Cranfield University

School of Industrial Manufacturing Science

Water Sciences

MRes Thesis

Academic Year 1999-2000

F. Wall

Evaluation of the Potential for Struvite and Calcite Formation at Seven Sewage Treatment Works within the Severn Trent Region

Supervisor: Dr S. Parsons

September 2000

This thesis is submitted in partial fulfillment of the requirements for the Degree of Masters of Research

Evaluation of the Potential for Struvite and Calcite Formation at Seven Sewage Treatment Works within the Severn Trent region.

Abstract

Scale formation on the pipes, pumps and dewatering equipment succeeding anaerobic digesters leads to reduced hydraulic capacity and increased downtime and pumping costs. The increasing use of biological nutrient removal (BNR), in particular biological phosphorus removal (BPR) leads to the production of phosphorus rich sludges. Anaerobic digestion solubilises ammonia, magnesium and orthophosphates (stored with micro-organisms) which are then available for scale formation.

Scale formation in pipes means either replacement or repeated scouring, the expense and inconvenience involved with such measures demand research into the extent of the problem within the Severn Trent region.

During this extensive study of seven full-scale sewage treatment works (STWs) throughout the Severn Trent region, the levels of scale forming elements within digested sludge liquors and centrate were monitored. Sampling took place on a weekly basis over a period of six weeks. A computer model was used to evaluate the struvite or calcite formation potential of the liquors and centrate. The model is affected by concentrations of the key elements phosphorus, calcium, magnesium and ammonia, in addition to pH, total dissolved solids and alkalinity.

A strong correlation has been found between the models predictions and reality. Four out of the seven works were predicted to have a scale problem by the model, and by the end of the project, this was indeed the case. The type of scale forming was also correctly predicted, though the degree of scale formation was not always as predicted.

Bench-scale experiments with real sludge liquors are planned to validate the precipitation potentials indicated by the model. This will allow Severn Trent to take a more proactive approach to the growing scale problem.

Acknowledgements

This project would not have been possible without the technical and financial support given by Severn Trent Water.

I would like to thank both project supervisors: Dr John Churchley of Severn Trent, and Dr Simon Parsons of Cranfield University. Thanks also to Kath Oldring for all her proof-reading and encouragement.

Special thanks to all members of the T & D team for their help and support throughout the duration of the project, and to Dan for keeping me sane.

Executive Summary

The formation of scale is a widespread problem within the wastewater treatment industry in the UK, and throughout the world. It is a growing problem in many other industries too, including pig farming and wine distillation.

At a sewage treatment works (STW) scale can form within the unit operations and pumps, most commonly centrifuges and any operations downstream from anaerobic digesters (Borgerding, 1972). The build-up of scale crystals can reduce the hydraulic capacity of a treatment works by restricting the flow of water. This can lead to an increase in pumping pressure requirements and pump wear, and therefore increased costs. STWs become less efficient as periods of operational downtime increase to allow pipework and pumps to be replaced or cleaned. This has a corresponding effect upon operational costs.

STWs concentrate the polluting elements of the wastewater into sludge, with a much smaller volume. The cost of sludge disposal is high, as are storage and transportation costs. If the volume of the sludge can be reduced, so can the handling costs. Anaerobic digestion reduces the sludge volume and also lessens odour and pathogen levels within the sludge. This makes the sludge more suitable for disposal to the land. Over a third of the sludge produced within the Severn Trent region is disposed to land, so digestion is a well used sludge treatment method.

Anaerobic digestion involves the decomposition of both organic and inorganic matter. This is carried out by anaerobic bacteria which breakdown around 40 % of the components in the sludge to the end products of carbon dioxide (CO_2) and methane (CH_4). The process releases ammonia, phosphorus and magnesium bound in the sludge. These, now soluble elements pass into the digested sludge liquor or supernatant. If the concentration of scale forming elements is high in the liquid pipelines and the pH raises, for example due to CO_2 evolution caused by turbulence at bends, or agitation of the liquid, scale can form. Formation of scale is based upon chemical equilibrium within the

sludge. The extent of supersaturation of scale forming elements and the pH within the water are the driving forces for crystallisation to occur.

Another potential area for scale formation is when the sludge is dewatered and more liquid drawn off to further reduce the volume. The centrate produced often contains concentrated level of ammonia, magnesium, calcium and orthophosphates, all scale forming elements. All of the STWs have one or more anaerobic digesters. Four out of the seven sites dewater the digested sludge on site, though this figure is set to rise as Severn Trent moves towards an increased level of sludge treatment.

High phosphorus and nitrogen levels in sludge are due to nutrient removal processes within STWs. Nutrient removal from wastewater is becoming more widespread as sewage effluent discharge consents to rivers are tightened, as called for in the Urban Waste Water Treatment Directive (EC Directive 91/271/EEC). An attempt is being made to reduce eutrophication in rivers, eutrophication occurs when levels of nutrients increase supporting the growth of nuisance algae.

Within the Severn Trent region, scale has been identified at two of the sewage treatment works (STWs) and a sludge destruction plant (SDP). The project will most importantly highlight any at-risk sites where scale formation has not yet become a significant problem. By identifying such sites, preventative measures can be taken before the scale takes hold and becomes unmanageable.

Analysis was carried out by Severn Trent Laboratories (STL) as per the Methods for the Examination of Waters and Associated Materials 1976 - 1992, HMSO, London.

All six sewage treatment works have anaerobic digesters. Samples were taken each week over a six-week period. The feed sludge to the digesters and the digested sludge were sampled, as well as digested sludge liquor or centrate.

The first samples taken on the sludge route were feed sludge into the anaerobic digesters. The percent dry solids (% DS) of the sludge were determined, along with calcium, magnesium and iron or aluminium, if dosed. The average % DS of the feed sludges over the six-week sampling period varied from 3.5 to 8.7. Within Severn Trent, digesters are ideally fed with sludges of between 5.5 and 6 % to ensure optimum performance.

The second samples taken were digested sludges. The average % DS of the digested sludge across the seven sites was 2.2 – 3.9. Digested sludge from an anaerobic digester is typically around 3.5 % (Metcalf and Eddy, 1991), however it is largely dependent upon feed concentration.

The liquor samples were pH adjusted on site to prevent scale formation within the sample vessel. Filtered samples were analysed for:

- ammonia
- magnesium
- calcium
- orthophosphate
- Total dissolved solids
- iron/aluminium if dosed on site

These determinands were chosen to enable the use of a computer model (Loewenthal, 1997) which predicts struvite and calcite precipitation potentials of samples. Struvite ($MgNH_4PO_4.6H_2O$) is a metal salt of the metal ammonium phosphate. Ammonium, phosphate and magnesium are all present in wastewater, so the formation of struvite is a widespread occurrence. Calcite is one of the polymorphic forms of calcium carbonate ($CaCO_3$). Calcium levels can be particularly high at works using lime dosing to control pH.

The results from the model will need to be treated cautiously, as the complex environment within the waste streams may not be represented fully by the computer model. For this reason laboratory-scale experiments were carried out in an attempt to actually form scale from waters which were identified by the model as having a potential to form scale. It was hoped that these results would verify the accuracy of the model.

Three sites included in the study undergo phosphorus removal (via iron dosing or alum dosing with biological). These sites expected to have a low phosphorus level in the sludge. Iron binds the phosphorus and so prevents the characteristic release of phosphorus during anaerobic digestion. One site undergoes biological nutrient removal and was expected to have a high phosphorus level in the liquor; however, two-thirds of the flow are treated with aluminium for phosphorus removal. Aluminium binds phosphorus in a similar way to iron, preventing release during digestion. This meant the overall phosphorus levels at this site were low.

Struvite and calcite potentials were calculated using the computer model. Potentials are quantified by their degree of deviation from zero. A potential of zero suggests that the system is on the brink of scale formation. For example, a value of 50 means the sample has the potential to produce 50 mg of scale per litre. A negative value of -200 means scale is very unlikely to form, whereas a value of -20 means no scale will form but scale formation is more likely if conditions within the waste stream change.

The potentials for each scale can be studied over the six-week sampling period (figures A and B).

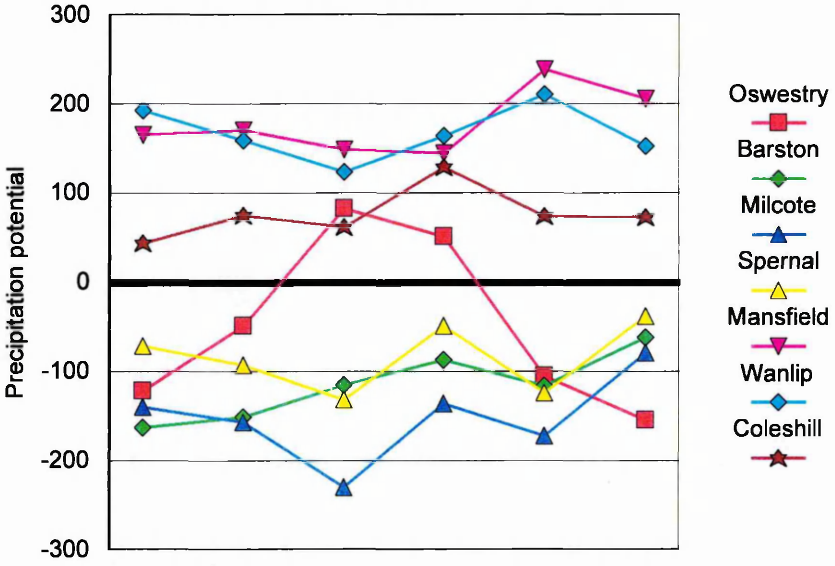


Figure A. Struvite potentials of the liquors sampled form all seven works over the six-week sampling period.

The struvite potentials are fairly consistent, each site is predicted to be either free of struvite or to suffer a considerable problem. Three sites: Barston, Milcote and Spernal have negative struvite formation potentials for all samples taken. This is attributed to the fact that these three sites undergo chemical phosphorus removal and therefore don't experience a solubilisation of phosphorus during digestion. This is indeed the case; the average orthophosphorus levels in the liquor or centrate at these sites were an order of magnitude lower than the sites with no phosphorus removal (Figure 5.18.). There is no known struvite problem at any of these works.

Three sites were predicted to have positive struvite potentials for all samples. Coleshill, Mansfield and Wanlip all suffer from struvite formation. These sites are the three with the highest average pH. This is probably a root-cause of the struvite problems at these works.

The remaining site, Oswestry, has a varying potential. The site has the lowest pH, and therefore would not be expected, and does not, have a scale problem. The peak in potential corresponds to a peak in both orthophosphate and magnesium.

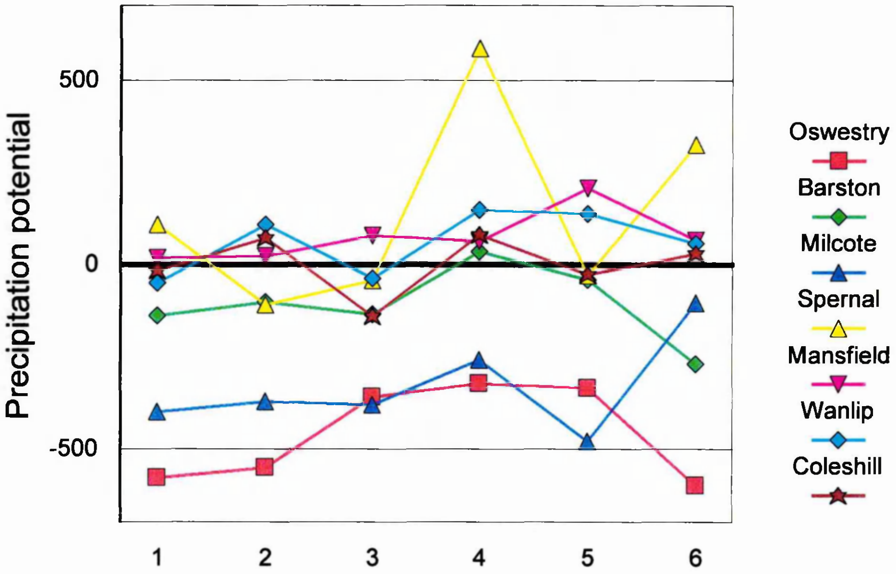


Figure B. Calcite potentials of the liquors sampled form all seven works over the six-week sampling period.

The calcite potentials are much more varied (Figure B). Milcote and Oswestry have negative potentials for all samples. Calcium levels are low at these works and no problem was anticipated. The low pH recorded on-site also contributes to the negative values. No scale problems exist at either site.

Mansfield was the only site with all samples showing a potential to form calcite. There is a considerable scale problem at Mansfield, though X-ray diffraction shows the scale to be struvite. It is possible that the sample analysed was unrepresentative or that the formation of struvite inhibits calcite crystal growth.

The remaining four sites all had variable calcite formation potentials. Wanlip and Coleshill are similar to Mansfield; struvite is formed on-site but the model predicts calcite formation. This may be due to a fault in the computer model or because struvite inhibits calcite formation.

Barston has only one positive sample; this peak does not appear to correspond to a rise in any measured parameter. No scale formation is experienced at Barston, and these results do not indicate a significant problem.

Spernal had varied calcite formation predictions and this raised concern. The positive values were very significant and scale formation was expected. There was no known scale problem at Spernal until the very end of the project. The pumps on the centrate line lost 20 % efficiency and were found to have a 3 mm layer of scale. X-ray diffraction confirmed the scale to be calcite.

Struvite and other scale formation in anaerobic digesters, pipework and any succeeding downstream processes is a significant problem. It has been reported that pipes at several sewage treatment works have to be frequently replaced, whilst others are pressure jet cleaned on a monthly basis. Pipework immediately after the digested sludge holding tank was reduced from 100 mm in diameter down to 50 mm.

The cost and inconvenience involved in managing a scale problem at a STW provides the need for this in-depth study, investigating the effects of many factors in scale formation across a number of works. The breadth of the project has enabled valuable comparisons and conclusions to be drawn.

Contents

Appendix I

Appendix II

List of Figures and Tables

Executive Summary

1. Introduction

2. Literature Review

4. Materials and Methods

5. Results

6. Discussion

1. Introduction

1.1. Scale formation

Scale formation is a widespread problem within the wastewater treatment industry throughout the world (Buchanan *et al.*, 1994) and is a growing problem in many other industries, including pig farming in Western Australia and wine distillation in South Africa (Webb and Ho, 1992, Loewenthal *et al.*, 1994).

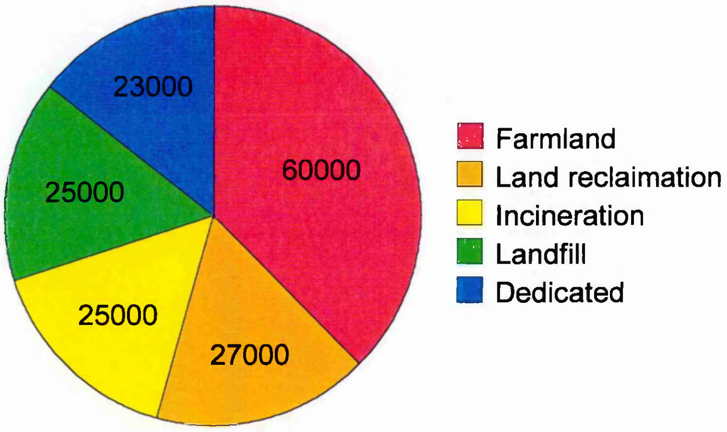
A build-up of scale on pumps and pipes at sewage works causes many problems (Williams, 1999). Scale also forms within the unit operations and fittings, most commonly centrifuges and any operations downstream from anaerobic digesters (Borgerding, 1972). Scale can reduce the hydraulic capacity of a treatment works by restricting the flow of water. This can lead to an increase in pumping pressure requirements and therefore increased cost, as well as greater pump wear. Operational downtime can increase as pipework and pumps are either replaced or cleaned, this has a corresponding effect upon operational costs (Buchanan *et al.*, 1994).

Many types of scale exist, including calcium phosphates, particularly hydroxyapatite (Battistoni *et al*, 1998) and to a lesser extent calcium hydrogen phosphate and β-Tricalcium phosphate (Popel and Jardin, 1993). Calcite is another calcium based scale, precipitating out of waste streams with high calcium levels (Habets and Knelissen, 1997). Another widely reported scale, causing problems all over the world is magnesium ammoniumphosphate or struvite (Horenstien *et al*, 1990) (Table 2.12.).

1.2. Anaerobic digesters and dewatering

At sewage treatment works (STWs), scale formation is most prevalent in pipes and fittings on the sludge route. Anaerobic digestion of the sludge releases ammonia, phosphorus and magnesium bound in the solid phase into the liquid phase. The digested sludge can be further dewatered and the liquid phase drawn off. The concentration of scale forming elements is high in the liquid pipelines and so if the pH raises, for example due to CO_2 evolution caused by turbulence at bends, or agitation of the liquid, scale can form. Scale can also form in the water, and be carried out of the system, or it may begin to form on the interior of pipes or fittings.

There were 20 dewatering plants in operation within the Severn Trent region in 1999. Dewatering aims to produce a high dry solids content in the sludge (Anderson and Nielson, 1993), therefore the main benefit is a reduced sludge volume, meaning lower transport and disposal costs, and easier storage. These points are significant when the disposal routes used by Severn Trent (Figure 1.1.) are considered. As can be seen, the landfill option is not preferred, the cost of land filling is directly proportional to the volume of sludge. All disposal routes require the transportation of sludge from the STW, the farmland disposal route often requires transportation to remote areas, further increasing costs



Total: 160,000 Tonnes dry solids per year

Figure 1.1. Disposal routes for the 160,000 Tonnes of dry solids (Tds) produced in the Severn Trent region in 1999.

1.3. Site background

Within the Severn Trent region, scale has been identified at several sewage treatment works (STWs) and a sludge destruction plant (SDP). Of the seven sites reported in this study, three are known to be susceptible to scale formation. The seven sites were chosen as relatively 'hard' or 'soft' sites. The hardness of water refers to the amount of calcium and magnesium contained within it; hard water will contain more of these components than soft. It was expected that Coleshill, Oswestry and Barston would be relatively 'softer' sites. All of the STWs have one or more anaerobic digesters. Four out of the seven sites dewater the digested sludge, though this figure is set to rise as Severn Trent moves towards an increased level of sludge treatment. Mounting environmental and financial pressures are leading to a greater awareness of the importance of dewatering (van der Roest *et al.*, 1993).

1.3.1. Barston STW

Barston STW has been in operation since 1911. It currently treats an average daily flow of 15,000 m^3 and serves a population of 74,000. Sewage is chemically dosed with ferric sulphate for phosphorus removal then settled. The biological treatment process is biological filtration, and sand filters provide tertiary treatment. Sludge produced on site (36 m^3/d) is mixed with imported sludges totalling 80 m^3/d and anaerobically digested in one of two digesters. The digested sludge is stored in secondary, pathogen-kill tanks where it settles out and is applied to land.

1.3.2. Coleshill SDP

Coleshill SDP treats sludge from Minworth STW (Birmingham) and surrounding areas. The plant is designed to incinerate 40,000 (Tds) of digested sludge per year. Sludge is centrifuged (dewatered), dried and incinerated. The incinerator ash is disposed via landfill and the liquors produced at all stages of treatment are returned to Minworth STW. Lamella clarifiers are provided to settle out solids from the liquors prior to return to Minworth. The lamella clarifiers have been severely affected by solids build-up, and for the duration of the project were being bypassed. An over ground plastic pipe carried centrate from the well directly to the effluent tank.

The scale problem is most prevalent in the post-centrifuge line. The cost of managing the scale problem is currently £16,500 per annum.

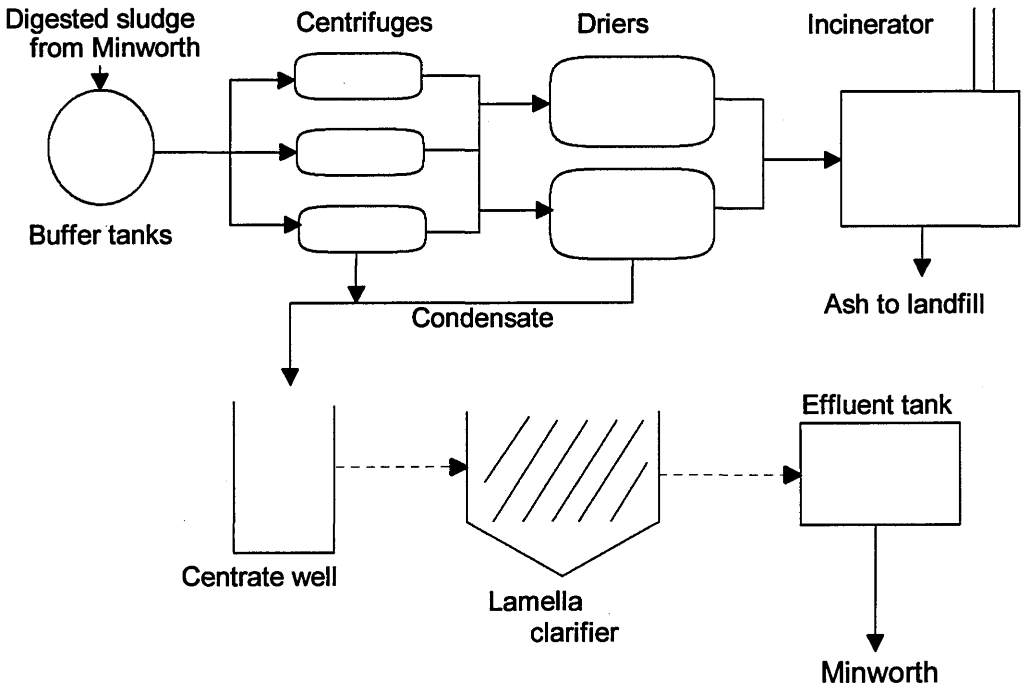


Figure 1.2. Schematic diagram of Coleshill SDP, ----- indicates pipework which is known to suffer scale formation.

1.3.3. Mansfield STW

Mansfield STW utilises various processes to treat incoming wastewater. Two digesters treat settled sludge anaerobically, before secondary digestion in large pathogen kill tanks (Figure 1.3.).

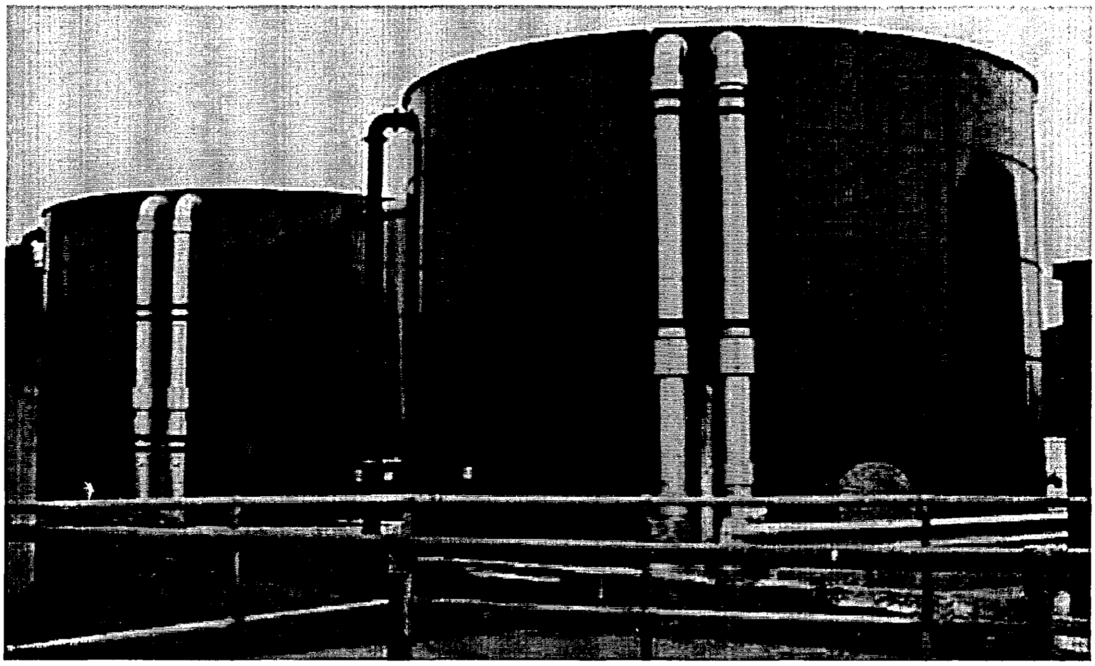


Figure 1.3. Sludge storage vessels at Mansfield STWs.

