“LIKE WATCHING PAINT DRY”: WATER RECYCLING IN THE PAINT INDUSTRY

Using chemistry to design & develop processes, which will help to create a "circular economy" in paint manufacturing

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by

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ABSTRACT

This thesis represents the cumulation of an industrially based project (KTP 10134) to find resource within manufacturing waste and develop a circular economy within industry. This work documents this collaborative project between Lancaster University's Chemistry and Engineering departments and an industrial partner (Crown Paints), highlighting specific milestones and outcomes of the project which may be of interest to wider industry and academia.

The manufacture of aqueous based paint (also known as emulsion, water based or latex paint) produces large volumes of waste, the largest stream by far is industrial effluent (estimated at Crown Paints alone to be approx. 30,000,000 l annually); produced primarily from the washing of production vessels.

Crown Paints is a leading UK based decorative paint manufacturer and part of the global Hempel Group. Crown Paints operates two production sites situated in Hull and Darwen, UK. The Hull site produces much more aqueous-based product and produces a larger volume of effluent waste (16,000 m^3, 2015). Currently, this effluent is pre-treated at each of the two sites' effluent plants, which flocculate any particulates producing an inert filtercake, which is currently sent for disposal in landfill.

To fully assess the paint manufacturing process, from a waste generation perspective a simple Value Stream Analysis (VSA) of the process was performed. This uses an already established Lean Six Sigma tool (i.e., VSA), which was applied from a unique wastewater perspective. Thus, a novel environmental application of VSA for establishing the origin of excessive water useage in industrial processes is presented.

Laboratory based modelling (via jar testing) of the current coagulation and flocculation based effluent process and subsequent plant trials suggested an ability to reduce the consumable useage of flocculant by 50%.

To improve the laboratory testing further and to focus on the filtration aspect of the process a novel automated stepped pressure filtration method was developed. This included an innovative design of a filtration apparatus and a new method to further characterise the process of filtration. The data interpretation method presented applies a multi-step systematic approach, with each step supported by statistical justification, to characterise filter cake particle stress, filtration diffusivity and cake hydraulic resistivity from a single stepped pressure experiment. Experimentally this new method showed no impact of the 50% flocculant reduction on the filtration parameters of interest.

Additionally, it was also shown that the raw effluent could be utilised as the "solvent" within the paint production process with limited effect on the paint's physical properties. From laboratory testing this was scaled to production volumes (circa. 9,000-19,000 l) and a method was developed to reduce virgin raw materials by up to 5%. A production batch (9,000 l) with 4% extra product (360 l) was produced. Testing of this trial batch showed no difference with a standardised paint formulation. This presents an exciting opportunity for water reuse within various Fast Moving Consumer Goods (FMCG) manufacturing processes.

DECLARATION OF AUTHORSHIP

The work described in this text was conducted at Lancaster University's Chemistry and Engineering Departments and Crown Paints' Darwen and Hull Sites. This thesis is the result of my own work and includes nothing, which is the outcome of work done in collaboration except where specifically indicated in the text. It has not been previously submitted, in part or whole, to any university of institution for any degree, diploma, or other qualification.

Signed:

Date: 30th September 2021

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I would like to express my gratitude to everybody at Crown Paints, the warmth, support, knowledge, and enthusiasm shown from everyone about this project has been fantastic. For fear of needing a second volume to this thesis, I feel unable to list all names but without their technical knowledge and expertise, use of labs supervision, help with data collection and general encouragement there can be no doubt this idea would have got off the ground. A special thanks must be given to Ian Coote & Rachel Demaine for giving me the support and encouragement to “get it done”.

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I probably should also thank my family for they rarely get enough praise, for all the grumpy phone calls, bacon butties and general family going above and beyond for the last 30 years. The support of my friends has also been essential throughout. And finally, to Tamsin Howarth for holding my hand & supporting me throughout, while giving me the final push I ever so needed at the end.

> *“The worst thing is watching someone drown and not being able to*
>
> *convince them that they can save themselves by just standing up”*
>
> *Serena Sprunk*

DEDICATION

To all those we lost along the way.

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LIST OF SYMBOLS

Symbols for Paint Chemistry

a^*	Red/Green
b^*	Blue/Yellow
I	Initiator
L^*	Brightness
M	Monomer
n	Degree of polymerisation
T	Tint
W	Whiteness
x & y	Chromaticity coordinate in the CIE 1931 colour space
x_n & y_n	Chromaticity coordinate of the perfect diffuser (reference white)
Y	Y tristimulus value (relative luminance

Symbols for Paint testing

		Dimensions
$\boldsymbol{A}$	Area	m^2
$\boldsymbol{CR}$	Contrast ratio	-
$\boldsymbol{L}$	Loss of mass per unit area	gm^{-2}
$\boldsymbol{L_{dft,}}$	Mean loss in dry-film thickness	µm
$\boldsymbol{m_1}$	Initial mass	g
$\boldsymbol{m_2}$	Mass following 200 scrub cycles	g
$\boldsymbol{r}$	Radius of the cone	m
$\boldsymbol{RB}$	Reflectance over black areas	-
$\boldsymbol{RW}$	Reflectance over white areas	-
$\boldsymbol{S}$	Scrub length	mm
$\boldsymbol{T}$	Torque	nm
$\boldsymbol{W}$	Scrub width	mm
$\boldsymbol{\Delta\lambda}$	Wavelength interval	m
$\boldsymbol{\vartheta}$	Cone angle	rad
$\boldsymbol{\rho_{df}}$	Dry film density	gcm^{-2}
$\boldsymbol{\Omega}$	Angular velocity	rad·s^{-1}

Symbols for effluent treatment

		Dimensions
a	Acceleration	m s^{-2}
C_D	Drag coefficient	-
d	Diameter of the settling particle	m
Fb	Boyancy force	N
Fd	Drag force	N
Fg	Gravitational force	N
g	Acceleration due to gravity (9.81 m s^{-2})	m s^{-2}
m	Mass	kg
$Py(\varphi)$	Compressive yield stress	M L^{-1} T^{-2}
Re	Reynolds number	-
$r(\varphi)$	Hydraulic resistivity	M L^{-3} T^{-1}
t	Time	s
V_p	Volume of particle	m^3
v	Dynamic viscosity	N s m^{-2} or kg m^{-1} s^{-1}
z	Height above filter membrane	Variable, typically m or l
ΔP	Piston pressure	Pa
μ	Kinematic viscosity	m^2 s^{-1}
ρ_p	Density of particle	kg m^{-3}
ρ_w	Density of water	kg m^{-3}
φ	Local volume fraction of solids	-

Symbols for Value Stream Analysis

NVA	Non-value adding
VA	Value adding
σ	Sigma Level

Symbols for stepped pressure filtration

		Dimensions
B_*	Specific coefficient of 2nd term of virial solids stress model	$L^5M^{-1}\theta^{-1}$
$B_{L,n}$	Coefficient of the nth term of Landman et al's late phase series solution	-
C	Coefficient of time independent terms fitting algorithm	variable
c	Solids concentration	$M\ L^{-3}$
$\tilde{c}_{gel}$	Gel concentration derived from virial solids stress model	$M\ L^{-3}$
c_*	Diffusivity weighted mean concentration at cake completion	$M\ L^{-3}$
D	Filtration diffusivity	$L^2\ T^{-1}$
$\mathcal{D}_*$	Specific coefficient of the nth term of virial solids stress model	variable
DoF	Degrees of freedom	-
E^2	Sum of squared residuals	variable
F	Fisher distribution	-
h	Measured height of filter piston above filter membrane	L
$\hat{h}$	Model estimated height of filter piston above filter membrane	L
M	Fitted coefficient of time dependent terms in fitting algorithm	variable
M_*	Nominal molecular mass of solid structures	M
n_{RZ}	Richardson and Zaki model exponent	-
n_v	Exponent of the nth term of virial solids stress model	-
ΔP	Filtration applied differential pressure	$M\ L^{-1}\ T^{-2}$
P_y	Concentration dependent inter particle stress	$M\ L^{-1}\ T^{-2}$
P_y	Concentration dependent inter particle stress gradient	$L^2\ T^{-2}$
r	Concentration dependent hydraulic resistivity	$M\ L^{-3}\ T^{-1}$

R_*	Nominal specific gas constant	$kJkg^{-1}\ K^{-1}$
r_0	Hydraulic resistivity of infinitely dilute suspension	$M\ L^{-3}\ T^{-1}$
t	Elapsed time	T
T	Absolute temperature	θ
α	Cake completion parameter	-
ρ_s	Solids density	$M\ L^{-3}$

Subscript for stepped pressure filtration

0	Initial (time zero)
∞	Infinite time asymptote
C	Pertaining to the moment of cake completion
$crit$	Critical value relating to rejection criteria in “F” and “t” tests
E	Early (cake growth) phase
L	Late (cake compression) phase
N	Number of fitted parameters
R	Pertaining to a stepped pressure run
RZ	Richardson and Zaki
s	Solid phase
$stat$	Statistic relating to “F” and “t” tests
U	Unweighted
v	virial

Symbols for water reuse

$Solids_{F},$	Total “Solids” in a formulation,
$Solids_{RM}$	Total Solids in Raw Materials
$Solids_{RW}$	Total Solids in Reclaimed Water

LIST OF ABBREVIATIONS AND ACRONYMS

AD	Anno Domini
aka	Also known as
ASTM	ASTM International (formally the American Society for Testing and Materials)
BS	British Standard
CFCs	Chlorofluorocarbons
CGE	Centre for Global Eco-Innovation
CIE	International Commission on Illumination (Commission internationale de l'éclairage)
COD	Chemical oxygen demand
CR	Contrast ratio
CSB	Chemical Safety Board (USA)
CTECH	Colloid Treatment Technologies Ltd
DAF	Dissolved air flotation
DI	Deionised
DRIPS	Decoration, Identification, Protection and Sanitation
EDL	Electrical double layer
EoS	Equations of state
EPA	Environmental Protection Agency (USA)
EPEA	Environmental Protection Encouragement Agency (Taiwan)
EQ	Equalisation Tank
EWC	European Waste Catalogue

FMCG	Fast Moving Consumer Goods
fps	Frames per second
HF	Hydrofluoric acid
HSE	Health and Safety Executive (UK)
IBC	Intermediate bulk container
ICI	Imperial Chemical Industries
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISO	International Organization for Standardization
KTP	Knowledge Transfer Partnership
LCA	Life Cycle Analysis
LSS	Lean Six Sigma
MRO	Maintenance, Repair and Overhaul
NAZ	Normal analytical zone
NVA	Non-Value adding
OED	Oxford English Dictionary
PLC	Programmable logic controller
PSA	Pressure-sensitive adhesive
PUR	Polyurethane
PVA	Polyvinyl acetate
QC	Quality Control
R & D	Research and Development
REF	Research Excellence Framework
RF	Radio frequency

rpm	Revolutions per minute
RSD	Relative standard deviation
SAP	Systems, Applications, and Products in Data Processing
SD	Standard deviation
SME	Subject Matter Expert
TDS	Total dissolved solids
TIMWOODS	Transportation, Inventory, Motion, Waiting, Overproduction, Defects Skills
TSS	Total suspended solids
USB	Universal Serial Bus
UK	The United Kingdom of Great Britain and Northern Ireland
USA	The United States of America
VA	Value adding
VBA	Visual Basic for Applications
Veo Va 10	Vinyl neodecanoate
VOC	Volatile Organic Compounds
VSA	Value Stream Analysis
WM3	Waste classification technical guidance

1 INTRODUCTION

1.1 Overall aims and objectives of this work

Many manufacturing processes produce large quantities of waste which are ultimately disposed of. This thesis presents the recording of an industrially based PhD to investigate the ability to extract any potential resource from this material and develop a circular economy within paint manufacturing.

The project was based at Crown Paints and funded with an intention of providing a benefit to this business which somewhat restricted the scope of the work. Whilst the work is specifically targeted towards Crown Paints it is not solely applicable for that specific business and provides potential solutions to issues arising with manufacturing waste across coatings and indeed other manufacturing industries.

1.1.1 Highlighted innovative outcomes of this research

In terms of “contribution to knowledge” this thesis presents three key novel outcomes from this research:

Firstly, within Chapter 3. a new application of a Value Stream Analysis (VSA) is presented. VSA is already an established Lean Six Sigma tool historically used for improving efficiencies of processes within organisations however more recently studies have utilised VSA to target environmental challenges. This work takes this environmental angle further by focusing specifically on the generation of wastewater within an industrial process perspective. The application for this technique within industrial processes is somewhat limitless (as it can be tailored towards areas of concern) however it could particularly be useful within any process which requires significant amounts of vessel washing, for example Fast Moving Consumer Goods (FMCG), Brewing etc.

Currently the material of concern (washwater from aqueous paint manufacturing, known as effluent) is treated by an effluent treatment process via a coagulation/flocculation stage followed by a filtration within a filterpress. Chapter 5. presents a method to model this process within a laboratory using an already established Jar Test methodology. No literature for the application of Jar Tests for paint effluent was identified and this work highlights some challenges with established methods. A plant trial also highlighted a limitation of the Jar Test methodology concerning the filtration stage of the process. To explore this element further a bespoke pressure filtration device was developed. Chapter 6. provides the details of this device and a mathematical method to fully characterise the flocculated material is presented. Notably, the model provided combines the need for two separate runs to determine compressive yield stress, ***Py(c)*** and resistivity, ***r(c)*** into a single run. This work was published in the preprint Wardrop et al.[1] and is currently being reviewed for publication within scientific journals. This application of this research would be useful in studying any processes involving filtration; notably water treatment, mining, polymer production, pharmaceutical manufacture etc. A simple benchtop device to study filtration (and thus make process improvements) could be revolutionary within many industries.

The final innovative outcome presented in this thesis is the use of the raw effluent as a material within a paint formulation with no significant negative impact on the paint product's properties. Chapter 7. gives an overview of laboratory testing of a new paint formulation followed by a full plant trial of a product which later entered the market. This method generated a trial batch, which provided an extra 4% of product for sale without the need for any additional raw materials (except some additional virgin water). This is a highly significant saving for any process as it improved batch size by 4% at insignificant cost. This outcome has the ability to completely revolutionise the production of aqueous paint and thus the impact of this is notably significant. Additionally, this outcome achieves the stated objective of the KTP project in "developing a process to recycle paint manufacturing" to develop a "circular economy" within paint manufacturing (paraphrased from Quote 1.). Outside of paint production this simple system has the potential for further application across various processes which require vessel washing such as many Fast-Moving Consumer Goods (FMCG) manufacturing processes.

The impact of this work has been significant and the success of the project has been highlighted in an Impact Case Study for the 2021 iteration of the Research Excellence Framework 2021 (REF 2021) titled: "Lancaster University research improves the monitoring, control and optimisation of paint wastewater processing at one of the UK's largest paint manufacturing companies"[2].

1.1.2 Overview of thesis structure

Here in Chapter 1. an overview of the thesis is provided with a contextualised overview of the Knowledge Transfer Partnership (KTP) project and the industrial challenge the project aimed to solve.

Chapter 2. gives an overview of the chemistry of paint providing the reader with an essential understanding of the material in question. The aim was to provide enough detailed information for the reader to fully understand the material as to be able to identify and apply the findings of this work with similar materials. An overview of the paint manufacturing process and effluent treatment is also provided to contextualise the process under investigation.

Chapter 3. fully quantifies the effluent and comprehensively maps the effluent generation and treatment process with the aim of identifying potential areas to focus on for maximum impact. It uses a Value Stream Analysis (VSA) tool with a unique industrial waste water perspective. This provides a baseline for the whole project to measure its successes and estimate its overall impact. Whilst also representing the first identified novel outcome of this work.

Chapter 4. builds off the process mapping provided in Chapter 3. and provides a range of possible solutions (illustrated in Figure 112.) these are ranked in a pyramid structure based on the philosophy of the Waste Hierarchy. The advantage of this approach is that it provides an idealised ranged of solutions to maximise the potential to recover resources without the inevitable practical limitations such as time, cost, additional processing etc. The aim of this Chapter is to show potential solutions to the problems of the process studied in Chapter 3., however due to the practicalities of this project some of the solutions were not investigated further. Nevertheless, they are provided here to spark further conversation and to present an argument to justify the research avenue pursued in this work.

Chapter 5. is a study to optimise the current effluent treatment process with an aim to identify the feasibility of reducing consumable consumption without any impact on the process. An overview of the Crown Paints Hull site's effluent treatment process is provided. This is followed by laboratory scale modelling of the Hull site's effluent treatment process using the already established Jar Test methodology. Based on these tests, Crown Paints were enthusiastic to explore the optimisation of their current process further and thus the reduction of PolyClay (the flocculant used within the process) by 50% was trialled for seven batches. This proved to be feasible but identified potential issues with the filtration stage of the process.

Chapter 6. presents a response to the limitations identified within Chapter 5.; a bespoke design for a benchtop pressure filtration device is given alongside a methodology to fully characterise the filtration process. This investigation further suggested no significant impact on the filtration process through reducing the PolyClay consumption by 50%. The stepped pressure filtration methodology presented here is the second identified novel outcome of this work.

Chapter 7. explores the ability to recycle the washings from the production process back directly into the production process. This solution is advantageous due to it requiring a simple, low effort alteration but ultimately results in a high reward activity. This work showed practically that all additional water in the "Letdown phase" (after dispersion) could be replaced with washing from another batch with no significant impact on necessary paint properties. The details of the standardised paint testing are provided. The Chapter explores basic formulation testing within a laboratory environment and eventually the scale up to a full plant trial batch of 9,000 l, generated with the same principle. This batch was quarantined to allow further testing of the trial batch, which is also detailed here before being supplied into the market.

Chapter 8. provides the conclusions to this work and explores the potential for further research. The overall impact of the project is also reviewed.

1.2 Introduction to the nature of this specific project

The project was initially a one-year (September 2014-September 2015) MSc by research working with a social enterprise Nimtech their partner Crown Paints and Lancaster University's Chemistry department with support with the Centre for Global Eco-Innovation (CGE). The vision was to find value in Crown Paints' waste streams. This feasibility study resulted in further funding (KTP 10134[3]) for a further three years (January 2016-January 2019) being sort under Innovate UK's Knowledge Transfer Partnership (KTP) scheme (Figure 1.). The project subsequently became a three-way partnership between, Crown Paints, and Lancaster University's Chemistry and Chemical Engineering departments to evaluate and reduce Crown Paints aqueous waste burden. It was established soon within the project that by far the largest waste stream for Crown Paints in terms of volume is that of wastewater (effluent) from their manufacturing sites at Darwen and Hull, estimated at 30,000,000 l, which is the equivalent of 12 Olympic size swimming pools annually.

Figure 1: The Knowledge Transfer Partnership (KTP) 10134 partners.

1.3 Project objectives

Given the nature of this industrially based project a specific objective was defined for the KTP (Quote 1.) project. This provided a framework for the KTP project while constricting the scope of this thesis. Interestingly, a stipulation of the funding was the requirement to focus on aqueous paint only (i.e., not high VOC solvent-based paint) however this did not restrict any potential research areas of interest in practice.

> *“To use chemistry to design and develop processes to reduce, reuse and recycle paint manufacturing and post-use waste, helping to create a "circular economy".*

Quote 1: THE KNOWLEDGE TRANSFER PARTNERSHIP STATED OBJECTIVES 2016

A significant limitation of the scope of the project was the commercial nature of the research and aim to maximise the benefit to Crown Paints’ needs as a business. This provided a clear and disciplined structure to the project but also restricted the avenue of investigation. Throughout this thesis where opportunities for further work are identified these are noted to the reader as they may be more applicable in other environments, whether in academia or industry.

As the project evolved the KTP objective morphed into a series of five deliverables where the research was targeted:

1. Identify the source of the wash water within the paint manufacturing process and characterise the quantity & composition of the material (this is detailed within Chapter 3.).
2. Identify potential solutions specifically for the process defined in Deliverable 1. without any commercial, logistic, or financial limitations (Chapter 3.5.).
3. Optimisation of the current effluent treatment process with a view of reducing consumable useage by 50% (Chapter 5.).
4. Develop a new method to study the filtration process which was neglected within Deliverable 3. (Chapter 6.).
5. Ascertain the feasibility of returning washwater into the manufacturing process and create a circular economy within the paint manufacturing process (Chapter 7.).

The structure of this thesis (as detailed in 1.1.2.) is built around the five deliverables described above with the three key “contributions to knowledge” (highlighted in 1.1.1.) included in the relevant deliverables.

1.4 Description of the challenge for Crown Paints' manufacturing process

The nature and size of Crown Paints' business inevitably results in the production of a substantial volume of waste, a large proportion of which, contains materials that have the potential to be re-used in the paint manufacturing process. Crown Paints, as a responsible manufacturer, is keen to increase the sustainability of its business. The aim of the KTP project was to support Crown Paints in identifying the potentially recyclable waste and to determine a route for possible resource recovery with the goal of reducing the environmental and economic burden of the manufacturing process. One of the higher volume waste streams (approx. 30,000,000 l) is wastewater (effluent) from Crown Paints' two manufacturing sites (based at Darwen and Hull, UK). This wastewater is currently pre-treated within effluent plants at both sites before being piped for secondary water treatment. The effluent treatment plants produce a by-product (filtercake) from the process, which although currently regarded as waste, potentially has value which is yet to be utilised. The aim is to help reduce the volume of this effluent at source whilst investigating possible uses for the by-product. Another waste stream with particular interest for the business is out of specification and surplus paint. Though the quantity of this is much less than the effluent, its quantity is still substantial (approximately 120 tonnes per year). This "waste paint" is an issue across the industry. Whilst legally defined as "non-hazardous" waterbased paint has a varied chemical composition of biocides, polymers, solvents, surfactants, and inorganic components which make it intrinsically difficult to reprocess, recycle or even treat. A fundamental grasp of the chemistry of paint is therefore required to identify and assess alternative treatments for these waste streams.

1.5 Waste as a resource and “the circular economy”

Our conventional linier “cradle to grave” (Figure 2.) based economic system has developed around a principle of taking natural resources, making a product for a use, and then disposing of the product when that use is fulfilled. This can be described as a “take-make-use-dispose” system. Economic drivers continuously force the increased consumption of these resources and there is a pressure for rapid redundancy on the products (e.g. planned obsolsence[4]) for the increased generation of profit.

With a continuingly growing population estimated to be 9.7 billion by 2050[5] the world will need to consume three times the planet’s natural resources to sustain current standards of living [6]. Additionally, waste generation is on course to increase by 70% by 2050[7]. With continued economic growth the consumption of natural resources is clearly unsustainable.

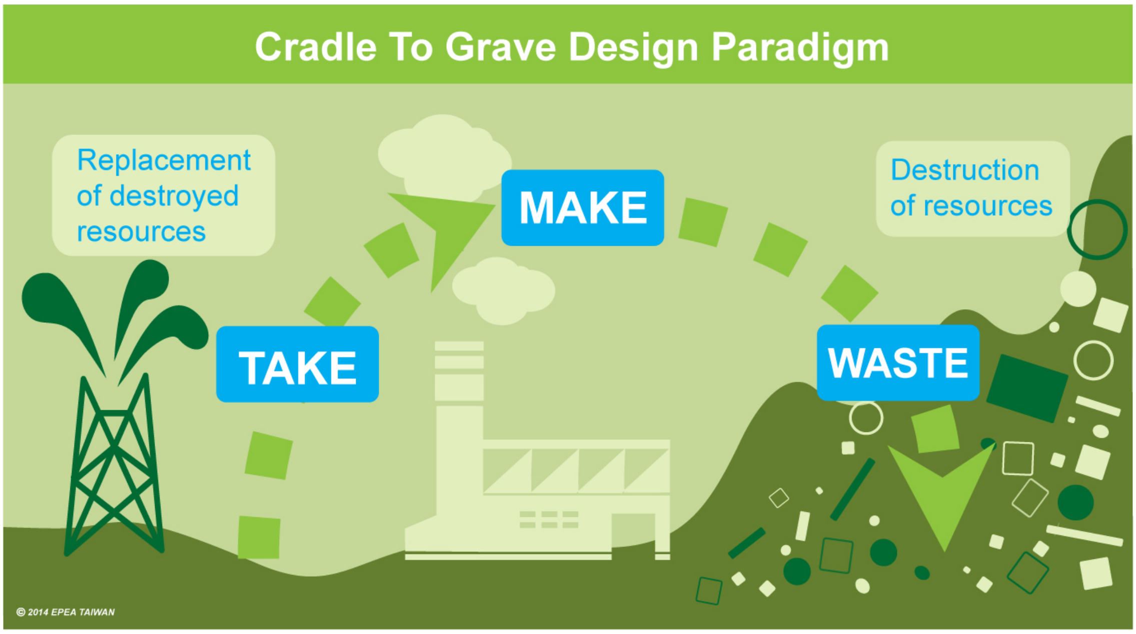


Figure 2: The Cradle to Grave Design Paradigm, from EPEA, 2020[8].

A circular economic model is an economic system which encourages a continuous flow of materials through the system. A circular economy can be illustrated in a butterfly model (Figure 3.), with biological or natural flows of resource to the left and human & industrial cycles to the right. The principle aim of the circular economic model is to maximise the time resources remain in the cycle to reduce the demand for additional virgin resources. Thus, increasing the duration of cycles and the number of cycles is essential.

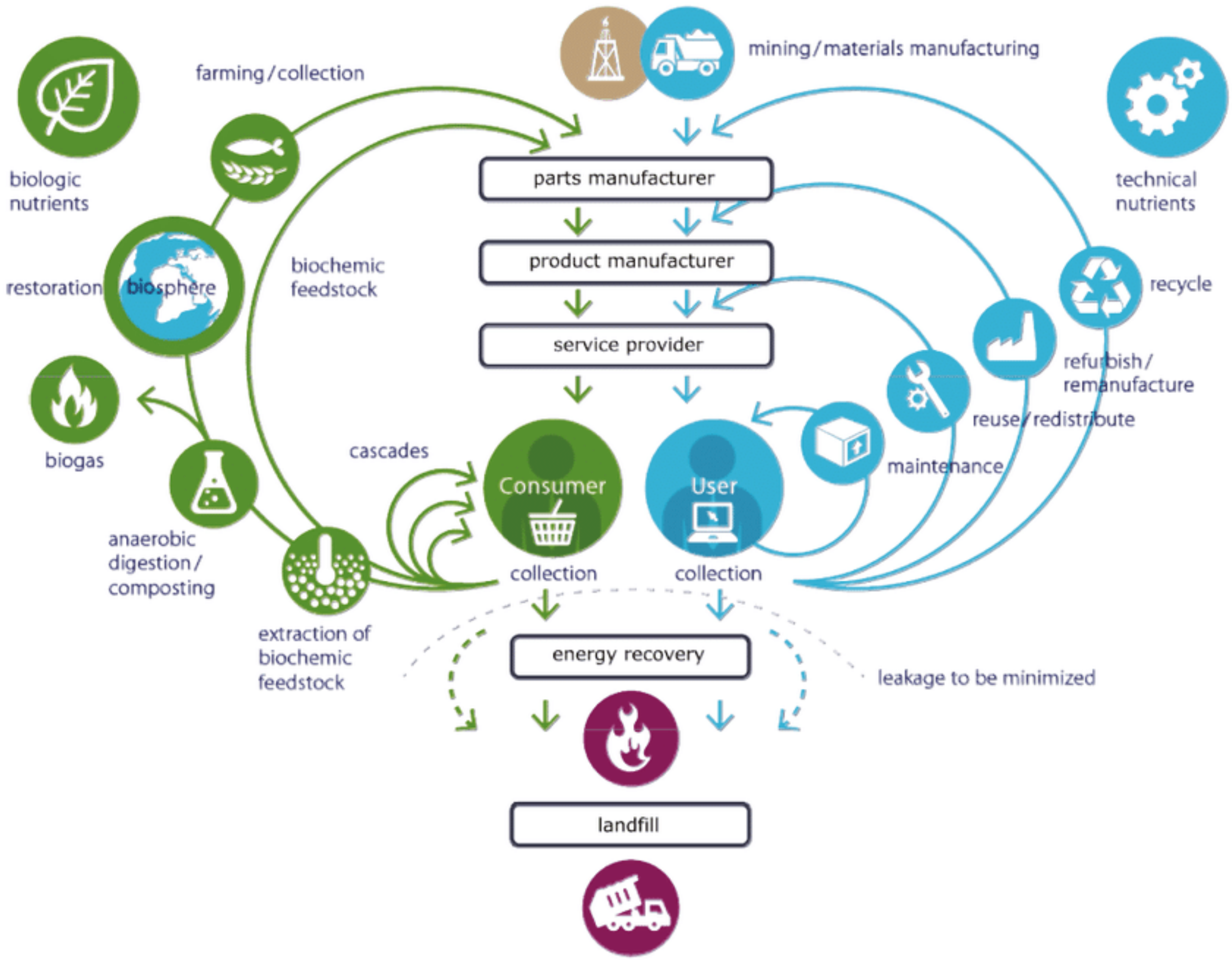


Figure 3: The Butterfly model for circular production and consumption, from Soldal, 2019[9].

1.5.1 Practicality of circular economic models in different sectors

With high value products a logical solution is to make them easier to update or repair [10]. Increased modularity of products and processes has been suggested to aid this shift [11,12]. However, this approach also constraints significant innovative improvements due to the need to standardise components. Products in automotive, aerospace and the tech sector may have an entire system developed around maintenance, repair and overhaul (MRO) operations to service a product to keep it functional.

Practically speaking decorative paint is manufactured, marketed, and distributed as a typical Fast-Moving Consumer Good (FMCG). It is manufactured & sold quickly and at a low cost to consumers (either to professional decorators or for domestic use). Modularity or repairability of the product is of limited practical application in such a system. Literature on increasing the circular nature of the FMCG sector is sparse with a focus on packaging and supply chain issues [13,14]. Paint is a distinctly separate substance to many FMCG products, i.e. it's isn't a food, toiletry or cosmetic and thus additional standards may not be as relevant. Without the constraints of other high-volume low-cost products this presents an interesting opportunity to investigate the possibility of making the manufacturing process circular. The paint industry also already has a notably modular feature, instore tinting of the product to the shade of a customer's preference. A practical solution could be to constrict paint production to an untinted neutral base, which is later tinted to the customers desired colour. This would minimise any excess production of less desired shades of paint and thus ultimately less waste. Additionally, such a move could limit the amount of vessel washings required because of less residual colourant within the vessels and the potential to move towards bigger batch (or continuous) production.

1.5.2 Paint Waste

Decorative paint waste has historically been separated into two distinct categories, those containing organic solvents (solvent based) and aqueous paint (waterbased). Indeed, the Waste Classification Guidance (WM3) [15] distinguishes between “waste paint and varnish containing organic solvents or other hazardous substances” (EWC: 08 01 11*) and “waste paint and varnish other than those mentioned in 08 01 11” (EWC: 08 01 12). This distinction between hazardous solvent-based paint and non-hazardous aqueous based paint presents an interesting divide between paint waste treatment methods.

Solvent based paint has an inherent calorific value and is typically recycled as a fuel for cement kilns. There is an economic value to this activity and thus solvent waste is often considered a by-product. Additionally, because the cost of virgin organic solvent is much higher than that of water there is a clear incentive to minimise the use of solvent within the manufacturing process [16]. Due to the cost of the virgin solvent attention is becoming more focused on recycling solvent based paint sludge into new paint[17]. The automotive industry will likely be the main driver of this research area due to the high volumes of solvent-based paint sludge produced and constant pressure to increase the efficiency of their processes. Aerospace has similar processes however it is unlikely recycled paint would meet necessary quality requirements (e.g. Nadcap accreditation[18]) and the sludge will also likely be contaminated with isocyanates.

Historically aqueous based paint has been difficult to dispose of as there is negatable calorific value and non-hazardous liquid waste isn't suitable for landfill[19]. The relatively high volumes of waste generated from the production of a low cost product has been a continual issue for the waste industry to meet the demands of coatings manufacturers. This isn't an issue solely for paint waste, low/non-hazardous liquids (e.g. shampoo, cosmetics, household cleaners etc.) present similar challenges and represent a significant proportion of waste generated.

The UK's waste sector developed two solutions for the treatment of this low/non-hazardous liquid waste. The first was to include the waste in composting material however environmental permitting legislation eventually prevented the inclusion of paint waste due to no evidence that it provided a benefit to the product. The other solution was to blend the liquid with inert solid waste until it was suitably dry and to landfill the blended material as a solid non-hazardous waste. This system was relatively primitive often utilising a front loader digger and colloquially known as a "pit of death" due to the risk of reactions within the mixing process. The literature on these previous practices is virtually non-existent however it remains an open secret within the waste industry.

Contemporary practice is to bulk the waste together (either manually, or by shredding the originally packaged goods), for safety the best practice is to include compatibility assessments (e.g. pH, oxidation, thermodynamic properties) before the mixing of different wastes streams[20]. This larger volume of liquid is then treated through conventional coagulation/flocculation followed by a dewatering processes. The residual "cake" is then normally forwarded to landfill. This practice is essentially Crown Paint's operation within their effluent plant. An alternative for aqueous paint is to use as an admixture within concrete[21] this has previously been done in the UK, where it was mixed with additional foundry waste, however it doesn't appear to have been a commercial success long term.

Another method has been suggested to use acid digestion[22] to extract TiO_2 from paint waste (but also potentially from other products also). Whilst possible the logistics of performing the activity on an industrial scale made the application of such an approach for this thesis unrealistic.

Utilising standard water treatment techniques to essentially dewater bulk low/non-hazardous liquids before landfill has been controversial for both the waste industry and manufacturers of the products. For the waste industry this activity is complex and costly for limited return. Manufacturers often see this as a potentially lost resource which can be returned into the supply chain. However, from a FMCG perspective most of their published interest in the circular economy has been focused on packaging waste [23–27] and not of the waste generated from the product itself. Plastic waste has been at the forefront of environmental discourse since being highlighted by David Attenborough in Blue Planet II[28]. Recently, a significant criticism of the corporate social responsibility practices of these corporations is that under pressure to be seen as "sustainable" brands (particularly within FMCG) are "greenwashing" dubious environmental claims to the public[29]. The perception and pressure from consumers has pushed a narrative to focus on reduction of packaging waste often at the expense of other environmental metrics[30–32]. Improving the efficiency of the manufacturing process may produce greater economic benefits to the business in addition to its sustainable targets however this is also less marketable to consumers who may not fully understand the complex nature of the supply chain. The use of recycled material within products is also likely seen as a risk to the brand's reputation due to the risk of variations in the quality of the product and subsequent customer dissatisfaction.

2 THE CHEMISTRY OF WATER BASED PAINT (AQUEOUS, EMULSION, LATEX PAINT) AND ITS MANUFACTURING PROCESS

Coatings are necessary to reduce the vulnerability of an object at its surface; to decorate and camouflage imperfections in materials. Whilst surface coatings represent a vast variety of different products (from Metallic plating to plastic sheeting and even wallpaper) the subject of “Paints” is a diverse domain in its own right; which results in a versatility whereby a product may be sort suitable for virtually any task in any environment. DRIPS is a coatings industry specific acronym to describe the four main purposes of coatings; Decoration, Identification, Protection and Sanitation.

A “Paint” may be loosely defined as “a substance which can be spread over a surface and dries to leave a thin decorative or protective coating” (Adapted OED[33]). Typically, classes of “Paints” include: enamels, lacquers, varnishes, primers, sealers, undercoats etc. However interestingly, by this definition, related but also usually classified as distinct products such as plasters, concrete and tar (which, conveniently are developed on the same principles and contain many of the same ingredients) could also in some instances be described as “Paints” (an obvious example would be bituminous paints).

“Waterbased paints” are a general classification, known typically as “Emulsion Paints” in the UK or “Latex Paints” in the USA (both in reference to the polymer component) and primarily as “Aqueous-based Paints” in a waste context (most likely due to a specific distinction between hazardous solvent containing coatings and non- hazardous aqueous based coatings in the Environment Agency’s technical guidance for classification[15] and thus the legal options for treatment), within this document and (as a general rule) in related literature it is safe to assume these terms are interchangeable.

A driving factor in the increased presence of waterbased coating within the market (at the detriment of their solvent-based equivalents) is the increased legislative requirement to lower the content of Volatile Organic Compounds (VOCs). VOCs are volatile organic substances defined by the EU as "any organic compound having an initial boiling point less than or equal to 250 °C (482 °F) measured at a standard atmospheric pressure of 101.3 kPa”[34]. Inconveniently these substances represent the solvent constituent of most paints, perfumes, inks etc. Adverse effects of VOC emissions vary based on their type, local concentration and interaction with other air pollutants. Chlorofluorocarbons (CFCs) are a textbook example of a VOC contained within a household product (i.e. refrigerators, freezers etc.), which once released migrates toward the stratosphere where it can be photolytically dissociated via sunlight in a process that ultimately results in the depletion of the ozone layer. Most VOCs are toxic (to a varying degree) and this is mainly controlled within developed countries via legislation. In late 2000 the “Decopaint” study of the potential for VOC reduction within the decorative paint industry was reported to the European Commission[35]. The consensus across the coatings industry was the desire for a harmonised product directive for decorative coatings; thus preventing competitive distortions due to market forces. The industry’s response has been multifaceted, of particular relevance to this research is the reformulation of alternative products matching the previous performance but with a much lower or totally avoiding VOC content (the rise in waterbased paints and powder coatings is seen as a response to this) but other interesting incentives such as recycling (which provides enormous economic benefits) and more environmentally considerate disposal routes has also been applied. In addition to the visible drive for manufacturers to decrease the VOC component of their products an economic drive has been seen from the simple perspective that “water is cheap” when compared to other raw materials.

2.1.1 The Solvent

A “solvent” in the paint industry is a very loosely defined term referring to “a liquid of significant volume used within the paint” and bares no relevance to the traditional definition within the field of chemistry (with respect to the substance’s ability to dissolve another substance). To increase confusion further the term in respect to “solvent-based paints” refers solely to (usually) high VOC organic solvents. Whereas in waterbased paints the principal “solvent” remains water. However other additional organic solvents are often added, these are usually non-volatile; typically with a boiling point >130°C, for example Texanol[36], (the primary organic solvent used in emulsion paints) has a boiling point between 255 - 261.5 °C. When these additional organic solvents are added these can also be described as “solvents”. Whilst within the literature this can be confusing, every attempt will be made to clarify the type of solvent referred to in every instance within this document.

