP 2) were added to four 15 cm^3 plastic centrifuge tubes (i.e. 2 grouts x 5 SP formulations and 3 adjuncts, plus blanks; 72 tubes in total). Each set of four tubes was denoted A, B, C and D.

A spike of each of the four isotopes being tested was added to the four separate sets of tubes (A-D). Four “blanks” were also produced which comprised the equilibrated water only. The spikes were as follows:

Ni(II) – A 100 µl aliquot containing 100 kBq ^{63}Ni in the presence of sufficient inactive nickel (II) chloride hexahydrate to generate a solution of ~1 x 10^{-3} mol dm^{-3} was added to each tube of Set A (actual concentration 9.5 x 10^{-4} mol dm^{-3}). The radioactive Ni(II) is used as a readily determinable (by liquid scintillation counting) tracer for the inactive Ni(II) carrier.

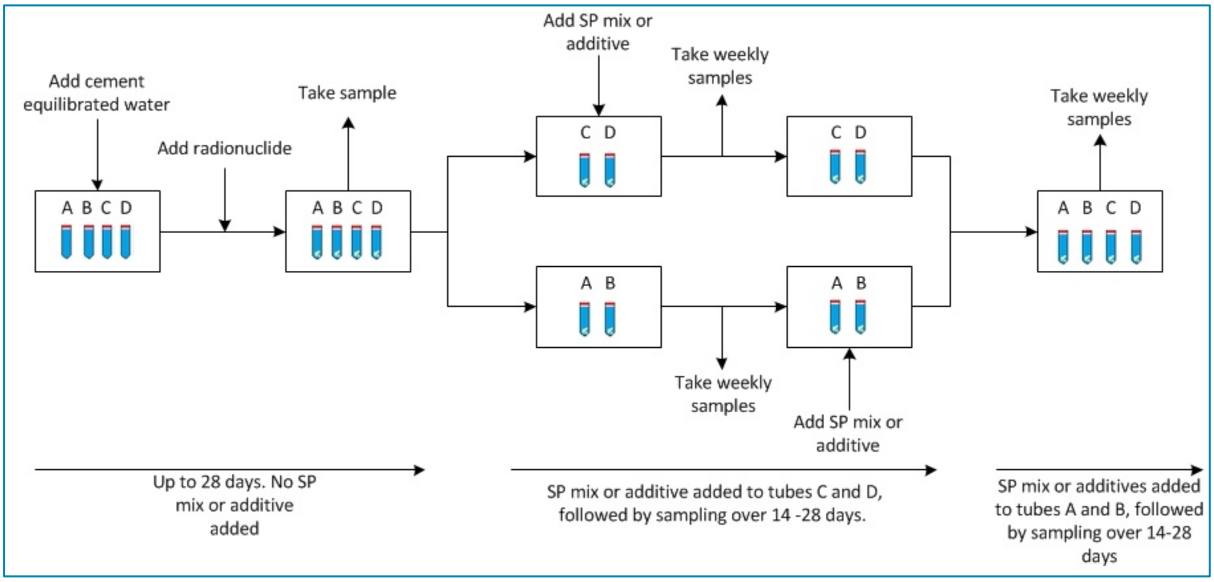
U(VI) – A 100 µl aliquot containing sufficient uranyl nitrate hexahydrate to generate a solution of ~ 1 x 10^{-3} mol dm^{-3} in each tube of Set B (actual concentration 8.0 x 10^{-4} mol dm^{-3} equivalent to ~50 Bq ^{238}U) was added to each tube.

^{239}Pu(IV) – A 100 µl aliquot containing a 15 kBq (2.7 x 10^{-4} mol dm^{-3}) spike of ^{239}Pu was added to each tube of Set C.

^{241}Am(III) – A 250 µl aliquot containing a 5 kBq (6.6 x 10^{-7} mol dm^{-3}) spike of ^{241}Am was added to each tube of Set D. Note that the Am solubility experiments were undertaken using a volume of 5 cm^3 of equilibrated water with the SP formulations and blanks only owing to limited availability of the isotope at the time.

Upon addition, precipitates were not visible in the Pu and Am sample tubes, a yellow precipitate was observed in the U sample tubes and a very small amount of precipitate accumulated over several days in the bottom of the Ni sample tubes. The sample tubes were not shaken during the experiment in the expectation that the precipitates would stay at the bottom of the tube and not be removed during sampling. A schematic diagram of the sampling procedure is shown in Figure 4 below.

Figure 4: Schematic Diagram of the Solubility Determination Sampling Procedure



The spiked tubes were allowed to stand for several days (see Tables 1 to 4 in Appendix A2 for details) before initial sampling. The sample size was 0.5 cm^3, taken after filtering approximately 0.7 cm^3 of the solution being investigated through a 0.2 µm PTFE disposable filter. After the initial samples had been taken, the SP and adjuncts were added to tubes C and D in each set, at a dose of 0.3% v/v of the solution as supplied. This involved adding 30 µl of the SP and adjunct solutions.

Two or three more samples were removed in the same way over a period of several weeks. Then, the SP formulations and adjuncts were added to tubes A and B (with appropriately reduced volume) and sampling continued until a total of at least six samples from each tube had been collected.

All work was undertaken in a nitrogen atmosphere glove-box and all samples were filtered using 0.2 µm syringe filters. Concentration determinations were by liquid scintillation counting using a Packard TR 2500 liquid scintillation counter for ^{63}Ni and ^{239}Pu, gamma counting using a Packard Cobra II Auto-Gamma counter for ^{241}Am and ICP-MS for ^{238}U using an Agilent Technologies 7700 ICP-MS.

The solubility before and after addition of the SPs and adjuncts was calculated and then plotted against the relevant experimental timescale for each radionuclide.

Results

The solubility results are shown graphically as Figures A2. 1 - 56 and Tables A2 1 - 4 in Appendix A2. The “empty” markers denote the concentrations of radionuclides prior to SP mix and adjunct addition; the “filled” markers denote concentrations post SP mix and adjunct additions. The blanks had no SP or adjunct present in the grout or the equilibrated water and the markers are coloured blue. In overview, it is clear that addition of the SP formulations caused an increase in concentration of all the radionuclides being investigated. However, with the exception of a small number of individual data points, the adjuncts did not appear to have any significant effect on solubility when added separately.

For Ni(II), the increase in solubility was between one and two orders of magnitude although for the PFA grout, the first results after the SP mix addition were noticeably higher before settling down to a lower value as the experiment proceeded. The data for the SP are summarised as maxima and minima in Table 12 below. The observed Ni(II) concentration rose from between 10^{-8} and 10^{-7} to between 10^{-5} and 10^{-4} mol dm^{-3} for both grouts. Nickel solubility in the GGBS equilibrated water of blocks cast both with and without additives was shown to be slightly higher than that of results gained from the PFA equilibrated waters. The adjuncts when added separately appeared to have a minimal or, at most, very limited effect on the concentration of the radionuclide in solution, contrasting with the much larger effect of the SP additions. The blanks were within the range of reported solubility values for Ni at high pH, which are between 5 $x10^{-9}$ and 7 x 10^{-5} mol dm^{-3} [13].The PCE SP LUSP 1 increased the solubility of the radionuclides by approximately one order of magnitude for both types of grout, compared to the two orders of magnitude increase witnessed for the W.R.Grace & Co products.

Table 12: Summary of Ni Solubility Data Showing the Effect of Adding SP

Cement	SP	Equilibrated water (mol dm^{-3})	Post SP addition (mol dm^{-3})
PFA	MPBDP	2.6E-08 - 4.8E-07	1.9E-05 - 2.0E-04
	WRBP	6.4E-09 - 1.8E-07	2.6E-06 - 7.8E-05
	WRBDP	2.6E-08 - 3.6E-07	3.0E-06 - 9.6E-05
	FWBFP	1.6E-08 - 1.5E-07	2.0E-06 - 3.4E-04
	LUSP1	1.3E-08 - 2.4E-07	1.1E-07 - 8.0E-06
GGBS	MPBDP	5.4E-08 - 4.8E-07	1.9E-05 - 2.0E-04
	WRBP	4.8E-08 - 5.1E-07	6.6E-06 - 5.5E-05
	WRBDP	4.2E-08 - 1.3E-05	1.3E-05 - 2.2E-04
	FWBFP	1.9E-08 - 1.4E-05	1.1E-05 - 1.5E-04
	LUSP1	1.9E-08 - 4.0E-05	1.2E-06 - 9.3E-05

For U(VI), there is a contrast between the results obtained for the two different types of grout. The data for the SP mixes are summarised as maxima and minima in Table 13 below. The PFA grout showed an increase of around one order of magnitude (from 10^{-6} to 10^{-5} mol dm^{-3}) for the SP mix samples but this was independent of the addition of SP mixes. This suggests that the agent responsible for increasing the solubility of U(VI) is already present in the equilibrated water at the start of the experiment. The results for the GGBS grout once again did not appear to be dependent upon the SP mix addition, and the blank results are higher than the equivalent PFA grout experiments. U(VI) solubility was generally higher for the GGBS experiments and the data spread increased from one to two orders of magnitude with increasing experimental duration. In contrast, the adjuncts when added separately appeared to have a minimal or, at most, very limited effect on the concentration of U(VI) in solution (Table 13). The blanks were within the range of reported solubility values for U at high pH which are between 10^{-6} and 10^{-5} mol dm^{-3} [6]. The SP LUSP 1 did not have a significant effect on U(VI) solubility in the presence of either grout, the results being indistinguishable from the blanks.

Table 13: Summary of U Solubility Data Showing the Effect of Adding SP

Cement	Additive	Equilibrated water (mol dm^{-3})	Post SP addition (mol dm^{-3})
PFA	MPBDP	4.4E-06 - 2.2E-05	4.6E-06 - 1.6E-05
	WRBP	1.4E-05 - 2.2E-05	8.2E-06 - 2.6E-05
	WRBDP	9.0E-06 - 2.5E-05	7.7E-06 - 3.3E-05
	FWBFP	7.7E-06 - 2.9E-05	7.9E-06 - 6.6E-05
	LUSP1	2.5E-06 - 7.4E-06	8.9E-07 - 4.9E-06
GGBS	MPBDP	2.4E-06 - 1.5E-05	8.9E-07 - 1.6E-05
	WRBP	6.2E-07 - 4.7E-05	1.8E-06 - 2.1E-05
	WRBDP	2.3E-06 - 4.2E-05	5.1E-07 - 4.7E-05
	FWBFP	1.4E-06 - 1.3E-05	2.8E-07 - 4.2E-05
	LUSP1	2.1E-06 - 7.1E-06	3.3E-07 - 8.7E-06

The ^{239}Pu(IV) experiments need to be considered differently as it was theoretically possible to dissolve all of the ^{239}Pu(IV) added (15 kBq of ^{239}Pu is 6.5 µg). Accordingly, an indication of the maximum concentration in solution is included in Figures 33 to 48 in Appendix A2. It should also be noted that in the later part of the experiment the maximum could be exceeded as earlier sampling will have reduced the volume of equilibrated water into which the ^{239}Pu(IV) precipitate has the potential to dissolve.

The Pu(IV) results for SP mixes with the PFA grout showed an initial increase in solubility of two orders of magnitude eventually increasing further to more than three orders over a total range of around 5 x 10^{-9} to 10^{-6} mol dm^{-3} over the 95 day period studied. The data for the SP mixes are summarised as maxima and minima in Table 14 below. By the end of the experiment all samples were close to dissolving all the ^{239}Pu(IV) introduced. There is also evidence that a substantial increase in ^{239}Pu(IV) solubility could be caused by the presence of the PFA equilibrated waters only. The adjuncts again did not produce any significant increase in solubility with the exception of a small potential enhancement in the PFA VMA system. The SP LUSP 1 also produced a solubility increase with the PFA grout of between two and three orders of magnitude.

The results are less consistent for the GGBS grout. The ^{239}Pu(IV) solubility observed in the blanks was, on average, an order of magnitude higher than the corresponding PFA blanks. The maximum concentrations reached are similar although MPBDP was consistently lower and WRBP achieved the maximum solubility in all samples taken. There was also evidence that an increase in ^{239}Pu(IV) solubility could be caused by the presence of the GGBS equilibrated waters. The PFA blanks were within the range of reported solubility values for ^{239}Pu at high pH, which are between 1x10^{-10} and 1.3x10^{-11} mol dm^{-3} [6], but the GGBS blanks were about a factor of five higher. The SP LUSP 1 did not produce an increase in ^{239}Pu(IV) solubility with the GGBS grout.

Table 14: Summary of Pu Solubility Data Showing the Effect of Adding SP Mixes

Cement	Additive	Equilibrated water (mol dm^{-3})	Post SP addition (mol dm^{-3})
PFA	MPBDP	3.6E-10 - 6.6E-07	1.1E-07 - 1.5E-06
	WRBP	4.2E-10 - 1.1E-07	7.6E-09 - 3.0E-06
	WRBDP	3.5E-10 - 2.3E-07	6.5E-08 - 1.7E-06
	FWBFP	3.2E-10 - 9.7E-08	1.2E-08 -6.7E-07
	LUSP1	2.9E-10 - 8.4E-08	4.2E-09 - 2.3E-07
GGBS	MPBDP	6.6E-09 - 9.3E-09	1.3E-08 - 1.1E-06
	WRBP	1.5E-06 - 3.7E-06	1.6E-06 - 3.5E-06
	WRBDP	2.3E-09 - 4.0E-08	9.7E-09 - 2.2E-06
	FWBFP	9.8E-10 - 3.8E-08	1.9E-08 - 1.9E-06
	LUSP1	6.7E-10 - 5.3E-09	6.1E-10 - 7.3E-09

The ^{241}Am(III) experiments were similar in nature to the ^{239}Pu(IV) experiments in that it was possible to dissolve all of the Am added (2.5 kBq ^{241}Am is 20 ng). In addition, the experiments were undertaken at a smaller scale; 5 cm^{3} of equilibrated water was used and the 0.5 cm^{3} samples represented a significant proportion of the overall volume. An indication of the maximum concentration in solution is given in Figures 49 to 56 in Appendix A2. It should also be noted that in the later part of the experiment the maximum could be exceeded as earlier sampling will have reduced the volume of equilibrated water into which the Am(III) precipitate has the potential to dissolve. The results for the SP mixes indicated that a solubility increase of two to three orders of magnitude occurred with both types of grout in the presence of the SP mixes when compared to blanks. The data for the SP mixes are summarised as maxima and minima in Table 15 below. The blanks were within the range of reported solubility values for Am at high pH which are generally between 10^{-12} and 10^{-10} mol dm^{-3} [7]. The maximum was only exceeded on the last two sampling events. Another factor could be the practical difficulties of sampling the small volume remaining at the end of the experiment.

Table 15: Summary of Am Solubility Data Showing the Effect of Adding SP Mixes

Cement	Additive	Equilibrated water (mol dm^{-3})	Post SP addition (mol dm^{-3})
PFA	MPBDP	1.4E-11 - 1.6E-10	1.0E-08 - 3.7E-08
	WRBP	1.3E-12 - 6.0E-09	7.5E-09 - 3.1E-08
	WRBDP	1.3E-11 - 4.1E-11	5.5E-09 - 2.8E-08
	FWBFP	3.1E-11 - 2.8E-10	9.4E-09 - 4.3E-08
GGBS	MPBDP	5.0E-11 - 2.2E-10	2.4E-08 - 8.2E-08
	WRBP	7.8E-12 - 1.0E-10	1.6E-09 - 5.0E-08
	WRBDP	5.2E-11 - 2.5E-10	1.5E-08 - 6.1E-07
	FWBFP	1.2E-10 - 3.3E-09	1.1E-08 - 5.7E-08

Conclusion

The solubility determinations undertaken showed that the W.R Grace & Co. SP formulations increased radionuclide solubility in cement equilibrated water by at least one and, in some cases, more than three orders of magnitude. The defoamer, biocide and viscosity modifier adjuncts, when tested in isolation, mostly showed no significant effect on the solubility of the radionuclides. It was also noted that one of the SP mixes (LUSP 1) had less of an effect on solubility than the commercial products. The reason for this is uncertain but the SP had been dialysed during its manufacture to remove low molecular weight material including residual monomer. Consequently, it is feasible that the low molecular weight materials present in the SP mixes contributed to increased radionuclide solubility. It should be noted that the ‘test tube’ measurements of solubility in free aqueous solution undertaken here, and in similar published studies, will not fully reflect pore water chemistry and its interactions with evolving mineral surfaces in a developing cement matrix. Consequently, consideration should be given to undertaking future experiments at pore water concentrations rather than in equilibrated water, and at more realistic solid to solution ratios.

These results indicate that the use of SP could result in increased solubility and hence mobility of the active species trialled in a GDF environment. It should be noted however, that this trial assumed that the active species were available in an aqueous form for solubilisation at the outset. In a GDF environment, this equates to the active species having escaped the confines of the cementitious wasteform. Further trials described below characterise the release and mobility of active species from cementitious grouts themselves.

Through-Diffusion Experiments

Objectives

The experiments undertaken in this work package aim to identify whether the presence of the SP formulations and adjuncts affect radionuclide migration by diffusion through cement monoliths. The experiments complement those in the solubility trials by determining whether any solubility changes in aqueous media are observed in the presence of the relevant solid grout. Thus, these trials provide information on whether the use of SP amended grouts could increase the mobility of the active species through a cement wasteform.

Experimental Methodology

For through-diffusion tests, cylindrical samples (40 mm diameter x 40 - 45 mm) of the grouts were cast using the individual SP mix or adjunct at 0.5% loading and cured for a minimum of 28 days under nitrogen-purged tap water in a N_2 atmosphere. A 10 mm diameter central hole was then cored to within 15 mm of the base and the upper and lower surfaces sealed with a wax coating (Figure 5 and 6). A 1.0 cm^3 aliquot containing a spike of the relevant isotope in deionised water was then added (10 kBq of ^{63}Ni(II), 1 kBq each of ^{241}Am(III) and ^{239}Pu(IV) and 8.5 mg uranyl nitrate hexahydrate, equivalent to ~50 Bq, ^{238}U(VI)) added. The hole was sealed with a plastic cap (Figure 5). The sample was then submerged in a plastic container with 200 cm^3 of a solution previously equilibrated with the appropriate solid grout matrix and replaced in the N_2 atmosphere glove box.

Figure 5: Schematic Diagram of the Diffusion Setup

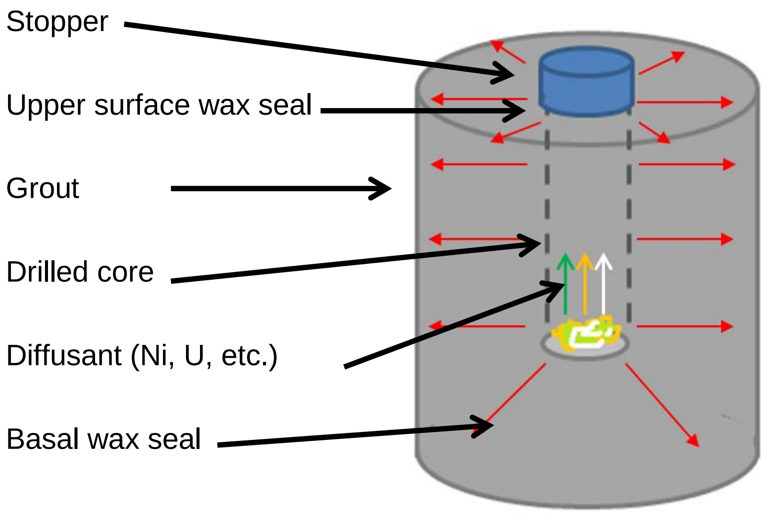


Figure 6: Through-Diffusion Samples

Periodic sampling of the solutions was undertaken weekly for four weeks and then monthly to a total duration of 6 months. All sub-samples were filtered using 0.2 µm syringe filters prior to analysis. Concentrations were measured by liquid scintillation counting for ^{63}Ni(II) and ^{239}Pu(IV), gamma counting for ^{241}Am(III) and ICP-MS for ^{238}U(VI).

After six months, one sample per set of each duplicate experiment was stopped and the grout cylinder removed from the container; the seal was broken and the liquid in the inner well removed. The cylinders were then allowed to dry overnight in the glove box. The following day, the cylinders were removed from the glove box and “wet cut” longitudinally using a mechanical diamond masonry saw. One half of each cylinder was selected and autoradiographed using Fuji BAS Plates and a Packard Cyclone reader. The autoradiography exposure times were determined by undertaking trials of between 4 and 60 hours on two types of plate: protectively coated and uncoated. The uncoated plates are highly sensitive and designed for low energy beta emitters, specifically tritium. They allow un-attenuated exposures to be undertaken and they can also be used for alpha emitters. In this work, the best results were obtained when coated plates were used for ^{241}Am(III) and ^{63}Ni(II) and uncoated plates were used for ^{239}Pu(IV) and natural isotopes of U(VI).

Results

Through-diffusion of the radionuclides was not detected in the receiving water over the six months of testing. Further, the autoradiographs showed no evidence of diffusion from the central core. All of the autoradiographs are presented in Appendix A3. Colour enhancement was undertaken using the freeware package, ImageJ. A black background was used for presentational purposes as it facilitates the removal of spurious information e.g. high activity spots most likely caused when cutting and handling the sectioned cylinders. Spots of this type are obvious and when removed make it easier to discern any diffusion that may have occurred.

A selection of the autoradiographs has been analysed further, again using ImageJ, to show intensity profiles and surfaces (Figure 7 and Figure 8). Photographs of the individual blocks are also included. In all cases, a steep drop off in intensity and hence, radionuclide concentration was observed at the edge of the inner core indicating no significant diffusion into the blocks. For comparison, autoradiographs of rapidly diffusing radionuclides (^{137}Cs^{+} and ^{125}I^{-}) can be found in the literature [14].

Figure 7 From top down, Photograph, Autoradiograph, Profile Plot and Surface Activity Plot for Through-Diffusion Tests on PFA. From left to right, PFA-BIO-U, PFA-Blank-Am and PFA-Pu-WRBP.

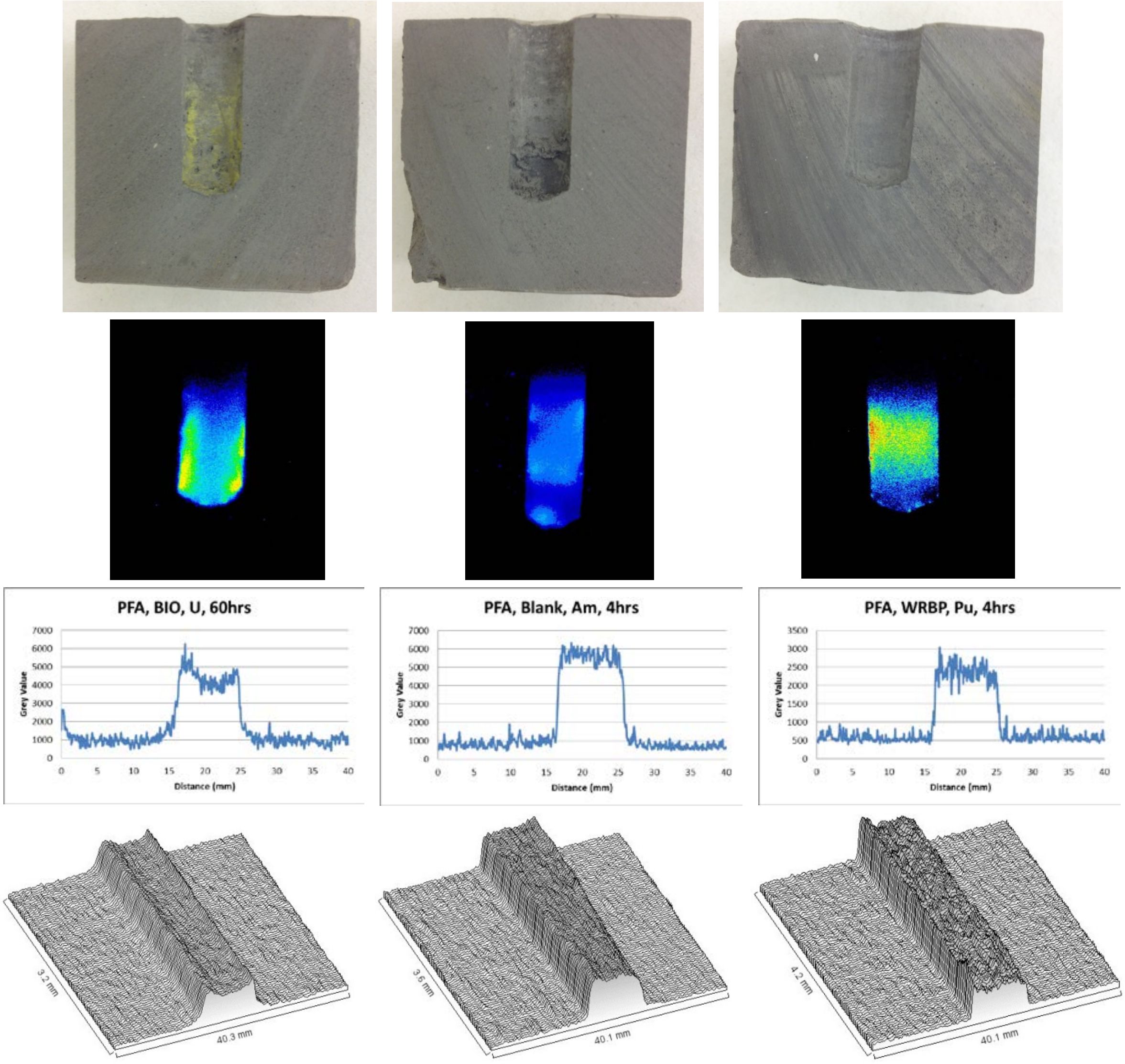
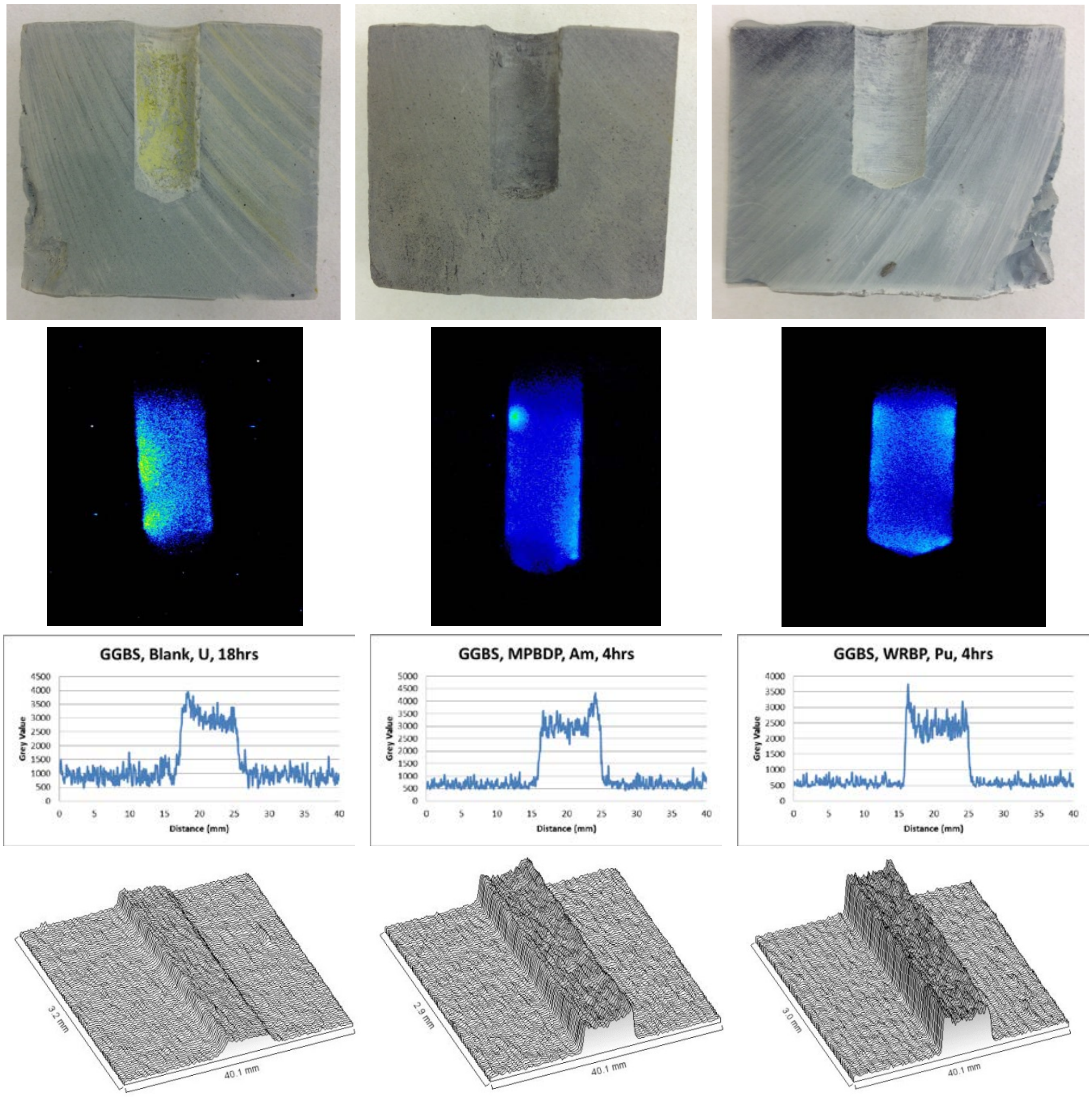


Figure 8: From top down, Photograph, Autoradiograph, Profile Plot and Surface Plot of Through-Diffusion Tests on GGBS. From left to right, GGBS-Blank-U, GGBS-MPBDP-Am, GGBS-WRBP-Pu.



Conclusion

The enhanced radionuclide solubility in free aqueous systems, observed in earlier trials, did not result in increased mobility of any the radionuclides in the presence of the solid grouts. Even where solubility increase substantially, e.g. ^{239}Pu(IV) in GGBS and WRBP, no evidence of diffusion was found over the six month duration of the experiments. It is clear from this work that the presence of the cementitious solid was crucial in minimising the migration of the radionuclides. The results indicated that, at least for the active species trialled, SP did not significantly enhance mobility within intact cement monoliths. The pixel size of the autoradiographs is ~50 microns which corresponds to the smallest degree of migration detectable via this method.

It should be noted that the grout samples manufactured for this programme were prepared at small scale utilising low-shear mixing and hence, may have different properties (e.g. microstructure) when compared to those prepared at the larger operational scale used in waste management. Nevertheless, the results may be considered indicative.

Intact Leaching Experiments

Objectives

The experiments undertaken in this work package aim to identify whether the presence of the SP formulations and adjuncts affect the leachability of radionuclides from cement monoliths. The experiments complement those in the solubility trials by determining whether any solubility changes in aqueous media are also observed in the presence of the relevant solid grout. The leaching experiments will help determine whether the primary function of a cementitious wasteform (radionuclide immobilisation) would be compromised by the use of SP by assessing the activity released from the wasteform surface. In essence, they are microcosm tests of leaching from intact grout wasteforms.

Experimental Methodology

Blocks were prepared in accordance with the method detailed earlier with the addition of 1.0 cm^3 aliquots containing; 10kBq ^{63}Ni(II), 1kBq ^{239}Pu(IV), 1kBq ^{241}Am(III) or 8.5 mg uranyl nitrate hexahydrate, equivalent to ~50 Bq ^{238}U(VI). After addition of the respective radionuclide, the blocks were allowed to cure over a 24 hour period. The bleed water was then decanted and tested for activity. Samples were de-moulded and placed into tap water to cure over a 28 day period in a N_2 atmosphere.

The bleed water was tested for the presence of radionuclides. The mass of bleed water per block is summarised in Table 16 and the percentage of the radionuclide lost from each block detailed in Table 17. A measurable quantity of radionuclide in the bleed water can be seen in most of GGBS water samples with the W. R. Grace and Co. SP mixes added. The radionuclides were not detected in any of the PFA bleed waters.

Table 16: Bleed Water obtained from Cement Blocks

	Bleed water obtained from spiked samples (g)							
	GGBS				PFA			
	Ni	U	Pu	Am	Ni	U	Pu	Am
WRBDP	18.1	17.6	16.3	18.3	16.5	14.7	15.2	15.3
MPBDP	14.0	13.6	13.8	13.5	12.4	12.1	11.3	10.8
FWBFP	14.1	14.1	13.7	13.8	13.6	13.4	13.7	13.2
WRBP	15.2	16.0	15.5	15.0	10.7	11.2	10.9	11.9
LUSP 1	2.5	2.9	3.3	2.2	7.6	8.8	7.6	6.7
LUSP 2	2.4	3.3	2.5	1.5	7.3	8.4	7.6	7.0
VMA	0.0	0.0	0.0	0.0	5.1	4.8	4.4	5.5
BIO	0.0	0.0	0.0	0.0	6.0	6.3	6.0	5.5
DEF	0.0	0.0	0.0	0.0	6.0	6.1	5.9	5.1
BLANK	0.0	0.0	0.0	0.0	5.2	4.8	4.8	4.7

Table 17: Radionuclide Spike Detected in Bleed Water

	% Original Spike in Bleed Water							
	GGBS				PFA			
	Ni	U	Pu	Am	Ni	U	Pu	Am
WRBDP	1.3	0.1	0.5	ND	ND	ND	ND	ND
MPBDP	7.6	0.2	1.1	0.6	ND	ND	ND	ND
FWBFP	0.5	0.2	0.1	ND	ND	ND	ND	ND
WRBP	1.9	0.1	0.1	ND	ND	ND	ND	ND
LUSP 1	ND	ND	ND	ND	ND	ND	ND	ND
LUSP 2	ND	ND	ND	ND	ND	ND	ND	ND
VMA	ND	ND	ND	ND	ND	ND	ND	ND
BIO	ND	ND	ND	ND	ND	ND	ND	ND
DEF	ND	ND	ND	ND	ND	ND	ND	ND
BLANK	ND	ND	ND	ND	ND	ND	ND	ND

ND – Not Detected

The doped blocks were removed from the curing water after 28 days and subjected to a standard monolithic leach test, BS EN 15863 [15]. The standard was modified owing to concerns with the volume of leachant required and the ability to detect the radionuclides in question. The leachant volume was changed from the published method where: $V_1 = (8 \pm 0.1) \times A$; V_1 is the volume of the leachant, in cm^3 and A is the surface area of the test portion, in cm^2. The altered protocol required each step to use 80 cm^3 deionised water as leachant since this was the minimum amount of water needed to fully submerge the samples. The water was changed, sampled and analysed at intervals of 2 hours, 1, 2.25, 8, 14, 15, 28 and 36 days in accordance with the standard.

Results

The results for the intact leaching test are presented in Appendix A3. The results show that, apart from two anomalous uranium results (59.3 and 14.4 ppb; highlighted in the tables), no consistent leaching from the cement blocks occurred with any of the SP mixes or adjuncts. The cause of the anomalously high results is not obvious but could include sampling error or faulty filters. When considered in their entirety, in the majority of cases the highest results shown in the tables were not from the leach test but from the curing water. When the radioactively doped blocks were cured it was possible to detect radionuclides in the curing water. This was particularly evident in the ^{63}Ni(II) and U(VI) PFA grout curing waters but ^{239}Pu(IV) and ^{241}Am(III) were also detectable for some SP mixes. One explanation may be radionuclide from the evaporated bleed water remaining on the external surface of the samples and subsequently dissolving in the curing water.

Conclusion

The enhanced solubility in free aqueous systems, observed in earlier trials, did not result in increased mobility of any the radioisotopes in the presence of the solid grouts. Even where the solubility increase was significant, e.g. ^{239}Pu(IV) in GGBS and WRBP, no evidence of leaching from the cement monolith could be found over the 36 day duration of the experiments. The cementitious solid appears to be important in controlling radionuclide retention when SP is present in the samples. As noted for the through-diffusion experiments, these results may be indicative of grout behaviour at the larger operational scale used for waste management although this remains to be confirmed.

Long term predictions cannot be made based on these short term trials. However, the results, combined with those from the through-diffusion tests, suggest that, although solubility is enhanced in aqueous systems, this is unlikely to translate to increased mobility within cementitious grouts or enhanced release of activity from its surface.

Crushed Leaching Experiments

Objectives

The experiments undertaken in this trial aim to identify whether irradiating SP formulations and adjuncts affects the leachability of radionuclides from crushed cement monoliths. The experiments complement those in the solubility trials by determining whether solubility changes in aqueous media are also observed in the presence of the relevant solid grout. These leaching experiments help determine whether the primary function of the cementitious wasteform (immobilisation) could be compromised by the use of SP by assessing radionuclide release from wasteform surfaces. The higher surface area resulting from crushing would be expected to result in greater leaching and thus can be considered a more conservative test than the previous example using monolithic samples. The use of crushed samples with higher surface area may be considered analogous to degraded wasteforms, although it is noted that newly exposed surfaces from crushing are not the same as those that have evolved over time.

The current generation of SP are organic compounds that consist of long aliphatic chains (Figure 1). These are likely to be readily degraded under long term irradiation ([16], [17]), as is likely to be experienced by waste packages both from self-irradiation and from the near field (typically considered to be 10 MGy over 300 years [18]). It is probable that, by the time of backfilling a GDF, the concentration of SP present in the waste packages will have reduced significantly due to degradation processes.

Historically, the concern over the use of SP for waste packaging has centred on radionuclide mobilisation in the longer term, during the post-closure phase of a GDF. Considering the timescales involved and the significant near field gamma dose, there is limited knowledge of the longevity of SP and the consequences of their degradation. Potentially, they may have degraded to such an extent that mobilisation is reduced or eliminated. Alternatively, there is the possibility that intermediate degradation products (i.e. prior to formation of hydrogen, carbon dioxide and water) could also promote radionuclide mobilisation.

By comparison to the results from un-irradiated samples, it should be possible to determine whether radiolytic SP degradation has an influence on radionuclide mobilisation.

Experimental Methodology

Two sets of identical samples were prepared in accordance with the method detailed earlier for intact leaching, and included the addition of a radionuclide mix comprising 10 kBq of ^{63}Ni, 1 kBq of ^{241}Am and 8.5 mg uranyl nitrate hexahydrate (approximately 50 Bq ^{238}U), in 1.0 cm^3 of deionised water. The water content in the initial grout mixes was reduced appropriately to account for the eventual addition of the radionuclides. ^{239}Pu was not included because of deconvolution issues with the subsequent liquid scintillation analyses and remote handling/transport concerns. The radionuclide mix was stirred in and the blocks were allowed to set over a 24 hour period. The bleed water was then decanted. Samples were de-moulded and placed into tap water to cure over a 28 day period under N_2 atmosphere.

The samples from one set were crushed so that 95% of the particles passed a 4 mm sieve for granular HazWAC leach testing according to BS EN12457-3:2002 (Part 3, two stage) [12]. This is a two stage leach test, the first stage being a 6 hour leach with a liquid to solid ratio of 2 dm^3/kg and the second stage, an 18 hour leach with a liquid to solid ratio of 8 dm^3/kg. The tests were performed in duplicate. The HazWAC analyses were conducted with the assistance of Enviras Ltd, a UKAS accredited laboratory at Loughborough University which specialises in the compliance testing of radioactive samples.

