# FORMATION AND ATTACHMENT OF SOLIDS WITHIN A PIPELINE EMANATING FROM A NUCLEAR EFFLUENT TREATMENT PLANT

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## **ABBREVIATIONS**

BAT	-	Best Available Technique
BST	-	Bulk Storage Tanks
BNFL	-	British Nuclear Fuel
CCTV	-	Closed Circuit Television
CfA	-	Condition for Acceptance
DI	-	Deionised water
EA	-	Environment Agency
EARP	-	Enhanced Actinide Removal Plant
EDX	-	Energy Dispersive X-Ray
GDF	-	Geological Disposal Facility
ICP-AES	-	Inductively Coupled Plasma Atomic Emission Spectroscopy
ILW	-	Intermediate Level Waste
HDPE	-	High-density polyethylene
LbL	-	Layer by Layer
MWCO	-	Molecular Weight Cut Off
NNL	-	National Nuclear Laboratories
OSPAR	-	Oslo and Paris Convention on the Protection of the Marine Environment of the North East Atlantic
РВО	-	Parent Body Organisation
PEM	-	Polyelectrolyte multilayers
РОСО	-	Post Operational Clean Out
pXRD	-	Powder X-Ray Diffraction
RBS	-	Rutherford Backscatter Spectroscopy
SCP	-	SIXEP Contingency Plant
SEM	-	Scanning Electron Microscopy
SIXEP	-	Site Ion Exchange Plant or Site Ion Exchange Effluent Plant
SL	-	Sellafield Limited
SLC	-	Site Licensed Company

#### **ABSTRACT**

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The Site Ion Exchange Plant (SIXEP) (Sellafield, Cumbria, UK) treats spent nuclear fuel storage pond liquors by utilising sand bed filtration to remove Mg containing particulates present in the effluent followed by an ion exchange process to remove Cs and Sr. Clinoptilolite (Na<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) the ion exchange media. After treatment the effluent is discharged to sea. During inspections of the discharge line a significant solid formation was encountered in the mid-2000s. The solid was poorly characterised and limited analysis was performed. At the time biofilm was suggested as the means of adhering a fine fraction of clinoptilolite to the pipeline surface.

Three areas of study were investigated in order to identify the source and means of these solids adhering to the discharge pipeline surface. These were: the precipitation of mineral phases from a variety of possible discharge effluent compositions; the dissolution/degradation of clinoptilolite under process like conditions including  $\gamma$ -radiation exposure; and the demonstration of the performance of polyelectrolyte as an adsorption medium when contacted with a clinoptilolite solution onto stainless steel surfaces.

Mineral phases from a range of likely SIXEP effluent compositions have been precipitated from static solution conditions. The predominantly aluminosilicate containing solids have similar characteristics (elemental composition and morphology) to the solid from the discharge line, but this is based upon limited and poor characterisation data from the recovered material. Dissolution studies of clinoptilolite displayed a fine fraction release into solution irrespective of the inclusion of a prewashing step. An incongruent release of Si from clinoptilolite was observed which was not considered in the original model put forward for this pipe fouling phenomenon. The presence of colloidal Si was found to increase in irradiated clinoptilolite samples (50 MGy total dose) when compared to unirradiated material. Polyelectrolyte was found to cause fine fractions of clinoptilolite to adhere to a stainless steel surface (304L) and as a result provides an additional attachment mechanism for solids within the pipeline to what has been previously proposed.

Following this work, it is suggested that the primary mechanism to justify this solids formation in the SIXEP discharge line is that the presence of polyelectrolyte and biofilms causes adsorption of clinoptilolite fines and colloids onto the inner pipe surface. Reprecipitation of aqueous species released through incongruent dissolution of the clinoptilolite should be considered as minor bulking agents to the main clinoptilolite fines solid.

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Chapter 1 – Introduction

#### 1) Introduction

The chapter seeks to provide a brief overview of the nuclear industry, along with an introduction to effluent management and the research undertaken on the effluent treatment plant.

#### a) Nuclear fuel cycle

The nuclear industry is well established (> 60 years) and at the heart of the industry is the nuclear fuel cycle. Within the UK nuclear reactor fleet there are two main types of fuel either natural uranium metal (Magnox fuel) or uranium oxide fuel used in advanced gas cooled reactor and pressurised water reactor. There are two options available to nuclear plant operators for the back end of the fuel cycle: either a once through cycle where nuclear material is placed into storage after use (for eventual disposal); or reprocessing of fuel for separation of fissile materials to recover reusable elements.

The Sellafield site (Cumbria, UK) has had a long association with the nuclear industry and its initial purpose was to produce plutonium for military uses[1]. Subsequently the site was used for civilian power generation and this in turn led to reprocessing operations of spent fuel[1]. More recently the site is transitioning from reprocessing to decommissioning operations. However there is a significant legacy in nuclear inventory that must treated and/or immobilised for subsequent disposal.

The fuel rods contain a cladding that must be removed prior to reprocessing. In the case of Magnox fuel elements the resulting swarf has been stored in "wet" conditions in silos. Reprocessing operations have been undertaken throughout the life of the industry and these endeavours have focused on the extraction of reusable fissile material[2] either for civilian or military purposes. Storage ponds have been utilised for the interim storage of fuel elements prior to reprocessing operations. The reprocessing of Magnox fuel was halted for a significant period of time and this has resulted in corrosion of the fuel cladding elements[3]. Due to extended periods of storage a corroded Magnox sludge formed that contained fuel cladding and fuel elements along with fission products[4]. These open air storage ponds along with other sources of effluent continuously generate a significant quantity of waste water. The effluent is treated prior to discharge to the Irish Sea.

Effluent management performs a vital function for site operations in both reprocessing and decommissioning activities. On the Sellafield site there are two main effluent treatment processes to enable safe discharge of treated liquors. These are Site Ion Exchange Plant (SIXEP) [Also known as site ion exchange effluent plant in some literature] and Enhanced Actinide Removal Plant (EARP). There are other low active effluent plants located on the Sellafield site but SIXEP and EARP are the main plants treating effluent and discharge to sea. Since commissioning of SIXEP (mid 1980s) and EARP (late 1980s) there has been a significant reduction in discharges to sea, with a reduction in Alpha ( $\alpha$ ) and Beta ( $\beta$ ) emitters recorded [5].

#### b) Site ion exchange plant

The primary purpose of SIXEP is to remove Cs and Sr from the first generation Magnox storage ponds. A continuous flow of effluent is produced as the ponds are purged daily producing around 3000 m<sup>3</sup> of highly alkaline effluent to be treated[3, 4]. SIXEP utilises two types of particulate removal. An initial sand bed filter[3, 4] dosed with a polyelectrolyte (currently polygold CL520) to remove larger Mg solids. Ion exchange[3, 4] is the second technique which removes Cs and Sr using Clinoptilolite, a natural mineral

part of the heulandite group[6]. A simplified schematic (Fig. 1.1) has been produced which includes the carbonation [3, 4] tower that reduces the pH from around pH 10 to 11 to achieve an optimal ion exchange performance at  $^{pH7}$ .

Several reports have been undertaken for the Sellafield site to characterise the pH and constituents. The area of interest to this research is the discharge line directly downstream of the SIXEP plant, i.e. the pipeline emanating from the discharge tank. To complicate matters there is a sea discharge line that takes numerous feed lines, of which the discharge line emanating from SIXEP is one such feed, from the whole Sellafield site.



Figure 1.1 - SIXEP schematic: high pH (pH ~10) incoming feed undergoes sand bed filtration to remove Mg rich particulates and then undergoes pH reduction (pH~7) in the carbonation tower, after which the effluent undergoes ion exchange to remove Cs and Sr prior to discharge to sea

#### c) The problem

Significant solids were encountered within the discharge pipeline following closed circuit television (CCTV) inspection surveys undertaken in April and November 2004. The solids recovered were characterised (Chapter 2) and were found to contain similarities to that of clinoptilolite, the ion exchange media utilised within the treatment plant. Due to the nature of the solids and radioactivity of these solids (Chapter 3) attempts were made to provide a mechanism for formation to provide justification for the formation of these solids to the environmental regulator (Environment Agency, EA).

The effluent plant treats a significant volume of effluent every day due to constant effluent feed from storage ponds. Losses from the ion exchange or sand beds, however small, can contribute to a significant mass of solids within the discharge pipeline due to the large volumes of bed masses (~7400 kg) and large volume of effluent treated per day (~ 3000 m<sup>3</sup>). The plant has been in operation since the mid-1980s therefore a significant mass of solids may have been retained within the discharge line. This was the assumption to be investigated by the mid 2000s CCTV inspections. A solid was recovered during a CCTV inspection from break in point G9 prior to the pipe bridge and after the SIXEP finals tank (Fig. 1.2).

A significant mass of solids was evident in the first CCTV inspection (April 2004) but a subsequent survey (November 2004) did not identify the solids in the same area. The problem has been encountered intermittently since these surveys and a pressure increase within the discharge line has been taken as indication of the occurrence of solids build-up.



Figure 1.2 - G9 break in point and extent of CCTV camera inspection undertaken in 2004. Location of deposit within the extent of the camera inspection. Exact location unknown.

Pipeline pressure build-ups have been used to identify increases in deposit mass within the pipeline[7]. These pressure build-ups and reductions have been used to identify solid formations and subsequent release of solids caused by flow induced shear in the solid formations. Recent observations have indicated a reduction of pressure within the line following a series of pressure increases and subsequent pressure drops[7].

### d) Research areas

The research aims are detailed after the review of existing Sellafield Ltd (SL) reports (Chapter 2) relating to the solid formations encountered in the discharge line. The research area that this work seeks to address relates to the geochemistry and mineralogical formation of likely and representative solids that could be encountered in the discharge line.

Furthermore the performance of the ion exchange mineral will be studied to determine whether the clinoptilolite could contribute to the solid formations encountered previously. Polyelectrolyte (Polygold CL520) as used within the plant, has been investigated as a means of attaching any possible solids found in the discharge line to pipeline surfaces.

#### e) Funding

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Industrial supervision of the project (as required by the Nuclear EngD) has been provided by National Nuclear Laboratory (NNL) through a separate funding agreement between Sellafield Ltd and NNL.

#### f) Thesis structure

This thesis is presented in the "alternative format" with a brief overview of the chapters:

- Chapter 2 Internal report review
  - A review of internal SL reports relating to the solid formation and associated characterisation efforts undertaken on the previously recovered solids including a review of the initial flow sheet development work for SIXEP.
- Chapter 3 Research context

- A requirement of the EngD qualification and how the research work undertaken for the thesis relates to the sponsor company (SL) and context discussions.
- Chapter 4 Experimental methods
  - A brief discussion of the key pieces of characterisation equipment and associated equipment used for the collection and characterisation for this work.
- Chapter 5 Precipitation of likely solids from analogous effluent constituents
  - Paper 1: A methodology to produce likely mineral phases with limited characterisation of previously recovered solids, undertaken using initial modelling and subsequent experimental work.
- Chapter 6 Congruent and incongruent dissolution of clinoptilolite
  - Paper 2: A means to determine whether fines generation could form part of the solid formations encountered within the discharge line. An investigation of incongruent dissolution that could lead to the generation of elemental concentrations leading to the formation of mineral phases.
- Chapter 7 The gamma irradiation effects on clinoptilolite
  - Paper 3: A follow up to paper 2 considering the effects of gamma irradiations (<sup>60</sup>Co source) and impacts upon the structure and dissolution performance against a non-irradiated sample.
- Chapter 8 Performance of polyelectrolyte as an adsorption mechanism for clinoptilolite
  - Paper 4: Investigation of stainless steel surfaces that have been immersed in a polyelectrolyte solution containing clinoptilolite to determine whether

polyelectrolyte could contribute to the adsorption of solids within the pipeline.

- Chapter 9 Concluding remarks
  - $\circ$   $\,$  Conclusions relating to problem under investigation and implications for

plant operations along with suggestions for further work in this area.

## Chapter 2 – Sellafield reports and project aims

#### 2) Internal report review

Due to the large number of internal reports relating to the Site Ion Exchange Plant (SIXEP) also known as Site Ion Exchange Effluent Plant and associated processes, a significant review of all work relating to the SIXEP is presented in this chapter. A wider literature review has not been presented. Published literature has been reviewed and incorporated in subsequent chapters to avoid repetition, forming part of the alternative thesis format, i.e. via papers.

Sellafield Ltd (SL) and companies previously responsible for managing the Sellafield site have undertaken numerous projects relating to: solid formations encountered within the discharge pipeline from SIXEP, and characterisation and performance enhancement of the ion exchange process used in SXIEP. All of the work undertaken on behalf of SL is presented in internal reports which the outside reader would usually be unable to access. As such this section aims to provide a detailed summary of work that is of relevance to further chapters contained herein. It attempts to provide justification of the chosen aims and objectives of the work described in this thesis investigated via experimentation and modelling.

Wherever possible the units used when describing various quantities and parameters have been a direct transposition of those presented in each report. Some anomalous units have been identified, specifically within the inorganic feed concentrations to SIXEP. There has been a case of unit error within one of the reports that has been identified via subsequent discharge line monitoring data undertaken for this project.

A review of reports has been undertaken and will be split into sections that relate to the nature of the content. The main focus for this work concentrates on characterisation of

solids, attachment mechanism (primarily bio films) and characterisation of the ion exchange medium (clinoptilolite).

#### a) Mud hills Clinoptilolite

The ion exchange medium used in the plant operations is a natural clinoptilolite mined from a specific location within the Mud Hills deposit from the Mojave Desert, California [8]. An idealised formula of Clinoptilolite is Na<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O. There are a number of different cations present within the exchange sites that have substituted for the Na. Typically these are K, Ca, and Mg. With these substitutions present the definitive formula of clinoptilolite is very difficult to pinpoint due to the heterogeneous state of the natural mineral [8].

Following the initial "Harwell trials" for the pilot plant trials and flow sheet development for the use of clinoptilolite as an ion exchange medium for the removal of radioactive Cs and Sr, there have been additional studies on Clinoptilolite performance. The most recent characterisation effort was undertaken in 1995 [8] which included both mineralogical and chemical composition data.

X- ray powder diffraction (pXRD) was undertaken on a clinoptilolite sample with the following minor mineral phases identified in addition to the bulk clinoptilolite; quartz, haematite, albite and possibly magnetite and an unassigned clay identified in addition to the bulk clinoptilolite[8]. Minor carbonate minerals, probably calcite or dolomite [8], have been identified via petrographic microscopy. The presence of Erronite in the Clinoptilolite was also suggested and as a consequence control measures during site operations are required due to the presence of this asbestos like fibre. However more recent studies [9] suggest anecdotally that Erronite is not present. With no obvious means to confirm the

presence of Erronite one must rely on the XRD identification of the crystalline minerals which was not reported. Detection limits for the characterisation of crystalline structures are quite high for pXRD typically thought to be around a few % of the sample. Some studies have been able to reduce detection limits to approximately 0.02% of the total sample (100s of ppm) with the aid of synchrotron based XRD measurements [10, 11]. Scanning Electron Microscopy (SEM) investigation of the sample revealed the particles to be made up of individual crystals of approximately 1 to 2 μm in size [8].

An analysis via X – ray fluorescence (XRF) spectrometry was undertaken on the Mud Hills clinoptilolite sample (Table 2.1) with the major components identified being Si and Al, as expected in the clinoptilolite structure. XRF appears to have been undertaken on a single sample rather than a composite of a number of samples. Due to the potential for a heterogeneous distribution of cations on the exchange sites this may have altered the component percentages. Minor trace elements [8] were also identified with the most significant concentrations present being Sr (2493ppm), Zr (138 ppm), and Rb (137ppm). All other traces including Cu (14ppm) were below 51ppm.

Table 2.1-X-ray fluorescence (XRF) of major compounds present inClinoptilolite [8]

Component	%
Na <sub>2</sub> O	2.76
MgO	0.63
Al <sub>2</sub> O <sub>3</sub>	11.21
SiO <sub>2</sub>	71.40
P <sub>2</sub> O <sub>5</sub>	0.02
K <sub>2</sub> O	1.68
CaO	2.24
TiO <sub>2</sub>	0.13
MnO	0.03
Fe <sub>2</sub> O <sub>3</sub>	0.91

An attempt [8] has been made to provide an approximate formula for the Mud Hills clinoptilolite with the following assumptions that the sample contained only a pure clinoptilolite and does not contain additional mineral phases like quartz, haematite, albite, etc. and the exchange sites are occupied by only the five most abundant cations, Na, Ca, K, Mg, and Sr. A formula of Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O has been suggested for the Mud Hills clinoptilolite used in SIXEP.

Leaching trials of the Mud Hills clinoptilolite were attempted using nitric acid[8]. (Table 2.2) The purpose of this experiment was to investigate ion exchange performance as opposed to determining the dissolution or degradation of clinoptilolite in a process environment. Analytes were selected including the main components of the representative formula and Ba. In the results a large percentage of Ca, K, Mg, Na, and Sr were leachable indicating that a nitric acid wash may be suitable to improve ion exchange performance.

Element	Concentration in Clinoptilolite	Leachable	Leachable
	mg.g <sup>-1</sup>	mg.g <sup>-1</sup>	%
Ва	Not determined	0.8	
Са	16.0	7.1	44
Fe	6.4	0.4	6.3
К	13.9	6.7	48
Mg	3.8	1.6	42
Na	20.5	17.0	83
Sr	2.5	1.8	72
AI	59.3	21.3	36
Si	333.8	2.3	0.7

Table 2.2 -	Clinoptilolite leaching	trials using 1 M nitric acid	[8]
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The acid wash was suggested as a means of increasing available ion exchange sites by removing previously attached cations present on the existing sites. Of interest was the leachable content of Al (36% leachable) and very low Si leaching (0.7%). A possible reason for the high Al leaching is most likely from loss from within the clinoptilolite lattice [8] with only minor amounts from dissolution of the silicates [8]. Dealumination is encountered in a study of Australian clinoptilolite[12] that has undergone sulfuric acid pre-treatment. In this instance bulk dissolution is discounted due to the presence of a similar silica mass present before and after leaching.

The leaching trials undertaken in the nitric acid wash study [8] differ substantially to the solution conditions to which the clinoptilolite bed is exposed during SIXEP in operations. Leaching in acidic conditions would be unrepresentative of the conditions encountered in SIXEP (pH > 7). Acidic conditions and dissolution of zeolites have been studied and very low levels of dissolution of Al[13, 14] from the lattice structure were observed. Some work during the Harwell development trials was undertaken to quantify the silicate loss in operation, with a value of 5% silicate loss at pH8 [15] indicated over the life of a bed with ~1.8 kg of dry mass loss obtained. No mechanism was suggested at the time of the trials or during the review report. One method of loss from the bulk mineral structure would be through ion exchange processes where the bulk clinoptilolite would undergo ion exchange from the simulants and process effluent used within the trials (full characterisation of the effluent/simulants was not provided). Cations could interact with the exchange site and by this interaction would release Si. The release of silicates from the Harwell trials was not characterised. Whether this is loss of fines from the bulk mineral or aqueous silicates has not been determined. Had this been quantified it could go some way to providing a candidate starting compound for future pipe fouling
mechanisms. Quantification of silicate loss at SIXEP operating conditions around pH7 to 8 was not achieved but was suggested as being significant [15]. No mechanism was suggested nor were these losses quantified. Near neutral pH conditions are of vital importance to the operation of SIXEP ion exchange beds and consequently the solid formations that are found to occur under these conditions within the discharge line need to be mitigated ideally without changing operational pH. To not accurately quantify this mass loss leaves doubts over the effectiveness of the study in relation to post ion exchange bed (i.e. discharge line fouling) performance. Loss of Al at high pH has been discussed as being unfavourable to the ion exchange performance but the impact of dealumination from clinoptilolite was not quantified. The reduction in Al content from the lattice structure has potential issues for the ion exchange performance. A loss of Al wold impact the availability of new exchange sites. New exchange sites are created by substitution of Si by Al creating a net negative charge that can be balanced by the adsorption of a cation. The loss of Al from the Si-O-Al lattice would create a mineral that was predominately Si and which could increase the resistance to dissolution as Al dissolution can be responsible for the breakdown of the mineral structure but is of no benefit to the ion exchange process. Quantification of the observed losses of clinoptilolite throughout its process lifetime has been lacking [15] but the studies conducted previously in this area do provide a starting point for future investigations.

Clinoptilolite fines generation in the ion exchange beds has been suggested as a route for solid formations in the SIXEP discharge line [16] with quantification of likely fines/silicate loss somewhat vague [15]. Attempts have been made to provide an indication of fines loss [17]. After washing, a figure of around 6% fines loss was suggested[17]. Further work has been undertaken that filtered the washed clinoptilolite across 10 steps. A total figure

of 0.3477 g out of a total mass of approximately 100 g of starting clinoptilolite was retained on the filters [17]. The study does not record the filter pore size, particle size distribution of the fines generated, or chemical composition of the fines or dissolved species in the filtrate. As such it is of limited impact as quantification of fines is not possible. What can be drawn from this study is that fines are possible and continue to be generated at modest rate after 10 wash cycles. Fines or dissolution of these fines (with one caveat that filtration within the discharge nozzle within the ion exchange bed may capture the fines) could readily form part of the solid formation within the SIXEP discharge line.

Significant work has been undertaken on characterising the Mud Hills clinoptilolite as part of the initial Harwell trials [15] and subsequent cation enhancement studies [8]. The five most abundant cations identified as most likely inhabiting the ion exchange sites are, Na, Ca, K, Mg, and Sr. Studies of dissolution of these cations from the clinoptilolite lattice are limited to dissolution in nitric acid and have not considered dissolution in operational ranges of around pH7 to 8. As such this is an area that requires further investigation to determine the likelihood of a re-precipitation of dissolved species. The loss of Al from the lattice is significant [8] albeit in nitric acid but suggestions of silicate loss at higher pHs [8] also point to some dissolution of silicate structures from the bulk clinoptilolite.

Fines losses are identified in some studies [16-18] as being encountered within the SIXEP discharge line. Generation of fines has been studied [17] but a full suite of characterisation techniques has not been adopted, limiting the conclusions that can be drawn as to the effects of washing and size distribution of fines.

The loss of elements present in the clinoptilolite lattice has not been considered within the reports. A link between loss of Al and ion exchange performance appears to be lacking in these reports. The quantification at near neutral pH conditions of these losses is again lacking. The loss and breakdown of the mineral structure at those conditions would appear to be vital to the functioning of the plant. Flow sheet development has given an upper bound figure for pH prior to entering the ion exchange beds but the result of these losses does not appear to have been considered. Typically the focus was on the generation of fines leading to entrainment in some media pre-existing within the pipe. Re-precipitation has been discussed but related experiments have not been undertaken. Indeed only a high level assessment of discharge effluent with regard to readily precipitating mineral phases has been undertaken. Further work is needed on the loss of elements within the lattice or indeed fines as a potential source of precursors for mineral precipitation.

### b) Washing procedure and ion exchange bed change

Historically the clinoptilolite was placed into the ion exchange beds in "as received" condition with no form of pre-treatment. A review of the quality plan [19] and improvement plan for materials handling[9] for SIXEP are presented here. The current quality plan [19] requires prewashing of the clinoptilolite beds prior to use in SIXEP. Further details are provided in a memorandum [20] detailing control measures for chloride removal from initial ion exchange beds. The quality plan [19] deals with all stages of a bed change. A simplified process chart (Fig. 2.1) has been constructed to replicate the quality document for incorporation into further work.

The washing procedure [19] for the clinoptilolite beds can be summarised as follows:

- Load fluidising vessel with 8 drums (205 L) of clinoptilolite and level bed and repeat a further four times resulting in a total of 40 drums (~ 7400 kg)
- Soak the clinoptilolite for 4 to 7 days (de-mineralised water not specified)
- Backwash fluidising vessel with 30m<sup>3</sup> of "demin" water
- Perform second backwash one or two days after first wash with 20m<sup>3</sup> of "demin" water and discharge water to foul drain

# c) Sand bed filtration

The presence of the sand bed provides a significant function in the plant. It removes larger Mg rich solids that would precipitate during the pH reduction undertaken in the carbonation tower and any Mg remaining in solution could act as competitor ions to Cs and Sr, as Mg may exist in solution in significantly greater concentrations than those of the radionuclides to be removed.



Sand bed filters have a much longer life between bed changes compared to the ion exchange columns. Up to 7 years [9] or between 9 and 10 years [21] has been suggested for sand bed changes compared to as little as 90 days for the clinoptilolite beds during current operations with a potential to reduce bed lifetimes even further with additional streams [9]. To regenerate the sand beds, a counter washing/backwashing technique is used with pressure differential [21] across the sand bed used to determine the point at which a bed change is required.

When inspected, one of the long duty cycle sand beds that was in operation for nine years, experienced an approximate 50% loss of sand [21]. This report focused on the engineering performance of the sand bed and did not consider mechanisms of dissolution, fines production or colloidal generation that could pass through the plant. It is unclear whether the sand had undergone some form of dissolution by the alkaline feeds but this is thought unlikely in that report. Anecdotal evidence was used to justify this decision rather than an understanding of the mechanism causing the sand loss. The loss was not encountered in Magnox stations using similar sand beds in similar conditions[21]. The more plausible reason for loss is that during backwashing some sand is removed each time it occurs due in some part to the air sparging undertaken to reduce the occurrence of "mud balls" [21] (Mud balls are typically formed on the top of the sand beds and are comprised of agglomerations of sand with some form of cementing agent). The lack of recording of the sand loss is problematic for both developing an understanding of solid deposit formation downstream of the sand beds and assessing overall plant performance. There is a suggestion that the sand bed filters can act as actinide abatement (90% of actinide abatement[22]) prior to entering the plant. A loss of 50% of the bed (~ 3,000 kg

of material ) could introduce a significant radiological risk for operators and the wider community.

# d) Polyelectrolyte

Polyelectrolyte has been utilised in SIXEP to condition the sand bed filters since its inception and significant time has been spent in the Harwell trials developing an appropriate dosing regime. The adoption of this material was based upon empirical evidence as opposed to an understanding of the mechanism of how the polyelectrolyte provides benefits to the filtration performance. The material chosen was a guaternary amine polyelectrolyte flocculent [22] trade name Magnafloc 1597. More recently polygold CL520, of similar composition with a different trade name, has been adopted for use in SIXEP. There is a postulated route through SIXEP for polyelectrolyte to act as attachment medium [18] for the solid deposit. The rationale for polyelectrolyte entering the discharge line via plant wash through is tenuous at present as no evidence exists for polyelectrolyte wash through. The presence of organic carbon in the recovered pipeline deposit has been assigned to one of two origins; biofilms or polyelectrolyte. This would provide an alternative to the biofilm formation and if polyelectrolyte was found to contribute to solid entrainment it would suggest that biocide dosing was not the most appropriate control measure. Biofilms have been suggested to form in the SIXEP discharge line by previous BNFL/Sellafield studies [18, 23]. A control measure to prevent the build-up of these films could be dosing using biocides. However as biofilms may already exist this has the potential to release a significant amount of retained activity and biocide dosing would be problematic. Biocide dosing would breakdown the extracellular growth that may have been acting as an adsorption medium. A release of retained activity that may be held within a biofilm would result in a significant discharge of radionuclides in a single discharge event that may result in an exceeded of permitted discharge levels from site and could pose issues to the surrounding environment.

The inclusion of polyelectrolyte, polygold CL520, into the feed tanks in SIXEP was developed from the Harwell trials. The improvements in filtration performance are substantial, with current work [21] suggesting that this is still the most appropriate option based upon the existing incoming feed composition. The rationale for polyelectrolyte inclusion is still one of empirical evidence with significant development works ongoing as to how and why the improvement in filtration performance occurs. The aggregation of colloidal material is suggested as occurring through interactions by van der Waals forces. The understanding of these interactions is limited at present, but there is an ongoing research project to develop a mechanistic understanding of sand bed – polyelectrolyte – solid interactions [22]. A lack of understanding of this mechanism poses issues. Without this understanding variations to the Conditions for Acceptance (CfA) for SIXEP require full development trials to establish whether new waste streams are acceptable. Low dosing of polyelectrolyte, flow sheet dosage 0.25 mg.L<sup>-1</sup> and actual 0.58 mg.L<sup>-1</sup>, is currently below detection limits with the techniques employed on plant. The inability to fully characterise the organic compound at present significantly hampers detection limit improvements and would rely on spectroscopy techniques using known calibration standards. There is a suggestion [21] that the polyelectrolyte makes its way into bulk storage tanks (BSTs). However this assumption cannot be confirmed, due to the problems with limits of detection of currently established methods that can ascertain polyelectrolyte concentrations on the plant.

The polyelectrolyte is introduced to the process upstream of the sand bed filters in the reception tank [21, 22]. The sand bed filters act as depth filters with filtration taking place between the pores of the sand grains with typical particulate flocs sizes between 0.5 and 1.5 µm retained between the pores created by the sand particles. One of the main purposes of the sand bed filter is to remove Mg rich solids which would dissolve [21] in the carbonation tower and act as competing ions within the clinoptilolite ion exchange tanks.

Polyelectrolyte detection in aqueous feeds has been studied previously [21] but limits of detection, >3mg.L<sup>-1</sup>, limit the use of these techniques as feed dosage is 0.58 mg.L<sup>-1</sup>. At present it is unclear how excess polyelectrolyte migrates through the SIXEP process with potential for the polyelectrolyte to pass into the SIXEP discharge line. Pilot scale and small scale studies [15, 21] have concentrated on the sand bed filtration performance with regard to improvements to filtration as opposed to wash through of excess polyelectrolyte. It is suggested [21] that excess polyelectrolyte makes its way into the BSTs but, like other work, this is based upon anecdotal evidence rather than demonstrable findings. The fundamental issue with polyelectrolyte detection is two-fold. One is finding an appropriate signal response that can be used to quantify polyelectrolyte content. Characterisation has been attempted on the polyelectrolyte using mass spectrometry and the findings were inconclusive due to a lack of any consistent, identifiable signalsThe other issue, should a trace spectroscopic signature be found for polyelectrolyte, is at current plant dose rates polyelectrolyte would undergo significant dilution effects from the effluent prior to any sampling and characterisation efforts.

#### e) Solid formation characterisation

Characterisation of the observed solid found in the SIXEP discharge line is based upon two sets of samples collected in 2004 [24] following CCTV inspection. Some analytical techniques were undertaken on these samples. There are problems with the level of characterisation effort and the lack of experimental repeats on the sample recovered that limits the ability to draw definitive conclusions as to the type and nature of these solid compositions.

Carbon content, organic and inorganic, was established from the recovered effluent with a total organic content (TOC) of 95 +/- 19ppm and a total inorganic content (TIC) of 15 +/-16 ppm determined from the liquid. [24] Large errors appear to exist on the inorganic carbon measurement with respect to the reported value. Particle size of the sampled solids was determined using sample filtration methods and ranged from 400 down to 0.2  $\mu$ m. [24]. Interestingly no solids passed the 50  $\mu$ m filter, indicating larger formations of particles rather than any colloidal type material. The sample recovered was described as being a soft solid with a light brown colour and orange tinge, with homogeneous texture[16]. Also it was described as "not gritty"[16]. The reference to a non-gritty sample may be an attempt to differentiate between clinoptilolite (which when being washed in a fine mesh filter has a gritty texture) and the received solid.

Settling trials were undertaken by mixing a solution containing the recovered discharge line solid filtrate passing the 185  $\mu$ m filter and sea water the resulting mixture settling within 17 hours. [24] Settling studies were based upon visual confirmation of settling being achieved. No aliquots of solution were drawn off to undertake further filtration to

determine the presence of colloidal-like material nor any elemental compositional analysis of the solutes.

A discussion was attempted regarding the representative nature of the sample [16] and whether a representative solid formation was collected in the sampling process. Discussion of how representative the characterisation of the solid was to the bulk solid recovered was lacking as only a single data point was collected through an elemental scan. Only surface deposits may have been collected. Below the collected soft surface deposit there may have been a harder solid. The possible presence of an underlying harder deposit is not supported by any experimental evidence though. Further elemental characterisation was undertaken on the obtained sample (Table 2.3) via Energy Dispersive X-ray (EDX) spectroscopy combined with SEM. An incomplete dissolution trial was undertaken where elemental composition data was obtained after dissolution of the recovered solid sample in acids. Nitric acid (HNO<sub>3</sub>; 2 and 4 M) and Aqua Regia (HCI & HNO<sub>3</sub>: 3 M each) were selected for dissolution experiments.

Concerns as to the applicability of dissolution were raised [16]. Only 6% of the solid was dissolved during these dissolution experiments. This quantity of dissolved solid would not realistically provide representative data from subsequent analysis. Additional and more effective dissolution trials were not performed and the unwillingness undertake further experimental work to fully dissolve the solid is unclear, but may be possibly due to the radiotoxicity of the samples. No Al was found by these poorly performed dissolution experiments. During an earlier study, dealumination was observed when clinoptilolite undergoes acid wash pre-treatment[8] and this should have been expected when the solid was contacted with the acid solutions if the solid was predominantly clinoptilolite.

Table 2. 3-Elemental compositions of previously recovered solid from SIXEPdischarge line [16].

SPECIES	DISSOLUTION (6 WT% OF TOTAL SOLID) %	ELEMENTAL SCAN %
Na	9.94	2.90
Са	0.52	3.50
Mg	2.62	1.10
К	7.81	0.00
Fe	24.34	7.40
Al	0.00	10.90
Si	54.77	67.50
Other(s)	(TIC & TOC)	P (5.3%) & S (1.5%)

No rationale for the lack of Al found in the recovered discharge pipeline solid was presented during the report most likely due to general lack of dissolution of the solid affecting the reliability of the data generated.

Both techniques to characterise the solid have errors associated with them. It is unclear as to the number of repeats undertaken whilst using the EDX probe and whether this is a single measurement or an average of a number of data points. EDX spectroscopy typically provides a point identification, however, due to the nature of the recovered solid this may not be fully representative. The general lack of representative characterisation of the solid could have been easily resolved. Whilst the activity would limit physical contact with the sample the mass of sample (and corresponding dose) could have been reduced. The reduced sample mass/volume could have been contacted with an alternative acid for dissolution, or highly alkaline solution. The contact time and subsequent radiological dose would have been limited. The inability to undertake additional EDX analysis appears to be a glaring omission from the study. The sample has already been visually characterised as heterogeneous but only one EDX data point has been collected. EDX data across numerous sampling points would have provided a more thorough understanding of the near surface elemental composition of the recovered solid. Instead, any discussion regarding the nature of the solid can only refer to "likely" and within the "envelope of constituents", as the characterisation effort undertaken on the recovered discharge line solid is poor and incomplete.

Comparisons were made between the solid recovered from the pipeline and that of clinoptilolite. Clinoptilolite has a similar Si:AI (by atom) of 6:1 to that of the recovered solid[16] using the EDX data point. Si:AI (by atom) is determined by the zeolite framework lattice and can be used as a good indicator of zeolite type. Other analytes were discussed including Fe and P which were both found in higher quantities in the discharge line sample by elemental scan than was found in naturally occurring clinoptilolite. Possible sources of Fe in the SIXEP effluent included scrubber condensates, corrosion from skips and pipes [16]. The presence of P was suggested as an indicator of biological activity [16] but this is said to "require further investigation". Sources of organic carbon were also suggested as originating from the feed itself, such as the presence of ethylene glycol from chillers or from polyelectrolyte additives used to condition the SIXEP sand beds[16]. A suggested alternative source of organic matter was bacteria and algae from the storage ponds[16]. The sources of the organic matter were merely suggested from likely inputs

and not determined by an exhaustive study as to the wash through performance of glycol/polyelectrolyte or algal growth from the ponds.

Clinoptilolite fines from the ion exchange bed entering the pipe was discussed as a potential source of fine solids in the effluent [16] the nature of the fines and mechanism for the generation of the fines were not discussed. Backwashing, according to the report [16] has not always been conducted and the suggestion was that this was from historic bulk fines wash through, as a larger proportion of fines are likely to be generated during early washes of the mineral rather than ongoing dissolution of the clinoptilolite mineral through a variety of means. When pre washing was not undertaken the effluent discharged from the new beds was of a yellow/orange appearance indicating a large proportion of fines being generated. Another source of the solids was discussed as the result of dissolution of clinoptilolite that then could re-precipitate as another mineral phase onto the pipework but this was not considered further.

The samples obtained from the discharge line were described as "not old i.e. not formed 15 years ago" [16]. This assumption of the age of the sample was taken by considering the isotopic Cs 137/134 and Sr 89/90 ratios which suggested that:

- the deposits are fresh, the phenomenon is likely ongoing but due to the effects of flow induced shear these are deposited and then removed and fresh deposits are likely encountered;
- the precipitate/solid is being formed then released by the action of shear from the flow;

 the sample was only from the outer surface of the formation due to the method of collection (from CCTV camera scrapings) and missed an older, potentially hard underlying formation.