The primary role of the paint’s “solvent” is to dilute and present a liquid medium carrier of the paints non-volatile components, to provide an appropriate viscosity to aid in the paint’s application and to aid in the paint’s stability while in a liquid state. As a carrier, the solvent does not form (ideally) any part of a paint film (however inevitably microscopic imperfections develop with residual “trapped” liquid) and thus the solvent must be volatile, evaporating to leave the remaining non-volatile component attached to the applicated surface. This process is the basis of the paint “drying” and leaving a paint film.

It should come as no surprise that the principal liquid ingredient within a waterbased paint is obviously water. Water can be used within emulsion paint in isolation or blended with additional alcohols or ether-alcohols (e.g. Texanol[36]) to aid in increasing the solvent polarity (and thus dispersion) when used with water-soluble resins. The advantages of water as a medium within paint stem from its non-toxicity, non-flammability, and odourless properties in addition to its cost and ready availability. Interestingly water however is not in fact a very suitable material from a purely chemistry perspective because it presents a poor miscibility with the other ingredients (thus requiring additional products to mitigate this), additionally specially developed miscible polymers remain sensitive to it; resulting in an eventual vulnerability at the film surface to hydrolysis.

2.1.2 The Binder (Polymer)

The polymer (or Binder) is the primary film forming element of a water-based paint. The terms Emulsion and Latex paints refer to this element directly as a water-borne dispersion of polymer particles (i.e. a latex) in a dual phase emulsion. As the binder represents the polymer backbone of the paint film, its properties have as significant impact eventually on the properties of the dry film. A suitable polymer is normally required to be resistant to mechanical abrasion and environmental effects, whilst still being easily applicable. Typically, synthetic polymers are utilised such as acrylics, vinyl acrylics (e.g. PVA), styrenes as the Binder within a paint formulation.

2.1.2.1 Film forming principles

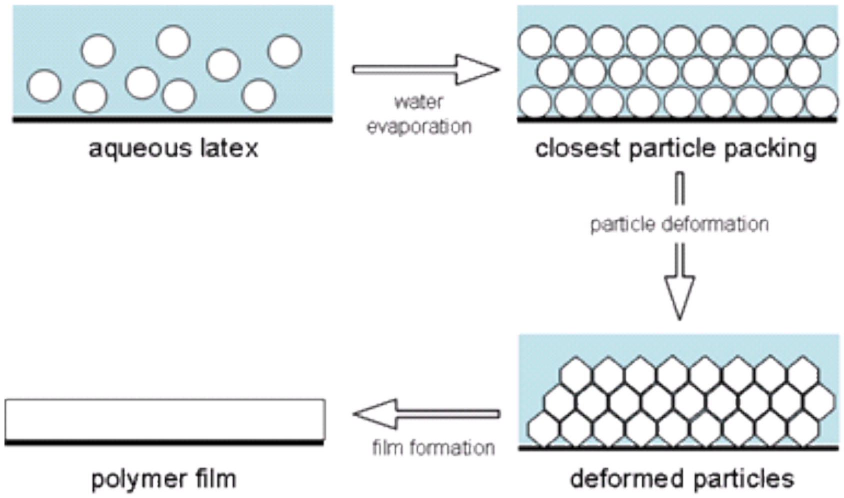


Figure 4: Basis of film formation.

2.1.2.2 Industrial Emulsion polymerisation overview

Emulsion polymerisation is a form of free radical polymerisation whereby the monomer is polymerised in an aqueous solution containing a surfactant to form a colloidal dispersion of polymer particles within aqueous medium (a latex).

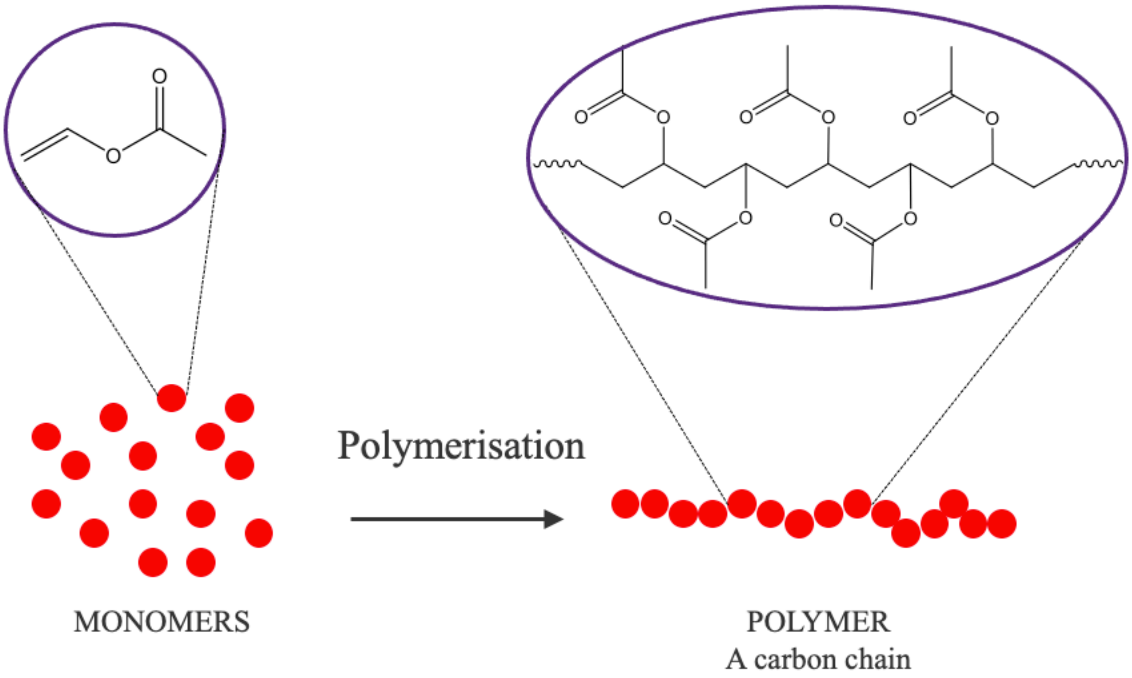


Figure 5: Polymerisation simplified.

Ingredients

For emulsion polymerisation water is the principal ingredient (approx. 40-50 wt%) within the continuous phase to maintain a low viscosity and good heat transfer whilst also acting as an isolating space for each polymerizing loci.

The emulsifier (approx. 0.5-3 wt%) refers to the surfactant which provides a site for particle nucleation whilst also providing colloidal stability to these growing particles. Typically, anionic surfactants are exclusively used in emulsion polymerisation although cationic or non-ionic surfactants can be occasionally utilised for niche applications.

Typically, the primary initiator (approx. 0.5 wt%) is an inorganic salt of persulphuric acid e.g. potassium persulphate, which can dissociate into two sulphate radical anions to initiate the polymerisation. Crown Paints however exclusively utilises a Redox couple initiator system where an oxidising agent and reducing agent react to form radicals (Equation 1.).

$$\boldsymbol{H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH} \tag{1}$$

Monomers build the polymer backbone (Figure 6.) and can be used to add additional properties such as better adhesion to surfaces or scrub resistance. Typical monomers used for emulsion polymerisation include vinyl esters, (meth) acrylic esters, styrene, acrylonitrile, acrylamides, butadiene etc. Monomers are selected according to the properties which they bring to the polymer, impact on polymerisation reaction and their cost.

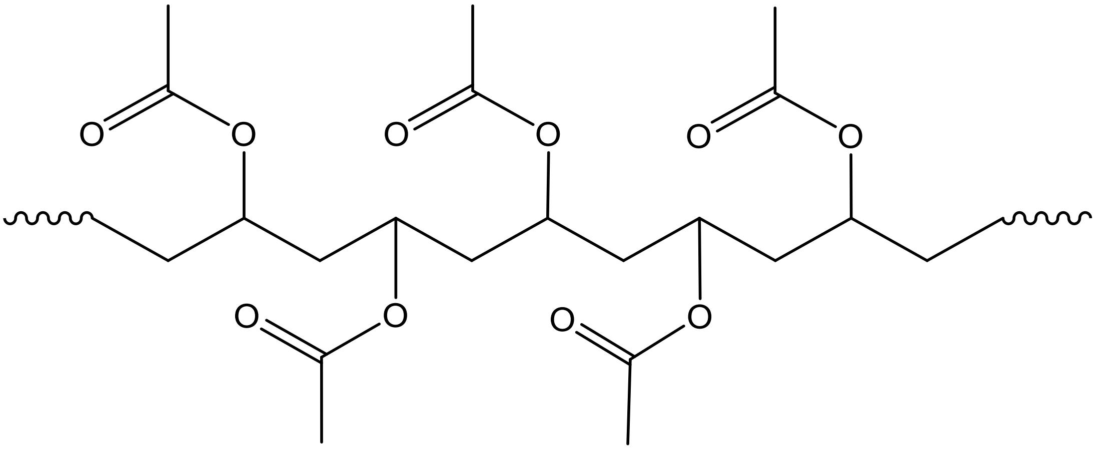
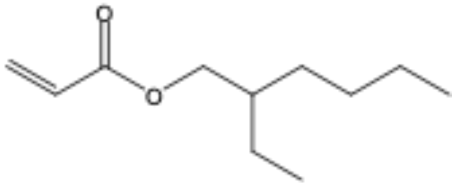
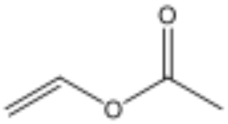


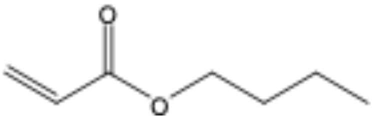
Figure 6: Structure of Poly Vinyl Acetate (PVA).



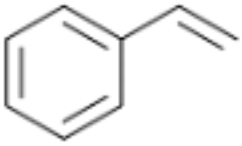
2-Ethylhexyl acrylate
(2-EHA)



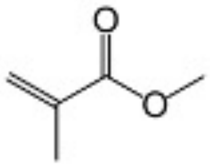
Vinyl acetate
(VA)



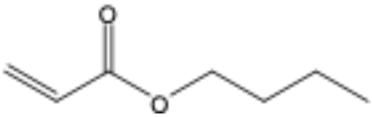
2-Ethylhexyl acrylate
(2-EHA)



Styrene
(Sty)



Methyl methacrylate
(MMA)



Butyl acrylate
(BA)

Figure 7: Examples of typical monomers used in emulsion polymerisation.

Monomers with low glass transition temperatures (T_g) such as ethylhexyl acrylate and butyl acrylate tend produce “soft” polymers which are used in pressure-sensitive adhesive (PSA) e.g. sticky tape, Post-it® notes. Monomers with higher glass transition temperatures such as styrene and methyl methacrylate.

Functional monomers are used to provide specific properties to the polymer, for example, polar monomers (e.g. methacrylic acid) aid the stability of a polymer and help adhesion, whereas crosslinking monomers increase polymer cohesion and its resistance to wear and solvents. Vinyl neodecanoate (Veo Va 10) is a co-monomer commonly used to create lattices during emulsion polymerisation. Veo Va 10 is very hydrophobic and in its branched structure (Figure 8.) protects adjacent vinyl acetate constituents from alkali hydrolysis.

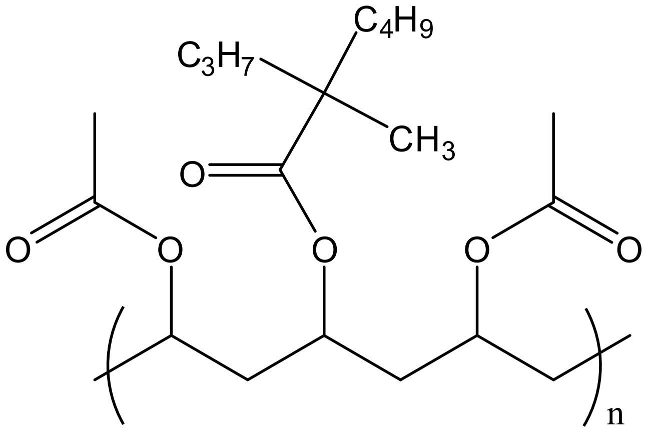


Figure 8: Structure of Vinyl neodecanoate (Veo Va 10).

Free-radical chain polymerization

Free radical polymerisation is the principal method for chain polymerisation used almost exclusively to form polymers from olefinic monomers. A free-radical polymerisation is typically divided into three distinct stages,

Initiation

An initiator is used to produce free radicals (Equation **2**.) which react with the olefinic monomer to initiate the reaction (Equation 3.).

$$\boldsymbol{I_2 \rightarrow 2I \bullet} \qquad \mathbf{2}$$

$$\boldsymbol{I \bullet + M \rightarrow IM_1 \bullet} \qquad \mathbf{3}$$

Where:

$\boldsymbol{I = Initator}$

$\boldsymbol{M = Monomer}$

Propagation

Each polymer chain propagates sequentially through the addition of subsequent monomer molecules at the “active centre” (the terminal free-radical reactive site) which consequently moves to the new terminus of the chain (Equation **4**.).

$$\boldsymbol{IM_n \bullet + IM_m \bullet \rightarrow IM_nM_mI} \qquad \mathbf{4}$$

Termination

Eventually the growth of the polymer is halted, typically by the coupling of two polymer chains (combination), deprotonation or chain transfer.

Combination (or coupling)

Where two free radicals join together (Equation **5**.) this significantly increases the molecular mass of the polymer chain.

$$IM_n \bullet + IM_m \bullet \rightarrow IM_nM_mI \qquad 5$$

Deprotonation

Alternatively, one radical can abstract a hydrogen atom from another forming a double bond (Equation **6**.). This has negligible effect on the molecular mass of the polymer.

$$IM_nCH\cdot + IM_mCH\cdot \rightarrow IM_nCH_2 + IM_m = CH \qquad 6$$

Chain transfer

The radical can also abstract a hydrogen atom from an adjacent molecule if this occurs within a polymer chain, this new radical may attack further molecules and branching will occur (Figure 9.).

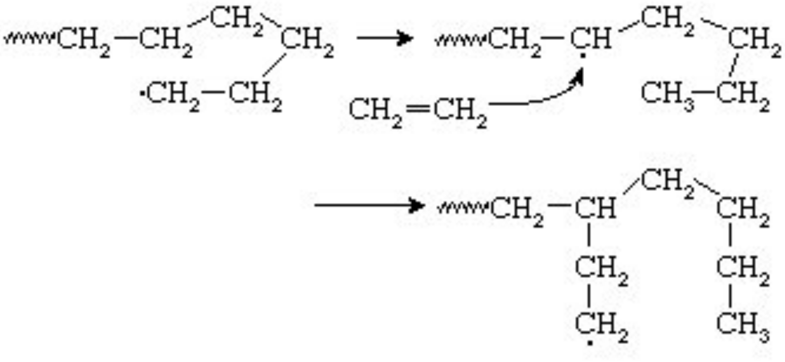


Figure 9: Chain Transfer and branching of Polymers, from Encyclopædia Britannica[37].

Controlling the degree of polymerisation

The degree of polymerisation, ***n*** in free radical polymerisation is dependent on the concentration of monomer, ***M***, and the concentration of initiator, **I** (Equation 7.).

$$\boldsymbol{n} = \frac{\boldsymbol{K}[\boldsymbol{M}]}{\sqrt{[\boldsymbol{I}]}} \qquad \textbf{\textit{7}}$$

Thus, a polymerisation may be controlled by varying the monomer concentration or varying the initiator concentration.

This ability to control the reaction is required to obtain the required molecular mass and thus the desired physical properties of the material. As with most reactions, thermodynamics are important, and all polymerisations are exothermic. In industrial applications especially this excess heat energy must be managed to maintain the desired process in addition to safety requirements. A number of serious incidents have occurred with runaway polymerisation reactions[38]. In a comprehensive report the US Chemical Safety Board (CSB) has shown that 15% of uncontrolled chemical reactions within the USA were from polymerisation reactions[39] and a similar study by the European Commission showed 13% of European major incidents were caused by polymerisation reactions[40]. Colloquially polymer reactors have been described as an “industrial bomb”.

One common method to control the reaction is to emulsify the monomer within water (emulsion polymerisation, shown in Figure 10.). In addition to varying the monomer and initiator concentration, compounds known as “Transfer agents” are used to control the reaction. Transfer agents require a high affinity for chain transfer such as mercaptans (Figure 11.) or halogenated compounds (e.g. carbon tetrabromide, Figure 12.)[41].

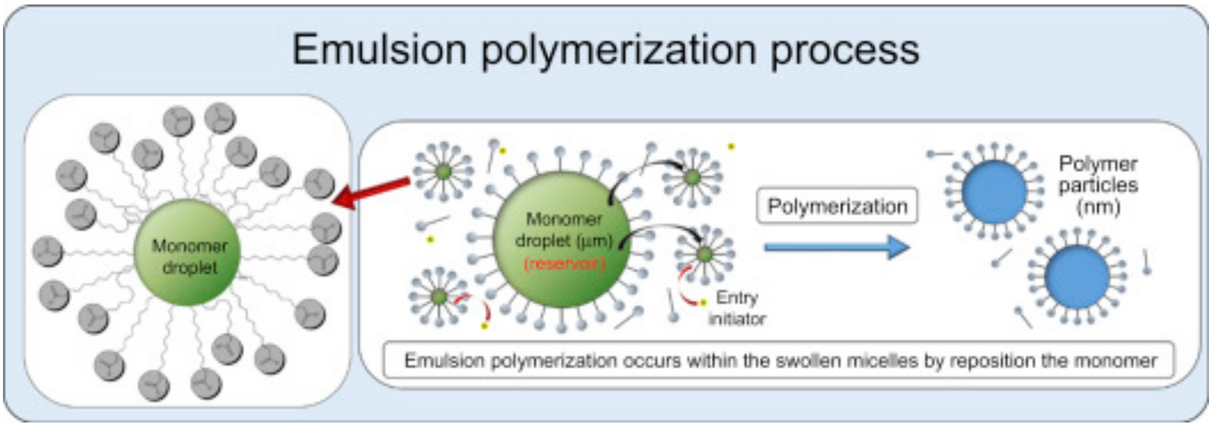


Figure 10: Emulsion polymerization process, from Jensen et al.[42]

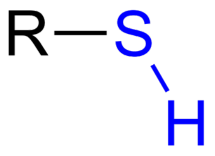


Figure 11: The mercaptan (or thiol) functional group.

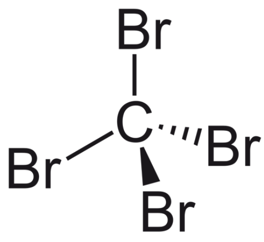


Figure 12: Structure of carbon tetrabromide.

Batch Emulsion Polymerisation (Harkins- Smith-Ewart Mechanism[43,44])

Initial situation

The monomer is dispersed (emulsified) in a solution of surfactant and water forming large droplets of monomer within the water. In the presence of excess surfactant (above what is known as the "critical micelle concentration") amphiphilic macromolecules known as micella form spontaneously (due to the hydrophobic effect) and small volumes of the slightly soluble monomer diffuse through the water into the micelle.

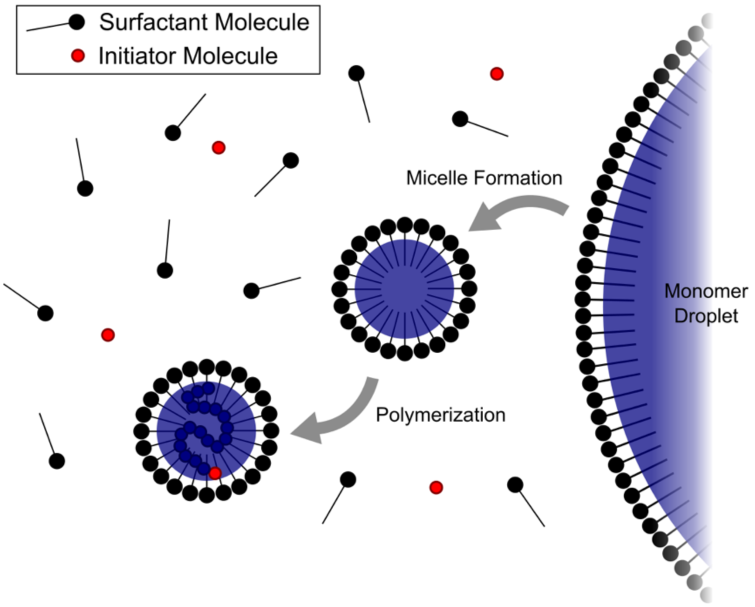


Figure 13:Overview of Emulsion Polymerisation, from Firesine, 2006[45].

Stage 1: Formation stage

Initiator radicals are generated within the aqueous phase (aka the water phase) and eventually migrate towards a micelle where they interact with the contained monomer (n.b. the total surface area of the micelle is far greater than that of the larger monomer droplets, therefore the reaction is typically restricted to the micelle and not the larger droplet) initiating the reaction. This conversion of monomer to polymer lowers the monomer concentration, generating a concentration gradient forcing monomer from any monomer droplets and uninitiated micella to defuse towards these growing polymer holding micella (thus any micelle that doesn’t interact with a radical gradually disappears). The formation stage is characterized by an increasing reaction rate as more monomer contained within the micelle is initiated.

Stage 2: Growth Stage

Eventually no micella remain and thus no new particles are formed, monomer continues to diffuse (through the aqueous phase) from monomer droplets towards the polymer particles. The overall reaction rate becomes constant as these particles continue to grow. Typically, additional monomer and initiator is added continuously to maintain their concentrations within the system as these particles grow.

Stage 3: Final Stage

The final stage begins as the reservoir of available monomer begins to dwindle and thus the reaction rate decreases. Figure 14. illustrates how the rate of reaction varies through the three stages of the polymerisation reaction.

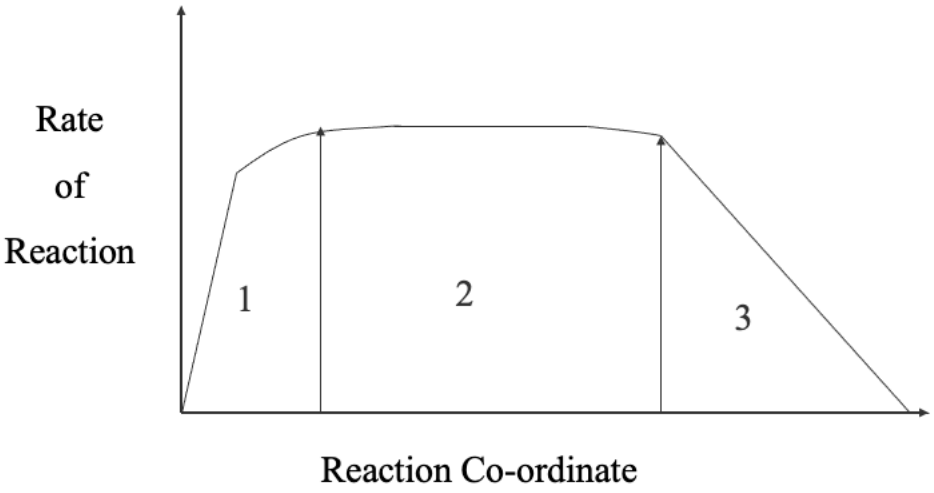


Figure 14: Illustration of the Batch Polymerisation stages (1.Formation, 2. Growth & 3. Final Stage).

2.1.3 Colourants

Typically, a paint is required to be of a specific shade whether it be white, black, yellow, blue, red, green or any mix between. A possible exception to this rule is within undercoats, although these still in reality require a level of quality control over a broader range of potential hues. The terms “pigments” and “colourants” are usually used interchangeably with respect to paint; with a slight bias for “pigments” referring to solid materials and “colourants” as liquid mixtures being applied both colloquially and within the literature. A pigment within a paint is usually utilised to provide the paint with a shade, to mask residue colours or to improve application and/or film durability properties.

2.1.3.1 Colour theory

Visible light (360-780 nm) is the region of the electromagnetic spectrum to which our eyes is sensitive to, in reality the human eye has poor sensitivity at the extremes of this range and thus the visible region can be assumed to be 380-720 nm. White light contains this whole range (however not necessarily of the same intensity), whereas the spectrum can be divided into regions which correspond to specific colours (Figure 15.), these colours can then be “mixed” to “synthesise” new colours (Figure 16.).

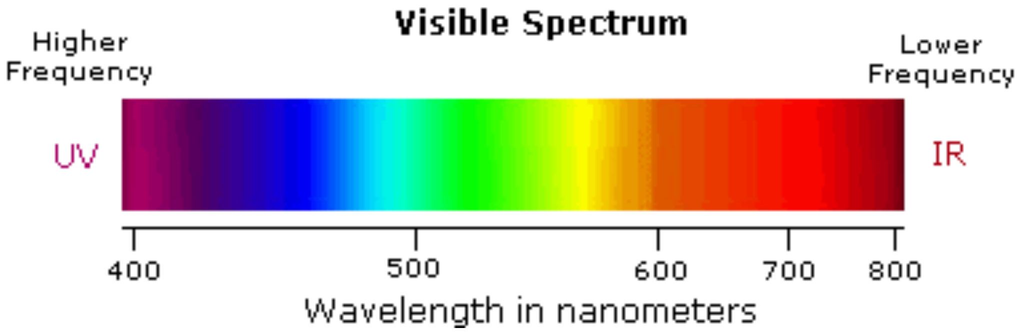


Figure 15: The Visible Spectrum, from Reusch[46].

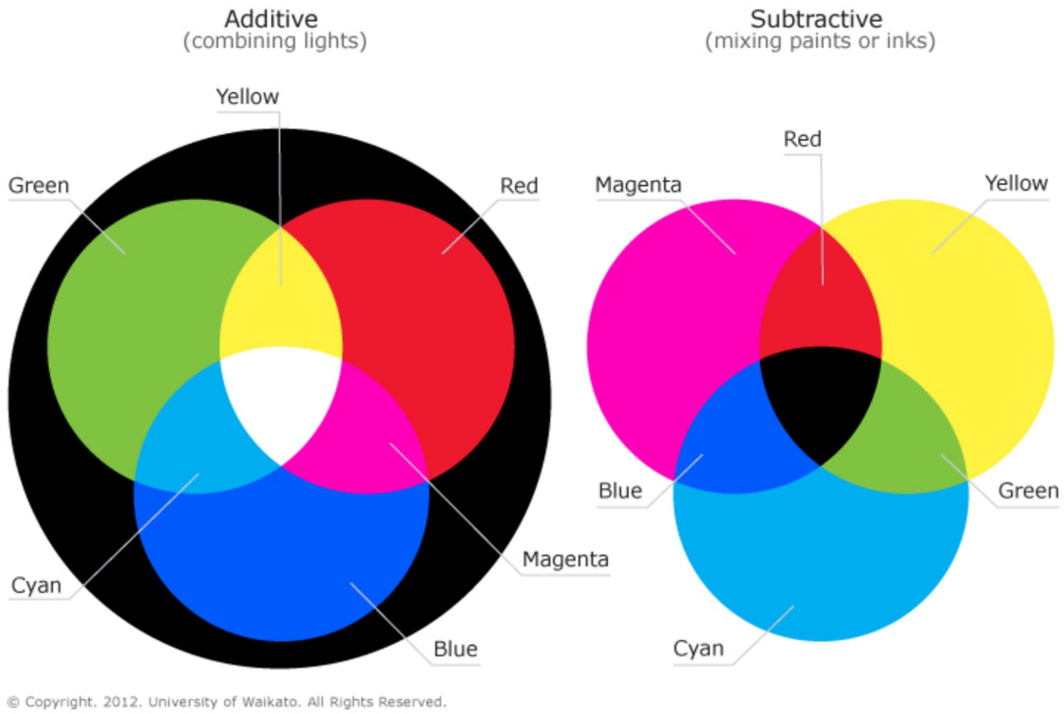


Figure 16: Additive and Subtractive "mixing", from Lakshmi[47].

There are two methods by which colours may be "mixed", known as additive and subtractive mixing (Figure 16.). Additive mixing is the blending of coloured lights of specific wavelengths so that the light is directly observed by the observer. Subtractive mixing is where a material is used to absorb specific wavelengths of reflected or transmitted light to produce a colour. Colour is provided to a paint via subtractive mixing.

Colour space

The concept of colour can be extremely subjective, the classic example of this subjectivity is the black and blue dress illusion[48]; a viral phenomenon in 2015 (with more than 10 million tweets referencing #thedress, #whiteandgold, and #blackandblue).

Figure 17: Simulated "white/gold" image (center) and "blue/black'" image (right) of the #theDress, from Kuriki[49].

The consistency of colour is essential in many fields (e.g. arts or textiles) colour spaces have therefore been developed to quantifiably measure the subjective concept of colour [50].

A colour space (e.g. HSV, Figure 18. & CIEL*A*B*, Figure 19.) is a mathematical model to provide a digital representation of a specific colour; an obvious benefit of this kind of system is the ability to convey information (in a standardised manner) regarding a colour to a third party without the need to actually observe the colour, whilst obtaining an exact match.. The Lab colour space is a method of describing all visible colours in a three-dimensional model (L; representing lightness, a; green-red, b; blue-yellow) which was developed primarily to approximate human vision.

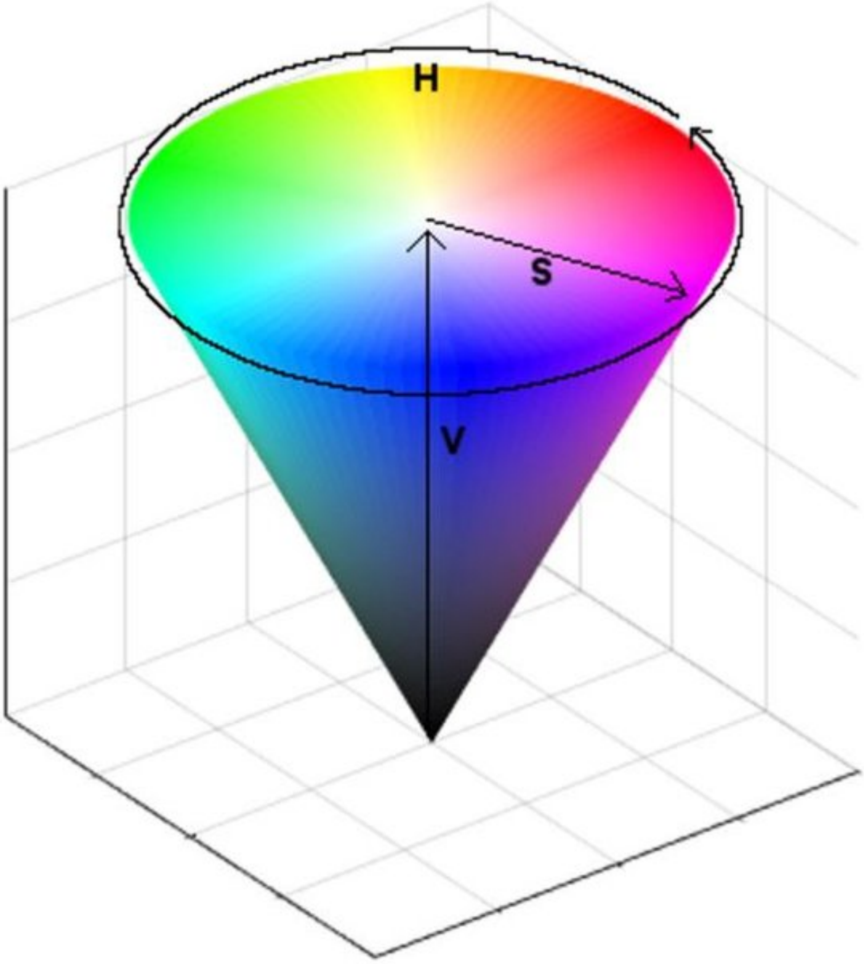


Figure 18: HSV colour space modelized with MATLAB. The hue, H is expressed in degree with a maximum of 360°. Saturation, S and the value, V in percentage from 0% to 100%., from Bertolino[51].

*CIEL*A*B**

The most regularly referred to method of a Lab interpretation of a colour space is the "CIEL*A*B* colour space" whereas L* =0 represents total darkness (or Black) and L*=100 total reflectance/transmission (white), the factors a* and b* representing the colour (a* negative values indicating green and positive red, while b* negative values indicate blue and positive yellow) theoretically these values can be infinitely large however in practice most values are capped at ±128. A simple plot of "CIEL*A*B* colour space" is shown in Figure 19. The method to calculate the L*A*B* coordinates is not described in this thesis however a detailed explanation is provided in ISO 11664-4:2011[52]. Additionally ISO 7724-3:1984 (BSI 3900-D10:1986[53]) specifies CIEL*A*B* as the standard measurement of colour for paints.

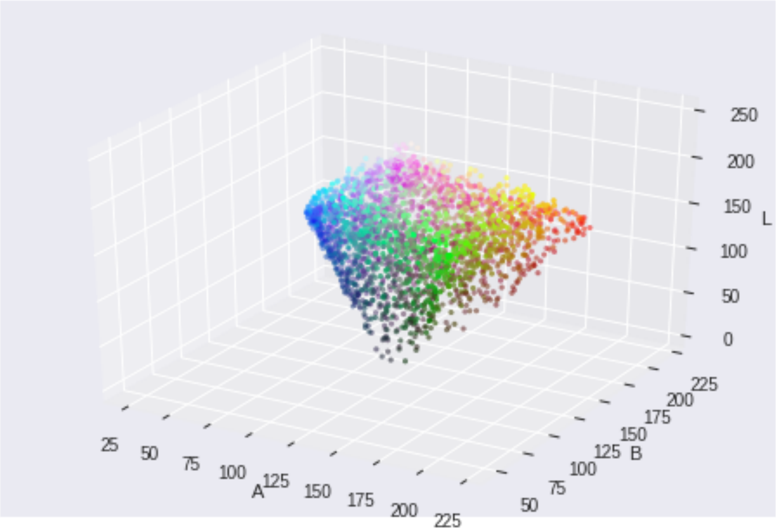


Figure 19: Demonstration of 3D plot of CIEL*A*B* on OpenCV, from Uzeda[54].

Where:

L *, Brightness;

a*, Red/Green;

*b**, Blue/Yellow;

As the coordinates increase in the a dimension (+a) the colour shifts to red (decrease, -a towards green), increase in b (+b) towards yellow (decrease, -b towards blue) and increase in L (+L) towards white (decrease -L towards black). A visual example of a Red Yellow plot (a*, b*) is provided in Figure 20.

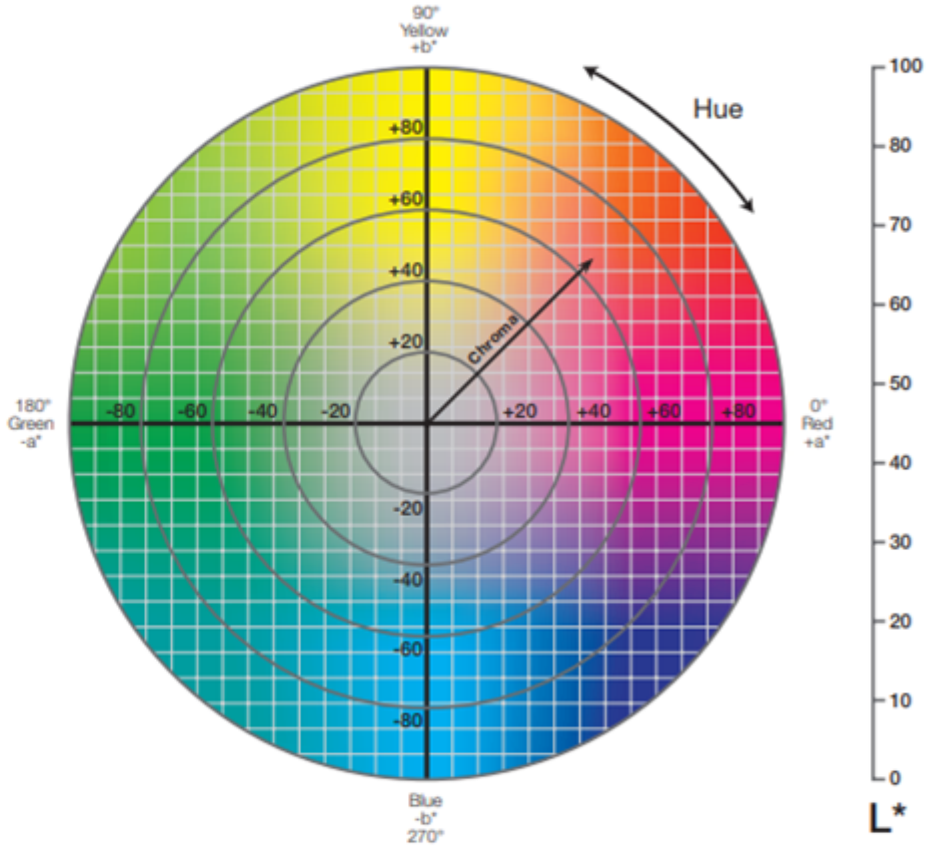


Figure 20: Colours represented by CIEL*A*B Colour Space, adapted from X-Rite Pantone[55].

Figure 20. shows the change in shade of a colour depending on the a* b* coordinates (brightness values, L* are excluded for simplicity).

CIE Whiteness

For white paints defining the degree to which a coating is “white” is essential. The International Commission on Illumination (Commission internationale de l'éclairage, CIE) describes whiteness as:

> *“To promote uniformity of practice in the evaluation of whiteness of surface colours, it is recommended that the formula for whiteness, W_2 or W_{10}, and for tint, $T_{w,2}$ or $T_{w,10}$, given below, be used for comparisons of the whiteness of samples evaluated for CIE standard illuminant D65. The application of the formulae is restricted to samples that are called "white" commercially, that do not differ much in colour and fluorescence, and that are measured on the same instrument at nearly the same time. Within these restrictions, the formula provide relative, but not absolute, evaluations of whiteness, that are adequate for commercial use, when employing measuring instruments having suitable modern and commercially available facilities.” CIE Publication 15:2018[56].*

Formulas for whiteness, ***W*** and tint, $\boldsymbol{T_w}$, from CIE Publication 15:2018[56]:

$$\boldsymbol{W_2 = Y_2 + 800(x_{n,2} - x_2) + 1700(y_{n,2} - y_2)} \qquad \mathit{8}$$

$$\boldsymbol{W_{10} = Y_{10} + 800(x_{n,10} - x_{10}) + 1700(y_{n,10} - y_{10})} \qquad \mathit{9}$$

$$\boldsymbol{T_{w,2} = 1000(x_{n,2} - x_2) - 650(y_{n,2} - y_2)} \qquad \mathit{10}$$

$$\boldsymbol{T_{w,2} = 900(x_{n,10} - x_{10}) - 650(y_{n,10} - y_{10})} \qquad \mathit{11}$$

Where:

Y, is the Y tristimulus value (relative luminance);

x & ***y***, is the chromaticity coordinate in the CIE 1931 colour space;

$\boldsymbol{x_n}$ & $\boldsymbol{y_n}$, is the chromaticity coordinate of the perfect diffuser (reference white);

The numbers in the subscript indicate the observer: two for the CIE 1931 standard observer and ten for the CIE 1964 standard observer.