The samples of the second set were placed in individual robust glass bottles with vented, filtered lids. The bottles were then mounted inside a secure aluminium case and transported to Synergy Health’s Swindon gamma irradiation facility. Initial trials were performed using an identical case with several inactive samples to ensure the system was adequately robust.

The cases were placed inside the irradiation cell (Figure 9) and gamma irradiated to a total dose of 1.04 MGy, delivered at an average dose rate of 0.85 kGy per hour from a ^{60}Co source. The case was rotated half way through the irradiation period to ensure that the gamma dose was evenly received by the samples. Harwell red polymethylmethacrylate (PMMA) dosimeters, mounted at several points within the cases, were used to record the total dose rates received by the samples.

Figure 9: Sample Irradiation

Results

Concentrations were measured by liquid scintillation counting (Packard TR 2500 liquid scintillation counter) for ^{63}Ni, gamma counting (Packard Cobra II Auto-Gamma counter) for ^{241}Am and ICP-MS for ^{238}U using an Agilent Technologies 7700 ICP-MS.

The crushed sample leaching results from the un-irradiated and irradiated samples are presented in Appendices 4 and 5, respectively. The L2 and L8 values (radionuclide concentrations from the 6 hour and 18 hour leach times) demonstrate that the majority of results were below the limit of detection or the blank. Where leaching was observed from the samples, the values did not differ significantly from the relevant blank. These concentrations render the A_2 and $A_{2\text{-}10}$ values normally associated with this test (see blank crushed sample leaching results) so low that they lack meaning.

Two ^{241}Am results for the GGBS irradiated grout have been highlighted in Table A5.1 as they appear anomalously high. Gamma counting for ^{241}Am can be sensitive to low energy background radiation and a range of counts for the blank subtraction is not uncommon. In this case, values under 12 counts per minute (equivalent to a maximum of 0.2 Bq in the sample) are assumed to be negligible.

There were minimal physical changes to the samples after gamma irradiation; no visible swelling, cracking or release of water. Some samples had small chips and particulates present in the bottles (e.g. Figure 10) but these were considered likely to have been generated during transport rather than as a result of irradiation. It should be noted that the shatterproof coating used on the outside of the bottles shown in Figure 10 discoloured to a dark brown. This is not unusual and was not an effect caused by or related to the samples.

Figure 10: GGBS Samples Post Irradiation

Conclusion

The solubility increases seen in free solution did not correlate with increased radionuclide leaching from crushed grout samples. Leaching from crushed grout samples was expected to be greater than from intact samples due to the increased surface area and exposure of fresh surfaces. However, as with the results from the intact and through-diffusion leaching, the presence of the cementitious solid appeared to be important in inhibiting radionuclide mobility. As noted in the through-diffusion experiments, these results, derived from small scale samples, may or may not be indicative of grout behaviour at the larger operational scale, such as used for waste management activities. It should also be noted that the intact leaching test involved 8 sampling points over 36 days whereas the standard crushed sample leaching procedure involved 2 sampling points over 24 hours.

Within the timescale of the trials, these results indicate that, even when the grout has a high surface area (analogous to a cracked, degraded wasteform), the active species did not leach to any measurable extent. The impact of gamma irradiation on the activity leached from the samples was negligible.

Porosity Measurements

Objectives

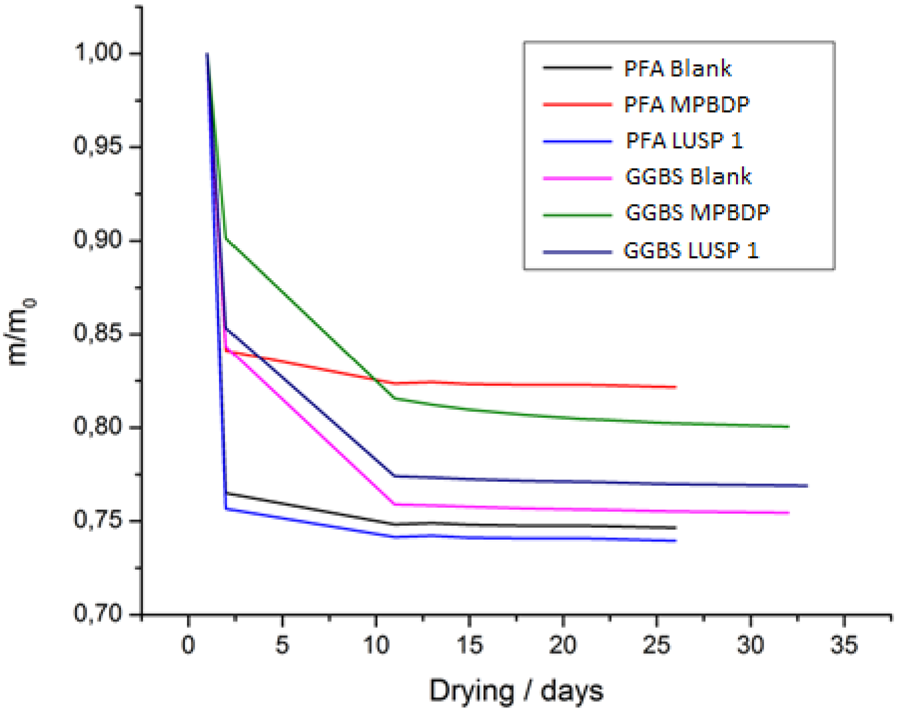
The purpose of this work package was first, to assess the effect of a limited number of SP products on total porosity in the GGBS and PFA grouts and second to ascertain whether they could exert an influence on microporosity and the connectivity of transmissive fracture networks. An increase in these parameters could be deleterious in a wasteform as it could result in increased groundwater penetration, thereby increasing the contact area with the waste and potentially increasing radionuclide mobility. These experiments were designed to assess the significance of this issue, albeit in a limited number of samples, and to indicate whether further work on the subject is warranted.

Experimental Methodology

Following agreement with NDA, a total of six samples comprising PFA or GGBS amended with either W.R Grace & Co. SP MPBDP or 'LUSP 1' SP, along with two blocks made without SP, were prepared as cylinders ca. 25mm diameter x 45mm.

The samples were prepared in a similar manner as detailed previously before shipping under normal atmospheric conditions to Helsinki University for testing. On receipt, the samples were dried under vacuum at 60°C to constant weight over approximately 30 days. Drying curves of the samples are shown in Figure 11.

Figure 11: Drying Curves m/m_0 as a Function of Time (m/m_0 is the mass of the block divided by the mass of the block at the beginning of the drying process)



A clear difference can be seen between the sample sets; the PFA samples dried faster than the GGBS in each case. Further, the loss on drying for the two MPBDP samples was significantly lower. The reasons for the differences in behaviour of the samples during the drying process have not been explored to date. It is notable that the PFA formulation had a higher initial water content than the GGBS formulation, yet dried more quickly. However, both formulations yielded bleed water so the increased initial water content may not have resulted in a proportional increase in pore water. Examination of the porosity results (Table 18) indicate that the PFA samples had higher porosity which may have allowed the water present to evaporate more quickly than the corresponding GGBS samples.

Argon Pycnometry

The equipment used to measure the porosity consists of two chambers - a measurement chamber and a reference chamber. A sample is placed in the measurement chamber and both chambers are evacuated until a gauge vacuum of -95 kPa is reached. The reference chamber is then pressurised with argon gas to a gauge pressure of 100 kPa, and finally the chambers are connected. When the pressure and temperature of both chambers is measured during all steps, the grain volume and thus the porosity of the sample can be determined by:

$$V_g = V_M - V_R \frac{(P_R T_M T_V - P_M T_V T_R)}{(P_M T_V T_R - P_V T_M T_R)}$$

where V_g is the grain volume of the sample; V_M and V_R are the volumes of the measurement and reference chambers, respectively; P_V and T_V are pressure and temperature, respectively, of the reference chamber after evacuation; P_R and T_R are the same quantities of the reference chamber after pressurisation and P_M and T_M are the same quantities of the measurement chamber after connecting the chambers. Porosity (ε) can be obtained from the expression:

$$\epsilon = \frac{V_b - V_g}{V_b}$$

where, V_b is the bulk volume of the sample, obtained by water immersion where a sample is weighed in air and immersed in water, using Archimedes' Principle. Data acquisition and weighing curve extrapolation were used to account for the water infiltrating the pores by capillary forces when the sample is submerged.

Some samples visibly deteriorated in the process of drying and pycnometry measurement. Photographs of the samples after pycnometry are shown in Figure 12 andFigure 13.

Figure 12: Deterioration of the PFA-series samples. Blank (left), MPBDP (centre) and LUSP 1 (right)

Figure 13: Deterioration of the GGBS-series samples. Blank (left), MPBDP (centre) and LUSP 1 (right)

Polymethylmethacrylate and Autoradiography

The ^{14}C-PMMA method involves the impregnation of centimetre-scale sample cores with ^{14}C-labelled methylmethacrylate (^{14}C-MMA) in a vacuum, polymerisation with a ^{60}Co or thermal source, autoradiography and optical densitometry using digital image-processing techniques. Impregnation with ^{14}C-MMA, a labelled, low molecular weight and low viscosity monomer that wets mineral surfaces well and which can be fixed by polymerisation, provides information about the accessible pore space that cannot be obtained using other methods [19].

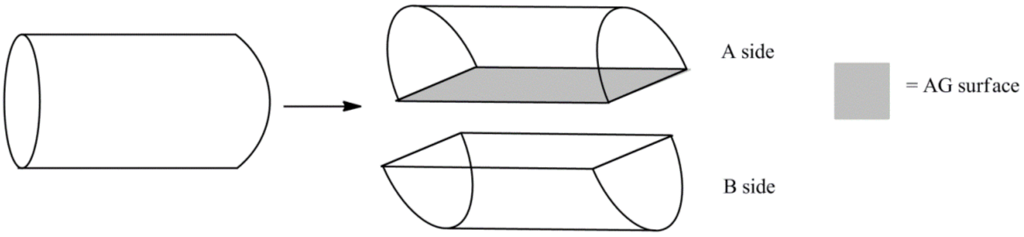
Total porosity is calculated using 2D autoradiographs of the sawn sample surfaces. The geometry of porous regions is then visualised. The conditions for applying this method are: (i) a known local bulk density; (ii) the presence of only two phases, i.e. sample and PMMA; and (iii) a homogeneous distribution of pores and minerals below the lateral resolution limit of autoradiography.

After completion of the argon pycnometry measurements described above, the samples were placed into polypropylene vials and moved to a vacuum canister where the samples were dried briefly under vacuum. They were impregnated with a ^{14}C-methylmethacrylate solution of activity 215 kBq/cm^3 and 0.5 wt-% of initiator (benzoyl peroxide). The impregnation time was three weeks.

In order to convert the ^{14}C-MMA solution to a solid within the pore structure, the samples were polymerized by placing the vials into a water bath for 16 hours at 55 °C. The vials were removed and opened in a fume cupboard to allow any residual monomer to evaporate.

The impregnated samples were cut in half lengthwise and the cut surfaces (Figure 14) prepared using a Kent 3 Automatic Lapping and Polishing Unit and Silicon Carbide 400 (P600) grit powder from Buehler. After polishing to improve contact with the autoradiography plate, the samples were washed in an ultrasonic bath and immersed in ethanol to remove the polishing powder. The ultrasonic bath was a Quantrex 140 from L&R Ultrasonics.

Figure 14: MMA Analysis. The Polished Grey Surface (AG) is placed on Autoradiographic Film



The polished surfaces were exposed on Kodak BioMax MR film, a high-performance autoradiographic film for ^{14}C and other low-energy β-emitting nuclides. The exposure time was 24 hours owing to the high porosity.

The nominal resolution of the β film is a few μm. The final spatial resolution achieved, about 20 μm, depends on the roughness of the sawn surface, the space between the sample and autoradiographic film and the range of the 155 keV beta particles in the matrix.

Interpretation of the results is based on digital image analysis of the autoradiographs. Digital image analysis commences by dividing the autoradiograph into pixel units. In this study, the 600 dpi (dots per inch) resolution used in the analysis resulted in a pixel size of 42.5 x 42.5 μm^2. Essentially, all the intensities of the sub-domains are converted into corresponding optical densities and these, in turn, converted into levels of activity with the help of the calibration curves measured for each exposure. Finally, the levels of activity are converted into their corresponding porosities. Thus, the interpretation is based on studying the abundance of tracer in each sub-domain.

The amount of tracer in the sample and the volumetric porosity can be derived from the blackening of the film caused by radiation emitted from the plane surface of the section. If the pore sizes are well below the resolution of the autoradiographic plate, the major fraction of the beta radiation emitted is attenuated by silicates. The tracer can thus be considered to be diluted by silicate.

Results

The results of argon pycnometry and ^{14}C-PMMA porosity determination are shown in Table 18 below. The errors for ^{14}C-PMMA autoradiography measurements are reported as 10% based on empirical findings. The main source of error occurs where digitisation of grey areas is non-linear at high porosities, leading to under-estimation. Within the linear region, the error is very small.

Table 18: Summary of Porosity Results.

Sample	Dimensions (cm)	Pycnometry porosity (%)	AG outer area porosity (%)	AG total porosity (%)
PFA Blank	4.6 x 2.6	57.8 ± 0.6	41.2 ± 4.2	25.5 ± 2.6
PFA LUSP 1	4.3 x 2.6	58.9 ± 0.7	38.9 ± 3.9	19.3 ± 2.0
PFA MPBDP	4.3 x 2.6	59.1 ± 0.6	51.0 ± 5.1	28.3 ± 2.9
GGBS Blank	4.6 x 2.6	44.6 ± 0.6	30.4 ± 3.1	14.3 ± 1.5
GGBS LUSP 1	4.4 x 2.5	29.1 ± 0.6	26.0 ± 2.6	12.7 ± 1.3
GGBS MPBDP	4.3 x 2.6	41.1 ± 0.7	27.7 ± 2.8	10.8 ± 1.1

AG = Autoradiography

Autoradiography results suggest that penetration of ^{14}C-MMA into the samples may not have been complete - the total porosity for each sample was significantly less than that of the outer margins (column labelled ‘AG outer area porosity’). Nevertheless, clear differences can be seen between the PFA and GGBS sample sets. The former gave significantly higher porosities in all cases. Differences within the sets are smaller though overall, cements prepared with LUSP 1 appeared to result in lower accessible porosity than either the blank or the W.R Grace & Co. product. The one exception from this limited set of samples is the GGBS prepared with MPBDP. Further, porosity patterns for the PFA samples are homogeneous whereas the GGBS samples contain fractures that are likely to dominate the measurements.

The PFA Blank shown in Figure 15 contains two zones with different porosities that are visible to the naked eye; the reason is probably imperfect impregnation. The porosity was therefore calculated for the total exposed area (25.5 ± 2.6 %) and the outer, well impregnated area (41.2 ± 4.2 %). Both values are lower than the gas porosity measured by argon pycnometry (57.8%).

Figure 16 is PFA grout amended with LUSP 1 and also showed evidence of imperfect impregnation with a slightly smaller outer zone and, possibly, three areas of different tone and porosity. PFA grout prepared with MPBDP shown in Figure 17 was more irregular with zones of different shade and porosity. It appeared to be better impregnated than the other two with PMMA measurements for the outer zone approaching the value obtained with argon pycnometry (Table 18). However, swelling and cracking were apparent, which could explain the greater degree of impregnation.

Figure 15: PFA Blank. Autoradiograph on left and Corresponding Photograph on the right

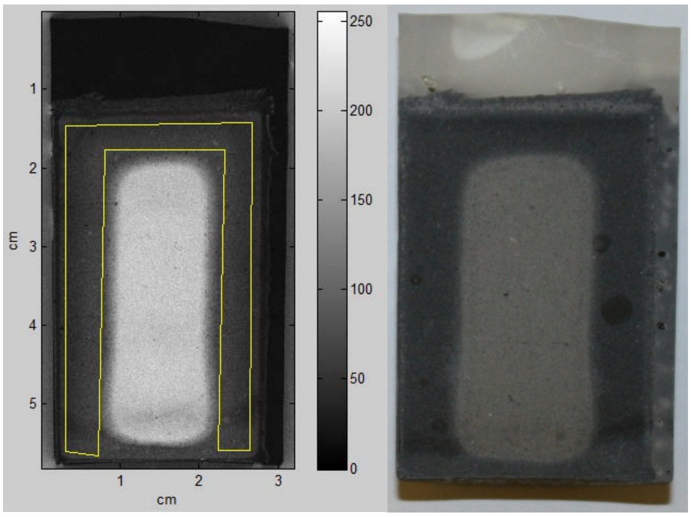


Figure 16: PFA LUSP 1. Autoradiograph on left and Corresponding Photograph on the right

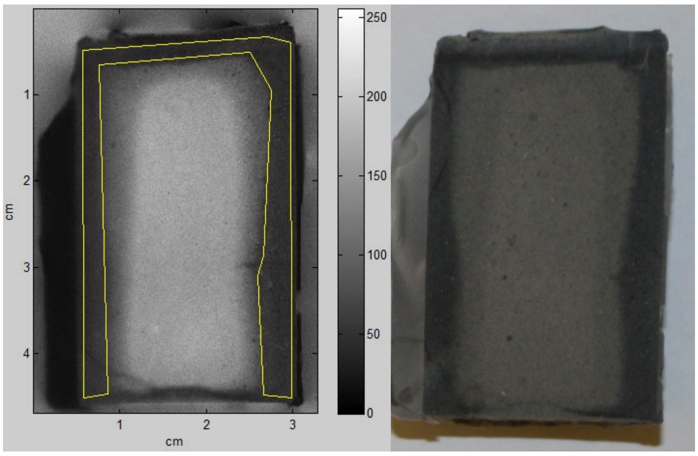


Figure 17: PFA MPBDP. Autoradiograph on left and Corresponding Photograph on the right

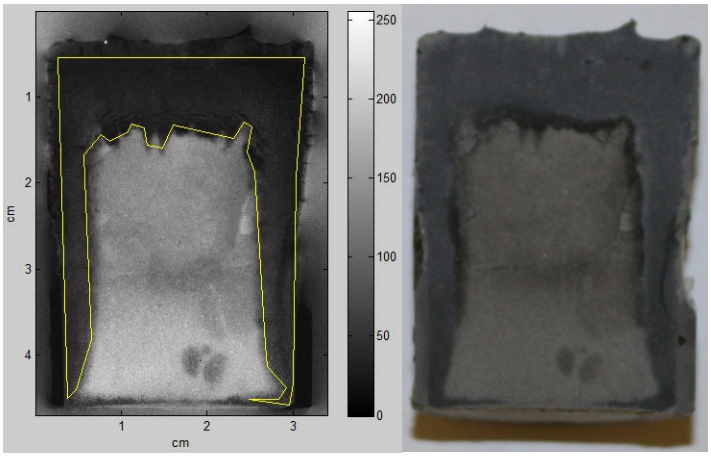


Figure 18 shows that the GGBS blank had a different pore network compared to the PFA set with numerous interconnected, porous cracks. Some of the cracks are visible in the photograph but even more evident in the autoradiograph. Notwithstanding the extent of cracking, the sample appeared to be imperfectly impregnated. However, pervasive zones of differing porosity are not clearly delineated; impregnation seems to have spread along the cracks. The total porosity for this sample was significantly lower than that of the corresponding PFA blank.

GGBS LUSP1 shown in Figure 19 has a distinct outer zone, as with the PFA samples. The inner zone appeared as two differently coloured areas on the photograph but these are not distinguishable on the autoradiograph. There seemed to be fewer cracks in this sample than in the GGBS blank. The cracks are of smaller aperture and only just visible to the naked eye. The total accessible porosity of this sample was determined to be only 12.7 ± 1.3 % with the outer area porosity 26.0 ± 2.6 %.

The final sample GGBS with MPBDP shown in Figure 20 appeared to have the narrowest well-impregnated outer area of all the samples analysed. The cracks had larger apertures than in GGBS LUSP 1 but they were fewer in number. The inner area appeared homogeneous away from the cracks. The total porosity of this sample was the lowest found at 10.8 ± 1.1 %, with the outer area similar within error to LUSP 1 (27.7 ± 2.8 %).

Figure 18: GGBS Blank. Autoradiograph on left and Corresponding Photograph on the right

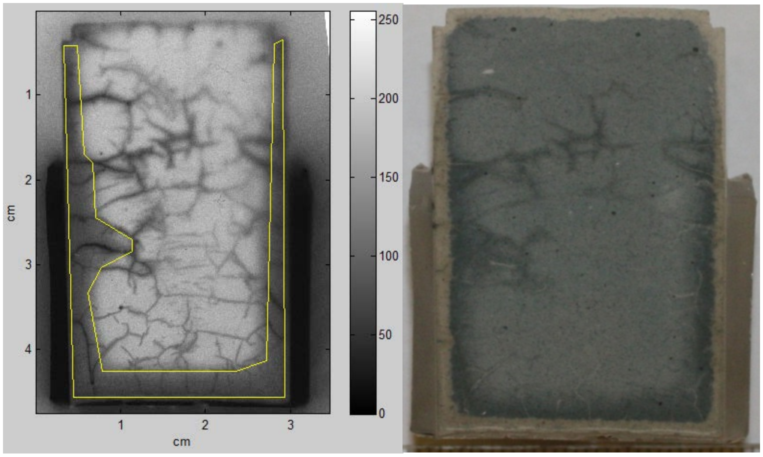


Figure 19: GGBS LUSP 1. Autoradiograph on left and Corresponding Photograph on the right

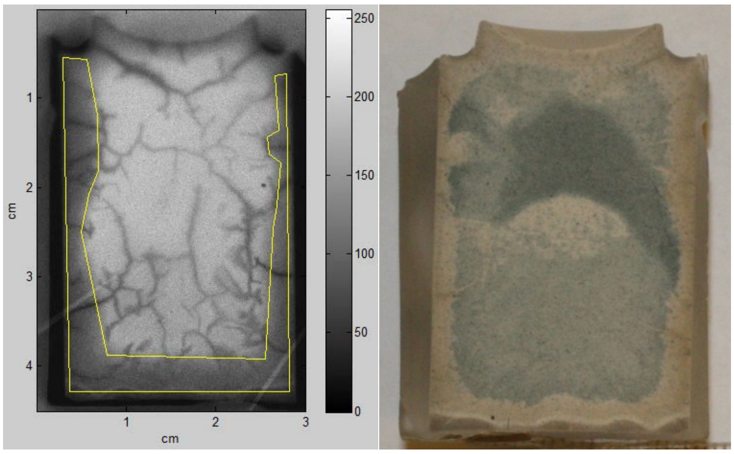
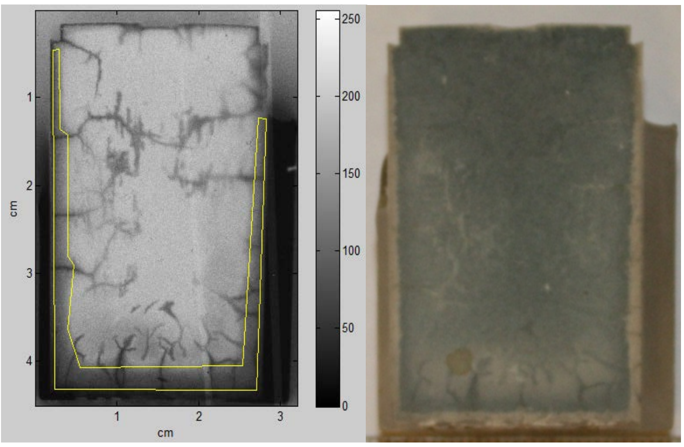


Figure 20: GGBS MPBDP. Autoradiograph on left and Corresponding Photograph on the right



Conclusion

Six cement samples, three of PFA and three of GGBS, were characterised using argon pycnometry and ^{14}C-PMMA autoradiography. All of the grout samples were highly porous and several showed evidence of incomplete mixing (e.g. stratification). The latter is not uncommon in small scale laboratory samples. Drum scale curing trials would be needed to confirm whether this is likely to constitute a problem in practice for waste encapsulation plants.

The PFA samples were observed to be more porous than the GGBS samples and the areas well-impregnated by PMMA are larger. Samples from the PFA set contained distinct zones with higher porosity towards the margins. Within the zones, they were relatively homogeneous with pores of small aperture. PFA amended with LUSP1 had the lowest accessible porosity of the PFA set but gas porosities were very similar. PFA amended with MPBDP was notable for showing signs of swelling and cracking.

Samples from the GGBS set had smaller well-impregnated areas. There were however, large and highly porous cracks throughout the material. GGBS LUSP 1 and GGBS MPBDP had fewer cracks than the GGBS blank and were quite similar in terms of cracking and porosity.

Overall, the differences within sets were much smaller than those observed between the two sample sets (PFA and GGBS). The addition of SP did not make a significant impact on porosity for either types of cement. Noting the potential variability of laboratory scale cement preparation, there nevertheless appears to be distinct differences in porosity between PFA and GGBS grouts.

Pore Water Extraction

Objectives

Residual water left over from the cement curing process resides in pores within the cement matrix. Should any radionuclide be immobilised within a wasteform in the GDF, it will be contained within the pore water. Therefore, being a vehicle for radionuclide release, the amount and chemical composition of pore water are of great interest. Additionally, it would add to the understanding of the mode of action of SP in cement systems if a comparison could be made between superplasticised and non-superplasticised grouts.

The objectives of this experiment were:

- To express pore water from PFA/OPC and GGBS/OPC cement samples dosed at two concentrations of SP;
- To assess the volume of pore water expressed;
- To identify appropriate analyses for the pore water (dependent on volume).

Experimental Methodology

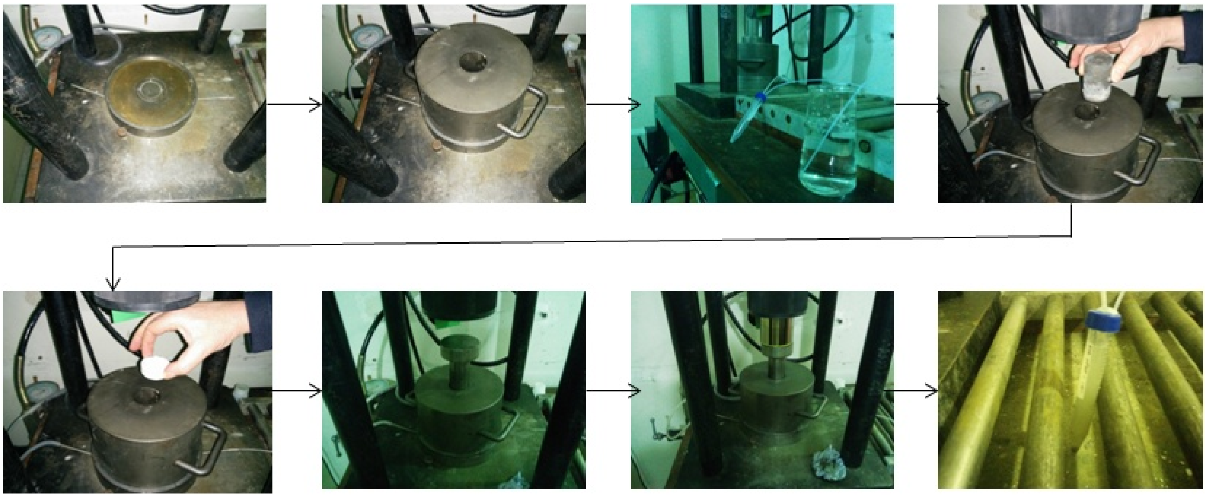
Cement samples were prepared as described earlier, but poured into larger moulds of suitable size for the pore squeezing rig.

Cylindrical samples of both PFA and GGBS grouts were cast with dimensions of approximately 49 mm diameter and 75 mm length. A total of 20 samples were made comprising duplicate samples of the two grouts with MPBDP or LUSP 1 dosed at 0.5% and 1% bwoc plus the corresponding blanks. The samples were allowed to cure for 28 days under nitrogen in an identical manner to other samples prepared for this project.

The samples were squeezed to extract pore water at Aberdeen University by Loughborough University staff (Figure 21).

Each specimen was placed on the base of the press and the pressure increased gradually through the piston to 4,000 psi (27 MPa). As pressure increased, water was expressed from the samples and flowed through a hypodermic needle via a tube into a collection vessel. This system ensured that the sample was not exposed to air and resulting carbonation [7].

Figure 21: Pore Squeezing Rig Setup



Two SP-amended PFA samples failed during the squeezing process. Although apparently intact and appearing identical to the other monoliths they reverted to a paste under moderate pressure and flowed down the collection tube, contaminating the equipment. Where this occurred, the samples were lost and consequently, samples that appeared likely to fail were not processed.

Results

The results from pore water extraction tests on the GGBS samples are detailed in Table 19. The result highlighted in red denotes a sample where some of the block mass was unrecoverable from the extraction rig, prior to weighing. The GGBS pore water TOC values are given in Table 21.

It was observed that the GGBS samples required pressures of around 3000psi before pore water was expressed whereas the PFA samples released pore water from several hundred psi onwards.

Table 19: Liquid Expressed from GGBS/OPC Samples

Sample Identity	Block Mass Pre Crushing (g)	Block Mass Post Crushing (g)	Mass Change (g)	% Mass loss	Mass Pore Water Collected (g)
MPDBD 0.5% 1	159.89	143.76	16.13	10.08	3.04
MPBDP 0.5% 2	168.43	164.64	3.79	2.25	2.40
MPDBD 1.0% 1	173.40	168.29	5.11	2.94	4.06
MPBDP 1.0% 2	171.19	166.70	4.49	2.62	2.71
LUSP 1 0.5% 1	160.49	156.59	3.90	2.43	7.75
LUSP 1 0.5% 2	177.39	165.99	11.40	6.42	9.37
LUSP 1 1.0% 1	163.35	154.23	9.12	5.58	4.23
LUSP 1 1.0% 2	167.51	161.98	5.53	3.30	4.28
Blank 1	176.42	164.28	12.14	6.88	7.56
Blank 2	168.12	157.61	10.51	6.25	8.39

The results from the pore water extraction of the PFA samples are given in Table 20. Rows highlighted in red denote where results were unobtainable due to the cement liquefying, or where it was suspected that the samples might liquefy resulting in a lengthy clean-up of the equipment. Blank 1 was squeezed successfully in a preliminary trial, but a water sample was not collected owing to a prior blockage in the equipment; this was remedied for subsequent tests. The PFA pore water TOC values are given in Table 21.

Table 20: Liquid Expressed from PFA/OPC Samples

Sample Identity	Block Mass Pre Crushing (g)	Block Mass Post Crushing (g)	Mass Change (g)	% Mass loss	Mass Pore Water Collected (g)
MPDBD 0.5% 1	148.03	129.47	18.56	12.53	16.05
MPBDP 0.5% 2	145.31	127.29	18.02	12.40	16.35
MPDBD 1.0% 1	141.24	122.25	18.10	13.44	16.60
MPBDP 1.0% 2	NR	NR	NR	NR	NR
LUSP 1 0.5% 1	161.91	154.23	7.69	4.74	6.52
LUSP 1 0.5% 2	NR	NR	NR	NR	NR
LUSP 1 1.0% 1	131.00	118.27	12.73	9.71	10.59
LUSP 1 1.0% 2	NR	NR	NR	NR	NR
Blank 1	161.10	150.07	NR	NR	NR
Blank 2	161.37	132.72	28.66	17.75	25.60

NR: No Result

Table 21: GGBS and PFA Pore Water TOC Values

	GGBS TOC (ppm w/w)	PFA TOC (ppm w/w)
MPBDP 0.5 %1	14.0	8.2
MPBDP 0.5% 2	29.0	11.4
MPBDP 1.0% 1	6.5	40.8
MPBDP 1.0% 2	8.7	No sample
LUSP 1 0.5% 1	18.9	No sample
LUSP 1 0.5% 2	10.8	NS
LUSP 1 1.0% 1	104.2	11.0
LUSP 1 1.0% 2	61.4	NS
Blank 1	1.6	NS
Blank 2	2.6	No sample

NR: No result

Conclusion

As noted in the porosity measurements, markedly different fracture porosity was shown by the PFA and GGBS grouts. These differences were apparent in the results of pore water squeezing tests carried out at pressures up to 4,000 psi. The PFA samples released greater volumes of pore water, particularly at lower pressures, and several SP-modified samples failed completely indicating false set.

The TOC analyses were difficult to interpret fully owing to the lack of a complete sample set and variability between duplicates. In general, the GGBS pore water showed higher TOC results than the corresponding PFA samples. The GGBS/ LUSP 1 SP showed the highest TOC values for any of the products analysed.

The TOC analyses identified clear differences in organic composition between the equilibrated water and the squeezed pore water. The GGBS results in the solubility trials had a maximum of 2.7 ppm in the solutions, whereas the expressed pore water had between 6.5 and 104 ppm. The PFA results were less marked, with a maximum of 8.9 ppm in the solubility experiments compared to 40.8 ppm in the expressed pore water. The reasons for the differences are not clear, especially as the surface chemistry behaviour of SP species under high pressure is not fully understood. However, these results do provide an insight into the nature of the surface and near surface chemistry of the cementitious grouts and the subsequent control of ion mobility and migration.

In summary, pore water was successfully extracted from the majority of the samples and the technique is clearly viable for the grout types being studied. Sufficient sample was expressed to enable TOC analyses, however the results do not allow for a confident interpretation of the quantity of organic content in the squeezed pore waters. It is suggested that a more comprehensive analysis could be achieved by squeezing larger samples to extract greater quantities of pore water for comprehensive chemical characterisation.

Discussion

A series of experiments have been undertaken to determine the behaviour of specific radionuclides in PFA and GGBS cement equilibrated pore water and solid monoliths. These were undertaken under laboratory conditions at small scale. It is recognised that the preparation of cement samples at small scale, utilising low shear mixing can result in cured products with differing properties to those prepared at larger scale using high shear mixing. However, the behaviour of radionuclides in SP modified grouts in samples manufactured for this programme may be indicative of behaviour at large scales as used in waste management activities.

Solubility determinations showed that commercial (W. R. Grace & Co.) SP formulations can increase the solubility of selected radionuclides over a range of oxidation states. The enhancement is at least one and, in some cases, more than three orders of magnitude in free solution. The defoamer and biocide and viscosity modifier adjuncts, when tested in isolation, showed no significant effect on radionuclide solubility, with the possible exception of one experiment involving Pu(IV) in the presence of VMA. A bespoke SP product, LUSP1, synthesised in a parallel programme, did not increase solubility to the same extent as the commercial products. The reason has not yet been confirmed; however, LUSP1 had been dialysed prior to the tests in order to remove low molecular weight material, including residual monomer. The commercial SP are unlikely to be dialysed as part of the manufacturing process and so it remains possible that the residual starting materials and short chain polymers may contribute to radionuclide solubility in disposal applications.

Intact leaching and through-diffusion experiments indicated that the enhanced solubility noted above did not produce a corresponding increase in the mobility of the radionuclides in the presence of solid grouts. Notwithstanding several anomalously high results from the leaching experiments, most likely caused by sampling constraints, the experiments with the SP mixes and adjuncts could not be differentiated from the corresponding blank experiments. Even where solubility enhancement observed in free solution was high (e.g. ^{239}Pu in GGBS and WRBP) there was no evidence of increased leachability from intact samples or detectable diffusion through monolithic grouts over the six month duration of the experiments. It appears that the presence of the cementitious solid is important in controlling radionuclide retention. Although the intact leaching and through-diffusion trials suggest that the mobility of the selected radionuclides would not be increased through a grout amended with these SP products, longer term tests are required for confirmation.

The crushed leaching trials looked at the effect on radionuclide mobility when the surface area of the SP amended grouts was increased. It would be expected that increased leaching would be witnessed due to the higher surface area and thus these trials could be considered a more conservative test than leaching from intact SP amended monoliths. In the event, the results of the trials showed no increase in leaching of active species from the crushed samples. However, it should be noted that the procedure for the crushed sample leaching trials only sampled 2 points over a period of 24 hours.

Analogous leaching trials were conducted on crushed samples which had first been gamma irradiated. These trials were undertaken for the purpose of simulating a wasteform that had been exposed to the irradiation expected during the operational period of a GDF. The activity leached from the samples was negligible.

Evidence of radionuclides in GGBS grout bleed waters was observed during the manufacture of doped samples, as noted in previous work. From practical experience, it is known that laboratory scale mixing is much less effective at controlling the generation of bleed water than large scale high shear techniques and, although the loss of radionuclides into the bleed water was quantified, no further investigation was undertaken owing to resource constraints.

It was possible to detect radionuclides in the curing water; the latter was retained and analysed. This was particularly evident in the ^{63}Ni(II) and U(VI) PFA grout curing waters but ^{239}Pu and ^{241}Am were also detectable for some SP mixes. This finding may be explained by radionuclides from the evaporated bleed water remaining on the external surface of the samples and subsequently dissolving. A series of autoradiographs of the samples used for through-diffusion tests provide confirmation that significant radionuclide migration had not occurred into the grout matrices.

Total (gas) and accessible porosity were determined by argon pycnometry and ^{14}C-methyl methacrylate injection, respectively. Markedly different fracture porosity was shown by the PFA and GGBS grouts. These differences were apparent in the results of pore water squeezing tests carried out at pressures up to 4,000 psi. The PFA samples released greater volumes of pore water, particularly at lower pressures, and several SP modified samples failed completely indicating false set. As with bleed, above, further work would be required to better understand the effect of the SP formulations on both physical durability and chemical retention.

Conclusions

The information produced within this experimental programme suggests that the SP mixes tested are capable of increasing the solubility of a range of radionuclides in cement equilibrated waters, which is consistent with previous work. However, the results of leaching trials suggest that this solubility enhancement does not translate into increased radionuclide leachability from solid PFA or GGBS grouts. Nor do they lead to measurable diffusion through the same cured grouts. The behaviour observed with the laboratory scale samples may be indicative of behaviour at larger scales and over similar timeframes.

These results suggest that the benefits of the use of PCE SP in waste management applications (e.g. waste encapsulation, concrete box waste container manufacture) could be potentially utilised without the deleterious effect of radionuclide mobilisation, though this is likely to require confirmation over the longer term and at larger scales than encompassed by this programme of work. The results may also be a useful input into decisions regarding the use of SP in the design of a GDF. It is important to note that construction of a GDF will not occur on the same short-term timescales as those for the packaging of waste.

There is some evidence that the initial bleed waters from the PFA and GGBS samples contain radionuclides, particularly in the case of GGBS blends. However, larger scale manufacturing techniques may be able to reduce or even eliminate bleed. In light of this, larger scale trials are recommended for confirmation and to assess other observed behaviour. Further consideration should also be given to experimental design to ensure representative solid to solution ratios in future solubility studies. It is also suggested that additional pore water squeezing tests on active samples are undertaken since, even the limited measurements undertaken in this work, highlight significant differences between equilibrated cement waters produced by batch methods and actual cement pore water.