Morphology of the discharge line solids was examined using SEM, which indicated an open and porous heterogeneous matrix with 10  $\mu$ m particles embedded in the porous structure[16] (Fig. 2.2 and 2.3). There is a suggestion that these sub 10  $\mu$ m particles were clinoptilolite fines embedded in a semi-organic matrix [16].



Figure 2.2 – SEM micrograph of previously recovered solid from SIXEP discharge line (scale bar 30  $\mu$ m) examined prior to this study by others [16]



Figure 2.3 – SEM micrograph of previously recovered solid from SIXEP discharge line (scale bar 10  $\mu$ m) examined prior to this study by others [16]

An initial hypothesis for the formation of solids and attachment to the pipe surface was postulated in the report, where the formation of the solids is due to either clinoptilolite fines or a dissolution of clinoptilolite followed by re-precipitation of an aluminosilicate material [16]. The subsequent mechanism for attachment to the pipe surface is due to the presence of organics either from polyelectrolyte and/or biological growth[16]. Both of these assumed solid formation and entrainment mechanisms are postulated through analysis of incoming feed stock constituents and the most likely conditions that relate to SIXEP as opposed to direct evidence as to the cause of this formation. Alternative mechanisms and solids could contribute to the solid formation and, due to the lack of definitive characterisation of the solids / attachment mechanisms, This poses questions as to the range of conditions in which potentially a wide variety of candidate species could form and result in similar solid formations of those observed on the SIXEP discharge line. The outcomes from this review of solid formation observed in the SIXEP discharge line report the identification of candidate materials from the characterisation attempted on the recovered, albeit limited, sample. The source of these solids would most likely be either through fines loss or caused by some form of dissolution of the clinoptilolite causing another mineral phase to precipitate.

# f) Mechanisms of solid formation

Initial formation mechanisms for the discharge line solids have been proposed in the early report [16] on solid formations within the SIXEP discharge line. Further work was undertaken to consider alternative solid formation mechanisms not solely relating to the clinoptilolite fines or re-precipitation of these fines into an alternative phase(s). Alternative mechanisms considered include those of physical, chemical, and biological origin. Each formation mechanism was discussed in various degrees of detail dependent upon the likelihood of its impact on the fouling process. Biofilm formation receives the most detailed discussion as to the method of fouling. The three basic mechanisms [18] suggested were:

- Chemical precipitation of inorganic components from SIXEP
- Deposition of particulates
- Biologically induced deposition of particulates attached to pipe surface via biofilms.

A summary of the feed constituents, the composition of the effluent and sources of the chemical components [18] was provided. There is concern over the units selected for the concentrations of the components as these are mg.mL<sup>-1</sup> as opposed to other concentration data that has been provided as mg.L<sup>-1</sup>. Further work was undertaken as

part of this thesis to establish the correct concentration range:  $mg.mL^{-1}$  or  $mg.L^{-1}$ . The monitoring work (one week additional monitoring) has been undertaken by SL for this project and has provided additional element data from the SIXEP discharge line. It appears that the correct unit for this data should have been  $mg.L^{-1}$  (Chapter 5).

Of interest to future planned experimental work are the concentrations of species present in the post SIXEP treated effluent [18]. These are: Na,  $4mg.L^{-1}$ ; Mg 1.6 mg.L<sup>-1</sup>; Ca 2.4 mg.L<sup>-1</sup>; Al <0.1 mg.L<sup>-1</sup>; Si 2 mg.L<sup>-1</sup> as SiO<sub>2</sub>; Fe <0.02 mg.L<sup>-1</sup>; SO<sub>4</sub><sup>2-</sup> 7 mg.L<sup>-1</sup>.

## i) Postulated option for pipe fouling

The three main hypotheses for pipeline fouling can be outlined as chemical precipitation, biofilm formation and attachment, deposit of Clinoptilolite fines through polyelectrolyte sorption. Of interest within this research project are the two alternative mechanisms to biofilm formation. This includes bulk precipitation of solids from the constituent effluent. Following a *"high level assessment"* [18] within the report, bulk precipitation from the effluent had been discounted. It has been noted within this report [18] that the precipitation of mineral phases may have contributed to the "deposit mass". Likewise the attachment mechanism of polyelectrolyte binding clinoptilolite fines, whilst not being discounted has been said to require confirmation experimentally[18].

Further consideration of the alternative hypotheses, other than biofilm formation, may prove fruitful in providing an overall assessment of the source of the solid formations observed in the SIXEP discharge line and subsequently to develop methods to mediate this formation and/or readily remove this material from the pipeline. Biofilm formation has been considered [18] and subsequent methods to remove biofilm attached solids have been proposed and implemented[23]. There is no reference to earlier studies which utilised infra-red spectroscopy measurements resulting in "no organic material being detected" in significant quantities[24].

The choice of biofilm formations receives much credence in later reports [18, 23]. It is unclear how these earlier infra-red spectroscopy measurements [24] have been incorporated into later reports [18, 23]. Perhaps differences arise from the approaches taken, as the earlier report is dedicated to the characterisation of the collected deposit [24] whereas later studies [18, 23] have considered the mechanism rather than direct analysis of the "soft solid".

Biofilm formation has been chosen as the means by which to attach solids to the pipeline surface. Biofilms are responsible for pipe fouling in the water industries and their presence cannot be discounted but, due to the intermittent and limited sampling regime adopted for the characterisation of the recovered solid, other mechanisms cannot be discounted, i.e. organic carbon originating from polyelectrolyte. Analysis of the sample to determine if the material contained living matter through DNA/RNA identification would have revealed whether the material containing organic carbon was of biological origin.

#### ii) Harwell trials and chemical precipitation

The SIXEP plant was developed in a pilot scale plant, undertaken at two locations in the late 1970s and early 1980s, known as the "Harwell trials". Following a review of Harwell trial data [15] a solid deposit was encountered within the pilot plant. The composition of this upon drying was found to contain 19.7% Mg and 3.7% Ca (by mass) with the remainder hydroxide, carbonate and combined water [15] the method of characterisation was not reported (dissolution, elemental scan). Dissolution in acid was not reported as being attempted on the "Harwell deposit". The study did not report a rationale for this

solid formation, reporting solid composition only. The conditions in which the solid were generated was not reported. Without those conditions and constituents it precludes any further interpretation as to why the solid formed. The nature of the solid formation reported in the Harwell trials would indicate, that as it contained a high Mg content, it would be upstream of any form of Mg control (sand bed filtration) or adjacent to pH control through carbonation, where a dramatic reduction in pH could lead to rapid precipitation of the Mg solid. The nature of the Harwell deposit was compared to the SIXEP discharge line solid with respect to thickness and water content [15] but not to dissolution or elemental compositions. The composition of the Harwell deposit (19.7% Mg and 3.7% Ca by mass) [15] differed considerably to that found in the SIXEP deposit (1.1% Mg and 3.5% Ca by mass) [16]. No further discussion as to conditions or constituent components was provided.

The addition of sodium silicate into the sand beds was studied during the Harwell trials at a concentration of around  $7mg.L^{-1}$  SiO<sub>2</sub> [21, 25]. It appears that this addition is not undertaken in the actual SIXEP process at present but may be introduced during future decommissioning feeds that may be processed through SIXEP.

#### iii) Bulk precipitation

Bulk precipitation studies considered the presence of, Ca, Mg and silica (SiO<sub>2</sub>) in the range of 0 to 32ppm (0 to ~32 mg.L<sup>-1</sup>) at pH8 and 11.4 in the effluent [18]. It was found at pH 8 that no solids were formed and at around pH 11 to 11.4 some Mg(OH)<sub>2</sub> precipitated [18]. The Ca, Mg and SiO<sub>2</sub> system chosen appeared to limit the range of likely mineral phases that could possibly form. The system studied here appears incomplete in not considering lower pH's of around 7 and the likely precipitation of Al phases if Al is present in the aqueous effluent. Al is present within the solid but not found within the discharge

monitoring perhaps due to having already precipitated out of solution. The report did not consider alternative forms of Si, in particular silicic acid (H<sub>4</sub>SiO<sub>4</sub>: polymer and monomer form), silicates released from dissolution of the clinoptilolite structure or colloidal silica globules that could form agglomerations of solids to aid precipitation and cause solid formations.

Simple settling of solids is considered but rejected due to the nature of the deposits [18]. The deposits being evenly spread around the pipework suggest that this is not the effect of a build-up of solids on the pipe bottom [18]. As such, suspension, or lack thereof, of particles within the system has not been considered further[18]. The assessment of settling of solids appears to be justified as if fouling was caused by this action, it would affect predominately areas of low flow rates instead of the main discharge pipe.

Scale fouling observations have been limited within the report [18] to Ca and Mg and the mechanism has been discounted due to the small temperature difference between the bulk liquid and pipe/vessel surface and the type of species present within the bulk effluent. The lack of scale fouling can be easily confirmed due to the lack of temperature gradient between the pipeline and treatment plant. Alterations to conditions within the pipeline for bulk precipitation are discussed and are limited to temperature variation due to seasonal changes and pH changes along with carbonate speciation caused by carbon dioxide loss from the supersaturated solution [18]. These condition alterations appear to be unfounded as the form of solids generation, due to the lack of likely candidate species and reliable effluent characterisation of the discharge liquor.

#### iv) Polyelectrolyte within SIXEP

An alternative mechanism for the adherence of solids through the sorption of the polyelectrolyte onto the stainless steel surface as opposed to biofilm growth has been suggested [18]. The mechanism for polyelectrolyte–sand-solids interactions and performance within the SIXEP sand beds is not currently fully understood. Steel polyelectrolyte – solid interactions are even less understood in the discharge line. Any assumptions regarding polyelectrolyte wash through are only hypothesised and have never been proven due to limits of detection and the inability to identify a signature pattern for mass spectroscopy analysis. This is one postulated route for clinoptilolite fines entrapment onto the pipework. This would have provided a means to achieve a comparable thickness (~1mm) to that encountered within the previous survey. The polyelectrolyte mechanism was not discounted [18] but requires further investigation. The preference for the biofilm mechanism as the most credible means of solid entrainment was likely due to the implicit limitations of sample characterisation undertaken on the recovered pipeline solid and inability to detect low concentrations of the polyelectrolyte, and biofilm formation has been found in other industries (water distribution). An earlier study [24] stating that no organics were encountered in significant quantities, would have given equal merit to the polyelectrolyte mechanism was given to the biofilm approach. However, given it has been postulated that the sample obtained was not representative of the entire adhered solid, this could account for a lack of organics (either biofilm or polyelectrolyte) observed in previous studies [16]. The lack of representative solids and gelation agent characterisation is a common problem throughout the studies and, in particular, the work undertaken on the discharge line

solids. Therefore, a significant range of starting conditions that could cause the solids encountered in the discharge line need to be considered.

The dosing rate for the polyelectrolyte is suggested as 0.25 mg.L<sup>-1</sup> [15, 21] from Harwell trials, with an actual plant dosing rate of around 0.58 mg.L<sup>-1</sup> [21, 25]. The strongly cationic polyelectrolyte with quaternary amine functional groups was chosen as it would not cause flocculation but a change in surface charge [21]. The main purpose of the polyelectrolyte is to condition the sand as opposed to the filtered solids[21, 25]. Conditioning, in the sense used here, is performed to create a more favourable surface through changes in the surface charge. A loss of polyelectrolyte from the feed tanks after 15 hours resulted in solids breakthrough[21] It was noted that when this occurred reintroducing polyelectrolyte did not stem the breakthrough of solids[21]. An accumulation of polyelectrolyte does not appearto be occurring. As polyelectrolyte must be continually added to the feed stock this would indicate that polyelectrolyte was being lost from the sand bed. Some polyelectrolyte would most likely be lost during sand bed recharging (air sparging and backwashing) while the remainder probably migrates through the plant itself. This loss through plant could be used as a justification for alternative mechanism for solid entrainment.

One source of organic carbon has been attributed to biofilm formations [18, 23] while another source may be the polyelectrolyte used within SIXEP. No information has yet been obtained [18] in relation to the effects of polyelectrolyte upon the sorption process for fines to a pipe surface. Biofilm as the cause of the solids appeared to be considered the candidate attachment mechanism of choice. To establish whether or not polyelectrolyte could be a plausible as an attachment compound. Further work is

required in this area to determine the effects upon sorption of clinoptilolite fines or bulk precipitates using polyelectrolyte as a binding mechanism.

### g) Review

Bulk precipitation or some form of fines attachment through an alternative organic solution, in this case polyelectrolyte, has not been ruled out as a candidate adsorption solution. Scale formation has been discounted, likewise bulk precipitation using Ca, Mg, and Si [18] has not been considered plausible and appears to be a realistic conclusion to draw.

The lack of credible characterisation of the recovered solid, complete effluent compositions and determination of the nature of the organic carbon (biofilm/polyelectrolyte) results in a number of assumptions made in the reports undertaken on the discharge line solids to date. Bulk precipitation of additional species that may include AI has not been considered, likely due to the poor dissolution of the recovered solid (6% by weight only). Due to the presence of AI within the single SEM elemental scan of the solid [16] and the presence of AI within the feed water [18] it is not unrealistic to consider AI within the discharge line system. Bulk precipitation should be investigated further after AI is included within the experimental elemental matrix.

Clinoptilolite fines has been discussed as one method of solid build-up [18]. Fines loss through the plant will need to be considered, as at present the postulated route for the presence of clinoptilolite is "historic residue" from "unwashed" samples. Re-precipitation from some form of clinoptilolite dissolution may provide some insight into the species encountered within the discharge line. The solids encountered in the SIXEP discharge line have been attributed to a biofilm growth that entrains a solid, either from clinoptilolite or through some form of bulk precipitation but there is little definitive proof to confirm that this occurred under SIXEP conditions. Other possible mechanisms have been considered and discounted due the very remote possibility of those mechanisms being responsible.. Bulk precipitation through species addition will be considered. This will be achieved through Al addition to the previously postulated Si, Mg elemental compositions.

# h) Origin of organic carbon

Studies have suggested that the presence of organics may be the cause of solid attachment onto the pipe surface. An alternative to biofilms could be the polyelectrolyte passing through the plant, as low concentrations of polyelectrolyte are dosed into the sand bed filters (0.58 mg.L<sup>-1</sup>), and an accumulation of polyelectrolyte within the system could occur. Layer by layer and polyelectrolyte multilayers are commonly utilised [26, 27] for nano-assemblies. The purpose of the polyelectrolyte is to alter the surface charge on the sand surface [22] and acts as a preconditioner to improve filtration performance and is continually dosed to act as conditioning agent as polyelectrolyte is not retained on the sand surface for long durations. An accumulation of polyelectrolyte on the pipe surface may be possible.

Biofilms have received the bulk of the attention for the likely formation of solids within the pipework [18, 23]. Typically these form in two stages[28]; a reversible attachment stage where temperature, pH and flow rates control formation; then an irreversible stage where extracellular matrix generation[29] occurs i.e. the bulk formation of the growth, with preferential sites created in zones of corroded or pitted pipework. The formation of

biofilms has been studied in some detail within drinking water systems [28, 30-32]. Formations can occur in a variety of temperatures (6 to 35 °C) and pH conditions (with pH 7 to 8 being optimum as encountered in SIXEP) and pipeline material leading to the growth of biofilms. Different types of biofilms form with variations in the surrounding conditions but it has been found that biological growth still occurs within most drinking water distribution systems.

Biofilm has been shown to form at temperatures (15 to 20 °C) and pressure conditions of drinking water distribution networks similar to that of the SIXEP discharge line. Typical biofilm formations have been encountered in a range of pipe materials including stainless steel grades, 304 [31, 32] and 316 [32]. Their presence in fresh water systems is considered highly likely to be independent of pipe type and the formation encountered in discharge pipelines could be of biofilm origin.

The presence of organic carbon has been determined during the limited characterisation efforts and as such it can be considered to be "likely" within the deposit mass. There are two means to demonstrate that biofilms are the cause of the solid entrainment:

- Direct proof, whereby a significant sampling campaign is undertaken throughout the discharge line in multiple locations and throughout the year with DNA/RNA testing undertaken on the organic carbon to demonstrate that this carbon is of biological origin;
- Or indirect proof, by showing that any likely alternative entrainment mechanisms do not occur. In this case, proving that polyelectrolyte cannot adhere solids to a stainless steel (grade 304) surface under SIXEP process conditions.

The justification of biofilms using approach 1 is outside the scope of this study. A significant sample collection programme would not be feasible for the size of this research project as it would require SIXEP discharges to be halted for significant periods of time (multiple days) per sampling campaign, needing multiple entries into the discharge line and require quarterly interventions to capture any solid deposit. The solids are transient and do not occur in one location. The solids form and are released sporadically from various locations. These entries would require operators to come into contact with potentially highly active solids (as encountered in the 2004 solid[24]) and this approach would not follow the As Low As Reasonably Practicable (ALARP) principle.

Approach two is the most credible, safe and efficient means to determine the origin of the organic carbon. Should it not be possible for polyelectrolyte to adhere solids to the surface of stainless steel then biofilms would be the "likely" candidate for the organic carbon and as such be the cause of the solid formations. This would enable confirmation that biofilms cause the solid build ups without requiring operators to be exposed to significant radiological doses through intrusive investigations. This study will not consider biofilm growth but will attempt prove the hypothesis that polyelectrolyte dosing causes particulates in the SIXEP discharge line to adhere to the pipeline surface. This work will focus on whether polyelectrolyte can act as a sorption mechanism for either clinoptilolite fines, or some form of re-precipitated solutes.

A comparable study on the role of biofilms in the solid entrainment mechanism under SIXEP discharge line conditions realistically requires the knowledge of the genus of the source biological organism for any likely biofilms that can form. This is because of the wide variety of biofilms that can form under the range of temperatures and pH conditions

within the SIXEP effluent. Establishing the genus of any biological organism, nor whether the source of the any found carbon was biological, was not achieved during the poor and limited characterisation of the recovered pipeline solid. Other related projects are ongoing on the Magnox storage ponds to undertake characterisation of the algal formations. Two research projects have been undertaken, one on characterisation and the second on growth of the organisms. This overall area of research would require significant effort, including the recovery of samples and the characterisation of potentially highly active solids that cannot be achieved within the scope of this project.

## i) Associated reports

A number of reports make reference to the SIXEP line but do not provide detailed information thus its relevance to this work is limited. These reports include sea discharge line modelling with respect to toxic bacteria produced via the Sellafield site laundry [33]. Simplistic modelling of solid formations encountered within the SIXEP discharge line [34] has been undertaken utilising a measurement of total dose at a certain point and extrapolating a thickness based upon mono-isotopic accumulation of <sup>137</sup>Cs within the pipeline deposits.

Dimensions of the SIXEP pipeline have been detailed as 20m of 300mm diameter, 700m of 200mm diameter, and 700m of 150mm diameter [35]. An attempt has also been made to define the surface roughness of the pipeline with a likely range of between 0.01 to 1.00 mm [35]. Surface roughness has not been measured within the pipeline and is an estimate based upon the age of the pipeline, commissioned in the mid-1980s. However this provides a starting point for attachment mechanism experiments.

#### j) Research areas

It appears from the review of the internal reports that much credence has been given to the biofilm route for fines entrainment. However there are a number of areas that require further investigation to establish whether alternative mechanisms may occur and are plausible. Likewise, it is necessary to investigate whether biofilm or polyelectrolyte is the sole source of the attachment mechanism, or a combination thereof. The areas for further investigation are closely related to areas discussed within the reports. There are a number of postulated mechanisms for various stages in the formation and retention of the solid. These can be split into three steps; solid formation, attachment mechanism, and entrained or bulking solids.

Solid formations should be defined as the initial solid formation occurring in the bulk effluent or near to pipe surface. This could take the form of chemical precipitation, clinoptilolite fines, or biological growth. Solid formations formed via chemical precipitation were initially discounted [18] but did not include any Al in the assessment, This was probably due to the poor dissolution of the recovered solid and a only single elemental scan using the EDX probe was performed. The presence of Al could readily form a precipitate itself and/or could co-precipitate with for example, Si to form a combined phase. The presence of Al, Si, Mg, and Fe have been encountered in the recovered solid [16] with the awareness of the poor and limited characterisation efforts undertaken previously, limiting any candidate elements to be termed "likely". A series of bulk precipitation experiments should be undertaken to establish if likely rapidly forming phases can occur in normal operating conditions i.e. temperature and pressure encountered in discharge lines. The chemical precipitation of phases from the bulk effluent would require a supply of aqueous species. There are two likely sources where these aqueous species could originate. They could either be wash through of species throughout the whole effluent treatment plant with effluent feed concentrations or the effluent pipeline concentrations present within the line post treatment plant. There are problems with selecting the starting point for concentrations at both extremes due to incomplete characterisation of the previously recovered solid. The treatment plant will reduce Mg solids in the sand beds and other species via ion exchange, with Si content likely to be increased during the process via the interaction of high pH solutions within the sand bed. The other option is to characterise the effluent collected from monitoring points. These are located downstream and if rapidly precipitating solids were formed these would not be identified. A matrix of likely solutions is therefore required to consider a range of starting concentrations and species.

Without a means of adhering the solid to the pipeline, any formed solid would be discharge into the open environment. The minimum settling velocity of solids had been examined and found to be considerably higher within the SIXEP discharge line. This means of solid formation on pipe surface was discounted [18]. With the minimum settling velocity condition not being met, the problem of solid attachment [18] has been distilled to a material that alters the surface charge of the pipeline surface and both polyelectrolyte and/or biofilm can act in such a manner.

The presence of polyelectrolyte downstream of the sand beds has been studied previously. The limits of detection:  $>3mg.L^{-1}$  is greater than dosing rate 0.58mg.L<sup>-1</sup>; have stalled any further investigation into the presence of polyelectrolyte within the plant.

Evidence of the role polyelectrolyte plays in the adherence of solids has been studied [26, 27] for assemblies. The interaction of stainless steel, polyelectrolyte and clinoptilolite fines should be investigated in this context.

Clinoptilolite fines losses are suggested as a route for initial solid formations [16-18]. The fine fraction from clinoptilolite may also be responsible for a significant increase in solid mass within the pipeline once an initial solid formation has formed on the pipeline. Therefore the determination of likely fine fraction from the ion exchange bed in near neutral pH conditions is needed. It appears that this mechanism coupled with biofilm is the preferred mechanism for justifying the solid formation observed in the SIXEP discharge line at present. Less understood is the role clinoptilolite plays in the formation of secondary phases through some form of dissociation of either Si or Al. Significant work has been undertaken on characterising clinoptilolite prior to use[8]. Leaching studies were carried out with nitric acid but did not consider a longer term release of species in near neutral conditions from the clinoptilolite lattice likely to be encountered in the ion exchange beds.

Studies have focused on either ion exchange capacity [8] or clinoptilolite fines losses [16-18] rather than the release of species from the lattice. Investigation of the dissolution behaviour of clinoptilolite in near neutral conditions would be beneficial. The use of this information would aid chemical precipitation work relating to rapidly precipitating mineral phases from the bulk mineral. Likewise it provides justification for a suggested reprecipitation mechanism for solid enhancement or solid bulking.

There are areas that require investigation to demonstrate that either the biofilm/fines mechanism is responsible for solids entrainment in the SIXEP discharge line or that an

alternative mechanism occurs. This can be achieved through a series of modelling and experimental studies across the areas of chemical precipitation, dissolution of clinoptilolite and polyelectrolyte sorption.

# k) Research aims

Three distinct areas exist for planned research relating to the operation of SIXEP and the materials utilised within the plant.

- Precipitation studies: Can Si<sub>(aq)</sub> and/or Al<sub>(aq)</sub> form precipitates in similar effluent compositions and concentrations to those encountered in the SIXEP discharge line and form similar solids to those encountered in the mid-2000s previously recovered solid?
- Performance of clinoptilolite: there has been an assumption that the solids are as
  a result of "clinoptilolite fines". The fines may be an indication of congruent
  dissolution but another option may be that an incongruent release of solutes may
  lead to an increase in Si or Al that may form representative solids to those
  encountered previously.
- Interactions of polyelectrolyte onto stainless steel surfaces: the adsorption of clinoptilolite onto a stainless steel surface with the aid of polyelectrolyte as a sorption medium may demonstrate that biofilms are the only cause of solid entrainment should polyelectrolyte be unable to adhere solids to stainless steel surfaces.

# Chapter 3 – Research context and Sellafield Ltd

# 3) Research context

The nature of the EngD qualification requires an awareness of the context for the research and its impact on the sponsor company. As such the chapter seeks to provide an overview of effluent management processes within Sellafield Ltd (SL), more specifically that of the spent fuel storage ponds and associated fouling issues, restrictions in effluent flow in processes will hamper ongoing operations, future decommissioning waste streams, and impact upon post operational clean out (POCO) decommissioning of the plant.

This chapter will only address issues relating to Sellafield rather than the nuclear industry as a whole and does not include "new build" operators who have different disposal routes for spent fuel. Likewise defence waste routes are not considered here. The ultimate preferred disposal route for all high level and intermediate level waste is geological disposal. The process of developing a geological disposal facility (GDF) in the UK, including site selection, facility design and waste containment, is being managed by the Radioactive Waste Management (RWM) which is a wholly owned subsidiary of the Nuclear Decommissioning Authority (NDA). A disposal route has been identified for high level and intermediate level waste via the GDF[36].

#### a) Sellafield site ownership

The Sellafield site has undergone many iterations and ownership models. Initially the Sellafield site was a munitions factory during the Second World War. Subsequently it was owned by the United Kingdom Atomic Energy Authority (UKAEA) until the 1970s when it became British Nuclear Fuels Ltd. The current owners of the site are the NDA. Due to the

nature of the UK's legislative framework the site owner and operator (Site Licensed Company, SLC) are separate legal entities.

The NDA took ownership of the site from BNFL in the mid 2000s. In 2008 the SLC transferred from the NDA to a parent body organisation (PBO) which won the contract to manage the site for a fixed period of time. The successful bidder was Nuclear Management Partners (NMP). At the commencement of this research (in 2013) NMP managed the Sellafield site through the PBO contract mechanism. Subsequently the ownership of the PBO was transferred back to the NDA.

# b) Project processes

A number of different operations are ongoing on the Sellafield site at present. To describe these processes the volume/variety model will be used. Where volume (from a process perspective) is low, this would typically describe a bespoke project with little or no repeatability to other processes. The variety on a project is high between one project and the next. In well-defined products or treatment processes there is low variability but much greater volume.

At SL there are a multitude of different process types. These include decommissioning activities. Demolition, clean up or new build to facilitate decommissioning would be described as project type work, where the attributes of the scheme are unique as to require a new set of requirements for each scheme, where variety is high and volume is low. Other operations ongoing include reprocessing (either batch or continuous operations) that have a repeated process (variability is low) where the process is well understood and the business focus is on repeatability (volume is high) and process control.

Effluent management has similarities to other industries (utilities; waste water, gas and electricity) where a continuous operation is required (very low variability and volume is high). However future waste streams may produce greater variability in the incoming effluent that may alter the process type to that of a mass customisation or jobbing area of the variability model. While the central effluent treatment process will most likely remain the same either through SIXEP or successor plant, however, the likely possibility of needed to treat alternative waste streams may require a change in ion exchange medium to account for high pH solutions and/or different radionuclides present in the effluent. Different environmental permitted discharge limits could be imposed on the Sea discharge pipeline that may affect the ability to treat effluent under the current regime. Discharge limits are set by the Environment Agency and are the regulator under the Radioactive Substances Act 1993.

#### c) Sellafield Ltd

The ownership of the parent body organisation has been transferred from Nuclear Management Partners back to the Nuclear Decommissioning Authority[37] on the 1<sup>st</sup> April 2016. A relationship diagram (Fig. 3.1) provides the current state of ownership, the Site licensed company and interfaces with the statutory regulatory organisations.

The relationship diagram does not provide an overview of inputs into SL operating license conditions. The Environment Agency (EA) is responsible for permitting any discharges from site, whether these are aqueous or gaseous. Other public bodies involved in the regulation are Public Health England and The Food Standards Agency. As the UK is a signatory to the Oslo and Paris Convention on the Protection of the Marine Environment of the North East Atlantic (OSPAR) convention there is a requirement to reduce radioactive and hazardous substances discharges to a level that is "close to zero" [38].

Funding for SL comes from the NDA and allocation of funds is based upon the NDA business plan. The most recent plan allocates significant funding to legacy ponds, and fuel swarf storage silos due to the prioritising high risk elements of work[39]. Approximately two thirds of the funding for the NDA is from the UK government the remainder is from commercial activities. At present these activities are spent fuel management and transport[39].



Figure 3.1 - Ownership and relationship diagram for Sellafield Ltd and Regulators
#### d) Sea line discharges and dose reduction

The discharges from SIXEP form part of the overall discharges from site. These are combined at the break pressure tanks (BSTs) which are then joined by other aqueous feeds (EARP being one such feed). The combined effluent feeds are discharged to sea using the Sea discharge line (or simply referred to as the pipeline in Sellafield reports) and the discharges at this point fall under the permitting regime as defined by the EA.

There are discharge limits for certain radionuclides which includes <sup>134,137</sup>Cs and <sup>90</sup>Sr that are treated by SIXEP (Table 3.1). The monitoring regime is based upon a total discharge from site as opposed to a single feed emanating from SIXEP. The monitoring report[38] discusses an increases in <sup>90</sup>Sr release due to ongoing works within the First Generation Magnox ponds.

The overall aqueous discharges from site for the three main radionuclides that are selectively removed by the clinoptilolite (as used in SIXEP) are considerably below authorised limits. The application of Best Available Techniques (BAT) requires consideration of the technological readiness (i.e. is it at concept stage or it has been implemented on a similar treatment plant previously?) of the proposed treatment technique, and the cost of implementation relative to the reduction in harm. For new build effluent plants there is a duty to ensure that the installation minimises impacts and emissions from facilities. When applying BAT to an existing plant this should encompass an element of as low as reasonably practicable that would consider the technological readiness of the process, and the economics of further intervention relative to the reduction in harm.

	Annual Dise	Authorised				
Radionuclides	2010	2011	2012	2013	2014	limits
						(ТВq)
<sup>90</sup> Sr	1.0	1.9	1.2	1.1	1.6	45.0
<sup>134</sup> Cs	0.11	0.09	0.06	0.08	0.06	1.6
<sup>137</sup> Cs	4.8	5.9	3.6	3.2	2.6	34.0

Table 3.1-Extract of annual aqueous discharges and authorised limits for afive year period from the Sellafield site [38] including SIXEP discharges

Nonetheless current methods for radioactive Cs and Sr removal from aqueous effluents appear to be very efficient with respect to discharge limits for open release to the environment. Any proposed modifications resulting from this work would be limited by the scale and size of the problem as emissions from the SIXEP plant are low. When comparing this to the cost and interventions required to add further control measures it could be considered to be disproportionate to the risks encountered. i.e. a new plant might not be considered but a small modification to the capturing of solids may be suitable and reasonable.

Dose elimination is a key requirement for any work that involves hazardous substances either radioactive or inactive. The risk hierarchy should be followed for all activities (when attempting to adopt BAT) where elimination of the risk is always the first and most desired outcome due to its effectiveness in removing the hazard. A collective control measure is always the more desirable measure compared to the protection of individuals as it is the least effective as it only protects the person and not everybody.

When considering the discharge line from SIXEP the observed solid formation in the pipeline may act as a means of accumulating radionuclides. Indeed the activity of the solids isolated from in the discharge line has been determined (Chapter 2) but only with minimal sampling. The impact of activity on POCO and future decommissioning works will be discussed as these solids could retain radionuclides that will impact future plans. The activity of the recovered pipeline solids was determined experimentally by dissolving the "wet solid" in nitric acid and was analysed for Alpha, Beta and Gamma content (Table 3.2). An increase in the activity of the April 2004 sample after it was aged for 8 months was due to a loss of water present in the sample during storage (but the magnitude of this water loss was not provided).

The waste arising from the discharge line would be likely to be characterised as Intermediate Level Waste (ILW) (>4 GBq tonne<sup>-1</sup> for  $\alpha$  emitters and 12 GBq tonne<sup>-1</sup> for  $\beta$ , and  $\beta$ ,  $\gamma$  [40, 41]). The waste would have a considerable cost in terms of resources associated with ILW disposal. The removal of solids from the discharge line would require considerable planning and resources for subsequent remediation/retrieval. The minimisation or elimination of the solids forming within the pipeline would reduce the volume of any waste arising. The waste would ultimately be deposited in the GDF. A reduction in activity contained within the discharge line would either eliminate or minimise the ionising radiation dose to workers tasked with the clean-up and decommissioning of the pipeline.

A pricing methodology has been adopted for new build power plants to facilitate pricing of ILW and High Level Waste (HLW)[42]. There is a cap of ~£50,000 tonne<sup>-1</sup> for ILW disposal[42] as a limit of any new build operator's liability for disposal costs. However the quantification only applies to new build works and does not include existing waste generators (such as SL).

The NDA retains the liability for waste as per the integrated waste management plan[43]. The disposal costs would be broadly similar to those of a new build operator, although there would not be a cap on the liability.

Costs associated with disposal of ILW waste are yet to be fully defined for legacy wastes, due to the uncertainties over the GDF and subsequent pricing models for waste generated on the NDA estate. However these costs are likely to be substantial and minimisation or elimination of waste is always preferable to identifying disposal routes.

The route for the waste recovered from the pipeline would be likely to be the same as that used for the used clinoptilolite and sand from SIXEP, in the form of ILW with a similar waste form as well. At present the preferred form is cementitious grout waste immobilisation[44].

Table 3.2-Total activity of samples after undergoing dissolution in nitric acidfrom SIXEP discharge solids collected in April and November 2004[24].

Type of Radioactivity	April 2004	April 2004	November 2004
	sample	(aged 8 months)	sample
Total alpha (Bq.g <sup>-1</sup> )	1.85x10 <sup>4</sup>	3.35x10 <sup>4</sup>	2.00x10 <sup>4</sup>
Total beta (Bq.g <sup>-1</sup> )	2.93x10 <sup>5</sup>	4.79x10 <sup>5</sup>	2.34x10 <sup>5</sup>
Total gamma (Bq.g <sup>-1</sup> )	7.50x10 <sup>4</sup>	1.09x10 <sup>5</sup>	7.59x10 <sup>4</sup>

Cementitious grouting is a common technique used for the immobilisation of many wastes originating on the Sellafield site. It has an advantage over other encapsulation techniques as it is a proven and well understood technique that has significant infrastructure already in place to receive the waste and transform it into an acceptable waste form for ultimate disposal. The purpose of any encapsulant is to immobilise the waste to prevent the migration of any radionuclides from the waste form to the surrounding environment. Clinoptilolite, sand and sludge would be treated separately with any liquid removed from the solids prior to encapsulation as the presence of free water would compromise the effectiveness of the cementitious grout. Alternative encapsulation techniques have been examined for SIXEP clinoptilolite, sand and associated sludges [45] by the NDA. These can be briefly summarised as:

- Geopolymer the waste is added to an aluminosilicate solution and heated (~80 °C) to form a solid immobilised form via polymerisation of the aluminosilicates and materials in the waste feed.
- Vitrification the dried waste is mixed with molten glass and once the mixture cools retains the waste in a glass matrix. This would typically be used for high level waste where the activity is much higher than that encountered in the SIXEP waste streams.

Dose minimisation or elimination would be the key concern of any POCO/ decommissioning work plan. As such a reduction in solids that can entrain radionuclides would provide considerable benefits to the long term operations in terms of waste minimisation and dose reductions.

#### e) Process improvements

Dose elimination and minimisation of costs associated with waste disposal are areas that research can support. Another significant area is process improvements. The efficient operation of SIXEP can be slowed by pressure build-ups within the discharge pipeline. A restriction of the diameter within the pipeline would result in one of two conditions either a) an increase in pumping pressure to maintain the same flow rate or b) a reduction in flowrate at the same pressure. The discharge pipeline has a maximum pressure rating and increases above this limit are not possible, thus if the pipeline diameter is reduced it will most likely result in a reduction in pipeline flow rates(condition b).

SIXEP takes a number of feeds not only from the first generation Magnox storage ponds. The "Conditions for Acceptance (CfA)"[22] are discussed but these are not readily defined in available literature. The waste streams incoming into SIXEP can contain a significant loading of solids[22]. However these solids are generally dealt with via settling tanks prior to entry into the sand bed filtration portion of SIXEP. A broader range of feeds falling outside the CfA for SIXEP may impact on fouling downstream of the plant. However there are no further details on the quantification of these feeds. The SL effluent management plan [46] indicates that in the future SIXEP will play a key role in the treatment of effluent in Legacy ponds and silos but does not provide comprehensive details as to the composition of these feeds.

