Understanding Wastewater from Hydraulic Fracturing to Minimise Environmental Risk

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Furthering the Knowledge Base for Reducing the Environmental Footprint of Shale Gas Development

This PhD Project was undertaken as part of **FracRisk**, a European Union Horizon 2020 Research and Innovation funded international research consortium aimed at understanding, preventing, and mitigating the potential environmental impacts of shale gas exploration and exploitation.

The main ambitions of **FracRisk** are to form a knowledge base and formulate scientific recommendations which will contribute to efforts aimed at minimising the environmental footprint of shale gas extraction, while addressing public concerns. The aim is to provide key scientific-based yet practical recommendations aimed at minimising the environmental footprint of shale gas extraction through effective planning and regulation, and also to address public concerns.

More information can be found at *www.fracrisk.eu*.

1 ABSTRACT

Hydraulic fracturing to extract shale gas is widely regarded to be socially, environmentally, and politically controversial due to the perceived negative impacts of the process. One issue of environmental contention is the management and fate of the wastewater generated by the fracturing process when fluids used to generate fractures in the rocks underground are returned to the surface. These waste fluids require appropriate storage, transportation, treatment, and discharge to ensure that overall fluid requirements are minimised, process efficiency is maximised, and risks to the environment are reduced. Prior understanding of the chemistry and volumes of waste that will require management are beneficial to operators, waste treatment professionals, and environmental regulators.

The effects of temperature, pressure, shale mineralogy, and injected fluid composition on the chemistry of waste fluids were investigated through a series of experiments. Experiments were designed to replicate the hydraulic, thermal, and chemical interaction between shale rocks and injected fluids in the subsurface to provide insight into the source of contaminants of concern in wastewaters. This work also modelled the economic and energetic cost of treating wastewater with varied composition under current regulatory conditions in the UK. The limited UK waste fluid composition data was compared with a wealth of waste fluid data from the USA to ascertain what lessons could be learned from legacy operations and their environmental impacts.

Experiments with injection fluids containing no chemical additives yielded waste fluids with few contaminants of concern. The greatest concentrations of contaminants of concern such as heavy metals, sulphates, and salts occurred during reaction with an injection fluid containing 10% HCl additive to the base injection fluid. Key factors affecting the release of contaminants into solution include solution pH, mineralogical

composition (particularly carbonates and sulphates), and oxidising conditions. Modelling of the volumes and chemistry of wastewater expected from operations in the UK concluded that the economic viability of any shale gas well is impeded by the cost of treatment. The cost of treating the salinity varied from 2 to 26% of well revenue, with a predicted median of ~ $495,472 per well. Additional costs of up to £163,450 per well will be incurred for disposal of NORM concentrated sludge in permitted landfill sites in line with UK regulations.

Based on the findings from this research, it is strongly recommend that this area receives further attention from the emergent unconventional gas industry, the established waste water management industry, and regulatory bodies in the UK, in order to produce a coherent strategy for the future management of wastewaters from hydraulic fracturing. This work has found that no such co-ordinated strategy currently exists, and limited management capacity in the UK will present a significant hurdle to future expansion of the industry unless it is urgently addressed.

2 LAY SUMMARY

Natural gas trapped in shale, a tightly packed sedimentary rock, has the potential to provide the UK with an indigenous fossil fuel resource, with inherently lower CO_2 emissions than any imported fuel, and lower CO_2 emissions than coal or Liquified Natural Gas (LNG).

Shale gas requires 'hydraulic fracturing' to enhance the permeability of the rock formation and allow trapped gas to flow to the surface. Hydraulic fracturing is achieved by pumping fluids into the subsurface to generate enough pressure to fracture the rock. These fluids contain a proppant to 'prop' fractures open under the ground, and are mixed with chemical additives to streamline the fracturing process.

During fracturing, these injected fluids mix with any formation water stored in the rocks, react with freshly fractured shale surfaces, and on returning to the surface after fracturing inherit salts, heavy metals, sulphates and naturally occurring radioactive materials from the subsurface. These returned waste fluids requiring appropriate management to ensure that environmental impact is limited, freshwater needs are reduced, and efficiency is maximised.

To inform decisions about how best to manage these wastewaters, this research aims to improve the understanding of the volumes and chemistry of wastewaters that will be generated by a UK hydraulic fracturing industry, by using data from the well-developed industry in the USA to make predictions. While treatment of these wastewaters will be possible, specialist facilities will be required and the energetic and economic cost are expected to be high.

Chemical reactivity experiments were conducted to understand what chemical reactions take place between fresh shale surfaces and injected fracturing fluids under subsurface temperature and pressure conditions. Field data from hydraulic fracturing wells in the UK and the USA are compared to the experimental fluids, with many of the constituents of environmental concern in field wastewaters not present at significant concentrations in experimental fluids.

The geochemistry of shales, specifically carbonate, pyrite and organic matter content, influence the release of heavy metals and sulphate into injected fluids. Oxidising reactions cause acidification of fluids which encourages mineral dissolution, and the presence of sulphate is likely to lead to the formation of sulphate scales. Sulphate scales can sequester natural occurring radionuclides from solution but also reduce equipment performance. The chemistry of formation water (water present in the shale formation since deposition) exerts a key control on the chemistry of wastewaters, and its influence is not reflected in the results from reactivity experiments.

Overall, the chemistry of returned wastewaters from hydraulic fracturing in the UK is treatable by existing technologies, however treatment will be costly, and specialist infrastructure will be required as the industry grows.

3 AUTHORS DECLARATION

I declare that this thesis has been composed solely by myself and that it has not been submitted, either in whole or in part, in any previous application for a degree. Except where otherwise acknowledged, the work presented is entirely my own.

Megan Catherine O'Donnell

August 2019

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To my supervisors, Dr Stuart Gilfillan, Dr Katriona Edlmann, and Dr habil Christopher McDermott – this work reflects a small portion of what I have learned from working with you. I am sincerely grateful to you all for your guidance, attention, and belief in me.

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And finally, thank you to my family and friends, who have supported me unwaveringly. Thanks to Murray, I always had a bit of perspective when I needed it most. Thanks to Kirsty, I never gave up when things got hard. And thanks to Mike and Claire, my standards were set so high that I always strove for better.

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6 TABLE OF ABBREVIATIONS

BS	Bowland shale, U- upper, L – lower
EC	Electrocoagulation
EUR	Estimate ultimate recovery
FP	Flowback and produced water
GHG	Greenhouse gas
IC	Ion chromatography
ICPOES	Inductively coupled plasma optical emission spectroscopy
KC	Kimmeridge clay
LLW	Low level waste (radioactive)
LNG	Liquified natural gas
LOI	Loss on ignition
MS	Marcellus shale
MVC	Mechanical vapour compression
NORM	Naturally occurring radioactive material
PH	Preese Hall (onshore hydraulic fracturing well in Lancashire)
PP	Polypropylene
RO	Reverse osmosis
RSR	Radioactive substances regulations
SF	Shorthand for experimental conditions (SF1 – 5)
SRM	Standard reference material
TDS	Total dissolved solids
TIC	Total inorganic carbon
TOC	Total organic carbon
USGS	United States Geological Survey
VLLW	Very low level waste (radioactive)
XRD	X-ray diffraction
XRF	X-ray fluorescence

7 INTRODUCTION

7.1 NATURAL GAS IN THE UK

Since the 1970s production of natural gas in the UK has steadily risen along with national demand until the peak of production in the 2000s (DUKES, 2014). In 2014 gas imports (477 TWh) began to exceed indigenous production (425 TWh), due to a gap between the demand for natural gas in the UK and the readily available national resources. With the exhaustion of local reserves, and increasing year-on-year consumption (DUKES, 2014), the demand for imported gas is set to increase.

The largest consumer of natural gas in 2014 was the domestic customer, closely followed by non-domestic heat and electricity generation (Figure 1). Most of the domestic demand for natural gas in the UK fuels gas-powered cooking and central heating and is unlikely to be readily replaceable by renewable energy sources in the near future without a costly, infrastructural overhaul. Due to a reduction in availability of conventional sources of natural gas, the UK has begun exploring the options available for exploiting their unconventional gas resources, such as shale gas and coal bed methane deposits.

SECTOR	**PERCENTAGE USE OF UK NATURAL GAS**
DOMESTIC	36%
ELECTRICITY AND HEAT GENERATION	32%
OTHER	13%
INDUSTRY	12%
ENERGY INDUSTRY USE	7%

FIGURE 1 – NATURAL GAS USE BY SECTOR, DIGEST OF UK ENERGY STATISTICS. SOURCE: DECC, 2014.

7.2 SHALE GAS IN THE UK

Shale gas is natural gas formed in tightly packed sedimentary rocks (shales) that contain high amounts of organic matter, specifically kerogen. Heat and pressure generated during the burial of these rocks produces hydrocarbons from the organic matter, which often migrate upward away from their source to become trapped in more porous overlying rocks – forming conventional oil and gas deposits. Due to the tightly packed structure of shale, some hydrocarbons remain trapped within the rock in pore spaces or associated with kerogen deposits (Passey *et al.*, 2010). The trapped hydrocarbons are termed 'unconventional' resources because they require some form of unconventional hydrocarbons engineering such as hydraulic fracturing, acid stimulation, or underground coal gasification to be extracted. However, the use of the term 'unconventional' is contentious due to the varied nature of its use across the conventional and unconventional hydrocarbon industry. Additionally, many conventional wells are stimulated using unconventional techniques to maximise recovery.

There are three main shale basins in the UK (Figure 2); The Weald Basin (South East England, Jurassic), The Bowland Shale (North West England and Yorkshire, Carboniferous) and the Midland Valley (Scotland, Carboniferous). The British Geological Survey (BGS) believes the Midland Valley to contain between 49.4 and 134.6 trillion cubic feet (tcf) natural gas reserves (Monaghan, 2014), and the Bowland Basin between 822-2281 tcf (Andrews, 2013), although recoverable reserves are likely to be much lower. The Weald Basin is not thought to have any significant shale gas potential as the shales have not reached thermal maturation (Andrews, 2014). The US Energy Information Administration estimates the UK's technically, although not necessarily economically, recoverable shale gas reserves to be 26 tcf (US Energy Information Administration, 2016a). The UK's annual gas demand in 2015 (DUKES, 2014) was 773 TWh, or 2.63 tcf, implying that the technically recoverable shale gas reserves could sustain a constant national gas demand for just under ten years. Hydraulic fracturing feasible shale reserves to produce natural gas has the potential to provide the UK with a new, indigenous fuel source.

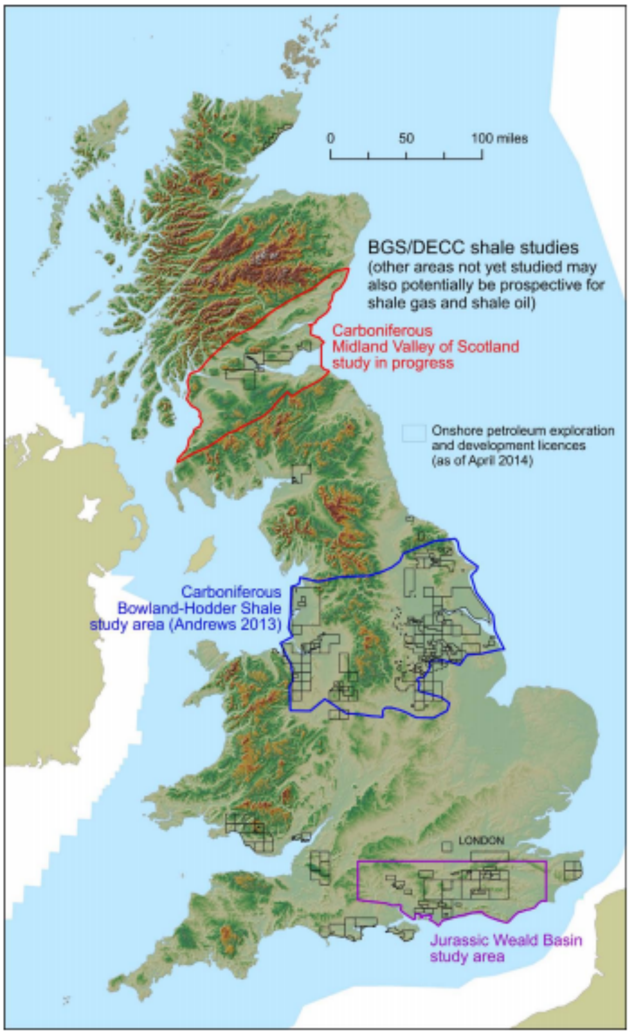

FIGURE 2 – THE UK'S ONSHORE UNCONVENTIONAL HYDROCARBON BASINS AND ONSHORE PETROLEUM EXPLORATION AND DEVELOPMENT LICENSES. SOURCE: BGS/DECC, 2014

7.3 HYDRAULIC FRACTURING

Shales are fine grained, tightly packed, clay-, and quartz-rich sedimentary rocks, that can contain hydrocarbons if their geological history and geochemistry permits. Unlike conventional hydrocarbon bearing rocks, shales have low to non–existent vertical permeability – inhibiting gas through-flow – and restricting hydrocarbon production through conventional techniques (Passey et al., 2010).

Since the 1990s the hydrocarbon industry has been using hydraulic fracturing to enhance the permeability of tight geological formations such as shales and ease extraction (The Royal Society, 2012). Since the 1950s the technique has been used for geothermal heat extraction, enhanced oil recovery from conventional sources, geological carbon sequestration, groundwater remediation and groundwater well development (Adams and Rowe, 2013). Since the 2000s the USA has been experiencing a shale gas 'boom' as vast onshore gas deposits have become more readily exploitable through developments in technology of drilling and fracturing.

To extract shale gas, hydraulically fracturing or 'fracking' the rock formation is required. Fluid pressure is utilised to generate an enhanced or artificial fracture network in the shale, improving its permeability and enabling the flow and production of hydrocarbons at the surface. Typically, a vertical well is drilled until the target formation is reached within the subsurface. Subsequently, horizontal drilling extends the lateral reach of the well (King, 2012). Horizontal drilling has enabled a greater proportion of shale gas deposits to be targeted for extraction in recent years, as thinner, laterally extensive formations can be reached with fewer wells at the surface.

The fluids used to generate fractures are often mixed with chemical additives that improve process efficiency and prolong the life of equipment used, as well as a proppant such as sand that 'props' the fractures open while gas is released from the rock formation. See appendix 15.1 (p232) for a list of the most common additives to fracturing fluids and their purposes. During the fracturing process the pressurised fluids react with the freshly exposed mineral surfaces in fractures, and mix with any inherent formation or pore water in the shale. On de-pressurisation between 10 and 70% of these fluids are returned to the surface having leached heavy metals, naturally occurring radioactive material (NORM), salts and hydrocarbons from the subsurface. The returned waters require appropriate management to ensure that they are stored, transported, treated, and disposed of in a way that minimises the need for fresh water, maximises the efficiency of the process, and reduces risks posed to the environment.

7.4 FRACTURING FLUIDS, FORMATION FLUIDS AND WASTE FLUIDS

Fluids injected to create the pressure required to undertake fracturing, which can be freshwater, saltwater, recycled or reused fluids, are mixed with a number of chemicals carefully chosen to streamline the fracturing process. These chemicals control fluid viscosity, inhibit the formation of bacteria or scale, control or adjust pH, and supress corrosion, among a number of other important tasks.

In the UK, only two chemical additives are permitted for use in hydraulic fracturing by the Environment Agency; a dilute hydrochloric acid (maximum 10% concentration) which acts as a solvent and as a control on pH, helping the fluid access the rock and gas in the subsurface, and acrylamide which reduces friction with the fluid to minimise the energy required to pump the fluid underground.

Hydrochloric acid dissolves carbonate minerals, releasing ions into solution (as well as CO_2 gas) and altering the chemistry of fluids downhole. It's purpose is to dissolve carbonate phases and enable fractures reach trapped gas within the rock formation. The reactions driven by this acid are likely to increase the concentration of dissolved constituents within fluids returned to the surface following fracturing, proportionally to the concentration used. This study investigates the relationship between hydrochloric acid and shale minerals and the implied effects on wastewater produced by the fracturing process.

Acrylamide is an organic chemical which is used to increase the viscosity of the injected fluids, thus reducing turbulent flow and friction when fluids are pumped underground at high pressures. Its chemical behaviour and interaction with shales has been studied by (Caulfield, Qiao and Solomon, 2002; Chen and Carter, 2017; Xiong *et al.*, 2018) - and is not investigated within this study.

During gas production, fluids that are injected to create fractures in the rock are returned to the surface having mixed with inherent formation or pore water contained within the shale. Formation and pore water chemistry is controlled predominantly by the chemical interactions between minerals and fluids present over geologic timescales, and to a lesser extent by dilution or mixing with meteoric waters. Mineral dissolution, leaching, redox reactions, ion exchange, and crystallisation within the water-rock system all exert a control on the geochemistry of formation water. Formation water often takes the form of a brine containing high concentrations of dissolved salts – derived from dissolution of mineral phases, and altered during diagenesis. Mixing of injected fluids with formation waters likely contributes much of the levels of dissolved contaminants in wastewaters generated by hydraulic fracturing.

Generally, levels of dissolved contaminants in initial flowback are low and increase over time (Hayes, 2009). Variations in TDS are thought to be due to natural chemical variations in the composition of the source rock and formation waters, as well as depending on the amount of time the fluid has spent downhole (Gaudlip and Paugh, 2008). In the Marcellus shale, Pennsylvania, salinity has been attributed to halite lenses or mixing with deep saline formation brines as opposed to local fracture dissolution (Blauch *et al.*, 2009) suggesting that salinity is controlled by basin-scale factors. The influence of local mineral dissolution on the chemistry of the returned waters reduces over time, eventually producing waters representative of in situ, saline formation brines (Haluszczak, Rose and Kump, 2012).

Rocks rich in organic matter, such as shales or other hydrocarbon source rocks, tend to contain naturally occurring radionuclides such as uranium (^{238}U) and thorium (^{232}Th). These radionuclides decay to form a number of daughter particles, notably radium, which is soluble in water. During hydraulic fracturing the injected fluids mix with the radium enriched formation waters within the rock, and subsequently contaminate the flowback water with naturally occurring radioactive material (NORM).

Injected fluids also react with freshly exposed shale surfaces created by fracturing, altering their chemistry by dissolving minerals, reacting with components in solution to produce new compounds, and by inheriting naturally occurring radiation prevalent in shale rocks. Dissolution of mineral phases releases constituent chemicals into solution (Ba, Si, Mg, Ca, K), while ion exchange between clay minerals and fracturing fluids releases cations and anions such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-}, and Cl^{-}. Fluids oversaturated with key mineral forming elements allow crystallisation to take place under certain conditions; reducing the concentration of mineral forming components within the fluids. Geochemical reactions taking place between formation fluids, injected fluids and shale minerals are affected by the major and minor geochemical components available to react within the system. The resulting chemistry of waste fluids returned is complex and influenced by many variables.

7.5 ENVIRONMENTAL CONCERNS

7.5.1 SUBSURFACE ENVIRONMENTAL CONCERNS

A number of environmental concerns exist associated with the process of hydraulic fracturing that have arisen from the legacy of operations in the USA. Regulations, permitting, and environmental conditions differ in the UK setting and therefore not all of these environmental concerns will be as relevant to the UK industry. Some of the key concerns are outlined and discussed in this section.

7.5.1.1 INDUCED SEISMICITY

Pressure changes in the subsurface caused by the additional hydraulic pressure during fracturing can induce seismicity at varying magnitudes; 1.0-3.8 M_L (Davies *et al.*, 2013). Although the majority of recorded induced seismicity associated with hydraulic fracturing in the USA is due to fluid injection of wastewater and not hydraulic fracturing operations (Keranen *et al.*, 2013; K.M. Keranen, M. Weingarten, G.A. Albers, B.A. Bekins, 2014), concerns exist over the potential for induced seismicity to cause damage at the surface, damage infrastructure underground such as well casings, and lead to unwanted fluid migration causing leakage or contamination. This concern is especially pertinent in the UK where population density is greater than in the USA and due to the events induced in Lancashire by hydraulic fracturing in 2011 (Clarke *et al.*, 2014).

To date, there have been two episodes of hydraulic fracturing of an onshore shale gas reservoir in the UK. The first, at the PH-1 well at Preese Hall in Lancashire, was drilled in August 2010, with fracturing commencing in March 2011. This well was drilled with the aim of testing the productivity of the Bowland Shale formation for gas. However, operations were suspended in May 2011 following two seismic events measured at 2.3 and 1.5 M_L (Clarke *et al.*, 2014), attributed to fault slip induced by fluid injection associated with the fracturing operations (de Pater and Baisch, 2011). One of these seismic events was felt at the surface, causing a year-long moratorium to be place on hydraulic fracturing in the UK until further review of best available techniques to prevent induced seismicity (Green, Christopher, Styles and Baptie, 2012). Hydraulic fracturing processes generally cause small, unfelt seismicity unlike the seismicity that can be associated with deep fluid waste injection (Davies *et al.*, 2013). Out of the hundreds of thousands of wells that have been fractured, only three cases of felt seismicity have been documented directly as a result of the fracturing process (Davies *et al.*, 2013).

All hydraulic fracturing in the UK currently operates under a seismicity 'Traffic Light System' whereby operators must take one of three defined actions depending on the magnitude of seismicity induced by operations. These options include, < 0 M_L; operations proceed as normal, ≥ 0.0 to < 0.5 M_L; operations proceed with caution at a reduced rate and monitoring is intensified, and ≥ 0.5 M_L; operations must cease and monitoring is highly intensified.

The second hydraulic fracturing operation in the UK commenced in October 2018 at Preston New Road. Seismicity has been measured between -0.8 and 1.1 M_L on 35 occasions over a one month period (19th October 2018-19th November 2018), with 'red light' events measured – and operations suspended – twice.

Some concerns exist over the validity of the regulatory 'traffic light' system due to the ability to measure and validate seismicity at <1.5 M_L. The method of magnitude calculation, statistical bias, and compound error from incorrect estimation of event location can mean that the error on a magnitude reported can be many times the value of magnitude itself (Nowacki, Curtis and Baptie, 2017). This has serious implications for decision making which is entirely dependent on reported magnitude values, and the method of estimating induced seismicity at very low magnitudes must be accurate and precise for any regulations relying on these measurements to be considered robust.

7.5.1.2 FLUID MIGRATION

Concerns also exist over fluid migration within the subsurface (e.g. stray gas, injection fluids, formation waters). The intention and purpose of hydraulic fracturing is to generate a fracture network within the shale formation allowing gas to be released and produced at the surface. However, concern exists over the reach of this fracture network and the potential for unwanted migration pathways to be generated whereby fluids could migrate to unwanted receptors (other geological units). A review of natural and stimulated fracture lengths determined that the probability of a stimulated fracture extending greater than 350m is ~1% (Davies *et al.*, 2012). If the vertical separation between the shale gas source rock and overlying potable water formations is known, this can determine the likelihood of stimulated fractures hydrogeologically connecting the two units.

To achieve contamination of overlying groundwater units stratigraphically above shale gas source rocks, feasible hydrogeological connectivity must exist, as well as a driving force to instigate and maintain fluid migration such as a hydraulic gradient. The overall likelihood that hydraulic pathways exist by way of natural or induced fractures is much lower than that presented by man-made infrastructure such as boreholes (Younger, 2016). Additionally the upward pressure gradients required to drive upward fluid migration from source rock to overlying units exist only during active fracturing (a few hours) and are therefore unlikely to be engaged long enough to sustain driving fluid migration over hundreds or thousands of meters in the subsurface (Younger, 2016).

7.5.2 SURFACE ENVIRONMENTAL CONCERNS

7.5.2.1 NOISE

Hydraulic fracturing can create noise disturbance within the surrounding area during construction (3-5 weeks), drilling (up to 1 month), fracturing (up to 1 month), and decommissioning (variable duration). For conventional hydrocarbon wells the entire exploratory drilling process is known to take between 12 and 15 weeks (Department for Communities and Local Government, 2013). Unwanted noise associated with such operations has been shown to have non-auditory health implications for populations located nearby (Hays, McCawley and Shonkoff, 2017); therefore reducing the impact of noise is imperative for any operator's social license. The legal limits for noise disturbances from shale gas operations in the UK are 55 dB between the hours of 07:30-18:30, and 42 dB at all other times (Stollery, 2014). It is essential that robust baseline measurements of noise levels in the area are measured before operations commence, as 55 dB can be lower than the sound of passing traffic, a lawnmower, or wind on the microphone. Noise impacts are typically addressed by implementing barriers such as industrial sound curtains, and restricting operation times to limit inconvenience to nearby communities.

7.5.2.2 TRAFFIC

As shale gas sites in the UK are likely to be focused in rural areas where infrastructure is limited; meaning equipment, chemicals, staff, and other physical site requirements will need to be transported by road to the site. This is expected to have environmental impacts including increasing the volume and intensity of traffic around sites, decreasing air quality by directly emitting greenhouse gases (GHG) from exhaust fumes, increasing noise associated with operations, and potential damage to rural road networks not designed for industrial load bearing (Goodman *et al.*, 2016). Factors affecting the volume and intensity of traffic vary widely; such as the volume of fluids required, the percentage of this that will return to the surface as waste fluid, and the volumes of gas produced – resulting in large compound uncertainty in the estimation of traffic related impacts on the environment. It has also been noted that the GHG emissions during the fracturing process may be negligible in comparison to the potential emissions from traffic related activity, with implications for the overall environmental impact from shale gas operations (Goodman *et al.*, 2016).

7.5.2.3 AIR POLLUTION

Hydraulic fracturing may have effects on local, regional, and global air quality. Locally, increased traffic and industrial works can cause significant atmospheric pollution by increasing levels of particulate matter and dust (Goodman *et al.*, 2016). In regions where shale gas is being exploited, air quality impacts such as fugitive methane leakages and increased GHG concentrations near areas with concentrated well pads, however the source of this decreased air quality is continually debated. Globally shale gas has the potential to increase air quality in areas where it replaces other hydrocarbon fuel sources such as coal mining, and may be able to contribute to the lowering of GHG emissions through alternative fossil fuel use.

7.5.2.4 SPILLS / UNPLANNED FLUID RELEASE

Spills of chemical additives, fracturing fluids, or returned waste fluids at the surface have the potential to cause significant environmental impact by pollution of surface waters. Clancy et al. 2018 estimated the likelihood of unplanned spills associated with hydraulic fracturing based on US data and discovered that there would likely be at least one spill for every 4-19 well pads developed at the surface. The likelihood of surface spills increases depending on the number of subsurface laterals attached to the well pad. Spills or ‘unplanned releases’ allow untreated fluids containing contaminants of concern for the surrounding environment to be released into the surface waters, soils, and even into near-surface groundwater reserves if a pathway for transport exists.

Spills onsite can be mitigated by installing subsurface lining of the site to obstruct any pathway between any pilled fluids and the subsurface. Fluids should be stored on site in bunded or double-walled sealed tanks, and using the best available standards of equipment combine with rigorous maintenance can help mitigate against unplanned fluid releases from faulty or malfunctioning equipment.

7.5.2.5 WATER REQUIREMENTS & SOURCING

The hydraulic fracturing process is driven by hydraulic pressure, and therefore water requirements can be significant (Figure 3). The volume of fluid required depends on the wettability of the shale, the extent of the well (laterally and vertically), and the fracture design (U.S. Environmental Protection Agency, 2016). Wells with greater extent have more perforation stages and therefore typically require larger volumes of water per length of well (Horner *et al.*, 2016). In the US water use varies by shale play and well length, with mean volumes ranging from 10,000-36,620 m^3 (Gallegos *et al.*, 2015). In the Sichuan Basin, China, the average water footprint is 34,000 m^3 per well (Zou *et al.*, 2018), and in Poland the average is 8000-19,000 m^3 (Vandecasteele *et al.*, 2015). The British Geological Survey estimate that the water requirements per well in the UK will be between 7000 and 18,000 m^3 (excluding 400-4000 m^3 of water required for drilling) (Stuart, 2012).

A study of the lifecycle consumption of fresh water during shale gas operations in the Marcellus Shale in the USA discovered that although the total consumptive water use of a shale gas well in the region was 6700-33,000 m^3, only 65% of that is utilised on site, with 35% consumed across the remainder of the supply chain (Jiang, Hendrickson and Vanbriesen, 2014).

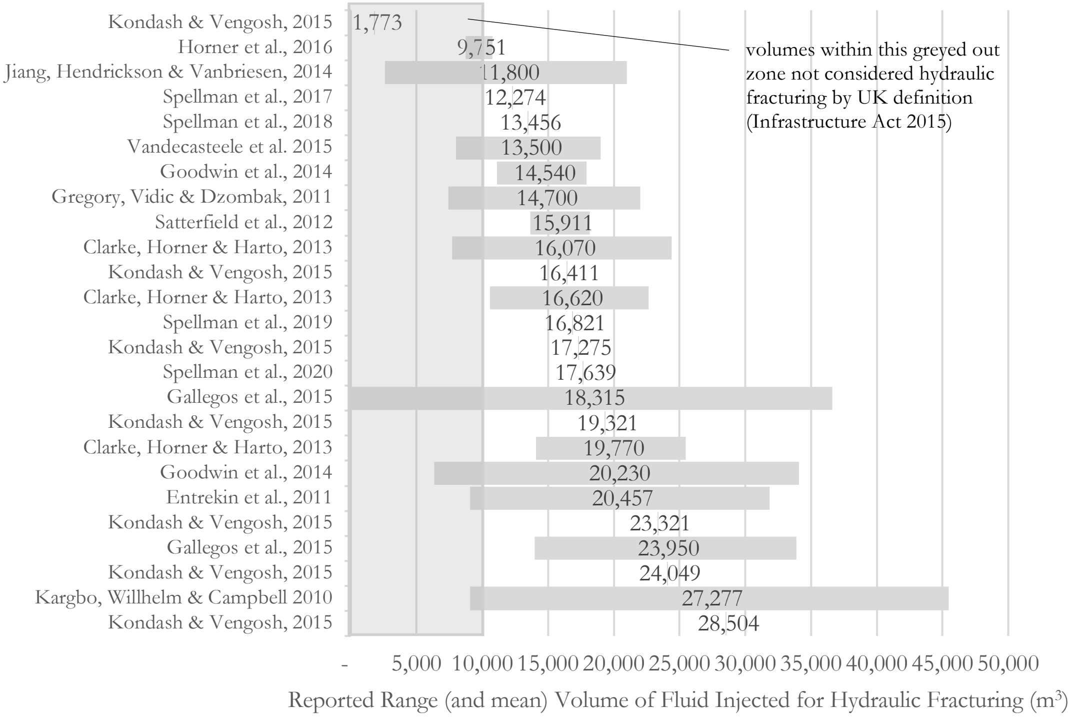

FIGURE 3 – TYPICAL VOLUMES OF FLUID REQUIRED FOR HYDRAULIC FRACTURING, AS REPORTED IN LITERATURE SHOWN AS GREY BAR AND ANNOTATED WITH MEAN.

The key risk posed by water requirements of the hydraulic fracturing process is not the consumption of fresh water, although in areas where demand and supply are unequal this will impose water demand stress, but more so by the availability of access to required water. As the UK water system is relatively limited to local supply, if water requirements for shale gas operations exceed local availabilities water will have to be transported in tankers causing additional traffic pressure (Marshall, 2013). In the UK, fracturing water will be drawn from the mains water supply – raising concern for water security in areas of low resilience., although abstraction is limited by the Environment Agency through licensing to protect drought sensitive areas.

In comparison to primary industries such as manufacturing and construction, water requirements for hydraulic fracturing are low. Additionally, consumptive freshwater requirements per unit of energy recovered are comparable onshore surface coal mining (Goodwin *et al.*, 2014). However, hydraulic fracturing requires a much greater volume of water over a much shorter timeframe than in coal operations as all water is required upfront, as opposed to over the lifetime of a well. Notably, there is over 13 times more water lost annually through mains system leaks ($1.2 x 10^9$ m^3) than would be required for UK fracturing needs ($8.7 x 10^7$ m^3) (Probert, 2012).

Following hydraulic fracturing, when the well is depressurised and between 10 and 70% of injected fluids are returned to the surface (American Petroleum Institute, 2010). The volumes of fluid waste returned vary depending on the volume of fluid injected, and local geological characteristics that control water retention in the subsurface. These fluids are returned with altered chemical characteristics that require dilution or treatment before subsequent re-use. This returned water could pose a significant environmental challenge to the industry if volumes expected are incorrectly predicted and therefore cannot be stored, treated or disposed of, or if specific chemical constituents are costly to remediate.

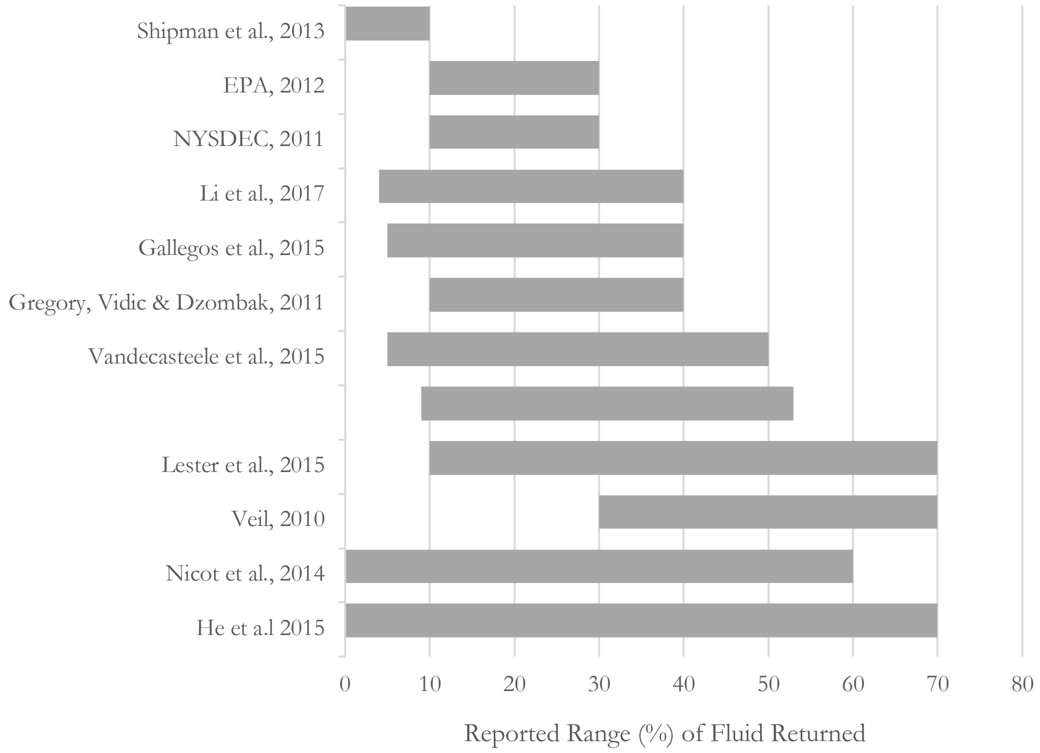

FIGURE 4 – RANGE IN PERCENTAGE OF INJECTED FLUID VOLUME RETURNED AT THE SURFACE AS REPORTED IN LITERATURE.

7.6 WASTEWATER MANAGEMENT OPTIONS

The management of fluids returned during the fracturing process is of particular importance in mitigating environmental risk from the hydraulic fracturing process. Due to geological, legislative, and financial restrictions, the options for management of these fluids are limited in the UK to dilution, treatment, discharge and recycling (Figure 5). This section outlines the management options available and discusses each within the context of the UK industry.

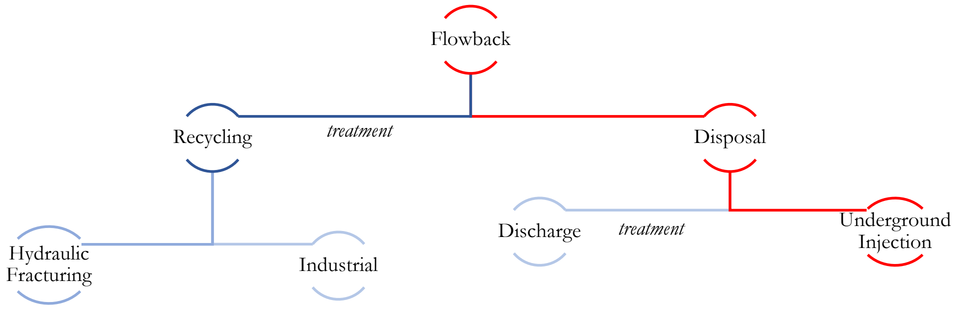

FIGURE 5 – SCHEMATIC REPRESENTATION OF THE MANAGEMENT OPTIONS AVAILABLE FOR WASTEWATER FROM HYDRAULIC FRACTURING IN THE UK (ADAPTED FROM ERM, 2014)

7.6.1 RECYCLING OR RE-USE

The most favoured management option for returned waters is to dilute them with fresh water and utilise them in a subsequent fracturing event (Environment Agency, 2016). This reduces fresh water consumption, but can lead to concentration of contaminants over time by repetitive exposure to fresh rock surfaces underground and mixing with fracturing additives (Zhang, Hammack and Vidic, 2015). Heavy scaling can occur due to re-use and concentration of contaminants which impacts the longevity of the infrastructure (Abualfaraj, Gurian and Olson, 2014).

In Pennsylvania, there are abundant shale gas resources however there is little geological capacity to dispose of flowback fluids underground, and operators are faced with high transportation and licensing costs associated with waste management (Clark and Veil, 2009). In two case studies analysed by Baker Hughes operators incurred a 43-58% saving by treating and recycling their flowback in future fracturing events instead of injecting it for disposal (Seth *et al.*, 2013). Reusing treated flowback fluids in future fracturing operations is currently the “preferred and sustainable option” of the UK Environment Agency’s Radioactive Substances Waste Management Plan (Environment Agency, 2013). This, combined with the financial incentive proven in the US, will ensure that some degree of fluid treatment is expected following hydraulic fracturing in the UK.

7.6.2 DISPOSAL

7.6.2.1 UNDERGROUND DISPOSAL

Another option is to inject the wastewaters into geological formations suitable for storage, such as depleted oil and gas reservoirs or saline aquifers. This method relies entirely on the geological suitability and available capacity of a region to store these waters, therefore cannot be relied upon uniformly. Concerns exist over the suitability of underground injection for the UK, due to increase in induced and triggered seismicity across the USA where the technique is practiced with high rates of injection (Weingarten *et al.*, 2015). Additionally, without prior treatment or separation, underground injection confines the large volume of fresh water utilised in the fracturing process to waste, which will significantly add to the water footprint of operations.

7.6.2.2 SURFACE DISPOSAL

Disposal can also include discharge to a surface water body such as a river, estuary or canal. Surface discharge requires the waters to be treated to an environmentally acceptable level before they can be released to the environment. In the UK, the parameters for environmentally acceptable discharge to the water environment are set by the Water Framework Directive (2000/60/EC) and the local environmental agency permits discharges of this kind on a case by case basis (see Section 15.2 – UK and USA Water Quality Limits). These agencies are: The Environment Agency (England); The Scottish Environmental Protection Agency (Scotland); Natural Resources Wales (Wales). Generally, to discharge the waters generated by hydraulic fracturing to the surface water environment without detriment to water quality extensive treatment will be required.

7.6.3 TREATMENT

Wastewaters from hydraulic fracturing operations must be treated to remove contaminants and reduce salinity unless the waters are being disposed of through deep geological disposal, or diluted and reused in further fracturing operations. Treatment of these waters is complex as they can contain total dissolved solids (TDS) of 50,000-250,000 mg/L, meaning that for every litre of water returned, between 5 – 25% comprises of dissolved contaminants. They also tend to contain heavy metals, naturally occurring radioactive material (NORM), oils and grease and a number of chemicals added prior to fracturing (see Section 15.1 – Table of Common Hydraulic Fracturing Additives).

7.6.3.1 REMOVAL OF TOTAL DISSOLVED SOLIDS (TDS)

Reducing or removing dissolved contaminants from flowback waters commonly occurs by distillation or reverse osmosis. Reverse osmosis (RO) utilises the osmotic pressure between two liquid streams of differing salinities to push the saline water across a filtration membrane, removing the contaminants of interest. RO is the less energy intensive and more cost effective option (Table 1 & Table 2), however its application is limited to waters with TDS below 50,000 mg/L. During RO two streams are generated, one fresh water stream, and a brine or concentrated stream which can be sent on for treatment by distillation to enhance fresh water recovery. Distillation involves using heat energy to evaporate the contaminated water in an enclosed environment whereby the potable water re-condenses leaving the contaminants contained within the residue. This process is energy intensive, due to the heat required for high-volume evaporation, and therefore also costly (Table 1 & Table 2). Reverse osmosis can recover 40–90% of the input volume as fresh water, whilst distillation has a slightly better recovery rate of 50–90%. The unrecoverable waste becomes concentrated with contaminants not targeted by this treatment such as heavy metals or naturally occurring radioactive materials and will require additional focused treatment or permanent disposal.

TABLE 1 – ESTIMATED ENERGY CONSUMPTION RANGE FOR REVERSE OSMOSIS AND THERMAL DISTILLATION TO REMOVE TOTAL DISSOLVED SOLIDS FROM WASTE WATER FROM HYDRAULIC FRACTURING (NIJMEIJER AND METZ, 2010).

TREATMENT	LOW	HIGH
REVERSE OSMOSIS	2 KWH / M^3	6 KWH / M^3
THERMAL DISTILLATION (MVC)	11 KWH / M^3	18 KWH / M^3

TABLE 2 – ESTIMATED COST RANGE FOR REVERSE OSMOSIS AND THERMAL DISTILLATION TO REMOVE TOTAL DISSOLVED SOLIDS FROM WASTEWATERS. SOURCE: DEPARTMENT OF ENERGY, NATIONAL ENERGY TECHNOLOGY LABORATORY REPORT.

TREATMENT	LOW	HIGH
REVERSE OSMOSIS	\$2.64 / M^3	\$18.8 / M^3
THERMAL DISTILLATION (MVC)	\$18.8 / M^3	\$31.4 / M^3

7.6.3.2 REMOVAL OF HEAVY METALS, SUSPENDED PARTICLES AND HYDROCARBONS

Human exposure to heavy metals in water can cause serious negative health effects, and therefore regulations exist to minimise exposure from discharged wastewaters (Barakat, 2011). Wastewater containing heavy metals is produced by a number of industries including manufacturing, mining, petroleum refining, photographic processing, as well as conventional and unconventional oil and gas operations.

A number of treatment techniques can remove particulate matter from returned waters. Filtration removes particles by passing the waste stream through a barrier screen designed to trap or block any particulate material. This process is limited by the efficiency and size restrictions of the filtration membrane. Flocculation removes metals from suspension by addition of a flaking agent that causes particles to coagulate in larger groups that must be sifted out. Oxidation utilises the strength of hydroxyl radicals to oxidise and eliminate organic compounds, and also metals in waste water. Oxidation requires a high volume of chemical input to reduce the heavy metal content of wastewaters and produces contaminated sludge that requires secondary treatment or long-term disposal (Barakat, 2011).

Heavy metals, suspended particulate matter and hydrocarbons within returned waters can also be removed by electrocoagulation (EC). EC alters the surface charge on contaminant particles held in the water causing them to separate and accumulate in an easily removable mass. EC does not require any external parts such as filters or chemical additives, offering a low waste, low maintenance treatment option. Typically EC requires 0.5-6.25 kWh/m^3 of energy depending on water conductivity and operating time, however novel methods of EC treatment utilising alternating instead of direct currents could bring the energy intensity down by 70% (Lobo *et al.*, 2016). Problems with EC include regular cleaning or replacement of the electrodes and appropriate handling and disposal of the sludge or accumulated contaminants.

7.6.3.3 REMOVAL OF NATURALLY OCCURRING RADIOACTIVE MATERIAL (NORM)

The decay of radionuclides causes radiation to be emitted prompting negative health impacts at critical doses, so monitoring and appropriate control of NORM in waste streams is extremely important.

NORM contaminated waste streams generated by the conventional offshore hydrocarbons industry can be re-injected into the source formation to provide pressure support or enhanced reservoir recovery, or can be diluted and dispersed offshore into the sea without major environmental implications (Gafvert *et al.*, 2007; Almond *et al.*, 2014). With the case of unconventional hydrocarbon production onshore, the waters have predominantly been introduced by the fracturing process and therefore re-injection into the source formation is not viable as there is very little available pore space to inject the waste water into. Dilution and dispersion of wastewaters from hydraulic fracturing at sea is unlikely to be feasible due to limitations on marine contamination enforced by the OSPAR Treaty (Convention for the Protection of the Marine Environment of the North-East Atlantic, 2007). Additionally, concentrations of radionuclides in unconventional waste streams are expected to be 1.5 times higher than in conventional hydrocarbon waste streams due to the direct contact with the radionuclide-rich hydrocarbon bearing shale rocks (International Association of Oil & Gas Producers, 2016). Any facility receiving flowback contaminated with NORM will have to consider how to suitably manage the risks posed to infrastructure and workers on site.

Naturally occurring radioactivity tends to be present in rocks as the parent radionuclides ^{232}U and ^{238}Th (Figure 6). The daughter particles ^{226}Ra and ^{228}Ra are highly soluble and tend to be mobilised by injected fluids during the interaction between the fluids and freshly fractured shale faces. Ra is chemically similar to other alkaline earth elements such as magnesium (Mg), barium (Ba), strontium (Sr), and calcium (Ca) and so readily co-precipitates once produced at the surface generating naturally occurring radioactive deposits. If any solids precipitate out as part of pre-treatment processes then these will also be contaminated with NORM, for example the evaporate deposit residue generated by distillation to remove dissolved contaminants.

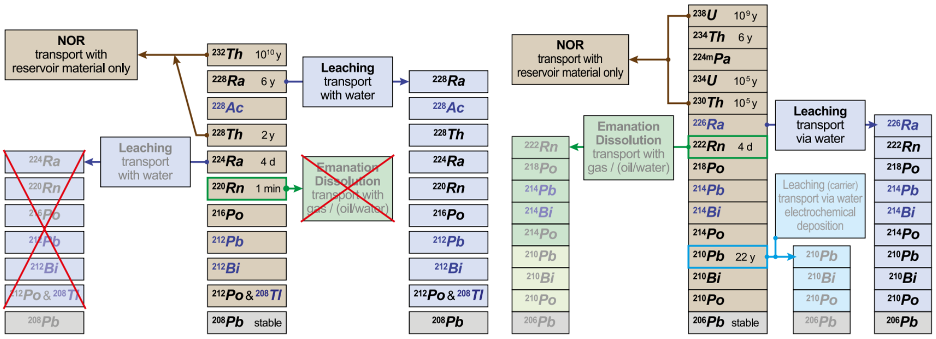

FIGURE 6 – FLOWCHART ILLUSTRATING THE DISTRIBUTION OF THE ^{232}TH AND ^{238}U RADIOACTIVE DECAY SERIES ACROSS UNCONVENTIONAL GAS OPERATIONS. GREY COLUMNS INDICATE GEOLOGICAL DECAY SERIES, BLUE COLUMNS INDICATE WHERE RADIONUCLIDES ARE PREVALENT IN AQUEOUS PHASE. SOURCE: (INTERNATIONAL ASSOCIATION OF OIL & GAS PRODUCERS, 2016)

8 THESIS OUTLINE

During hydraulic fracturing, the fluids injected into the subsurface are chemically altered during their time underground. The fluids that return to the surface following fracturing require appropriate management to minimise risk posed to the environment by unplanned release (spills, blowouts, etc.) and through improper treatment and discharge.

Since the hydraulic fracturing industry in the UK is in its infancy, data on the volume and composition of these waste fluids are lacking, making preparation for the management of this waste complex and subject to many unknowns. This thesis aims to improve upon the understanding of the potential composition of these fluids and their management options by combining novel experimental research with data collected from extensive operations in the USA to better confine the composition of these returned fluids.

Secondly, laboratory-based experiments were conducted to replicate the sub-surface conditions during fracturing and investigate the source and fate of constituents of concern within these wastewaters (Chapter 10). The influence of temperature, pressure, geology and chemistry of injected fluids were investigated in a number of experiments. Fluids produced during these experiments were analysed for a suite of chemical constituents to determine what reactions had taken place during interaction between the rocks and fluids. Additionally, aggregate data from the USA was used to mathematically predict the expected volumes and chemistry of waste to be produced in the UK should a fully-fledged shale gas industry develop. This was used to infer the economical and energetic cost implication of treatment (Chapter 9), giving socio-economic context to our understanding of the management of this waste.

9 VIABILITY AND COST OF MANAGING WASTEWATER FROM HYDRAULIC FRACTURING IN THE UK

The following chapter was first published as an article in 'Environmental Science: Water Research & Technology', November 2017.

Title: Assessing the Viability and Cost of Managing Wastewater from Hydraulic Fracturing in the UK
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9.1 ABSTRACT

The safe and effective management of wastewaters from unconventional hydrocarbon production using the hydraulic fracturing (fracking) process poses a major challenge (Gaudlip and Paugh, 2008; Gregory, Vidic and Dzombak, 2011; Rahm *et al.*, 2013; Kondash, Albright and Vengosh, 2017a; Zhang *et al.*, 2017). Exploitation of unconventional hydrocarbons, such as shale gas, remains controversial in the UK primarily due to concerns surrounding the hydraulic fracturing process required to extract the resource. The key issue of how waste fluids produced by hydraulic fracturing in the UK will be safely managed has yet to be adequately addressed, and the capacity for the specialist treatment required is currently uncertain. To address this critical knowledge gap we review, for the first time, the available management options for these waste fluids in the UK. We find that these are limited in comparison to the options available in the U.S., due to uncertainty surrounding whether wastewater injection wells will be permitted in the UK. Consequently, it is highly probable that these fluids will need to be treated and safely disposed of at the surface. In order to constrain the composition of wastewater which will require treatment in the UK, we analyse the only existing data set of returned waters from hydraulic fracturing (n = 31). We supplement this with measurements of wastewater from UK conventional onshore hydrocarbon (n = 3), and offshore hydrocarbon (n = 14), operations which produce water from similar formations as those currently targeted for shale gas exploration. Comparison of this limited UK data to the more extensive unconventional production dataset from the United States (n = 3092) provides confidence in our projected UK wastewater compositions. We find that the high level of salinity and concentration of naturally occurring radioactive material (NORM) in UK wastewaters will be problematic to treat for disposal into a freshwater environment. We use our data compilation to estimate costs of treating such wastewaters in a number

of relevant scenarios. We find that the projected salinity in FP waters from UK hydraulic fracturing operations can be treated at a cost of between \$107 683 (~£80 000) and \$1 376 093 (~£1 047 000) per well, with a P_{50} value of \$459 472, requiring between 2 and 26% of expected revenue. Additional costs, specific to the UK of up to £163,450 per well, will be incurred due to the legislative requirement for disposal of NORM concentrated sludge in permitted landfill sites. We find that existing capacity to receive NORM waste at currently permitted UK treatment facilities is limited, and that this will pose management problems if wastewaters are generated from multiple unconventional wells simultaneously.

9.2 OVERVIEW

Hydrocarbon production from shale formations has become an increasingly prominent source of energy over the last decade, yet exploitation of the resource remains controversial. The majority of this controversy is due to concerns surrounding the hydraulic fracturing (fracking) process which is required to extract the hydrocarbons, and the management of resulting wastewater (Gaudlip and Paugh, 2008; Gregory, Vidic and Dzombak, 2011; Rahm *et al.*, 2013; Kondash, Albright and Vengosh, 2017a; Zhang *et al.*, 2017). During the process, injected fluids (typically consisting of 99.5% fresh water and proppant to maintain fracture connectivity), and 0.5% chemical additives such as biocides, surfactants, viscosity adjusters, cross-linkers, breakers, corrosion inhibitors, bactericide, and friction reducers (ERM, 2014) react with the freshly fractured and exposed minerals and mix with the formation fluids within the shale rocks being targeted. On de-pressurisation of the well following the fracturing process, these fluids are returned to the surface having inherited heavy metals, naturally occurring radioactive material (NORM), salts and hydrocarbons from interaction with the rocks and fluids at depth. The chemistry of fluids returned is determined by the base chemistry of fracturing fluid, geochemistry of the rock, and the fluid chemistry of any formation waters residing in the pore space (Capo *et al.*, 2014), with potential influence from the chemistry of residual drilling fluid. Volumes of fluid returned vary depending on (1) the volume of fluid injected, (2) local geological characteristics that control water retention in the subsurface such as imbibition and extent of fracture network (Zhou *et al.*, 2016) and (3) well length (Schmid and Yoxtheimer, 2015). We collectively define and refer to these fluids as flowback and produced water (FP water), after (Nicot *et al.*, 2014).

FP waters generated by unconventional hydrocarbon operations – such as hydraulic fracturing or coal bed methane extraction – require appropriate management to ensure that they are stored, transported, treated and disposed of in a way that minimises the operational need for fresh water, maximises the efficiency and cost of the processes and reduces risks posed to the environment. The expected volumes and chemistries of FP water, or the capacity for their treatment (The Royal Society, 2012) or disposal in the UK is poorly understood, as outlined in a recent joint report from the Natural Environment Research Council (NERC), National Science Foundation (NSF), and Royal Society of Chemistry (RSC). This is the only literature published in the public domain that covers the management of FP waters from shale gas extraction in the UK to date, and concludes that the potential cost of treatment of FP waters could render extraction of shale gas reserves in the UK uneconomic (Reible and Davies, 2015). However, this conclusion was based on a limited review of available data that made no comprehensive assessment of UK FP water management options. To address this critical knowledge gap we review the available options for management of these wastes in the UK.

9.3 OPTIONS FOR WASTEWATER MANAGEMENT IN THE UK

Section 7.6.3 from Chapter 7 of this thesis appeared at this point in the published version of this paper, it is not repeated, however can be read on page 35.

9.4 PREDICTING VOLUMES OF WASTEWATER GENERATED FROM HYDRAULIC FRACTURING IN THE UK

The volume of fluid injected to undertake the hydraulic fracturing process depends on; the depth and length of well to be fractured, the number and length of stages to be perforated, the properties of the fracturing fluid, and the geological characteristics of the formation (Scanlon, Reedy and Nicot, 2014; The Environmental Protection Agency, 2015). Concurrently, volumes of FP water produced vary according to the volume of fluid injected, local geological characteristics that control water retention in the subsurface such as imbibition and extent of fracture network, and the well length (Schmid and Yoxtheimer, 2015; Zhou *et al.*, 2016). To date, only one well, targeting the Carboniferous Bowland Shale Formation, located at Preese Hall in Lancashire, England, has been subjected to high volume hydraulic fracturing in the UK. In 2011, Cuadrilla Resources injected 8399 m^3 of fluids, and perforated six fracturing stages in this well, before operations ceased and approximately 8000 m^3 of FP water was produced at the surface. As this operation provides the only FP water volume datum for the UK at present, additional estimates of the likely volume of FP water returned to the surface can be made using injection volume estimates from the British Geological Survey and published ranges of percentages of injected fluid returned by the in the following equation (1).

$$V_{returned} = V_{injected} \cdot \%_{returned} \qquad 1$$

Where; V = volume.

9.5 CALCULATING COSTS OF WASTEWATER TREATMENT

The cost of FP water treatment can be determined by equation 2 (adapted from Webb and Woodfield 1981):

$$C=R+VP+(\frac{S_s}{S_t}.S) \qquad 2$$

Where;
C is the total cost to the operator,
R is the cost of receiving the waste at the facility in question including storage and transport costs,
V is the volumetric cost of waste treatment imposed by the plant,
P is the cost per volume of the primary treatment applied to the waste,
St is the Total Suspended Solid (TSS) concentration of the waste,
Ss is the Total Dissolved Solid (TDS) concentration of the waste,
and S is the cost of the treatment of solids.

To forecast the cost of treatment of wastewater (C), the volume of waste to be treated (V) and the chemistry, or solid salinity, (St, Ss) must be determined and combined with the cost of auxiliary treatment (R, P, S).

We apply the results of the volume calculation (1) to a simplified cost projection equation (3) to identify the expected range in cost of treatment for our simulated range of FP water volumes. To provide a contextual and holistic estimate of the likely cost of treatment, published costs ($C_{treatemnt}$) for reverse osmosis (RO) and distillation by mechanical vapour compression (MVC), were used (Alleman and ALL Consulting, 2010) (Section 15.4.1). These costs were supplemented with a cost range provided by a specialist treatment plant in Pennsylvania, U.S. which uses a combination of chemical adjustment, filtration, settling, and distillation to produce dischargeable and re-usable effluent (Gilfillan and Haszeldine, 2016).