Finally, all of the analyses presented in this report are the result of relatively short-term trials. Therefore, they may not be representative of long term behaviour and there is a case for retaining some tests materials for possible re-examination at a future date.

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Glossary

Additive	Refers to all organics added to cements, including superplasticiser and adjuncts
Adjunct	Refers to the biocide, viscosity modifying agent and defoamer
BFS	Blast Furnace Slag
Blank	Indicates samples without additive present
BWOC	By Weight of Cement
DOC	Dissolved Organic Carbon
DRP	Direct Research Portfolio
GC-MS	Gas Chromatography – Mass Spectrometry
GDF	Geological Disposal Facility
GGBS	Ground Granulated Blast Furnace Slag
HAW	Higher Activity Waste
HazWAC	Hazardous Waste Acceptance Criteria
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
ILW	Intermediate Level Waste
LHGW	Low Heat Generating Waste
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
NDA	Nuclear Decommissioning Authority
ND	Not Detected
Non active	Indicates samples with no radionuclides present
NSG	NSG Environmental Ltd
NR	No Result
NS	No Sample
OPC	Ordinary Portland Cement
PCE	Polycarboxylate ether
PFA	Pulverised Fly Ash
PMMA	Polymethylmethacrylate
RWM	Radioactive Waste Management Limited
SLCs	Site Licence Companies

SP	Superplasticiser
TOC	Total Organic Carbon
SP mix	Refers to the commercial SP formulations

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Appendix 1: Preliminary Leach Trial Results

Table A1. 1 ICP-MS Derived A_2 Values for the GGBS:OPC Cement

	Ni	Se	Cs	Eu	Th	U
GGBS:OPC	A_2	A_2	A_2	A_2	A_2	A_2
Units	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}
Additive						
WRBDP 1	42	6.5	87	0.5	0.5	ND
WRBDP 2	38	3.1	75	0.5	0.4	ND
MPBDP 1	79	7.5	130	0.8	1.1	ND
MPBDP 2	84	6.8	117	0.8	0.9	ND
FWBFP 1	77	7.8	113	0.7	0.7	ND
FWBFP 2	85	10.7	99	0.7	0.5	ND
WRBP 1	101	7.4	98	0.9	0.5	ND
WRBP 2	96	11.7	117	0.9	0.5	ND
LUSP 1 1	110	11.2	227	0.8	0.5	ND
LUSP 1 2	103	9.9	182	0.7	0.4	ND
LUSP 2 1	87	8.1	195	0.7	0.3	ND
LUSP 2 2	90	10.2	250	0.8	0.2	ND
BIO 1	101	8.3	104	0.6	0.2	ND
BIO 2	83	10.8	94	0.5	0.1	ND
DEF 1	93	11.2	104	0.7	0.2	ND
DEF 2	98	8.5	86	0.7	0.2	ND
VMA 1	103	9.8	184	0.7	0.2	ND
VMA 2	126	12.8	281	0.9	0.3	ND
BLANK 1	89	6.3	81	0.5	0.1	ND
BLANK 2	81	7.1	66	0.5	0.1	ND

The methodology produces results that are reported as 'A_2' and 'A_{2-10}'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 2: ICP-MS Derived A_2 values for the PFA:OPC Cement

	Ni	Se	Cs	Eu	Th	U
PFA:OPC	A_2	A_2	A_2	A_2	A_2	A_2
Units	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}
Additive						
WRBDP 1	162	133	1002	ND	ND	0.5
WRBDP 2	158	116	776	ND	ND	ND
MPBDP 1	120	108	1043	ND	ND	ND
MPBDP 2	128	137	989	ND	ND	ND
FWBFP 1	127	29	890	1	ND	1.0
FWBFP 2	139	24	830	1	ND	ND
WRBP 1	130	53	856	ND	ND	ND
WRBP 2	117	46	647	ND	ND	ND
LUSP 1 1	115	65	1190	ND	ND	ND
LUSP 1 2	120	62	1261	ND	ND	ND
LUSP 2 1	131	21	1235	1	ND	ND
LUSP 2 2	105	19	1001	1	ND	ND
BIO 1	135	107	1402	1	ND	ND
BIO 2	176	115	1786	ND	ND	ND
DEF 1	131	23	993	1	ND	ND
DEF 2	132	26	989	1	ND	ND
VMA1	119	97	1078	ND	ND	ND
VMA 2	133	93	1255	ND	ND	ND
BLANK 1	153	95	1379	ND	ND	ND
BLANK 2	145	93	1355	ND	ND	ND

The methodology produces results that are reported as 'A_2' and 'A_{2-10}'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 3: ICP-MS Derived $A_{2\text{-}10}$ values for the GGBS:OPC Cement

	Ni	Se	Cs	Eu	Th	U
GGBS:OPC	$A_{2\text{-}10}$	$A_{2\text{-}10}$	$A_{2\text{-}10}$	$A_{2\text{-}10}$	$A_{2\text{-}10}$	$A_{2\text{-}10}$
Units	μg kg^{-1}	μg kg^{-1}	μg kg^{-1}	μg kg^{-1}	μg kg^{-1}	μg kg^{-1}
Additive						
WRBDP 1	38	13	112	1.2	0.4	ND
WRBDP 2	36	9	94	1.0	0.4	ND
MPBDP 1	62	10	141	1.4	ND	ND
MPBDP 2	63	9	132	1.4	ND	ND
FWBFP 1	62	18	131	1.3	ND	ND
FWBFP 2	64	17	101	1.1	ND	ND
WRBP 1	86	11	109	1.6	ND	ND
WRBP 2	85	16	123	1.7	ND	ND
LUSP 1 1	81	17	231	1.5	ND	ND
LUSP 1 2	77	17	197	1.4	ND	ND
LUSP 2 1	66	17	202	1.3	ND	ND
LUSP 2 2	75	17	282	1.7	ND	ND
BIO 1	NS	NS	NS	NS	ND	ND
BIO 2	60	16	115	1.2	ND	ND
DEF 1	67	15	111	1.4	ND	ND
DEF 2	68	12	90	1.3	ND	ND
VMA 1	70	12	205	1.4	ND	ND
VMA 2	91	12	279	1.7	ND	ND
BLANK 1	64	6	87	1.1	ND	ND
BLANK 2	60	10	76	1.0	ND	ND

The methodology produces results that are reported as 'A_2' and '$A_{2\text{-}10}$'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 4: ICP-MS Derived A_{2-10} values for the PFA:OPC Cement

	Ni	Se	Cs	Eu	Th	U
PFA:OPC	A_{2-10}	A_{2-10}	A_{2-10}	A_{2-10}	A_{2-10}	A_{2-10}
Units	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}	µg kg^{-1}
Additive						
WRBDP 1	273	418	3550	0.8	ND	ND
WRBDP 2	101	224	1779	0.5	0.1	ND
MPBDP 1	189	371	3840	0.6	ND	ND
MPBDP 2	69	272	2413	0.5	ND	ND
FWBFP 1	242	139	2315	7.0	ND	ND
FWBFP 2	146	88	1329	4.9	ND	ND
WRBP 1	216	210	2269	2.0	ND	ND
WRBP 2	121	160	1773	1.9	0.1	ND
LUSP 1 1	191	266	3931	1.9	ND	ND
LUSP 1 2	103	166	2875	1.7	ND	ND
LUSP 2 1	264	101	2740	5.4	0.3	ND
LUSP 2 2	194	89	2255	5.8	ND	ND
BIO 1	209	376	4340	1.8	0.3	ND
BIO 2	93	278	3167	1.5	0.1	ND
DEF 1	314	114	2408	8.9	0.3	ND
DEF 2	191	89	1482	7.0	0.1	ND
VMA 1	209	366	4422	1.8	0.2	ND
VMA 2	92	239	3053	1.0	0.1	ND
BLANK 1	237	342	4047	1.7	0.3	ND
BLANK 2	114	236	3070	1.6	ND	ND

The methodology produces results that are reported as 'A_2' and 'A_{2-10}'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 5: ICP-OES Derived A_2 and A_{2-10} values for the GGBS:OPC Cement

	K	Na	K	Na
GGBS:OPC	A_2	A_2	A_{2-10}	A_{2-10}
Units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Additive				
WRBDP 1	372	220	510	292
WRBDP 2	339	199	459	263
MPBDP 1	516	304	676	403
MPBDP 2	470	276	609	359
FWBFP 1	447	263	601	347
FWBFP 2	467	280	513	295
WRBP 1	330	187	434	239
WRBP 2	408	225	532	288
LUSP 1 1	671	361	874	462
LUSP 1 2	563	304	713	376
LUSP 2 1	727	380	907	495
LUSP 2 2	888	483	1087	596
BIO 1	462	262	627	362
BIO 2	491	282	NS	NS
DEF 1	510	334	644	416
DEF 2	429	270	605	356
VMA 1	644	354	805	437
VMA 2	784	435	759	527
BLANK 1	413	246	529	319
BLANK 2	386	233	728	307

The methodology produces results that are reported as 'A_2' and 'A_{2-10}'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 6: ICP-OES Derived A_2 and $A_{2\text{-}10}$ values for the PFA:OPC Cement

	K	Na	K	Na
PFA:OPC	A_2	A_2	$A_{2\text{-}10}$	$A_{2\text{-}10}$
Units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Additive				
WRBDP 1	1083	353	1802	524
WRBDP 2	1080	363	1282	360
MPBDP 1	1254	404	2138	613
MPBDP 2	1195	393	1663	473
FWBFP 1	995	291	1145	316
FWBFP 2	900	267	611	168
WRBP 1	932	296	1247	361
WRBP 2	936	298	807	222
LUSP 1 1	1483	443	2182	601
LUSP 1 2	1455	431	1451	391
LUSP 2 1	1346	384	1536	421
LUSP 2 2	1369	394	840	239
BIO 1	1501	437	2267	615
BIO 2	1461	423	1734	465
DEF 1	1050	294	1180	316
DEF 2	1030	290	697	196
VMA 1	1335	398	2065	566
VMA 2	1341	401	1538	418
BLANK 1	1418	425	1971	538
BLANK 2	1334	394	1308	341

The methodology produces results that are reported as ‘A_2’ and ‘$A_{2\text{-}10}$’. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 7: Ion Chromatography Derived A_2 Values for the GGBS:OPC Cement

GGBS:OPC	F		Cl		NO_3		SO_4	
	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)
Units	mg kg^{-1}							
Additive								
WRBDP 1	3.6	1.8	34.8	20.2	14.9	8.9	9.3	0.7
WRBDP 2	1.5	1.3	24.6	17.5	8.5	7.7	9.7	8.7
MPBDP 1	1.2	1.2	26.8	26.1	6.6	6.7	8.8	8.4
MPBDP 2	1.2	1.4	26.5	22.4	7.2	6.5	8.6	7.6
FWBFP 1	1.7	2.2	21.7	22.6	5.7	5.5	7.5	7.9
FWBFP 2	1.5	0.7	25.7	21.6	6.4	5.6	8.4	8.3
WRBP 1	1.8	1.5	20.3	13.5	28.4	27.6	8.4	8.0
WRBP 2	1.2	1.3	20.7	20.9	7.5	6.9	7.4	8.3
LUSP 1 1	1.4	2.0	35.7	36.4	6.4	5.7	10.1	10.3
LUSP 1 2	1.6	1.8	32.0	30.6	5.5	4.9	11.5	10.4
LUSP 2 1	5.1	1.1	83.6	82.0	12.6	12.2	21.0	21.6
LUSP 2 2	3.0	1.4	28.1	28.1	10.7	10.2	12.2	11.8
BIO 1	0.5	3.6	4.1	5.8	5.7	7.9	2.1	1.9
BIO 2	0.3	1.1	34.3	30.1	9.0	8.4	1.2	14.2
DEF 1	1.2	2.5	30.0	29.5	6.0	5.2	10.5	9.5
DEF 2	1.3	1.5	27.5	28.8	5.7	6.7	12.4	11.6
VMA 1	2.3	2.0	36.5	32.5	9.0	6.3	12.2	13.6
VMA 2	1.5	1.3	41.5	40.4	6.7	6.6	11.8	11.6
BLANK 1	1.8	1.4	27.2	23.9	11.1	8.4	11.1	8.4
BLANK 2	1.3	1.0	24.5	21.9	10.8	10.6	10.8	10.6

The methodology produces results that are reported as ‘A_2’ and ‘A_{2-10}’. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 8: Ion Chromatography Derived A_2 Values for the PFA:OPC Cement

PFA:OPC	F		Cl		NO_3		SO_4	
	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)	A_2 (1)	A_2 (2)
Units	mg kg^{-1}							
Additive								
WRBDP 1	4.1	2.0	111	103	24	21	74	70
WRBDP 2	3.1	2.0	108	105	21	20	94	96
MPBDP 1	2.3	2.6	107	106	15	15	75	75
MPBDP 2	3.0	1.6	114	112	16	17	95	95
FWBFP 1	2.1	1.5	86	85	18	17	8.0	5.0
FWBFP 2	1.9	1.6	81	83	21	19	6.0	6.0
WRBP 1	1.7	1.0	55	53	10	10	24	22
WRBP 2	1.4	1.5	55	52	11	10	23	22
LUSP 1 1	3.5	2.5	96	91	18	18	44	44
LUSP 1 2	4.9	2.7	94	87	18	18	38	39
LUSP 2 1	2.6	1.6	66	64	12	12	6.0	5.0
LUSP 2 2	1.3	1.2	54	53	10	10	4.0	3.0
BIO 1	2.8	2.2	111	109	18	18	56	60
BIO 2	2.5	3.0	126	126	24	23	72	73
DEF 1	2.0	2.5	54	54	13	13	5.0	1.0
DEF 2	2.5	2.4	56	54	12	12	8.0	7.0
VMA 1	2.6	2.8	85	86	19	18	42	42
VMA 2	2.3	2.4	82	82	17	17	38	37
BLANK 1	2.7	2.2	71	67	12	14	36	37
BLANK 2	1.9	1.9	91	90	12	12	31	31

The methodology produces results that are reported as ‘A_2’ and ‘A_{2-10}’. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 9: Ion Chromatography Derived $A_{2\text{-}10}$ Values for the GGBS:OPC Cement

GGBS: OPC	F		Cl		NO_3		SO_4	
	$A_{2\text{-}10}$ (1)	$A_{2\text{-}10}$ (2)	$A_{2\text{-}10}$ (1)	$A_{2\text{-}10}$ (2)	$A_{2\text{-}10}$ (1)	$A_{2\text{-}10}$ (2)	$A_{2\text{-}10}$ (1)	$A_{2\text{-}10}$ (2)
Units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Additive								
WRBDP 1	5.3	4.3	57	44	22	18	73	90
WRBDP 2	3.1	3.1	37	17	11	10	70	68
MPBDP 1	3.8	3.0	57	52	14	15	46	49
MPBDP 2	6.8	5.2	65	49	8	8	58	55
FWBFP 1	5.9	4.6	46	45	7	6	58	60
FWBFP 2	4.9	3.9	38	36	10	10	83	86
WRBP 1	3.2	3.2	37	33	28	24	37	39
WRBP 2	3.6	3.9	36	36	17	11	64	66
LUSP 1 1	21.4	10.3	131	83	16	10	89	84
LUSP 1 2	5.1	3.5	55	51	10	12	56	54
LUSP 2 1	6.5	2.3	104	93	14	12	62	50
LUSP 2 2	6.9	2.1	75	71	13	12	45	49
BIO 1	5.1	6.0	67	65	11	11	79	87
BIO 2	2.9	2.8	60	51	12	12	62	65
DEF 1	6.1	8.0	60	53	11	11	77	79
DEF 2	2.4	3.3	47	46	14	14	63	75
VMA 1	5.7	3.0	57	60	15	14	44	54
VMA 2	2.7	2.9	67	64	11	10	57	55
BLANK 1	5.9	2.3	57	44	13	10	67	64
BLANK 2	4.8	2.9	49	21	12	10	71	69

The methodology produces results that are reported as 'A_2' and '$A_{2\text{-}10}$'. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 10: Ion Chromatography Derived A_{2-10} Values for the PFA:OPC Cement

PFA:OPC	F		Cl		NO_3		SO_4	
	A_{2-10} (1)	A_{2-10} (2)	A_{2-10} (1)	A_{2-10} (2)	A_{2-10} (1)	A_{2-10} (2)	A_{2-10} (1)	A_{2-10} (2)
Units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Additive								
WRBDP 1	12.3	5.8	201	168	37	35	898	905
WRBDP 2	3.1	2.5	171	160	55	53	231	224
MPBDP 1	7.6	5.0	157	152	31	30	282	284
MPBDP 2	5.8	4.3	163	158	29	27	443	441
FWBFP 1	5.0	3.0	141	132	31	31	178	171
FWBFP 2	8.2	5.7	142	145	30	30	165	161
WRBP 1	6.2	5.5	102	104	18	18	543	545
WRBP 2	5.0	2.4	101	89	18	17	21	149
LUSP 1 1	6.5	5.0	146	136	28	27	378	366
LUSP 1 2	6.8	2.8	142	135	30	27	187	180
LUSP 2 1	5.2	5.7	151	142	32	29	113	115
LUSP 2 2	3.8	3.3	127	125	25	24	115	99
BIO 1	11.1	4.4	174	163	27	27	305	298
BIO 2	4.6	4.9	163	157	29	33	428	432
DEF 1	7.7	4.8	113	110	20	22	73	71
DEF 2	7.9	6.3	120	111	24	22	205	195
VMA 1	3.9	3.5	139	138	29	27	182	182
VMA 2	8.7	8.9	144	134	28	30	323	324
BLANK 1	11.0	6.4	182	145	24	21	205	200
BLANK 2	7.0	6.0	131	123	21	19	417	418

The methodology produces results that are reported as ‘A_2’ and ‘A_{2-10}’. The former relates to the release of a constituent at a liquid/solid ratio of 2 and the latter evaluates the cumulative release at a cumulative liquid/solid ratio of 10.

Table A1. 11: pH Values for the GGBS:OPC and PFA:OPC Cements

	pH			
	Liquid : Solid = 2		Liquid : Solid = 8	
GGBS:OPC	**1**	**2**	**1**	**2**
WRBDP	12.6	12.7	11.9	11.8
MPBDP 1	12.6	12.8	11.8	11.8
FWBFP 1	12.8	12.6	11.8	11.7
WRBP 1	12.7	12.3	11.7	11.6
LUSP 1 1	12.6	12.5	11.7	11.7
LUSP 2 1	12.5	12.5	11.8	11.7
BIO 1	12.3	12.5	NS	11.7
DEF 1	12.6	12.3	11.7	11.7
VMA 1	12.3	12.4	11.7	11.7
BLANK 1	12.2	12.2	11.7	11.7
PFA:OPC	**1**	**2**	**1**	**2**
WRBDP	12.5	NS	11.6	11.5
MPBDP 1	12.3	12.4	11.6	11.6
FWBFP 1	12.4	12.5	11.8	11.8
WRBP 1	12.4	12.3	11.8	11.7
LUSP 1 1	12.5	12.5	11.7	11.7
LUSP 2 1	12.7	12.7	11.9	11.9
BIO 1	12.4	12.4	12.6	11.9
DEF 1	12.5	12.5	12.0	12.0
VMA 1	12.4	12.4	11.8	11.8
BLANK 1	12.5	12.4	11.7	11.9