The feed compositions will have an effect on the likely solids formed downstream of the plant. An increase in cation concentration could induce a faster rate of Si – Al substitutions in the clinoptilolite tetrahedral arrangements in the structure. The impact of

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this on clinoptilolite is that it may undergo significant incongruent dissolution possibly increasing the rate at which solids build-up downstream. An understanding of the likely performance of clinoptilolite in the present feed conditions will allow input into the "SIXEP process models"[22].

Process improvements can also be achieved by a reduction of solids within the discharge line leading to an increase in throughput of the plant. A reduction in treated volume through solids build-up would result in a reduction in alternative effluent feeds that could be treated in addition to the constant Magnox ponds feed. The impact would be felt on future plans for decommissioning waste effluent feeds[46] resulting in an increased timescale for retrieval of wastes from the silos and legacy ponds or potential interim storage of this effluent prior to subsequent treatment.

Any improvements to the plant discharge line through a decrease in solid formations within the pipeline would improve the throughput of SIXEP that would in turn lead to potential savings for decommissioning projects. A reduction in project duration should result in a saving in cost and the associated resources. Due to the nature of the NDA's mission (and by nature of the new ownership model of SL) a reduction in duration would enable other schemes to be accelerated or the commencement of additional schemes.

# f) Successor plant

SIXEP has a planned operating programme until at least the mid-2020s[46] with a requirement for effluent treatment on the Sellafield Site until at least the 2050s[47]. There is a plan for an additional ion exchange effluent treatment plant adjacent to SIXEP, the Site Ion Exchange Contingency Plant (SCP). The SCP will replicate functions performed by SIXEP[47].

The successor plant could be configured in such a way as to allow alternative ion exchange media to be utilised, potentially allowing the removal of other cationic species.

Alternative ion exchange media would enable greater variability in conditions for acceptance with regards to incoming pH thus removing the carbonation tower requirements. Further benefits would be to allow a greater range of ionic species to be removed from the effluent as currently the plant must place strict limits on incoming competitor species. It may also improve process efficiency by, for example, increasing decontamination factors and/or extending the number of cycles between bed changes. There is an ongoing research project (M.Herbas) funded by Sellafield Ltd through the University of Manchester examining the options for alternative ion exchange media. The key requirements for any alternative media would be:

- Maintenance of ion exchange performance irrespective of high pH, as this would allow a much broader range of incoming feeds in particular silo discharge effluent from the Magnox Swarf Storage Silos.
- The degradation and dissolution of the proposed media should be less than clinoptilolite reducing the build-up of any solids within the discharge line
- A greater efficiency of ion exchange of the primary species to be removed (Cs and Sr) and a capacity for secondary species removal
- Ability to process effluent without additional treatment steps (pH reduction), would lessen the likelihood of precipitation of solids through a pH change within the treatment plant. However any high pH effluent would still require pH adjustment prior to discharge. This would cause environmental damage if left

unaltered and as such could potentially increase solid formations within the discharge line.

The detailed design of SCP (planned date 2019) has not commenced yet. As such, details involving ion exchange media and plant process are not readily available. However recommendations relating to incongruent release of Si and Al would be pertinent to that phase of the design selection as alternative ion exchange media may produce less solids resulting in a corresponding reduction in solid formations.

The disposal route for the treated effluent has not been identified yet. The discharge pipeline would likely be the most suitable route. However if fouling of the existing pipeline becomes too great and the dose encountered prohibits satisfactory enhancement works, there exists the possibility of additional discharge lines.

# g) Conclusions

This chapter has sought to provide an overview and context for the subsequent research activities. The review of internal reports (Chapter 2) undertaken or funded by SL (or previous incarnations) has identified research themes: precipitation of solids from likely effluent compositions encountered in the SIXEP discharge line, performance of clinoptilolite and subsequent release of fines (congruent dissolution) or release of solutes (incongruent dissolution) and the performance of polyelectrolyte as an alternative means of adsorption onto surfaces to biofilms.

Solid formations have been encountered in the discharge pipeline and these formations have an impact on plant performance. The activity of the solids (Table 3.2) appeared to suggest that significant control measures would be required when decommissioning the discharge line and subsequent increases in resources that could be utilised on other schemes. Due to the nature of the NDA funding, there are limited resources and prioritisation of these identified risks is required. Waste elimination is always the priority.

A reduction in the treated volume of effluent through the plant as a result of solid formations would potentially impact on future POCO waste streams and would be likely to increase the project durations and costs in addition to worker dose rates. Solid formations ideally should be eliminated and an understanding of the formation of these solids together with a means to address attachment and increases in the solid mass would enable mitigation measures to be made possible. These findings could inform future plant operations through the SCP project where alternative arrangements of ion exchange media may be utilised.

# Chapter 4 – Method development and characterisation

# 4) Experimental methods

### a) Introduction

The internal Sellafield Ltd (SL) reports have highlighted three areas that may prove fruitful in addressing the solid build-up in the discharge lines emanating from the effluent treatment plant. Initially this project was intended to focus on the chemical engineering aspects of solid formation. However following reviews of existing work it has become apparent that a more fundamental approach is required. Solid formations have been suggested as originating from clinoptilolite fines or some form of re-precipitation from bulk effluents held in a biofilm matrix adhered to the pipeline's surface. Three areas (Fig. 4.1) have been highlighted in this work as requiring investigation:

- initial solid formation possibly due to chemical precipitation from bulk effluent, clinoptilolite fines or biofilm growth;
- ii) whether polyelectrolyte provides a means of attaching these solids to the pipeline surface. If not, then the attachment mechanism will most likely be some form of biofilm;
- iii) once the initial solids have attached to the surface, whether there is a bulk solid generation phase of entrained solids from clinoptilolite fines wash through, chemical precipitation from the effluent and/or clinoptilolite dissolutions.

Significant work was undertaken on attempting to produce likely mineral phases that could precipitate from discharge effluent. This section will not replicate data presented in subsequent sections but instead will focus on the development of the methodologies.



Figure 4.1 – Overview of solid generation, attachment and bulk solid formations.

Where equipment has not been operated by the author there will be a brief discussion as to the role the author played in collecting the data. In particular usage of the ion beam accelerator and Rutherford Back Scatter end station has been performed by experimental officers due to the complex and safety critical nature of these operations.

Sections of experimental work will broadly follow the subsequent chapters; lab scale precipitation formations, clinoptilolite dissolution experiments and polyelectrolyte adsorption studies. There will be some discussion as to data interpretation, in particular the ternary diagram format used within the precipitation studies section. The flow loop that was created for this project will be discussed and method development discussions will be undertaken. The flow loop will be revisited in the future work section as the remainder of this work attempts to better understand the fundamental processes driving solid formations within the pipeline.

#### i) Precipitation studies

The aim of this study has been to attempt to replicate solids that contain similar elemental compositions to those encountered in the discharge line. A three stage process has been adopted, firstly modelling of elemental species using geochemical modelling (PhreeqC), secondly condition narrowing using small volume experiments to create a large number of samples (>180 vials), and finally larger volume samples with three experimental matrices (10 to 11 experiments per matrix).

At the commencement of this study, limited effluent composition data has been provided by SL. A screening exercise was undertaken utilising small sample volumes with greater variability in pH and elemental concentration. To commence the condition narrowing exercise, modelling composition data was undertaken using the PhreeqC geochemical code[48] provided by the United States Geological Survey. The model suggested that Si and Al despite not being present in the effluent discharge data these elements played a key role in producing likely precipitates (Chapter 5 details modelling and plant compositional data). Subsequent monitoring data has been provided, around mid-2015, from the discharge line which has been incorporated into "precipitation studies".

#### ii) Clinoptilolite dissolution

Mineralogical investigations have been previously undertaken on the Mud Hills clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) as part of investigations into process improvements in SIXEP[8]. There were strong elemental similarities between solids found in the discharge pipeline and that of clinoptilolite [23, 24]. This conclusion was reached in spite of extremely limited characterisation efforts on the recovered sample. The case for clinoptilolite fines has been best made using Scanning Electron Microscope images indicating the morphology of the recovered solid. The aim of this

series of experiments was to examine the role of clinoptilolite fines (congruent dissolution) in the solid build-up and also aqueous elements released from the clinoptilolite structure (incongruent dissolution). In addition  $\gamma$ -irradiated clinoptilolite at a high total dose (50 MGy and dose rate of ~ 5 Gy.s<sup>-1</sup>) samples have been examined at similar concentrations and conditions of previous aqueous experiments and mineralogical examinations.

#### iii) Polyelectrolyte

Polyelectrolyte (polygold CL520) is dosed into the incoming SIXEP effluent prior to its reaching the sand bed filters at ~0.58 mg.L<sup>-1</sup> to aid solid filtration. Some work has been undertaken on the polyelectrolyte adsorption on the sand bed filters[22] but has been limited to the simulations and modelling of colloid – polyelectrolyte sand particle – polyelectrolyte interactions. The work [22] considered how the polyelectrolyte interacted with the particles only. This does not provide additional insight from the plant perspective as it did not consider release of the polyelectrolyte once attached nor polyelectrolyte stainless steel interactions. Improving detection limits downstream of the sand bed filters or wash through the plant affecting the discharge line were not considered by the Owens study[22]. The presence of organic carbon has been identified in the discharge line by a previous study[16]. Organic carbon could originate from a number of sources, either from wash through from the storage ponds of algal blooms that are present for long periods of the year or through the introduction of organic compounds within the plant. The presence of an organic compound within the discharge effluent is the most likely means of creating an initial solid formation within the discharge line. The low concentration present within the discharge line and the inability to measure the concentration of polyelectrolyte in line has previously limited the willingness to investigate the

contributory factor of polyelectrolyte in solution. The origin of this organic matter has been postulated as either biofilms or the dosed polyelectrolyte[16, 18]. The aim of this study will be to investigate adsorption of clinoptilolite particles/fines onto stainless steel surfaces using a broad range of polyelectrolyte solution concentrations. The main focus of the work will be to determine whether polyelectrolyte can adhere solids to stainless steel surfaces.

# b) Main characterisation techniques

A number of techniques have been utilised for characterisation of the solutions and solids produced during these studies. For brevity the four major techniques have been presented here: Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX); Powder X-Ray Diffraction (pXRD); Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) and Rutherford Back Scattering (RBS).

# i) Scanning Electron Microscopy

The use of Scanning Electron Microscopy (SEM) has been extensive within this work. Morphology of samples was determined using a FEI Quanta FEG 250 microscope using a 1mbar vacuum at 20keV electron beam with a working distance of 10 mm. An Energy Dispersive X-ray (EDX) detector has been used where elemental composition data was required. The EDX detector used for this work was an Oxford Instruments system, with analysis via Aztec software utilising the appropriate standard characterisation data set for the electron energy level (5 or 20 keV). Investigations were typically undertaken in environmental mode, i.e. with water to increase the surface conductivity of samples. Initial samples were carbon coated with a ~10 nm coating layer performed by thermal evaporation of a carbon road to generate a conductive surface coating for analysis of morphology and/or elemental compositions. Carbon coating and high vacuum SEM observations were undertaken in work relating to precipitation studies (Chapter 5) with the remainder of the work undertaken in environmental mode (Chapter 6-8).

The operation of a SEM requires an electron gun to generate the electrons. These electrons are passed through a series of focusing and deflecting lenses. The electron beam is rastered across the sample retained on the sample working stage with electrons collected in a secondary electron detector for subsequent analysis. A representation of the sample is produced from signals generated in the electron detector that identifies shapes and variations within the samples. The majority of the studies in this work were performed at 20keV with the exception of precipitation studies which were performed at 5keV due to the nature of the samples and surface coating (Chapter 5).

#### ii) Energy Dispersive X-Ray Spectroscopy

Collection of elemental compositional data is possible whilst using the SEM in conjunction with the EDX detector. An Oxford Instruments X-Max 80 EDX detector has been used to obtain elemental characterisation data to enable characterisation of samples. The generation of X-rays in the sample requires a source, in the case of SEM-EDX the electrons from the electron gun bombard the sample, which generates an identifiable characteristic X-ray from electron transitions within the solid being investigated. A localised characteristic X-ray is generated that is detected by the semi-conductor contained in the EDX probe.

The detector then generates a signal that is processed to produce spectra containing counts against energy level (keV). The energy levels can be assigned to a specific element by comparing the levels recorded experimentally to the K and/or L energy bands for the

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corresponding element. In these studies the internal characterisation data set provided with the Oxford Instruments Aztec software was utilised to provide elemental compositional data for the solids at the corresponding energy levels (5 or 20 keV).

There has been significant debate [49-52] as to whether EDX can be quantitative when considering "rough" heterogeneous samples. The accuracy of readings in "rough" heterogeneous samples as encountered in the majority of these studies depends upon whether the element in question was a major (> 10% of element present in solid, or atomic percent (by atom) or minor (>1%, <10% by atom) constituent of the solid. Trace analysis (<1% by atom) is not considered suitable for this form of characterisation with no prior surface preparation due to the irregular and heterogeneous nature of the solids found in these studies.

In this body of work, contrary to the sample characterisation methodology undertaken on the recovered pipeline solid, a substantial number of data points has been collected for each sample to attempt to overcome the weaknesses associated with rough samples and to ensure a more accurate representation of a potentially heterogeneous sample. Each collected data point indicates the elemental composition at that location. Data has been presented in a number of formats. Ternary diagrams have been used to provide elemental information of precipitated solids (Chapter 5 and 7). Due to the unusual use of axes of these diagrams a simplified diagram is presented to indicate what each axis represents (Fig. 4.2).



Figure 4.2 - A ternary diagram presenting Si, Al and Mg elemental data which has been used extensively in this work. The diagram represents three variables (elements), the red star indicates a solid that contains 50 % Si, 35% Al and 15% Mg, whilst the blue triangle indicates a solid that contains 25% Si, 75% Al and 0% Mg.

When considering ternary diagrams the reader should be aware that the percentages relate to only those elements present on the diagrams and that these may in fact be minor elements, part of a much wider elemental composition containing a significant variance in elemental composition.

#### iii) Powder X-Ray Diffraction

Powder X-ray diffraction (pXRD) using a Bruker D8Advance diffractometer (Cu source) has been used to identify crystalline mineral phases in precipitation studies (Chapter 5) and to determine clinoptilolite structure (Chapter 6-8). Initial precipitation study samples were investigated using a borosilicate microscope slide. However, because the composition of the samples contained a mixture of crystalline and amorphous Si and Al solids there was significant difficulty in identifying phases present in the samples. Once the samples were transferred to a non-diffracting silicon sample holder the phases became more easily identifiable.

An X-ray diffractometer consists of a source of X-rays, a sample holder and X-ray detector. When X-rays satisfy the Bragg equation (Eq. 4. 1) they produce constructive interference and provide information relating to the spacing between the atoms present in the solid. By altering the angle of incidence a characteristic diffraction pattern can be produced that allows identification of the crystalline phases present in the sample. When compared to reference samples previously identified, this allows phases present in the sample to be characterised.

# $n\lambda = 2 dsin\theta$ - Equation 4.1

#### iv) Inductively Coupled Plasma Atomic Emission Spectrometer

ICP-AES was undertaken to determine the concentration of solutes present and was operated by the Manchester analytical geochemistry unit located in the Williamson Research Centre. Solutions requiring such analysis were obtained for the clinoptilolite studies (Chapter 6 and 7).

A Perkin-Elmer Optima 5300 dual view inductively coupled plasma atomic emission spectrometer was used with operation of the equipment undertaken by the analytical staff located at the geochemistry unit.

The sample is introduced into the spectrometer, where the sample is atomised, the atomised vapour is then turned into a plasma along with a carrier gas with thermal excitation of the electrons in the outer shell of the element. When these electrons return to a ground state they emit a photon that has a characteristic that can be used to identify the element. ICP-AES was used almost exclusively for aqueous element concentration determination, as all of the solutes investigated were in the ppm concentration range (with the exception of Cs concentration (ppb range) in Chapter 6).

## v) Rutherford Back Scattering

The use of Rutherford Back Scattering (RBS) requires the use of a pelletron ion accelerator. The basic principle of RBS is to use a beam of  $\alpha$  –particles (He<sup>2+</sup>) where each ion impacts on the surface of the sample resulting in an elastic collision between the ion and the particle located in the sample[53]. The backscattered ions generate a cross section that provides data that can be used to determine elemental composition. To quantify the elemental composition, a simulation of the energy cross section produced experimentally is used to allow fitting based upon estimated elemental compositions.

Experiments were performed using the RBS end station attached to the dual beam 5 MeV pelletron ion accelerator[54, 55] located at the Dalton Cumbrian Facility (Fig. 4.3). The energy of the ions was 2 MeV. Experiments were performed by staff at the DCF with data simulation performed using SimNRA [56] by a Research Associate also located at DCF.

There were some issues using the RBS technique, in particular for very low concentration solid dosing with the beam size of ~1 mm diameter combined with low amounts of sample on the substrate containing with only small particles ~(<100s  $\mu$ m) would not generate significant backscatter due to the majority of the beam interacting with the substrate itself. This was rectified to some extent in the main RBS experiments (Chapter 8) where higher dosing of solids was undertaken such that a greater amount of sample was deposited on the substrate compared to these initial experiments.



Figure 4.3 - Tandem Pelletron Ion accelerator located at the Dalton Cumbrian Facility. The Rutherford Backscatter end station was located on one of the main 5 MeV accelerator beam lines and has been identified as RBS.

# c) Gamma irradiation source

A <sup>60</sup>Co  $\gamma$ -source was utilised for the irradiation of clinoptilolite in a dry state. This was performed at the Dalton Cumbrian Facility[54] with a total dose of 50 MGy at a dose rate of ~5Gy.s<sup>-1</sup> (or ~300 Gy.min<sup>-1</sup>). The irradiator was operated and dose determined by a DCF experimental officer using Fricke dosimeter[57] where absorption is measured due to the change from ferrous ions (Fe<sup>2+</sup>) into ferric ions(Fe<sup>3+</sup>) caused by radiation. Fricke solutions are the most common form of dosimetry for radiation studies and has been used for this work.

# d) Experimental methods

The three broad areas of research have been addressed over four papers presented in subsequent chapters. These sections will discuss some of the specific method development work undertaken to produce the presented work along with discussion of characterisation equipment and techniques.

All work that had the potential to create solutes of Si was performed in beakers or containers of high density polyethylene (HDPE) to prevent any leaching of Si from the borosilicate glassware, however remote the possibility, at the near neutral pH conditions at which the majority of the experiments were undertaken.

# i) Precipitation studies

An initial experimental screening exercise was undertaken to confirm whether solutions containing Si, Al and Mg could form precipitates and was based upon modelling outputs from PhreeqC[48] based upon plant monitoring records (detailed in Chapter 5). At each elemental concentration the pH was adjusted using 0.1 M HCl and 0.1 M NaOH as required to 7.0, 8.0, 9.0 and 10.0 ( $\pm$ 0.5) pH using a Mettler Toledo pH meter and electrode (Inline expert pro probe) under normal laboratory temperature (~25 °C) and pressure (1 bar) conditions. The experiments were undertaken in small sample volumes (20 mL). Stock solutions were created by dissolved MgCl<sub>2</sub>, AlCl<sub>3</sub>.6H<sub>2</sub>O, Na<sub>2</sub>SiO<sub>3</sub>.5H<sub>2</sub>O which were supplied by Sigma Aldrich and were used as received, in deionised water (Elga purelab classic 18.2 MΩ-cm).

Table 4.1 details the range of elemental compositions of the series of experiments using the stock solutions created previously. For each experimental concentration an appropriate amount of stock solution was introduce into a DI water solution and the pH was adjusted for each experiment (7, 8, 9 and 10 pH) to provide four samples per elemental concentration. The samples were stored without agitation for 1 month in normal pressure and temperature conditions and prior to filtering the samples were

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inspected for visible precipitates. Some of the samples contained a visible formation in the vials (Table 4.2). The visible formation was most noticeable in the high starting elemental concentrations (> $5.0 \text{ mg.L}^{-1}$ ).

Table 4.1 - Elemental compositions for initial screening exercises undertaken on small volume samples (20 mL) at ambient conditions ( $25^{\circ}$ C) and normal pressure (1 bar) with pH adjusted to between 7 and 10 pH using 0.1 M NaOH and 0.1 M HCl.

	Min.	Max.		Min.	Max.		Min.	Max.
Series 1	(mg.L <sup>-1</sup> )	(mg.L <sup>-1</sup> )	Series 2	(mg.L <sup>-1</sup> )	(mg.L <sup>-1</sup> )	Series 3	(mg.L <sup>-1</sup> )	(mg.L <sup>-1</sup> )
Si	0.1	0.5	Si	0.5	2.0	Si	5.0	25.0
Al	2.0	10.0	Al	2.0	10.0	Al	5.0	25.0
Mg	1.0	10.0	Mg	2.0	10.0	Mg	5.0	25.0

Table 4.2 - Samples containing visible precipitates after ageing for 1 month in static conditions First number indicates number of samples that contained visible precipitates, second (number) indicates total number of samples created for the corresponding pH.

	рН	7.0	8.0	9.0	10.0
	Si	2 (5)	2 (5)	2 (5)	2 (5)
Series 1	Al	0 (5)	0 (5)	0 (5)	0 (5)
	Mg	0 (5)	0 (5)	0 (5)	0 (5)
	Si	1 (5)	1 (5)	1 (5)	1 (5)
Series2	Al	0 (5)	0 (5)	0 (5)	`0 (5)
	Mg	0 (5)	0 (5)	0 (5)	0 (5)
	Si	5 (5)	5 (5)	5 (5)	5 (5)
Series 3	Al	5 (5)	5 (5)	5 (5)	5 (5)
	Mg	5 (5)	5 (5)	5 (5)	5 (5)

After a visual inspection each sample was passed through a 0.8 µm track etched polycarbonate filter for subsequent characterisation. Characterisations were performed on a selected small sample size (~6 samples) using Powder X-Ray Diffraction (pXRD) and Scanning Electron Microscopy (SEM) complemented by Energy Dispersive X-Ray (EDX) spectroscopy.

Characterisation by pXRD was difficult in these trials due to the limited quantity of solids produced and either: a) interference from the substrate of the sample holders; or b) an amorphous solid that produced a typically broad and shallow bulge between  $20^{\circ}$  and  $30^{\circ}$ (Fig. 4.4)  $2\theta$ . Crystalline solids (Fig. 4.5) were identified as gibbsite (Al(OH)<sub>3</sub>) and the phase was produced in high concentration solutions (> 5mg.L<sup>-1</sup> Al, Si and Mg) at near neutral pH (~7.4). The sample holders were changed to non-diffracting backing for the main experimental work (Chapter 5) to identify whether the bulge was as an amorphous solid or as a result of interference. The former was the case in the main precipitation studies (Chapter 5) as confirmed by SEM-EDX measurements.



stnuoC

Figure 4.4 - Powder X-Ray diffraction of sample produced during method development trials.



struoJ

Figure 4.5 - Powder X-Ray diffraction of sample containing gibbsite produced during method development trials.

#### ii) Clinoptilolite dissolution

An initial set of experiments was undertaken on clinoptilolite to investigate dissolution effects and whether clinoptilolite fines could be responsible for solid formations within the discharge pipeline. Actual experimental results are presented in Chapter 6.

Clinoptilolite (Na2.2Mg0.40K0.89Ca0.99Sr0.07Al6Si30O72.24H2O)[8] as supplied by Sellafield Ltd was used in an unwashed "as received" condition. 2.00g of clinoptilolite was added to a pH adjusted solution (1000 mL) of 9, 10 and 11 (±0.5) pH. High pH solutions had been chosen as clinoptilolite was thought to be stable at near neutral pH conditions and maloperation and/or fault conditions were suspected of causing dissolution of the mineral structure. The adjustment of pH was undertaken using 0.1 M HCl and 0.1 M NaOH to the required pH and measurements were obtained from a Mettler Toledo pH meter and electrode (Inline expert pro probe). The experiments were performed in normal atmosphere as the effluent undergoes carbonation to control pH prior to entering the ion exchange beds. The decision was taken to provide no  $CO_{2(g)}$  control in order to reflect the conditions encountered on plant. CO<sub>2</sub> dosing was considered in the experiments. However this would not have reflected the conditions under which the ion exchange beds received incoming effluent i.e. carbonation and pH already reduced prior to contact with clinoptilolite. The solutions were placed on a shaker bed (100 rpm) and subjected to continuous agitation during the experiment.

Aliquots were drawn off at regular intervals (24, 72 and 240 hours) and were centrifuged (3000 rpm, 10 min) using a Grant-bio LMC-3000 centrifuge to remove any large solids. The aliquots were then sent for analysis for the following solutes: Na, Mg, K, Ca, Si, Al and Fe by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with appropriate solutions standards. The development trials indicated that significant solutes were released after an initial 24 hours with some reduction encountered in solutes at the 72 hour measurements. The solutes have been expressed as a percentage solute lost compared to starting mass of clinoptilolite (2.00g) and have been volume corrected for reduced solution volume after drawing off aliquots (Fig. 4.6). A Si solute of ~1% could generate significant solids within the discharge pipeline of SIXEP. Likewise ~0.1% Al could form either simple Al hydroxides or more complex aluminosilicate solids (Chapter 5 and 6).



Figure 4.6 - Solutes expressed as a % loss of mass of clinoptilolite (2.00 g) after undergoing pH adjustment (9, 10 or 11 pH) and undergoing continuous agitation (100 rpm shaker bed)

#### iii) Polyelectrolyte adsorption

Polyelectrolyte adsorption experiments were undertaken using small stainless steel coupons (1 cm x 1 x 0.09 cm) of type 304L (1.4307) received to a 2B finish from Aalco Manchester. The majority of the SIXEP discharge line is fabricated from 304L stainless steel with a small section of carbon steel after the pipe bridge towards the end of the discharge line (see Fig. 1.2). Solid formation was encountered in a section of 304L stainless steel pipeline prior to pipe bridge. The sheet had been hot rolled, heat treated at 1100 °C, solution annealed by quenching with water/air and lastly the mill scale was removed. The steel was then cut to size. An initial method development experiment was undertaken utilising a solution containing a range of polyelectrolyte concentrations. Polygold CL520 as supplied by Goldcrest Chemicals and used in the sand bed filtration system of SIXEP was used as the polyelectrolyte for all experiments. Characterisation of the polyelectrolyte at the commencement of this work was attempted by the School of Chemistry analytical service. Mass Spectrometry (MS) did not identify any consistent compounds present in solution. The MS characterisation may indicate that the polyelectrolyte as used in SIXEP was an agglomeration of a number of organic phases that do not provide an identifiable phase. Instead the high molecular weight compounds break down and recombine in solution in a disordered manner.

Coupons (1 x 1 x 0.09 cm) were introduced into a solution of deionised water and polyelectrolyte (0.1, 1 and 10% v/v) with a small quantity (<1 mg) of previously prepared and dried gibbsite. The solutions were stored in static conditions under normal temperature (25  $^{\circ}$ C) and pressure (1 bar) in an air atmosphere. After two weeks of storage the solution was drawn off using a syringe through a hole in the side of the container. The solution containing polyelectrolyte and mineral (gibbsite in initial trials)

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was drawn off in a controlled manner in order to avoid disturbing the surface solids retained on the stainless steel coupon. The coupons were transferred to a microscope slide and dried for 24 hours in a vacuum oven at 40  $^{\circ}$ C.

An additional set of coupons was also prepared that contained only polyelectrolyte within a solution concentration of 10% and 100% v/v. A further control sample containing no polyelectrolyte solution but with the mineral (gibbsite) was examined. These control polyelectrolyte samples were prepared by pipetting out a small volume (~1 mL) of solution which was deposited onto the coupon. These prepared coupons were dried in the same manner as the polyelectrolyte/mineral coupons.

Characterisation was performed on the coupons after drying using the Rutherford Backscattering (RBS) end station attached to the dual beam 5 MeV pelletron ion accelerator[54, 55] located at the Dalton Cumbrian Facility. Other characterisation techniques were also performed and are detailed in Chapter 8.

The rationale for a solution containing gibbsite (Al(OH)<sub>3</sub>) as opposed to clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) had been to investigate a link between gibbsite and polyelectrolyte adsorption in similar plant concentration conditions. However after characterisation using RBS it became apparent that very low sample volumes of gibbsite replicating likely solid quantities produced in the discharge pipeline would prove problematic from a data collection perspective. Outcomes of the characterisation through RBS for the polyelectrolyte only samples (10 and 100% v/v) proved more fruitful as it indicated suppression of the underlying stainless steel elemental components. There was no evidence of gibbsite material overlaying the stainless steel sample on the polyelectrolyte free control sample. Gibbsite was not

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encountered in the samples containing gibbsite/polyelectrolyte mix as well. Therefore, either the limits of detection for gibbsite are being reached using RBS, or polyelectrolyte cannot bind solids to the surface indicating that biofilm is the likely cause of the solid formation entrainment. The suppression of the signals from Fe, Cr and Mn indicated that the technique would be suitable for further clinoptilolite/polyelectrolyte studies.

Clinoptilolite was chosen for the main study as opposed to gibbsite. The previously recovered pipeline solid contained an organic carbon content and the purpose of this study was to identify whether polyelectrolyte could bind solids to the steel surface.

# e) Flow loop

A bespoke flow loop was fabricated for this work (Fig. 4.7) in parallel to the other studies undertaken and presented in the subsequent chapters. However due to the significant areas of "unknowns" associated with formation mechanisms and likely solids this necessitated further investigation in laboratory scale prior to pilot scale/flow loop experiments. A brief overview of flow loop design and fabrication has been presented here as an introduction to further work described in Chapter 9.

The flow loop consists of a recirculating loop of ~25 mm diameter stainless steel pipework with a peristaltic pump (Verderflex Dura 35) and a storage tank (~ 50 L capacity). A high volume and flow rate pump was selected as this would allow investigation of both low flow simple settling of solids, representative velocities and turbulent flow encountered on plant and high flow rate conditions that may be suitable to simulate removal of retained solids. The flow loop is designed so it can obtain similar flow velocities (~1.75 m.s<sup>-1</sup>) for the effluent to that of the SIXEP discharge line (0.49 to 1.98 m.s<sup>-1</sup>). The maximum Reynolds number (Re) that can be produced in the flow loop is 4.4 x10<sup>4</sup>, whilst the

discharge line pipeline has maximum Re value of  $3.01 \times 10^5$  (150 mm diameter pipe) and  $1.24 \times 10^5$  (300 mm diameter pipe).

Initial commissioning trials were undertaken on the flow loop and some further development work was undertaken with a solution of starting concentration of 0.025 mg.L<sup>-1</sup> Si, 9.2 mg.L<sup>-1</sup> Al and 10.0 mg.L<sup>-1</sup> Mg with a total solution volume of 50 L. A flow restrictor formed by the use of fine mesh (0.65 mm opening) was used during these trials and did not indicate the presence of solid formations on the filter. However more work should be undertaken on the flow loop following conclusion of the laboratory studies involving precipitation (Chapter 5), clinoptilolite dissolution (Chapters 6 and 7) and polyelectrolyte adsorption (Chapter 8).



Figure 4.7 - Flow loop created for this project with 25 mm diameter stainless steel pipework, a tank (~50 L capacity) discharges analogous effluent which is pumped around the system using a peristaltic pump (Verderflex Dura 35) with a pulsation damper.

# f) Outcomes

#### i) Precipitation studies

Solids can be formed from aqueous solutions containing relatively low concentrations Al and Si. However precipitates were more noticeable from solutions with higher concentrations of these elements (>5.0 mg.L<sup>-1</sup>). When samples are being examined using pXRD the sample holders should be of a non-diffracting backing in order to determine the nature of the samples whether amorphous or crystalline. SEM-EDX investigations can be used for major (>10% by atom) and minor (<10% by atom) elemental constituents however trace elemental analysis (<1% by atom) should not be undertaken with rough heterogeneous samples by this technique. A significant number of data points should still be collected by SEM-EDX to obtain quantitative information for elemental constituents >1% (by atom) to minimise errors that are inherent in a non-polished sample.

#### ii) Clinoptilolite dissolution

Dissolution of clinoptilolite occurs to a greater extent at a higher pH than that encountered in the ion exchange beds of SIXEP (pH ~ 7). Nonetheless, the relatively small extent of clinoptilolite dissolution that is observed experimentally at pH neutral (~1% Si by starting mass) may still provide the original source of material leading to the solids formation observed in the discharge line. Over the cycle time (> 90 days) of an ion exchange bed (~7400kg bed), even small relative amounts of clinoptilolite dissolution may contribute significantly to the solids encountered within the effluent discharge line. Work is required to establish the nature of either fines or aqueous species and quantity of solutes at near neutral conditions. ICP-AES can be used to determine the mass of solutes in the ppm range and above.  $\gamma$ - irradiation of clinoptilolite will be performed at the DCF using a <sup>60</sup>Co source in a dry non-aqueous system.

# iii) Polyelectrolyte adsorption

The RBS characterisation technique can be used as a means to determine the composition of solids adsorbed and/or deposited onto the surface of a stainless steel coupon (304L grade). Sample preparation has been developed using a syringe to draw off the solution prior to drying to minimise disturbance of the prepared coupons. Other techniques (FT-Raman and FTIR) have been included in Chapter 8. However for brevity these have not been discussed in this section.

# Chapter 5 – Precipitation studies paper
# A methodology to identify likely mineral phases that cause pipeline solid formations in nuclear effluent treatment plants

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# Author Contributions

R S Jones – First Author, principal researcher, model development, experimental data collection and data analysis.

D. Trivedi – Initial model, co-supervisor including method development discussions, manuscript review; C.A. Sharrad – Manuscript review, Principal supervisor; S. Kellet – Provision of data for modelling and funding.

# **Relevance:**

Establishes: i) pipeline solids originating from bulk effluent as a credible means of solid formation; ii) highlights the range of precipitates that can occur within similar starting conditions; iii) that limited pre-characterisation data can be used to generate plausible solid formations.

The presented work addresses some of the gaps in the pipeline solid formation discussion that was previously undertaken on the discharge line emanating from the effluent treatment plant. This approach can be used to address other nuclear pipeline solid buildup problems where restricted access and dose minimisation are required.

#### a) Abstract

Pipeline flow restrictions due to unforeseen solid formations in process liquors occur in all manner of systems and industries. These can usually be cleaned easily and flow restrictions removed. In contrast, within nuclear effluent pipelines these solid build-ups can be problematic to access and remove due to radiation doses from radionuclide contamination limiting access points. A lack of characterisation data of the solids formed from these nuclear effluents limits the ability to control solid build-up inside pipelines. A methodology to predict the formation of mineral phases by utilising effluent composition data has benefits across nuclear and effluent treatment industries, where preventative measures and solids removal strategies may be developed without having to obtain difficult-to-access samples from the pipelines.

The SIXEP (Site Ion Exchange Plant or Site Ion Exchange Effluent Plant) process, which is used to remove radioactive caesium and strontium from aqueous nuclear effluents by ion exchange with the zeolite clinoptilolite, is an example where pipeline flow restrictions due to solids formation has been observed as an oscillating pressure increase in the discharge line of 0.5 bar at 160 m<sup>3</sup>.hr flow rate. Precipitation from the bulk effluent is one of a number of potential sources for solid formations. There have been few previous studies identifying likely mineral phase formation with the elemental constituents found in SIXEP effluents, particularly under ambient temperature (25 °C) and pressure systems (<10 bar) used in plant operations and the relatively short duration (<2 hours) that liquors will be held in pipelines before release. Initial condition narrowing was undertaken using geochemical modelling code from post treatment SIXEP effluent composition data in combination with elements identified from limited characterisation of a single recovered solid sample. Beaker scale experiments were performed where solid phases were produced by altering starting solution compositions within the condition window identified through modelling. The solids were characterised by multiple techniques and found to have a high degree of heterogeneity. Crystalline Al(OH)<sub>3</sub> phases have been encountered as well as non-crystalline amorphous solids which predominantly contain Si. Various solution compositions were found to form solids which were similar to those previously sampled from the discharge pipeline.

#### b) Introduction

Process operations that treat aqueous effluents by removing identified contaminants to sufficient levels allowing water discharges back to the open ecosystem are essential in allowing most chemical industries to remain sustainable. Many approaches are used to successfully aqueous effluents. Examples treat include ion-exchange[58], electrochemical [59, 60] and distillation methods [61], but in many cases pipeline solids and blocking near the point of discharge can occur. This solids build-up can originate from a number of sources including the wash through of fines from a solid phase material, biofilm formation[28, 32] or chemical precipitation[62] from bulk effluent. For most effluent treatment plants the inspection, identification and removal of such solid formations in process pipelines is relatively simple. However, in the case of nuclear effluent treatment plants the potential hazards involved in sampling pipelines due to radiation exposure and limited access points means that inspecting pipelines is highly problematic, if not impossible. Therefore, in order to pinpoint the causes and identify mitigation measures to counter solids build-up in nuclear effluent treatment, investigations using computational and laboratory studies need to be undertaken.