TREATMENT	SOURCE	COMPARATIVE MEAN	*UNITS*	MINIMUM	*UNITS*	MAXIMUM	*UNITS*
REVERSE OSMOSIS <50,000 MG/L	(IGUNNU AND CHEN, 2014)	2.16	$\$/M^3$	0.19 10,000 MG/L	$/BBL	0.50 35,000 MG/L	$/BBL
	(HARTO, 2014)	2.14	$\$/M^3$	0.13	$/BBL	0.21	$/BBL
	(MITTAL *ET AL.*, 2012)	5.03	$\$/M^3$	0.2	$/BBL	0.6	$/BBL
	(ALLEMAN AND ALL CONSULTING, 2010)	12.33	$\$/M^3$	0.42	$/BBL	3.5	$/BBL
MECHANICAL VAPOUR COMPRESSION >50,000 MG/L	(IGUNNU AND CHEN, 2014)	0.5	$\$/M^3$	0.08 >40,000PPM	$/BBL	0.08	$/BBL
	(HARTO, 2014)	1.32	$\$/M^3$	0.21	$/BBL	0.21	$/BBL
	(ALLEMAN AND ALL CONSULTING, 2010)	25.16	$\$/M^3$	3.00	$/BBL	5.00	$/BBL
	(LARA, OSUNSAN AND HOLTZAPPLE, 2011)	0.83	$\$/M^3$	0.42	$\$/M^3$	1.24	$\$/M^3$
UNDERGROUND DISPOSAL BY INJECTION	(HARTO, 2014)	1.20	$\$/M^3$	0.19	$/BBL	0.19	$/BBL
	(HAGSTROM *ET AL.*, 2016)	16.98	$\$/M^3$	0.05	$/BBL	2.65	$/BBL
	(JIANG, HENDRICKSON AND VANBRIESEN, 2014)	6.8	$\$/M^3$	0.59	$\$/M^3$	13.00	$\$/M^3$
	(MITTAL *ET AL.*, 2012)	10.50	$\$/M^3$	0.07	$/BBL	1.6	$/BBL
	(MOORE, WANG AND ACHARYA, 2010)	25.16	$\$/M^3$	1	$/BBL	3	$/BBL
	(FAKHRU'L-RAZI *ET AL.*, 2009)	16.98	$\$/M^3$	0.05	$/BBL	2.65	$/BBL

TABLE 3 - REPORTED RANGE IN COST OF TREATMENT TECHNIQUES USED TO TREAT WASTEWATER FROM HYDRAULIC FRACTURING.

A Monte Carlo simulation (n = 10,000) was performed to estimate the range in total cost likely to arise from changes in expected injected and returned volumes of fluid, and to estimate the sensitivity of each parameter within the calculation to the total cost of treatment. Each Monte Carlo simulation was run with 10,000 iterations using R. The input parameters used are listed in Table 4, and the input equations are described in Table 5.

Uniform distributions were assumed between end-member data points. Results are presented in Section 9.5.1 & 9.5.2. Table 6 & Table 7 show the $P_{2.5}$, P_{50} and $P_{97.5}$ values, indicating the 95% confidence interval ($P_{2.5}$ – $P_{97.5}$) and the median (P_{50}) of each simulation. Cumulative frequency distributions (CDFs) are also shown, with the $P_{2.5}$ and $P_{97.5}$ values marked in solid colour corresponding lines, and the P_{50} values with dashed lines (Figure 7, Figure 8, Figure 9).

$$C_{total}=V_{injected}.\%_{returned}.C_{treatment} \tag{3}$$

Where;
C = cost.

		MINIMUM	MAXIMUM	SOURCE
VOLUME$_{INJECTED}$		7,000M^3	18,000M^3	SEE S.I.4
PERCENTAGE$_{RETURNED}$		10%	70%	SEE S.I.5
COST$_{TREATMENT}$	RO	\$0.50/M^3	\$12.33/M^3	SEE S.I.3.1
	MVC	\$0.47/M^3	\$25.16/M^3	SEE S.I.3.1
	CBD	\$50.31/M^3	\$164.50/M^3	EUREKA RESOURCES (GILFILLAN AND HASZELDINE, 2016)
ENERGY$_{TREATMENT}$	RO	0.13 KWH/M^3	6.4 KWH/M^3	SEE S.I.3.2
	MVC	6 KWH/M^3	16.26 KWH/M^3	SEE S.I.3.2
	CBD	*UNKNOWN*	*UNKNOWN*	*NA*
COST$_{DISPOSAL}$	INJECTION	\$1.2/M^3	\$25.16/M^3	SEE S.I.3.1

TABLE 4 - INPUT PARAMETERS FOR MONTE CARLO SIMULATIONS TO PREDICT COST OF TREATMENT

$$\text{Volume } (V_{returned}) = \text{Volume } (V_{injected}) \ . \ \text{Percentage } (P_{returned})$$

$$\text{Cost } (C_{total}) = \text{Volume } (V_{injected}) \ . \ \text{Percentage } (P_{returned}) \ . \ \text{Cost } (C_{treatment})$$

$$\text{Energy } (E_{total}) = \text{Volume } (V_{injected}) \ . \ \text{Percentage } (P_{returned}) \ . \ \text{Energy } (E_{treatment})$$

TABLE 5 - INPUT EQUATIONS FOR MONTE CARLO SIMULATIONS TO PREDICT COST OF TREATMENT

9.5.1 VOLUME SIMULATION RESULTS

PROJECTED VOLUMES (M^3) (95%^{CI})	$P_{2.5}$	P_{50}	$P_{97.5}$
INJECTED	7287.02	12527.297	17748.43
RETURNED	1253.07	4676.047	10544.74
RETAINED	3035.46	7037.632	13889.07

TABLE 6 - PROJECTED VOLUMES OF INJECTED, RETURNED (WASTEWATER) AND RETAINED (IN THE ROCK FORMATION) FROM EACH HYDRAULIC FRACTURING WELL IN THE UK., P2.5 - P97.5 REPRESENTS THE 95% CONFIDENCE INTERVAL AND P50 REPRESENTS THE MEDIAN.

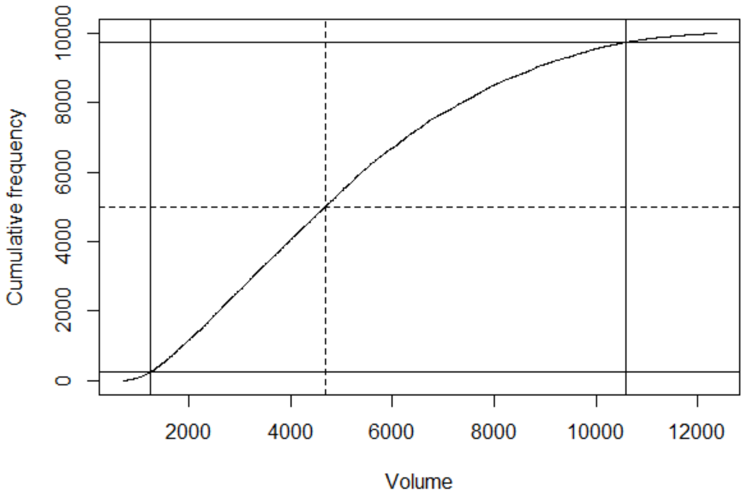


FIGURE 7 - CUMULATIVE FREQUENCY PLOT OF THE PREDICTED VOLUME OF RETURNED WASTEWATER

9.5.2 COST SIMULATION RESULTS

PROJECTED COSTS ($)	P_1	$P_{2.5}$	P_{50}	$P_{97.5}$	P_{99}
REVERSE OSMOSIS	814.96	2,701.73	24,846.46	94,815.38	132,904.08
MECHANICAL VAPOR COMPRESSION	955.61	3,952.76	50,506.23	196,484.74	270,996.33
COMBINED (EUREKA RESOURCES)	57,815.40	107,683.1	459,472.27	1,376,093.80	1,819,846.90

TABLE 7 - PROJECTED RANGE IN COST FOR TREATMENT OF WASTEWATER FROM A SINGLE HYDRAULIC FRACTURING WELL IN THE UK. P1 - P99 REPRESENTS THE 99% CONFIDENCE INTERVAL, P2.5 - P97.5 REPRESENTS THE 95% CONFIDENCE INTERVAL AND P50 REPRESENTS THE MEDIAN.

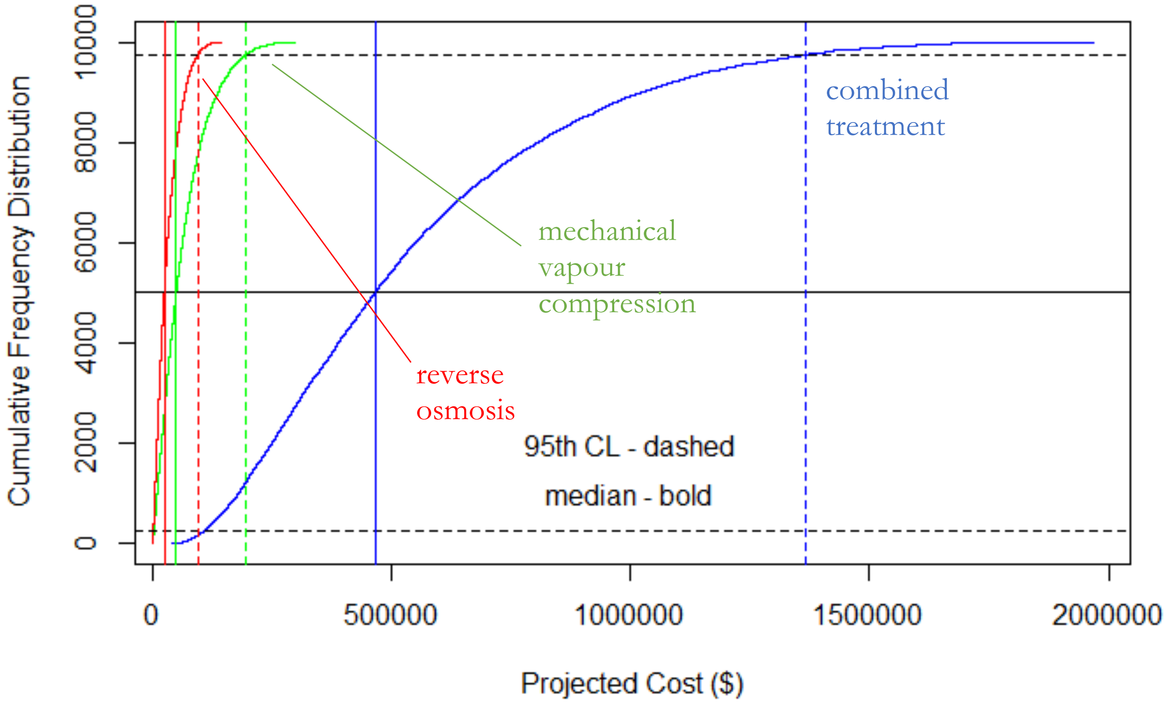


FIGURE 8 - CUMULATIVE FREQUENCY DISTRIBUTION OF CALCULATED COST FOR EACH TREATMENT METHOD AS PER TABLE ABOVE.

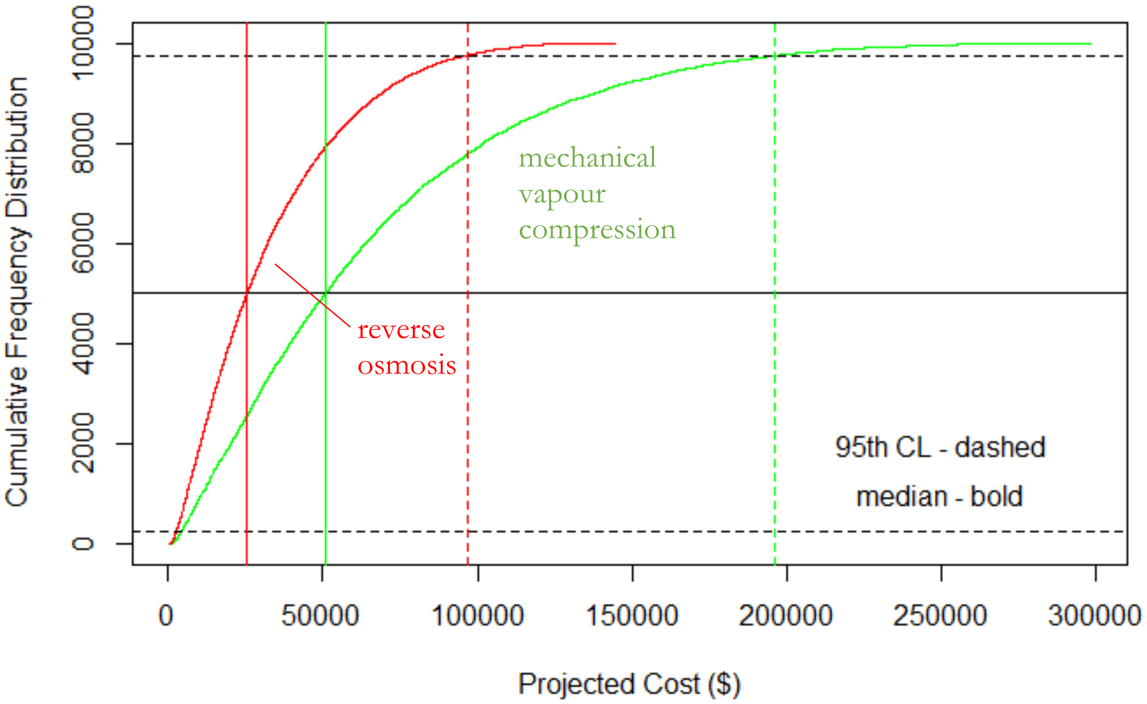


FIGURE 9 - CUMULATIVE FREQUENCY DISTRIBUTION OF CALCULATED COST - FOR REVERSE OSMOSIS AND MECHANICAL VAPOUR COMPRESSION ONLY)

9.6 ASSESSING THE CAPACITY FOR WASTEWATER TREATMENT IN THE UK

Non-specialist public treatment works in the UK are unable to treat highly saline and NORM contaminated waters (Vidic *et al.*, 2013; Zhang, Sun and Duncan, 2016). Hence, the removal of salinity (TDS) and NORM can only be undertaken at specially permitted treatment facilities (Department of Energy and Climate Change, 2014). There are currently four treatment facilities in the UK that are appropriately permitted to handle liquid waste containing NORM (The Environment Agency, 2000, 2010b, 2010a, 2013). Publicly available permitting documents for these four sites provide information on the environmentally agreed limits for accumulation and disposal of aqueous radioactive waste on a daily, monthly and annual basis. Amalgamating these provides the total daily accumulation and disposal limits for the UK (correct at time of publication). Using the measured radioactivity in FP waters from the 2011 hydraulic fracturing at Preese Hall and the projected volumes of FP water, we estimate the range in radioactivity expected to be received and disposed of by the sites listed (Equation 4).

$$A_{\text{projected}} = A_{\text{measured}} \cdot V_{\text{projected}} \qquad 4$$

Where;
A = radioactivity.

Supporting information for the methods described in this Chapter can be found in Sections 15.3 - 15.6.

9.7 RESULTS

9.7.1 VOLUMES OF FP WATER

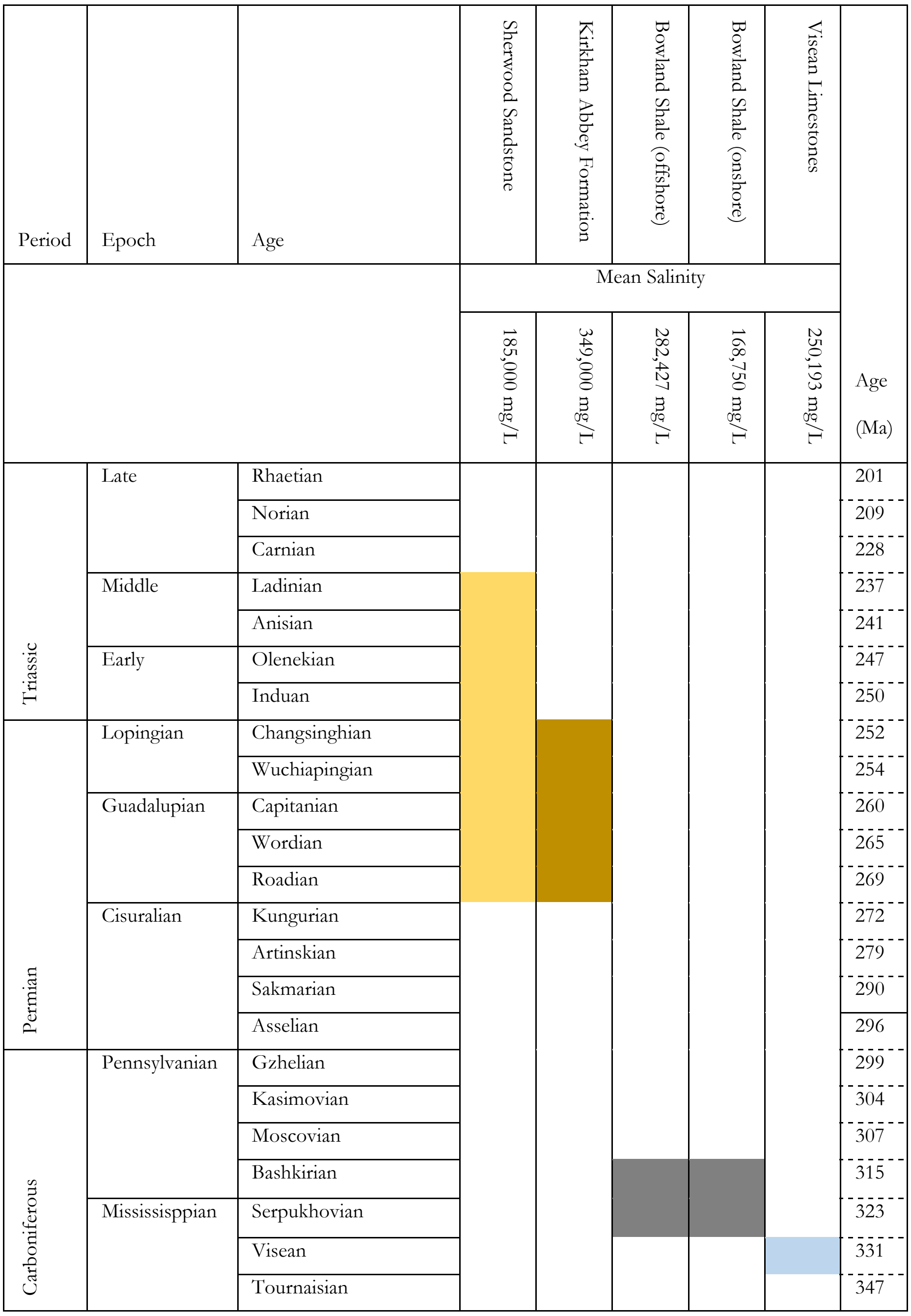
The British Geological Survey estimate between 7000 m^3 and 18,000 m^3 of injection fluid will be required for each UK hydraulic fracturing operation (Stuart, 2012) (See Section 15.5 for further data relating to the water requirements of hydraulic fracturing). The American Petroleum Institute cite that between 10% and 70% of this fluid typically returns to the surface (American Petroleum Institute, 2010) (See Section 15.6 for further data relating to the percentage of water returned during hydraulic fracturing). Using Equation 1 with the bounding values listed allows calculation of expected return water volumes of between 700 m^3 and 4900 m^3, if 7000 m^3 is injected. If the volume injected is nearer to the upper bound of 18,000 m^3, then the range of returned waters increases to 1800 m^3-12,600 m^3. These do not represent exhaustive volume limits, as corroborated by the wider range of volumes recorded in the U.S. (The Environmental Protection Agency, 2015), but provide reasonable estimates within the confines of existing data for the UK.

To improve upon this volume estimate, a Monte Carlo analysis (n=10,000) was performed on this volume projection to determine the 95% confidence intervals, given a uniform probability distribution assumed between the BGS end-member values. These simulations determine that in 95% of cases the FP water volume is likely to be between 1253 m^3 and 10,544 m^3, and only in 1% of cases will the FP water volume exceed 12,224 m^3. The volume of water retained by the formation could vary from 2227 m^3 to 12,754 m^3 under these injection volume scenarios (Table 6).

In comparison, the return of 8000 m^3 fluids from the 8399 m^3 injected by Cuadrilla Resources in the only hydraulic fracturing of a shale formation in the UK to date highlights that 95% of the injected fluids returned to the surface. However, this well was not completed and produced in the planned fashion, with no shut-in period due to the triggered seismic events, and hence these ratios are not representative and are not used in the modelled volumes of FP water. The fluid volume injected at Preese Hall is well within the 5th and 95th percentile volumes of fluids injected for hydraulic fracturing in 38,530 wells in the U.S. between 1st January 2011 and 28th February 2013 which range from 135 m^3 to 32,700 m^3 respectively, with a median volume of 6800 m^3 (The Environmental Protection Agency, 2015). However, these data include volumes for fractured vertical wells and coal bed methane operations, which typically use significantly less fluids. A higher and more concise volume range would be expected should the hydraulic fracturing of only high volume, horizontally drilled wells be considered, but unfortunately, the U.S. data is not reported by well type.

9.7.2 COST OF WASTEWATER TREATMENT

The expense and energy intensity of FP water treatment is dependent on the composition of the water to be treated. The minimum, mean, and maximum, levels of dissolved solids measured in the FP waters collected by Cuadrilla for treatment, at Preese Hall were; 94,000 mg/L, 128,750 mg/L and; 210,000 mg/L, respectively (Cuadrilla Resources, 2011). Whilst these data are limited by being from a single well, this provides the best estimates of future compositions of UK FP waters currently available. Confidence in this salinity range is provided from examination of data from offshore operations that produce waters from wells drilled to the Bowland Shale or underlying Visean limestone formations. The salinities of these waters range from 164,460 mg/L to 398,240 mg/L (CDA, no date), indicating that higher salinities may be possible from fracturing of other areas of the Bowland Shale. These offshore produced waters are typically discharged directly to the sea, and are only treated to separate co-produced hydrocarbons to the limit of 30 mg/L (National Measurement System, no date).



Period	Epoch	Age	Sherwood Sandstone	Kirkham Abbey Formation	Bowland Shale (offshore)	Bowland Shale (onshore)	Visean Limestones	Age (Ma)
			Mean Salinity					
			185,000 mg/L	349,000 mg/L	282,427 mg/L	168,750 mg/L	250,193 mg/L	
Triassic	Late	Rhaetian						201
		Norian						209
		Carnian						228
	Middle	Ladinian	■					237
		Anisian	■					241
	Early	Olenekian	■					247
		Induan	■					250
Permian	Lopingian	Changsinghian	■	■				252
		Wuchiapingian	■	■				254
	Guadalupian	Capitanian	■	■				260
		Wordian	■	■				265
		Roadian	■	■				269
	Cisuralian	Kungurian						272
		Artinskian						279
		Sakmarian						290
		Asselian						296
Carboniferous	Pennsylvanian	Gzhelian						299
		Kasimovian						304
		Moscovian						307
		Bashkirian			■	■		315
	Mississisppian	Serpukhovian			■	■		323
		Visean					■	331
		Tournaisian						347

Figure 10 - Stratigraphic chart annotated with mean salinities (mg/L) of fluid produced from shale formations in the UK.

Additionally, produced waters from conventional onshore production at Kirby Misperton in Yorkshire, England from the Permian Kirkham Abbey and Permo-Triassic Sherwood

Sandstone Formations overlying the Carboniferous Bowland Shale exhibit a range of salinities from 180,000 mg/L to 349,000 mg/L (Third Energy, 2014). These comparisons provide confidence that the salinity levels measured at Preese Hall are comparable, on average lower, than salinities measured from fluid produced during offshore Carboniferous production and onshore Permo-Triassic production as outlined in Figure 10.

The cost of treatment is dependent on feedwater chemistry (Equation 2) meaning estimates of overall cost are limited by the assumption that FP water chemistry will not change throughout the life of the well. However, salinity is known to vary significantly within the first weeks of production and then increase with time as fluids are produced (Barbot *et al.*, 2013). Measured TDS values in FP waters from the U.S. range from 35 to 358,000 mg/L (Madalyn S. Blondes, Kathleen D. Gans *et al.*, 2016), so scenarios beyond those considered in this analysis are possible. However, this is the best data available at present, until further UK hydraulic fracturing operations are undertaken and can easily be adapted when additional FP water chemistry data becomes available.

Using the data outlined, a Monte Carlo simulation was performed to predict the range of costs that will be incurred by operators for treatment of FP waters from a single UK well using Equation 3 (Table 7). The calculated costs range from $553 (low volume reverse osmosis for <50,000 mg/L TDS waters) up to $2,023,797 (high volume combined treatment techniques of high TDS waters) per well, with a 95% confidence interval of $2,701-$1,376,093. Only in 1% of cases where combined treatment techniques are used will the cost exceed $1,819,846 per well. The method of treatment and volume of water to be treated play a significant role in determining the overall cost of treatment. The variability in cost of treatment projected is greatest when the volumes of water produced are the highest. The range in cost of the treatment techniques considered is inherently linked to the energy requirements of those techniques. FP water containing a higher concentration of dissolved solids requires more energy to treat (more pressure for osmosis and greater heat for distillation) and therefore is more costly per unit. The range of costs applied in this analysis show the variability in treatment cost due to range in chemistry of feedwater and processes utilised for treatment (Section 15.4.1).

NORM are removed from FP water during treatment by mechanical vapour compression (MVC) when radioactive nuclides are precipitated within the sludge generated as a by-product. Consequently, any sludge produced during MVC of FP waters is contaminated with NORM and must be disposed of to a Radioactive Substances Regulations (RSR) permitted landfill site or to the LLW (Low Level Waste) Repository, in Cumbria. The cost of landfill disposal in the UK (gate fee plus landfill tax) per tonne varied from £89- 35, with a median of £100/tonne, in 2014/15 (Waste and Resources Action Programme, 2015). Due to the cost incurred by obtaining a RSR permit to receive LLW there is likely to be an additional charge for NORM contaminated waste corresponding to the radioactivity level of the waste (The Environment Agency, 2017). The LLW Repository pricing structure declares that the price for receipt of waste is based on "weight, volume, material type, radioactivity levels, hazardous content, packaging requirements, transportation mode and location". They estimate a charge to the operator of £500/m^3 for very low level radioactive waste (VLLW, < 4 MBq/tonne), and £3038/m^3 for low level waste (LLW, < 4 GBq/tonne alpha & < 12 GBq/tonne beta or gamma), with an additional charge per mega-Becquerel of £9 for ^{238}U, and £55 for ^{232}Th, including ^{226}Ra (LLW Repositroy LTD, 2015). Additional costs will be incurred due to the need to transport the NORM contaminated sludge for disposal offsite.

9.7.3 CAPACITY FOR TREATMENT OF NATURALLY OCCURRING RADIOACTIVE MATERIAL IN THE UK

Collation of publicly available data (The Environment Agency, 2000, 2010b, 2010a, 2013) allows calculation of a total daily accumulation limit for NORM in the UK to be 1.92x10^8

Bq for the ^{238}U group, and 3.82x10^{7} Bq for the ^{232}Th group. The total daily disposal limits are 1.15x10^{7} Bq for the ^{238}U group, and 4.09x10^{7} Bq for the ^{232}Th group. These limits apply to the parent radionuclides and groups of daughter radionuclides within the same decay chain. Although there are no limits placed upon the volume of treated waste discharged from these plants, there are volumetric limits imposed upon the quantity of waste containing NORM that can be received per day, equating to 826 m^{3} or (826,000 L) per day. The maximum radioactivity per volume of waste that can therefore be received is 232 Bq/L for the ^{238}U group and 46 Bq/L for the ^{232}Th group.

The maximum activity of ^{226}Ra (^{238}U group) recorded in FP waters from hydraulic fracturing in the UK is 90 Bq/L (day 158), with activities of 14, 6, and 17 Bq/L measured 0, 50, and 70 days respectively from initial flowback. As these values are only from one fracturing event they should not be considered as exhaustive or necessarily representative figures for the UK (Department of Energy and Climate Change, 2014). However, the recorded ranges in activity, and their increase in time as FP water is generated at the surface, are consistent with other studies of NORM in FP waters (Rowan *et al.*, 2011). ^{226}Ra levels of up to 626 Bq/L have been recorded in U.S. unconventional FP waters, with a median value of 39 Bq/L. U.S. conventional hydrocarbon produced waters have been reported to have activities of up to 196 Bq/L, with a median of 12 Bq/L (Madalyn S. Blondes, Kathleen D. Gans *et al.*, 2016). Comparatively, the activity of from offshore disposal of produced water from conventional oil and gas operations to the UK sector of the North Sea from 2005-2012 was 5.9x10^{8} and 13.3x10^{8} Bq per day, for the ^{238}U and ^{232}Th group, respectively.

Using the activity data from the Preese Hall well, a Monte Carlo simulation was used to predict the likely range of activities of FP waters using Equation 4. The results indicate that the total ^{226}Ra activity per hydraulically fractured well in the UK will range from 9.5x10^{4} Bq to 1.3x10^{6} Bq in 95% of cases, and will only exceed 1.5x10^{6} Bq in 1% of cases.

These values lie within the current calculated treatment capacity for the ^{238}U group, though only when considering the projected activity for the parent radionuclide. Constraining the implications of multiple daughter radionuclide groups on the accumulation and disposal capacity is not possible at present due to the limited data available. These results show that it is unlikely that FP waters produced from a single well will cause significant stress to the existing treatment facilities, provided they are divided between all available treatment plants. However, the uncertainty surrounding the volume of waste generated during fracturing could pose a threat to the capacity to treat NORM in the medium to longer term.

The Environment Agency enforce volumetric as well as activity limits on the volume of aqueous waste containing NORM that can be received at available treatment sites, currently amounting to 825 m^3/day across the UK. If the volume of FP water produced during fracturing exceeds this the capacity of the available treatment facilities could become critically stressed. Hence, without alternate storage options or emergency treatment capacity, operations would be forced to cease until the fluids can be appropriately handled.

9.8 IMPLICATIONS

9.8.1 COST OF SALINITY TREATMENT

The values of salinity measured in FP waters from the hydraulic fracturing of the Bowland Shale in the UK range from 98,000 to 210,000 mg/L. Salinity of FP water can vary geographically within a single shale basin due to lithological heterogeneity and distribution of relatively saline horizons (Blauch *et al.*, 2009; Rowan *et al.*, 2011). However, these values lie well within the reported salinity ranges observed in FP waters from unconventional production in the Haynesville, Marcellus and Barnett shale plays of the U.S. (35-358,000 mg/L). Additionally, they are lower than measured salinities of produced water from conventional hydrocarbon extraction onshore (180,000-349,000 mg/L) and offshore (164,000-398,240 mg/L) in similar formations in the UK (Figure 10).

It is clear that FP water with higher levels of contaminants, including TDS, will be more costly and energy intensive to treat. Waters with TDS levels above 50,000 mg/L can only be treated by distillation (MVC), as filtration and osmosis has been proven to be ineffective at high salinities (Horner, Halldorson and Slutz, 2011).

The 95% confidence range of estimated costs of desalination, per well, for FP waters from fracturing of the Bowland Shale in the UK by MVC range from \$3952 to \$196,484. Disposal of desalination by-products such as sludge contaminated with NORM will significantly increase the cost projections. The U.S. Energy Information Administration calculate that the mean estimated ultimate recovery (EUR) from shale gas wells is 1.8×10^6 MMBtu (US Energy Information Administration, 2016b). With the current price for natural gas at \$2.94/MMBtu (correct as of November 2017), each well can be estimated to generate *on average* \$5,292,000 in revenue. Therefore, up to 3.7% of the total revenue from a single shale gas well could be absorbed by desalinising treatment costs alone.

Variations in the price of natural gas can cause the percentage of expected revenue required for FP water treatment by MVC to vary from 2% up to 5%.

Additionally, if multiple treatment processes are required to target multiple contaminants within the waste, the cost can increase significantly. Eureka Resources, a specialised FP water treatment company based in Williamsport (PA), typically charge \$50.30/m^3-\$164.50/m^3 to treat FP water at their designated facility (Gilfillan and Haszeldine, 2016). If these prices are to reflect the total combined treatment cost in the future for the UK, between \$107,683 to \$1,376,093 (95% CL), or up to 26% of the estimated revenue per well would be required. The U.S. has also benefitted from the use of portable treatment facilities that reduce salinity and remediate against some contaminants on-site before re-use. These reduce the transport requirements associated with off-site waste treatment, but increase the likelihood of onsite spills as a result of increased on site waste handling.

9.8.2 COST OF NATURALLY OCCURRING RADIOACTIVE MATERIAL TREATMENT

Aqueous NORM waste in the UK is treated by following the principal of 'dilute and disperse' within the sewerage and water treatment system (Department of Energy and Climate Change, 2014). Given that underground disposal of FP waters has been discounted as an option for the UK to date, treatment for re-use or effluent discharge will be required.

It is also pertinent to consider the volume of solid or sludge NORM waste generated as a by-product. Radium, the most common NORM in FP water, is chemically similar to other alkaline earth elements such as magnesium (Mg), barium (Ba), strontium (Sr), and calcium (Ca) and so readily co-precipitates generating NORM concentrations in scale and sludge produced during MVC treatment. This sludge by-product will require disposal to landfill with the appropriate radioactivity permits unless exempt due to low activity by the Radioactive Substances Regulations (2011).

Within the context of Equation (2), the S value for FP water containing NORM will be inflated by the cost of obtaining and maintaining a RSR permit, with application fees for 2017 ranging from £980-£2640, and subsistence costs ranging from £154 to £3940 per year depending on the conditions and nature of the mining waste activity proposed (The Environment Agency, 2017). Additionally, disposal of these sludge wastes at landfill will incur a 'gate fee' and landfill tax, between £89-£135 per tonne in 2014. Utilising the known salinity of waters returned at Preese Hall, the total mass of solids available for removal from waters returned during fracturing of a single well can be projected to be between 10 and 3269 kg (53-2053 kg, 95% CL). Between 1 and 99% of the volume of sludge is comprised of residual wastewater and therefore the total volume to be disposed of varies in proportion to the percentage water content (Andreoli, von Sperling and Fernandes, 2007). Dewatering processes significantly reduce the volume of waste to be disposed, but if 100% recovery of solids is assumed and no dewatering performed the volume of sludge to be disposed varies from 10-329,600 kg (0.01-326.9 t). This equates to an additional cost of £1.00-£326.90 in regular landfill gate fees per well, or up to £163,450 (£500 per m^3 of sludge) at the LLW Repository exclusive of permitting levies for the cost incurred in obtaining an RSR permit, transportation costs, and radioactivity charges such as those imposed at the LLW Repository (LLW Repositroy LTD, 2015). The maximum projected disposal cost of NORM waste of £163,450 equates to an additional 3% of the estimated overall revenue generated from a single well. Therefore under these scenarios is unlikely that the additional costs of disposing this low level radioactive sludge will render unconventional extraction uneconomic, however the issue of available capacity remains pertinent.

9.9 LESSONS FROM THE U.S.

A number of the FP water management options practised in the U.S. have caused surface contamination, which has impacted the ecology and environment. It is crucial that the UK learns from the mistakes and subsequent regulatory improvements made in the U.S. to prevent similar problems occurring in the UK.

Treating waters returned by hydraulic fracturing operations at centralised or municipal treatment works in the U.S. has led to increased concentrations of contaminants such as TDS, bromide, and chloride in the receiving waters due to the incompatibility of the treatment facilities with the waters concerned (Gregory, Vidic and Dzombak, 2011; Olmstead *et al.*, 2013; Warner *et al.*, 2013). Inadequate treatment of these waters has also been shown to reduce water quality downstream from treatment works (Ferrar *et al.*, 2013; Vidic *et al.*, 2013; Warner *et al.*, 2013; Wilson and Van Briesen, 2013; Hladik, Focazio and Engle, 2014). Consequently, treatment of water in public or municipal works has since been banned by the U.S. Environmental Protection Agency, and treatment may now only be performed by specialist or designated treatment works (US EPA, 2016).

Leaks and spills associated with transport and storage of these waters can also cause detriment to water quality, as well as due to casing failure or poor well integrity at deep injection sites (Yuan *et al.*, 2013). Containment of waters within unlined surface ponds or impounds can allow leaching into the water table and contamination of nearby ground and surface waters (DiGiulio *et al.*, 2011). However, this practice will not be permitted in the UK (Environment Agency, 2013), and regulatory changes in some states in the U.S. mean that full lining of any hydraulic fracturing site is now required , which combined with a means of secondary containment of FP water has significantly reduced contamination risks (Kuwayama *et al.*, 2015).

9.10 CONCLUSIONS & RECOMMENDATIONS

We find that disposal options in the UK are limited by current restrictions on the underground injection of waste. Hence it is certain that some form of treatment will be required before waters will be re-usable, either for hydraulic fracturing operations or externally, or for safe to discharge to the environment. We find that whilst the salinity and NORM levels in future FP waters from UK hydraulic fracturing operations can be treated, this will cost between $2701 and $1,376,093 per well for salinity. This will require up to 26% of the revenue generated by a typical shale gas well, and up to £163,450 (3% of revenue) for NORM management.

We have found that there is currently limited treatment capability for receiving returned waters from unconventional gas operations in the UK that are contaminated with NORM, and no uniquely dedicated treatment plants currently exist. As the UK shale gas industry is in its infancy, the limited treatment capacity for returned waters should not pose a problem in the short term, unless especially high volumes of FP water are experienced that cannot be received at the currently permitted facilities.

However, significant expansion of the shale gas industry resulting in simultaneous FP water production from multiple wells would critically stress the current capacity to receive, treat and dispose of NORM contaminated, highly-saline wastewaters. We strongly recommend that this area receives further attention from the emergent unconventional gas industry, the established waste water management industry and regulatory bodies in the UK, in order to produce a coherent strategy for the for the future management of FP waters. Our work has found that no such co-ordinated strategy currently exists, and limited FP management capacity in the UK will present a significant hurdle to future expansion of the industry unless it is urgently addressed.

We advise that future shale gas activities in the UK make their returned water composition data publicly available so as to improve upon the estimates presented in this study. We further recommend that future treatment options are reviewed in light of new data once it becomes available.

10 LABORATORY METHODS

HYDROGEOCHEMICAL BATCH REACTIONS

To investigate the geochemical interaction between freshly fractured shale rocks and injected fracturing fluids at realistic pressures and temperatures in the subsurface, batch reaction experiments were designed to replicate the physical and chemical conditions during hydraulic fracturing.

Batch reaction experiments are closed chemical reactivity experiments where two or more reactants are placed under controlled temperature and pressure conditions. They allow the operator to define the ratios of reactants in the system, making it easy to cross compare the results of reactions taking place at differing times, and the duration of experiments is flexible to suit requirements.

Batch reactors can be configured to relatively basic design and can be constructed with ease from readily available parts – the vessels for this research were constructed entirely from Swagelok stainless steel parts and can therefore be easily reconstructed to replicate experiments. They are easy to take apart and clean, however require significant labour to prepare, set up and clean in preparation for and after each experiment. This also means that during cleaning or preparation the vessels cannot be used, resulting in forced 'down-time' where experiments cannot take place.

The closed nature of batch reactor vessels means that they are hard to retrieve samples from without perturbing the system during an experimental run. This offers the benefit of ensuring a closed chemical system for the duration of experiments, however prevents the system from being temporally sub-sampled without altering the conditions in the vessel.

The batch reactors used for experiments in this thesis were designed to enable periodic sampling of the aqueous solution within the vessel to determine temporal change during each experiment, however this feature was not widely successful utilised due to residual shale material clogging the sampling tap and blocking fluids from passing through the sampling tap.

Batch reactions can be used to replicate the pressure and temperature conditions within the subsurface. The batch reactor vessels and the experimental conditions were designed to mimic the hydro-geo-chemical conditions during hydraulic fracturing as closely as possible so that any shale rock could be reacted with any fracturing fluid to determine the chemical changes likely to occur during hydraulic fracturing operations. These experiments were designed so that without any field-scale fracturing operations taking place, the chemistry of any waste or residual fluid produced at the surface following operations could be better predicted and the overall geochemical interaction between shale and injected fluids in the subsurface could be better understood.

10.1 ROCK SAMPLES

Eighteen shale rock samples were collated for conducting batch reactions (Table 8). Shales from the UK (n = 15) and the USA (n = 3) were obtained, and both rocks from outcrop (n = 3) and core (n = 15) were selected. Shale samples ranged in age from the Devonian Marcellus Shale (n = 3) to the Jurassic Kimmeridge Clay (n = 1), with the majority of samples from the Carboniferous Bowland Shale (n = 14). Twelve core samples of the Bowland Shale were obtained from the Preese Hall 1 well (*LJ/05-5*) in Lancashire (UK); six from the British Geological Survey records and six from Cuadrilla Resources Ltd. private holdings. Outcrop samples were collected of the Upper and Lower divisions of the Bowland Shale in Little Mearley Wood, near Clitheroe, Lancashire. Two core samples of the Marcellus Shale were acquired from the Snow Shoe 4 well (*SS4-8HG*), and one outcrop sample was collected from the Forgy Quarry, Newton Hamilton, Pennsylvania. A single core sample of the Kimmeridge Clay from a well in the East Brae offshore oil field in the North Sea (*16/3a-E1*) was also used.

SAMPLES	LOCATION	DMS COORDINATES	WELL NUMBER	GEOLOGICAL AGE	DEPTH
PH1-6	PREESE HALL, UK	53°49'19.006"N / 2°56'56.576"W	LJ/05-5 (BGS)	CARBONIFEROUS	2348 – 2500 M
BS1-6	PREESE HALL, UK	53°49'19.006"N / 2°56'56.576"W	LJ/05-5 (CUADRILLA)	CARBONIFEROUS	2086 – 2348 M
BS-U	LANCASHIRE, UK	53° 52' 12.36" N / 2° 20' 23.1025" W	-	CARBONIFEROUS	OUTCROP
BS-L	LANCASHIRE, UK	53° 52' 12.36" N / 2° 20' 23.1025" W	-	CARBONIFEROUS	OUTCROP
MS$^{\diamond}$	PENNSYLVANIA, USA	40°23'51.7"N / 77°49'32.5"W	-	DEVONIAN	OUTCROP
MS-C	PENNSYLVANIA, USA	41° 3' 34.0596" N / 77° 57' 58.9392" W	SS4-8HG	DEVONIAN	2521 – 2660 M
KC-EB	SUSSEX, UK	58° 52' 34.433" N / 1° 31' 36.845" E	16/3A-E1	JURASSIC	3910 – 3918 M

TABLE 8 – LIST OF ROCK SAMPLES UTILISED IN EXPERIMENTS, INCLUDING LOCATION OF SAMPLE, GEOLOGICAL AGE, WELL NO AND DEPTH.

10.1.1 DEVONIAN MARCELLUS SHALE

Marcellus Shale (MS) outcrop samples were collected from the Forgy Quarry on Ferguson Valley Road, North East of Newton Hamilton, Pennsylvania, 40°23'51.7"N / 77°49'32.5"W by Dr. Stuart Gilfillan and Prof. Stuart Haszeldine (University of Edinburgh) in April 2016 (Figure 11).

The exposures at the sampling site were described as "Bedded (5-20 mm), platy, very dark black 'Marcellus Shale'. No fauna or flora visible of any type. A lot of pale iron brown on the bedding layers. No pyrite, no jarosite weathering. Low density, and easy brittle fracture." (Haszeldine, 2016).

Data from wells drilled into the MS formation across Pennsylvania indicate porosities of 5 – 15% in the southwest and 4 – 10% in the northeast, with permeabilities ranging from 130 to 2000 nD (Range Resources, 2016).

FIGURE 11 – MARCELLUS SHALE OUTCROP SAMPLING LOCATION: FORGY QUARRY, NEWTON HAMILTON, PENNSYLVANIA. LEFT: DR. STUART GILFILLAN STANDS WITH THE EXPOSURE KNOWN TO HAVE BEEN DUG OUT WITHIN ONE MONTH OF SAMPLING (APRIL 2016). RIGHT: EXPOSURE WITH SCALE CARD SHOWS SCALE AND FREQUENCY OF LAYERING, AND STYLE OF WEATHERING IN THE SHALE.

10.1.2 CARBONIFEROUS BOWLAND SHALE

Bowland Shale (BS) subsurface samples were taken from drillcore and cuttings of the Preese Hall 1 well (*LJ/06-5*) held by the British Geological Survey (BGS), in 2016, and from Cuadrilla Resources private holdings, in 2017. The Preese Hall 1 well is located adjacent to Preese Hall Farm on the Fylde Coast of North West Lancashire, 53°49'19.006"N / 2°56'56.576"W (Clarke and Hird, 2012). Details of each sample collected, including depth, lithology, and sample source are provided in Table 9.

SAMPLE	DEPTH	FORMATION	NOTES	SOURCE
PH_1	2348.02 M	UPPER BOWLAND SHALE	*PERFORATED ZONE, GAMMA LOG ~110 API*	*BGS*
PH_2	2348.06 M	UPPER BOWLAND SHALE	*PERFORATED ZONE, GAMMA LOG ~110 API*	*BGS*
PH_3	2348.97 M	UPPER BOWLAND SHALE	*PERFORATED ZONE, GAMMA LOG ~110 API*	*BGS*
PH_4	2015.52 M	UPPER BOWLAND SHALE	*NON-CALCAREOUS,* R_0*<1.1%*	*BGS*
PH_5	2594.15 M	LOWER BOWLAND SHALE	*N/A*	*BGS*
PH_6	2499.97 M	UPPER BOWLAND SHALE	R_0 *>1.1%, PRODUCING ZONE NOT PERFORATED*	*BGS*
BS_1	2348.15 M	UPPER BOWLAND SHALE	*PERFORATED ZONE/CORE AVAILABLE*	*CUADRILLA*
BS_2	2348.48 M	UPPER BOWLAND SHALE	*PERFORATED ZONE/CORE AVAILABLE*	*CUADRILLA*
BS_3	2347.78 M	UPPER BOWLAND SHALE	*PERFORATED ZONE/CORE AVAILABLE*	*CUADRILLA*
BS_4	2347.17 M	UPPER BOWLAND SHALE	*PERFORATED ZONE/CORE AVAILABLE*	*CUADRILLA*
BS_5	2086.23 M	UPPER BOWLAND SHALE	*HIGH GAMMA LOG*	*CUADRILLA*
BS_6	2086.23 M	UPPER BOWLAND SHALE	*HIGH GAMMA LOG*	*CUADRILLA*

TABLE 9 - LIST OF CORE SAMPLES COLLECTED FROM THE BOWLAND SHALE. NOTES EXPLAIN SAMPLING CHOICE AND CORRELATE TO WELL LOG DATA PROVIDED BY CORE HOLDERS (BGS AND CUADRILLA).

The Bowland Shale can be described as "Mainly dark grey fissile and blocky mudstone, weakly calcareous, with subordinate sequences of interbedded limestone and sandstone, fossiliferous in more-or-less discrete bands." (British Geological Survey, 2017).

Average effective porosity is 2.39% for the Upper Bowland Shale (UBS) and 2.82% for the Lower Bowland Shale (LBS), while total porosity is 3.31% and 3.70% respectively. Permeability was measured at 150 nD for the UBS and 115 nD for the LBS (Clarke and Hird, 2012).

Outcrop samples of the UBS and LBS were collected from surface exposures of each formation in Little Mearley Wood, Clitheroe, Lancashire, 53° 52' 12.36" N / 2° 20'

23.1025" W. Permission to sample rocks in this area was obtained from Natural England and the landowner (Mr George Dobson) due to the exposures being within a Site of Special Scientific Interest (Section 15.7 – Pro-Forma for Unconditional Consent for Sampling). Sampling was carried out by Dr. Andrew Fraser Harris and Dr. Xander Lightbody in October 2017.

10.1.3 JURASSIC KIMMERIDGE CLAY

Kimmeridge Clay (KC) samples were obtained in 2008 from drillcore of the East Brae well (*16/3a-E1*) drilled by Marathon Oil PLC and held by the University of Edinburgh. The East Brae well extends into a gas condensate reservoir within the western margin of the South Viking Graben, and the KC-EB sample was taken from the caprock formation between 3910 m and 3918 m (Edlmann, Haszeldine and McDermott, 2013).

The Kimmeridge Clay is a clay-rich siltstone with micaceous laminae with porosities ranging between 5 and 20%, decreasing with depth, and permeabilities between 0.09 and 4 ηD (Okiongbo, 2011).

10.2 REACTION FLUIDS

The rock samples were reacted with fluids of varying composition to reflect the range of fluids that are permitted for use during hydraulic fracturing in the UK. First, the samples were reacted in the batch reaction vessels with distilled water. Distilled water is vaporised and then re-condensed – removing any minerals, or other impurities. Although it is expected that most hydraulic fracturing operations will take place using locally sourced mains water, which has a higher mineral content than distilled water, it was anticipated that using distilled water as a base fluid would make any changes in the chemical composition of the reactant fluid easier to detect and interpret. A notable drawback of using distilled water in the batch reaction vessels is that it is more likely to react with any impurities surrounding it and therefore may cause higher than expected reactivity between shales and fluids. This was accounted for by the use of a blank batch reaction vessel which was set up to run with only distilled water – any material inherited by the water during this blank run would quantify any interactivity between the reaction vessel and the distilled water. The results of chemical analyses of product water were corrected for the chemicals detected in the blank batch reaction vessels.

The effect of using distilled water over mains water in the reaction vessels was not able to be quantified, however it is anticipated that a greater proportion of minerals would be leached from the rock using distilled water and therefore results of these batch reaction experiments could be considered ‘worst case’ leaching scenarios compare to the use of mains water.

During experimental development it became apparent that to conduct experiments with chemical additives used in the fracturing process alternative reaction vessels would be required. The primary chemical additive of interest; utilised for well clean-up, acid fracturing, and hydraulic fracturing, and the only chemical additive to be permitted for use within the UK at time of research was hydrochloric acid or HCl (King, 2012; The Environment Agency, 2014).

Due to the known interaction of hydrochloric (HCl) acid with stainless steel, especially at elevated temperatures and pressures (Jessen, 2011), the designed batch reactors were not fit to conduct experiments with complex fluids including HCl. Thus, for experiments with HCl additive, alternative glass apparatus was used – which removed the ability to replicate sub-surface pressure in experiments using fluids containing HCl additive – as glass could not be pressurised to 1500 psi (103 bar).

10.3 ROCK SAMPLE PREPARATION

Rock samples were cut to remove outer oxidised layer. Elongate slices of 5mm thickness were made into thin sections for optical and electron microscope analysis. The remaining samples were washed and left to air dry for a period of one week. Samples were passed through a dodge jaw crusher three times to crush to 1 mm chips. A Carboniferous shale from Spireslack Quarry in Glenbuck, Scotland (sampled from just below the index limestone marking the top of coal units) was passed through the rock crusher before each rock processing session to ensure cleanliness of crushing and milling equipment.

After crushing, samples were sieved to separate the fractions. Crushed fractions of 1mm, 0.5 – 1 mm, 0.18-0.5 mm and <0.18 mm were weighed (Table 10). The fraction distribution can determine crushing performance. Optimal crusher performance is achieved when 40% of the crushed material is finer than ½ the size of the crusher setting, and when 80% of the crushed material is slightly below the size of the crusher setting. Between 69 and 76% of the crushed material was returned as 1 mm chips, indicating slightly lower than expected crusher performance. This was not overly problematic for sample preparation since following crushing, as most material was milled to a much finer fraction using a tungsten carbide milling unit to maximise the available reactive rock surface (see p82 for more detail).

Crusher performance may also be related to the abundance of brittle rock minerals, which determine the overall 'fracability' of a shale. A higher concentration of more brittle minerals means the rock is more likely to fracture easily and therefore gas recovery from hydraulic fracturing will be more successful, therefore typically, productive gas shales are more brittle than other softer sedimentary rock types.

For all samples (with the exception 15 g of 1 mm KC rock chips) the crushed material was ground using a tungsten carbide milling unit. The milling unit was also flushed with the carboniferous Spireslack shale and acetone in between each sample. The 1mm KC fraction was retained for a single experiment to determine the impact of particle size and surface area, while the remaining material was milled to a fine powder. The 1 mm fraction was washed with distilled water and left to air dry so as to remove any finer material from the surface of the shale chips. All samples were stored in airtight sample bags, out of direct sunlight, and away from harsh chemicals in the laboratory.

The majority of rock samples used were recovered from geological core, and therefore the overall availability of material was limited. Core is expensive to obtain and store – and only a quarter of the overall cylinder of core is made available for sampling at the British Geological Survey Core Store. Much greater amounts of rock were able to be collected when samples were recovered from surface outcrops such as in the case of the samples from the Marcellus Shale. As illustrated by the data in Table 10, when sampling core, typically only 20 – 60 g was recovered for use in experiments. This meant that the number of experiments and replicates for each sample were limited by the amount of available rock.

Experimental vessels were designed with this restriction in mind – and required only 15 g of sample to conduct a batch reaction at a rock:fluid ratio of 1:20. However for some samples this did mean that only one experiment was able to be conducted before the sample was used up.

The samples of Kimmeridge Clay held by the University of Edinburgh were more abundant than core samples or those brought from the USA and were available for immediate processing.

Arranging for access to and collecting the other samples was time consuming and logistically challenging. After the Kimmeridge Clay samples, the next rock samples were not available for processing until May 2016, eight months after initially commencing this research, and three months after the experimental vessels were ready.

Additionally, an experimental run time of 28 days also requires sample processing, preparation, equipment cleaning and set up, and cleaning and re-set time in between experiments which was imperative to the successful re-use of batch reaction vessels.

Three identical batch reactors were built so that multiple experiments could be conducted simultaneously, two containing rock an fluid and a single blank vessel containing only fluid. The vessel that was the blank was rotated to ensure effectiveness of the cleaning process across all vessels.

To obtain a single set of results from one batch reaction took around four months, however some processes such as rock crushing and milling, as well as fluid analysis could be conducted simultaneously. Between finishing the batch reaction vessels in March 2016, and obtaining the first samples in April 2016, the first results of geochemical analyses of the fluids generated during batch reactions were obtained in September 2017.

SAMPLE CODE/ FRACTION	>1 MM	1 - 0.5 MM	0.5 - 0.18 MM	<0.18 MM	TOTAL (G)
MS	109.7	16.3	14.3	9.7	150.0
KC	77.8	16.4	11.1	7.3	112.6
PH1	28.9	4.2	3.3	2.5	38.9
PH2	33.5	4.5	3.6	2.1	43.7
PH3	47.3	7.1	5.6	4.6	64.6
PH4	17.5	3.1	2.1	1.0	23.7
PH5	27.3	4.5	3.1	2.0	36.9
PH6	32.4	4.4	3.2	2.1	42.1

TABLE 10 – DISTRIBUTION OF SIEVED FRACTION FOR EACH SHALE SAMPLE BY MASS.

10.4.1.1 RESERVOIR PRESSURE AND TEMPERATURE (EXPERIMENTS (SF1)

A pressurised batch reaction cell was designed and constructed to undertake batch reactions at representative sub-surface pressures and temperatures. The equipment was designed to be filled with a mixture of shale and fluid (ratio variable by experimental design), withstand and maintain pressurisation up to 2000 psi (138 bar), and be heated to 100 °C in an oven. Three replicate batch reactors were designed to allow the simultaneous run of a control, a closed system batch reaction, and a batch reaction that allows the fluids to be repetitively sampled throughout the experiment duration.

The equipment required to build these vessels was supported financially by an award from the Moray Endowment Fund, awarded annually by the University of Edinburgh to support original research.

The batch reactors were constructed entirely of stainless steel Swagelok parts (Table 11), in the Laboratory 2.18 of the Grant Institute, University of Edinburgh. The batch reactors were designed to receive inflow from a pump, infill and pressurise the batch reactor cylinder, be shut off from the pump by on/off valves at each end of the cylinder, and be sampled from an on/off tap (Figure 12).

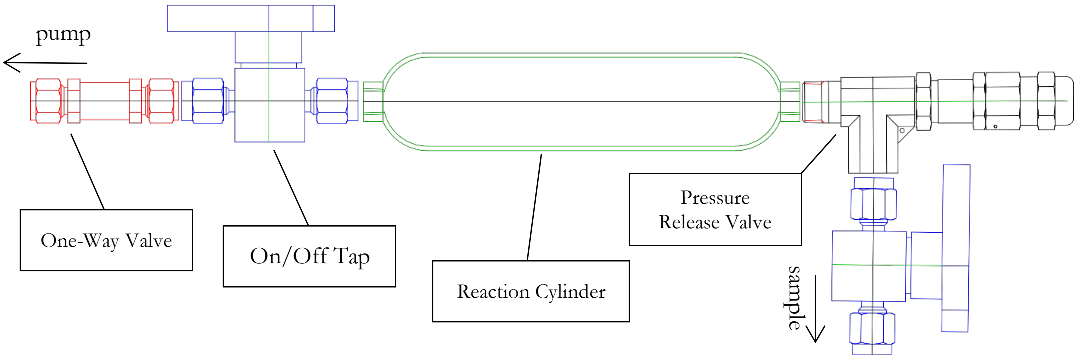


FIGURE 12 – DESIGN DRAFT OF EXPERIMENTAL EQUIPMENT, EXCLUDING ALL PIPING AND CONNECTORS FOR CLARITY.