Appendix 2: Solubility Results

Figure A2. 1: Ni - PFA - MPBDP vs Blank

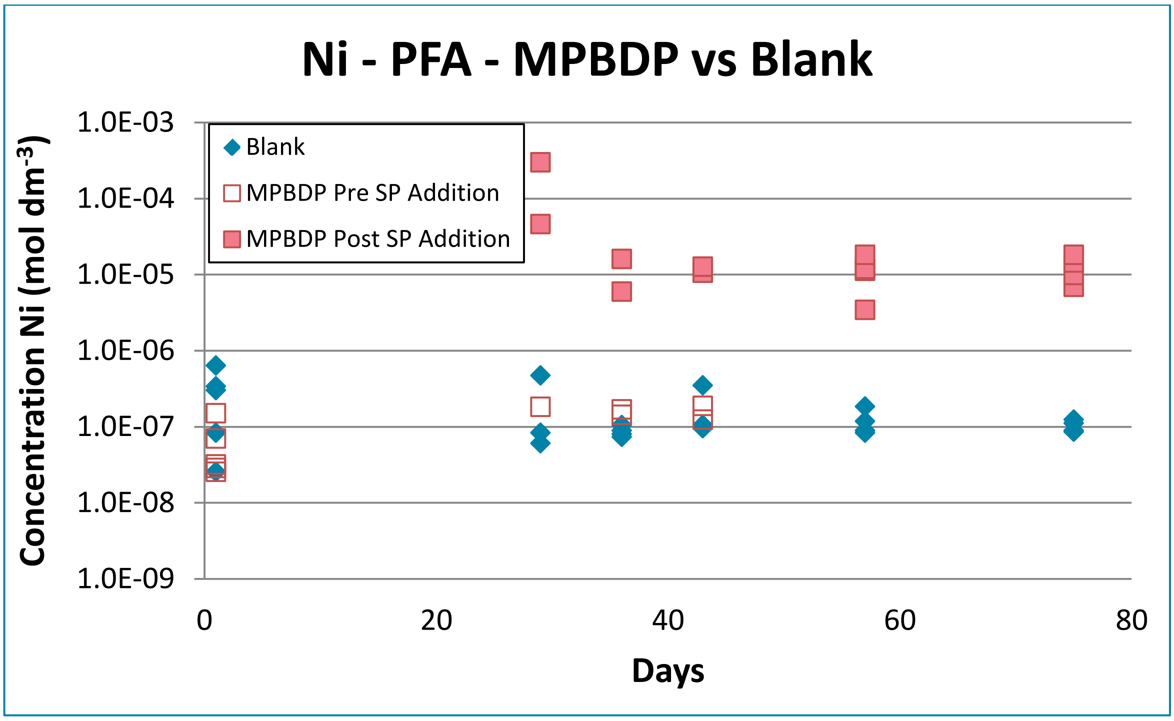

Figure A2. 2: Ni - PFA - WRBP vs Blank

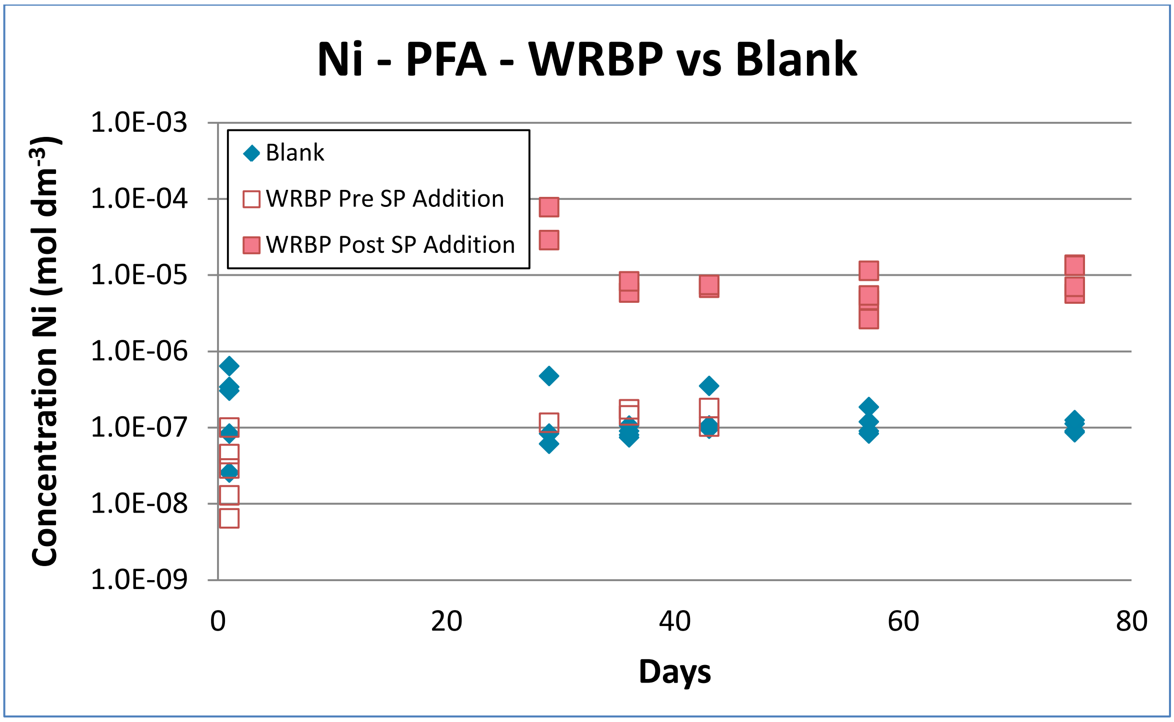

Figure A2. 3: Ni - PFA - WRBDP vs Blank

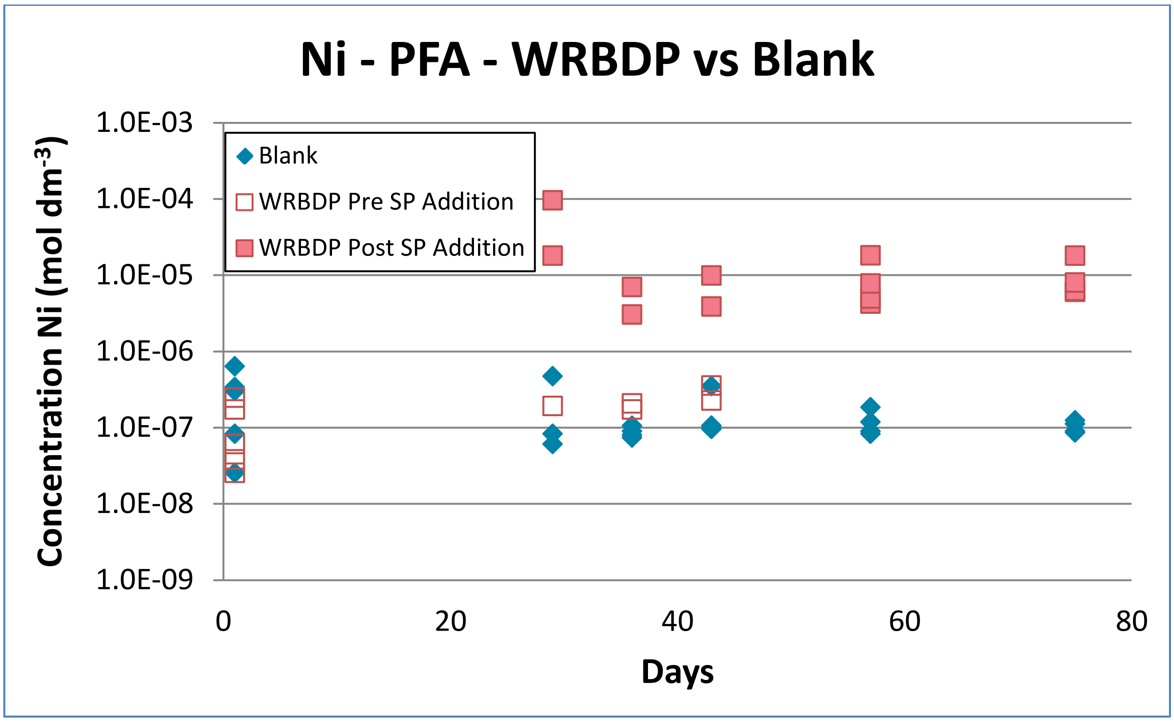

Figure A2. 4: Ni - PFA - FWBFP vs Blank

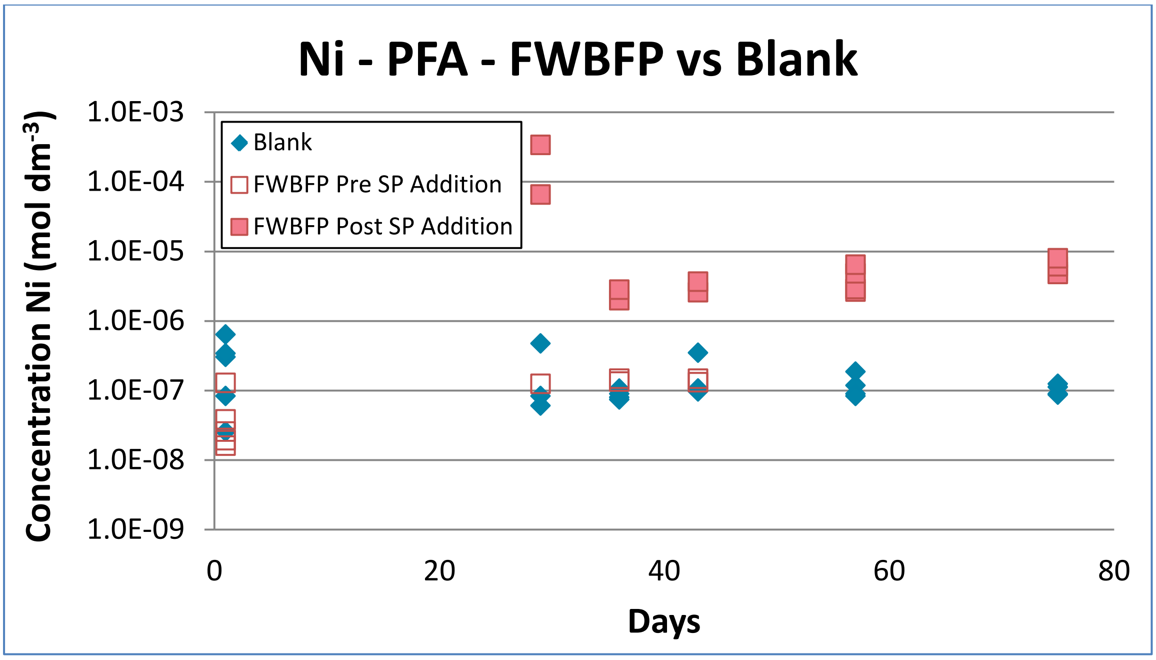

Figure A2. 5: Ni - PFA - BIO vs Blank

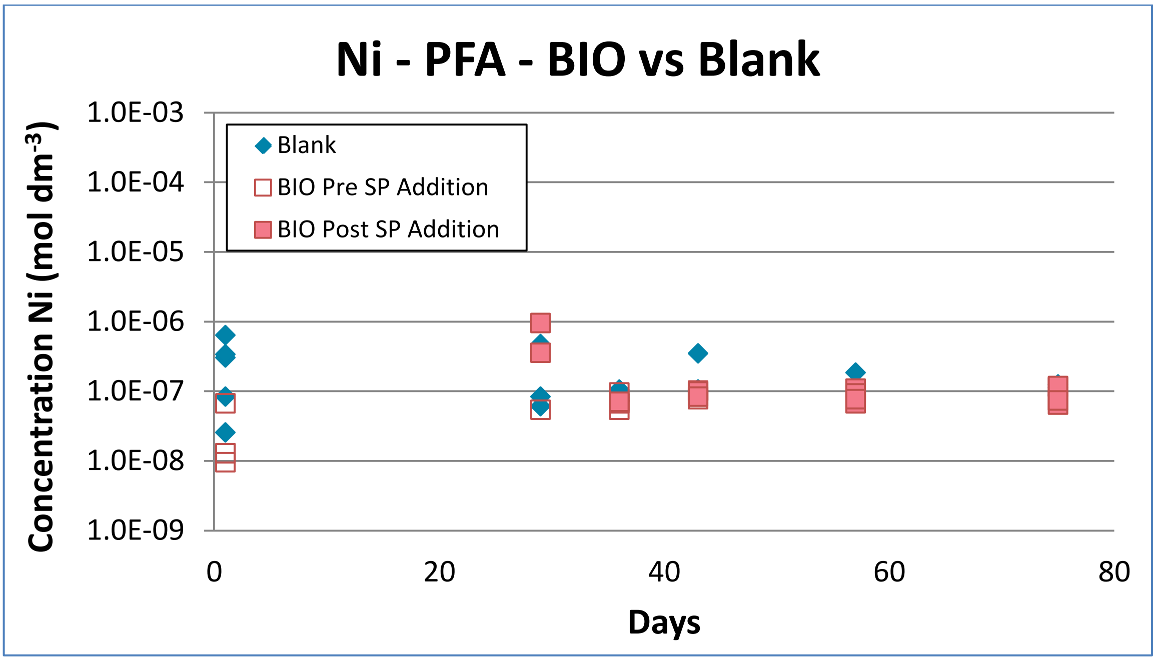

Figure A2. 6: Ni - PFA - VMA vs Blank

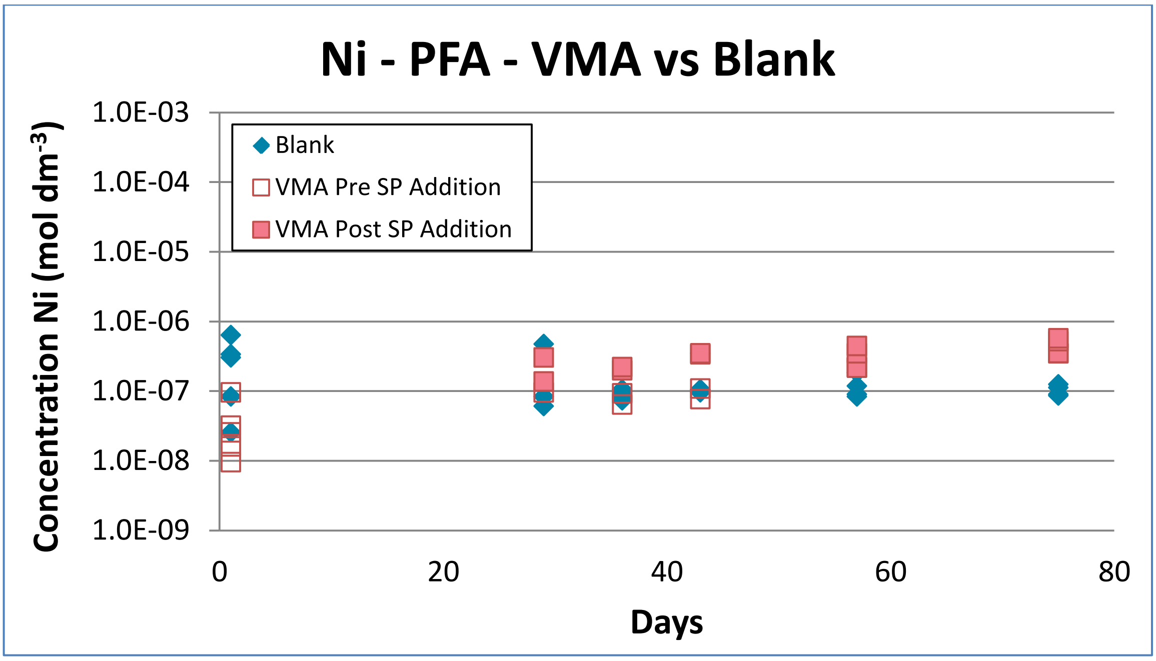

Figure A2. 7: Ni - PFA - DEF vs Blank

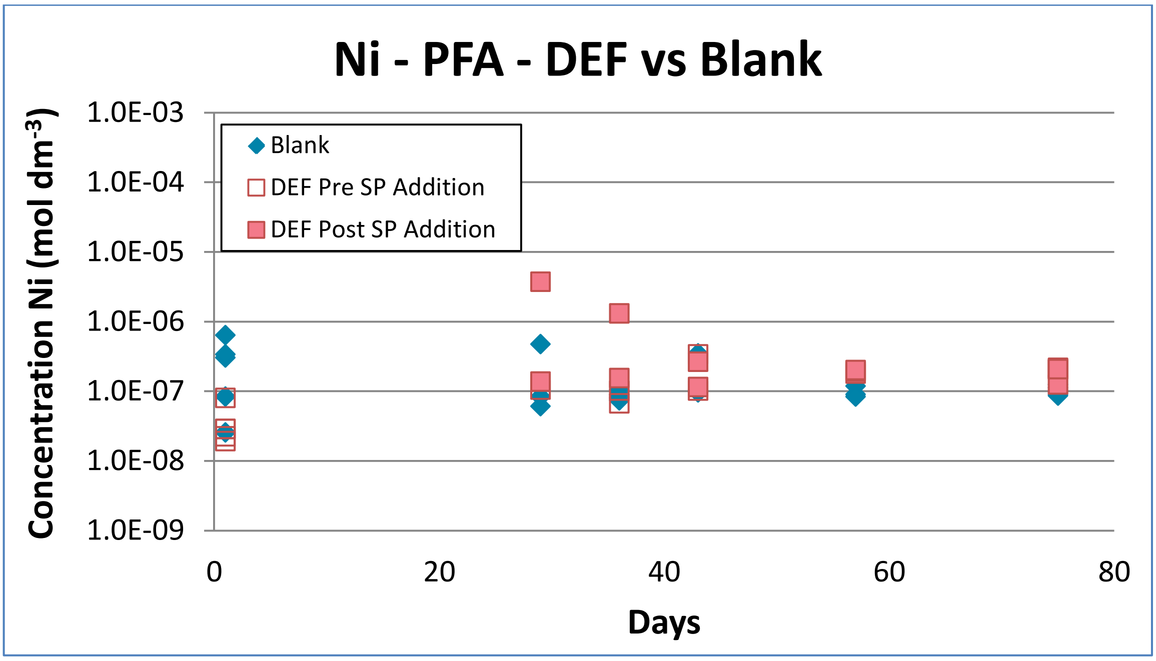

Figure A2. 8: Ni - PFA – LUSP 1 vs Blank

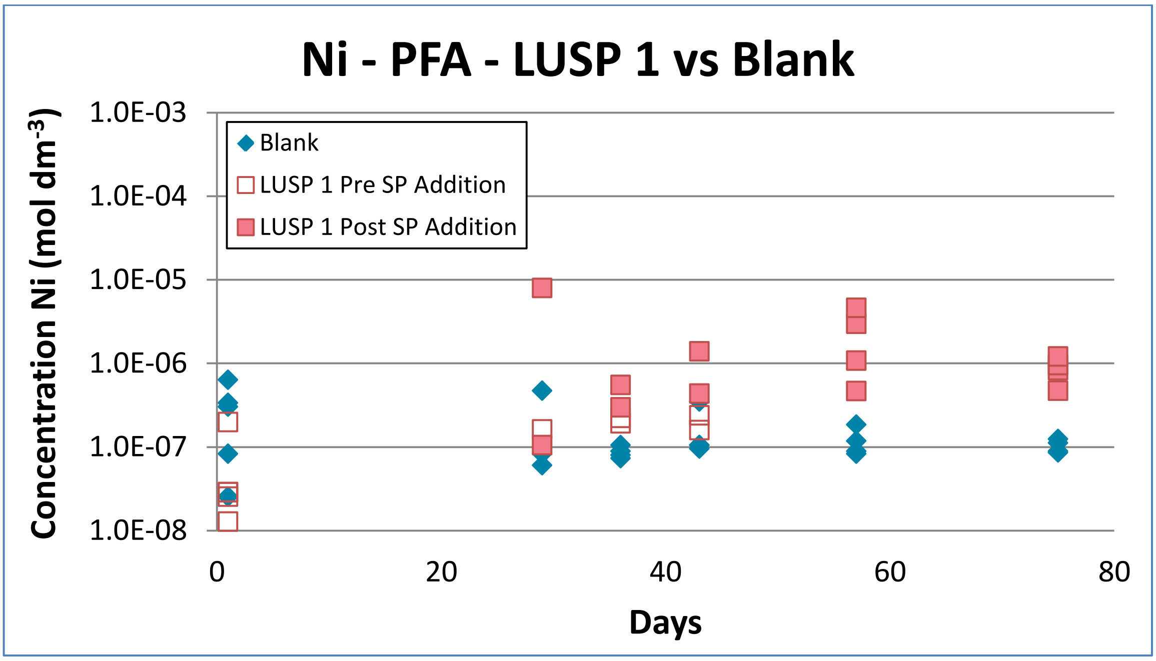

Figure A2. 9: Ni - GGBS - MPBDP vs Blank

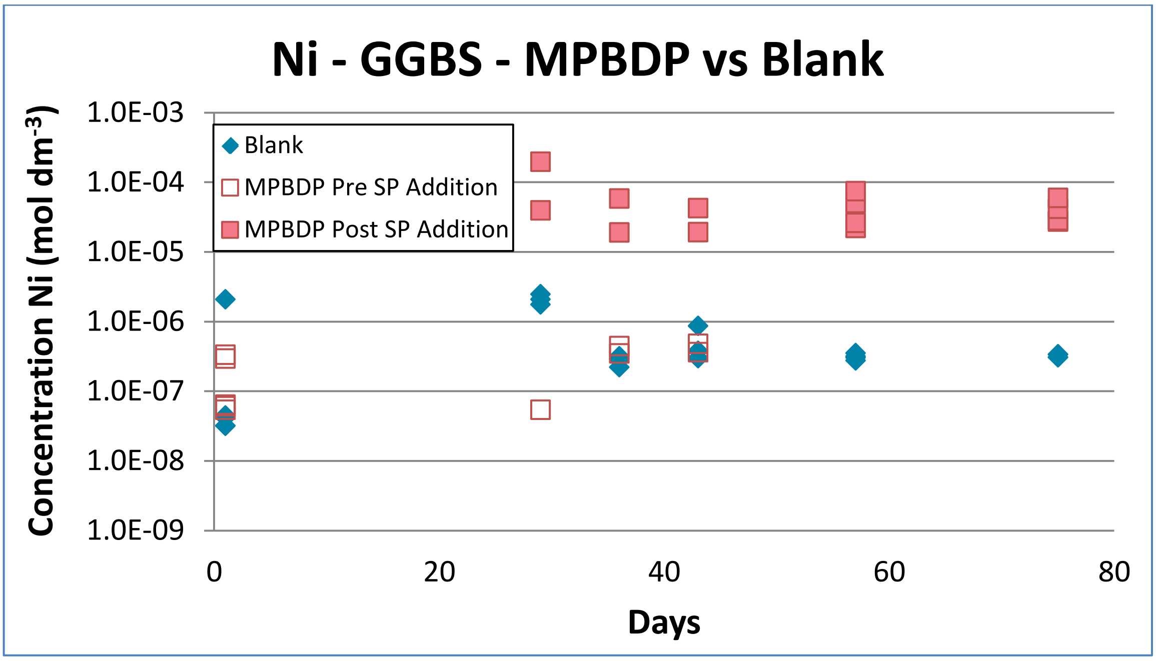

Figure A2. 10: Ni - GGBS - WRBP vs Blank

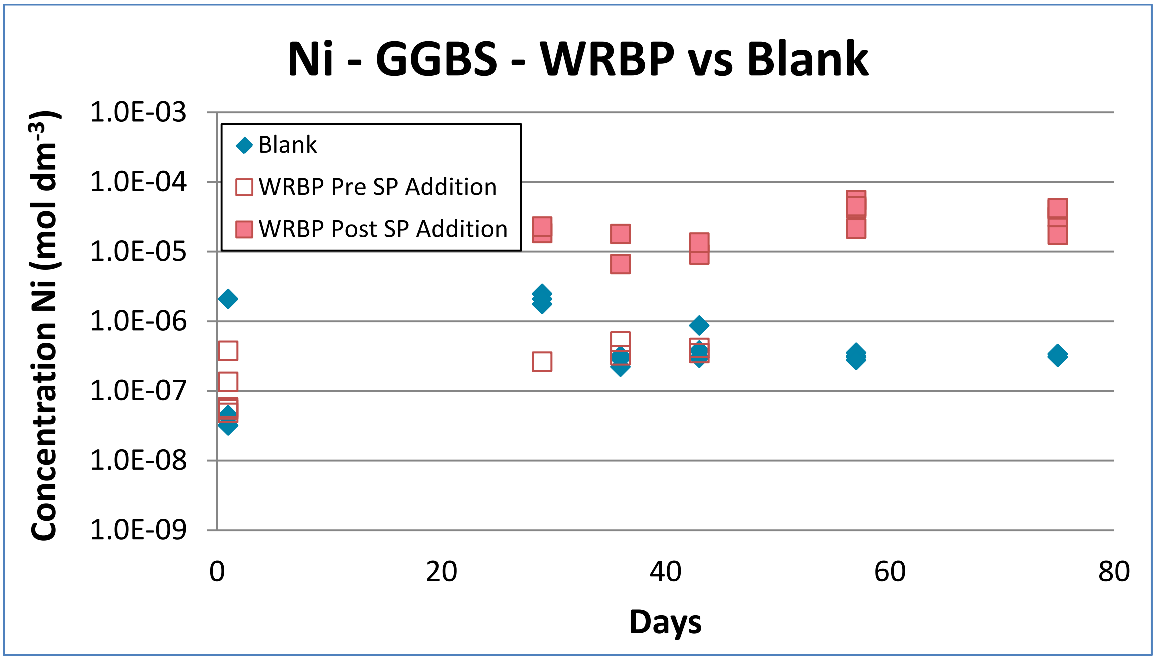

Figure A2. 11: Ni - GGBS - WRBDP vs Blank

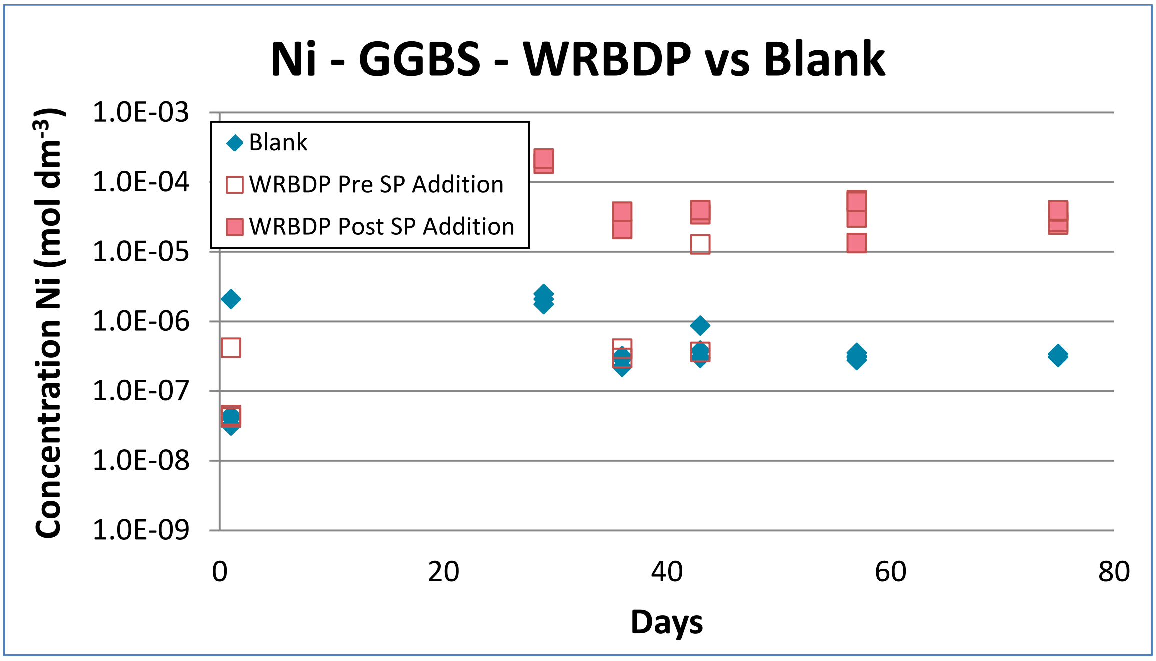

Figure A2. 12: Ni - GGBS - FWBFP vs Blank

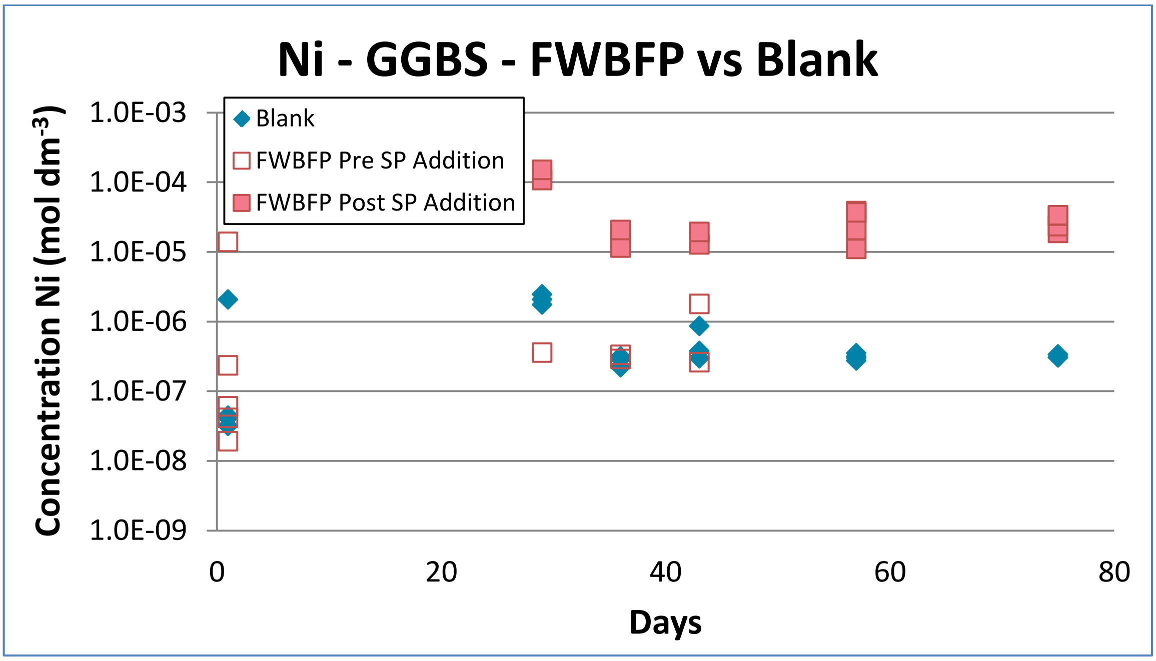

Figure A2. 13: Ni - GGBS - BIO vs Blank

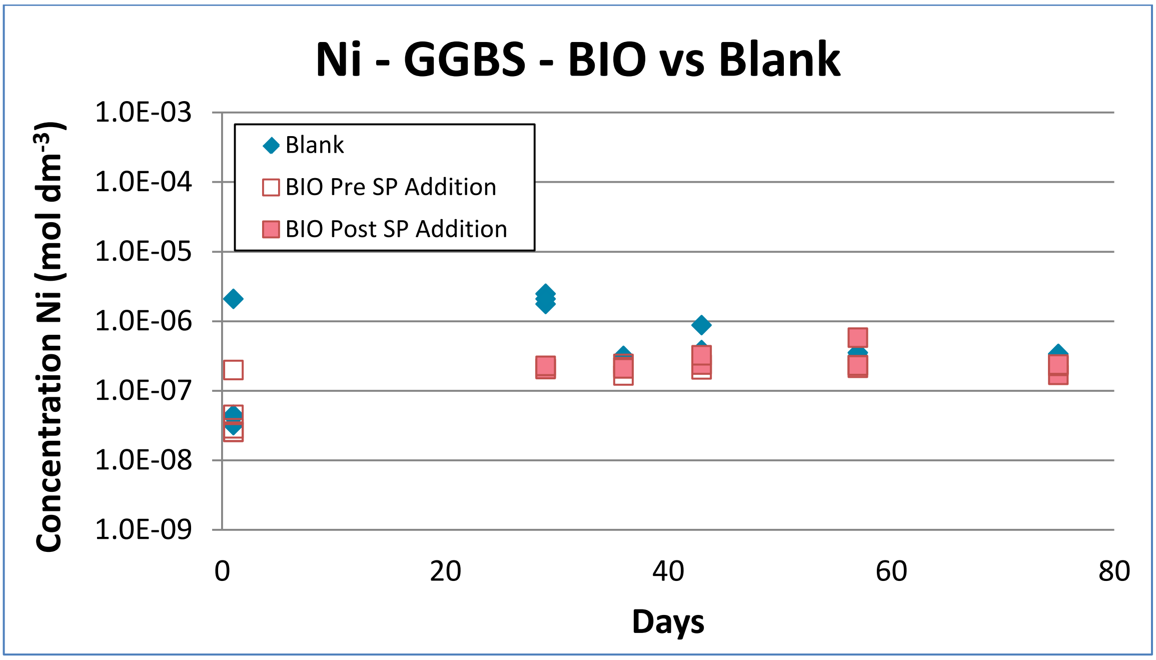

Figure A2. 14: Ni - GGBS - VMA vs Blank

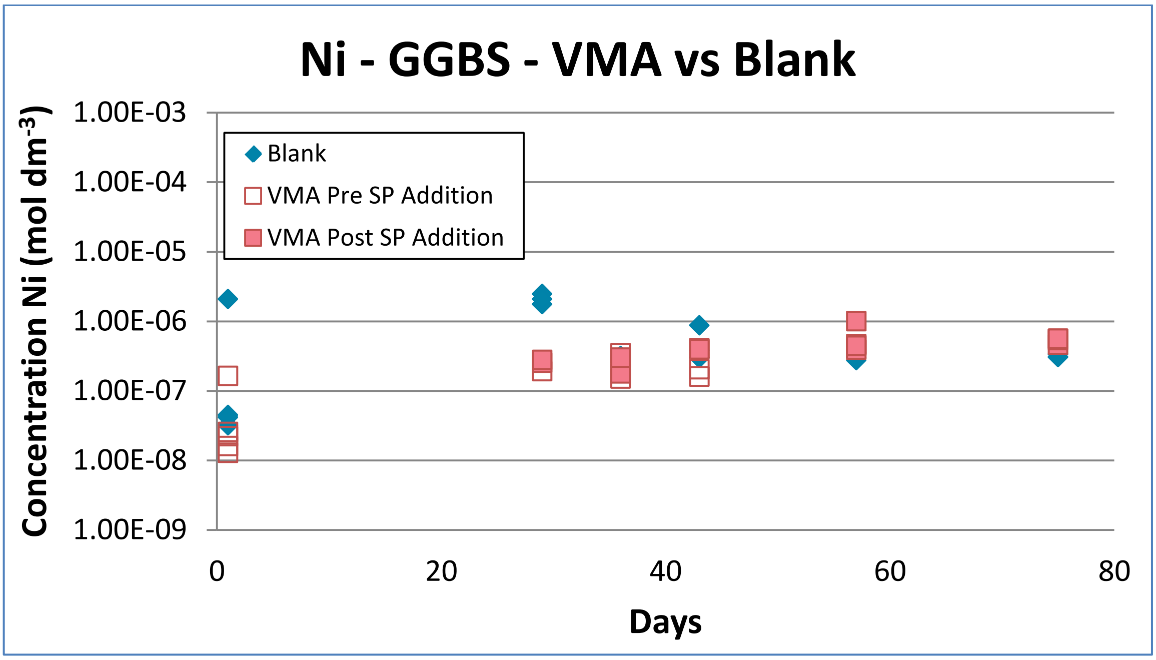

Figure A2. 15: Ni - GGBS - DEF vs Blank

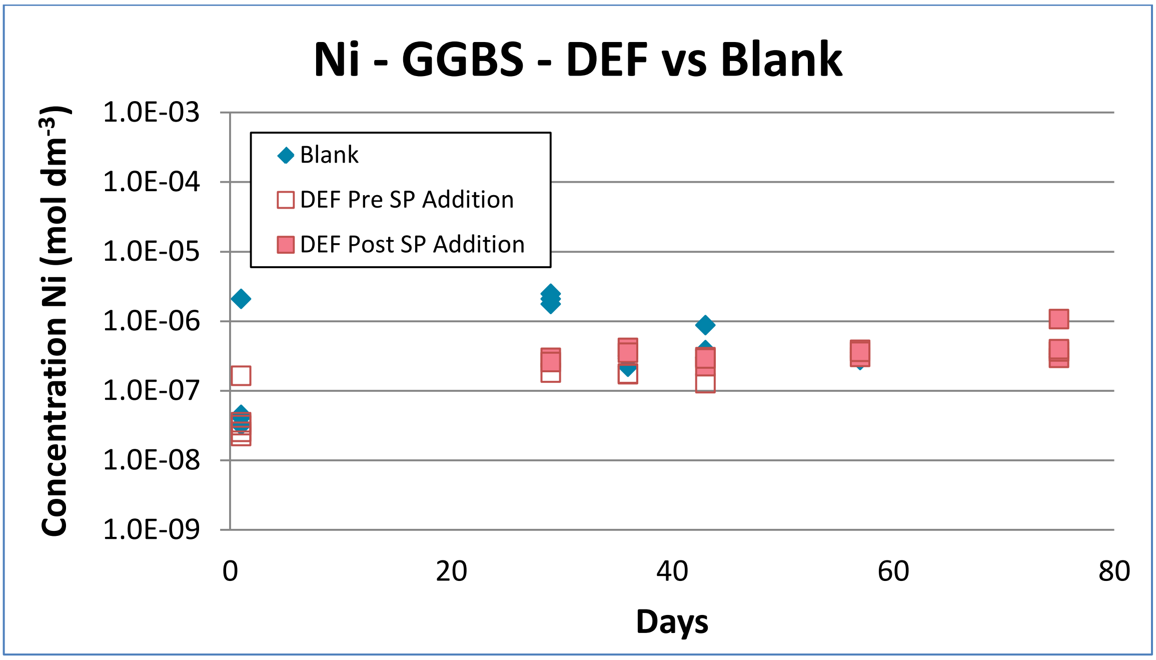

Figure A2. 16: Ni - GGBS - VMA vs Blank

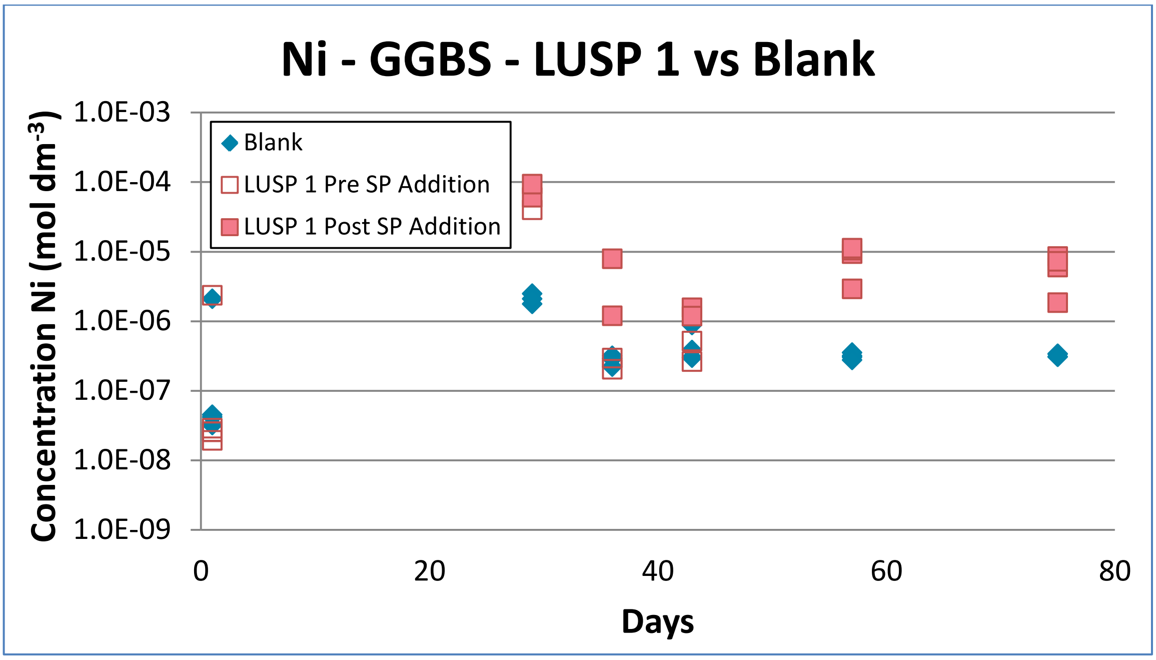

Figure A2. 17: U - PFA - MPBDP vs Blank

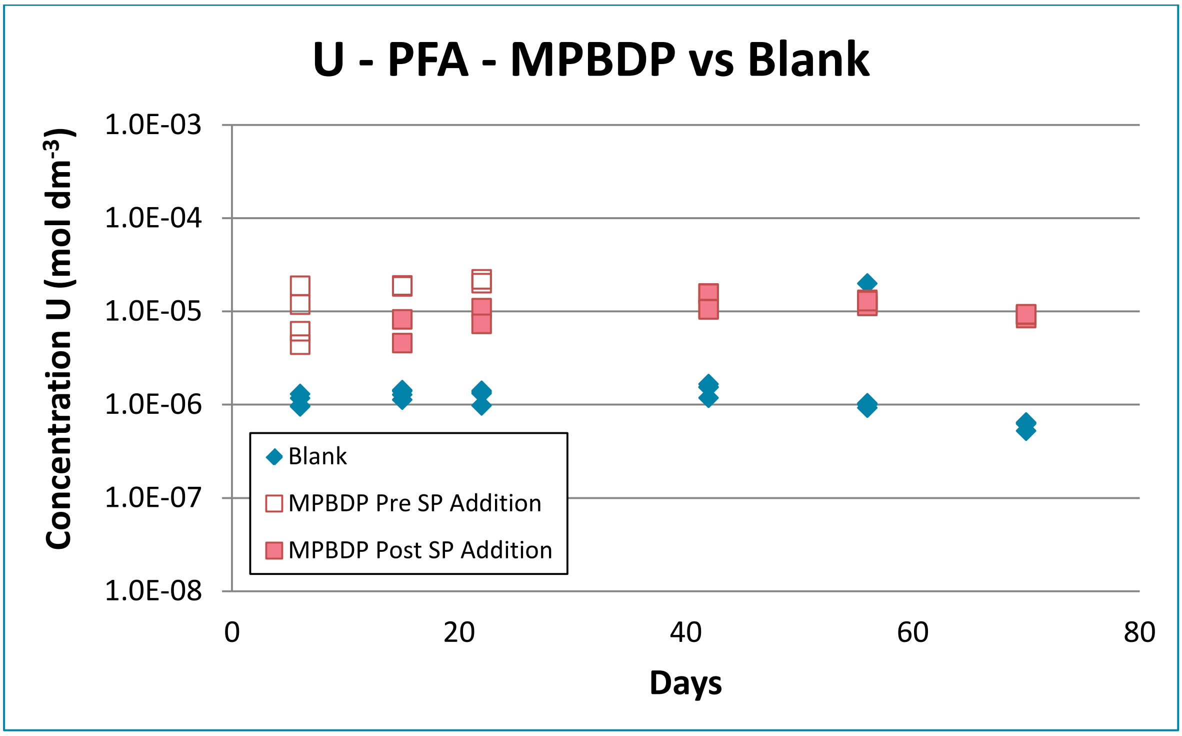

Figure A2. 18: U - PFA - WRBP vs Blank

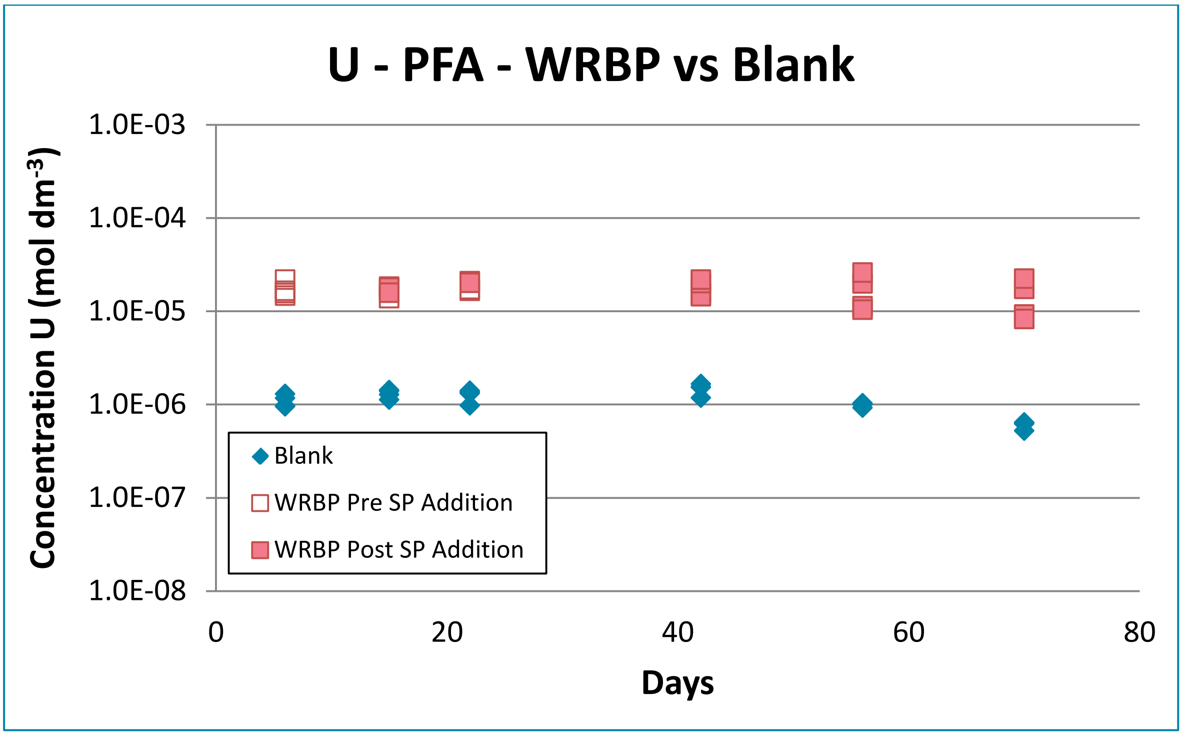

Figure A2. 19: U - PFA - WRBDP vs Blank

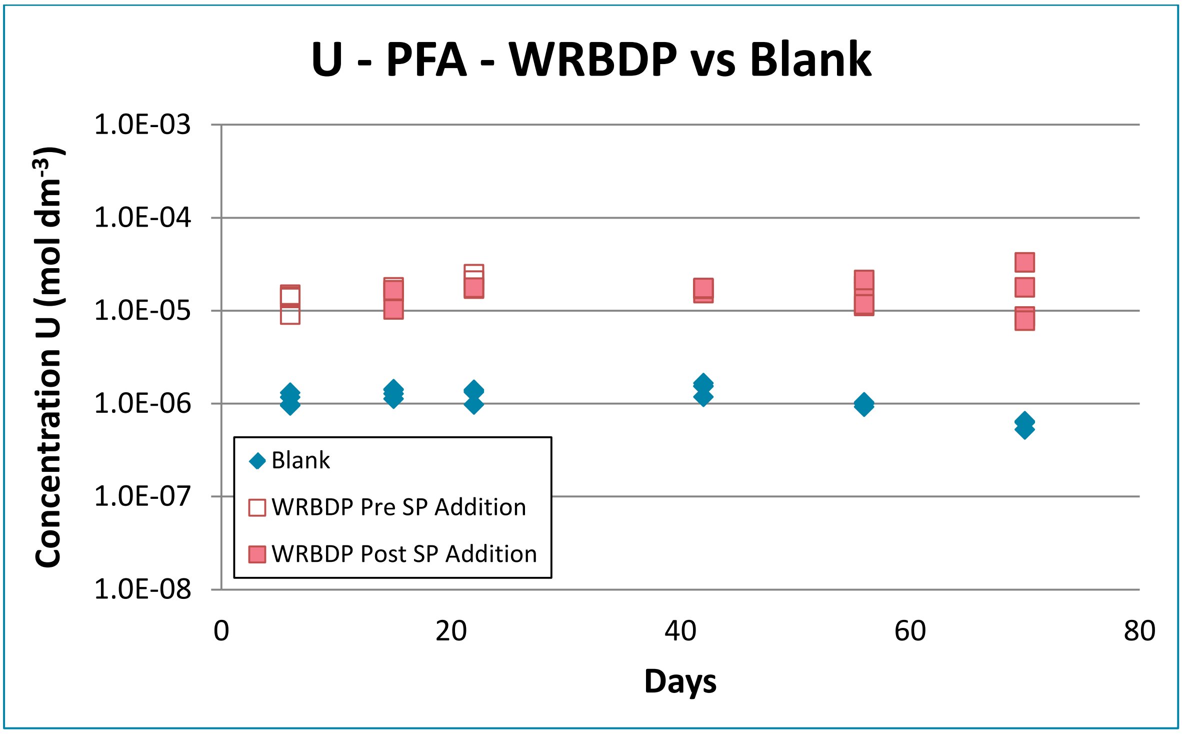

Figure A2. 20: U - PFA - FWBFP vs Blank

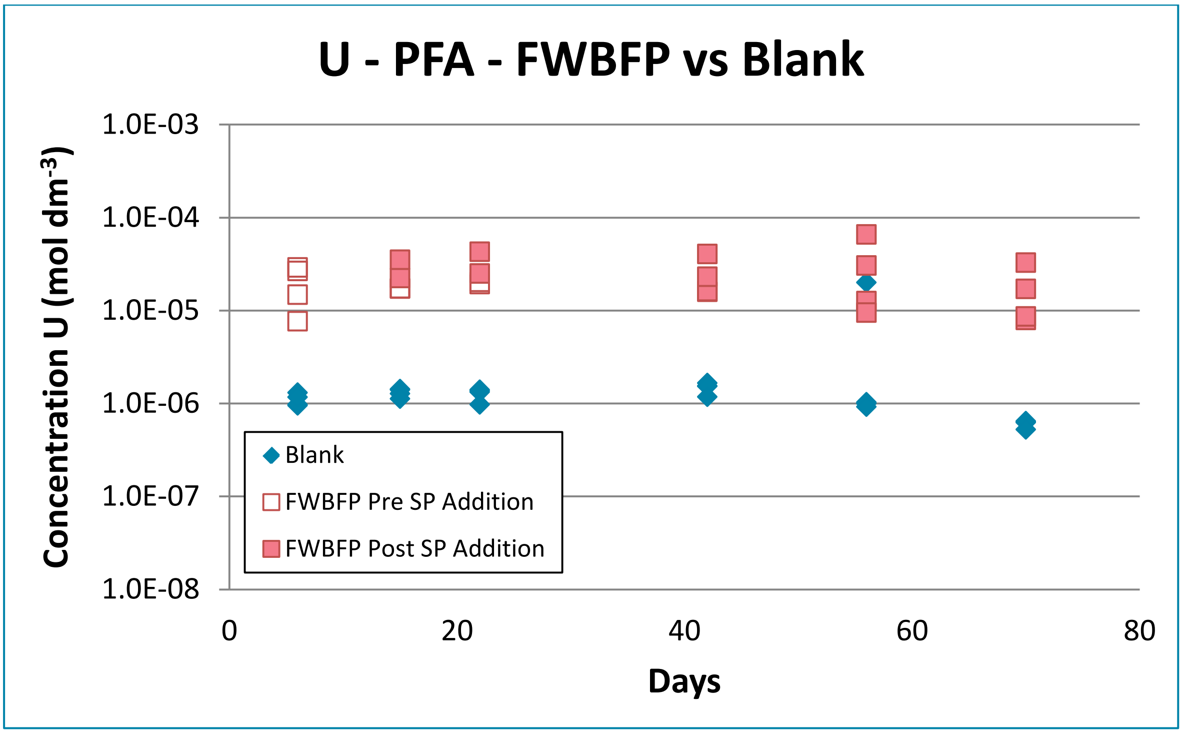

Figure A2. 21: U - PFA - BIO vs Blank

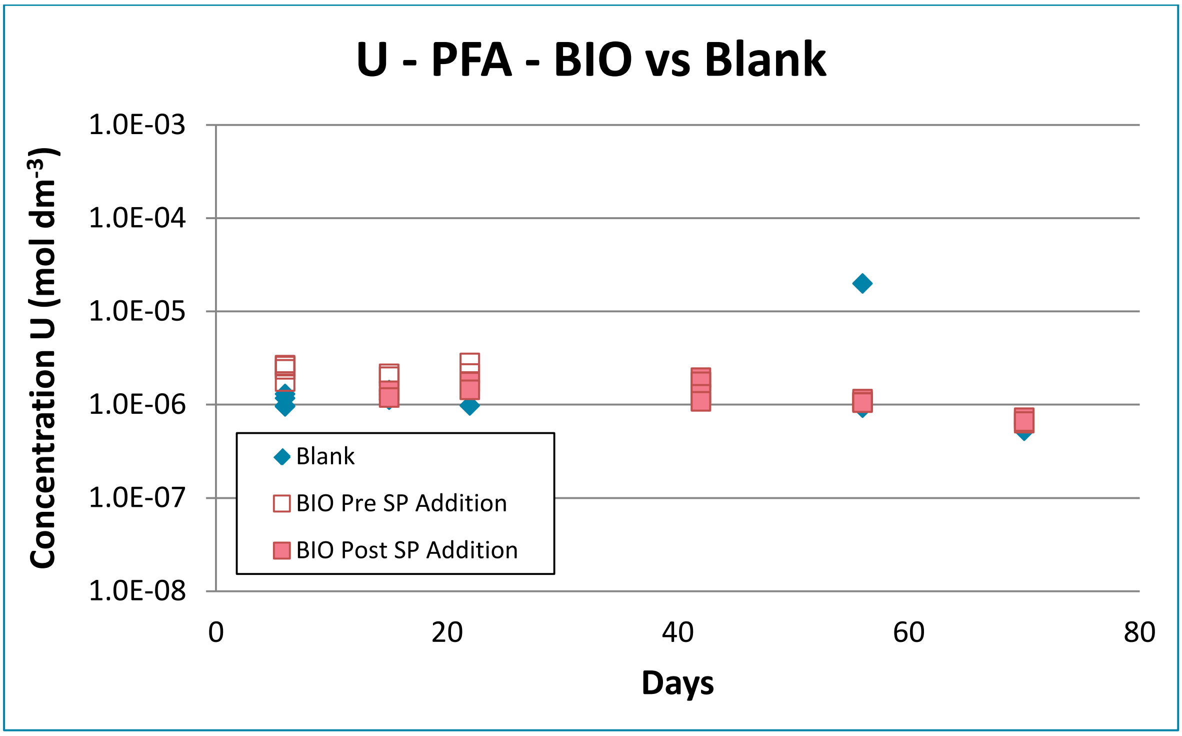

Figure A2. 22: U - PFA - VMA vs Blank

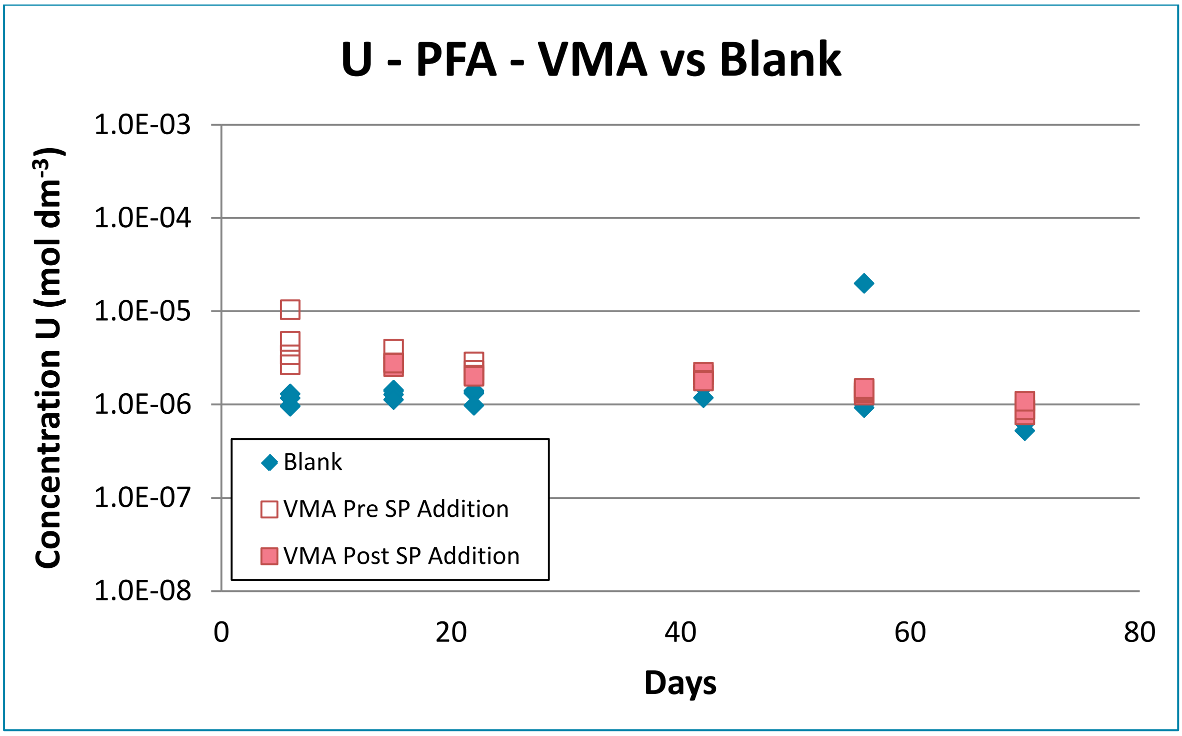

Figure A2. 23: U - PFA - DEF vs Blank

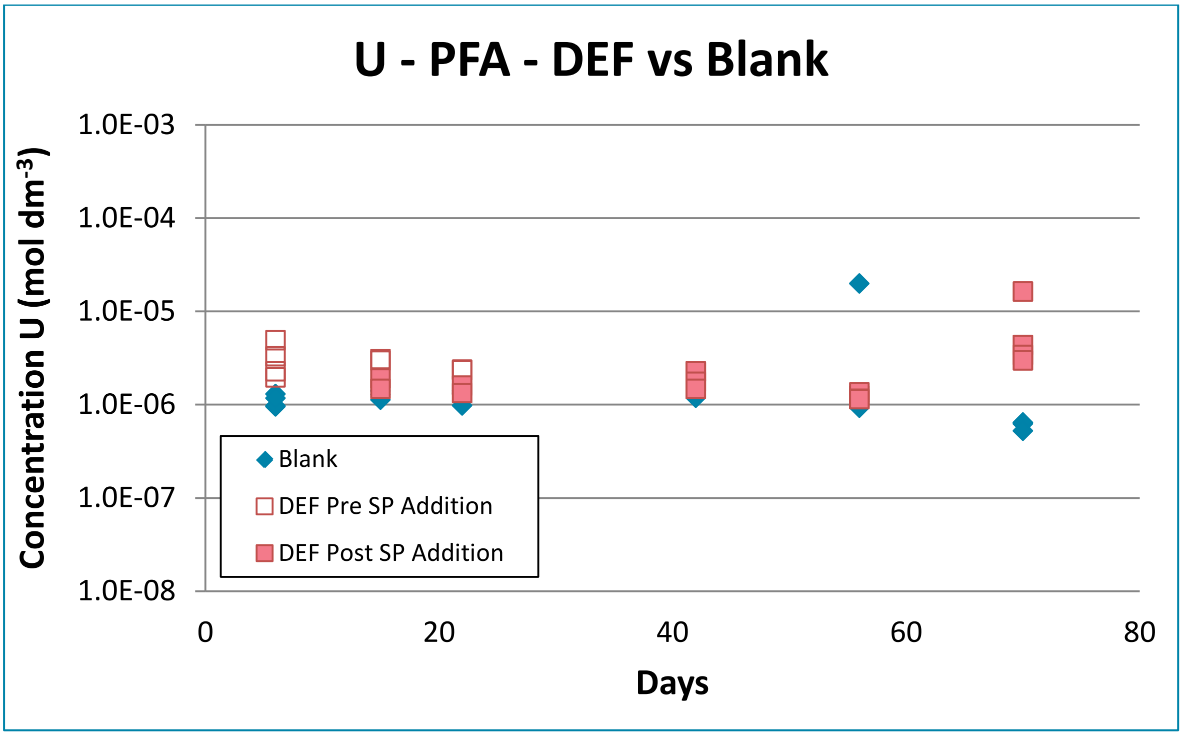

Figure A2. 24: U - PFA – LUSP 1 vs Blank

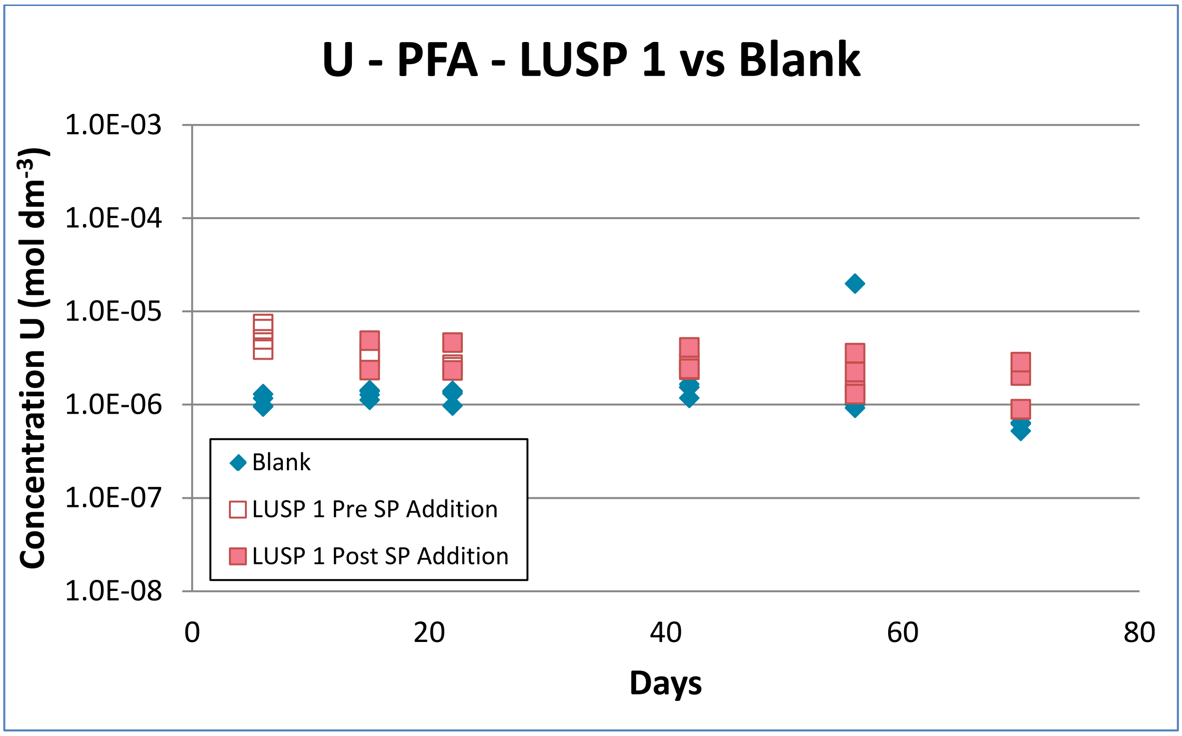

Figure A2. 25: U - GGBS - MPBDP vs Blank

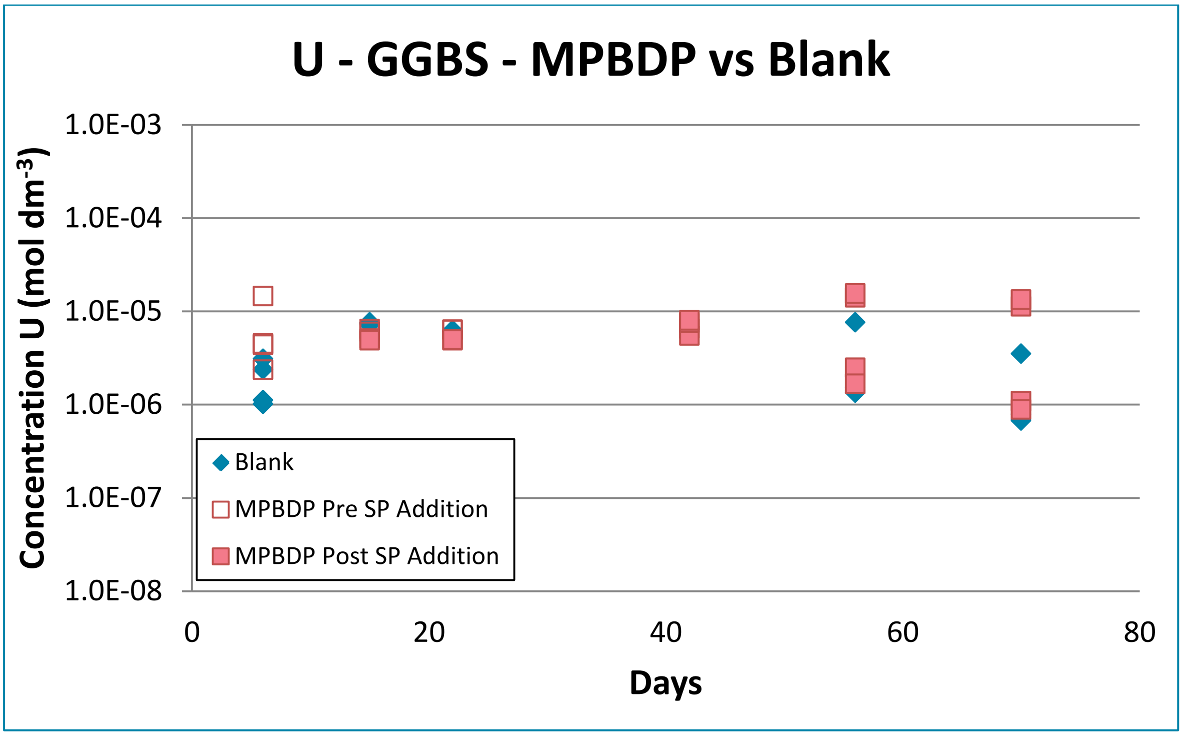

Figure A2. 26: U - GGBS - WRBP vs Blank

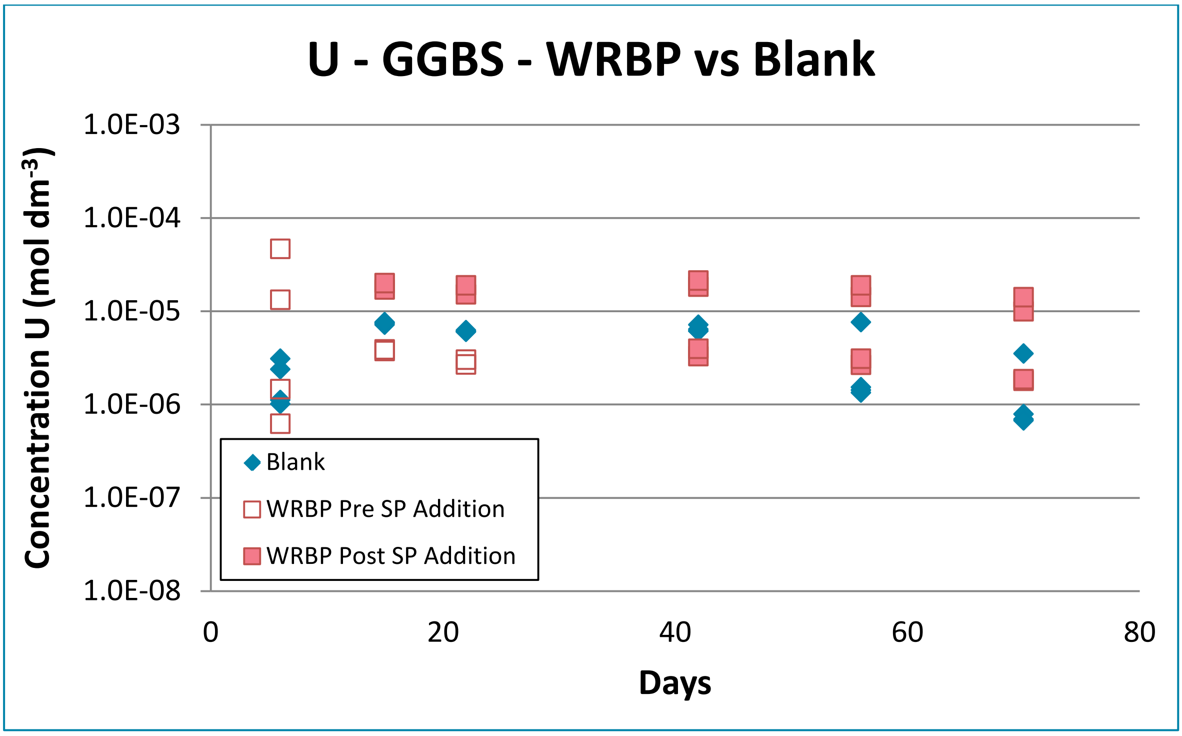

Figure A2. 27: U - GGBS - WRBDP vs Blank

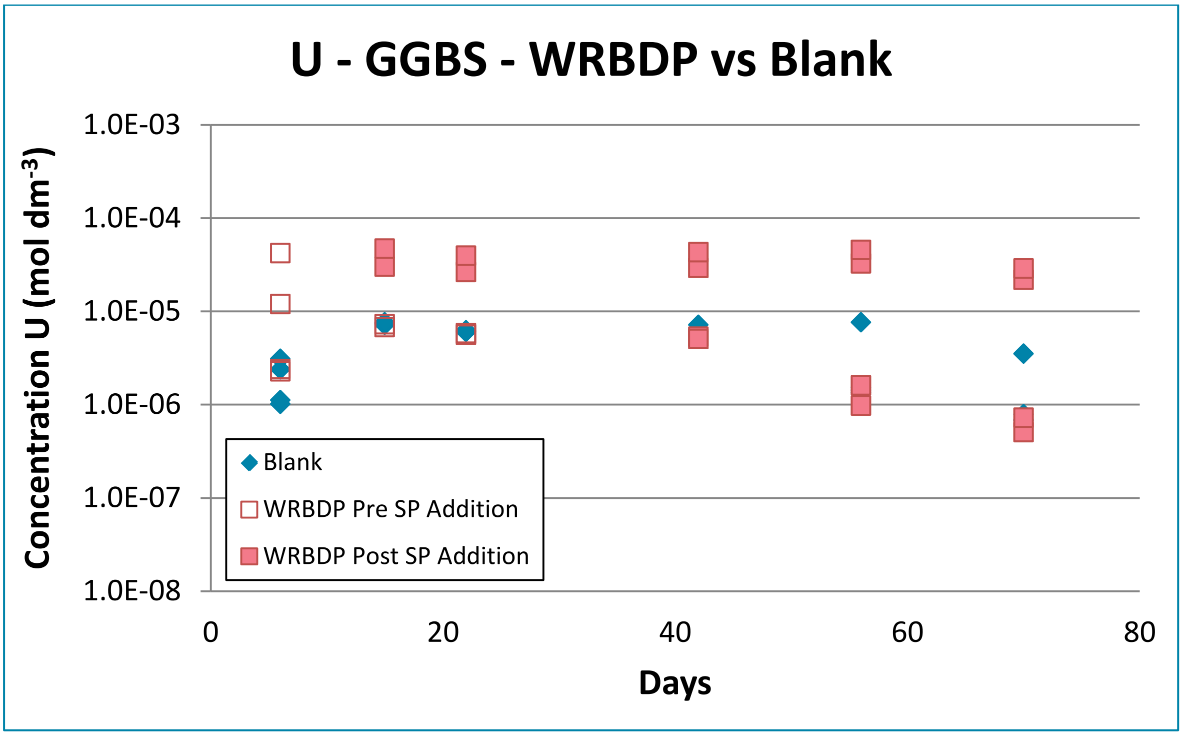

Figure A2. 28: U - GGBS - WRBDP vs Blank

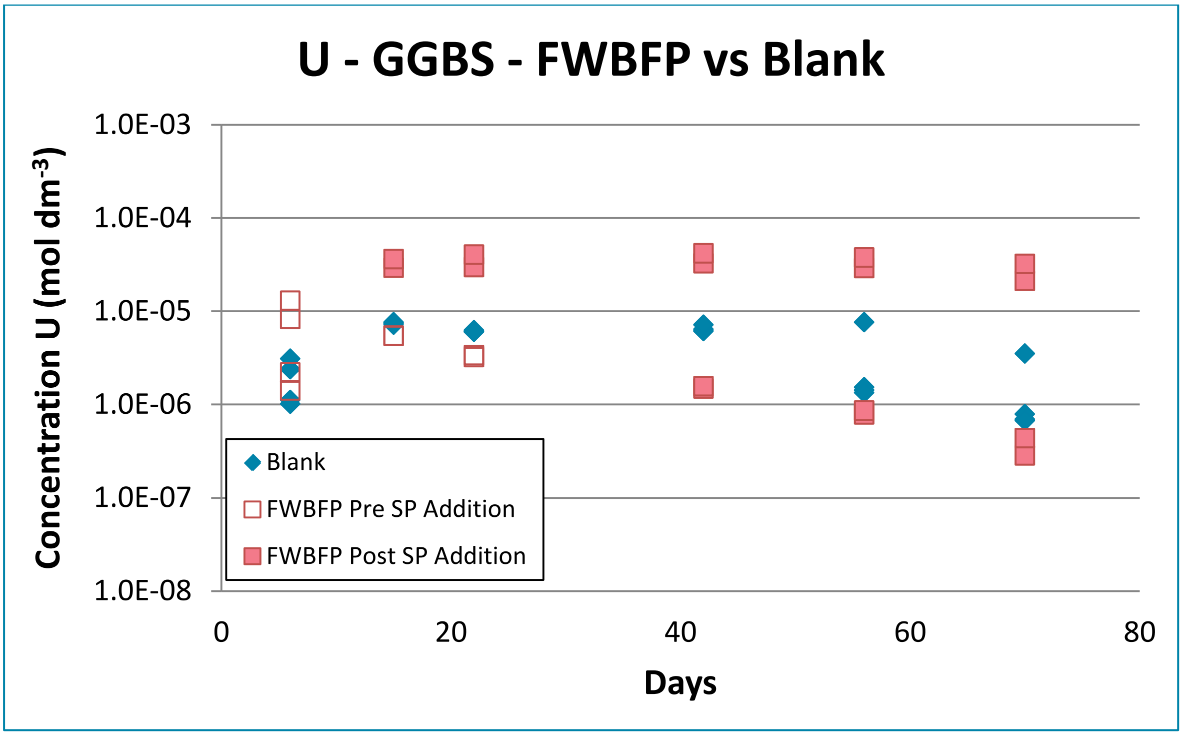

Figure A2. 29: U - GGBS - BIO vs Blank

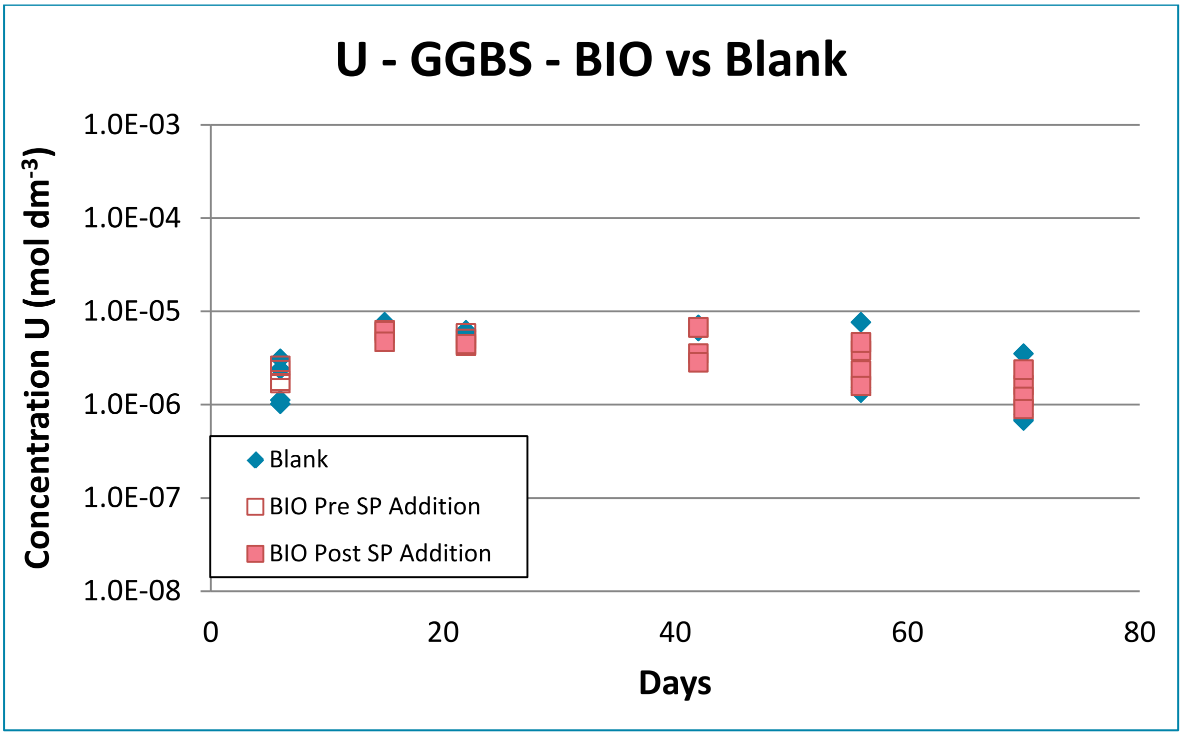

Figure A2. 30: U - GGBS - VMA vs Blank

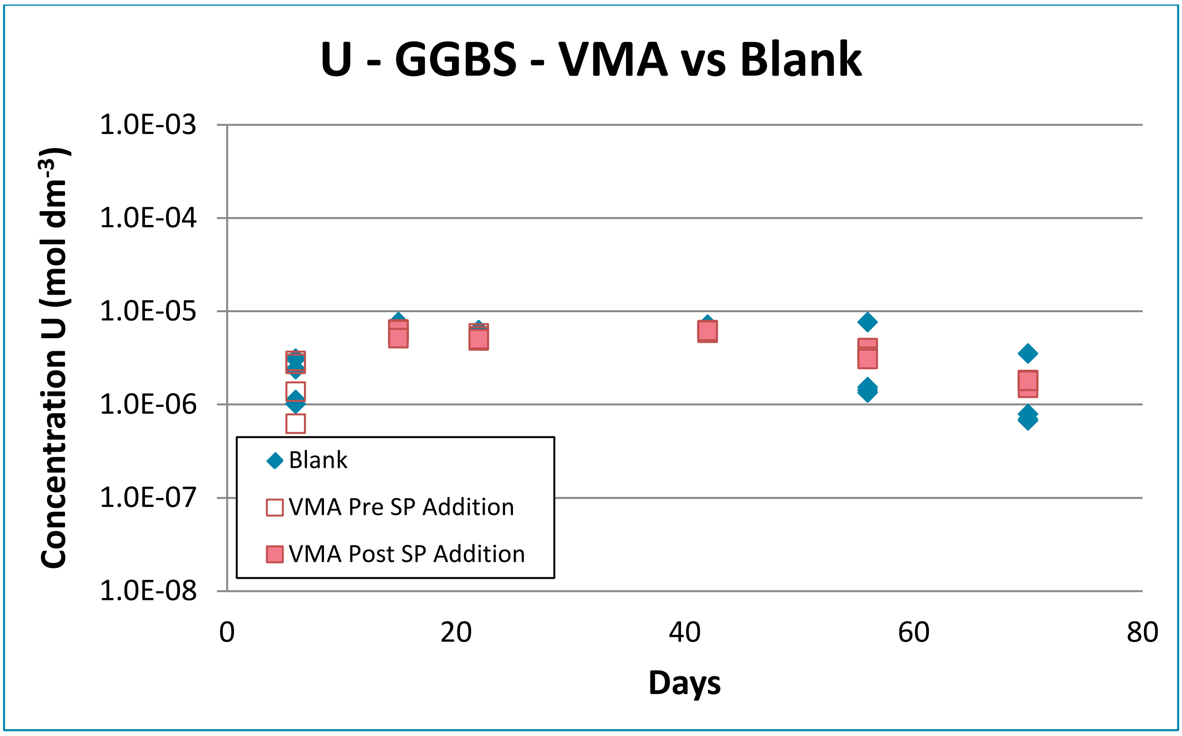

Figure A2. 31: U - GGBS - DEF vs Blank

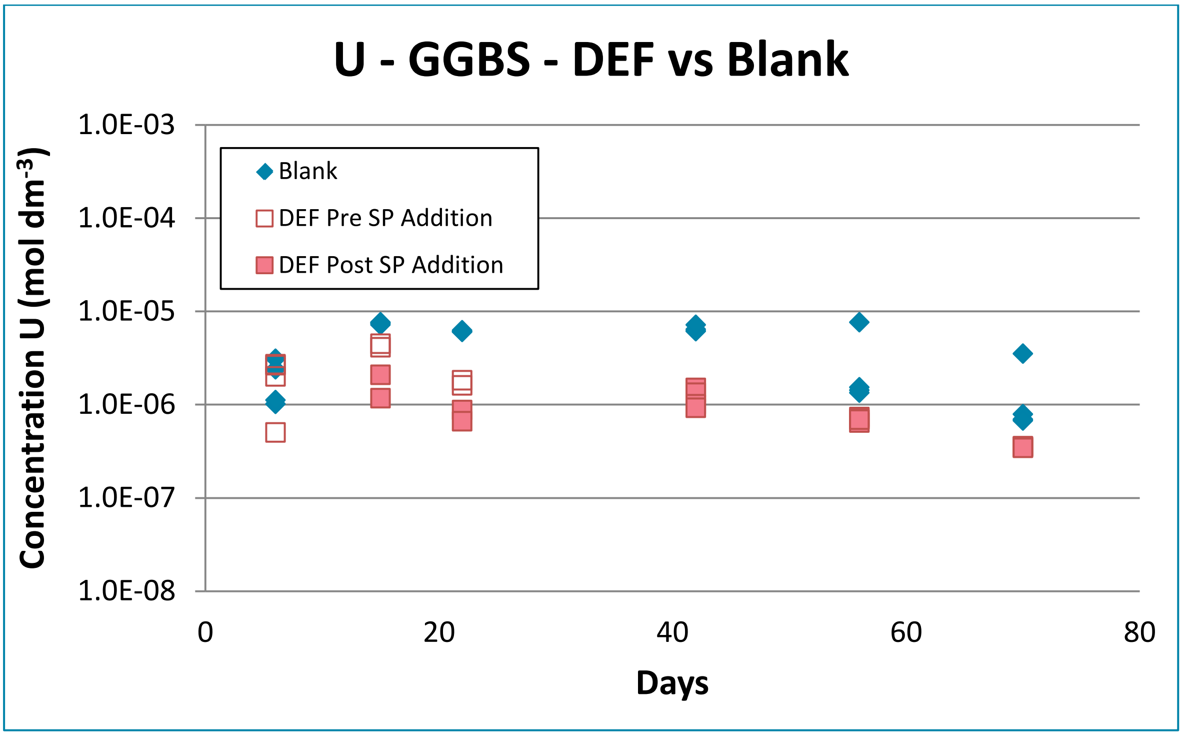

Figure A2. 32: U - GGBS - LUSP 1 vs Blank

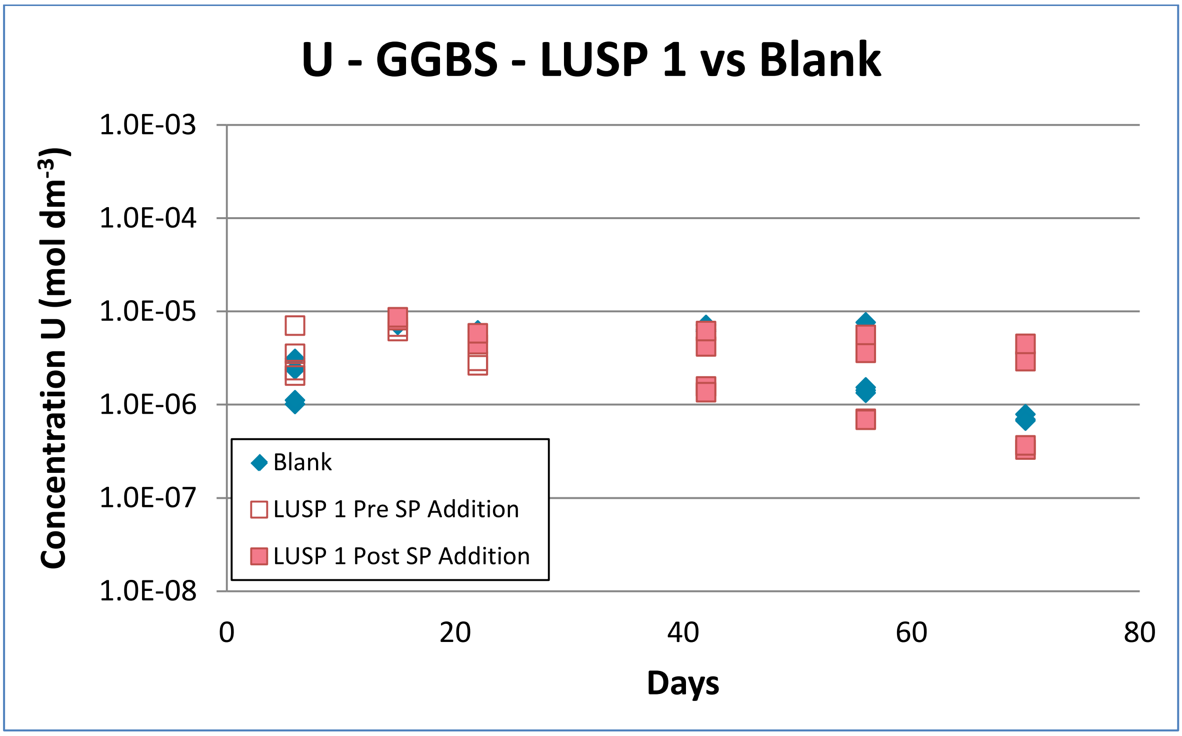

Figure A2. 33: Pu - PFA - MPBDP vs Blank

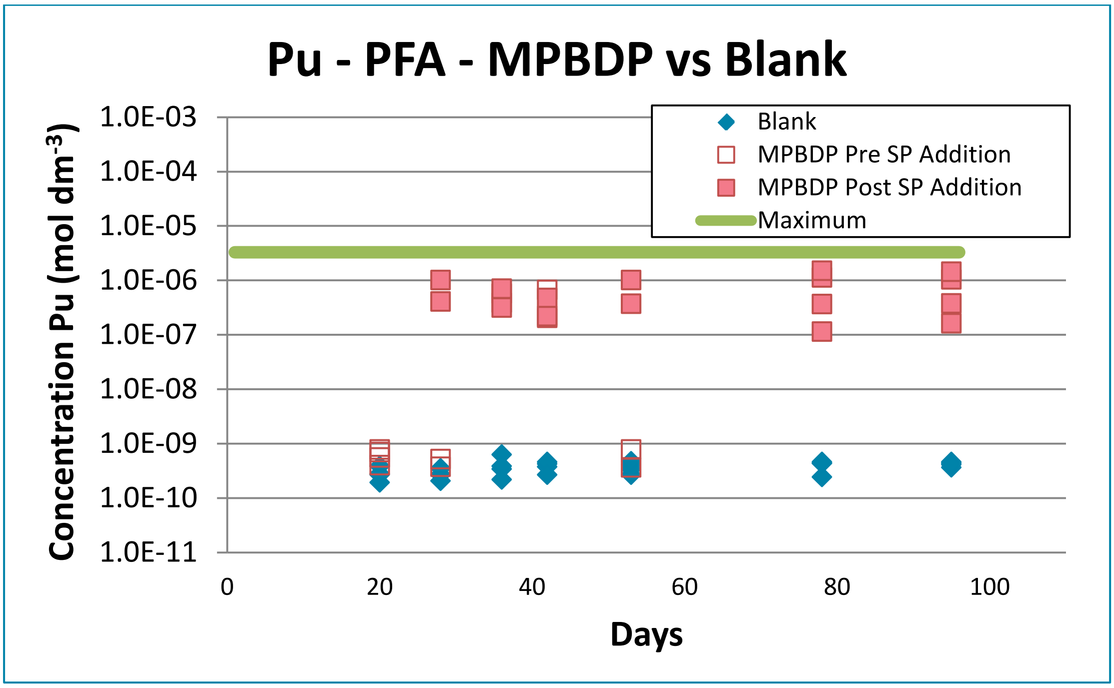

Figure A2. 34: Pu - PFA - WRBP vs Blank

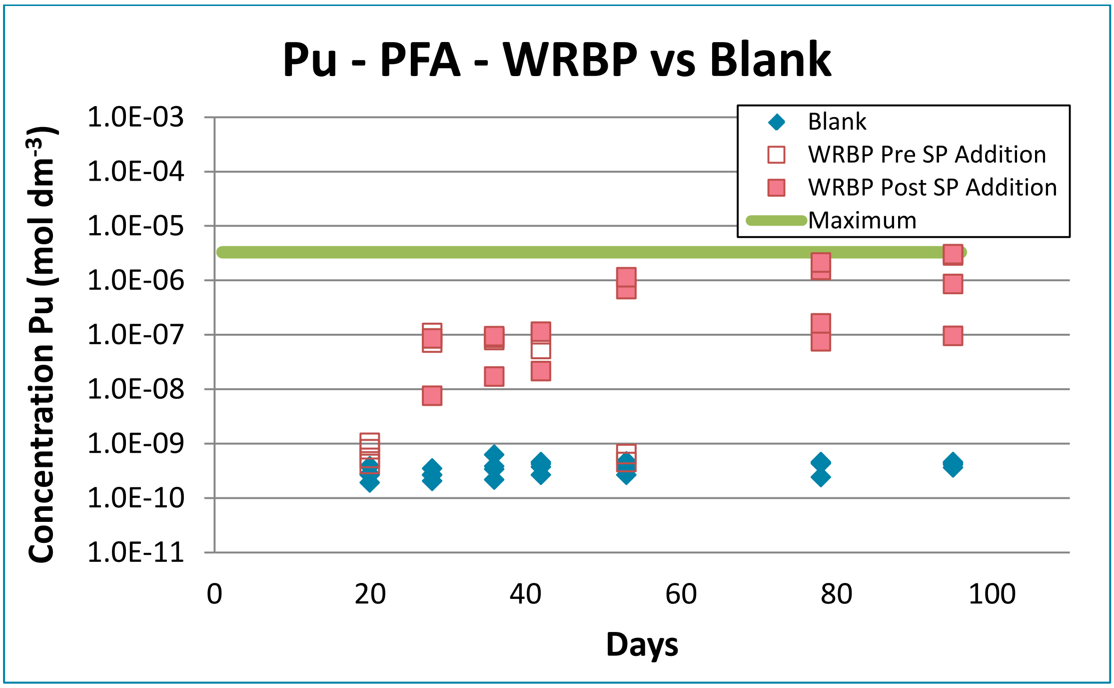

Figure A2. 35: Pu - PFA - WRBDP vs Blank

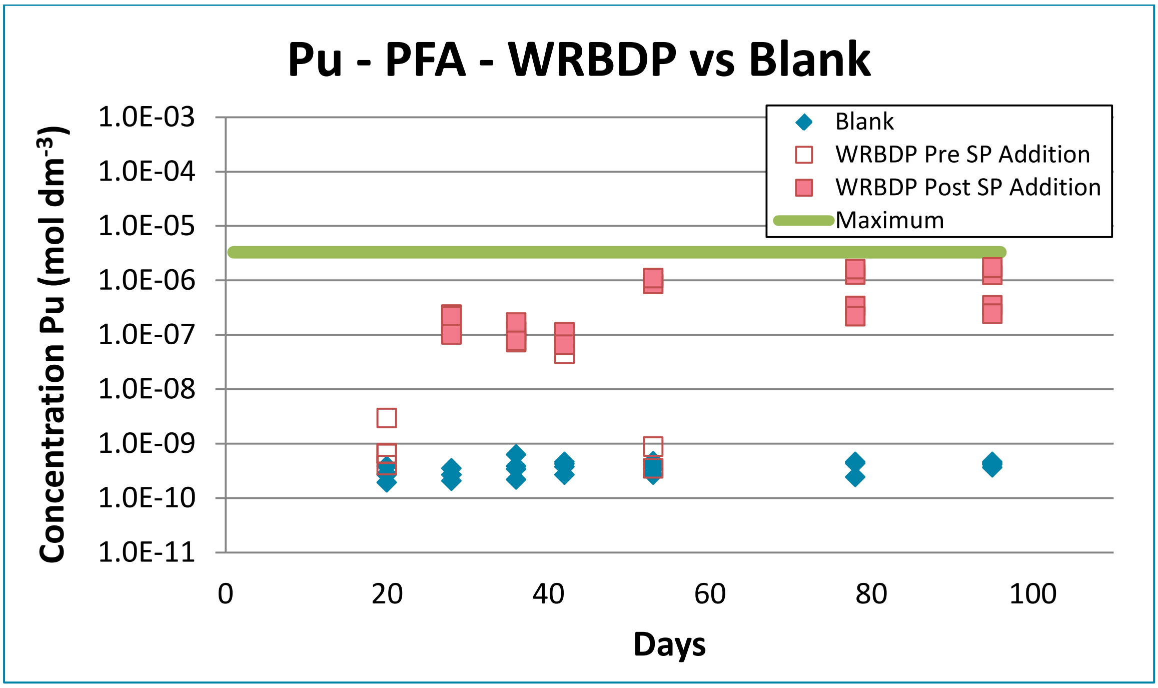

Figure A2. 36: Pu - PFA - FWBFP vs Blank

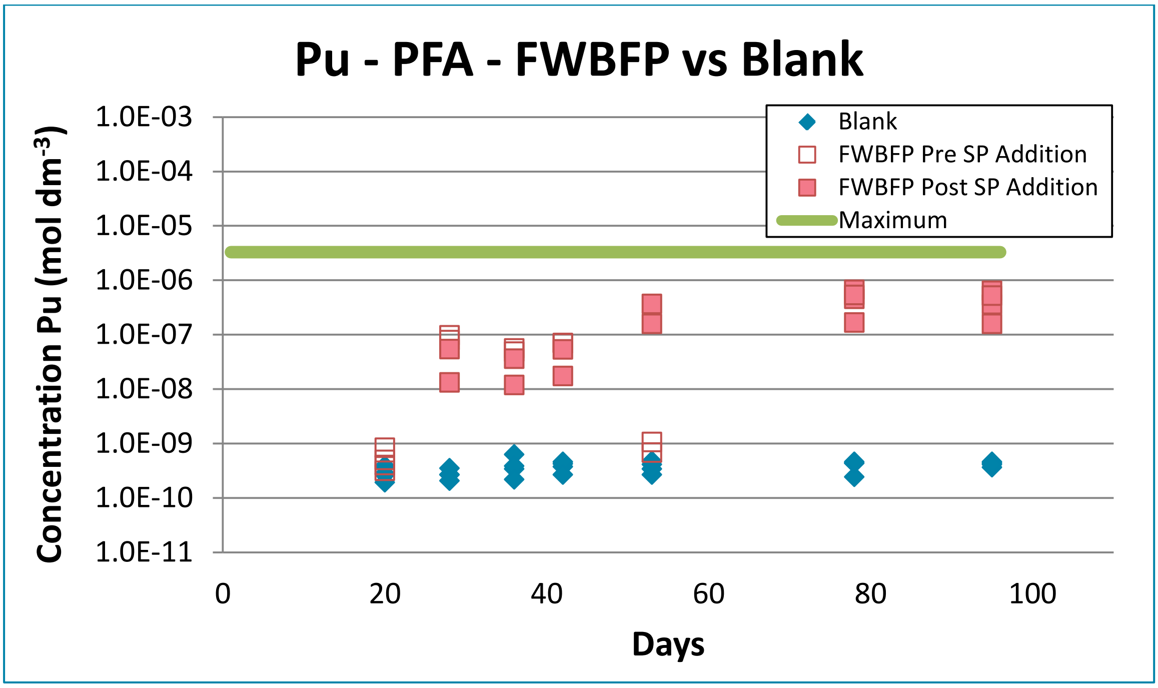

Figure A2. 37: Pu - PFA - BIO vs Blank

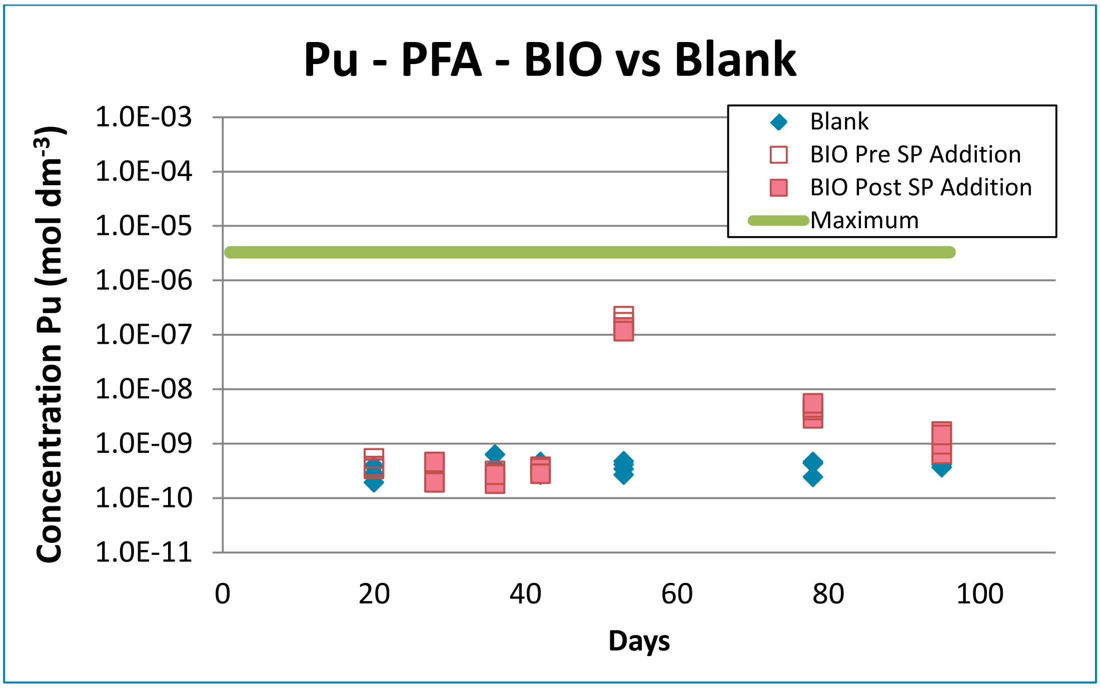

Figure A2. 38: Pu - PFA - VMA vs Blank

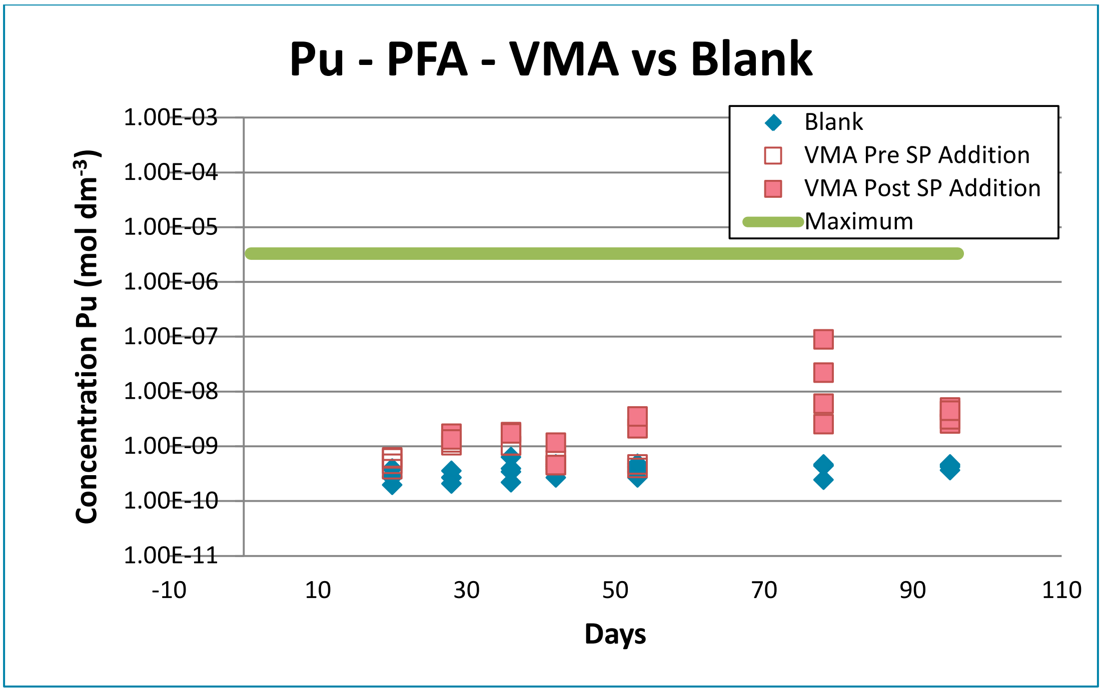

Figure A2. 39: Pu - PFA - DEF vs Blank

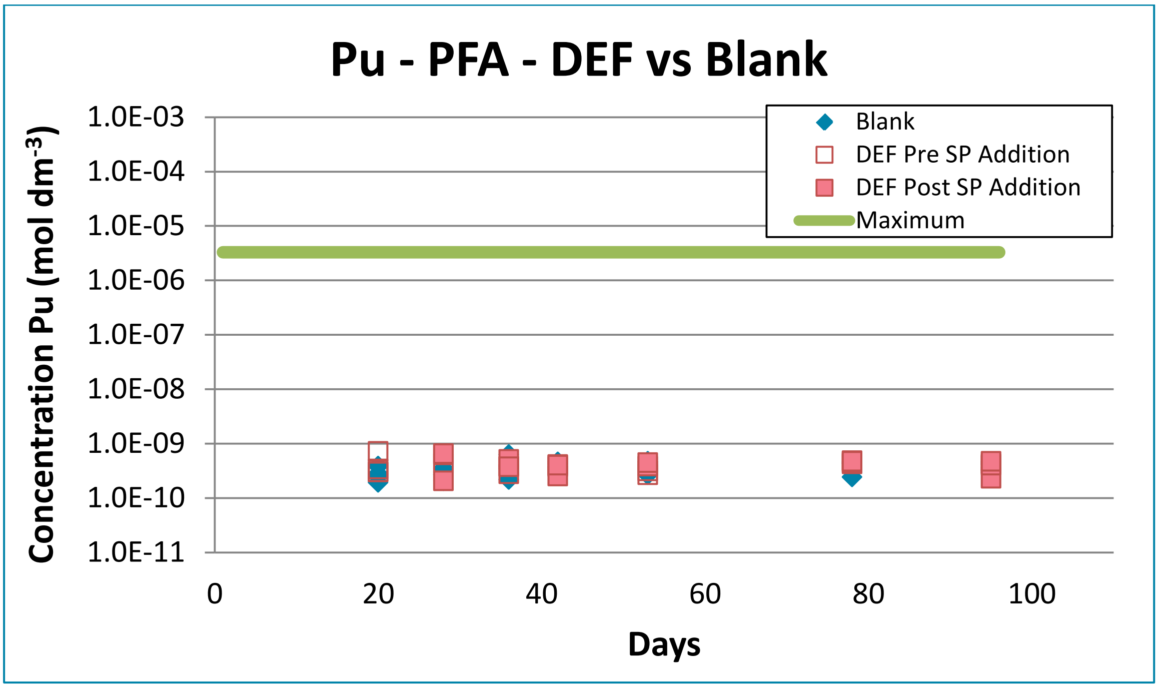

Figure A2. 40: Pu - PFA – LUSP 1 vs Blank

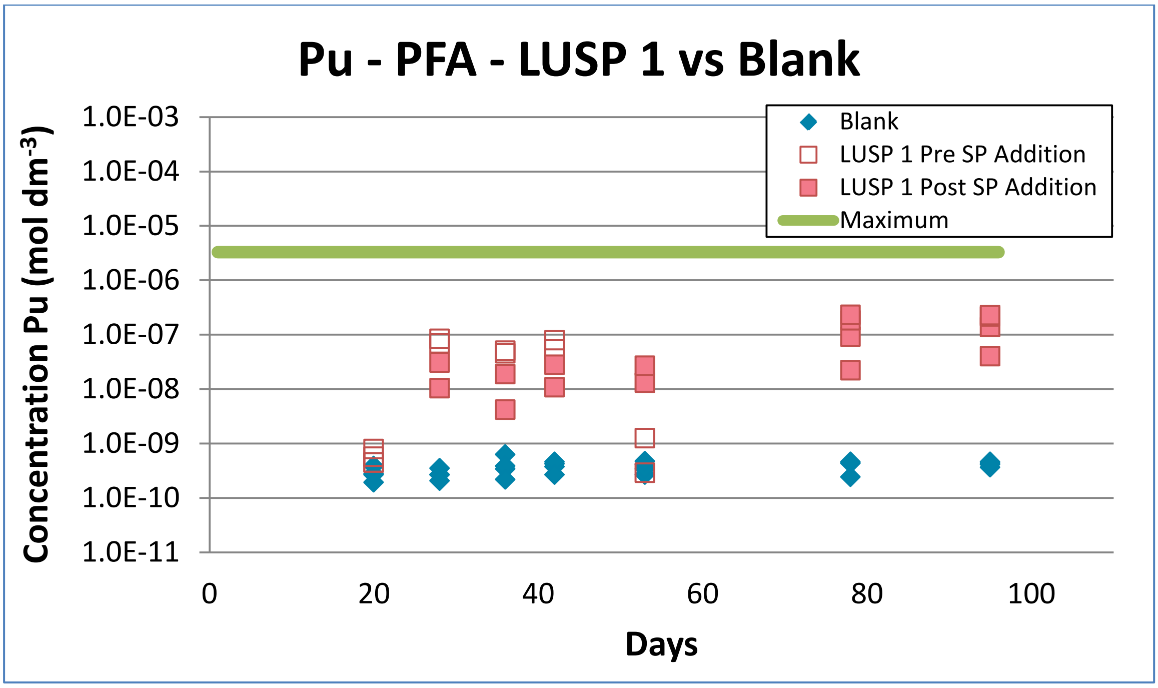

Figure A2. 41: Pu - GGBS - MPBDP vs Blank

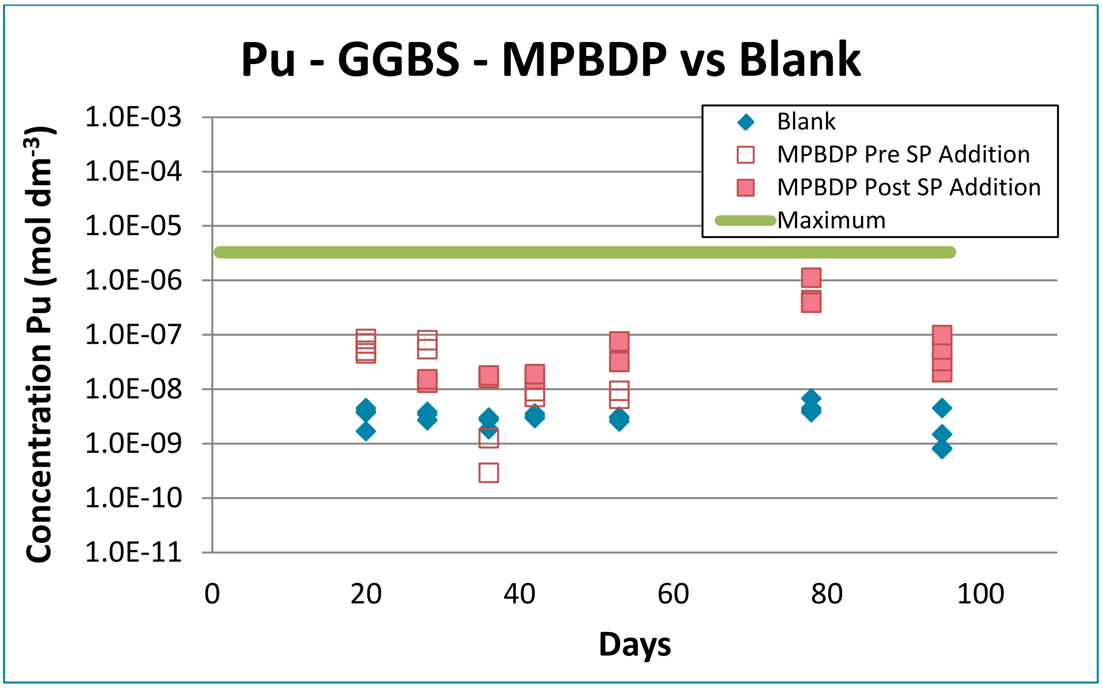

Figure A2. 42: Pu - GGBS - WRBP vs Blank

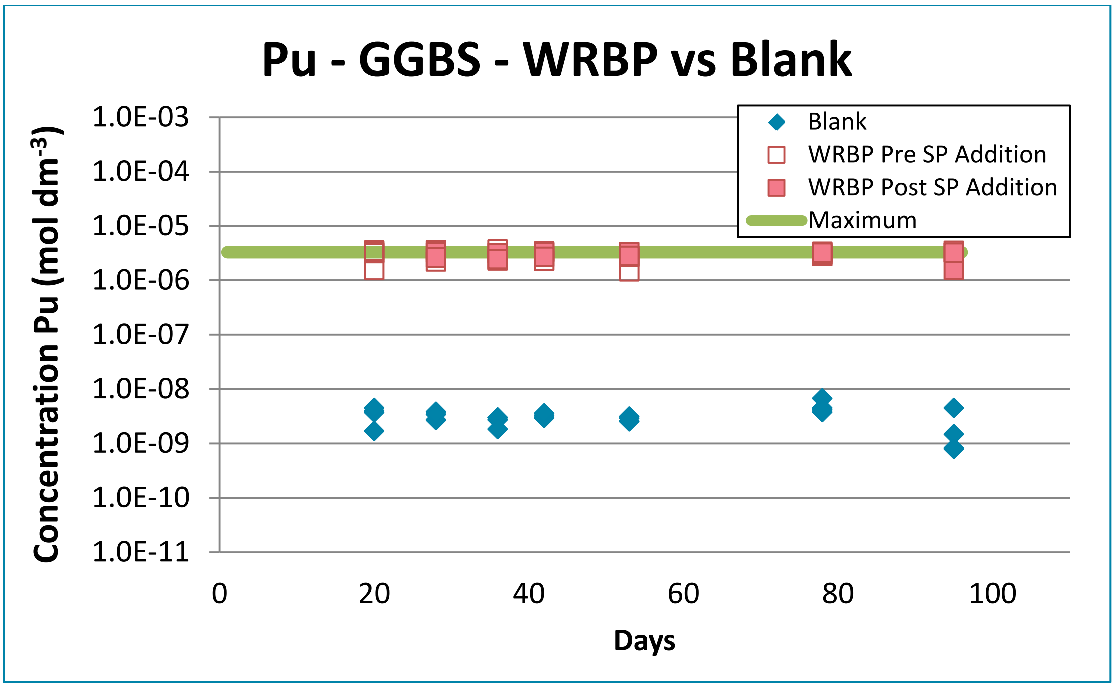

Figure A2. 43: Pu - GGBS - WRBDP vs Blank

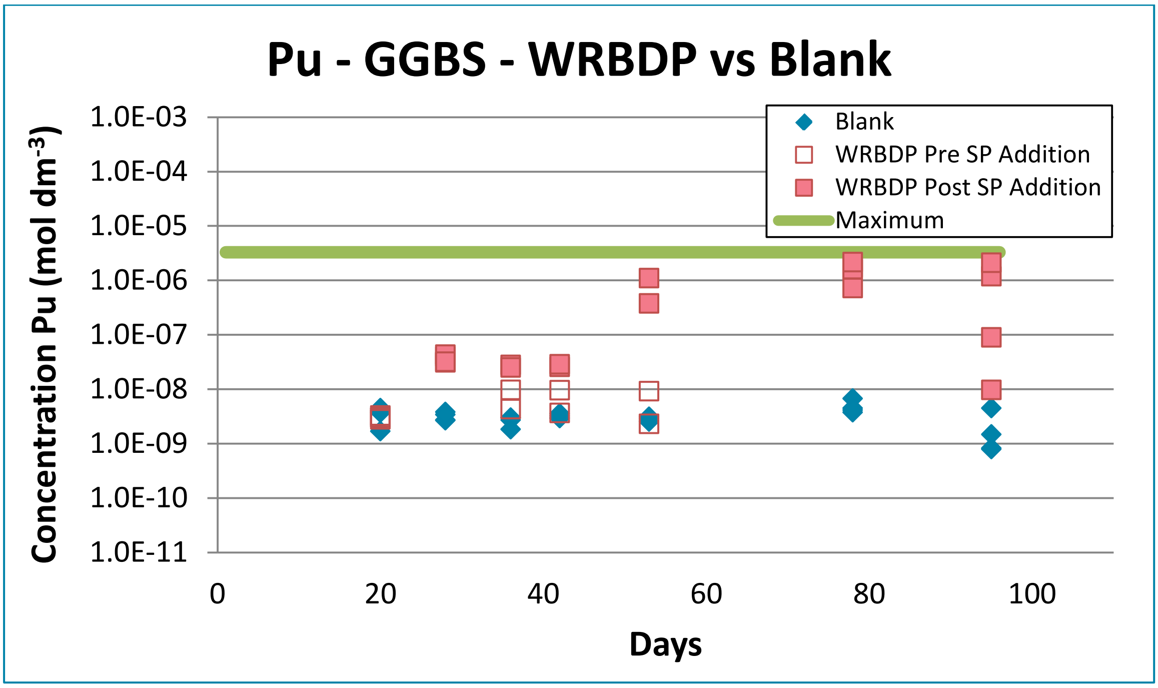

Figure A2. 44: Pu - GGBS - FWBFP vs Blank

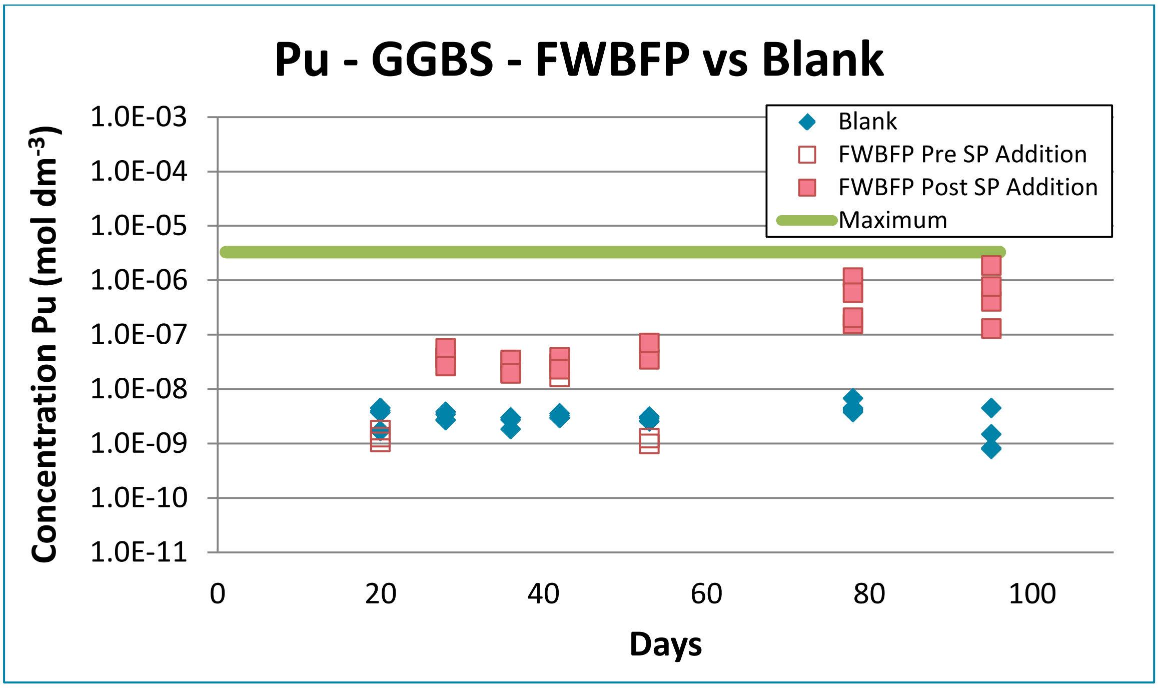

Figure A2. 45: Pu - GGBS - BIO vs Blank

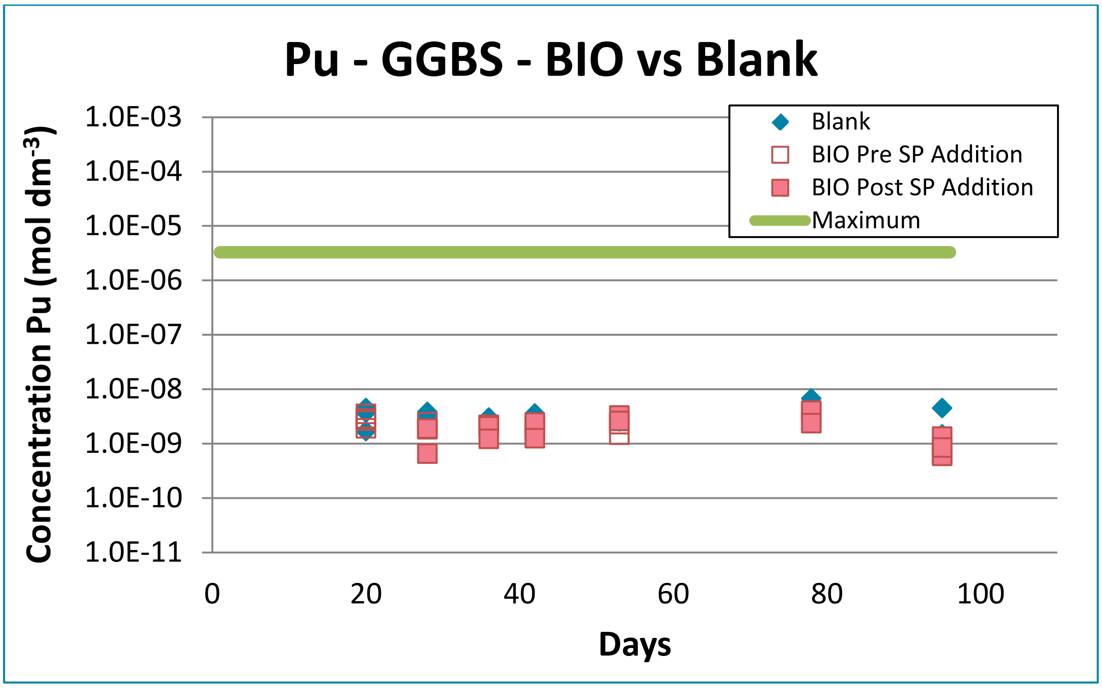

Figure A2. 46: Pu - GGBS - VMA vs Blank

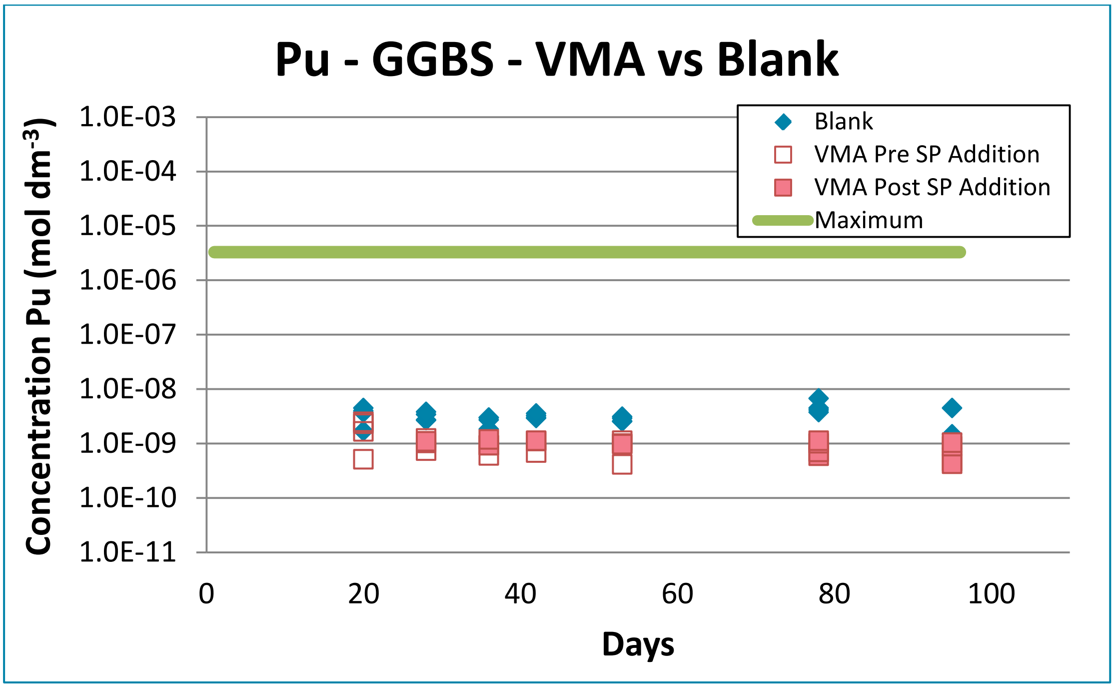

Figure A2. 47: Pu - GGBS - DEF vs Blank

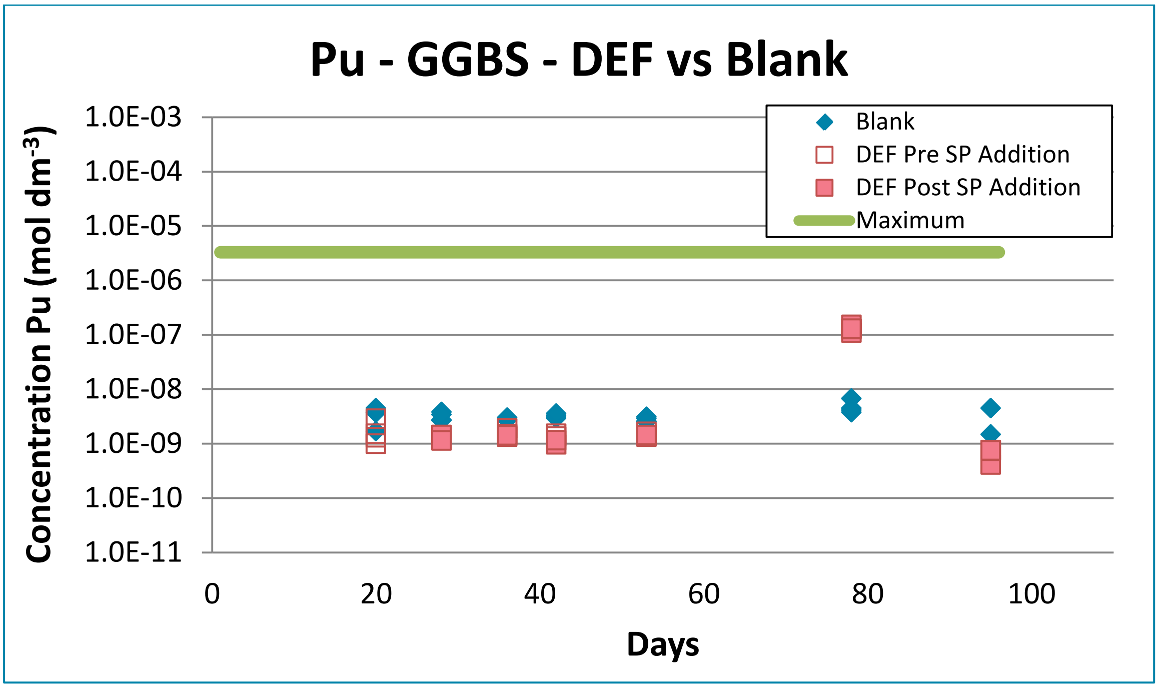

Figure A2. 48: Pu - GGBS – LUSP 1 vs Blank

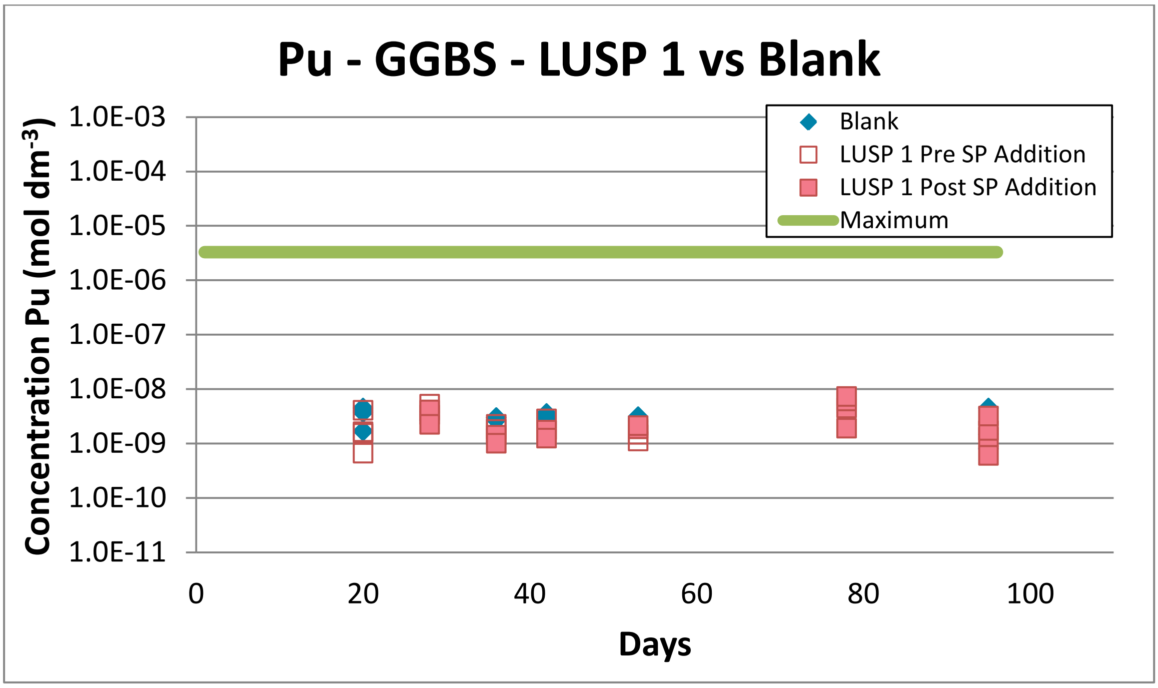

Figure A2. 49: Am - PFA - MPBDP vs Blank

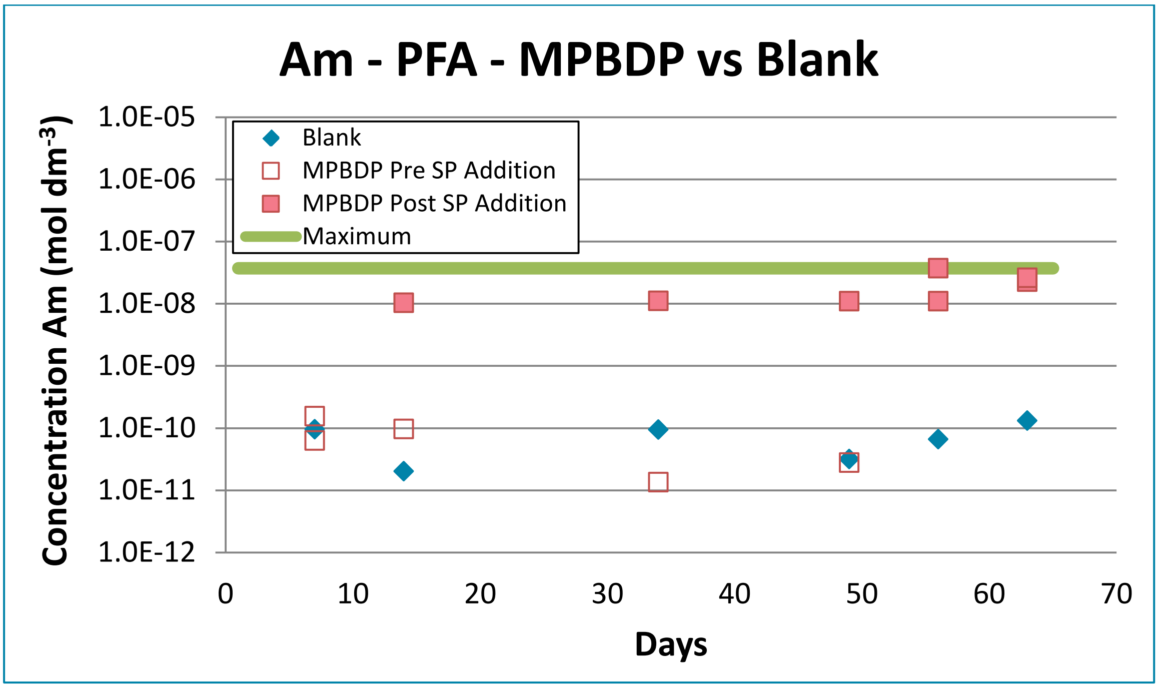

Figure A2. 50: Am - PFA - WRBP vs Blank

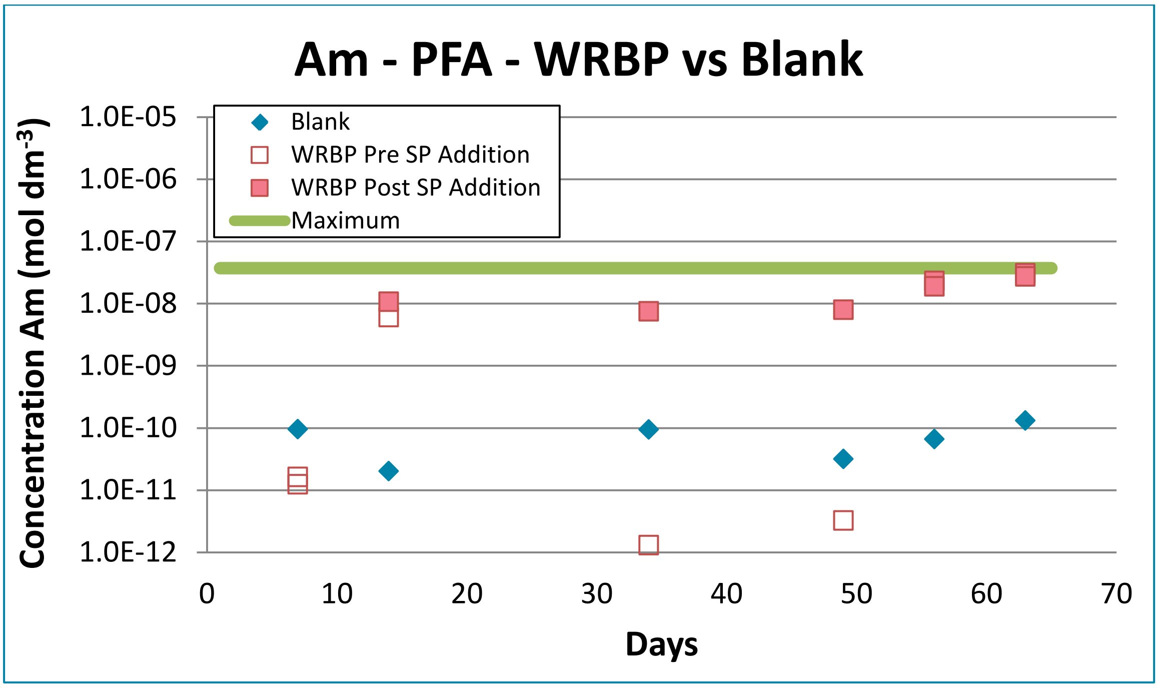

Figure A2. 51: Am - PFA - WRBDP vs Blank

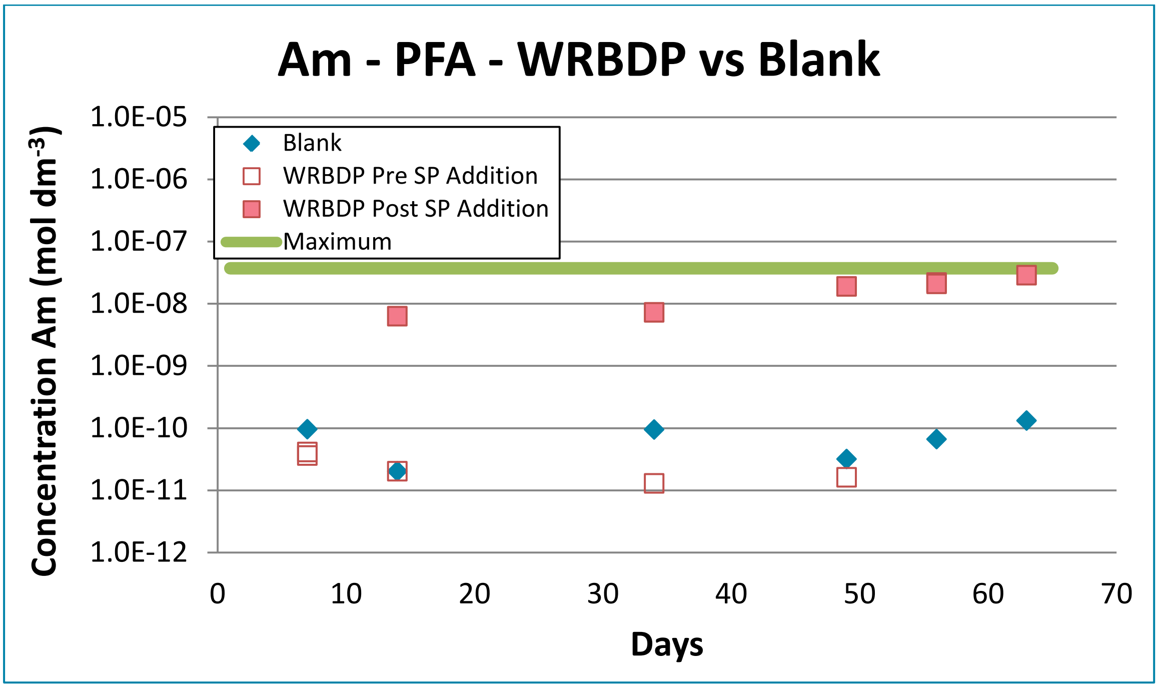

Figure A2. 52: Am - PFA - FWBFP vs Blank