The SIXEP[58] (Site Ion Exchange Plant or Site Ion Exchange Effluent Plant) process, located on the Sellafield site in Cumbria (UK), is an example of a nuclear effluent treatment plant where solid formation has been observed in the discharge line. It treats effluent containing active beta emitters prior to sea discharge. The plant receives aqueous streams between approximately pH 10 to 11 [3, 4]. The feed is passed through a number of sand bed filters to remove large particles of predominately Mg rich solids originating from nuclear fuel cladding[3, 4]. The filtered effluent is passed through a carbonation tower where  $CO_{2(g)}$  is bubbled through the effluent to lower the pH to

around a neutral pH[3, 63]. The effluent is transferred into ion exchange vessels containing Na-clinoptilolite (Na<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O). Radionuclides undergo cationic exchange and are removed from solution. The treated effluent is discharged to the Irish Sea. A build-up of solids within the discharge line was observed during the mid-2000s. At that time a few limited samples of the solid were obtained. The principle indicator that a solids build-up occurred was increased pressure readings while monitoring effluent discharge. A number of investigations were undertaken to characterise the solids but sampling was limited due to radiation doses and physical access restrictions [16, 18, 23, 24]. The limited findings from these studies performed on the actual sample recovered from the discharge line prove extremely problematic. The characterisation efforts were very limited and of poor quality. The data produced is limited as only one measurement was taken, repeat readings were not performed and the range of analytical techniques used do not include relatively simple measurements that could readily resolve the origin and nature of this material (e.g. X-ray diffraction). Likewise, elemental composition determinations using EDX across multiple sites in the sampled solid would have provided a wealth of information on which to baseline any experimental findings produced in this study. Instead, only broad conclusions can be drawn from the scoping studies presented in this work due to the variable nature of the conditions in the observed solid was formed in the SIXEP discharge line. Consequent reductions in flow due to the reduction in the pipeline diameter with solid formation may result in reduced effluent treatment rates unless mitigation measures are instigated. Such restrictions could have an impact upon future treatment of waste streams planned during decommissioning pond clearances [64, 65]. Options for treatment of the effluent discharge lines are limited. For instance

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mechanical cleaning is not possible due to the need to continuously treat incoming effluent streams emanating from storage of nuclear waste.

This study seeks to produce a methodology for the investigation of bulk precipitation in ambient temperature (~25 °C) and pressure (~10 bar) systems using the SIXEP process as a case study. The approach to understanding solids build-up can be split into three distinct areas: i) chemical precipitation from the bulk effluent, ii) a solids attachment mechanism that may arise due to materials used in effluent processing, or materials of biological origin and iii) a means of increasing the bulk mass through solid entrainment. This work will seek to test whether chemical precipitation from the bulk effluent to bulk effluent may contribute to the solid mass.

Investigation of chemical precipitation normally requires detailed composition data from the effluent. However in this case effluent monitoring during plant operations has focussed almost entirely on the radionuclide content (e.g. <sup>90</sup>Sr and <sup>137</sup>Cs) in order to restrict the release of activity into the environment and only limited information has been obtained on the content levels of the non-radioactive species present that are likely to be the cause of the observed solids build-up. Low concentration non-hazardous materials are not routinely monitored within the discharge line. Consequently the approach adopted in these studies is to use computation modelling to determine likely solution conditions where precipitates occur based upon plant monitoring data that were available. Experiments were then performed to generate and characterise precipitates formed from solution conditions identified by modelling and were compared to the few samples obtained and characterised from the discharge line. Although this study aims to understand specific issues encountered at an effluent treatment plant, it has wider applications in the nuclear industry and beyond where limited characterisation and sample collections are either difficult or impossible to obtain. The ultimate application of this work is to facilitate the mitigation and treatment of uncontrolled particulate build-up, when encountered in the nuclear process.

# c) Previously recovered solid characterisation

Solids collected from the SIXEP discharge pipeline in the mid-2000s were characterised by BNFL/Sellafield prior to this work. These previous characterisation efforts form the basis of this investigation. The characterisation of the previously obtained solids was used to narrow the input conditions for modelling and used as a comparison against solids formed experimentally in these studies.

Characterisation of the precipitates recovered in the discharge line identified various elements. Techniques utilised to characterise the recovered solid included chemical analysis of solutions formed by dissolving the recovered solid in 3M Aqua Regia (HNO<sub>3</sub> & HCl) [16] and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) spectroscopy of the solid[16]. It should be noted that it was observed the solid did not completely dissolve (~6 % dissolved by mass) in Aqua Regia, therefore results for this chemical analysis should be treated with caution

The characterisation of the previously recovered discharge solid has provided elemental atomic percentages (by atom; first value from chemical analysis of dissolved solid, second value from EDX of the solid): Si (62.1%, 70.3%), Al (0%, 11.8%), Mg (3.4%, 1.3%) and Fe (13.9%, 3.9%). The recovered solid composition data has been used to compare against those data from experimentally produced precipitated solids.

The sources of these elements formed in the recovered solid formations originate from the plant and the preceding storage ponds. Si may originate from sand beds or dissolution of the ion exchange material. Al may originate from dissolution of the ion exchange material. Mg may be from wash through the treatment plant or dissolution of the ion exchange material. Fe may originate from either corrosion products from the treatment plant or dissociation of the ion exchange material. Unfortunately, X-ray diffraction (XRD) studies were not undertaken on the recovered sample to determine the presence of any crystalline mineral phases present due to the radioactivity limitations and as such severely limit the ability to make definitive conclusions regarding the nature of the solids. Any candidate mineral phase can only be defined as likely to occur. SEM scans(Fig. 5.1a and 5.1b) of the recovered sample indicated small particles  $(1 - 10 \ \mu m)$  held in a porous heterogeneous matrix[16].



Figure 5.1a – SEM micrograph of previously recovered solid from SIXEP discharge line (scale bar 30  $\mu$ m) examined prior to this study by others [16]



Figure 5.1b – SEM micrograph of previously recovered solid from SIXEP discharge line (scale bar 10  $\mu$ m) examined prior to this study by others [16]

The measured element content within the recovered solid varies depending upon the limited and poor sampling methodology. Al was not observed by solution chemical analysis of the dissolved solid trial but was found within the SEM elemental scan but only a single data point was obtained. As the solid was heterogeneous in nature this does not accurately inform the overall composition of the recovered pipeline solid. Al may have remained undissolved following the dissolution process used in the study and a lack of repeat dissolution trials or attempts to use alternative digestion methods for the solid renders much of the data of little use. Any solid that is produced during these experimental trials can only be considered as a possible contributor to the solids formation found in the SIXEP discharge line.

# d) Methodology

#### i) Modelling

The aim of the modelling was to undertake a condition-narrowing exercise to identify the most likely effluent compositions that would form precipitated solids similar to those found in the discharge line with the caveat of "likely" due to the poor characterisation of the previously recovered solid.

The PhreeqC geochemical code[48], provided by the US Geological Survey, was used to model and predict precipitation process from multi-component solutions[66]. The code has been used on a limited basis for studies of scale formations [66-68] with the main output being saturation indices (SI) of the mineral phase (Eq 1).

$$SI = log \frac{IAP}{K}$$
 - Eq 1

where IAP is the Ion Activity Product and K is the stability constant, for the idealised reaction shown in Eq. 2.

K defined as the stability constant, which in turn is calculated by the equation displayed in Eq. 3.

$$X^+ + Y^- \rightleftharpoons XY$$
 -Eq. 2

$$K = \frac{[XY]}{[X^+][Y^-]} - \text{Eq 3}$$

The model used the Hatches18\_noredox database provided by the Nuclear Decommissioning Authority for: logK, stability constant, and enthalpy values. The input element concentrations were chosen from available plant monitoring records provided prior to this work. Mean values (A) and maximum recorded values (B) of the element concentrations found in the discharge effluent by plant monitoring were used as input

data (Table 5.1) into the model. An initial model based on the presence of Na, K, Mg and Ca predicted that no likely precipitates could occur. Consequently Si and Al were introduced into the model, despite not being identified as present in the discharge effluent. Without these additions the likely mineral phases identified by previous characterisation efforts were not indicated as occurring in the output model. Si and Al are likely to be present in the discharge effluent due to potential incongruent dissolution of the clinoptilolite and sand bed filters (See chapter 6).

Additional plant monitoring was undertaken for seven days commencing on the 27/2/2015 for which minimum (Set C) and maximum (Set D) concentrations of each of the analysed elements over the timeframe of the study are provided in Table 5.2. The sampling point was not located immediately after the ion exchange bed and Al was not detected

Table 5.1 – Screening model input parameters as elements; temperature and pH;  $25^{\circ}$ C and 7.5 respectively for all models.  $CO_{2(g)}$  has been added to replicate the plant conditions encountered with the partial pressure (pCO<sub>2</sub> -0.35): (a) – Estimate concentrations not provided by plant monitoring records

Element	Na	К	Mg	Са	Al <sup>(a)</sup>	Si <sup>(a)</sup>
A (mg.L <sup>-1</sup> )	78.3	0.33	0.03	0.18	0.1	0.1
B (mg.L <sup>-1</sup> )	96.1	0.87	0.13	0.48	1.0	1.0

Table 5.2 – Monitoring data from pipeline collected over a period of one week minimum (C) and maximum (D) values are presented: Al and Fe have not been encountered in solution at the monitoring point

Species	Na	К	Mg	Са	Al	Si	Fe	TIC	рН
C (mg.L <sup>-1</sup> )	72.1	0.07	0.16	0.18	0.00	0.02	0.00	38	6.7
D (mg.L <sup>-1</sup> )	86.0	0.13	0.20	0.23	0.00	0.44	0.00	48	7.5
Mean error	4.5	0.23	0.05	0.06	0.01	0.01	0.39	6	0.1

#### ii) Experimental

A simplified analogous effluent based upon the modelling, plant monitoring data and previous characterisation of the recovered solid produced two sets of precipitation experiments, both with Mg (II), Al(III) and SiO<sub>3</sub><sup>-</sup>, and the other with the addition of Fe(III). The modelling conditions were chosen as a starting point for the experimental work with a broader range of starting experimental element concentrations selected to include the modelling conditions and those thought likely to produce representative solids.

Stock solutions were created by dissolved MgCl<sub>2</sub>, AlCl<sub>3</sub>.6H<sub>2</sub>O, Na<sub>2</sub>SiO<sub>3</sub>.5H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, which were all supplied by Sigma Aldrich and were used as received, in deionised water (Elga purelab classic 18.2 MΩ-cm). Stock solution concentrations have been determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Perkin-Elmer Optima 5300 dual view ICP-AES). Appropriate quantities of stock solution were then mixed together to provide sample solutions of the targeted element concentrations. The order of stock solution additions to form sample solutions was Mg, Al, Si and Fe (if included). The solutions were mixed for 1 hour. The samples were not degassed due to the abundance of  $CO_2$  within the actual effluent treatment system. Solutions were then transferred to 100 mL HDPE screw cap bottles and pH adjusted to the

desired level, pH 7 to 8. The adjustment of pH was undertaken using aqueous solutions of 0.1 M NaOH and 0.1 M HCl with measurements obtained using a Mettler Toledo pH meter and electrode (Inline expert pro probe). Sample solutions were not filtered after mixing. No precipitates were visible during the mixing phase.

The three-component system (labelled as Si-Al-Mg) had a solution volume of 100 mL for each experiment. Each experiment contained Mg, Si and Al with some Na and Cl from pH adjustment. The Si concentration ranged from 2.00  $\times 10^{-2}$  to 25.0 mg.L<sup>-1</sup> and the Al concentration ranged from 0.1 to 10.0 mg.L<sup>-1</sup>. For all experiments Mg concentration was maintained at 10 mg.L<sup>-1</sup>.

A four-component system (labelled as Si-Al-Mg-Fe) was also investigated (100 mL solution per experiment) which contained Mg (10 mg.L<sup>-1</sup>), Si, Al and Fe with some Na and Cl from pH adjustment. The Si concentration ranged from 1.0 to 5.0 mg.L<sup>-1</sup> and the Al concentration fell between 5.0 and 6.0 mg.L<sup>-1</sup>. The Fe concentration was between 0.1 and 2.5 mg.L<sup>-1</sup>.

The samples were stored without agitation for 1 month in normal pressure and temperature conditions. The solid precipitate encountered in the plant effluent[16] was referred to as "above colloidal size" therefore each sample was passed through a 0.8  $\mu$ m track etched polycarbonate filter. Element concentrations in the remaining filtrate were determined using ICP-AES. The retained solids were transferred to a microscope slide and dried in a vacuum oven for 24 h at 35 °C.

Some solution samples produced only a very small amount of solid therefore characterisation of the solid was restricted. The headspace of the samples was not subject to an inert atmosphere.

#### iii) Solid phase characterisation

A sample of the dried solid was lightly ground and mounted on a non-diffracting mounting disc for characterisation by Powder X-ray diffraction (pXRD) using a Bruker D8Advance diffractometer.

For characterisation using Scanning Electron Microscope (SEM) samples of the previously lightly ground dried solid were mounted onto SEM stubs after pXRD characterisation and carbon coated for SEM and Energy Dispersive X-ray (EDX) analysis. Morphology was determined in each sample via SEM (FEI Quanta FEG 250) in high vacuum mode using 5kV electron beam. Specimens were coated with carbon (10nm C layer). Oxford Instruments energy dispersive X-ray (EDX) spectrometer was used to determine elemental composition of the solids studied with analysis via Aztec software using the "5keV standard characterisation data set".

Some morphology changes will have occurred by lightly grinding the solids required for optimal pXRD results. However for the SEM studies performed the interpretation of the results obtained was predominately based upon elemental composition data by EDX therefore lightly grinding of the sample would not unduly impact these interpretations.

#### e) Results

#### i) Modelling

The identification of species and their concentration in the discharge effluent required rationalisation in order to allow experimental studies to be effective in determining likely effluent compositions that could cause the observed solid formations in the discharge line. Modelling, using the PhreeqC geochemical code, was performed to determine likely solution compositions where precipitation could occur. Input solution conditions were based upon previously collected composition data of the discharge effluent (Table 5.1) and set to pH 7.5. The model outputs a significant number of precipitated mineral phases that could form based upon the Saturation Index (SI) where the greater the SI value, the more likely precipitation of the particular mineral phase will occur. A manual sense check of the outputted parameters was performed to select the precipitates most likely to occur under discharge line conditions (i.e. short duration and conditions ~25 °C and ~10 bar pressure). Based upon previously established conditions the formation of the mineral phases was identified in the model outputs. The selected phases that would be encountered within the pipe system with mineral phases indicated in decreasing order of SI are presented in Table 5.3.

Mineral precipitation occurs when the solution becomes supersaturated, i.e. SI >0. The definition of "likely" is those minerals that would be indicated to form within relatively low temperature and pressures and in short timescales (i.e. <1 year) as is found within the piped system.

Table 5.3 - Likely mineral phase formations where saturation index (SI)>0 indicates precipitation within the discharge effluent based upon mean (A) and maximum (B) values (See Table 5.1) at pH 7.5.

Mineral Phase	Formula	SI	SI	
		Condition A	Condition B	
Gibbsite	AI(OH) <sub>3</sub>	2.16	3.15	
Analcime	$Na_{0.96}AI_{0.96}Si_{2.04}O_6$ :H <sub>2</sub> O	-2.72	0.36	
Amorphous silica	SiO <sub>2</sub>	-3.07	-2.07	
Heulandite-Ca	$CaAl_2Si_7O_{18}$ :6 $H_2O$	-12.36	-2.95	

Modelling of conditions C (minimum values based upon 1 week of monitoring data collected in 2015; Table 5.2) and D (Maximum pipeline values collected in 2015; Table 5.2), based upon the most recent monitoring results, do not indicate any likely mineral phase precipitation, i.e. SI is <0.

The presence of Al has been demonstrated within the elemental scan of the previously recovered solid[16] and indicates that Al should be considered as a likely species present in the effluent. However, at the monitoring point, Al was not encountered in the recently sampled effluent. Despite not being found in the effluent at the sampling point, Al was introduced into the model at 0.2 mg.L<sup>-1</sup> and indicated a Gibbsite mineral phase (Table 5.4). The minimum concentration values based upon 1 week of data collection in 2015 (Table 5.2) with the addition of 0.2 mg.L<sup>-1</sup> Al is labelled condition E. Condition F describes the maximum concentration values (Table 5.2) with 0.2 mg.L<sup>-1</sup> Al. Al may be forming a hydroxide of either Gibbsite or Bayerite prior to the sample collection point that could explain the lack of Al present in the most recent sampling data.

Table 5.4-Likely mineral phase precipitation indicated wheresaturation index (SI)>0 and followed Al addition (0.2 mg.L<sup>-1</sup>) based upon recent dischargeeffluent minimum (E) and maximum (F) [Table 5.2 (minimum C plus Al addition = E; andmaximum D plus Al addition = F)].

Mineral Phase	Formula	SI	SI
		Condition E	Condition F
Gibbsite	AI(OH) <sub>3</sub>	3.36	2.66
Analcime	$Na_{0.96}AI_{0.96}Si_{2.04}O_6:H_2O$	N/A	-0.85
Amorphous Silica	SiO <sub>2</sub>	-3.74	-2.41

# f) Experimental results and discussion

# i) Three component system (Al - Si - Mg)

Solution conditions for the three-variable system containing AI, Si and Mg were chosen following modelling conditions (PhreeqC model) that indicated the formation of solids representative of those found previously in the SIXEP discharge line. The solutions were stored for 1 month, filtered and the isolated solids dried (Vacuum oven 35 °C, 24 hours). The dried solids were characterised using pXRD and SEM-EDX and found to contain a range of Al and Si compositions.

Crystalline phases were identified in some samples, whilst other samples contained an amorphous non-identifiable phase (Fig. 5.2a). For several samples, even although precipitation was observed visually, there was insufficient solid isolated to provide definitive characterisation by pXRD [Note: halite was found in some samples due to the presence of chlorides in starting solutions]. The principal phases encountered were either gibbsite and/or bayerite, both forms of Al(OH)<sub>3</sub> (Fig. 5.2b-c)with different structural characteristics. Further pXRD patterns are presented in Appendix A.



Figure 5.2a - Crystalline phases from isolated solids identified using pXRD. Noncrystalline solids assigned to all other samples that contained sufficient sample for SEM analysis but did not produce a diffraction pattern.



struoC

Figure 5.2b - Crystalline phases from isolated solids identified using pXRD from a sample with starting solution Al>Si.





Figure 5.2c - Crystalline phases from isolated solids identified using pXRD from a sample with starting solution Si>Al.

There was a reduction in the number of high Si starting concentration samples (where Si > Al content by mass) that contained crystalline phases as identified by pXRD compared to starting solutions where concentration of Al was greater than Si. The majority of solids, where Si starting concentration was greater than Al, did not provide an identifiable diffraction pattern, indicating a predominantly amorphous or non-crystalline phase.

Elemental composition data from solid samples was obtained using an EDX detector present on the SEM. A significant number of data points (>10 per location) were collected in a number of areas (~ 5 to 10 locations per sample) for each sample providing approximately 50 -100 data points per sample.

The data has been presented in a ternary diagram format to facilitate the understanding of the composition of elements, Mg, Al, Si, present in the isolated solids. The data has been separated into results where solids were obtained from starting solutions where the concentration of Al>Si (Fig. 5.3) by mass and starting solutions where the concentration of Si>Al (Fig.5.4) by mass. In both these examples Fe was not present in solution. Precipitates were formed which provided similar elemental compositions to those encountered in the previously characterised solid found in the discharge line. These were obtained for solutions that had a high abundance of Si relative to Al irrespective of the absolute concentration of these elements in solution. The presence of Mg, up to 10 mg.L<sup>-1</sup>, did not generally form any type of a combined ternary (Si-Al-Mg) solid. Some Mg incorporation (up to 50%) into the solid formations was found in predominantly Al containing solids where Al>Si by mass.

Typically, the higher Al content solution system (Al>Si) created a greater variability in formed solid compositions, with up to 50% Mg incorporated into the solid. In these

instances, the Si content in the solid phase was below 5%. Samples displayed a greater heterogeneous nature where the starting concentrations of Al were greater than Si.

Previous characterisation efforts on the recovered pipeline solid provided an insight into the nature of this material but only two elemental content data points were collected on this solid. In this study a large number of data points (>2000) have been collected on the element content of solids obtained from various solution conditions that may be encountered in the SIXEP discharge line.



Figure 5.3 - Starting solutions containing Al>Si previously recovered solid are provided for comparison. Elemental scan of recovered solid composition Si 84.2%, Al 14.2%, Mg 1.6%



Figure 5.4 - Starting solutions containing Si>Al (by mass) previously recovered solid are provided for comparison. Elemental scan of recovered solid composition Si 84.2%, Al 14.2%, Mg 1.6%

This study shows substantial variability of solid compositions (see Fig. 5.3 and 5.4) that may form in possible SIXEP discharge effluents. Without extensive sampling of the solids in the discharge line and given the observations from these studies it is most likely the solids formation in the pipeline do have similar variable compositions to those found experimentally. The solution conditions that produced similar solid compositions in the Al>Si solution system to that of the previously recovered pipeline solids are presented in Table 5.5. It would indicate that as starting compositions are varied there was little effect upon encountered solids produced. Al incorporated into the solid as encountered in the phase characterisation, was predominantly Bayerite and/or Gibbsite. However, that would discount the effect of other non-crystalline phases that have been encountered in the solids produced in this study.

Table 5.5-Starting solution concentrations that generated solids thatprovided representative solids to those encountered in the previously recovered SIXEPdischarge line solid

Si (mg.L <sup>-1</sup> )	Al (mg.L <sup>-1</sup> )
0.2	9.20
0.1	9.20
$4.4 \times 10^{-2}$	4.60
4.0x10 <sup>-2</sup>	9.20
2.2 x 10 <sup>-2</sup>	4.61

In one isolated location on the edge of a predominately Al containing solid from a starting solution concentration of 2.5 x 10<sup>-2</sup> mg.L<sup>-1</sup> Si, 9.2 mg.L<sup>-1</sup> Al and 10.0 mg.L<sup>-1</sup> Mg, a high elemental composition Si (~54%) and Mg (~45%) solid was observed using SEM-EDX. The Si-Mg solid (Fig. 5.5a) was encountered at the edge of the bulk Al solid on the near vertical face of the solid as opposed to the horizontal surface on the top of the solid. The Si-Mg solid was not observed in pXRD analysis and has only been recorded at one site. However the presence of a Si-Mg solid may be significant as it could indicate the formation of a proto-clay that could be the precursor assemblages[69] to a more complex mineral phase formation. In addition the presence of a Si-Mg solid indicated that the solid formations can be heterogeneous, with a broader range of mineral phases formed than were encountered in the previous pipeline solid characterisation efforts.

Typically, the solutions with starting concentrations of Si>Al by mass showed less incorporation of Mg into the formed solid than those from the higher Al containing solutions (Fig. 5.4). Similar solid compositions to those encountered from the previous SIXEP discharge line solids were also found from solutions containing 10.0 mg.L<sup>-1</sup> of Si and 4.6 mg.L<sup>-1</sup> of Al, 10.0 mg.L<sup>-1</sup> of Si and 1.8 mg.L<sup>-1</sup> of Al. Where the starting solution had a concentration 11.0 mg.L<sup>-1</sup> of Si and 0.9 mg.L<sup>-1</sup> of Al, it did not produce a representative

solid when compared against the previously recovered SIXEP pipeline solid. In both the Si>Al and Al>Si systems, Al crystalline phases were formed.

In the high Si content solutions (Si>AI) there was a distinct grouping of solid compositions where each of the elements (Mg, Si and AI) were found of compositions above 10% with AI content of around 50 to 60% and up to 25% Mg incorporation with the remainder as Si. This could have been in the form of co-precipitated independent AI and Mg phases or incorporation into a single ternary solid. Surface data (pXRD) was collected on the composition of the solids along with elemental compositional data (EDX). This tended to indicate a combined Mg-AI-Si solid with some effect of an amorphous Si phase acting as a binder.

The morphology of Al(OH)<sub>3</sub> has been studied[70-72]. It indicated a rod-like/rectangular shape as being a likely gibbsite phase and a triangular or cone-like shape as Bayerite. The significance of this for this study is that if the elemental composition matches that of Al(OH)<sub>3</sub> then the morphology can be used to differentiate between the two mineral phases. Some solids have a clearly defined triangular structure that could indicate the presence of Bayerite formations (Fig. 5.5b). Solids formed in this study had both a triangular and rectangular/octahedral morphology. These morphologies indicate the presence of both Gibbsite (rod-like) and Bayerite (triangular) and were encountered in two different starting concentration solutions (Fig. 5.5c, 5.5d). Two general solid compositions were found (Fig. 5.5e) from starting solutions of 2.0 mg.L<sup>-1</sup> Si, 9.2 mg.L<sup>-1</sup> Al and 10.0 mg.L<sup>-1</sup> Mg where a near even atomically distributed Si – Al solid (Si:Al ratio (by atom) 1:1.5) and an overlaying high Si content solid (Si:Al (by atom) 36:1) was observed.



Figure 5.5: a - Proto-clay formation encountered on the side of the bulk precipitate from starting solution with starting concentration of  $2.5 \times 10^{-2}$  mg.L<sup>-1</sup> Si and 9.2 mg.L<sup>-1</sup> Al and 10.0 mg.L<sup>-1</sup> Mg (Magnification. 4485x); b - Triangular particles retained within a larger matrix of the bulk precipitate. (Mag. 27,319x) (4.4 x  $10^{-2}$  mg.L<sup>-1</sup> Si and 4.6 mg.L<sup>-1</sup> Al); c - Bayerite (triangular) and Gibbsite (rectangular) formations from Al>Si solution. (Mag. 101,303x (2.2 x  $10^{-2}$  mg.L<sup>-1</sup> Si and 4.6 mg.L<sup>-1</sup> Al); d - Bayerite (triangular) and Gibbsite (rectangular) formations from Al>Si solution. (Mag. 10<sup>-2</sup> mg.L<sup>-1</sup> Si and 4.6 mg.L<sup>-1</sup> Al); d - Bayerite (triangular) and Gibbsite (rectangular) formations from Al>Si solution, at different starting compositions of 4.4 x  $10^{-2}$  mg.L<sup>-1</sup> Si and 4.6 mg.L<sup>-1</sup> Al (Mag. 130,361x); e - Bulk precipitate from a solution starting concentration of 2.0 mg.L<sup>-1</sup> Si and 9.2 mg.L<sup>-1</sup> Al. Red area has a high Al content solid (Si:Al of 1:1.5) and is underlain by a high Si solid (Si:Al 36:1) (Mag. 6540x); f - Bulk precipitate from Si>Al starting solution (2.21 mg.L<sup>-1</sup> Si and 0.92 mg.L<sup>-1</sup> Al). (Mag. 538x).

The variability in the solid compositions observed in the high Al system (Al>Si) could indicate a highly heterogeneous system where surface composition may mask or be substantially different to that of the underlying bulk solid. The formations were an agglomeration of solids with various Si:Al ratios. Typically, this was encountered in the elemental compositions encountered in solutions where Al>Si (Fig. 5.3).

A bulk sample at higher Si starting concentrations (Si>Al) has been examined which contained various elemental compositions (Fig. 5.5f). The images of the sample, with EDX analyses indicated that there was a bulk amorphous-like solid (likely to be Si) containing smaller Al crystalline phases. Two independent phases may be co-precipitated where a crystalline Al phase and an amorphous phase was produced. Al<sub>2</sub>O<sub>3</sub> has been found to be a precursor to formation of a crystalline Al phase[71]. The amorphous phases may have been Si and/or Al and that could have impacted upon Mg incorporation into the solid due to the reaction with O in preference to Mg.

## ii) Four component system (Al - Si - Mg - Fe)

Following on from the three component system, Fe was added to the experimental matrix. Fe has been added to solution in amounts corresponding to similar Si:Fe ratios that have been encountered in the recovered pipeline solid. All solutions were prepared and solids isolated and characterised as described in the three component system.

Less crystalline solid formations were encountered (Fig. 5.2a) than in comparable concentrations Si-Al-Mg experiments, with a greater number of samples that identified no crystalline phases. There was some indication of distinct and potentially crystalline solids being encountered in a bulk solid (Fig. 5.6a) at starting solution concentrations of 2.00 mg.L<sup>-1</sup> of Si, 5.00 mg.L<sup>-1</sup> of Al, 1.00 mg.L<sup>-1</sup> of Fe and 10.00 mg.L<sup>-1</sup> of Mg. The

morphology of some of the crystalline phases, typically less than 1 or 2  $\mu$ m, may have indicated the presence of Bayerite due to similar morphology to that of previous observations (Figs. 5.5 b, c, d). EDX data and SEM micrographs (Fig. 5.6b) indicated that this same starting concentration solution produced a bulk solid that was amorphous in nature with smaller geometric solids with both triangular and rectangular morphologies observed which were retained on the surface of the bulk solid and EDX indicated that these were Al phases, likely to be Bayerite and/or Gibbsite.

As there are four components present for these experiments compositional analysis by SEM/EDX is presented across two ternary diagrams that each included Al and Si content while the third axis displays either Mg (Fig. 5.7) or Fe (Fig. 5.8) content. To further aid comparison, the compositional data for the recovered pipeline solid (mid-2000s origin) where Fe content was also determined was also displayed in the figures.



Figure 5.6 – SEM micrographs of solids produced from a starting solution of 2.00mg.L<sup>-1</sup> of Si, 5.00 mg.L<sup>-1</sup> of Al, 1.00 mg.L<sup>-1</sup> of Fe and 10.00 mg.L<sup>-1</sup> of Mg; a - the morphology of the solids indicates some crystalline phases that have similarities to the bayerite mineral phase identified previously in Figure 5.5 with a typical particle size of ~1 or 2  $\mu$ m (Magnification 4493x); b in the same solution concentrations indicating both a bulk amorphous solid with some triangular and rectangular solids indicating crystalline Al phases (Mag. 32213x)

The solids obtained from these four component experiments showed a significant incorporation of Mg (Fig. 5.7) more so than those found in the three component (Si-Al-Mg) system. There were also a greater number of sample solids consisting of only Mg and Si than in any of the three component Si-Mg-Al systems. The distribution of observed solid compositions, with respect to Si, Al and Mg content (Fig. 5.7), with three general areas all defined by the relative Al content: 0-50% 50-75%, 75-100%.

A 75-100% Al cluster corresponds to Gibbsite/Bayerite formations identified by pXRD. Solid compositions found in this cluster were obtained from starting solutions containing  $1.0 \text{ mg.L}^{-1}$  Si and  $5.0 \text{ mg.L}^{-1}$  Al for both sets of Fe experiments that contained starting Fe concentrations of 0.6 and 1.4 mg.L<sup>-1</sup>.

The compositions with 50 to 75% Al content with Mg content varying across 0 to 100%, was not encountered in the three component (Si, Al, Mg) system. This most likely indicates an effect from increasing ionic strength of the solution from the Fe that was present in the experiment. Increased ionic strength of solutions can promote higher Saturation Indices (indicating that minerals may precipitate where Saturation Indices (SI) >0) whereas at low ionic strengths the solutions may be in partial equilibrium, as has been encountered in Waste Isolation Pilot Plant geological studies[73].

There was a trend towards less binary (Si – Al) solids in the range 0% to 50% Al content. The system had become less binary when previously Si-Al solids dominated the solid formations encountered in the three-component system (Si-Al-Mg). General Si incorporation was less in the Fe-Al-Si-Mg system. The incorporation of Fe into the bulk solid produced a ternary system instead of Si-Al solids encountered previously.

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Figure 5.7 – Si, Al, Mg ternary diagram for Si-Al-Mg-Fe experiments. Elemental scan of recovered solid composition Si 84.2%, Al 14.2%, Mg 1.6%

In the Si-Al-Mg-Fe experiments there were less similarities between previously recovered solids and the precipitated solids encountered in the experiments. There appeared to be a preference towards Al phases along with a secondary Mg-Si solid. The characterisation data for the pipeline solid was extremely limited (2 data points) which may mask the heterogeneous nature of likely pipeline solids that may be encountered. In this study the concentrations used for the Si-Al-Mg-Fe component experiments did not produce an exact representative solid to that previously encountered in the discharge pipeline from the mid 2000s sample. However as has been observed in the three component system (Fig. 5.5e) starting concentrations of 2.0 mg.L<sup>-1</sup> Si and 9.2 mg.L<sup>-1</sup> Al there was a significant variability in the solids produced. A similar level of variability was observed in the four component system, albeit with no exact match between EDX data and the previously

recovered solids. The incorporation of Fe into the bulk solid was observed up to a maximum Fe content of 40% (Fig. 5.8).

Elemental data of the previously recovered solid (mid 2000s sample) was a poor match to the bulk solids produced in these sets of experiments. A large proportion of solids showed no incorporation of Fe into the solid. There was also a large accumulation of solids in the 50% to 75% range of Al content, up to 25% Fe content and between 25% and 50% Si content. Solids found in this compositional range were found to be amorphous, therefore the formations may be either a ternary Fe-Al-Si solid or co-precipitated independent Al and Si-Fe phases.



Figure 5.8 – Si, Al, Fe ternary diagram for Si-Al-Mg-Fe experiments. Elemental scan of recovered solid composition Si 81.8%, Al 13.7%, Fe 4.5%

The lack of crystalline Fe phases found in these solid formations was unexpected from modelling of the experimental parameters with elemental concentrations of 10 mg.L<sup>-1</sup> Mg, 5 mg.L<sup>-1</sup> Al, 5 mg.L<sup>-1</sup> Si and 2.5 mg.L<sup>-1</sup> Fe in pH 7.4 and 21°C conditions. The model predicted a number of crystalline phases that included gibbsite, goethite, hematite and Mg-ferrite (Table included in supplementary information). The model also indicated the formation of phases that only contained Fe (e.g. goethite, hematite, ferric hydroxide). Characterisation of the solids obtained in this study found no examples that contained exclusively Fe. As such the most likely forms that the Fe phases could take are amorphous and were found to co-precipitate with other Si, Al and/or Mg containing phases as indicated by EDX (Fig. 5.8).

### g) Amorphous silica

In the four component experiments (Si-Al-Mg-Fe) elemental observations using the EDX probe indicated a high Si >75% and low Fe <25% solid (Fig.5.8). The presence of a predominately Si solid with the lack of crystalline solids following investigation using pXRD (Fig. 5.2a) would indicate the presence of a predominately amorphous solid. As such the Si solid would most likely be  $SiO_{2(am)}$ .

Likewise the three component system observations by pXRD indicated that at high Si starting solutions concentrations relative to Al, amorphous non-crystalline phases were produced. These non-crystalline phases were observed in starting solutions that contained 11.0 mg.L<sup>-1</sup> of Si and 0.9 mg.L<sup>-1</sup> of Al and 10.0 mg.L<sup>-1</sup> of Si and 1.8 mg.L<sup>-1</sup> of Al. In the Al-Si-Mg component system a Saturation Indices was suggested for  $SiO_{2(am)}$  of ~-2.42. This indicated an under-prediction in SI's against experimental observations. One possible explanation for this was that PhreegC treated Si as monosilicic acid rather than the more

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likely polymerised polysilicic acid[74]. Polymerised silicic acid has been suggested as being the primary form of silicic acid due to the presence of precipitated Si globules (~50 nm) that would not be predicted to precipitate under the monosilicic acid form. Monosilicic acid is present within the PhreeqC database and the polymer form is not present. To overcome this omission where Si is under saturated, with respect to its SI, this should be confirmed experimentally.

# h) Findings for plant operations

Solids have been produced that have similar compositions to those encountered in the previously recovered pipeline solids from the mid-2000s[16]. Due to the poor and limited characterisation efforts of the original pipeline sample undertaken, any solids formed can only be considered candidate mineral phases. There were a number of starting solutions that formed representative candidate precipitates when compared to the recovered solid. This was particularly evident in Al>Si starting conditions where the Al concentration was greater than that of Si concentration, which appeared to be counterintuitive as the major elemental component present within the recovered pipeline solid was Si. A low concentration of Si was found to form a representative solid, either from a reaction between Al-Si forming a simple aluminosilicate phase or by co-precipitation of Al(OH)<sub>3</sub> and a Si rich phase.

There was a much weaker link to the pipeline solid when considering Fe in the system. It appeared that Fe was retained within the bulk solid phases and was usually amorphous in nature. The addition of Mg into solution had little impact on the phases produced. It was a similar mechanism to that encountered with Fe, where Mg (and Fe) were retained in the amorphous solid but did not form a predicted crystalline phase that was recognisable.