Generally, the higher the luminance factor of a substance the whiter the substance will appear. However, substances with a luminance factor >100% will likely appear fluorescent rather than white[57]. It is important to note that luminance isn't the only factor and that the "bluer" (-b*) the shade the whiter the substance will appear. Thus, brightening agents are occasionally used to absorb ultra-violet light and re-emit it as a visible blue.

A criticism[58] of CIE whiteness is that the system doesn't clarify whether the whiteness has any component of blue or yellow. The CIE recommends that CIE whiteness should only be used for a relative whiteness value for a single instrument at a given time, comparative analysis of samples with standards is therefore necessary as opposed to a "whiteness scale".

2.1.3.2 Inorganic Pigments

Inorganic pigments, traditionally from minerals, have been used since the prehistoric period with a few notable examples (e.g. iron oxides) being highly significant today. Traditionally mined, it is characteristic that mineral pigments often bare geographical names such as Umber and Sienna derived from their original sources (in Umbria and Siena, Italy respectively), however the renaissance and industrialisation introduced a number of synthesised inorganic pigments (e.g. Vermilion, Prussian Blue & French Ultramarine Blue).

The colour of inorganic pigments originates from a range of different electron transfer processes in a manner very different from their organic counterparts. Charge transfers between ligand-metal (e.g. cadmium sulphates & lead chromates) or metal-metal (e.g. tungstates[59] & Prussian Blue [60]) are two typical examples of this.

Table 1: Examples of historically and commercially important inorganic pigments.

Colour		Pigments			
⬜	White	Titanium dioxide, TiO_2	Zinc sulfide	Calcium carbonate	China clay
⬛	Black	Carbon Black	Mars Black, Iron oxide		
🟥	Red	Red Orchre, Iron (II) oxide	Cadmium Red, Cadmium selenide	Minium (Red Lead), Lead tetroxide	Vermillion, Mercury sulfide
🟧	Orange	Cadmium Orange, Cadmium sulfoselenide			
🟨	Yellow	Chrome Yellow, Lead chromate	Zinc Yellow, Zinc chromate	Yellow Ochre, Hydrated iron hydroxide	
🟩	Green	Veridian Green, Hydrated chromium oxide	Cadmium green	Terre verte, Celadonite & Glauconite,	
🟦	Blue	Prussian Blue, Ferric hexocyanoferrate	Ultramarine Blue, $Na_{810}Al_6Si_6O_{24}S_{2–4}$		
🟪	Purple	Manganese violet, $NH_4MnP_2O_7$	Cobalt violet Cobalt (II) phosphate		

White pigments: Titanium dioxide (TiO_2, Pigment White 6) and others

Titanium dioxide (also known as titanium (IV) oxide) is a naturally occurring substance (usually in the minerals rutile, anatase and brookite) primarily used as a brilliant white pigment with applications from paint to toothpaste due to its very high refractive index offering a high degree of opacity (i.e. maximum light scattering with minimal light absorption). Approximately 4.6M tonnes of TiO_2 is utilized as a pigment annually worldwide.

Pure zinc sulfide (ironically, despite the pure substance being strongly white due to impurities it is usually found as black) is another pigment used for some specialist applications however its lower refracting index means it is far less efficient at producing opacity. White lead was also a traditional white pigment which has now been rendered obsolete due to inferior performance and its toxicity.

Other white pigments are also utilized, known as extenders or fillers, these are sometimes used in large quantities often to reduce the required quantities of titanium dioxide. Typically, white powders of relatively low refractive indexes, they provide little benefit in regard to opacity, however they can assist in adapting the flow and mechanical properties of a paint. Commonly used extenders include calcium carbonate ($CaCO_3$), talc (hydrated magnesium silicate) and China clay (hydrated aluminium silicate).

Iron oxides and other Coloured Oxides

Iron oxides are arguably the most versatile and useful inorganic pigments. Additionally, other factors such as their relative natural abundance has resulted in the extensive useage of iron oxides for pigmentation throughout history.

Pigments with dull yellow to red/brown shades are called ochres within the fields of geology, mining and painting[61]. The pigment "Yellow Ochre" ($FeO(OH)\cdot nH_2O$) is perhaps almost synonymous with the term "ochre". However, the use of Red Ochre (Fe_2O_3) as a pigment is also culturally significant as it can be traced to the palaeolithic Red Landy of Paviland (circa. 31,000 B.C.) [62]. Indeed, its abundance amongst Neolithic burials has been suggested as a representation of the returning to the earth or symbolism of bloodied soil. Ochres were notably also used for skin decoration and sun protection by societies across the globe (e.g. the Picts, Himba, Egyptians and Aboriginal Australians). From a specifically decorative paint pigment function iron oxide ochres have been found frequently within murals at Pompeii, Egyptian tomb paintings and historic cave paintings.

Figure 21: Yellow ochre pigment, from KREMER PIGMENTE[63].

Figure 22: Hands painted on cave wall in Argentina, from Lesso[64].

2.1.3.3 Organic Pigments

Azo dyes

Azo dyes are the quintessential and most widely used organic colourant (representing an estimated 60-70% of organic colourant applications, [65]. Whilst the common structural azo group (-N=N-) normally links two aromatic rings, the vast structural variety available can practically provide virtually any hue required. Azo dyes produce high intensity colours and also provide reasonable technical properties (such as durability when exposed to environmental factors) whilst, being economically reasonable.

Copper phthalocyanine

Copper phthalocyanines provide a significant variety of blue/green pigments. Copper phthalocyanine is extremely widely used (possibly the single most prevalent organic pigment) due to its brilliant blue colour and low manufacturing cost. The β-form of copper phthalocyanine (Figure 23.) is the predominant pigment for cyan ink. Halogenated derivatives of copper phthalocyanine are also used for additional strong green/blue pigments (Figure 24.).

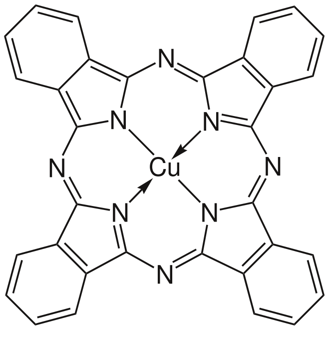


Figure 23: Copper phthalocyanine.

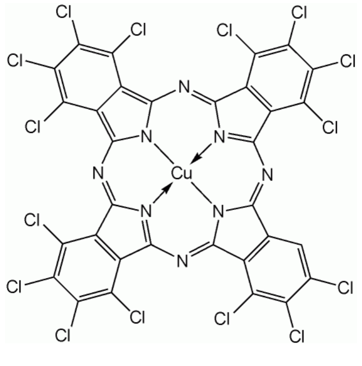


Figure 24: Phthalocyanine Green.

2.1.4 Biocides

As previously shown, aqueous paint consists of a mixture of organic substances dispersed within a liquid medium (“solvent”) of water. These chemical features coupled with an extended shelf life presents an obvious opportunity for microbial growth. Interestingly, this is much less of an issue within solvent-based paint, where the medium is usually toxic to these lifeforms. The function of biocides within aqueous paint is typically two-fold, as an “in-can” preservative (preventing growth while the product is stored in its packaging) and also as a film preservative post application.

Bacteria, yeast and fungi can all cause deterioration of liquid paint[66] however of these classifications of microbe bacteria are seen to be more of an issue when the paint is in a liquid medium. Bacteria typically cause gassing, viscosity reduction and also potentially colour drifts. High standards of plant hygiene and regular sterilization is essential to minimise the potential for contamination (notably, Crown Paint’s hygiene procedure is of a standard far greater than that of brewing). All water used within the plant needs to be chlorinated (or otherwise sterilized) before use. “In-can” biocides are used at low concentrations as an ongoing defence against microbial growth, these tend to be mixtures of various chemicals to provide adequate protection for the widest range of bacterial classes for a sustained shelf life.

Microbes can be monitored simplistically using Dipslides (Figure 25.), the advantage of their use is that they provide a relatively quick method that requires limited training or equipment and the equipment's availability and cost effectiveness (as the HSE recommends this method for legionella detection[67]). As the fundamental aim is to reduce microbial contamination to a minimum specific microbial testing or classification is rarely required.

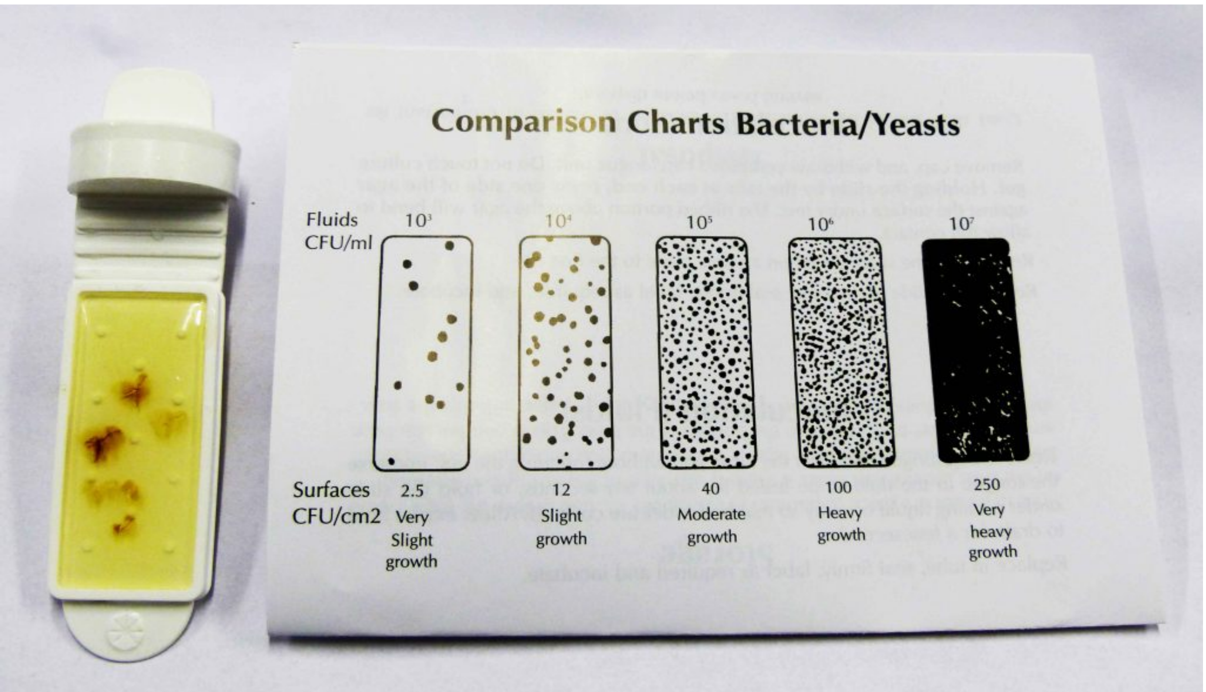


Figure 25: Standardised Dipslide for Microbial Growth, from Hydro X[68].

After the paint's application, fungi and algal spores present a greater risk to the paint film. These develop colonies which can cause aesthetic and odour issues in addition to structural damage to the film. Protection is therefore provided through a mixture of algicides and fungicides (typically consisting of both organic and organometallic complexes) to limit the development of these colonies.

2.1.5 Thickeners

The rheology of coatings is a field in its own right[69]. For a coating to be effective it must be free from any defects and thus a careful balance must be made to ensure a continuous film of the required thickness can be easily applied and maintained whilst in storage a high viscosity is preferred to prevent sedimentation. Post application behaviour is also a concern and any "running", "sagging" or "dripping" of material may ultimately weaken the desired film. Thickeners (also known as rheology modifiers or rheology control additives) are used to achieve the desired rheological properties.

Figure 26: Flow of different coloured paints, from SOLVAY[70].

2.1.5.1 Cellulose based thickeners

Cellulose based thickeners have been used for several decades with over 35,000 t of cellulose used annually worldwide in emulsion paint[71]. Cellulose thickeners thicken the water phase of the emulsion paint by the formation of chain entanglements between the dissolved cellulose molecules via intra and intermodular hydrogen bonding.

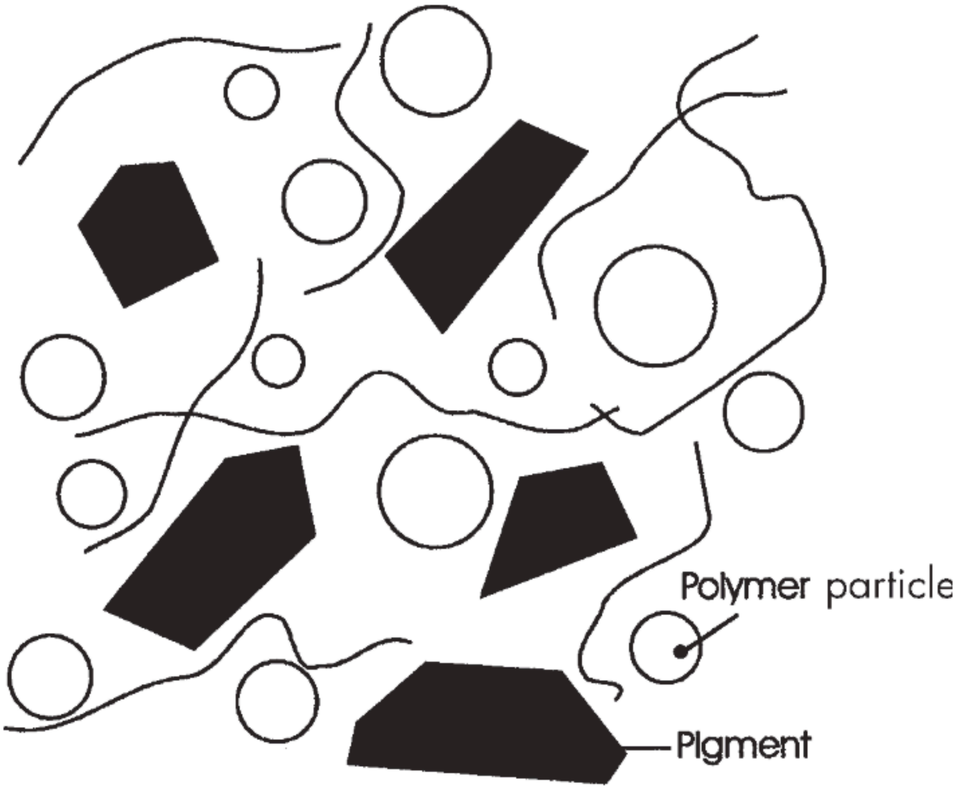


Figure 27: Thickening of emulsion paint showing the entanglement of cellulose thickeners, from Bieleman[71].

2.1.5.2 Polyurethane (PUR) thickeners

Polyurethane (PUR) thickeners are becoming increasingly used within emulsion paints, especially within gloss emulsions (due to appearance properties). These thickeners tend to have better flow and levelling properties than cellulose thickeners. PUR thickeners are non-ionic low molecular weight polymers with a combination of hydrophobic and hydrophilic functional groups.

The thickening mechanism is due to the interaction of these hydrophobic and hydrophilic functional groups with the other components of the paint. Notably they couple with the binder's (polymer) surface forming a complex network across the paint increasing its viscosity.

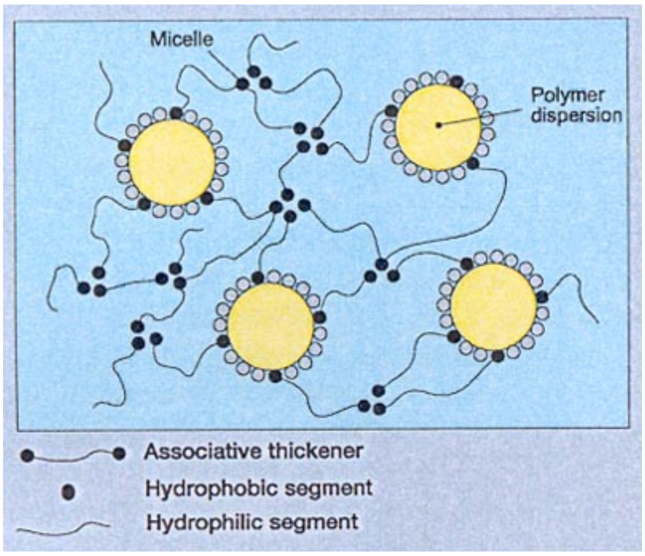


Figure 28: Thickening Mechanism of 2.1.5.2 Polyurethane (PUR) thickeners, from SpecialChem[72].

2.1.6 Properties and Paint Testing

2.1.6.1 Viscosity & Rhenology

Using a Cone and Plate viscometer

The determination of viscosity using a cone and plate viscometer is defined by two standards ISO 2884-1:2006[73] and ASTM D4287-9400[74]. The method is used to determine the rheology of a coating under high sheer conditions similar to those encountered during application.

Apparatus

The apparatus required is a cone and plate viscometer ASTM D4287-9400 recognises both analogue (Figure 29.) and digital (Figure 30.) viscometers. Whilst Crown paints have both analogue and digital viscometers available, only digital equipment was used in the work described within this thesis for consistency.

Figure 29: An analogue cone and plate viscometer, from ASTM D4287-9400[74].

Figure 30: A digital cone and plate viscometer, from ASTM D4287-9400[74].

The geometry of the cone and plate apparatus is shown in

Figure 31.

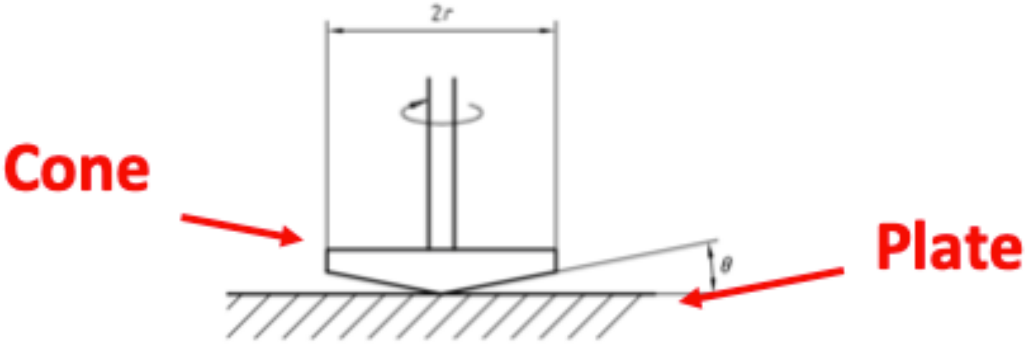


Figure 31: Geometry of cone and plate device, adapted from ISO 2884-1:2006[73].

Where:

T, is the torque, in newton metres;

Ω, is the angular velocity, in radians per second;

r, is the radius of the cone, in metres;

θ, is the cone angle, in radians.

The following viscometric values can be calculated:

n.b. within this thesis only the viscosity (Equation 14.) was considered, which was determined by the instrument itself.

$$\boldsymbol{Shear\ rate\ (s^{-1}) = \frac{\omega}{tan\theta}} \tag{12}$$

$$\boldsymbol{Shear\ stress\ (Pa) = \frac{3T}{2\pi r^3}} \tag{13}$$

$$\boldsymbol{Viscosity\ (Pa\ s) = \frac{3Ttan\theta}{2\pi\omega r^3}} \tag{14}$$

For viscosity, the unit poise (P) is commonly used and is equivalent to 0.1 Pa s (or 1 cm^{-1} g s^{-1}). Interestingly, the viscosity of water is 0.00890 P (at 25°C and 1 atmosphere)[75].

Method

The equipment is regularly calibrated using standardised refined mineral oils with Newtonian characteristics and known viscosities and zeroed before each use. The cones are checked for any wear before use and are thoroughly cleaned following any use to prevent any residual coating remaining on the instrument. The digital instruments maintain the temperature of the sample at 25°C ± 0.3°C (unless another temperature is required).

With the cone in a down position the equipment is allowed to reach temperature over a period of at least 5 minutes, (practically this tends to be closer to 20-30 minutes due to other preparation activities). The coating is homogenised, and a representative sample is taken. n.b. samples containing large particles can produce anomalous results and damage the instrument[73] and are thus best avoided. The cone is then raised and adequately large sample to cover the plate is transferred. Care is made to avoid adding additional air bubbles. The cone is lowered onto the sample, which pushes excess sample away from the plate. The plate warms the sample to the required temperature before rotating. The viscosity is recorded on an analogue device once the pointer becomes steady, whereas a digital viscometer typically records the measurement once the viscosity stabilises.

Using a rotary viscometer (“Rotaball”)

A rotary viscometer, commonly referred to as a “Rotaball” is used to determine the viscosity of a paint while within the paint tin, known as “in-can viscosity”. These conditions are relevant while mixing the paint within the tin and the application of the paint to a brush from within the tin. The “in-can viscosity” is also useful to predict the sedimentation behaviour of a paint while in storage.

Similar to using a Cone and Plate viscometer, the method for using a “Rotaball” to determine a paints viscosity is defined in the standard ISO 2884-2:2006[76].

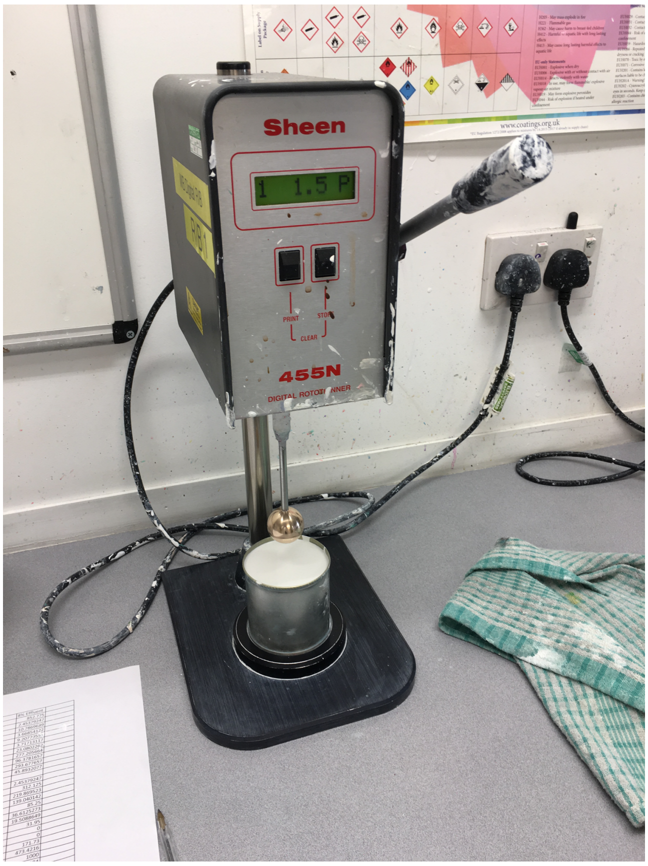


Figure 32: A "Rotaball" at Crown Paints.

Apparatus

ISO 2884-2:2006[76] defines the apparatus required as shown in Figure 33. A single speed digital viscometer operating at 562 rpm (±2%) is used throughout the work described in this thesis (Figure 32.)

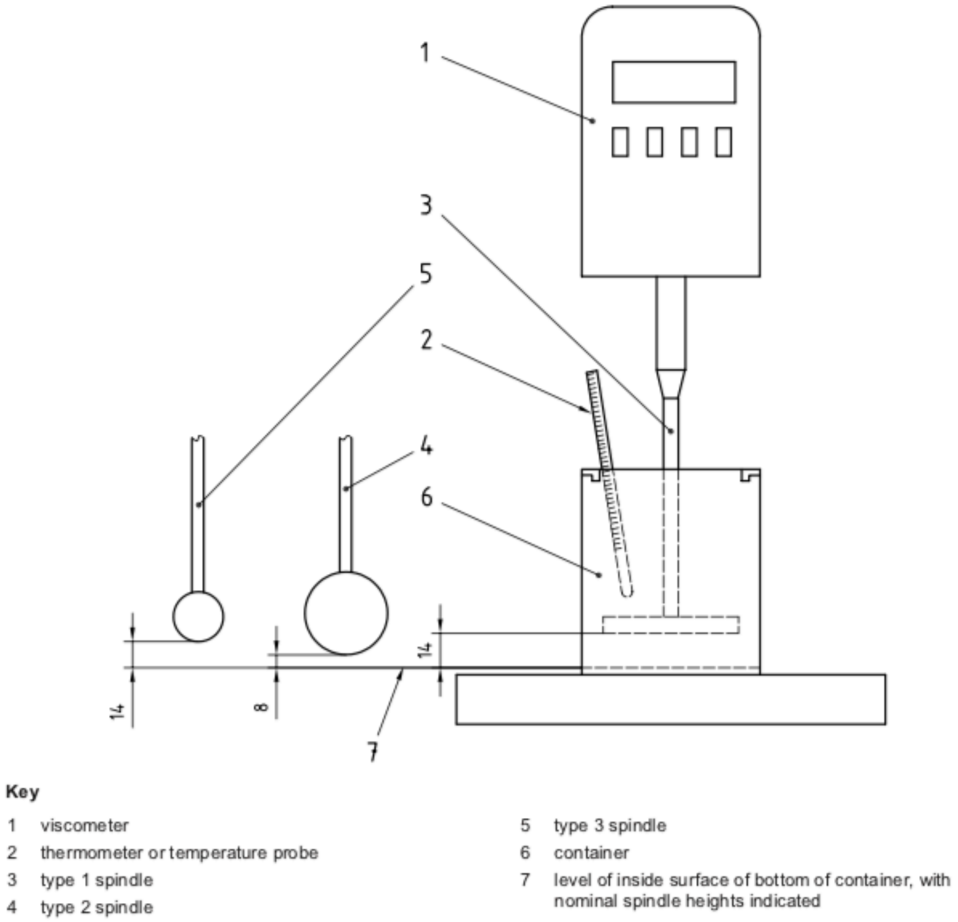


Figure 33: A rotary viscometer as defined in ISO 2884-2:2006[76].

A series of spindles are defined in ISO 2884-2:2006[76] a "Type 2" spindle as defined in Table 2. was used throughout this work.

Table 2: Ball spindle specification, from ISO 2884-2:2006[76].

Spindle	Viscosity range	Diameter, D
Type 2	0 mPa·s to 6,500 mPa·s (6.5 Pa·s)	31.75 mm
Type 3	0 mPa·s to 34,000 Pa·s (34 Pa·s)	19.05 mm

The container is a modified 250 ml round paint tin. Within ISO 2884-2:2006[76] the standardised tin used has an internal diameter of 74 mm, a height of 74 mm and an internal aperture of 61 mm (Figure 34.). At Crown Paints a standard tin without the 61 mm aperture (simply 74 mm x 74 mm) is used for ease. Whenever a new container is used the viscometer is calibrated accordingly.

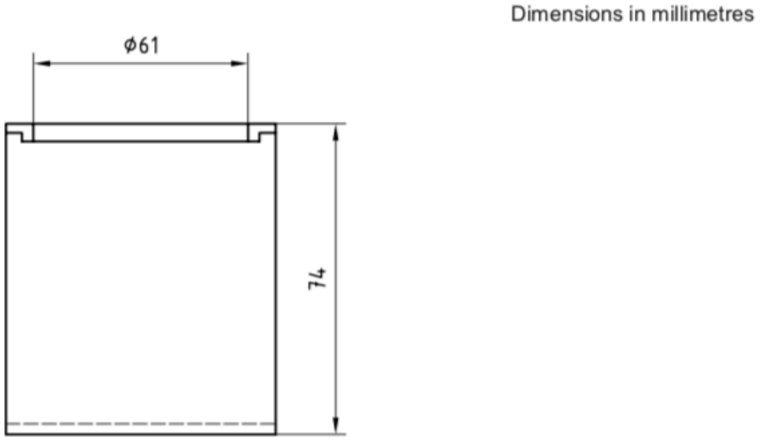


Figure 34: Standardised container, from ISO 2884-2:2006[76].

Method

The equipment is regularly calibrated using standardised refined mineral oils with Newtonian characteristics and known viscosities and zeroed before each use.

The digital instruments maintain the temperature of the sample at 25°C ± 0.3°C (unless another temperature is required). The coating is homogenised, and a 250 ml representative sample is taken to fill the standardised container (Figure 34.) to a point approximately 20 mm from the lip (usually marked). The sample is placed into a waterbath to regulate the temperature at 23°C ± 0.5°C. The container is then placed in a central position under the spindle and the spindle lowered into the sample until the level (shown in Figure 33. as position 7.) is reached. A line marked on the spindle should be level with the surface of the sample, additional paint may be added to reach this level. The equipment is left for a sufficient to reach thermal equilibrium. Once reached the spindle is turned at 562 rpm (±2%), once the viscosity stabilises a reading of the value is made.

After the reading is made the spindle is removed and the temperature of the sample is checked with a thermometer. If the temperature of the sample is not 23°C (± 0.5°C) the process is repeated at the required temperature.

Samples can be thinned or thickened to quality specifications through adding additional water or thickeners to the sample and homogenised. The test would then be repeated to determine the new viscosity.

2.1.6.2 Colourimetry

There appears to be no current standardised method to measure the colour of a paint within the literature, however the now withdrawn (as of 18/11/2013) ISO 7724-2:1984[77] provided a standardised method which Crown Paints has adopted.

Apparatus

A double-beam reflection spectrophotometer with prism and a photometer head is used. The method uses photoelectric tristimulus colorimetry with three filters, an established system as originally described in Hunter, 1942[78].

Figure 35: A Crown Paints spectrophotometer.

The spectrophotometer is calibrated with a primary standard; representing a “perfect diffuser” as recommended by CIE and defined as an ideal uniform diffuser at all wavelengths. Because an ideal uniform diffuser cannot be realised in practice a secondary standard with known a spectral reflectance value close to the primary standard is additionally used. Typically, a compressed barium sulphate powder is used as this secondary standard.

The sample paint is homogenised and test panels of 120 µm film thickness (Figure 36) are made of the sample paint on a transparent polyethylene sheet (approx. 50 µm thick) using an applicator under a standardised pressure and speed.

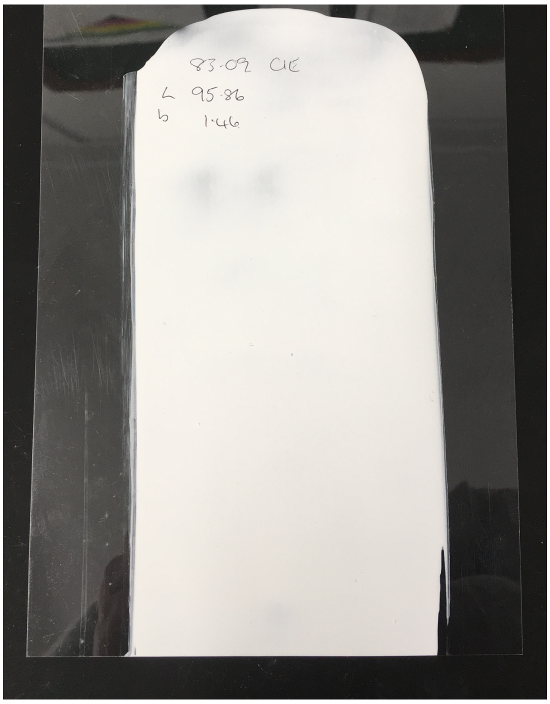


Figure 36: A 120µm paint film on transparent sheet.

n.b. in Figure 36. the values for CIE whiteness, L^**, and* b^* *are recorded at the top of the sample.*

Measurements are made in wavelength intervals (Δλ = 10 nm) across the 380 - 770 nm range using monochromatic light. The L^*, a^*, b^* and CIE whiteness values are recorded.

2.1.6.3 Opacity

The contrast ratio is a measurement of opacity or “hiding power” is the physical property that evaluates the transmittance of light through a substance. In terms of paint this is a key aesthetic feature which is often desired by the user. The method to determine the contract ratio is defined in ISO 2814:2006 (BS 3900-D4:2006[79]) and is a comparison of the contrast ratio of paint films of equal wet film thickness drawn on a black and white substrate.

There is a choice of substrates used, either a transparent polyethylene sheet (approx. 50 µm thick), where black (reflectance less than 5%) and white plates (reflectance between 84-86%) are used or specific contrast ratio cards (these are treated to be resistant to solvent and water) with black (reflectance less than 5%) and white areas (reflectance between 75-86%)[79]. Crown Paints have both substrates available however the black and white card method was used throughout this work for ease.

Before testing the cards are stored individually for at least 24 hours under testing conditions at 23°C (± 0.5°C) and 50% (± 5%) relative humidity. The cards are only ever handled by their edges, in practice normally at the labelled area shown at the top of Figure 37.

The sample paint is homogenised and a paint film of 120 µm thickness is drawn down on the cards (Figure 37.) using an applicator under a standardised pressure and speed. In all contrast ratio testing described in this thesis a sample is compared to a standard paint, which is drawn with the same applicator at the same time.

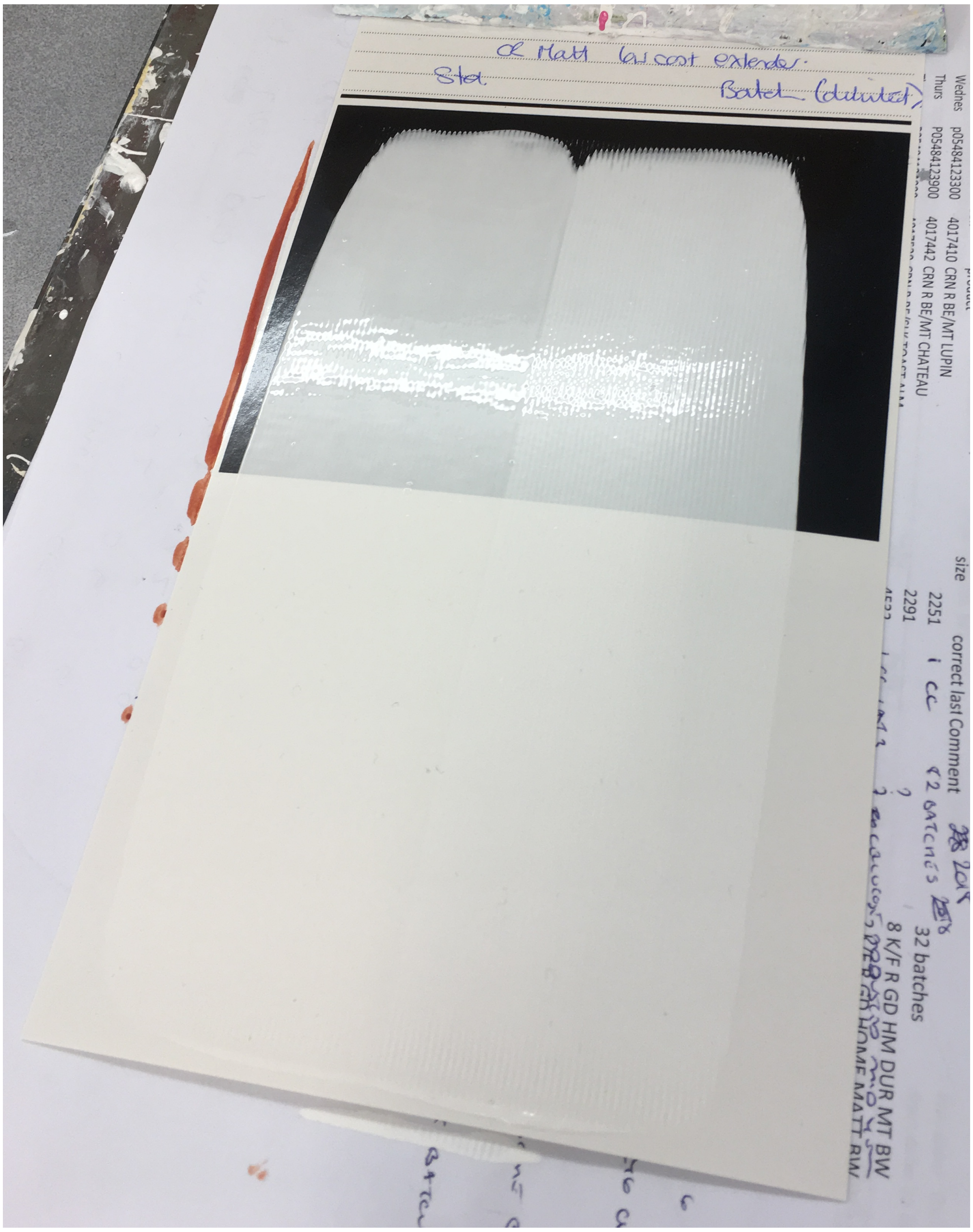


Figure 37: A 120 µm paint film on a contrast ratio card.

The films are left to dry in conditions of 23°C (± 0.5°C) and 50% (± 5%) relative humidity for at least 16 hours but no longer than 168 hours[79]. At Crown Paints this is standardised to 72 hours.

After this drying period reflectance measurements of the paint films are made. at a minimum of four test positions over each of the black and white substrates. In this work five test positions were randomly selected for each substrate. The average values of reflectance over the black areas, $\boldsymbol{R_B}$ and over white areas, $\boldsymbol{R_w}$ is then used to determine the contrast ratio, $\boldsymbol{CR}$:

$$\boldsymbol{CR = \frac{R_B}{R_W}} \qquad 15$$

2.1.6.4 Scrub resistance

The ability of a coating to withstand general abrasion and physical wearing by a repeated action (for example for cleaning) is an important factor for users. From a decorative paint perspective, the paint film's scrub resistance can have a significant impact on the durability and therefore practicability of the product's application.