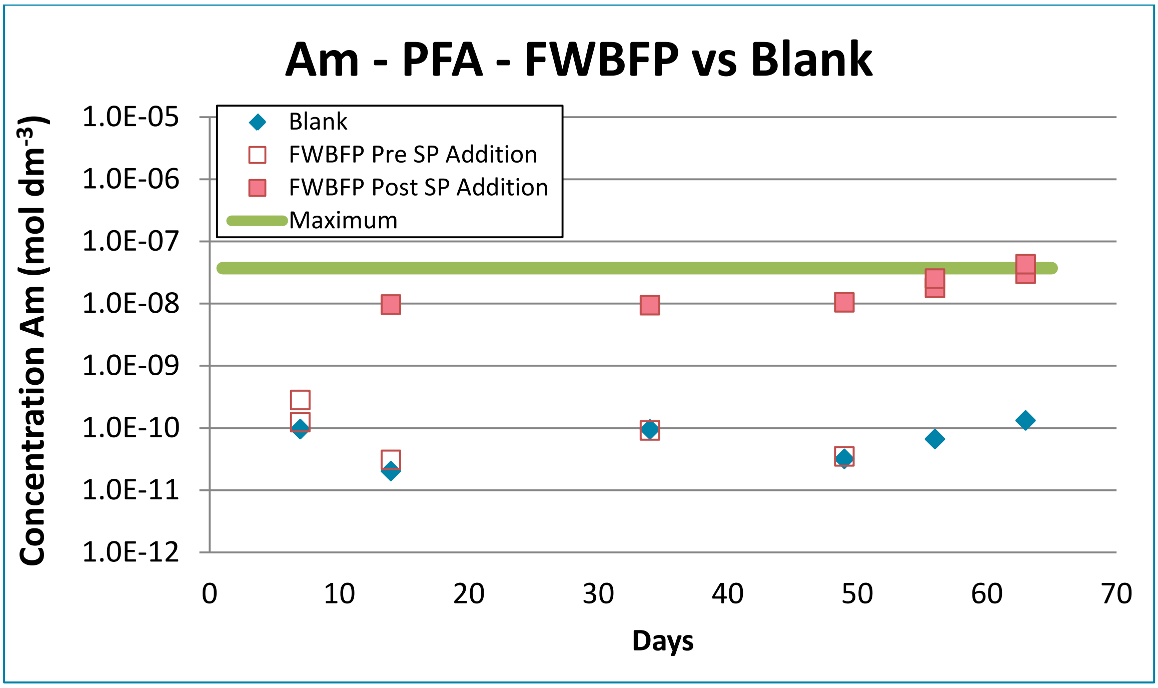

Figure A2. 53: Am - GGBS - MPBDP vs Blank

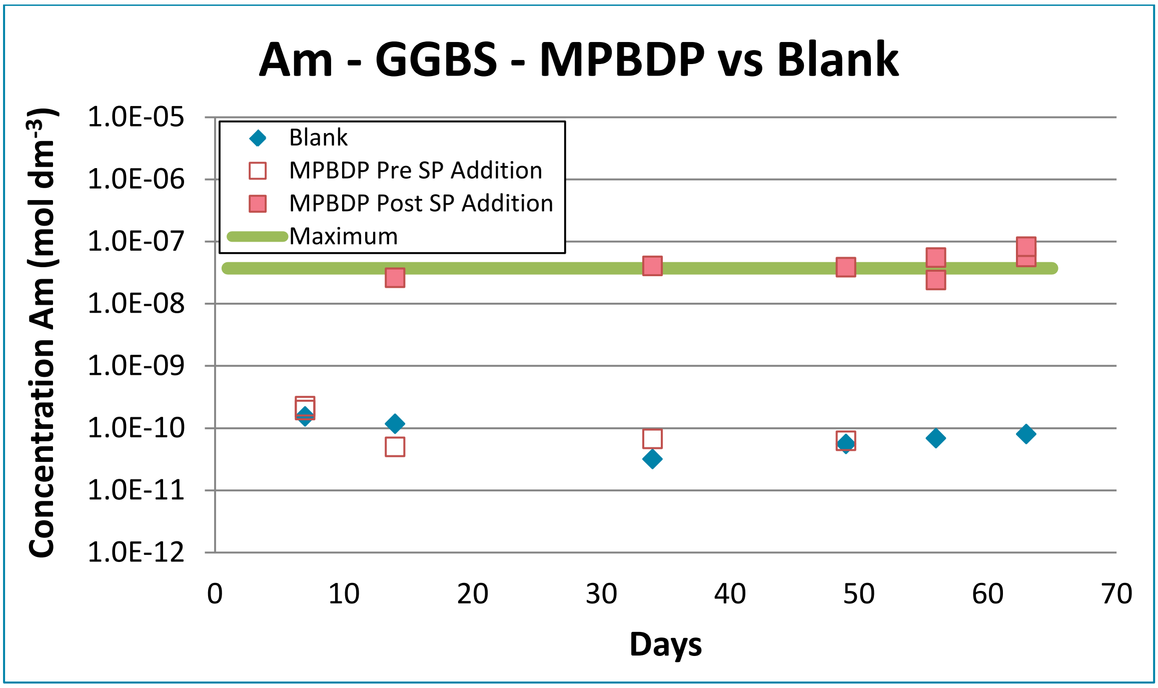

Figure A2. 54: Am - GGBS - WRBP vs Blank

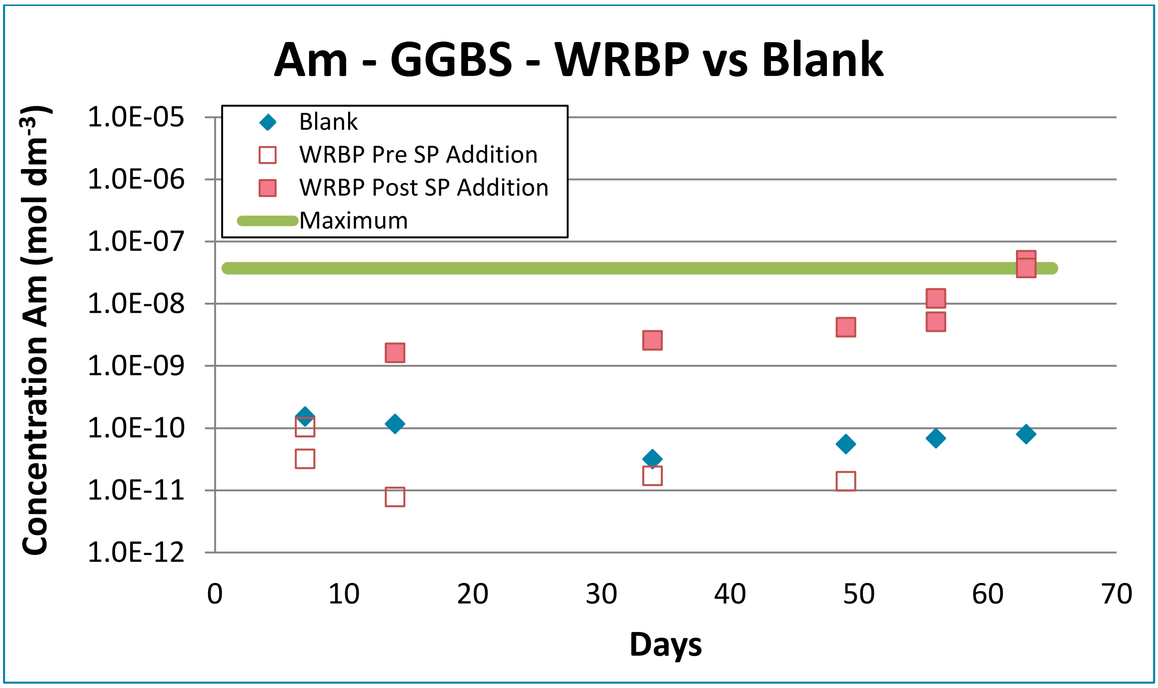

Figure A2. 55: Am - GGBS - WRBDP vs Blank

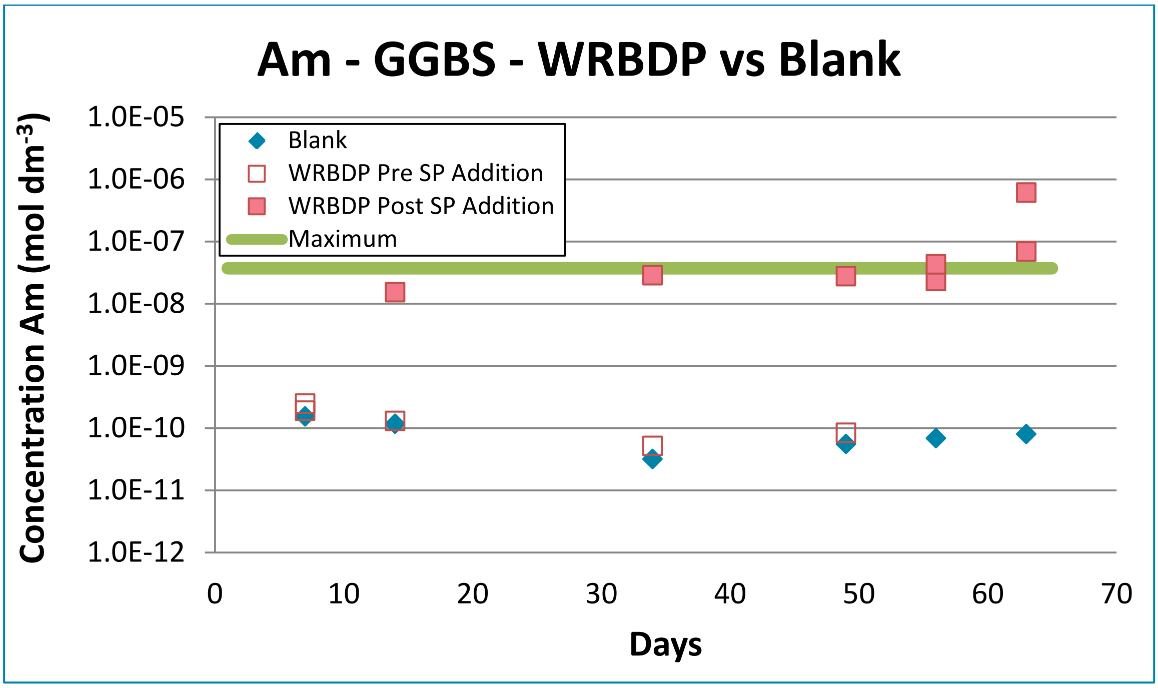

Figure A2. 56: Am - GGBS - FWBFP vs Blank

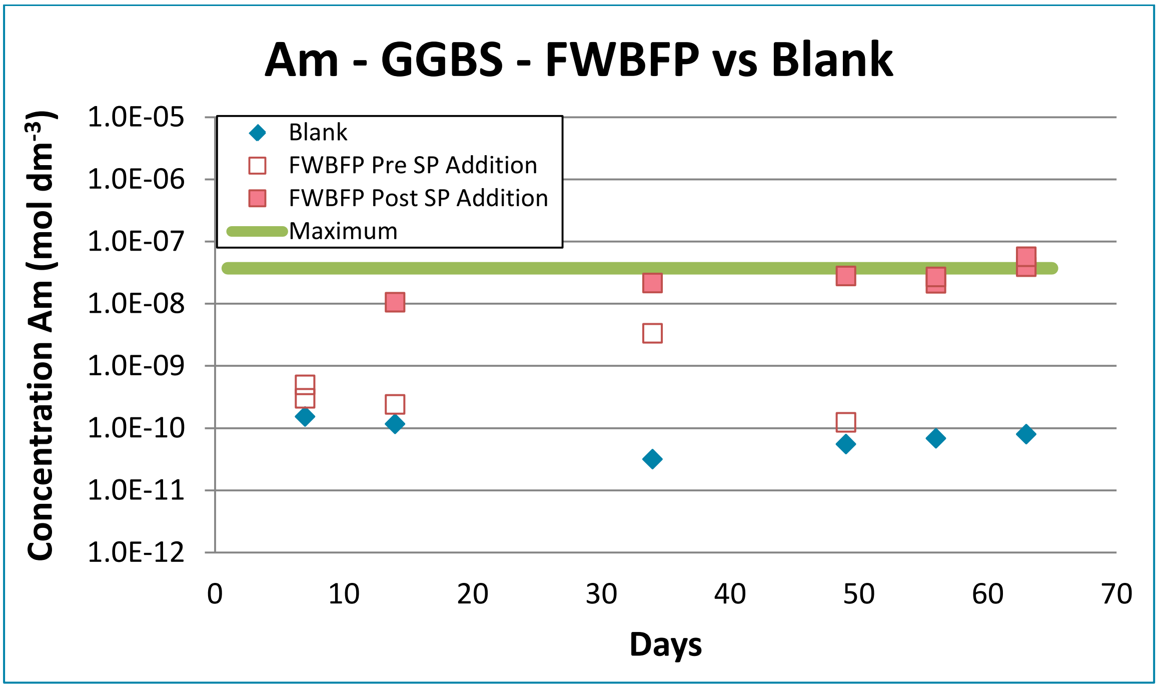

Table A2 1: Nickel Solubility Results

Cement	Additive	Sample	1 day	29 days	36 days	43 days	57 days	75 days
PFA	MPBDP	A	2.9E-08	3.3E-07	3.5E-07	3.6E-07	2.2E-05	2.7E-05
		B	7.0E-08	5.4E-08	4.4E-07	4.8E-07	2.6E-05	2.8E-05
		C	2.6E-08	3.9E-05	1.9E-05	1.9E-05	5.0E-05	4.2E-05
		D	3.2E-08	2.0E-04	5.9E-05	4.2E-05	7.4E-05	6.0E-05
	WRBP	A	1.3E-08	9.9E-08	1.4E-07	1.0E-07	2.6E-06	5.7E-06
		B	6.4E-09	1.2E-07	1.7E-07	1.8E-07	4.7E-06	7.0E-06
		C	4.5E-08	2.9E-05	5.9E-06	6.8E-06	1.1E-05	1.4E-05
		D	2.9E-08	7.8E-05	8.2E-06	7.4E-06	5.4E-06	1.3E-05
	WRBDP	A	3.8E-08	2.5E-07	1.7E-07	3.6E-07	4.2E-06	6.1E-06
		B	6.1E-08	1.9E-07	2.1E-07	2.3E-07	5.0E-06	6.2E-06
		C	2.6E-08	1.8E-05	3.0E-06	3.9E-06	7.8E-06	8.0E-06
		D	1.7E-07	9.6E-05	7.0E-06	9.9E-06	1.8E-05	1.8E-05
	FWBFP	A	1.9E-08	1.3E-07	1.5E-07	1.3E-07	2.6E-06	5.1E-06
		B	2.6E-08	1.2E-07	1.3E-07	1.5E-07	2.9E-06	4.7E-06
		C	1.6E-08	6.5E-05	2.0E-06	2.6E-06	4.8E-06	6.1E-06
		D	3.8E-08	3.4E-04	2.8E-06	3.7E-06	6.4E-06	7.9E-06
	BIO	A	0.0E+00	6.7E-08	5.4E-08	7.7E-08	6.7E-08	6.4E-08
		B	1.3E-08	5.4E-08	9.6E-08	1.0E-07	1.1E-07	1.2E-07
		C	1.3E-08	9.5E-07	6.7E-08	9.9E-08	9.3E-08	1.2E-07
		D	9.6E-09	3.5E-07	7.0E-08	8.3E-08	7.7E-08	7.3E-08
	VMA	A	1.6E-08	9.6E-08	6.4E-08	7.7E-08	2.2E-07	3.5E-07
		B	9.6E-09	9.6E-08	9.3E-08	1.1E-07	2.2E-07	3.5E-07
		C	3.2E-08	1.4E-07	2.0E-07	3.4E-07	3.5E-07	5.2E-07
		D	2.6E-08	3.0E-07	2.2E-07	3.5E-07	4.4E-07	5.7E-07
	DEF	A	2.9E-08	8.0E-08	6.7E-08	3.4E-07	1.8E-07	2.0E-07
		B	2.9E-08	1.1E-07	1.0E-07	1.0E-07	1.9E-07	2.2E-07
		C	2.2E-08	3.7E-06	1.3E-06	1.2E-07	1.9E-07	1.2E-07
		D	1.9E-08	1.4E-07	1.5E-07	2.7E-07	2.0E-07	2.1E-07
	LUSP 1	A	2.9E-08	2.0E-07	2.2E-07	2.4E-07	4.7E-07	4.7E-07

		B	2.6E-08	1.6E-07	1.9E-07	1.6E-07	1.1E-06	8.3E-07
		C	2.9E-08	1.1E-07	3.0E-07	4.3E-07	3.0E-06	9.6E-07
		D	1.3E-08	8.0E-06	5.5E-07	1.4E-06	4.6E-06	1.2E-06
	Blank	**A**	2.6E-08	8.3E-08	1.1E-07	1.1E-07	1.2E-07	1.1E-07
		B	3.0E-07	4.7E-07	7.3E-08	3.5E-07	8.9E-08	8.6E-08
		C	6.4E-07	6.1E-08	8.0E-08	9.6E-08	8.3E-08	8.9E-08
		D	3.4E-07	8.3E-08	8.9E-08	1.1E-07	1.9E-07	1.2E-07
GGBS	**MPBDP**	**A**	5.4E-08	3.3E-07	3.5E-07	3.6E-07	2.2E-05	2.7E-05
		B	6.1E-08	5.4E-08	4.4E-07	4.8E-07	2.6E-05	2.8E-05
		C	6.4E-08	3.9E-05	1.9E-05	1.9E-05	5.0E-05	4.2E-05
		D	2.9E-07	2.0E-04	5.9E-05	4.2E-05	7.4E-05	6.0E-05
	WRBP	**A**	5.8E-08	3.7E-07	3.2E-07	3.5E-07	2.1E-05	1.8E-05
		B	5.4E-08	2.6E-07	5.1E-07	4.1E-07	5.5E-05	3.1E-05
		C	1.3E-07	1.8E-05	6.6E-06	9.0E-06	4.2E-05	4.0E-05
		D	4.8E-08	2.3E-05	1.8E-05	1.3E-05	4.5E-05	4.2E-05
	WRBDP	**A**	4.2E-08	4.2E-07	3.0E-07	3.6E-07	1.3E-05	2.5E-05
		B	4.2E-08	NS	4.1E-07	1.3E-05	3.1E-05	2.7E-05
		C	4.5E-08	1.8E-04	2.1E-05	3.4E-05	5.5E-05	3.8E-05
		D	4.5E-08	2.2E-04	3.7E-05	3.9E-05	5.2E-05	3.9E-05
	FWBFP	**A**	6.1E-08	2.4E-07	2.9E-07	2.6E-07	1.1E-05	1.9E-05
		B	4.2E-08	3.6E-07	3.3E-07	1.8E-06	2.1E-05	2.3E-05
		C	1.9E-08	1.1E-04	1.2E-05	1.3E-05	3.9E-05	3.3E-05
		D	1.4E-05	1.5E-04	2.1E-05	1.9E-05	3.7E-05	3.4E-05
	BIO	**A**	2.6E-08	2.0E-07	1.7E-07	2.0E-07	2.3E-07	1.7E-07
		B	2.9E-08	2.1E-07	2.4E-07	2.4E-07	2.1E-07	2.4E-07
		C	2.6E-08	2.0E-07	2.2E-07	2.4E-07	2.3E-07	2.3E-07
		D	4.5E-08	2.3E-07	2.1E-07	3.2E-07	5.8E-07	2.4E-07
	VMA	**A**	1.3E-08	1.6E-07	1.5E-07	1.6E-07	3.9E-07	4.6E-07
		B	2.2E-08	1.9E-07	3.5E-07	2.0E-07	1.0E-06	5.3E-07
		C	2.6E-08	2.5E-07	1.8E-07	4.1E-07	4.7E-07	5.6E-07
		D	1.6E-08	2.8E-07	3.0E-07	4.0E-07	4.4E-07	5.6E-07

	DEF	**A**	3.2E-08	1.6E-07	1.8E-07	1.3E-07	3.1E-07	3.0E-07
		B	3.5E-08	1.8E-07	1.7E-07	3.0E-07	3.7E-07	3.6E-07
		C	2.2E-08	3.0E-07	4.1E-07	2.2E-07	3.9E-07	1.1E-06
		D	2.6E-08	2.6E-07	3.5E-07	2.9E-07	3.6E-07	4.0E-07
	LUSP 1	**A**	2.6E-08	2.3E-06	2.0E-07	5.1E-07	2.9E-06	1.8E-06
		B	2.9E-08	4.0E-05	2.9E-07	2.6E-07	9.3E-06	5.9E-06
		C	2.6E-08	6.0E-05	1.2E-06	1.5E-06	1.0E-05	8.4E-06
		D	1.9E-08	9.3E-05	7.8E-06	1.2E-06	1.1E-05	7.2E-06
	Blank	**A**	3.2E-08	2.1E-06	2.2E-07	3.8E-07	3.0E-07	3.4E-07
		B	4.5E-08	2.5E-06	3.2E-07	8.7E-07	3.2E-07	3.4E-07
		C	3.2E-08	1.8E-06	2.9E-07	3.0E-07	3.5E-07	3.1E-07