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Conditions encountered in the piped system are very different to those encountered in the open environment. Typically, residence time in the system is very short <1 hour for the effluent. This limits phases that can occur in the system. A rapidly precipitating precursor phase would be required to commence the particulate build-up within the pipe. Only once a solid is rapidly formed could a more complex phase be produced. In some instances, the lack of solid recovered for determination of crystalline phases may indicate conditions that would be unfavourable for production of rapidly precipitating crystalline or precursor amorphous phases. Solution conditions with starting concentrations 11.0 mg.L<sup>-1</sup> of Si and higher and 0.9 mg.L<sup>-1</sup> Al did not produce representative solid precipitates when compared to those found in the discharge line solid. The poorly characterised recovered solid had a Si:Al ratio (by atom) of around 6:1 which was produced in a wide variety of starting solutions, typically with starting solutions where the concentration of Al is greater than that of Si.

Limited and poor quality characterisation of the previously recovered solid by others[16] may mask the heterogeneous nature of the solid that would have been encountered if further measurements had been undertaken. This would have provided a much clearer target for any potential solid phase and would have allowed significant back analysis of the solid to enable starting constituents to be more accurately produced. The starting solutions studied in these experiments produced a variety of precipitated phases, both crystalline and non-crystalline/amorphous. Similar phases can be produced in the effluent with quite different starting concentrations of Si and Al. Very low concentrations of Si present in the system can provide a source of SiO<sub>2(am)</sub> to precipitate, forming part of the bulk solid formation. This can contribute to the bulk formation of solids within the pipeline. The presence of Al provides typically crystalline hydroxide phases that may also

produce representative solids with particle sizes in the same order as those encountered in the SEM scan of the recovered solid (1 to 10  $\mu$ m).

# i) Conclusions

Little published work exists in relation to rapidly forming precipitates at ambient temperatures and pressures within a piped system. This work has undertaken laboratory studies to replicate and understand the causes leading to the formation of solids encountered in an effluent discharge system, in a situation where there was a very limited ability to take samples and to characterise recovered solids and effluent compositions.

Experimental results in the three (Si-Al-Mg) and four component (Si-Al-Mg-Fe) systems produced solids similar to those predicted in the modelling (by condition narrowing).  $SiO_{2(am)}$  was under-saturated with respect to the model but was encountered during the precipitate experiments. This scenario was also encountered in the previous work[74] predicting  $SiO_{2(am)}$ .

A wide variety of starting compositions of solids can produce likely solids that share similarities with those of a previously recovered discharge pipeline solid from the mid 2000s. In starting solutions where the Al concentration (by mass) is greater than that of Si, these have tended to form a greater number of representative solids of the recovered pipeline solid than those at higher Si concentrations. The presence of precursor phases that form more complex species has been encountered in limited instances.

Where Fe was introduced into the experimental concentration matrix there was less overlap between the representative pipeline solid (mid 2000s) to that produced experimentally. One possible reason for this was that the solids in the actual system have been present in the pipeline for decades, which allows slow long-term processes, such as recrystallization and remobilisation of some components to occur.

All experimental systems produced a broad range of elemental compositions that demonstrated a heterogeneous nature. The recovered pipeline solid exhibited some variability, though with limited elemental data with respect to SEM and elemental compositions after dissolution in acid. A broad range of elemental starting concentrations may lead to similar solids to those encountered within the pipeline. Co-precipitation of Bayerite/Gibbsite and amorphous Si phases appear to be the most likely cause of bulk solid formations.

SiO<sub>2(am)</sub> saturation indices were under-predicted within the PhreeqC models of experimental and pipeline conditions. The occurrence of this under-prediction has been encountered previously [74] and should be considered as a likely solid formation that would be encountered within the pipeline.

Production of precipitates from bulk effluent conditions encountered in the pipeline had not been considered prior to this work as a credible means of producing solids that could contribute to the bulk mass of the solid formation. This could be due to the lack of accurate and sufficient solid characterisation data. Here it can be demonstrated that under similar kinetics, as encountered within the piped system, solids can be generated similar to those previously characterised from the discharge pipeline. A greater heterogeneity is experienced in experimental results than is encountered in the characterisation of the recovered solid. This was thought to be due to the small number of samples undertaken on the previously recovered solid. Precipitates can occur in these conditions and are likely to form within the pipeline.

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The adopted methodology of identifying plausible solids formation conditions through thermodynamic modelling and subsequent laboratory based precipitation studies appears to be a credible means of identifying mechanisms and reproducing solids formation. The solids produced in this manner are similar to those encountered in effluent pipeline samples. The methodology was attempting to solve a problem using poor quality and limited previously recovered solid characterisation information.

To refine the list of "likely" mineral phases further, additional characterisation data, from EDX data points (of which there was one) and pXRD information would be of assistance. Despite limited characterisation information, this study has been able to narrow down the chemical conditions that lead to the precipitation of mineral phases similar to those found to occur in the effluent pipeline. Such information will help inform management decisions concerning physical (flow) and chemical treatment options to mitigate the effects of solids build-up. The nature of the solid formation would have a bearing upon the treatment regime undertaken. Where a solid was formed that could be easily sheared from the pipe surface, a simple increase in flow rate may allow removal of this solid which would be retained downstream of the pipeline. For tightly bound solids chemical dosing may be required. Any chemical dosing would require significant consideration as to the effects upstream within SIXEP and may pose issues regarding wash through of active species. Wash through may pose problems with downstream recovery of these radionuclides. Further flow sheet development would be required if this approach were adopted.
# j) Acknowledgements

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# k) Supporting information

PhreeqC modelling conditions on which additional table mineral phases was populated

```
#Model to predict likely phases of EXP 6 11E6
#Database used for model - Hatches Noredox_18
PHASES
fix_pH
H+ = H+
log_K 0.0
END
SOLUTION 1
units mg/l
Mg
    10
Al
    5
Si
    5
Fe(3) 2.5
Cl 0.1 Charge #Added as Cl present in Al, Mg stock solutions
N(5) 1.88
                       #Added as present in Ferric Nitrate
C(4) 1
                      #Approximate to indicate 1 month storage in
closed
cap conditions
temp 21.7
рН 4.597
EQUILIBRIUM_PHASE 1
fix_pH -7.4 NaOH 10
END
```

Additional Table – Output from model from a single experiment, comparing model against experimental results (in solution concentrations Mg 10 mg.L<sup>-1</sup>, Al 5 mg.L<sup>-1</sup>, Si 5 mg.L<sup>-1</sup> and Fe 2.5 mg.L<sup>-1</sup>

Mineral Phase	Formula	Saturation INDEX
Gibbsite	AI(OH) <sub>3</sub>	4.10
Goethite	FeOOH	7.46
hematite	Fe <sub>2</sub> O <sub>3</sub>	15.31
Ferric hydroxide	Fe(OH) <sub>3</sub>	2.32
ferrite-mg	MgFe <sub>2</sub> O <sub>4</sub>	5.95
Analcime	$Na_{0.96}Al_{0.96}Si_{2.04}O_6$ :H <sub>2</sub> O	1.92
Amorphous Silica	SiO <sub>2</sub>	-1.36

## PhreeqC modelling conditions on which the table mineral phases was populated

```
#Model to predict likely phases of EXP 5 6E5
#Database used for model - Hatches Noredox_18
PHASES
fix_pH
H+ = H+
log_K 0.0
END
SOLUTION 1
units mg/l
    10
Mg
Al
    4.61
Si 0.442
Cl
    0.1 Charge #Added as Cl present in Al, Mg stock solutions
                      #Approximate to indicate 1 month storage in
C(4) 1
closed cap conditions
temp 23
рН 4.711
EQUILIBRIUM_PHASE 1
fix_pH -7.49 NaOH 10
```

END

# Chapter 6 – Clinoptilolite dissolution paper

# Congruent and incongruent dissolution behaviour of clinoptilolite in ion

# exchange effluent treatment plant conditions

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**Author Contributions** 

R S Jones – First Author, principal researcher, experimental data collection and data analysis.

C.A. Sharrad – Manuscript review, Principal supervisor; D. Trivedi –co-supervisor, manuscript review; S. Kellet –context discussion.

#### <u>Relevance</u>

This work addresses a potential source of  $Si_{(aq)}$  that has been proven to cause solid formations at <1 mg.L<sup>-1</sup> concentrations. Here the concentration of  $Si_{(aq)}$  is >10 mg.L<sup>-1</sup> at the end of long duration experiments and >1 mg.L<sup>-1</sup> at the end of 24 h experiments. The presence of fines (congruent dissolution) has been suggested as a cause of solid formations with the combination of an organic layer (Polyelectrolyte or Biofilm) in the pipeline in previous reports. However incongruent dissolution was not previously suggested as a means of a source of aqueous species at near neutral conditions.

#### a) Abstract

Ion exchange materials are used extensively in waste treatment and in particular in nuclear effluent treatment facilities. Clinoptilolite is a naturally occurring aluminosilicate based ion exchange material which is used to remove mono-valent and di-valent radionuclides from effluent at process scale. In nuclear effluent treatment plants, it is particularly important to have a thorough understanding of process operations in order to minimise the radiological risks associated with managing such plants as well as conventional process risks. One manner in which this manifests is the minimisation of maloperations that require person ingress into the plant to identify and/or mitigate the maloperation event. In the case of effluent treatment plants that use ion exchange processes, dissolution of the ion exchange mineral has the potential to cause blockages or flow restrictions downstream of the plant. There are limited studies on the congruent and incongruent dissolution of high Si:Al ratio aluminosilicates at near neutral pH and temperature (25 °C) in which these plants typically operate.

A series of experiments has been undertaken using unwashed (as received) and pre – washed clinoptilolite at near pH neutral conditions. Long duration (21 days) and short duration (<24 hour) studies were performed. The effect of Cs loaded clinoptilolite was investigated over long durations to investigate whether ion exchange was a possible means of incongruent dissolution.

Significant quantities of Si were released into solution in unwashed and washed long duration experiments with both congruent, from the release of fines from the clinoptilolite, and incongruent dissolution, where Si is present as silicic acid, occurring. A greater amount of congruent dissolution was observed in the unwashed samples. Similar quantities of Si<sub>(aq)</sub> were present in washed and unwashed conditions. Short duration experiments (washed only) produced particulate fines and aqueous Si with very little incongruent dissolution of Al observed from the mineral structure. The generation of fines and aqueous species at near neutral conditions has relevance to effluent treatment plant that utilise a high Si:Al ratio zeolite. The incongruent dissolution of the mineral may cause pipeline diameter reductions and corresponding flow restriction downstream of the plant resulting in reduced throughput.

#### b) Introduction

Natural mineral ion exchange materials have been utilised extensively within the nuclear industry worldwide for either treating contaminated waters or selectively removing valuable elements[63]. One such ion exchange material is clinoptilolite  $(Na_6Al_6Si_{30}O_{72}.24H_2O)$ . Clinoptilolite minerals are part of the heulandite group[6], with a high silicon content with respect to aluminium content (i.e. 4 < Si:Al <5.5 by atomic content) within the structure, a key characteristic of clinoptilolites[75]. Ion exchange sites in clinoptilolite minerals occur as a result of Al<sup>3+</sup> ions replacing Si<sup>4+</sup> sites, thereby creating a net negative charge in the tetrahedral coordinated structure[76-78]. The net negative charge is then balanced by a monovalent or divalent cation[76-78]. The study of clinoptilolite as an ion exchange material to remove cationic species from solution has been extensive [76, 77, 79-82]. Such studies where measurements of the cation exchange capacity of relevant materials are undertaken are commonplace throughout the area of water treatment. This parameter is typically the major factor used to determine the efficiency of materials in a given ion exchange process, and thereby the selction of the material to be deployed in the targeted process. The study proposed here differs from those previous studies as it seeks to understand what happens to the mineral formation undergoing contact with various likely influent solutions. The degradation performance is lacking from these studies which instead focus on the ability to exchange various cationic species. The cationic exchange capacity of clinoptilolite is well known and does not form the basis of this work.

Waste water treatment processes using clinoptilolite as an ion exchange material operating at near neutral pH conditions are utilised at the Sellafield site to reduce the content of radionuclides prior to sea discharge[63]. This process, known as SIXEP (Site Ion

Exchange Plant), takes an incoming feed from spent fuel storage pond water which is alkaline (pH >10)[3, 4]. The feed undergoes sand bed filtration to remove larger Mg rich solids originating from fuel cladding[3, 4] stored in the ponds. The filtered effluent passes through a carbonation tower[63] where  $CO_{2(g)}$  is bubbled through the effluent reducing the pH to between 7 and 8 prior to its entering the ion exchange beds[3, 63]. The neutralisation step is required in order to optimise the performance of the ion exchange beds and the entire process is operated at ambient temperatures and pressures.

Clinoptiloilte was contacted with a SIXEP feed solution to investigate the impact of radionuclide uptake on colloidal material [58]. Leonard et al [58] focused on radionuclide uptake of beta (<sup>137</sup>CS, <sup>90</sup>Sr) and alpha (<sup>239,240</sup>Pu, <sup>241</sup>Am) emitters on a clinoptilolite contacted solution. No mechanism was proposed by which colloidal clinoptiolite could be encountered in plant operation and the study did not consider the effects of degradation or dissolution of the mineral phase but on the generation of clinoptilolite colloids with adsorbed radionuclides.

As such the study [58] has limited use relating to the degradation of clinoptilolite as their experiment was undertaken under short durations (16 hours) and did not collect data relating to the mineral structure. It has been included here as it is one of very few studies that explores clinoptilolite behaviour with regards to the release of particles and radionuclide re-mobilisation under SIXEP conditions. That study did not consider the degradation of clinoptilolite or the means by which colloidal material could be generated.

There exists a possibility for congruent or incongruent dissolution of the mineral structure to release Si and/or Al. This might have an impact on downstream effluent processing, as management of effluent flow may be required to mitigate restrictions due to solids buildup. Such a solids build-up in a nuclear effluent treatment plant may have a profound effect as access points to identify potential problems and develop resolution strategies are typically restricted due to radiological safety concerns.

This work sought to understand whether under typical plant temperatures and near neutral pH conditions whether solutes could be produced that may contribute to bulk solid formations encountered in effluent treatment plants that use clinoptilolite. Previous studies have considered the dissolution of high Si content synthetic zeolites in alkaline conditions at temperatures >60 °C [83-85] which are not encountered under SIXEP plant operating conditions and will not be considered in this study. These synthetic zeolites do not contain the range of impurities that are encountered in the natural mineral form present in the mud hill deposit clinoptilolite. Under these synthetic conditions amorphous silica (SiO<sub>2(am)</sub>) was encountered during the dissolution process[84] and may indicate that a natural mineral solid may undergo similar incongruent dissolution of the structure. Other work on a range of zeolites [13, 14] considered the impact of the Si vs Al content of these materials on their propensity towards dissolution in HCl solutions (> 8.0 M) where it was found that zeolites with Si:Al ratios >3 tend not to dissociate. That study considered that Al content within the lattice structure was responsible for the dissolution behaviour of zeolites when contacted with strong HCl solutions over a maximum experimental duration of 2 hours. The 8.0 M HCl dissolution experiments have little relevance to the study of clinoptilolite performance in near neutral and mildly basic pH conditions except that it suggests that a preferential order of incongruent dissolution based on element type may occur. Clinoptilolite is considered to be stable (i.e. not soluble) when introduced into a saturated amorphous silica solution at 25°C[86] and this would suggest that removal of Al from the lattice structure is responsible for dissolution behaviour rather than substitution of Al by Si. The work presented in this study is of broad relevance for any plant that utilises natural mineral ion exchange media for effluent treatment as previous work has not considered near neutral pH dissolution of clinoptilolite under ambient temperature (25 °C) and pressures (1 Bar).

# c) Experimental methods

#### i) Materials

Clinoptilolite, supplied by Sellafield Ltd, was originally sourced from the Mud Hills deposit, California, USA and is the same material that is used in SIXEP. Previous work[8] has given a non-idealised formula for clinoptilolite as Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O with some minor trace elements also found. Examination of the "as supplied" mineral by powder X-ray diffraction (pXRD) confirmed the material was clinoptilolite (Fig. 6.1). It also identified small quantities of quartz and mordenite impurities. From a study prior to this work undertaken by Sellafield/BNFL, using X- ray fluorescence spectroscopy, it has been identified that the clinoptilolite predominately contained Na on the exchange sites[8]. Subsequent studies used the "as supplied" clinoptilolite or after the mineral was washed according to the procedure described below. All other chemicals were supplied by Sigma-Aldrich and used without any further purification. All beakers and flasks used in these studies were made of high density polyethylene (HDPE) to remove any possible interference of silicates leaching from glassware however insignificant under the conditions studied.



Figure 6.1 – Powder X-ray diffraction pattern of as received material from Sellafield limited indicating that the sample is clinoptilolite.

#### ii) Washing procedure

Washing of clinoptilolite was undertaken using deionised (DI) water (Elga purelab classic 18.2 M $\Omega$ -cm) at ~ 7.0 pH (adjusting the pH of the DI water was not found to be necessary). The bulk mineral (~ 200 g) was washed through a mesh sieve (100  $\mu$ m sieve size) with DI water (~ 1000 mL). The "wash" fines in the filtrate after initial washing were collected for analysis. The washing procedure was repeated once. The washed clinoptilolite was stored as a wet solid in a screw top HDPE beaker until use. Immediately before experiments were performed, the washed and unwashed clinoptilolite materials were dried for 24 hours in a vacuum oven at 40 °C.

#### iii) Dissolution/degradation procedures

DI water was used to prepare the clinoptilolite dissolution solutions with pH adjustment undertaken after contact with the mineral phase using 0.1 M HCl and 0.1 M NaOH, where necessary, to ensure a starting pH 7.0  $\pm$  0.5.

Dried clinoptilolite (1.00 g) was added to a beaker containing DI water (200 mL) adjusted to pH 7.1, covered and placed on a shaker bed (100 rpm) for 21 days. Experiments were performed in triplicate using both washed and unwashed clinoptilolite and were conducted under an ambient atmosphere with no control of CO<sub>2</sub> to reflect conditions encountered on plant. Aliquots (5 mL) were collected from each sample with a total of ten aliquots drawn off at regular time intervals over 21 days for analysis. After 21 days, the covered solutions were removed from the shaker and left to stand still for a further 58 days giving a total contact time of 79 days.

To consider the potential impact of Cs loading on clinoptilolite dissolution (congruent or incongruent), the procedure described above was repeated with unwashed clinoptilolite

only in contact with a solution with a starting of Cs concentration of  $1.00 \text{ mg.L}^{-1}$  obtained using CsCl.

Experiments focussing on short term (0 - 24 hours) dissolution behaviour of washed clinoptilolite were performed as described previously with the pH adjusted to 7.3 and no Cs added to the solution. This was conducted in duplicate. Aliquots (15 mL) were collected for analysis at the following time intervals: 0, 0.25, 0.5, 1, 4, 8 and 24 hours.

# d) Characterisation and analysis

Characterisation of solid materials by pXRD was performed using a Bruker D8Advance powder diffractometer. Examination of solids was also conducted by a FEI Quanta FEG 250 scanning electron microscope (SEM) in environmental mode using a 20 keV electron beam with a working distance of 10 mm where samples were maintained under vacuum at 1 mbar. The SEM was coupled with an Oxford Instruments energy dispersive X-ray (EDX) spectrometer with supporting analysis provided by Aztec software and utilised the "20 keV standard characterisation data set".

Solution analysis was performed using a Perkin-Elmer Optima 5300 dual view inductively coupled plasma atomic emission spectrometer (ICP-AES) to determine the concentration of the solutes Na, Mg, Si, Al, Fe, and Ca. Concentration determinations of Cs were conducted using an Agilent 7500cx inductively coupled plasma atomic mass spectrometer (ICP-MS). Measurements of pH from aqueous solutions were undertaken using a Mettler Toledo pH meter and electrode (Inline expert pro probe). Inorganic carbon content of selected solutions was determined using an Analytic Jena Multi N/C 2100S analyser calibrated using sodium bicarbonate (NaHCO<sub>3</sub>).

Before analysis, all 5 mL aliquots were centrifuged (3000 rpm, 10 min) using a Grant-bio LMC-3000 centrifuge such that the supernatant does not contain any large sized clinoptilolite fines that may have been present. Alternate solution preparation was also performed from the aliquots obtained from the 24 hour study and the final solutions obtained after contact with the clinoptilolite for 79 days. In addition to directly centrifuging the sample, a 5 mL sample was filtered using a 0.45 µm syringe filter while another 5 mL sample was filtered using a VIVASPIN 6 3000 Molecular Weight Cut-Off (MWCO) colloid filter (pore size <5nm) where the sample was centrifuged at 3000 rpm for 35 minutes.

# e) Results and Discussion

# i) Experimental

Currently, clinoptilolite is washed prior to use on the SIXEP plant in accordance with the procedure summarised in the simplified process chart displayed in Figure 6.2. Historically though, the unwashed, as received, mineral was used on plant with very minor pre-treatment[58]. Hence, both washed and unwashed samples of clinoptilolite were used to explore dissolution and degradation behaviour. The washing procedure employed in these studies reflects the method used to currently prepare clinoptilolite for deployment at SIXEP.

The washing procedure used in this work typically removed ~1.25% (by mass s.d. 0.01) of the clinoptilolite. Studies were undertaken to ascertain both the short term (< 24 hours) and long term behaviour of clinoptilolite (up to 79 days) that could lead to congruent and/or incongruent dissolution of this material resulting in the presence of inorganic species in the discharge effluent causing the formation of undesirable solids. Solution conditions used in these studies (pH 7, ambient atmosphere and temperature) were chosen to reflect plant conditions. Clinoptilolite containing solutions were agitated for 21 days and then allowed to stand with solution samples periodically removed for analytical purposes to determine element content and the nature of any fines/colloids/precipitates formed that could pass through the filters used on plant and into the discharge effluent.

All solutes are reported as a percentage loss of species relative to starting mass of clinoptilolite (typically 1.00g). The reporting method was chosen to account for solution loss via collection of aliquots for subsequent analysis and to provide comparisons between experiments.



Figure 6.2 – Process chart detailing existing washing procedure undertaken at the SIXEP plant to remove contaminants (mainly Cl) and to condition the mineral (clinoptilolite) prior to use on plant (all washing and soaking undertaken using deionised water)

#### f) Long term clinoptilolite behaviour

#### i) Si:Al ratio and loss of Si from structure

Long duration experiments were undertaken (up to 79 days). The purpose of these experiments was to determine washed and unwashed performance of the clinoptilolite with respect to the generation of solutes from the bulk structure of the clinoptilolite. Atomic Si:Al ratios are used to ascertain the nature of any clinoptilolite dissolution where a solution content with a Si:Al ratio (by atom) of around 5:1 would indicate congruent dissolution by the formation of clinoptilolite fines being washed from the bulk solid.

The Si and Al content present in centrifuged solution samples obtained after agitation of clinoptilolite (up to 21 days at pH 7.1) is presented in Figures 6.3 and 6.4, respectively. All numeric data are provided in supplementary information and data points are presented as mean values with error bars denoting the standard error associated with the duplicate samples. Both washed and unwashed clinoptilolite produced solutions which showed an increase in Si and Al content over time (Figs. 6.3 and 6.4), especially evident after four days of contact. Consistently lower Si and Al content was present in the solution from washed clinoptilolite compared to the unwashed material, but the difference between both the Si and Al solution content during the entire time the clinoptilolite was in contact with solution essentially remained constant.

Unwashed samples tended to have a Si:Al ratio (At %) of between 5 and 6 for the majority of the experimental duration suggesting that the bulk dissolution was congruent (Fig. 6.5). However, this was not the case when considering the washed clinoptilolite where the Si:Al ratio (by atom) remained greater than nine for the duration of the study (Fig. 6.5). This indicated that a simple bulk loss (congruent dissolution) of clinoptilolite mineral into solution was not occurring in the washed material and instead Si was being released into solution in preference to Al.

The expected loss of Si from the structure of clinoptilolite has been considered in low pH [6, 87] conditions (pH 5.5  $\pm$  0.5) with cation exchange capacity studied. Deallumination was suggested, resulting in a loss of AlO<sup>-</sup> surface sites resulting in an increase in dissociation of Al prior to likely Si sites[12] when undergoing acid pre-treatment. This does not appear to be the case at pH 7 where Si release was considerably higher than Al. Indeed near neutral pH conditions have reported a similar release of Si (~1.4 mg.g<sup>-1</sup> or ~ 0.14 % of solute relative to starting mass) [87] and a loss of metal ions expressed as total ion content into solution at 0.204 wt%[78] from the clinoptilolite at elevated pH (pH 8.7).



Figure 6.3 – The percentage of Si relative to the starting clinoptilolite mineral (1.00g) observed in solution when exposed to agitation (shaker bed – 100 rpm) for 504 hours with a solution (pH 7.1, 200 mL) in ambient conditions (25  $^{\circ}$ C and 1 bar pressure).



Figure 6.4 – Percentage of Al present relative to starting mass of clinoptilolite (1.00 g) in observed solution (pH 7.1, 200 mL) in ambient conditions (25  $^{\circ}$ C and 1 bar) undergoing continuous agitation (100 rpm shaker bed) for 504 hours.



Figure 6.5 – Atomic Si:Al ratio content found in aqueous solutions prepared from 1.00 g of clinoptilolite at pH 7.1 in ambient conditions (25 oC and 1 bar) undergoing continuous agitation (100 rpm shaker bed).

A suggested reason for this was the presence of cations forming inner sphere[88] complexes with Si-O<sup>-</sup> and SiOH groups [78, 87, 89]. However, in our studies the presence of cations or anions capable of forming complexes was unlikely due to the lack of any added cations in the majority of the experiments. Instead these charged sites were likely be filled with protons drawn from the solutions. H<sup>+</sup> may have been exchanging into the structure with Si<sup>4+</sup> being released[12] from the available Si-O<sup>-</sup> site.

Measurements of pH were undertaken with an initial phase of a rapidly increasing pH between 1 and 4 hours with a ~0.5 pH increase (Fig. 6.6) in both washed and unwashed samples. The rate of change in pH lessened in washed and unwashed clinoptilolite samples after the initial 4 hour period. The pH of both washed and unwashed samples underwent a much lower rate of change after the initial 4 hour period, indicating that the samples were close to equilibrium. An equilibrium effect was observed in another study [78] where pH underwent the maximum rate of change in pH at 4 hours. However that experiment was undertaken in basic conditions (pH 11) that subsequently buffered to pH 10 after a 4 hour period[78].

The increase in pH in these experiments could have indicated an increased uptake of  $H^+$  onto the exchange sites created by the Al – Si substitution in the structure. The  $H^+$  reaction was experienced at early stages of equilibrium in other studies (up to 2 minutes [78] in high pH situations >pH 10).

A small reduction in pH was also encountered in all samples between the ~400 and ~500 hour pH readings. The 200 hour pH reduction did not correspond to a reduction in % solute released as a total % starting mass of clinoptilolite (Fig. 6.3 & 6.4). The effect of a small change of pH in near neutral conditions would have little effect on the solubility of

these solids but could indicate a congruent dissolution event creating new surface exchange sites. Adsorption of  $H^+$  onto the exchange sites present in the clinoptilolite structure is the most likely cause of the observed increase in pH. Where  $H^+$  is being adsorbed this would correspond to an increase in Si release. This would have been due to the Al – Si substitution creating a net negative charge that would have been balanced by  $H^+$ .

The reduction of pH at around 200 hours (Fig. 6.6) in both washed and unwashed contacted solutions may originate from dissolution of the clinoptilolite. This may be followed by a release of  $H^+$  thorough deprotonation of fresh surface sites created by congruent dissolution of the mineral, reducing the pH of the solution. The released H<sup>+</sup> could then bind to surface exchange sites resulting in an increase in pH as more  $H^{\star}$  is removed from solution. An increase in pH from 0 to 200 hours indicates that exchange sites are undergoing proton donor acceptance through exchange of  $H^{+}$ . Around the 100 to 200 hour duration a reduction in Si release is encountered that may indicate that  $H^{+}$  is not reacting with the exchange sites as they are occupied, resulting in a reduction in uptake of  $H^{+}$  from solution and followed by a release of a fine fraction (congruent dissolution) event that would create a relative abundance of  $H^{+}$ . Proton donor reactions would then occur that would release an increased rate of additional Si (Fig. 6.3) into solution post 200 hours occupying the freshly created exchange sites. The pH drop was experienced to a greater extend in unwashed samples that undergo a greater proportion of congruent dissolution (fine fraction loss) to that of washed samples. A further minor reduction in pH was experienced post 400 hours and this may indicate another point of  $H^{+}$  adsorption declining due to fully occupied exchange sites and an increase in  $H^{\dagger}$  through continued dissolution.

The concentration of Si through loss from the clinoptilolite matrix through dissolution was significant over the period of the study when considering that SIXEP utilises 7400kg of clinoptilolite per ion exchange bed. A percentage loss against starting mass for Si of 0.10% (washed) and 0.14% (unwashed) was reported and could be in either an amorphous colloidal silica (SiO<sub>2</sub>) form or Si<sub>(aq)</sub> in the form of silicic acid (H<sub>4</sub>SiO<sub>4</sub>).

In low temperature (25°C) and pressure conditions (1 bar), as encountered in long duration experiments and those in the effluent plant, silicic acid should complex with available Al<sup>3+</sup> to form simple aluminosilicate complexes[90]. That may be the reason for lack of Al in solution. However the presence of lower Si:Al ratio (by atom) (1:1) solids has not been detected in SEM-EDX data in the long duration experiments. pXRD was not undertaken (high detection limits inherent in XRD would preclude the detection of small sample volumes of secondary precipitates) due to the bulk sample being predominately clinoptilolite masking any subsequent secondary phases.

All solids isolated during the clinoptilolite dissolution studies have been examined using SEM (Fig. 6.7) and EDX to determine elemental compositions. The elemental compositions of Mg, Si, Al, Fe and Ca have been determined from samples collected from the initial washing procedure (labelled "first wash") (Fig. 6.8). The first wash sample has been compared with clinoptilolite in "as received" condition, washed prior to experimental work and post experimental work. Post experimental samples were taken after 21 days of solution contact.



Figure 6.6 – pH readings obtained from triplicate observations for washed and unwashed experiments following the addition of 1.00 g of clinoptilolite into a pH neutral aqueous solution (200 mL) undergoing continuous agitation (100 rpm shaker bed) in ambient conditions ( $25^{\circ}C$  and 1 bar).

Elemental compositions of the clinoptilolite pre and post experiments do not reveal significant differences between the Si and Al compositions. The surface of the clinoptilolite is most likely to undergo significant loss of either Si or Al in the process of ion exchange. SEM-EDX has a relatively high uncertainty even in major constituents [49-52] with ongoing debate as to whether it can be a quantifiable technique without calibrated standards and rough particulate, non-polished material (as was the case in these experiments).

The effect of pre equilibrium conditions producing Al dissociation had been suggested previously with gibbsite [87] suggested as occurring due to early Al dissociation but was not found experimentally here. It did not appear to occur in the long duration experiments where AI concentration in solution was low and SEM – EDX data did not indicate the presence of  $AI(OH)_3$  phases in the recovered solids.



Figure 6.7 –SEM micrographs of clinoptilolite samples from long duration experiments: a - as received (mag. 7833x), b – first washings (mag. 7290x), c – unwashed pre-use (mag. 9324x), d – washed pre-use (mag. 2535x), e. washed sample after 21 days dissolution (mag. 2536x), f – unwashed sample after 21 days dissolution (mag. 6553x)



Figure 6.8 – Elemental compositions of clinoptilolite obtained via SEM-EDX (environmental mode 1mbar vacuum, 20 keV) at various stages; first wash is after initial washing collected from filtrate (100  $\mu$ m sieve), unwashed and washed priors are immediately prior to dissolutions experiments, 21 day samples are collected post dissolutions trials on washed and unwashed.

In the Doula [87] study the mechanism of Si release was Cu<sup>2+</sup> would interact with an exchange site, which would then create complexes with the Si-O<sup>-</sup> and Si-OH groups. The free proton obtained by the deprotonation of the surface lattice would then react with another Si-OH site and cause the release of Si. The release of Si in preference to Al from the structural lattice differs from the findings of Hartman [13, 14] where that study concluded that zeolite with a Si:Al ratio of above 3:1 did not dissolve in highly

concentrated acid solutions (~ 8.0 M HCl) over short durations (< 2 h). The Hartman study [13, 14] suggested the mechanism of dissolution as removal of Al from the lattice structure resulting in breaking of the remaining lattice structure as below a 3:1 Si:Al ratio there are significant Si-Al bonds. Whereas in zeolites with Si:Al ratios above 3:1, there are a majority of Si-Si bonds rather than Si-Al bonds. The breaking of the Si-Al bonds releases Si in addition to Al. A different mechanism is at work in the zeolite dissolution studied by Doula [87] due to near neutral pH conditions employed.

The study presented here does not contain a significant amount of starting cations that can create complexes with only Na<sup>+</sup> added to solution in the form of 0.1 M NaOH to adjust pH. It has been suggested that in operation at SIXEP due to the relatively short periods of operation ~180 days Cs tends to occupy the surface exchange sites[22] only and diffusion into the inner sphere/channels tends not to occur. The location of Cs was used to justify a modelling approach as opposed to dissolution behaviour of clinoptilolite and their model did not consider longer term effects nor breakdown of the structure. The presence of some H<sup>+</sup> at near neutral conditions could be expected. The majority of any H<sup>+</sup> would rapidly react with  $OH^{-}$  but some  $H^{+}$  would be available to react with the exchange sites to promote the release of Si in preference to Al as found in the Doula study [87] undertaken at pH 7.25. An increase in incongruent release in Al could indicate complexing agents (likely to be Cl<sup>-</sup> in the experiments undertaken in this study) as the Doula study [87] found that Al was released in preference to Si when subjected a complexing agent. An increase in Al content and corresponding decrease in Si:Al ratio (by atom) was not experienced. Instead a release of Si was encountered indicating that near surface exchange sites were being occupied, leading to deprotonation (and corresponding increase in  $H^{\dagger}$ ), as experienced in 200 hour and 400 hour pH readings (Fig. 6.6). This may

create conditions where Si forms  $H_4SiO_{4(aq)}$  (silicic acid) [87]. The set of reactions may go some way to explain the lack of Al and the high concentration of Si present in solution in non Cs-experiments.

# g) Effect of monovalent metal ion addition on release of species

Cs was added to one set of experiments (1 mg.L<sup>-1</sup> starting concentration) to investigate the role of Cs in clinoptilolite dissolution processes. The only monovalent metal ion additions to the solution in contact with clinoptilolite were Na from pH adjustment (NaOH) (Fig. 6.9) and Cs (as CsCl) (Fig. 6.10). The solution concentration of Cs increased throughout the duration of the experiments indicating that the majority of Cs was adsorbed by clinoptilolite in initial stages of contact and was gradually released back into solution as contact with solution was maintained.

Cs concentration prior to the commencement of the experiment was 1.00 mg.L<sup>-1</sup>. In solution at 24 hours the concentration of Cs ranged between 5 to 7.5  $\mu$ g.L<sup>-1</sup> and reached 20 to 35  $\mu$ g.L<sup>-1</sup> at 504 hours (21 days) (Fig.6.9).

The effect of ion exchange by Cs loading of clinoptilolite leading to the possible loss of Si from the mineral structure has been considered. Cs was added to solution in contact with clinoptilolite and has been compared to unwashed samples at pH 7 and pH 8. The unwashed clinoptilolite Cs experiments contained significantly higher Si:Al ratios (by atom) than those non-Cs analogue controls. The Si:Al ratio (by atom) in solution was 8.6:1 when Cs was present and 4.6:1 without Cs addition. After the 24 hour contact period in the Cs loaded samples the Si:Al ratio (by atom) in solution dropped to below that expected of the clinoptilolite mineral ~5:1 (Fig. 6.11a).



Figure 6.9 – The percentage of Na relative to the starting mass of clinoptilolite in washed and unwashed states (1.00 g) in pH 7.1 solutions both with Cs present (1.00 mg) and without in solution all in ambient conditions (25 °C and 1 bar).

When considering Na levels (Fig. 6.9), less Na was released into solution in the first 200 hours of solution contact with the Cs loaded mineral phases than those with the Cs free mineral phase. Si was being preferentially released into solution (Fig. 6.11a). After a period of approximately 24 hours a significant increase in Al released (Fig. 6.11b) into solution and a corresponding decrease in Si:Al ratio (by atom) are observed (Fig. 6.11c).

After 200 hours a greater % of Na was released from the Cs loaded clinoptilolite at pH 7 than pH 8 Cs loaded clinoptilolite solutions. Clinoptilolite loaded with Cs at pH 8.0 released less Na into solution than those at pH7.0 and those of non-Cs analogue unwashed experiments at the termination of the study (>79 days). It would tend to indicate that Na and Cs were not being retained in the clinoptilolite over long durations but were retained on surface exchange sites that is consistent with the modelling approach[22] for ion exchange in the SIXEP process with a rapid sorption of Na<sup>+</sup> and Cs<sup>+</sup>

during initial contact with clinoptilolite, followed by a slow release of these ions back into solution. These "released" exchange sites were then most likely occupied by H<sup>+</sup>.