ITEM	ITEM SPECIFICATION	ITEM CODE	UNITS
ONE-WAY VALVE	STAINLESS STEEL POPPET CHECK VALVE, FIXED PRESSURE, 1/8 IN. SWAGELOK TUBE FITTING, 1 PSIG (0.07 BAR)	SS-2C-1	1
ON/OFF FLOW TAP	STAINLESS STEEL QUARTER TURN INSTRUMENT PLUG VALVE, 1/8 IN. SWAGELOK TUBE FITTING, 0.10 CV	SS-2P4T	2
BATCH CYLINDER CONNECTOR	STAINLESS STEEL SWAGELOK TUBE FITTING, MALE TUBE ADAPTER, 1/8 IN. TUBE OD X 1/4 IN. MALE NPT	SS-2-TA-1-4	2
BATCH CYLINDER	316L STAINLESS STEEL DOUBLE ENDED DOT-COMPLIANT SAMPLE CYLINDER, 1/4 IN. FNPT, 300 CM3, 1800 PSIG (124 BAR)	316L-HDF4-300	1
PRESSURE RELEASE VALVE	STAINLESS STEEL HIGH PRESSURE PROPORTIONAL RELIEF VALVE, 1/4 IN. SWAGELOK TUBE FITTING, BUNA N SEAL	SS-4R3A-BU	1
PRESSURE RELIEF VALVE CONTROL	BROWN SPRING KIT FOR R3A SERIES PROPORTIONAL RELIEF VALVE, 2250 TO 3000 PSIG (155 TO 206 BAR)	177-R3A-K1-E	1
END CAP	316 STAINLESS STEEL CAP FOR 1/8 IN. OD TUBING	SS-200-C	1
CONNECTION SIZE REDUCER	STAINLESS STEEL SWAGELOK TUBE FITTING, REDUCING PORT CONNECTOR, 1/4 IN. X 1/8 IN. TUBE OD	SS-401-PC-2	2
CONNECTOR	316 SS NUT AND FERRULE SET (1 NUT/1 FRONT FERRULE/1 BACK FERRULE) FOR 1/8 IN. TUBE FITTING	SS-200-NFSET	15
TUBING	316/316L STAINLESS STEEL SEAMLESS TUBING, 1/8 IN. OD X 0.028 IN. WALL X 20 FEET	SS-T2-S-028-20	1

TABLE 11 – LIST OF SWAGELOK PARTS, SPECIFICATION AND PRODUCT CODES, REQUIRED TO CONSTRUCT EXPERIMENTAL BATCH REACTOR CELLS.

All experimental equipment was soaked in a sonic bath with Mucasol™ alkaline laboratory detergent and rinsed three times with deionized (DI) water before drying in an oven overnight prior to set up. In between experiments all parts were deconstructed, rinsed for debris and then sonicated until visually clean. The control vessel was rotated after each experiment to ensure effectiveness of the cleaning process and fluids sampled from control vessels showed very little contamination from previous experiments (Figure 13). The highest concentration of any element measured in a control experiment was 0.76 mg/L potassium in the initial control, however subsequent control fluids showed concentrations below those measured in unreacted distilled water. Generally, the control experiments showed that the cleaning process was effective and minimal variation was detected from the composition of unreacted distilled water. Largest variations in concentration with reference to distilled water were observed in calcium, potassium, magnesium, sodium, iron and lead. No chromium, nickel, or molybdenum was detected indicating the stainless steel batch reactors remained chemically stable throughout experiments.

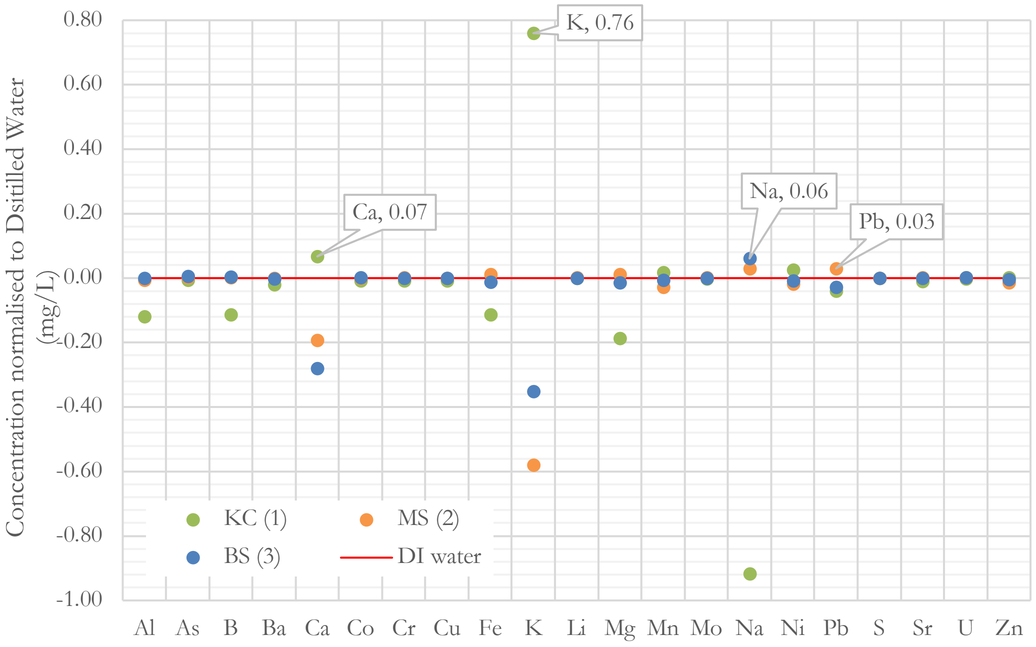


FIGURE 13 – CONCENTRATION OF ELEMENTS MEASURED IN CONTROL EXPERIMENTS NORMALISED TO COMPOSITION OF DISTILLED WATER (RED REFERENCE LINE). BRACKETED NUMBER IN LEGEND REFERS TO EXPERIMENTAL ORDER.

EVALUATING THE EFFECT OF PARTICLE SIZE, AND TEMPORAL SUB-SAMPLING

Initially, the effects of particle size were tested in the batch reactors. The first experiment compared the reaction between 1 mm KC shale chips with KC shale powder. Subsequently, the ability to sub sample from the experiments was trialled; a closed batch reaction was compared with one that was sub-sampled after 24 hours. Sub-sampling during the experiments was largely unsuccessful due to the mixture of shale powder and fluid clogging the sampling tap and preventing flow. The amount of fluid able to be sampled from both SF1 experiments was not sufficient for obtaining analytical results.

Despite issues with sub-sampling from the RPT equipment, the vessels were used to conduct three rounds of experiments at reservoir pressures and temperatures with distilled mains water and three difference shale samples (MS, BS1, KC).

For each experiment, 15.0 ± 0.1 g of shale was weighed using a Cole Palmer Symmetry ED-1200 portable balance. The shale was transferred into a glass beaker where it was mixed with 285 ml of distilled water until homogenised and poured into an upstanding batch reaction vessel (Figure 15). Once filled, the batch reactor is sealed with the check valve and on/off flow tap and attached to a Varian 2510 HPLC Fluid Pump. The pump was run at a flow rate of 0.1ml/min until the pressure on the attached Additel ADT 680 Pressure Gauge read 1500 ± 25 psi (103 bar), at which point the reactor is sealed using the on/off flow tap and disconnected from the pump. The ends of the vessel are sealed off with cap pieces and placed in a Memmert UNB500 oven at 65.0 ± 0.1 °C (Figure 15). All glassware and plastic used was cleaned in 10% HNO_3, rinsed with DI three times and dried in an oven overnight prior to use.

For sub-sampling the sample tap at the base of the upstanding reaction vessel was opened into a borosilicate glass collection beaker. During sampling the pressure was released from the system, so after sampling the pump was used to re-pressurise the vessel using the same method as during experimental set up. For final sampling the reaction vessel was detached from the pressure release valve and the contents poured out into screw-cap 15 ml Fisherbrand conical polypropylene centrifuge tubes.

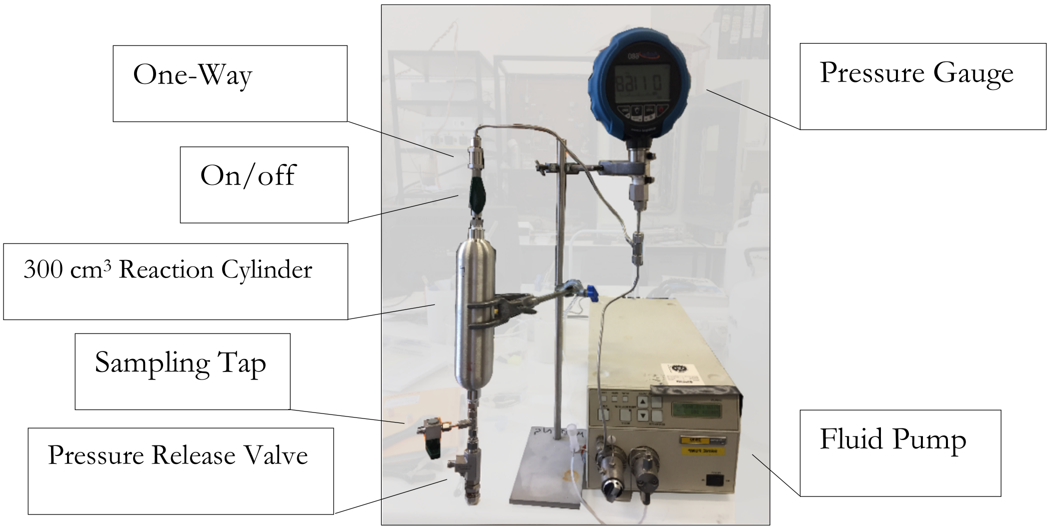


FIGURE 14 – EXPERIMENTAL BATCH REACTOR ATTACHED TO FLUID PUMP AND PRESSURE GAUGE – READY FOR PRESSURISATION.

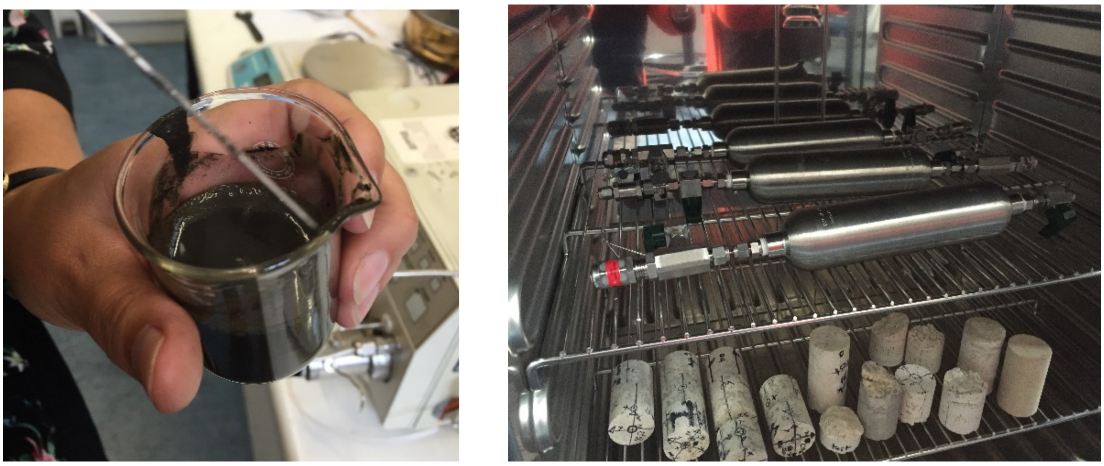


FIGURE 15 – SHALE AND FLUID MIXTURE READY FOR FILLING BATCH REACTOR (LEFT) AND FILLED AND PRESSURISED BATCH REACTORS IN THE OVEN FOR HEATING (RIGHT).

10.4.1.2 AMBIENT PRESSURE AND TEMPERATURE EXPERIMENTS (SF2)

Stainless steel corrodes in contact with HCl, the acid permitted for use in UK fracturing fluids. Therefore, a set of experiments were conducted at ambient pressure and temperature to compare with the pressurised and heated batch reactions in the stainless steel equipment.

With the aim of developing a method of conducting experiments using dilute HCl additive without degrading the stainless steel batch reactors, these experiments were carried out in 50 ml Staestedt polypropylene conical screw-cap vials (Figure 16). First, experiments were run without any HCl additive to determine comparability to elevated temperature and pressure experiments. The same shale–fluid ratio (1:20) was used in all experiments to allow for comparative results across experiments despite the difference in scale.

For each experiment, 2.5 ± 0.1 g of powdered shale (MS, KC, PH3, PH4, PH6) was weighed into each vial and mixed with 50 ml distilled water. Samples were sealed with a screw-cap and agitated vigorously before being stored in ambient temperature and pressure conditions for 28 days.

Vials were cleaned in a 10% HNO_3 bath, rinsed three times with DI and left to dry in an oven overnight before use.

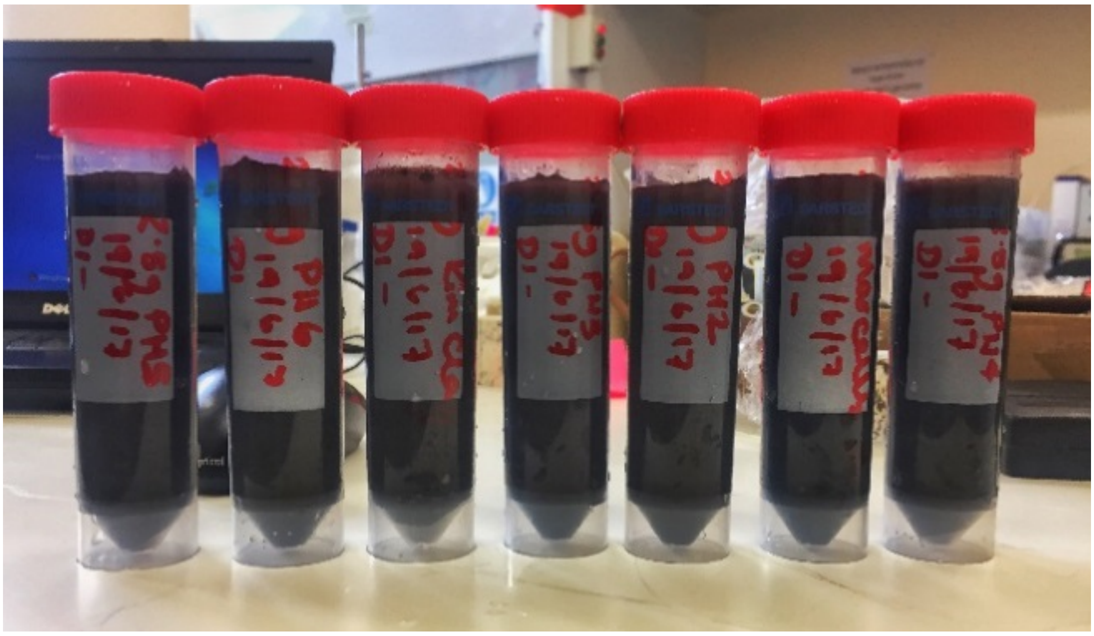


FIGURE 16 – 50ML STAESTEDT POLYPROPYLENE CONICAL SCREW-CAP VIALS FILLED WITH 2.5G POWDERED (<50µM) SHALE AND 50ML DISTILLED WATER

10.4.1.3 AMBIENT PRESSURE AND RESERVOIR TEMPERATURE EXPERIMENTS (SF3- 5)

Within the budgetary and time constraints of this PhD, it was unfeasible to reconstruct the RPT batch reaction pressure vessels to be capable of conducting experiments with acidic fluids such as dilute HCl, by coating them or rebuilding them from inert gold parts. Instead, these experiments were carried out in polypropylene (PP) conical screw-cap vials, and then later in Quickfit conical flat-bottomed glass flasks. PP vials were sufficient for conducting experiments at ambient pressure and temperature however under prolonged heated conditions the seals would warp and allow air exchange outside the reaction vessel – compromising the closed nature of the batch reaction system. Qucikfit® glassware is made of borosilicate heat resistant glass with ground glass joint connection systems, allowing for a sealed closed system batch reaction at elevated temperatures.

Experiments were conducted with both 0.125% and 10% HCl, mimicking the concertation of HCl permitted for hydraulic fracturing at Preese Hall in 2011 (UK Department of Energy and Climate Change, 2014), and the maximum permissible concentration allowed at Preston New Road in 2018 (The Environment Agency, 2014).

10.5 SUMMARY OF EXPERIMENTAL WORK

A total of 24 experiments were conducted and experimental conditions are summarised in Table 12. These consisted of –

SAMPLED FLUID	EXPERIMENT DETAILS
SF1	3 batch reactions at reservoir temperatures and pressures (RPT) with distilled water containing no additives
SF2	5 batch reactions at ambient temperature and pressure (APT) with distilled water containing no additives
SF3	7 batch reactions at reservoir temperature and ambient pressure (APRT) with distilled water containing no additives
SF4-5	9 batch reactions at reservoir temperature and ambient pressure (APRT) - with varying concentrations of HCl additive (0.125 – 10%)

SHALE SAMPLE(S)	FLUID	BATCH REACTOR VESSEL	TEMPERATURE (± 0.1°C)	PRESSURE (PSI)	DURATION (DAYS)	AGITATION (DAYS SINCE START)	RATIO	SHALE—FLUID DILUTED AFTER SAMPLING?
KC-EB	DISTILLED WATER	300 CM^3 STAINLESS STEEL PRESSURE CYLINDER	65 ^{0}C	1515 - 1516 ± 25	21	0, 5, 12, 19, 24	1:20	N
MS	DISTILLED WATER	300 CM^3 STAINLESS STEEL PRESSURE CYLINDER	65 ^{0}C	1542 - 1620 ± 25	28	0, 7, 14, 21	1:20	N
BS [PH1]	DISTILLED WATER	300 CM^3 STAINLESS STEEL PRESSURE CYLINDER	65 ^{0}C	1500 ± 25	28	0, 7, 14, 21	1:20	N
PH3, PH4, PH6, MS, KC	DISTILLED WATER	50 ML PP SCREW-TOP VIALS	~20 ^{0}C	14.7*	28, 49	0, 28	1:20	Y (28)
PH2, PH3, PH4, PH5, PH6, MS, KC	DISTILLED WATER	50 ML PP SCREW-TOP VIALS†	65 ^{0}C	14.7*	28	0, 7, 14, 21	1:20	N
PH2, MS, KC	DISTILLED WATER + 0.125% HCL	50 ML QUICKFIT GLASS FLAT-BOTTOM FLASK	65 ^{0}C	14.7*	29, 56, 157, 189	INITIAL, THEN AFTER SAMPLING	1:20	Y (29, 56)
PH2, MS, KC	DISTILLED WATER + 10% HCL	50 ML QUICKFIT GLASS FLAT-BOTTOM FLASK	65 ^{0}C	14.7*	28, 160, 161	INITIAL, THEN AFTER SAMPLING	1:20	Y (28)
BS-U, BS-L, MS-C	DISTILLED WATER + 10% HCL	50 ML QUICKFIT GLASS FLAT-BOTTOM FLASK	65 ^{0}C	14.7*	31, 40	INITIAL	1:20	N

*TABLE 12 – DETAILS OF EXPERIMENTAL CONDITIONS. †EXPERIMENTS WERE EXPOSED TO OXIDIZING CONDITIONS AND FLUID LOSS THROUGH EVAPORATION DUE TO POOR EXPERIMENTAL SEAL. *ATMOSPHERIC PRESSURE = 14.7PSI.*

10.6 EVALUATION OF METHOD

10.6.1 DESIGN IMPROVEMENTS

Experimental method was iteratively improved within the constraints of the research budget and time available. However, some improvements that would advance this work are described here:

- Design of a pressurised batch reactor cylinder inert to fluids with complex chemistry including HCl, biocides, acrylamides, and other fracturing fluid additives
- Achieve temporal sub-sampling success through design improvements.

Difficulty in obtaining experimental vessels inert to HCl additive that were sealable during prolonged heating delayed experimental progress significantly.

10.6.2 SHALE SAMPLES

With the aim of replicating hydro-geo-chemical conditions during hydraulic fracturing, shale samples should be taken wherever possible from drillcore, within the prospective horizon to be fractured. Samples obtained from surface exposures are much less likely to reflect downhole conditions due to weathering and surface alteration. Both drillcore and surface exposure samples were compared in experiments in this study to determine the difference. Where possible core samples were cut from the centre of the cored section (far from the cored edge) to avoid contamination with drilling or other well fluids used in the coring process. Due to limited sample availability for the shales of interest, the ideal sampling conditions (as described above) were not always possible.

10.6.3 EXPERIMENTAL FLUIDS

Although distilled water is the base fluid used in experiments, the proposed base fluid for hydraulic fracturing in the UK is local mains water, or even groundwater if the correct abstraction permits apply (UK Department of Energy and Climate Change, 2014). As distillation removes minerals, bacteria, and chemicals from the water, it is likely that the base fluid utilised in operations will contain a greater number and concentration of components affecting the chemistry of fluids returned. Distilled water was chosen for its purity, so even trace amounts of contaminants released during reactions could be detected above a relatively low 'background' fluid. Additionally, at depth in the sub surface, shales contain inherent formation water and pore fluids not present in any of the samples utilised for these experiments due to drying out during storage at the surface. Both the lack of pore and formation water, and the use of distilled water as a base fluid, affects the comparability of experimental results with field data.

10.6.4 OXIDISING CONDITIONS

Experiments conducted in polypropylene screw top vials at reservoir temperatures (SF2 & SF3) were exposed to more oxygen rich environments due to poor sealing of the screw top closure. This allowed air to freely enter the reaction vessel and oxidise the atmosphere inside. Some evaporation of the experimental fluid was observed during the course of these experiments - skewing the concentration of analytical results in comparison to other experiments where no fluid loss occurred. Whilst fluids injected for fracturing are likely to be slightly oxygenated, it is unlikely that there will be free exchange of oxygen throughout the system. Therefore, the close-system batch reactions (SF4 & SF5) with no atmospheric exchange are more likely to represent the hydro-geo-chemical sub-surface conditions.

10.7 SUMMARY

Overall, the aim of the experiments conducted was to replicate the hydro-geo-chemical interaction taking place in the sub-surface between freshly fractured shale rocks and injected hydraulic fracturing fluids. Despite some of the noted limitations to our experimental methods, confidence in the experimental results is high. These experiments indicate what, if any, contaminants of concern can be mobilised during hydraulic fracturing with limited to no chemical additives. This helps to build a picture of the source of contaminants of concern in fluid produced at the surface following fracturing, and can help us to rule out the rock as a source of many of these. If the contaminants are not mobilised during these experiments then their source can be determined to be outside the rock/water system.

11 ANALYTICAL METHODS

To understand the changes taking place during batch reaction experiments, detailed geochemical characterisation of the shale sample material was carried out. Mineralogy was determined by X-Ray Diffraction, elemental composition was analysed by X-Ray Fluorescence, carbon content (both organic and inorganic) was analysed, thin sections were examined under the electron and optical microscope, and full acid digestions of rock samples was undertaken to characterise complete elemental composition by Inductively Coupled Plasma Optical Emissions Spectroscopy (ICP-OES).

Additionally, pre- and post- experimental fluids were analysed using ICP-OES for dissolved elemental concentrations, and by Ion Chromatography for concentration of cations. Temperature and pH of fluids was measured on sampling.

11.1 SHALE CHARACTERISATION

11.1.1 X-RAY DIFFRACTION (XRD)

Mineralogy of rock samples was characterised using X-Ray Diffraction (XRD), carried out within the X-Ray Laboratories of the School of Geoscience, University of Edinburgh with the assistance of Dr Nicholas Odling.

XRD is an analytical technique that utilises the diffractive properties of crystalline minerals to quantify the mineral content of a rock sample to 1 wt.% accuracy.

Rock samples were cut to remove outer oxidised surfaces, crushed in a dodge jaw crusher to ~1 mm chips, and then ground using a tungsten carbide rock milling unit.

Samples were given a final grinding using an agate mortar and pestle and acetone to ensure adequate particle size for analysis before being mixed with a gelling agent and pressed into powder pellets.

Pressed powder pellets were loaded into a Bruker D8 Advance x-ray diffractometer. Sample identification was performed in Bruker EVA 3.0 and Rietveld analysis in TOPAS 3.0. Final data was obtained in the form of percentage abundance of each mineral phase detected, with a detection limit of 1 wt.% for crystalline phases.

The precision of the x-ray diffraction technique is a measure of the reproducibility of the results. This is affected by both the instrumental precision and the heterogeneity of the sample. Instrumental precision is determined during the Reitveld analysis and reported alongside individual measurements in Section 12.1.1.

11.1.2 X-RAY FLUORESCENCE (XRF)

Rock samples were characterised by XRF to determine their major and trace elemental composition. Analysis was carried out within the X-Ray Laboratories of the School of Geoscience, University of Edinburgh with the assistance of Dr Nicholas Odling.

Crushed and milled samples were weighed to 1.0 ± 0.1 g in platinum crucibles. These were placed in a 450 °C oven overnight to ignite organic material within the sample. The crucible weight before and after ignition was recorded to determine organic content by loss-on-ignition, see Total Organic Content by Loss on Ignition (TOC) for further detail. Spectroflux 105 – a mix of Li-borate, Li-carbonate and La-oxide – was added proportionally to each sample (five times the weight of each sample) to act as a kind of internal standard (heavy absorber). Each sample was heated in a 1100 °C furnace until molten before being well agitated to ensure homogenisation of the sample and flux mixture. The mixture was transferred into a mould and cooled to a single fusion bead or glass disc. This process homogenises the material within the sample in a crystalline form which reduces matrix effects during XRF analysis & combats the effects of sample heterogeneity (Nakayama and Wagatsuma, 2017).

The precision of XRF is a function of the reproducibility of measurements which relates to both the instrumental precision and the sample heterogeneity. The precision of major elemental analysis by XRF is less susceptible to sample heterogeneity than the measurement of trace elements. Typical instrument reproducibility and accuracy of the XRF analytical method are outlined in Table 13.

	Instrument Reproducibility		Sample Reproducibility		
Major Elements (wt.%)	Mean (n=5)	σ	Mean (n=5)	σ	Accuracy (rsmd)
SiO2	39.42	0.03	33.39	0.06	0.22
Al2O3	11.33	0.02	11.33	0.05	0.12
Fe2O3	14.30	0.02	14.27	0.05	0.05
MgO	13.26	0.03	13.24	0.06	0.08
CaO	12.76	0.01	12.75	0.06	0.05
Na2O	3.68	0.03	3.64	0.10	0.06
K2O	1.151	0.007	1.149	0.005	0.02
TiO2	2.454	0.009	2.450	0.013	0.01
MnO	0.215	0.002	0.216	0.003	0.01
P2O5	0.932	0.003	0.941	0.023	0.01
Total	99.51	0.08	99.42	0.14	
Trace Elements (ppm)	Mean (n=5)	σ	Mean (n=5)	σ	Accuracy (rsmd)
Nb	52.4	0.6	52.6	0.4	2.4
Zr	166.7	0.9	166.9	1.0	14.8
Y	29.3	30.3	29.1	0.3	3.4
Sr	1070	2.1	1070.0	2.9	9.6
Rb	30.4	0.4	30.4	0.4	3.5
Zn	123.4	0.7	123.3	0.8	5.0
Cu	84.6	1.1	84.7	0.9	5.3
Ni	310.3	2.6	310.6	2.6	4.3
Cr	488.4	2.1	487.7	1.1	11.0
V	300.3	2.3	300.4	2.8	11.5
Ba	745.8	9.3	746.4	6.7	39.0
Sc	29.7	0.9	29.2	1.5	2.4

TABLE 13 - TYPICAL REPRODUCIBILITY AND ACCURACY DATA FOR XRF ANALYTICAL METHOD (MAJOR AND TRACE ELEMENTS). ACCURACY WAS QUANTIFIED BY ROOT MEAN SQUARE DEVIATIONS (RMSD) EXPRESSED IN WT.% OR PPM OF THE CALIBRATION DATA ABOUT THE REGRESSION LINE (N. ODLING, PERS COMMS).

11.1.3 TOTAL ORGANIC CONTENT BY LOSS ON IGNITION (TOC)

During sample preparation for XRF, powdered samples undergo ignition in an oven at 450 °C overnight (>8 hours) to remove organic matter before preparation into a glass bead. Equation 5 illustrates the method for calculating the percentage loss on ignition. This method has been used to quantify organic carbon in powdered rock and soil samples (De Vos *et al.*, 2005; Wood, 2015). There remains some question as to it's application as a quantitative analytical method due to interference with other volatile losses during ignition (Santisteban *et al.*, 2014), but can at least be utilised as a tool to provide qualitative organic carbon content.

$$\mathrm{LOI}(\%) = \left(\frac{w_u - w_i}{w_s}\right) * 100 \qquad 5$$

Where;
w_u = weight of the unignited crucible and sample
w_i = weight of the ignited crucible and sample
w_s = weight of the sample ($w_u - w_{crucible}$).

Analysing rocks or soils for total organic carbon (TOC) by 'Loss-On-Ignition' (LOI) is limited by the potential to overestimate organic carbon due to incomplete combustion of organic matter, the loss of structural water from clay minerals, or CO_2 release from carbonates (De Vos *et al.*, 2005; Hoogsteen, 2015). CO_2 release from carbonate minerals can be assumed to remain negligible at ignition temperatures of 500 °C or less (450 °C for this method). And a clay correction factor can be applied to account for the loss of mass from structural water (Equation 6) after Jensen et al. (2018). This correction essentially accounts for a decrease in the effect of clay with increasing clay content and was developed using the TOC/LOI relationship between two independent sets of samples, which was successfully corroborated against a third set of samples not used to calculate the correction factor. Other factors, such as the one proposed by De Vos et al. (2005) or the common conversion factor of 0.58 are now believed to be inaccurate following the work of Jensen et al. (2018). Minerals loose most of their structural water above 450 °C and therefore the LOI method of TOC estimation at 450 °C tends to overestimate the organic content without this correction.

$$\mathrm{TOC} = 0.513.\mathrm{LOI} - (0.047.\mathrm{Clay} - 0.00025.\mathrm{Clay}^2) \qquad 6$$

11.1.4 TOTAL INORGANIC CARBON BY COULOMETER (TIC)

The Total Inorganic Carbon (TIC) content of a select subset of shale samples was measured using a CM5012 CO_2 Coulometer. Assistance and training was provided by Dr Clare Peters.

Samples were weighed to 80 ± 5 mg into glass sample boats using the Sartorius BP221S Balance. Samples were placed into glass test tubes and fitted with plastic attachments for connection to the Coulometer. Once a seal has been established the system is purged of atmospheric CO_2 for 3 minutes. Using the built-in pump unit, 5 ml of 2N perchloric acid is added to the sample tube and the ‘reset’ button is pushed to start analysis. As the sample reacts with the perchloric acid it gives off CO_2 which passes through a KOH and a KI scrubber to remove common interferent gases before reaching the analytical module.

The analytical module of the coulometer contains a mixture of ethanol amine and a colorimetric indicator solution. CO_2 released reacts with the ethanol amine to form a titratable acid; changing the colour of the indicator solution. An electrically driven titration unit generates a base to return the solution to its original colour in between samples.

The sample tube is manually inserted into the heating unit and the analysis runs for 10 minutes to allow all of the CO_2 released from the sample to evolve and titrate.

The instrument continually displays the cumulative amount of Carbon in μg detected, after 10 minutes this value is sufficiently stable and can be recorded.

Data was converted from cumulative TIC to TIC(%) using Equation 7.

$$\mathrm{TIC}(\%)=\frac{\mathrm{TIC}_{\mathrm{cumulative}}-\mathrm{TIC}_{\mathrm{blank}}}{\mathrm{Mass}_{\mathrm{sample}}} \tag{7}$$

11.1.5 SCANNING ELECTRON MICROSCOPY WITH ENERGY DISPERSIVE SPECTROSCOPY (SEM-EDS)

Slices of whole rock (BS1, BS2, BS3, BS6) were made into thin sections and carbon coated. These sections were analysed on a Zeiss Sigma HD Field Emission Scanning Electron Microscope (SEM) to view detailed textural and compositional information about each sample (down to 1 μm). Energy Dispersive Spectroscopy (EDS) was used to determine and map elemental distribution of sections. Oxford Instruments Aztec software was used to interpret and analyse data obtained by the EDS. Operating voltage, detector used, and visual scale can be found on the information bar at the base of each SEM image. Training and assistance was provided by Dr John Craven.

11.1.6 WHOLE ROCK DIGESTION FOR TRACE COMPONENT ANALYSIS

A select number of shale samples were analysed by full acid digestion to detect trace components otherwise undetected in analysis by XRD and XRF. Training and assistance was provided by Dr Laetitia Pichevin and Steve Mowbray.

16 samples were weighed to 25 ± 5 mg in Teflon vials. A replicate set of three samples (3x BSU), two internal standards (PACS and SGR) and two blanks (Yttrium spike, no

sample) were also prepared. 3 ml of HNO_3, 2 ml HCl, and 0.5 ml HF was added to the vials and after a few minutes of settling time lids were placed on the samples before moving to the hotplate (100 °C) for storage overnight (>8 hours). After this initial digestion, a noticeable amount of refractory organic matter remained undissolved in the samples and so an additional digestion of this material was required. Samples were evaporated on the hotplate to remove HF and 50 µl perchloric acid was added to the vials. These were enclosed again and left on the hotplate for another few hours before a final evaporation. 5 ml of 1M HNO_3 was added to the vials for the final step of the digestion on the hotplate before diluting with 2% HNO_3 for analyses by ICP-OES. This process is summarised step by step in Figure 17.

Digestion Step 1

1. 25 ± 5 mg sample weighed into Teflon vial
2. Add 3 ml HNO_3, 2 ml HCl, 0.5 ml HF
3. Store at 100 °C, >8 hours, enclosed

Digestion Step 2 *(dissolution of organic matter)*

4. Evaporate HF, at 100 °C, open
5. Add 50 µl perchloric acid
6. Store at 100 °C, 2-4 hours, enclosed

Digestion Step 3

7. Add 5 ml 1M HNO_3
8. Store at 100 °C, >8 hours, enclosed

FIGURE 17 – STEP BY STEP METHOD FOR FULL ACID ROCK DIGESTIONS

Replicate analyses of the BS-U sample were conducted to determine instrumental and procedural precision during digestion and measurement on ICP-OES. Greater absolute error occurred when absolute concentration is greater, however relative error was greater at smaller concentrations (Figure 20). The instrumental error ranged from 0.10% to 0.56%. For every element measured for, except Li, the coefficient of variation was within 0.10-0.20% (Figure 20).

The analysis of standard reference material (SRM) PACS-2 and SGR in comparison with measured concentrations determines instrumental accuracy. All of the elements within the SGR standard were measured within their certified error except for Li (Figure 18). Generally, concentrations were consistently underestimated with respect to the reference material. In comparison with the PACS-2 reference material, concentrations were also consistently underestimated, perhaps indicating a systematic underestimation of concentrations by this method. Four elements in PACS-2 were underestimated with respect to the SRM concentration; S, Cr, Pb, and Cu (Figure 19).

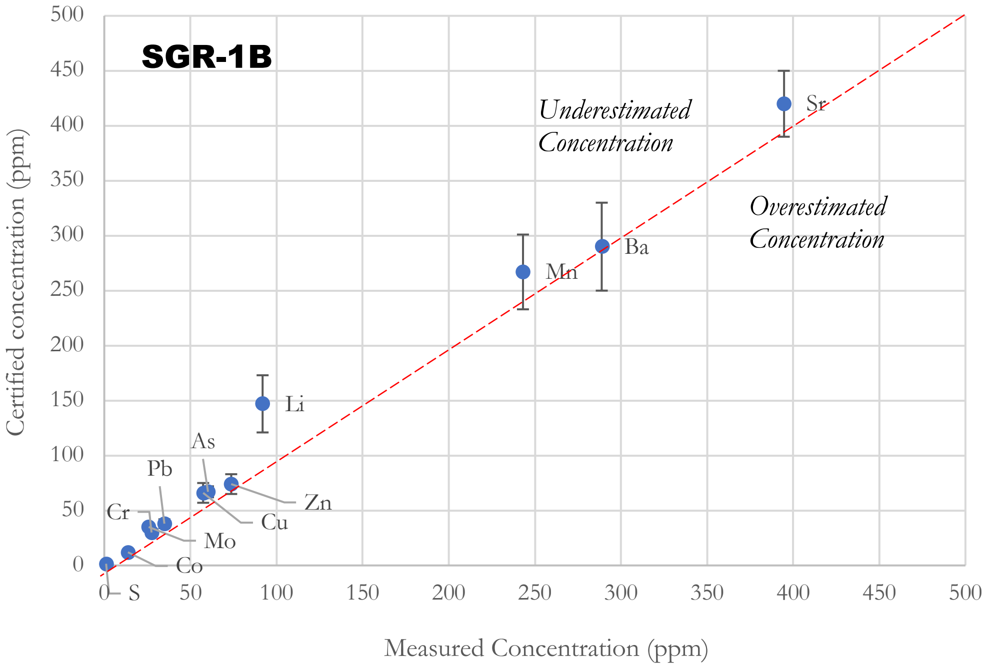


FIGURE 18 – SCATTERPLOT COMPARING THE MEASURED CONCENTRATIONS WITH THE CERTIFIED REFERENCE VALUES FOR SGR-1B SRM.

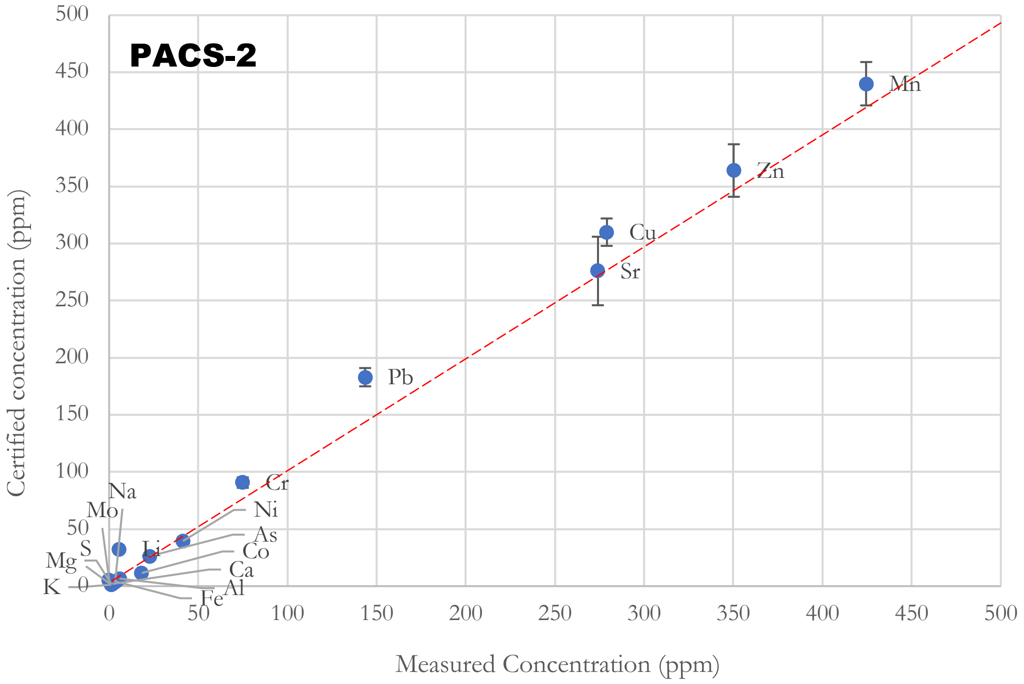


FIGURE 19 – SCATTERPLOT COMPARING THE MEASURED CONCENTRATIONS WITH THE CERTIFIED REFERENCE VALUES FOR PACS-2 SRM.

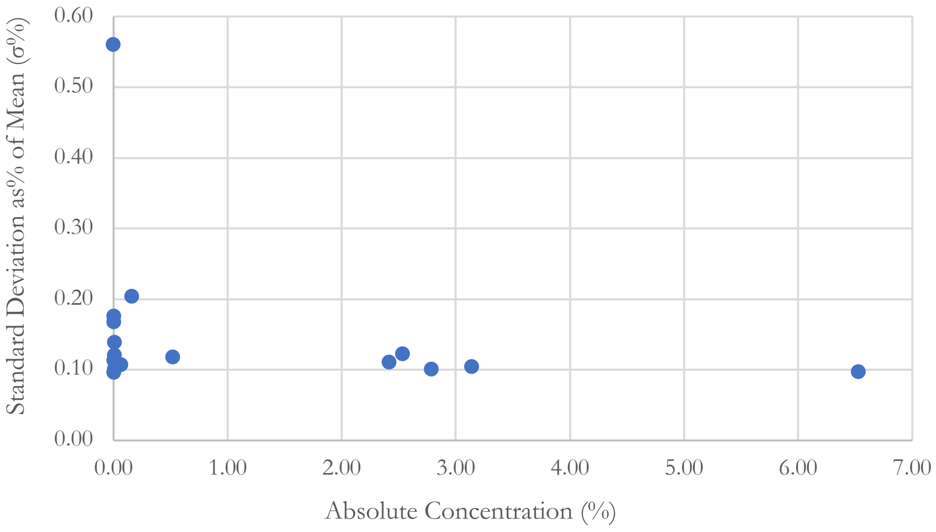


FIGURE 20 – STANDARD DEVIATION AS PERCENTAGE OF THE MEAN, PLOTTED AGAINST ABSOLUTE MEASURED CONCENTRATION. THE PERCENTAGE DEVIATION IS GREATER WHEN CONCENTRATIONS ARE LESS.

11.2 EXPERIMENTAL FLUID CHARACTERISATION

11.2.1 PH AND TEMPERATURE

The pH and temperature of sampled experimental fluids was measured using a Hanna HI 2210 Benchtop pH Meter with an accuracy of ± 0.1 pH and ± 0.5 ºC. The resolution, or limit of detection, of the meter was 0.01 pH and 0.1 ºC. To ensure the pH of fluids measured at different temperature are comparable, measured values are automatically compensated for the effects of temperature using ATC (Automatic Temperature Compensation) built into the meter functionality. This means that pH values measured using the meter's temperature probe are directly comparable regardless of the temperature of fluid at the time of measurement.

pH and temperature were only measured in SF1 fluids as for other experiments there was not enough fluid to set some aside for pH measurement. During pH measurement the insertion of the probe would contaminate the samples before they had been analysed on the ICP-OES leading to inaccurate results. Estimation of the precision of pH and temperature measurement was limited by the fluid sample volume (preventing simultaneous replicate measurements) and the constant change in temperature and pH of samples with time (preventing comparability of sequential replicate measurements).

11.2.2 INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Fluid samples collected from hydro-geo-chemical reaction experiments were analysed using ICP-OES in the Grant Institute of the School of Geosciences at the University of Edinburgh. Training and assistance was provided by Dr Alex Thomas, and Dr Laetitia Pichevin. Four analytical runs were completed in (1) February 2017, (2) September 2017, (3) April 2018 and (4a & b) July 2018. Analytical runs 1 and 2 were repeated in run 3 due to suspected contamination and inconsistencies found in original data processing. Final data analysed in this thesis is taken from runs 3 & 4. A list of fluid samples collected and corresponding ICP-OES order of analysis is summarised in Table 15.

The suite of elements analysed for were chosen for their applicability to shale gas operations, for their environmental implications, for their complex management requirements, for their ability to convey information about water rock reactions taking place, and for their ability to be measured effectively on the ICP-OES. To determine which elements to analyse for elements of interest to shale gas operations from existing literature were considered, then elements which have been studied in other similar experiments, and finally any other components of interest such as potential tracer elements were added. This was then correlated with the availability and interference of analytical determinands on the ICP-OES to determine the final analyte list (Table 16 & Table 17).

11.2.2.1 SAMPLE PREPARATION & STORAGE

Fluid samples were collected into laboratory glassware and filtered to 0.45 μm using BD Plastipak polypropylene syringes and MILLEX MF-Millipore MCE Membrane filter units. Samples were acidified to 2% with HNO_3 and stored in screw-cap 15 ml Fisherbrand conical polypropylene centrifuge tubes and refrigerated at 4 °C.

11.2.2.2 INSTRUMENT SPECIFICATION & OPERATION

Elemental concentrations of each sample were measured using a Varian Vista Pro ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy). Aliquots of 3 ml were pipetted into an auto sampling rack. Each sample is individually drawn into the instrument and dispersed across an argon plasma beam. The interaction of the sample with the plasma excites atoms in the sample, producing characteristic electromagnetic radiation at diagnostic wavelengths for each element present. The intensity and wavelength of emitted radiation is measured and analysed to determine elemental concentrations down to μg/l (ppb) concentration.

For any single element, multiple wavelengths were analysed to account for different sensitivities and interferences between elements present at similar wavelengths. Across all four runs a range of wavelengths were analysed for resulting in a variety of concentrations associated with different wavelengths. Where possible, the wavelengths set out by US EPA Standard Method 200.7 for analysing metals in wastewater (Martin *et al.*, 1994) were chosen, and where not possible the next appropriate wavelength was used. For Ca analysis a combination of wavelengths 315.880 and 616.216 were used because a single wavelength was not successful across both analysis runs.

ICP-OES instrumentation can be negatively affected by samples containing very high concentrations of dissolved solids. If the salinity of a sample is expected to be higher than 300,000 ppm it is good practice to dilute samples to protect the instrumentation and auto-sampler from build-up which can impact quantification. Following dilution, the concentrations measured can be re-adjusted to give accurate quantification for un-diluted fluids. In all four analytical runs, no sample dilution was required as all determinands were within the limits of calibration of the standards prepared, and contained relatively low TDS (max 6000 ppm).

A record of any instrumental or analytical issues encountered during analysis are detailed in the '*Status*' column of Table 16. Where issues were encountered during analysis resulting in an unreliable result, the data were not reported in the results section.

11.2.2.3 PROCEDURAL BLANKS & INTERNAL STANDARDS

A minimum of three procedural blanks were analysed per run. All samples (and blanks) were spiked with 20 µl of Yttrium as an internal standard and to account for matrix effects. Matrix effects are incurred when there are differences between the matrices of samples and blanks. Internal standards are the most common method of countering these effects and are reliable and relatively quick – any matrix effects can be quickly realised when the internal standard concentration is not what expected. Internal standards improve the analytical accuracy of the ICP-OES method as the difference between the measured concentration and the known concentration can highlight any discrepancies.

11.2.2.4 INSTRUMENT CALIBRATION & ACCURACY

Instrument calibration was performed against a custom made multi-element standard composed of 100 µl Merck IV multi-element ICP standard containing 1000 ppm Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn, and 100 µl each of 1000 ppm Mo, 1000 ppm As, and 1000 ppm U Fisherbrand single-element ICP standards in a matrix of 2% HNO_3. Instrumental accuracy was maintained by analysing the concentrations of known multi element standards for each run.

11.2.2.5 PRECISION

Three replicate blank reagent sample analyses were conducted to determine precision of the ICP-OES method (%RSD). The RSD ranged from 2.0 – 27.4% but for most (16 out of 20) analytes was below 10%, and for all except Cu was below 20% (Table 14).

	RSD %		RSD %
AL	11.8	LI	4.7
AS	5.4	MG	10.9
B	2.2	MN	2.4
BA	2.3	MO	4.5
CA	3.2	NA	4.0
CO	3.2	NI	4.1
CR	9.0	PB	7.5
CU	27.4	S	8.8
FE	19.3	SR	6.2
K	2.0	ZN	3.5

TABLE 14 - RELATIVE STANDARD DEVIATION (RSD) FOR THREE BLANK REAGENT SAMPLES ANALYSED ON ICPOES TO DETERMINE METHOD PRECISION FOR EACH ANALYTE.

		ICP-OES RUN #									
#	SAMPLE CODE	1	2	3	4	#	SAMPLE CODE	1	2	3	4
1	DI	▨		▨		25	PH6_T0		▨	▨	
2	KC1.1	▨		▨		26	MS_T0		▨	▨	
3	KC2.1	▨		▨		27	KC_T0		▨	▨	
4	KC3.1	▨		▨		28	PH2_0.125HCL(28)			▨	
5	MS1.2	▨		▨		29	MS_0.125HCL(28)			▨	
6	MS2.2	▨		▨		30	KC_0.125HCL(28)			▨	
7	MS3.2	▨		▨		31	PH2_0.125HCL(56)				▨
8	BS1.3	▨		▨		32	MS_0.125HCL(56)				▨
9	BS2.3	▨		▨		33	KC_0.125HCL(56)				▨
10	BS3.3	▨		▨		34	PH2_0.125HCL(157)				▨
11	PH3_A4		▨	▨		35	MS_0.125HCL(157)				▨
12	PH4_A4		▨	▨		36	KC_0.125HCL(157)				▨
13	PH6_A4		▨	▨		37	PH2_0.125HCL(189)				▨
14	MS_A4		▨	▨		38	MS_0.125HCL(189)				▨
15	KC_A4		▨	▨		39	KC_0.125HCL(189)				▨
16	PH3_A7		▨	▨		40	PH2_10HCL(28)				▨
17	PH4_A7		▨	▨		41	KC_10HCL(28)				▨
18	PH6_A7		▨	▨		42	MS_CORE(31)				▨
19	MS_A7		▨	▨		43	BS_UPPER(31)				▨
20	KC_A7		▨	▨		44	BS_LOWER(31)				▨
21	PH2_T0		▨	▨		45	MS_CORE(40)				▨
22	PH3_T0		▨	▨		46	BS_UPPER(40)				▨
23	PH4_T0		▨	▨		47	BS_LOWER(40)				▨
24	PH5_T0		▨	▨							

TABLE 15 – COMPLETE LIST OF FLUID SAMPLES COLLECTED FROM EXPERIMENT – DENOTING WHICH ICP-OES ANALYTICAL RUN EACH WERE ANALYSED ON.

RUN 1	STATUS	RUN 2	STATUS	RUN 3	STATUS	RUN 4A & (*4B*)	STATUS
AL 396.152	✓	AL 308.215	✓	AL 396.152	✓	AG 328.068	✓
AS 188.980	✓	AL 396.152	✓	AS 188.980	✓	AL 237.312	✓
AS 193.696	✓	AS 188.980	✓	AS 193.696	✓	AS 193.696	✓
B 249.678	✓	AS 193.696	✓	B 249.678	✓	BA 493.408	✓
BA 455.403	✓	B 249.678	✓	BA 455.403	✓	BE 313.042	PROBLEM
BA 493.408	✓	BA 455.403	✓	BA 493.408	✓	CA 315.887	✓
CA 393.366	INTERFERENCE	BA 493.408	✓	CA 317.933	✓	CA 317.933	✓
CA 396.847	✓	CA 393.366	✓	CA 616.217	✓	CD 226.502	✓
CO 228.615	✓	CA 396.847	PROBLEM	CO 228.615	✓	CO 228.615	✓
CO 238.892	✓	CA 422.673	✓	CO 238.892	✓	CR 267.716	✓
CR 205.560	✓	CA 616.217	✓	CR 205.560	✓	CU 327.395	✓
CR 267.716	✓	CR 205.560	✓	CR 267.716	✓	FE 259.940	✓
CU 327.395	✓	CR 267.716	✓	CU 327.395	✓	HG 184.887	✓
CU 327.395	✓	CU 327.395	✓	CU 327.395	✓	HG 194.164	✓
FE 238.204	✓	CU 327.395	✓	FE 238.204	✓	K 766.491	✓
FE 259.940	✓	FE 238.204	✓	FE 259.940	✓	LI 610.365	✓
K 766.491	✓	FE 259.940	✓	K 766.491	✓	MG 279.800	✓
LI 610.365	✓	K 766.491	✓	LI 610.365	✓	MN 260.568	✓
MG 279.800	✓	K 769.897	✓	MG 279.800	✓	MN 294.921	✓
MG 383.829	✓	LI 610.365	✓	MG 383.829	✓	MO 202.032	✓
MN 260.568	✓	MG 279.800	✓	MN 260.568	✓	NA 588.995	✓
MN 294.921	✓	MG 383.829	✓	MN 294.921	✓	NI 231.604	✓
MO 204.598	✓	MN 260.568	✓	MO 204.598	✓	P 213.618	✓
NA 568.821	✓	MN 294.921	✓	NA 568.821	✓	PB 220.353	✓
NI 216.555	✓	MO 204.598	✓	NI 216.555	✓	S 181.972	✓
NI 231.604	✓	MO 204.598	✓	NI 231.604	✓	S 182.562	✓
PB 220.353	✓	NA 568.821	✓	PB 220.353	✓	SN 189.927	✓
PB 405.781	✓	NA 588.995	✓	PB 405.781	✓	SR 421.552	✓
S 181.972	✓	NI 216.555	✓	S 180.669	✓	SR 460.733	✓
S 189.965	BAD CALIBRATION	NI 231.604	✓	S 181.972	✓	TI 334.941	✓
SR 421.552	✓	PB 220.353	✓	S 182.562	✓	TI 336.122	✓
SR 460.733	✓	PB 405.781	✓	S 189.965	✓	TI 337.280	✓
U 367.007	INTERFERENCE	PB 405.781	✓	SI 250.690	✓	V 292.401	✓
U 385.957	INTERFERENCE	S 181.972	??	SI 251.611	✓	ZN 202.548	✓
Y 360.074	✓	S 189.965	UNCALIBRATED	SI 288.158	✓	ZN 213.857	✓
Y 371.029	✓	SC 335.372	✓	SR 421.552	✓	*B 182.577*	✓
ZN 202.548	✓	SC 361.383	✓	SR 460.733	✓	*B 249.678*	✓
ZN 213.857	✓	SI 250.690	✓	U 367.007	INTERFERENCE	*B 249.772*	✓
		SI 251.611	✓	U 385.957	INTERFERENCE	*CA 315.887*	✓
		SI 288.158	✓	ZN 202.548	✓	*CA 317.933*	✓
		SR 421.552	✓	ZN 213.857	✓	*FE 238.204*	✓
		SR 460.733	✓		✓	*FE 259.940*	✓
		U 367.007	INTERFERENCE			*K 766.491*	✓
		U 385.957	INTERFERENCE			*MG 279.800*	✓
		ZN 202.548	✓			*MN 260.568*	✓
		ZN 213.857	✓			*MN 294.921*	✓

						NA 588.995	✓
						NA 589.592	✓
						P 213.618	✓
						S 181.972	✓
						S 182.562	✓

TABLE 16 – LIST OF ANALYTES AND WAVELENGTHS MEASURED IN EACH RUN OF ICP-OES ANALYSIS. THE 'STATUS' COLUMN PROVIDES DETAILS OF ANY ISSUES ENCOUNTERED DURING THE ANALYTICAL PROCEDURE RENDERING DATA UNUSABLE.

11.2.2.6 INSTRUMENTAL LIMITS OF DETECTION

Instrumental limits of detection were calculated for each wavelength using equation 8 & are detailed in Table 17.

$$LOD=3\sigma*y \tag{8}$$

Where;

σ = standard deviation of blank

y = calibration slope

To calculate the calibration slope equation 9 is used:

$$y=\frac{(C_{max}-C_{min})}{(I_{max}-I_{blank})} \tag{9}$$

Where;

C = concentration

I_{max} = maximum intensity

I_{blank} = mean intensity of blanks

ELEMENT & WAVELENGTH	LOD (UG/L)						
AG 328.068	0.059	**HG 194.164**	0.25	**S 182.562**	0.11	**B 249.772**	0.065
AL 237.312	0.0092	**K 766.491**	0.0036	**SN 189.927**	0.012	**CA 315.887**	0.0040
AS 193.696	0.016	**LI 610.365**	0.00055	**SR 421.552**	0.00026	**CA 317.933**	0.037

BA 493.408	0.00013	**MG 279.800**	0.0040	**SR 460.733**	0.00077	**FE 238.204**	0.0094
CA 315.887	0.056	**MN 260.568**	0.00022	**TI 334.941**	0.00018	**FE 259.940**	0.0098
CA 317.933	0.047	**MN 294.921**	0.00020	**TI 336.122**	0.0031	**K 766.491**	0.0031
CD 226.502	0.00057	**MO 202.032**	0.015	**TI 337.280**	0.00029	**MG 279.800**	0.0083
CO 228.615	0.00025	**NA 588.995**	0.021	**V 292.401**	0.00088	**MN 260.568**	0.011
CR 267.716	0.00045	**NI 231.604**	0.00020	**ZN 202.548**	0.0031	**MN 294.921**	0.0098
CU 327.395	0.00054	**P 213.618**	0.0061	**ZN 213.857**	0.0027	**NA 588.995**	0.0039
FE 259.940	0.00059	**PB 220.353**	0.0038	**B 182.577**	0.077	**NA 589.592**	0.0045
HG 184.887	0.26	**S 181.972**	0.022	**B 249.678**	0.065	**P 213.618**	0.014
						S 181.972	0.021
						S 182.562	0.12

TABLE 17 – CALCULATED LIMITS OF DETECTION FOR EACH ELEMENT AND WAVELENGTH, REPORTED TO TWO SIGNIFICANT FIGURES.

11.2.3 ION CHROMATOGRAPHY (IC)

The samples listed in Table 15 were selected for analysis by Ion Chromatography to determine concentrations of the following anions; Fluoride (Fl^{-}), Chloride (Cl^{-}), Nitrite (NO$_2^{-}$), Bromide (Br^{-}), Nitrate (NO$_3^{-}$), Phosphate (PO$_4^{3-}$) and Sulphate (SO$_4^{2-}$). This analysis was conducted with the help of Miss Louise Hogg, in the Environmental Engineering Laboratories, William Rankine Building, School of Engineering, University of Edinburgh.

Analytes were limited to those filtered, but not acidified with HNO_3 for analysis by ICP-OES, meaning that due to limited sample availability in some cases both IC and ICP-OES analysis of the same fluid was not possible.