		D	4.2E-08	2.1E-06	2.9E-07	3.0E-07	2.7E-07	3.1E-07

Yellow highlighted area indicates SP mix or adjunct present

Table A2 2: Uranium Solubility Results

Cement	Additive	Sample	6 days	15 days	22 days	42 days	56 days	70 days
PFA	MPBDP	A	1.9E-05	1.9E-05	2.2E-05	1.6E-05	1.3E-05	9.1E-06
		B	1.2E-05	1.8E-05	2.0E-05	1.5E-05	1.2E-05	8.5E-06
		C	6.1E-06	8.2E-06	1.1E-05	1.1E-05	1.1E-05	9.2E-06
		D	4.4E-06	4.6E-06	7.3E-06	1.1E-05	1.3E-05	9.3E-06
	WRBP	A	1.6E-05	1.8E-05	1.7E-05	1.6E-05	1.1E-05	9.2E-06
		B	1.7E-05	1.4E-05	1.7E-05	1.4E-05	1.0E-05	8.2E-06
		C	1.5E-05	1.8E-05	2.1E-05	2.0E-05	2.0E-05	1.7E-05
		D	2.2E-05	1.6E-05	2.0E-05	2.2E-05	2.6E-05	2.2E-05
	WRBDP	A	9.0E-06	1.6E-05	2.1E-05	1.5E-05	1.1E-05	8.6E-06
		B	1.4E-05	1.8E-05	2.5E-05	1.7E-05	1.2E-05	7.7E-06
		C	1.5E-05	1.0E-05	1.7E-05	1.7E-05	1.8E-05	1.8E-05
		D	1.4E-05	1.7E-05	1.8E-05	1.7E-05	2.1E-05	3.3E-05
	FWBFP	A	1.5E-05	1.7E-05	2.0E-05	1.6E-05	1.3E-05	7.9E-06
		B	7.7E-06	1.7E-05	1.9E-05	1.6E-05	9.5E-06	8.6E-06
		C	2.9E-05	2.2E-05	2.5E-05	2.3E-05	3.0E-05	1.7E-05
		D	2.7E-05	3.5E-05	4.3E-05	4.0E-05	6.6E-05	3.3E-05
	BIO	A	2.6E-06	2.0E-06	2.2E-06	1.9E-06	1.1E-06	7.0E-07
		B	2.6E-06	2.1E-06	2.8E-06	1.8E-06	1.1E-06	7.2E-07
		C	1.8E-06	1.4E-06	1.7E-06	1.3E-06	1.1E-06	6.3E-07
		D	2.4E-06	1.2E-06	1.4E-06	1.1E-06	1.0E-06	6.6E-07
	VMA	A	4.8E-06	2.8E-06	2.3E-06	2.1E-06	1.3E-06	8.9E-07
		B	1.0E-05	3.9E-06	2.9E-06	2.2E-06	1.3E-06	7.7E-07
		C	2.7E-06	2.5E-06	2.1E-06	1.8E-06	1.4E-06	8.7E-07
		D	3.4E-06	2.8E-06	2.0E-06	1.8E-06	1.5E-06	1.1E-06
	DEF	A	4.9E-06	3.1E-06	2.4E-06	2.2E-06	1.3E-06	1.6E-05
		B	3.3E-06	3.0E-06	2.3E-06	2.3E-06	1.3E-06	4.4E-06
		C	2.0E-06	1.9E-06	1.6E-06	1.8E-06	1.2E-06	3.4E-06
		D	2.3E-06	1.5E-06	1.3E-06	1.5E-06	1.1E-06	3.0E-06

	LUSP 1	A	5.0E-06	3.7E-06	2.7E-06	2.8E-06	1.4E-06	8.9E-07
		B	7.4E-06	3.1E-06	2.5E-06	2.4E-06	1.3E-06	9.0E-07
		C	3.9E-06	2.4E-06	2.3E-06	2.4E-06	2.2E-06	2.1E-06
		D	6.5E-06	4.9E-06	4.6E-06	4.1E-06	3.6E-06	2.9E-06
	Blank	A	9.5E-07	1.4E-06	1.4E-06	1.7E-06	1.0E-06	6.4E-07
		B	9.7E-07	1.4E-06	1.3E-06	1.5E-06	2.0E-05	6.2E-07
		C	1.3E-06	1.3E-06	1.4E-06	1.5E-06	1.0E-06	6.4E-07
		D	1.2E-06	1.1E-06	9.7E-07	1.2E-06	9.2E-07	5.2E-07
GGBS	MPBDP	A	2.4E-06	6.5E-06	6.3E-06	6.5E-06	2.5E-06	1.1E-06
		B	4.5E-06	6.0E-06	6.3E-06	5.5E-06	1.7E-06	8.9E-07
		C	4.4E-06	5.1E-06	4.9E-06	7.5E-06	1.4E-05	1.1E-05
		D	1.5E-05	4.9E-06	5.0E-06	8.0E-06	1.6E-05	1.3E-05
	WRBP	A	6.2E-07	3.9E-06	2.7E-06	3.3E-06	2.7E-06	1.8E-06
		B	1.5E-06	3.7E-06	3.0E-06	4.0E-06	3.1E-06	1.9E-06
		C	1.3E-05	1.7E-05	1.5E-05	1.8E-05	1.4E-05	1.0E-05
		D	4.7E-05	2.0E-05	1.9E-05	2.1E-05	1.9E-05	1.4E-05
	WRBDP	A	2.4E-06	7.3E-06	5.6E-06	5.4E-06	9.8E-07	5.1E-07
		B	2.3E-06	6.8E-06	5.8E-06	5.0E-06	1.6E-06	7.3E-07
		C	1.2E-05	3.0E-05	2.6E-05	2.9E-05	3.3E-05	2.2E-05
		D	4.2E-05	4.7E-05	4.0E-05	4.3E-05	4.6E-05	2.9E-05
	FWBFP	A	1.4E-06	5.5E-06	3.2E-06	1.5E-06	7.8E-07	2.8E-07
		B	2.2E-06	5.4E-06	3.4E-06	1.6E-06	8.6E-07	4.4E-07
		C	8.3E-06	2.9E-05	3.0E-05	3.3E-05	2.9E-05	2.1E-05
		D	1.3E-05	3.6E-05	4.0E-05	4.2E-05	3.8E-05	3.2E-05
	BIO	A	2.3E-06	6.3E-06	5.0E-06	6.8E-06	3.8E-06	1.6E-06
		B	1.8E-06	5.9E-06	5.8E-06	6.7E-06	4.6E-06	2.4E-06
		C	1.7E-06	6.1E-06	4.3E-06	3.5E-06	2.3E-06	1.2E-06
		D	2.6E-06	4.7E-06	4.5E-06	2.8E-06	1.6E-06	8.9E-07

	VMA	**A**	1.4E-06	6.4E-06	5.4E-06	6.2E-06	3.8E-06	1.8E-06
		B	2.7E-06	5.7E-06	5.8E-06	6.3E-06	4.0E-06	1.8E-06
		C	2.9E-06	6.3E-06	4.9E-06	5.9E-06	3.3E-06	1.5E-06
		D	6.2E-07	5.1E-06	5.0E-06	6.2E-06	3.1E-06	1.8E-06
	DEF	**A**	2.7E-06	4.1E-06	1.6E-06	1.5E-06	6.4E-07	3.5E-07
		B	2.6E-06	4.5E-06	1.8E-06	1.3E-06	7.4E-07	3.5E-07
		C	2.0E-06	2.1E-06	8.8E-07	1.0E-06	7.0E-07	3.6E-07
		D	5.0E-07	1.2E-06	6.6E-07	9.2E-07	6.9E-07	3.4E-07
	LUSP 1	**A**	2.1E-06	6.9E-06	2.9E-06	1.6E-06	7.1E-07	3.3E-07
		B	2.4E-06	6.2E-06	2.6E-06	1.4E-06	6.9E-07	3.7E-07
		C	3.5E-06	8.1E-06	4.5E-06	4.2E-06	3.6E-06	2.9E-06
		D	7.1E-06	8.7E-06	5.8E-06	6.2E-06	5.6E-06	4.5E-06
	Blank	**A**	1.0E-06	7.4E-06	6.1E-06	6.2E-06	1.4E-06	7.0E-07
		B	2.4E-06	7.1E-06	6.0E-06	6.4E-06	1.5E-06	7.9E-07
		C	3.1E-06	7.7E-06	6.3E-06	6.1E-06	1.3E-06	6.7E-07
		D	1.1E-06	7.5E-06	6.0E-06	7.2E-06	7.6E-06	3.5E-06

Yellow highlighted area indicates SP mix or adjunct present

Table A2 3: ^{239}Pu Solubility Results

Cement	Additive	Sample	20 days	28 days	36 days	42 days	53 days	78 days	95 days
PFA	MPBDP	A	4.0E-10	3.8E-10	3.9E-07	2.1E-07	3.6E-10	1.1E-07	1.6E-07