Deallumination was observed from Cs loaded clinoptilolite on contact with pH neutral aqueous solutions as indicated by an increasing AI concentration and lower Si:AI ratios over longer durations ( >24 hours). Cs concentration in solution increased (Fig.6.10) throughout the duration that the Cs loaded clinoptilolite was in contact with solution, indicating that Cs was being released from the ion exchange sites. The increase in Cs in solution may indicate that Cs was initially adsorbed onto the clinoptilolite and subsequently released back into solution throughout the duration of the experiment. This is in agreement with the findings of Doula [87] where, in that study, complexes were formed by the addition of  $Cu^{2+}$  that reacted with the exchange sites creating a complex which reached a peak absorption after 24 hours and after which time some  $Cu^{2+}$  was subsequently released back into solution. A corresponding increase in Na<sup>+</sup><sub>(aq)</sub> during the experiments was also in agreement with the Doula study [87] (Fig. 6.9), indicating that the Na<sup>+</sup> that was present on the exchange sites was being released through a combination of  $Cs^{+}$  exchange and  $H^{+}$  interaction with the surface exchange sites. After 24 hours the Si:Al ratio of the Cs contacted solutions (Fig. 6.11c) decreased indicating that a greater proportion of AI was being released into solution (Fig. 6.11b).

Doula [87] found that absorption of the cation ( $Cu^{2+}$ ) was responsible for the release of Si and that an increase in Cl<sup>-</sup> would favour complexes with Al-OH groups and release Al from surface groups. Whilst complexing agents are not the cause of the non-Cs loaded clinoptilolite dissolution it appears that after an initial 24 hour period with the  $Cs_{(aq)}$ supply exhausted, the Cl<sup>-</sup> that remained in solution may be forming complexes to liberate

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a greater quantity of Al in preference to the Si as found in the non-Cs experiments. Cl was present in the non-Cs experiments but in significantly lower concentrations. There are a number of processes of dissolution occurring during the experiment. Throughout the duration of the experiment there was a significant increase in solute concentrations in all dissolution experiments with Cs loaded clinoptilolite relative to those found for Cs free clinoptilolite where elevated levels of both congruent and incongruent dissolution is likely to be occurring. A likely process by which incongruent dissolution of the clinoptilolite occurs is as follows:

- 0 24 hours: Cs<sup>+</sup> binds to exchange sites on the near surface and this near surface cation exchange promotes an incongruent dissolution releasing Si (Fig. 6.11a);
- After 24 hours: The majority of the Cs has been absorbed onto the exchange sites. An increase of Al in solution (Fig. 6.11b) is likely due to an Cl<sup>-</sup> in solution relative to Cs<sup>+</sup>. This relative increase in Cl then creates complexes with Al-OH on the surface of the clinoptilolite (as Si has already been removed from the surface in the 0-24 hour period) similar to that found in Doula [87] where Cl was responsible for the release of Al in preference to Si. ; Due to a low Si:Al ratio (by atom) this is likely to be an incongruent release of Al.



Figure 6.10 – The concentration of Cs present in solution after 24 hours up to 504 hours in pH 7 and pH 8 solutions containing clinoptilolite (1.00 g) undertaken in ambient conditions (25  $^{\circ}$ C and 1 bar) in a non-inert atmosphere (no CO<sub>2</sub> control). Cs was added to solution prior to the experiments at a concentration of 1.00 mg.L<sup>-1</sup>.



Figure 6.11a – The percentage of Si relative to the starting clinoptilolite mineral (1.00g) observed in solution when exposed to agitation (shaker bed – 100 rpm) for 504 hours in ambient conditions (25 °C and 1 bar pressure) in three conditions: Unwashed Clinoptilolite without Cs addition (Non Cs unwashed); with 1.00 mg.L<sup>-1</sup> Cs and pH adjusted to 7.0 (pH 7 Cs); with 1.00 mg.L<sup>-1</sup> Cs and pH adjusted to 8.0 (pH 8 Cs).



Figure 6.11b – The percentage of Al relative to the starting clinoptilolite mineral (1.00g) observed in solution when exposed to agitation (shaker bed – 100 rpm) for 504 hours in ambient conditions (25  $^{\circ}$ C and 1 bar pressure) in three conditions: Unwashed Clinoptilolite without Cs addition (Non Cs unwashed); with 1.00 mg.L<sup>-1</sup> Cs and pH adjusted to 7.0 (pH 7 Cs); with 1.00 mg.L<sup>-1</sup> Cs and pH adjusted to 8.0 (pH 8 Cs).



Figure 6.11c – Atomic Si:Al ratio content found in aqueous solutions prepared from 1.00 g of clinoptilolite at pH 7.0 and 8.0 in ambient conditions (25  $^{\circ}$ C and 1 bar) undergoing continuous agitation (100 rpm shaker bed) Cs was added to solution prior to the experiments at a concentration of 1.00 mg.L<sup>-1</sup>.

#### h) Comparisons between washed and unwashed samples

The clinoptilolite sample that underwent an initial wash (Fig. 6.8) predominately produced similar elemental compositions to that encountered in the bulk unwashed "as received" samples. The relative content of Si was lower in the clinoptilolite samples after a single wash than that of all other samples. This may have indicated that some aluminosilicate mineral was being washed from the sample in the first instance with a lower Si:Al ratios than that of clinoptilolite. However impurities encountered in the "as received" samples contained Quartz (SiO<sub>2</sub>) and mordenite (Ca<sub>2.5</sub>, Na<sub>2</sub>Al<sub>7</sub> Si<sub>41</sub>O<sub>96</sub>.24H<sub>2</sub>O) which have either wholly Si or very similar Si:Al ratio (by atom) to clinoptilolite. The first wash may have indicated that deallumination occurred to some degree, with a bulk release of clinoptilolite fines. The rapid adsorption of H<sup>+</sup> has been encountered in the first 2 minutes of aluminosilicate mineral phases contact with deionised water [12, 78].

The total inorganic carbon (TIC) has been determined for all solutions obtained after contact with clinoptilolite for 79 days (agitation of samples ceased at 21 days) taking triplicate measurements from each of the three samples from both washed and unwashed mineral. Washed clinoptilolite produced a percentage mass of 4.80  $\times 10^{-2}$  % of dissolved TIC when compared to the starting mass of clinoptilolite while unwashed clinoptilolite yielded 3.95  $\times 10^{-2}$  % of dissolved TIC compared to the starting mass of clinoptilolite. There were some observed effects of carbonation and CO<sub>2</sub> buffering in the solutions. A small reduction was observed in pH measurements (Fig. 6.6) however this did not significantly alter the dissolution/degradation process of the clinoptilolite mineral.

## i) Colloidal and aqueous species present in 79 day samples

To investigate the nature of these species in solution the long duration experiments have undergone a step-wise filtration process with results presented for washed and unwashed samples post experiments at 79 days (Table provided in supplementary information). From 21 days to the collection of the filtrate, samples were stored in static conditions. There is Si present in solution in both washed and unwashed samples at the end of the experiments with 2.18x10<sup>-1</sup> % and 3.09x10<sup>-1</sup>% of Si transferred from solid phase into solution, respectively. The presence of higher Al content in the supernatant after centrifuging in the unwashed sample (2.84x10<sup>-2</sup> % of solute compared to starting mass of clinoptilolite) compared to washed sample (1.18x10<sup>-2</sup> % of solute) may indicate congruent dissolution and/or the presence of clinoptilolite fines in unwashed samples.

The supernatant obtained after centrifuging solution mixtures was subsequently passed through colloidal filters (3000MCWO) which showed significant Si content in the filtrate for unwashed ( $1.55 \times 10^{-1}$  %) and washed ( $6.9 \times 10^{-2}$ %) clinoptilolite samples. Congruent dissolution of soluble species is most probably occurring as the Si:Al ratios (by atom) in the colloid removed solution were around 5:1. When subtracting Al aqueous species from the centrifuged only samples for washed and unwashed samples a Si:Al ratio of 5.2:1 (unwashed) and 5.7:1 (washed) was observed.

An increase in Al in solution was experienced in the Cs loaded clinoptilolite aliquots. This was evidenced by a reduction in Si:Al (by atom) ratios for solutions passing a 0.45  $\mu$ m filter (12.50:1) and sub-micron 3000 MWCO filters (242.17:1). The reduction in Si:Al ratio was as a result of an increase in Al content as opposed to a reduction in Si.

The abundance of Si present in solution after being passed through colloidal filters tended to indicate that particulate SiO<sub>2</sub> was not present in significant amounts. Studies have suggested amorphous silica globules exist in the <50 nm range[74, 91] and dissolution of olivine[92] that results in SiO<sub>2(am)</sub> falls in the particle size range of 10 nm to 25 nm. Similar reductions are reported in Si concentrations [93] when passed through ultrafiltration medium (5000 MWCO in that case). The amorphous silica globules if present would be expected to be retained in 3000 MWCO (<2 nm filters). Instead the Si present in solution was likely to be Si<sub>(aq)</sub> in the form of silicic acid.

# j) Short term clinoptilolite behaviour

Contact of clinoptilolite with the pH neutral aqueous solutions over 24 hours have been used to explore the short term release of Si (Fig. 6.12a) and Al (Fig. 6.12b) into solution and is based upon the three stage filtration methodology (centrifuge only, 0.45 µm and 3000MWCO ultrafiltration). The solution Si and Al content is expressed as a % of solute relative to starting mass of clinoptilolite (1.00 g). At each time interval the samples underwent all three filtration techniques. The Si:Al ratio (by atom) (Fig. 6.12c) of each sample has been determined using the concentration data with errors expressed as multiplicative errors.

Previous work[94] suggested that a significant proportion of silicate release occurred in the first 30 minutes of contact with solution. In the studies performed here, the three filtration methodologies produced similar concentrations of Si in solution within the first 30 minutes of solution contact with clinoptilolite. This tended to indicate initially that Si was likely to be undergoing incongruent dissolution as a greatly increased Si:Al ratio by atom was encountered.



Figure 6.12a – The percentage of Si in solution (pH 7.3) compared to starting mass of clinoptilolite (1.00 g) in ambient conditions (25  $^{\circ}$ C and 1 bar) undergoing continuous agitation (100 rpm shaker bed). Solutions were centrifuged, followed by 0.45  $\mu$ m filtration and then colloid filtration (3000MWCO).



Figure 6.12b – The percentage of Al compared to starting mass of clinoptilolite (1.00 g), in ambient conditions (25  $^{\circ}$ C and 1 bar) undergoing continuous agitation (100 rpm shaker bed). Solutions were centrifuged, followed by 0.45  $\mu$ m filtration and then colloid filtration (3000MWCO).
The filtrate data for Al (Fig. 6.12b) colloid filtration (3000MWCO) indicated that Al<sub>(aq)</sub> was not present in significant quantities. This was to be expected if Al was not undergoing incongruent dissolution but was being released as part of congruent dissolution of the clinoptilolite. The lack of Al in the aqueous filtrate did not allow comparisons between long duration and short duration experiments. In the long duration experiments the Si:Al ratios (by atom) were above 1000:1 with different mixing conditions.



Figure 6.12c – Si:Al ratios (by atom) of particulates and colloids in short duration experiments (<24 hour) in pH 7.3 solutions undertaken at ambient conditions (25  $^{\circ}$ C and 1 bar) undergoing continuous agitation (100 rpm shaker bed). The determination of Si:Al ratio of the aqueous species was not possible due to the very low Al concentrations present in the samples.

#### i) Release of Si into solution

After initial incongruent dissolution (up to 30 minutes) congruent dissolution was observed, where clinoptilolite fines were released into solution in addition to  $Si_{(aq)}$ . After a period of four hours there was evidence for significant release of fines (congruent dissolution) into the bulk liquid, as demonstrated by Si:Al ratios (Fig. 6.12c) for centrifuge only sample filtration, where the ratio tended to reduce to around 5 – 6 Si:Al ratio (by atoms) at four hours and remained near this ratio for the remainder of the experiment.

After the four hour period there was evidence of both fines release (congruent) and silicic acid formation (incongruent). The Si:Al ratios of the centrifuged samples suggested a bulk release of fines (Fig. 6.12c) demonstrating congruent dissolution. A release of Si from the mineral structure may be occurring in parallel to a simple congruent release of small particulates of clinoptilolite after four hours of solution contact.

## k) Ostwald ripening

Monomers of silicic acid with a particle size of 1nm can occur [94]. A particle size of 1nm would pass through a 3000 MWCO colloidal filter. There was a suggestion that Si was present in the silicic acid form  $(H_4SiO_4)$  [74]. Whether this was in the monomeric or polymeric form has not been determined experimentally in the study undertaken here.

There was a suggestion that in environmental conditions (25°C and 1 bar) silicic acid tends to exist in the polymeric form[74] and a suggestion that up to 50% may be in polymeric form[95]. The progression from nano cluster to nano particles and then onto bulk phases in an Ostwald ripening [92, 96] stepwise transformation did not appear to be occurring in the short duration experiments (24 Hr) in the initial stages. The colloidal Si particles encountered after the 0.45  $\mu$ m filters and before 3000MWCO filters did not significantly increase as a ratio to that encountered for the species present in the aqueous phase.

When considering congruent dissolution, after the initial release of a greater proportion of Si to Al indicating incongruence, the bulk phases released tended towards the Si:Al ratio of clinoptilolite and would generate large particulates. The 0.45  $\mu$ m filtrate indicated a colloidal material that possessed similarities to Clinoptilolite. However a Si:Al ratio (by atom) of above 10:1 immediately after 24 hours of contact with pH neutral aqueous solutions, would indicate colloids are a combination of both Clinoptilolite fines and Si<sub>(aq)</sub> likely to be in the silicic acid form [74, 94] possibly indicating Ostwald ripening towards the end of the initial 24 hour contact period.

### **I)** Conclusions

Washed and unwashed clinoptilolite in contact with pH neutral aqueous solutions over long duration underwent both congruent and incongruent dissolution and produced solutions containing both particulates and aqueous species. Step-wise filtration (centrifuge only, 0.45  $\mu$ m filter and 3000 MWCO filters) indicated that there was considerable Si<sub>(aq)</sub> likely to be in the form silicic acid [74]. The long duration experiments yielded similar percentages of solute compared to starting mass of clinoptilolite for Si 1.50x10<sup>-2</sup> % (washed) and 1.54x10<sup>-2</sup> % (unwashed). A greater percentage of particulates was encountered in unwashed conditions compared to washed samples and was to be expected due to the lack of prewash steps that would have removed a considerable quantity of fines.

A mass balance can be undertaken using the experimental data collected on the 79 day long duration experimental data, applied to SIXEP process scale. A total Si solids content of 32.26 kg and 2.22 kg of Si<sub>(aq)</sub> could be generated from the ion exchange beds during this period. Making a further assumption that the dissolution rates were similar throughout the lifetime of the plant since commissioning a total of 4760 kg of Si solids may have entered the discharge line since plant operations commenced. This assumes that washed clinoptilolite has always been utilised for the ion exchange beds which may not have been the case during early stages of the plant operation and that a linear dissolution rate occurs after 79 days. Bed changes are typically undertaken every 180 days. Dissolution of clinoptilolite could account for a significant contribution to the solids build up within the discharge pipe.

Assuming that all of the clinoptilolite has been deposited on the inner surface of the discharge line and that the discharge line is ~1500 m long with an internal diameter of 240 mm this would create a 1.91 mm solid layer on the entire length of the pipe. This assumes no solids loss and that all solids remain adhered to the pipe surface which is not the case in service as shearing of the retained solids occurs as demonstrated through pressure build ups and pressure lowering during normal operations. However this build-up of material has been experienced when undertaking localised inspections. As a similar thickness of material has been encountered in service in localised areas it is feasible that the origin of the solids build up is due to congruent dissolution of the bulk clinoptilolite ion exchange beds.

The solids collected from the first wash (in the pre-treatment step of washed clinoptilolite) yielded lower Si:Al (by atom) ratios than that of unwashed and washed clinoptilolite. It may indicate impurities (quartz and mordenite) were either being retained in the bulk clinoptilolite or that significant Si<sub>(aq)</sub> was being lost due to the

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washing process. However  $Si_{(aq)}$  loss from the first wash step (in 100 µm sieve) for the retained bulk solid was unlikely as the bulk characterisation (SEM –EDX) of the starting solids (washed prior – Figure 6.8) was comparable with that of unwashed clinoptilolite pre and post experiments. Overall, the results suggested that when unwashed commercial clinoptilolite was utilised during effluent treatment, a fine fraction was washed out containing clinoptilolite and/or other solids also contained within the bulk preparation.

Short duration experiments (<24 hours) indicated that Si was present in solution, likely to be in the silicic acid form. The Si:Al ratio (by atom) suggested that congruent dissolution releasing fines into the bulk solution contributed to Si concentration in solution. The presence of incongruent dissolution of Si from the clinoptilolite matrix was shown to occur at near neutral solution conditions. This has implications for plant operations that utilise clinoptilolite, as this may result in precipitation down-stream of the plant or contribute to the solids entrainment encountered in another bulk solid formation. Concerning the release of solutes from clinoptilolite, dissolution may result in reprecipitate in downstream processes, via a quite complex set of reactions resulting in the precipitation of secondary solids. This study has identified that small amounts of simple Al hydroxides and Fe oxides may precipitate, even over the short duration conditions encountered in the pipeline. Such solids could cumulatively increase over many years of plant operations. Rate dependent processes, such as Ostwald ripening[92, 96] may explain the propagation of silicic acid nanoclusters to bulk particulates.

The aim of this work was to investigate whether dissolution of clinoptilolite could occur in near neutral pH conditions. There appears to be both congruent and incongruent dissolution taking place. In the instances of incongruent dissolution these were Si phases

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typically silicic acid. Al<sub>(aq)</sub> was not encountered to the same extent as Si. The presence of Si in abundance to Al is unlikely to be due to rapid re-precipitation of Al into a hydroxide phase as the Si:Al ratios would remain similar to 6:1 in the colloid filtrate. Deallumination does not appear to be occurring in these experiments, with a preferential release of Si compared to Al.

A Cs analogue has been introduced to examine the effects of the presence of a representative cation on the process of dissolution and degradation of the mineral. A significant increase in Si content in solution over an initial 24 hour period occurs and for durations over 24 hours an increase in Al solution concentration is observed. This is not thought to be congruent dissolution of the bulk clinoptilolite mineral structure as the Si:Al ratio (by atom) is lower than 5:1. Instead, it is likely that Al is being released along with congruent release of bulk clinoptilolite fines. This is likely due to a reaction between the Cl<sup>-</sup> present in solution (from the initial CsCl compound added at commencement of the study) and Al-OH sites present on the surface and bulk inner lattice. Control of Cl on the SIXEP plant is exercised due to Cl attack of the vessels leading to corrosion and pitting. This provides further justification for control of Cl as it can cause an increased Al release that can form insoluble hydroxides in simulant effluent which can contribute to the deposit mass.

Congruent dissolution of the clinoptilolite was encountered in addition to the release of Si from the mineral structure. The majority of the fines generated were >0.45  $\mu$ m. However there was a proportion of <0.45  $\mu$ m colloidal particles that may prove problematic downstream of the plant. The <0.45  $\mu$ m particles and incongruent dissolution releasing Si

will contribute to solid build-up and solid formation issues in discharge lines unless mitigation measures are put in place to prevent release.

## m)Acknowledgements

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# n) Supplementary information

Filtration data from long duration experiments obtained using three types of filtration to determine presence of fines, colloids and aqueous elemental species data is presented as % loss of species relative to starting mass of clinoptilolite (1.00g).

	Mg (sd) %	Na (sd) %	Si (sd) %	Al (sd) %	Fe (sd) %	Ca (sd) %	Si:Al ratio (error)					
Washed Samples												
Centrifuge	1.27E-03 (1.27E-05)	9.35E- 02 (7.95E- 04)	1.22E- 01 (9.70E- 04)	1.16E- 02 (5.99E- 05)	5.85E-03 (2.11E-05)	2.72E- 03 (2.53E- 05)	10.1 (0.1)					
0.45um filter	3.27E-04 (8.08E-06)	8.25E- 02 (2.15E- 04)	7.50E- 02 (2.06E- 04)	3.20E- 03 (2.14E- 05)	1.96E-03 (1.40E-05)	7.98E- 04 (1.83E- 04)	22.5 (0.2)					
colloid filter	1.63E-04 (1.62E-05)	7.31E- 02 (1.44E- 03)	5.60E- 02 (4.58E- 04)	2.33E- 05 (2.91E- 05)	0.00E+00 (1.40E-05)	1.37E- 03 (4.28E- 04)	2303.7 (2877.4)					
Centrifuge	1.54E-03 (1.32E-05)	2.69E- 01 (2.72E- 03)	3.72E- 01 (1.60E- 03)	1.42E- 02 (8.89E- 05)	6.66E-03 (9.65E-05)	3.08E- 03 (1.76E- 05)	25.3 (0.2)					
0.45um filter	3.87E-04 (8.08E-06)	2.22E- 01 (1.88E- 03)	2.70E- 01 (2.25E- 03)	3.92E- 03 (8.08E- 06)	2.20E-03 (2.42E-05)	6.16E- 04 (1.40E- 05)	66.3 (0.6)					
colloid filter	6.53E-05 (8.08E-06)	2.35E- 01 (4.79E- 03)	2.88E- 01 (2.57E- 03)	2.10E- 04 (2.80E- 05)	1.87E-05 (8.08E-06)	4.71E- 04 (1.44E- 04)	1315.5 (175.8)					
Centrifuge	1.04E-03 (6.89E-06)	1.33E- 01 (4.54E- 04)	1.61E- 01 (7.05E- 04)	9.60E- 03 (3.94E- 05)	5.21E-03 (3.28E-05)	2.30E- 03 (2.37E- 05)	16.1 (0.1)					
0.45um filter	2.94E-04 (3.70E-05)	1.10E- 01 (1.70E- 03)	1.09E- 01 (1.42E- 03)	2.84E- 03 (5.05E- 05)	1.90E-03 (3.52E-05)	5.74E- 04 (5.60E- 05)	36.9 (0.8)					
colloid filter	1.35E-04 (8.08E-06)	1.05E- 01	1.04E- 01	5.13E- 05	-4.67E-06 (8.08E-06)	8.31E- 04	1940.9 (1617.2)					

		(2.06F-	(4.54F-	(4.28F-		(6.31F-						
		03)	04)	05)		(05)						
Unwashed Samples												
Centrifuge	3.57E-03 (3.85E-05)	1.17E- 01 (1.33E- 03)	2.04E- 01 (1.33E- 03)	2.92E- 02 (3.10E- 04)	1.68E-02 (1.66E-04)	6.41E- 03 (6.60E- 05)	6.7 (0.1)					
0.45um filter	7.70E-04 (7.27E-05)	1.04E- 01 (1.20E- 03)	7.39E- 02 (3.87E- 04)	5.53E- 03 (7.18E- 05)	4.27E-03 (6.10E-05)	1.08E- 03 (7.71E- 05)	12.8 (0.2)					
colloid filter	1.45E-04 (2.14E-05)	9.16E- 02 (1.60E- 03)	4.23E- 02 (5.44E- 04)	6.53E- 05 (4.92E- 05)	4.67E-06 (8.08E-06)	9.52E- 04 (1.61E- 04)	621.4 (467.7)					
Centrifuge	3.44E-03 (3.71E-05)	1.11E- 01 (6.68E- 04)	1.98E- 01 (2.26E- 03)	2.79E- 02 (3.80E- 04)	1.66E-02 (2.31E-04)	6.20E- 03 (7.37E- 05)	6.8 (0.1)					
0.45um filter	6.72E-04 (1.40E-05)	9.68E- 02 (9.82E- 04)	7.31E- 02 (6.29E- 04)	5.27E- 03 (9.32E- 05)	4.00E-03 (1.40E-05)	1.03E- 03 (8.08E- 06)	13.3 (0.3)					
colloid filter	1.45E-04 (8.08E-06)	8.70E- 02 (1.23E- 03)	4.38E- 02 (5.95E- 04)	4.67E- 05 (2.91E- 05)	0.00E+00 (0.00E+00)	8.03E- 04 (9.53E- 05)	901.3 (563.0)					
Centrifuge	3.63E-03 (6.59E-05)	3.39E- 01 (1.01E- 02)	5.26E- 01 (8.42E- 03)	2.82E- 02 (4.76E- 04)	1.76E-02 (2.28E-04)	5.89E- 03 (1.49E- 04)	17.9 (0.4)					
0.45um filter	7.56E-04 (0.00E+00)	2.78E- 01 (3.83E- 03)	3.35E- 01 (1.26E- 03)	5.20E- 03 (1.07E- 04)	4.56E-03 (6.42E-05)	8.21E- 04 (5.66E- 05)	61.9 (1.3)					
colloid filter	6.53E-05 (8.08E-06)	3.20E- 01 (3.92E- 03)	3.78E- 01 (2.92E- 03)	2.75E- 04 (5.66E- 05)	9.33E-05 (8.89E-05)	3.97E- 04 (1.62E- 05)	1320.4 (271.5)					

# Chapter 7 – Gamma irradiation of clinoptilolite paper

## Gamma irradiation effects on a natural ion exchange zeolite used in a

## nuclear effluent treatment plant

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C.A. Sharrad – Manuscript review, Principal supervisor; D. Trivedi –co-supervisor; S. Kellet –context discussion.

## <u>Relevance</u>

This work addresses high dose effects on clinoptilolite in dry irradiation conditions and congruent and incongruent dissolution of the mineral. (Work by others is considering wet irradiation conditions) In this work it suggests only minor differences in the clinoptilolite structure post irradiation. Reductions in the release of ions (likely to be from exchange sites) have been observed indicating a radiation induced reduction of surface cations and solutes, potentially reducing amounts of available sites for exchange. An overall reduction in Si<sub>(aq)</sub> is beneficial from a pipeline fouling perspective as it reduces elemental Si that has been found to generate precipitates that have similarities to the previously recovered pipeline solid. However an increase in colloidal Si (likely to be SiO<sub>2</sub>) may be a route for radionuclide transport through the plant.

#### a) Abstract

Clinoptilolite (Na<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) is a naturally occurring mineral (part of the Heulandite group) and is used in many applications. One such use is as an ion exchange media to remove cation species where a net negative charge is created by substitution of Si by Al within the tetrahedral lattice structure and this negative charge is usually filled by a monovalent cation. Typically Na<sup>+</sup> or Cs<sup>+</sup> or divalent cations can also occupy these sites. Clinoptilolite originating from the mud hills deposit (California, USA) is used within an ion exchange plant at Sellafield (Cumbria, UK) to selectively remove Cs and Sr from effluent prior to discharge. The behaviour of clinoptilolite subjected to high total gamma doses has been limited to <10 MGy in previous studies. This study has sought to examine the effect of  $\gamma$  total dose up to 50 MGy from a <sup>60</sup>Co source in order to identify any structural alterations through characterisation of the dry mineral and assess the dissolution/degradation of the irradiated mineral when contacted with process-like solutions.

Characterisation of the dry clinoptilolite was performed using powder X-Ray Diffraction (pXRD). The relative intensities and peak positions were similar between  $\gamma$  -irradiated mineral (50 MGy) and the control sample. The lack of a distinct change indicated that a 50 MGy total dose does not adversely affect the crystalline structure of the mineral. Elemental composition of the near surface of the material by scanning electron microscopy/energy dispersive X-ray spectroscopy indicated similar Si/Al ratio (~5:1 by atom) between the control (non-irradiated) and irradiated 50 MGy total dose samples. As Si/Al substitutions are responsible for the exchange performance then this would indicate that a limited effect of  $\gamma$ -radiation on the mineral structure has been experienced. Minor cations present on the near surface (few µm) have decreased upon exposure to the  $\gamma$ -radiation.

The nature of solutes (particles, colloids or aqueous species) from the clinoptilolite contact solutions have been examined through a series of filtration experiments. A reduction in total solutes and a significant reduction in aqueous species (passing <2 nm filters 3000 MWCO) was found in 50 MGy clinoptilolite contacted solutions. An increase in colloidal species as a proportion of total solutes was found in irradiated samples. The increase in colloidal material post irradiation has not been observed in other studies. Limited effects are encountered in the structural arrangement and any changes were likely due to the loss of structural water resulting in shrinkage of the lattice structure. This indicates that exposure to high doses of  $\gamma$  radiation has minimal impact on ion exchange performance. However, an increase in colloidal material content from the degradation of the ion exchange material may prove problematic for waste isolation as these colloids could enhance radionuclide mobility in the effluents.

#### b) Introduction

Zeolites are utilised as inorganic ion exchange media within numerous industries. The nuclear industry in particular has a long history[97] of utilising zeolites as a form of ion exchange to remove radionuclides[63]. Clinoptilolite (Na<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) is one such zeolite used to remove mono and di-valent radionuclides from effluent prior to discharge at the Site Ion Exchange Plant (SIXEP)[3, 4] located on the Sellafield site in Cumbria, UK.

Clinoptilolite has been found to be selective for Cs and Sr which is present in effluent treated in SIXEP. Ion exchange occurs in the bulk clinoptilolite structure as a result of Al<sup>3+</sup> ions replacing Si<sup>4+</sup>, resulting in a net negative charge in the tetrahedral coordinated structure [76-78].

The clinoptilolite mineral is part of the heulandite group[6], with a high silicon to aluminium ratio (by atom) of around 5:1. In the process environment of SIXEP, the clinoptilolite receives a pH neutral feed (after pH reduction through a carbonation tower) containing radionuclides [3, 4, 63]. Previous work has characterised the clinoptilolite used at SIXEP[8] with a representative formula for the mineral (Mud Hills deposit, California, USA) as Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O. The clinoptilolite ion exchange beds are changed at intervals > 90 days with the initiation of bed changes based upon performance of the exchange bed which are subjected to a significant radiation dose during the lifetime of the clinoptilolite. The beds are currently pre-conditioned prior to use on plant to remove a significant quantity of Cl<sup>-</sup>. Historically the clinoptilolite was used in an "as received" condition in an unwashed state with little pre-treatment[58].

Clinoptilolite has been utilised on the SIXEP for many years and the work has relevance for that plant and any nuclear treatment or remediation plant that utilises clinoptilolite. The study of degradation of the mineral structure has many applications, including inservice and potential decommissioning legacy issues. The in-service performance and corresponding dissolution performance can cause potential solid formations within discharge pipelines resulting in flow restrictions. Along with longer term decommissioning and waste immobilisation strategies that may be proposed for spent exchange media.

The effects of radiation on clinoptilolite have been previously considered. Previous studies have investigated gamma ( $\gamma$ ) [77, 98-101] (total doses: 0.7MGy[98], 10MGy [99], 1MGy [100] and 10kGy [101]) and beta ( $\beta$ ) radiation damage [77, 98]. The effects from radiation on the leaching performance[99], ion exchange performance[77, 98] and adsorption of ions onto the structure [100, 101] of the clinoptilolite have all been studied. However, none of these studies considered changes in the mineral structure subjected to radiation effects , with studies focusing instead on ion exchange performance. An increase in lattice spacing of 0.110 Å[102] has been reported in monovalent metal ion exchange capacity experiments after being subjected to a total dose of 0.7 MGy of  $\gamma$ -radiation. The increase in lattice spacing appears to be due to Cs<sup>+</sup> substitution in place of Na<sup>+</sup>, with the former having a large cation radii rather than as a direct effect of 0.7 MGy of  $\gamma$ -radiation and resulting in a "stretch" or relaxation of the lattice structure to accommodate the larger cation.

Cations with a higher ionic radius were found to be more favourably exchanged [77] into the clinoptilolite structure when subjected to  $\gamma$  and  $\beta$  irradiations due to the displacement of H<sub>2</sub>O contained within the structure and a breaking of Si-O-Al, Si-O-Si and Al-O-Al bonds.

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The breaking of bonds and displacement of H<sub>2</sub>O would create a greater number of net negative charge sites which can be filled with larger ionic radii cations. The breaking of the bonds and removal of H<sub>2</sub>O would create a pathway for the cations to penetrate into the bulk structure as they are currently retained on the near surface, thereby increasing the available number of exchange sites. The study considered exchange properties of clinoptilolite with <sup>137</sup>Cs and <sup>90</sup>Sr post irradiation and did not consider the release of cations present on the ion exchange sites or dissolution of the bulk clinoptilolite.

The radiolytic effects on bound or free (i.e. not contained in the mineral structure) water[57, 100, 103-105] at high doses may produce significant quantities of ionic species ( $H^+$  and  $OH^-$ ) that would react with the exchange sites Incongruent dissolution has been found to occur in near neutral pH (7 ± 0.5) resulting in degradation of the clinoptilolite through loss of Si from the structure (See chapter 6). As such, studies should be undertaken in a dry state in the first instance.

#### c) Experimental methods

The clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) was supplied by Sellafield Ltd and was used in an "as received" condition without further preparation or grading steps i.e. no pre-washing or sample drying. The clinoptilolite was mined from the Mud Hills deposit in California. The mineral was examined prior to use using powder X-ray diffraction (pXRD) to confirm the mineral phases present in the sample. It was predominately Clinoptilolite with minor impurities of quartz and mordenite. All other chemicals were supplied by Sigma-Aldrich and used without any further purification. All containers for aqueous experiments were made of high density polyethylene (HDPE) to remove any potential interference from silicates leaching from glassware.

#### i) y irradiation

Two samples (5.00 g each) of clinoptilolite were placed into glass vials (~5 mL) with screw top lids in ambient lab conditions (25  $^{\circ}$ C, air atmosphere). No degassing was performed on the samples. These were placed into a  $^{60}$ Co irradiator[54] located at the Dalton Cumbrian Facility (DCF) and exposed to a total dose of 50 MGy over a time period of three months. Dose rate was 5 Gy.s<sup>-1</sup> determined using Fricke dosimeter[57].

#### ii) Dissolution experiments

A series of experiments was undertaken on non-irradiated (0 MGy) and irradiated (50 MGy) clinoptilolite. The clinoptilolite samples (1.00 g) were introduced into an aqueous solution (200 ml) and adjusted to near pH neutral (pH 7  $\pm$  0.5) where necessary. Deionised water (Elga purelab classic 18.2 M $\Omega$ -cm) was used with pH adjustment undertaken using 0.1 M NaOH and 0.1 M HCl supplied by Sigma-Aldrich. Measurements of pH from aqueous solutions were undertaken using a Mettler Toledo pH meter and electrode (Inline expert pro probe).

The solutions containing clinoptilolite were placed on a shaker bed (100 rpm) for 21 days. Aliquots of the solution (5 mL) were drawn off at regular intervals (total of 10 aliquots) and analysed for various solutes (Na, Mg, Ca, Fe, Al and Si). The solutes were determined using a Perkin-Elmer Optima 5300 dual view inductively coupled plasma atomic emission spectrometer (ICP-AES). The experiment was undertaken in ambient conditions (25 °C and 1 bar pressure) and there was no control of CO<sub>2</sub> as this more accurately reflects the SIXEP plant operations where CO<sub>2</sub> was introduced upstream of the ion exchange beds to control pH. The initial sample filtration was undertaken using centrifuge tubes placed into a Grant-bio LMC-3000 centrifuge (3000 rpm, 10 min). After 21 days the solutions were left to stand and at a total duration of 79 days further aliquots (15 mL) were drawn off with a series of sample filtration techniques undertaken. The presence of aqueous species was defined as liquid passing VIVASPIN 6 3000 Molecular Weight Cut-Off (MWCO) filters. Colloidal material was defined as material passing a0.45 µm syringe filter. Small particulates was defined as any material remaining in solution after centrifuging in sample tubes)

## d) Characterisation

#### i) Mineral structure

The clinoptilolite (0 MGY and 50 MGy) samples were examined using pXRD using a Bruker D8Advance powder diffractometer. Characterisation was undertaken in triplicate. To assist in identifying changes in the mineral structure a reference silicon powder was added to the sample to allow samples to be compared against a known reference point. Many characteristic powder diffraction peaks were identified for clinoptilolite (17 peaks) and for the reference silicon powder four peaks were used for comparative purposes. The intensity relative to the most intense peak and angle (2 $\theta$ ) relative to the silicon reference samples was examined using a manual peak fitting approach.

To account for drifts in the pXRD readings, offsets were calculated for each clinoptilolite peak to the four reference silicon peaks. This value was then compared against the nonirradiated sample, again using the four reference silicon peaks obtained from the silicon added to that sample. The peak position values observed for the irradiated and nonirradiated clinoptilolite were subtracted from each other for each corresponding peak. The sum of the offsets (Eq. 1) for each unique peak was then divided by the original nonirradiated offset value (Eq. 2) to determine a percentage change relative to original position of that peak.

$$P_{offset}^1 = \sum_{i=1}^4 \left( P_{Clino}^1 - P_{Si}^i \right)$$
- Eq. 1

$$V_{offset}^{1} = \frac{\left(P_{offset(Clino50MGy)}^{1} - P_{offset(Clino0MGy)}^{1}\right)}{P_{offset(Clino0MGy)}^{1}}$$
-Eq. 2

#### Where

P is the peak positon in  $2\theta$  of the designated peak (No. of peak 1, 2, 3 .....)