Test method

The wet-scrub resistance and cleanability of a coating has several methods defined in standards e.g. ISO 11998:2006 (BSI 2007[80]) & ASTM D2486-06 (ASTM International 2006[74]). The basic method remains the same with a test coating applied to a test panel using a film applicator to produce a uniform film thickness. The test panel is clamped to a standardised wet-scrub tester apparatus which makes repeated scrubs (from a moist brush or abrasive pad) at a standardised speed, distance, and pressure.

ISO 11998:2006 specifies an apparatus more similar to that used in this thesis (Figure 38.) however ASTM D2486-06 provides an easier to understand diagram (Figure 39.) of the equipment.

Figure 38: A scrub resistance test.

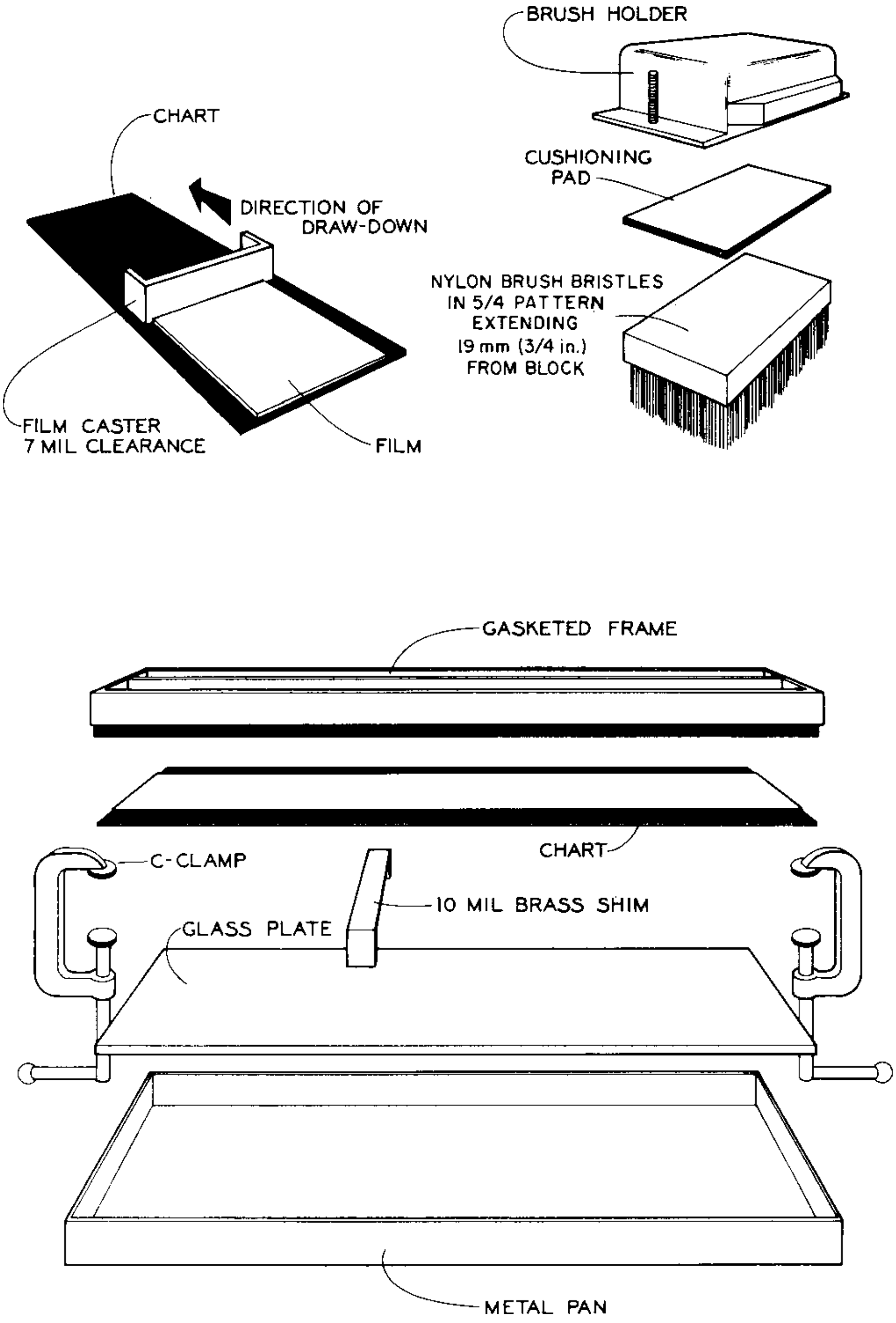


Figure 39: Apparatus for Scrub Test, from ASTM D2486-06[74].

Figure 39. shows the apparatus for the Scrub Test. The coating is applied to a uniform film thickness (7 mm). The moist brush (an abrasive pad was used within this thesis) then makes repeated scrubs along the gasketed frame.

Eventually a continuous mark will be scrubbed across the paint film (Figure 40.) at which point the film is said to have “failed” and the number of scrubs made is recorded. The test is restarted and the cycles to failure of each film on the test panel are also recorded.

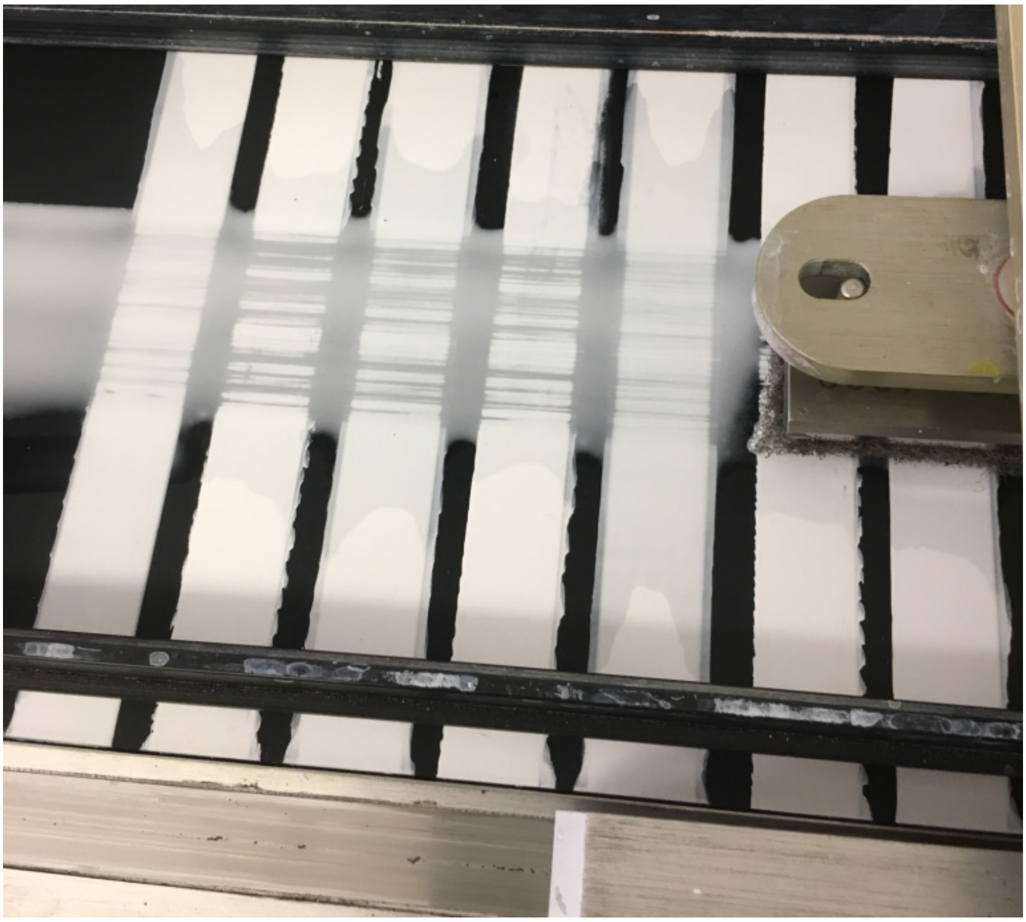


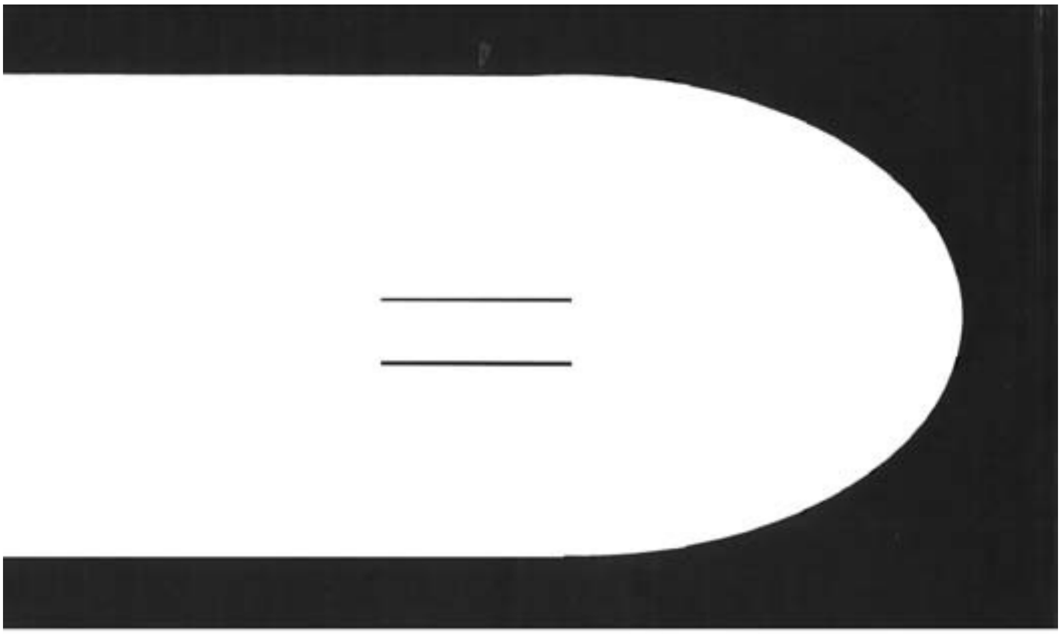
Figure 40: A scrub test showing the “failure” of several paint films.

Potential Variations of Method

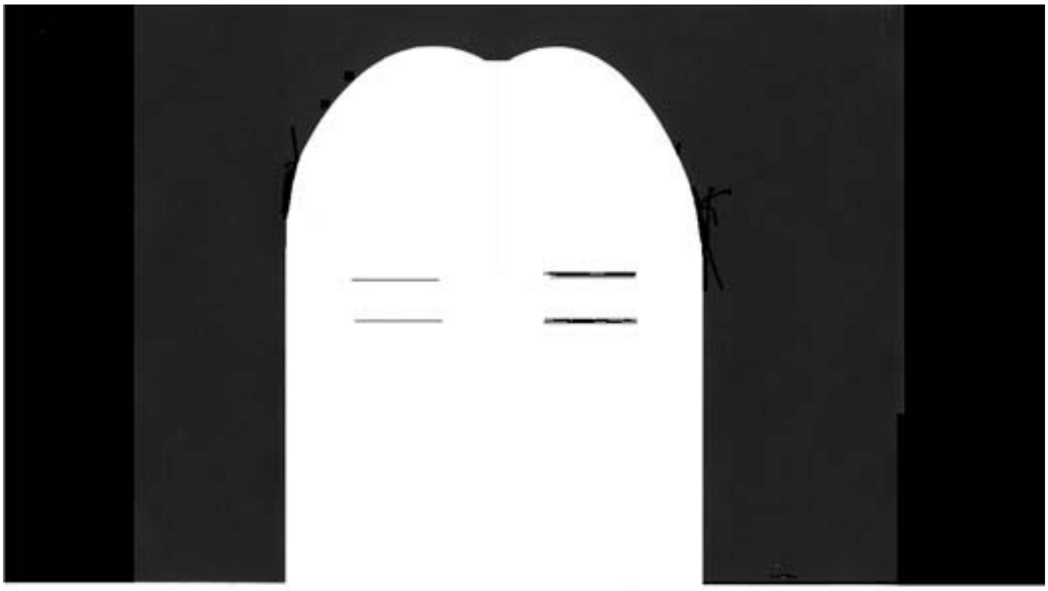
ASTM D2486-06[74] defines two variations on the method (Figure 41.):

Method A based on a cycle to failure concept of the test paint, which has reasonably poor reproductivity (due to variations of various environmental and applicational factors). A single test paint is applied, and scrubs are made to compare with a library of recorded reference paints.

Method B is similar to Method A however, it also includes a comparison of the test paint with a standardised reference paint to improve reproducibility. Two paints are thus required; a standardised paint (the “Reference Paint”) and the paint requiring testing (the “Test paint”). The advantage of this method is that the impact of confounding variables on the test is minimised.



Test Method A: Cycles to Failure on Test Paint



Test Method B: Ratio of Cycles to Failure of Test Paint and Reference Paint

Figure 41: Comparison of D2486-06 Method A & Method B, from ASTM D2486-06[74].

Within the work presented in this thesis a variation of Test Method B has been used (however it is notable that the apparatus used more closely reflects that described in ISO 11998:2006). This adapted Method B was chosen to simplify the procedure to a direct comparison between the test paint and standard in a reproducible manner.

Alternatively, standards such as ISO 11998:2006[80] present a failure after a standardised number of cycles perspective (200 cycles in the case of ISO 11998:2006). Whilst this is useful to classify a paint films scrub resistance to a specific standard, it presents limited value to products with lower scrub resistance and direct comparisons between films.

ISO 11998:2006 also presents a numerical method to calculate the loss in coating mass which could be highly valuable (though would also suffer the same reputability issues as D2486-06').

$$\boldsymbol{A = \frac{S \times W}{10^6}} \qquad \textbf{16}$$

Where:

A, is scrub area (m^2);

S, is scrub length (mm);

W, is scrub width (mm);

$$\boldsymbol{L} = \frac{\boldsymbol{m_1} - \boldsymbol{m_2}}{\boldsymbol{A}} \qquad \textbf{\textit{17}}$$

Where:

$\boldsymbol{L}$, is the loss of mass per unit area (g m^{-2});

$\boldsymbol{m_1}$, is initial mass (g) of the dry coating film;

$\boldsymbol{m_2}$, is mass (g) of the dry coating film following 200 scrub cycles;

$$\boldsymbol{L_{dft}} = \left(\frac{\boldsymbol{m_1} - \boldsymbol{m_2}}{\boldsymbol{A} \times \boldsymbol{\rho_{df}}}\right) = \frac{\boldsymbol{L}}{\boldsymbol{\rho_{df}}} \qquad \textbf{\textit{18}}$$

Where:

$\boldsymbol{L_{dft}}$, is mean loss in dry-film thickness (µm);

$\boldsymbol{\rho_{df}}$, is dry film density (g cm^{-2});

The method described above (Equation 16-18) to determine the loss of material as a result of scrubbing has not been applied within this thesis as the principal purpose of measuring scrub resistance for this project is the comparison of a test paint with a standardised sample where maintaining reproducibility is key. Therefore, the method isn't suitable beyond a statistical evaluation of the method within this context, however it is included to provide a useful example for future investigation.

2.2 Overview of Paint Manufacturing

A comprehensive review of the manufacturing of aqueous paint is a notoriously difficult task[81] due to the wide variety of manufacturers operating under different conditions. This overview will present a general method for paint production using Crown Paints as an example.

Figure 42: The filling of Crown Paints tins.

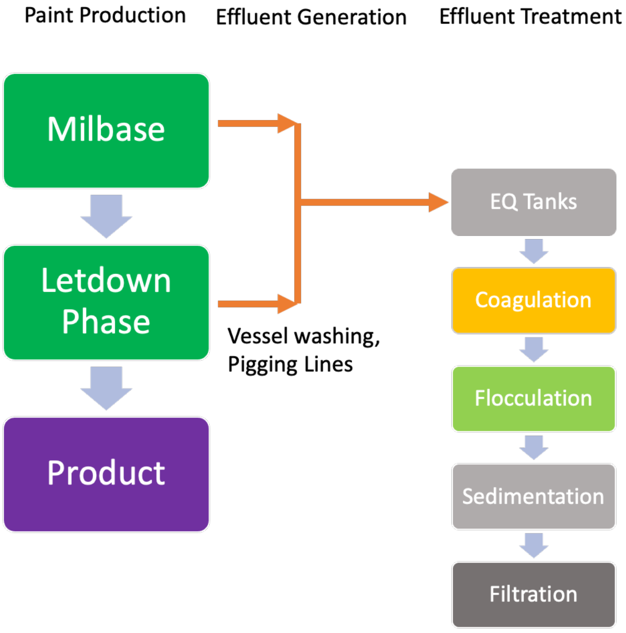


Figure 43: A simplified process diagram for paint production.

Figure 43. shows a general paint production process (as performed at Crown Paints) and where the effluent processes links with production.

Dören[81] notes that aqueous binders (see 2.1.2.) are more problematic within aqueous systems than their alternatives in solvent systems due to increased sheer stability (i.e. resistance to mechanical effects), chemical stability and limited resistance to bacterial attack. The dispersal process is thus a fundamental element of paint manufacturing as pigments and fillers that are not optimally dispersed tend to settle. Typically, this is described as a two-phase process known as the Millbase and Letdown.

Figure 44: Mixing vessels at Crown Paints Darwen site.

2.2.2 The Millbase

The first phase of the process focuses on dispersing the material into an emulsion (Figure 45.). Many additives are added in this stage such as wetting and dispersal agents before the addition of bulk pigments (e.g. TiO_2, Talc etc.). The particles must be “wetted, where air/moisture trapped within the dry pigment is replaced by the liquid medium being used within the product (typically water with aqueous paint). This is often described as “the pigment air interface becoming a pigment liquid interface”. Interestingly, the surface tension of the liquid can be a concern and thus wetting agents and mechanical mixing are often used. Wetting is far more effective at lower viscosities of liquid and ineffective wetting results in issues with dispersion and stabilisation further into the process.

Following the wetting stage, the wetted pigment agglomerates (i.e. individual particles stuck together) are spilt into separate individual pigment particles through mechanical energy (impact and shear forces).

These particles have a tendency to flocculate back into agglomerates and thus need stabilisation to keep individual pigment particles at a sufficient distance so that they cannot congregate[82]. Dispersal agents are used to obtain optimally pigment stabilisation.

Figure 45: Dispersion of pigments to form a Millbase at laboratory scale.

2.2.3 The Letdown

Once the material is optimally dispersed additional material such as thickeners, additional water, binders etc. are added. This is known as the letdown phase. Notably it is in this phase pH control is conducted and rheology adjustments made. Finally, any additional colourants are added to tint the product to the required shade (Figure 46.).

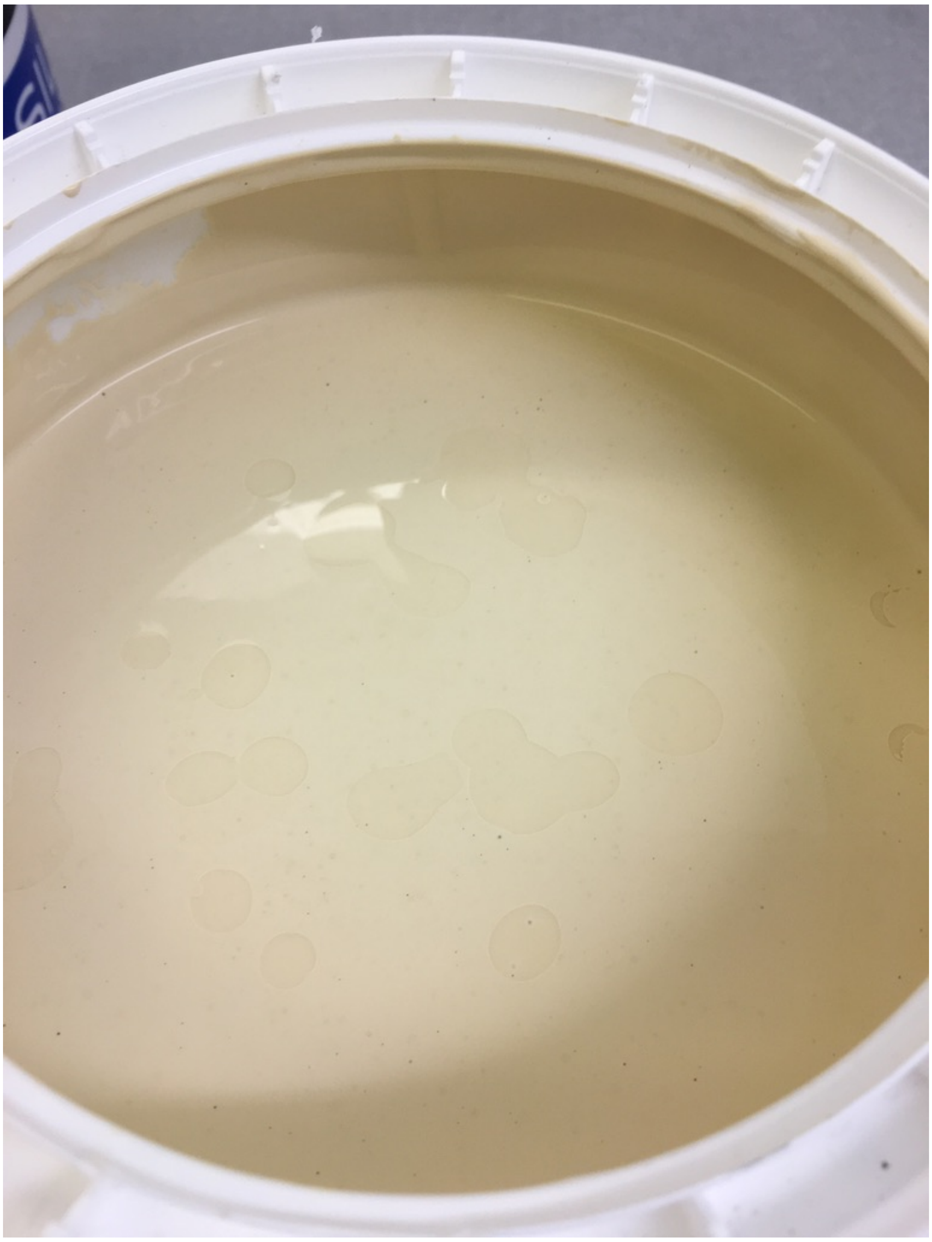


Figure 46: A shaded paint (magnolia).

2.2.4 Paint manufacturing plant designs

Within the literature Rotstein et al.[83] working with ICI Paints, Slough (which is now under AkzoNobel with the decorative brand Dulux[84]) compared the design of three types of paint manufacturing plant concepts:

1. A conventional “fixed-mixer” plant
2. A Pipeless plant
3. An “In-can” plant

This three-concept design is particularly interesting within Crown Paints as their processes can be argued to incorporate all three.

An idealised conventional plant would be automated with a continuous flow of raw material pumped into the vessels through the process and into paint tins. Whilst none of the Crown Paints factories have a perfect automated design the processes used are clearly designed with this in mind. The Darwen manufacturing site is a typical conventional plant for high volume production resulting in larger batches, low manufacturing costs and higher stocks. It is also highly automated relying on a PLC system (which was useful for the work described in Chapter 3.) and the material is pumped across the facility in a series of separate pipes (Figure 47.). Overall, the assumption based on Rotstein et al.[83] is that the cost per unit capacity would be lower than the other designs. The Hull manufacturing site has a single Line (Line 1) dedicated to this methodology for very high output products (typically white or magnolia paint). Similarly, this line is also virtually fully automated including “robotic filling lines” for the “canned” product (Figure 48. & Figure 49.).

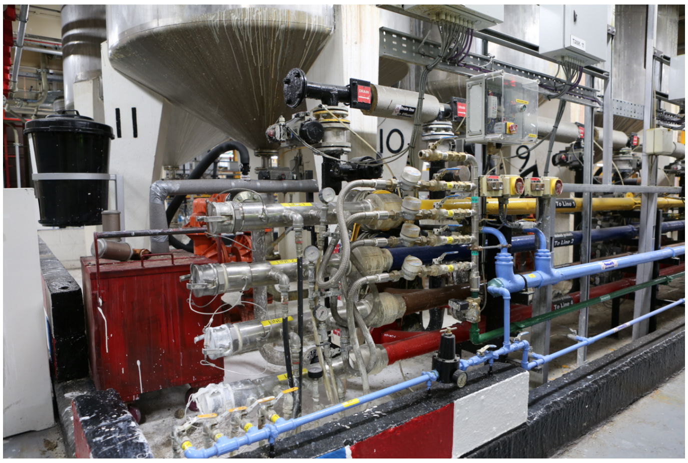


Figure 47: Complex series of separate pipes at Crown Paints Darwen Site.

Figure 48: Automated filling line at Crown Paints Hull site Line 1.

Figure 49: Robotic palletising of product at Crown Paints Hull site Line 1.

Interestingly, most of the Hull manufacturing lines operate on a “Pipeless Plant” model where material is pumped (shown in Figure 50.) from vessels to another vessel using temporary flexible hoses (indeed within this work the trial detailed in 7.3. used this method). The batch sizes are significantly large enough (circa. 9,000 - 30,000 l) to warrant conventional plant design and the plant produces significantly larger volumes of material than the Darwen site however this remains the plant design.

Rotstein et al.[83] suggests this method results in higher manufacturing cost but lower lead-times which could have been an advantage at the plant’s design. Overall, the capital cost per unit capacity is higher than with a conventional plant. This is likely the result of a legacy design feature and an idealised plant producing the volumes expected at the Hull site would likely feature a more “conventional plant” design.

Figure 50: An example of a "portable pump station" at Crown Paints Hull site.

Colour matching[85] is a service provided within Crown Paints' retail stores to provide a match to a diverse range of niche colours (Figure 51.). Typically, a spectrophotometer is used to identify the desired colour and a colourless "base" is tinted using small amounts of colourants within a colour mixing machine (Figure 52.). Mixing is provided "in can" by shacking the product vigorously. Interestingly, each can therefore is a single batch. Rotstein et al.[83] estimates this manufacturing method has the highest per unit cost however it results in extremally low volumes of stock. Notably for this project this method generates limited amounts of waste as the product is manufactured in a vessel which also acts as the packaging of a product made specifically for the customers' requirements practically at the point of sale.

Figure 51: A "fan deck" of available colours of Crown Trade Paint.

Figure 52: A typical paint mixing machine.

2.2.5 Plant Hygiene

In addition to the “in-can” biocides described in 2.1.4. the vessels are extensively washed before and after use with chlorinated virgin water. While all Pipes are flushed and pigged to remove any residual material. The generated wash water is then typically treated as waste effluent.

Figure 53: Vessel cleaning at Crown Paints Hull site.

2.2.6 Effluent treatment

At Crown Paints, the washwater generated from the paint manufacturing process is treated within their onsite effluent treatment plants. However, it is notable that for some smaller paint manufacturers the effluent is sent directly for treatment with other liquid wastes at external facilities. Chapter 3. provides a detailed evaluation of the effluent process for Crown Paints from generation to disposal (cradle to grave). However, in this section (2.2.6.) a general overview of a typical effluent treatment process is provided.

On a basic level, the purpose of effluent treatment is to remove contaminants from wastewater thus producing an effluent that is suitable for discharge into the environment (or an additional treatment process) or alternatively reused (e.g., greywater recycling). Globally, it is estimated that 52% of sewage is treated before discharge[86]. Whilst there are various effluent treatment processes available (e.g. Dissolved Air Flotation, Ozonation, Chlorination, Denitrification etc.[87]) Crown Paints utilise a standard coagulation/flocculation, settling and filtration based system. For Crown Paints the process requires the removal of suspended solids whilst keeping the chemical oxygen demand (COD) within specification. The method chosen; coagulation and flocculation grows larger particles (Flocs), which are more likely to sediment from the suspension and thus be removed from the water into a sludge layer. This sludge layer is then dewatered via pressure filtration using a filterpress.

2.2.6.1 Coagulation and flocculation processes

The fundamental factor affecting the separation of a suspension is the particle size and the form of the separated solid; when the particle size is small both the gravitational and centrifugal sedimentation rates are usually low and filtration is often slow. This produces a high resistance cake that is subsequently difficult to de-liquor and wash. Increasing the particle size of these fine and colloidal suspensions is therefore advantageous. The addition of a chemical agent can encourage an aggregation process through altering either the surface properties of the particles, the properties of the suspending liquid or the way the particles and liquid interact.

"Coagulation" is the process whereby destabilization (aggregation) of a suspension is affected by reducing the electrical double layer (EDL) repulsion between particles through changes in the nature and concentration of the ions in the suspending electrolyte solution. A "Coagulant" refers to the chemical or substance added to the suspension to affect the destabilization.

"Flocculation" is the process whereby a long chain polymer (or polyelectrolyte) causes particles to aggregate, often by forming "bridges" between them. A "Flocculent" refers to the chemical or substance added to a suspension to accelerate the rate of flocculation or to strengthen the flocs formed during the flocculation.

Optimizing coagulation is often seen as the most cost-effective way to decrease treated water turbidity.

Coagulation

Multivalent metal ions

Inorganic salts containing multivalent metal ions of Aluminium or Iron are the most widely used coagulants in water and wastewater treatment. The most commonly added coagulants are aluminium sulphate (Alum), ferric chloride and ferric sulphate

The use of these chemicals in this manner is ancient, with references to Alum being used as a coagulant to purify water being traced to the great Roman scientist and statesman Pliny the Elder (circa 77 AD)[88]. Chemically the addition of these inorganic salts increases ion absorption by the particles

Coagulation mechanisms

It is believed that the method by which colloidal particles are coagulated can be categorised by four distinct mechanisms:

- Enmeshment,
- Adsorption,
- Charge neutralization/destabilization,
- Complexation/precipitation.

A conceptual view of these mechanisms is provided in Figure 54.

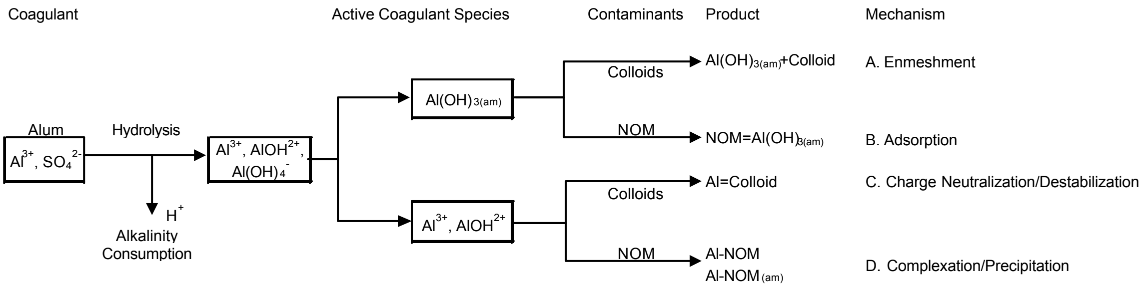


Figure 54: Conceptual View of Coagulation Reactions with Alum, adapted from Pernitsky[89].

Enmeshment (or “sweep floc”) is a mechanism by which the precipitated hydrous metal ion salts literally sweep the majority of the colloids and some dissolved solids enmeshing them within their settling hydrous metal oxide floc. This requires a relatively large dose of coagulants and a slightly higher pH,

Absorption of species with the same polarity (co-ion) augment the particles original charge whilst those with different polarity (counter-ions) may negate or sometimes even cause charge reversal (Charge Destabilization). Ultimately whilst these two mechanisms may slightly differ, their overall effect is to lower EDL repulsions and thus reduce the potential energy barrier to coagulation.

Complexation is a mechanism in which the destabilized particles are bridged together in a form of polymerisation further promoting destabilisation. Once precipitated this mechanism can aid the overall coagulation effect further through enmeshment of the particulates by the ever-expanding structure.

Factors affecting coagulation

The pH at which the coagulation process occurs is the most influential factor in coagulate performance. Aluminium coagulants perform best at pH values close to the pH of minimal solubility of the coagulant (typically close to 6) this maximises the presence of hydrous metal oxide for complexation and enmeshment whilst providing a source of dissolved Al ions for charge destabilisation (Figure 55.).

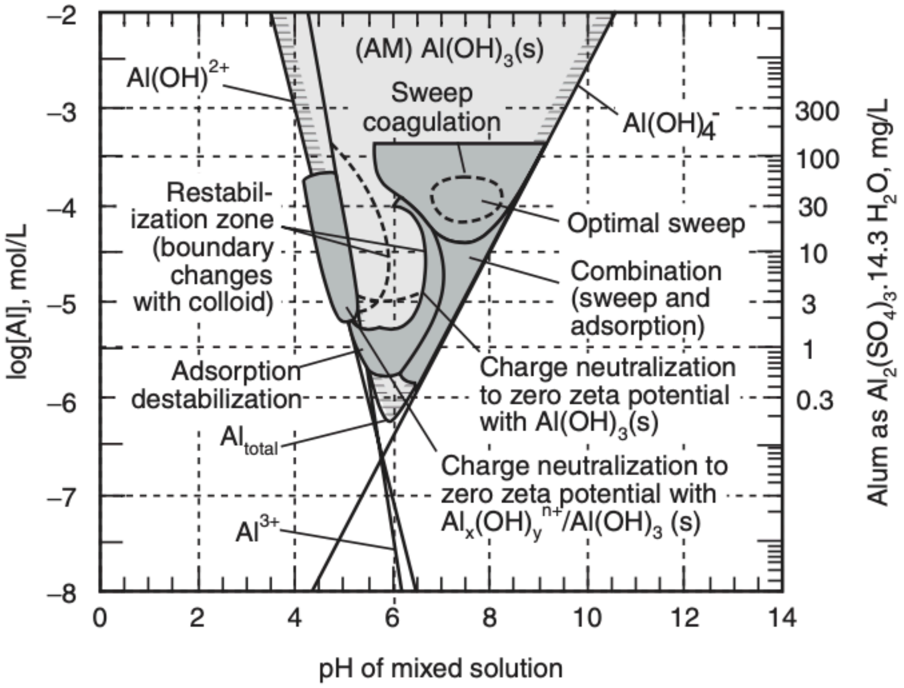


Figure 55: A solubility diagram for Al(III) at 25°C, adapted from Howe et al[90].

Flocculation

Flocculation occurs when long-chain (typically synthetic) polymers are used to overcome the potential energy barriers preventing the spontaneous aggregation of the particles. If these polymers contain functional groups which carry a charge, they convey an anionic (-ve) or cationic (+ve) charge across the polymer chain. This can also occasionally result in an amphoteric character where both anionic and cationic charges are expressed. These polymers act as aggregates and the coagulated particles form a floc around them (Figure 56. & Figure 57.).

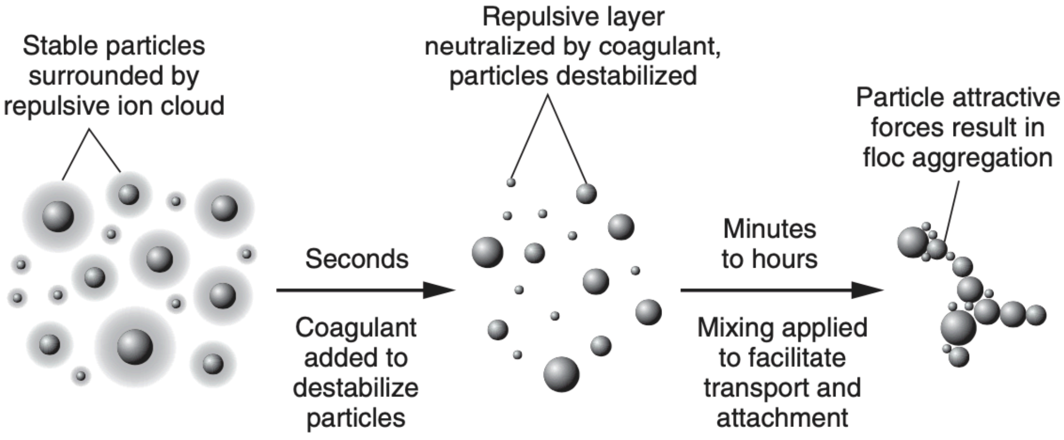


Figure 56: Schematic of coagulation and flocculation process,

from Crittenden et al.[91].

Figure 57: Flocs at Crown Paints Darwen effluent plant.

Jar testing

Jar test are the standard tool for chemical selection/dosing of physical chemical wastewater treatment processes[92]. Jar tests are used to mimic the coagulation and flocculation processes on a smaller scale typically within a laboratory environment. Jar tests are used extensively to predict optimum coagulant conditions due to their simplicity for operators to conduct.

A standardised method for Jar Tests is provided in ASTM D2035-19[93]. For this work however a simplified method (detailed in Chapters 5. & 6.) of a single 500 ml beaker of effluent was agitated to simulate the treatment tanks. This was done to mirror the situation at Crown Paints as accurately as possible (the Jar Test at Crown Paints' Hull effluent plant is shown in Figure 58.)

Figure 58: A jar test setup at Crown Paint Hull effluent plant.

2.2.6.2 Dewatering

Sedimentation

Following coagulation and flocculation the suspended solids (in the form of "Flocs") are separated from the aqueous phase using gravity forming a sludge. As the sedimentation process was not a significant focus of the project (due to the limited observed impact on the process during plant trials) only a general overview of sedimentation theory is presented here.

In a dilute suspension, an individual particle settles based on its size and density with limited particle interactions. These are known as discrete particles (i.e. those that do not continue to flocculate during sedimentation). For discrete particles, the Type I model is used[94] as described on the following pages. Additionally, Buscall and White[95] described a theory of sedimentation for concentrated suspensions, which is of interest as the origin of the concept of compressive yield stress, ***Py(φ)*** that is reinvent to the filtration modelling described in Chapter 6. particularly.

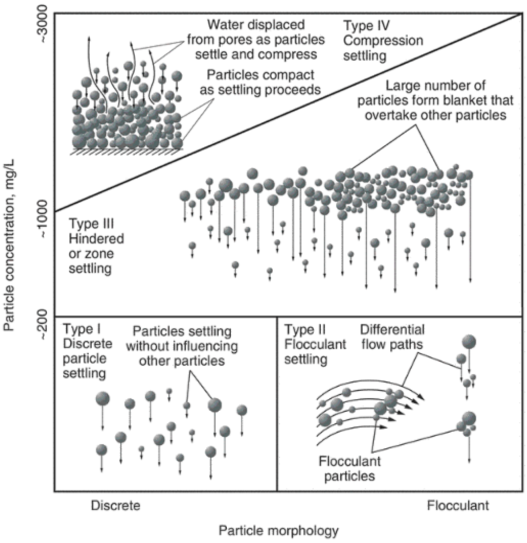


Figure 59: Relationship between settling type, concentration, and flocculent nature, from Crittenden[96].