		B	5.6E-10	5.2E-10	5.7E-07	6.6E-07	7.8E-10	3.7E-07	3.8E-07
		C	7.8E-10	4.1E-07	7.0E-07	4.8E-07	3.7E-07	1.1E-06	1.0E-06
		D	7.0E-10	1.0E-06	3.2E-07	2.2E-07	1.0E-06	1.5E-06	1.4E-06
	WRBP	A	5.5E-10	7.2E-08	8.0E-08	5.5E-08	4.6E-10	7.6E-08	9.6E-08
		B	4.2E-10	1.1E-07	8.8E-08	1.0E-07	6.4E-10	1.6E-07	8.6E-07
		C	7.9E-10	8.5E-08	9.4E-08	1.1E-07	7.0E-07	1.6E-06	2.9E-06
		D	1.0E-09	7.6E-09	1.7E-08	2.1E-08	1.1E-06	2.1E-06	3.0E-06
	WRBDP	A	4.0E-10	1.2E-07	7.3E-08	4.4E-08	3.5E-10	3.4E-07	3.4E-07
		B	6.4E-10	2.3E-07	1.2E-07	8.0E-08	8.9E-10	2.2E-07	2.4E-07
		C	6.7E-10	2.2E-07	1.7E-07	1.1E-07	8.6E-07	1.3E-06	1.2E-06
		D	2.9E-09	1.0E-07	7.7E-08	6.5E-08	1.1E-06	1.6E-06	1.7E-06
	FWBFP	A	3.2E-10	8.0E-08	4.9E-08	7.0E-08	1.1E-09	1.7E-07	1.6E-07
		B	5.0E-10	9.7E-08	5.6E-08	6.9E-08	6.8E-10	4.6E-07	3.6E-07
		C	4.0E-10	5.4E-08	3.6E-08	5.3E-08	1.6E-07	6.7E-07	6.4E-07
		D	8.4E-10	1.3E-08	1.2E-08	1.7E-08	3.7E-07	5.3E-07	5.2E-07
	BIO	A	5.3E-10	4.2E-10	3.2E-10	3.8E-10	1.7E-07	2.9E-09	6.4E-10
		B	3.4E-10	4.5E-10	2.8E-10	3.2E-10	2.2E-07	4.1E-09	9.7E-10
		C	3.9E-10	4.6E-10	1.8E-10	3.5E-10	1.4E-07	4.6E-09	1.7E-09
		D	3.5E-10	1.9E-10	2.7E-10	2.8E-10	1.2E-07	5.5E-09	1.4E-09
	VMA	A	5.9E-10	1.2E-09	1.0E-09	5.6E-10	4.6E-10	2.5E-09	2.6E-09
		B	3.8E-10	1.0E-09	1.0E-09	4.5E-10	4.0E-10	5.9E-09	3.1E-09
		C	4.7E-10	1.7E-09	1.8E-09	1.2E-09	2.1E-09	2.2E-08	5.1E-09
		D	6.2E-10	1.3E-09	1.7E-09	4.5E-10	3.5E-09	8.8E-08	4.4E-09
	DEF	A	3.4E-10	4.4E-10	3.9E-10	4.1E-10	2.7E-10	4.9E-10	4.2E-10
		B	3.0E-10	6.2E-10	2.8E-10	3.8E-10	3.2E-10	4.2E-10	2.3E-10
		C	7.2E-10	6.5E-10	5.1E-10	2.5E-10	3.9E-10	4.5E-10	4.0E-10
		D	3.0E-10	2.1E-10	3.8E-10	4.0E-10	4.5E-10	4.7E-10	4.7E-10
	LUSP 1	A	4.5E-10	8.4E-08	4.5E-08	8.0E-08	2.9E-10	2.2E-08	4.0E-08

		B	5.7E-10	6.9E-08	5.1E-08	5.4E-08	1.2E-09	9.2E-08	1.4E-07
		C	4.5E-10	3.1E-08	1.9E-08	2.8E-08	1.3E-08	1.8E-07	2.1E-07
		D	7.9E-10	1.0E-08	4.2E-09	1.1E-08	2.7E-08	2.3E-07	2.3E-07
	Blank	A	1.9E-10	2.7E-10	3.4E-10	3.8E-10	2.7E-10	2.4E-10	4.4E-10
		B	2.7E-10	2.7E-10	6.3E-10	4.2E-10	4.1E-10	4.4E-10	3.6E-10
		C	2.8E-10	3.5E-10	3.9E-10	4.6E-10	3.4E-10	4.4E-10	4.6E-10
		D	3.9E-10	2.1E-10	2.2E-10	2.7E-10	4.7E-10	4.6E-10	4.1E-10
GGBS	**MPBDP**	A	7.2E-09	7.4E-09	6.6E-09	7.4E-09	7.0E-09	1.1E-06	2.0E-08
		B	9.1E-09	8.3E-09	9.2E-09	9.0E-09	7.7E-09	3.9E-07	3.3E-08
		C	6.7E-09	1.3E-08	1.6E-08	1.5E-08	3.1E-08	4.3E-07	5.4E-08
		D	9.3E-09	1.5E-08	1.8E-08	1.9E-08	7.5E-08	3.9E-07	9.8E-08
	WRBP	A	1.5E-06	2.2E-06	2.3E-06	2.3E-06	1.5E-06	2.8E-06	1.6E-06
		B	3.2E-06	3.6E-06	3.7E-06	3.4E-06	2.7E-06	3.0E-06	3.3E-06
		C	3.5E-06	3.3E-06	3.1E-06	3.2E-06	3.3E-06	3.3E-06	3.5E-06
		D	3.3E-06	2.6E-06	2.4E-06	2.7E-06	2.8E-06	3.2E-06	3.2E-06
	WRBDP	A	3.0E-09	4.0E-08	4.3E-09	3.7E-09	2.3E-09	7.3E-07	9.7E-09
		B	3.3E-09	3.1E-08	9.7E-09	9.5E-09	9.2E-09	1.7E-06	9.0E-08
		C	2.8E-09	4.3E-08	2.8E-08	2.6E-08	3.8E-07	1.6E-06	1.2E-06
		D	3.0E-09	3.2E-08	2.5E-08	2.9E-08	1.1E-06	2.2E-06	2.1E-06
	FWBFP	A	1.1E-09	3.6E-08	2.0E-08	1.7E-08	9.8E-10	1.6E-07	4.1E-07
		B	1.3E-09	3.8E-08	3.2E-08	3.0E-08	1.3E-09	1.1E-06	1.9E-06
		C	1.8E-09	5.6E-08	3.4E-08	3.8E-08	3.5E-08	5.8E-07	7.6E-07
		D	1.8E-09	2.7E-08	1.9E-08	2.3E-08	7.0E-08	2.0E-07	1.3E-07
	BIO	A	3.5E-09	1.8E-09	2.2E-09	1.7E-09	1.5E-09	3.9E-09	1.3E-09
		B	2.6E-09	2.5E-09	2.2E-09	2.2E-09	2.3E-09	2.6E-09	6.3E-10
		C	2.9E-09	1.9E-09	2.1E-09	2.4E-09	3.3E-09	4.0E-09	5.9E-10
		D	1.9E-09	6.5E-10	1.2E-09	1.2E-09	2.6E-09	2.4E-09	8.5E-10
	VMA	A	5.1E-10	7.4E-10	6.1E-10	6.8E-10	4.1E-10	5.9E-10	4.7E-10
		B	2.5E-09	1.2E-09	9.3E-10	NR	1.1E-09	7.0E-10	4.2E-10
		C	1.7E-09	1.0E-09	9.3E-10	1.1E-09	9.9E-10	1.0E-09	9.0E-10

		D	2.3E-09	1.1E-09	1.2E-09	1.1E-09	9.7E-10	1.1E-09	1.0E-09
	DEF	**A**	9.9E-10	1.4E-09	1.5E-09	1.3E-09	1.3E-09	1.1E-07	4.1E-10
		B	1.5E-09	1.4E-09	1.9E-09	1.5E-09	1.6E-09	1.3E-07	7.6E-10
		C	1.3E-09	1.4E-09	1.3E-09	9.7E-10	1.4E-09	1.5E-07	7.4E-10
		D	2.9E-09	1.1E-09	1.4E-09	1.2E-09	1.4E-09	1.3E-07	7.5E-10
	LUSP 1	**A**	6.7E-10	3.4E-09	1.8E-09	1.8E-09	1.1E-09	1.9E-09	1.3E-09
		B	1.6E-09	5.3E-09	2.2E-09	2.8E-09	1.5E-09	4.5E-09	1.7E-09
		C	1.5E-09	4.1E-09	1.4E-09	1.8E-09	1.9E-09	6.0E-09	3.2E-09
		D	4.1E-09	2.2E-09	1.0E-09	1.2E-09	2.1E-09	7.3E-09	6.1E-10
	Blank	**A**	3.7E-09	3.8E-09	3.0E-09	3.2E-09	2.9E-09	6.7E-09	8.2E-10
		B	3.9E-09	2.7E-09	2.7E-09	2.9E-09	2.5E-09	4.5E-09	1.5E-09
		C	1.7E-09	2.7E-09	3.0E-09	3.0E-09	3.1E-09	3.8E-09	7.9E-10
		D	4.5E-09	3.4E-09	1.8E-09	3.6E-09	2.6E-09	4.1E-09	4.5E-09