The IC column was prepared for anion analysis and equilibrated before use. Calibration was performed against five dilutions of a Thermo Scientific™ Dionex™ Combined Seven Anion Standard II containing 99.9% water and 20 mg/l fluoride, 100 mg/l chloride, nitrite, bromide, nitrate, and sulphate, and 200 mg/l phosphate (Product No. 057590, Lot No. 40-85AS). The limit of detection is equal to the lowest concentration of standard used during calibration equalling 0.02 mg/l fluoride, 0.1 mg/l chloride, nitrite, bromide, nitrate, and sulphate, and 0.2 mg/l phosphate.

Analysis of the standards as samples quantified the analytical accuracy of for each element (Table 18). The variance between the known concentration of the standard was calculated as a percentage of the measured concentration and an average variance for each element determined. The accuracy, or variance between measured and standard concentration, of IC analysis was between 5 and 7% for all ions except nitrate which was measured to 20%. Precision was calculated from replicate analyses of a select number of standards (Cl, NO3, SO4). In all three cases the RSD was 5% or less, inferring good analytical precision.

3 ml of each sample was loaded into an autosampling rack. The sample is drawn into the instrument by a pump and passed to the stationary phase column where anions of interest are bound by the solution of positively charged particles (cations) in place within the column. The anion concentrations are detected by observing changes in conductivity across the column, and interpreted using chromatographic data system software.

	MEASURED CONCENTRATION (PPM)	STANDARD CONCENTRATION (PPM)	VARIANCE	VARIANCE AS% OF MEASURED CONCENTRATION	AVERAGE VARIANCE AS%
FL	0.26	0.20	0.06	23%	7%
	0.40	0.40	0.00	0%	
	2.07	2.00	0.07	3%	
	4.01	4.00	0.01	0%	
	9.41	10.00	0.59	6%	
CL	13.73	15	1.27	9%	6%
	14.73	15	0.27	2%	
	21.62	20	1.62	7%	
	29.63	30	0.38	1%	
	54.22	50	4.22	8%	
BR	-	1			5%
	1.80	2	0.20	11%	
	10.57	10	0.57	5%	
	20.72	20	0.72	3%	
	50.03	50	0.03	0%	
NO3	17.87	15	2.87	16%	20%
	18.87	15	3.87	21%	
	26.61	20	6.61	25%	
	36.48	30	6.48	18%	
	62.05	50	12.05	19%	

S04	16.24	15	1.24	8%	7%
	16.26	15	1.26	8%	
	21.94	20	1.94	9%	
	28.69	30	1.31	5%	
	47.19	50	2.81	6%	

TABLE 18 - ACCURACY (VARIANCE) OF MEASURED CONCENTRATIONS OF STANDARDS BY ION CHROMATOGRAPHY.

	MEASURED CONCENTRATION (PPM)	AVERAGE CONCENTRATION (PPM)	STANDARD DEVIATION	RSD (%)
CL	13.73	14.23	0.71	5.0%
	14.73			
N03	17.87	18.37	0.71	3.9%
	18.87			
S04	16.24	16.25	0.01	0.1%
	16.26			

TABLE 19 - PRECISION (%RSD) OF ANALYSIS BY ION CHROMATOGRAPHY FOR A SELECT GROUP OF IONS.

11.3 UNCERTAINTY

Sources of uncertainty exist in both the experimental and analytical methods. Instrumental uncertainty is reported with measurements in ' Chapter 12 Results'.

As variability exists within all natural systems, experimental work involving natural samples will provide results with some inherent inconsistencies. It is important to characterise all known and quantifiable sources of uncertainty in method and in results so as to minimise the input from these in experimental results.

Instrumental accuracies can determine uncertainty in experiment preparation and set up. Weighing of samples was carried out on calibrated laboratory balances with accuracies of at least ± 0.1 g, liquid volumes above 5ml were measured into marked laboratory glassware and below 5 ml were pipetted using Eppendorf Research Plus Pipettes. Care was taken during these procedures to minimise human induced error, especially during pipetting.

Statistical error (or precision) is inherent to all measurements and can be estimated by comparing replicate measurements. Replicate measurements of one rock sample were conducted for full rock digestions, allowing statistical error to be calculated, however as rock samples are heterogeneous then some natural variability will be reflected in this. Replicate blank samples were run on the ICP-OES and TIC Coulometer for the same purposes.

Systematic experimental error was be identified and corrected for by using control experiments (Figure 13).

The ICP-OES, IC, and pH meter were all calibrated against certified standard reference material (SRM). Instrumental detection limits are reported alongside data wherever applicable (calculated LODs for ICP-OES). Procedures of experimental set-up, agitation, sampling, and measuring were all standardised to minimise human induced error, and records kept.

12 RESULTS

This chapter presents the results of pre-experimental analysis on shale sample texture and composition as well as pre- and post-experimental fluid chemistry characterisation.

To study the hydro-geo-chemical interaction between shales and fluids at varied pressures and temperatures pre-experimental (or baseline) chemistry was determined through analysis of shale samples by XRD, XRF, Coulometry, LOI, SEM and full rock acid digestion and analysis of ICP-OES (Table 20). Following experiments, fluid samples were collected and analysed by ICP-OES, Ion Chromatography, and tested for pH and temperature (Table 29).

The analysis of experimental fluids can identify chemical reactions taking place during the interaction of shale samples and added fluids under subsurface temperature and pressure conditions within the batch reactors. These fluids can indicate what, if any, constituents of environmental concern are leached from the rock or generated by reaction with fluids during hydraulic fracturing.

The key results are summarised below, and described in more detail along with data in the following Section.

- The depositional setting and source material that makes up a shale, as well as the fluids trapped within the rock during formation, control the geochemistry of the components available to react with any injected fluids during hydraulic fracturing. It is essential to characterise these well to understand the potential geochemical contribution to wastewater generated. The rate of deposition, oxygen conditions, and source material affect shale mineralogy and formation fluid.

- Total organic carbon in shale samples varied, with only two samples containing sufficient TOC to be believed as a prospective shale gas reservoir by industry norms. Even within a single formation, such as the six samples from the Bowland Shale in this study, TOC varied between 0.5% 4.2%. This reinforces the vertical heterogeneity of shale geochemistry, and implies subsequent variation in wastewater produced depending on the horizons and lithologies accessed during fracturing.

- Inorganic carbon, a proxy for the carbonate mineral content, were low in all samples used in this study. Carbonate mineral species buffer the effects of acidizing reactions such as the oxidation of pyrite, which can lead to accelerated mineral dissolution during hydraulic fracturing. Inorganic carbon was highest in PH6 (2.2%) which also contained the highest organic carbon content (4.2%). Inorganic carbon content in shales could indicate the buffering potential against acidizing reactions, and therefore predict the extent of mineral dissolution during interaction with fracturing fluids.

- The distribution, size and texture of the minerals as observed by SEM determines the surface area of each mineral phase available to react with injected fluids during fracturing. Sulphur was observed to only exist in conjunction with Fe, confirming that organic matter was not the source of and S released into solution. As shales were crushed and milled for experiments a greater mineralogical homogeneity than would be expected in field conditions was able to be accessed.

- Digestion of shale samples using a series of acidic solutions determined absolute chemical composition of shales. Fe and S were linearly correlated – supporting the hypothesis that pyrite dissolution is the main source of S in experimental solutions. Outcrop samples were shown to have high Ca with higher proportions of Sr and Mn than other samples. Metal abundance of Cu, Ni, Mo, Pb, Co and As were clustered with Fe and S concentrations – indicating their release may be associated with pyrite dissolution. Zn is clustered with carbonate elements (Sr, Mn, Ca), and is negatively correlated with Na, suggesting preferential association with carbonate over silicate minerals. Al and Cr are associated with Na and Li, and dissolution of silicate phases containing these elements. Ba, a major component of wastewater from hydraulic fracturing which was not present at representative concentrations in experimental solutions, was released from whole shale dissolution in association with K and other elements common to silicate mineral phases.

- The pH of experimental solutions (MS and BS) decreased with time – indicating the release of H+ ions into solution. This is likely due to the dissolution of atmospheric CO_2 into sampled fluids, which are approaching equilibrium with the ambient surroundings (in contrast with the experiential vessels which are at elevated temperature and pressure). This effect is more pronounced in experiments where the shale has higher pyrite content, as dissolution of pyrite within residual shale powder is accelerated by the increasing acidity due to dissolution of CO_2. In experimental solutions which have interacted with shale containing low pyrite (BS and KC) the pH is initially low, as CO_2 is initially dissolved, and then gradually increases again as the carbonate content of the shales buffer the acidity of the sampled solutions. The interplay between pyrite and carbonate content could have implications for the management of wastewater in the field during hydraulic fracturing. Shales with high pyrite content, known to produce more acidic wastewaters could be treated with a buffer material to reduce acidity and prevent further dissolution affects.

- Experiments were designed to mimic the hydrogeochemical conditions during hydraulic fracturing as closely as possible – however due to restrictions in experimental design, budget, shale availability, and sampling strategy some discrepancies between the lab conditions and the field conditions are acknowledged. These have been discussed in greater detail in Section 10.6.

- Much lower concentrations of elements are released during experiments with outcrop shale samples than those conducted with core shale samples. This implies that 'fresh' mineral surfaces exposed by the milling of core samples are more reactive than those already exposed to surface weathering.

- When hydrogeochemical batch reactions were conducted with distilled water, the key elements released into solution are those that make up the main rock forming elements present in the shale samples (Ca, K, Mg, Na, S, and Si). Constituents of concern in wastewaters from hydraulic fracturing such as Ba, heavy metals, and high concentration salts (i.e. NaCl ~100,000ppm), are not released during interaction at reservoir conditions between shales and simple fluids with no additives. These constituents must be derived either from mixing of inherent formation and pore water with injected fluids (not represented in this experimental system) or the reaction of specific chemical constituents of injected fluids and rock components.

- Experiments conducted at ambient pressure enable greater release of constituents into solution. This is most likely to the continual exchange of oxygen and CO_2 from the atmosphere into the experimental set up, which was not suitably sealed off. Evaporation of some experimental solution provided evidence for this. Dissolution of CO_2 during the experiments (similar to that observed on sampling with SF1 experiments) will have increased the acidity of the experimental solution dissolving, in some cases, up to 15 times the concentration of elements into solution. This is supported by the greater concentration of Ca and S, both correlated with greater dissolution of carbonate minerals and pyrite which are accelerated under acidic conditions.

- The addition of hydrochloric acid as an additive to the injected fluid composition in batch reactions released a greater variety of elements into sampled solutions. Metals such as As, Pb, Cu and Zn were all present in experiments with HCl additive, however negligible in experiments without. While greater concentrations of elements were released on interaction with fluids containing HCl additive, concentrations overall were still supressed in comparison with measured wastewaters from active operations.

- Ba, an element of particular concern in for the treatment of wastewater, was released in greatest abundance after short time periods (24h) of interaction with stronger concentrations of HCl. Shale samples with greater overall proportion of carbonate minerals (KC) released more and more elements with reaction time and the addition of the fresh HCl additive. Samples with less carbonate minerals (BS) released the most elements into solution early, after which additions of HCl only diluted the overall concentration of elements in solution.

- Ion chromatography analysis revealed that fluoride concentrations were higher than advised limits in drinking and surface water for a number of samples, and although high, sulphate concentrations were not above advised environmental limits. Sulphate concentrations are in agreement with the previously proposed mechanism of pyrite dissolution and pH control dominating the geochemistry of experimental fluids.

12.1 SHALE CHARACTERISATION

Due to available sample volumes and date of receipt of some samples not all analysis was able to be performed on all samples. Table 20 provides an overview of the shale samples used in this study and the analytical techniques applied to each.

	XRD	XRF	TOC	TIC	SEM	ACID DIGESTIONS
PH1-6	✓	✓	✓	✓	✓	✓
BS1-6				✓		✓
BS-U				✓		✓
BS-L				✓		✓
MS$^{\diamond}$	✓	✓	✓	✓		✓
MS-C						
KC-EB	✓	✓	✓	✓		✓

TABLE 20 – MATRIX OF SHALE ROCK SAMPLES AND ANALYTICAL METHODS APPLIED.

12.1.1 X-RAY DIFFRACTION (XRD)

Limits of detection for quantitative XRD analysis are 1 wt.%, and results were processed such that any showing mineral content below 1 wt.% (inclusive of error) were removed from final results presented. Therefore the compositional results do not add up to 100% – with the difference representing minerals present in quantities below the limits of detection. The error in each measurement is reported by the diffraction analysis software in most cases the error is less than 1 wt.%. Samples PH1-6, KC and MS were analysed by XRD and results presented in (Table 21).

	PH1		**PH2**		**PH3**		**PH4**	
MINERAL	WEIGHT%	±	WEIGHT%	±	WEIGHT%	±	WEIGHT%	±
QUARTZ	69	2.00	79	1.40	74	1.80	62	1.80
CALCITE	LOD		3	0.23	LOD		3	0.27
DOLOMITE	LOD		3	0.24	LOD		LOD	
PYRITE	3	0.22	3	0.20	2	0.20	7	0.39
ALBITE	3	0.43	LOD		3	0.40	4	0.50
ILLITE	8	0.76	3	0.39	8	0.71	7	0.62
KAOLINITE	3	0.32	LOD		LOD		3	0.40
CHLORITE	3	0.44	LOD		2	0.40	2	0.52
MICROCLINE	1	0.34	LOD		LOD		ND	
MUSCOVITE	6	0.62	3	0.42	6	0.60	5	0.59
CARNALLITE	LOD		LOD		LOD		LOD	
GYPSUM	LOD		LOD		LOD		1	0.21
ANORTHITE	ND		ND		LOD		LOD	
ORTHOCLASE	LOD		LOD		LOD		LOD	

	PH5		**PH6**		**MS**		**KC**	
MINERAL	WEIGHT%	±	WEIGHT%	±	WEIGHT%	±	WEIGHT%	±
QUARTZ	54	2.50	56	1.90	50	1.90	63	2.30
CALCITE	2	0.23	14	0.88	LOD		LOD	
DOLOMITE	LOD		LOD		LOD		1	0.23
PYRITE	5	0.33	4	0.25	LOD		4	0.36
ALBITE	5	0.61	3	0.44	3	0.44	LOD	
ILLITE	10	0.87	6	0.58	18	1.00	8	0.79
KAOLINITE	7	0.70	2	0.32	2	0.35	5	0.55
CHLORITE	3	0.63	2	0.51	3	0.57	3	0.59
MICROCLINE	2	0.51	LOD		3	0.49	LOD	
MUSCOVITE	6	0.72	5	0.64	13	0.82	8	0.84
CARNALLITE	2	0.35	LOD		2	0.32	1	0.36
GYPSUM	LOD		LOD		LOD		LOD	
ANORTHITE	ND		1	0.43	LOD		ND	
ORTHOCLASE			2	0.44	2	0.44	2	0.40

TABLE 21 – MINERAL CONTENT OF SAMPLES (WT.%), ERROR REPORTED TO 100TH PLACE (0.01).

Mineralogy varied between samples taken from different depths within the Bowland Shale core (Figure 21). Samples PH1-6 were predominantly composed of quartz (54 – 79%), illite (3 – 10%), calcite (2 – 14%), muscovite (3 – 6%), and pyrite (3 – 4%), with accessory minerals making up less than 5%. Samples PH1-3, and PH6, were taken from the gas producing zone of the Upper Bowland Shale, $R_o > 1.1\%$, PH4 was taken from the non-calcareous section of the UBS where the $R_o < 1.1\%$, PH5 was taken from the Lower Bowland Shale. R_o is vitrinite reflectance (%), an indicator of thermal maturity of organic matter and indicates the productive gas zone within a shale (Harvey and Gray, 2012). PH1-3 were sampled from horizons within the shale core that were hydraulically fractured by Cuadrilla Resources in 2011.

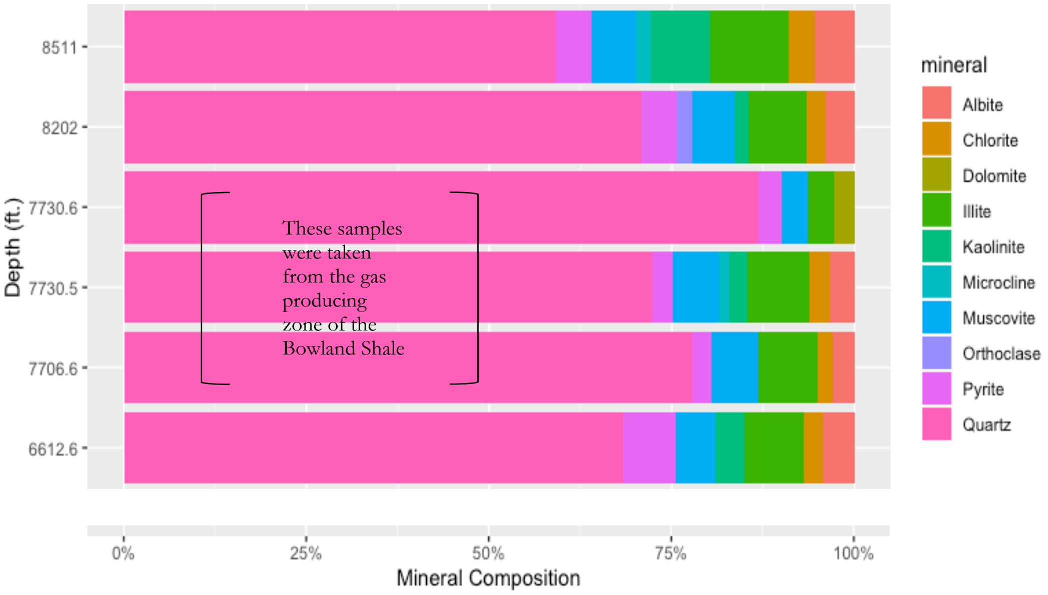


FIGURE 21 – MINERALOGICAL COMPOSITION OF CORE SAMPLES OF THE BOWLAND SHALE BY DEPTH ANALYSED BY XRD AND CORRECTED TO TOTAL 100%.

As PH1-3 were taken from corresponding fractured depths, they are expected to most closely reflect the mineralogical content of the shales fractured for gas at the Preese Hall 1 well in Lancashire, UK in 2011. Their geochemical profile, as determined by XRD, XRF, and whole rock digestion analysis is expected to most accurately represent the chemical make-up of the rocks which will have interacted with the injected fluids during fracturing. Samples PH5 & PH6 were collected from outside the gas producing zone, to reflect the wider composition of the shale, and to offer insight into how variety in mineralogical content will affect the geochemical reactions taking place between shales and injected fluids.

The mineralogical composition of MS is 54% quartz, 17% illite, 13% muscovite with accessory minerals such as kaolinite, chlorite, carnallite, microcline, and albite (each <5%). No calcareous minerals were detected in this sample, however calcareous mineral content is reported up to 30% in other analyses of Marcellus Shale material (Enomoto *et al.*, 2015), therefore either the MS sample comes from a carbonate poor zone, or weathering may have leached carbonate content prolonged surface exposure. Water present at the surface reacts with carbon dioxide in the atmosphere resulting in carbonic acid ($CaCO_3$). This reacts with calcareous minerals, dissolving the calcium carbonate, see equations 10 & 11 below.

$$CO_2 + H_2O = H_2CO_3 = HCO_3 + H^+ \tag{10}$$

carbon dioxide + water = carbonic acid = bicarbonate + hydrogen

$$CaCO_3 + H_2CO_3 = HCO_3 + Ca^{2+} \tag{11}$$

calcium carbonate + carbonic acid = bicarbonate + calcium

KC is made up of 63% quartz, with 8% illite, 8% muscovite, 5% kaolinite, and 4% pyrite, as well as <5% orthoclase, carnallite, chlorite and dolomite. It is the only sample used in batch reactions that contains dolomite, and is also geochemically distinct from PH1 and MS as it contains no albite.

The most calcareous sample analysed by XRD is PH6, containing 14% calcite, however three samples contain no calcareous material at all - PH1, PH3, and MS. Pyrite is present (2 – 7%) in all samples except MS. The precipitate minerals carnallite ($KCl.MgCl_2 \cdot 6(H_2O)$) or gypsum ($CaSO_4 \cdot 2H_2O$) are detected in all samples except those collected from the Upper Bowland Shale (PH1-3, and PH6).

Irrespective of the causes, the variability in shale composition geographically, with depth, and between formations highlights the importance of thorough shale characterisation when trying to understand the hydro-geo-chemical reactions taking place in the subsurface during hydraulic fracturing. Figure 22 compares the mineral composition of samples used in batch reactions at reservoir temperatures and pressures.

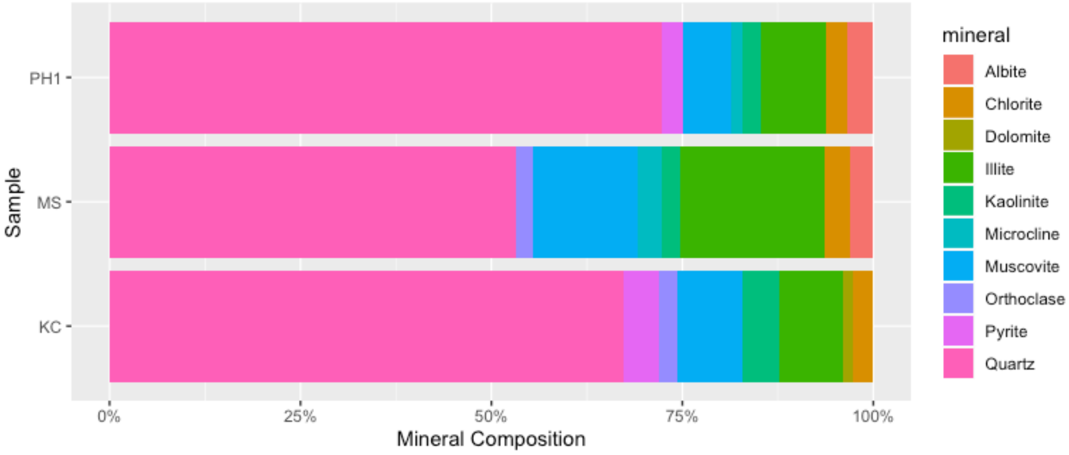


FIGURE 22 – MINERALOGICAL COMPOSITION OF THE THREES SHALE SAMPLES USED IN BATCH REACTION EXPERIMENTS AT RESERVOIR PRESSURE AND TEMPERATURE WITH DISTILLED WATER (RPT) AS DETERMINED BY XRD.

12.1.2 X-RAY FLUORESCENCE

Samples were predominantly composed of the rock forming elements silicon (63.2-81.9%), aluminium (5.14 – 19.0%), calcium (0.17-10.5%), iron (1.93-5.27%), potassium (0.82-4.66%), with less than 2% magnesium + sodium, and less than 1% titanium, manganese and phosphorus respectively. These compositions largely reflect the chemistry of minerals present in the samples as determined by XRD (Table 22).

MINERAL	FORMULA	% RANGE OF MINERAL ABUNDANCE IN SHALE SAMPLES (XRD)
QUARTZ	SiO_2	50-79
ILLITE	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}$	3-18
CALCITE	$CaCO_3$	2-14
MUSCOVITE	$KAl_2(AlSi_3O_{10})(FOH)_2$ or $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$	3-13
PYRITE	FeS_2	2-7
KAOLINITE	$Al_2Si_2O_5(OH)_4$	2-7
ALBITE	$NaAlSi_3O_8$	3-5
CHLORITE	$(Mg,Fe)_3(Si,Al)_4O_{10}\ (OH)_2\cdot(Mg,Fe)_3(OH)_6$	2-3
DOLOMITE	$CaMg(CO_3)_2$	1-3
MICROCLINE	$K(AlSi_3O_8)$	1-3
CARNALLITE	$KCl.MgCl_2\cdot{}_6(H_2O)$	2
ORTHOCLASE	$KAlSi_3O_8$	2
GYPSUM	$CaSO_4\cdot 2H_2O$	1
ANORTHITE	$CaAl_2Si_2O_8$	1

TABLE 22 – TABLE OF MINERALS AND THEIR CHEMICAL FORMULAE, SORTED BY DESCENDING PERCENTAGE OF COMPOSITION OF EACH SAMPLE.

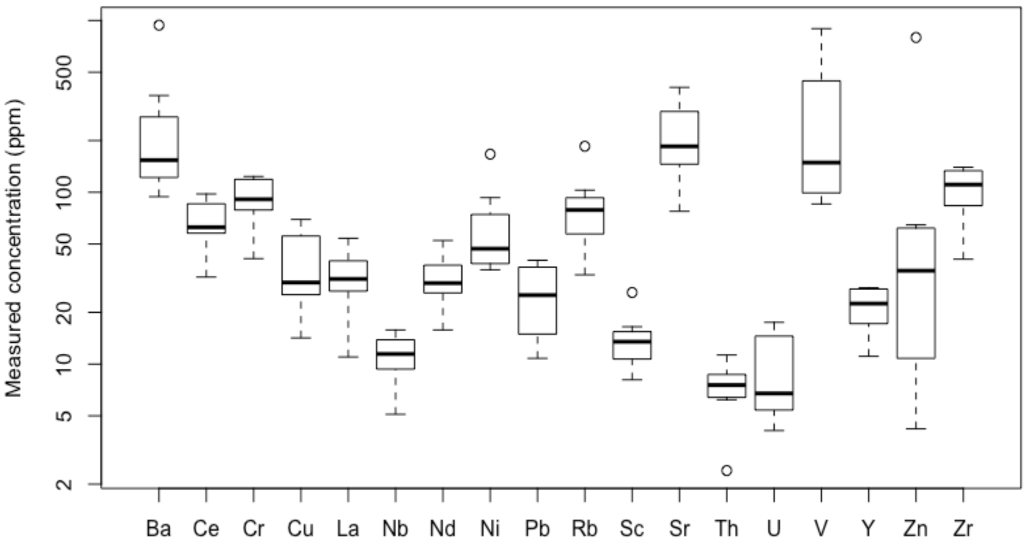


Figure 23 – Log scale box and whisker plot showing the relative concentrations (ppm) of trace elements detected in shale samples by XRF analysis.

Although major element analysis is essential for shale characterisation, and useful for corroborating geochemical analysis of the samples by XRD, the minor chemical analysis of the samples are more likely to reveal details of the subtle geochemical alterations occurring during batch reactions. Results from the XRF analysis of (minor) elements, Zn, Cu, Ni, Cr, V, Ba, Sc, La, Ca, Nd, U, Th, Pb, Nb, Zr, Y, Sr and Rb detected in parts per million, are listed in Table 24 and plotted on Figure 23.

Most of the minor elements were measured at concentrations below 100 ppm (0.01%) except Ba, V, Zr, Sr for all samples and Rb and Cr in MS and PH-5. PH-2 was comparatively low in most trace elements compared to the other samples. KC was relatively high in heavy metals Zn (797 ppm), Ni (167 ppm), and V (897 ppm). Zn is known to be high in oil shales (Wedepohl, 1978), while black shales (organic rich shales with <1% carbonates) are the main source of commercially extracted V in China (LI *et* *al.*, 2010), and are known to contain elevated traces of a variety of metals (Cu, V, U, and Ni).

The Ti, Mn and P fractions, although measured at <1% are important factors in shale geochemistry. P has been linked to the hydrocarbon source potential of shale formation (Sheldon, 1987), while Ti and Mn are known to be enriched in shales relative to coarser sedimentary rocks (Salminen *et al.*, 2005).

Rb is held within the clay fraction of shales, in this case illite, and is strongly associated with K. Cr tends to be enriched in micaceous minerals, most likely mica in these samples, but also readily substitutes for Fe and Mg and can be present in amphiboles and pyroxenes (Salminen *et al.*, 2005).

Differentiation between rock and mineral dissolution, and the transformation or formation of new chemical components, can be aided by understanding the behaviour of minor chemical constituents of the shales. The baseline geochemistry of the shale samples used as determined by XRD and XRF gives essential context to the analysis of any fluids sampled from experiments reacting the shale samples and fluids.

%	SI02	AL203	FE203	MGO	CAO	NA20	K20	TI02	MNO	P205	LOI	TOTAL
KC	70.7	12.7	4.97	1.21	2.1	0.05	2.52	0.53	0.03	0.19	4.9	99.9
MS	69.7	19.0	1.93	1.01	0.17	N.D.	4.66	0.9	0	0.05	2.67	100
PH-1	77.6	11.7	3.11	0.68	0.49	0.5	1.99	0.59	0.01	0.1	3.02	99.8
PH-2	71.2	12.1	6.51	0.82	3.1	0.57	1.55	0.47	0.01	0.07	3.72	100
PH-3	79.4	10.9	2.82	0.58	0.31	0.58	1.88	0.57	0.01	0.09	2.52	99.6
PH-4	81.9	5.14	2.92	0.49	2.28	0.13	0.82	0.23	0.01	0.07	5.91	99.9
PH-5	64.9	18.5	5.27	0.72	1.76	0.73	1.94	0.82	0.02	0.09	4.92	99.6
PH-6	63.2	9.1	4.17	0.76	10.5	0.35	1.37	0.46	0.02	0.11	9.47	99.5

TABLE 23 – RESULTS OF XRF ANALYSIS OF THE MAJOR ELEMENTAL COMPOSITION OF SHALE SAMPLES USED IN BATCH REACTION EXPERIMENTS

(PPM)	ZN	CU	NI	CR	V	BA	SC	LA	CE	ND	U	TH	PB	NB	ZR	Y	SR	RB
KC	797	69.5	167	116	897	366	14.4	39	82.3	36.5	17.5	8.5	15.9	14.6	102	26.3	199	103
MS	11.2	14.2	35.4	124	701	939	26.1	54	97.8	52.4	13.6	8.9	40.2	15.8	140	27.8	77.5	185
PH1	17.6	42	55.4	94.6	168	154	14.2	31.7	65.4	30.5	6.1	7.8	35	11.8	119	18.7	172	83
PH2	10.4	26.2	36.5	41.1	85.5	94.3	8.1	11	32.1	15.8	7.4	2.4	38.3	5.1	40.8	11.1	131	33.1
PH3	4.2	29.5	44.4	87.5	129	154	12.8	30.9	59.8	28.7	5.7	7.3	32.8	11.1	133	18.4	161	76.7
PH4	64.6	69.3	93.1	78	190	114	9.2	26.9	56.5	24	15.5	6.2	14	10	65.1	16	235	56.9
PH5	52.3	30.2	49.5	121.9	109	183	16.5	40.8	89.1	38.8	4.1	11.3	17.6	13.1	134	27.1	408	81.1
PH6	59.2	24.5	40.4	79.7	89.8	130	12.2	26.3	59.1	27.9	5.1	6.6	10.8	8.7	103	27.6	356	57.6

TABLE 24 – RESULTS OF XRF ANALYSIS OF MINOR ELEMENTAL COMPOSITION MEASURED IN SAMPLES USED IN BATCH REACTION EXPERIMENTS.

12.1.3 LOSS ON IGNITION

The total organic carbon of each shale sample analysed for XRF was measured by calculating Loss-on-Ignition (LOI) during sample preparation. As discussed in Section 11.1.3, LOI as a method of estimating TOC is limited due to its susceptibility to lost volatiles as well as organic matter during ignition. Nonetheless, it is possible to correct for the loss of structural water based on the known clay content of the shale sample (XRD Results – Section 12.1.1). Details of the correction applied can be found in Section 11.1.3. Measured LOI (%) and calculated TOC (%) are displayed in Table 25.

Estimated total organic carbon ranged from 0.1% (MS) to 4.2% (PH-6), with a mean of 1.5% and a standard deviation of 1.2%. 0.5% is the minimum TOC expected in a hydrocarbon source rock, however for a shale gas reservoir this is 2%.

SAMPLE	LOI (%)	CLAY† (%)	TOC (%)
PH1	3.0 ± 0.3	18.9 ± 2.1	0.75
PH2	3.7 ± 0.4	6.5 ± 0.8	1.52
PH3	2.5 ± 0.3	15.8 ± 1.7	0.57
PH4	5.9 ± 0.6	18.2 ± 2.1	2.26

PH5	4.9 ± 0.5	26.3 ± 2.9	1.46
PH6	9.5 ± 1.0	14.5 ± 2.1	4.28
MS	2.9 ± 0.3	36.4 ± 2.7	0.14
KC	4.9 ± 0.5	23.0 ± 2.8	1.57

TABLE 25 – TOTAL ORGANIC CARBON (TOC) CONTENT FOR EIGHT SHALE SAMPLES ANALYSED BY LOSS ON IGNITION AND CORRECTED FOR CLAY CONTENT. †CLAY CONTENT =% TOTAL CONTENT OF MUSCOVITE, KAOLINITE, CHLORITE, ILLITE FROM XRD ANALYSIS.

12.1.4 CO_2 COULOMETRY

Total inorganic carbon (TIC) was measured with a CO_2 coulometer. Calculated TIC (%) is displayed in Table 26. Total inorganic carbon is a combination of the carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3) and carbonate (CO_3^{2-}) species detected in the sample (Equation 12). Inorganic carbon is stored in rocks as carbonate minerals such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) and therefore can be indicative of carbonate mineral content. TIC measured ranged from 0.04% (PH-3) to 2.17% (PH-6) with a mean of 0.59%, a median of 0.46%, and a standard deviation of 0.63. For all samples except PH-6 the TIC was below 1%.

$$TIC=CO_2+H_2CO_3+ HCO_3^-+CO_3^{2-} \tag{12}$$

SAMPLE	TIC (%)
PH-1	0.33
PH-2	0.58
PH-3	0.04
PH-4	0.57
PH-5	0.41
PH-6	2.17
KC	0.52
MS	0.07

TABLE 26 – CALCULATED TIC (%) VALUES FROM CO_2 COULOMETRY.

12.1.5 SCANNING ELECTRON MICROSCOPY (& ENERGY DISPERSIVE SPECTROSCOPY)

Samples PH-1, -2, -3 and -6 were analysed on the Scanning Electron Microscope to determine texture and distribution of certain elements within the shale matrices. Specifically, the distribution of sulphur was investigated to determine any mineralogical association.

Organic carbon was observed in equant and elongate form, the elongate matter is concordant with the overall texture of the shale. Elongate needles of muscovite mica also follow this laminar texture while cracks or deformities in the rock mostly conform to the same orientation (Figure 25). Pyrite is observed in 'framboids' of minerals grown in spherical lenses or recesses within the shale matrix (Figure 24), and both Fe and S are only found in conjunction with each other indicating that S is not found in association with organic matter. Grain size varies from 1-20 μm, and are fairly consistently sized by mineral type. Pyrites tended to be the smallest at around 0.1-2 μm. The largest particles in the shales are the deposits of organic carbon (20-50 μm). The muscovite grains are long, 20-100 μm, however very thin (<5 μm). Quartz, feldspar and clay material varies in shape and size.

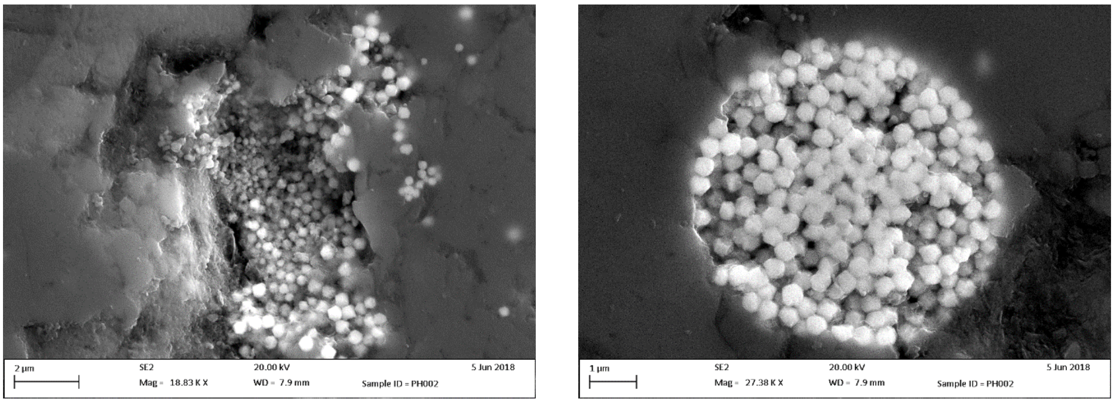


FIGURE 24 – SEM IMAGES OF PYRITE FRAMBOIDS IN SHALE SECTION PH-2, MOST ARE SPHERICAL (RIGHT) BUT SOME ALSO FILL RECESSES IN SHALE SAMPLE (LEFT). THE SAME PYRITE TEXTURE WAS OBSERVED IN PH-3 AND PH-6.

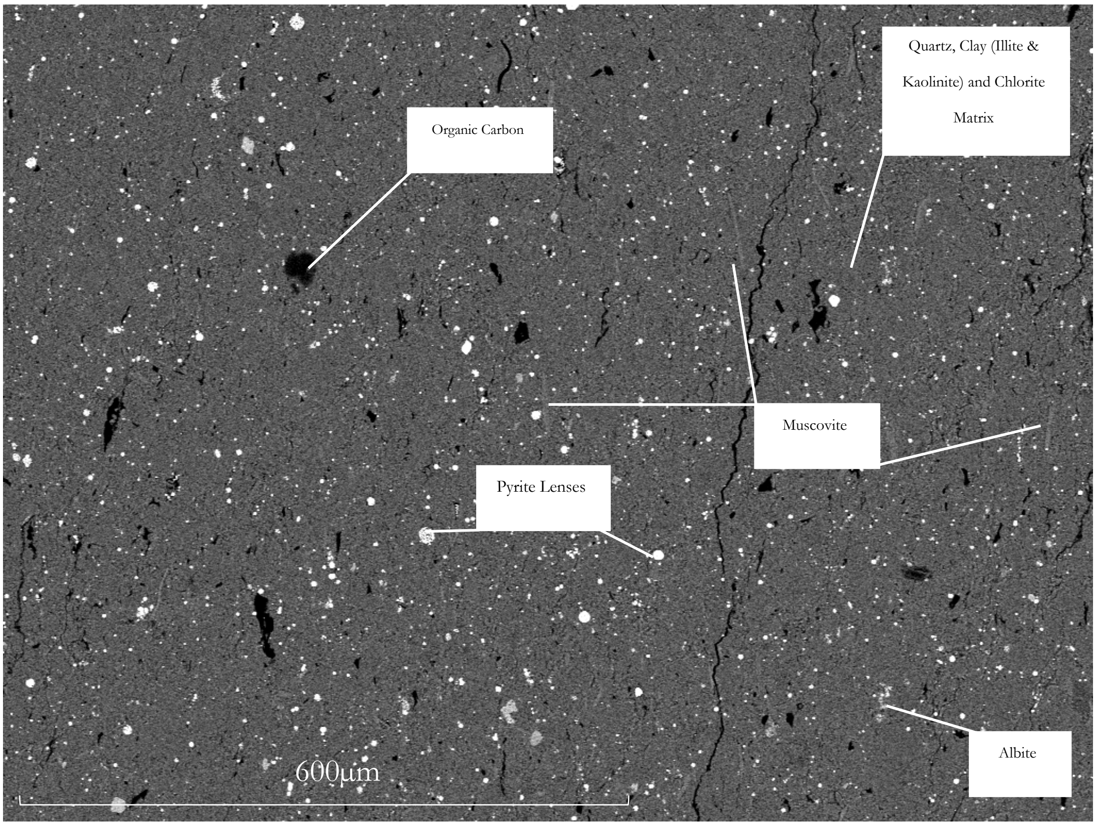
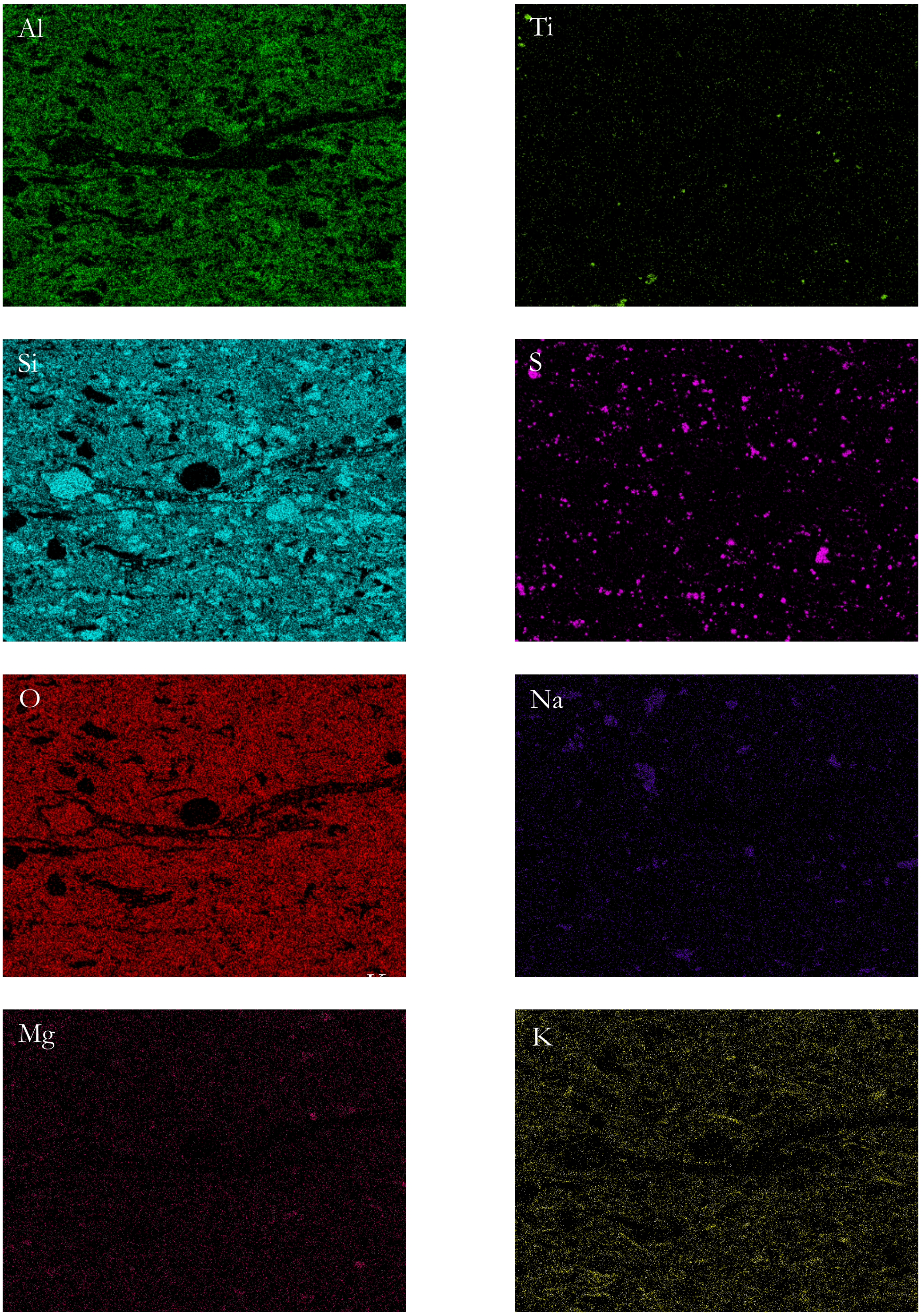


FIGURE 25 – SCANNING ELECTRON MICROSCOPE IMAGE OF PH-1 SHOWING TYPICAL COMPOSITION AND TEXTURE. DARK BLACK AREAS OF VARYING MORPHOLOGY AND SIZE ARE ORGANIC CARBON. LIGHT GREY ELONGATE, NEEDLE-LIKE, MINERALS (RUNNING NORTH TO SOUTH) ARE MUSCOVITE. CIRCULAR WHITE AREAS, AND CLUSTERS OF WHITE CIRCLES ARE FRAMBOIDS OF PYRITE. BLOCKY AND ANGULAR WHITE CRYSTALS ARE ALBITE. AND THE DARKER GRAY MOTTLED MATRIX IS MADE UP OF QUARTZ, ILLITE AND KAOLINITE.

Elemental maps of a section of sample PH-6 (Figure 26) indicate the relative groupings of elements detected in the sample. Combining this information with the measured mineralogy of the sample allows us to map out the distribution and abundance of each element. Clear associations can be seen between Al and Si (indicating the presence of aluminosilicates such as plagioclase feldspar), clear distinctions between Si and O (the difference between siliceous matrix and organic carbon deposits), and associations between Fe and S (indicating the presence of pyritic framboids). Sparse Ti is observed which may indicate the presence of rutile in the sample at levels undetected by XRD analysis. Na, Ca and Al indicate the distribution of anorthite (Ca-rich feldspar) and albite (Na-rich feldspar). Elongate needles of K pick out the placement of muscovite mica. Understanding the distribution of elements and minerals in the shale samples helps us to identify the source of dissolved elements after reaction with fluids during experiments.



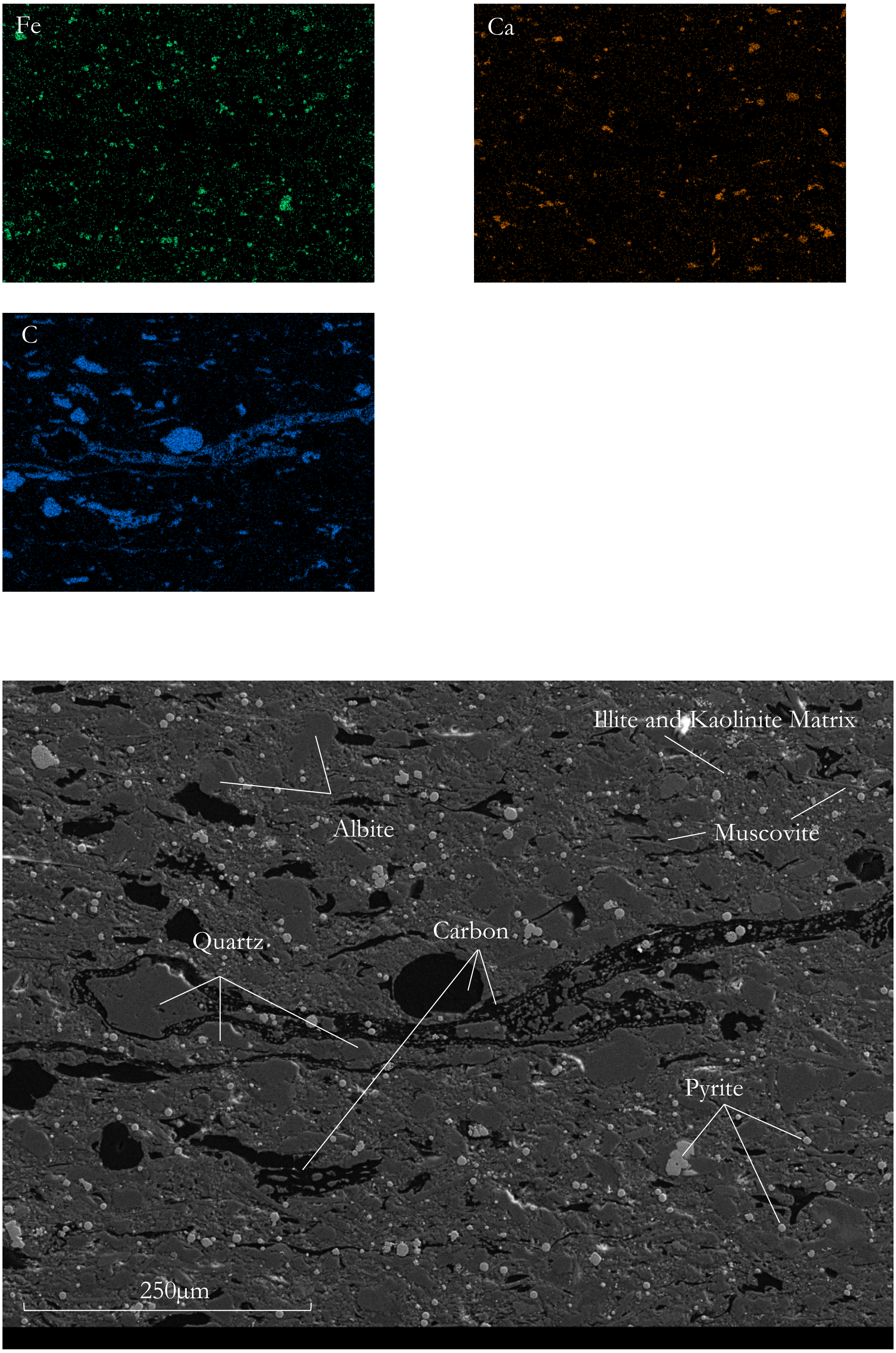


FIGURE 26 – ELEMENTAL MAPS PRODUCED BY EDS FOR A SECTION OF THE PH-6 SAMPLE (ELEMENT DETECTED ANNOTATED IN TOP RIGHT HAND CORNER OF EACH MAP) – AND THE CORRELATED SEM IMAGE ANNOTATED WITH MINERALS IDENTIFIED FROM ELEMENTAL MAPS. NB – SCALE IN ELEMENTAL DISTRIBUTION MAPS SAME AS LARGER SEM IMAGE.

Fe and S were shown by elemental mapping to be spatially correlated indicating pyrite (FeS_2) abundance and location. Pyrite cubes were observed on the SEM in framboidal structures of varying size and distribution. Most were in spherical form, showing as bright white circles at larger scales (100-600 μm) and clearly differentiated as groups of overlapping crystals at scales of 1-5 μm (Figure 24). As S was one of the predominant components released into solution during experiments, the source and nature of this S is of key interest.

Texture and elemental distribution is also relevant due to the nature of material that can be accessed by the injected fluids during fracturing. As shales were crushed and milled to a fine powder for experiments – material accessed is more homogenous – however the geochemistry of available minerals accessed during fracturing will most likely be more restricted by fracture geometry and mineralogical heterogeneity.

12.1.6 WHOLE ROCK DIGESTION

Samples were completely digested in acidic solutions to determine whole rock composition by ICP-OES. This provides a comparative data set with which we can better understand the source of certain dissolved species released during experiments. Elemental concentrations for each sample are reported in percent (%) for more concentrated elements (Table 27) and in parts per million (ppm) for less concentrated elements (Table 28).

SAMPLE / ELEMENT CONCENTRATION (%)	AL	CA	FE	K	MG	NA	S
PH1	5.62	0.87	2.18	1.37	0.50	0.44	1.89
PH2	2.45	1.54	1.86	0.55	0.27	0.17	1.77
PH3	5.14	0.21	1.76	1.21	0.30	0.45	1.64
PH4	5.22	1.80	3.70	0.96	0.40	0.40	3.83
PH5	8.28	1.08	3.07	1.25	0.40	0.56	2.92
PH6	4.26	6.14	2.61	0.94	0.41	0.37	2.50
KC	4.23	1.02	1.70	0.96	0.57	0.06	1.52
MS	7.31	0.28	1.11	2.46	0.48	0.06	0.34
BS1	5.13	2.46	2.78	1.15	0.62	0.41	2.59
BS2	4.81	2.64	2.31	1.14	0.77	0.44	1.84
BS3	4.12	1.50	1.78	0.98	0.41	0.44	1.49
BS4	4.50	2.66	2.05	1.08	0.59	0.39	1.73
BS5	5.16	0.33	6.92	1.02	0.25	0.34	8.22
BS6	5.50	0.36	2.02	1.31	0.38	0.40	1.80
BS-L	4.45	9.46	2.18	0.94	0.53	0.32	1.43
BS-U	2.79	6.53	2.42	0.52	3.14	0.16	2.53

TABLE 27 – MAJOR ELMENTAL CONCENTRATIONS MEASURED IN ACID-DIGESTED ROCK SAMPLES ON ICP-OES, REPORTED IN PERCENT (%).

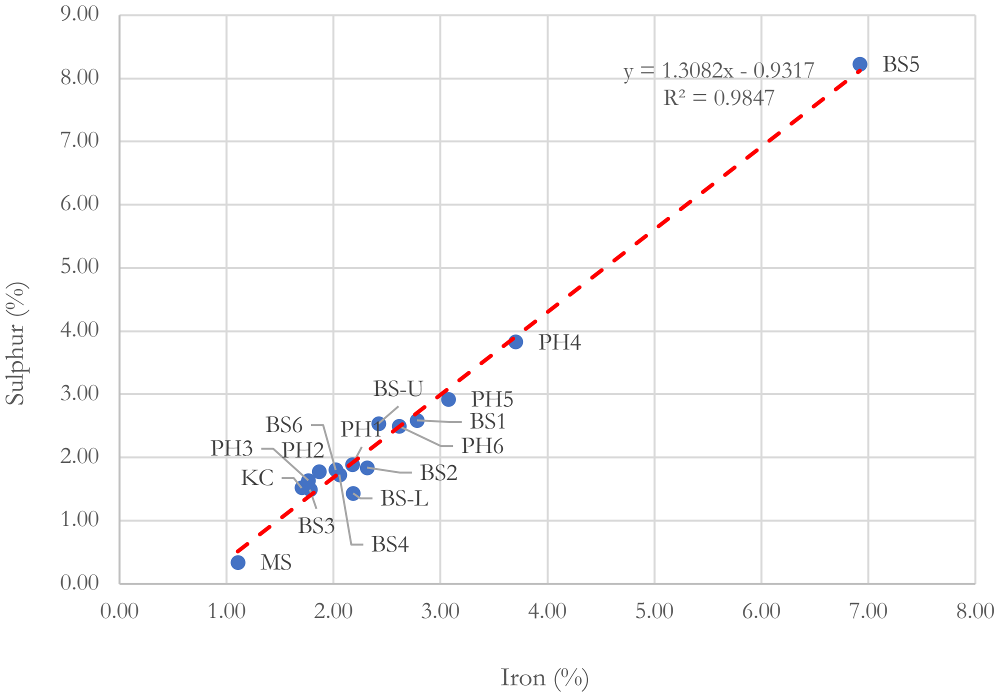


FIGURE 27 – SCATTERPLOT OF MEASURED IRON (FE) AND SULPHUR (S) CONCENTRATIONS MEASURED IN EACH ROCK SAMPLE.

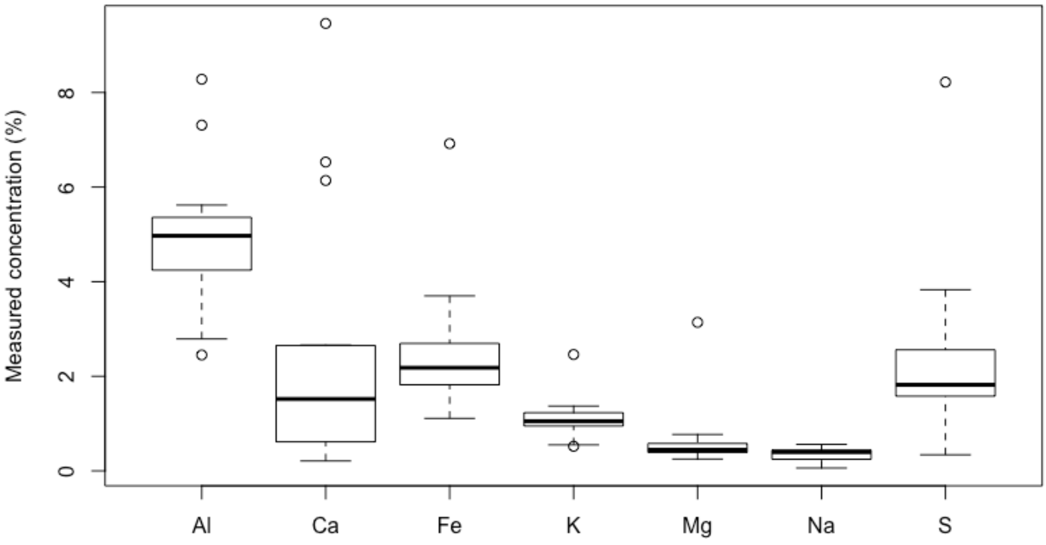


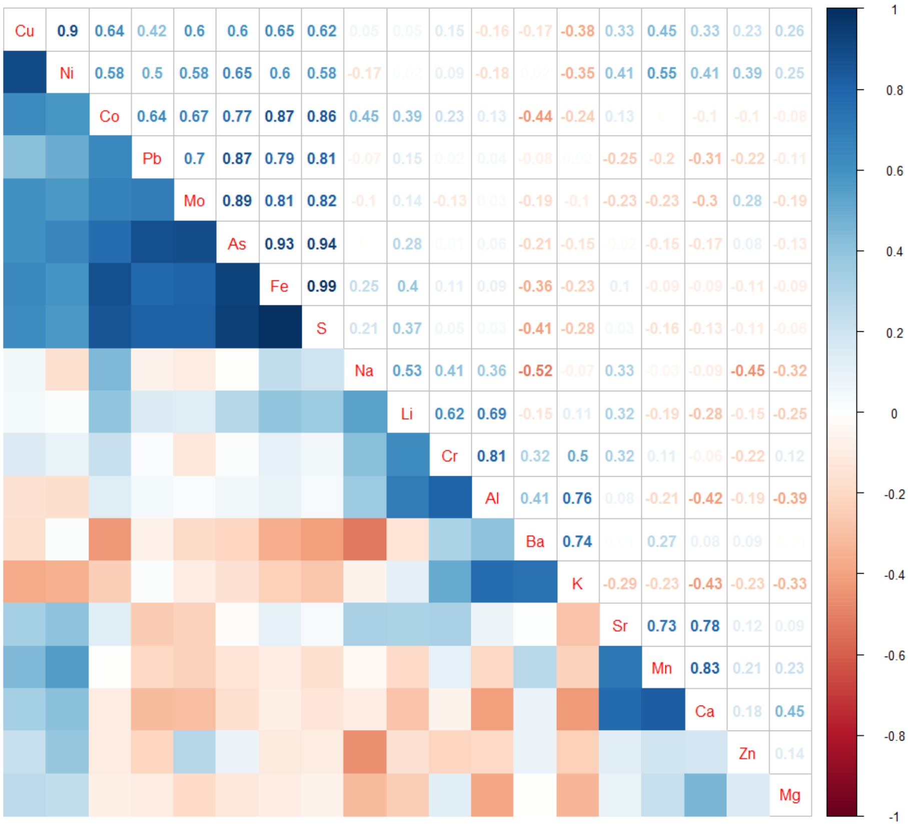
FIGURE 28 – BOX AND WHISKER PLOT SHOWING THE % CONCENTRATION OF MAJOR ELEMENTS MEASURED ON ICP-OES FOLLOWING FULL ROCK DIGESTION AND ANALYSIS (N=1).