1.3.4. Milcote STW

A third of the flow is treated on a BNR activated sludge plant, with two-thirds dosed with aluminium for phosphorus removal, followed by biological filters. The sludge produced by the biological processes is digested anaerobically in two digesters. The digested sludge is stored and settled in four pathogen kill tanks. The top water is returned to the head of works and the sludge is tankered to land.

1.3.5. Oswestry STW

Oswestry is another activated sludge works. The surplus activated sludge (SAS) from the process is thickened to between 6 % and 9 % dry solids with a belt thickener. The thickened sludge is mixed with settled primary sludge and fed to the single anaerobic digester. The works accepts imports from small works in the surrounding area. The digester is operated under 'fill and spill' conditions. Digested sludge is stored and allowed to settle in four pathogen kill tanks, and the top water is returned to the head of works whilst the sludge is tankered to land.

1.3.6. Spernal STW

The sludge handling facilities at Spernal STW are currently undergoing a renovation program, with the commissioning of four anaerobic digesters.
In the summer the flow is split evenly between biological filters and an activated sludge plant. Ferric sulphate is dosed into the humus tank feed, and ferrous chloride into the ASP to remove phosphorus. These processes produce a third of the plants total sludge intake. The remaining two-thirds of the sludge is imported, therefore undergoing no iron dosing for phosphorus removal compared to the indigenous sludge.

1.3.7. Wanlip STW

Situated north-east of Leicester, Wanlip STW (Figure 1.4.) treats an average of 120 Ml of wastewater per day. The main means of wastewater treatment at Wanlip is the activated sludge process. Sludge is digested on site using four anaerobic digesters. The digested sludge liquor is pumped to open lagoons were it is allowed to settle out. The top water is drained off and returned to the head of the works, and the sludge is centrifuged. Two centrifuges produce a 20-25% dry solids cake.

Figure 1.4. General site view of Wanlip STW, showing banks of trickling filters (front left), activated sludge tanks (rear left) and large circular digesters (right).

1.4. What Will This Study Achieve?

Scale is known to form at three of the sites included in this study. Any other sites which are at risk from scale formation can also be identified and the problem avoided or minimised at design. Pipework at STWs is often underground and pumps and tanks are sealed making regular inspection impossible. If the scale gradually builds-up, the problem may not be recognised until pump efficiencies and hydraulic capacities are reduced to a significant extent. The main body of the study involved sampling from all seven sites over a six week period. Weekly samples were taken of digester feed sludge, digested sludge and either digested sludge liquors or centrate, if a centrifuge is active on site. The ionic balance of these streams was determined and the results from the liquor or centrate were fed into a computer model (Loewenthal, 1997). The model enables the prediction of struvite and calcite formation (or precipitation) potentials. This is done using chemical equilibrium formulae to predict the scale formation potential of the water. The model specifically addresses struvite and calcite formation, and gives a positive or negative result. For example, a value of 50 means the sample has the potential to produce 50 mg of scale per litre. A negative value of -200 means scale is very unlikely to form, whereas a value of -20 means scale formation is unlikely but may occur if conditions within the waste stream change.

The results from the model will need to be treated cautiously as the complex environment within the waste streams may not be represented fully by the computer model. For this reason laboratory-scale experiments were carried out in an attempt to actually form scale from waters which were identified by the model as having a positive precipitation potential. It was hoped that these results would verify the accuracy of the model.

The main study will also provide the basis for an investigation into the consequences of the installation of dewatering equipment at a site. The turbulence of centrifugation drives off CO_2 causing a pH rise in the liquor which may provoke the formation of various scales (Borderding, 1972). This may be particularly relevant at Spernal, with a new sludge treatment facility. Laboratory-scale experiments using simple aeration equipment will show the possible pH rises in liquors achievable via aeration and turbulence, hopefully simulating centrifugation. As a pH rise is conducive to scale formation (figure 1.5.) this would highlight any sites where a scale problem would be likely if sludge dewatering were to occur.

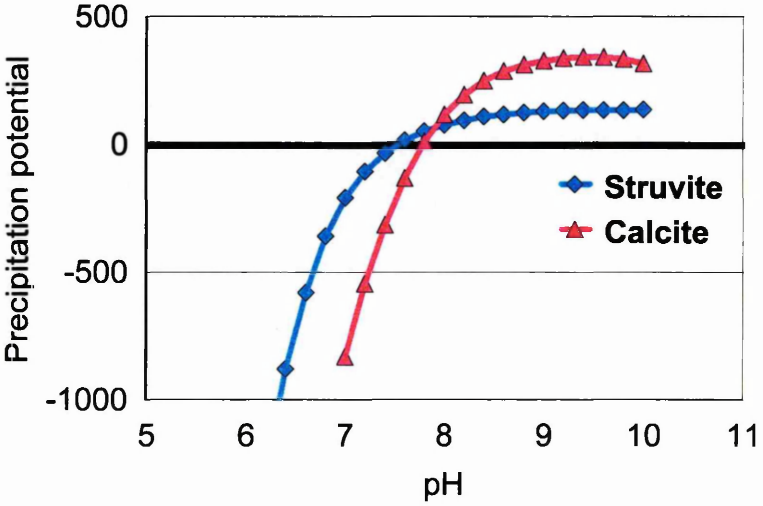


Figure 1.5. Struvite and calcite formation potential with pH, as predicted by the computer model (Loewenthal, 1997). All other variables remain constant.

This additional study was very significant because Severn Trent is moving towards a more complete sludge treatment program. The addition of further sludge treatment facilities e.g. dewatering, at works with anaerobic digesters will become more common. Dewatering reduces the volume of sludge, and so reduces transport and disposal costs (Melcalf and Eddy, 1991). With the recent moves to drive down costs within water companies, dewatering will become a popular option.

The project will most importantly highlight any 'at-risk' sites where scale formation has not yet become a significant problem. By identifying such sites, preventative measures can be taken before the scale takes hold and becomes unmanageable.

2. Literature Review

2.1. Introduction

At most stages during domestic and industrial wastewater treatment, sludges are produced (Figure 2.1.). These sludges contain both settleable and non-settleable solids from primary treatment; organic matter from secondary treatment; and specific elements such as nitrogen and phosphorous (if an advanced tertiary treatment has been used).

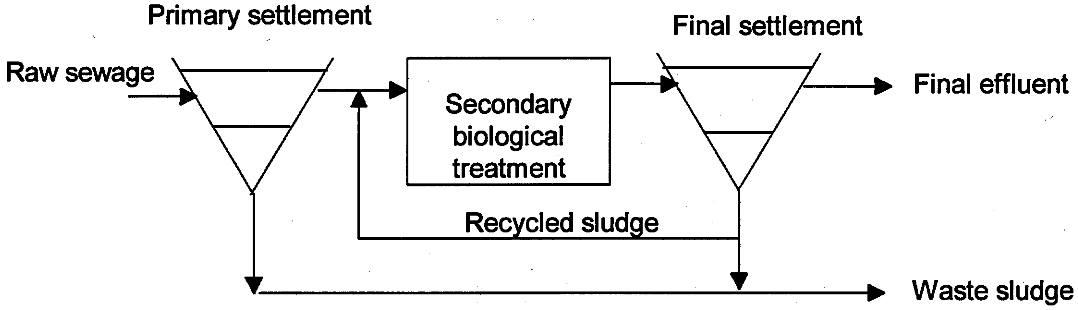


Fig. 2.1. Schematic of basic sewage treatment works with primary settlement, biological treatment and final settlement.

The traditional UK route of sludge disposal to sea has been closed off by European Union (EU) legislation (EU Directive 97/271/EEC) providing additional pressure upon water companies to reduce the volume of sludge produced. In the Severn Trent region, sea disposal isn't used for geographical reasons but the pressure to reduce sludge volumes still remains, with sludge production expected to increase by 50 % by the year 2005 (Hall, 1995). The 64 sludge treatment plants in the Severn Trent region treat a total of 240,000 tonnes of dry solids each year (Tds/y). The sludge treatment facilities range from a capacity of 500 Tds/y up to the largest, Coleshill sludge destruction plant (SDP), at 40,000 Tds/y.

The disposal of sludge is very costly, and can account for up to half of the running cost of a wastewater treatment plant. Once treated the sludge has to be transported, before being land filled or stored for use on farmland. All options are costly therefore it is desirable to dispose of the smallest volume of sludge possible. Reducing the volume of sludge produced at a sewage treatment works can be done using several methods, either thickening and/or dewatering. Physical or chemical conditioning of sludge (or stabilisation) can further aid dewatering (IWPC, 1981). The most widely used method of sludge stabilisation is digestion (Fig. 2.2.), carried out in aerobic or most commonly, anaerobic conditions (Metcalf and Eddy, 1991).

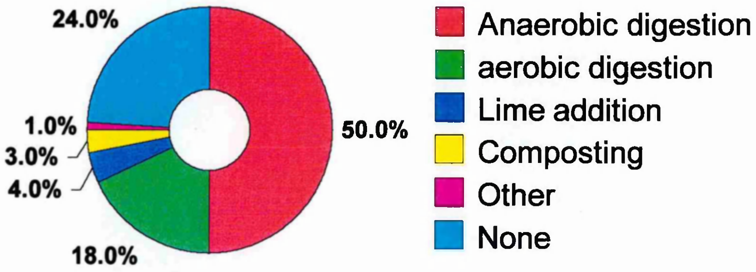


Figure 2.2. Sludge stabilisation methods as % of STWs in the European Union. Adapted from Hall (1995).

Sludge digestion is a biological process, relying upon complex microbiology and biochemistry to function. The micro-organisms retained within the digesters are responsible for the breakdown of components in the incoming sludge.

After stabilisation, the sludge may be dewatered. Many methods exist, including centrifugation, belt presses, filter presses and vacuum filters (IWPC, 1981). These processes generally produce a cake containing greater than 15% dry solids, however, this can be increased considerably depending upon the origin of the sludge; primary, waste activated, digested etc. (Metcalf and Eddy, 1991). As the sludge becomes more concentrated, the elements within it may begin to reach their products of solubility and then may precipitate out as salts, forming scale on pipework and pumps (Ohlinger *et al.*, 1998, Maqueda *et al.*, 1993). This scale can cause many operational problems in industry.

Ever-tightening standards are being imposed by the Environment Agency and the EU upon discharges from sewage works. Plants are adopting a nutrient removal stage into the current process to meet these new demands (Cooper *et al.,* 1995). This will lead to increasing volumes of sludge being produced that contain high levels of nitrogen and phosphorus, which, under the right conditions, are scale forming elements.

2.2. Nutrient removal

Nutrient removal from wastewater is becoming more widespread as sewage effluent discharge consents to rivers tighten (Table 2.3.). As instructed in the Urban Waste Water Treatment Directive (UWWTD), many water courses are being classified as 'sensitive', originally by the National Rivers Authority (NRA), as an attempt is made to reduce eutrophication in rivers (EC Directive 91/676/EEC). Eutrophication occurs when levels of nutrients increase supporting the growth of nuisance algae. Nitrogen is more specifically dealt with in the Nitrates Directive, with designated 'vulnerable zones' throughout Europe. Discharges into these sensitive or vulnerable zones are limited and have new, higher standards. The UWWTD currently only affects STWs with a population equivalent (PE) of over 10,000 which discharge into a sensitive watercourse.

Table 2.3. Requirements of the EC Urban Wastewater Treatment Directive 91/271/EEC, for sewage works discharging into nutrient sensitive waters (Farrimond and Upton, 1993).

	Total Phosphorus		**Total Nitrogen**	
Population Equivalents (PE)	10,000-100,000	100,000 +	10,000-100,000	100,000 +
Concentration (mg/l)	2	1	15	10
Minimum Reduction (%)	80	80	70-80	70-80

Lind (1993) observed that eutrophication can be considered in two ways, as a lake ageing naturally over thousands of years, or as the associated algae blooms, altered fish life, taste and odour problems. The growth of algae is dependent upon nitrogen and phosphorus, but is rate limited only by the latter.

It is therefore necessary to specifically address the phosphorus in the wastewater before discharge. Phosphorus can be removed from a wastewater via several methods (Table 2.4.), physico-chemically, biologically or, though only as a side-stream process, crystallisation (Metcalf and Eddy, 1991, Cooper *et al.*, 1995 and Battistoni *et al.*, 1997 respectively).

Table 2.4. Phosphorus removal efficiencies by process, adapted from Metcalf and Eddy (1991).

Process/Operation	% Removal of incoming phosphorus	% Removal of incoming nitrogen
Conventional treatment		
Primary	10-20	5-10
Activated sludge	10-25	10-30
Trickling filter	8-12	
Biological phosphorus removal alone	70-90	0
Biological phosphorus and nitrogen removal via nitrification	70-90	5-20
Biological phosphorus and nitrogen removal via denitrification	70-90	70-95
Chemical precipitation, metal salts, lime	70-90	20-30
Physical removal		
Filtration	20-50	20-40
Carbon adsorption	10-30	10-20
Reverse osmosis	90-100	80-90

2.2.1 Physico-chemical Phosphorus Removal

Physico-chemical removal involves the precipitation of the phosphorus from the wastewater as an insoluble phosphate by the addition of a metal salt. Aluminium or iron, in either the chloride or the sulphate form are most commonly used (Brett *et al.*, 1997). Lime dosing is also effective (IWEM, 1974), as are polymers when dosed with alum or iron salts (Metcalf and Eddy, 1991).

The stage in the process at which the dosing occurs determines the type of precipitation; pre-precipitation binds the phosphorus into the primary sludge during primary treatment; co-precipitation contains the phosphorus within a biological sludge and post-precipitation allows the phosphorus to be removed during a final or tertiary treatment stage such as effluent filters (Metcalf and Eddy, 1991).

Using iron dosing as an example, a very simplified reaction schematic (Equation 2.5.) illustrates the basic principle behind phosphorus removal via chemical dosing.

$$\mathbf{Fe^{3+} + HPO_4^{3-} \Leftrightarrow FePO_4 + H^+}$$ Equation 2.5. Metcalf and Eddy, 1991.

Many reactions take place once a chemical is dosed into wastewater, so the reaction cannot be considered in isolation. Equation 2.5. indicates a theoretical one to one ratio of iron to phosphorus, but in reality a much greater ratio of iron is required to compensate for iron uptake during auxiliary reactions.

A chemical sludge is produced whatever form of precipitation is used. Recommendations within the UWWTD call for a reduction in the frequency of chemical addition during wastewater treatment (EC Directive 91/271/EEC). For this reason, many plants are turning to biological nutrient removal (BNR) including biological phosphorus removal (BPR).

2.2.2. Biological Phosphorus removal

2.2.2.1. The Activated Sludge Process (ASP)

BNR is an adaptation of the conventional activated sludge process. As noted by The Institute of Water Pollution Control (IWPC) (1987), activated sludge is "the flocculant microbial mass which is produced when sewage is continuously aerated". Aeration provides oxygen to support the living organisms but also a means of mixing the incoming sewage with the micro-organisms within the sludge (Hanel, 1988). The flocs consist mostly of micro-organisms which are responsible for the breakdown of biodegradable elements of the wastewater (IWPC, 1987).

Having undergone primary treatment, sewage enters the activated sludge plant (Figure 2.6.) and is retained for up to 6 days. The treated sewage is allowed to settle to remove the microbial flocs before passing on to the next treatment stage.

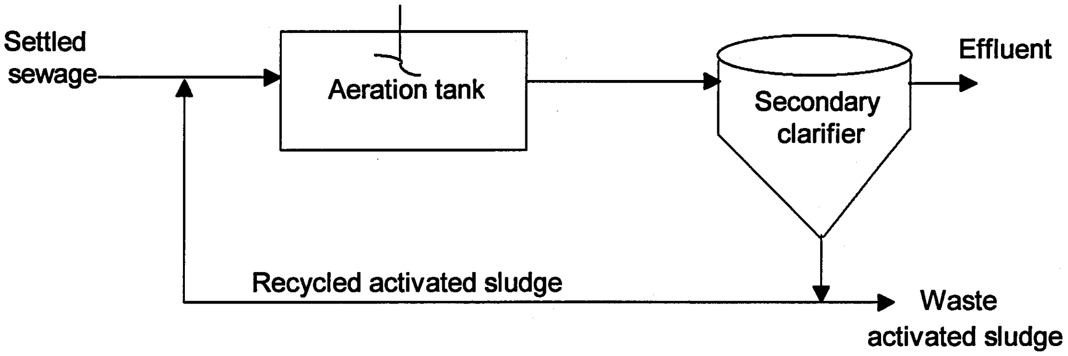


Figure 2.6. Schematic of an activated sludge plant (ASP) (Metcalf and Eddy, 1991).

The biodegradable elements within the sewage are quantified as Biochemical Oxygen Demand (BOD), and an 85-95 % BOD removal can be expected from a conventional ASP (Metcalf and Eddy, 1991).

2.2.2.2. ASPs for Nitrogen Removal

Alongside BOD removal, ASPs can also nitrify, i.e. convert ammonia to nitrate (Equation 2.7. shows the conversion of ammonia to nitrate, via nitrite).

$$\mathbf{NH_3 \Rightarrow NO_2^- \Rightarrow NO_3^-}$$ Equation 2.7. Metcalf and Eddy, 1991.

This can be achieved by encouraging the growth of the nitrifying bacteria, *Nitrosomonas* and *Nitrobacter*, in the activated sludge (Albertson, 1994). The activated sludge process has to be tailored to suit the nitrifiers, as they require more specific conditions (Table 2.8.) than the faster growing heterotrophs (Hanel, 1988).

Table 2.8. shows a comparison of the optimum conditions for BOD removal and nitrification in an activated sludge plant.

Parameter	BOD Removal	Nitrification
Energy source	organic carbon	ammonia and nitrite
Carbon source	organic carbon	carbon dioxide
Substrate	organic carbon	ammonia
pH	5.5-9.0	7.2-8.0
Alkalinity	low	high
Temperature	2°C	35°C
Oxygen requirement per kg degraded	1 kg	4.3 kg
Sensitivity to inhibitors	low	high
Sludge age, days	4-6	6-10
Hydraulic retention time, hours	2+	6+

Further modifications to the activated sludge process can produce conditions which are selective for micro-organisms which can achieve denitrification (Equation 2.8.). For example, the addition or creation of an anoxic zone within an ASP starves heterotrophs of a source of oxygen. This can be done by simply disabling the aeration system in one section of the ASP and has been traditionally done more often as a means of saving energy, than to meet a nitrogen discharge consent (Farrimond and Upton, 1993). Anoxic means that the majority of dissolved oxygen now available to the micro-organisms, is in the oxidised forms of nitrogen produced by nitrification (Hanel, 1988). Oxygen is essential as an electron acceptor in the respiratory chain. The bacteria breakdown the oxidised form of nitrogen (nitrite), use the oxygen and release nitrogen gas (Metcalf and Eddy, 1991).

$$\mathbf{NO_2^- \Rightarrow NO \Rightarrow N_2O \Rightarrow N_2} \qquad \text{Equation 2.8. Metcalf and Eddy, 1991.}$$

As this biological process is carried out in open tanks, the nitrogen gas is released to the atmosphere leaving the wastewater with reduced nitrogen levels.

2.2.2.3. ASPs for Phosphorus Removal

Levin and Shapiro (1965) noted that when an aerobic sludge is allowed to become anaerobic, an uptake of phosphorus takes place. Phosphorus can be stored within the micro-organisms in two distinct ways. Physiologically, as an integral part of the nucleic acids and nucleotides of a cell, or as phospholipids, the constituent of cell walls. Secondly, additional phosphorus can be stored within the cell as polyphosphates (Jardin and Popel, 1996).

Acinetobacter sp. is a species of bacteria which can store phosphorus. It utilises polyphosphates as an energy source (Wedi, 1994, Kavanaugh, 1994). When exposed to anaerobic conditions, the bacteria take up short chain fatty acids (SCFA's) and store them as the energy source, poly-B-hydrobutyrate (PHB). The energy required to build up the large store of carbon is directly derived from the breakdown of polyphosphates. This causes a release of phosphorus, which leaves the cell and enters the surrounding wastewater. Buchan (1981) noted that "Sludges were also investigated which had been left anaerobic for 24 hours, thereby releasing up to 40 % of the total phosphorus in the sludge into the supernatant as orthophosphate".

If the bacteria are subjected to aerobic conditions they take up vast amounts of phosphorus to drive the reaction in the opposite direction, enabling themselves to breakdown the stores of PHB. The degradation of PHB yields CO_2 and H_2O, which can then be used by the micro-organism for growth (Greaves *et al.*, 1999).

This phenomenon can be exploited by manipulation of the sequence and type of zones within an activated sludge plant. Mino *et al,* (1994) state "Introduction of anaerobic zone into the influent end of the conventional activated sludge process is known to facilitate the proliferation of PAOs (phosphate accumulating organisms) and lead to the improvement of the phosphate removal efficiency". Many complex arrangements of aerobic, anaerobic and anoxic zones, along with recycle loops, exist, enabling the removal of both phosphorus and nitrogen biologically, without the addition of chemicals (Figure 2.9.). Many ASPs have been converted to allow for BPR, not only does this reduce chemical precipitation costs, it also reduces the volume of sludge produced (Wedi, 1994).

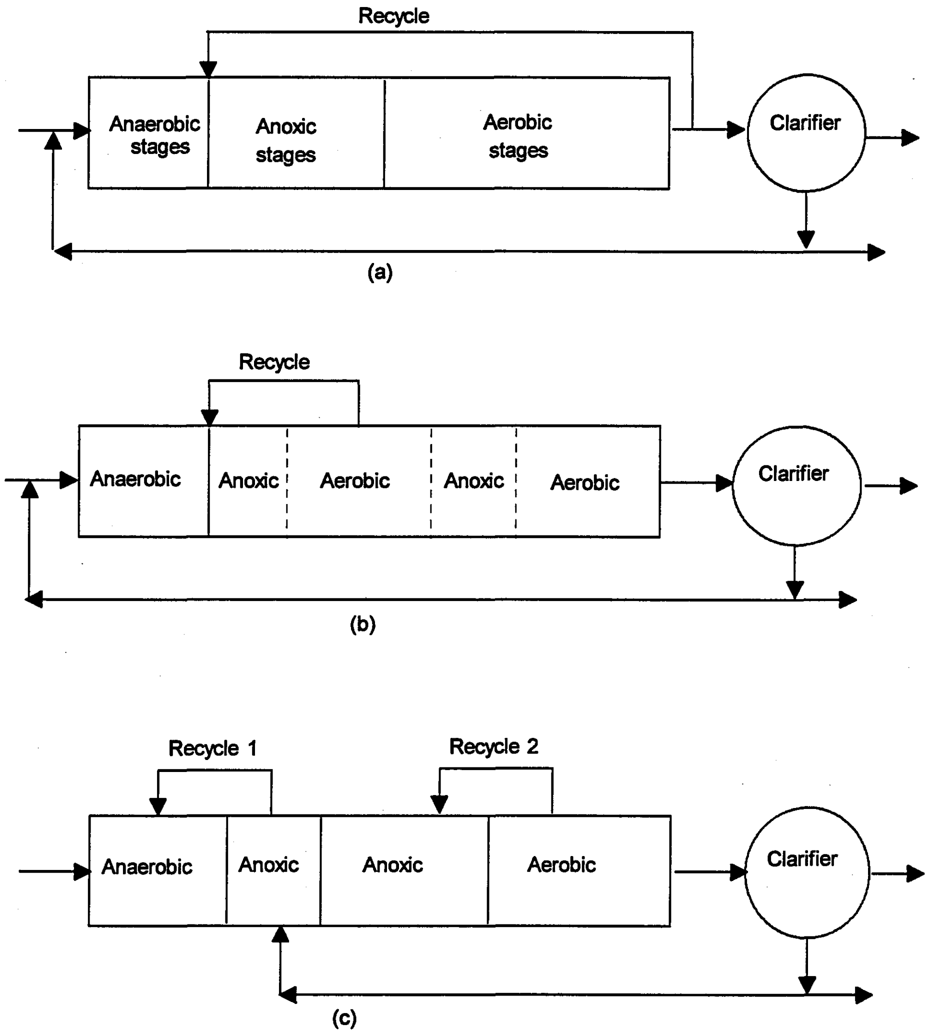


Figure 2.9. Schematic of activated sludge plants for combined nitrogen and phosphorus removal. (a) A_2O process (b) five-stage Bardenpho process (c) UCT process (developed at the University of Cape Town).