The Type I sedimentation model

For dilute suspensions (assumed to contain discrete particles) a single particle moving through a fluid is subjected to both gravitational, F_g (and buoyancy, F_b) and drag forces, F_d.

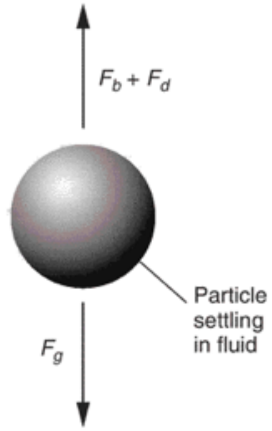


Figure 60: The forces acting on a discrete settling particle, from Crittenden[96].

The force balance is normally written so that the direction of gravitational force is positive (i.e. a positive settling velocity results in a settling particle)[96].

$$F_g = ma = \rho_p V_p g \tag{19}$$

$$F_b = ma = \rho_w V_p g \tag{20}$$

Where:

m = mass, kg

a = acceleration, m s^{-2}

ρ_p = density of particle, kg m^{-3}

ρ_w = density of water, kg m^{-3}

V_p = volume of particle, m^3

g = acceleration due to gravity, 9.81 m s^{-2}

Mathematically, the most important parameter of the settling process is the settling velocity of a particle, **v_s**.

$$v_s = \left[\frac{4g(\rho_s - \rho_w)d}{3C_D\rho_w}\right]^{1/2} \qquad 21$$

Where:

ρ_s = density of the settling particle, kg m^{-3} **C_D** = drag coefficient

d = diameter of the settling particle, m

The drag coefficient, **C_D** is determined experimentally by measuring the settling velocity within laboratory conditions.

$$Re = \frac{\rho_w v_s d_p}{\mu} = \frac{v_s d_p}{\nu} \qquad 22$$

Where:

Re = Reynolds number **ν** = kinematic viscosity m^2 s^{-1}

μ =dynamic viscosity, N s m^{-2} or kg m^{-1} s^{-1}

Figure 61. shows the experimentally derived drag coefficient, **C_D** for a spherical particle.

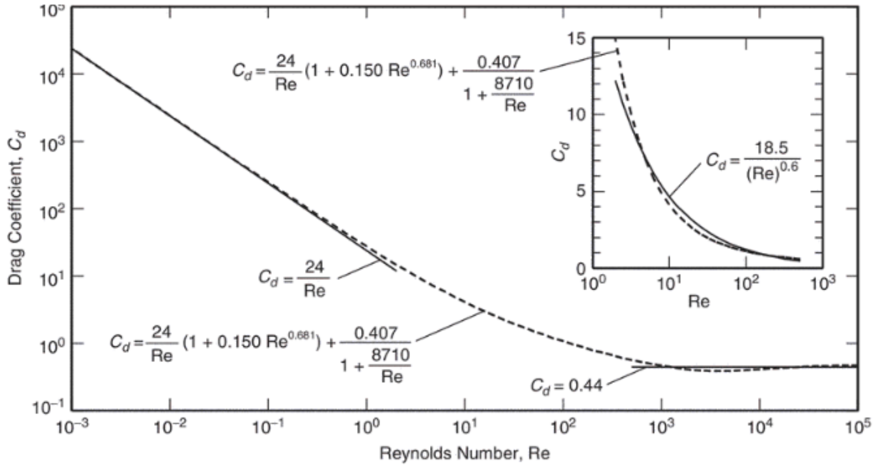


Figure 61: The drag coefficient for different Reynolds numbers, from Crittenden[96].

Filtration

After the sedimentation process the sludge is pumped into a filterpress where it is filtered through a membrane under pressure. The filterpress is a simple device that has a large variety of applications from iron ore extraction to blood plasma fractionation[97]. A standard filter press (illustrated in Figure 62.) consists of three main elements, a strong frame which can resist high pressure (especially cyclical loading and fatigue stresses), a series of filter plates with a cloth covering and channels for filtrate, and a mechanism to apply pressure and to open and close the plate pack for cake discharge and cleaning operations.

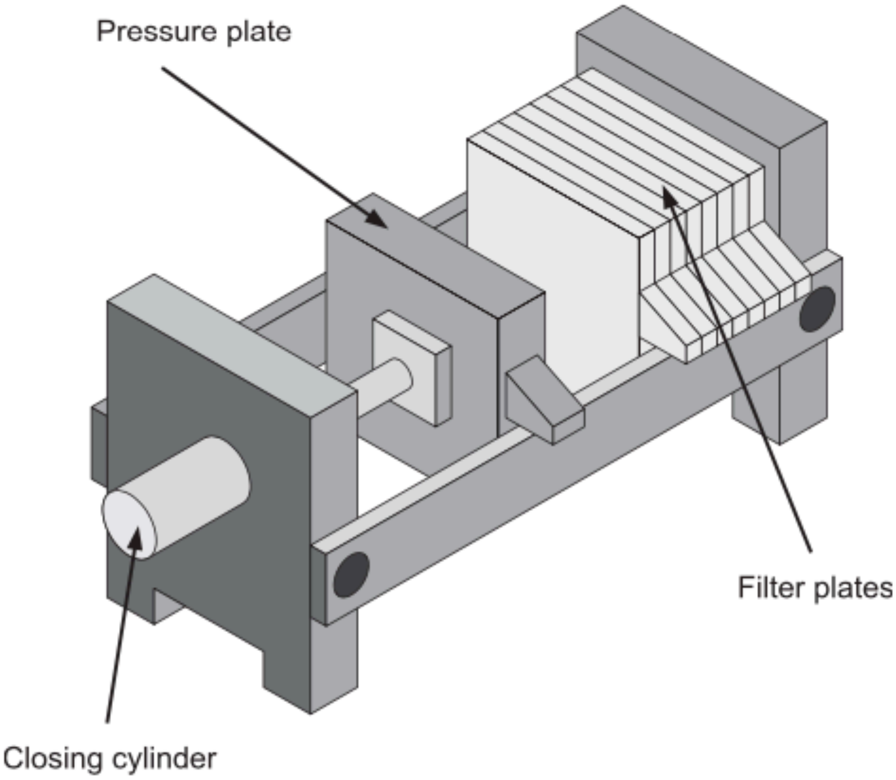


Figure 62: A basic filter press, from Sparks & Chase[97].

The structure can be envisioned in a simplified manner with an arrangement of alternate frames and clothes forming a series of filtration chambers when placed together under pressure (Figure 63.).

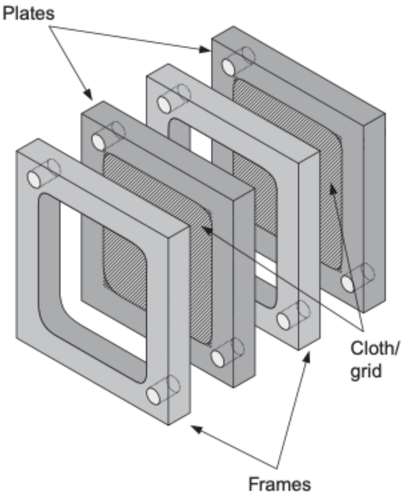


Figure 63: A simplified structure of filtration chambers within a filterpress, from Sparks & Chase[97].

Within the plates, a channel is formed which acts as a "pipe" throughout the series of plates (known as the "plate pack"). The sludge is pumped into each filtration chamber from this "pipe". Figure 64. shows a filter press plate at Crown Paints with the central "pipe" hole clearly visible.

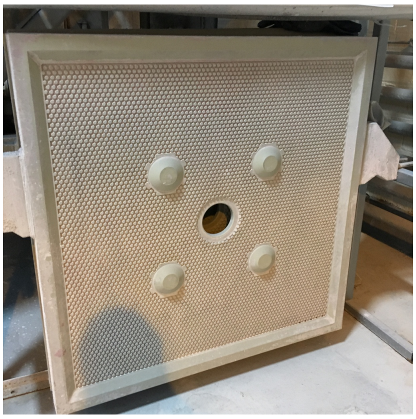


Figure 64: A filterpress plate at Crown paints.

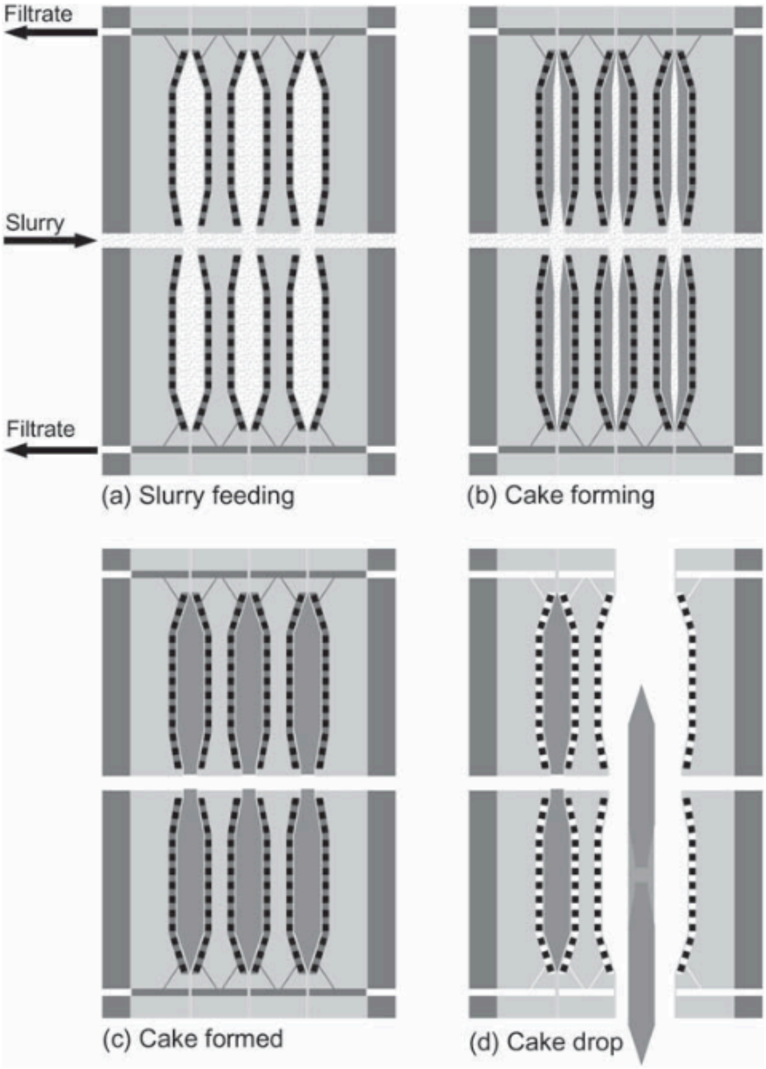


Figure 65: The filter press cycle, from Sparks & Chase[97].

Figure 65. shows a cross section of the filterpress chamber plates during a filtration cycle. The sludge (or slurry) is pumped into the plate pack through the “pipe” and directed into each of the filtration chambers (A). The filtrate then exits through channels separated by the filter cloth and out of the filter press (shown in Figure 66.). As the cake begins to form (B) the resistance across the cake increases leading to an increase in pressure and a drop in the flowrate of the sludge. Once a cake is fully formed (C), the sludge channel is blown clean to remove any sludge before the pack is opened to drop the filter cake out of the press.

Figure 66: The filtrate vacating the filter press.

Filtration modelling

With jar tests being the standard method to simulate the effluent treatment process the filtration stage is thus routinely neglected in both industry and academia. This section will provide an overview of filtration modelling to provide a background for the work contained within Chapter 6. (which is adapted from Wardrop et al.[1]).

The modelling of pressure filtration using compressional rheology and compressive yield stress, ***Py(φ)*** and hydraulic resistivity, ***r(φ)*** (where: ***φ*** is the local volume fraction of solids) was developed by Landman and White[98,99] expanding on Buscall and White's work[95] introducing compressive yield stress in sedimentation processes. Landman and White[92] simplified the process into a one-dimensional model (illustrated in Figure 67.) which required the determination of ***φ(z,t),*** i.e. the volume fraction, ***φ*** at height, ***z*** above the filter membrane as a function of time, ***t***. A consent piston pressure, ***ΔP*** is applied and the initial volume fraction, ***φ_0*** is equal to the initial piston height, ***h_0***.

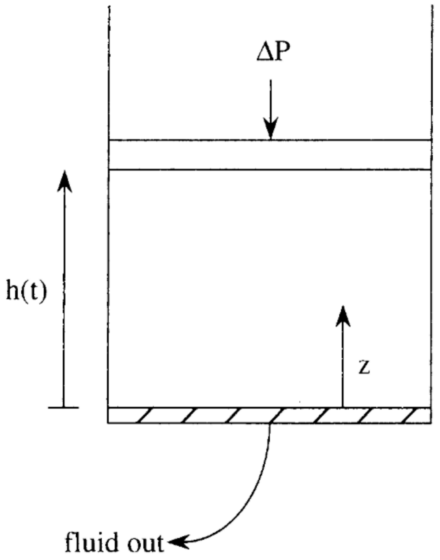


Figure 67: The simplified geometry of the one dimensional filter press model, from Landman & White[99].

Green et al.[100] builds from this work illustrating a design for a constant pressure filtration device (Figure 68.) and reports results for ZrO_2 suspensions. The device was built at the University of Melbourne, pressure was applied via a pneumatic cylinder with a line pressure range of 0-600 k Pa (with a lower limited pressure approx. 50 k Pa). ZrO_2 was chosen as a model suspension due to its chemical stability and the preparation of the ZrO_2 suspension was carefully controlled for repeatability.

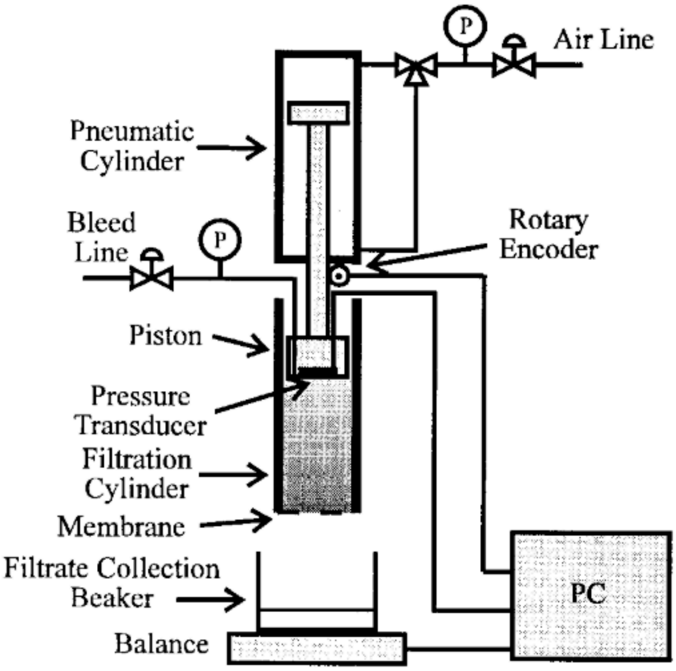


Figure 68: The constant pressure filtration device, from Green et al.[100]

A typical set of raw data consisted of ***t/V*** verses ***V*** plots for the relevant applied pressure (shown in Figure 69.). Whilst Landman and White predicted that the ***t/V*** verses ***V*** plot would be linear with the slope, $\mathbf{m_1}$[98,100]**.** Green et al.[100] notes a linearity in the data at low ***V*** followed by a deviation and then full equilibrium.

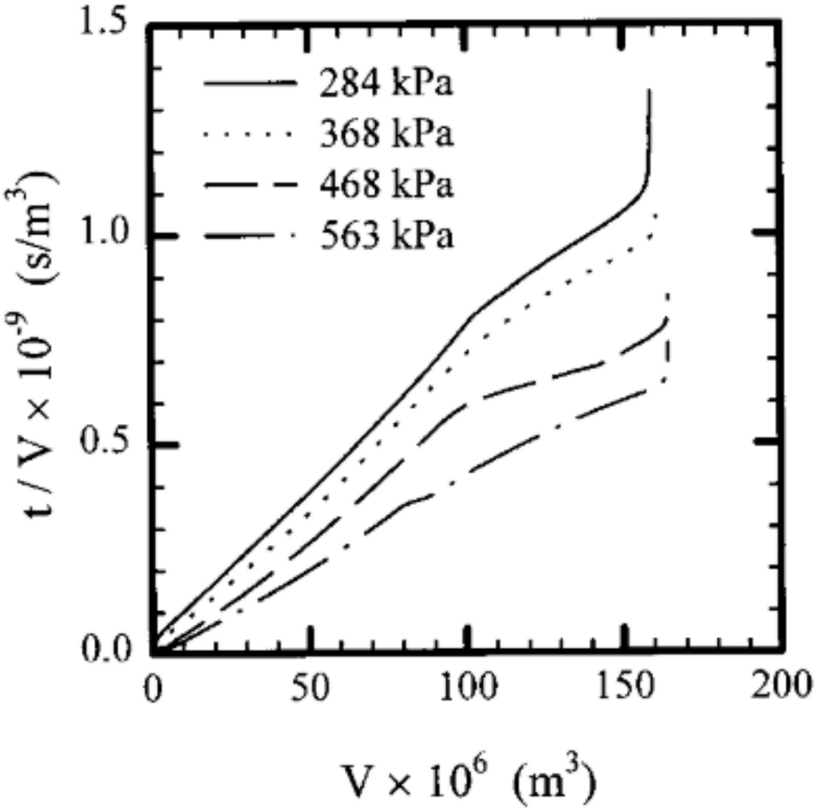


Figure 69: Typical filtration rate data for ZrO_2 from Green et al.'s constant pressure filtration device[100]

The filtration apparatus described in De Kretser et al.[101] (Figure 70.) is almost identical to the design in Green et al.(Figure 68.) with the author noting this inspiration but also “substantial modifications” which appear to relate to the introduction of a Double Ended Pneumatic Cylinder and Linear Encoder. Additionally, the scale of the filtration experiment (and thus filter cake thickness) was reduced to reduce the time required for each filtration run.

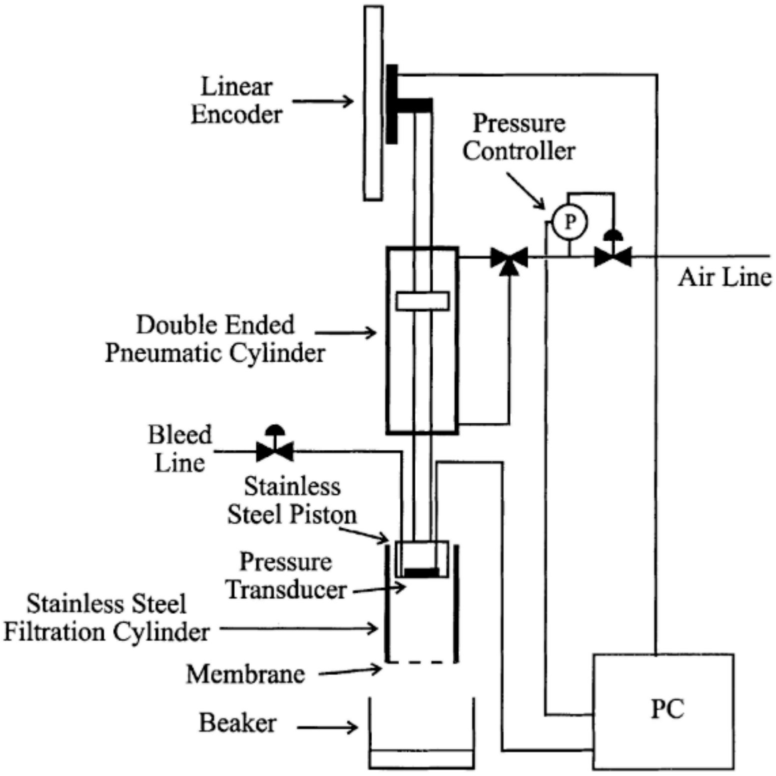


Figure 70: filtration apparatus, from De Kretser et al.[101]

Experimentally De Kretser et al.[101] notes that historic filtration testing (implying the method described in Green et al.[100]) was time extensive; taking in the region of several days. Thus, they targeted reducing the required time for compressive yield stress, ***Py(φ)*** and hydraulic resistivity, ***r(φ)*** characterisation from at least five individual filtration experiments into a new method that required only two separate filtration experiments over a range of pressures.

In their method a “compressibility test” (to determine compressive yield stress) is conducted at the lowest pressure desired and the filtration is run to equilibrium. Once equilibrium is reached the pressure is “stepped up” to the next desired pressure until the compression reaches equilibrium once again. This is repeated until each desired pressure has been conducted (Figure 71.). This method of increasing the pressure in sequential steps, is known as “stepped pressure filtration”. The purpose of this test is to produce an experiment determining the final solids concentration for the full range of desired pressures and thus ***Py(φ)***.

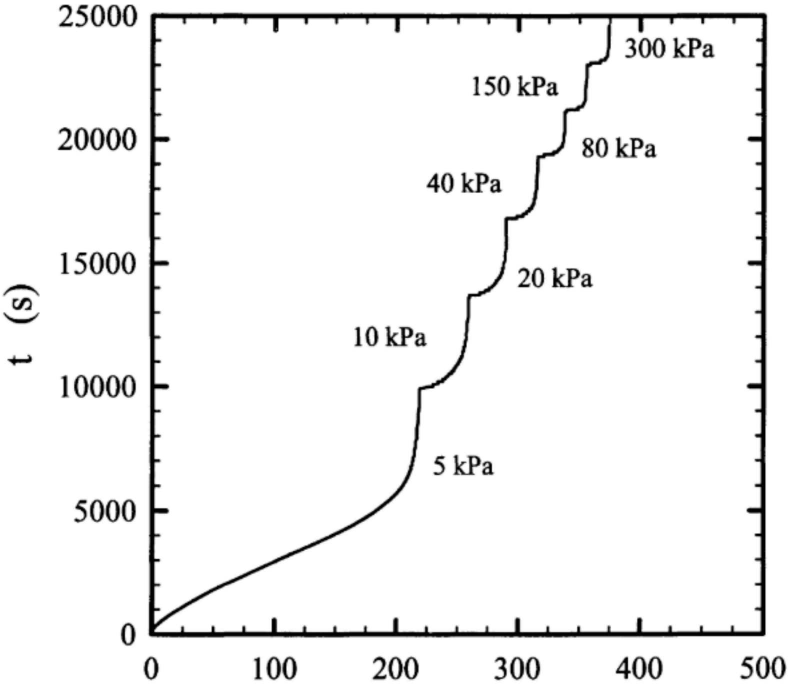


Figure 71: Example of t vs. V^2 for stepped pressure filtration compressibility test, from De Kretser et al.[101]

The “permeability test” from De Kretser et al.[101] functions in much the same way, using a “stepped pressure filtration” methodology. **β^2** values are determined for the same pressures used in the “compressibility test”. A linear ***t*** vs. ***V^2*** plot is made for the lowest pressure desired, once this slope becomes “stable” the pressure is then stepped to the next pressure increment. This is followed by a “transition region of filtration behaviour” before a new linear region. Once this slope becomes stable in the linear region again the pressure is once again “stepped up” etc. (shown in Figure 72.). From this test the value of, ***r(φ)*** can be calculated.

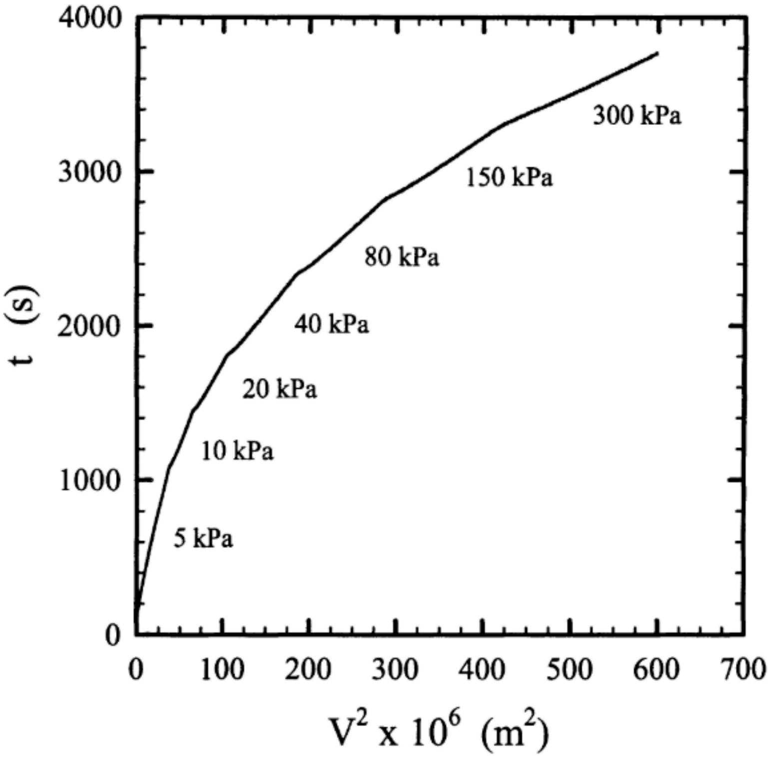


Figure 72: Example of t vs. V^2 for stepped pressure filtration permeability test, from De Kretser et al.[101]

The work described within Chapter 6. of this thesis takes the work of De Kretser et al.[101] and combines the two experiments required via that method into a single experiment.

3 GETTING A BASELINE: THE VALUE STREAM ANALYSIS

The primary activity of the first stage of the KTP project was to analyse the effluent and to attempt to fully map Crown Paint's emulsion plant processes; to establish the origin of this waste stream, its costs and reduction potential. This represents the first deliverable of the KTP project as defined in 1.3. This section therefore provides an overview of this process and provides a holistic overview of the waste situation within Crown Paints emulsion paint manufacturing process with respect to wastewater.

A simple Value Stream Analysis (VSA) methodology was used. The basis of this methodology is the definition that only an activity that physically changes the shape or character of a product or assembly can add value (value adding) and that any activity that does not change the product or assembly is waste (non- value adding). By separating the process into value added and non-value added components it has been possible to characterize the process as such to identify any areas where resource usage could be minimised[102].

This value stream analysis provides a unique approach by focusing on water consumption from an industrial process. It specifically quantifies the useage of water within the production of a product (i.e. paint) and subsequent vessel washings, in addition to the effluent treatment of waste water and ultimately disposal (as a filter cake) of waste flocculated material contained within the effluent. This chapter therefore reports the first identified novel outcome of this highlighted within this thesis.

3.1 Overview of Value Stream Analysis (VSA)

3.1.1 Introduction to Lean & Six Sigma (LSS) methodologies

Lean Six Sigma (LSS) is a series of methodologies to improve a process' performance and to reduce waste. Historically "Six Sigma" originated in organisational improvement with Motorola in 1980s Japan and was combined in the early 2000s with "Lean" manufacturing ideals from the 1950s Toyota Production System[102].

The Lean philosophy simply is the reduction of unnecessary activity & avoidance of "waste" within a process. A Lean practitioner's task is to evaluate a process from the "customers" perspective, the value of an activity is one which the customer is willing to pay for.

From a customer's perspective:

Any activity is said to be "**Value adding**" **(VA)** if it is essential for the customer needs. Any activity which isn't essential to the customer is said to be "**Non-Value adding**" **(NVA)**. This from a lean perspective represents "waste".

Although this definition is very intuitive, a strict definition can be problematic as Quality Control (QC), Maintenance and Testing activities are considered “non-value adding” and thus waste. Six-sigma is therefore often implemented as a series of tools to help reduce the occurrence of defects and thus the reliance on inspection and quality processes. Strictly speaking a Six-Sigma process is one where 99.99966% of activities are free from defects (as detailed in Table 3). Mathematically it means an error would occur at six standard deviations from the mean (hence the name). A typical normal distribution chart demonstrating this is shown in Figure 73.

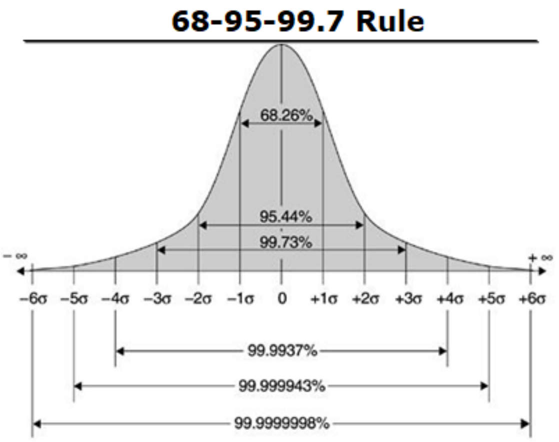


Figure 73: The percentage of values that lie within a band around mean in a normal distribution with a width of 2,3,4,5 & 6 standard deviation respectively, from Ramana[103].

Table 3: The Expected yield at each sigma level

Sigma Level	Short term yield (without 1.5 σ shift)	Long-term yield (with1.5 σ shift)
1σ	68.6%	30.9%
2σ	95.44%	69.1%
3σ	99.73%	93.3%
4σ	99.9937%	99.4%
5σ	99.999943%	99.98%
6σ	99.9999998%	99.9997%

3.1.1.1 The original seven wastes (Muda) of Lean

The “seven wastes” or “Muda” (from the Japanese term for “wasteful”, “useless or “futility”) is a cornerstone of lean philosophy. In English the mnemonic “TIMWOODS” is sometimes used.

The Seven Wastes (Muda):

1. Transportation

   Unnecessary transport of materials, tools or personnel from one area to another. Solutions include changing locations of equipment/activities or alternative transport methods.

2. Inventory

   Costs associated with the storage and capital tied up with unprocessed inventory. Moving towards “just in time manufacturing” minimises this waste.

3. Motion

   Unnecessary movement of machines and people, machines can wear out and people over-burdened.

4. Waiting

   The process being slowed or halted due to other steps in the supply chain. The slower process can be made more efficient, more resource can be applied on the slower process and better coordination of the process can reduce waiting time.

5. Overproduction

Often results in additional inventory. Excessive capital is inevitably tied up in unsellable product. Market research and adequate scheduling reduces this impact.

6. Over processing

Over-engineering a process to add more value than the customer expects. This can also raise customer expectations and compound this aspect.

7. Defects

Products or services not meeting the customers’ expectations. Defective products are often replaced at an additional cost and require processing. A more effective and efficient production system often can reduce the complexity of a process in addition to the numbers of defects.

Although not defined in the Toyota production system it is commonly accepted that there is an 8th waste, essentially the human potential of the workforce[104].

8. Skills

Without engaging with staff’s expertise, it is difficult to improve any process. Placing employees in positions below their skills and talent or poorly training staff for their role are common examples of this waste.

Figure 74: The Eight Wastes of Lean, commonly known as "TIMWOODS", adapted from Skhmot [104].

3.2 Contextualising the value stream analysis study and opportunities for future research

Whilst there has been a wealth of operational research studies using value stream mapping tools [105,106] its application to environmental problems has been extremely limited. Those limited studies focused predominantly on energy useage[107,108]. When this study was completed the research was completely unique and there was limited literature for the application of value stream mapping with the perspective of environmental performance[109,110,111]. Value stream mapping of water consumption has since developed[112] but methods remains fairly simplistic and not realising the true potential of the tool.

An alternative to the Value Stream Analysis (VSA) would be the use of a Life Cycle Analysis (LCA). Developed by Zhang et al.[113], LCA is a methodology to assess the environmental impact associated with all stages of the life cycle of a commercial product (or alternatively process or service) from raw material extraction (cradle) through manufacture, distribution, use and disposal (grave). Notice how a circular economy philosophy attempts to extend the lifecycle and move towards a cradle-to-cradle model. Whilst the LCA has merits the focus of this work is on improving production with an aim to reduce production waste. The VSA is more focused on the specific processes involved and thus more useful for this purpose. A LCA is however of interest when considering the whole circular nature of the ecosystem, but it is not detailed within this work.

Objectively, chemical processes are unique in the level of analytics we can apply to them. If we were to combine analytical techniques with mass and energy balances across a chemical process, we would have access to a highly powerful tool for understanding the application of the chemical process. From a true lean perspective, this activity would be totally over-processed for its intended purpose within this work. However, the application in this manner, considering all variables (all raw materials, by-products & intermediates) could be invaluable in understanding a chemical process.

3.3 The Darwen manufacturing site's effluent Value Stream Analysis (VSA)

3.3.1 Methodology

3.3.1.1 Process map of effluent generation at the Darwen site

First the process was observed, defined and any inputs and outputs identified (Figure 75.).

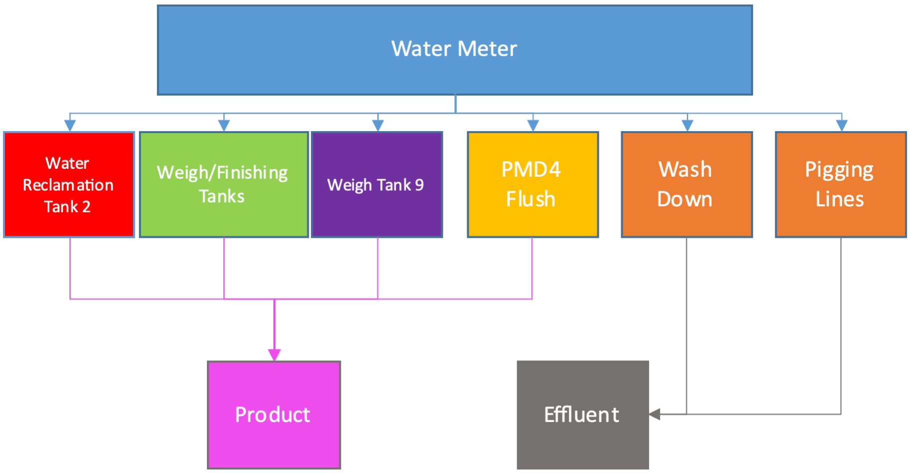


Figure 75: The process map of the generation of Effluent at Crown Paints Darwen Emulsion Plant.

The process described in Figure 75. is an isolated system which establishes the total throughput of water entering Crown Paints Darwen Emulsion Plant. The process map defines the water's use as either a Value Added (VA) component within the product or as a Non Value Added (NVA) component, directed to the effluent plant. At the time of this study the emulsion plant accounted for the entire volume of effluent generated at the Darwen site.

Utilizing the assumption that “any input must either add value to the process or not” we can determine the “wastage” of the process using:

$$\boldsymbol{Influent\ water = Value\ Added + Non\,Value\ Added} \qquad \textbf{23}$$

3.3.1.2 Emulsion Plant’s water usage

The Emulsion Plant contained an isolated water meter Figure 76., which recorded volumes of water entering the plant. This record of the influent water provides an understanding of the water usage within both the product and waste. At the onset of the project, a number of irregular readings had been recorded. However, the project has moved towards a regular daily recording (shown as total weekly volumes in Figure 77.) of the water meter (at approximately 07:20).

Figure 76: The water meter for Crown Paints’ Darwen Emulsion Plant.

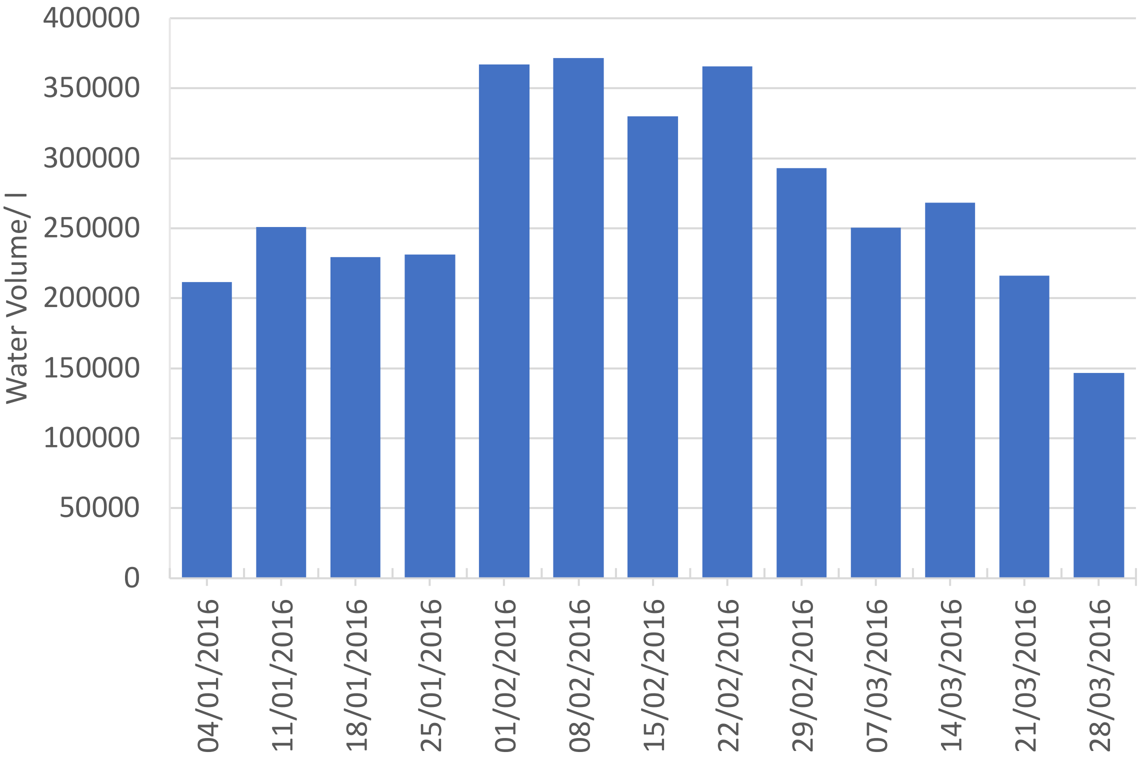


Figure 77: Darwen Emulsion Plant Weekly Water Usage.

3.3.1.3 Plant Data

The Emulsion Plant operates on a Programmable Logic Controller (PLC) system, which records every individual input of “virgin” water into each of the formulations produced by the plant (defined as Value Added, VA). The individual batch data was mined and consolidated to identify the different sources of Value-Added water into the process. The data (Figure 78.) demonstrates the different sources of water into the formulations for the start of 2016.