The major elements detected in the samples included Al, Ca, Fe, K, Mg, Na and S. In outcrop samples of the Bowland Shale (BS-U & BS-L) the most abundant element was Ca (6.53, 9.46%). BS-U contained the most Mg of all samples (3.14%) suggesting the presence of dolomite ($CaMg(CO_3)_2$). For most other samples (PH-1, -2, -3, -4, -5, KC, MS, BS-1, -2, -3, -4) Al is the most abundant element analysed for (2.45-8.28%). Major elements measured (ppm concentration) constitute between 8.60 and 22.3% of the sample composition. For all samples, the correlation of Fe to S is linear, indicating direct relation between the concentrations of both elements. This suggests that pyrite (FeS_2) is the major source of sulphur in experimental fluids.

The correlation between Fe and S is the strongest in the dataset with a correlation co-efficient of r(14) = 0.99 (p-value = $4.2x10^{-14}$), statistically significant at $\alpha = 0.01$. The correlation matrix produced for the whole rock digestion data set (Figure 29) displays the calculated correlation coefficients for each pair of elements, indicating whether or not each element displays a statistically significant positive or negative linear correlation. The concentration of metals such as Cu, Ni, Co, Pb, Mo, As, S and Fe are all positively correlated suggesting that the dissolution of Pyrite (the source of Fe and S) may be associated with the release of these metals into solution. Other statistically significant positive correlations exist between Ca, Mn and Sr (Ca, Mn (0.83) and Mn, Sr (0.73) and Sr, Ca (0.78)) perhaps indicating co-dissolution of phases bearing these elements. Negative correlations exist between Na and Ba (-0.52) and Na and Zn (-0.45) indicating that dissolution of one may restrict the presence of the other. Larger proportions of Zn and Ba are detected when less Na is detected.

Generally, stronger positive correlations exist in the dataset than negative ones. Positive correlations in whole rock digestion data suggest that certain elements may be co-released during dissolution however negative correlations do not suggest inhibition of elemental dissolution, but perhaps that mineral abundance restricts the co-presence of certain minerals and exerting a more gentle control on overall fluid composition.

Hierarchical clustering of the correlation data discerns groups of elements associated by the strength of their correlation. The height of the dendrogram bar indicates the strength of the correlation between elements; lower height splits indicate stronger correlation (Figure 30). Fe and S are most strongly correlated, followed by Cu and Ni, with most metals (As, Mo, Pb, Co) clustered at a height of 1, and all the elements stated clustered below a height of 2. This suggests an association of metals with pyritic material. Sr, Mn, and Ca are clustered below 2, indicating the co-presence of Sr and Mn in calcareous material. Both Sr and Mn are common trace elements found in carbonate minerals (Society of Economic Paleontologists and Mineralogists, 1983).



Cu	0.9	0.64	0.42	0.6	0.6	0.65	0.62	0.05	0.05	0.15	-0.16	-0.17	-0.38	0.33	0.45	0.33	0.23	0.26
	Ni	0.58	0.5	0.58	0.65	0.6	0.58	-0.17	0.02	0.09	-0.18	0.02	-0.35	0.41	0.55	0.41	0.39	0.25
		Co	0.64	0.67	0.77	0.87	0.86	0.45	0.39	0.23	0.13	-0.44	-0.24	0.13	0	-0.1	-0.1	-0.08
			Pb	0.7	0.87	0.79	0.81	-0.07	0.15	0.02	0.04	-0.08	0.02	-0.25	-0.2	-0.31	-0.22	-0.11
				Mo	0.89	0.81	0.82	-0.1	0.14	-0.13	0.03	-0.19	-0.1	-0.23	-0.23	-0.3	0.28	-0.19
					As	0.93	0.94	0	0.28	0.01	0.06	-0.21	-0.15	-0.02	-0.15	-0.17	0.08	-0.13
						Fe	0.99	0.25	0.4	0.11	0.09	-0.36	-0.23	0.1	-0.09	-0.09	-0.11	-0.09
							S	0.21	0.37	0.05	0.03	-0.41	-0.28	0.03	-0.16	-0.13	-0.11	-0.06
								Na	0.53	0.41	0.36	-0.52	-0.07	0.33	-0.03	-0.09	-0.45	-0.32
									Li	0.62	0.69	-0.15	0.11	0.32	-0.19	-0.28	-0.15	-0.25
										Cr	0.81	0.32	0.5	0.32	0.11	-0.06	-0.22	0.12
											Al	0.41	0.76	0.08	-0.21	-0.42	-0.19	-0.39
												Ba	0.74	0.01	0.27	0.08	0.09	-0.01
													K	-0.29	-0.23	-0.43	-0.23	-0.33
														Sr	0.73	0.78	0.12	0.09
															Mn	0.83	0.21	0.23
																Ca	0.18	0.45
																	Zn	0.14
																		Mg

FIGURE 29 – CORRELATION MATRIX SHOWING THE PEARSON PRODUCT MOMENT CORRELATION VALUES BETWEEN EACH VARIABLE IN THE WHOLE ROCK DIGESTION DATASET. TOP-RIGHT GIVES R VALUES AND BOTTOM LEFT SHOWS STRENGTH OF CORRELATION BY COLOUR SCHEME DISPLAYED BY TEMPERATURE BAR ON RIGHT. CORRELATION DATA HAS BEEN GROUPED BY HIERARCHICAL CLUSTERING TO ORDER ELEMENTS BY ASSOCIATION OF CORRELATION COEFFICIENT (N=8).

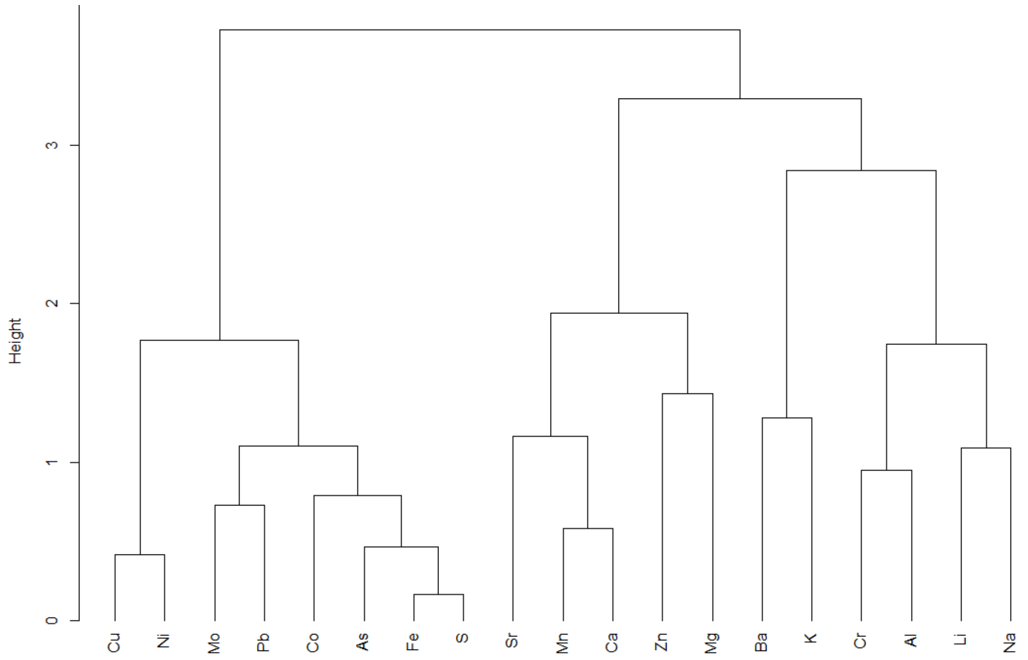


FIGURE 30 – HIERARCHICAL CLUSTER DENDROGRAM SHOWING GROUPS OF CORRELATED ELEMENTAL CONCENTRATIONS FROM WHOLE ROCK DIGESTIONS AND THEIR RELATIVE GROUPING STRENGTH (INDICATED BY 'HEIGHT' ON THE Y-AXIS (N=8).

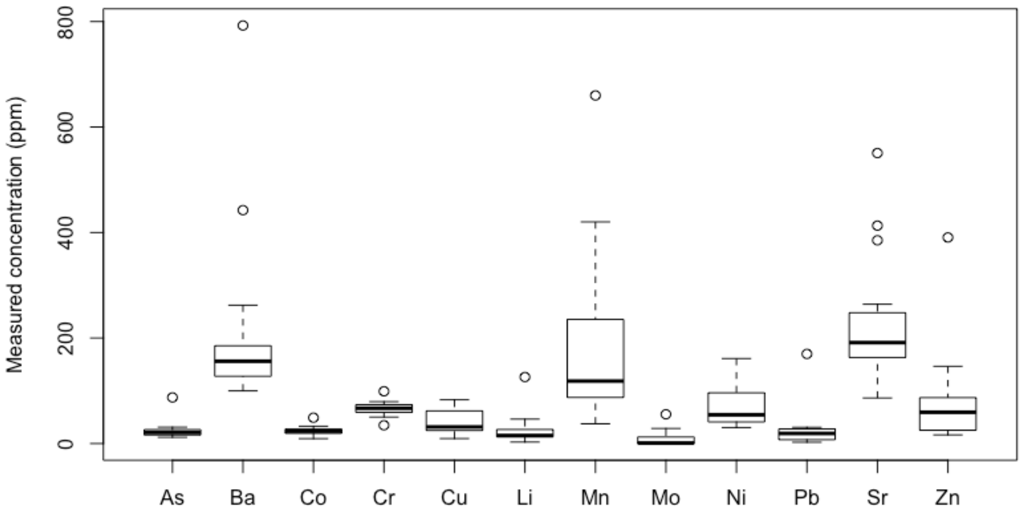


FIGURE 31 – BOX AND WHISKER PLOT OF THE MINOR (PPM) ELEMENTAL CONCENTRATIONS OF WHOLE ROCK DIGESTIONS AND ANALYSIS BY ICP-OES. NB-THE OUTLIER OF 2210PPM MN MEASURED IN BS-L IS OUTSIDE THE PLOTTING RANGE OF THE Y AXIS OF THIS PLOT (N=8).

SAMPLE / ELEMENTAL CONCENTRATION (PPM)	AS	BA	CO	CR	CU	LI	MN	MO	NI	PB	SR	ZN
PH1	24.3	185	20.4	76.2	58.3	25.3	143	10.3	66.0	24.5	191	79.8
PH2	17.3	100	12.4	34.6	23.8	14.0	84.2	1.51	41.1	28.6	136	30.3
PH3	15.7	158	19.6	69.7	29.0	15.0	88.2	0.0	49.8	29.8	160	20.1
PH4	31.1	121	32.8	66.2	70.0	35.7	86.7	28.5	95.7	7.78	232	94.2
PH5	26.3	186	27.9	99.0	29.1	126	136	0.0	56.5	12.5	413	59.7
PH6	26.7	124	19.1	55.1	21.4	12.8	150	0.0	42.5	2.42	385	65.3
KC	30.8	262	18.8	50.1	38.1	8.39	108	26.8	96.7	6.75	146	391
MS	13.5	792	9.27	79.4	9.41	12.9	37.4	1.12	30.3	30.8	86.4	17.3
BS1	22.2	154	24.4	67.3	49.0	28.1	340	14.7	52.5	LOD	212	58.9
BS2	11.8	146	26.8	64.3	28.2	16.5	420	0.7	40.7	4.91	197	61.4
BS3	16.7	131	26.1	57.2	20.3	15.3	118	0.0	38.2	19.1	173	16.4
BS4	12.4	136	19.5	61.1	25.8	14.6	321	3.57	40.1	7.91	192	42.7
BS5	87.4	115	49.0	66.3	83.0	46.2	64.0	55.4	161	170	172	36.2
BS6	18.9	160	30.2	74.9	33.8	23.0	108	0.0	58.4	26.8	167	17.0
BS-L	19.7	442	24.2	71.5	76.2	11.6	2211	0.0	160	5.96	551	146.4
BS-U	22.3	184	22.6	72.4	65.4	2.8	660	0.0	117	25.6	264	103.4

TABLE 28 – ELEMENTAL CONCENTRATIONS MEASURED IN ACID-DIGESTED ROCK SAMPLES ON ICP-OES, REPORTED IN PARTS PER MILLION (PPM).

12.2 EXPERIMENTAL RESULTS

Fluids produced by the hydrogeochemical batch reactions were collected at the end of each experiment. pH and temperature was measured at 1 minute intervals for those conducted at reservoir pressures and temperatures (p146). Experiments conducted at ambient pressure were sub-sampled at 28, 31, 40, 56, 157, and 189 days, and topped up with fresh distilled water to maintain the rock:water experimental ratio. Samples were filtered and either acidified to 2% with HNO_3 for analysis on ICP-OES or left unacidified for analysis by IC. Table 29 provides a summary of the analysis performed on experimental fluids collected.

SAMPLE	PH	TEMPERATURE	ICP-OES	IC
DI			✓	
KC1.1	✓	✓	✓	✓
KC2.1	✓	✓	✓	✓
KC3.1	✓	✓	✓	✓
MS1.2	✓	✓	✓	✓
MS2.2	✓	✓	✓	✓
MS3.2	✓	✓	✓	✓
BS1.3	✓	✓	✓	✓
BS2.3	✓	✓	✓	✓
BS3.3	✓	✓	✓	✓
PH3_A4			✓	
PH4_A4			✓	
PH6_A4			✓	
MS_A4			✓	
KC_A4			✓	
PH3_A7			✓	
PH4_A7			✓	
PH6_A7			✓	
MS_A7			✓	
KC_A7			✓	
PH2_T0			✓	
PH3_T0			✓	
PH4_T0			✓	
PH5_T0			✓	
PH6_T0			✓	

MS_T0	✓	
KC_T0	✓	
PH2_0.125HCL(28)	✓	✓
MS_0.125HCL(28)	✓	✓
KC_0.125HCL(28)	✓	✓
PH2_0.125HCL(56)	✓	✓
MS_0.125HCL(56)	✓	✓
KC_0.125HCL(56)	✓	✓
PH2_0.125HCL(157)	✓	
MS_0.125HCL(157)	✓	
KC_0.125HCL(157)	✓	
PH2_0.125HCL(189)	✓	
MS_0.125HCL(189)	✓	
KC_0.125HCL(189)	✓	
PH2_10HCL(28)	✓	✓
KC_10HCL(28)	✓	✓
MS_CORE(31)	✓	
BS_UPPER(31)	✓	
BS_LOWER(31)	✓	
MS_CORE(40)	✓	
BS_UPPER(40)		
BS_LOWER(40)		

TABLE 29 – MATRIX OF FLUID SAMPLES AND ANALYTICAL TECHNIQUES APPLIED.

12.2.1 PH & TEMPERATURE

Fluids samples collected from reservoir temperature and pressure (SF1) experiments were measured for pH and temperature at 1 minute intervals from the moment of sampling. Figure 33, Figure 34, and Figure 35 display the measured pH across the 10 minute measuring period.

Temperatures ranged from 21.8-55.3 ± 0.5 °C (experiments were conducted at 65 °C) indicating a 10 – 40 °C temperature drop on sampling that could drive mineral precipitation from solution, therefore every effort was made to acidify the samples with HNO_3 as quickly as possible so as to maintain the dissolution of any trace metal phases.

The pH of fluids sampled from control experiments ranged from 6.49 to 7.99 ± 0.01 at the moment of sampling, dropping off to 5.89-6.81 ± 0.01 after ten minutes (Figure 33,

Figure 34, Figure 35). For the experiments conducted with shale material under reservoir conditions, the highest pH was measured in the experiment with 1 mm chips Kimmeridge Clay (8.41 ± 0.01) and the lowest in the experiment with powdered Marcellus Shale, sampled after 24h (5.06 ± 0.01) (Figure 32).

The pH of both experiments with Kimmeridge Clay shale are higher than the pH measured in the control by ~ 2 pH units (Figure 34). The pH of the experiments with the Marcellus Shale are lower than the control by ~ 2.5 pH units (Figure 33). The pH of the experiments conducted with Bowland Shale measure above and below that of the control until 2 minutes after sampling when the pH gradually increases above that of the control which, unexpectedly decreases with time (Figure 35).

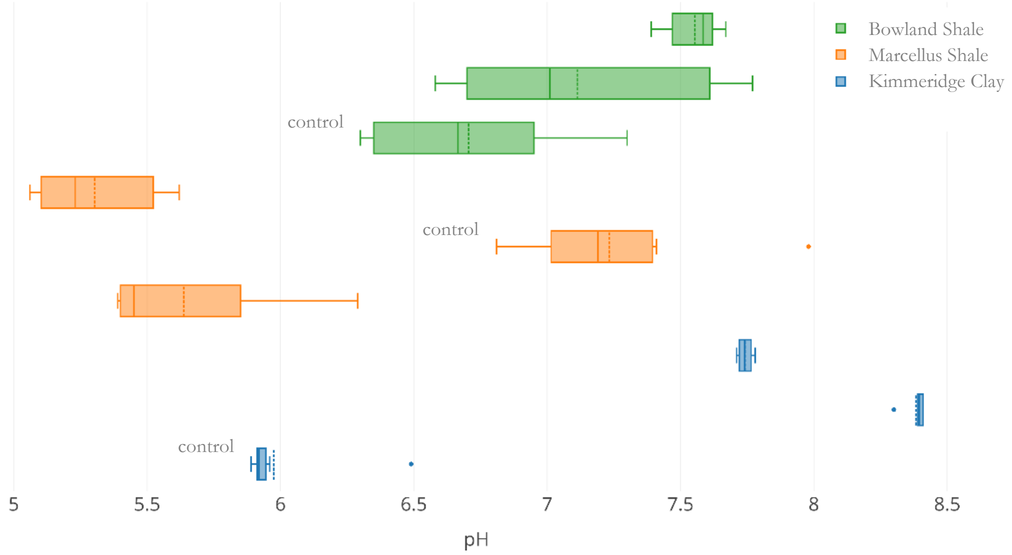


FIGURE 32 – BOXPLOTS OF PH MEASURED ACROSS 10 MINUTE TIME INTERVALS FOLLOWING EXPERIMENT END (CONTROL EXPERIMENTS HIGHLIGHTED BY TEXT LABEL, N=3).

pH decreases when H+ ions are released into solution. A number of chemical reactions can decrease solution pH, including the dissolution of pyrite in oxygenated water (Equation 13) or the dissolution of CO_2 and dissociation of carbonic acid (Equation 14).

$$FeS_2 + H_2O + O_2 \rightarrow Fe^{2+} + SO_4^{2-} + 2H^+ \qquad 13$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO3^- \qquad 14$$

It is possible that the increase in pH observed in both the SF1-BS and SF1-KC fluids is due to counterbalancing chemical reactions causing release of H+ ions (pyrite dissolution or similar) before buffering by bicarbonate (HCO_3^-) back to carbonic acid ($H_2CO_3^-$). This buffering effect is more likely to take place if the carbonate content of the shales is greater. It is also possible that the change in pH observed in the SF1-MS fluid (first increase then decrease) is due to dissolution of pyrite as the fluids become oxygenated during sampling.

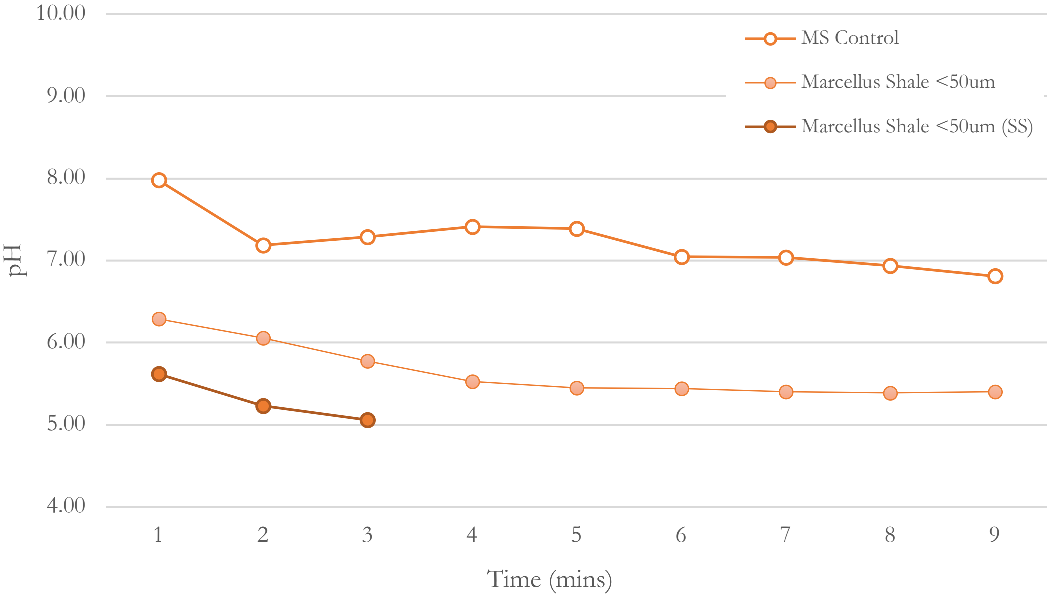


FIGURE 33 – PH OF MARCELLUS SHALE FLUID SAMPLES (1 MINUTE INTERVALS) FROM RESERVOIR CONDITIONS EXPERIMENTS WITH RESPECT TO CONTROL. (N=1).

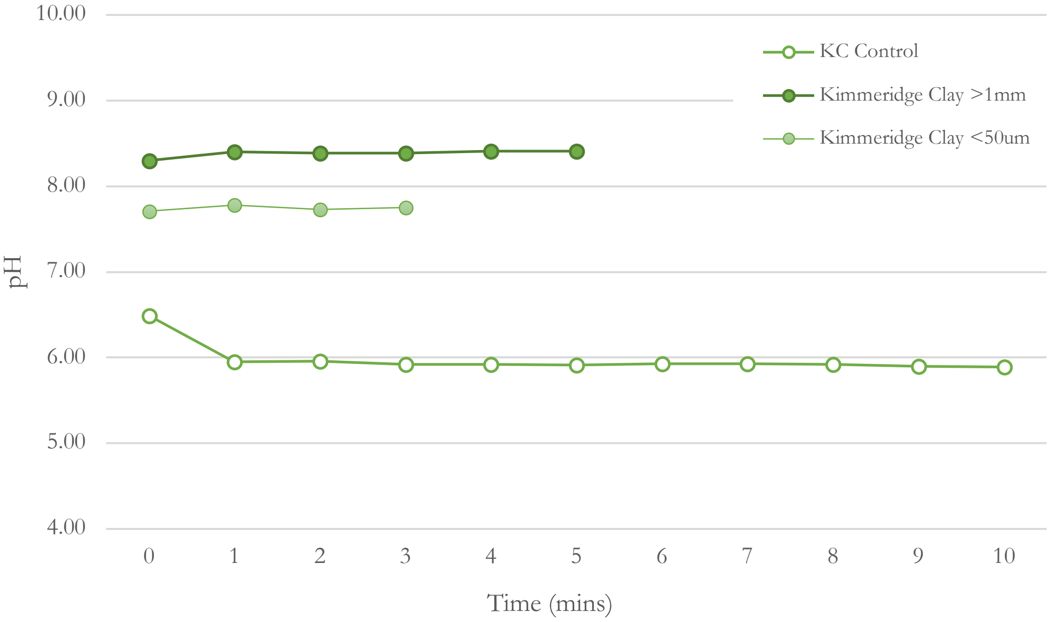


FIGURE 34 – PH OF KIMMERIDGE CLAY FLUID SAMPLES (1 MINUTE INTERVALS) FROM RESERVOIR CONDITIONS EXPERIMENTS WITH RESPECT TO CONTROL (N=1).

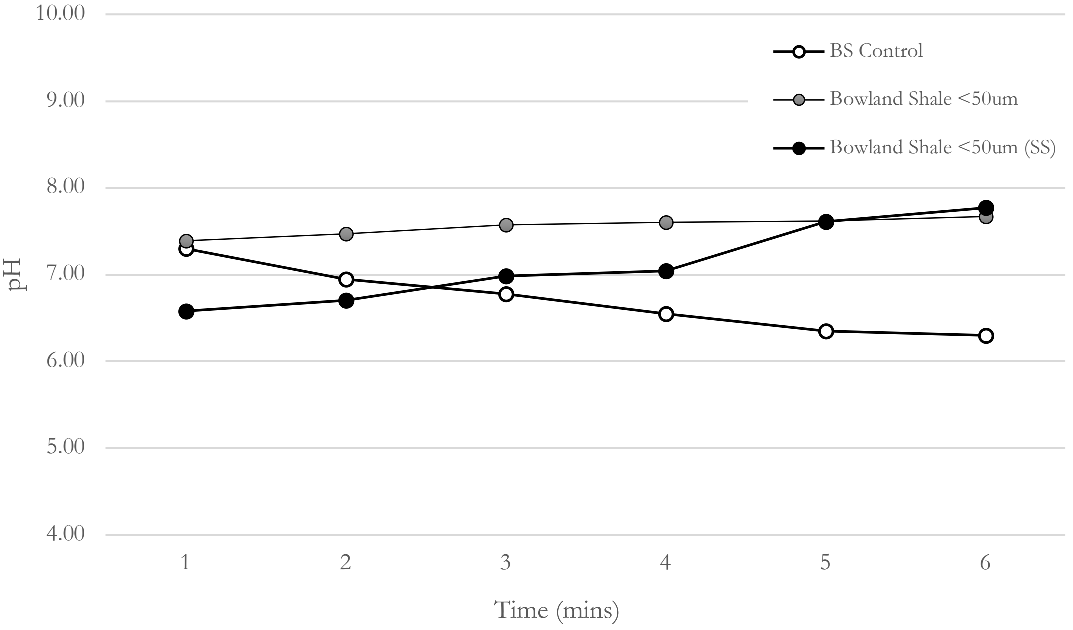


FIGURE 35 – PH OF BOWLAND SHALE FLUID SAMPLES (1 MINUTE INTERVALS) FROM RESERVOIR CONDITIONS EXPERIMENTS WITH RESPECT TO CONTROL (N=1).

12.2.2 ICP-OES

Fluid samples collected from experiments were analysed on the ICP-OES to determine dissolved elemental concentrations for a suite of analytes. Samples were tested for Ag, Al, As, B, Ba, Cs, Ca, Co, Cr, Cu , Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, S, Si, Sr, Ti, V, and Zn. The concentration of each element is calculated by measuring the intensity of the light produced at diagnostic wavelengths for each element and calibrating against standards of known concentrations run before each analysis.

Five different experimental conditions were set (SF1-5). SF1 most closely replicated subsurface temperature and pressure conditions however limitations with the experimental equipment meant that only distilled water could be used as the fracturing fluid in this set up. SF2 comparatively investigated the effect of reducing the pressure at which SF1 experiments were conducted to ambient air pressure, keeping all other variables the same. SF3 experiments were conducted at ambient pressures and temperatures. SF4 and SF5 were conducted at reservoir temperature, ambient pressure, and with 0.125% and 10% HCl chemical additive to the fracturing fluid respectively.

Within these experimental conditions some additional variables were investigated. During SF1 the effect of shale particle size was investigated. The effects of sample depth and source (surface outcrop or core) were investigated in SF2-5. Temporal sub-sampling was achieved with varying degrees of success in all experiments; SF1 after 24 hours, SF3 after 7 weeks, SF4/5 after 8, 22.5, and 27 weeks, and all experiments were sampled after 4 weeks.

Three replicate SF1 experiments were run. Two, SF1-MS & SF1-BS, were run for four weeks and one, SF1-KC, was terminated after 3 weeks due to equipment issues. SF1-KC compared the effect of 1mm shale chips with powdered shale on reaction rates. SF1-MS and SF1-BS were both conducted with shale powder due to the greater reactivity observed in SF1-KC powdered shale experiment.

12.2.2.1 CONTROL EXPERIMENTS

Overall, elemental concentrations measured in control analyses were minimal (0-0.34 ppm) indicating little evidence of contamination from equipment or set up. As SF1 experimental equipment was made of 313L stainless steel, elements of particular concern were Cr, Ni, Mn and Mo which are all primary constituents of 316L stainless steel. Cr, Ni, and Mn all measured 0 ppm or below the limit of detection suggesting corrosion was not responsible for 0.1-1.6 ppm Mo measured in the fluids, as these elements would be expected to be co-released if corrosion was occurring.

As experimental equipment was re-used for each SF1 experiment, the effectiveness of the cleaning process was tested by comparing the results of the control experiments with time Figure 36. All concentrations of elements measured decrease between the first and the third control experiment, however Mn, Ni, Si and Zn all increase temporarily in the second control. Most elements detected in control analyses were less than 0.1 mg/L except Ca, K and S.

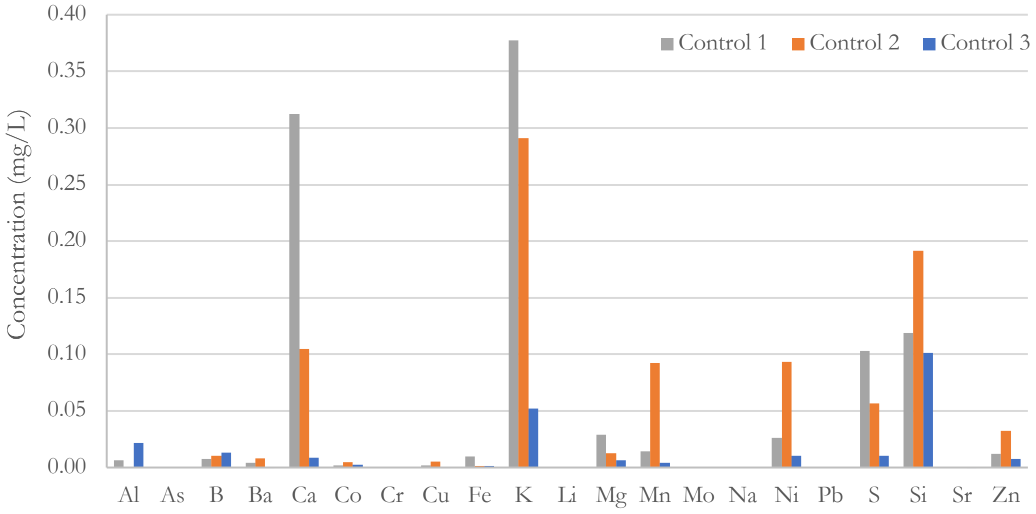


FIGURE 36 – ELEMENTS MEASURED IN CONTROL REACTIONS RUN WITH DISTILLED WATER AND NO SHALE FOR 4-WEEK PERIODS. CONTAMINATION BETWEEN EXPERIMENTS WOULD BE ILLUSTRATED BY PROGRESSIVELY INCREASING CONCENTRATIONS BETWEEN CONTROLS 1, 2, AND 3 (WHICH CORRESPOND TO SEQUENTIAL EXPERIMENTS SF1-KC (CONTROL 1), SF1-BS (CONTROL 2), AND SF1-MS (CONTROL3).

12.2.2.2 SF1 EXPERIMENTAL RESULTS

For each SF1 experiment the results of fluid analysis from a synchronous control experiment containing fluid but no rock sample, are subtracted from the concentrations measured dissolved constituents to counter the effects of any contamination by method. Tabulated results are presented on p156.

The dissolved constituents greater than 1ppm within the fluids analysed from SF1-KC experiments performed with shale powders are Ca (36.7 ppm), K (17.3 ppm), Mg (5.6 ppm), Mo (1.2 ppm), Na (51.4 ppm), S (14.0 ppm), and Si (4.3 ppm). In comparison to the SF1-KC experiments conducted with 1mm rock chips the concentrations are between 0.2 and 5 times higher (Figure 37).

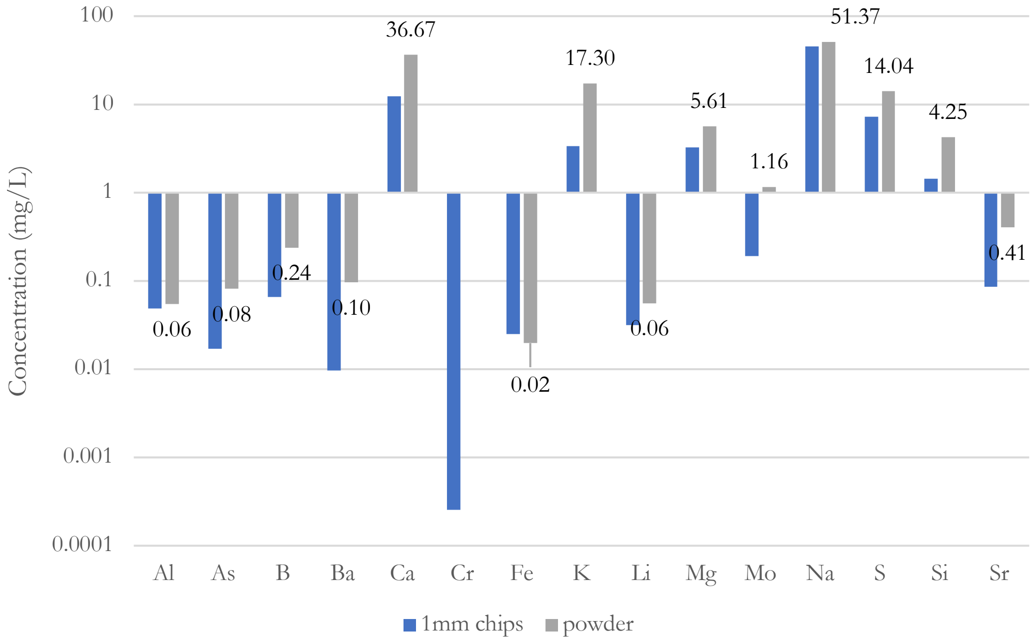


FIGURE 37 – CONCENTRATION OF ELEMENTS MEASURED IN FLUIDS SAMPLED FROM BATCH REACTIONS WITH KIMMERIDGE CLAY SHALE MATERIAL, 1MM CHIPS AND POWDER. NB: LOG SCALE AXIS.

Dissolved constituents greater than 1 ppm in the SF1-BS experiments closely mirrored those measured from the SF1-KC fluids with measured concentrations of Ca (57.6 ppm), K (11.2 ppm), Mg (11.7 ppm), Na (82.3 ppm), S (25.2 ppm), and Si (3.6 ppm), however only 0.05 ppm Mo was detected. The SF1-BS experiment that was opened for sub-sampling after 7 days and then refilled with fresh reaction fluid before re-pressurisation contained lesser concentrations of all elements measured.

For the SF1-MS experiments, all elements measured are present in lesser concentrations than the previous two experiments (SF1-KC and SF1-BS). The >1 ppm concentration elements are Ca (1.20 ppm), K (2.55 ppm), and Si (2.1 ppm), S is also present at 0.95 ppm. The SF1-MS experiment sub-sampled after 24h shows greater concentrations overall of elements measured than in the experiment that remained closed for the entire duration, suggesting that the subsampling process may be altering the chemical interaction between the fluids and the shale. This is the opposite outcome to the SF1-BS experiment sampled after 7 days, where concentrations are less after 7 days than when experiments are left closed for the full duration.

Fluids sampled from SF1 experiments are Na and Ca dominated for KC and BS however MS fluids are relatively depleted in dissolved elements in comparison. If Na and Ca are derived from feldspar dissolution then Al would be expected at greater concentrations than is measured. The next most abundant elements are K, Mg and S, with some Si detected. K and Si are proportionally concentrated depending on shale sample, as are Na and Ca and S, suggesting they are co-released depending on shale composition (Figure 38). B and Sr are also concentrated proportionally with Na, C and S, but at much lesser concentrations (Figure 39).

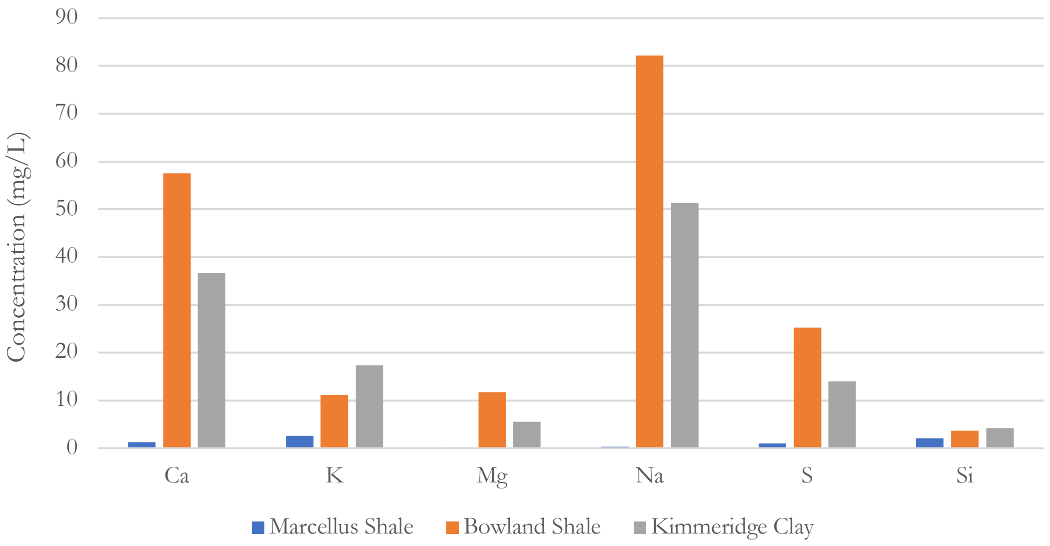


FIGURE 38 – CONCENTRATION OF MAJOR ELEMENTS MEASURED IN SF1 BATCH REACTIONS AT REPRESENTATIVE RESERVOIR PRESSURES AND TEMPERATURES (N=1).

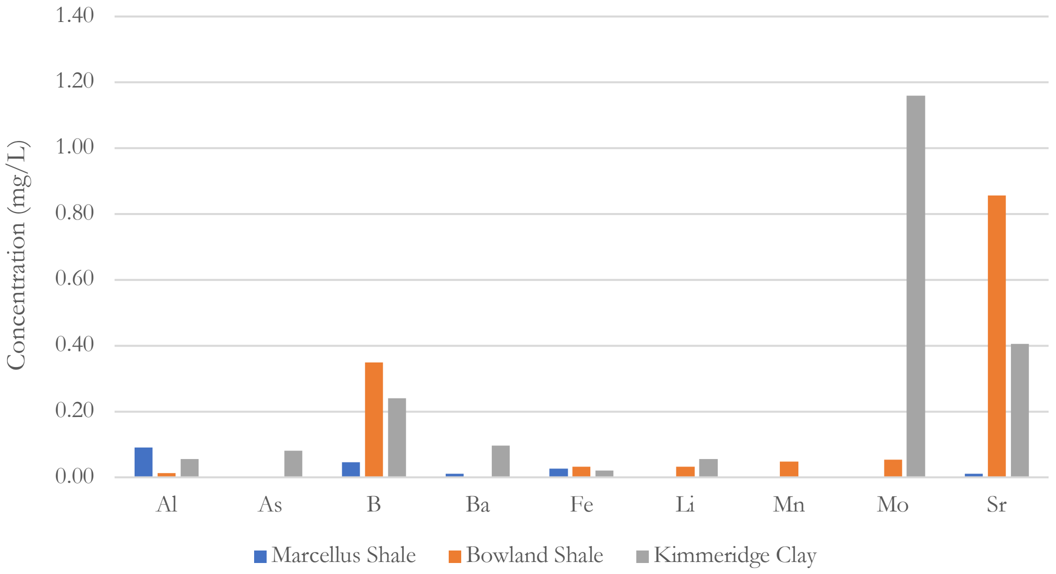


FIGURE 39 – CONCENTRATION OF MINOR ELEMENTS MEASURED IN FLUIDS SAMPLED FROM BATCH REACTIONS AT RESERVOIR PRESSURES AND TEMPERATURES (N=1).

Summary of SF1 Experimental Results:

- Contamination from corrosion of experimental equipment is non-existent.
- Contamination between runs of experiments is low to negligible. Cleaning process is effective.
- Marcellus Shale (outcrop sample) is much less reactive than Kimmeridge Clay and Bowland Shale (core samples).
- Sub-sampling experiments after 24 hours results in increased concentrations of most constituents, however after 7 days results in decrease, in comparison to the same experiments that remain closed for the 28 day duration
- Constituents released into solution are mainly elements found in rock forming mineral matrix – no elements of environmental concern released during reaction at pressure and temperature with distilled water.

Theoretically if hydraulic fracturing was performed with distilled water the expected produced fluids would be of this composition. – however, no pore of formation water is present in these shales and geological heterogeneity is not accounted for.

SF1-KC

(MG/L)	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
1 MM CHIPS	0.05	0.02	0.07	0.01	12.4	0.00	0.00	LOD	0.03	3.34	0.03	3.27	LOD	0.19	45.5	LOD	0.00	7.30	1.45	0.09	LOD
POWDER	0.06	0.08	0.24	0.10	36.7	0.00	0.00	LOD	0.02	17.3	0.06	5.61	LOD	1.16	51.4	LOD	0.00	14.0	4.25	0.41	LOD

TABLE 30 - MEASURED CONCENTRATION OF ELEMENTS IN SF1 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH KC SHALE.

SF1-BS

(MG/L)	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	PB	S	SI	SR	ZN
1 WEEK	0.01	0.00	0.28	0.00	40.8	0.00	0.00	0.00	0.02	8.03	0.02	8.17	0.04	0.05	50.7	0.00	16.0	3.08	0.56	0.00
4 WEEKS	0.01	0.00	0.35	0.00	57.6	0.00	0.00	0.00	0.03	11.2	0.03	11.7	0.05	0.05	82.3	0.00	25.2	3.64	0.86	0.00

TABLE 31 - MEASURED CONCENTRATION OF ELEMENTS IN SF1 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS SHALE.

SF1-MS

(MG/L)	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
24H	0.01	LOD	0.05	0.04	4.65	0.00	LOD	0.00	0.11	3.76	0.00	0.78	LOD	LOD	0.48	LOD	0.00	2.87	2.33	0.04	0.01
4 WEEKS	0.09	LOD	0.05	0.01	1.20	0.00	LOD	0.00	0.03	2.55	0.00	0.24	LOD	LOD	0.35	LOD	0.00	0.94	2.05	0.01	0.00

TABLE 32 - MEASURED CONCENTRATION OF ELEMENTS IN SF1 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH MS SHALE.

12.2.2.3 SF2 EXPERIMENTAL RESULTS

SF2 experiments, in comparison to SF1, were conducted at ambient air pressure, while maintaining representative reservoir temperature (65 °C). Results from geochemical analysis of fluids collected after 4 weeks are tabulated on p158. Similarly to SF1 experiments, the elements present in greatest concentration are Ca (30.6-829 ppm), K (13.8-55.5 ppm), Mg (4.37-74.0 ppm), Na (2.18-171 ppm), S (13.4-285 ppm), and Si (1.22-18.3 ppm), however overall the concentrations of contaminants measured are higher, in some cases by up to 15 times the concentrations measured in SF1 experiments (Figure 40 & Figure 41).

This suggests that either pressure inhibits elements from dissolution during rock water interaction at reservoir pressures and temperatures, or the mixing with oxygenated air in the SF2 experiments encourages dissolution, further discussion of the results of SF2 experiments can be found in Section 12.2.2.3 SF2 Experimental Results.

SF2 experiments were conducted in polypropylene screw top vials, which may be susceptible to air exchange throughout the duration of the experiments. On sampling, 5-60% fluid loss from each experiment was detected and therefore it is proposed that contamination with oxygenated air may have occurred as the screw top closures warped in the oven. This has the potential to significantly bias any results obtained from SF2 experiments, as fluid volumes were not kept constant throughout. Due to widespread anomalous concentrations measured in SF2-BS3 fluids – relatively low Ca, Na, and S concentrations, and high Al, Fe, and Si compared to other shale samples – the data was not plotted in Figure 40 & Figure 41, however is included in data tables on p161 for reference.

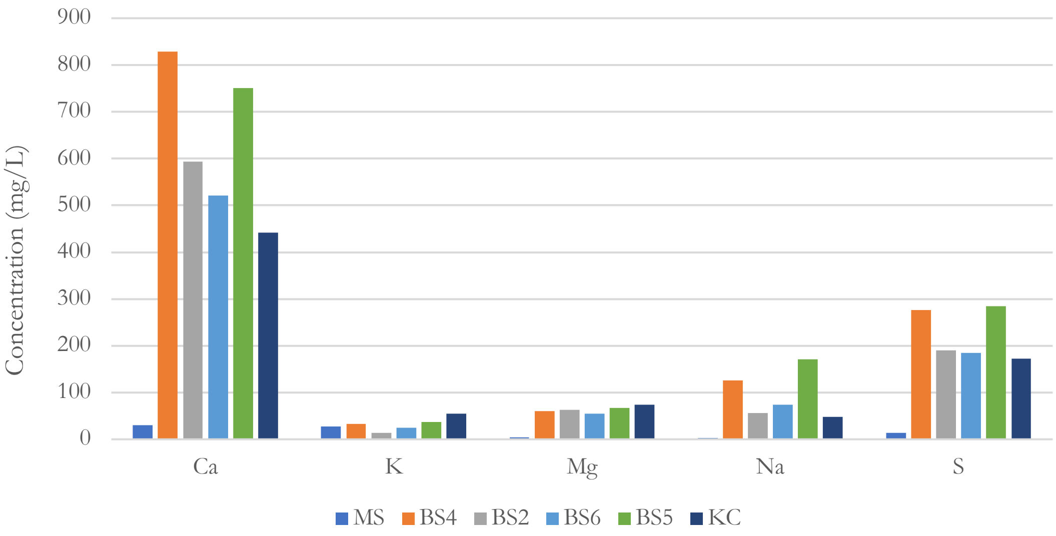


FIGURE 40 – MAJOR ELEMENTAL COMPOSITION OF FLUIDS SAMPLED FROM SF2 EXPERIMENTS (N=1).

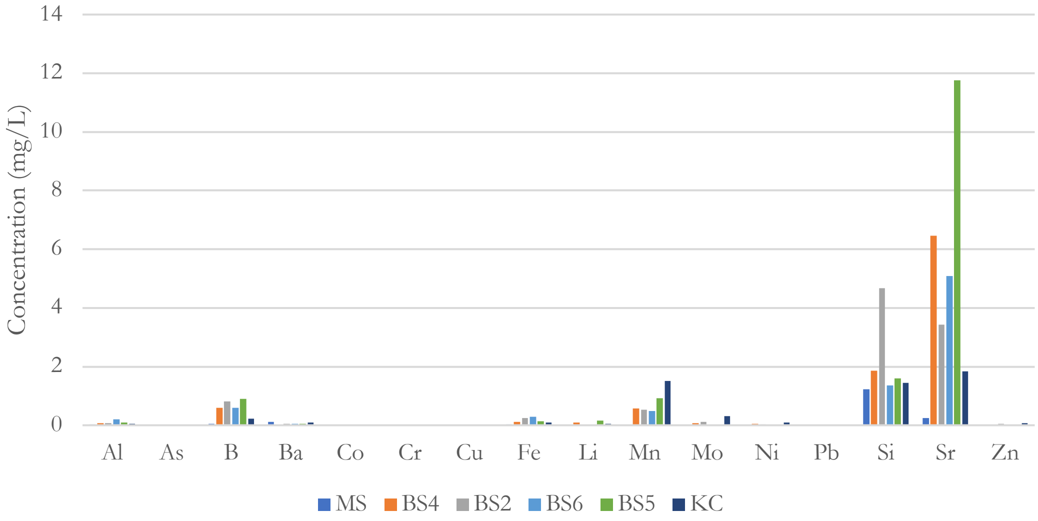


FIGURE 41 – MINOR ELEMENTAL COMPOSITION OF ELEMENTS DETECTED IN FLUIDS FROM SF2 EXPERIMENTS (N=1).

SF2

SAMPLE	DEPTH (M)	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
MS	0	0.03	LOD	0.06	0.12	30.6	0	LOD	0	0.03	27.0	0	4.37	0.01	LOD	2.18	0	LOD	13.4	1.22	0.25	0.01
BS4	2016	0.07	LOD	0.59	0.01	829	0.02	LOD	0	0.12	32.9	0.1	60.2	0.57	0.08	125	0.06	LOD	276	1.87	6.47	0.01
BS2	2348	0.08	0.01	0.82	0.06	594	0.01	LOD	0.01	0.24	13.8	0.01	62.8	0.52	0.11	56.5	0.03	LOD	191	4.68	3.43	0.04
BS3	2349	33.6	0.07	0.65	0.12	138	0.9	0.02	1.51	393	31.5	0.07	39.2	3.77	LOD	122	2.8	0.16	252	18.3	2.67	0.58
BS6	2500	0.21	LOD	0.59	0.04	520	0.01	LOD	0.01	0.29	24.9	0.01	55.5	0.49	LOD	73.7	0.02	0	185	1.36	5.09	0.02
BS5	2594	0.09	LOD	0.91	0.05	750	0.01	LOD	0	0.14	36.8	0.15	67.3	0.93	LOD	171	0.01	0	285	1.59	11.8	0.01
KC	3901	0.05	LOD	0.23	0.09	442	0.02	LOD	0.01	0.09	55.5	0.05	74.0	1.5	0.31	48.4	0.09	LOD	172	1.45	1.83	0.08

TABLE 33 -MEASURED CONCENTRATION OF ELEMENTS IN SF2 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH A RANGE OF SHALE SAMPLES. ALL VALUES IN MG/L.

12.2.2.4 SF3 EXPERIMENTAL RESULTS

SF3 experiments, conducted at ambient pressure and temperature provided context to both SF1 and SF2 experimental results. Five shale samples were reacted with fracturing fluids consisting of distilled water and sampled after both 4 and 7 weeks. Analytical results from these experiments are displayed on p161. There was not enough sample remaining to conduct any further experiments with sample BS2 after SF1 & SF2 were complete. Similarly to SF1 and SF2 the predominant dissolved constituents in fluids sampled from SF3 experiments are Ca, K, Mg, Na, S and Si. Sr is more abundant than was measured in SF1 fluids, comparable with concentrations measured in SF2 experiments. After 7 weeks the SF3-MS experiment showed much greater Ca, Na and Sr concentrations than have been observed through any batch reaction at reservoir pressure and temperature. The Sr concentration of 5.18 ppm (SF3-MS) after 7 weeks at ambient conditions is the highest measured in all fluids sampled from experiments SF1 to SF3 (using no chemical additives). SF3 experiments with BS4 and MS samples elicited higher concentrations of Sr in comparison to other shales after both 4 weeks and 7 weeks duration.

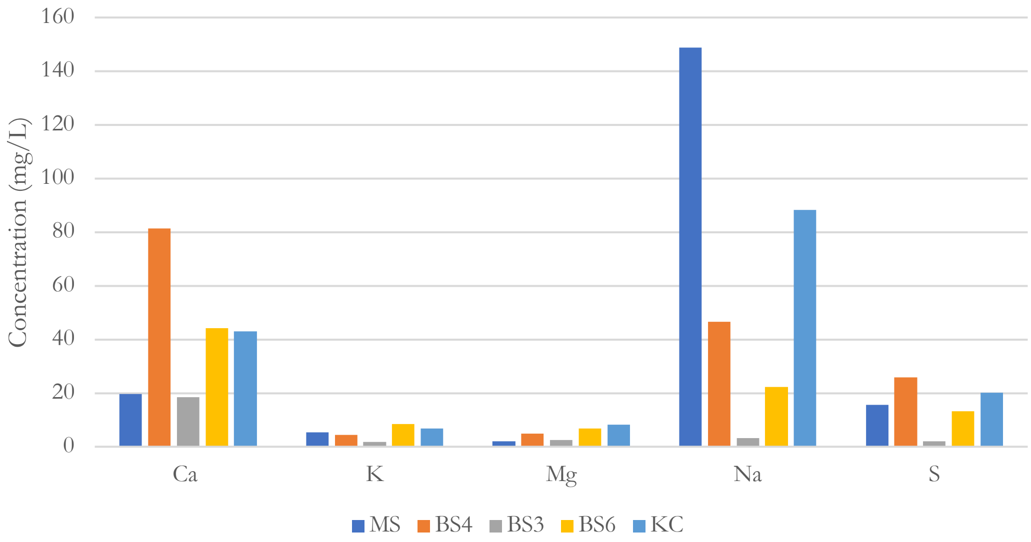


FIGURE 42 – MAJOR ELEMENTAL COMPOSITION OF FLUIDS SAMPLED FROM SF3(28) EXPERIMENTS (N=1).

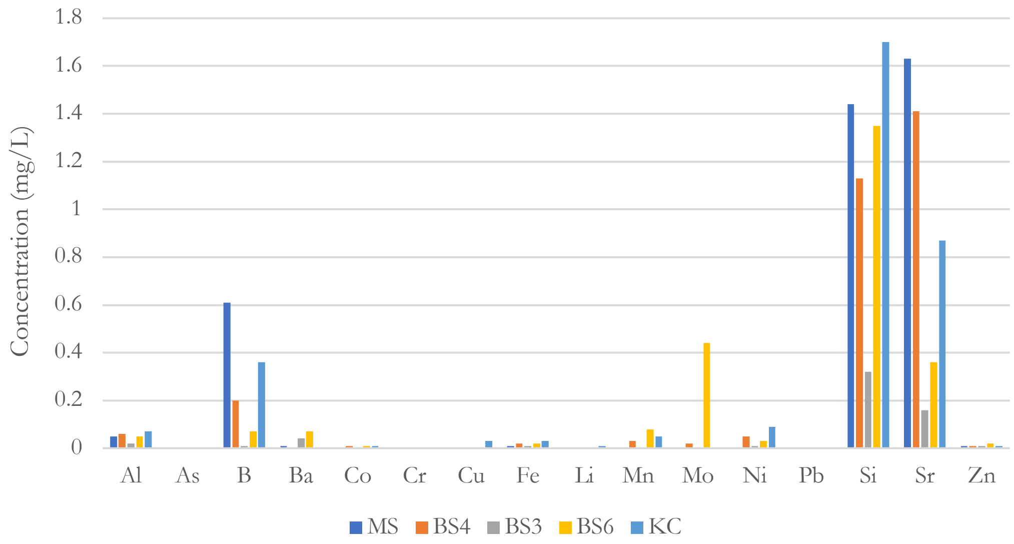


FIGURE 43 – MINOR ELEMENTAL COMPOSITION OF FLUIDS SAMPLED FROM SF3 EXPERIMENTS (N=1).

SF3 - 28 DAYS

DEPTH (M)	SAMPLE	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
0	MS	0.05	0.00	0.61	0.01	19.7	0.00	0.00	0.00	0.01	5.34	0.00	1.92	0.00	LOD	148.7	0.00	0.00	15.7	1.44	1.63	0.01
2016	BS4	0.06	0.00	0.20	0.00	81.3	0.01	0.00	0.00	0.02	4.36	0.00	4.99	0.03	0.02	46.6	0.05	0.00	25.8	1.13	1.41	0.01
2349	BS3	0.02	LOD	0.01	0.04	18.6	0.00	0.00	0.00	0.01	1.89	0.00	2.55	0.00	LOD	3.15	0.01	0.00	2.14	0.32	0.16	0.01
2500	BS6	0.05	LOD	0.07	0.07	44.2	0.01	0.00	0.00	0.02	8.37	0.00	6.91	0.08	0.44	22.2	0.03	0.00	13.2	1.35	0.36	0.02
3901	KC	0.07	LOD	0.36	0.00	43.1	0.01	0.00	0.03	0.03	6.85	0.01	8.26	0.05	LOD	88.3	0.09	0.00	20.1	1.70	0.87	0.01

TABLE 34 - MEASURED CONCENTRATION OF ELEMENTS IN SF3 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH A SELECTION OF SHALE SAMPLES, SAMPLED AFTER 28 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES. MS – MARCELLUS SHALE, BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

SF3 - 49 DAYS

DEPTH	SAMPLE	AL	AS	B	BA	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
OUTCROP	MS	0.16	LOD	0.83	0.03	71.9	0.01	0.00	0.00	0.03	8.65	0.01	7.70	0.04	LOD	174	0.00	0.00	20.5	2.14	5.18	0.01
2016	BS4	0.06	LOD	0.27	0.01	156	0.01	0.00	0.00	0.05	5.89	0.01	9.35	0.11	0.10	59.6	0.10	0.00	41.7	1.54	2.27	0.64
2349	BS3	0.05	LOD	0.06	0.10	54.5	0.00	0.00	0.00	0.03	4.31	0.00	8.11	0.03	LOD	8.00	0.02	0.00	10.8	0.70	0.44	0.02
2500	BS6	0.05	LOD	0.08	0.07	72.8	0.02	0.00	0.00	0.03	8.06	0.00	10.4	0.22	0.46	20.3	0.07	0.00	17.4	1.41	0.50	0.07
3901	KC	0.05	0.01	0.52	0.01	99.1	0.01	0.00	0.01	0.05	9.63	0.01	18.6	0.28	LOD	111	0.12	0.00	37.3	2.40	1.67	0.01

TABLE 35 - MEASURED CONCENTRATION OF ELEMENTS IN SF3 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH A SELECTION OF SHALE SAMPLES, SAMPLED AFTER 49 DAYS.. VALUES IN MG/L, N=1 FOR ALL SAMPLES MS – MARCELLUS SHALE, BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

12.2.2.5 SF4 EXPERIMENTAL RESULTS

The SF4 experiments were conducted in sealed Quickfit glassware with 0.125% HCl additive to distilled water base fluid. This minor chemical change in the reaction fluid was enough to produce distinct results in the elemental concentrations of fluids sampled. Notable concentrations of B (0.70-1.34 ppm), Ba (0.03-1.96 ppm), Al (0.04-36.3 ppm), Cu (0.06 ppm), Li (0.04-0.12 ppm), Pb (0.01-0.34 ppm), and Zn (0.15-0.21 ppm) are present in the sample fluids from SF4 reactions, even after just 4 weeks, where in SF1, SF2 and SF3 these were negligible or measured at significantly lower concentrations.