These processes all have recycle loops for the sludge, however waste sludge (WAS) is still produced. The sludge is hard to treat because stabilisation and thickening results in solubilisation of magnesium and phosphorus (Jardin and Popel, 1996). This is a problem because these soluble elements are available for scale formation. The release of magnesium and phosphorus can lead to the precipitation of struvite (Jardin and Popel, 1996).

2.2.3. Crystallisation as a Method for Phosphorus Removal

Crystallisation was developed as a method of phosphorus removal from wastewaters (Joko, 1984). Trial experiments were done with both synthetic and real secondary effluents and digested sludge liquors (Kaneko, 1988, Battistoni *et al,* 1997). Joko (1984) removed phosphorus via crystallisation as calcium phosphate using phosphate rock as a seed crystal. The author concluded that phosphorus and calcium levels, along with pH were the key parameters controlling crystallisation (Joko, 1984).

Kaneko (1988) formed calcium phosphates, but using activated magnesia clinker as a seed material. The clinker was treated with a calcium chloride solution to provide a source of calcium for crystallisation, however, the clinker needed regeneration twice a year (Kaneko, 1988).

In 1988, the first full-scale (160,000 PE) fluidised-bed reactor became operational in the Netherlands (Eggers et al, 1991). The Crystalactor® produces a small amount of calcium phosphate granules which can be reused. Lime is dosed to raise the pH (Eggers et al, 1991). Work was undertaken by Battistoni (1997) to carry out struvite crystallisation without chemical use at all. Quartz sand was the seed material, providing sites for nucleation of struvite crystals within the FBR (Battistoni et al, 1997). Struvite was successfully formed without chemical addition from real digested sludge supernatant (Table 2.10.). The key parameter influencing struvite formation was pH. Simply by raising pH using aeration, scale formed within the supernatant, it was concluded that "continuous external aeration represents the best operative condition for reducing the crystallisation time" (Battistoni et al, 1997).

Table 2.10. Physio-chemical characteristics of the digested sludge supernatant (Battistoni, 1997).

Determinand	Value in supernatent
Initial pH	7.3
Orthophosphate, mg/l	18
Magnesium, mg/l	53
Calcium, mg/l	184
Ammonium, mg/l	220
Alkalinity, mg/l as $CaCO_3$	1,430

Further work by Battistoni (1998) found phosphate removal efficiency to be related to pH and sand contact time. The addition of calcium or magnesium was not necessary for crystallisation, only to influence the most prevalent scale. For example, both struvite and calcium phosphate will form in the liquor so the dosing of either calcium or magnesium will determine the most prevalent crystal (Battistoni *et al.*, 1998).

2.3. Sludge digestion

2.3.1. Introduction

A sludge treatment and disposal system is selected with the aim of reducing any detrimental effect on the environment and maximising any potential benefit the sludge may hold. These points have to be achieved at an acceptable cost. The purpose of sludge treatment is to produce a sludge suitable for disposal via the available routes and to minimise the disposal cost. Treatment may be carried out specifically to achieve one or more of the following aims:

- produce a less offensive sludge and reduce any potential health hazard the sludge may pose (achievable via anaerobic digestion or lime conditioning)

- produce a reduced pathogen level sludge, suitable for use in agriculture (via anaerobic digestion)

- produce a reduced volume of sludge to reduce the cost of transportation and disposal, or to reduce the volume prior to further treatment

- alter the nature of the sludge to enhance the dewatering properties (via conditioning, although anaerobic digestion is the most widely used method of sludge stabilisation, it doesn't tend to improve the dewatering properties of sludge (IWPC, 1981).)

The cost of sludge disposal is ever increasing, therefore water companies endeavour to produce less and less sludge from their works. This is done using various treatments that fall into the categories of thickening and dewatering. One method is sludge digestion, which can be operated under aerobic or anaerobic conditions.

2.3.2. Aerobic digestion

In conventional aerobic digestion the sludge is aerated, however the sludge can alternatively be oxygenated. The latter providing increased volatile solids reduction, but a corresponding increase in cost (Metcalf and Eddy, 1991). The aerobic conditions support the growth of bacteria which breakdown the organic constituents in the sludge, resulting in reduced levels of solids, improved filterability and a reduction in unpleasant odours (IWPC, 1979). The bacteria, fungi and some protozoa, only remove a proportion of the biodegradable fraction of the sludge. The organic matter is converted to carbon dioxide (CO_2), water and simple salts.

The process can also be operated at above ambient temperatures, using thermophilic bacteria. Thermophilic systems are capable of high reaction and growth rates, and can achieve up to 80% removal of the biodegradable fraction (Metcalf and Eddy, 1991). This enables use of a smaller vessel and shorter sludge retention times.

2.3.3. Anaerobic digestion

Anaerobic conditions can occur within an aerobic digester if an aerator ceases to function or if inadequate stirring allows the sludge to stand and become stagnant. Anaerobic digestion can occur because some aerobic micro-organisms are capable of facultative respiration, they are the facultative anaerobes (IWPC, 1979).

In the United Kingdom (UK), anaerobic digestion is most commonly operated as a suspended-growth, completely-mixed process, though many reactor configurations exist. Reactors are sealed to prevent the entry of air, but are fitted with valves to allow release of the methane gas produced during the degradation process. The dry solids level in a typical feed sludge was found to be 3.6 %, and digested 1.7 % (Mamais, 1994). The sludge retention time within the vessels is long, ranging between 30 and 60 days (Metcalf and Eddy, 1991). The process involves the decomposition of both organic and inorganic matter.

Digestion is carried out by anaerobic bacteria which breakdown around 40 % of the components in the sludge to the end products of carbon dioxide (CO_2) and methane (CH_4)(IWPC, 1978). The breakdown occurs in three distinct stages:

- hydrolysis
- non-methanogenesis
- methanogenesis.

2.3.3.1. Hydrolysis

The components in the sludge, proteins, polysaccharides and lipids (fats) are too large to pass through the cell membranes of the micro-organisms. Therefore before uptake can occur, these components have to be broken-down. This is done by extra cellular hydrolytic enzymes released by the bacteria. Components are hydrolysed to the simple building blocks they are composed of; proteins to amino-acids, polysaccharides to monosaccharides (simple sugars) and lipids to glycerol and long chain fatty acids. These molecules are then free to pass into the bacterial cells.

2.3.3.2. Non-methanogenesis

Metabolic pathways within the cell allow conversion of the molecules from the sludge to acid (also known as acid forming stage). This conversion is also accompanied by an increase in the biosynthesis of bacterial biomass. This stage is carried out by the facultative anaerobes, but mainly by the obligate (strictly anaerobic) anaerobes (IWPC, 1979).

2.3.3.3. Methanogenesis

The final stage involves the conversion of acid formed during non-methanogenesis into the end-products of anaerobic digestion, carbon dioxide and methane. This stage proceeds solely due to the obligate anaerobes, and again biosynthesis of bacterial biomass occurs (IWPC, 1979). As for aerobic digestion, the process can be operated mesophilically at temperatures of 30-38 °C or thermophilically at 49-57 °C (Metcalf and Eddy, 1991, Noone, 1982).

2.3.3.4. The Effect of Anaerobic Digestion on Scale Forming Elements

The action of digestion affects insoluble nitrogenous compounds within the sludge; they are partially degraded and the released ammonia is then a soluble source of nitrogen. This is also the case for phosphorus. A proportion of the phosphorus taken up by micro-organisms with be released (Jardin and Popel, 1996). Carliell and Wheatley (1997) noted that digestion of sludge dosed with ferric sulphate for chemical phosphorus removal did not increase the soluble phosphorus (orthophosphate) levels in the digested sludge liquors. The phosphorus was retained as inorganic phosphorus in the sludge. However, digestion of sludge produced during biological phosphorus removal produced an increase in soluble and water extractable phosphorus when compared to a control digester receiving domestic sewage alone (Carliell and Wheatley, 1997).

2.4. Scale

2.4.1. Introduction

"Scaling refers to the formation of hard deposits, usually on hot surfaces, which reduce the efficiency of heat exchange" (Metcalf and Eddy, 1991). The most common example being lime scale or calcium carbonate build up. Many types of scale exist, including calcium phosphates, particularly hydroxyapatite (Battistoni *et al*, 1998) and to a lesser extent calcium hydrogen phosphate and β-Tricalcium phosphate (Popel and Jardin, 1993). A widely reported scale, causing problems all over the world is magnesium ammonium phosphate, or struvite (Horenstien *et al*, 1990). (Table 2.11.).

Table 2.11. Different types of scale and their properties.

Scale	**Chemical formula**	**Solubility product**	**Comments**
Struvite	$MgNH_4PO_4.6H_2O$	12.36 13.26	Buchanan *et. al.* 1994 Ohlinger *et. al.* 1998
Hydroxyapatite	$Ca_5(PO_4)3OH$	55.9	Popel and Jardin, 1993 Slow growing crystals, can form as any of three types with hydroxyl, fluorine or chlorine dominating.
Calcium carbonate	$CaCO_3$		Angel, 1999 Three different polymorphs: calcite, aragonite and vaterite Franke and Mersmann, 1994
Calcium hydrogen phosphate	$CaHPO_4$	6.5	Greaves et al, 1999
Flour-apatite	$Ca_5(PO_4)3F$	60.4	Greaves et al, 1999
Octacalcium phosphate	$Ca_4H(PO_4)3$	46.9	Greaves et al, 1999
β-Tricalcium phosphate	β-Ca3(PO4)2	26	Greaves et al, 1999

2.4.2. Scale in Industry

Scale is a growing problem in many industries, including pig farming (Webb and Ho, 1992), wine distillation (Loewenthal *et al.*, 1994) and the wastewater treatment industry (Buchanan *et al.*, 1994).

The waste and wastewater produced by a western Australian piggery was treated very simply using a system of 4 lagoons (Webb and Ho, 1992). However when the water from the final lagoon was diverted for irrigation purposes, the new pipeline began to block up. The blockage was caused by a build-up of the scale struvite and residual organic material. The outfall from the final lagoon was found to be pH 7.8, above the critical pH for struvite formation as predicted by the computer model used in this study (Figure 1.5.)

Similarly, the waste from wine distilleries when treated anaerobically has a high potential for struvite formation. This is due to the high levels of the constituents of struvite, that is, orthophosphates, ammonia and magnesium ions found in these two types of waste water (Loewenthal et al., 1994).

During anaerobic digestion a proportion of ammonium, magnesium and phosphate bound within the sludge will be released (Jardin and Popel 1996). Digester supernatant is commonly high in ammonium (Nyberg et al, 1993). When levels of these three components rise above the level of saturation, struvite can begin to form on pipes, pumps and fittings succeeding the digester (Ohlinger *et al*, 1998, Maqueda *et al*, 1993).

Many operational problems in sewage works have been reported as a result from a build-up of scale on equipment (Loewenthal et al., 1994). Most commonly pumps and pipes (Williams, 1999) but also within digesters (Borgerding, 1972) and on dewatering machinery (Horanstein et al., 1990). The hydraulic capacity of a works can be reduced dramatically by scale deposits (Buchanan *et al.*, 1994). The replacement or cleaning of pipes is also very costly, both in time and money (Mohajit et al, 1989).

2.4.3. Struvite

Struvite is a metal salt of the metal ammonium phosphate species, containing a single magnesium ion (Bridger *et al*, 1962), and is the best known of this type of salt (Booker *et al.*, 1998). Struvite has been found in many areas of nature, peat beds and soils, organic-rich sediments, guano deposits and basalt, diatomite and phosphorus caves (Abbona and Boistelle, 1978). Struvite is also common in medical terms too as it is known to form in urinary tracts and as 'stones' in human and animal kidneys, intestine and even lungs (Abbona and Boistelle, 1978).

Ammonium, phosphate and magnesium are all present in wastewater, so the formation of struvite is a widespread occurrence. The white scale is incredibly hard, described as "too tough to break up" by Borderding (1972) when attempting to clear pipelines.

Composed of around 50% water, the values in the literature for the other components of struvite are very similar for magnesium and nitrogen, though do differ considerably for phosphorus and consequently, water (Table 2.12.).

Table 2.12. Composition of struvite and reference.

Magnesium, %	Orthophosphate, %	Nitrogen, %	Water, %	Reference
10	29	6	55	Bridger *et al*, 1962
9.9	12.7	7.34	70.06	Taylor *et al.*, 1963 (experimental)
9.91	12.62	7.35	70.12	Taylor *et al.*, 1963 (theoretical)
9.8	38.8	7.3	44.1 (water and organic compounds)	Borderding, 1972 (theoretical)
12.3	33.5	5.7	42.8	Borderding, 1972 (experimental)
10	35.1	4.9	33.2 (water) 8.4 (Ca,Na,Cl)	Liberti et al, 1986

2.4.4. Calcite

Calcium carbonate has three polymorphic forms: vaterite, aragonite and calcite (Franke and Mersmann, 1995). Impurities can have an effect upon crystal nucleation and can determine the appearance of these three different forms (Meyer, 1984). Calcite is the thermodynamicallystable polymoph (van Langerak et al, 1999).

Calcite precipitation is a significant problem for the waste paper industry as there tends to be high calcium levels in the waste streams. This is often exerbated by closed loops for wastewater reuse within the paper mill (Habets and Knelissen, 1997).

2.4.5. Formation mechanism.

Formation of scale is based upon chemical equilibrium within the sludge. The extent of supersaturation within the water is the driving force for crystallisation to occur (van Langerak, 1999). A water solution can be saturated with a maximum amount of solute, beyond this point the solution becomes supersaturated (Chang, 1994). Supersaturated solutions are very unstable and the addition of a small 'seed crystal' leads to rapid crystallisation of the excess solute (Chang, 1994). A precipitate will not form in a supersaturated solution spontaneously; precipitation first requires nucleation, which may then be followed by the growth of a crystal (Ohlinger *et. al.*, 1999). Donnert (1999) developed a means of phosphorus removal from wastewater "which involves a direct precipitation of calcium phosphate induced by calcite as the seeding material (Donnert and Salecker, 1999).

2.4.5.1. Induction period

Nucleation occurs during the "induction period" (Franke and Mersmann, 1995) and is expected to be via a heterogeneous mechanism. Homogeneous nucleation only occurs in pure solutions and so is very unlikely during wastewater treatment (Ohlinger *et. al.*, 1999). The charged ions in solution will be associated with water molecules and these have to be displaced for an ion pair to form (Gunn, 1976). The force of attraction between the scale molecules has to be greater than that of the water molecules. The ion pairs then begin to associate with other free ions in solution and a crystal lattice forms (Ohlinger *et. al.*, 1999). Gunn (1976) noted that "this theory of precipitation by preliminary ion association provides a satisfactory explanation for the kinetics of growth of slightly soluble precipitates in aqueous solutions for ... magnesium ammonium phosphate".

2.4.5.2. Growth period

The crystals may form aggregates and once formed, struvite is highly insoluble (pKsp 12.36-13.26) (Buchanan *et. al.* 1994a, Ohlinger *et. al.* 1998).

High turbulence has been highlighted as a possible trigger to struvite formation. This is due to the production of areas of low pressure and the corresponding release of CO_2. The reduction in partial pressure of CO_2 causes a pH change and a corresponding change in the potential to form struvite (Loewenthal 1994). However more recent work by Ohlinger suggests that "Evaluation of the effect of pH change resulting from CO_2 evolution in high turbulence areas showed that it had a minor influence on the [struvite] crystal growth rate" (Ohlinger, 1994).

2.4.6. Problems associated with scale formation

Struvite and other scale formation in anaerobic digesters, pipework and any succeeding downstream processes is a significant problem. It has been reported that pipes at several sewage treatment works have to be frequently replaced, whilst others are pressure jet cleaned on a monthly basis to relieve the build up of struvite on the inside. The struvite can build up to such an extent that an 8 inch-diameter pipe is reduced to only 2 or 3 inches within a six-month period.

A similar problem is faced by Thames Water at a new activated sludge plant. Pipework immediately after the digested sludge holding tank was reduced from 100 mm in diameter down to 50 mm. This problem is being overcome in the short term by dissolving the struvite inside the pipe in 10% sulphuric acid. The use of magnetic softening devices are currently being evaluated as a long-term method of preventing struvite formation (Williams1999).

Struvite also poses a problem in livestock waste management where systems have been developed with acid injection networks. The acid dissolves any scale forming on the pipework or equipment within the system. The inconvenience and hazards involved with the acid-injection system prompted work by Buchanan *et al. al.* on the possibilities of injecting anti-scalants into the waste management system instead (Buchanan *et. al.* 1994).

Scale formation can result in long periods of downtime, a reduction in the hydraulic capacity of a works and often increased pumping costs as the internal diameter of pipes reduces.

2.4.7. Control mechanisms

Dilution of flow with secondary effluent at Hyperion, Los Angeles (to prevent supersaturation and limited pH drops at areas of high turbulence), aerobic treatment of some of the flow and increase of velocity to 'scour' lines (Borderding, 1972). PVC pipes were found to be better than cast iron, glass fibre reinforced plastic and Techite (Borderding, 1972). All is working well and no future problems are anticipated.

Ion exchange can be used to remove calcium and magnesium and therefore reduce the scaling propensity of the wastewater, however the expense involved with such measures means that they are rarely used (Metcalf and Eddy, 1991).

2.4.8. Benefits and Recovery

The high level of phosphorous and nitrogen present in struvite make its recovery for fertilisers feasible. Studies have shown that struvite has excellent agronomic properties. Struvite was found to be an effective source of all three of its components (NH_3, Mg and P) for plants, even though its solubility in water and soil solutions is slight (Booker *et. al.* 1998). This work considers the formation of struvite, specifically for this purpose and concludes that "despite such attractive agronomic properties, struvite is not widely used in the fertiliser industry, the main reason appearing to be its high cost of production from the raw chemicals". This cost could be written off if naturally occurring struvite in wastewater treatment plants could be utilised. However the recovery of struvite from a treatment works not specifically designed for this purpose would be virtually impossible, remembering that the method employed by Thames Water to remove struvite involved dissolving the scale in acid. As struvite has already been outlined as a useful substance (Booker *et. al.* 1998) it would be beneficial if the potential of the struvite forming in the

Severn Trent region could be harnessed. Research has shown that struvite can be encouraged to form in beneficial places (Maquada, 1994). The introduction of a seed material into the wastewater can form a nucleation site for crystal formation.

For example, a cylindrical reactor (The Crystalactor®) has been developed which 'grows' struvite crystal on a sand or mineral seed material. Pellets of approximately 1 mm in size are produced, which can easily be filtered out of solution (Giesen, 1999). Earlier work by Rodriguez (1992) "studies the influence of clay minerals used as supports in anaerobic digester on the precipitation of ammonium magnesium phosphate [struvite]". This technique is based on the fact that the cation in the clay is magnesium, providing a source of magnesium, allowing struvite to form. The use of supports such as stevencite, showed precipitation of calcium ammonium phosphate (Rodriguez, 1992).

If scale formation were desirable in a designated area, crystal growth can be enhanced in several ways:

- Non-agitation of the sludge
- Insertion of rough areas for crystal growth, such as joints
- A vibration passing through the sludge
- Pressure reduction to evolve CO_2, at bends or venturies (Borderding, 1972).

All of these removal methods may only be of real use for new works as the modification of older works to accommodate new systems is costly. However when the cost of constant replacement of pipework or acid jet washing and the corresponding downtime is taken into account, as well as the increased pumping costs and reduced hydraulic capacity, these measures may seem favourable.

3. Aims and objectives

3.1. Aims

The aim of this project is to assess the ionic balances of digested sludge liquors with respect to scale formation potential. This involved a six-week sampling regime at seven sites with anaerobic digesters and numerous lab-scale experiments. A computer model was used to predict the scale forming potential of sludge liquors and also centrate, where possible.

The project aims to be able to highlight sites which either have a slight, as yet undetected, scale problem or identify those which may encounter problems in the near future.

3.2. Objectives

- Sample seven sites and analyse for key scale forming elements.
- Use computer model to identify scale forming potential of liquors.
- Confirm those sites which currently experience scale formation, identify 'at risk' and 'low risk' sites.
- Use laboratory scale tests to confirm models predictions.
- Suggest possible remedial measures, both for the short and long-term.

4. Materials and Methods

4.1. Sampling procedure

4.1.1. Main sampling regime

All six sewage treatment works have anaerobic digesters. Samples were taken each week over a six-week period. The feed sludge to the digesters and the digested sludge were sampled, 500 ml samples were collected in sludge pots.
Two litres of centrate and/or liquor samples were collected into 1 l plastic bottles.

Barston STW

Feed sludge was collected in a 500 ml sludge pot. The sludge was diverted away from the digester into a sump, where a sample was taken using a sampling can (steel 1 l can on a length of rope). To ensure a representative sample was collected, the sludge was allowed to flow for long enough to clear the line of any debris or stale sludge. This was the case at all sites where samples were taken from similar points. Feed was then redirected back to the digesters.

Digested sludge was drained off from the very base of the digester. Two digesters are in operation and samples were taken from each one and combined in a 500 ml sludge pot.

There is no dewatering at Barston, and the digested sludge is settled in four secondary digesters or pathogen-kill tanks. These tanks allow settlement of the sludge, producing a thicker sludge and a top water. The top water is returned to the head of works and the sludge is tankered to land. Samples were taken with a sampling can from the surface of the fullest (and therefore the most settled) tank. Two litres of top water was collected.

Coleshill SDP

Coleshill SDP receives post-digested sludge as well as digested sludge liquors. For this reason only digested sludge was sampled. Centrifuge cake was sampled on three occasions.

The digested sludge was sampled from a direct sampling point in the line from the sludge balancing tank.

Centrifuges are in operation on-site allowing both centrate and cake samples to be taken. Centrate samples were taken from the centrate well, a sump where the centrate collects before being mixed with condensate from the incinerators and pumped back to Minworth STW. Cake was collected from a holding tank. Samples were taken from a sampling point near the base of this tank. A sample of approximately 500 ml in volume was collected into a sludge pot.

Samples were also taken of the return to Minworth prior to mixing with the incinerator liquor. These samples were collected from the temporary over ground pipe which bypasses the lamella clarifiers. This was purely for comparative purposes with the centrate sampled entering the well.

Mansfield STW

Feed sludge was sampled from the line to the digesters, at a fixed sampling point. Digested sludge was collected from a similar sampling point on the heat exchange unit (Sludge is digested at around 35 °C (Noone, 1982)).

Centrate was collected from the line taking centrate directly from the centrifuge. Again 2 l were collected.

Milcote STW

The feed sludge was taken from a sampling point in the line to the digesters and digested was taken from sampling points on the heat exchanger. Two digesters are in operation so samples were taken from both heat exchangers and mixed.

There are no centrifuges on site so top water was collected, using a sampling can, from the top of the tanks. Samples were taken from the surface of the fullest (and therefore the most settled) tank.

Oswestry STW

Primary sludge was collected from a sampling point in the feed line to the single digester.

It was necessary to sample surplus activated sludge (SAS) as well, to get a representitve sludge sample, as this is mixed with the primary sludge prior to digestion. SAS was sampled from the belt thickener, 500 ml was collected in a sludge pot.

Digested sludge was sampled from the overflow on the top of the digester.