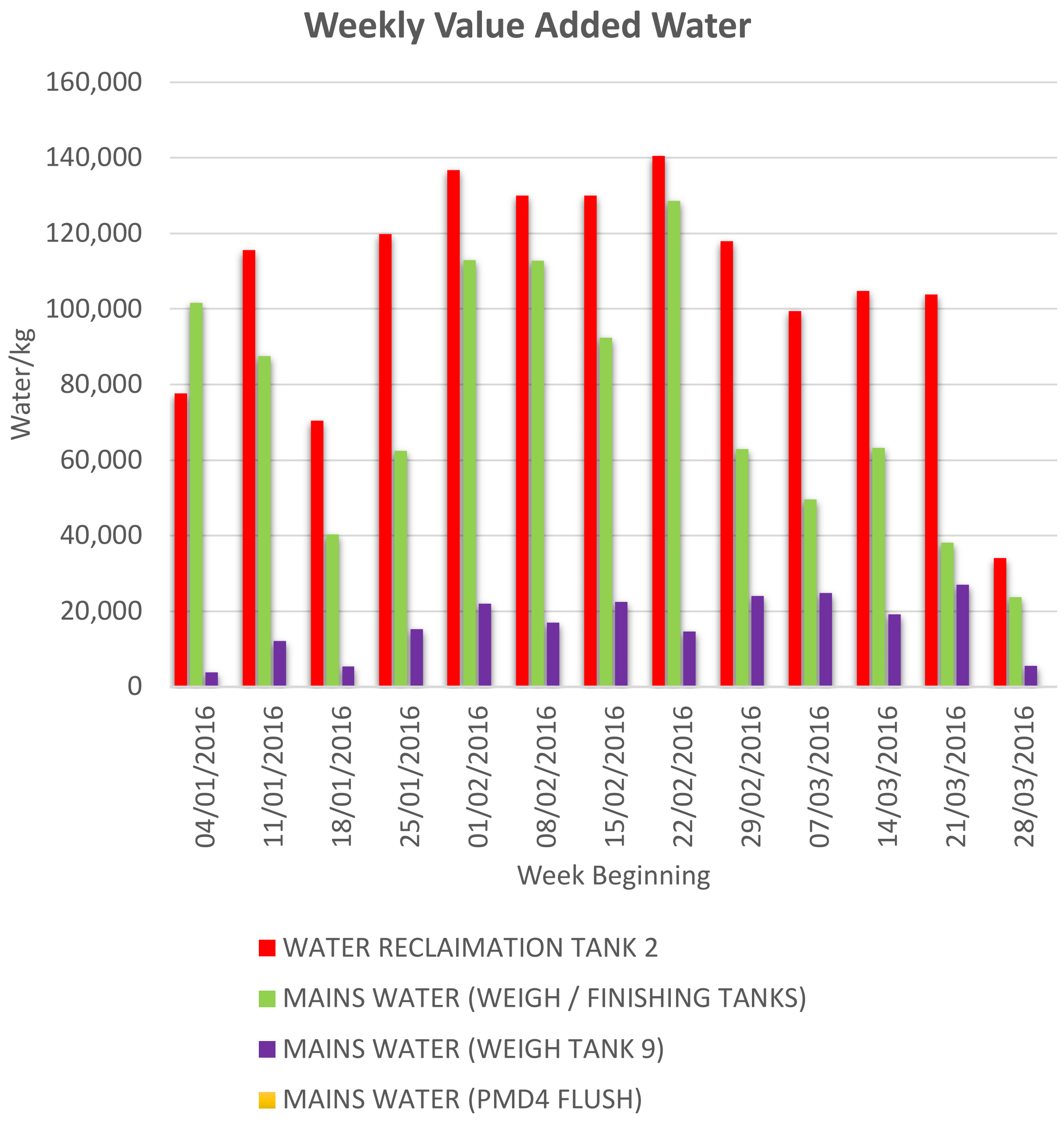


Figure 78: Consolidated PLC data from Darwen Emulsion Plant of all different inputs of water into product.

3.3.1.4 Calculation of Value Added (VA) and Non Value Added (NVA) Component

Utilising Equation 23. the ratio between VA and NVA components can be determined.

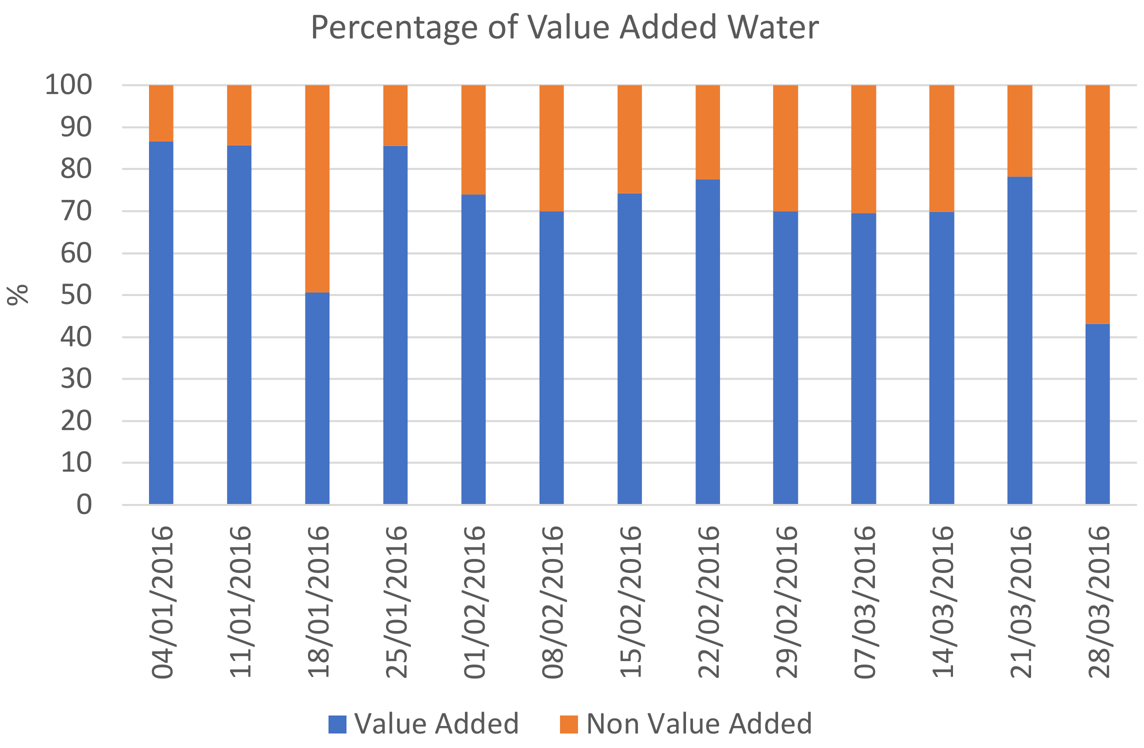


Figure 79: Comparison of Value Added and Non Value Added components of water within the Darwen Emulsion Plant.

Figure 79. compares the data extracted from Crown Paints' Emulsion Plant PLC system as a proportion of the recorded influent volumes. It shows a variable proportion of water being used within the formulations (VA) and wastage (NVA) this could be representative of a variation in washing water volumes. The mean values for the Value Added and Non-Value Added components are 71.91 and 28.09 respectively (S.D. 12.80) suggesting influent water wastage of approximately 28%, which is ultimately being treated by the effluent plant. The NVA component comes primarily from vessel and line washing (both of which are unmetered).

Interestingly, as the VA component by definition represents all the water within the product (due to the PLC control system). The concentration of water contained within the paint formulations can also be estimated by comparing the PLC data with the production volume data:

At Crown paints Darwen Site:

$$\boldsymbol{Percentage\ of\ Water\ in\ Paint} = \frac{\boldsymbol{Volume\ of\ Water\ in\ Formulation}}{\boldsymbol{Production\ Volume\ of\ Product}} \qquad \textbf{\textit{24}}$$

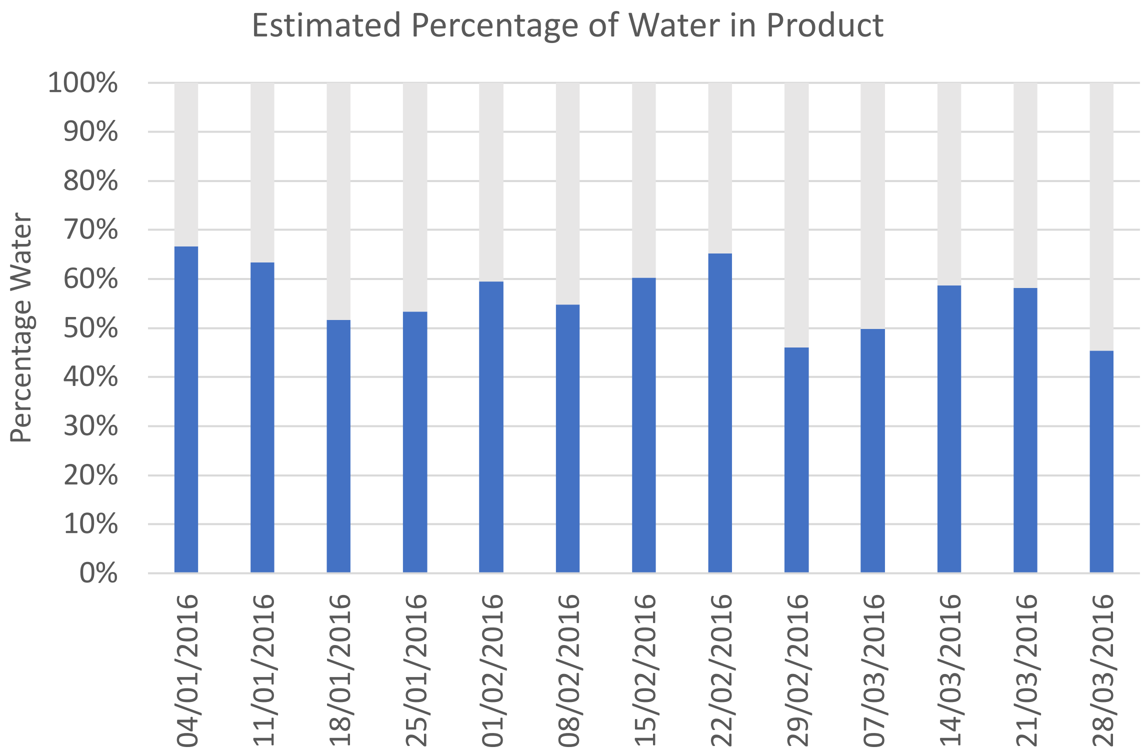


Figure 80: Estimated percentage of water in product produced in Darwen's emulsion plant.

Figure 80. illustrates that approximately 50% (mass/volume) of the product is virgin water (Mean: 56.40%, SD:6.90) this would correspond well with Crown Paints often cited assumption that there is "50% water within their emulsions". This value would expectedly vary depending on the products produced on the plant (due to changes in formulation); however, the values would support the assumption that the PLC system provides the total water input into the product and thus the VA Component (i.e. none of the water used for washings). This supports the accuracy of the PLC and thus VA data.

3.3.1.5 Effluent Plant log

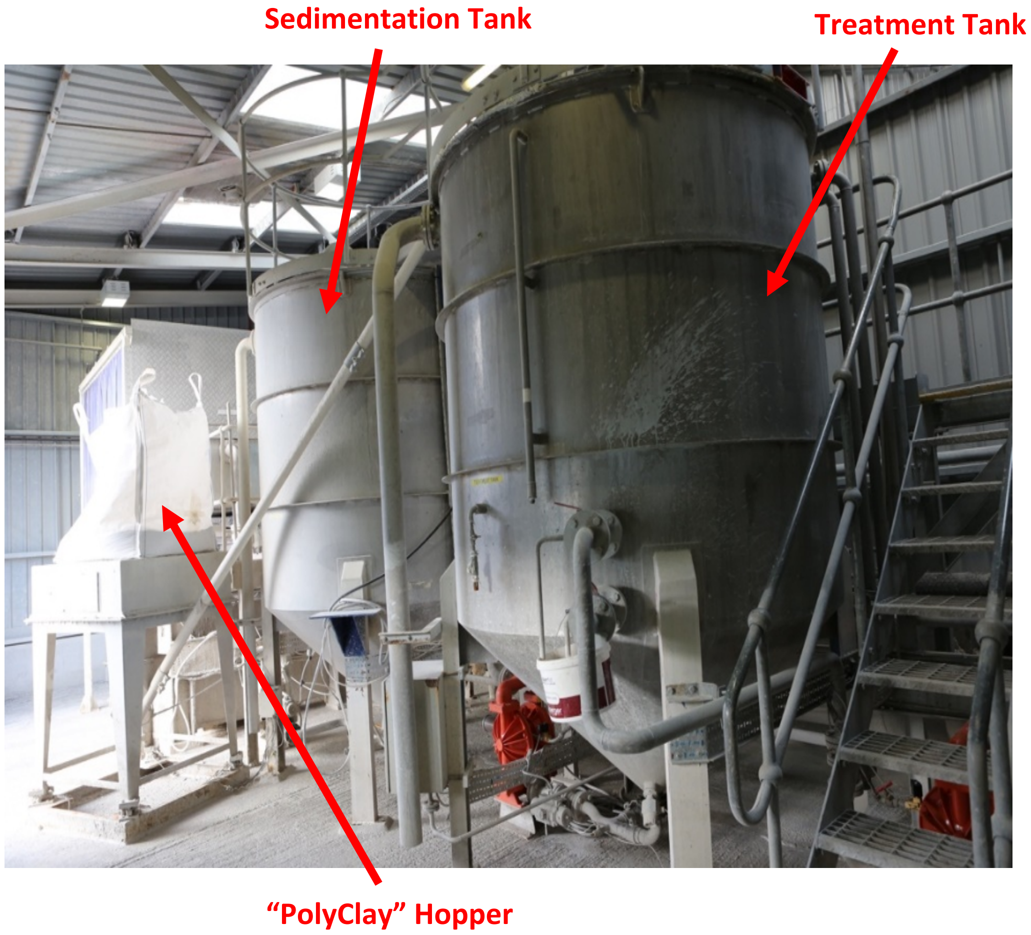


Figure 81. Crown Paints' Darwen Effluent Plant.

Before this study there had been no regular recording of the throughput of effluent within the effluent plant at Crown Paints Darwen site. Therefore, a system based on the Hull Plant's effluent logging method was implemented at the first opportunity. Each batch size is recorded along with the untreated effluent's initial pH and the final pH after the flocculent has been dosed.

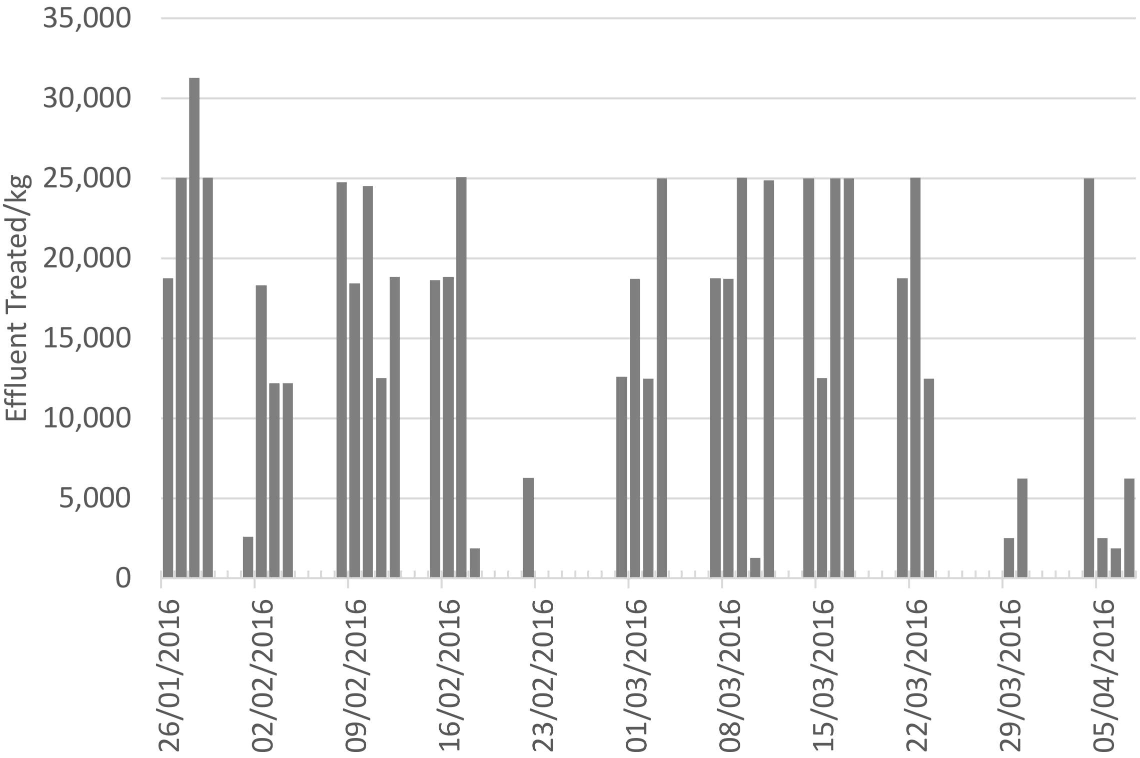


Figure 82: Daily log of treated Effluent at Darwen Effluent Plant.

The data provided by this log (Figure 82.) is of high value to this VSA study as it gives a clear indication of the volumes of effluent produced and treated by Crown Paints. The system was simple but relies on the Effluent plant operator to record each value which has resulted in a number of “gaps” in the data. Therefore, the total volumes provided cannot be seen to be highly accurate and the values should be viewed as more of a guide. Despite its shortcomings, these data are still valuable and provides a much better understanding of the stresses placed on the plant. In addition, during this study water meters were installed on the Effluent plant providing a much more accurate record specifically of the volume of effluent being treated at the Darwen plant.

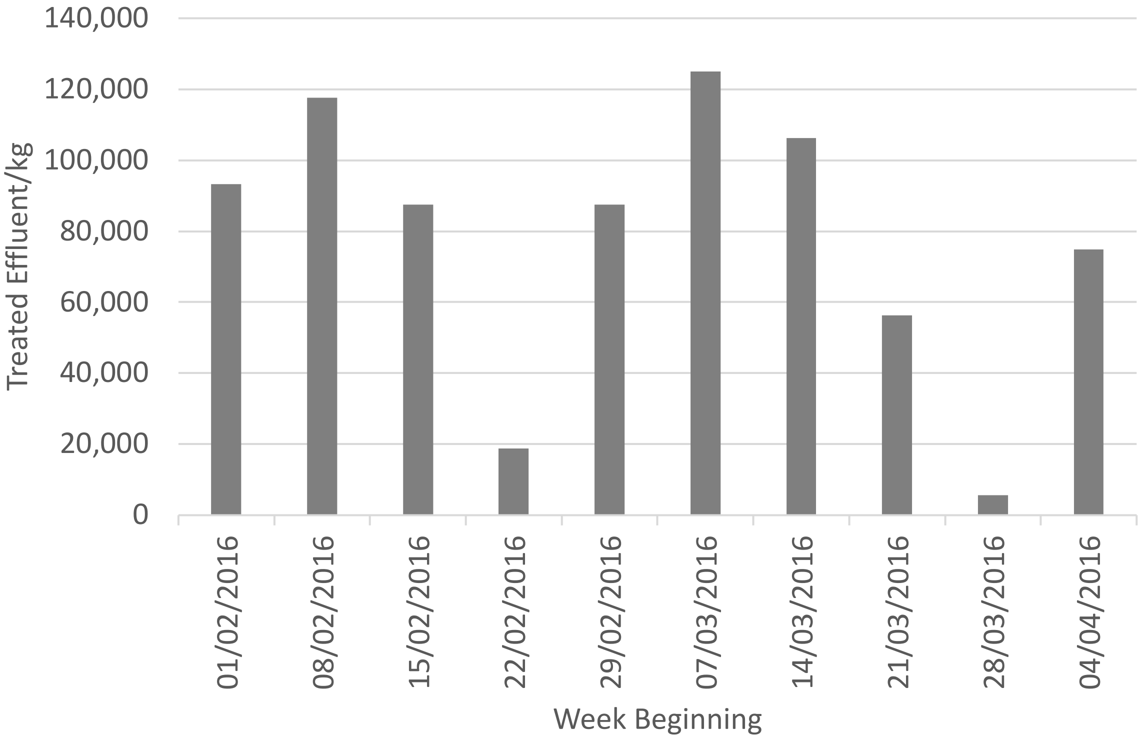


Figure 83: Weekly log of Treated Effluent at Darwen Effluent Plant.

The daily-recorded Treated Effluent volumes were converted into weekly volumes to aid in comparative analysis with other available data (Figure 83.). The week beginning 22/02/16 clearly has a much lower treated effluent volume which is assumed to be anomalous (most likely due to human factors and the omission of the recording), the weeks beginning 21/03/16 and 28/03/16 are also noticeably lower than expected. This is potentially due to the Easter weekend and thus a shortened production schedule during these weeks.

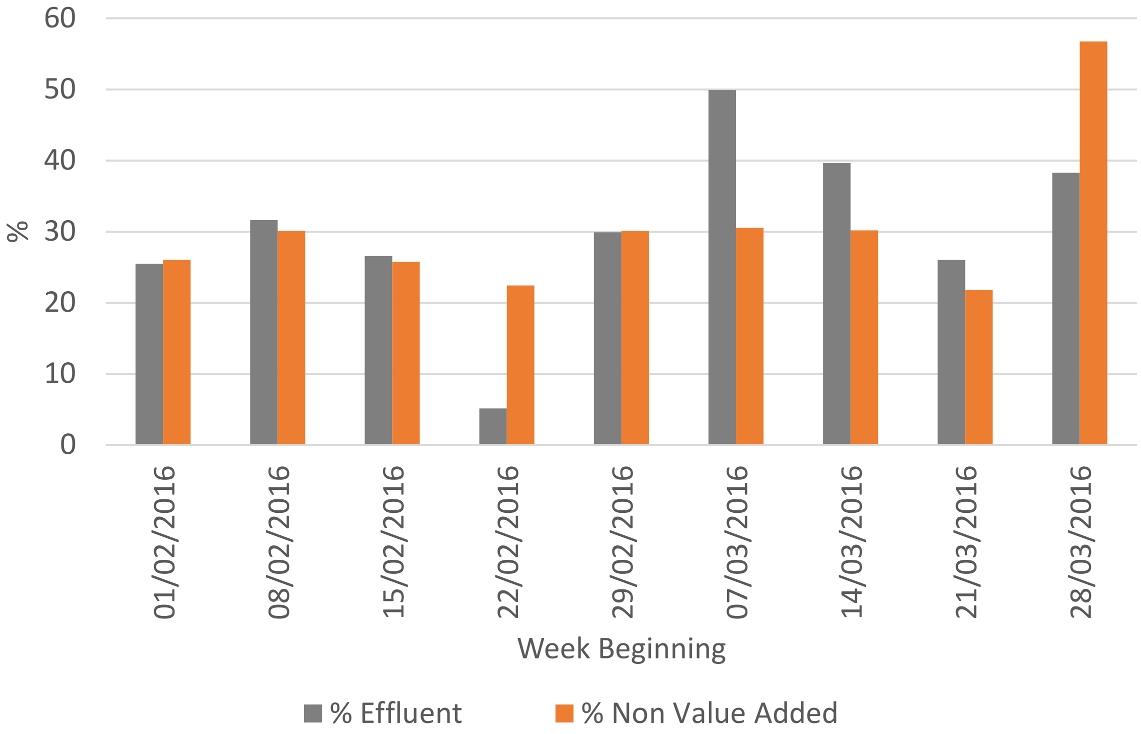


Figure 84: Comparison of Non Value Added component of water and Treated Effluent at the Darwen Plant.

Figure 84. compares the calculated NVA component (wastage) of the Darwen Emulsion Plant's process with the recorded treated effluent for the Effluent Plant. The expected values should be approximately the same based on the assumptions that all the treated effluent originates from the Emulsion Plant and the effluent concentration is approximately 100% water. The only additional source of effluent in addition to the Emulsion Plant is a small volume of rainwater collected around the Effluent Plant area (which was deemed negligible). The concentration of effluent for the Darwen Site tends to be approximately 98 wt% volatile material (primarily water). However due to the accuracy of the meters available a 2% variation is minimal. The values for the NVA and the volume of treated effluent are relatively similar suggesting an accuracy in the method of calculation of the NVA component, of note is the week beginning 22/02/2016 where the NVA is significantly higher than the treated effluent. This would support the previous assumption that the treatment data was incomplete for that week. In weeks where the total volume of effluent is much larger than the NVA (e.g. weeks beginning 07/3/2016 & 14/03/16) it would suggest that excess product from the batches was being washed into the effluent stream.

3.3.1.6 Filtercake

Filtercake (Figure 85.), the principal product of the waste treatment process is an inert clay-like substance, which is designed to be disposed of in a conventional (i.e. non-hazardous) landfill site.

Figure 85 Darwen filtercake.

Monitoring of filtercake production is difficult due to a lack of measuring equipment; a solution to this issue was devised using the skip weight measurements, which at Crown Paints Darwen site occur approximately monthly. Figure 86. illustrates the quantities of filtercake produced in 2015 and 2016 for comparison.

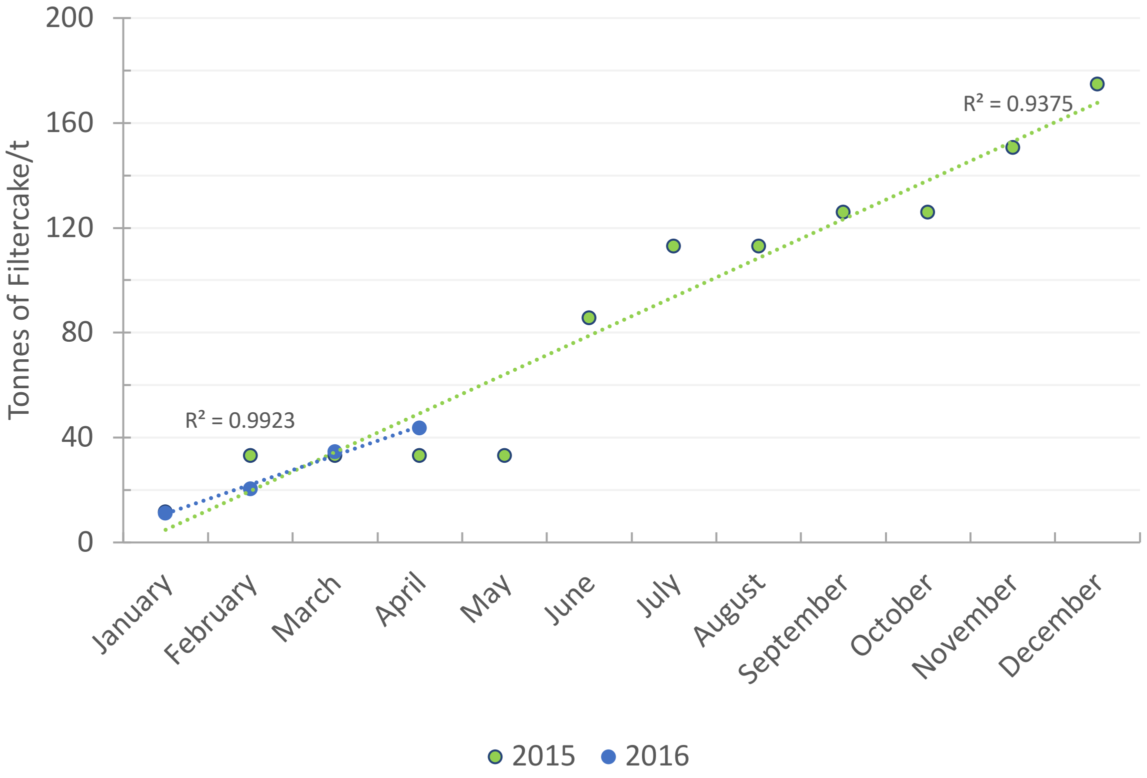


Figure 86: Comparison of Darwen Effluent Plant Filtercake production per year.

3.3.2 Conclusions from Value Stream Analysis (VSA)

The completed value stream map of the Darwen Emulsion Plant’s water usage (Figure 87.) illustrates the origin and average volumes of effluent arising for the first quarter of 2016 (for reference weekly data has been provided within Table 4.).

The production data suggests that approximately 28% of the Emulsion Plant’s influent water is “wasted” as wash water utilized for the washing of vessels and for line washings, which is then ultimately treated by the site’s effluent plant. As expected, observation of the emulsion plant’s processes would suggest that this wash water is the primary source of the plant’s effluent (Figure 84.). Despite being an essential element of the plant’s processes, any effective effluent reduction strategy needs to focus on minimizing this “wash water”.

Potential solutions include: using less water in vessel and line washings; reuse of any wash water within paint formulations; or potentially moving from a batch production system to a continuous or semi-continuous one.

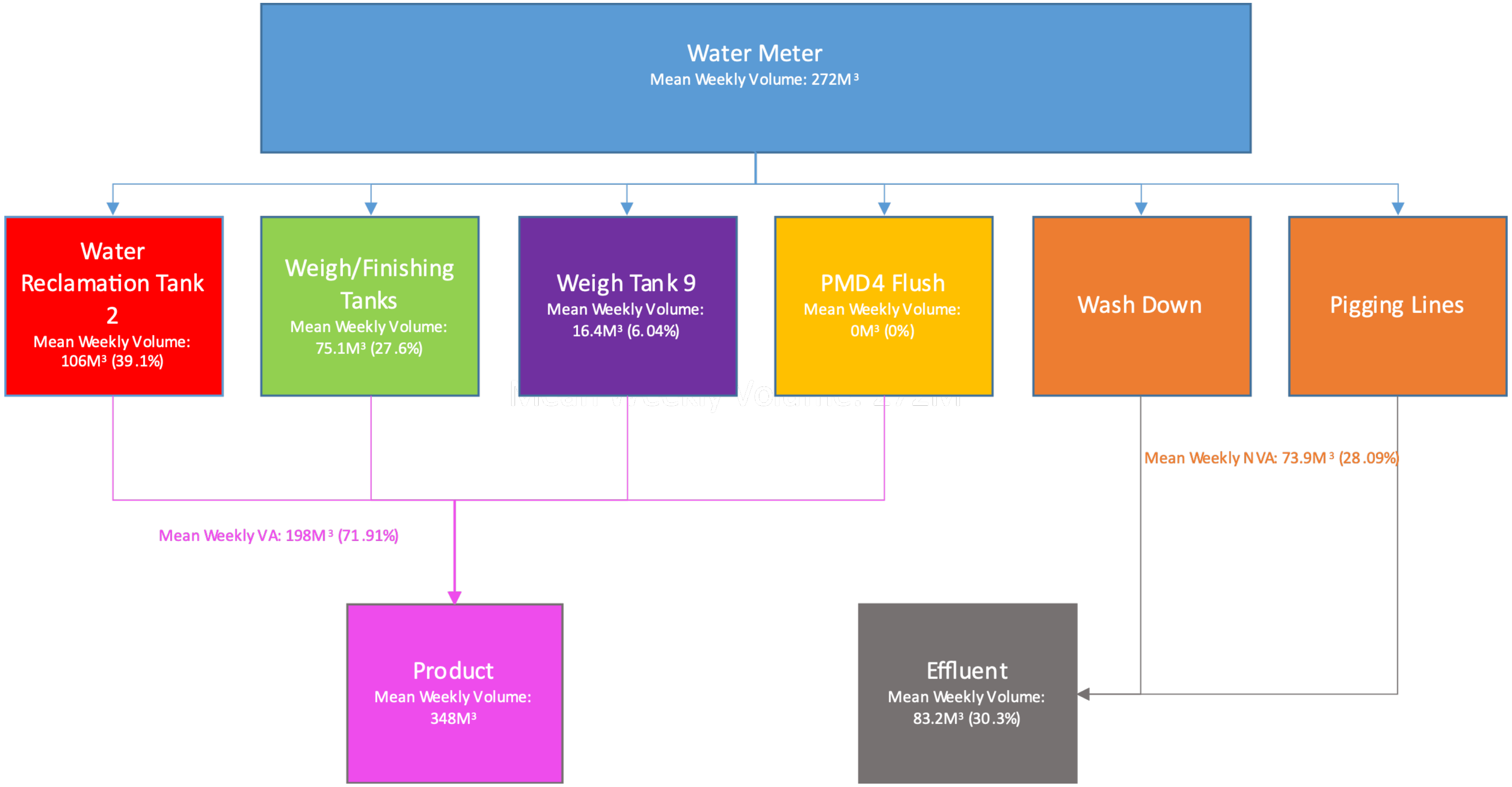


Figure 87. Value Stream Map of Darwen’s Emulsion Plant.

Table 4. Weekly data for the Darwen Emulsion Plant Value Stream Map.

	04/01/16	11/01/16	18/01/16	25/01/16	01/02/16	08/02/16	15/02/16	22/02/16	29/02/16	07/03/16	14/03/16	21/03/16	28/03/16
WATER RECLAIMATION TANK 2/kg	**7.76 x10^{4}**	**1.16 x10^{5}**	**70.4 x10^{4}**	**1.10 x10^{5}**	**1.37 x10^{5}**	**1.30 x10^{5}**	**1.30 x10^{5}**	**1.40 x10^{5}**	**1.18 x10^{5}**	**9.95 x10^{4}**	**1.05 x10^{5}**	**1.04 x10^{5}**	**3.40 x10^{4}**
MAINS WATER (WEIGH / FINISHING TANKS)/kg	**1.017 x10^{5}**	**8.75 x10^{4}**	**4.039 x10^{4}**	**6.25 x10^{4}**	**1.13 x10^{5}**	**1.13 x10^{5}**	**9.23 x10^{4}**	**1.29 x10^{5}**	**6.29 x10^{4}**	**5.00 x10^{4}**	**6.32 x10^{4}**	**3.82 x10^{4}**	**2.38 x10^{4}**
MAINS WATER (WEIGH TANK 9)/kg	**3830**	**12100**	**5330**	**15300**	**21900**	**17000**	**22400**	**14600**	**24100**	**24900**	**19200**	**27000**	**5600**
MAINS WATER (PMD4 FLUSH)/kg	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Total Value Added/kg	**1.83 x10^{5}**	**2.15x10^{5}**	**1.16 x10^{5}**	**1.98 x10^{5}**	**2.72 x10^{5}**	**2.60 x10^{5}**	**2.45 x10^{5}**	**2.84 x10^{5}**	**2.05 x10^{5}**	**1.74 x10^{5}**	**1.87 x10^{5}**	**1.69 x10^{5}**	**6.34 x10^{4}**
Influent Water/L	**2.12 x10^{5}**	**2.51 x10^{5}**	**2.30 x10^{5}**	**2.31 x10^{5}**	**3.67 x10^{5}**	**3.72 x10^{5}**	**3.30 x10^{5}**	**3.66 x10^{5}**	**2.93 x10^{5}**	**2.51 x10^{5}**	**2.68 x10^{5}**	**2.16 x10^{5}**	**1.47 x10^{5}**
Effluent Treated/L	**-**	**-**	**-**	**-**	**9.34 x10^{4}**	**1.18 x10^{5}**	**8.75 x10^{4}**	**1.88 x10^{4}**	**8.75 x10^{4}**	**1.25 x10^{5}**	**1.06 x10^{5}**	**5.63 x10^{4}**	**5.61 x10^{4}**
% Value Added	**86.5**	**85.7**	**50.6**	**85.5**	**74.0**	**69.9**	**74.2**	**77.6**	**70.0**	**69.5**	**69.9**	**78.2**	**43.2**
% Effluent	**-**	**-**	**-**	**-**	**25.4**	**31.6**	**26.5**	**5.15**	**29.9**	**49.9**	**39.6**	**26.0**	**38.3**
% Non Value Added	**13.5**	**14.3**	**49.4**	**14.5**	**25.0**	**30.1**	**25.8**	**22.4**	**30.0**	**30.5**	**30.1**	**21.8**	**56.8**
Paint Production/L	**2.75 x10^{5}**	**3.39 x10^{5}**	**2.25 x10^{5}**	**3.70 x10^{5}**	**4.57 x10^{5}**	**4.74 x10^{5}**	**4.06 x10^{5}**	**4.35 x10^{5}**	**4.46 x10^{5}**	**3.49 x10^{5}**	**3.19 x10^{5}**	**2.90 x10^{5}**	**1.40 x10^{5}**
% Water in Paint	**66.7**	**63.4**	**51.7**	**53.4**	**59.5**	**54.8**	**60.3**	**65.3**	**46.0**	**49.9**	**58.7**	**58.2**	**45.4**
% Non Water	**33.3**	**36.6**	**48.3**	**46.6**	**40.5**	**45.2**	**39.7**	**34.7**	**54.0**	**50.1**	**41.3**	**41.8**	**54.6**

3.4 The Hull Manufacturing site's effluent Value Stream Analysis (VSA)

3.4.1 The Hull site's water usage

Historic data of the influent water usage for Crown Paints' Hull site were readily available via the site's Yorkshire Water maintained "smart meter". Regular readings have been made consistently every 15 minutes since 2010 (producing over 210,000 individual readings). Problematically, the meter developed a fault on 10th October 2015 and wasn't re-operational until 12th April 2016, preventing data collection for the initial stage of this project (January 2016-April 2016). Figure 88. illustrates a summary of the meter readings.