V is variance of the designated peak (No. of peak 1, 2, 3 .....)

## ii) Elemental compositions

Examination of the samples was also undertaken using a scanning electron microscope (SEM) operated in environmental mode using a 20 keV electron beam with a working distance of 10 mm where samples were maintained under vacuum at 1 mbar. Elemental compositions of the clinoptilolite (0 MGy and 50 MGy) were determined using an Oxford Instruments energy dispersive X-ray (EDX) spectrometer. Data analysis was undertaken using Aztec software (Oxford Instruments) utilising the "20 keV standard characterisation data set".

#### iii) Aqueous experiments

Irradiated (50 MGy) and non-irradiated solutions were filtered and then examined using a ICP-AES to determine the concentration of solutes: Na, Mg, Si, Al, Fe, and Ca. At the termination of the experiments (79 days) the inorganic carbon content of the solutions was determined using an Analytic Jena Multi N/C 2100S analyser calibrated using sodium bicarbonate (NaHCO<sub>3</sub>).

The solutes have been presented as a percentage loss relative to starting mass of clinoptilolite (1.00 g) as this provided a means of comparing samples between various conditions. Another study (Chapter 6) has been undertaken comparing pre-washed and unwashed clinoptilolite performance. In the study presented here all samples are in an unwashed state.

## e) Results and discussion

#### i) y irradiation mineral structural changes

Irradiation of clinoptilolite samples took place over a period of many months. Control (0 MGy) and post irradiation (50 MGy) clinoptilolite samples were examined using pXRD (Fig. 7.1). Peak fitting of the powder diffraction patterns was undertaken manually based upon a standardised set of peak positions determined at the start of the experiments (non-irradiated sample) and these positions were compared against the powder diffraction pattern of the Si reference material, which was added to each sample. Quantification of the shifts in peak positions of the powder diffraction patterns between irradiated and non-irradiated clinoptilolite was performed using Eq.1 and 2.

The peak position (2 $\theta$ ) from the powder diffraction patterns were determined for the two irradiated clinoptilolite samples and both experienced the same total dose (50 MGy) and

dose rate (~5 Gy.s). A mean average has been presented, undertaken in triplicate for each irradiated sample. The non-irradiated "reference peak positions" have been provided (Table 7.1).



Figure 7.1 – X-ray diffraction patterns (background subtracked) from non irradiated clinoptilolite (a), clinoptilolite that has received a 10MGy total dose (b) and two clinoptilolite samples (c and d) that have each received a total dose of 50MGy at a dose rate of ~5 Gy.s<sup>-1</sup>.

Table 7.1 – Peak positions (2 $\theta$ ) from the powder X-ray diffraction pattern of the non-irradiated clinoptilolite sample (Peaks 1 – 17). Peak positions (2 $\theta$ ) from the powder X-ray diffraction pattern of the silicon reference sample (Silicon Peaks 1 – 4) are also included.

Clinoptilolite (0 MGy)																
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	1 6	1 7
9.7410	11.0911	13.0026	13.3768	16.8790	17.3067	19.0444	22.3461	23.8164	25.0462	25.6611	26.6235	30.0321	31.9837	32.7188	35.6997	37.0230
Silicon reference																
1	2	3	4													
28.4280	47.3156	56.1378	69.1572													

Peak positions (20) from the powder diffraction patter of the 50MGy irradiated clinoptilolite have been analysed against the reference samples (Table 7.1) and are presented as a percentage shift from the peak positions observed for the non-irradiated samples (Fig. 7.2). The shift in irradiated clinoptilolite diffraction peaks when compared to non-irradiated diffraction peaks are generally <1% against the non-irradiated reference position. Previous studies [77, 98-101] of clinoptilolite have not reported any shift in peak diffraction positions. It has been previously observed that clinoptilolite exposed to a total dose of 1 MGy of  $\gamma$  radiation effects has a reduced crystal lattice size[100] due to a contraction of the lattice through the loss of structural water and a small loss of crystallinity noted in clinoptilolite samples exposed to similar  $\gamma$  doses in other experiment. The subtle change in structure was attributed to the loss of H<sub>2</sub>O present in the

lattice[100]. It has been reported that radiolysis of water [57, 100, 103-105] results in changes in structural coordination[98] with the lattice framework of Si-O and Al-O through interactions with radiolytic products ( $H^+$  and  $OH^-$ ).

Figure 7.2 indicates small changes within the peak positions with the majority of these peak shifts within 1% of the corresponding 20 peak from the non-irradiated sample. A higher peak number indicates a greater 20. The higher peak numbers appear to have a greater percentage shift against lower numbers. This could indicate structural changes within the lattice structure. A greater percentage shift is encountered in greater 20 angle peaks that have lower relative intensities than those of lower 20 angle peaks (Fig. 7.3). An oscillation of positive and negative shifts is encountered in the samples. This could indicate a margin of instrument error/miss calibration but this is thought unlikely as each sample is calibrated against a Si standard during the characterisation of each specimen. There are greater uncertainties over peak positions in higher 20 peaks due to higher signal to noise ratios for those peaks. This may indicate a real effect on the structural coordination in certain planes but as the majority of peaks show only a small shift (<0.5 %), if at all,it can be concluded that there is little effect on the structure of clinoptilolite by exposure (up to 50 MGy) to y radiation. A loss of structural water reducing d - spacingbetween the lattice could be the cause of this small alteration in certain peak positions as encountered in previous studies [77, 100].



Figure 7.2 – Peak shift of  $\gamma$  irradiated clinoptilolite samples (5.00g) using <sup>60</sup>Co source (total dose 50 MGy with a dose rate of 5 Gy.s) against a non-irradiated clinoptilolite sample (0 MGy). The data presented as an offset position relative to a silicon powder.

Relative intensities of the diffraction peaks have also been examined and were compared to the most prominent peak, peak 8 ( $2\theta = 22.3461^{\circ}$ ) in non-irradiated clinoptilolite (Fig. 7.3). The relative intensity of most peaks in the majority of samples (0 MGy reference and 50 MGy samples) are similar. Some samples (e.g. Sample 2: 50 MGy) exhibited an increase in relative intensities for some peaks and this is likely to be due to orientation of the specific planes present in the structure rather than to a significant change in the structure of the mineral. Any increase in peak width would have indicated a change in crystallinity i.e. greater amorphous component of the sample. No such peak width increases or changes were observed in these studies, indicating a similar crystalline structure after irradiation.



Figure 7.3 – Peak intensities of  $\gamma$  irradiated clinoptilolite using <sup>60</sup>Co source (total dose 50 MGy : dose rate of 5 Gy.s) relative to peak 8 (usually the most prominent peak) with a reference sample included (non-irradiated – 0 MGy) Peak numbers refer to clinoptilolite assigned peaks (Table 7.1).

Elemental scans were undertaken using the EDX probe present on the SEM (environmental mode) on the non-irradiated (0 MGy) and post irradiated samples (50 MGy). These are presented as ternary diagrams (Fig. 7.4a – d). The distribution elements in the post irradiated sample differed from that observed for the non-irradiated sample. When considering Si-Al and-Mg distributions (Fig. 7.4a) there was very little Mg present in the post irradiated sample together with a greater percentage of Al compared to Si. The total % of element composition obtained from EDX must equal 100% when plotted in ternary diagram format. For minor elements (Ca, Mg and Fe) a small change in elemental composition can result in a large change in relative % to those other minor elements.

Clinoptilolite has a typical Si:Al (by atom) ratio range of 4.5:1 to 6:1. The higher Si:Al ratio in the non-irradiated sample may indicate other phases such as quartz (SiO<sub>2</sub>). A reduction in Mg in the post irradiated sample was experienced which indicated a reduction in retained Mg on the surface. The reduction in Mg present on the surface of the irradiated samples may be due to a reduction in H<sub>2</sub>O caused by radiolysis in the mineral structure [100] resulting in a reaction between radiolytic products (H<sup>+</sup>) on the exchange sites with H<sup>+</sup> adsorption liberating cations previously retained on the structure.

A similar outcome was experienced with Fe (Fig. 7.4b) and Ca (Fig. 7.4c) to that of Mg (Fig. 7.4a) where less Fe and Ca was present on the clinoptilolite surface post irradiation. Fe (Fig. 7.4b) differed to Ca and Mg post irradiation as up to 12.5% of Fe remained on the surface of the samples post irradiation. In contrast Ca and Mg showed little or no elemental retention on the surface of the post irradiated samples.

The minor (Mg, Ca and Fe) elements (Fig. 7.4d) provided a similar outcome to other results (Fig. 7.4 a - c) where the irradiated sample produced less variability in elemental composition. Provided less scatter indicating a reduction in retained Mg and to a lesser extent Ca on the structure. Fe was still evident on the surface post irradiation and appeared as the most abundant of the minor elements present on the clinoptilolite surface. Fe may be retained as it forms part of the mineral structure rather than interacting with just the exchange sites. A strongly distorted tetrahedral environment has been suggested in 10 kGy  $\gamma$  irradiation studies of clinoptilolite as a possible location for a Fe(III) complex to associate[101]. A general reduction in minor elemental content was experienced in post irradiated samples on the surface (or near surface ~ 1 or 2  $\mu$ m) when subjected to SEM-EDX investigations.

The results in this study are similar to those experienced in previous experiments where the impact of gamma doses on the ion exchange properties of clinoptilolite were explored [98]. It was found that Mg affinity decreased and Ca affinity remained unchanged with  $\gamma$  doses of 0.7 MGy, with Fe content not being recoded in these previous studies clinoptilolite sample.



Figure 7.4 – Elemental scan data (EDX) collected from SEM using standard characterisation data set contained in Aztec software on non-irradiated (0 MGy - Green) and irradiated (50 MGy – Magenta) samples to examine the effects of  $\gamma$  irradiation on the distribution of elements within the near surface (~ 1 or 2  $\mu$ m). Data presented as a ternary diagram showing the relative content of three elements for each diagram: a)Si, Al and Mg; b) Si, Al and Fe; c) Si, Al and Ca; d) Ca, Mg, Fe.

Significant differences to the structure (tetrahedral coordination of Si – O –Al) in the clinoptilolite have not been encountered in this study (50 MGy -  $\gamma$  irradiation). The changes in the structure were minor from peak position and relative intensity of peaks and are most likely due to a reduction in structural water and minor contractions of the lattice as experienced in earlier studies [77, 100]. No peak broadening was encountered to indicate a change in crystallinity. The results encountered in this study were similar to those of earlier work where a limited extent of framework atoms[100] had been altered not as a result of structural damage through radiation but through the loss of structural water creating a shrinkage effect within the lattice. A significant reduction in Mg content likely to have been initially present on exchange sites was experienced. This was in agreement with previous work [100] where the effects of  $\gamma$  irradiation were more pronounced on cations present on ion exchange sites. A reduction in Mg affinity[98] has been previously observed that may explain the reduction in surface Mg present on the post irradiated samples observed via EDX in this study.

#### ii) Aqueous experiments

Significant changes to the tetrahedrally coordinated Si-O-Al structure of clinoptilolite caused by  $\gamma$  irradiation have not been observed in a dry state in this study. Aqueous experiments have been undertaken where samples of the irradiated clinoptilolite have been contacted with aqueous solutions (pH 7.1) to investigate potential dissolution and/or leaching of the mineral phase. The performance of washed and unwashed clinoptilolite has been studied in other work (See chapter 6 – Clinoptilolite dissolution). Here the clinoptilolite has been studied in an unwashed "as received" state. The study has been undertaken using non-irradiated (0 MGy) and irradiated (50 MGy total dose : dose rate 5 Gy.s) samples of clinoptilolite.

Solute content has been determined using ICP-AES and included the elements Si (Fig. 7.5a), Al (Fig. 7.5b), Na (Fig. 7.5c), Mg (Fig. 7.5d), Ca (Fig. 7.5e), Fe (Fig. 7.5f). The Si:Al (by atom) ratio (Fig. 7.5g) has been calculated using the molar mass of Si and Al. All the solute data has been presented as a % loss of the starting mass of clinoptilolite (1.00g) with corrections made for volume reductions as aliquots were drawn off. The mass loss from both non-irradiated (black) and irradiated clinoptilolite (red) into solution have been compared for each element investigated. Overall the irradiated clinoptilolite generated less mass loss into solution compared to non-irradiated sample.

A reduction in the percentage of solutes in the  $\gamma$  irradiated samples (50 MGy) may indicate that there is an effect from the  $\gamma$  irradiation. However these differences were quite small. In particular, Si (Fig. 7.5a) and Al (Fig. 7.5b) expressed as a % solute release compared to starting mass of clinoptilolite were within the error range of one standard deviation. That could indicate that there was little effect on the structural coordination of Al or Si within the clinoptilolite framework. The Si:Al ratio (by atom) of non-irradiated reference sample and the 50 MGy samples (Fig. 7.5g) also indicated a similar lack of structural change to the coordination between Si – O – Al in the bulk mineral structure.

The tetrahedral structure remained unaffected post irradiation. However when considering the minor elements present on the ion exchange sites a reduction was encountered in post irradiation samples for Mg (Fig. 7.5d) and Fe (Fig. 7.5f) expressed as a % solute release compared to starting mass. This was particularly evident in sample aliquots of durations up to 100 hrs. The reduction in cationic species located on the exchange sites released into solution could be an indication of a reduction in mobile cations present on the exchange sites.



Figure 7.5 – Elemental loss by dissolution trials (100 rpm shaker bed from non-irradiated (0 MGy – Black) and irradiated (50 MGy – Red) clinoptilolite (starting mass of 1.00g) over a contact period of 21 days at pH 7.1 in ambient conditions ( $25^{\circ}$ C and 1 bar) a) Si; b) Al; c) Na; d) Mg; e) Ca; f) Fe; g) Si:Al ratio (by atom)

The reduction in Mg<sup>2+</sup> affinity from post irradiated (0.7MGy -  $\gamma$ ) clinoptilolite has been reported [98], where the order of preferential incorporation into the structure was Sr<sup>2+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> [98]. A decreased solute % of Mg found in this study may indicate an increase in the retained Mg within the bulk clinoptilolite. However in post irradiation samples it was found that Mg (Fig. 7.4a and 7.4d) was less prevalent on near surface elemental compositions by SEM-EDX.

The reduction in Fe (Fig. 7.5f) was similar to that encountered with Mg (Fig. 7.5d) expressed as a % solute compared to starting mass of clinoptilolite. There exists the

possibility that the tetrahedral coordination of Si – O – Al could have been altered and may have incorporated some Fe(III) into the main lattice structure [101]. However we have not been able to confirm this as occurring in this study. Instead following SEM-EDX investigation of the near surface (~ 1 or 2  $\mu$ m) we have observed a reduction in Fe content in clinoptilolite samples exposed to 50 MGy relative to non-irradiated clinoptilolite.

## f) Nature of solutes

An additional set of sample filtration has been performed on aqueous solutions containing non-irradiated and irradiated clinoptilolite samples after 79 days. The solutions have undergone three filtration steps, a centrifuge only, 0.45 µm filtration and 3000 MWCO filters. Each filtration step would indicate the presence of different configurations (solids, colloids or aqueous) of elements present as solutes. The solutes (Na, Mg, Al, Si, Ca and Fe) were determined using the same analytical technique (ICP-AES) as the aqueous experiments and are presented in the same format as a % solute relative to starting mass of clinoptilolite.

The irradiated and non-irradiated samples have been analysed (Fig. 7.6) with the solutes presented (Fig. 7.5). Both sets of solute data generated comparable quantities of solutes expressed as a total % of solute relative to the starting mass of clinoptilolite (1.00 g). The total % of solute relative to starting mass for the irradiated samples was marginally less than the non-irradiated reference samples. The composition of the solutes: particles, colloidal or aqueous, only differed when considering elemental Si and Na between non-irradiated samples.



Figure 7.6 - Solutes presented as a % of starting mass of clinoptilolite (1.00 g) from pH 7.1 in ambient conditions (25 °C and 1 bar). With two sets of samples: non-irradiated and irradiated (50 MGy total dose). Solutes were obtained via ICP-AES analysis. The samples were filtered to provide compositional data for fines/particles remaining in solution after centrifuge, colloids were determined as passing a 0.45 μm filter. Aqueous species were determined as passing a 3000MWCO filter.

An increased release of colloidal Si after the clinoptilolite underwent irradiation has not been encountered previously [77, 98-101]. Instead a number of phenomenon have been reported when clinoptilolite is exposed to a considerable radiation dose including amorphisation of the bulk crystalline structure and a reduction in lattice spacing.

When considering the SIXEP plant operations, colloidal particles can be problematic due to their ability to adsorb radionuclides [106, 107] and the difficulty in removing these from plant process liquors[58]. The aqueous species released expressed as a % solute were considerably lower in the irradiated samples possibly indicating a reduction in mobile cations present on exchange sites.

Congruent dissolution of clinoptilolite has been determined in similar experimental conditions where the ratio of Si:Al has been used to ascertain the nature of the fines/particles (Chapter 6). The elemental composition ratio of Si and Al in both sample groups (irradiated and non-irradiated) tended to indicate congruent dissolution was occurring in similar volumes ,i.e. particulates (Fig. 7.6). Thus it appeared that congruent dissolution was independent of any effects from  $\gamma$ -radiation and was based instead upon solution conditions (pH 7, 25 °C) that were comparable between the irradiated and non-irradiated samples.

## g) Conclusions

The effects of *y*-radiation on clinoptilolite has been studied previously [77, 98-101] however those studies have considered ion exchange performance of clinoptilolite as opposed to dissolution and/or degradation of clinoptilolite and have not considered a very high dose, 50MGy *y*-radiation (Dose rate 5 Gy.s). This study has sought to characterise structural damage using pXRD data. Peak identification and manual peak

fitting was undertaken to provide offsets against a non-irradiated reference sample. In ambient temperature and pressure conditions (25°C and 1 bar) and in normal atmosphere (i.e. not inert) a small variance of  $\sim$  0.5 to 1% in the peak position has been encountered in the irradiated samples against a non-irradiated reference sample. The crystallinity of the irradiated samples was not altered as peak broadening was not experienced in the irradiated samples when compared to the non-irradiated reference sample. Small variances encountered in the peak positions and a lack of peak broadening along with similarly small changes in relative intensities, indicated that the clinoptilolite mineral was largely unaffected by radiation in the conditions in this study and minor alterations in peak position are likely to be due to loss of structural water within the mineral. Other studies may report changes in the structure of clinoptilolite but these are most likely the result of radiolysis of water [57, 100, 103-105] resulting in cationic species being produced that react with the ion exchange sites or the loss of structural water present within the lattice structure. The structural change would result from promoting tetrahedrally coordinated AI in place of Si [76-78] through  $H^{+}$  adsorption and the loss of lattice water from the structure.

Minor cations present on the near surface (~ 1 or 2  $\mu$ m) following SEM-EDX investigations differed between irradiated (50 MGy) and non-irradiated samples. Mg showed the greatest change between the 50MGy and non-irradiated reference sample, possibly indicating the effect of "locking in" [100] as found previously.

Aqueous experiments were performed at pH 7.1 and at 25°C conditions and the reduction in surface cations were evident for Mg and Fe in that set of experiments. The reduction in % solute released when compared to starting mass of clinoptilolite for Mg and Fe was

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lower in the irradiated samples indicating that less Fe and Mg was being released from the exchange sites.

There was little effect on the release of Si and Al in aqueous experiments irrespective of radiation dose. The reference sample (0 MGy) generated similar quantities (expressed as % solute) of Si and Al, most likely indicating that little structural damage has been encountered in the Si-O-Al coordination in the clinoptilolite structure but that any changes were as a result of loss of structural water.

Congruent dissolution was as found in previous studies (Chapter 6). Behaviour of the irradiated samples, was similar to the non-irradiated reference sample. An increase in colloidal Si was encountered in the irradiated samples. The increase in colloidal content could cause recovery problems due to difficulties in plant process filtration of colloidal material with incorporation/adsorption of radionuclides a possibility. A reduction in aqueous species, determined as elements remaining in solution after filtration through a 3000 MWCO filters, was encountered. The reduction in Si<sub>(aq)</sub> and Na<sub>(aq)</sub> was partially offset by the increase in colloidal material. However the total of % solute release per element was below that of the non-irradiated reference sample. The reduction in aqueous species in the case of Si was most likely due to reduction in ion exchange sites because of radiation effects resulting in less Si being released into solution. Na was most likely retained and "locked in" to the structure.

Small quantities of aqueous Si and/or Al have been found to generate mineral phases (Chapter 5) that could lead to pipeline restrictions resulting in solids build-up and flow restrictions. A reduction in release of aqueous species has benefits for plant operations where a reduction in % solute released would reduce the pipeline fouling that has been

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previously encountered within the SIXEP discharge pipeline. The performance of clinoptilolite as an ion exchange material has not been studied here. A reduction in surface cations present on exchange sites and a reduced % solute release indicates a reduction in ion exchange capacity that will require further investigation.

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Chapter 8 – Mineral adsorption using polyelectrolyte paper
# Mineral adsorption onto stainless steel surfaces using a polyelectrolyte

# solution

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**Author Contributions** 

R S Jones – First Author, principal researcher, experimental data collection and data analysis(SEM-EDX, FTIR, FT-Raman).

S.M. Shubeita – RBS Data collection and modelling of RBS data to determine elemental compositions, manuscript review

C.A. Sharrad – Manuscript review, Principal supervisor; D. Trivedi –co-supervisor; S. Kellet –context discussion.

## Relevance

Investigates polyelectrolyte as a solid attachment mechanism. If it cannot adhere solids then biofilms are the cause of solid entrainment within the discharge pipeline. Polyelectrolyte may cause solids to adhere to the surface of the pipeline instead of biofilms. It addresses this by considering clinoptilolite fines (congruent dissolution) adsorption to a stainless steel surface using a range of polyelectrolyte dosing (10% down to  $1 \times 10^{-6} \% \text{ v/v}$ ). Congruent dissolution has been identified as a potential source of solids in previous work.

## a) Abstract

Water effluent treatment plants routinely use polyelectrolyte solutions during process chemistry operations. The Site Ion Exchange Plant (SIXEP) (Sellafield site, Cumbria, UK) utilises polyelectrolytes to precondition the sand bed filter in order to improve filtration performance. The role of mobilised polyelectrolyte in the adsorption of solids onto the stainless steel surface in the discharge line has been studied in this work.

The adsorption of clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) in the form of fines, onto stainless steel coupons (304L) from aqueous solutions containing a range of polyelectrolyte concentrations ( $1x10^{-6}$ % to 10% v/v) has been investigated. Stainless steel coupons have been prepared and characterised using a range of techniques that include Rutherford Backscattering Spectrometry (RBS) to determine the species adsorbed to the steel surface.

Si and Al were detected on the surface of the steel coupons using RBS in a range of starting concentrations of polyelectrolyte solutions. This indicated that RBS was able to detect clinoptilolite on a stainless steel surface and that clinoptilolite was being retained on the steel surface which was corroborated by SEM investigations. Direct detection of polyelectrolyte was not possible using RBS, FTIR nor FT-Raman.

Coupons were subjected to a simple washing in deionised water to determine whether solid attachment was due to settling or adsorption onto the steel surface. It appeared that the starting concentration of polyelectrolyte had a limited effect on post-washed deposits retained on the coupon. However the sample dispersions were not uniform as the solid was allowed to settle onto the coupon from a static solution. The RBS measurements may have reflected this by only partially identifying the retained Si and Al on the steel surface.

The presence of polyelectrolyte had an effect on clinoptilolite post-washing in certain cases which would indicate that polyelectrolyte should be considered to be a credible means of adhering solids to stainless steel surfaces.

## b) Introduction

Solid formations inside pipelines are a significant issue for many industries. Biofilms are thought to contribute significantly to this build up by acting as the cementing agents to which solids may adhere [28-32] with temperature and pH of the bulk liquid affecting the initial attachment of solids onto surfaces. The cells typically have an affinity to the pipeline surface dictated by the net surface charge which in turn is affected by the pH of the bulk liquid. Temperature and pH cannot be easily controlled in discharge lines and if the conditions prove favourable to biofilm growth significant problems can result from these formations. However each instance of solids build-up is case-specific and alternative mechanisms may exist as the means to adsorb to the internal surface. Effluent treatment plants routinely use polyelectrolyte solutions during process chemistry operations. Typically polyelectrolytes are used to either facilitate flocculation or coagulation[108]. An alternative use of polyelectrolyte is to condition filters as a pretreatment step to remove larger solids. One such plant that utilises the filtration pretreatment technique is located on the Sellafield site, Cumbria, UK, where high pH (>10) incoming effluent contains a significant proportion of Mg rich solids. Filtration is performed via sand beds. Development trials were undertaken in proof of concept studies, showing that low levels (<0.5 mg.L<sup>-1</sup>) of polyelectrolyte dosing into the incoming feed significantly improved filtration performance. The study was undertaken to support the operation of the Sellafield Site Ion Exchange Plant (SIXEP) [63] where there was some historical evidence of solid adhesion onto discharge pipelines. During routine inspection of the SIXEP discharge line (mid 2000s) solid deposits were encountered that were thought to be adsorbed to the inner surface of the pipeline by an organic compound. Polyelectrolytes at <1.0 mg.L<sup>-1</sup> concentration are difficult to determine accurately in

discharge effluent[109] due to the relatively high limits of detection for techniques that are typically used to quantify polyelectrolyte content (e.g. fluorescence spectroscopy). Detection of polyelectrolyte will prove problematic for very dilute polyelectrolyte conditions in both static lab-based experiments and in-line monitoring during effluent treatment operations. Establishing that polyelectrolyte can cause solids to adhere to pipeline surfaces would provide justification for further work to develop methods to quantify polyelectrolyte levels at process concentrations. In this case, the effluent discharge pipeline diameters range between 150 to 300 mm and are constructed from stainless steel. Direct measurements of the surface roughness inside the pipeline have not been possible due to access restrictions to mitigate radiation doses to workers.

The settling of mobilised polyelectrolyte may contribute to the adsorption of encountered solids to the stainless steel surface in the discharge line. The solids were thought to form either by chemical precipitation from the effluent or by congruent or incongruent dissolution from the mineral clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O). This work seeks to understand the stainless steel-polyelectrolyte-mineral phase interactions. Significant work [26, 27, 110-116] has been undertaken on polyelectrolyte multilayers (PEM) and layer by layer (LbL) in nanoscale assemblies with interactions between stainless steel surfaces or meshes. Little work exists on mineral particle – polyelectrolyte interactions. Some studies [117-119] have considered mineral phase precipitation in the presence of a polyelectrolyte and others [120-122] have considered adsorption onto mineral surfaces. None of these studies has considered polyelectrolyte as a means to facilitate the adhesion of solids onto metal surfaces.

Polyelectrolyte adsorption causing solids to adhere to the pipeline surface has been proposed as an alternative mechanism to biofilms and will be considered in this work. Understanding the adhesion mechanisms during solids build-up in effluent pipelines is important as it dictates the method/s to mitigate this build-up. For instance, a biocide would be effective in treating biofilm growth but not in removing solid build ups that were formed by polyelectrolyte adsorption of solids to stainless steel surfaces. The pipeline has been in service from the mid 1980s therefore it is assumed there will be significant surface roughness.

### c) Experimental methods

#### i) Sample preparation

Stainless steel coupons (304 L) 1 cm x 1 cm were prepared prior to use by an acid wash and were left in 0.1 M HCl (Sigma Aldrich) solution for 1 hour. Grade 304 L stainless steel was chosen to replicate the pipeline material. Coupons were then removed, rinsed in deionised water (Elga purelab classic 18.2 M $\Omega$ -cm) and placed in a water bath sonicator for 1 hour. The coupons were washed again under deionised water, dried in a vacuum oven and then stored in a sealed container prior to use. Surface preparation was not undertaken on the coupons in order to replicate the pipe surface where any smoothing of the surface would be unrepresentative of the in-service conditions of the pipeline.

Clinoptilolite (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) was provided by Sellafield Ltd and used in an "as received" condition. The bulk clinoptilolite was characterised utilising powder X-ray diffraction (pXRD, Bruker D8Advance) to confirm the phases present. The mineral was predominately Na-clinoptilolite with small quantities of quartz and mordenite impurities. The clinoptilolite was washed in deionised water (18.2 MΩ-cm) through a 100  $\mu$ m mesh sieve. The washed fines were collected and dried in a vacuum oven (40°C) overnight and were stored in an airtight container.

Using the polyelectrolyte (polygold CL520) provided by Goldcrest Chemicals, solutions were created by diluting polyelectrolyte in deionised water (18.2 M $\Omega$ -cm) by volume. Solutions with the following polyelectrolyte concentrations were prepared; 10, 1, 0.1, 0.01, 0.001, 1x 10<sup>-4</sup> and 1 x 10<sup>-6</sup> % v/v. A blank sample was also prepared using deionised water only.

Each solution was split into two vials (25 mL each), with two coupons added to each vial. Into each vial 1 mg or 10 mg of prepared clinoptilolite fines (small sized <100  $\mu$ m particles) was added. The solutions were stored at room temperature conditions (25 °C) for two weeks to allow settling/adsorption to take place onto the stainless steel surface of the coupons. The coupons were left in a horizontal position throughout the experiment.

After two weeks the solution was drawn off via a syringe inserted into the vials above the coupons. The rationale was to retain the integrity of the deposited surface of clinoptilolite and polyelectrolyte. The coupons were then removed and were dried in a vacuum oven for two days at 40°C with care taken not to disturb the wet surface film on the coupon surface, preceding surface characterisation.

After characterisation, some coupons were selected to undergo washing. These samples were placed in vials and 20 mL of deionised water (18.2 M $\Omega$ -cm) was added. Coupons were removed from the water after 1 hour and dried using the vacuum oven (40 °C) with additional characterisation performed on the washed coupons.

#### ii) Characterisation

#### eSEM

Environmental scanning electron microscopy (eSEM) was performed using a FEI Quanta FEG 250 microscope using a 1 mbar vacuum at 20 keV electron beam with a working distance of 10 mm. Energy Dispersive X-ray (EDX) Spectra were obtained using an Oxford Instruments system, with analysis via Aztec software utilising the "20keV standard characterisation data set".

#### FTIR

All stainless steel coupon samples were investigated using Fourier Transform Infrared (FTIR) spectroscopy and was performed using a Bruker Vertex 70 with DLaTGS detector. Background reflectance was obtained from a representative blank stainless steel coupon (304L) prior to any spectra measurements. Spectra were obtained for undiluted polyelectrolyte (CL520) and clinoptilolite fines to aid identification and interpretation of the spectra of the coupons. The stainless steel coupons were investigated by a diffuse reflectance stage (Pike Technologies Vee Max II) and single reflection diamond stage (Bruker Platinum ATR) was used for polyelectrolyte and clinoptilolite. Data analysis was undertaken using OPUS spectroscopy software (Bruker).

#### FT Raman

Raman spectroscopy was performed using a FT-Raman (RAM II module part of Bruker Vertex 70 FTIR) instrument. Spectra were obtained for clinoptilolite fines and wet undiluted polyelectrolyte samples to aid identification and interpretation of the spectra, prior to the coupons. The laser power (1064 nm continuous wave laser) of between 350 mW and 700 mW was selected to maximise the intensity of the spectral profile and

to minimise sample degradation (through burning). Results were collected using OPUS spectroscopy software (Bruker).

## Rutherford Backscattering Spectrometry

Rutherford backscattering (RBS)[53] was attempted in all samples to characterise and quantify the deposits present on the surface of the stainless steel coupons. This technique has been used previously in the investigation of mineral/rock interfaces with strontium adsorption[123] and also in studies involving polyelectrolytes [116](LbL assemblies and PEM's). The experiments were carried out with a 5 MeV tandem Pelletron Ion Accelerator [54, 55] (National Electrostatics Corp. USA) located at the Dalton Cumbrian Facility. A 2 MeV He<sup>+2</sup> beam (normal incidence) with beam spot diameter of approximately 2 mm was used in the experiments. A total charge of 7  $\mu$ C was accumulated in each irradiation. Backscattered particles were collected by a detector positioned at 165° from the incident beam.

Data analysis was performed by the use of the SimNRA 6.06 software[56]. Surface roughness was introduced in the fitting model to account for possible non uniform distribution of the clinoptilolite/polyelectrolyte surface layer, which results in the partial exposure of the metallic substrate and also introduces a source of uncertainty to the quantification of the elements present on the samples. Uncertainties in the quantification of the elements were more pronounced in the lighter elements (C, N, O) in comparison to the heavier elements (Fe, Cr, Ni from coupons), with Al and Si in between the uncertainty range (5-7%).

# d) Results and discussion

## i) SEM

Polyelectrolyte detection has been undertaken on stainless steel coupons (304L), dosed with clinoptilolite at 1 and 10 mg and at various polyelectrolyte starting concentrations from  $1 \times 10^{-6}$  to 10% by volume with deionised water making up the remainder of the solution.

The presence of deposits on the surface had been determined on all samples using eSEM. Investigation of the elemental composition of these deposits indicated that these were clinoptilolite particles with Si:Al (by atom) ratios around 5:1. High polyelectrolyte dosing (10% v/v) with high clinoptilolite content (10 mg) generated a relatively large amount of solids on the surface (Fig. 8.1a). In contrast, low polyelectrolyte dosing (1 x  $10^{-6}$  % v/v) and low clinoptilolite content (1 mg) produced far less solid formations on the stainless steel surface (Fig. 8.1b). Additional eSEM micrographs are presented in Appendix B.



Figure 8.1 - Stainless steel coupons with surface formations of clinoptilolite. Clinoptilolite has been retained at a) high polyelectrolyte concentration (10% v/v) (mag. 1783x) with 10 mg dosing of clinoptilolite and b) low polyelectrolyte ( $1 \times 10^{-6} \% v/v$ ) concentration (mag. 2295x) with 1 mg dosing of clinoptilolite A range of polyelectrolyte and clinoptilolite concentrations has been investigated in this study. High concentration samples (10% v/v polyelectrolyte and 10 mg Clinoptilolite) had a significant surface coating that obscured the underlying stainless steel substrate (Fig. 8.1a). Low concentration (1 x  $10^{-6}$  % v/v and 1mg Clinoptilolite) samples contained some surface particles but the stainless steel substrate is clearly visible (Fig. 8.1b). The rough surface profile in the unprepared stainless steel coupons is clearly visible.

Elemental compositions of the particles on the surface indicate that these were predominately clinoptilolite as identified by EDX analysis comparing Si:Al (by atom) ratios encountered on the surface to that in the idealised formula (idealised Si:Al = 5:1 by atom). There is some evidence of localised incongruent dissolution of the particles deposited on the surface with Si:Al ratios >6:1 (by atom) encountered (Fig. 8.2).



Figure 8.2 – Chart displaying the distribution of Si:Al composition of deposits found on stainless steel exposed to various solution of clinoptilolite fines and polyelectrolyte sample compositions % of polyelectrolyte and mg of clinoptilolite.

The majority of the elemental compositions of the surface deposits contained similar Si:Al (by atom) ratios to those of the bulk idealised clinoptilolite (Fig. 8.2). However there was a significant proportion of data points in the samples in the broad range of experimental conditions (Polyelectrolyte % and clinoptilolite mass) that contained Si:Al(by atom) above that of the idealised elemental composition. This may be due to incongruent dissolution of the mineral phase or the shallow depth the EDX can analyse (few  $\mu$ m at 20keV). However the latter explanation is thought unlikely as clinoptilolite particles can exist in the few  $\mu$ m size range after undergoing congruent dissolution as discussed (Chapter 6). The majority of the data points tended to exhibit a similar elemental composition to that of clinoptilolite. The low concentration of polyelectrolyte 1 x10<sup>-6</sup>% by v/v and 10mg of clinoptilolite samples appeared to have a lower Si:Al ratio than that of other samples but this result is not thought to be significant due to the low number of data points collected at low concentrations.

## ii) FTIR

All samples were analysed using the FTIR (Fig. 8.3). The undiluted polyelectrolyte (100%) provided some characteristic IR bands (Fig. 8.3a). The majority of samples contained a characteristic IR band that can be assigned to clinoptilolite (Fig. 8.3b) at around 1050 cm<sup>-1</sup> (very strong) assigned to Si-O-Si bending frequency. The polyelectrolyte reference sample provided a very broad IR band at 3350 cm<sup>-1</sup> that could be assigned to OH stretch from the polyelectrolyte solution. When examining the polyelectrolyte there were further IR bands that provided a reference for further identification. These IR bands are at 1100 (CH<sub>3</sub> rocking vibration or C-O-C), 1480 (-O-CH<sub>3</sub> or OH) and 1640 cm<sup>-1</sup> (OH).