It was not viable to sample the sludge liquors directly from the pathogen kill tanks, therefore samples were taken from the outlet into a sump, after the line had been flushed through with top water.

Spernal STW

The feed sludge was taken from a sampling point in the line to the digesters and digested was taken from sampling points on the heat exchanger.

Centrate was collected from a sampling point in the line directly from the centrifuge. Two centrifuges were present, running alternately.

Wanlip STW

Feed sludge was collected using a sampling can from a sump where sludge was drawn off into the four digesters. Digested sludge, as at Redditch, was sampled from only two of the four digesters before mixing. Sampling points were positioned on the outlet pipe from each digester.

Top water was collected as it drained from the settlement tanks (figure 4.1.)

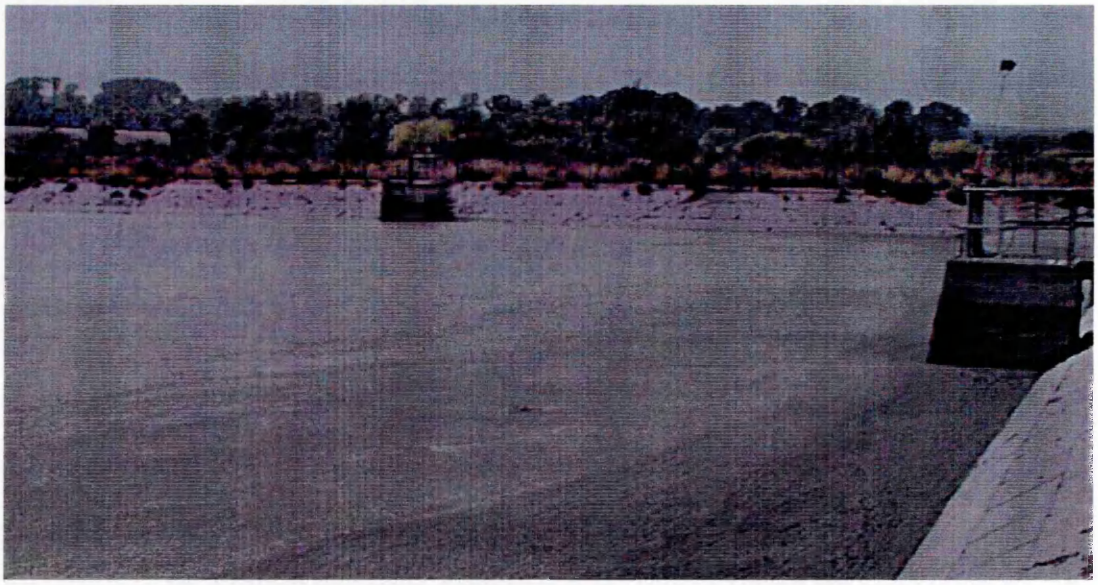


Fig 4.1. Settlement tanks for digested sludge at Wanlip STW.

Centrate was also sampled on few occasions. This was collected from a sump which couldn't be opened single-handedlyand so required the help of operators on site.

4.1.2. Preparation of liquor samples

A minimum of two 1 litre samples were taken on site of liquor and/or centrate. The pH was recorded immediately and then adjusted using 1M HCl. The pH must be kept below

7 to minimise struvite formation and below 6.5 for calcite. The amount of acid added varied with site, initial pH and condition of sample i.e. liquor or centrate and suspended solids levels, though was approximately 2 - 3 ml. Regular calibration of the pH meter was carried out using standard solutions of pH 4 and pH 7.

Once returned to the laboratory, one sample was filtered or centrifuged depending on the settleability of the solids. One remained unfiltered to allow for alkalinity analysis. The centrifuge used was a WIFUG, LABOR 50, and the samples were run at 4,500 rpm. The filtered samples were analysed for:

- ammonia
- magnesium
- calcium
- orthophosphate
- Total dissolved solids
- iron/aluminium if dosed on site

These determinands were chosen to enable the use of a computer model (Loewenthal, 1997) which predicts struvite and calcite precipitation potentials of samples.

4.2. Procedure for Laboratory-scale Experiments

4.2.1. pH Elevation

The experiment was carried out using samples from Wanlip and Barston (sites with and without an existing centrifuge, respectively).

At least 3 l of the top water was collected from each site and the pH recorded. pH adjustment was done using 1 % Nitric acid, to below 6.5. In the laboratory the samples were centrifuged to remove any larger suspended solids. 300 ml of the centrate was aerated in a beaker using an air stone. The air stone was connected to a small pump. The pH was recorded every minute until an equilibrium was reached. This was repeated three times for each site with fresh centrate.

4.2.2. Scale Formation Experiment

This experiment was carried out using centrate from Coleshill and Mansfield. Five litre samples were collected from each site and the pH recorded and adjusted to below pH 6.5 on site. This involved a reduction of around 1.5 pH units. In the laboratory, the samples were filtered to remove large suspended solids.

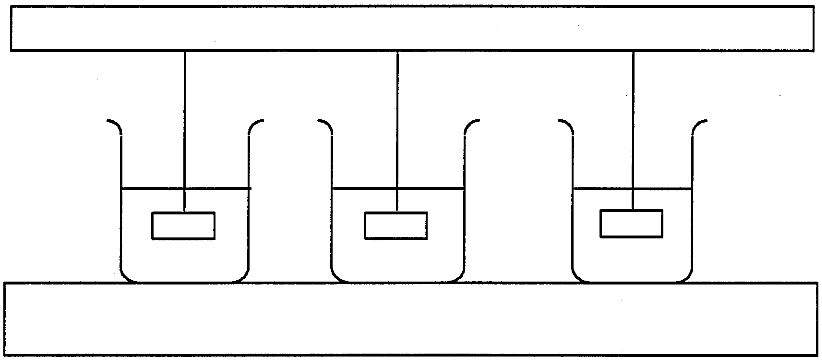


Figure 4.2. Schematic of flocculator and sample set-up.

Four 2 l beakers were each filled with 500 ml of centrate. The paddles were lowered fully into the sample and rapid mixing (250 rpm) occured for 20 minutes (figure 4.2.). The pH of three samples was raised to over pH 8 using Sodium hydroxide, and the mixing speed reduced to 25 rpm. A control was set up with no pH adjustment at all, the pH was recorded throughout.

After 30 minutes of slow mixing, the paddles were switched off and the samples left to stand for 10 minutes. The liquid was then filtered using a vacuum filter and Whatmann filter papers. The liquid samples, along with the control were sent to Severn Trent laboratories (STL) for analysis of the standard determinands reported in this study.

4.3. Sample Analysis

Analysis was carried out by Severn Trent Laboratories (STL) as per the Methods for the Examination of Waters and Associated Materials 1976 - 1992, HMSO, London.

4.3.1. Sludge analysis

- **Total dry solids**

  The conditionability, filterability, settleability and solids content of sludge, 1984. A compendium of methods and tests. Book 83, p 6.
- **Calcium**

  Methods for the determination of metals in soils, sediments, and sewage sludge, and plants by hydrochloric-nitric acid digestion, with a note on the determination of insoluble metal contents, 1986. Book 93, p 20.
- **Magnesium**

  Methods for the determination of metals in soils, sediments, and sewage sludge, and plants by hydrochloric-nitric acid digestion, with a note on the determination of insoluble metal contents, 1986. Book 93, p 20.
- **Iron**

  Methods for the determination of metals in soils, sediments, and sewage sludge, and plants by hydrochloric-nitric acid digestion, with a note on the determination of insoluble metal contents, 1986. Book 93, p 20.

- **Aluminium**

  Methods for the determination of metals in soils, sediments, and sewage sludge, and plants by hydrochloric-nitric acid digestion, with a note on the determination of insoluble metal contents, 1986. Book 93, p 20.

4.3.2. Liquid analysis

- **Total dissolved solids**

  Suspended, settleable and total dissolved solids in waters and effluents, 1980. Book 105, p 25.

- **Alkalinity**

  The determination of alkalinity and acidity in water, 1981. Book 44, p 10.
- **Ammonia**

  Ammonia in waters, 1981. Book 48
- **Aluminium**

  Emission spectrophotometric multielement methods of analysis for waters, sediments and other materials of interest to the water industry, 1980. Book 1, p 6.
- **Calcium**

  Emission spectrophotometric multielement methods of analysis for waters, sediments and other materials of interest to the water industry, 1980. Book 1, p 6.
- **Magnesium**

  Magnesium in waters and sewage effluents by atomic absorption spectrophotometry, 1977. Book 8, p 4.
- **Orthophosphate**

  The determination of anions and cations, transition metals, other complex ions and organic acids and bases in water by chromatography, 1990. Book 140, p 123.
- **Iron (filtered)**

  Iron in raw and potable waters by spectrophotometry (using 2,4,6 - tripyridal _ 1,3,5 - triazine), 1977. Book 11, p 4.

5. Results

5.1. Sludge data

5.1.1. Barston

Barston had a fairly varied feed sludge to the two digesters on site. The range in dry solids was the greatest of all the sites. The calcium levels vary by over 2,000 mg/l, whereas the difference in magnesium was only 100 mg/l.

The site uses iron dosing for chemical phosphorus removal. The iron levels in the feed were very variable, ranging from nearly 3,000 mg/l to over 10,000 mg/l.

Table 5.1. Composition of Barston feed sludge

	Minimum	Maximum	**Average**
% Dry solids	5.7	11.1	**8.7**
Calcium, mg/l	1,112	3,265	**1,795**
Magnesium, mg/l	164	263	**205**
Iron, mg/l	2,930	10,111	**7,022**

The dry solids in the digested sludge is fairly constant, being more stable than the feed sludge. The range between minimum and maximum values is only 1.5 %. The difference between the two average concentrations is exactly 5 %.

The average calcium level for digested sludge was generally lower than that of feed by 500 mg/l, however this was not always the case. The digested sludge calcium levels have a 5-fold variability. This is due to one, unusually low result of under 600 mg/l. All other results were above or close to 1000 mg/l.

The magnesium levels in the digested sludge are much more variable than those in feed, with a range of nearly 300 mg/l between minimum and maximum values. The average, like calcium, was lower in digested sludge.

The average iron concentration was also lower in digested sludge, on average over 4,000 mg/l lower. Again, not all of the digested sludge levels were lower than feed across the six samples.

Table 5.2. Composition of Barston digested sludge

	Minimum	Maximum	Average
% Dry solids	2.8	4.4	**3.7**
Calcium, mg/l	574	2,610	**1,301**
Magnesium, mg/l	79	345	**171**
Iron, mg/l	875	5,117	**2,884**

The variability seen in dry solids and calcium in the feed sludge may be due to the sludge imported to Barston. Variations in the weekly imports are to be expected, as there may not be imports from the same source every week.

The iron levels in the digested sludge are lower than those in the feed. This could be due to the binding of iron within the digester by phosphorus released during the digestion process (Carliell and Wheatley, 1997). No conclusions can really be drawn due to the variability of the iron levels in general, across both feed and digested. Also the long retention time in the digester makes direct comparison of weekly samples impossible (30 - 60 days (Metcalf and Eddy, 1991)).

5.1.2. Coleshill

The sludge destruction plant (SDP) at Coleshill receives digested sludge from Minworth sewage treatment works. For this reason, no data for feed sludge is given.

The dry solids level in the digested sludge is consistent, ranging over 1.2 % only.

Calcium levels are also consistent, with a range of 300 mg/l, compared with the range of over 2,000 mg/l found at Barston. Magnesium is similarlystable.

Table 5.3. Composition of Coleshill digested sludge

	Minimum	Maximum	Average
% Dry solids	3.2	4.4	**3.5**
Calcium, mg/l	1,080	1,379	**1,193**
Magnesium, mg/l	146	177	**163**

The calcium and magnesium results are quoted as g/kg, not mg/l because of the solid form of the cake.

All data for the centrifuge cake is variable, except dry solids. Dry solids are incredibly static, ranging over only 1 %. However the variability of the calcium and magnesium levels is hard to analyse because only three samples were taken over the six-week sampling period, therefore the results must be treated cautiously because an erroneous result would have a more significant effect upon this small data set.

The maximum calcium and aluminium levels in the cake are double the minimum values, giving a large range of results. As only three samples were taken of centrifuge cake, the results must be treated cautiously. The effect of an erroneous result will be much greater on this small data set.

Table 5.4. Composition of Coleshill centrifuge cake

	Minimum	Maximum	**Average**
% Dry solids	21.2	22.2	**21.7**
Calcium, g/kg	37.6	97.8	**61.2**
Magnesium, g/kg	4.7	7.3	**5.7**

The components of the digested sludge, dry solids, calcium and magnesium, are all very stable across the six samples. This wasn't expected as Coleshill receives solely imported sludge. The site is a sludge destruction plant and therefore has no indigenous sludge. The regularity of imports may account for the varied results.

5.1.3. Mansfield

Mansfield has the most consistent feed dry solids level of all sites, with a range between maximum and minimum values of less than 1 %.

Both calcium and magnesium levels are fairly stable, ranging under 200 mg/l and 60 mg/l respectively.

Table 5.5. Composition of Mansfield feed sludge

	Minimum	Maximum	**Average**
% Dry solids	2.9	3.8	**3.5**
Calcium, mg/l	832	1,112	**952**
Magnesium, mg/l	177	237	**195**

Despite the consistent dry solids content of the feed at Mansfield, the digested sludge is actually one of the most variable, even though it only has a range between minimum and maximum values of 1.9 %.

The calcium and magnesium levels of the digested sludge are as consistent as the feed, with very similar levels being recorded.

Table 5.6. Composition of Mansfield digested sludge

	Minimum	Maximum	**Average**
% Dry solids	1.1	3	**2.2**
Calcium, mg/l	947	1,100	**1,017**
Magnesium, mg/l	186	244	**214**

The dry solids, calcium and magnesium levels in both feed and digested sludges are very consistent. This may be due to the lack of sludge imports and therefore digestion of indigenous sludge alone.

5.1.4. Milcote

The feed into the two digesters at Milcote is variable, ranging over more than 2 %. Calcium and magnesium levels are similar to Mansfield, that is, stable across the six week sampling period.

Aluminium is also measured because at Milcote, two-thirds of the settled sewage is dosed with alum for chemical phosphorus removal.

Table5.7. Composition of Milcote feed sludge

	Minimum	Maximum	Average
% Dry solids	2.8	5.1	**4.1**
Calcium, mg/l	809	1,127	**963**
Magnesium, mg/l	88	138	**114**
Aluminium(total), mg/l	739	1,647	**1,250**

The digested sludge is fairly consistent, considering the variability of the feed concentrations. The average calcium level in the sludge is similar to the feed, however the results over the six weeks have a range of over 1,000 mg/l. The magnesium is also very variable, the second most variable of all the sites, after Spernal.

The aluminium content of the sludge is higher than the calcium, and is fairly inconsistent, ranging 2,500 mg/l. Not all six samples were analysed for aluminium and therefore the range may be misleading as the few samples taken could be erroneous.

Table 5.8. Composition of Milcote digested sludge

	Minimum	Maximum	**Average**
% Dry solids	1.8	2.9	**2.3**
Calcium, mg/l	740	2,000	**1,100**
Magnesium, mg/l	95	350	**181**
Aluminium(total), mg/l	774	3,388	**1,724**

The dry solids of the feed at Milcote is very variable, though the digested sludge is fairly stable, suggesting that the digester is running well.

Aluminium levels were measured in the sludge because alum is dosed into two-thirds of the flow at Milcote for chemical phosphorus removal. As the only site in the study with aluminium dosing, it is impossible to draw any parallels with the other six sites.

5.1.5. Oswestry

The feed to the single digester at Oswestry was variable for all determinands. The dry solids content rose and fell quite dramatically over the sampling period, beginning at 2.2 % and rising up to 7.6 %, before dropping to 4.8 %.

The calcium levels within the feed were very consistent until the end of the study, when the level rose by nearly 2,000 mg/l. The magnesium ranges over 100 mg/l, in a similar way to Barston.

Table 5.9. Composition of Oswestry primary sludge

	Minimum	Maximum	**Average**
% Dry solids	2.2	7.6	**5.8**
Calcium, mg/l	724	2,789	**1,220**
Magnesium, mg/l	107	202	**158**

The indigenous primary sludge is mixed with thickened surplus activated sludge (SAS) in a 60/40 ratio respectively. This hybrid sludge is combined with imported sludge from local smaller works, before co-digestion. The dry solids level of the SAS had a range of nearly 3 %.

Table 5.10. Composition of Oswestry SAS

	Minimum	Maximum	**Average**
% Dry solids	6.8	9.4	**7.8**
Calcium, mg/l	1,519	2,008	**1,736**
Magnesium, mg/l	238	335	**285**

The digester at Oswestry consistently produces a very stable dry solids content, with a range of only 0.3 %. This is by far the most consistent digester of all those studied. The average calcium and magnesium levels are similar in all three types of sludge, but the feed and digested are far more variable than the SAS across the six samples. The range in magnesium levels in the digested sludge are huge, a massive difference of 550 mg/l was found.

Table 5.11. Composition of Oswestry digested sludge

	Minimum	Maximum	**Average**
% Dry solids	2.8	3.1	**3**
Calcium, mg/l	693	3,100	**1,380**
Magnesium, mg/l	72	620	**244**

The large range in % DS of feed sludge may be due to the imports taken at Oswestry. The volume and consistency of the imported sludge will influence that of the feed sludge. The thickened SAS ranges 6.8 % - 9.4 %; this variability may also influence the feed sludge. The single digester copes very well with the varying primary and SAS, consistently producing sludge of 2.8 % - 3.1 %.

5.1.6. Spernal

The percent dry solids of the feed to the four digesters at Spernal was very consistent (ranging 5.2 % - 5.6 %) except for one occasion in the second week of sampling. This value at 2.8 % was considerably lower than the rest. The average calcium level was the second highest of all the sites. Magnesium concentrations vary over a range of 200 mg/l, though the value of 350 mg/l seems high when compared to the second highest value of only 240 mg/l.

Analysis for iron was carried out on three occasions. This was because iron dosing is in place at Spernal for chemical phosphorus removal. The iron levels in the feed sludge are lower, on average, than at Barston (the other iron dosed site), whereas the range of values is similar for both sites.

Table 5.12. Composition of Spernal feed sludge

	Minimum	Maximum	**Average**
% Dry solids	2.8	5.6	**5**
Calcium, mg/l	1,378	2,302	**1,659**
Magnesium, mg/l	150	350	**213**
Iron, mg/l	3,030	7,155	**4,505**

The range in the dry solids content of the digested sludge is similar to that of the feed. A value of 7.7 % was given for the fourth sample. This value is 2.7 % above the next highest value.

The variations in the calcium and magnesium values are the largest of all the sites at 2,500 mg/l and 380 mg/l respectively. The iron levels in the digested sludge are also very variable. The highest value is more than twice that of the equivalent value at Barston (10,850 mg/l and 5,117 mg/l respectively).

Table 5.13. Composition of Spernal digested sludge

	Minimum	Maximum	**Average**
% Dry solids	1.8	5	**3.9**
Calcium, mg/l	463	2,957	**1,707**
Magnesium, mg/l	67	391	**243**
Iron, mg/l	1,400	10,850	**5,708**

All the feed samples were consistently averaging just above 5 % except one sample at 2.8 %. This would seem to be uncharacteristically low, and may be due to a sludge import (two-thirds of the sludge at Spernal is imported). Laboratory analysis may be incorrect, or the sample may have just been unrepresentative due to inadequate draining of the sample tap.

The digested sludge is very unstable. This may be because there are four digesters at Spernal and samples were collected from several heat exchangers and mixed. This may have lead to an unrepresentative sample being submitted for analysis.

5.1.7. Wanlip

Wanlip has a range of feed dry solids levels, but no results appear to be anomalies.

Both calcium and magnesium levels vary a little, ranging across 500 mg/l and 150 mg/l respectively.

Table 5.14. Composition of Wanlip feed sludge

	Minimum	Maximum	**Average**
% Dry solids	3.3	5.1	**4.2**
Calcium, mg/l	861	1,357	**1,062**
Magnesium, mg/l	150	336	**215**

Despite the inconsistent dry solids content of the feed at Wanlip, the digested sludge is actually one of the most stable, ranging 2.4 % - 3.7 %.

The calcium levels are more variable in the digested sludge than in the feed, ranging over 1,600 mg/l. The average calcium value of the digested sludge is higher than the average feed concentration. A direct comparison is hard to draw between the two sets of data due to the long retention time during anaerobic digestion. The average magnesium level is also higher in the digested sludge, though this is probably due to a very high anomalous result. One sample showed a magnesium level 10-fold higher than the next highest result of 228 mg/l. The sample was reanalysed and the result was confirmed.

Table 5.15. Composition of Wanlip digested sludge

	Minimum	Maximum	**Average**
% Dry solids	2.4	3.7	**2.9**
Calcium, mg/l	1,007	2,600	**1,500**
Magnesium, mg/l	192	2,358	**583**

There was little variation in the feed or digested sludges at Wanlip; this may be due to the low level of imports. Anaerobic digesters have long residence times, spanning several days, so the four large digesters on site would 'smooth-out' any inconsistencies in the feed sludge. This appears to be the case for all determinands in all samples, except the second sample (Appendix I), where the magnesium level is very high. The sample was reanalysed by the laboratory and the result confirmed, so lab error is unlikely. This anomalous result may then have been caused by contamination of the sample. A high magnesium level in the raw sewage entering the works could cause this peak, though as mentioned earlier, the long retention time within the digester lessen the impact of such an influx on the sludge.

5.2. Liquor data

The liquors and/or centrates were analysed for levels of ammonium, orthophosphate, calcium and magnesium, pH, total dissolved solids and alkalinity. The elements within the water all have varying effects upon the scale formation potential predicted by the computer model (Table 5.16.)

Table 5.16. Factors required by the computer model for determining struvite and calcite precipitation potentials (Loewenthal, 1997).

	Struvite formation potential	Calcite formation potential
pH	√	√
Ammonium	√	
Calcium		√
Orthophosphate	√	
Magnesium	√	
Total dissolved solids		√
Alkalinity	√	√

An approximation of the 'hardness' of water can be made from the levels of calcium and magnesium. Harder water has more calcium and magnesium than softer. Figure 5.17. shows the average relative 'hardness' of the liquors from the seven sites studied.

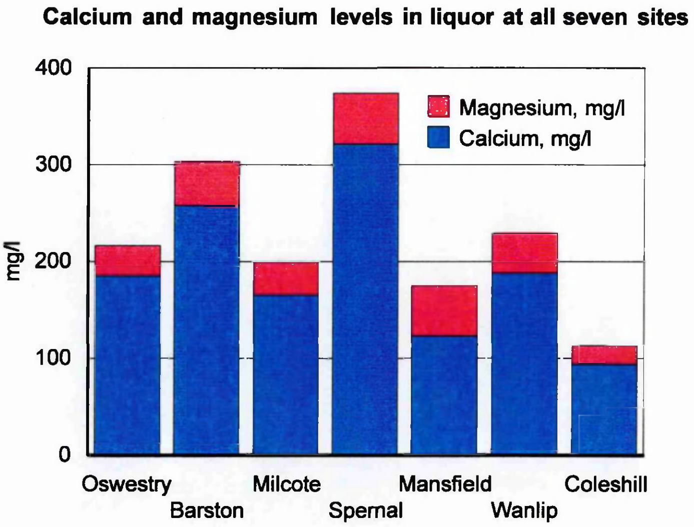


Figure 5.17. Relative hardness of the water in the region of each site, by potable water supplied.

It is clear that Barston, originally labelled 'soft' was indeed the hardest liquor, second to Spernal. These two sites were the relatively most 'hard', Coleshill was the softest, and the remaining four sites were all very similar, being slightly soft. The range of hardness levels is quite large, spanning over 250 mg/l. The lowest and highest being 113 mg/l and 374 mg/l, respectively. The central group of four sites ranged across just 30 mg/l.