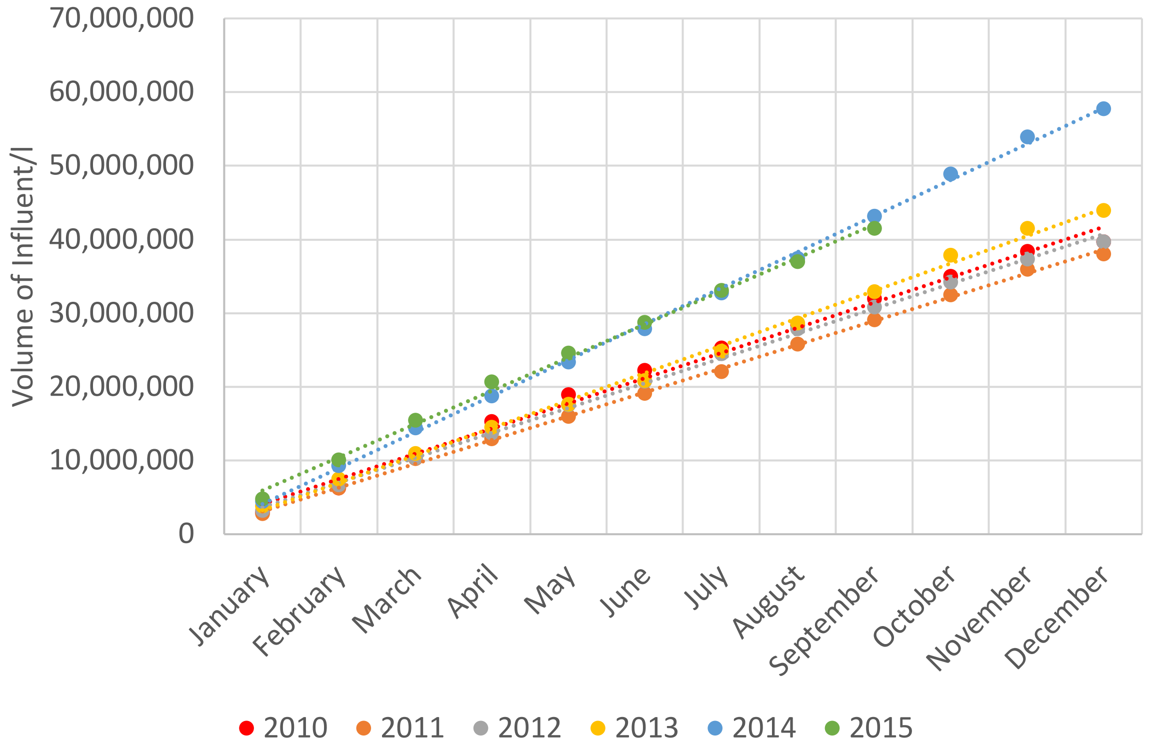


Figure 88: Cumulative Influent Water for Crown Paints' Hull manufacturing site.

Table 5: Summary of Trendlines for Figure 88.

Year	Equation	R^2
2010	y=3E+06x + 652487	0.9934
2011	Y=3E+06x -130142	0.99897
2012	y=3E+06x + 274316	0.99848
2013	y=4E+06x - 467760	0.99728
2014	y=5E+06x - 790878	0.99883
2015	y=5E+06x + 1E06	0.99669

Where:

x, is a date serial number from 01/01/1990 (i.e. x = 2, 02/01/1990)

Figure 88. clearly illustrates the similarity in the volume of influent water required for 2010-2013, whilst a significantly greater volume of water has been required since 2014. This would be expected due to the implementation of the "high speed filling line" at the Hull site and a move towards greater volumes of water-based paint during early 2014.

3.4.2 Paint Production

Due to the failure of the "smart meter" in 2015 it was decided to compare production data from 2013 and 2014 as representative years. This was because of the quantity of corresponding data that was available.

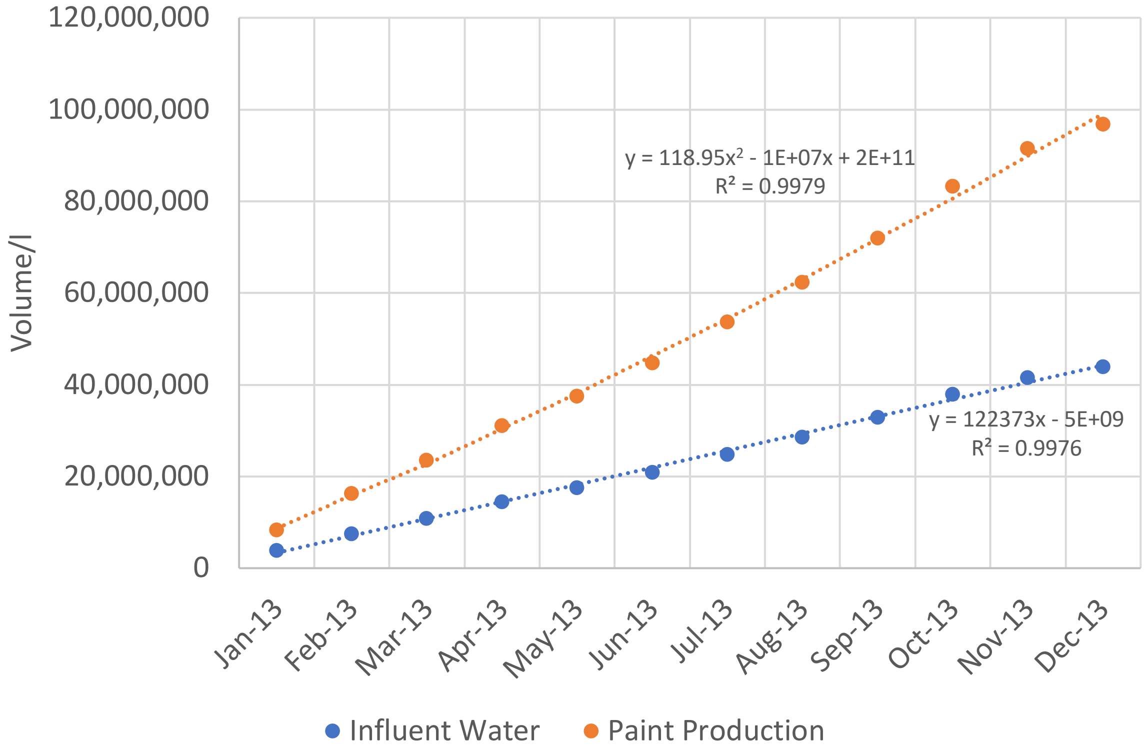


Figure 89: Cumulative volume of Influent water and Paint Production, 2013.

Figure 89. implies a much lower volume of water entering the plant compared to the volume of Paint produced in 2013, it would suggest that all the influent water to the site contributes to approximately 46% of the volume of Paint produced; this value would be expected to be significantly greater than 50% (assuming a 50% water concentration within the product) due to additional influent water requirements such as washings, excess product, and domestic uses. This unexpectantly low value is curious because the production data extracted specifically isolates solvent based and Emulsion paint productions.

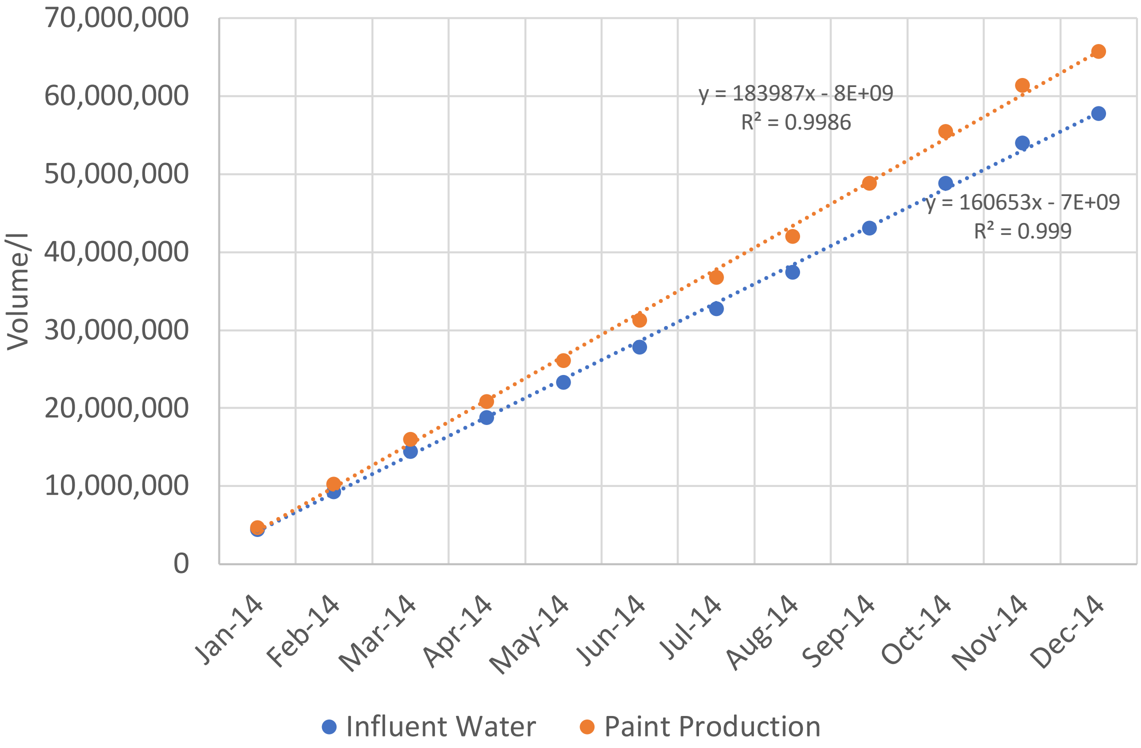


Figure 90: Cumulative volume of Influent water and Paint Production, 2014.

Figure 90. however, shows a much higher relative value of Influent Water as expected, where approximately 88% of the Paint production volume consists of influent water. Assuming 50% of this produced emulsion paint's composition being water it would suggest approximately 43% of all influent is being used for alternative uses. These uses are defined as of "no added value" (NVA) to the paint production process.

3.4.3 Value Added component

Unlike Crown Paints' Darwen Site, the lack of a PLC within the Hull manufacturing site required an alternative method to identify the inputs of "virgin" water into the Paint formulations to be necessary. The suggested method was to use the data available on Crown Paints' SAP system which contains a record of material usage inputted from individual production batch cards.

Similar to the previous Value Stream Analysis for the Crown Paints Darwen manufacturing site, this inputted water used within formulations was defined as the Value Added component of the process (VA). Thus using the assumption that "any input must either add value to the process or not" we can determine the "wastage" of the process using Equation 24.

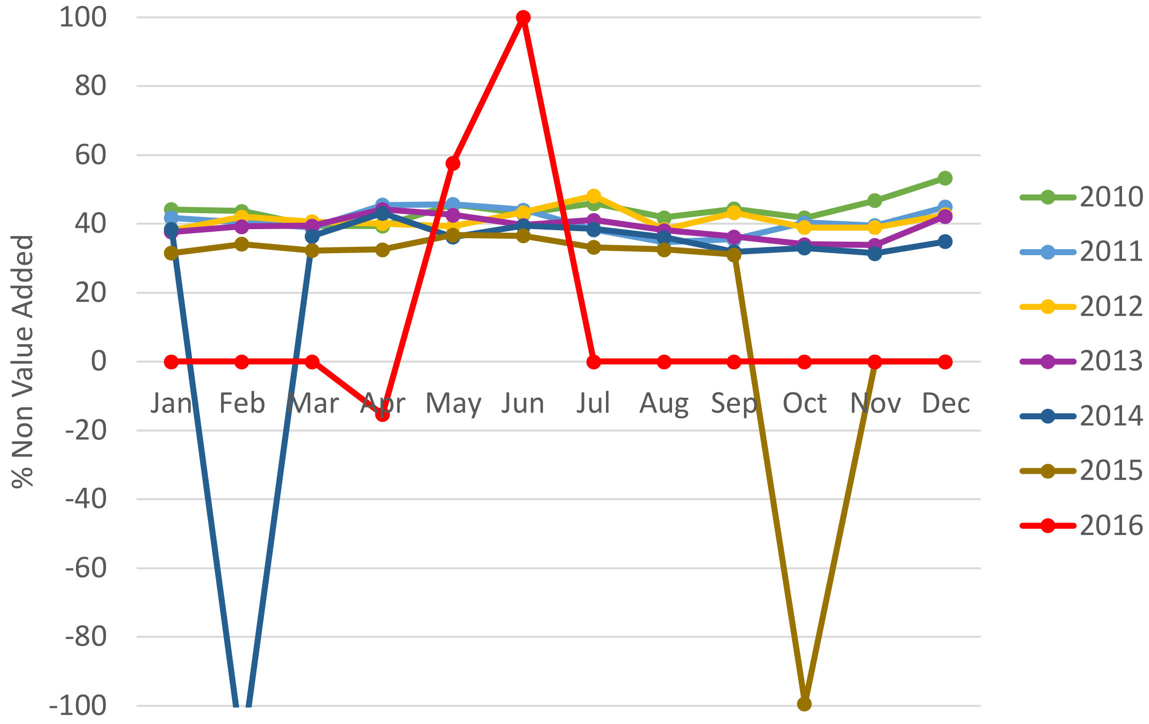


Figure 91: Comparison of the Non Value Added component for Crown Paints Hull Manufacturing site.

Figure 91. shows the calculated NVA for the Hull manufacturing site. The substantial quantities of data allow the easy explanation of anomalies clearly visible within the graph; the failure of the water meter in October 2015 caused this distinctive drop in the NVA component and insufficient SAP data (due to the slight delay in inputting batch cards) produced the spike in June 2016. The significant decrease in NVA for February 2014 (%NVA+-113.74) is particularly unexpected, suggesting a higher volume of water being used within the product than the volume of influent water to the site (this is obviously impossible unless there is an additional water source), the error can be sourced by analysing the daily data of this month (Table 6.) which would suggest a data input error on the SAP system for 10/02/2014 & 11/02/2014 (highlighted). This demonstrates the ability to identify errors in the data due to the robustness of this methodology.

Table 6: Comparison of SAP and Influent water for February 2014.

Date	SAP Data/ kg	Influent water/l	Date	SAP Data/ kg	Influent water/ l
01/02/2014	55,974	128,320	24/02/2014	149,137	220,020
02/02/2014	111,591	108,410	25/02/2014	126,832	214,080
03/02/2014	159,401	227,650	26/02/2014	151,613	207,770
04/02/2014	111,847	180,100	27/02/2014	103,354	181,190
05/02/2014	132,045	216,880	28/02/2014	70,870	112,370
06/02/2014	140,369	197,360			
07/02/2014	66,897	108,580			
08/02/2014	81,490	133,950			
09/02/2014	114,617	123,270			
10/02/2014	3,867,948	219,830			
11/02/2014	3,590,459	244,890			
12/02/2014	126,862	215,360			
13/02/2014	107,127	172,670			
14/02/2014	77,875	110,570			
15/02/2014	131,949	151,550			
16/02/2014	82,801	137,390			
17/02/2014	144,128	222,610			
18/02/2014	131,038	212,120			
19/02/2014	119,737	186,090			
20/02/2014	140,420	213,680			
21/02/2014	36,379	110,180			
22/02/2014	121,100	151,380			
23/02/2014	97,333	134,520			

Through isolating calculated NVA values for January 2010-September 2015 and excluding February 2014 a more distinct trend is visible (Figure 92.).

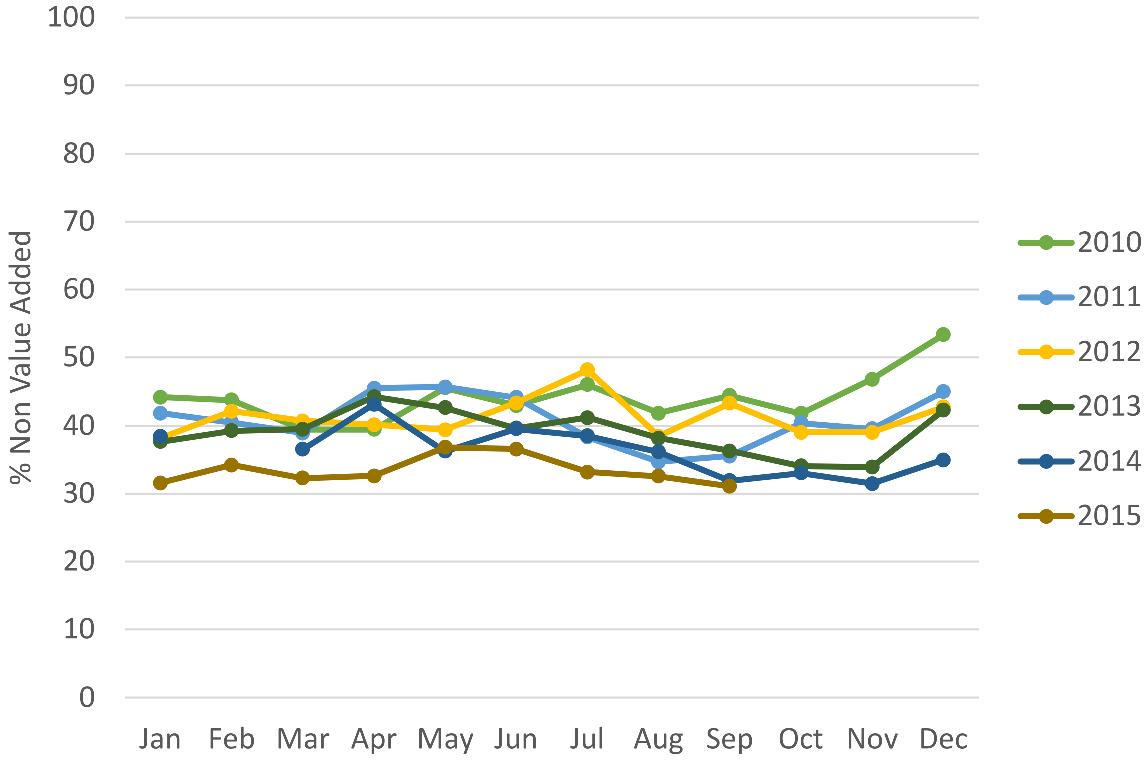


Figure 92: Comparison of Non Value Added for the Hull Manufacturing site, January 2010 - September 2015 (excluding February 2014).

Figure 92. provides a clearer illustration that despite the changes in production volumes within the plant, the %NVA and thus “wastage of water” has remained relatively similar since 2010.

Table 7. illustrates the mean values for NVA for each year for the Hull site with the addition of the mean of the available data for the Darwen site (Q1 2016). For comparison though, the %NVA for the Darwen site appears more variable than that of the Hull site. It also appears that the wastage of water within the Darwen site is lower than that for the Hull site. Additionally, the sole record of %NVA for the Hull site for 2016 (May: 57.69%) is much higher than that of any reading throughout 2010 - 2015, although this was omitted from the graph and represents only a single reading; it is suggested that potentially the %NVA may have increased during the period with which the “smartmeter” was non-operational.

Table 7: Average Value Added Components for the Hull site, 2010-2015.

Year	Mean Value Added/%	Mean Non Value Added/%	RSD
2010	55.89	44.11	3.59
2011	59.18	40.82	3.56
2012	58.81	41.19	2.77
2013	60.95	39.05	3.12
2014	63.67	36.33	3.33
2015	66.59	33.41	1.93
Darwen Q1 2016	71.91	28.09	12.8

3.4.4 Estimation of percentage of water within Paint Product

The percentage of water contained within the paint can then be estimated by comparing the water input data with the production volume data:

At Crown Paints Hull site:

$$\boldsymbol{Percentage\ of\ Water\ in\ Paint} \sim \frac{\boldsymbol{Volume\ of\ Water\ used\ in\ Production}}{\boldsymbol{Production\ Volume\ of\ Product}} \qquad \textbf{25}$$

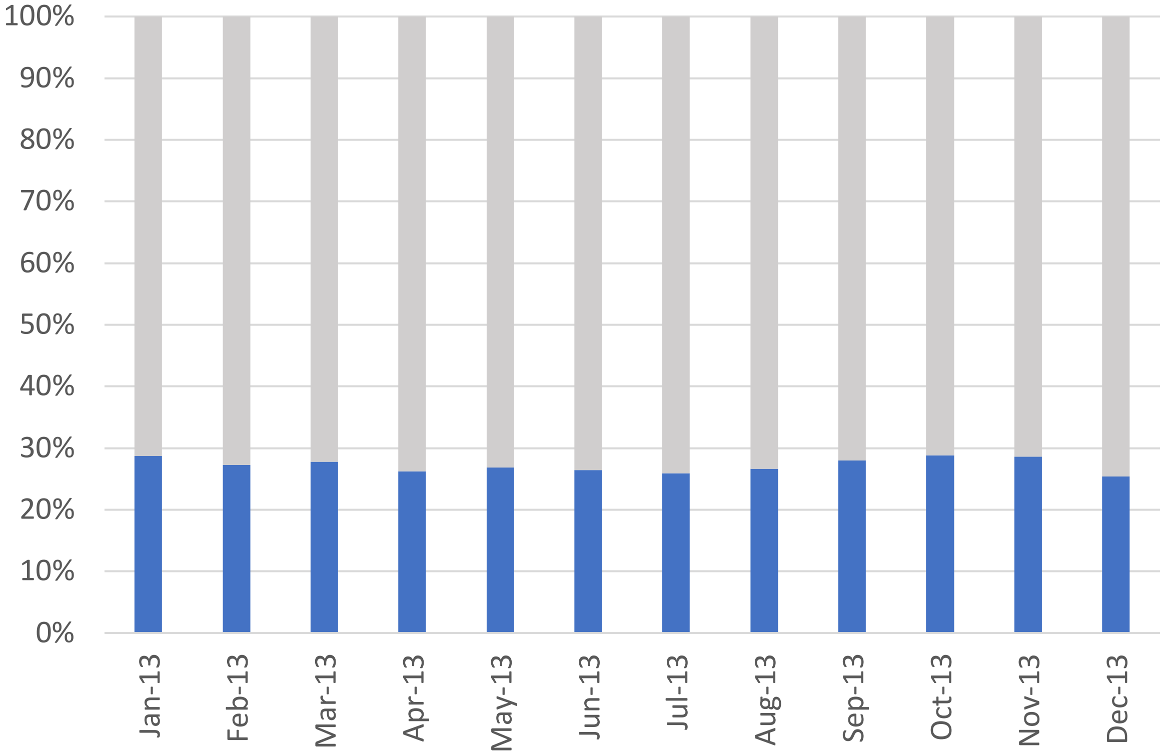


Figure 93: Estimated percentage of water in Paint Product produced in 2013 at Crown Paints' Hull Site.

From the data available, the percentage of water within the paint formulations for 2013 remains relatively standardized (Mean: 27.22, SD: 1.15), this however would contradict the basic assumption by Crown Paints' employees that "approximately 50% of their paint formulations consist of water". This would be consistent with the data illustrated within Figure 89. however, suggesting a much lower percentage of water within the paint formulations produced in 2013. A potential explanation for this unexpected result (as previously mentioned) would be the addition of solvent-based paint production figures within the "production data" however, the records show that solvent-based paint volumes are specifically excluded and therefore it is safe to assume that this isn't the case. Another issue is the human factor of manually inputting volumes from a batch card, which is prone to input errors. Assuming that the data is accurate, it would be expected that the quantity of water within the product has increased after 2013; potentially due to a dramatic shift in product types produced at the Hull manufacturing site.

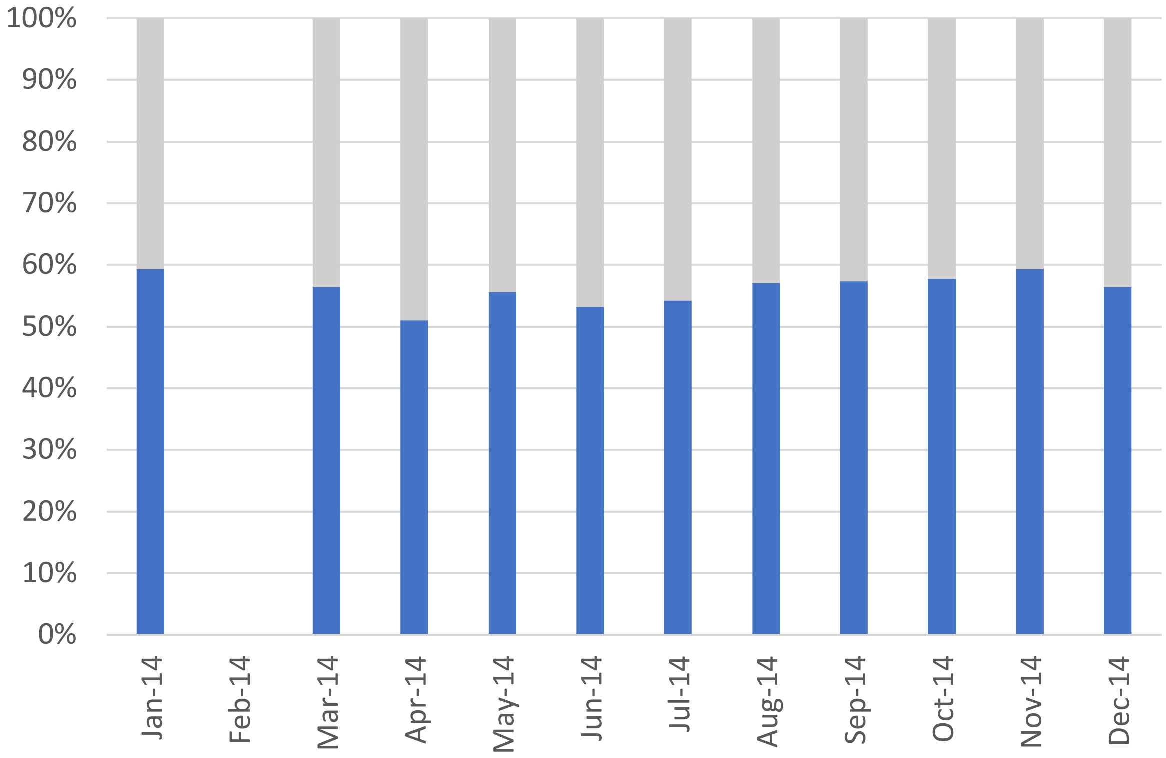


Figure 94: Estimated percentage of water in Paint Product produced in 2014 at Crown Paints' Hull Site.

Figure 94. presents results more consistent (compared with Figure 93.) with the assumption that an emulsion paint's formulation contains approximately 50% water (Mean: 56.14, SD: 2.54) suggesting that the proportion of water within the formulations increased post 2013.

3.4.5 Volumes of Raw "Liquid" Effluent treated

The volumes of the liquid effluent requiring treatment have been collected and recorded by the effluent plant's operators and provide a clear record of the effluent plant's historic activity.

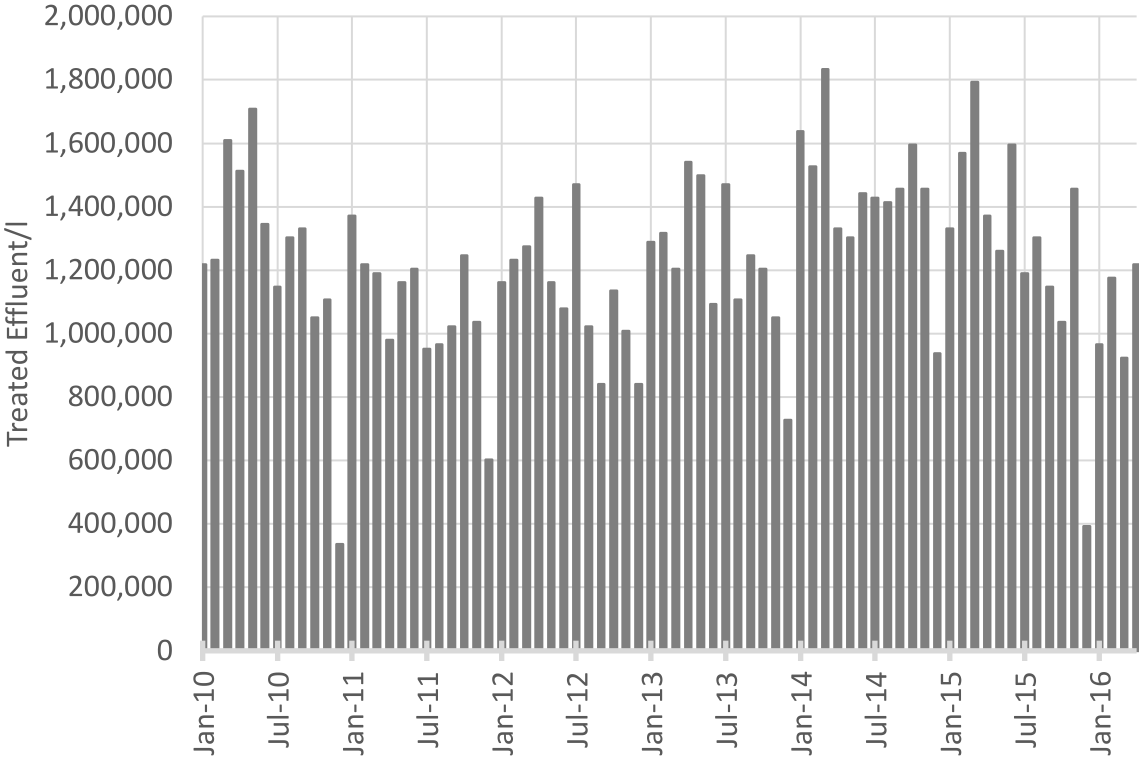


Figure 95: Monthly Treated Effluent volumes at Crown Paints' Hull Site, Jan 2010 - Apr 2016.

Table 8: Summery table of the monthly Treated Effluent volumes at Crown Paints' Hull Site, Jan 2010 – Apr 2016.

	Treated Effluent volume/ l						
	2010	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
Jan	1,218,000	1,372,000	1,162,000	1,288,000	1,638,000	1,330,000	966,000
Feb	1,232,000	1,218,000	1,232,000	1,316,000	1,526,000	1,568,000	1,176,000
Mar	1,610,000	1,190,000	1,274,000	1,204,000	1,834,000	1,792,000	924,000
Apr	1,512,000	980,000	1,428,000	1,540,000	1,330,000	1,372,000	1,218,000
May	1,708,000	1,162,000	1,162,000	1,498,000	1,302,000	1,260,000	
Jun	1,344,000	1,204,000	1,078,000	1,092,000	1,442,000	1,596,000	
Jul	1,148,000	952,000	1,470,000	1,470,000	1,428,000	1,190,000	
Aug	1,302,000	966,000	1,022,000	1,106,000	1,414,000	1,302,000	
Sep	1,330,000	1,022,000	840,000	1,246,000	1,456,000	1,148,000	
Oct	1,050,000	1,246,000	1,134,000	1,204,000	1,596,000	1,036,000	
Nov	1,106,000	1,036,000	1,008,000	1,050,000	1,456,000	1,456,000	
Dec	336,000	602,000	840,000	728,000	938,000	392,000	
Total	14,896,000	12,950,000	13,650,000	14,742,000	17,360,000	15,442,000	4,284,000
Mean	1,241,333	1,079,167	1,137,500	1,228,500	1,446,667	1,286,833	1,071,000
SD	348,103	199,823	198,720	224,962	215,348	351,725	147,499

Because of the variability of demand placed on both the emulsion plant, and the effluent plant the proportion of influent water which inevitably gets treated by the effluent plant was calculated (Figure 96.). shows that approximately 28 - 45% of the total water entering the plant requires effluent treatment. The anomalous spike in October 2015 is due to the failure of the "smartmeter" during this period and does not represent a huge increase in effluent production.

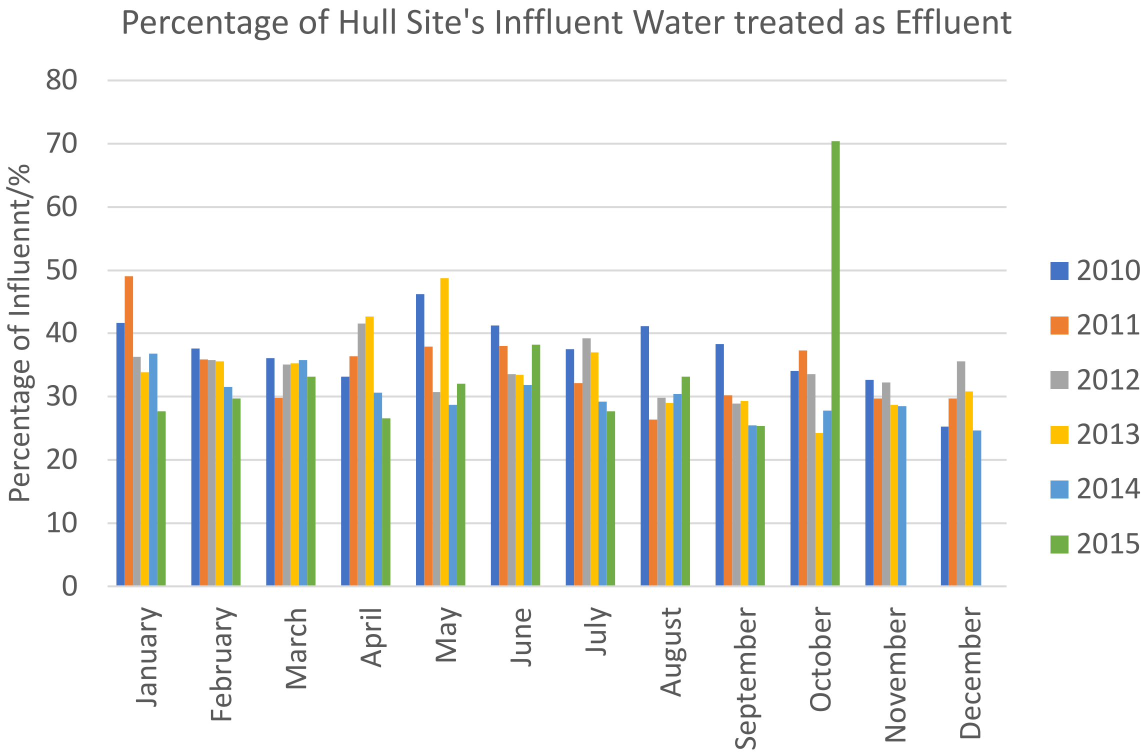


Figure 96: Percentage of Crown Paints' influent water treated as effluent.

Ideally, the percentage value of Non Value Added (NVA) water and treated effluent (of the total influent water) should be equal due to the assumption that all water not used within the product should be treated via the effluent plant. Using NVA component data from Table 5. and data from Figure 96. the volume of treated effluent and NVA water may be compared. The data is summarized within Figure 97. however, Table 9. provides a more comprehensive visualization of the available data.

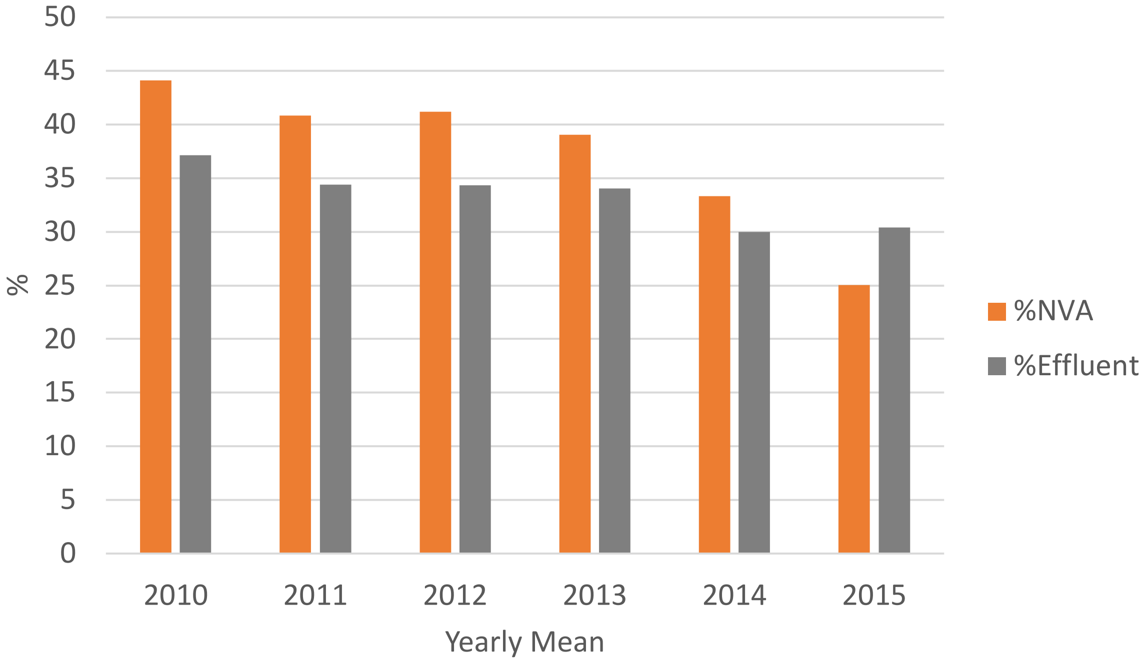


Figure 97: Comparison of Non Value Added Water and volume of Treated Effluent for Crown Paints Hull production site.

In Figure 97. the NVA usually appears higher than the effluent which would suggest a potential loss of excess water before the effluent plant. A potential explanation would be that some of the NVA component may end up in the product, however the quantities appear too large for this. The most probable reasons are errors regarding the accuracy of either the record of the volumes of effluent or potentially the manual SAP inputs from the route cards (likely due to human factors).

The variation in 2015 is easily explained by the addition of the high-speed filling line (in mid 2014) which additionally diverted a large volume of excess product directly to the effluent plant that has since been recaptured as a result of the previous Nimtech project (September 2014 - September 2015); 2016 therefore, should continue the trend of a higher % NVA based on this method.

Table 9: Summary table of mean values of Non Value Added water and effluent for Crown Paints' Hull production site.

Year	Non Value Added		Effluent	
	% Mean	RSD	% Mean	RSD
2010	44.11	3.75	37.13	5.40
2011	40.82	3.72	34.37	6.08
2012	41.19	2.89	34.35	3.72
2013	39.05	3.26	34.06	6.65
2014	33.30	11.00	29.98	3.78
2015	25.06	15.21	30.42	4.07

3.4.6 Coagulant and Flocculent usage

Similar to the Darwen Effluent Plant (but on a larger scale) the Hull Effluent Plant operates on a 2-step batch effluent treatment process utilizing aluminium sulphate (colloquially known as “acid” by the operatives presumably based on its effect on the effluent’s pH) as the coagulant and a Bentonite clay and unspecified polymer as the flocculent (“PolyClay”). Quantities of coagulant and flocculent used are recorded in a similar manner to the effluent volumes and records of historic data are extensive (providing detailed information for every batch treated since January 2011).