The secondary sampling of these experiments after 56, 157, and 189 days allowed a temporal evaluation of the interactions between rock and fluid under these conditions occurring after the 28-day duration of other experiments. After a sample of fluid was taken the experiment was refilled with fresh 0.125% HCl to maintain the water:rock ratio. This meant that while concentrations would be slightly diluted immediately following subsampling, overall there would be slightly more fresh HCl available for reaction following this.

As 100 days passed between the first phase of sampling (28 and 56 days) and the second (157 and 189 days) the samples were analysed on the ICP-OES separately. A number of analytes were not measured for in all four temporal samples – including Si which was only measured in the 28 and 56 day samples, and As, Cd, Ti and V which were only measured in the 157 and 189 samples. Incomplete temporal data for these elements was limiting to the evaluation of their behaviour with time in SF4 experiments.

Out of all three samples reacted with 0.125% HCl fluids, concentrations of all elements except Si and Ba were detected in their highest concentrations in SF4-KC fluids. Si and Ba were higher in SF4-MS fluids, both starting more concentrated and depleting over time. This suggests that following sampling after 28 days (and after 56 days for Ba) the addition of fresh 0.125% HCl fluid did not release any additional Si or Ba from the MS matrix.

Li, Mg, Mn, B, S, Ni and Pb all show a similar trend in concentrations – decreasing between 28 and 56 days, before increasing above the initial concentration by 157 days, before increasing again (typically at a similar rate) by 189 days of reaction. A greater proportion of these elements are therefore released with time, despite a dip in their concentration measured after 8 weeks (Figure 44).

Experiments conducted with KC exhibit a more marked increase in concentration with time than the batch reactions conducted with BS and MS rock samples.

The concentration trend with time of Ca and Na are similar in each experiment, however the concentrations remain much more steady in SF4-BS and SF4-MS fluids than with SF4-KC which is much more variable. The concentration of Ca and Na in SF4-KC drop between 4 weeks and 8 weeks by around half, however in SF4-BS and SF4-MS the concentration remains more constant fluctuating by only ~20%.

SF4-MS has a steady concentration of between 0.3 and 0.4 mg/L Pb, however the SF4-KC fluid contains no Pb until 157 days where the concentrations are 0.7-0.8 mg/L. This implies, not all elements are certain to be released within the first 4 or 8 weeks of reaction, and that concentrations do have the potential to change, albeit by less than 1 mg/L, up to 22 weeks after initiation.

Sr decreases with time in SF4-BS and -MS fluids, suggesting that the initial concentrations detected after 4 weeks may be scavenged from solution. Ca and Ba concentrations decrease with time in all SF4 fluid samples. Ca and Ba are often associated with Sr, particularly in Ca-feldspars such as anorthite, which may dissolve into solution between 0 and 28 days, however Ca and Sr are possibly withdrawn from solution with time as secondary minerals form incorporating heavier alkali elements (Salminen *et al.*, 2005).

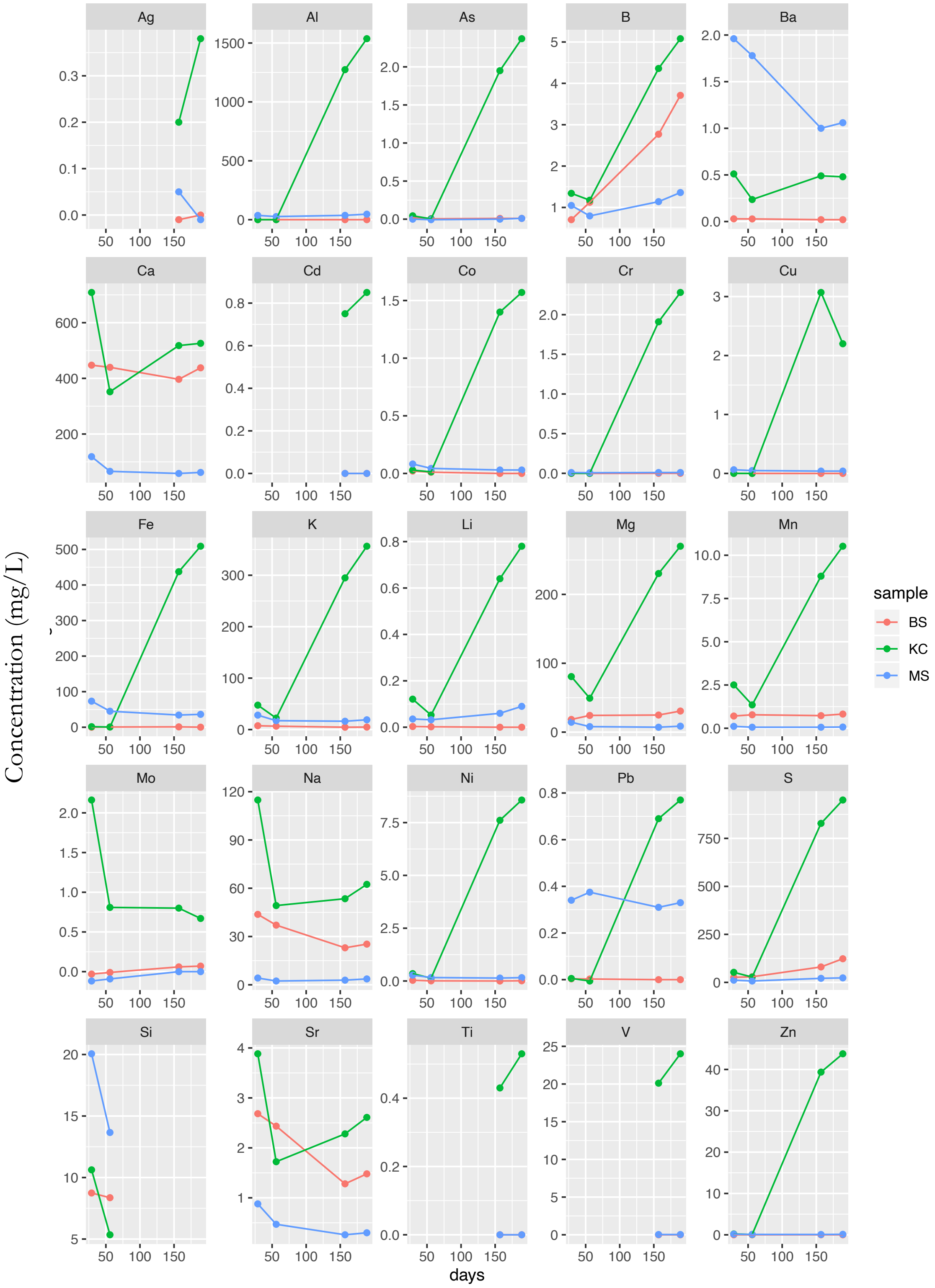


FIGURE 44 – COMPARISON OF ELEMENTAL RELEASE (CONCENTRATION IN MG/L) WITH TIME (28, 56, 157 AND 189 DAYS) IN SF4 EXPERIMENTS.

SF4-KC

DAYS	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	TI	V	ZN
29		0.11	0.04	1.34	0.51		9	0.03	0.00	0.00	1.58	47.5	0.12	80.7	2.51	2.16	115	0.35	0.01	52.3	10.6	3.88			0.21
56		0.17	0.00	1.17	0.24		352	0.01	0.00	0.00	0.62	22.3	0.05	49.2	1.35	0.81	49.2	0.13		27.6	5.35	1.72			0.09
157	0.20	1270	1.95	4.36	0.49	0.75	518	1.40	1.91	3.07	437	295	0.64	230	8.79	0.80	53.5	7.61	0.69	828	NA	2.28	0.43	20.1	39.4
189	0.38	1540	2.37	5.08	0.48	0.85	526	1.57	2.28	2.20	509	356	0.78	270	10.5	0.67	62.4	8.57	0.77	950	NA	2.61	0.53	24.0	43.8

TABLE 36 - MEASURED CONCENTRATION OF ELEMENTS IN SF4 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH KC SHALE, SAMPLED AFTER 29, 56, 157 AND 189 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

SF4-BS

DAYS	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	TI	V	ZN
29		0.04	0.02	0.70	0.03		447	0.02	0.00	0.00	0.06	7.46	0.00	18.4	0.71		43.77	0.03	0.00	26.3	8.74	2.68			0.21
56		0.04	0.00	1.12	0.03		440	0.01	0.00	0.00	0.70	6.57	0.00	24.3	0.78		37.08	0.01	0.00	29.2	8.36	2.44			0.09
157	LOD	0.02	0.01	2.77	0.02	0.00	397	0.00	0.00	0.00	1.04	4.54	0.00	24.8	0.73	0.06	23.00	0.00	0.00	80.3		1.28	0.43	20.1	39.4
189	0.00	0.04	0.01	3.71	0.02	0.00	438	0.00	0.00	0.00	0.20	4.82	0.00	30.6	0.82	0.07	25.28	0.01	0.00	123		1.48	0.53	24.0	43.8

TABLE 37 - MEASURED CONCENTRATION OF ELEMENTS IN SF4 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS SHALE, SAMPLED AFTER 29, 56, 157 AND 189 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES BS = BOWLAND SHALE, (SEE SECTION 10.1).

SF4-MS

DAYS	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	TI	V	ZN
29		36.3	0.00	1.05	1.96		119	0.08	0.01	0.06	73.4	28.1	0.04	14.4	0.11	LOD	4.22	0.28	0.34	11.4	20.1	0.88			0.15
56		26.4	LOD	0.79	1.78		65.9	0.04	0.01	0.05	45.1	17.3	0.03	8.02	0.06	LOD	2.36	0.16	0.37	7.15	13.7	0.47			0.09
157	0.05	36.8	0.00	1.14	1.00	0.00	58.4	0.03	0.01	0.04	34.3	16.2	0.06	7.13	0.06	0.00	2.89	0.14	0.31	21.0	NA	0.26	0.00	0.03	0.08
189	LOD	46.8	0.01	1.36	1.06	0.00	62.0	0.03	0.01	0.04	36.3	19.0	0.09	8.66	0.07	0.00	3.65	0.16	0.33	23.4	NA	0.30	0.00	0.03	0.12

TABLE 38 - MEASURED CONCENTRATION OF ELEMENTS IN SF4 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH MS SHALE, SAMPLED AFTER 29, 56, 157 AND 189 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES MS – MARCELLUS SHALE, (SEE SECTION 10.1).

12.2.2.6 SF5 EXPERIMENTAL RESULTS

SF5 experiments were conducted with 10% HCl additive and reflect the highest permitted concentration of chemical additive for hydraulic fracturing operations in the UK. These experiments were conducted with BS and KC core samples (28, 160 and 161 days duration), and MS core and BS outcrop shale samples (31 and 40 days duration). Results are tabulated on p167.

Between the 28 and 160 day sample times (132 day period) there is a more marked increase in element concentration than between 160 and 161 days (1 day period), indicating that reaction time may be proportional to elemental concentration. It also provides useful insight into the difference between short- and long-term reactions taking place during interaction 10% HCl fluids.

In all SF5 experiments the Ba concentration reduces with time suggesting initial release and then scavenging of Ba. Concentrations of heavy metals (Co, Cu, Cr, Ni, Pb, V, Ti, Zn) increase with time and are measured at their peak concentration in fluids sampled from SF5 experiments. This suggests heavy metal release may be greatest when greater acidized fluids are utilised during fracturing.

Each fluid sample is referred to by sample code in capital letters and experiment duration in days in brackets. Concentrations of Al range from 563 ppm in KC(28) to 2310 ppm in KC(161). As is below 1 ppm in all fluids, ranging from 0.05 ppm in BSU(30) to 0.95 ppm in KC(160). B ranges from 2.32 ppm in KC(28) to 7.02 ppm in KC(161). Ba is greatest in MSc(40) at 15.0 ppm and lowest in BSc(28) at 1.72 ppm. Highest concentrations of Ca are observed in fluids sampled from BSU and lowest from KC. Fe ranges from 131 ppm to 359 ppm, and is correlated with S (0.78) at a ratio of around 2Fe:1S. K ranges from 187 ppm to 464 ppm with the second lowest and highest concentrations measured in KC(28/161). Li is present in most fluids below 1ppm, except in BSL(40) at 1.03 ppm. Mg is notably higher in fluids sampled from BSU (31/40) at 1210 ppm-1350 ppm. In all other samples Mg ranges from 91.7 ppm to 348 ppm. Mn is greatest in fluids reacted with BSU and BSL at 23.0-94.9 ppm, and between 1.98 and 5.87 ppm in all other fluids. Mo is greatest in MSc fluids at 5.15-5.20 ppm, and ranges between 0.03 ppm and 1.48 ppm in other samples. Na is lower in SF5 experiments than in comparable SF4 experiments (32.6-94.8 ppm). Ni values vary widely across fluids sampled from all SF5 experiments and with no discernible trend (0.86-6.67 ppm). Pb varies in correlation with Na concentrations (0.78) from 0.22 ppm-2.40 ppm. S ranges from 15.7 ppm to 175 ppm with MSc samples resulting in two of the top three concentrations measured. Sr varies between 2.72 ppm and 18.8 ppm, with the four largest concentrations measured in fluids reacted with BSU and BSL, and the two lowest concentrations measured in BSc.

SF5-BSU fluids are depleted in most elements compared to the SF4-BSL fluids. The difference between concentrations highlights the importance of working with representative shale samples when conducting batch experiments to replicate subsurface conditions.

The SF5-MSc fluid was enriched in As, Cd, Mo, Ni, P, V and Zn compared to those reacted with surface samples of the Bowland Shale (SF5-BSU & -BSL). Core samples that have not been surface weathered may be more reactive, however the differing composition of the Marcellus Shale and the Bowland Shale may mean that metals are not released into solution unanimously between shale formations.

For fluids SF5-BSU, -BSL, and -MSc between 28 and 40 days sampling time most elemental concentrations exhibit the same trend except from Ba, Ca and Cr (Figure 45). Ca and Cr decrease in SF5-BSU and increase very slightly in SF5-BSL.

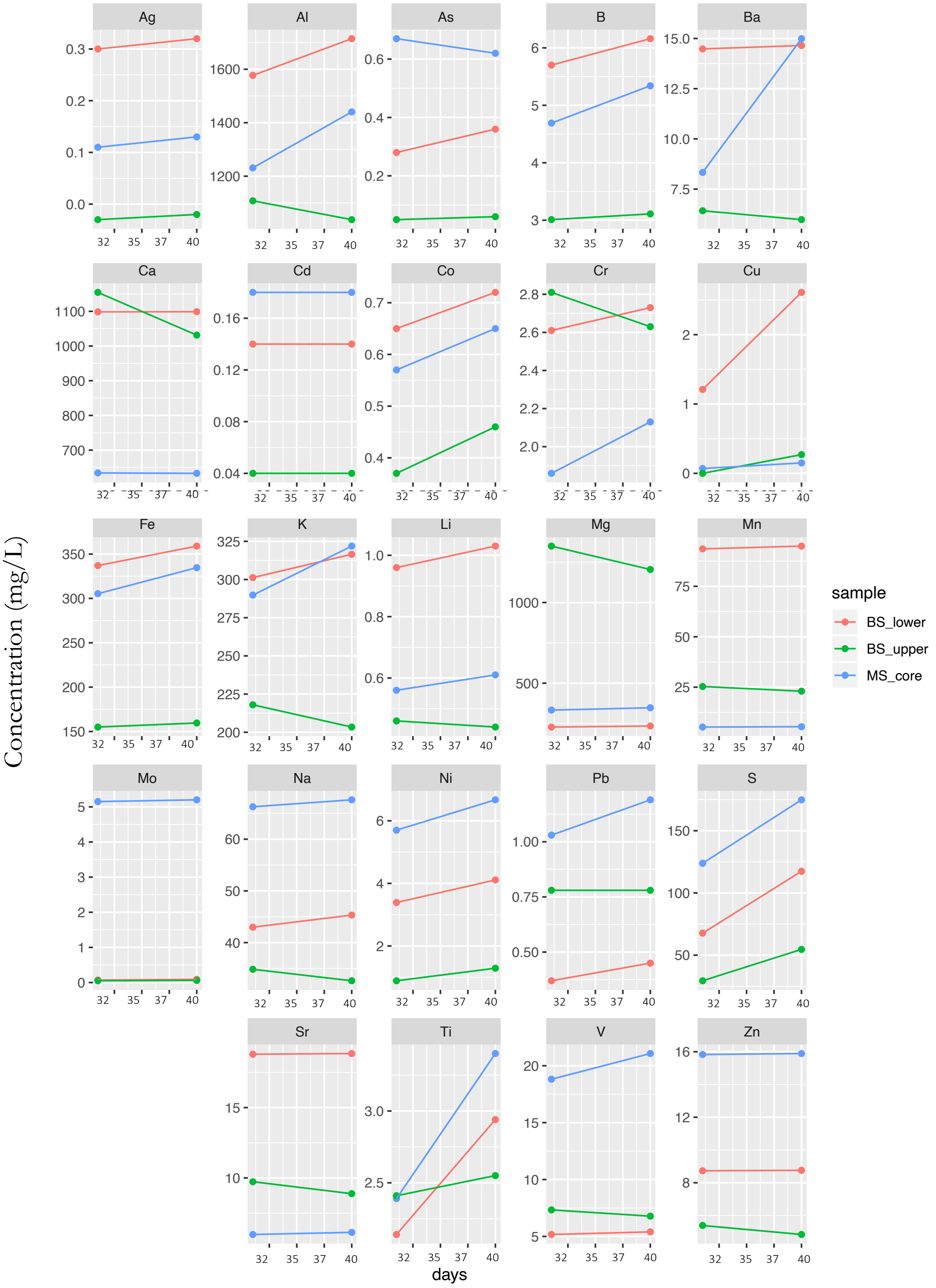


FIGURE 45 – COMPARISON OF CHANGE IN ELEMENTAL CONCENTRATION (MG/L) N SF5 EXPERIMENTS WITH OUTCROP SAMPLES OF THE BOWLAND SHALE AND A CORE SAMPLE OF THE MARCELLUS SHALE.

SF5 – BS CORE / KC CORE

28 DAYS

	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SI	SR	ZN
BS_CORE		682	0.34	3.58	1.72		1250	0.59	1.18	0.00	192	187	0.40	122	2.69	0.11	94.9	1.27	2.41	32.8	53.4	5.65	0.89
KC_CORE		563	0.32	2.33	3.70		311	0.39	1.17	0.06	131	191	0.39	117	2.45	0.53	34.4	2.00	0.22	15.7	16.6	2.86	14.2

TABLE 39 - MEASURED CONCENTRATION OF ELEMENTS IN SF5 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS AND KC CORE SAMPLES, AFTER 28 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

160 DAYS

	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SR	TI	V	ZN
BS_CORE	LOD	879	0.10	3.92	2.56	0.03	515	0.29	1.29	0.00	166	196	0.45	91.7	1.98	0.03	57.6	0.86	1.28	75.8	2.72	2.54	2.76	0.59
KC_CORE	0.18	2250	0.95	7.02	8.31	0.43	421	0.85	3.16	0.53	330	439	0.94	251	5.84	1.48	65.8	5.17	0.54	150	7.52	10.2	30.0	25.9

TABLE 40 - MEASURED CONCENTRATION OF ELEMENTS IN SF5 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS AND KC CORE SAMPLES, AFTER 160 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

161 DAYS

	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SR	TI	V	ZN
BS_CORE	LOD	881	0.07	4.01	2.61	0.03	526	0.29	1.28	0.00	168	197	0.46	92.3	1.98	0.03	57.7	0.88	1.30	79.7	2.77	2.58	2.76	0.56
KC_CORE	0.11	2310	0.87	6.69	9.72	0.46	457	0.80	3.31	0.15	319	464	0.99	265	5.87	1.39	68.3	4.31	0.49	102	7.93	10.4	32.0	28.0

TABLE 41 - MEASURED CONCENTRATION OF ELEMENTS IN SF5 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS AND KC CORE SAMPLES, AFTER 161 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES. BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

SF5 - MS CORE / BS-UPPER & -LOWER OUTCROP

30 DAYS

	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SR	TI	V	ZN
MS_CORE	0.11	1230	0.67	4.69	8.33	0.18	634	0.57	1.86	0.07	305	290	0.56	333	5.24	5.15	66.3	5.70	1.03	124	5.98	2.39	18.8	15.8
BSL_OUTCROP	0.30	1580	0.28	5.70	14.48	0.14	1100	0.65	2.61	1.21	337	301	0.96	228	93.6	0.07	43.0	3.39	0.37	67.7	18.8	2.14	5.17	8.73
BSU_OUTCROP	LOD	1110	0.05	3.01	6.42	0.04	1160	0.37	2.81	0.00	155	218	0.46	1350	25.3	0.05	34.8	0.89	0.78	29.4	9.73	2.41	7.33	5.39

TABLE 42 - MEASURED CONCENTRATION OF ELEMENTS IN SF5 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS AND MS OUTCROP SAMPLES, AFTER 30 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES MS – MARCELLUS SHALE, BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

40 DAYS

	AG	AL	AS	B	BA	CD	CA	CO	CR	CU	FE	K	LI	MG	MN	MO	NA	NI	PB	S	SR	TI	V	ZN
MS_CORE	0.13	1440	0.62	5.34	15.0	0.18	633	0.65	2.13	0.15	335	322	0.61	348	5.41	5.20	67.6	6.67	1.19	175	6.13	3.40	21.1	15.9
BSL_OUTCROP	0.32	1710	0.36	6.16	14.7	0.14	1100	0.72	2.73	2.61	359	317	1.03	235	94.9	0.09	45.3	4.11	0.45	117.4	18.8	2.94	5.40	8.76
BSU_OUTCROP		1040	0.06	3.11	5.98	0.04	1030	0.46	2.63	0.27	160	203	0.44	1200	23.0	0.06	32.6	1.29	0.78	54.6	8.88	2.55	6.78	4.84

TABLE 43 - MEASURED CONCENTRATION OF ELEMENTS IN SF5 HYDROGEOCHEMICAL BATCH REACTION FLUIDS FROM INTERACTION WITH BS AND MS OUTCROP SAMPLES, AFTER 40 DAYS. VALUES IN MG/L, N=1 FOR ALL SAMPLES MS – MARCELLUS SHALE, BS = BOWLAND SHALE, KC = KIMMERIDGE SHALE (SEE SECTION 10.1).

Between 28 and 160 days much greater concentration differences were observed than between 28 and 40 days. SF5-KC and SF5-BS were both core samples of UK shales, however reacted quite differently to the addition of 10% HCl solution. Ag, Cd, Ti and V were only measured in the 160 days samples to temporal comparison cannot be made for these elements. However, concentrations of Ti and V were highest in SF5-KC fluids after 160 days than any others at 10.4 mg/L (Ti) and 31.6 mg/L (V).

Similar trends between SF5-KC and -BS are present for the release of all elements except As, Ca, Co, Fe, Pb, Sr and Na. These elements show conversely increasing or decreasing trends depending on the shale sample – with BS typically exhibiting negative concentration trends with time, and KC positive (Figure 46).

Samples collected 1 day apart between 160 and 161 days were taken to determine the change in elemental concentration over a short time period after prolonged shale–fluid exposure had already taken place. This scenario mimics a short term refracturing, where fresh fluids are injected to refracture a well which has already been in long term contact with injected fluids and fractured shale. This short term temporal sample was only collected from the SF5-KC and SF5-BS experiments.

Trends were much less severe than between longer term temporal samples, see Figure 46 (132 day sampling period) and Figure 47 (1 day sampling period). Typically SF5-KC contained higher concentrations of all elements except Pb.

Increasing Ca concentrations and decreasing S in SF5-KC fluids were the most notable change taking place between 160 and 161 days – potentially signalling the short term dissolution of carbonate minerals by fresh acidic fluids, and the formation of sulphate salts removing S from solution. Sampling and the addition of fresh HCl fluids expose the rock:water batch solution to increased free oxygen which can encourage sulphate salt or scale formation.

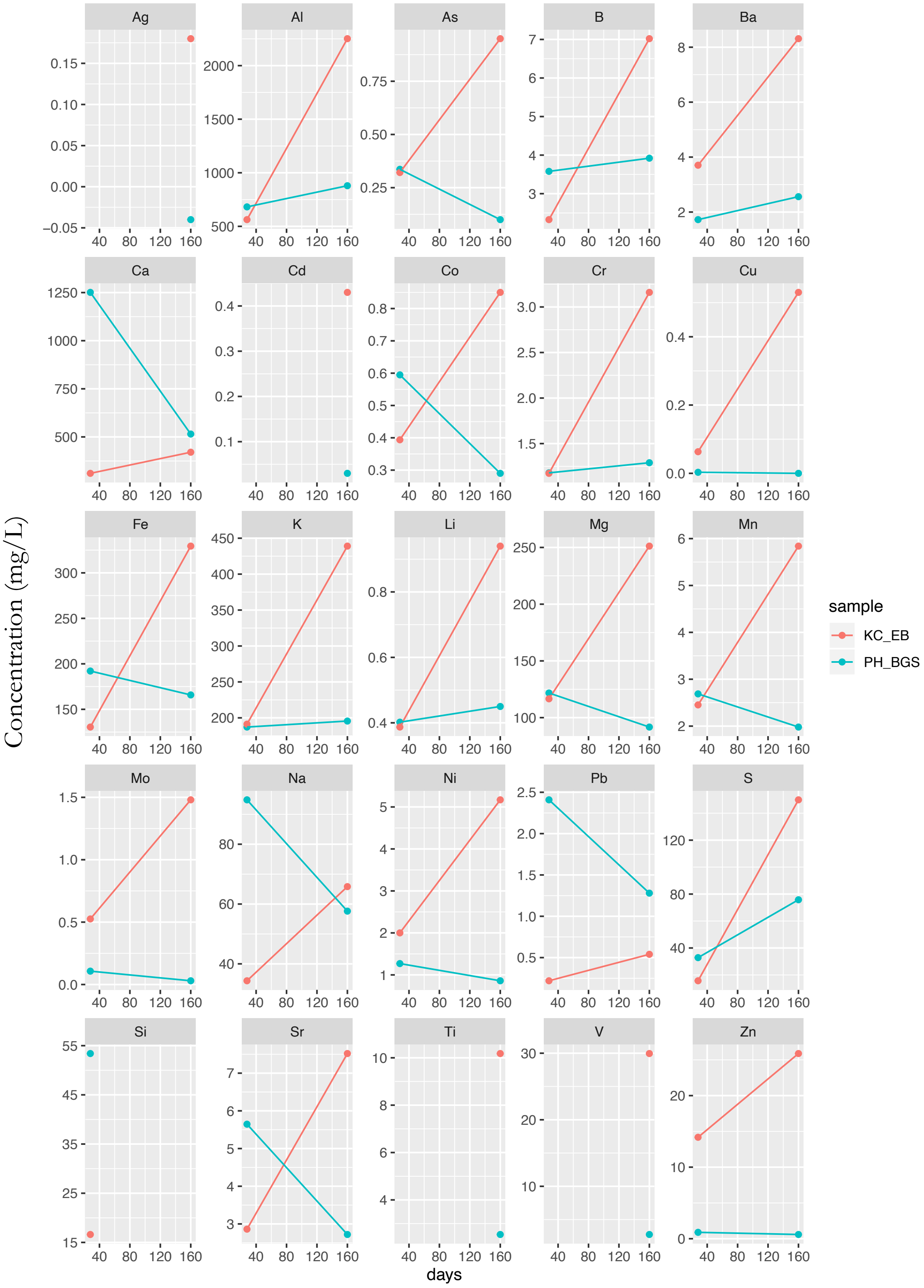


FIGURE 46 – COMPARISON OF THE ELEMENTAL CONCENTRATION IN FLUIDS SAMPLED FROM SF5 EXPERIMENTS AFTER 28 AND 160 DAYS (PH_BGS - BOWLAND SHALE AND KC_EB - KIMMERIDGE CLAY SAMPLES).

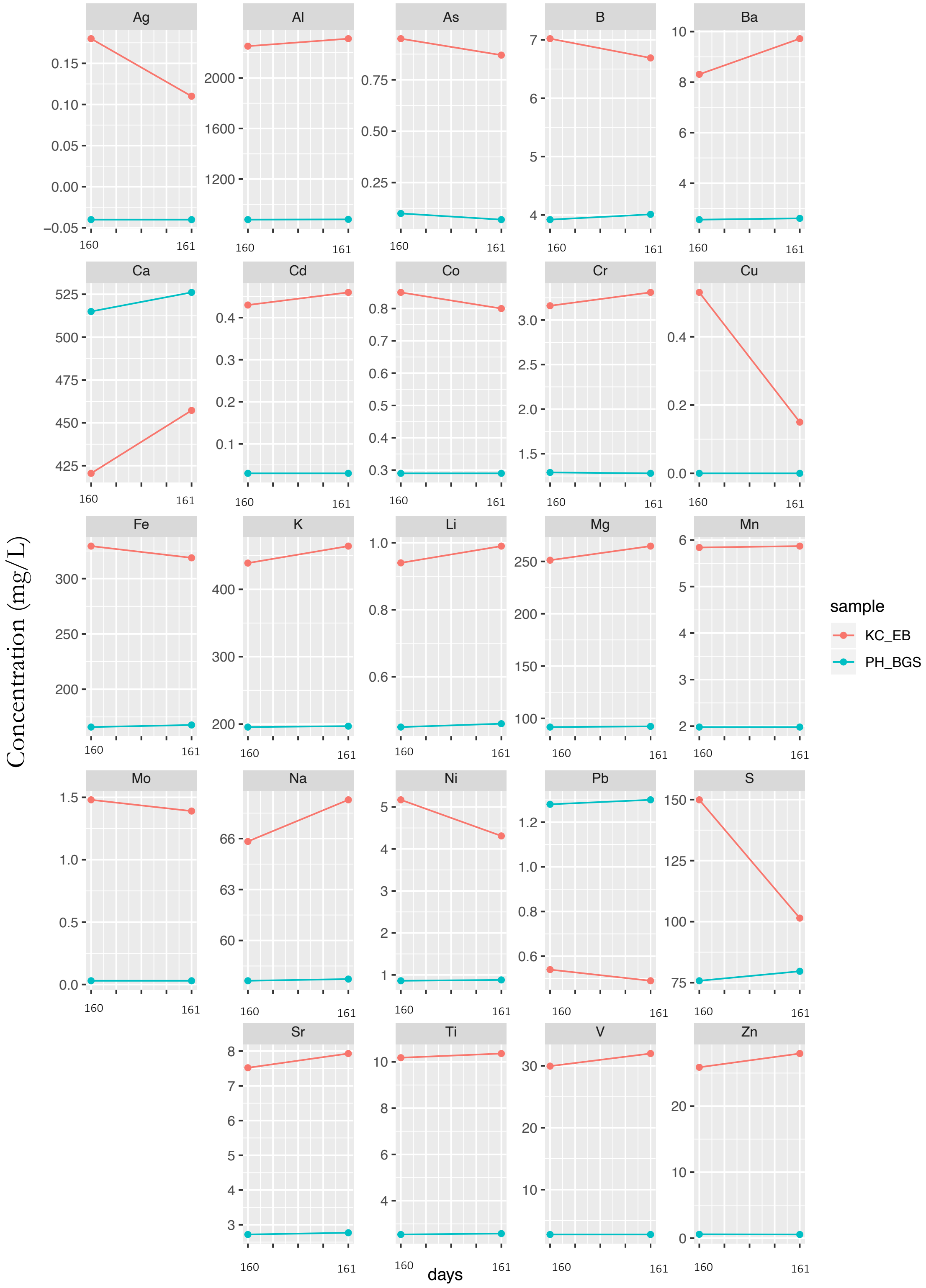
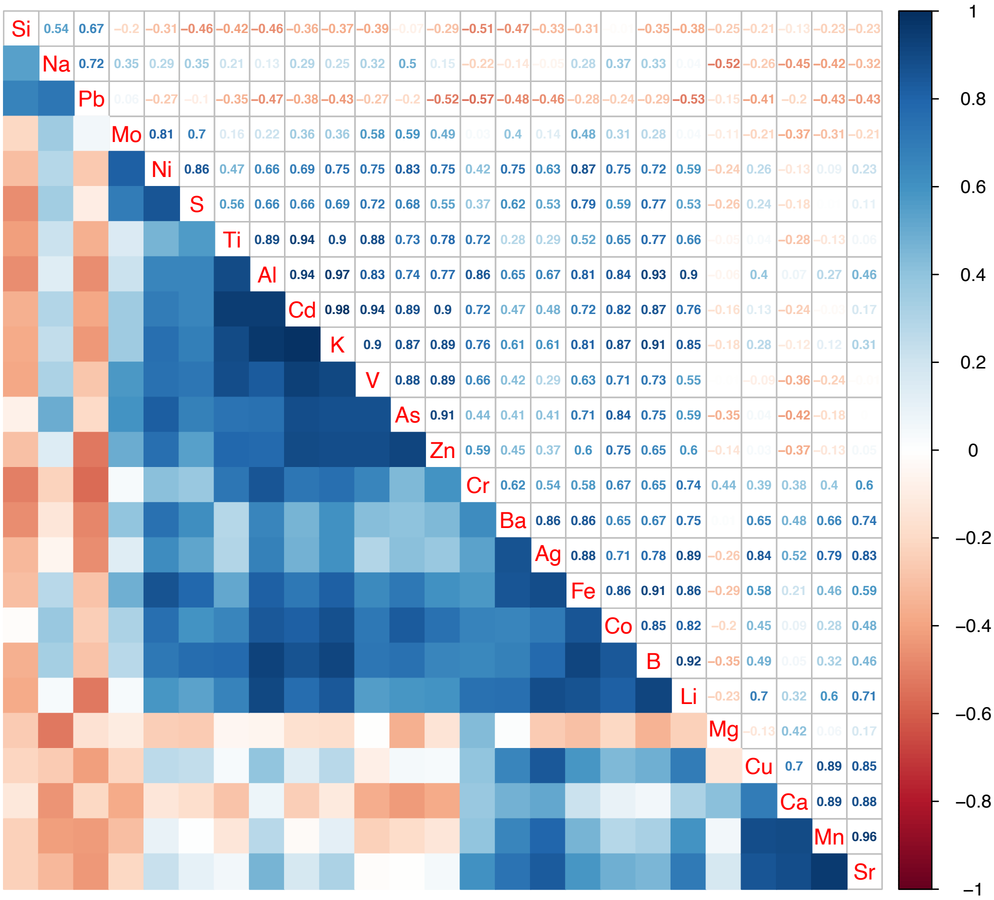


FIGURE 47 – COMPARISON OF THE ELEMENTAL CONCENTRATION IN FLUIDS SAMPLED FROM SF5 EXPERIMENTS AFTER 160 AND 161 DAYS (PH_BGS - BOWLAND SHALE AND KC_EB - KIMMERIDGE CLAY SAMPLES).



Si	0.54	0.67	−0.2	−0.31	−0.46	−0.42	−0.46	−0.36	−0.37	−0.39	−0.07	−0.29	−0.51	−0.47	−0.33	−0.31	−0.01	−0.35	−0.38	−0.25	−0.21	−0.13	−0.23	−0.23
	Na	0.72	0.35	0.29	0.35	0.21	0.13	0.29	0.25	0.32	0.5	0.15	−0.22	−0.14	−0.05	0.28	0.37	0.33	0.04	−0.52	−0.26	−0.45	−0.42	−0.32
		Pb	0.06	−0.27	−0.1	−0.35	−0.47	−0.38	−0.43	−0.27	−0.2	−0.52	−0.57	−0.48	−0.46	−0.28	−0.24	−0.29	−0.53	−0.15	−0.41	−0.2	−0.43	−0.43
			Mo	0.81	0.7	0.16	0.22	0.36	0.36	0.58	0.59	0.49	0.03	0.4	0.14	0.48	0.31	0.28	0.04	−0.11	−0.21	−0.37	−0.31	−0.21
				Ni	0.86	0.47	0.66	0.69	0.75	0.75	0.83	0.75	0.42	0.75	0.63	0.87	0.75	0.72	0.59	−0.24	0.26	−0.13	0.09	0.23
					S	0.56	0.66	0.66	0.69	0.72	0.68	0.55	0.37	0.62	0.53	0.79	0.59	0.77	0.53	−0.26	0.24	−0.18	0.01	0.11
						Ti	0.89	0.94	0.9	0.88	0.73	0.78	0.72	0.28	0.29	0.52	0.65	0.77	0.66	−0.05	0.04	−0.28	−0.13	0.06
							Al	0.94	0.97	0.83	0.74	0.77	0.86	0.65	0.67	0.81	0.84	0.93	0.9	−0.06	0.4	0.07	0.27	0.46
								Cd	0.98	0.94	0.89	0.9	0.72	0.47	0.48	0.72	0.82	0.87	0.76	−0.16	0.13	−0.24	−0.03	0.17
									K	0.9	0.87	0.89	0.76	0.61	0.61	0.81	0.87	0.91	0.85	−0.18	0.28	−0.12	0.12	0.31
										V	0.88	0.89	0.66	0.42	0.29	0.63	0.71	0.73	0.55	−0.01	−0.09	−0.36	−0.24	−0.01
											As	0.91	0.44	0.41	0.41	0.71	0.84	0.75	0.59	−0.35	0.04	−0.42	−0.18	0
												Zn	0.59	0.45	0.37	0.6	0.75	0.65	0.6	−0.14	0.03	−0.37	−0.13	0.05
													Cr	0.62	0.54	0.58	0.67	0.65	0.74	0.44	0.39	0.38	0.4	0.6
														Ba	0.86	0.86	0.65	0.67	0.75	0.01	0.65	0.48	0.66	0.74
															Ag	0.88	0.71	0.78	0.89	−0.26	0.84	0.52	0.79	0.83
																Fe	0.86	0.91	0.86	−0.29	0.58	0.21	0.46	0.59
																	Co	0.85	0.82	−0.2	0.45	0.09	0.28	0.48
																		B	0.92	−0.35	0.49	0.05	0.32	0.46
																			Li	−0.23	0.7	0.32	0.6	0.71
																				Mg	−0.13	0.42	0.06	0.17
																					Cu	0.7	0.89	0.85
																						Ca	0.89	0.88
																							Mn	0.96
																								Sr

FIGURE 48 - CORRELATION MATRIX SHOWING THE PEARSON PRODUCT MOMENT CORRELATION VALUES BETWEEN EACH VARIABLE IN THE SF5 DATA. BOTOTM-LEFT GIVES R VALUES AND TOP RIGHT SHOWS STRENGTH OF CORRELATION BY COLOUR SCHEME DISPLAYED BY TEMPERATURE BAR ON RIGHT. CORRELATION DATA HAS BEEN GROUPED BY HIERARCHICAL CLUSTERING TO ORDER ELEMENTS BY ASSOCIATION OF CORRELATION COEFFICIENT.

Summary of SF5 Results:

- Greatest concentrations of most elements measured in SF5 experiments – greater acid concentration as additive releases more constituents into solution.
- Fluids sampled from reaction with MS core have notably high Mo concentrations compared to other SF5 experiments
- Sr is highest in fluids reacted with BS outcrop samples (both upper and lower BS) – perhaps correlated with sample depth or source, but most likely related to carbonate content
- Fe and S show good correlation (0.79) across all SF5 experiments as with SF1 – 4 experiments; as do Mn, Sr and Ca; B and Li; and Al, Cd, K, As, V and Zn (Figure 48).
- Mg is highest in experiments with BS-U shale
- For most elements experiment duration increases concentration in sampled fluid (except Ba which decreases with time in all SF5 experiments)
- Heavy metals detected in greater concentrations in SF5 experiments than in SF1-4 experiments

12.2.3 ION CHROMATOGRAPHY

Analysis of the concentration of certain elements and compounds including Cl, Br, Fl, NO_2, NO_3, PO_3, SO_4, in sampled waters was not possible on the ICP-OES due to poor reproducibility and insufficient instrumental sensitivity. Particularly, in the case of Cl the diagnostic ICP-OES wavelength is easily absorbed by other molecules before detection. Therefore Ion Chromatography was used to determine concentrations of these components.

Fluid samples from experiments SF1, SF4, and SF5 were analysed on the IC and results are displayed on p178. NA denotes no observable peak during measurement which indicates that the element is below the limit of detection.

Fluoride is detected at 0.36 ppm in the SF1-MS experiment but 3.01 ppm in the SF5-KC experiment, suggesting Fl concentrations may be proportional to fluid acidity. Generally the Fl concentrations in SF1 fluids are the lowest (0.36-1.37 ppm), with the SF4 concentrations slightly higher (0.46-2.89 ppm) and the SF5 concentrations the highest of all (2.31-3.01). The WHO advised limit for Fl in drinking water is 1.5 mg/l (Liteplo *et al.*, 2002), expected surface water concentrations are between 0.01 ppm and 0.3 ppm, while seawater concentrations average 1.2-1.5 ppm. The largest Fluoride concentration measured was in the SF1 control experiment (4.18 ppm).

Chloride ranged from 0.66 ppm (SF1-MS) to 634 ppm (SF4-BS). No Cl was detected in both SF5 fluids, which is unexpected as these experiments were conducted with 10% HCl reaction fluid. Background concentrations of Cl between 0.60 and 0.73 ppm were detected in control SF1 experiments. Cl was distinctly variable depending on shale sample, with variances across orders of magnitude even between the SF1 experiments. SF1-MS experiments reflected background concentrations (0.66-0.73 ppm), SF1-KC experiments contained Cl at an orders of magnitude greater (3.12-3.73 ppm) and SF1-BS experiments yielded Cl concentrations at an order of magnitude greater still (28.5-41.4 ppm). In SF4 experiments the Cl concentrations differ according to shale sample, in the range of 543 ppm and 634 ppm, however the difference between experiments is less pronounced. The differentiation between Cl concentrations by shale sample is less marked in SF4 experiments.

Nitrite (NO_2^-) is present above 1ppm only in experiments SF4 and SF5 (those conducted with acidized reaction fluids). It is present in SF1-BS at a concentration of 0.417 ppm. In SF4 experiments it is concentrated between 5.50 and 8.52 ppm. In the two SF5 experiments samples it is measured in much greater concentrations of 94,100 ppm and 94,900 ppm, however the source of this anomaly is unknown.

Bromide was not detected in most samples, except for both SF1-BS (0.50-0.52 ppm) experiments and the SF1-KC control experiment (1.02 ppm). Br was analysed with the aim of comparing Br/Cl ratios between experimental and field wastewaters (Johnson and Graney, 2015; Vengosh *et al.*, 2015; Rosenblum *et al.*, 2017). Unfortunately, with such poor rates of detection this comparison is not possible.

Nitrate levels are mostly low, around or below 1 ppm for all fluids except those sampled from SF5 experiments (6.93-48.8 ppm). Nitrate is highest in SF1-MS and SF4-MS fluids and comparable between KC and BS for all except SF5 fluids.

Phosphate concentrations were detected in seven out of the seventeen samples measured on the IC, all below 10 ppm. 1.43 ppm was detected in the SF1-KC control experiment, all other concentrations measured were above this background level. No relationship is apparent between phosphate and shale sample, reaction fluid or reaction time.

Background levels of sulphate measured in control experiments were relatively low (0.40-0.79 ppm) compared to those measured in reacted fluids (13.3-242 ppm). Generally, MS experiments in both SF1 and SF4 showed less concentrated sulphate than KC and BS reactions under the same experimental conditions. SF5 experiments show the least sulphate concentrations of all experiments, despite containing the highest HCl acid concentration in reaction fluid. BS samples generated the highest concentrations of sulphate in SF1 experiments (171-222 ppm), while in SF4 experiments KC samples exhibited the highest sulphate concentrations (215-242 ppm). In SF5 experiments, KC samples led to concentrations of 27.7 ppm, while BS samples generated 13.3 ppm sulphate. All sulphate concentrations measured are within suggested drinking water secondary maximum contaminant levels (250 ppm) and are therefore unlikely to pose any environmental contamination threat, however the concentrations can be indicative of oxidation and reduction conditions within each experiment. Sulphide rich minerals such as pyrite (FeS_2) can release sulphate into solution, acidifying fluids and encouraging the release of heavy metals into solution. However, oxidation of organic matter with SO_4 can lead to release of bicarbonate and elevation of pH (Miao *et al.*, 2012).

IC RESULTS

EXPERIMENT CODE	DAYS	NOTES	FLUORIDE (PPM)	CHLORIDE (PPM)	NITRITE (PPM)	BROMIDE (PPM)	NITRATE (PPM)	PHOSPHATE (PPM)	SULPHATE (PPM)
SF1-BS	21	POWDER	0.69	28.5	NA	0.50	0.56	NA	171
SF1-BS	21	POWDER, SUB-SAMPLED 7 DAYS	0.73	41.4	0.42	0.52	NA	NA	222
SF1-BS	21	CONTROL	4.18	0.73	NA	NA	0.42	NA	0.40
SF1-MS	28	POWDER	0.36	0.66	NA	NA	NA	1.45	17.5
SF1-MS	28	CONTROL	NA	0.60	NA	NA	NA	NA	0.79
SF1-MS	28	POWDER, SUB-SAMPLED AFTER 24H	NA	0.73	NA	NA	1.21	NA	28.0
SF1-KC	28	CONTROL	NA	0.78	NA	1.02	NA	1.43	0.52
SF1-KC	28	POWDER	0.46	3.12	NA	NA	0.67	NA	57.1
SF1-KC	28	1 MM CHIPS	1.37	3.73	NA	NA	0.78	NA	159
SF4-BS	29	0.125% HCL	2.59	634	6.19	NA	0.55	1.57	194
SF4-BS	56	0.125% HCL	1.14	633	7.42	NA	0.59	NA	227
SF4-MS	29	0.125% HCL	1.05	543	7.87	NA	1.25	NA	61.7
SF4-MS	56	0.125% HCL	0.73	587	8.52	NA	1.17	8.79	59.5
SF4-KC	29	0.125% HCL	0.72	549	5.50	NA	0.42	2.64	215
SF4-KC	56	0.125% HCL	1.19	613	6.61	NA	0.53	NA	242
SF5-KC	28	10% HCL	3.01	NA	94900	NA	6.93	3.81	27.7
SF5-BS	28	10% HCL	2.31	NA	94100	NA	48.8	4.17	13.3

TABLE 44 - MEASURED ION CONCENTRATIONS OF A SELECT NUMBER OF UNACIDIFIED SAMPLES COLLECTED FROM HYDROGEOCHEMICAL BATCH REACTIONS.

13 DISCUSSION

13.1 SHALE GAS IN THE UK

Gas currently provides the UK with around 30% of its energy, offering a dependable source of heat, fuel and electricity to 80% of the UK's 25 million homes. In 2019, 40% of the UK's electricity was generated from gas (Department for Business Energy & Industrial Strategy, 2019). It is an important feedstock for many chemicals and petroleum by-products such as plastics, however it is also a finite 'fossil' fuel resource. Gas is a light hydrocarbon that is combusted, generating energy and releasing, water and carbon dioxide (CO_2) which is emitted to the atmosphere, increasing global atmospheric CO_2 levels.

Carbon dioxide is a key atmospheric gas, reflecting and absorbing infrared radiation from the sun to maintain the global surface temperature of the planet. However, since the advent of large scale hydrocarbon combustion in the industrial revolution, our anthropogenic contribution to the CO_2 concentrations in the atmosphere has been steadily increasing, from an average of 315 ppm in 1959, to 408 ppm in 2018 (Tans and Keeling, 2019).

The UK currently imports 46% of its natural gas from Europe, with 21% sourced from Norway and 36% from Russia (Department for Business Energy & Industrial Strategy, 2017). Gas produced indigenously does not require international transportation, and has an inherently lower carbon footprint than any imported gas. The carbon footprint of shale gas is comparable to that of conventional gas, lower than Liquified Natural Gas (LNG), and much lower than that of coal (MacKay and Stone, 2013). The UK's main source of indigenous fuel is currently North Sea oil and gas reserves, where resources are mature and technology is well developed, however recently there has been a movement to explore the UK's 'unconventional' hydrocarbon resources following the success of their exploitation in the USA. The dominant fuel in the USA has shifted in recent years away from coal, towards natural gas which became more economical to exploit due to advancements in technology and engineering.

Shale gas, or natural gas trapped in shale rocks, is produced using 'unconventional' methods. Although these methods are termed 'unconventional' they are used widely in hydrocarbon engineering in both conventional and unconventional settings to enhance the recovery.

Hydraulic fracturing is an unconventional exploitation method, where fluid is pumped underground to generate and enhance fractures in the brittle and tightly structured shale rock, allowing trapped gas to flow out. To generate the high pressures required to overcome the mechanical strength of the rocks and generate fractures, large volumes of water are required to carry out this process in relatively short periods of time.

13.2 FRACTURING FLUIDS

Fluids injected to create the pressure required to undertake fracturing, which can be freshwater, saltwater, recycled or reused fluids are mixed with a number of chemicals carefully chosen to streamline the fracturing process. These chemicals control fluid viscosity, inhibit the formation of bacteria or scale, control or adjust pH, and supress corrosion, among a number of other important tasks. A wide variety of chemicals are utilised in the USA to perform hydraulic fracturing, with specific combinations and chemical formulations protected from public knowledge by law as they can directly affect shale gas recovery rates. Guidelines introduced in 2015 by the US Environmental Protection Agency (USEPA) require companies operating on public land to disclose what chemicals they are using in the 'Fracfocus Database' (www.fracfocus.org). This has made it easier for the EPA to monitor the environmental impact of operations as they can focus their monitoring on chemicals disclosed for use.

In the UK, only a small number of chemical additives are permitted for use by the Environment Agency; a dilute hydrochloric acid (maximum 10% concentration) which acts as a solvent and as a control on pH, helping the fluid access the rock and gas in the subsurface, and acrylamide which reduces friction with the fluid to minimise the energy required to pump the fluid underground. This means that the chemistry of returned fluids in the UK is likely to be much less varied than is experienced in the USA where a much greater variety of chemicals are used in the process. The chemistry of waste returned from hydraulic fracturing is not only influenced by the chemistry of injected fluids. The chemistry of the rocks and any inherent subsurface fluids play in important role in the composition of the waste too.

These carefully curated chemical mixtures are then mixed with a proppant, which 'props' fractures open to allow gas to flow out. This often takes the form of a natural or manufactured pure silica sand with high sphericity.

The fluid and proppant mixture is then pumped down a drilled well, which extends vertically to the target formation before continuing horizontally along the shale laterally to maximise contact with the prospective horizon. The farthest section of the well from the surface is fractured, or 'perforated', first with each subsequent section following back towards the well head. Drilling can take 4 weeks, fracturing typically takes up to a month, and a well will produce waste water and gas for as long as the well is commercially viable before it is shut down and decommissioned – with the entire construction process lasting anywhere between 12 and 25 weeks (Department for Communities and Local Government, 2013).

13.3 WASTEWATER OR PRODUCED FLUIDS

The composition of wastewaters from hydraulic fracturing in the UK, are often predicted be similar to those generated in the USA. Comparison of the geochemical data for wastewaters available for both countries shows that some variability exists that could have implications for how this wastewater is managed at the surface (Table 45).

The maximum salinity of wastewaters is higher in the USA (345,000 mg/L) than in the UK (210,000 mg/L), however the current UK mean is higher (168,750 mg/L). Salinity is controlled initially by the composition of formation water and latterly by the dissolution of minerals. When wastewater is first produced, salinity is high, mimicking the composition of formation water within the shale. As time passes the salinity lowers the chemistry becomes more dominated by the fluid–rock reactions taking place between the injected fluids and the shale. Salinity is one of the most expensive components of wastewaters to treat, as above 50,000 mg/L only evaporative treatment is effective. The levels of salinity in both UK and USA wastewaters are many times that of seawater (35,000 mg/L) and are therefore energy intensive and costly to treat. The cost of treating saline wastewater is proportional to its salinity, and therefore the salinity of recovered wastes will impact the overall economic prosperity of any shale gas well (O'Donnell *et al.*, 2018).

Higher levels of arsenic are reported in wastewaters produced from UK operations than in the USA, with a mean of 0.97 mg/L versus a mean of 0.07 mg/L respectively. Arsenic is released into wastewaters following the oxidation of pyrite and dissolution of associated metal sulphides such as arsenopyrite, galena, and sphalerite. Arsenic water quality limits for the UK are currently set at 0.05 mg/L for fresh water, and therefore treatment by reverse osmosis, biochar, filtration, or distillation will be required to reduce arsenic levels before discharge. Arsenic is associated with organic matter, sulphides and clays in shales – and are released into solution during oxidative dissolution, which can be significantly accelerated by microbial action (Paikaray, 2012). Minimising the oxygen content of injected waters, and controlling microbial action could reduce the release of arsenic into solution. Arsenic, like many of the other heavy metal contaminants, is easily and commonly treatable by existing wastewater treatment processes (Barakat, 2011).

Barium is much lower in wastewaters from the UK (19.0 mg/L UK mean, versus 1076 mg/L USA mean). While the source of Ba in wastewaters was previously thought to be from mixing of saline formation waters containing Ba (Warner *et al.*, 2012; Capo *et al.*, 2014; Engle and Rowan, 2014), an experimental investigation into the source of Ba determined that between 55 and 75% of the Ba is partitioned to clay minerals and released over time as injected fluids and shales interact (Renock, Landis and Sharma, 2016). Ba and radium (Ra) are geochemically similar. If Ba/Ra waters are also enriched in sulphate insoluble barite scale ($BaSO_4$) is formed, sequestering both Ba and Ra from solution. Although beneficial to water quality, as dissolved Ba and Ra concentrations are reduced, the scale is radioactive and must be managed appropriately to ensure human exposure is minimised and release to the environment is prevented.

Wastewaters from the USA exhibit higher mean concentrations of heavy metals such as Cu, Co, Cr, Fe, Ni, and Zn. Heavy metals are released into solution through the dissolution of metal bearing sulphides on reaction with O_2 rich fluids, increasing metal concentrations and dissolved sulphate. Although toxic at high concentrations, metals are relatively easy and common to treat, and will be removed as a by-product of liming, filtration, flocculation, or distillation. Heavy metals have also been known to be efficiently (50-70%) reduced in concentration by reaction with retorted (spent) oil shale which can absorb dissolved metals in wastewaters (Pimentel *et al.*, 2010). The fact the heavy metal concentrations are lower in the UK means that it is likely their treatment will be addressed with ease as a by-product of salinity treatment, or by existing and effective industrial wastewater treatment methods.

Much higher sulphate levels were detected in wastewaters from the UK (570 mg/L max.) than in the USA (375 mg/L max.) indicating that UK wastewaters have a higher potential for sulphate scale formation. Scale can reduce the efficiency and longevity of fracturing equipment, impacting the recovery and operational success off a shale gas well (Horner, Halldorson and Slutz, 2011).

The mean concentration of Cl is higher in the UK than in the USA (84, 541 mg/L vs. 51,714 mg/L), however the maximum reported Cl in USA wastewaters is almost double that of the UK dataset (196,000 mg/L vs. 100,000 mg/L). Chloride in wastewaters is derived from the dissolution of chloride salts in formation water. It is one of the most concentrated elements in oil and gas wastewaters, and along with Na, can constitute more than 50% of the total dissolved solids content (Sun *et al.*, 2019). It is a primary challenge for wastewater treatment, as the concentrations of Na and Cl render most treatment options, except for evaporation methods, ineffective. High concentrations of Cl^- can also cause corrosion.

Finally, the pH of wastewaters generated in the UK is lower (5.78) than is typical in the USA (7.55). The lower pH of UK wastewaters could impact their ability to be received without any pre-treatment at biological wastewater treatment plants – as the microbes are sensitive to influent pH. Lower pH wastewaters are also more likely to contain metal and other major cations as anion adsorption is more prevalent in acidic conditions (Willis D. Weight P.E., 2019).