Liquors were analysed over six weeks, an average result for each determinand is shown for each site (Figure 5.18.). (A full list of results appears in appendix I)

Figure 5.18. Average Determinands within Liquors, across all seven sites

	Oswestry	Barston	Milcote	Spernal	Mansfield	Wanlip	Coleshill
pH	7.2	7.6	7.5	7.6	7.9	7.7	7.9
TDS, mg/l	622	1425	1360	2323	902	918	1200
Alkalinity, mg/l	2795	2226	1883	3267	3700	3267	3382
Ammonia, mg/l	658	523	426	660	872	957	888
Calcium, mg/l	185	257	165	321	123	188	94
Magnesium, mg/l	31	46	34	53	52	41	19
Orthophosphate, mg/l	80	2	9	8	65	99	96

5.2.1. Barston

With an average pH of 7.6, Barston was one of the sites at the lower end of the pH scale. Total dissolved solids (TDS) levels were fairly variable across sites, ranging over nearly 2000 mg/l. The top water at Barston had a reasonably central TDS value of just over 1400 mg/l. Alkalinity also varied across sites over a range of around 2000 mg/l. Barston was the second lowest in alkalinity, after Milcote.

Barston also has the second lowest average ammonium level, again behind Milcote. The ammonium level across the six samples taken at Barston were all very similar, ranging over just 50 mg/l. Calcium level were found to be very high, much higher than expected. Barston was originally chosen for this project as a 'soft' water site. The high calcium level contributes most significantly to the hardness of the top water, as the magnesium is no higher than average. An average magnesium level of 46 mg/l is one of the central values across the seven sites. The orthophosphate at Barston is the lowest of all sites, nearly 100 mg/l below the average at Wanlip.

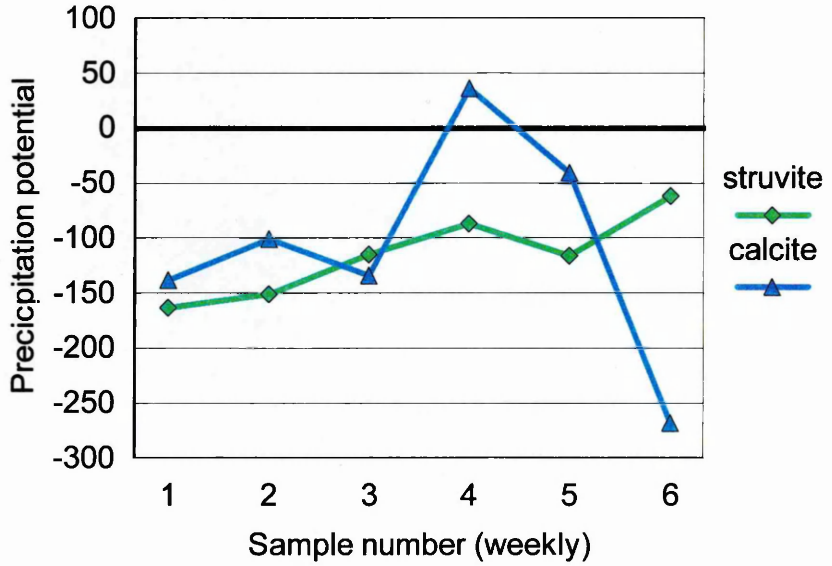


Figure 5.19. Struvite and calcite formation potnetials of the top water at Barston

The variation in struvite and calcite precipitation potential of the top water at Barston is shown (figure 5.19.). Samples taken over a six-week period were fed into a computer model (Loewenthal, 1997) to predict the scale formation potential of each sample.

The higher than expected calcium levels in the top water at Barston may be due to sludge imports. The site produces primary and secondary settled sludge, which is then mixed with imported sludge prior to on-site digestion. Local works are the main source of sludge; works often dose lime ($CaCO_3$) as a means of pH adjustment. This may account for these findings. It was thought that these high calcium levels would lead to a high potential to form calcite, this has, however, not been the case.

The results are expressed as mg/l, that is the maximum potential amount of scale, in mg, which could be formed by 1 litre of sample. As can be seen, the results for all samples were negative for struvite, and only one was positive for calcite. The positive result is fairly significant at 36 mg/l, a rise of 77 mg/l from the second highest at -41 mg/l.

All six samples were found to have a negative struvite formation potential, this would be expected with the highest orthophosphate level being only 2.7 mg/l. Borderding (1972) suggests 65 mg/l of orthophosphate as the minimum level of orthophosphate required for struvite formation. The pH may also be low enough to reduce the likelihood of struvite formation (figure 1.5.). An average of pH 7.5 may suggest this, but when all six results are considered, the pH peaks twice to above average levels; once to 7.67 and once to 7.87 (Appendix I). These peaks do appear to influence the struvite formation potential, but do not correspond to the peak in calcite potential (figure 5.20.).

The relatively invariable calcium levels cannot be the cause of the peak, and no other patterns can be seem to offer an explanation. The peak may be due to a parameter not measured within the study. It could be possible that an electrical or operational fault in the pH meter lead to the high pH recorded for the final sample. If this were an erroneous result, then pH could account for the peak in calcite potential. This brings to question, why the elevated pH of 7.87 didn't lead to a large increase in calcite precipitation potential. This may be due to the low alkalinity of only 454 mg/l. The value of 454 mg/l was substituted for a more average value of 2500 mg/l to observe the effect this would have on the prediction. The struvite potential decreased by only 3 mg/l to -65 mg/l, but the calcite potential increased from -268 mg/l up to a huge 174 mg/l. This would seem appropriate as this sample had the highest pH.

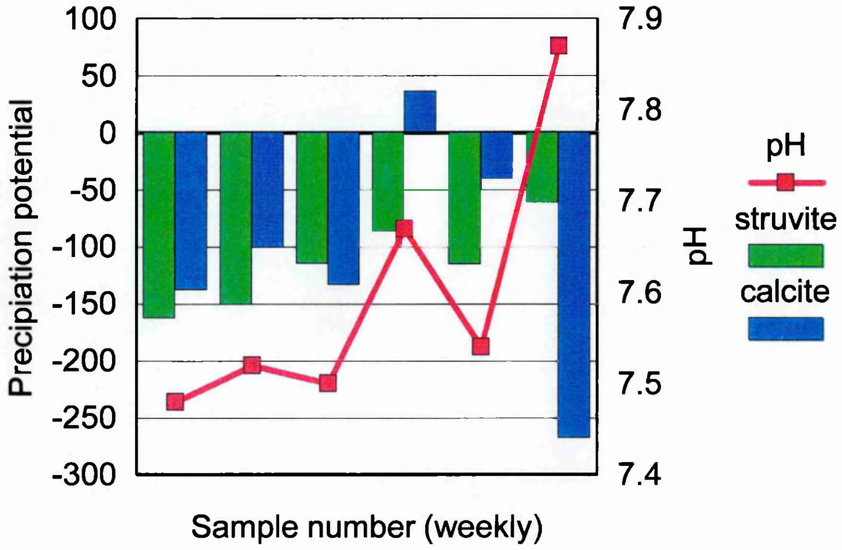


Figure 5.20. Struvite and calcite formation potentials of the top water at Barston over the six-week sampling period, with top water pH.

There is no known scale problem at Barston, however the consistently high calcium levels may lead to a calcite problem if coupled with an increase in pH. The consistently negative struvite potential clearly corresponds to pH, a point will have to be considered if dewatering facilities were to be installed, because the turbulence involved usually leads to a pH rise (Borderding, 1972).

5.2.2. Coleshill

The pH of centrate at Coleshill was matched at Mansfield as the highest of all sites, averaging at 7.9. Consistently high, the pH ranged between 7.88 and 8.08. The TDS was slightly lower than average, and alkalinity one of the highest. The average ammonium level was also one of the highest at 888 mg/l. Coleshill was the 'softest' of all sites with both calcium and magnesium levels below all other sites. The average calcium and magnesium levels were at least 30 mg/l and 10 mg/l below the other sites, respectively. The orthophosphate however, was the second highest at 96 mg/l.

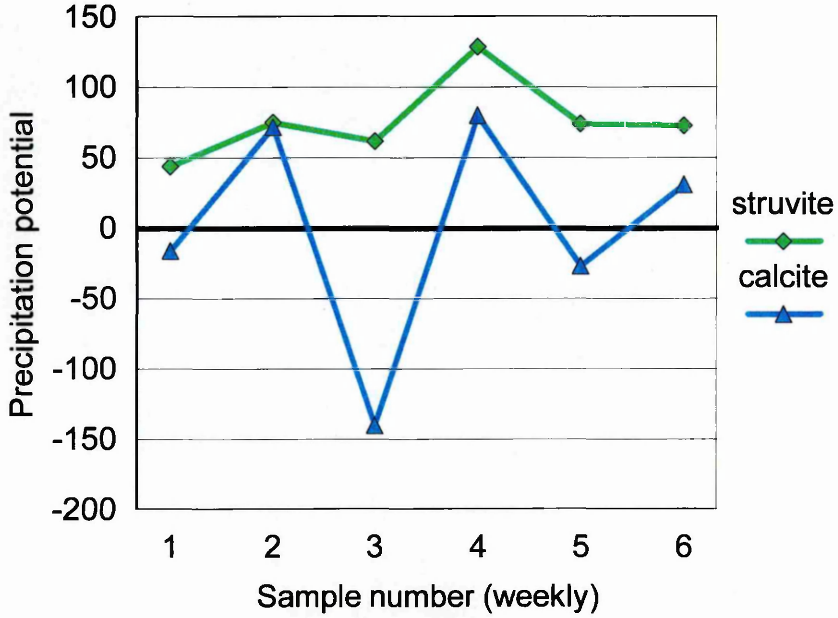


Figure 5.21. Struvite and calcite formation potentials at Coleshill

The graph of scale formation potentials tells a different story for struvite than for calcite (Figure 5.21.). The struvite potentials are predicted to all be positive, ranging between 44 mg/l and 129 mg/l. The calcite potentials are much less ordered, ranging hugely between -140 mg/l and 80 mg/l, a span of 220 mg/l. Every other sample was predicted to have a positive calcite formation potential, causing great fluctuations in the graph.

The centrate at Coleshill was high in pH, immediately implying a possible scale problem (Figure 1.5.). This was coupled with a high ammonium level, but low calcium and magnesium levels. Though the calcium and magnesium were the lowest of all sites (Coleshill being the softest water site tested) all six samples showed a positive struvite potential. The potentials were fairly similar, except for a peak in the fourth sample. This doesn't appear to follow pH, because though a pH peak is seen in sample four, there is also one in sample six, with no corresponding rise in potential. The peak may actually be in response to a rise in magnesium (Figure 5.22.).

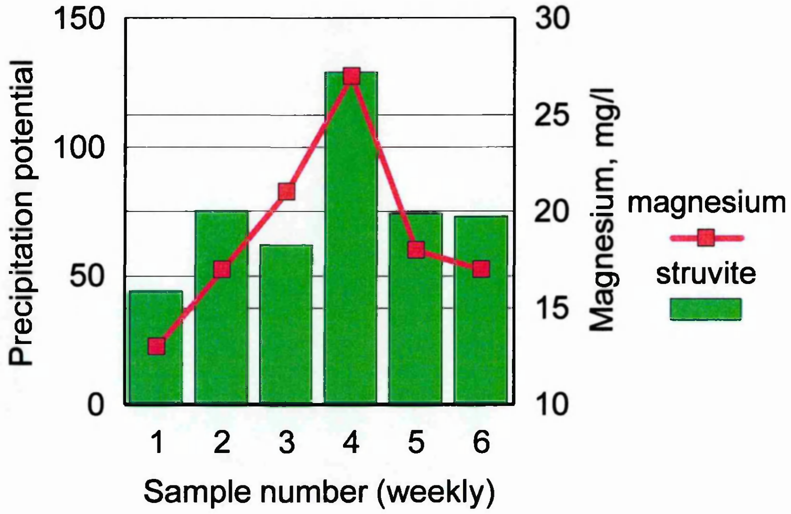


Figure 5.22. Struvite potentials of the centrate at Coleshill, with magnesium

The calcite potentials are very variable, ricocheting between –140 mg/l and 80 mg/l (Figure 5.23.). These peaks and troughs correspond well with the fluctuations in pH. Though only small, the change in pH may be crucial if all other factors influencing calcite formation are maximal. The calcium in the centrate is variable, but appears to have little effect upon the calcite potential. This is probably because the minimum value is high enough to promote calcite formation, therefore any rise above this level has little effect if the pH remains too low.

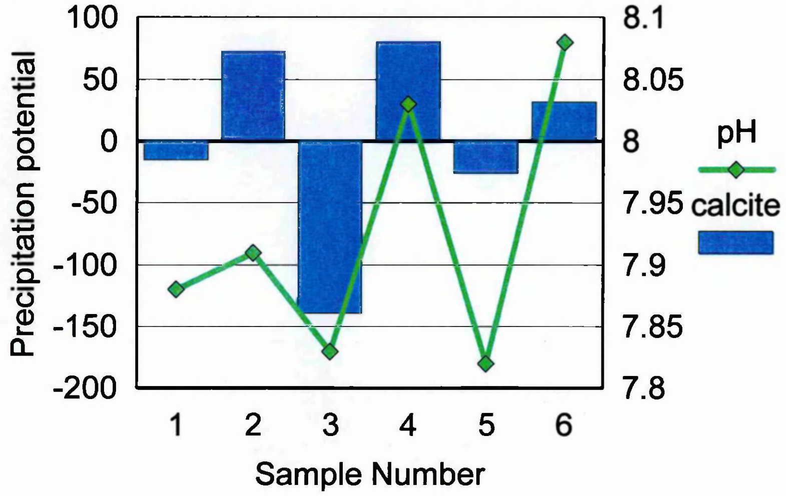


Figure 5.23. Calcite potentials of the centrate at Coleshill, with pH

Samples were taken from a point further down the centrate line for comparison. The 'secondary' centrate has been drawn out of the centrate well, and pumped over ground to a secondary tank where the condensate from the incinerators is added. A sample is taken before the addition of condensate. The pH is slightly higher than in the centrate, an average of 7.95, compared to 7.93. Though only a small change, it may be due to the increased turbulence evolving CO_2 from the water and raising the pH.

Coleshill has suffered from struvite precipitation within the pumps and pipes following the centrate well. The current cost of managing the problem is £ 16,500 per annum. The scale formed at Coleshill has been confirmed as struvite by X-ray diffraction (Appendix II). No trace of calcite has been found. This may be because it is embedded in the struvite sample and has not been detected. Or, because the high orthophosphate level inhibits calcite formation (Meyer, 1994). The model could be inaccurate or this difference may be due to an environmental factor, not considered by the model.

5.2.3. Mansfield

As mentioned earlier, this site had the joint highest pH, averaging 7.9. A fairly low TDS is coupled with the highest average alkalinity level.

High ammonium and magnesium levels can be seem, along with the second lowest average calcium value. The orthophosphate level is central, with respect to the values at the other sites.

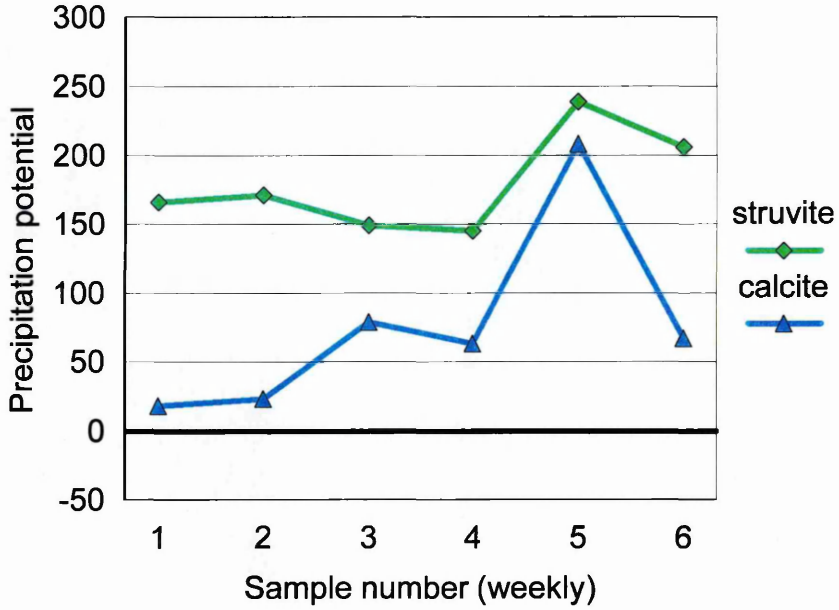


Figure 5.24. Struvite and calcite potentials of the centrate at Mansfield

The scale formation potentials (fig 5.24.) tell the same story for both struvite and calcite. The struvite potentials were positive for all six samples, ranging between 145 mg/l and 239 mg/l, all very significantly positive values. The calcite values range 18 mg/l to 208 mg/l. Though the maximum values for each scale are similar, the lowest value is significantly lower for calcite than for struvite, 18 mg/l and 145 mg/l, respectively. The values are all positive but there is still reasonable fluctuation across the six-week sampling period.

High levels of orthophosphates, magnesium and high pH, along with an average ammonium level would indicate a scale problem, and this is indeed the case at Mansfield.

The model states that all six samples have a positive struvite and calcite potential, though the struvite potentials are all higher than all but one of the calcite potentials. The potentials don't appear to follow the pattern of any one determinand, but in a highly complex system of equilibrium, as is found in wastewater, this is to be expected. The two particularly high struvite potentials occurring in samples five and six appear to be due to a rise in pH and magnesium. The calcite potentials are fairly similar, except for a peak in the fifth sample up to over 200 mg/l. This may be due to a rise in calcium, coupled with an increase in pH.

5.2.4. Milcote

This site had the second lowest average pH at 7.5. The TDS and alkalinity were both fairly central, compared to the other sites.

The ammonium level was nearly 100 mg/l below the other six sites, at 426 mg/l. This was accompanied with the third lowest average levels of calcium, magnesium and orthophosphate.

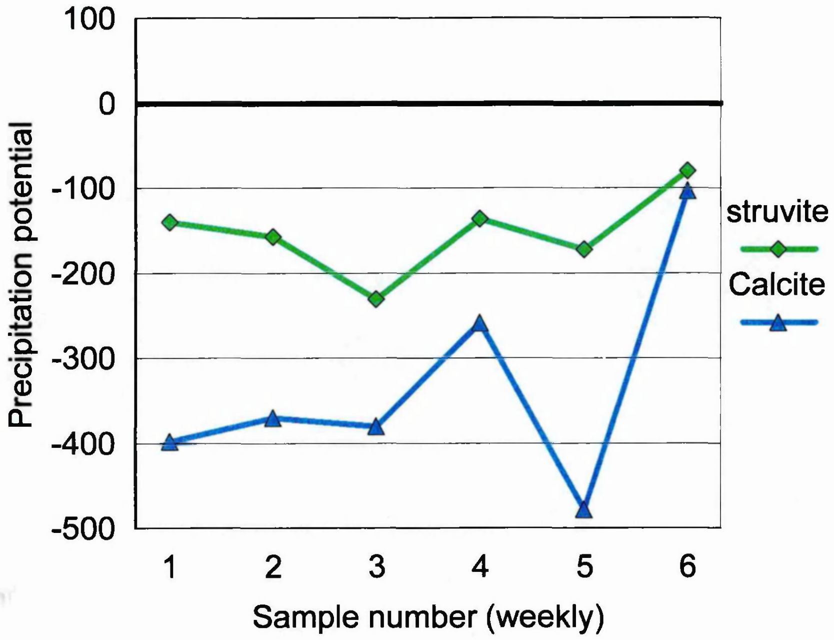


Figure 5.25. Struvite and calcite potentials of the top water at Milcote

The graph (Figure 5.25.)shows the complete opposite of the previous site, Mansfield. Here at Milcote, all of the six samples had negative scale formation potentials. The computer model predicted no scale problem, either struvite or calcite, at Milcote. The predictions for struvite vary between -79 mg/l and -163 mg/l. A range of only 74 mg/l, compared to a range of 375 mg/l for calcite (lowest being -478 mg/l and highest being -103 mg/l).

The top water at Milcote has a reasonably low pH, averaging only 7.5. The lowest ammonium level, fairly low calcium and magnesium levels, coupled with a very low orthophosphate level suggest that scale shouldn't be a problem at this site. This is indeed the finding of the model; both struvite and calcite precipitation potentials are significantly negative for all sites. There is no known scale problem at Milcote, so the predictions from the model seem accurate.

The average orthophosphate result of only 9 mg/l is lower than expected. As mentioned earlier, two-thirds of the flow is chemical dosed for phosphorus removal, while a phosphorus-removing ASP treats the other third. This would have the effect of harnessing the phosphorus in the sludge, within micro-organisms that then release this store of phosphorus upon anaerobic digestion (Jardin and Popel, 1996). This should normally result in elevated solubilised phosphorus levels in the digested sludge, and therefore in the sludge liquors. It is possible that this phosphorus, released from the biologically treated third of the sludge, is being 'mopped-up' by the excess aluminium in the chemically dosed two-thirds. This would explain the low orthophosphate levels in the top water.

5.2.5. Oswestry

The top water from Oswestry had the lowest average pH, at 7.2 with little fluctuation around this value (minimum pH 7.09, maximum pH 7.23). It also had the lowest TDS at 622 mg/l. The alkalinity, ammonium and calcium were all reasonably central, but the magnesium was the second lowest, and orthophosphate was quite high at 80 mg/l.

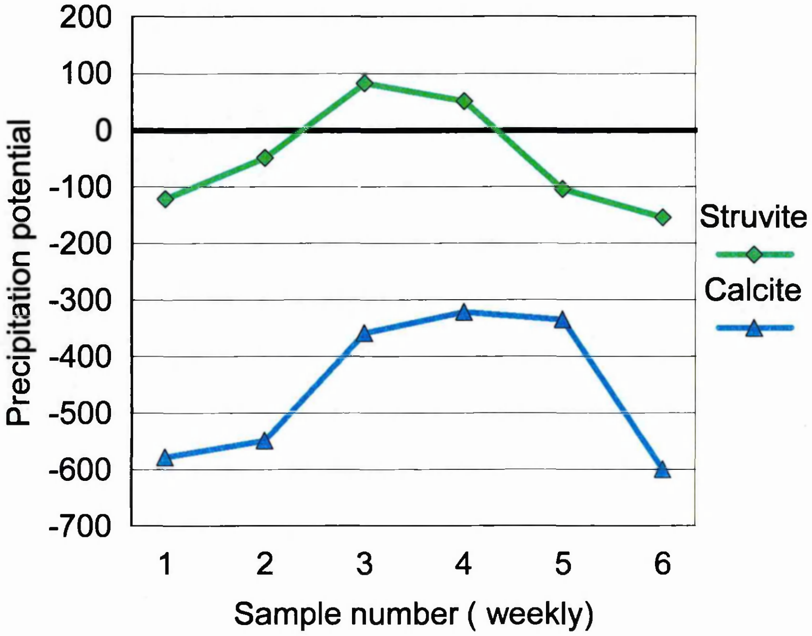


Figure 5.26. Struvite and calcite potentials of the top water at Oswestry

As figure 5.26. shows, there is a difference in the models predictions for the two types of scale. All samples had very negative precipitation potentials for calcite, the 'highest' being -322 mg/l. Struvite however, is rather different. Chronologically, the first sample was negative, the second was also negative though to a lesser degree. The third sample was very positive, at 83 mg/l, then the fourth dropped to 51 mg/l. This decline in struvite formation potential continued with the final two samples of -105 mg/l and -155 mg/l.

The consistently negative calcite potential is probably due to the low pH at Oswestry. The clear effect of pH upon the precipitation potential of both calcite and struvite can be seen (figure 1.5.).