The clinoptilolite reference sample had additional IR bands at 600 (Si-O-Si) and 1625 cm<sup>-1</sup> (OH – possible from lattice water or H-O-H bending). There were overlaps between the IR bands of clinoptilolite at 1625 cm<sup>-1</sup> and polyelectrolyte at 1640 cm<sup>-1</sup>.

There appeared to be little evidence for polyelectrolyte retained on the stainless steel coupons. All coupons (Fig. 8.3c – 8.3i) exhibited a peak that matched that of clinoptilolite at around the 1050 cm<sup>-1</sup> (Fig. 8.3b). There were further peaks that matched the clinoptilolite reference at 600 and 1625 cm<sup>-1</sup>.

#### iii) FT Raman

The samples have been analysed using FT Raman with a reference sample containing a stainless steel coupon prepared with a 100% polyelectrolyte solution together with a blank stainless steel coupon, to allow the surface effects from the stainless steel to be discounted from the samples. The FT-Raman results indicated a broadening of a peak centred around 2950cm<sup>-1</sup> wavenumber on a 100% polyelectrolyte coupon. When attempting to use this peak to identify polyelectrolyte retained on other stainless steel coupons the peak was not present. Therefore FT-Raman results were inconclusive with respect to characterisation of polyelectrolyte.

#### i) Rutherford Backscattering Spectrometry

From the samples characterised by RBS a subset was subjected to washing after initial characterisation. The designation of washed will be used where samples have undergone further washing to investigate the effects of the polyelectrolyte as a means of adhering clinoptilolite to the steel structure. Without this designation the samples should be considered in "as prepared" condition i.e. unwashed coupons.





Figure 8.4 depicts some typical RBS spectra obtained from the samples analysed. Some of the elements present in the samples are indicated in their expected energy positions considering their presence as in the surface. The presence of a fraction of Fe in the surface is an indication of a possible nonhomogeneous distribution of the clinoptilolite/polyelectrolyte surface layer which partially exposes the metallic coupons. A range of starting concentrations of polyelectrolyte (10% to  $1 \times 10^{-6}$ % v/v) and clinoptilolite (1 mg and 10 mg) explored in this work produced similar plots.

Fitting procedures using the SimNRA 6.06 software[56] were undertaken in order to characterise and quantify the elements present in the samples. Figure 8.5 presents a simulation output from one of the samples analysed. Selected elements and the total spectra are presented.

There was an indication that the samples contained clinoptilolite prior to the RBS experiments. However attempts to quantify the level of the mineral phase retained on the surface were not possible with the other techniques. An atomic percentage figure has been produced that relates to the near surface (~3  $\mu$ m). The surface roughness of the samples makes accurate quantification of these deposits difficult.



Figure 8.4 – RBS plots of counts against Energy for stainless steel coupons exposed to solutions of clinoptilolite fines and polyelectrolyte



Figure 8.5 – Typical simulation output from SimNRA. This produced characterisation data to determine elemental compositions of the samples. Note, simplified plot not showing the 17 elements present in some samples.

The analysis of the data has been presented as atomic percentages (At%) for O, Al, Si and Fe (Fig. 8.6). The broad variation observed in the amount of Fe is direct evidence of the non-uniform distribution of the clinoptilolite/polyelectrolyte surface layer, since the energy edge corresponding to Fe is not shifted to lower energies. The suppression of Fe signal did not appear to be related to a significant change in Si (At%) present on the surface of the sample.

The starting concentration of the polyelectrolyte solutions did not have a significant impact upon the suppression of Fe that is present in the underlying coupon material with a higher by atomic % Fe encountered in low starting concentrations of clinoptilolite (Fig.8.6). This indicated that the surface build-up and suppression of Fe present in the coupon was dependent upon the starting clinoptilolite concentration as opposed to polyelectrolyte dosing.

There was a large range of oxygen present in the samples (Fig. 8.6). The amount of O present appeared to be independent of the starting polyelectrolyte concentration relating instead to the clinoptilolite dosing at the start of the experiments. When the starting concentration of clinoptilolite was 1 mg the O (At%) was significantly lower than the 10 mg samples. The O found in the experiments was likely to be from the clinoptilolite structure or adsorbed H<sub>2</sub>O present on the mineral as polyelectrolyte concentration had little effect on the atomic %. The RBS confirms the presence of Si on the surface of the coupons and was in agreement with the elemental findings from SEM-EDX (Fig. 8.2). The At% of Si present on the surface of the coupons ranged from between 13% to 22% (At%) and it appeared independent of the starting concentration of clinoptilolite.

The Al (At%) followed a similar trend to the Si, with Al of between 3% to 6% (At%) encountered in the surface deposits. The corresponding range of Si:Al ratios (by atom) was 3.2:1 to 4.9:1. This differed from the EDX data that had a Si:Al ratio (by atom) of >4.5:1 in approximately 80 to 90% of the sampled data points. The difference between the experimental Si:Al ratios for EDX and RBS can be attributed to the penetration depths of the different techniques. EDX has penetration depth of ~1  $\mu$ m whilst RBS had a penetration depth of ~ 3  $\mu$ m. A lower atomic percentage figure for Al was observed using EDX and as a result there was an increase in Si:Al ratios observed using this technique. Whereas the RBS produced a lower Al content compared to EDX giving a reduced Si:Al ratio. The lower Al content observed in the near surface by EDX readings indicates that surface dealumination may have occurred.



Figure 8.6 – Atomic % of samples for a range of polyelectrolyte (Poly.) concentrations from 1x10-6 to 10% by volume and clinoptilolite (Clino.) with either 1 or 10 mg present in the starting solution. Observations obtained from RBS cross section data and reported values based upon simulated outputs from simNRA model providing elemental compositions.

The reduction in surface AI has been previously encountered in other clinoptilolite studies where AIO<sup>-</sup> has been lost from the surface of the mineral structure [12] caused by interactions between the framework AI and acid prewash treatment or cations causing breakdown of the lattice structure. However neither appears to be the cause of the loss of surface AI. This is likely due to an increased Si near the surface due to interaction between the polyelectrolyte solution and the exchange sites liberating Si from the lattice structure. Significant characterisation of the surface deposits has been undertaken using the RBS technique. There was a reasonable fit between RBS and other techniques when considering Si and Al ratios and heavier elements. Lighter elements have proved problematic to characterise with the RBS technique due to higher uncertainties associated with lighter elements. There appeared to be a significant quantity of O present in the majority of samples, possibly originating from the clinoptilolite or potentially from the polyelectrolyte but due to the abundance of O present in the clinoptilolite structure (Na<sub>2.2</sub>Mg<sub>0.40</sub>K<sub>0.89</sub>Ca<sub>0.99</sub>Sr<sub>0.07</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>.24H<sub>2</sub>O) it is most likely the source of the recorded O found in the RBS experiments.

## e) Surface washing

The samples were studied using the RBS in pre- and post-washed states. They have been presented as separate plots showing pre- and post-washing effects (Fig. 8.7). The significance of undertaking the washing experiments was to quantitatively consider the strength of adherence of solids onto the stainless steel coupon. Simple settling of solids on the surface would have resulted in a very low amount of retained solids post-washing. This would have been determined by a significant increase in Fe (At%) present in samples post-washing i.e. samples would have had less material on the surface that interacted with the impinging a -particles.

Washing experiments produced a reduction in retained solids on the surface. High polyelectrolyte starting solution (1 % v/v) (Fig. 8.7a) retained a significant amount of solids post-washing. The RBS data provided a small step at the Fe energy band (1530 keV) in the unwashed sample where the majority of the Fe was suppressed by the solids present on the coupon. After the sample washing there was a more pronounced step

indicating that Fe was more visible on the surface, in turn indicating that less overlaying solid remained on the surface. A step at 1149 keV remained in the washed RBS data indicating that Si remained on the sample, in turn indicating that simple washing was ineffective in removing the solid formation.

The retained solids present after washing were not encountered on the sample (Fig. 8.7b) which had a starting concentration of 0.001 % polyelectrolyte and 10 mg of clinoptilolite. There was a significant increase in the amount of Fe exposed from the metallic coupon indicating a significant change in the surface layer. Further evidence of the loss of solid retained on the surface was the lack of Si, Al and O in the washed coupon.

A similar trend to high polyelectrolyte starting solution (Fig. 8.7a) was encountered in the lowest starting concentration polyelectrolyte solutions of 0.0001 % (Fig. 8.7c) and 1x10<sup>-6</sup> % (Fig. 8.7d). In both samples there were less retained solids on the surface after washing. However in the 0.0001 % polyelectrolyte coupon there was evidence of the presence of Si, Al, and O post-washing, indicating that washing was ineffective on that sample. In the lowest polyelectrolyte solution (Fig. 8.7d) there was a more pronounced step at the Fe energy level indicating that washing was more successful than the previous sample (0.0001%). However there appeared to be an indication that Si was still encountered on the sample (Fig. 8.7d, small step around 1100 keV). There was little evidence for O on the washed sample.

In the washing experiments there were a number of coupons that retained significant quantities of surface deposits. The high concentration polyelectrolyte (1 % v/v) solution prior to washing contained 21 % (At%) of Si and after washing 17 % (At%). Any increase in Fe after washing would indicate that less of the overlying solid remained. A significant

washing effect was observed on the 0.001 % v/v and 10 % v/v polyelectrolyte samples. It was also observed in the lower polyelectrolyte dosing samples (0.0001 % v/v and 1 x  $10^{-6}$  % v/v), although not as significant.

The variability in washing performance could indicate that polyelectrolyte as a means of adhering solids to the surface is not dependent upon starting concentrations of polyelectrolyte. Alternatively, due to the dispersion of clinoptilolite in solution being nonuniform, there may be areas of higher and lower concentrations of clinoptilolite when deposited upon the coupon.



Figure 8.7 – Pre- (Black) and post-washed (Red) experiments utilising the RBS as a means of sample characterisation. Red points are washed samples and black points are unwashed samples. a) 1 % v/v polyelectrolyte 10 mg clinoptilolite, b) 0.001 % and 10 mg, c) 0.0001 % and 10 mg, d) 1 x10<sup>-6</sup> % and 10 mg.

The effect of washing the coupons in some samples suggested that simple settling of clinoptilolite was the cause of the surface build-up (significant exposure of the metallic substrate after washing) whereas in other samples solids remained adhered to the coupon surface suppressing the Fe present in the sub surface stainless steel coupon. The seemingly random nature of the conditions leading to clinoptilolite adherence on stainless steel surfaces requires further investigation.

Presence of Si-rich (and suppression of Fe) solids after washing indicated that clinoptilolite was adsorbed onto the surface of the stainless steel coupon as opposed to the simple settling of solids in some samples. Direct detection of the polyelectrolyte through identification of C and N was not possible. However the presence of retained solids post-washing would indicate that the presence of polyelectrolyte in solution can lead any formed solids to adhere to the surface of a pipeline.

## f) Conclusions

There was evidence of adsorption of clinoptilolite onto the stainless steel coupons in a range of polyelectrolyte starting concentration solutions from  $1 \times 10^{-6}$  to 10% by volume. The evidence for this was the effect of washing. If simple settling of solids was the main mechanism of formation then the clinoptilolite would have been removed from the surface after washing. Where significant solids remained after washing they were present in a range of polyelectrolyte solutions. Significantly the lowest concentration of polyelectrolyte ( $1 \times 10^{-6} \%$  v/v) suppressed a significant amount of the signals used to identify the presence of Fe in the sub surface coupon indicating that solids were retained on the coupon.

Direct measurement of the polyelectrolyte on the surface was problematic. In pre- and post-washed samples there was little direct evidence of polyelectrolyte retained on the surface. When considering FTIR data there were overlapping IR bands that may be assigned to either the clinoptilolite or polyelectrolyte. Indirect measurement of the effect of polyelectrolyte on the adsorption of clinoptilolite has been possible using RBS.

When considering whether polyelectrolyte can act as a mechanism for adsorption of clinoptilolite onto the stainless steel surface, it appeared that the starting concentration of polyelectrolyte had a limited effect on post-washing suppression of Fe below the surface of the deposits retained on the coupon. However the sample dispersions were not controlled i.e. they were allowed to settle onto the coupon naturally and did not use any form of coating to provide a uniform distribution of particulates.

The presence of polyelectrolyte had a positive effect on clinoptilolite post-washing in certain cases which would indicate that polyelectrolyte should be considered to be a credible means of adhering solids to stainless steel surfaces. However a comparable study of biofilm adsorption would be required to definitely determine the mechanism of attachment and entrainment of pipeline formations. If polyelectrolyte wash through SIXEP was the cause of solid entrainment and attachment, the use of biocides within the SIXEP pipeline would have little impact on the removal of solids retained through a polyelectrolyte mechanism.

### g) Further work

Polyelectrolyte as a means of adhering solids to the stainless steel appears to be credible. A uniform dispersion of clinoptilolite would provide significantly clearer evidence of the effects of washing on the retained solids on the surface. A piped system or some form of couette device that would provide the uniform coatings would make direct comparisons easier. However the couette device would not be representative of the formation dynamics present in the piped system. A flow system would allow the coatings to be studied further without the heterogeneous dispersions present in the static system.

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## i) Supplementary information

FT Raman spectrographs from polyelectrolyte investigation. The only sample that suggested a different peak was the 100% polyelectrolyte wet sample.

There was a significant change in the peak profile at 2850 cm<sup>-1</sup> compared to the blank sample (100% polyelectrolyte). The peak was significantly broader than the blank sample indicating that the polyelectrolyte created a different peak profile than that of the stainless steel. An additional peak was encountered in the blank at 2700 cm<sup>-1</sup>, yet absent from the 100% polyelectrolyte sample. This indicated that the polyelectrolyte was of sufficient depth to mask the characteristic peak present at 2700 cm<sup>-1</sup> from the stainless steel. In the dried experiments the peak at 2700 cm<sup>-1</sup> was not suppressed to the same extent as that in the wet sample. The noise present in the samples was significant and most likely due to the rough surface of the unprepared samples.



Selected FT Raman data – a) Steel coupon blank (without polyelectrolyte), b) stainless steel coupon with fresh polyelectrolyte (i.e. not dried), c) Coupon with 1 x10<sup>-6</sup>% v/v polyelectrolyte and 1 mg clinoptilolite starting solution, , d) 1 1 x 10<sup>-6</sup>% v/v and 10 mg, e) 1 x 10<sup>-4</sup>% v/v and 1mg, f) 1 x 10<sup>-3</sup>% v/v and 1 mg, g) 0.01% v/v and 1 mg, h) 0.1%v/v 10mg, i)1% v/v 1mg

The table below indicates the atomic % of Fe present after RBS characterisation and SimNRA simulations. The presence of Fe within the sample originates from the bulk stainless steel substrate material. Therefore changes in atomic % can be used as an indication of overlaying deposits with a reduction in Fe (At%) indicating a greater amount of solids remaining on top of the steel substrate supressing the Fe signal from the RBS readings. Where there is a higher atomic % of Fe it indicates that less retained solids on top of the coupon due to a reduction in signal from retained solids on the surface of the steel. The atomic % of Fe in the steel substrate remained unchanged by these experiments as such any changes in At% of Fe was indicative of an increase in retaining solids on top of the steel substrate.

The At% of Fe in unwashed and washed selected samples (volume of Polyelectrolyte (%) and mass Clinoptilolite (mg)). A significant increase in Fe At % after washing would indicate that the majority of the surface coating has been removed from the sample

Polyelectrolyte	10 %	1%	0.001%	0.0001%	1 x10 <sup>-6</sup> %
Clinoptilolite	10 mg	10 mg	10 mg	10 mg	10 mg
Unwashed	1.5%	1.1%	0.9%	0.1%	2.3%
Fe (At%)					
Washed	44.0%	5.6%	27.0%	3.3%	13.5%
Fe (At%)					

# Chapter 9 – Conclusions and further work

# 9) Conclusions

This work has sought to address solid formations and associated problems within the discharge line emanating from SIXEP. The three research aims have been to consider: (1) the resistance of clinoptilolite in near neutral and ambient conditions (pH, temperature and pressure) and the nature of any dissolution whether congruent or incongruent; (2) the precipitation of  $Si_{(aq)}$  and/or  $Al_{(aq)}$  from the bulk effluent; and (3) whether formations through polyelectrolyte adsorption can lead to adherence of any formed solids onto a pipeline surface. Should polyelectrolyte not adhere solids to the pipeline surface, solid formations would most likely result from biofilm growth and subsequent solid entrainment.

Significant upstream biocide dosing to control algal blooms should not be undertaken after solids are found within the pipeline. This could release retained activity in one discharge, potentially causing breakthrough in the downstream filters prior to sea discharge. Biocide dosing would only be effective as a preventative measure to avoid solid formations that are instigated by biofilms. A polyelectrolyte instigated solid formations are unlikely to be prevented by biocide dosing but would be effective in algal control of upstream ponds.

The results indicated that both congruent (fine fraction) and incongruent (aqueous species) dissolution were encountered in clinoptilolite  $(Na_{2.2}Mg_{0.40}K_{0.89}Ca_{0.99}Sr_{0.07}Al_6Si_{30}O_{72}.24H_2O)$  contacted solutions under process conditions. Aqueous species were generated at near neutral starting conditions (pH 7.0 ± 0.5) and experiments were undertaken at room temperature (25°C) with a small percentage loss when compared to the starting clinoptilolite mass (1.00 g) in solution (200 mL). Aqueous

species released into solution after 79 days for Si were reported as  $1.50 \times 10^{-2}$  % (washed) and  $1.54 \times 10^{-2}$  % (unwashed) and would be significant when considering bed volumes used in the SIXEP ion exchange columns (~7400 kg). The aqueous Si was most likely to be in the silicic acid form due to SiO<sub>2</sub> colloids being retained in the 3000 molecular weight cut off filters. In addition to the aqueous species a proportion of fine fraction clinoptilolite was recorded that may contribute to the solids build-up encountered in the discharge line.

An increase in Si colloidal material was encountered in the  $\gamma$ - irradiated clinoptilolite (total dose 50 MGy) compared with the non-irradiated control sample. Another effect encountered in the irradiated sample was a reduction in the release of cations (which would inhibit the exchange sites) when added into a near neutral pH solution. This could indicate a reduction in available sites for exchange by a reduction in near surface (~ 1 or 2 µm) cations and would require further investigation. The tetrahedral structure of clinoptilolite (Si-O-Al bonds) appeared unaffected by a high dose (50 MGy) when considering a reduction in crystallinity and any shift in peak position and any minor alterations to the structure are most likely as a result of a change in lattice water content.

The effect of near neutral pH dissolution and the generation of additional colloidal material in  $\gamma$ - irradiated samples has implications for existing SIXEP operation and successor plants that may replicate the ion exchange mineral and treatment techniques and processes. Limited mitigation measures can be implemented to combat the release of aqueous species in the current process flow sheet i.e. ion exchange using clinoptilolite. Removal of solids in the discharge line is required using the present flow sheet. For the successor plant either a different ion exchange media should be selected that does not

release Si<sub>(aq)</sub> or one that includes an extra process to remove the silicic acid generated from incongruent mineral dissolution.

An approach was adopted to replicate solid formations from extremely limited and incomplete characterisation data of the recovered pipeline solid (mid 2000s). The solids produced in precipitation studies had similarities to the previously recovered solid. The solids produced in this study had a high degree of variability within the same starting sample concentrations. Where the starting concentration of AI was greater than Si (by mass) these solutions produced a greater number of representative solids (than Si>AI) to that encountered within the discharge line. Characterisation of a number of samples indicated solids were amorphous and will contribute to the solid formations within the discharge line. The assumption that the pipeline solids may be wholly clinoptilolite fines has been challenged by this work as it can be shown that similar solid elemental compositions can be created in a wide variety of starting solution concentrations and constituents.

When solute concentrations remained the same the heterogeneity of the resulting solid samples was extensive in these studies. This could be also be representative of the range of elemental compositions encountered within the discharge line solid characterised previously[16, 18] with the proviso that the previous characterisation efforts were incomplete. However with only very limited characterisation data (elemental and incomplete dissolution analysis) this hypothesis cannot be validated. Further sample collection from the discharge line would be required to determine if the previous solids were actually representative of the bulk solid encountered in the discharge line, but due to the radioactivity of the samples and access restrictions this would be unlikely to occur.

The adopted methodology undertaken in this study has applications for other NDA sites where limited characterisation data can be obtained. However a greater amount of characterisation data than that provided in this study would be beneficial as a starting point for any future investigations. Recommended changes to SIXEP operating procedures have not been suggested in this work. However control of species entering the SIXEP discharge line would greatly reduce solids build-up and could be included within successor plants. Routine monitoring of Si and Al is not currently undertaken in the discharge line and was requested specifically for this project, with significant variability of Si encountered within the 7 days of monitoring data. This would allow a more accurate model of the discharge line to be developed. These elements (Al and Si) should be included in the routine monitoring, along with the current mono- and di-valent metal cations already included in the monitoring regime.

Organic carbon was detected during the limited characterisation of the previously recovered solid. The most likely cause of this was either biofilm growth or polyelectrolyte. The purpose of the polyelectrolyte study was to avoid, where possible, further sampling within the discharge line to minimise radiological dose uptake by operators surveying the discharge line and to mitigate plant outages caused by offline inspections of the discharge line. If proven that polyelectrolyte does not cause the adherence of solids to a stainless steel surface, it can be stated that biofilm formation is the most likely cause of any solids present to attach to pipeline surfaces, and that biocide dosing would be effective in mitigating this phenomenon without the need for future pipeline inspections. In this study it can be demonstrated that the presence of polyelectrolyte has led to the adsorption of clinoptilolite solids to a stainless steel surface. The clinoptilolite solids were retained on some samples after washing indicating that a relatively strong interaction

between the solid particulates and the steel surface has taken place. Therefore potentially both polyelectrolyte adsorption and biofilms may contribute to the growth of the solids within the discharge line. Consequently, biocide dosing may not be the most appropriate control measure to remove solids from the discharge line.

The study of polyelectrolyte wash through SIXEP has been limited due to issues surrounding limits of detection associated with polyelectrolyte. Polyelectrolyte is dosed at 0.58 mg.L<sup>-1</sup> prior to the effluent entering the sand bed filtration in SIXEP. In this study a starting sample concentration of 1  $\times 10^{-6}$ % by volume of polyelectrolyte generated an adsorption effect on solids onto the stainless steel surface. The RBS analysis technique proved useful in determining effects from adhered solids by considering the suppression of Fe present in the substrate. Further work on sample preparation can prove extremely useful.

Recommendations relating to the polyelectrolyte studies for plant operation are currently limited by a lack of evidence of wash through the plant. Polyelectrolyte is likely to be encountered within the discharge line. However, currently this is below limits of detection for current techniques used to quantify polyelectrolyte levels. Nonetheless, the use of polyelectrolyte has been found to be a credible means of adhering fine fraction clinoptilolite solids to a stainless steel surface.

## a) Recommendations for further work

#### i) SIXEP discharge line

To enable more accurate determination of the nature and composition of the solids, additional samples should be collected from the SIXEP discharge line along with routine monitoring of Al and Si prior to entry and at the regular monitoring points. Collection of solids can be problematic due to the transient nature of the solids within the line as encountered when attempts were made to collect additional solids in the mid 2000s. This study has demonstrated that polyelectrolyte can adhere solids to stainless steel surfaces at very low concentrations therefore there are currently two potential sources of entrainment, polyelectrolyte and biofilm. Previous work has favoured biofilms as the cause of solids entrainment. Should algal bloom issues affect the upstream storage ponds there are limited control measures that can be adopted at present due to the potential for the sudden release of activity within the discharge lines. A safety case should be created to undertake significant monitoring of the discharge line at regular time intervals and locations to undertake a targeted campaign to collect and identify the nature of the organic carbon present within the solids.

Determination of the mineral phases present in the discharge line solids through XRD analysis would greatly increase the accuracy of the model presented here and refine the elemental components and starting concentrations. However this is unlikely to be undertaken due to radioactivity and access restrictions.

Polyelectrolyte wash through investigation in SIXEP has ceased due to issues surrounding limits of detection. Work relating to significantly reducing limits of detection may prove fruitful to determine whether polyelectrolyte and/or biofilms are the true cause of the adsorption media.

#### ii) Dynamic experiments

Currently all precipitation experiments have been undertaken in static conditions. The use of a flow loop was envisaged at the commencement of this research project. Other avenues were first investigated to enable future work on dynamic systems to be more representative. Initial studies in the dynamic system were undertaken but these proved inconclusive as without there being a means of adhering precipitated solids to the surface these would most likely be transported around the system.

It has been found in this work that polyelectrolyte can act as an adsorbent when considering static conditions. Combined polyelectrolyte/precipitation study solution concentrations and polyelectrolyte/fine fraction clinoptilolite should be investigated. Treatment techniques, both mechanical through flow/pressure control and chemical, could also be investigated once a solid has been adhered to the surface of the flow loop pipeline.

An alternative surface preparation technique for mineral adsorption was suggested (Chapter 8) as a couette device (to investigate Taylor–Couette flow) which would provide a more uniform distribution of clinoptilolite. A uniform distribution would enable greater quantitative accuracy with regard to surface washing performance in the stainless steel coupon experiments.

#### iii) Performance of clinoptilolite

Dissolution of clinoptilolite has been found to be both congruent (fine fraction) and incongruent (aqueous species) in near neutral pH conditions without significant metal cation additions. Other studies have sought to model SIXEP performance[22]. None have considered the release of solutes. Specific work should be undertaken relating the operation of a bench scale SIXEP to solutes formed by its operation.

The  $\gamma$  -irradiation of clinoptilolite at high doses (50 MGy) suggests an effect on cations present on exchange sites. Other work is currently ongoing (within the University of Manchester) relating to the wet performance of  $\gamma$  -irradiated clinoptilolite.

A study could be undertaken relating to ion exchange performance at very high doses as currently most studies do not consider total doses beyond 10 MGy [77, 98-101]. It may prove fruitful for alternative radionuclides in successor plants albeit not representative when considering ion exchange performance for SIXEP of  $\beta$ -emitting Cs and Sr.

#### b) Relevance and outcomes relating to Sellafield Ltd

This work has direct relevance to SL as it relates to the operational performance of SIXEP and in turn has an important role in planning decommissioning and effluent management on the Sellafield site. Direct recommendations have been limited as outcomes relate to providing evidence for alternative mechanisms of formation that have not been considered previously. This work has sought to increase the knowledge base around pipeline solid formations as opposed to increasing the technology readiness level of any specific processes. The following should be taken as considerations following this work:

- Clinoptilolite dissolution can occur at near neutral conditions. When envisaging
  successor plants careful consideration as to ion exchange media and/or mitigation
  measures to control fine fractions and aqueous species should be incorporated
  into the flow sheet design from the outset.
- Routine monitoring of Si and Al for effluent prior to entering and within the discharge line should be undertaken along with attempts to recover additional samples from the discharge line.
- Polyelectrolyte adsorption is a credible means of adhering fine fraction clinoptilolite solids to a stainless steel surface, therefore dosing of biocides may not be the correct measure for control of a polyelectrolyte adsorption mechanism.

A further study is required on polyelectrolyte wash through and a comparable biofilm investigation on stainless steel interaction is suggested.

• Monitoring of the discharge line should be undertaken in multiple locations and at regular and frequent time intervals including the collection of representative samples. Once samples are collected undertake a full characterisation suite on these samples to include: elemental composition of the solid by complete dissolution of representative samples with subsequent determination of solution content (e.g. ICP-MS); multiple elemental scans of the solid in multiple sample locations using SEM/EDX; and XRD to identify any crystalline mineral phases. Examination of any organic carbon content within the solid needs to be performed to determine whether the sample is of biological origin or otherwise.

## c) Most likely cause of solid formations

Solids have been previously recovered from the discharge pipeline in the mid 2000s. The solid recovered was poorly characterised with only morphology used to identify clinoptilolite and a single elemental scan of the solid. The preferred mechanism of solid formation was clinoptilolite fines wash through (historic from unwashed clinoptilolite or ongoing was not specified) which then adhered to the pipe surface through a form of biofilm growth (origin and genus unknown).

The characterisation of the recovered solid poses many issues relating to an attempt to recreate the solid formation found within the discharge line and in particular whether AI should be considered as a likely candidate species or not. Within the study undertaken here, AI should be considered as a probable major constituent of the solid found in the SIXEP discharge line due to the dissolution of clinoptilolite releasing both a fine fraction

and an incongruent release of both Al and Si. During an analogue trial using Cs loaded clinoptilolite, an increase in Al release into solution was observed indicating that during SIXEP operations Al would be released into solution as well as Si. The significance of Al in solution is that it has been shown to rapidly precipitate as gibbsite/bayerite in static experiments. A rapidly precipitating simple mineral phase could be easily entrained in a precursor bulk solid formation.

Experimental evidence indicates that the dissolution of clinoptilolite is ongoing throughout the lifetime of the bed and appears to occur irrespective of whether the bed is pre-washed or not. The release of a fine fraction of clinoptilolite was observed and fits within the previously postulated solid formation model proposed shortly after the solids were recovered. The incongruent dissolution of the mineral phase does not fit within this model. Should dissolution rates occur in plant conditions as in the static experiments undertaken in this study a significant loading of clinoptilolite (~4,700kg Si bearing phases) could either be present within the discharge line or have passed through the line. Of this, a smaller proportion of aqueous Si could be present that may form secondary phases or precipitate out as amorphous silica.

The previously suggested model of solid formation did not consider the creation of secondary phases of either Si and or Al adding to the bulk solid formations. The concentration of these aqueous species has been found to be very low. Therefore the creation of secondary phases, whilst important, does not appear to be the main cause of solid formation. The bulk dissolution of the mineral releasing a significant fine fraction appears to be the most credible explanation of the solids observed within the discharge line. This is in agreement with the SEM micrographs taken of the solid during the limited
characterisation efforts of the recovered solid that indicated a similar morphology to a natural clinoptilolite sample.

Biofilms were considered to be the method of adsorption onto the pipe surface and this study sought to prove that polyelectrolyte cannot adhere solids. This would have avoided the requirement for extensive monitoring and sampling regime on the discharge pipeline. Polyelectrolyte induced adsorption of solids onto a stainless steel surface does occur in the static experiments undertaken in this study. The postulated mechanism of solid entrainment and adsorption was biofilm growth, resulting in capture and retention of the clinoptilolite fines. This could still have validity but polyelectrolyte induced adsorption is also possible. It was not possible to undertake comparative studies of biofilms due to lack of characterisation of the organic carbon and any resulting DNA/RNA assignments confirming biological origin. This was not the case, therefore a revised mechanism of solid entrainment should include polyelectrolyte adsorption of clinoptilolite fines in addition to biofilm growth leading to solid entrainment.

The agglomeration of polyelectrolyte and biofilm would readily attract solids to the surface through a charged surface that would interact with ion exchange sites present on the clinoptilolite surface. The increasing presence of Si colloids post irradiation would also contribute to the solid formations as the colloids would be readily attracted to the charged surface created by the agglomeration of biofilm and polyelectrolyte.

A primary mechanism of biofilm and polyelectrolyte adsorption of clinoptilolite fines and colloids onto the inner pipe surface is suggested following this work. Reprecipitation of aqueous species released through incongruent dissolution of the clinoptilolite should be considered which would act as secondary phases within the solid formations found in the discharge line. These secondary phases would make only minor contributions to the bulk

solid within the discharge line.

Chapter 10 – Bibliography

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# Appendix A

Supplementary pXRD patterns from precipitation paper (Chapter 5)

Si>Al starting solution







sinuoO



sinuoO



Si>Al starting solution

MFile: BE5.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 26 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - C Operations: Background 0.037,1.000 | Import

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File: 5E4.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 36 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - C Operations: Background 0.380,1.000 | Import





100-033-0018 (I) - Gibbsite, syn - Al(OH)3 - Y: 2.07 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitive 01-077-0250 (C) - Bayerite - Al(OH)3 - Y: 6.35 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.01000 - b 8.68000 - c 4.76000 - alpha 90.000 - beta 90.000 - gamma 90.000 - Base-center



M File: 11E5.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 25 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Operations: Background 0.120, 1.000 | Import





Al>Si starting solution



III 00-033-0018 (II) - Gibbsite, syn - Al(OH)3 - Y: 16.34 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitiv
 III 01-077-0250 (C) - Bayerite - Al(OH)3 - Y: 15.33 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.01000 - b 8.68000 - c 4.76000 - alpha 90.000 - beta 90.000 - gamma 90.000 - Base-cent



MFile: 3E5.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 24 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - C Operations: Background 0.098, 1.000 | Import

0.003-0018 (I) - Gibbsite, syn - Al(CH)3 - Y: 12.71 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitiv 01-077-0250 (C) - Bayerite - Al(CH)3 - Y: 20.66 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.01000 - b 8.68000 - c 4.76000 - alpha 90.000 - beta 90.000 - gamma 90.000 - Base-cent



File: 4E5.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 25 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - C Operations: Background 0.068,1.000 | Import

 Image: Image:



Al>Si starting solution

File: 6E5.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 35 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - C Operations: Background 0.120,1.000 | Import

100-033-0018 (I) - Gibbsite, syn - Al(OH)3 - Y: 13.96 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitiv 01-077-0250 (C) - Bayerite - Al(OH)3 - Y: 22.70 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.01000 - b 8.68000 - c 4.76000 - alpha 90.000 - beta 90.000 - gamma 90.000 - Base-cent



M File: 8E5b.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 764.7 s - Temp.: 25 °C (Room) - Time Started: 24 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Operations: Background 0.068, 1.000 | Import

100-019-0770 (I) - Talc-2M - Mg3Si4O10(OH)2 - Y: 1.10 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.28700 - b 9.17100 - c 18.96400 - alpha 90.000 - beta 99.610 - gamma 90.000 - B



Fe solutions

[M] File: 1E6b.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 305.9 s - Temp.: 25 °C (Room) - Time Started: 24 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - Phi: 0.00 ° - X: 0.0 mm - Operations: Background 0.120,1.000 | Import

Defaultis. Description of response of resp



M File: 7E6.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 24 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - X: 0.0 mm - Y:
 Operations: Background 0.120,1.000 | Import

Dependitors. Decargoon 0.1 c2, 1.000 (migoritic sport al (0.01)3 - Y: 25.28 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 5.06200 - b 8.67100 - c 4.71300 - alpha 90.000 - beta 90.270 - gamma 90.000 - Primitive - P21/a (14) - 4 - 206.864 - F30= 2 0.00-020-0011 (i) - Bayevine, syn - Al(OH)3 - Y: 10.25 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitive - P21/n (14) - 8 - 425.167 - I/k CPD



Dependions. Background 0.120, 1.000 [mitpoint 0.120, 1.000] [mitpoint 0.120, 1





Li 00-033-0018 (I) - Gibbsite, syn - Al(OH)3 - Y: 71.08 % - d x by: 1. - WL: 1.5406 - Monoclinic - a 8.65520 - b 5.07220 - c 9.71610 - alpha 90.000 - beta 94.607 - gamma 90.000 - Primitive - P21/n (14) - 8 - 425.167 - I/lc PD



File: 11E6.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 24 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - Yhi: 0.00 ° - X: 0.0 mm - Operations: Background 0.068, 1.000 | Import



File: 10E6.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 25 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - Phi: 0.00 ° - X: 0.0 mm - Operations: Background 0.068, 1.000 | Import



File: 4E6.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 69.994 ° - Step: 0.020 ° - Step time: 76.5 s - Temp.: 25 °C (Room) - Time Started: 25 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - X: 0.0 mm - Y: Operations: Background 0.068,1.000 | Import

# Appendix B

Polyelectrolyte surface adsorption eSEM micrographs

### 10% v/v polyelectrolyte 1 mg Clinoptilolite





1% v/v polyelectrolyte 1 mg Clinoptilolite



#### 1% v/v polyelectrolyte 10 mg Clinoptilolite


## 0.1% v/v polyelectrolyte 1 mg Clinoptilolite





0.01% v/v polyelectrolyte 1 mg Clinoptilolite





0.001% v/v polyelectrolyte 1 mg Clinoptilolite



0.001% v/v polyelectrolyte 10 mg Clinoptilolite



0.001% v/v polyelectrolyte 10 mg Clinoptilolite



## $1 x 10^{\text{--4}} \ \% \ v / v$ polyelectrolyte 1 mg Clinoptilolite



 $1 x 10^{\text{--4}} \ \% \ v/v$  polyelectrolyte 10 mg Clinoptilolite



 $1 x 10^{\text{-6}} \ \% \ v / v$  polyelectrolyte 1 mg Clinoptilolite



 $1 \times 10^{-6}$  % v/v polyelectrolyte 10 mg Clinoptilolite



 $1 \times 10^{-6}$  % v/v polyelectrolyte 10 mg Clinoptilolite