Despite the salinity of wastewaters from shale gas operations being largely similar to that of waste produced during conventional hydrocarbons extraction – differences in geography play a key role in the challenges of managing these wastes. Waters produced offshore from conventional hydrocarbon production are often dispersed and diluted at sea with little requirement for any pre-treatment. However the wastes produced onshore cannot be diluted or dispersed at sea owing to environmental protection offered by the

OSPAR Treaty (Convention for the Protection of the Marine Environment of the North-East Atlantic, 2007). Therefore wastes generated onshore must be treated and disposed of onshore, despite their origin (organic rich rocks in the subsurface) and geochemistry (high salinity, heavy metals and naturally occurring radioactive material) being similar.

TABLE 45 – MEAN, MINIMUM AND MAXIMUM CONCENTRATIONS OF COMPARABLE CONSTITUENTS IN WASTEWATERS FROM SHALE GAS OPERATIONS IN THE USA (N = 3092) AND UK (N=31) (MADALYN S. BLONDES, KATHLEEN D. GANS *ET AL.*, 2016).

	UK			USA		
	MINIMUM (MG/L)	*MEAN (MG/L)*	*MAXIMUM (MG/L)*	*MINIMUM (MG/L)*	*MEAN (MG/L)*	*MAXIMUM (MG/L)*
PH	5.40	5.78	6.10	3.20	7.55	11.8
ALKALINITY AS HCO_3^-	41.0	81.2	133	76.9	191	440
TOTAL SUSPENDED SOLIDS	230	1,387	2,600	4.00	316	5,290
TOTAL DISSOLVED SOLIDS	94,000	168,750	210,000	221	88,198	345,000
CHEMICAL OXYGEN DEMNAND	120	1302	3240	10.00	5863	51,000
SILVER		<1.00		0.00	0.04	0.10
ARSENIC	0.48	0.97	1.40	0.01	0.07	0.15
BARIUM	9.20	19.03	30.00	0.06	1,076	13,600
VANADIUM		<5.00	0	0.00	0.00	0.00
COBALT	0.02	0.04	0.05	0.00	1.43	25.0
CHROMIUM	0.00	0.05	0.30	0.00	1.80	156
MANGANESE	1.60	2.09	2.80	0.01	4.04	24.0
IRON	4.20	13.42	23.00	0.18	58.3	220
MERCURY		<0.20		0.00	0.00	0.00
NICKEL	0.16	0.32	0.88	0.00	0.94	19.2
COPPER	0.08	0.13	0.30	0.01	0.25	1.57
ZINC		<0.50		0.04	2.00	182
CADMIUM	0.12	0.12	0.12	0.00	0.03	0.10
LEAD	0.03	0.05	0.05	0.00	0.05	0.65
FLUORIDE		<50.0		0.01	3.06	58.3
CHLORIDE	48,000	84541	100,000	18.0	51,714	196,000
SULPHATE	570	570	570	0.78	58.8	374
NITRATE		<10		0.02	2.17	15.9

13.4 DATA SCARCITY

In 2016, the USA had 670,000 producing unconventional wells. The UK has fractured two wells, neither of which produced gas commercially. The first, located at Preese Hall in Lancashire, was drilled and fractured in 2011 before closing down due to issues with induced seismicity. The second, at Preston New Road in Lancashire, was drilled in 2017 and fractured in 2019, with flow testing completed in February 2019. Both of these wells were drilled to access prospective shale gas horizons of the Carboniferous Bowland Shale rock formation. Cuadrilla Resources undertook sampling and chemical analysis of fluids produced at both these wells which is the only 'field' data available for wastewaters generated by unconventional operations in the UK. Field data for wastewater compositions in the UK is very limited in comparison to the USGS database of produced water chemistry data for more than 3000 wells (Madalyn S. Blondes, Kathleen D. Gans *et al.*, 2016). However even the USA dataset only accounts for 0.5% of all producing unconventional wells, therefore more data is essential to improving our ability to analyse and understand the environmental risk posed by mis-management of these wastewaters (Sun *et al.*, 2019).

Comparing these two datasets, while limited by the relatively small sample size in the UK, offers the only comparison of field data possible between the two countries at this time.

13.5 ENVIRONMENTAL IMPACTS: LESSONS FROM THE USA

The waste fluids produced during hydraulic fracturing operations have the potential to negatively affect the environment in which they are stored, treated and disposed of if they are not managed effectively. The environmental legacy of operations in the USA, including pollution of surface water, reduced efficiency at wastewater treatment plants, and seismicity induced by the disposal of wastewater in underground wells has diminished the industry's reputation. There are a number of lessons that the UK can learn from the legacy of operations in the USA.

- Salinity will be high due to the mixing of injected fluids and inherent formation brine, regardless of the mineralogical composition of the shale. This salinity will pose a greater challenge to the UK industry as regulations prohibit the injection of waste underground for disposal, as is commonplace in the USA. This means that all waste will have to be treated before it can be released or reused, adding significant energetic and economic costs to the process in the UK.
- The fewer additives permitted for use in the UK will most likely simplify the geochemistry of waste generated, and could reduce the overall variability of the chemistry of waste from well to well. Wastes are more likely to be predictable if limited chemical additives are permitted for use, rendering management simpler in the UK than in the USA where any number of undisclosed additives can be present in wastes.
- The pH of wastewaters restricts their ability to be received at non-specialist biological treatment facilities in the UK. Treatment at non-specialist works in the USA has caused significant environmental degradation and any UK facility should learn from the well documented cases in the USA.

The waste fluids produced during hydraulic fracturing operations have the potential to negatively affect the environment in which they are stored, treated and disposed of if they are not managed effectively. The environmental legacy of operations in the USA, including pollution of surface water, reduced efficiency at wastewater treatment plants, and seismicity induced by the disposal of wastewater in underground wells has diminished the industry's reputation.

Hydraulic fracturing for shale gas in the UK will take place under different environmental, geological, regulatory, and social conditions than in the USA. Due to the lower population density in the USA, the surface footprint of operations can be much greater than would be possible in the UK where land more densely utilised. It is likely that multiple lateral wells would stem from a single vertical well more often in a UK industry – significantly reducing the impact of shale gas wells at the surface compared with the USA.

Water requirements can vary depending on well length, well type, operator specifications, rock formation, number of fractured stages and the percentage of onsite water recycling taking place. Water use has increased year on year in every USA shale basin except the Marcellus, even when normalised to well length or energy recovered, since 2011 (Kondash, Lauer and Vengosh, 2018). Since more water injected implies more water returned as waste, as the industry develops the demand for storage, treatment or disposal of wastewater produced at the surface will increase. If water requirements for hydraulic fracturing in the UK follows the patterns of the USA, the requirements for effective and efficient water management will increase with time.

The regulations surrounding storage, treatment and disposal of wastewaters produced in the UK vary significantly from those in place in the USA. Many of the wastewater management practices that are commonplace will not be suited to the UK, such as disposal of wastewater in deep underground injection wells, or storage of waste in open, lined pits. Freshwater effluent limits also vary slightly between the USA and the UK (p233) and therefore the treatment required before wastewaters can be discharged to surface waters will also vary.

Most wastewater produced in the USA is re-injected into porous rock formations for geological disposal, however re-use or recycling of wastewater is more prevalent in states where injection is not geologically suitable, such as in the Marcellus Shale (Ma, Geza and Xu, 2014). Re-use and recycling of wastewaters for fracturing, other industrial applications such as dust suppression or de-icing, or even agricultural irrigation is becoming more favourable due to the proven economic incentive offered by secondary use of fluids that would otherwise be confined to waste. On site management, including treatment before re-use and recycling, is more popular in the USA than off site management. Transport of waste off site adds significant cost and carbon emissions that can be avoided by conducting the majority of processing onsite. Onsite management requires specialist roaming treatment facilities and capability to service the onsite treatment needs of the industry. Conversely to the USA, the preferred method of management at present in the UK is transportation of waste to an offsite treatment plant. This is due to a number of factors, including but not limited to the legality of deep well injection in the UK, the availability of capable treatment infrastructure, and a lack of onsite treatment capability.

13.6 EXPERIMENTAL DESIGN

Experimental work undertaken for this thesis aimed to determine the geochemical influence on the overall chemistry of wastewaters that reactions between shales and fracturing fluids have. Novel experimental equipment was designed to react shale samples with synthetic fracturing fluids at representative pressures and temperatures in the subsurface. The equipment tested the interaction of distilled water and shale samples from a variety of geological settings and depths from both the UK and the USA. Due to their stainless steel construction HCl additive could not be used in these pressurised batch reactors without corrosion occurring and contaminating the fluids. Experiments were adapted to test the interaction with HCl in polypropylene (PP) to remove the risk of corrosion of the metal batch reaction vessels, however these PP vessels could not be pressurised.

Care was taken to ensure the reaction vessels were as representative of conditions in the subsurface during hydraulic fracturing as was possible within the restrictions imposed by time, sample availability, vessel construction materials, and budget. A number of improvements could be made to the experimental set up to increase the representativeness of condition. A batch reactor receptive to HCl fluids made from an inert material such as gold, or titanium would allow the behaviour of shales with acidized fluids to be tested under representative pressure conditions, however these were too expensive to be considered for use in this study. Improvements in experimental design to enable successful temporal sub-sampling of fluids would enable a time series of chemical data to be collected – offering more detailed temporal understanding of the reactions taking place. A system similar to the one described in (Marcon *et al.*, 2017a) would effectively achieve this, however was outside the budget prescribed for this work.

Experiments conducted for this thesis investigated the interaction of hydrochloric acid with representative shale rocks for the UK, however the effect of acrylamide or polyacrylamide was not investigated as it was outside the scope of this study to analyse both organic and inorganic geochemistry in detail.

13.7 SHALE GEOCHEMISTRY

Shale samples used for experiments described in this thesis are compared to US Geological Survey standard reference material SBC-1 (Figure 49). Samples PH1-6 are taken from drill core and cuttings from the PH-1 hydraulically fractured well at Preese Hall in Lancashire. KC is taken from drillcore of the Kimmeridge Clay formation from the East Brae well and MS was taken from a weathered road cutting sample of the Marcellus Shale formation in Pennsylvania, USA. The SBC-1 reference material is a Carboniferous marine shale collected from a fresh surface exposure in Greensburg, Pennsylvania (USA). Notably, all samples used for experiments greater quantities of quartz than the SBC-1 shale reference material. Since quartz is understood to be relatively stable below temperatures of 100°C it is not expected to play a major role in reactivity reactions between shales and synthetic fracturing fluids. Greater quantities of quartz indicate lesser proportions of minor minerals available to react with fracturing fluids, but also infer better mechanical conditions for fracturing as quartz rich or silicified shales tend to be easier to fracture (Jafary Dargahi, 2013). Ultimately, shale mineralogy impacts the geochemical reactivity of the rock, however reactive minerals may not be the predominant source of many of the constituents dissolved in wastewaters.

The geochemical behaviour of minerals at the surface can provide insight into probable subsurface reactivity, however the elevated temperatures and pressures experienced by rocks and fluids deep in the subsurface may alter mineral behaviour. Some rocks preferentially dissolve under increased pressures and temperatures, while for others dissolution declines under the same physical conditions (Hong *et al.*, 2018). Experiments conducted at elevated temperatures and pressures, representative of subsurface conditions during fracturing, were designed to investigate the contribution of minerals to the chemistry of wastewater and to better understand the reactions taking place.

The mineralogy of shale samples vary geographically, by shale basin, with depth within a single shale unit, and between difference facies. The mineralogy of any shale unit determines the major elements available to react with fracturing fluids during hydraulic fracturing.

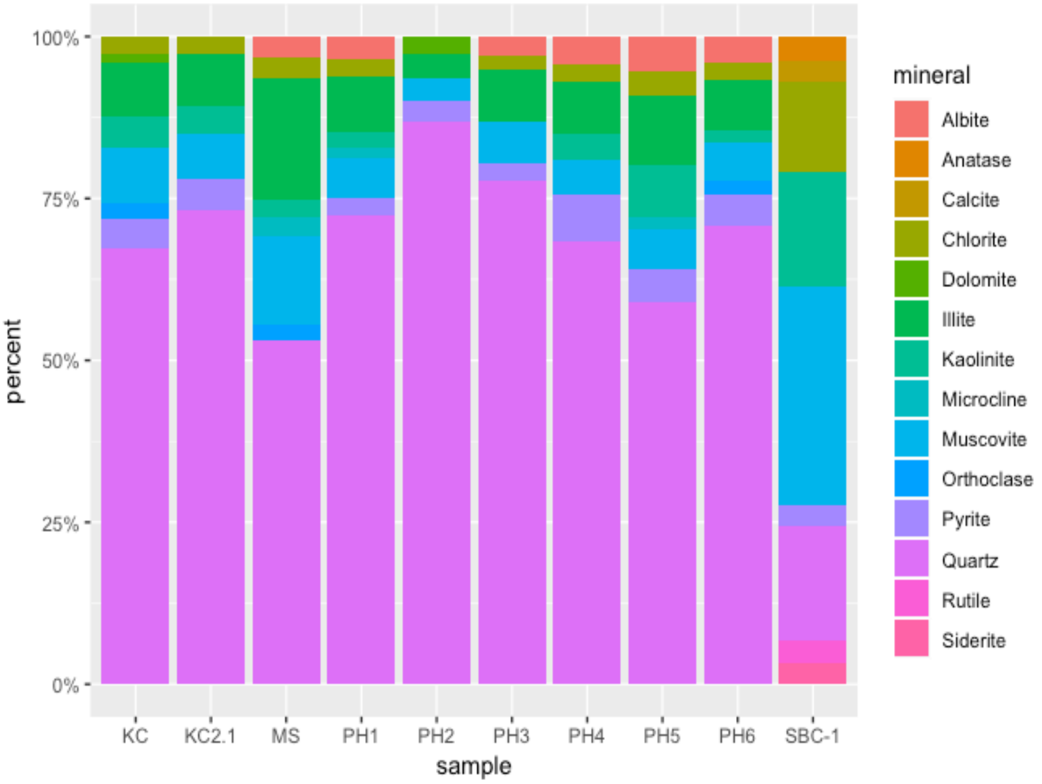


Figure 49 – Percentage mineralogical composition of shale samples compared with the mineralogy of SBC reference material.

13.7.1 SILICATE & CLAY MINERALS

The three most abundant minerals across all samples used for experiments in this study are quartz, illite and muscovite. The greatest abundance of illite and muscovite are detected in the MS sample, with 18 ± 1 wt. % and 13.0 ± 0.8 wt. % respectively (mean ± s.d. wt %). Both illite and muscovite are clay minerals typically formed from the weathering of other primary minerals and their greater abundance in the MS sample material is likely due to surface weathering, as MS was collected from a fresh cutting at a quarry. While the MS sample contains the least quartz (50 ± 1.9 wt. %), PH2 contains the greatest with 79 ± 1.4 wt. %. PH2 also shows low clay mineral content, indicating lesser overall weathering, and a more mature sedimentary system, which is consistent with a drillcore source.

Zr and Ti are typically fractionated by sorting that during sediment transport. Zirconium is typically contained with Zircons associated with SiO_2 minerals (quartz and feldspars), whereas Ti is typically found associated with clay materials in sediments with smaller grain sizes (Garcia, Coelho <, & Perrin, 1991).

13.7.2 CARBONATE MINERALS

All samples collected for reactivity experiments contained relatively little carbonate minerals, with PH6 containing the most; 14 ± 0.88 wt. % calcite. KC contains just enough dolomite to reach the detection limit of XRD (1 ± 0.23 wt. %), and MS contains no detected carbonate at all. In all other samples carbonate content ranged between 2 ± 0.23 and 3 ± 0.27 wt. %. Carbonate content plays an important mechanical and chemical role in gas shales. Carbonate content can infer good fraccability, similarly to quartz content (Jafary Dargahi, 2013), but also acts as the main chemical buffer to acidity in fluids which can increase dissolution of minerals susceptible to interaction with acids.

Carbonate content is a proxy indicator of the neutralising capacity of the rock in acidic fluids. During interaction with fracturing fluids shales may experience chemical weathering at increased rates with respect to natural or surface conditions. Pyrite oxidation, degradation of clay material, and carbonate dissolution can alter the chemistry of the rocks and fluids underground, with potential to release constituents of concern to the environment should they be managed poorly.

The lack of carbonate material detected by XRD in these samples suggests that, compared to other more carbonate bearing shales, they may have less capacity to neutralise acidic conditions caused by the oxidation of pyrite leading to hyper-acidic fluid conditions. This would further increase the rate and penetration of chemical weathering into the rock matrix leading to dissolution of a higher volume and suite of contaminants to be released into solution. Low carbonate content in gas shales could result in a greater environmental threat from waste fluids produced at the surface by offering limited buffering capacity to acidic fluids and therefore greater dissolution of minerals susceptible to acidic conditions.

13.7.3 TRACE ELEMENT GEOCHEMISTRY

XRF analysis of shale samples offered insight into the major and trace chemical constituents present. The suite of elements detected reflects the variety of constituents available to be released into solution during water rock interaction experiments. As expected, the major elemental chemistry largely mirrored the elemental components of mineralogy detected by XRD with no anomalous elements or concentrations. The minor or trace chemistry was dominated by the presence of Ba, V, Zr and Sr. Ba and Sr are often found in high concentrations in wastewaters from the USA and are thought to originate from clay material (Figure 50), released on interaction with high ionic strength injected fluids (Renock, Landis and Sharma, 2016).

The overall mineralogical distribution obtained by XRD analysis provides insight into the geological history and weathering conditions of each sample, however this mineralogical profile alone it is not enough to offer a thorough understanding of water rock reactions taking place during fracturing.

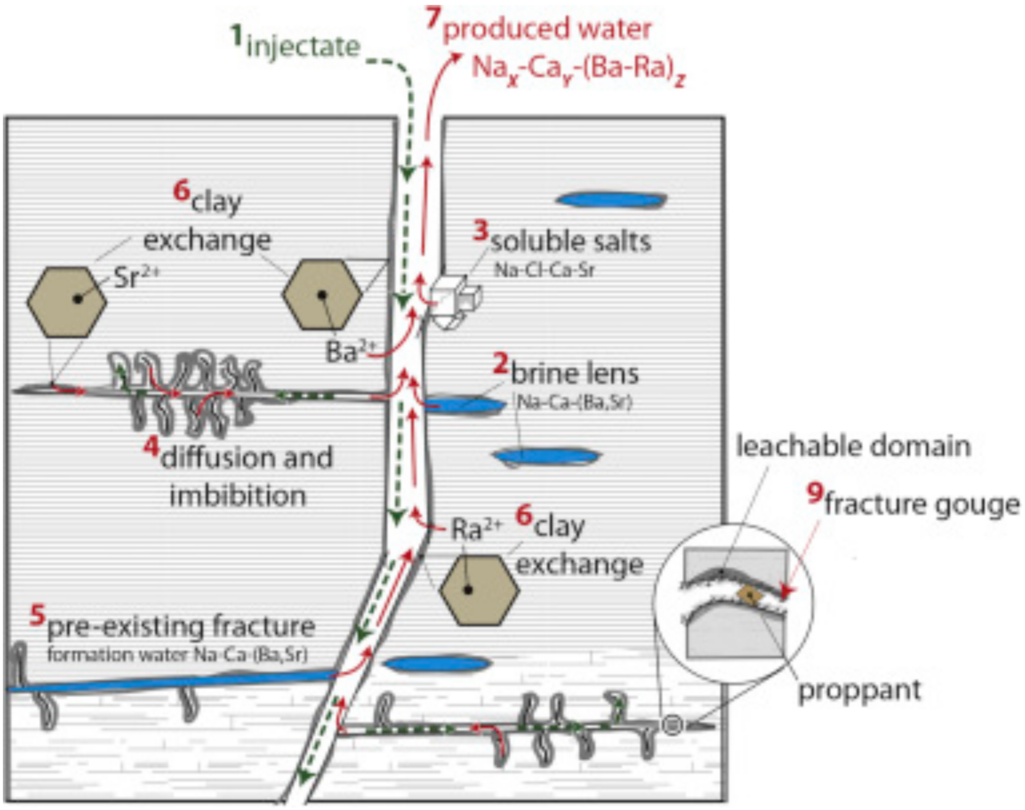


FIGURE 50 – SCHEMATIC INDICATING THE POTENTIAL SOURCES CONTRIBUTING CA, SR, BA, RA TO THE CHEMISTRY OF PRODUCED WATER. IMAGE REPRODUCED FROM (RENOCK ET AL., 2016).

13.7.4 REACTIVE SURFACE AREA

Mineral reaction rates are strongly linked to the available reactive surface area at the rock/water interface, which can be highly variable depending on grain size, mineralogy, oxide coating, weathering history, or biological effects (Brantley, White and Hodson, 1999). Surface area can be estimated by calculating the dimensions of the geometric shape of grains, or more precisely quantified by gas adsorption – however neither can quantify the reactive proportion of the mineral surface area which can anything from one to three orders of magnitude lower than physical surface areas (White and Peterson, 2009). Depending on the distribution and orientation of minerals within a shale matrix, the surface area of a sample at the molecular level can vary significantly – with discernible effects on the actual or modelled geochemical reactivity (Pearce, Turner and Pandey, 2018). Reactive surface area and the kinetic rate constants of components in the system strongly influence the rate and extent of reactivity between any injected fluid and a shale. Due to the heterogeneity of physical and reactive surface area within fractures, accurately accounting for these effects at the laboratory scale was not feasible. To maximise the opportunity to access reactive material within each shale sample, rock powders were used in batch reaction experiments. A single batch experiment compared the effect of powder vs. shale chips on the chemistry of fluids produced during experiments. While chipped shale material has a macro-scale surface area more close to that of fractures, reactivity was much higher when shale samples were powdered, giving greater chance of accessing the full heterogeneity of the shale composition and improving the chances of reaction taking place within the experimental timeframe. Dissolved constituents measured in sampled fluids were between 0.2 and 5 times more concentrated when shale material was powdered versus when the shale material was in 1 mm chips.

13.8 ANALYTICAL SENSITIVITY

Following the batch reaction experiment conducted with 1 mm chips of KC shale material, and distilled water at elevated temperature and pressure (SF1); the remnant solids were collected, crushed, milled and pressed for comparative analysis by XRD. The results of this comparative analysis are displayed in Figure 51 & Figure 52. After consideration of the analytical error a 0.6 wt.% change in quartz abundance was measured, with a greater relative percentage of quartz detected in fluids after the reactivity experiment. This may be due to a decrease in abundance of other minerals leading to a calculation of a greater proportion of quartz overall by semi-quantitate XRD analytical software.

Of the shale material analysed following the batch reaction experiment, only 6 minerals are detected, whereas 9 minerals were present in unreacted shale. Orthoclase, carnallite and colomite were detected in unreacted shale material, however were not present after reaction, indicating either dissolution or presence below the detection limit of XRD analysis (<1%), perhaps due to mineralogical heterogeneity within the shale sample.

Dissolution of carnallite is plausible under experimental conditions since evaporite minerals easily dissolve in water (Tavares *et al.*, 2018). Dolomite is known to dissolve in water at low temperatures by the mechanism described in Equations 15 & 16 (Zhang *et al.*, 2007):

$$\mathrm{CaMg(CO_3)_2}\,(s) = \mathrm{MgCO_3}\,(s) + \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \tag{15}$$

$$\mathrm{Mg(CO_3)_2}\,(s) = \mathrm{Mg^{2+}} + \mathrm{CO_3^{2-}} \tag{16}$$

Orthoclase, while soluble in water, is more chemically stable than both dolomite and carnallite. It can be subject to hydrolysis (see Equation 17) in acidic waters (containing excess H+ ions) and due to its monoclinic crystal structure is more soluble than other (Na- or Ca-) feldspars.

$$4KAlSi_3O_8 + 4H^+ + 2H_2O = 4K^+ + Al_4Si_4O_{10}(OH)_8 + 8SiO_2 \qquad (17)$$

orthoclase + hydrogen ion + water = potassium ion + kaolinite + quartz

Apart from these three minerals, all other change in mineral abundance was within the analytical error of the XRD technique. Overall, due to the lack of precision offered by XRD, it is limited in the evaluation of rock water reactions during experiments as changes in rock and fluid chemistry may be taking place at less than the 1% detection limit of the XRD technique. More detailed geochemical analysis was required to analyse the rock water reactions taking place during experiments, and hence XRD was not used for any further analysis.

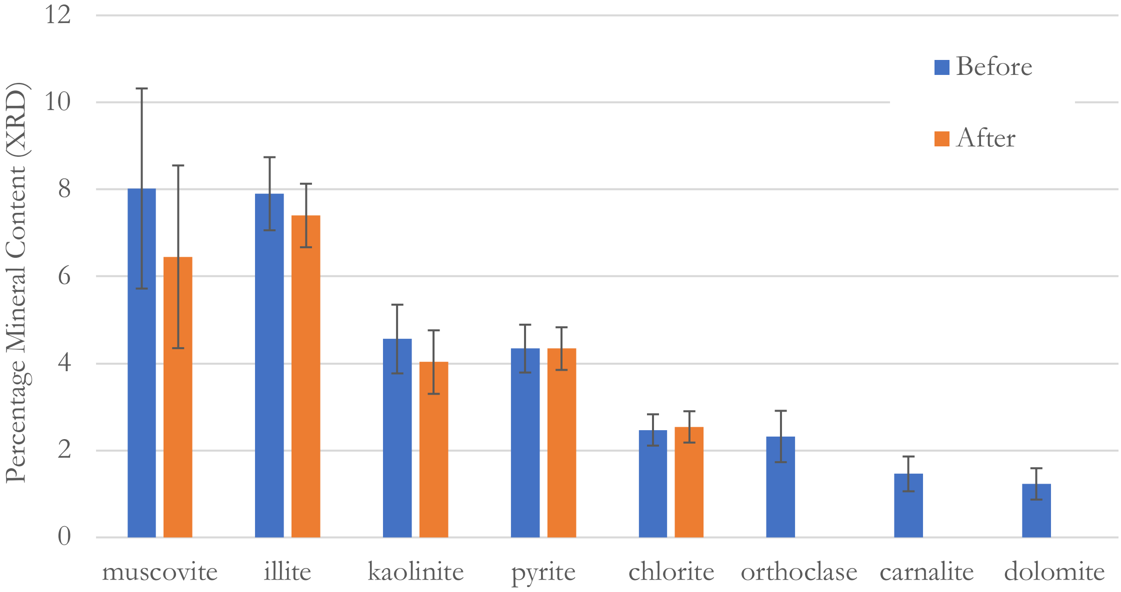


FIGURE 51 – RESULTS OF COMPARATIVE XRD ANALYSIS OF KIMMERIDGE CLAY SHALE MATERIAL BEFORE AND AFTER REACTION WITH DISTILLED WATER AT RESERVOIR TEMPERATURES AND PRESSURES (EXCLUDING QUARTZ).

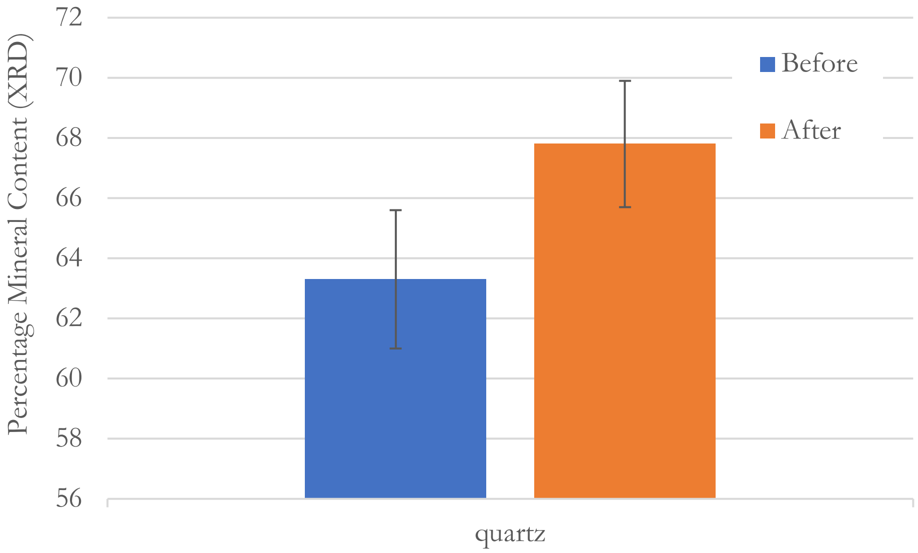


FIGURE 52 – RESULTS OF COMPARATIVE XRD ANALYSIS OF KIMMERIDGE CLAY SHALE MATERIAL BEFORE AND AFTER REACTION WITH DISTILLED WATER AT RESERVOIR TEMPERATURES AND PRESSURES (QUARTZ ONLY).

13.9 CONTROLS ON FLUID CHEMISTRY DURING HYDRAULIC FRACTURING

Aside from the geochemical reactions between shales and injected fluids during fracturing, mixing between injected fluids and inherent pore or formation water contained within shales exerts a dominant control on the major geochemistry of fluids generated (Barbot *et al.*, 2013; Capo *et al.*, 2014; Stewart *et al.*, 2015; Phan *et al.*, 2016). The trace element geochemistry of wastewaters is more likely to be influenced by shale–fluid interactions observed in these experiments which are discussed in this section.

13.9.1 INORGANIC CARBON

The acidity of natural water systems is predominantly controlled by the inorganic carbon system or carbonate weathering. In experiments which are open to atmospheric exchange, and therefore able to continually dissolve CO_2, this is likely the key driver of acidity generation and mineral dissolution. The inorganic carbon system is governed by the following three reactions which describe the dissolution of atmospheric CO_2 in water to produce carbonic acid (Equation 18). Carbonic acid dissociates to create bicarbonate and excess H^+ ions, reducing the fluid pH (Equation 19). Eventually bicarbonate can dissociate to generate carbonate and hydrogen ions (Equation 20). Low pH fluids can induce silicate, carbonate or sulphate mineral dissolution – releasing greater volumes of rock forming elements into experimental fluids.

$$CO_2(g) + H_2O = H_2CO_3(aq) \tag{18}$$

$$H_2CO_3(aq) = HCO_3^- + H^+ \tag{19}$$

$$HCO_3 = CO_3^{2-} + H^+ \tag{20}$$

13.9.2 DISSOLUTION AND PRECIPITATION

Carbonate, silicate and sulphide minerals dissolve in the presence of weak acids and oxygen releasing their constituent ions into solution, and sometimes forming secondary minerals. Calcite, dolomite and potassium feldspar dissolve to release ions into solution and produce secondary mineral products (e.g. potassium feldspar degrading to kaolinite and quartz, see Equations 21-23). Chlorite, while less reactive than other minerals, releases Mg and Si congruently under elevated temperature conditions. Typically calcite dissolves most easily and rapidly in acids, followed by feldspars and micas, however exact reaction kinetics are affected by a number of factors and can be difficult to predict in natural systems. The extent of dissolution of each mineral present depends on the duration of contact, and the saturation of the fluid with respect to these minerals.

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \tag{21}$$

$$CaMg(CO_3)_2 + H_2CO_3 = Ca^{2+} + Mg^{2+} + HCO_3^- \tag{22}$$

$$KAlSi_3O_8 + H_2CO_3(aq) + H_2O = K^+ + Al_2Si_2O_5(OH)_4 + SiO_2 + HCO_3^- \tag{23}$$

13.9.3 CATION EXCHANGE AND ADSORPTION

Charged mineral surfaces can attract or release ionic species into, or out of, solution. Clay minerals such as illite, muscovite and kaolinite are particularly prone to attracting cations due to their strong negative surface charge. If cations from the clay surface are exchanged for those in solution due to differential strengths of ionic attraction this is termed cation exchange. Clay minerals depend to host different ions depending on their environment of formation (Na^+ on marine clays and Mg^+ or Ca^+ on terrestrial) and readily exchange these on interaction with a high ionic strength solution. Cation exchange can occur during or after mineral dissolution as ions released into solution can be exchanged with those in place, or adsorbed onto free surfaces. High pH waters encourage cation adsorption, and conversely low pH waters tend to be higher in dissolved cations, with anions (except SO_4) commonly low or absent all together.

13.9.4 REDOX REACTIONS

The last way minerals and fluids are likely to interact in the subsurface during fracturing is through redox reactions, whereby electrons are transferred from one species to another. During pyrite oxidation, iron sulphide reacts with oxygen and water to release iron, sulphate and protons (hydrogen ions) into solution. The release of hydrogen ions reduces the fluid pH and can drive the dissolution of other mineral species susceptible to low pH fluid conditions (Equation 24). Pyrites are often found in association with other metal sulphides that can undergo similar oxidation reactions to release a variety of metals into solution e.g. arsenopyrite (arsenic), galena (lead), sphalerite (zinc), chalcopyrite (copper), etc.

$$FeS_2 + O_2 + H_2O = Fe(OH)_3(s) + SO_4^{-2} + H^+ \qquad 24$$

The hierarchical clustering of the elements detected in experimental solutions illustrates three key groups or 'clusters' of elements which are released into solution on interaction with (A) sulphides, (B) carbonates, or (C) silicates (Figure 53). The release of metal and sulphate ions into solution by the oxidation of sulphide minerals is likely responsible for the varying concentrations of Cu, Ni, Mo, Pb, Co, As, Fe and S (as sulphate) in experimental solutions. As oxygen was freely available within the experimental systems in SF2 and SF3 experiments, these elements are generally more concentrated in these metals as a result of increased sulphide oxidation.

The dissolution of carbonates by acidic fluids releases Sr, Mn, Ca, Zn and Mg into solution at varying concentrations depending on the carbonate mineral composition and extent of dissolution. As the dissolution of carbonate minerals can also buffer the fluid pH – the amount of constituents released through carbonate dissolution depends on the limit of the buffering capacity (or bicarbonate formation capacity) of the shale.

Silicate minerals such as quartz, feldspars and clays can be dissolved by injected fluids to release Al, Ba, K, Na, Li and Cr into solution. Clays such as illite and kaolinite are responsible for the cation exchange of Na, K, and Al into solution, while feldspars degrade to secondary minerals such as quartz and kaolinite as well as releasing elements into solution.

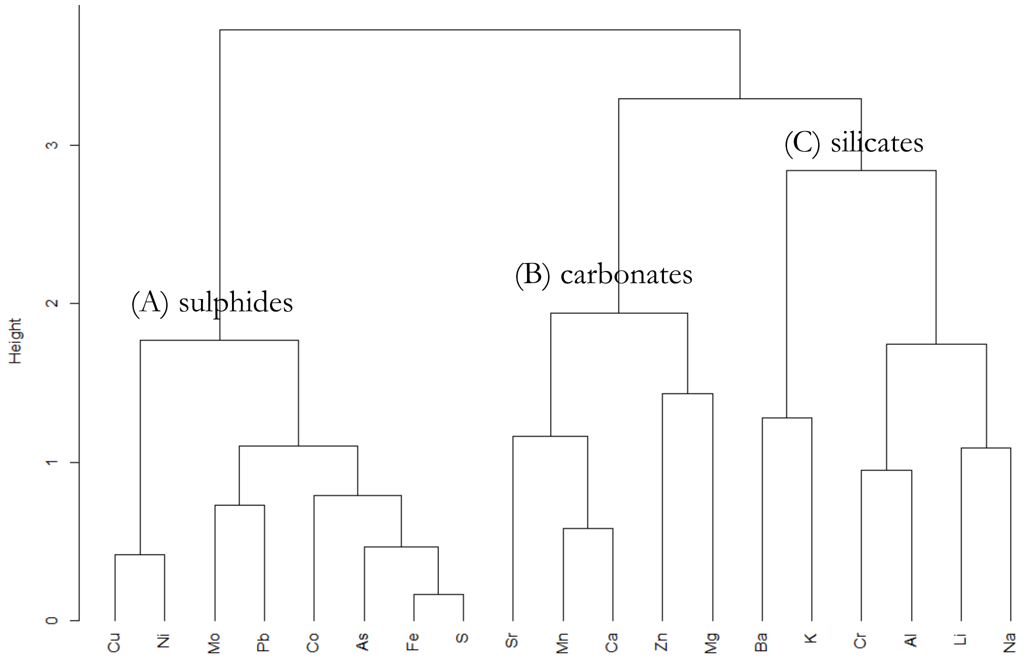


FIGURE 53 – HIERARCHICAL CLUSTER ANALYSIS ILLUSTRATED BY GROUPING OF CORRELATED ELEMENTAL CONCENTRATIONS FROM WHOLE ROCK DIGESTIONS AND THEIR RELATIVE GROUPING STRENGTH.

13.9.5 DURATION

Most experiments were conducted for a period of four weeks to mimic the typical length of a fracturing job and the residence time of fluids in the subsurface. Although experimental equipment was designed to enable temporal sub-sampling of the fluids throughout the experiments – this was not widely achieved due to blockages in the sampling pipework.

During the SF1 experiment with Marcellus Shale, a single temporal sample was retrieved after 24 hours at reservoir pressures and temperatures. This sample had higher or the same concentrations of all elements except Al, in comparison with concentrations in the fluids sampled from the same experiment run for four weeks Figure 54. A similar experimental study to this that successfully achieved sub-sampling throughout, concluded that the majority of chemical reactions took place within the first 24-72 hours, with concentrations of most elements at their peak during this time (Marcon *et al.*, 2017b). Marcon et al. derived that the initial spike and subsequent reduction in concentrations of constituents indicated primary dissolution followed by secondary mineral precipitation and scavenging of dissolved elements. It is unclear from the limited temporal sub-sampling data for these experiments whether secondary precipitation was taking place – however many flowback fluids have been known to exhibit oversaturation with respect to secondary minerals therefore depending on kinetic limitations secondary precipitation is plausible (Paukert *et al.*, 2015; Paukert Vankeuren *et al.*, 2017). Kinetic effects of pressure on precipitation of barite scale have been known to slow formation by up to two orders of magnitude under experimental settings (Bhandari *et al.*, 2016), and therefore the pressure conditions could be inhibiting secondary mineral precipitation from taking place. If pressure is inhibiting precipitation during SF1 batch reactions, then it follows that when sampling any supersaturated minerals would be most likely to form after the initial sampling period when fluids return to ambient pressure and temperature conditions. Samples were acidified immediately on collection with HNO_3 to maintain dissolution of components in solution for analysis.

The SF1 experiment with Bowland Shale material was sub-sampled successfully after a week and then again after 4 weeks. Figure 55 shows the difference in concentrations between the two samples. Unlike the constituents detected in fluids sampled after 24h in SF1-MS, all elements are either equal or greater in concentration after 4 weeks in comparison with the fluids sampled after 1 week. This suggests that, in concurrence with the Marcon et al. study, dissolved constituents have stabilised or continue to be released following the initial period of reactivity in the first 24 – 72h of mixing. If secondary precipitation was occurring throughout the experiment duration, a drop in some elemental concentrations would be expected as they are scavenged from solution to form precipitates.

The elements that continued to change concentration in solution were the major rock forming elements Ca, Mg, K, Na, Si, as well as some minor elements such as B, Ba, Fe, Sr and Zn gradually increasing – suggesting continual dissolution of rock forming minerals throughout experiment duration.

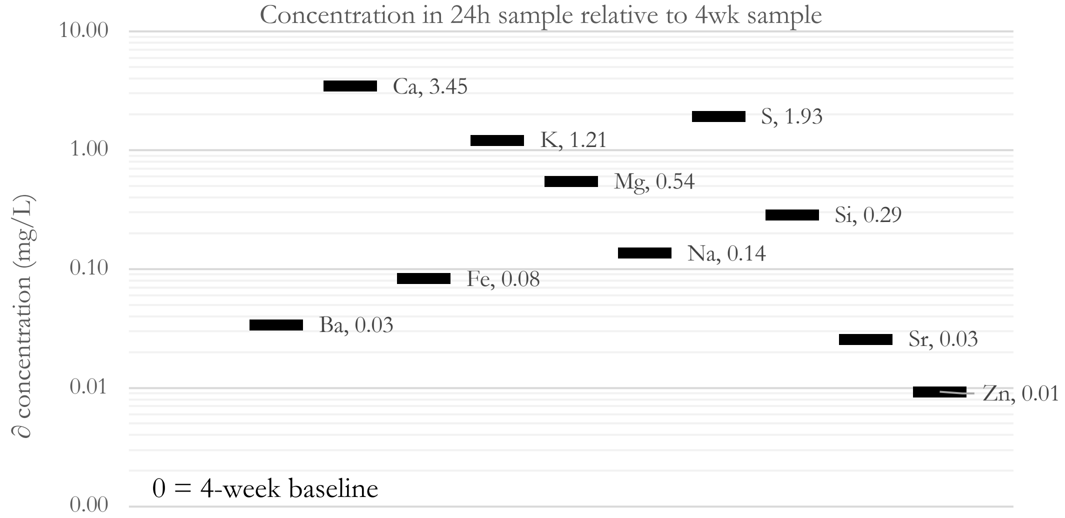


FIGURE 54 – RELATIVE CONCENTRATION AFTER 24 HOURS RELATIVE TO 4 WEEKS, FOR DETECTABLE ELEMENTS WHERE RATIO >1.0, NORMALISED TO 4 WEEK CONCENTRATIONS IN MG/L.

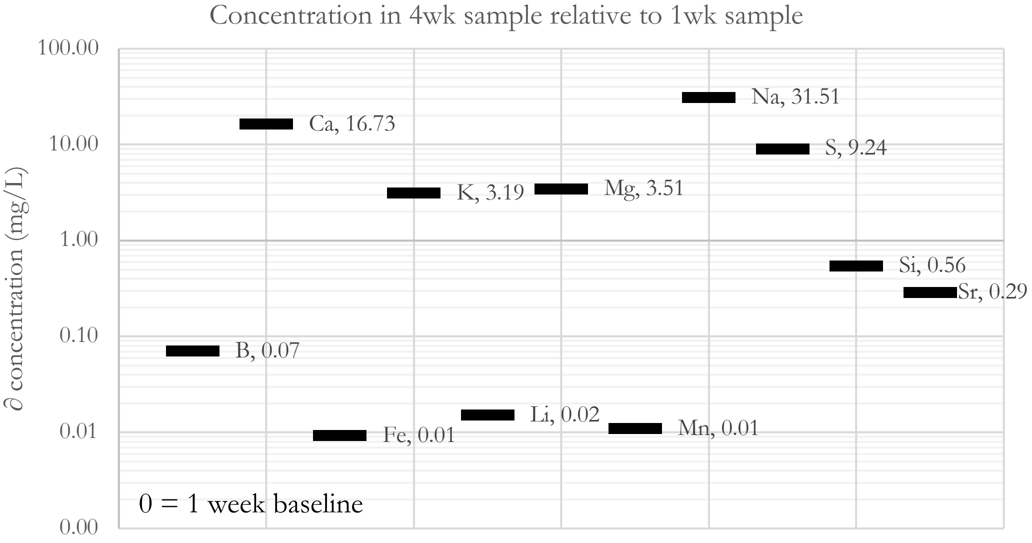


FIGURE 55 – PLOT OF CONCENTRATIONS OF ELEMENTS WHICH ARE HIGHER AFTER 4 WEEKS THAN WHEN SAMPLED AFTER 1 WEEK. CONCENTRATIONS IN MG/L.

13.9.6 TEMPERATURE

Temperature had a significant effect on the concentration of elements released into solution during the interaction of shales and injected fluids. Temperature comparison experiments were conducted at ambient pressure, in experimental equipment that was not sealed from the surrounding atmospheric oxygen, resulting in significant pyrite oxidation, fluid acidity, and the associated dissolution of Na- and Ca- bearing carbonate and silicate minerals. Iron (393 ppm), cobalt (0.90 ppm), copper (1.51 ppm), and nickel (2.80 ppm) were most concentrated in fluids sampled from high temperature, ambient pressure experiments in comparison to all other experimental conditions – suggesting that the potential to dissolve heavy metals into solution is greatest when elevated temperatures accelerate the oxidation of sulphide minerals (Figure 57).

The only element released into solution above 5 mg/L in ambient pressure and temperature experiments was calcium (Figure 56), most likely derived from the reaction between calcium carbonate, atmospheric carbon dioxide (carbonate weathering) which is known to readily take place under atmospheric conditions, at rates proportional to temperature.

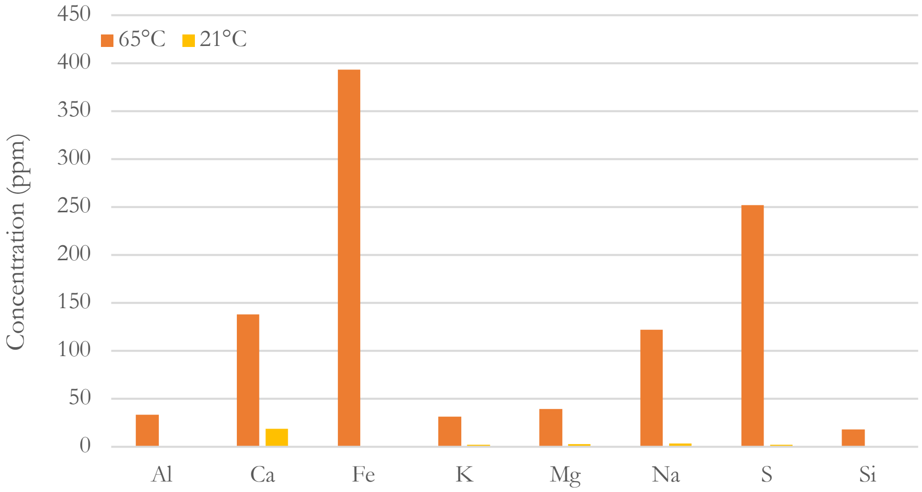


FIGURE 56 - CONCENTRATION OF MAJOR ELEMENTS MEASURES IN SOLUTION AFTER EXPERIMENTS CONDUCTED AT AMBIENT (21°C) AND RESERVOIR (65°C) TEMPERATURES (N=1).

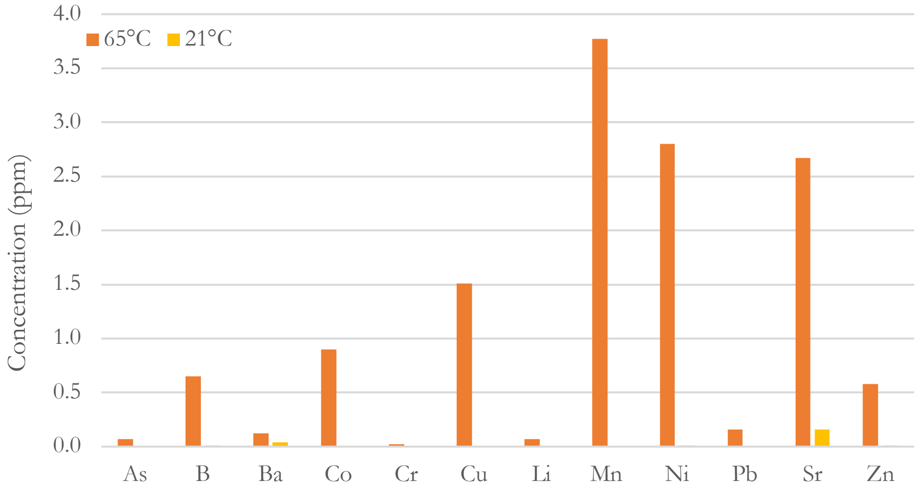


FIGURE 57 - CONCENTRATION OF MINOR ELEMENTS MEASURES IN SOLUTION AFTER EXPERIMENTS CONDUCTED AT AMBIENT (21°C) AND RESERVOIR (65°C) TEMPERATURES (N=1).

13.9.7 PRESSURE AND AVAILABLE OXYGEN

Experiments conducted in Swagelok pressure rated stainless steel are closed batch reaction systems, however the fluids injected to pressurise these containers are somewhat oxygenated as they are not purged prior to injection – similarly to fracturing fluids pumped into wells in the field. The solubility of oxygen in water is proportional to pressure increase and therefore any oxygen in the batch reactors will be more likely to dissolve in pressurised systems than in any of the batch reactions at atmospheric pressure. The maximum dissolved oxygen concentration in atmospheric pressure batch reactors is 9.2 mg/L, whereas in the batch reactors pressurised to 1500 psi (103 bar) the maximum dissolved oxygen concentration is closer to 1100 mg/L. Higher temperature waters restrict the dissolution of oxygen so counter the effects of pressure, however the influence of pressure on the oxygen solubility is more dominant.

Dissolved oxygen in water encourages oxidation of mineral species, which can often release hydrogen ions, lowering the pH. Pyrite, formed alongside organic matter and often correlated with gas in shales, was observed using a SEM microscope to be framboidal in texture – resulting in a very large surface area. Pyrite is easily oxidised in water in the presence of O_2 to release sulphate, iron and hydrogen ions, reducing the solution pH. It has been suggested that this reaction could actually help improve shale gas recovery rates, as dissolution of pyrite (which tends to form closely with organic matter) could increase access to gas within the fractured shale (You *et al.*, 2017).

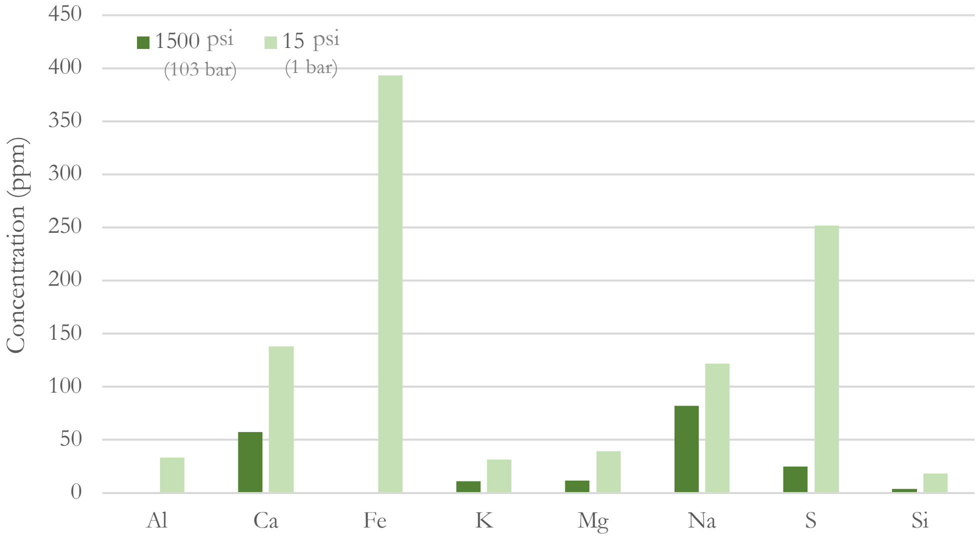


FIGURE 58 - CONCENTRATION OF MAJOR ELEMENTS MEASURED IN EXPERIMENTAL FLUIDS AFTER 1 MONTH UNDER VARYING PRESSURE CONDITIONS. 15 PSI = AMBIENT (SF2), AND 1500 PSI = ELEVATED PRESSURE (SF1).

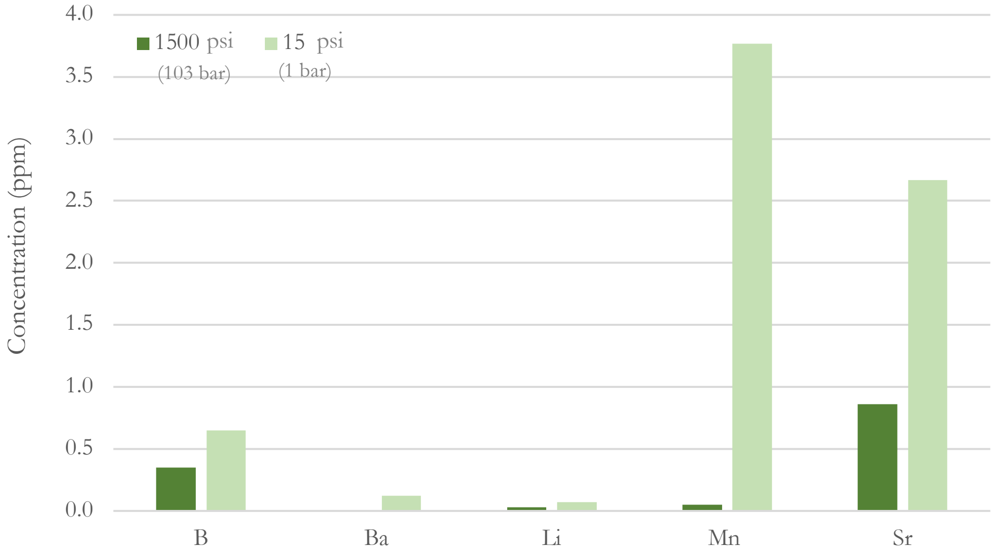


FIGURE 59 - CONCENTRATION OF MINOR ELEMENTS MEASURED IN EXPERIMENTAL FLUIDS AFTER 1 MONTH UNDER VARYING PRESSURE CONDITIONS. 15 PSI = AMBIENT (SF2), AND 1500 PSI = ELEVATED PRESSURE (SF1).

Concentrations of all comparable major and trace elements were higher in fluids sampled from experiments conducted under ambient conditions than those conducted at representative reservoir pressures (Figure 58 & Figure 59). This is most likely an effect of the available oxygen in the two batch reactor systems and not a direct effect of pressure kinetics on mineral fluid reactions. The only available oxygen in pressurised experimental systems was that carried by the injected fluids, however in low pressure batch reactions the seals were found to be faulty resulting in free oxygen exchange throughout the experiment duration. This available oxygen most likely enabled the oxidation of pyrite (evidenced by high Fe and S concentrations in low pressure experimental solutions), generating acidic fluid conditions and driving the dissolution of other minerals. As adsorption is more prevalent under alkaline conditions, it is expected that cation concentrations will be higher in low pH fluid systems.

Ca (138 ppm), Mn (3.77 ppm), and Sr (2.67 ppm) are also higher in the low pressure experiments indicating dissolution of carbonate mineral phases – which are easily dissolved under weak acidic conditions. In order to compare the results of experiments at reservoir and ambient pressure conditions, equipment that ensures no atmospheric exchange was required.

Overall, greater concentrations of dissolved elements were measured in batch reaction experiments conducted at ambient pressures than at reservoir pressures. This is likely due to batch experiments at ambient pressures in plastic or borosilicate glass being more oxygen rich than experiments conducted in sealed stainless steel pressure rated equipment. There was no headspace or free air present in the stainless steel batch reactors, unlike the PP vials and borosilicate glassware which both contained air in their headspace. Batch reactions in PP vials were most susceptible to oxygen exchange, with between 5 and 60% evaporation occurring from within the vial during the experimental run. These experiments are least likely to represent subsurface conditions due to the degree of oxygen exchange and ambient pressure conditions. Quickfit borosilicate glassware vessels did not allow exchange of oxygen with the atmosphere, however they dud did have ~25 ml headspace containing ambient air. As mains water used for synthesising fracturing fluids is already oxygenated, purging the headspace with N_2 or any inert gas would reduce the free oxygen in the system and limit oxidation.

13.9.8 PH

Additional aliquots of fluid, separate to those collected for ICP-OES analysis, were collected and their pH measured at one-minute intervals over a 10-minute period. These data can indicate whether mineral dissolution or precipitation taking place in the period following sampling, when pressure conditions are reduced and kinetic effects are altered. In oxidising conditions, shales containing high surface area framboidal pyrite will form sulphate, dissolved iron and sulphur, releasing excess H^+ ions. This reduces the pH and causes dissolution of acid sensitive minerals such as silicate and carbonate minerals, increasing the concentration and variety of elements in solution. Impurities and secondary elements contained within or associated with major minerals are released in to solution in much smaller concentrations than the major elemental components – altering the minor geochemical signatures of fluids. These minor geochemical components are not present at concentrations high enough to influence the overall geochemical profile of fluids.

The pH of fluids reacted with KC chips was higher than that in the fluid reacted with KC powder. This implies that a greater volume of acidizing reactions were able to take place when material had a greater reactive surface area made available by the powdering of the sample. Overall, the pH of fluids reacted with KC sampled were the highest, which correlates with the highest carbonate mineral content measured in any of the SF1 samples (1 ± 0.2% dolomite). It is likely that dissolution of the dolomite buffered the production of acid generated by the oxidation of pyrite (4 ± 0.4% in KC).

The pH in SF1-MS was the lowest of all three batch reaction fluids, despite containing no pyrite and one of the lowest sulphur contents. Additionally, the pH of fluids sub-sampled after 24h was even lower than the batch reactor which remained closed for 4 weeks, indicating early acid conditions in the batch system. MS is predominantly composed of quartz and muscovite, with the highest clay content of any SF1 sample (~33 %). The clay minerals kaolinite, illite and chlorite are susceptible to degradation when in contact with acidic fluids (Simon and Anderson, 1990) – making them more likely to release dissolved solids into solution under acidic conditions.