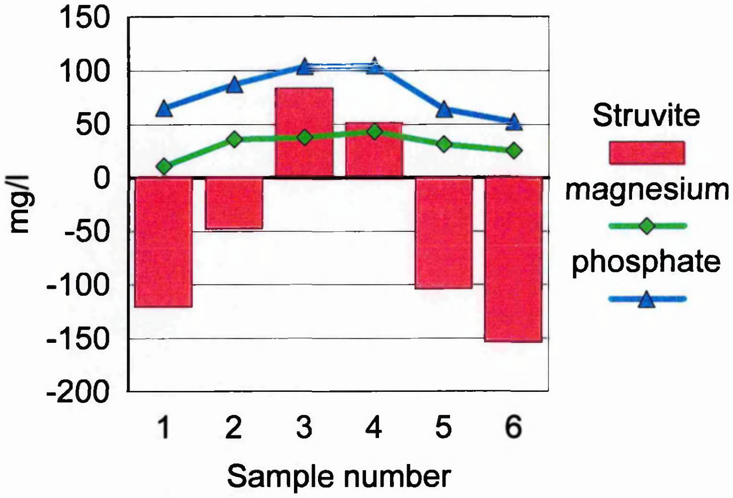


Figure 5.27. Struvite potentials of the top water at Oswestry, with magnesium and orthophosphate

The struvite potential was mostly negative but there were two samples with positive potentials (Figure 5.27.). The values for magnesium and orthophosphate for the samples are also shown. The levels of these two known struvite constituents match the peak in struvite potential. If this rise in magnesium and phosphorus is indeed responsible for the positive struvite potential, then this has implications for Oswestry; if these components were to rise significantly again, a scale problem may emerge. A rise of less than 20 mg/l of orthophosphate, coupled with a small rise in the magnesium level of 2 mg/l has resulted in a rise in struvite potential from –49 mg/l up to 83 mg/l. There is currently no known scale problem on site.

5.2.6. Spernal

With an average pH of 7.6 and fairly central values of alkalinity, TDS and ammonium, the centrate at Spernal seemed unremarkable. However, the highest values of both calcium and magnesium were found here, totalling 374 mg/l, the hardest of all waters tested in this report. The centrate had the second lowest orthophosphate level.

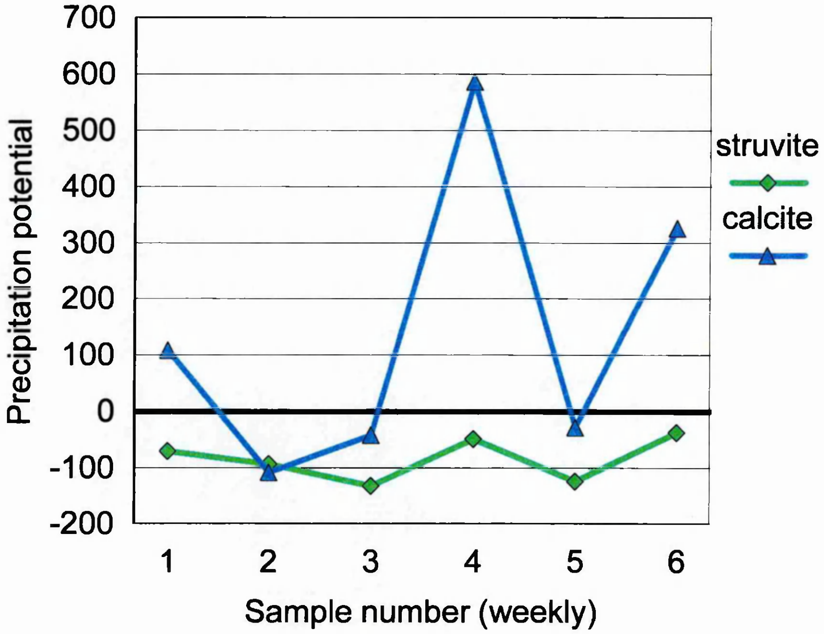


Figure 5.28. Struvite and calcite potentials of the centrate at Spernal

The graph of struvite formation potential is fairly stable (figure 5.28), only varying across less than 100 mg/l. The calcite potentials are however, far from stable. The potential ricochets between negative and very positive values, ranging -108 mg/l up to the largest potential predicted for any of the samples; 587 mg/l, a massive range of nearly 700 mg/l.

The low pH, ammonium and orthophosphate may contribute to the negative struvite potentials predicted by the model for the centrate at Spernal. Though the highest average magnesium level of all the sites would point to a more positive potential. The fluctuations seen in the struvite potentials correlate with the rises in pH (Figure 5.29.). The low orthophosphate level is due to the iron dosing for phosphorus removal, the iron binds the phosphorus and doesn't release it, even during anaerobic digestion.

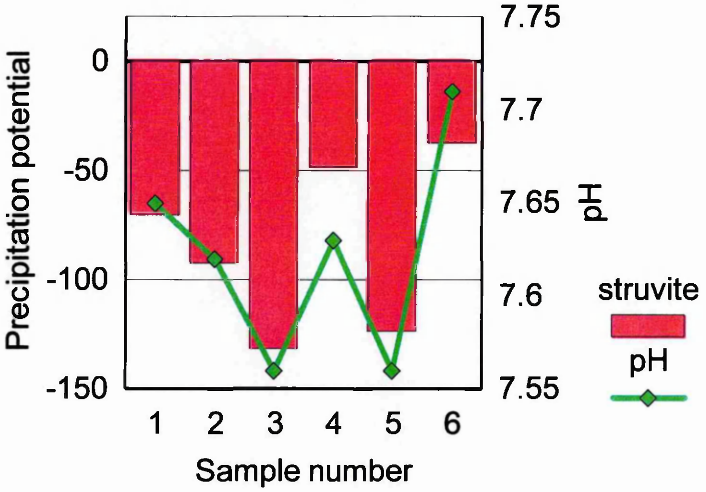


Figure 5.29. Sruvite potentials of the centrate at Spernal, with pH

The calcite potentials are much more interesting; ranging between –42 mg/l and a massive 587 mg/l. This trend mirrors the rise and fall of calcium levels within the centrate (Figure 5.30.). All negative samples had less than 287 mg/l of calcium, whereas positive samples had level greater than 336 mg/l. pH seems less influential upon calcite potential at this site.

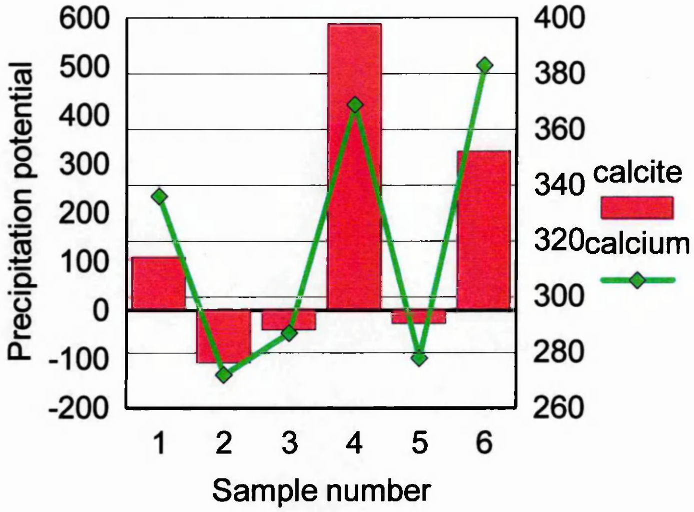


Figure 5.30. Calcite potentials of the centrate at Spernal, with calcium

Up until two months ago, Spernal had no problem with scale. The findings of this project lead to a possible reason for the recent loss of 20 % efficiency of the pumps. On lifting of the pumps a 5-mm thick layer of scale was discovered. This was removed and analysed using X-ray diffraction. The sample was confirmed to be calcite.

5.2.7. Wanlip

The pH of the liquor from Wanlip was the third highest, as was the alkalinity (joint with Spernal, curiously with exactly the same average value). The TDS is fairly low at 918 mg/l.

The ammonium and the orthophosphate levels are the highest of all the sites, the orthophosphate reaching nearly 100 mg/l on average. The magnesium and calcium levels are central, giving an above average hardness.

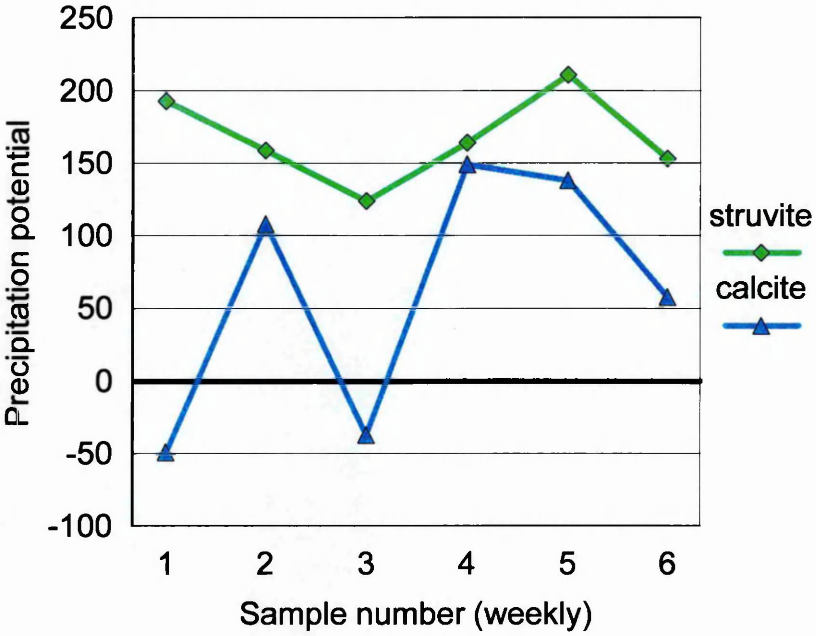


Figure 5.31. Struvite and calcite potentials of the liquor at Wanlip

The struvite formation potentials are positive for all of the six samples (figure 5.31). The lowest value was a rather large 124 mg/l, ranging up to 211 mg/l for the fifth sample, a very similar range of values as Mansfield. The calcite potential must more varied, ranging over nearly 200 mg/l. Two of these values are negative, however the other four samples are all significantlypositive, the lowest being 58 mg/l and the highest, 149 mg/l.

High levels of orthophosphates, magnesium and high pH, along with an average ammonium level suggest a significant struvite problem and this is indeed the case at Wanlip. No obvious pattern emerges to explain the calcite predictions.

5.3. Laboratory-scale experiments

5.3.1. pH adjustment

Figure 5.32. shows the results from the first lab-scale experiments with the liquor from Wanlip. The pH of the liquor was elevated from below 7.5 using aeration. The three sets of data are all consistent, levelling off at pH 8.5. This equilibrium was reached slightly earlier by the first sample, after about 15 minutes, compared to around 20 minutes for the second and third samples. The highest rate of pH increase occurred during the first 5 minutes of aeration.

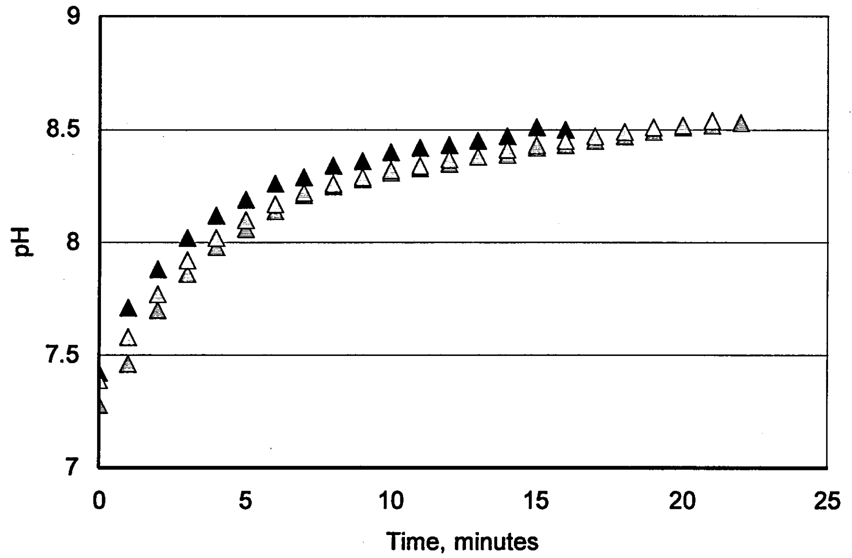


Figure 5.32. pH elevation of liquors from Wanlip, using aeration alone

Figure 5.33. shows the results from the aeration experiment at Barston. The protocol used for the liquor from Wanlip was followed here. Very similar patterns are shown by the liquors from both sites. The pH of the liquor from Barston appears to rise more rapidly, all three samples beginning to level off after only 10 minutes, compared to 15 to 20 minutes for the Wanlip liquor. Two data sets reach their peak just above pH 8.5, however one set rises slightly higher than this, peaking at pH 8.59. Again the greatest

rate of pH increase occurred during the first 5 minutes of aeration, reaching a minimum of 8.06 after this time.

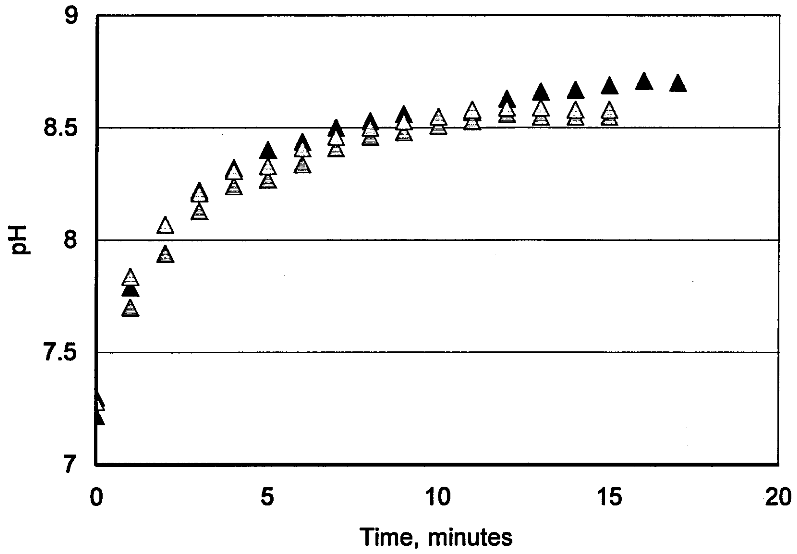


Figure 5.33. pH elevation of top water from Barston, using aeration alone

These findings are very relevant to Severn Trent when considering the expansion of the sludge treatment process. This would most likely involve the addition of dewatering facilities, such as centrifuges, to the end of the existing digestion process. The turbulence involved in centrifugation often causes evolution of CO_2 and a corresponding pH increase (Borderding, 1972). This would be of great concern when the effect a pH increase has on the precipitation potential of struvite and calcite (Figure 1.5.).

5.4.2. Scale formation

This set of experiments, carried out using a floccluator, had two aims. Firstly to form a scale which could be analysed to confirm the type, and secondly, to produce liquors with lowered level of scale forming elements. Scale type is identified using X-ray diffraction (XRD), this result can then be compared to the scale type predicted by the computer model.

The amount of scale produced from 1 litre of pH adjusted liquor was negligible. Once filtered from solution and dried, the liquor from Mansfield did not form enough scale for analysis. The liquor from Coleshill formed slightly more, allowing for XRD analysis. The scale formed in the Coleshill liquor was found to be struvite (XRD plot).

The second aim of the experiment was achieved more successfully. Experimental liquors from both sites showed a reduced level of some scale forming elements when compared to the control (Tables 5.34. and 5.35.).

Coleshill

The liquors were originally all approximately the same pH. Sodium hydroxide was added after 20 minutes of rapid mixing to raise the pH of the two experimental liquors. Prior to pH adjustment, all samples had experienced a pH increase. This was probably due to the evolution of CO_2 caused by the turbulent mixing in the flocculator. The final pH was about one pH unit above the final pH of the control.

Table 5.34. Results showing effect of scale formation upon liquors, data given before and after scale formation

Determinand, mg/l	Control no pH adjustment	Data set 1 pH adjustment	Data set 2 pH adjustment
Initial pH	7.2	7.1	7.1
pH immediately after adjustment	7.6	8.74	8.72
Final pH	7.65	8.61	8.58
Total Dissolved Solids	2,050	2,810	2,780
Alkalinity	1,100	1,000	1,200
Ammonium	987	926	969
Calcium	80	81	85
Magnesium	15	9	7
Orthophosphate	96.3	79.6	78.7

The experimental liquor (pH adjusted) showed a significantly reduced level of ammonia, magnesium and orthophosphate (significant within 97.5 % confidence levels). Levels of total dissolved solids and calcium are higher in both experimental liquors than the control, though it is not a significant rise for calcium.

These results are consistent with the formation of struvite within the centrate.

Mansfield

The pH was approximately the same for all three samples before pH adjustment took place. Again, all three samples experienced a pH increase due to the evolution of CO_2 by the turbulence of mixing. After sodium hydroxide addition the pH of both of the experimental liquors was one pH unit above the control, this dropped to three-quarters of a unit by the end of the experiment.

Table 5.35. Results showing effect of scale formation upon liquors, data given before and after scale formation

Determinand, mg/l	Control no pH adjustment	Data set 1 pH adjustment	Data set 2 pH adjustment
Initial pH	7.06	7.1	7.13
pH immediately after adjustment	7.89	8.8	8.85
Final pH	8.01	8.78	8.81
Total Dissolved Solids	2,440	1,880	1,840
Alkalinity	1,500	2,100	1,900
Ammonium	831	798	795
Calcium	105	58	57
Magnesium	43	25	24
Orthophosphate	30.8	8.9	8.7

The experimental liquors from Mansfield have reduced levels of total dissolved solids, ammonium, calcium, magnesium and orthophosphate when compared to the control (significant within 97.5 % confidence levels). The alkalinity is higher in both experimental liquors than the control.

These results are consistent with the formation of both struvite and calcite.

6. Discussion

6.1. Hardness data

The sites chosen were selected originally as relatively hard or soft water sites. Oswestry, Barston and Coleshill were expected to have lower hardness, that is calcium and magnesium. It was discovered that Barston wasn't as 'soft' as originally thought, and was in fact the second hardest site studied (Table 6.1.). The relative hardness was assessed using data from drinking water in the surrounding areas of each site because this would be the main source of water.

Table 6.1. Hardness data for drinking water supplied to the sites and their surrounding areas (Severn Trent, 2000) and hardness of digested sludge liquors or centrate as found in this study.

Area	Average Calcium, mg/l	Average Magnesium, mg/l	**Sum of calcium and magnesium, mg/l**	**Sum of calcium and magnesium, (this study), mg/l**
Coleshill	16.85	1	**18**	**113**
Oswestry	25.72	3.27	**29**	**216**
Milcote	49.5	9	**59**	**199**
Sperna l	55	8.5	**64**	**374**
Mansfield	48.5	23.5	**72**	**175**
Barston	61	11	**72**	**303**
Wanlip	82	16	**98**	**229**

The two sets of data for hardness in the table above do correlate for the 'softer' sites: Coleshill, Oswestry and Milcote. The hardness of the water supply to the area that feeds Spernal sewage treatment works is average, with respect to the other six sites. However, the hardest centrate found in this study; with nearly 400 mg/l of combined calcium and magnesium, was at Spernal. This is probably due to the large number of imports taken at Spernal; accounting for two-thirds of the sludge digested. It is possible that an import received from a harder water area would elevate the average hardness of the centrate.

6.2. General sludge discussion

The first samples taken on the sludge route were feed sludge into the anaerobic digesters. The percent dry solids (% DS) of the sludge were determined, along with calcium, magnesium and iron or aluminium, if dosed. The average % DS of the feed sludges over the six-week sampling period varied from 3.5 to 8.7. Within Severn Trent, digesters are ideally fed with sludges of between 5.5 and 6 % to ensure optimum performance.

The average % DS values for the sludges at the sites studied are shown (Table 6.2). The % DS for the feed sludges were all higher than in the study by Mamais (1994), except one site. This was Mansfield, which was only 0.1 % lower.

Table 6.2. Table comparing average feed and digested sludge dry solids levels from these seven sites with another study.

Site	Percentage dry solids in feed sludge	Percentage dry solids in digested sludge	Reference
Barston	8.7	3.9	This study, 2000
Coleshill	(no feed sampled)	3.5	This study, 2000
Mansfield	3.5	2	This study, 2000
Milcote	4.1	2.3	This study, 2000
Oswestry	5.8	3	This study, 2000
Spernal	5	3.9	This study, 2000
Wanlip	4.2	3	This study, 2000
Other	3.6	1.7	Mamais *et al.,* 1994
Other	3.6	2	Mamais *et al.,* 1994

The second samples taken were digested sludges. The average % DS of the digested sludge across the seven sites was 2.2 – 3.9. Digested sludge from an anaerobic digester is typically around 3.5 % (Metcalf and Eddy, 1991), however it is largely dependent upon feed concentration. The results from this study show that digested sludge is

generally 2 – 4 % lower than the feed concentration. The digested sludges all had a greater or equal dry solids content to the comparative study.
The scale formation potential was only measured for the liquor samples taken during this project. The scale formation potential of the sludges could not be predicted by the computer model as parameters such as alkalinity were not measured. The model is also designed for waters from wastewater plants, not sludges (Loewenthal, 1997).

Ohlinger et al (1998) carried out a study at the Sacramento Region Wastewater Treatment Plant (SRWTP) on the struvite formation potential of the sludge route. Anaerobic digester feed and digested sludges were sampled, along with sludge from sludge storage basins (SSB) and the top water from these tanks. The compositions of these streams are not revealed, however the conditional solubility products are calculated. This enabled the authors to predict the struvite formation potential of each stream. They found "saturation and supersaturation conditions for the SSB supernatant and undersaturation conditions for the other process fluids". This finding was consistent with the Sacramento plant; scale formation only occurs on the SSB supernatant system, that is equipment and pipe walls in contact with the supernatant.

This is the case for three sites in this study with a known scale problem; no scale has been identified in the feed sludge to the anaerobic digesters or in the digested sludge. Problems are only experienced in the dewatering equipment and pipelines after dewatering. The fourth site known to have a scale formation problem is Mansfield. At this site scale forms in the granular form, within the secondary digesters.

6.3. Influence of Chemical Phosphorus removal on Struvite and Calcite formation potentials

Iron dosing is used at Spernal and Barston, both hard water sites, and aluminium dosing occurs at Milcote, a soft water site. At Milcote, only two-thirds of the flow is alum dosed, the final third undergoes biological phosphorus removal. The three sites with phosphorus removal (via iron dosing or alum dosing with biological) were expected to have a high phosphorus level in the sludge. Iron is known to bind phosphorus and so prevents the characteristic release of phosphorus during anaerobic digestion; Fujimoto et al (1991) used ferric chloride as a source of iron to fix the phosphorus in sludge during digestion. The sludge from these two iron dosed plants would have a high phosphorus level. Moreover the phosphorus would not be released upon dewatering because it would be bound by the iron. At Milcote, some of the phosphorus in the sludge would be bound biologically. However, this will "deposit the phosphorus in the digestion process where it increases struvite precipitation potential (Ohlinger et al 1998). A study by Battistoni (1997) found average orthophosphate levels of 282 mg/l in digested sludge liquors from a BNR plant, compared to 9 mg/l found during this study at Milcote. As two-thirds of the flow is treated with aluminium dosing the phosphorus would be fixed in a similar way to the iron at Spernal and Barston. The overall effect at Milcote is difficult to predict. It is likely that an overdosing of alum accounts for the low orthophosphate level, meaning that aluminium is free to bind the phosphorus, as it is released in the digester.

The level of orthophosphate predominantly chemically dosed sludge liquors would be expected to be lower than undosed. This was indeed the case; the average values of orthophosphates in these three liquors were all an order of magnitude below the sites with no phosphorus removal (Table 6.3.).

Table 6.3. Composition of anaerobic digester supernatant from Ballarat South BNR plant (Webb et al, 1995).

Average centrifuged liquor (5000 rpm, Webb et al or 4500 rpm, this study)	Barston	Wanlip	Ballarat
Ammonia, mg/l	523	957	805
Orthophosphate, mg/l	2	99	282
Magnesium, mg/l	46	41	19.1
Calcium, mg/l	257	188	50
Reference	This study, 2000	This study, 2000	Webb et al, 1995

Digested sludge liquor analyses from Ballarat, Australia are also shown (Table 6.3.). The levels of ammonia are lower at Barston, which also has the highest calcium level. The orthophosphate level is most variable. The value of 282 mg/l at Ballarat is more than twice that of the highest in this study (Wanlip, 99 mg/l). This is because the Ballarat plant uses biological nutrient removal (BNR) and therefore the sludge produced releases the stored phosphorus during anaerobic digestion (Ohlinger et al, 1998). Barston is included for comparison as a site undergoing iron dosing to removal phosphorus. The phosphorus levels in the liquor are predictably low (2 mg/l) as the iron binds the phosphorus, preventing release during anaerobic digestion (Carlliel and Wheatley, 1997).