Yellow highlighted area indicates SP mix or adjunct present

Table A2 4: ^{241}Am Solubility Results

Cement	Additive	Sample	7 days	14 days	34 days	49 days	56 days	63 days
PFA	MPBDP	A	1.6E-10	9.6E-11	1.4E-11	2.8E-11	3.7E-08	2.3E-08
		B	6.3E-11	1.0E-08	1.1E-08	1.1E-08	1.1E-08	2.6E-08
	WRBP	A	1.2E-11	6.0E-09	1.3E-12	3.3E-12	2.3E-08	3.1E-08
		B	1.6E-11	1.1E-08	7.5E-09	8.0E-09	1.9E-08	2.7E-08
	WRBDP	A	4.1E-11	2.0E-11	1.3E-11	1.6E-11	1.9E-08	2.1E-08
		B	3.6E-11	5.5E-09	6.2E-09	7.3E-09	2.2E-08	2.8E-08
	FWBFP	A	1.2E-10	3.1E-11	9.1E-11	3.5E-11	1.8E-08	3.0E-08
		B	2.8E-10	9.7E-09	9.4E-09	1.0E-08	2.5E-08	4.3E-08
	Blank	A	9.6E-11	2.0E-11	9.4E-11	3.2E-11	6.6E-11	1.3E-10
GGBS	MPBDP	A	1.9E-10	5.0E-11	6.7E-11	6.3E-11	2.4E-08	5.6E-08
		B	2.2E-10	2.6E-08	4.0E-08	3.9E-08	5.5E-08	8.2E-08
	WRBP	A	3.2E-11	7.8E-12	1.7E-11	1.4E-11	1.2E-08	5.0E-08
		B	1.0E-10	1.6E-09	2.6E-09	4.2E-09	5.1E-09	3.8E-08
	WRBDP	A	1.9E-10	1.3E-10	5.2E-11	8.3E-11	2.3E-08	6.1E-07
		B	2.5E-10	1.5E-08	2.9E-08	2.8E-08	4.3E-08	6.9E-08
	FWBFP	A	3.0E-10	2.4E-10	3.3E-09	1.2E-10	2.1E-08	4.0E-08
		B	5.0E-10	1.1E-08	2.2E-08	2.8E-08	2.7E-08	5.7E-08
	Blank	A	1.5E-10	1.2E-10	3.2E-11	5.5E-11	6.8E-11	8.0E-11

Yellow highlighted area indicates SP mix or adjunct present

Appendix 3: Through-Diffusion and Intact Leaching Results

Key for autoradiography plates:

A) WRBDP
B) MPBDP
C) FWBFP
D) WRBP
E) LUSP 1
F) LUSP 2
G) BIO
H) DEF
I) VMA
J) Blank

Figure A3. 1: GGBS ^{63}Ni Autoradiographs 60hr Exposure on a Coated Plate

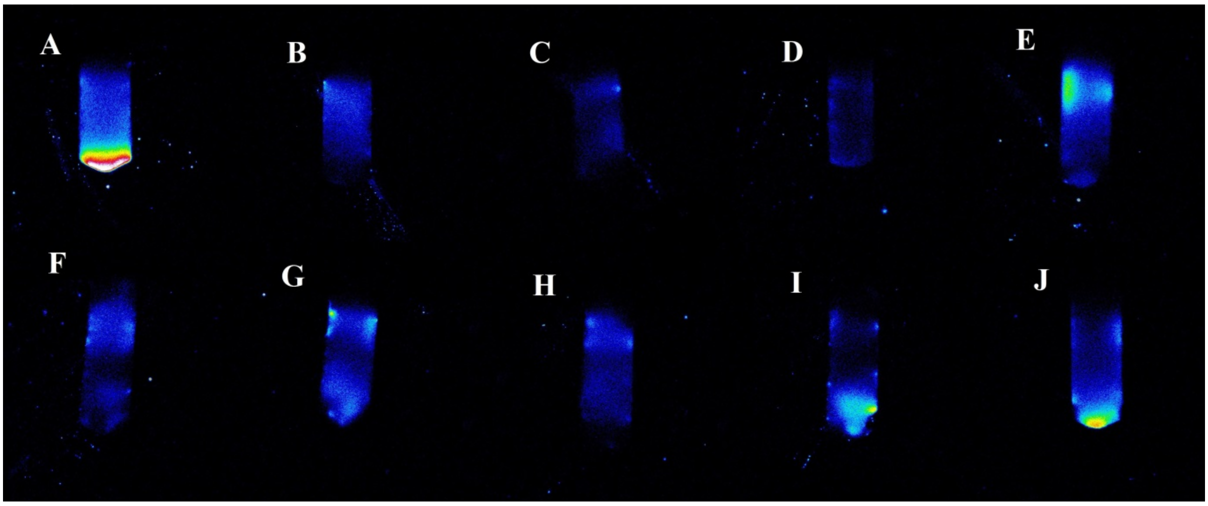

Figure A3. 2: PFA ^{63}Ni Autoradiographs 60hr Exposure on a Coated Plate

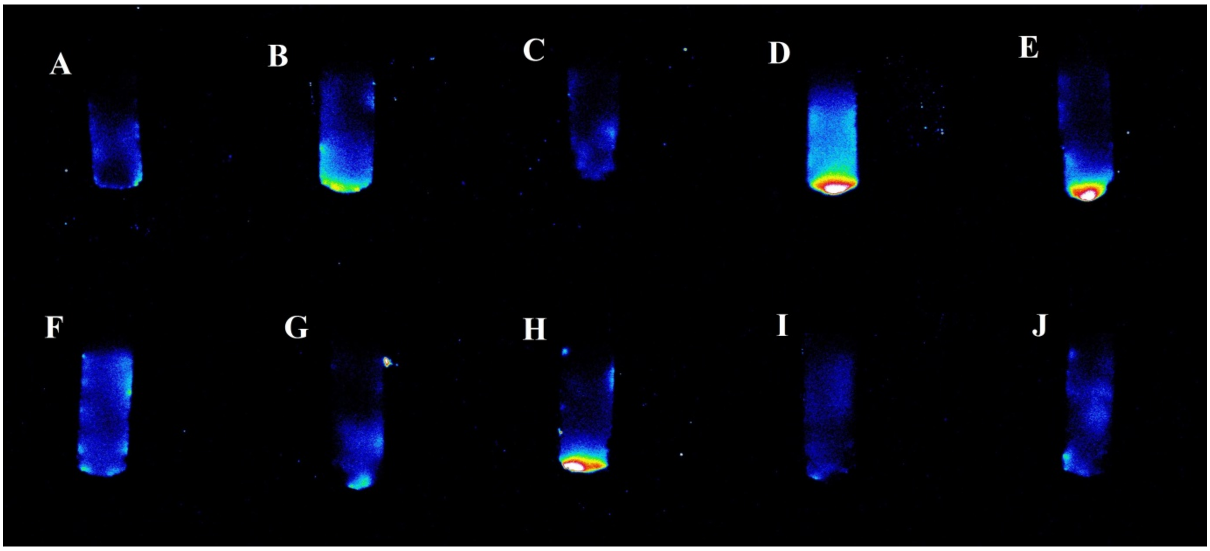

Figure A3. 3: GGBS Uranium Autoradiographs 18hr Exposure on an Uncoated Plate

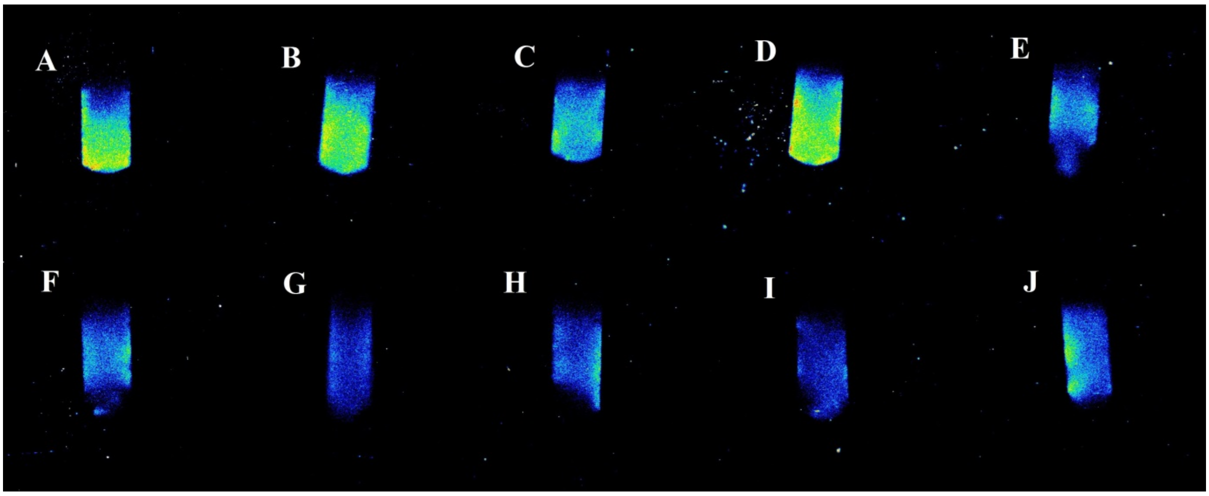

Figure A3. 4: PFA Uranium Autoradiographs 18hr Exposure on an Uncoated Plate

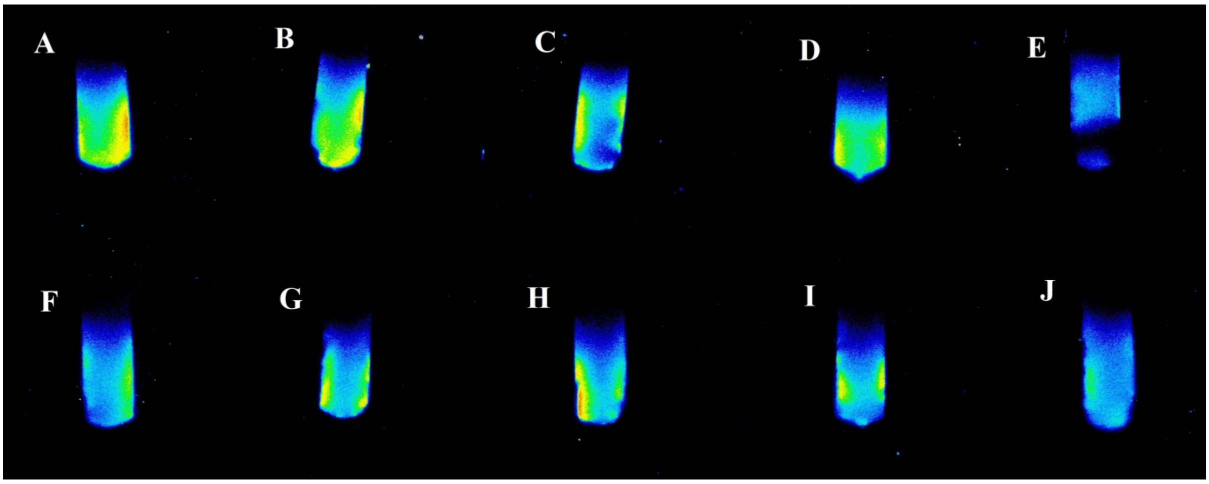

Figure A3. 5: GGBS ^{239}Pu Autoradiographs 4hr Exposure on an Uncoated Plate

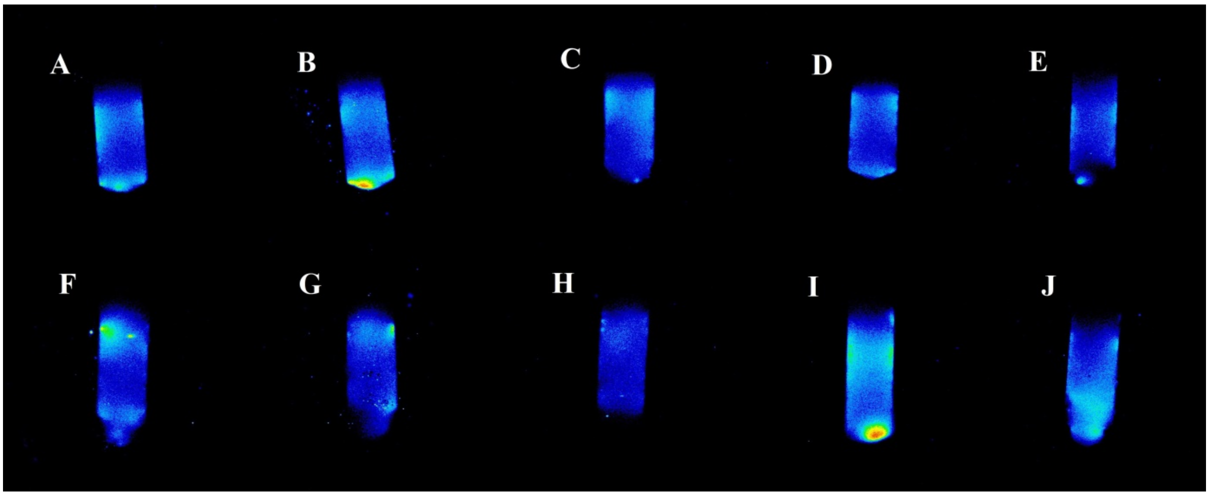

Figure A3. 6: PFA ^{239}Pu Autoradiographs 4hr Exposure on an Uncoated Plate

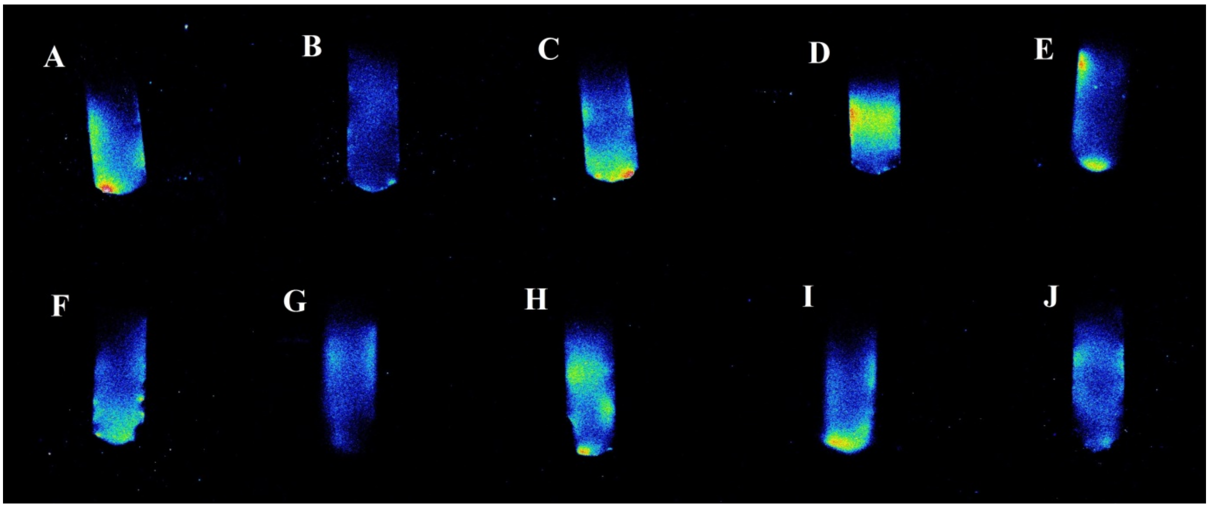

Figure A3. 7: GGBS ^{241}Am Autoradiographs 4hr Exposure on a Coated Plate

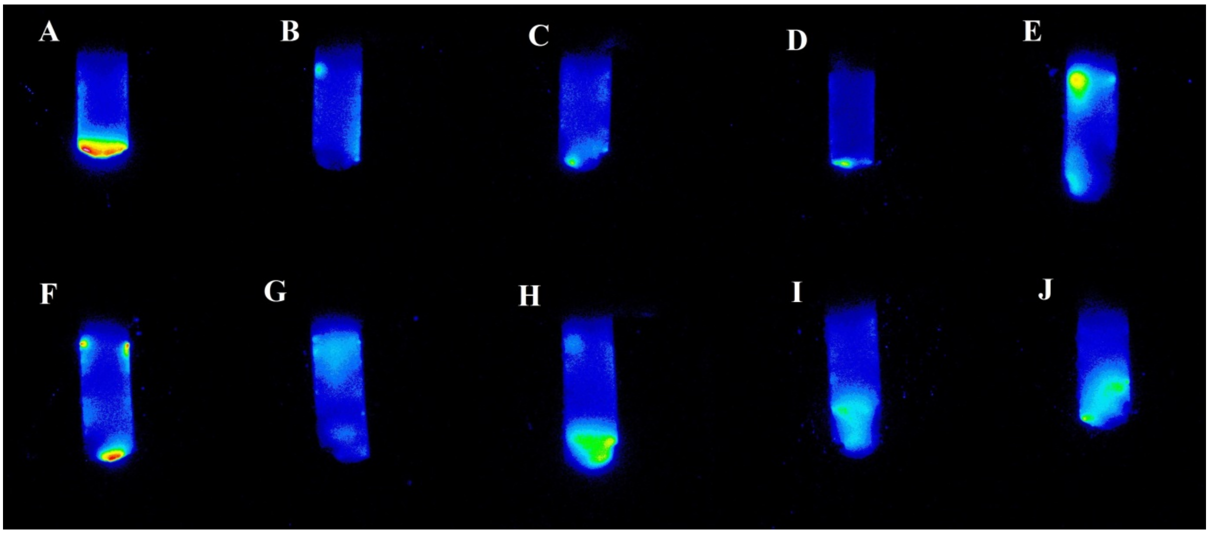

Figure A3. 8: PFA ^{241}Am Autoradiographs 4hr Exposure on a Coated Plate

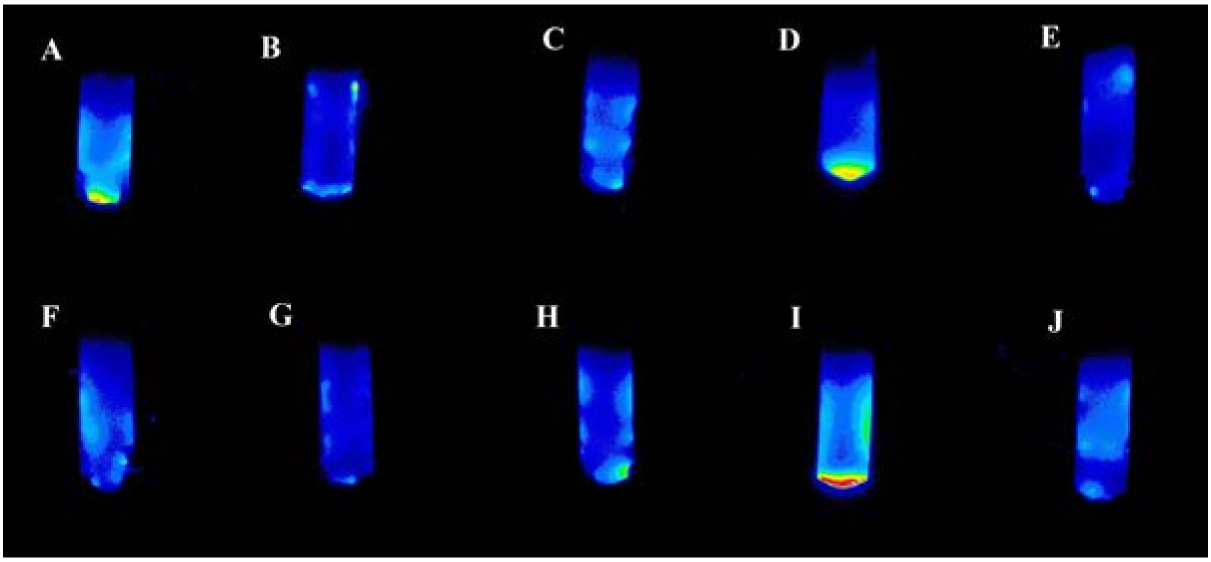

Table A3. 1: GGBS Uranium Intact Leach Results

GGBS - U	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(ppb)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	0.05	0.06	0.08	0.06	0.01	0.02	0.02	0.12	0.09	0.09	0.02	0.15	0.57	0.04	0.05	0.13	0.20
MPBDP	0.13	0.10	0.07	0.05	0.05	0.06	0.04	0.10	0.04	0.02	0.02	0.14	0.36	0.03	0.02	0.07	0.13
FWBFP	0.96	0.45	0.39	0.56	0.06	0.20	0.23	0.40	0.09	0.57	1.27	0.52	0.85	0.18	0.12	0.37	0.43
WRBP	10.91	0.39	0.37	0.49	0.12	0.23	0.33	0.60	0.07	0.18	1.13	59.30	0.62	0.31	1.58	0.59	0.27
LUSP 1	0.03	ND	ND	0.02	ND	ND	0.05	ND	ND	ND	ND	0.15	0.22	ND	0.07	2.36	0.06
LUSP 2	ND	0.02	ND	0.07	ND	ND	ND	0.04	ND	0.00	0.08	0.23	ND	0.12	14.40	ND	ND
BIO	ND	ND	ND	ND	ND	ND	ND	0.01	ND	ND	0.05	0.55	0.04	ND	ND	0.03	0.11
DEF	ND	0.00	ND	ND	ND	ND	0.01	0.05	ND	ND	0.08	0.53	0.16	0.19	0.00	0.10	0.19
VMA	0.02	0.09	0.09	0.12	0.04	0.07	0.07	0.17	0.09	0.04	0.18	0.27	0.47	0.04	0.14	0.07	0.09
Blank	0.02	0.07	0.05	0.05	0.27	0.02	0.05	0.07	0.03	0.03	0.10	0.18	0.24	0.15	0.10	0.35	0.07

Table A3. 2: PFA Uranium Intact Leach Results

PFA - U	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(ppb)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	6.43	0.32	0.22	0.43	0.64	0.45	0.44	0.51	0.49	0.31	0.32	0.45	0.23	0.24	0.22	0.20	0.21
MPBDP	6.14	0.14	0.11	0.82	0.96	0.93	0.98	1.28	1.22	0.88	0.78	0.59	0.47	0.78	0.73	0.48	0.49
FWBFP	4.71	0.84	0.92	1.43	0.84	0.49	0.45	0.60	0.50	0.37	0.36	0.57	0.54	0.31	0.37	0.23	0.24
WRBP	20.26	0.89	0.78	2.07	2.20	2.11	2.29	3.34	3.42	2.49	2.63	1.58	0.93	1.94	1.96	1.48	1.48
LUSP 1	4.57	0.01	0.14	0.11	0.22	0.50	0.85	1.21	1.92	1.02	1.98	0.64	1.67	1.45	2.16	1.16	1.28
LUSP 2	2.72	ND	0.02	0.10	0.01	0.12	0.06	0.30	0.27	0.26	0.23	0.02	0.07	0.28	0.26	0.19	0.17
BIO	4.64	0.10	ND	0.54	ND	0.70	0.31	1.32	1.16	0.90	1.04	0.72	0.15	1.06	1.02	0.92	0.93
DEF	3.18	ND	ND	0.12	ND	0.34	0.06	0.75	0.66	0.67	0.73	0.53	1.06	0.76	0.66	0.83	0.51
VMA	2.43	0.03	ND	0.34	ND	0.53	0.22	0.89	0.94	0.87	0.83	0.52	0.14	1.04	0.96	0.90	0.63
Blank	3.83	0.19	0.01	0.49	0.03	0.45	0.40	0.86	0.79	0.03	ND	0.07	0.37	0.86	0.80	0.84	0.65

Table A3. 3: GGBS Nickel Intact Leaching Results

GGBS - Ni-63	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	11.4	ND	ND	ND	ND	5.2	ND	0.6	ND	ND	5.2	ND	18.8	ND	ND	ND	0.2
MPBDP	2.6	ND	ND	0.8	ND	ND	ND	ND	ND	1.2	ND	0.4	ND	ND	ND	ND	ND
FWBFP	ND	ND	ND	ND	ND	ND	ND	0.6	ND	ND	3.8	ND	0.8	ND	1.4	ND	ND
WRBP	11.4	ND	ND	ND	ND	0.8	1.6	3.4	2.4	3.2	ND	1.4	ND	0.6	ND	1.2	ND
LUSP 1	ND	2.0	ND	ND	ND	ND	ND	ND	ND	ND	1.6	ND	ND	ND	ND	1.6	1.4
LUSP 2	ND	ND	1.6	ND	ND	ND	0.8	10.4	ND	ND	1.6	ND	ND	ND	ND	ND	ND
BIO	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6	ND	ND	ND	1.8	ND	ND	0.2
DEF	ND	0.8	ND	ND	1.6	ND	ND	ND	0.4	ND	ND	ND	ND	1.6	ND	ND	ND
VMA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND
Blank	ND	3	ND	0.8	ND	ND	2.2	ND	ND	ND	ND	ND	ND	ND	4.0	ND	ND

Table A3. 4: PFA Nickel Intact Leaching Results

PFA - Ni-63	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	20.8	0.6	2.8	ND	ND	2.4	ND	0.8	ND	1.4	9.2	ND	ND	3.2	ND	ND	0.8
MPBDP	33.2	0.6	2.4	0.2	0.4	ND	0.4	0.6	2.4	ND	ND	5.4	ND	ND	ND	2.8	ND
FWBFP	24.8	ND	0.4	ND	1.6	ND	3.2	2	0.2	ND	0.6	ND	ND	0.4	0.2	ND	ND
WRBP	28.8	ND	ND	ND	4.8	0.8	1.6	ND	ND	0.8	5.2	3.2	4.4	3.2	0.2	0.2	1.2
LUSP 1	1.4	ND	ND	ND	0.2	ND	ND	0.8	ND	ND	ND	ND	ND	4.2	ND	2.8	0.2
LUSP 2	4.6	4.8	ND	0.6	ND	ND	ND	7.0	ND	1.0	ND	ND	ND	3.0	1.8	0.2	ND
BIO	3.0	0.2	ND	ND	0.6	ND	4.0	ND	0.8	ND	ND	14.6	ND	ND	ND	ND	0.6
DEF	0.2	ND	ND	ND	0.4	ND	ND	2.2	ND	0.6	ND	ND	6	ND	0.2	ND	0.8
VMA	1.6	ND	ND	ND	ND	ND	ND	1.6	ND	ND	1.8	ND	12.6	ND	ND	2.8	7.8
Blank	ND	4.8	6.6	3.2	ND	ND	ND	2.8	44.8	ND	0.6	1.4	0.2	0.8	0.6	2.2	1.4

Table A3. 5: GGBS Plutonium Intact Leaching Results

GGBS - Pu-239	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	0.6	ND	0.4	ND	0.4	1.4	ND	ND	ND	2.2	ND	ND	ND	ND	ND	ND	2.2
MPBDP	ND	1.6	0.4	ND	ND	ND	0.4	ND	ND	0.6	ND	0.2	0.8	0.6	ND	ND	ND
FWBFP	ND	ND	0.4	ND	0.6	ND	0.4	2.6	1.8	1.6	ND	ND	0.4	ND	ND	0.6	ND
WRBP	1.8	1.6	ND	3.0	ND	ND	ND	0.2	ND	1.8	ND	ND	ND	2.8	1.2	0.8	ND
LUSP 1	2.6	ND	ND	0.8	0.6	1.6	1.2	2.2	ND	0.6	ND	ND	ND	ND	ND	ND	ND
LUSP 2	1.6	ND	ND	0.2	ND	ND	ND	2.0	ND	0.4	ND	ND	1.8	2.6	ND	ND	ND
BIO	ND	ND	ND	2.8	0.4	ND	1.0	ND	0.4	2.2	ND	ND	ND	0.4	ND	ND	ND
DEF	0.4	ND	1.0	ND	ND	ND	1.4	0.6	1.2	ND	ND	ND	1.8	ND	0.8	0.8	0.2
VMA	ND	ND	0.4	ND	ND	ND	1.2	0.4	ND	2.0	ND	ND	ND	ND	ND	ND	ND
Blank	0.2	ND	0.4	0.2	1.2	ND	1.2	1.8	ND	ND	1.2	ND	0.6	ND	ND	ND	ND

Table A3. 6: PFA Plutonium Intact Leaching Results

PFA - Pu-239	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	1.4	1.0	ND	ND	ND	ND	0.6	ND	2.2	0.2	ND	ND	ND	2.2	0.8	1.4	1.0
MPBDP	1.8	0.2	1.2	0.6	0.6	0.4	ND	0.6	ND	0.8	ND	ND	1.4	ND	2.2	2.0	1.4
FWBFP	1.6	ND	ND	ND	2.0	0.6	ND	0.4	ND	0.6	ND	1.6	0.6	0.4	ND	0.6	1.0
WRBP	0.2	ND	ND	0.6	0.4	0.6	1.8	0.4	1.0	1.6	1.6	1.8	ND	2.4	0.6	0.6	1.2
LUSP 1	ND	ND	ND	ND	ND	2.0	ND	ND	ND	1.2	1.6	0.6	0.6	1.8	0.8	0.8	ND
LUSP 2	ND	0.4	ND	ND	ND	ND	0.8	2.2	0.8	0.2	1.4	1.2	0.4	ND	2.2	0.4	2.0
BIO	0.8	0.2	ND	ND	1.6	1.4	0.2	2.0	ND	ND	ND	2.0	ND	1.6	ND	1.8	ND
DEF	ND	ND	ND	2.2	ND	ND	2.0	0.8	1.2	ND	ND	0.4	2.2	0.2	1.6	ND	ND
VMA	2.2	ND	2.2	ND	ND	ND	ND	ND	ND	0.4	0.8	3.2	2.2	2.8	0.8	ND	ND
Blank	ND	0.8	ND	ND	2.2	2.8	1.8	ND	1.6	ND	0.6	1.2	ND	ND	3.2	0.6	1.6

Table A3. 7: GGBS Americium Intact Leaching Results

GGBS - Am-241	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	ND	ND	1.8	ND	ND	1.0	ND	ND	3.4	ND	ND	ND	ND	ND	ND	1.4	2.6
MPBDP	ND	ND	ND	ND	1.0	ND	ND	3.4	1.2	5.4	2.2	2.4	ND	ND	ND	4.6	6.4
FWBFP	3.4	ND	ND	ND	ND	ND	ND	ND	5.2	2.0	ND	2.6	ND	ND	ND	0.7	4.2
WRBP	1.8	ND	ND	ND	0.4	ND	2.8	ND	2.4	ND	ND	3.4	ND	ND	7.7	2.6	2.8
LUSP 1	ND	ND	ND	1.8	ND	ND	ND	7.6	ND	ND	ND	ND	1.4	ND	3.8	0.2	ND
LUSP 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.6	5.6	ND	ND	2.4	2.6	1.2	2.0
BIO	ND	ND	ND	ND	ND	3.0	ND	ND	0.4	ND	2.8	0.2	ND	1.4	3.2	0.4	0.8
DEF	2.4	ND	2.0	ND	ND	ND	ND	ND	2.4	4.6	4.2	ND	ND	2.0	1.4	ND	3.4
VMA	ND	ND	ND	ND	ND	ND	ND	1.2	ND	6.4	3.0	2.0	ND	ND	2.2	4.4	1.4
Blank	ND	ND	0.2	4.2	ND	ND	0.4	ND	ND	ND	2.4	ND	ND	ND	6.0	1.2	ND

Table A3. 8: PFA Americium Intact Leaching Results

PFA - Am-241	Curing Water	0.08 days		1 days		2.25 days		8 days		14 days		15 days		28 days		36 days	
(CPM)		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
WRBDP	0.4	ND	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6	ND	ND	ND
MPBDP	1.2	ND	ND	ND	2.2	ND	ND	ND	ND	ND	ND	ND	2.4	ND	ND	5.2	ND
FWBFP	ND	1.4	0.6	2.6	ND	ND	ND	0.2	0.6	ND	ND	ND	ND	ND	ND	ND	ND
WRBP	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.6	ND	0.4	ND	ND	2.8	ND	2.0
LUSP 1	ND	ND	ND	ND	ND	ND	ND	ND	0.6	ND	1.6	7.6	4.6	ND	ND	ND	1.4
LUSP 2	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.8	1.4	1.2	2.4	ND	4.4
BIO	5.4	ND	ND	ND	ND	ND	5.0	ND	0.6	ND	ND	3.8	0.8	ND	2.8	ND	ND
DEF	1.4	ND	2.2	ND	ND	ND	ND	ND	ND	ND	ND	5.0	2.2	3.0	ND	ND	3.4
VMA	0.4	0.8	ND	ND	ND	ND	ND	ND	ND	2.0	ND	2.4	0.8	ND	ND	0.4	ND
Blank	1.8	ND	ND	1.2	ND	ND	ND	ND	ND	ND	1.8	3.2	ND	ND	2.0	ND	ND

Appendix 4: Un-Irradiated Crushed Sample Leaching Results

Table A4. 1: GGBS Mixed Isotope Crushed Sample Leaching Results

	Ni (cpm)		U (ppb)		Am (cpm)	
GGBS Non-Irradiated	**L2**	**L8**	**L2**	**L8**	**L2**	**L8**
WRBDP 1	ND	ND	0.52	0.10	ND	ND
WRBDP 2	ND	ND	0.03	0.25	ND	ND
MPDBP 1	ND	ND	0.03	0.05	ND	ND
MPBDP 2	ND	0.60	0.04	0.01	ND	ND
FWBFP 1	ND	ND	0.01	0.09	ND	ND
FWBFP 2	ND	ND	0.01	0.02	ND	ND
WRBP 1	ND	ND	0.02	0.04	ND	ND
WRBP 2	ND	ND	0.01	0.01	ND	ND
LUSP 1 1	ND	ND	0.06	0.01	2.00	ND
LUSP 1 2	ND	ND	0.04	0.02	ND	ND
LUSP 2 1	ND	ND	0.01	0.02	ND	ND
LUSP 2 2	ND	ND	0.04	0.05	ND	ND
BIO 1	ND	ND	0.39	0.09	ND	ND
BIO 2	ND	ND	0.41	0.15	ND	ND
DEF 1	ND	ND	0.32	0.09	ND	1.00
DEF 2	ND	ND	0.27	0.07	ND	ND
VMA 1	ND	ND	0.30	0.07	ND	ND
VMA 2	ND	ND	0.62	0.08	ND	ND
Blank 1	ND	ND	0.61	0.08	ND	ND
Blank 2	ND	ND	2.77	0.16	ND	ND
Blank Non-active1	ND	ND	0.67	0.03	ND	ND
Blank Non-active2	ND	ND	0.14	0.02	ND	ND

Blank Non-active refers to sample with no additive and no radionuclides added

Table A4. 2: PFA Mixed Isotope Crushed Sample Leaching Results

	Ni (cpm)		U (ppb)		Am (cpm)	
PFA Non irradiated	**L2**	**L8**	**L2**	**L8**	**L2**	**L8**
WRBDP 1	ND	ND	0.07	0.09	ND	ND
WRBDP 2	ND	ND	0.25	0.25	ND	ND
MPDBP 1	ND	ND	0.10	0.23	ND	ND
MPBDP 2	ND	ND	0.18	0.23	ND	ND
FWBFP 1	ND	ND	0.17	0.17	ND	ND
FWBFP 2	ND	ND	0.32	0.16	ND	ND
WRBP 1	ND	0.20	1.27	0.28	ND	ND
WRBP 2	ND	ND	0.40	0.16	ND	ND
LUSP 1 1	0.30	ND	0.39	0.17	ND	ND
LUSP 1 2	ND	ND	0.29	0.12	ND	ND
LUSP 2 1	ND	ND	0.16	0.07	ND	ND
LUSP 2 2	ND	ND	0.09	0.03	ND	1.00
BIO 1	ND	ND	0.56	0.27	ND	ND
BIO 2	ND	ND	0.29	0.43	ND	1.00
DEF 1	ND	ND	0.32	0.28	ND	1.00
DEF 2	ND	ND	0.35	0.35	ND	ND
VMA 1	ND	ND	0.16	0.18	ND	ND
VMA 2	ND	ND	0.19	0.28	ND	4.00
Blank 1	ND	ND	0.80	0.12	ND	ND
Blank 2	ND	ND	0.26	0.11	ND	ND
Blank Non-active1	ND	ND	0.04	ND	ND	ND
Blank Non-active 2	ND	ND	ND	0.09	ND	ND

Blank Non-active refers to sample with no additive and no radionuclides added

Appendix 5: Irradiated Crushed Sample Leaching Results

Table A5. 1: GGBS Mixed Isotope Irradiated Crushed Sample Leaching Results

	Ni (cpm)		U (ppb)		Am (cpm)	
GGBS Irradiated	**L2**	**L8**	**L2**	**L8**	**L2**	**L8**
WRBDP 1	ND	ND	0.52	0.10	1.20	2.60
WRBDP 2	ND	ND	0.03	0.25	ND	4.80
MPDBP 1	ND	ND	0.03	0.05	6.40	2.80
MPBDP 2	ND	ND	0.04	0.01	ND	3.40
FWBFP 1	ND	ND	0.01	0.09	0.00	4.60
FWBFP 2	ND	ND	0.01	0.02	2.20	5.00
WRBP 1	ND	ND	0.02	0.04	ND	ND
WRBP 2	ND	ND	0.01	0.01	2.60	1.40
LUSP 1 1	ND	ND	0.06	0.01	ND	6.40
LUSP 1 2	ND	2.80	0.04	0.02	1.00	8.80
LUSP 2 1	ND	ND	0.01	0.02	2.60	7.20
LUSP 2 2	ND	ND	0.04	0.05	ND	14.80
BIO 1	ND	ND	0.39	0.09	4.20	7.40
BIO 2	ND	ND	0.41	0.15	1.80	6.00
DEF 1	ND	ND	0.32	0.09	4.60	11.20
DEF 2	ND	ND	0.27	0.07	2.20	10.20
VMA 1	9.80	ND	0.30	0.07	10.20	8.20
VMA 2	9.60	ND	0.62	0.08	3.00	9.00
Blank 1	8.60	ND	0.61	0.08	2.20	5.80
Blank 2	ND	ND	2.77	0.16	5.60	17.20
Blank Non-active 1	ND	ND	0.67	0.03	2.20	11.80
Blank Non-active 2	ND	ND	0.14	0.02	3.80	5.80

Blank Non-active refers to sample with no additive and no radionuclides added

Table A5. 2: PFA Mixed Isotope Irradiated Crushed Sample Leaching Results

	Ni (cpm)		U (ppb)		Am (cpm)	
PFA Irradiated	**L2**	**L8**	**L2**	**L8**	**L2**	**L8**
WRBDP 1	ND	ND	0.04	0.19	ND	ND
WRBDP 2	ND	ND	ND	0.11	ND	ND
MPDBP 1	ND	ND	0.09	0.11	2.00	ND
MPBDP 2	ND	ND	0.10	0.19	ND	ND
FWBFP 1	ND	ND	0.09	0.13	ND	1.80
FWBFP 2	ND	ND	0.06	0.05	ND	ND
WRBP 1	ND	2.00	0.07	0.07	ND	1.60
WRBP 2	ND	ND	0.15	0.11	ND	ND
LUSP 1 1	ND	ND	0.17	0.10	ND	ND
LUSP 1 2	ND	ND	0.14	0.18	ND	ND
LUSP 2 2 1	ND	ND	0.17	0.23	ND	2.80
LUSP 2 2	ND	ND	0.41	0.06	ND	ND
BIO 1	ND	ND	0.00	0.01	ND	ND
BIO 2	ND	ND	0.10	0.06	ND	ND
DEF 1	ND	ND	0.04	ND	ND	ND
DEF 2	ND	ND	0.06	ND	ND	ND
VMA 1	ND	ND	0.21	0.12	1.00	ND
VMA 2	ND	ND	0.13	0.06	ND	3.40
Blank 1	ND	ND	0.17	0.06	1.00	ND
Blank 2	ND	ND	0.25	0.19	2.60	ND
Blank Non-active 1	ND	ND	0.57	0.47	ND	ND
Blank Non-active 2	ND	ND	1.03	0.51	ND	0.20

Blank Non-active refers to sample with no additive and no radionuclides added