The greatest variance in pH measured between two fluids reacted with the same shale sample is in SF1-BS batch reactions. The 1 week SF1-BS sample had a pH of 6.3 and the 4 week SF1-BS fluid had a pH of 7.8 in comparison with the control which had a pH of 7.3. Similarly to the SF1-MS experiment, the fluid sampled at the 1 week mark had a lower pH than the fluid sampled at 4 weeks, indicating early acidic conditions. After five minutes, the pH of SF1-BS samples (both 1 week and 4 week fluids) converged at 7.6, while the control had dropped to 6.3. It is unclear what caused the pH of the SF1-BS 1 week fluid to rise immediately following sampling, it is possible that the geochemical mechanisms driving the pH down, such as oxidation, cease to be dominant once the pressure is reduced. It is also possible that pressure could be inhibiting dissolution of some mineral phases within the sample, that become more readily dissolved once pressure is reduced. For example, limestone is less susceptible to dissolution when pressure and temperature increase, however conversely dolomite dissolves more readily (Hong *et al.*, 2018).

The pH of wastewaters from hydraulic fracturing could impact their ability to be received at wastewater treatment plants in the UK. Biological water treatment utilises bacteria and micro-organisms to break down the organic material in wastewater, however their health is severely impacted by acidic waters. Biological treatment systems are easily damaged by acidic or high salinity waters, two common features of wastewaters from hydraulic fracturing. Acidity may have to be treated before waters can be received at existing waste treatment facilities or specialist infrastructure will be required at additional cost. Liming, or the addition of calcium or magnesium carbonate to acidic waters can neutralize pH, whilst also effectively reducing dissolved metal mobility (Jeng, 1992; Pearce, Turner and Pandey, 2018).

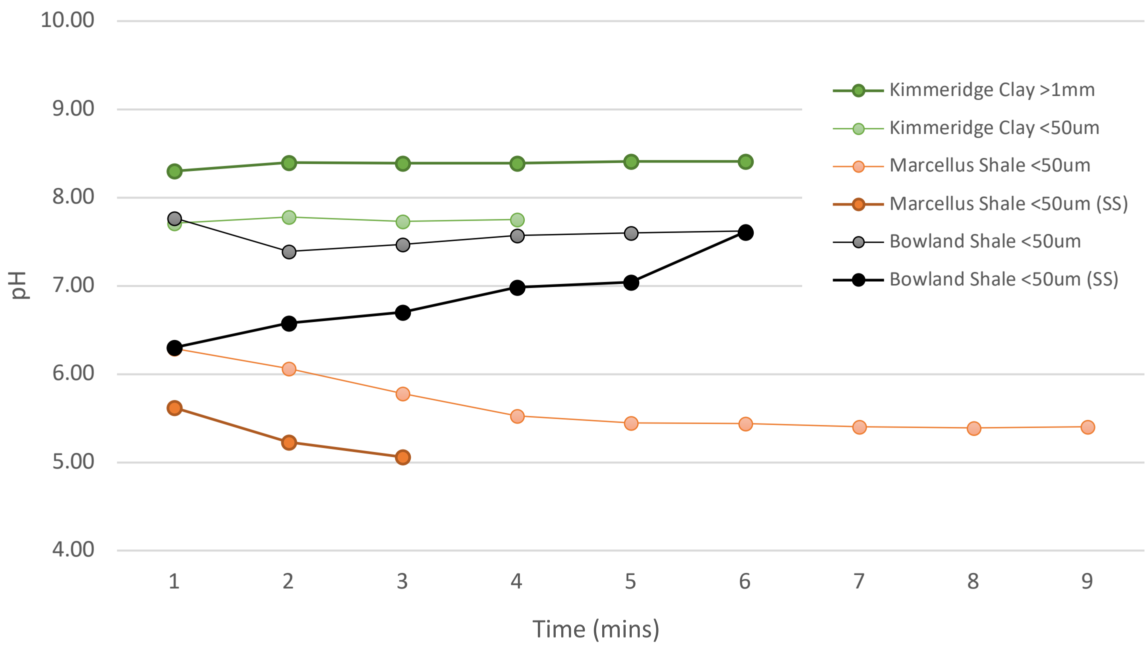


FIGURE 60– THE PH OF EXPERIMENTAL FLUIDS MEASURED OVER TIME (1-MINUTE INTERVALS) FROM MOMENT OF SAMPLING HIGH PRESSURE AND TEMPERATURE EXPERIMENTS (DATA AUTOMATICALLY TEMPERATURE COMPENSATED BY INSTRUMENT). SS = INDICATES 'SUB-SAMPLED' AFTER 24 HOURS OR 1 WEEK AND THEREFORE EXPOSED TO ATMOSPHERIC EXCHANGE BEFORE FULL EXPERIMENT DURATION.

13.9.9 ORGANIC CARBON

Organic carbon in shales can drive microbial activity, scavenging oxygen from the subsurface environment. Many of the reactions controlling pH, and affecting the dissolution of minerals are directly linked to oxygen content, and therefore could be slowed by high microbial activity. Temperature can increase microbial activity to certain point, before the temperatures become generally hostile to such organisms.

Microbes can metabolise organics within wastewaters, contributing to the formation of and breaking down chemical components in fluids. Limited strains of microbes can survive in this environment as they must be resistant to temperature, dissolved metals, high salinity and changes in pressure, however some have been observed in a number of studies (Mohan *et al.*, 2013; Morono *et al.*, 2019).

Organic carbon is common in hydraulic fracturing wastewaters can cause fouling during membrane desalination if not treated (Shaffer *et al.*, 2013). An additional targeted treatment step for organics which uses activated carbon or aerated degradation will be required before desalination can take place by membrane methods (Butkovskyi *et al.*, 2018).

13.9.10 HYDROCHLORIC ACID

The use of HCl additive in synthetic fracturing fluids mobilised significantly more elements from the experimental system than any reaction without. Even in experiments where only 0.125% HCl was added to the fluid (SF4), notably greater concentrations of elements such as Al, B, Ba, Cu, Li, Pb, Zn were detected where in experiments without HCl (SF3) these were much lower or negligible (Figure 61 & Figure 62). In SF4-MS and SF4-BS some concentrations of elements decreased with time, however most in SF4-KC increased. This implies that reaction progression with time is not uniform and does depend – to some extent – on shale composition.

In SF5 experiments with 10% HCl, the longer a batch reaction was left to run for, the more elements were released into solution, insinuating that an equilibrium between the synthesised fracturing fluid and the rock was not reached in either a 4- or 7-week period. This implies that should SF5 fluids spend a greater period of time downhole, they would inherit greater and greater concentrations of dissolved constituents, until a chemical equilibrium was reached. However the results of SF4 suggest that at lower HCl concentrations this may not always be the case, and dissolution may be limited by shale composition.

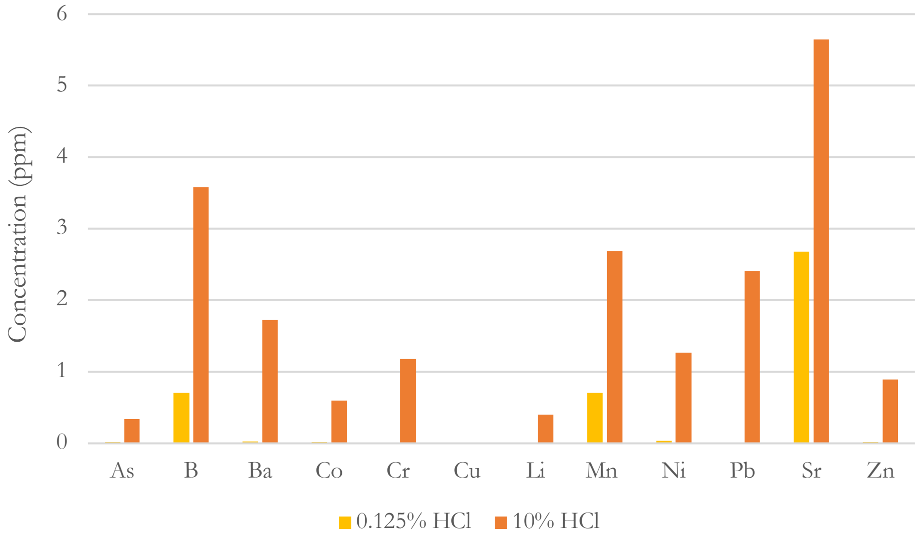


FIGURE 61 – COMPARISON OF THE CONCENTRATION OF MINOR ELEMENTS IN SOLUTION AFTER REACTION WITH DIFFERING CONCENTRATIONS OF HYDROCHLORIC ACID.

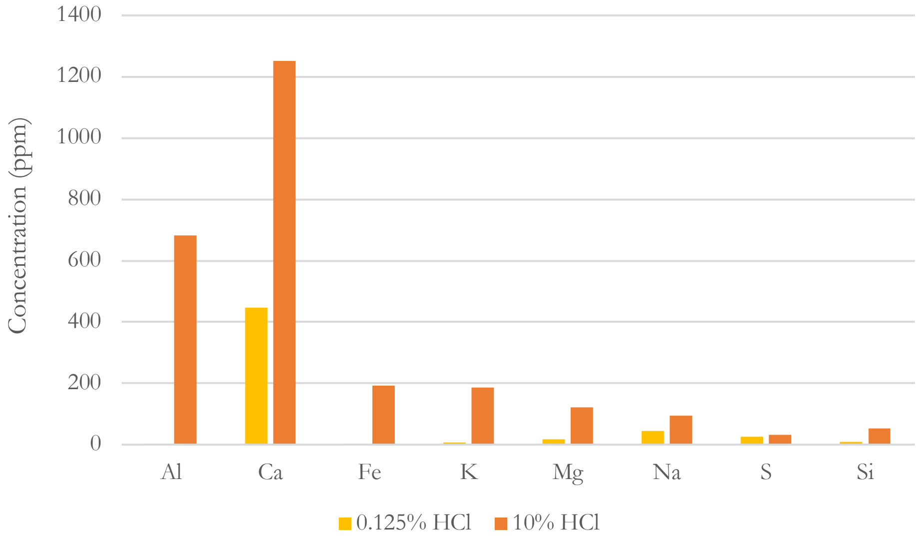


FIGURE 62 - COMPARISON OF THE CONCENTRATION OF MAJOR ELEMENTS IN SOLUTION AFTER REACTION WITH DIFFERING CONCENTRATIONS OF HYDROCHLORIC ACID.

The addition of varying amounts of hydrochloric acid (HCl) from the minimum permissible concentration (0.125%) to the maximum (10%) illustrates the effects of using varying concentrations of fluid additives on the resultant wastewater chemistry. Hydrochloric acid is a strong and soluble acid, which is used in hydraulic fracturing to improve dissolution and increase the access of fractures to the rock mass. For this reason, it was expected to increase the concentrations of most solutes in experimental fluids proportionally to its concentration.

Experiments conducted with 10% HCl released the highest concentrations of all constituents of concern into solution with a few notable exceptions of Fe, S, Mn, Co, Cu and Ni. These elements are released into solution by the oxidation of pyrite and other metal sulphides and the subsequent dissolution of Ca- bearing mineral phases which was enabled by the free exchange of atmospheric oxygen within the SF2 experiment. In SF4 and SF5 experiments, the concentrations of major rock forming elements (Al, Ca, K, Mg, Na and Si) were highest of any experimental conditions, with Sr, B, Ba, Pb and Zn present at higher trace concentrations than in any other experiment.

Concentrations of dissolved constituents increase with time as a well produces gas and wastewater (Barbot *et al.*, 2013), however the volumes of wastewater produced by a well drop off with time (Kondash, Albright and Vengosh, 2017b). This means that there will be a high volume of low salinity wastewater generated in the immediate period following fracturing, with a much lower concentration of high salinity wastewater to follow. As fluids spend longer in the subsurface they have more time to react with the rock and dissolve minerals into solution. Additionally, as time passes most of the injected water becomes imbibed into the shale and the fluids returned at the surface are only made up of formation water (Osselin *et al.*, 2018). This well reported field occurrence matches with the limited batch reaction data in this study, and concentrations of most elements increase with contact time with the rock when a higher concentration HCl additive is used. When no additives of lower concentration additive is used, the elemental concentrations are much more variable with time, and generally concentrations of most elements are much lower.

13.9.11 SHALE HETEROGENEITY

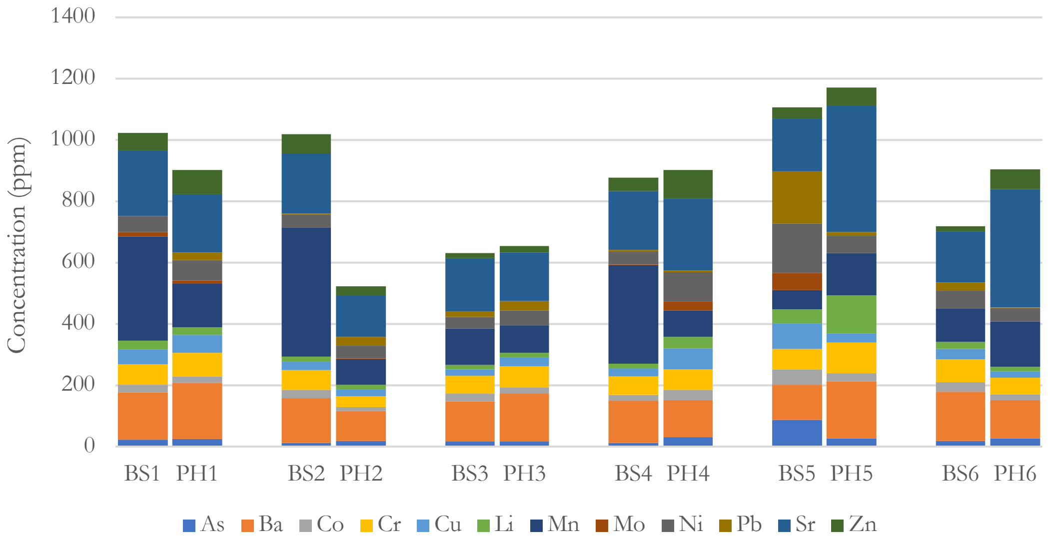


FIGURE 63 - COMPARISON OF THE MINOR ELEMENTAL COMPOSITION OF SHALE SAMPLES TAKEN FROM THE SAME HORIZON WITHIN THE SAME CORE, BUT FROM TWO STORAGE LOCATIONS. VARIABILITY INDICATES THE HETEROGENEITY OF SHALE EVEN WITH SAMPLING HORIZONS.

Significant heterogeneity exists even within samples collected from the same horizons within the two sets of shale quarter cores (Figure 63). Trace elements, while on the whole comparable, vary by up to 500 ppm in some samples. Ternary plots (Figure 64 & Figure 65) compare the trace geochemistry of experimental shale samples to US shales. Experimental shales exhibit higher quartz and feldspar and lower carbonate content than is seen in a range of US samples. Despite heterogeneity, which will affect the trace geochemistry of shales and resulting fluids, the composition of major elements in shales that are available to react with injected fluids are largely comparable. Key reactions that affect fluid chemistry involving calcite, pyrite, feldspars and clays can be expected to take place to a greater or lesser extent depending on their prevalence and exposure in the subsurface. These will affect fluid chemistry to a stronger extent during latter stages of fluid production when the majority of formation mixed fluids have already been returned.

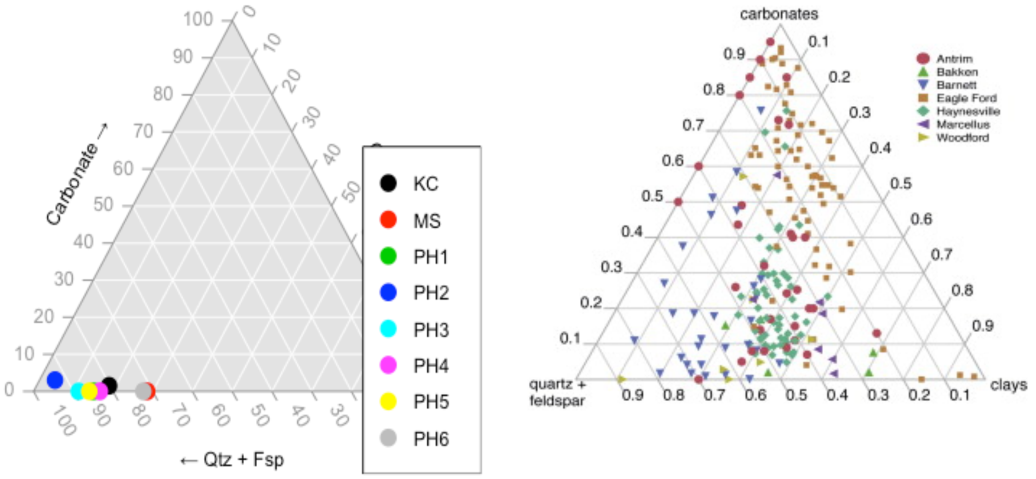


FIGURE 64 – CONTENT OF SILICATE (QTZ) PLUS FELDSPAR (FSP) AND CARBONATE PLUS CLAY FOR SHALE SAMPLES IN THIS STUDY (LEFT) COMPARED TO THE USA (AGGREGATE SHALE MINERALOGY DATA, RIGHT). DATA FOR USA REPRODUCED FROM (CHERMAK AND SCHREIBER, 2014).

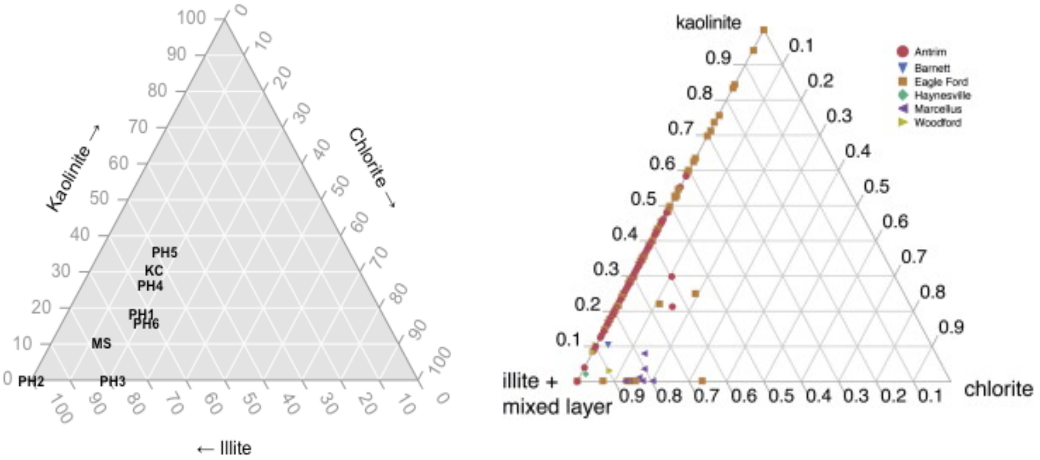


FIGURE 65 – TERNARY PLOTS OF RELATIVE PROPORTION OF ILLITE, KAOLINITE AND CHLORITE CLAYS IN SAMPLES COLLECTED FOR THIS STUDY (LEFT) COMPARED TO AGGREGATE SHALE DATA FROM THE USA (RIGHT). PLOT ON RIGHT OF SHALE MINERALOGY REPRODUCED FROM (CHERMAK AND SCHREIBER, 2014).

The Marcellus Shale sample was taken from a quarry in the USA and the BS-U and BS-L samples were taken from field exposures in England. Generally, the surface samples were much less reactive in batch experiments than the core samples. In SF1, despite exhibiting a much lower fluid pH than the other experiments, SF1-MS fluids exhibited some of the least concentrated elemental signatures. MS may have spent a significant amount of time exposed to weathering at the surface before being collected for sampling. Although every effort was made to remove outer oxidised layers, the many of the minerals that would have reacted in batch reactions may have already dissolved out from prolonged surface exposure. In SF5 experiments the BS-U and BS-L fluids were similarly depleted in all of the major rock forming elements, however fluids reacted with BS-U and BS-L contained much higher Mn than any other samples. BS-U and BS-L were also high in Sr, which tends to associated with Ca, Mg and Ba in calcareous rocks (Salminen *et al.*, 2005). It is possible that the surface exposures of the Bowland Shale contain more calcareous minerals than the core samples as calcareous content varies widely within the formation – which is evident even in samples taken from differing core depths. Samples taken from core were able to be correlated with well logs, and fracturing data making them the most likely to be representative of downhole conditions. At the start of experimental work, the only sample of Marcellus Shale available was from a surface exposure, and the sample of core material was not received until near the end of experimental runs.

Overall, samples from core will be much more representative of the geochemistry of downhole shales, however they are harder to access and more expensive to obtain. Any further experimental work to determine geochemical reactivity between shales and injected fluids should be carried out with core samples from prospective shale gas zones wherever possible.

13.9.12 EXPERIMENTAL GEOCHEMISTRY VS FIELD GEOCHEMISTRY

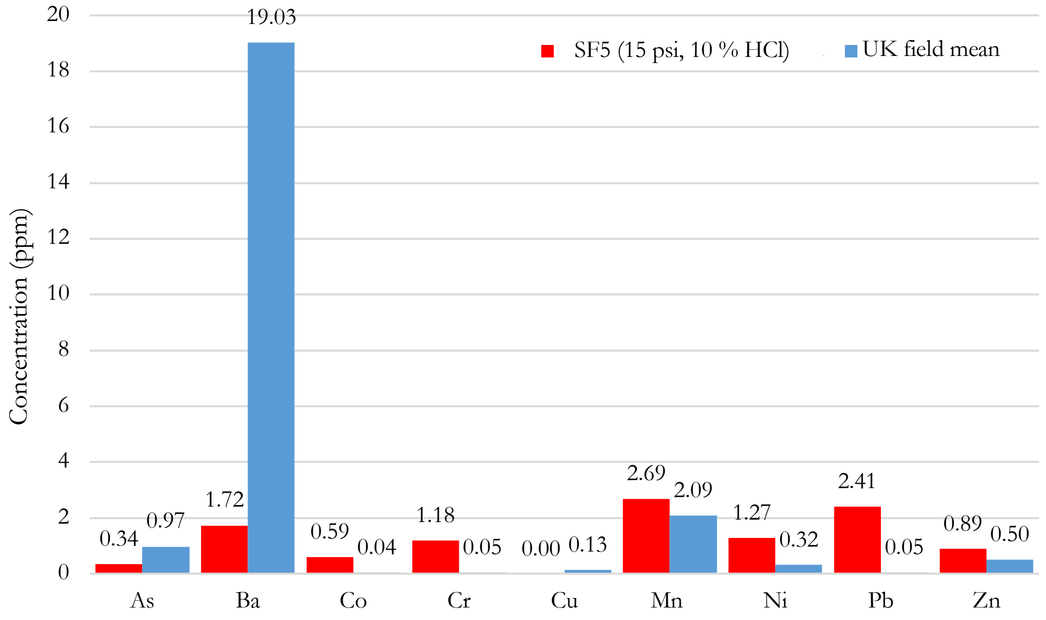


FIGURE 66 - EXPERIMENTAL VERSUS UK FIELD CONCENTRATION FOR KEY ELEMENTS (MEANS) WITH REFERENCE TO SF5 STANDARD.

The concentration of trace elements measured in UK field samples are comparable to those generated during SF5 experiments with a few notable exceptions (Figure 66). Ba was ten times more concentrated in field measurements than in experiments, whereas the metals Pb, Cr, Co, Ni and Zn were more concentrated in experiments than in field samples. The ratio of fluids to shales, the reactive surface area of powdered samples, and the lack of pore or formation water present affects the comparability of experiments to field measurements.

Although distilled water is the base fluid used in experiments, the proposed base fluid for hydraulic fracturing in the UK is local mains water, or even groundwater if the correct abstraction permits apply (UK Department of Energy and Climate Change, 2014). As distillation removes minerals, bacteria, and chemicals from the water, it is likely that the base fluid utilised in operations will contain a greater number and concentration of components affecting the chemistry of fluids returned. Distilled water was chosen for its purity, so even trace amounts of contaminants released during reactions could be detected above a relatively low ‘background’ fluid. Additionally, at depth in the sub surface, shales contain inherent formation water and pore fluids not present in any of the samples utilised for these experiments due to drying out during storage at the surface. Both the lack of pore and formation water, and the use of distilled water as a base fluid, affects the comparability of experimental results with field data.

13.10 EXPERIMENTAL SUMMARY

Experiments conducted for this thesis showed that under a variety of pressure and temperature conditions the composition of fluids after reaction with shale samples was dominated by the chemistry of the major rock forming elements. Trace elemental chemistry of these fluids was more susceptible to variation than any major element, however overall, concentrations of elements detected were much lower than in field data from the UK or the USA. Reactivity was lower in experiments with fluids containing no additives, than those conducted with a varying concentration of HCl. HCl encouraged dissolution of minerals, releasing a much wider variety and stronger concentration of elements into solution than when they experiments were conducted without any additives. Under reservoir pressure and temperature conditions the most concentrated elements released into solution were Ca, K, Mg, Mo, Na, S and Si. None of these elements are of any particular treatment concern, and all at concentrations well below the current EU drinking water quality limits.

14 CONCLUSIONS

The main findings of this thesis are:

- Disposal options for wastewater produced by onshore oil and gas operations in the UK are limited by restrictions on the underground disposal of waste.
- The predicted geochemistry of waste generated by hydraulic fracturing in the UK is treatable by existing methods, however this will cost between 2 and 26% of expected well revenue – with additional fees of up to £163,450 applicable for waste containing NORM.
- The UK has limited treatment capacity at present, with no dedicated facilities, which could pose a threat to a rapidly growing industry.
- Constituents of concern in wastewater produced by hydraulic fracturing must come from either the rock, the formation water, the injected fluids, or the chemical products generated during the interaction of these components.
- Industry disclosure of chemical use and data availability in the USA has enabled environmental regulators and treatment professionals to develop effective waste management practices for these wastes.
- Limited chemical additives are permitted in the UK in comparison with the USA, implying that the chemistry of wastes produced in the UK will be less influenced by injection fluid additives and their chemical by-products.
- The salinity of wastes will influence the economic viability of any well.
- Available oxygen during experiments significantly increased the dissolution of rock forming minerals into solution and therefore the concentration of constituents within experimental wastes. Minimising the oxygen content of

injected fluids could limit dissolution, oxidation, microbial action and ion exchange in the subsurface during fracturing.

- Heavy metal concentrations in UK field and experimental wastewaters are lower than those detected in the USA, well within treatable limits.
- Chloride concentrations in UK field wastewaters indicate salinity could be a significant treatment challenge.
- pH of wastewaters in the UK is lower than those measured in the USA – with impacts for receipt at non specialist treatment plants.
- Surface footprint of UK operations will be lower than in the USA.
- Most wastewater in the USA is reinjected for disposal, whereas this is not permitted in the UK, and treatment will be needed to manage all wastes produced.
- Silicate minerals were most abundant in shale samples however relatively unreactive, with very little Si measured in synthesised wastes.
- Clay minerals such as illite and muscovite represent up to ~ 10% of each shale sample and are the key driver of ion exchange between shales and injected fluids during fracturing.
- Carbonate minerals, while higher in US field shales, were mostly low in samples used for experiments in this study (< 3%). Carbonate minerals dissolve in the presence of HCl – releasing rock forming elements into solution such as Mg, Ca, etc. But they also act as a buffer to the acidic conditions created through the oxidation of pyrite and dissolution of CO2 during fracturing.
- The fracturing of lower carbonate content shales could result in greater concentration of constituents of concern being released into solution due to the lower buffering capacity of the rock.

- The trace geochemistry of shale minerals is dominated by Ba, V, Zr and Sr – Ba and Sr are particularly prevalent in USA wastewaters (released from exchangeable clay sites), however were not released at comparable levels in experiments.
- Surface area, as expected, significantly affected the concentration of elements released into solution – with powdered shales releasing between 0.2 and 5 times more constituents into solution than chipped shales.
- The major control on geochemistry of wastewaters produced during hydraulic fracturing is the mixing of inherent formation or porewater with injected fluids and their respective chemical by-products. The interaction between injected fluids and rock forming minerals is more likely to influence trace geochemistry.
- Temporally sampled fluids suggest an initial period of reactivity (~24h) releasing the majority of constituents into solution, followed by a scavenging of key rock forming elements such as Ca, Mg, K, Na, and Si up to one week after.
- Over a longer time period, these same elements are continually released into solution at concentrations that eventually exceed those measured after 24h.

15 APPENDICES

15.1 TABLE OF COMMON HYDRAULIC FRACTURING ADDITIVES

ADDITIVE	PURPOSE[1,2]	MAIN COMPOUND(S)
ACID[1,2,3,4]	Cleans up perforation intervals of cement and drilling mud prior to fracturing fluid injection, and provides accessible path to formation.	Hydrochloric acid or muriatic acid
BIOCIDE[1,2,3,4]	Inhibits growth of organisms that could produce gases (particularly hydrogen sulfide) that could contaminate methane gas. Also prevents the growth of bacteria which can reduce the ability of the fluid to carry proppant into the fractures.	Glutaraldehyde
BREAKER[1,2,4]	Reduces the viscosity of the fluid in order to release proppant into fractures and enhance the recovery of the fracturing fluid.	Ammonium persulfate
CLAY STABILISER[2,4]	Prevents swelling and migration of formation clays which could block pore spaces thereby reducing permeability.	
CORROSION INHIBITOR[1,2,3,4]	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid).	N, n-dimethyl fomamide
CROSSLINKER[1,2,4]	The fluid viscosity is increased using phosphate esters combined with metals. The metals are referred to as crosslinking agents. The increased fracturing fluid viscosity allows the fluid to carry more proppant into the fractures.	Borate salts
FRICTION REDUCER[1,2,3,4]	Allows fracture fluids to be injected at optimum rates and pressures by minimising friction.	Polyacrylimide or Mineral oil
GEL[1,4]	Increases fracturing fluid viscosity, allowing the fluid to carry more proppant into the fractures.	Gura gum or Hydroxyethyl
IRON CONTROL[1,2,3,4]	Prevents the precipitation of metal oxides which could plug off the formation.	Citric acid
SALTS[1,3]	Creates a brine carrier fluid.	Potassium chloride
OXYGEN SCAVENGER[1,4]	Removes oxygen from the fluids to prevent corrosion of infrastructure.	Ammonium bisulphate
PH ADJUSTMENT[1,3]	Maintains the effectiveness of other additives, such as crosslinkers.	Sodium or potassium carbonate
PROPPANT[1,2,3,4]	"Props" open fractures and allows gas / fluids to flow more freely to the well bore.	Silica, quartz sand
SCALE INHIBITOR[1,2,3,4]	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation.	Ethylene glycol
SURFACTANT[1,2,3,4]	Reduces fracturing fluid surface tension thereby aiding fluid recovery.	Isopropanol

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15.2 UK AND USA WATER QUALITY LIMITS

CONTAMINANT	UG/L (UNLESS OTHERWISE DENOTED)					UG/L (UNLESS OTHERWISE DENOTED)	
	UK					USA	
	FRESH WATER		SALT WATER		DRINKING WATER	DRINKING WATER	
	LONG-TERM (MEAN)	SHORT-TERM (95^{TH}%-ILE)	LONG-TERM (MEAN)	SHORT-TERM (95^{TH}%-ILE)	PRESCRIBED CONCENTRATION VALUE (PCV)	MAXIMUM CONCENTRATION LIMIT (MCL)	PUBLIC HEALTH GOAL
ALPHA PHOTON EMITTERS†						15PCI/L	0
BETA PHOTON EMITTERS†						4 MILLIREMS/YR	0
AMMONIA * Φ (UNIONISED)			21		500		
ALUMINIUM◊Φ	15		15		200	200	
ANTIMONY†Φ					5	6	5
ARSENIC*†Φ	50		25		10	10	0
ASBESTOS†						7 MILLION FIBRES PER LITRE (MFL)	7 MFL
BARIUM†						2000	0
BERYLLIUM†						4	4
BORONΦ					1000		
BROMATE†Φ					10	10	0
BROMINE	2	5	NONE	10			
CADMIUM†Φ	0.25		0.2		5	5	5
CHROMIUM (III) *†Φ	4.7	32			50	100	100
CHROMIUM (VI) *†Φ	3.4		0.6	32	50		
CHLORINE*†◊Φ	2	5		10	NONE	4000	4000
CHLORIDE◊Φ	250000				250000		
COBALT	3	100	3	100			
COPPER*†◊Φ	1 (BIOAVAILABLE)		3.76 WHERE DOC ≤1MG/L		2000	1300	1300
CYANIDE*†	1	5	1	5		200	200
FLUORIDE†◊Φ	1000 (<50 MG CACO3/L) 5000 (>50 MG CA\CO3/L)	3000 (<50 MG CACO3/L) 15000 (>50 MG CA\CO3/L)	5000	15000	1500	4000	4000
IRON*◊Φ	1000		1000		200	300	
LEAD†◊Φ					10	15	0
MANGANESE*◊Φ	123 (BIOAVAILABLE)				50		
MERCURY†Φ					1	2	2
NICKELΦ					20		
NITRATE†◊Φ					50000	10000	10000
NITRITE†◊Φ					500	1000	1000
RADIUM$^{226+228}$†						5 PCI/L	0
SELENIUM†Φ					10	50	50
SILVER	0.05	0.1	0.5	1			
SODIUM ◊Φ	NONE PROPOSED	NONE PROPOSED	NONE PROPOSED	NONE PROPOSED	200000		
SULPHATE ◊Φ	4000000	-	NONE PROPOSED	-	250000		
THALLIUM†						200	0.5
URANIUM†						30	0
VANADIUM	20 (CLASS 1) - 60 (CLASS 2)	-	100	-			
ZINC*	10.9 (BIOAVAILABLE) + AMBIENT BACKGROUND		7.9				

* Water Framework Directive implementation in England and Wales: new and updated standards to protect water environment (May 2014)

† United States Environmental Protection Agency, National Primary Drinking Water Regulations (May 2009)

◊ Scottish Water – Water Quality Standards Explained, Factsheet 2 (March 2015)

Φ Anglian Water – Drinking Water Standards according to the Water Supply (Water Quality) Regulations (2000)

15.3 MONTE CARLO SIMULATION METHODS

Each Monte Carlo simulation was run with 10,000 iterations using R[1]. The input parameters used are listed in the following table, and the input equations are also described below. Uniform distributions were assumed between end-member data points. Results are presented showing the $P_{2.5}$, P_{50} and $P_{97.5}$ values, therefore indicating the 95% confidence interval and the median of each simulation. Cumulative frequency distributions (CDFs) are also provided, with the $P_{2.5}$ and $P_{97.5}$ values marked in solid colour corresponding lines, and the P_{50} values with dashed lines.

15.3.1 COST SIMULATION RESULTS

PROJECTED COSTS ($)	P_1	$P_{2.5}$	P_{50}	$P_{97.5}$	P_{99}
REVERSE OSMOSIS	814.96	2,701.73	24,846.46	94,815.38	132,904.08
MECHANICAL VAPOR COMPRESSION	955.61	3,952.76	50,506.23	196,484.74	270,996.33
COMBINED (EUREKA RESOURCES)	57,815.40	107,683.1	459,472.27	1,376,093.80	1,819,846.90

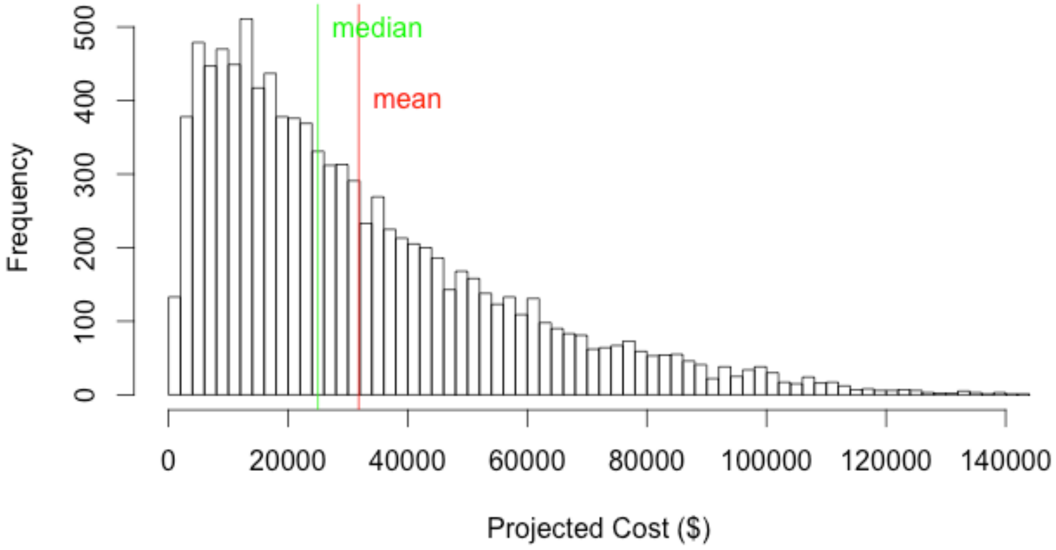


FIGURE 67 –PROJECTED COSTS FOR REVERSE OSMOSIS WITH MEAN AND MEDIAN MARKED

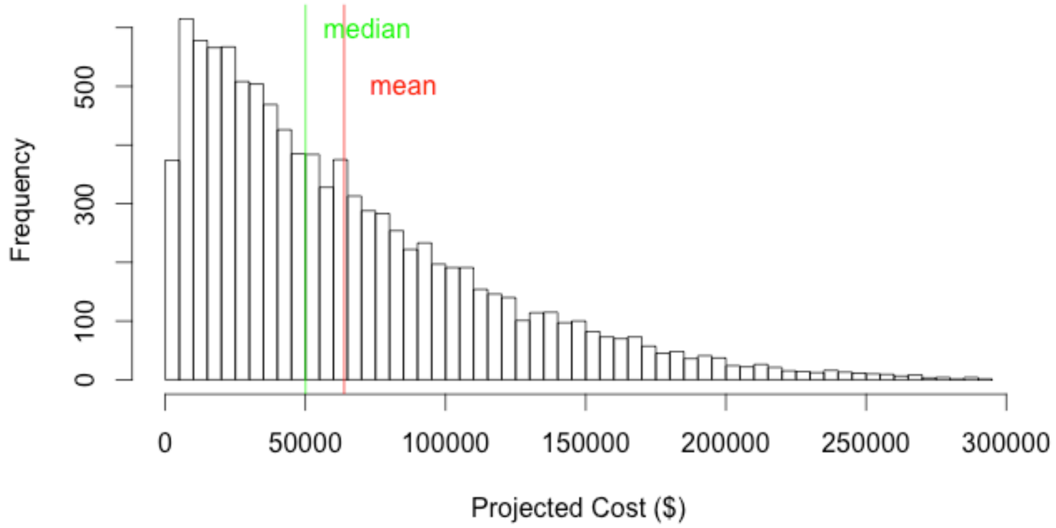


FIGURE 68 – PROJECTED COSTS FOR MECHANICAL VAPOUR COMPRESSION, MEAN AND MEDIAN MARKED

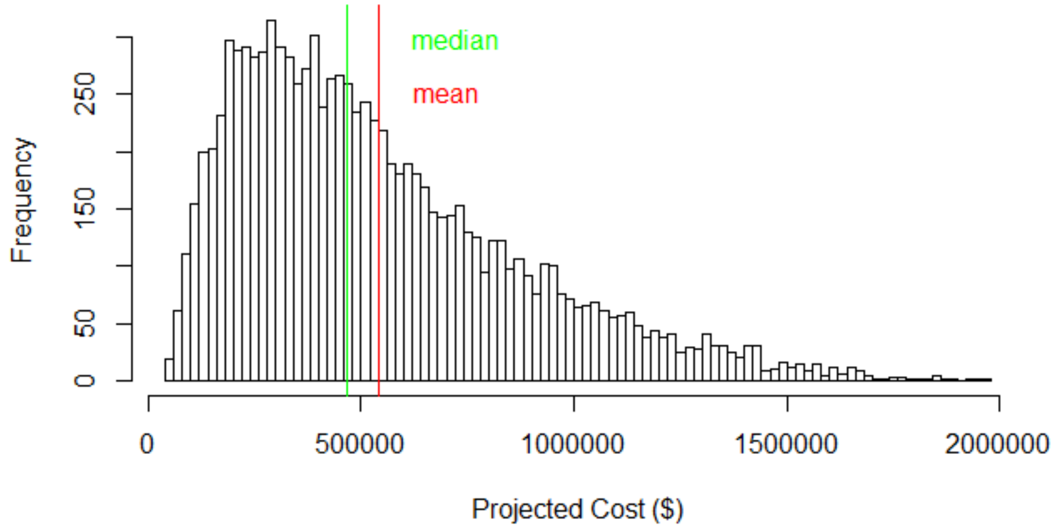


FIGURE 69 – PROJECTED COSTS FOR COMBINED TREATMENT TECHNIQUES, MEAN AND MEDIAN MARKED

15.4 TREATMENT TECHNOLOGIES: ENERGY AND COST INTENSIVENESS

15.4.1 REPORTED RANGE IN COST OF TREATMENT TECHNIQUES

TREATMENT	**SOURCE**	**COMPARATIVE MEAN**	***UNITS***	**MINIMUM**	***UNITS***	**MAXIMUM**	***UNITS***
REVERSE OSMOSIS <50,000 MG/L	(IGUNNU AND CHEN, 2014)	2.16	$\$/M^3$	0.19 10,000 MG/L	$/BBL	0.50 35,000 MG/L	$/BBL
	(HARTO, 2014)	2.14	$\$/M^3$	0.13	$/BBL	0.21	$/BBL
	(MITTAL *ET AL.*, 2012)	5.03	$\$/M^3$	0.2	$/BBL	0.6	$/BBL
	(ALLEMAN AND ALL CONSULTING, 2010)	12.33	$\$/M^3$	0.42	$/BBL	3.5	$/BBL
MECHANICAL VAPOUR COMPRESSION >50,000 MG/L	(IGUNNU AND CHEN, 2014)	0.5	$\$/M^3$	0.08 >40,000PPM	$/BBL	0.08	$/BBL
	(HARTO, 2014)	1.32	$\$/M^3$	0.21	$/BBL	0.21	$/BBL
	(ALLEMAN AND ALL CONSULTING, 2010)	25.16	$\$/M^3$	3.00	$/BBL	5.00	$/BBL
	(LARA, OSUNSAN AND HOLTZAPPLE, 2011)	0.83	$\$/M^3$	0.42	$\$/M^3$	1.24	$\$/M^3$
UNDERGROUND DISPOSAL BY INJECTION	(HARTO, 2014)	1.20	$\$/M^3$	0.19	$/BBL	0.19	$/BBL
	(HAGSTROM *ET AL.*, 2016)	16.98	$\$/M^3$	0.05	$/BBL	2.65	$/BBL
	(JIANG, HENDRICKSON AND VANBRIESEN, 2014)	6.8	$\$/M^3$	0.59	$\$/M^3$	13.00	$\$/M^3$
	(MITTAL *ET AL.*, 2012)	10.50	$\$/M^3$	0.07	$/BBL	1.6	$/BBL
	(MOORE, WANG AND ACHARYA, 2010)	25.16	$\$/M^3$	1	$/BBL	3	$/BBL
	(FAKHRU'L-RAZI *ET AL.*, 2009)	16.98	$\$/M^3$	0.05	$/BBL	2.65	$/BBL

15.4.2 REPORTED RANGE IN ENERGY INTENSITY OF TREATMENT TECHNIQUES

TREATMENT TECHNIQUE	ABBREVIATION	SINGLE VALUE	LOW	HIGH
		KWH/M3	KWH/M3	KWH/M3
MECHANICAL VAPOUR COMPRESSION	MVC(SHAFFER *ET AL.*, 2013)	13.6		
MECHANICAL VAPOUR COMPRESSION	MVC(SHAFFER *ET AL.*, 2013)		10.4	11.2
MEMBRANE DISTILLATION	MD(SHAFFER *ET AL.*, 2013)	680		
MEMBRANE DISTILLATION	MD(SHAFFER *ET AL.*, 2013)	40		
MULTI-STAGE FLASH DISTILLATION	MSF(ABDEL-JAWAD, 2001)		15.32	16.72
MULTI-EFFECT DISTILLATION	MED(ABDEL-JAWAD, 2001)		9.73	13.65
MECHANICAL VAPOUR COMPRESSION	MVC(ABDEL-JAWAD, 2001)		11	12
THERMAL VAPOUR CRYSTALLISATION	TVC(ABDEL-JAWAD, 2001)	14.56		
REVERSE OSMOSIS	RO(ABDEL-JAWAD, 2001)		2.1	6.4
ELECTRODIALYSIS	ED(ABDEL-JAWAD, 2001)		2.64	5.5
MULTI-STAGE FLASH DISTILLATION	MSF(AL-KARAGHOULI AND KAZMERSKI, 2012)		19.58	27.25
MULTI-EFFECT DISTILLATION	MED(AL-KARAGHOULI AND KAZMERSKI, 2012)		14.45	21.35
MECHANICAL VAPOUR COMPRESSION	MVC(AL-KARAGHOULI AND KAZMERSKI, 2012)		7	12
THERMAL VAPOUR CRYSTALLISATION	TVC(AL-KARAGHOULI AND KAZMERSKI, 2012)	16.26		
SEA-WATER REVERSE OSMOSIS	SWRO(AL-KARAGHOULI AND KAZMERSKI, 2012)			
BRACKISH WATER REVERSE OSMOSIS	BWRO(AL-KARAGHOULI AND KAZMERSKI, 2012)			
ELECTRODIALYSIS	ED(AL-KARAGHOULI AND KAZMERSKI, 2012)			
NANOFILTRATION	NF(IGUNNU AND CHEN, 2014)	0.50		
SEA-WATER REVERSE OSMOSIS	SWRO(IGUNNU AND CHEN, 2014)		2.89	4.21
BRACKISH WATER REVERSE OSMOSIS	BWRO(IGUNNU AND CHEN, 2014)		0.13	0.82

MULTI-STAGE FLASH DISTILLATION	MSF(IGUNNU AND CHEN, 2014)		21.07	29.56
MECHANICAL VAPOUR COMPRESSION	MVC(IGUNNU AND CHEN, 2014)		26.42	66.04
MECHANICAL VAPOUR COMPRESSION	MVC(ZIMERMAN, 1994)	6.1		
MECHANICAL VAPOUR COMPRESSION	MVC(VEZA, 1995)		10.4	11.2
MECHANICAL VAPOUR COMPRESSION	MVC(ALY AND EL-FIQI, 2003)		6	16
MECHANICAL VAPOUR COMPRESSION	MVC(AL-SAHALI AND ETTOUNEY, 2007)		10	14
MULTI-EFFECT DISTILLATION	MED(AL-SAHALI AND ETTOUNEY, 2007)	15		
MULTI-STAGE FLASH DISTILLATION	MSF(AL-SAHALI AND ETTOUNEY, 2007)	18		
REVERSE OSMOSIS	RO(AL-SAHALI AND ETTOUNEY, 2007)	5		
MULTI-STAGE FLASH DISTILLATION	MSF(AL-KARAGHOULI AND L.KAZMERSKI, 2013)		19.58	27.25
MULTI-EFFECT DISTILLATION	MED(AL-KARAGHOULI AND L.KAZMERSKI, 2013)		14.45	21.35
MECHANICAL VAPOUR COMPRESSION	MVC(AL-KARAGHOULI AND L.KAZMERSKI, 2013)	16.26		
REVERSE OSMOSIS	RO(AL-KARAGHOULI AND L.KAZMERSKI, 2013)		1.5	2.5
ELECTRODIALYSIS	ED(AL-KARAGHOULI AND L.KAZMERSKI, 2013)		0.7	5.5

15.5 REPORTED RANGE IN WATER VOLUMES REQUIRED FOR HYDRAULIC FRACTURING

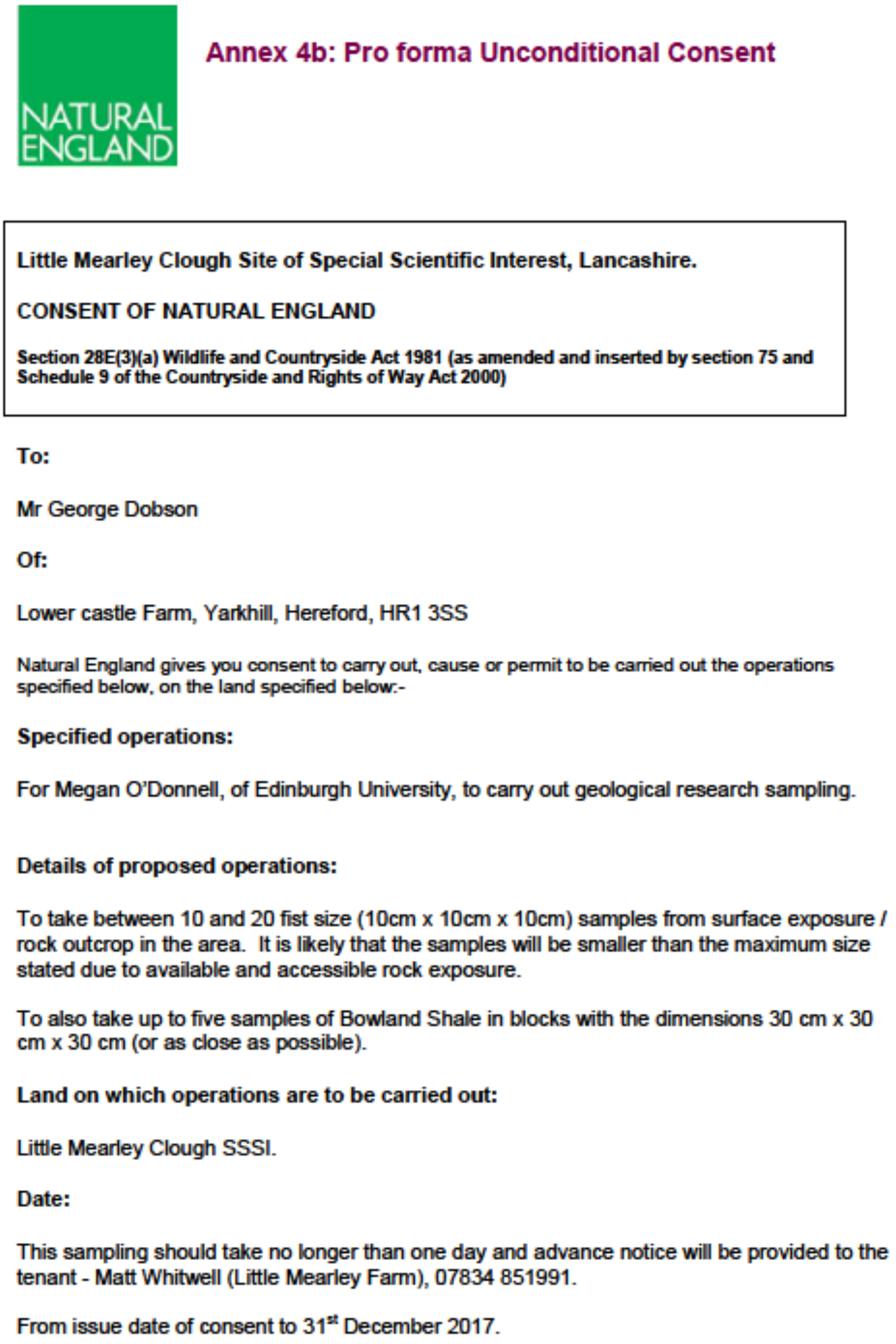
	DRILLING (M^3)		FRACTURING (M^3)		TOTAL (M^3)	
LOCATION$^{(SOURCE)}$	LOW / INDIVIDUAL	HIGH	LOW / INDIVIDUAL	HIGH	LOW / INDIVIDUAL	HIGH
BARNETT(SPELLMAN, 2017)	1818		10,465		12,274	
FAYETTEVILLE(SPELLMAN, 2017)	273		12,814		13.456	
HAYNESVILLE(SPELLMAN, 2017)	4546		12,274		16,821	
MARCELLUS(SPELLMAN, 2017)	364		17,275		17,639	
MARCELLUS(GREGORY, VIDIC AND DZOMBAK, 2011)	400	4,000	7,000	18,000	7400	22,000
U.S.A.(GALLEGOS AND VARELA, 2015)					14,000	33,900
U.S.A.(GALLEGOS AND VARELA, 2015)					10	36,620
BARNETT(CLARK, HORNER AND HARTO, 2013)	920		6800	23,500	7720	24,420
FAYETTEVILLE(CLARK, HORNER AND HARTO, 2013)	70		14,000	25,400	14,070	25,470
HAYNESVILLE(CLARK, HORNER AND HARTO, 2013)	1,080		129,000	334,000	130,080	335,080
MARCELLUS(CLARK, HORNER AND HARTO, 2013)	670		9900	22,000	10,570	22,670
COLORADO(GOODWIN *ET AL.*, 2014)	311	764	10,820	17,184	11,131	17,948
COLORADO(GOODWIN *ET AL.*, 2014)					6365	34,096
BAKKEN(HORNER *ET AL.*, 2016)					8728	10,744
MARCELLUS(JIANG, HENDRICKSON AND VANBRIESEN, 2014)	300	380	3500	26,000	2600	21,000
MARCELLUS(KARGBO, WILHELM AND CAMPBELL, 2010)					9,092	45,461
BARNETT(NICOT AND SCANLON, 2012)			10,600			
HAYNESVILLE(NICOT AND SCANLON, 2012)			21,500			
EAGLEFORD(NICOT AND SCANLON, 2012)			16,100			
MARCELLUS(VIDIC *ET AL.*, 2013)			9,092	31,823		
U.S.A.(COOLEY *ET AL.*, 2012)	182	4546	10,456	17,275		

BARNETT(NICOT *ET AL.*, 2011)			<4546	36,369		
HAYNESVILLE/BOSSIER(NICOT *ET AL.*, 2011)			4546	45,461		
EAGLEFORD(NICOT *ET AL.*, 2011)			<4546	59,099		
WOODFORD/PEARSALL(NICOT *ET AL.*, 2011)			<4546	22,730		
MARCELLUS(COOLEY *ET AL.*, 2012)			11,365			
U.S.A.(ENTREKIN *ET AL.*, 2011)					9,092	31,823
POLAND(VANDECASTEELE *ET AL.*, 2015)					8,000	19,000
BARNETT(KONDASH AND VENGOSH, 2015)					17,275	
EAGLEFORD(KONDASH AND VENGOSH, 2015)					16,411	
FAYETTEVILLE(KONDASH AND VENGOSH, 2015)					24,049	
HAYNESVILLE(KONDASH AND VENGOSH, 2015)					19,321	
MARCELLUS(KONDASH AND VENGOSH, 2015)					17,73	
NIOBARRA(KONDASH AND VENGOSH, 2015)					28,504	
WOODFORD(SETH *ET AL.*, 2013)					13,638	36,369

15.6 REPORTED RANGE IN WASTEWATER VOLUMES AS PERCENTAGE OF INJECTED FLUIDS

LOCATION	LOW / INDIVIDUAL	HIGH	REFERENCE
MARCELLUS SHALE, USA	10	40	GREGORY, VIDIC & DZOMBAK, 2011
USA	5	40	GALLEGOS ET AL., 2015
USA	9	53	
BARNETT SHALE, USA	60		NICOT ET AL., 2014
MARCELLUS SHALE, USA	10	30	NYSDEC, 2011
POLAND	5	50	VANDECASTEELE ET AL., 2015
USA	10	30	EPA, 2012
	4	40	LI ET AL., 2017
	70		HE ET A.L 2015
USA	10		SHIPMAN ET AL., 2013
USA	10	70	LESTER ET AL., 2015
USA	30	70	VEIL, 2010

15.7 PRO-FORMA OF UNCONDITIONAL CONSENT FOR GEOLOGICAL RESEARCH SAMPLING



NATURAL ENGLAND

Annex 4b: Pro forma Unconditional Consent

Little Mearley Clough Site of Special Scientific Interest, Lancashire.

CONSENT OF NATURAL ENGLAND

Section 28E(3)(a) Wildlife and Countryside Act 1981 (as amended and inserted by section 75 and Schedule 9 of the Countryside and Rights of Way Act 2000)

To:

Mr George Dobson

Of:

Lower castle Farm, Yarkhill, Hereford, HR1 3SS

Natural England gives you consent to carry out, cause or permit to be carried out the operations specified below, on the land specified below:-

Specified operations:

For Megan O'Donnell, of Edinburgh University, to carry out geological research sampling.

Details of proposed operations:

To take between 10 and 20 fist size (10cm x 10cm x 10cm) samples from surface exposure / rock outcrop in the area. It is likely that the samples will be smaller than the maximum size stated due to available and accessible rock exposure.

To also take up to five samples of Bowland Shale in blocks with the dimensions 30 cm x 30 cm x 30 cm (or as close as possible).

Land on which operations are to be carried out:

Little Mearley Clough SSSI.

Date:

This sampling should take no longer than one day and advance notice will be provided to the tenant - Matt Whitwell (Little Mearley Farm), 07834 851991.

From issue date of consent to 31st December 2017.

15.8 COMPARISON OF TRACE ROCK GEOCHEMISTRY FROM XRF AND WHOLE ROCK DIGESTION

(mg/l)

FIGURE 70 – COMPARISON BETWEEN THE ANALYTICAL RESULTS OF THE SAME SHALE SAMPLE BY XRF AND WHOLE ROCK ACID DIGESTION, FOLLOWED BY ICP-OES. GREY BARS SHOW RESULTS OBTAINED BY ROCK DIGESTION AND ICP-OES, AND WHITE BARS SHOW RESULTS AS PER XRF. RESULTS ARE COMPARABLE, WITH XRF OVERESTIMATING BA, CR, NI AND ZN SLIGHTLY.

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