The scale precipitation model consistently predicted negative values for all three of these chemical phosphorus removal sites. The liquors from Barston and Milcote and the centrate from Spernal were collected over six weeks and the six sets of data fed into the model. All six values for these sites were negative for struvite, ranging from -230 mg/l to -38 mg/l.

Milcote was chosen as a site for this study because it had BNR, and therefore a possible scale problem had been predicted. It is common for waste BNR sludge to release phosphorus, as well as magnesium and potassium, upon thickening and stabilisation (Jardin and Popel, 1996). If a greater proportion of the flow were to undergo biological phosphorus removal as opposed to chemical, there would be a struvite problem at Milcote. This is because if the orthophosphate level in the sludge were to rise above 77 mg/l (Lower than the average value at three sites) and all the other parameters remained the same, the model predicts that struvite will begin to precipitate. This fact must be considered if a move to reduce chemical dosing were made at Milcote, which is likely as more calls are made for reduced chemical dosing.

Spernal wasn't predicted to suffer struvite formation, the model did however indicate a very positive calcite formation potential. The digested sludge at Spernal is centrifuged, and when this project began, no scale problem had been identified, either within the dewatering equipment or the surrounding pipelines. Spernal had the highest level of calcium in centrate or liquor, an average of 321 mg/l. The peaks and falls in calcium level over the six weeks of sampling are followed directly by the calcite precipitation potential. This high predicted formation potential caused concern on site. The new sludge disposal route at Spernal has only been running for a few months, there was definitely no scale problem 2 months ago. After the sampling had finished, the pumps at Spernal began to lose efficiency. Once a 20 % loss in efficiency was reached, the pumps were examined. A layer of scale was discovered inside the pump, about 3 mm thick. The scale was chipped away and sent for analysis. It was confirmed to calcite by XRD analysis (Appendix II).

6.4. Effect of pH upon scale precipitation model.

The pH of the top water or centrate from each site was recorded for every sample. An average of these results is shown (figure 6.4.). The graph also shows the struvite and calcite formation potentials, as predicted by the computer model. An average value is shown.

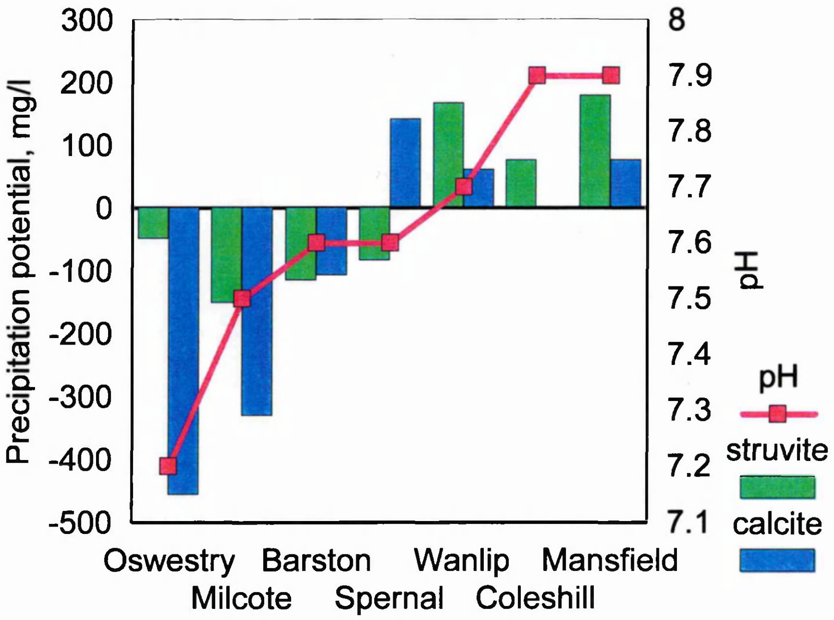


Figure 6.4. Graph of struvite and calcite formation potentials with average site pH.

The rise in scale formation potential across the sites corresponds to a general rise in pH. This finding is similar to that of Webb and Ho (1992) whilst studying piggery effluents in Australia. The wastewater from the piggery is treated via a series of four anaerobic lagoons. A new pipeline from the final lagoon suffered struvite formation along its length, rendering it useless. The study included monitoring the pH, orthophosphate, ammonia and magnesium levels. The results (table 6.5.) are shown from four sampling points along the treatment route.

Table 6.5. Analysis of data gathered from a piggery effluent treatment system (Webb and Ho, 1992).

Determinand, average	Inflow to 1st lagoon	Outflow from 1st lagoon	Outflow from 2nd lagoon	Outflow from final lagoon
pH	7.1	7.2	7.6	7.8
Orthophosphate, mg/l	43	37	31	16
Magnesium, mg/l	67	63	60	49
Ammonia, mg/l	970	910	980	800
Struvite potential for this liquor using computer model, mg/l (Loewenthal, 1997)	**-15**	**-8**	**68**	**19**

The pH clearly rises through the lagoon system. Webb and Ho concluded that the rise in pH across the treatment system caused a corresponding rise in struvite formation potential. This conclusion was reached using conditional solubility constants, predicting whether struvite was likely to form 'thermodynamically'. Finally, the study indicates a possibility of struvite formation at points 2, 3 and 4 Webb and Ho, 1992). The data published by Webb and Ho (1992) was analysed using the computer model used during this study (Loewenthal, 1997). The values stated for pH and struvite forming elements were used, along with a temperature of 30 °C (the temperature at the piggery). A value of 1500 mg/l was used for alkalinity. This was because no alkalinity levels were quoted in the research. The resulting struvite precipitation potentials (table 6.5.) show a rise from negative to positive potentials across the lagoon system. This is due to the rise in pH. The final sampling point has a reduced struvite potential, this is probably because the level of the other determinands have dropped: ammonia by nearly 200 mg/l, magnesium by over 10 mg/l and the orthophosphate level has halved. If the previously high levels are combined with the elevated pH, a struvite potential of 92 mg/l is predicted by the model.

The data from the Australian study shows only a little variance between the sampling points except pH, while this is not the case for this study, a correlation between pH and scale formation potential is clear in both studies.

This correlation is further confirmed by a new study by Ohlinger at the Sacramento works. The study concludes that it is supersaturation, and thus pH, which controls struvite crystal nucleation and induction (Ohlinger, 2000).

To enable a direct comparison of the seven sites, the pH of the average liquor composition was normalised. All sites were set to pH 7.5. The other average determinands in the liquor were kept the same (Figure 6.6.).

The pH normalisation allows the consideration of the effects of other parameters upon scale formation potential. The key determinand influencing struvite potential appears to be orthophosphate. The three sites undergoing chemical phosphorus removal have low orthophosphate levels as expected. They also have very negative struvite potentials. The magnesium and ammonium levels don't fluctuate enough to have a significant effect upon the potential.

Table 6.6. The struvite and calcite formation potentials at all seven sites, calculated using the average constituent levels in the liquors and a normalised pH of 7.5.

Site	Struvite formation potential	Calcite formation potential
Barston	72	-70
Coleshill	-126	-117
Mansfield	-142	-313
Milcote	-105	79
Oswestry	128	-120
Spernal	148	-54
Wanlip	32	-251

The calcite potentials do not show such a clear pattern. The three lowest potentials are at the sites with the lowest average calcium level. Spernal, the site with a known calcite problem and the highest calcium levels is the only site with a positive potential. Wanlip and Oswestry have virtually identical average calcium levels and similar calcite potentials. Barston however, has high calcium levels, yet a low calcite formation potential. This must be due to another factor, not pH, possibly the lower TDS level. TDS does have an effect upon calcite potential (figure 5.16.). The dissolved solids may provide a nucleation site for the calcite crystal growth. Interestingly, Spernal, the site with the highest calcite potential also has the highest TDS level.

6.5. Further experiments

6.5.1. Scale formation

The scale formation experiments in a flocculator were carried out using centrate form Coleshill and Mansfield. The centrate after the scale had formed showed reduced levels of a number of parameters. At Coleshill, reductions in orthophosphates, ammonium and magnesium were recorded. At Mansfield, reductions in these determinands were seen, as well as a significantreduction in calcium levels (Figure 6.7.).

Table 6.7. Percentage removal of phosphorus form phosphorus-rich side streams (Moriyama, 2000) and liquors sampled from two sites in this study.

Approximate % reduction in liquor	Coleshill	Mansfield	Japan
Experimental pH	8.6	8.8	8
Calcium	0	50	
Orthophosphate	**18**	**72**	**80**
Magnesium	53	44	
Reference	This study, 2000	This study, 2000	Moriyama, 2000

The table also shows the results from an experiment in Japan using phosphorus rich side streams as a means of phosphorus recovery as calcium phosphates (Moriyama, 2000). The pH chosen in these experiments and within this study are very similar. The centrate from both sites in this study contained a higher phosphorus level than used in the Japanese study, however the initial calcium levels are fairly similar: 105 mg/l at Mansfield, 80 mg/l at Coleshill and 80 mg/l in Japan (Moriyama, 2000). A reduction in calcium at Mansfield, coupled with the reduced orthophosphate would suggest the formation of a calcium phosphate scale. This was indeed the case in Japan, unfortunately, the scale formed in the liquor at Mansfield was too small an amount to allow for analysis. The reductions seen at Coleshill suggest no calcium based scale has formed, they point towards the formation of struvite. This was confirmed by XRD analysis of the scale formed (Appendix II). The percentage removal of phosphorus was greater in the Japanese study, this is probably due to the seed material (calcium silicate hydrate) used to encourage crystal formation by providing a nucleation site.

6.5.2. pH Elevation

Samples of digested sludge liquors were aerated to investigate the rise in pH which could be achieved by aeration alone. This is relevant to Severn Trent when considering the expansion of the sludge treatment process. This would most likely involve the addition of dewatering facilities, such as centrifuges, to the end of the existing digestion process. The turbulence involved in centrifugation often causes evolution of CO_2 and a corresponding pH increase. This would be of great concern when the effect a pH increase has on the precipitation potential of struvite and calcite (Figure 1.5.).

Battistoni (1997) also used CO_2 stripping to raise the pH of digested sludge liquors. The aim here was to precipitate the phosphorus out of solution as struvite, using no chemical addition. Purely by aerating the liquor, the pH raised enough to cause struvite precipitation (Battistoni, 1997).

Table 6.8. Composition of digested sludge liquors sampled in Italy (Battistoni, 1997) and from two sites in this study.

	Wanlip	Barston	Italy
Initial pH	7.59	7.95	7.3
Final pH	8.5	8.5	8.3 - 8.6
Orthophosphate, mg/l	99	2	18
Magnesium, mg/l	41	46	53
Calcium, mg/l	188	257	184
	This study, 2000	This study, 2000	Battistoni, 1997

The three sets of data (Table 6.8.) are similar across all fields except phosphorus. The digested sludge liquors used by Battistoni (1997) showed an 80 % reduction in orthophosphates upon aeration. It was concluded that CO_2 stripping by aeration alone can "enable effective phosphate removal and recovery as struvite from bio-P sewage works digester or sludge treatment supernatants" (Battistoni, 1997). A removal efficiency of 80 % of orthophosphate was observed by Battistoni. This is an important point for Severn Trent, if struvite precipitation were to be considered, either for phosphorus recovery and recycling, or to form scale in a chosen area to relieve formation in pipes and fittings downstream of the anaerobic digester.

7. Conclusion

Six sewage treatment works and a sludge destruction plant were sampled within the Severn Trent region. Feed sludge to anaerobic digesters, digested sludge and digested sludge liquors or centrate were sampled. The ultimate aim of this project was to investigate the scale formation potential of the digested sludge liquors or centrate.

Three of the works chosen were known to suffer with scale formation: Coleshill, Mansfield and Wanlip. The cost of managing the scale problem at Coleshill alone was £16,500 last year. The sites with a known scale problem were included to test the accuracy of the computer models predictions. Did the model predict scale at sites with an existing problem? Could it predict the degree of scaling that occurred? And could it determine whether struvite or calcite would form?

The model successfully identified all the sites with an existing scale problem and all those with no current problem. Another aim was to identify 'at-risk' sites, perhaps with varying potentials. This was indeed the case at Spernal, which, when the practical work was undertaken, definitely did not suffer scale formation. The computer model was predicting a varied but none the less significant calcite potential. When the pumps returning centrate to the head of works began to lose efficiency they were immediately inspected and a layer of scale discovered. XRD analysis confirmed the scale to be calcite. The model predicted predominantly struvite at Coleshill. Scale samples taken from Coleshill were identified via XRD as struvite, as was the scale formed during laboratory-scale experiments using liquor from Coleshill (Appendix II). The scale formed on site at Mansfield has been confirmed as struvite (Appendix II), unfortunately the amount scale formed from the centrate in the laboratory was insufficient for analysis. The model predicted predominantly struvite.

The degree of scale formation is predicted by the model, and is dictated by the size of the potential. The site with the most significant scale problem is currently Coleshill, though this site is predicted by the model to suffer the least struvite formation. Mansfield and

Wanlip have similar problems, in agreement with the models predictions. The site with the highest predicted scale problem is Spernal. Scale has only been identified at this site since the commencement of this project, so the immensity of the problem cannot yet be gauged.

The project has fulfilled the aims set at the beginning of the study, and has provided a valuable insight into the ever-growing scale problem. The consideration of seven different sites has allowed a full, in-depth study of the factors effecting the formation of struvite and calcite.

8. Further Work and Recommendations

This project has provided the basis for a considerable amount of further work. It has highlighted some significant points for both Severn Trent and the Water Industry as a whole.

An investigation at Spernal STW is required to establish the full extent of the newly discovered calcite problem. This should involve further sampling and analysis of the centrate at different points along the effected pipework. Remedial measures are already being considered, and the effectiveness of magnetic treatment and anti-scalent dosing are to be investigated.

The dosing of anti-scalents to prevent struvite formation is also to be explored at Coleshill. An on-site pilot plant is planned, to enable the effectiveness of anti-scalents on real centrates to be measured. The findings of this pilot trial may be applicable to Spernal, though the scale recently identified there is calcite.

Laboratory-scale investigations during this study indicated that the centrate at Mansfield was capable of forming both struvite and calcite. The model predicts that both types of scale should form; yet XRD analysis of a scale sample taken from Mansfield identified struvite only. This difference may be because the scale collected was an unrepresentative sample, or because the two types of scale are forming in different areas of the works. More thorough investigations using centrate need to be carried out to establish the ability of the centrate to form struvite, calcite or both. The nature of scale at the site must be determined to allow permanent remedial measures to be taken.

9. References

Abbona, F. (1978). Growth morphology and crystal habit of struvite crystals. *J. of crystal growth,* Vol. 46, pp. 339-354

Albertson, O. and Stensel, H. D. (1994). Aerated Anoxic Biological Nitrification and Denitrification Process. *Wat. Sci. Tech.,* Vol. 29, No. 7, pp. 167-176

Anderson, I. and Nielson, B. (1993). A Comparative Study of Full-scale Sludge Dewatering Equipment. *Wat. Sci. Tech.,* Vol. 28, No. 1, pp. 37-45

Angel, R. (1999). Removal of Phosphate from Sewage as Amorphous Calcium Phosphate Environmental Technology, Vol. 20, pp. 709-720

Battistoni, P., Fava, G., Pavan, P., Musacco, A. and Cecchi, F. (1997). Phosphate Removal in Anaerobic Liquors by Struvite Crystallization without Addition of Chemicals: Preliminary Results. *Wat. Res.,* Vol. 31, No. 11, pp. 2925-2929

Battistoni, P., Pavan, P., Cecchi, F. and Mata-Alvarez, J. (1998). Phosphate Removal in Real Anaerobic Supernatants: Modelling and Performance of a Fluidized Bed Reactor. *Wat. Sci. Tech.,* Vol. 38, No. 1, pp. 275-283

Brett, S., Morse, G. K. and Lester, J. N. (1997). Phosphorus Removal and Recovery Technologies. Selper Publications, London.

Booker, N. A., Preistley, A. J. and Fraser, I. H. (1998). Struvite Fromation in Wastewater Treatment Plants: Opertunities for Nutrient Removal. *Environmental Technology,* Vol. 20, No. 7, pp. 777-782

Borderding, J. (1972). Phospate deposits in digestion systems. *J. Water Poll. Cont. Fed.,* Vol. 44, pp. 813-819

Bridger, G. (1962). Metal Ammonium Phosphates as Fertilizers. *Agricultural and Food Chemistry.* Vol. 10, No. 3, pp. 181-188

Buchanan, J.R., Mote, C.R. and Robinson, R.B. (1994). Thermodynamics of Struvite Formations. *Transactions of the ASAE* ,. Vol. 37, No. 2, pp. 617-621

Buchanan, J.R., Mote, C.R. and Robinson, R.B. (1994). Struvite control by chemical treatment. *Transactions of the ASAE*,. Vol. 37, No. 4, pp. 1301-1308

Buchan, L. (1981). The Location and Nature of Accumulated Phosphorus in Seven Sludges from Activated Sludge Plants which Exibit Enhanced Phosphorus Removal. *Water SA.,* Vol. 7 No. 1, pp.1-7

Carliell, C. M. and Wheatley, A. D. (1997). Metal and phosphate speciation during anaerobic digestion of phosphorus rich sludge. *Water Sci. Tech.*, Vol. 36, No. 6-7, pp. 191-200

Chang, R. (1994). Chemistry 5th Ed. Mc-Graw Hill Inc., New York.

Cooper, P., Upton, J.E., Smith, M. and Churchley, J. (1995). Biological Nutrient Removal: Design Snags, Operational Problems and Costs. *J.IWEM* Vol. 9, pp. 7-18

Council of European Communities (1991) *Directive Concerning Urban Wastewater Treatment (91/271/EEC)* Off. J. L135/40, (1991)

Council of European Communities (1991) *Directive Concerning the Protection of Waters Against Pollution Caused by Nitrates from Agricultural Sources (91/676/EEC)* Off. J. L375/1, (1991)

Donnert, D. and Salecker, M. (1999). Elimination of Phosphorus from Waste Water by Crystallisation. *Environmental Technology* Vol. 20, pp. 735-742

Eggers, E., Dirkzqager, A.H. and van der Honing, H. (1991). Full-Scale Experiences with Phosphate Crystallisation in a Crystalactor. *Wat. Sci. Tech.*, Vol. 24, No. 10, pp. 333-334

Farrimond, M. and Upton, J. (1993). A Strategy to Meet the Nutrient (N and P) Standards of the Urban Wastewater Directive. *Wat. Sci. Tech.*, Vol. 27, No. 5-6, pp. 297-306

Franke, J. and Mersmann, A. (1995). The Influence of the Operational Conditions on the Precipitation Process. *Chemical Engineering Science*, Vol.50, No. 11, pp. 1737-1753

Fujimoto, N., Mizuochi, T. and Togami, Y. (1991). Phosphorus Fixation in the Sludge Treatment System of a Biological Phosphorus Removal Process. *Wat. Sci. Tech.*, Vol. 23. Kyoto. pp. 635-640

Giesen, A. (1999). Crystallisation Process Enables Environmental Friendly Phosphate Removal at Low Costs. *Environmental Technology* Vol. 20, pp. 769-775

Greaves, J., Hobbs, P., Chadwick, D. and Haygarth, P. (1999). Prospects for the Recovery of Phosphorus from Animal Manures: A Review. *Environmental Technology* Vol. 20, pp. 697-708

Gunn, D. J. (1976). Mechanism for the formation and growth of ionic precipitates from aqueous solutions. *Chemistry society*. Vol. 61, pp. 133-140

Hall, (1995). Sewage Sludge Processing, Treatment and Disposal in the EU. *J.CIWEM.,* Vol. 9. No. 4, pp. 335-343

Hanel, K. (1988). Biological treatment of sewage by the activated sludge process. John Wiley and Sons, New York.

Horenstein, B.K., Hernandez, G.L., Rasberry, G. and Crosse, J. (1990). Successful Dewatering Experience at Hyperion Wastewater Treatment Plant. *Wat. Sci. Tech.*, Vol. 22, No. 12, pp. 183-191

Habets, L. H. A. and Knelissen, H. J. (1997). In line biological water regeneration in a zero discharge recycle paper mill. *Wat. Sci. Tech.* Vol. 35, pp. 41-48

IWEM Manuals of British Practice in Water Pollution Control. Tertiary treatment and Advanced Wastewater Treatment, 1974

IWPC Manuals of British Practice in Water Pollution Control. Sewage sludge III: Utilisation and Disposal, 1978.

IWPC Manuals of British Practice in Water Pollution Control. Sewage sludge I: Production, PreliminaryTreatment and Digestion, 1979.

IWPC Manuals of British Practice in Water Pollution Control. Sewage sludge II: Conditioning, dewtering and thermal drying, 1981.

IWPC Manuals of British Practice in Water Pollution Control. Activated sludge, 1987

Jardin, N. and Popel, J.H. (1996). Behavior of Waste Activated Sludge from Enhanced Biological Phosphorus Removal During Sludge Treatment. *Water Environment Research* Vol. 68, No. 6, pp. 965-973

Joko, I. (1984). Phosphorus Removal from Wastewater by the Crystallization Method. *Wat. Sci. Tech.,* Vol. 17, pp. 121-132

Kaneko, S. and Nakajima, K. (1988). Phosphorus Removal by Crystallization using a Granular Activated Magnesia Clinker. *JWPCF* Vol. 60, No. 7, pp. 1239-1243

Kavanaugh, R. G. and Randall, C. W. (1994). Bacterial Popualtions in a BNR Plant. *Wat. Sci. Tech.,* Vol. 29, No. 7, pp. 25-34

Van Langerak, E. P. A., Beekmanns, M. M. H., Beun, J. J., Hamelers, H. V. M. and Lettinga, G. (1999) Influence of Phosphate and Iron on the Extent of Calcium Carbonate Precipitation During Anaerobic Digestion J. Chem. Biotechnol. Vol. 74, pp. 1030-1036

Levin, G. V. and Shapiro, J. (1965). Metabolic Uptake of Phosphorus by Wastewater Organisms. *J. Wat. Pollut. Control Fed.* Vol. 37, pp. 800-821

Liberti, L., Limoni, N., Lopez, A., Passino, R. and Boari, G. (1986). The 10 m^3 h^{-1} Rim-Nut Demonstration Plant at West Bari for Removing and Recovering N and P from Wastewater. *Wat. Res.*, Vol. 20, No. 6, pp. 735-739

Lind, O. T. (1993). Permissible Charge of Nutrients and Organic Compounds in Relation to Other Processes in Reservoirs. *Wat. Sci. Tech.,* Vol. 28, No. 6, pp. 1-4

Loewenthal, R. E. (1994). Modelling struvite precipitation in anaerobic treatment systems. *Wat. Sci. Tech.*, Vol. 30, No. 12, pp. 107-116

Loewenthal, R. E. (1997). A Caclculator for Struvite Precipiation/Dissolution. Developed for the Water Research Commission

Mamais, D. (1994). Determination of ferric chloride dose to control struvite precipitation in anaerobic digestors. *Wat. Environ. Res.* 66, 411-416

Maqueda, C., Perez Rodriguez, J.L. and Lebrato, J. (1994). Study of Struvite Precipitation in Anaerobic Digesters. *Wat. Res.*, Vol. 28, No. 2, pp. 411-416

Metcalf and Eddy, (1991). Wastewater Engineering: Treatment, Disposal, Re-use. McGraw-Hill Inc., New York

Meyer H J 1983 The influence of impurities on the growth rate of calcite *J. of crystal growth*, 66, 639-646

Mino, T., Satoh, H. and Matsuo, T. (1994). Metabolisms of Different Bacterial Populations in EBPR Processes. *Wat. Sci. Tech.,* Vol. 28, No. 7, pp. 67-70

Mohajit, K, (1989). Struvite deposits in pipes and aerators *Biol. wastes,* Vol. 30, pp. 133-147

Moriyama, K. (2000). P-recovery as Calcium Phosphates. *Scope Newsletter, CEEP* , Vol 36, pp. 5

Noone, G. P. (1982). Anaerobic sludge digestion *J. Effluent and Water Treat.* Vol. 22, No. 5, pp. 193

Nyberg, U., Jes la Cour Jansen, Aspegren, H. and Andersson, B. (1993). Handling of anaerobic digester supernatant combined with full nitrogen removal. *Wat. Sci. Tech.,* Vol. 27, No. 5-6, pp. 391-403

Ohlinger, K. N., Young, T. M. and Schroeder, E. D. (1998). Predicting Struvite Formation in Digestion. *Wat. Res.*, Vol. 32, No. 12, pp. 3607-3614

Ohlinger, K. N. (1999). Kinetic efffects on preferential struvite accumulation in wastewater. *J. of Environmental Engineering*, Vol. 125, No. 8, pp. 730-737

Ohlinger, K. (2000). Struvite Precipitation Kinetics. *Scope Newsletter, CEEP.*, Vol 36, pp.6

Popel, J.H. and Jardin, N. (1993). Influence of Enhanced Biological Phosphorus Removal on Sludge Treatment. *Wat. Sci. Tech.*, Vol.28, No. 1, pp. 263-271

Rodriguez, P. J. L., Maqueda, C., Lebrato, J. and Carretero, M. I. (1992). Influence of Clay Minerals, used as Supports in Anaerobic Digesters, in the Precipitation of Struvite. *Wat. Res*. Vol. 26, No. 4, pp. 497-506

van der Roest, H. F., Salome, A. A., Koornneef, E. (1993). New genration belt presses and decanters for sludge dewatering. *Wat. Sci. Tech.,* Vol. 27, No. 1, pp. 21-28

Taylor, A. W. (1963). Solubility Products of Magnesium ammonium and Magnesium potassium phosphates. *Trans. Faraday Soc.*, Vol. 59, pp. 1580-1584

Webb, K. M., Ho, G. E. (1992). Struvite Solubility and its Application to a Piggery Effluent Problem. *Wat. Sci. Tech.* Vol. 26, No. 9-11, pp. 2229-2232

Webb, K., Bhargava, S., Fraci, Priestley, A. J., Booker, N. A. and Cooney, E. (1995). Struvite Precipitation: Potential for Nutrient Removal and Re-use from Wastewaters. *Chemistry in Australia,* Vol. 62, No. 10, pp. 42-44

Wedi, D. and Konig, E. (1993). Elimination of Nitrogen and Phosphorus from Sludge Liquor. *Wat. Sci. Tech.* Vol. 28, No. 1, pp. 283-287

Williams, S. (1999). Struvite Precipitation in the Sludge Stream at Slough Wastewater Treatment Plant and Opportunities for Phosphorus Recovery. *Environmental Technology* Vol. 20, pp.743-747

Appendix I

A full list of all results form six-week sampling regime at seven site within the Severn Trent region

Barston	FEED	**31/05/00**	**07/06/00**	**14/06/00**	**21/06/00**	**28/06/00**	**05/07/00**
	dry solids, %	5.7	8.8	9.7	11.1	9.7	7
	Fe, mg/kg		114900		26400	123000	44500
	calcium, mg/kg	19500	37100	19400	14370	17200	17800
	magnesium, mg/kg	3070	2990	2150	1950	2070	2340
	DIGESTED						
	dry solids	2.9	2.8	4.4	4.4	3.5	4.1
	Fe			48600	116300	25000	83100
	calcium	90000	34500	25000	31720	16400	28300
	magnesium	11900	4630	3190	4080	2250	3780
	TOP WATER						
	pH	7.48	7.52	7.5	7.67	7.54	7.87
	TDS			3070	2040	1590	1850
	alkalinity	2600	2600	2900	2500	2300	454
	ammonia	499	488	536	535	540	537
	iron		<0.6	<0.6	0.8	1.5	<0.6
	calcium	258	253	262	253	282	234
	magnesium	44	46	48	42	48	45
	phosphate	2.7	2.2	2.1	1.8	1.8	1.6
	struvite	-163	-151	-115	-87	-116	-62
	calcite	-138	-101	-134	36	-41	-268

Coleshill	DIGESTED	31/05/00	07/06/00	14/06/00	21/06/00	28/06/00	05/07/00
	dry solids	3	3.7	3.4	4.4	3.4	3.2
	calcium	36200	29200	32000	31350	36200	40400
	magnesium	4850	4330	4460	4020	4980	5420
	Al				9620	12900	16400
	CENTRATE						
	pH	7.88	7.91	7.83	8.03	7.82	8.08
	TDS		940	3340	760	680	1480
	alkalinity	4250	4200	3340	2300	3200	3000
	ammonia	838	940	935	810	927	876
	Al (tot)				3.7	3.1	4.9
	calcium	62	98	94	134	86	91
	magnesium	13	17	21	27	18	17
	phosphate	87.6	108	105	93.5	89.1	91.2
	struvite	44	75	62	129	74	73
	calcite	-16	72	-140	80	-27	31
	CENTRIFUGE CAKE	using 940					
	dry solids		22.2			21.2	21.8
	calcium		48200			97800	37600
	magnesium		7260			4680	5130
	Al					33100	14100
	LAMELLA						
	pH	7.91	7.95	7.88	8.01	7.92	8.05
	TDS		1160	2490	500	733	736
	alkalinity	5000	4300	4700	3400	3100	3700
	ammonia	906	944	911	878	949	807
	Al (tot)				3.5	2.4	2
	calcium	76	95	90	90	81	88
	magnesium	15	17	17	18	16	16
	phosphate	96.6	103	102	92.7	80.4	84.1
	struvite	44	74	54	86	66	70
		-3	73	3	78	-4	86

Mansfield	FEED	**01/06/00**	**08/06/00**	**15/06/00**	**22/06/00**	**29/06/00**	**06/07/00**
	dry solids	2.9	3.6	3.8	3.7	3.4	3.4
	calcium	28700	30900	24800	28380	25500	26700
	magnesium	6240	6580	5270	5010	5220	5620
	DIGESTED						
	dry solids	3	1.8	1.1	2.6	2.4	2.4
	calcium	35700	55200	100000	36420	43000	39900
	magnesium	7480	11700	22200	7170	8840	8540
	CENTRATE						
	pH	7.8	7.8	7.76	7.87	7.96	7.92
	TDS		867	965	1400	1150	1030
	alkalinity	3500	3700	4100	3300	4500	3100
	ammonia	919	961	867	799	884	800
	calcium	106	103	128	132	147	121
	magnesium	45	45	53	53	57	57
	phosphate	65.7	67.3	53.9	56.3	78.3	66.6
	struvite	166	171	149	145	239	206
	calcite	18	23	79	63	208	67

Milcote	FEED	30/05/00	06/06/00	13/06/00	20/06/00	27/06/00	04/07/00
	dry solids	3.4	4.1	4.2	4.9	2.8	5.1
	calcium mg/kg	26200	25900	21900	19740	28900	22100
	magnesium	3100	3360	2980	2320	3140	2280
					27840	26400	32300
	DIGESTED						
			0.6				
	dry solids	1.8	2	2	2.9	2.2	2.7
	calcium	41100	100000	37400	31420	43600	46100
	magnesium	5270	17500	5170	3950	5490	5140
	Al			38700	32460	154000	66400
	TOP WATER						
	pH	7.5	7.44	7.53	7.58	7.32	7.57
	TDS		1260	4020	910	1220	750
	alkalinity	1200	1700	2300	1900	1900	2300
	ammonia	398	407	410	414	463	465
	aluminium			1.5	1.9	4.5	2.6
	calcium	182	181	185	102	171	167
	magnesium	37	37	36	16	41	39
	phosphate	7.5	8.5	7.7	9.5	10.1	8.2
	struvite	-140	-157	-230	-136	-172	-79
		-398	-370	-380	-258	-478	-103

Oswestry	FEED	26/05/00		05/06/00		19/06/00		26/06/00		03/07/00		11/07/00
			mg/l		mg/l		mg/l		mg/l		mg/l	
	dry solids %	2.2		5.2		7.6		7.1		7.6		4.8
	calcium mg/kg	32900	723.8	15300	795.6	14120	1073.12	14560	1033.76	11900	904.4	58100
	magnesium	5570	122.54	2610	135.72	2610	198.36	2850	202.35	2420	183.92	2230
	DIGESTED											
				0.8								
	dry solids	2.8		3.1		3		2.8		2.8		3
	calcium	67000		100000		29300		24740		33900		26100
	magnesium	13300		20000		4740		4020		5200		2392
	SAS											
	dry solids	6.8		9.3		9.4		7.3		6.9		7.1
	calcium	23500		20300		18000		27500		24800		21400
	magnesium	4220		3600		2990		4120		3900		3350
	TOP WATER											
	pH	7.21		7.2		7.2		7.23		7.11		7.09
	TDS			1280		120		840		890		600
	alkalinity	3270		2500		2200		2200		4100		2500
	ammonia	885		586		596		693		653		535
	calcium	89		190		160		318		202		153
	magnesium	11		36		38		43		31		25
	phosphate	65.3		87.5		104		105		64.4		52.3
	Struvite	-122		-49		83		51		-105		-155
	Calcite	-578		-549		-359		-322		-335		-599

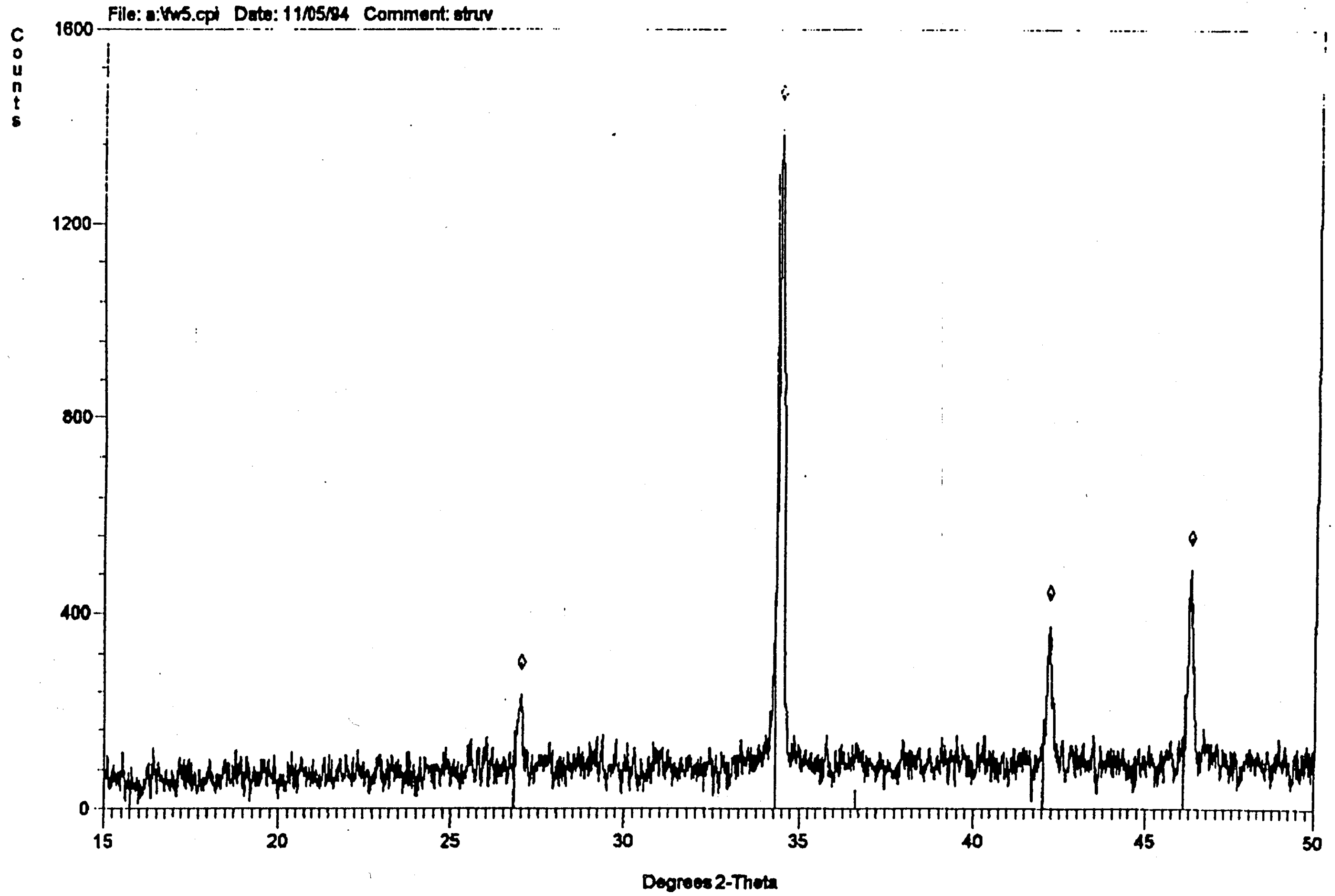
Spernal	FEED	30/05/00	06/06/00	13/06/00	20/06/00	27/06/00	04/07/00
	dry solids	5.2	2.8	5.4	5.5	5.3	5.6
	Fe				60570	135000	54100
	calcium	29200	82200	28800	25540	26000	32100
	magnesium	4630	12500	3800	3060	3080	2680
	DIGESTED						
					8.2		
	dry solids	1.8	1.4	3.7	7.7	5	3.7
	Fe		100000		102000	217000	73700
	calcium	25700	100000	44400	38400	40600	47300
	magnesium	3720	22100	6020	5080	4890	6010
	CENTRATE						
	pH	7.65	7.62	7.56	7.63	7.56	7.71
	TDS		2690	3070	2550	2900	2730
	alkalinity	2500	2100	2800	6300	2900	3000
	ammonia	653	653	647	676	659	673
	iron		<0.6	<0.6	1.1	<0.6	16.9
	calcium	336	272	287	369	278	383
	magnesium	55	51	47	54	53	60
	phosphate	9.2	6.1	3.6	15.9	1.7	13
	struvite	-71	-93	-132	-49	-124	-38
	calcite	108	-108	-42	587	-28	326

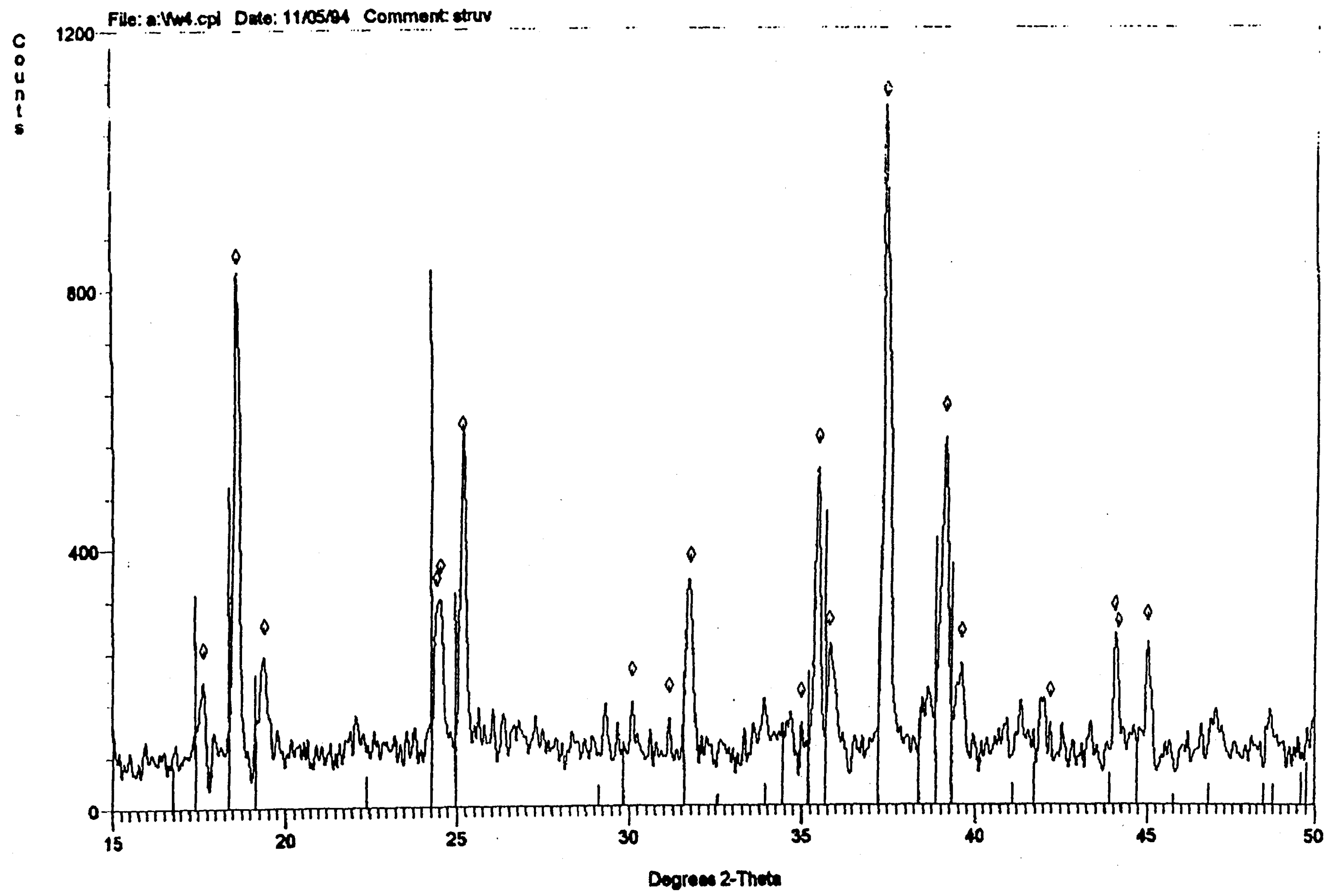
Wanlip	FEED	**01/06/00**	**08/06/00**	**15/06/00**	**22/06/00**	**29/06/00**	**06/07/00**	
	dry solids	3.3	4.2	3.6	5.1	4.1	4.9	
	calcium	26100	27700	28300	20200	23000	27700	
	magnesium	5260	3560	6920	3210	8200	4500	
	DIGESTED							
			0.2					
	dry solids	3.7	2.6	2.4	2.9	2.6	3.3	
	calcium	30900	100000	54900	42110	65800	30500	
	magnesium	5430	90700	8010	7070	12100	6910	
	LIQUORS							
	pH	7.82	7.8	7.53	7.81	7.83	7.39	
	TDS		1020	750	1290	1470	980	1030
	alkalinity	1900	3700	3700	3300	2800	4200	4500
	ammonia	896	1020	966	951	1020	888	928
	calcium	176	151	147	191	218	247	175
	magnesium	43	34	35	39	47	47	46
	phosphate	98.7	110	89.6	88.9	99.5	110	119
	struvite	193	159	124	164	211	153	
	calcite	-49	108	-37	149	138	58	
		using 1020						
	CENTRATE							
	pH		7.57	7.62	7.75		7.67	
	TDS		1110	1090	1290		1240	
	alkalinity		3400	3500	2300		3000	
	ammonia		883	876	779		857	
	calcium		126	109	91		125	
	magnesium		35	26	19		37	
	phosphate		71.2	70.1	70.2		64.5	
	struvite		92	64	41		101	
			-113	-99	-189		-93	

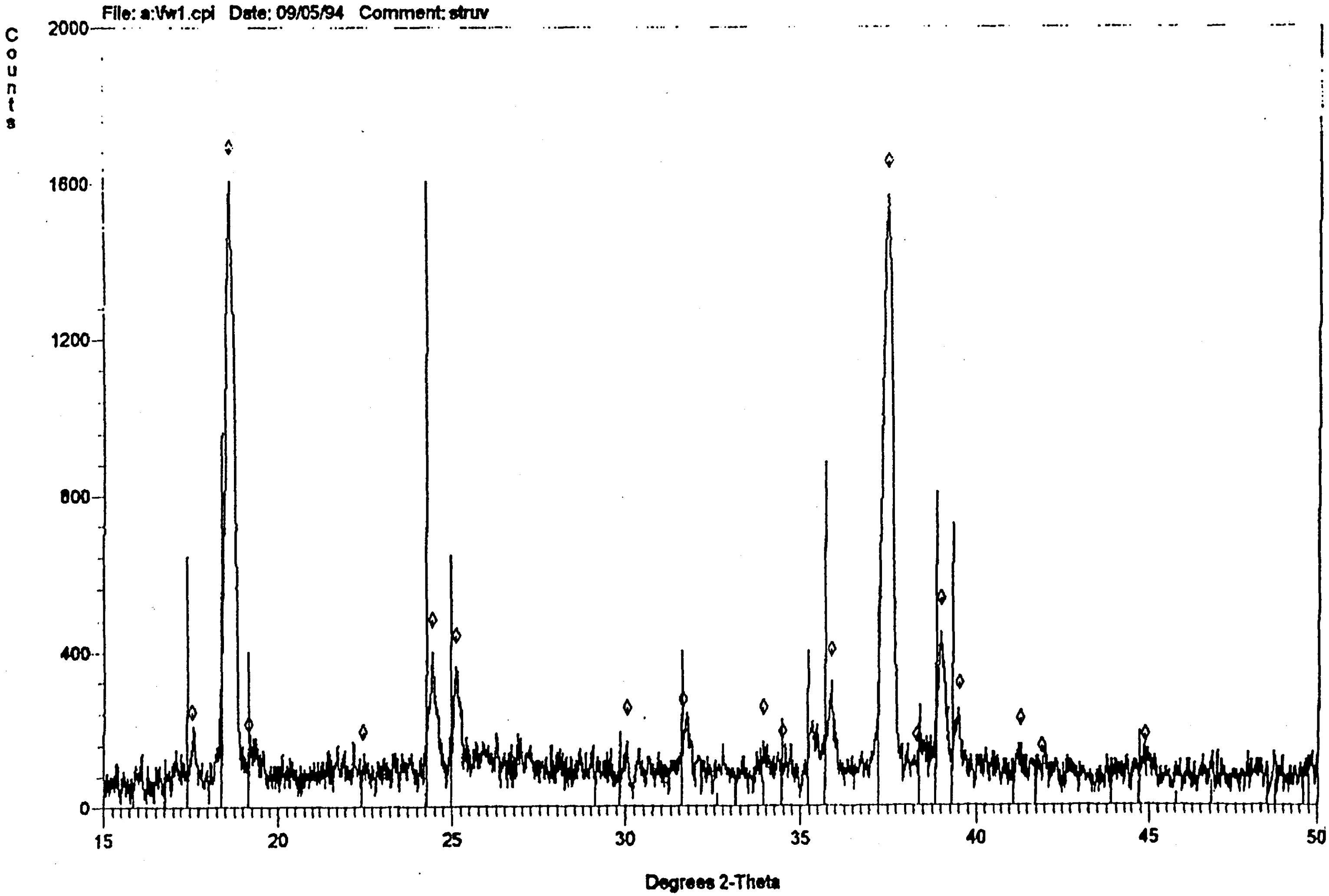
Appendix II

Results from X-ray diffraction analysis upon three scale samples:

- Struvite from Mansfield (sampled on site)
- Calcite form Spernal (sampled on site)
- Struvite from Coleshill (manufactured using liquors in laboratory)


File: a:\Vw5.cpi Date: 11/05/94 Comment: struv
Counts
1600
1200
800
400
0
15
20
25
30
35
40
45
50
Degrees 2-Theta


File: a:\Vw4.cpl Date: 11/05/94 Comment: struv
Counts
1200
800
400
0
15
20
25
30
35
40
45
50
Degrees 2-Theta


File: a:\Vw1.cpi Date: 09/05/94 Comment: struv
Counts
2000
1600
1200
800
400
0
15
20
25
30
35
40
45
50
Degrees 2-Theta