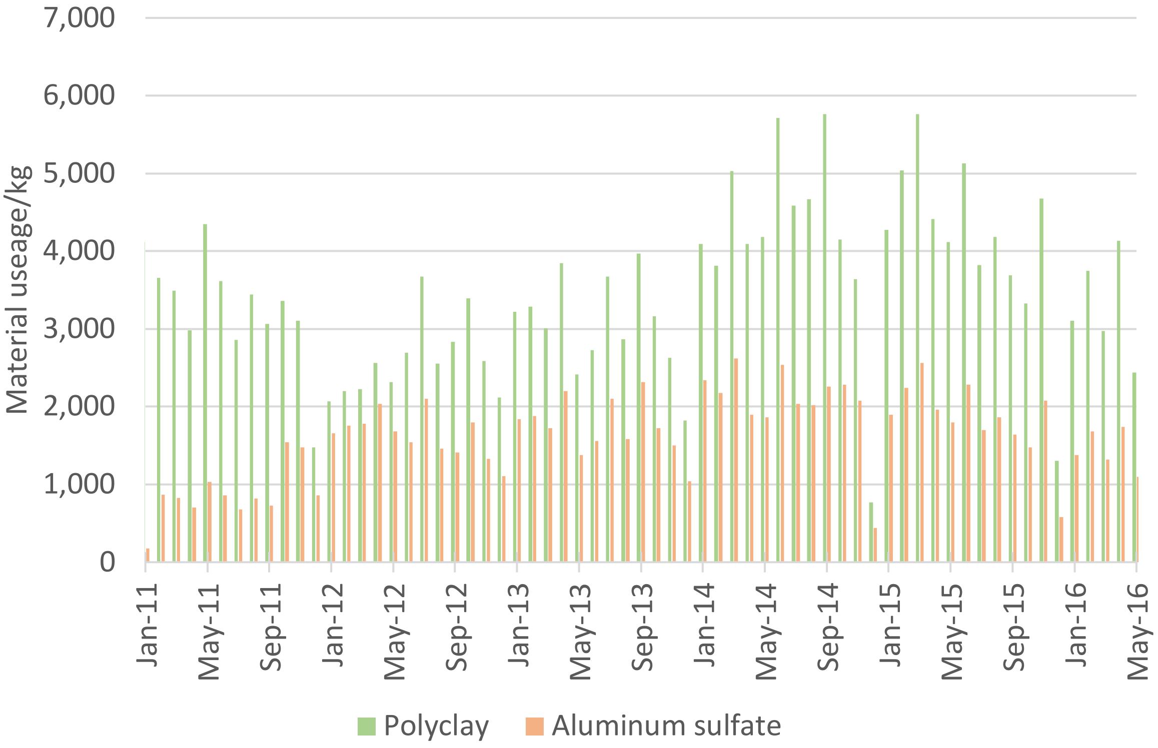


Figure 98: Flocculant and Coagulant useage for Crown Paints' Hull production site.

3.4.6.1 Average Polyclay and aluminium sulphate dosages

Due to the heavy variation of effluent volumes (Figure 95.), the quantities of coagulant and flocculent required (Figure 98.) will vary heavily dependent on this demand. The quantities of these materials required to treat a volume of effluent is therefore seen as a more useful measure. It also provides an indication of the composition of the effluent (based on the reasonable assumption that the effluents with higher concentrations of "solids" require more coagulant and flocculent dosages).

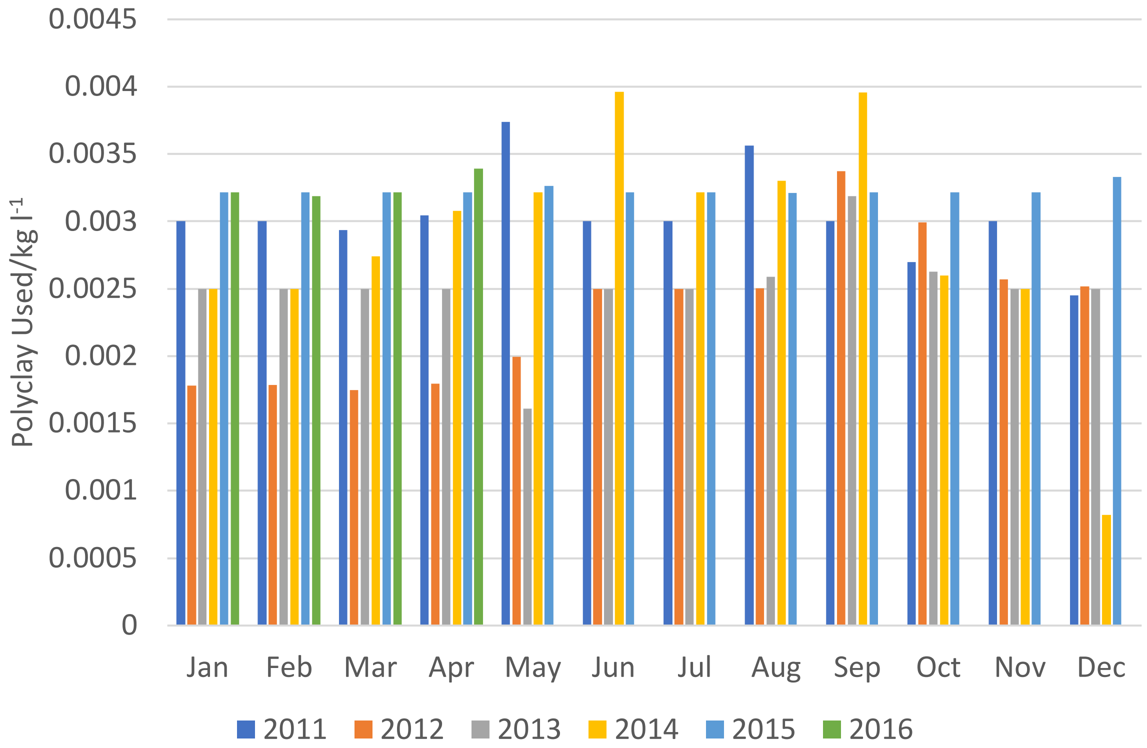


Figure 99: Average quantity of "PolyClay" required to treat 1 litre of effluent.

The Flocculent (“PolyClay”) usage within the Hull Effluent Plant is reasonably variable batch by batch with relatively similar dosages month-on-month reflecting similar practices and products in the short term, seasonally more “PolyClay” appears to be required in “Summer months” (approximately May-September) every year (except 2013).

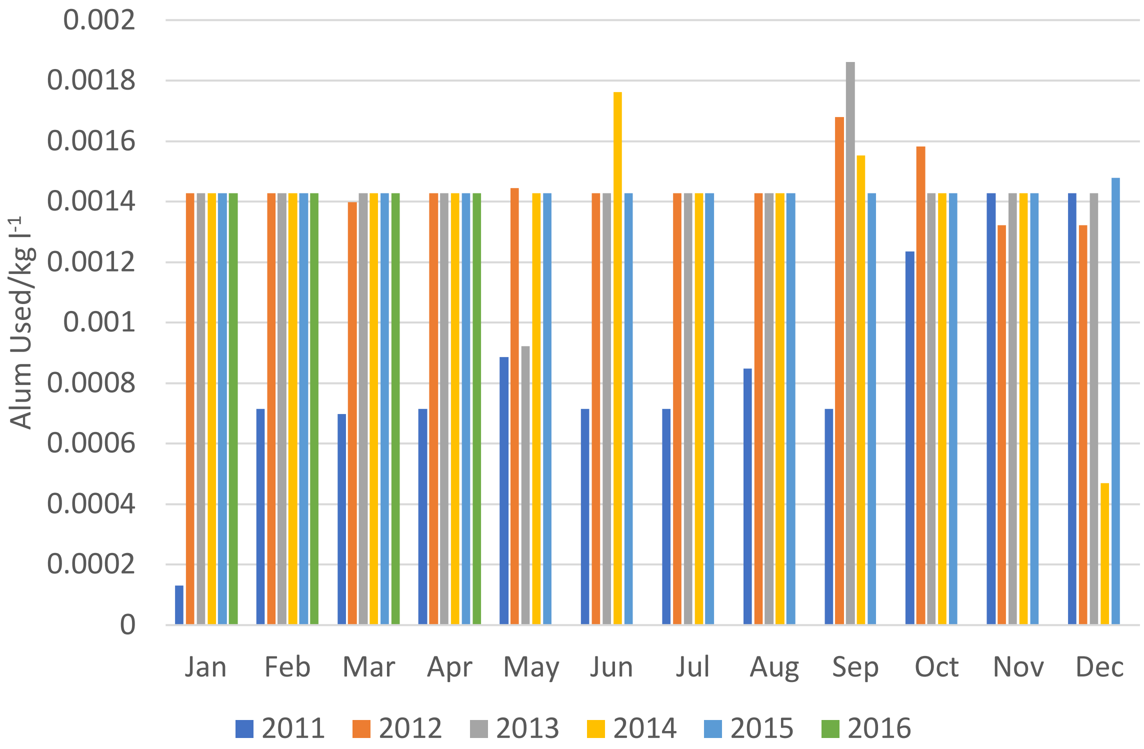


Figure 100: Average quantity of aluminium sulphate required to treat 1 litre of effluent.

Figure 100. illustrates a more standardized dosage of aluminium sulphate than that of "PolyClay" with a mode value of approximately 0.00143 kg l^{-1} of aluminium sulphate, which would contradict with the Effluent Plant operatives that "acid (coagulant) dosage was controlled by the pH of the effluent". From Figure 100. it is suggested that until November 2011 the coagulant dosage was pH determined however post 2011 the dosage became much more standardized and is visible in Figure 101.

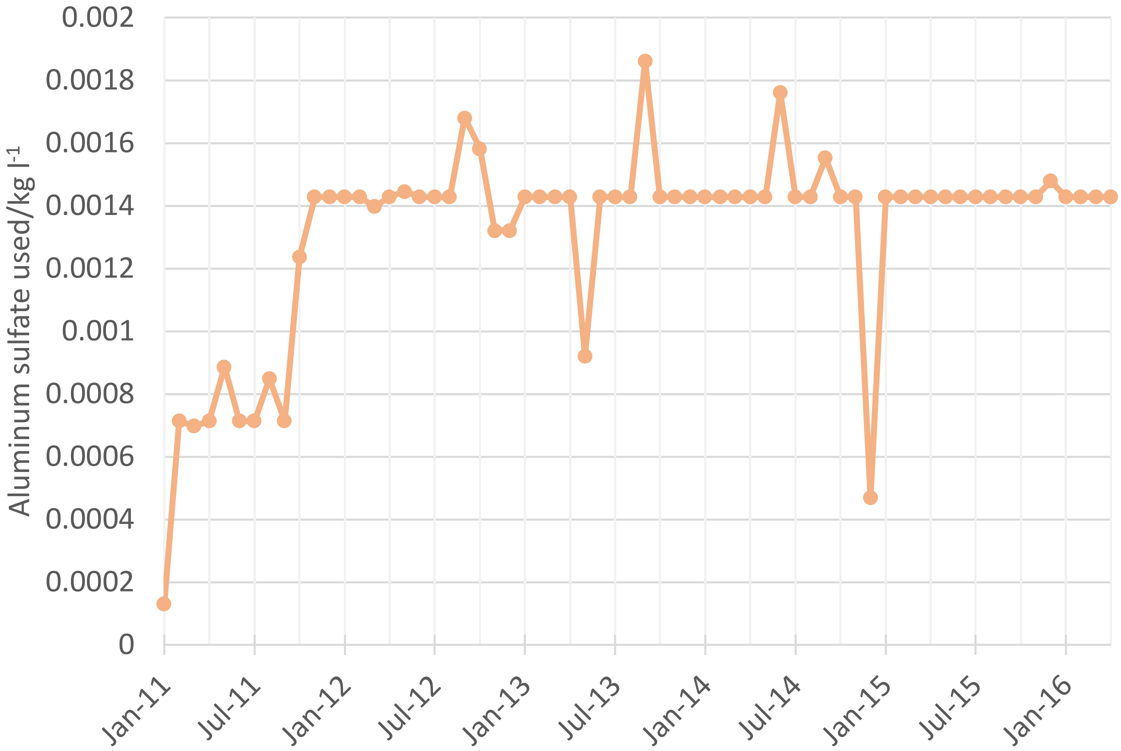


Figure 101: Variation in average aluminium sulphate dosage (kg) required to treat 1 litre of effluent.

3.4.6.2 Cost of coagulant and flocculent

The cost of the coagulant and flocculent is easily calculated using the assumption that 1,000 kg of “PolyClay” cost £1,245 and an IBC (assumed to be 1,000 kg within the figures) of aluminium sulphate costs £231.35; both as of 2016 for easier comparison.

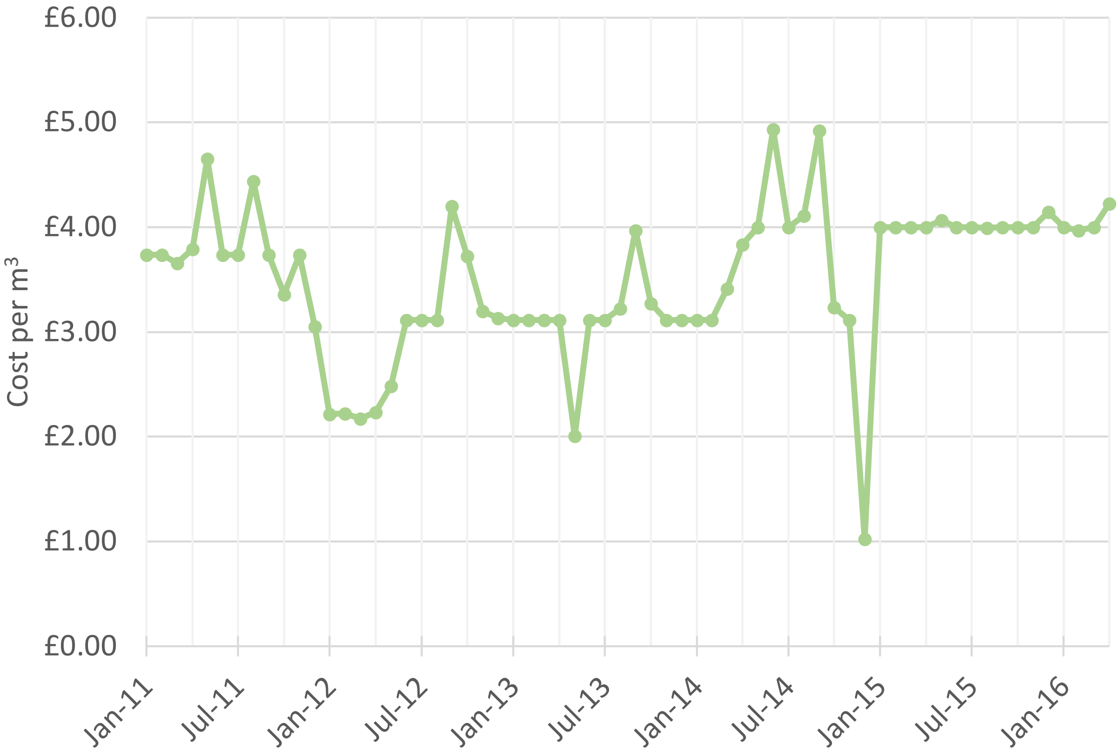


Figure 102: Average “PolyClay” cost per m^3 of effluent

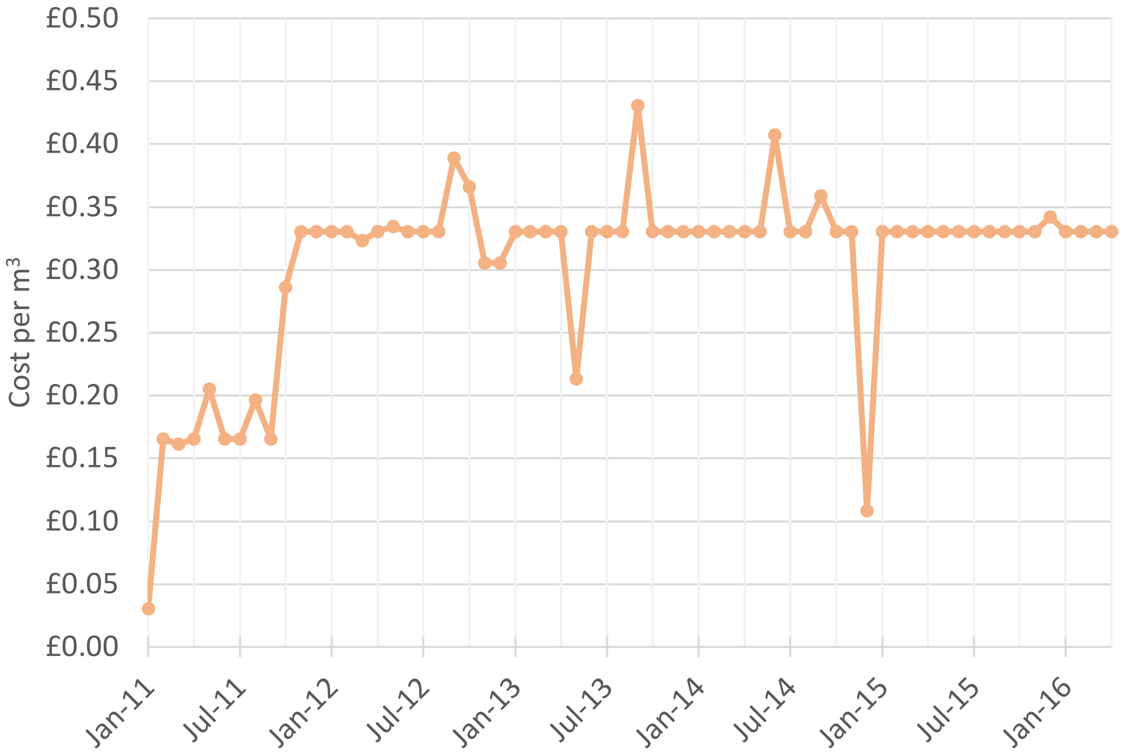


Figure 103: Average aluminium sulphate cost per m^3 of effluent

Figure 102. and Figure 103. provide an estimate of the cost of material required to treat a cubic metre of effluent (equivalent to an IBC; a standardized volume within the waste/chemical industry). The cost of the raw materials required for the treatment of the effluent is relatively low. However, due to the large volumes of effluent the total cost is not negligible (Figure 104 and Figure 105.), it is also important to note that this figure is based on an average composition of effluent (which in reality is approximately >97% water) and not a reflection that the effluent plant can treat all material as cheaply.

The total yearly material costs for “PolyClay” and aluminium sulphate are provided in Figure 104. and Figure 105. respectively.

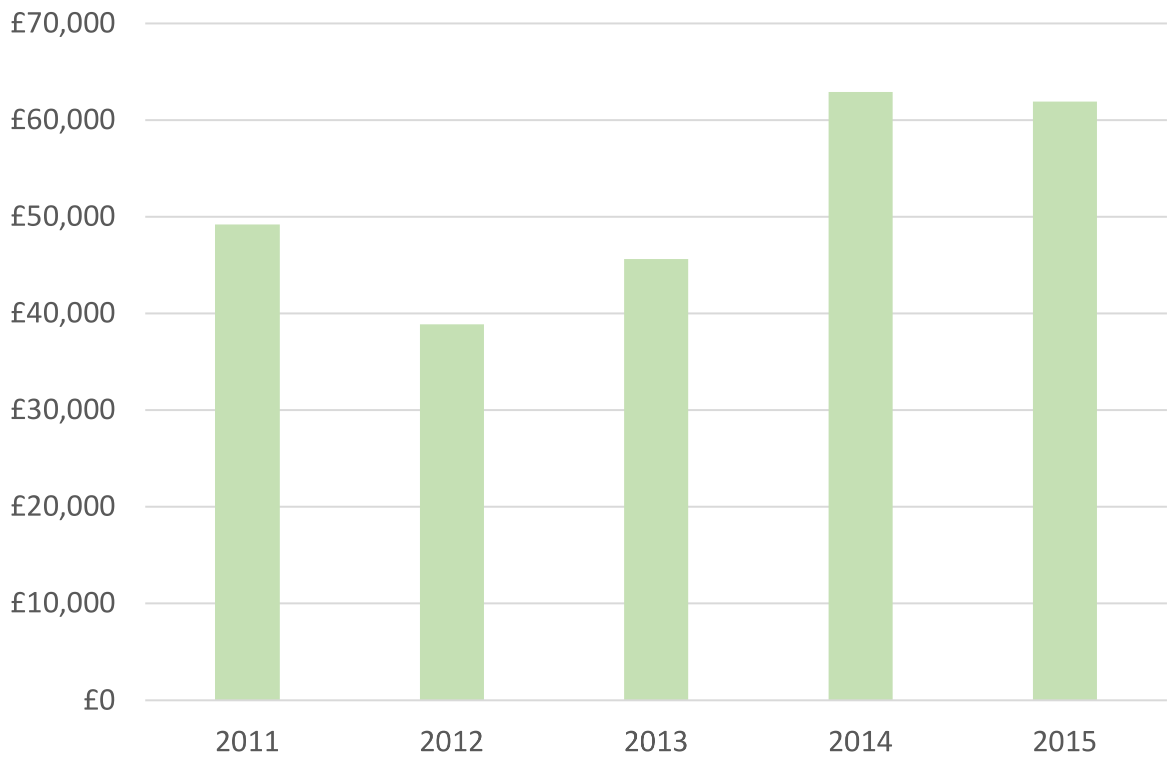


Figure 104: Total annual “PolyClay” cost for Crown Paints' Hull production site.

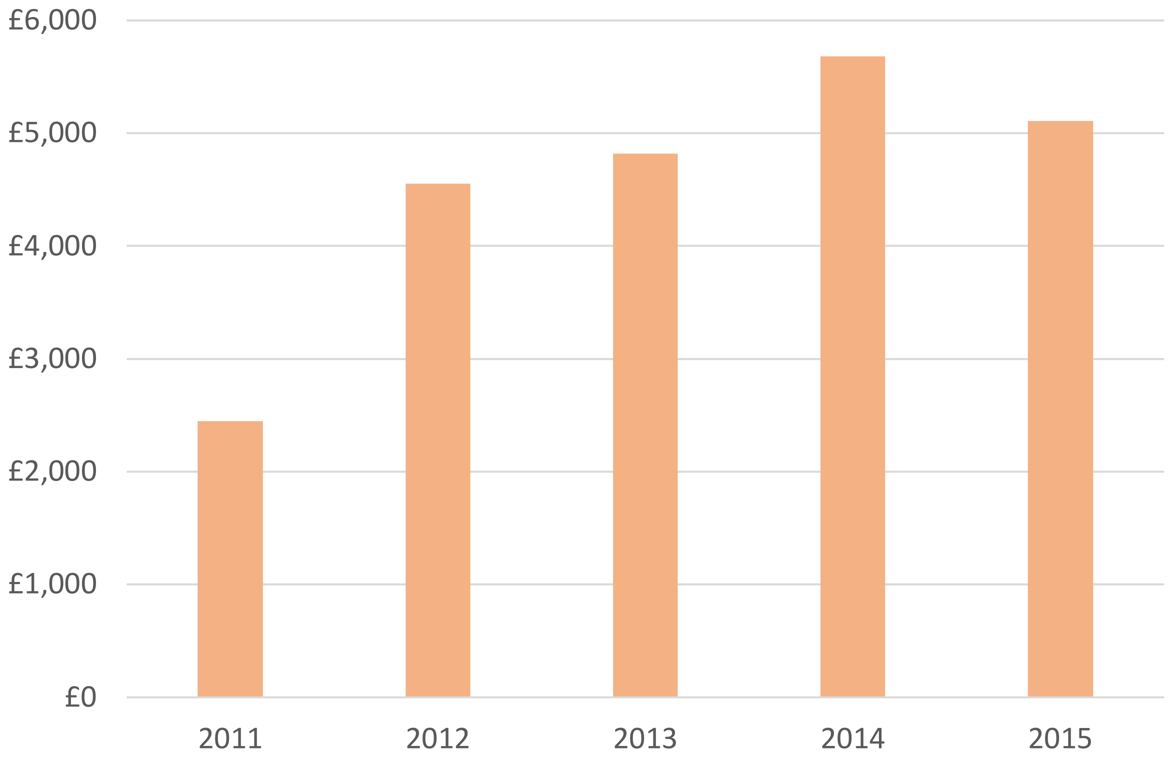


Figure 105: Total annual aluminium sulphate cost for Crown Paints' Hull production site.

3.4.7 Effluent cake

Weighbridge records were extracted from Crown Paints SAP system to provide details of the volume of effluent cake removed from the Hull Site (Table 10. and Figure 106.).

N.b. Data were deficient from February 2014; however, it is assumed effluent cake was produced in this period (i.e. presumably an omission due to operator error).

Table 10: Effluent cake production at Hull production site.

	Mass of effluent cake/kg		
	2014	2015	2016
January	39020	48820	49040
February	-	91100	60260
March	66240	92000	41000
April	85710	106240	71620
May	125380	90220	-
June	115920	77580	-
July	49700	88580	-
August	140840	75030	-
September	92160	60660	-
October	66950	85990	-
November	77240	66100	-
December	67350	50220	-
Mean	84228	77712	55480
SD	31874	17999	13348

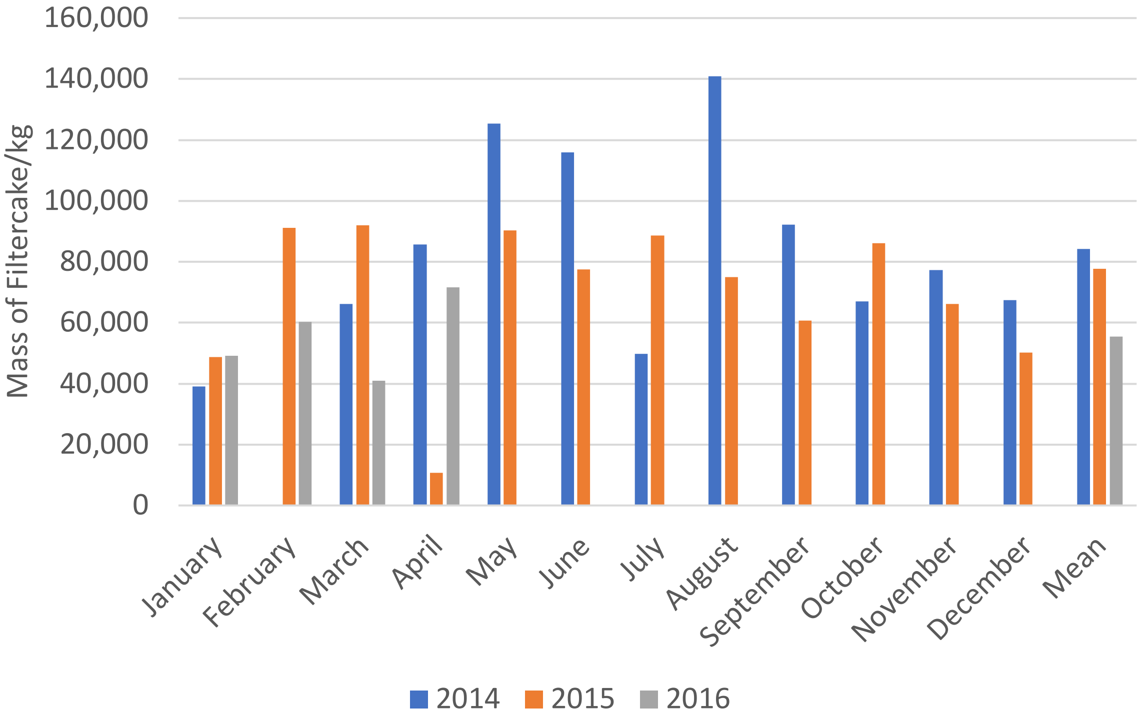


Figure 106: Effluent cake production.

The data provided in Table 10. suggests that although variable, the volumes of effluent cake produced for 2014 and 2015 are relatively similar (as visible in Figure 106.); the site appears to be producing much less effluent cake in 2016 however, and it is of clear interest to monitor the development of this trend.

Utilizing the records of effluent cake production, it is possible to estimate the proportion of the effluent cake which is composed of aluminium sulphate and “PolyClay” (assuming total containment of flocculent and coagulant within the cake) and thus the quantity of solid material removed from the effluent.

Figure 107. and Figure 108. show that whilst a relatively low percentage of the effluent cake is composed of these materials, they still represent a significant proportion of this waste material and thus these materials have an inherent cost associated with their addition. It is worth noting that the “effluent” proportion also includes excess water which can be expected to reach 50% of the total mass of the effluent cake.

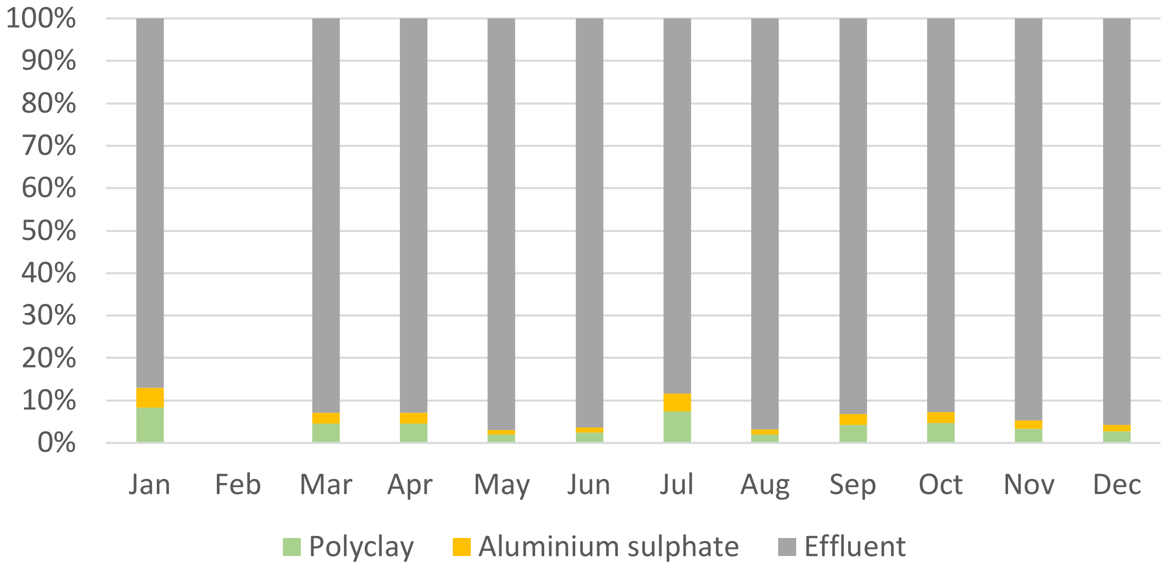


Figure 107: Estimation of the proportion of Effluent Cake composed of "Polyclay" & aluminium sulphate, 2014.

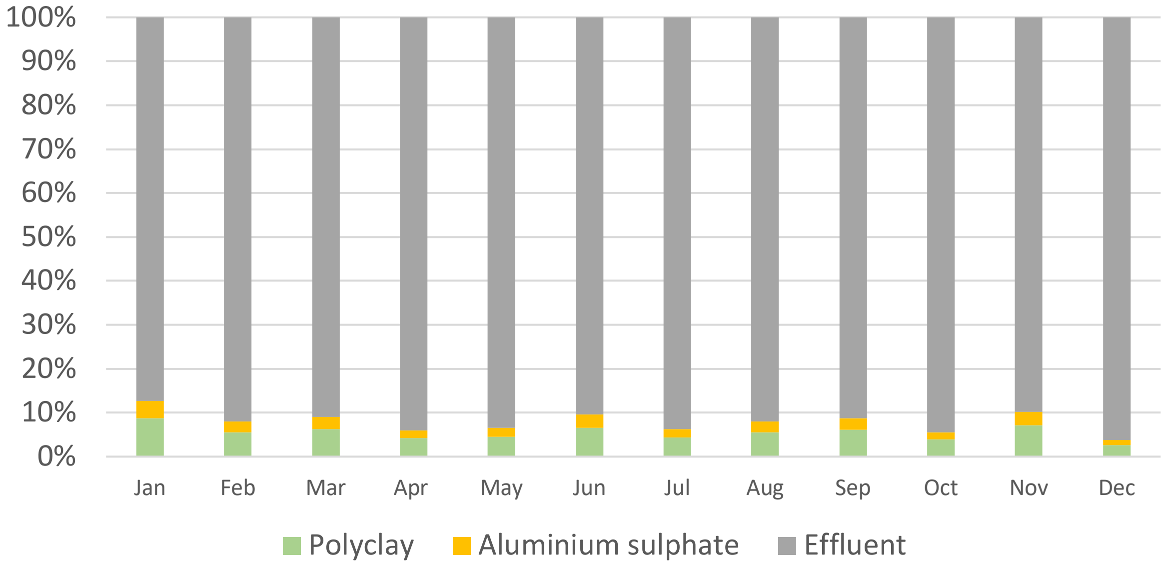


Figure 108: Estimation of the proportion of Effluent Cake composed of "Polyclay" & aluminium sulphate, 2015.

Table 11: Summary table of estimated composition of Crown Paints Hull site's Effluent Cake for 2014 &2015.

	2014			2015		
	"PolyClay" /%	Alum/%	Effluent/%	"PolyClay" /%	Alum/%	Effluent/%
Jan	8.25	4.72	87.03	8.76	3.89	87.35
Feb	-	-	-	5.53	2.46	92.01
Mar	4.54	2.60	92.86	6.26	2.78	90.96
Apr	4.49	2.57	92.94	4.15	1.84	94.00
May	1.93	1.10	96.97	4.56	2.00	93.44
Jun	2.36	1.35	96.30	6.61	2.94	90.45
Jul	7.39	4.23	88.38	4.32	1.92	93.76
Aug	2.03	1.12	96.84	5.57	2.48	91.95
Sep	4.31	2.52	93.17	6.08	2.70	91.21
Oct	4.73	2.57	92.70	3.87	1.72	94.41
Nov	3.40	1.94	94.66	7.08	3.15	89.77
Dec	2.70	1.54	95.75	2.60	1.15	96.25
Mean	4.19	2.39	93.42	5.45	2.42	92.13
SD	2.08	1.19	3.27	1.66	0.74	2.40

3.4.8 Conclusions

The value stream maps (Figure 109. and Figure 110.) for Crown Paints Hull site illustrate the quantities of effluent arising across the Hull Plant. Approximately 30 - 40% of the sites influent water is treated as effluent.

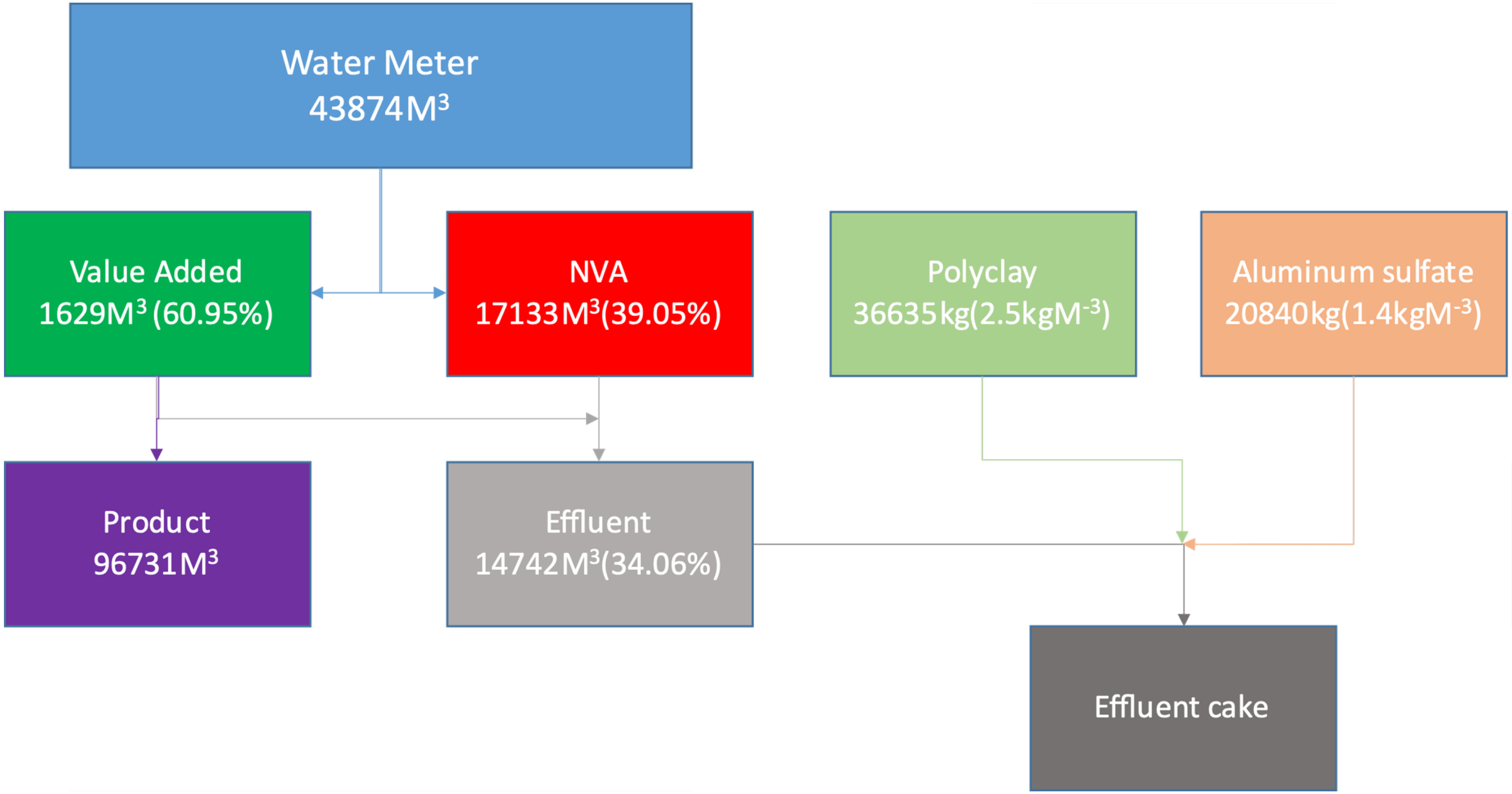


Figure 109: Value Stream Map for Hull site 2013

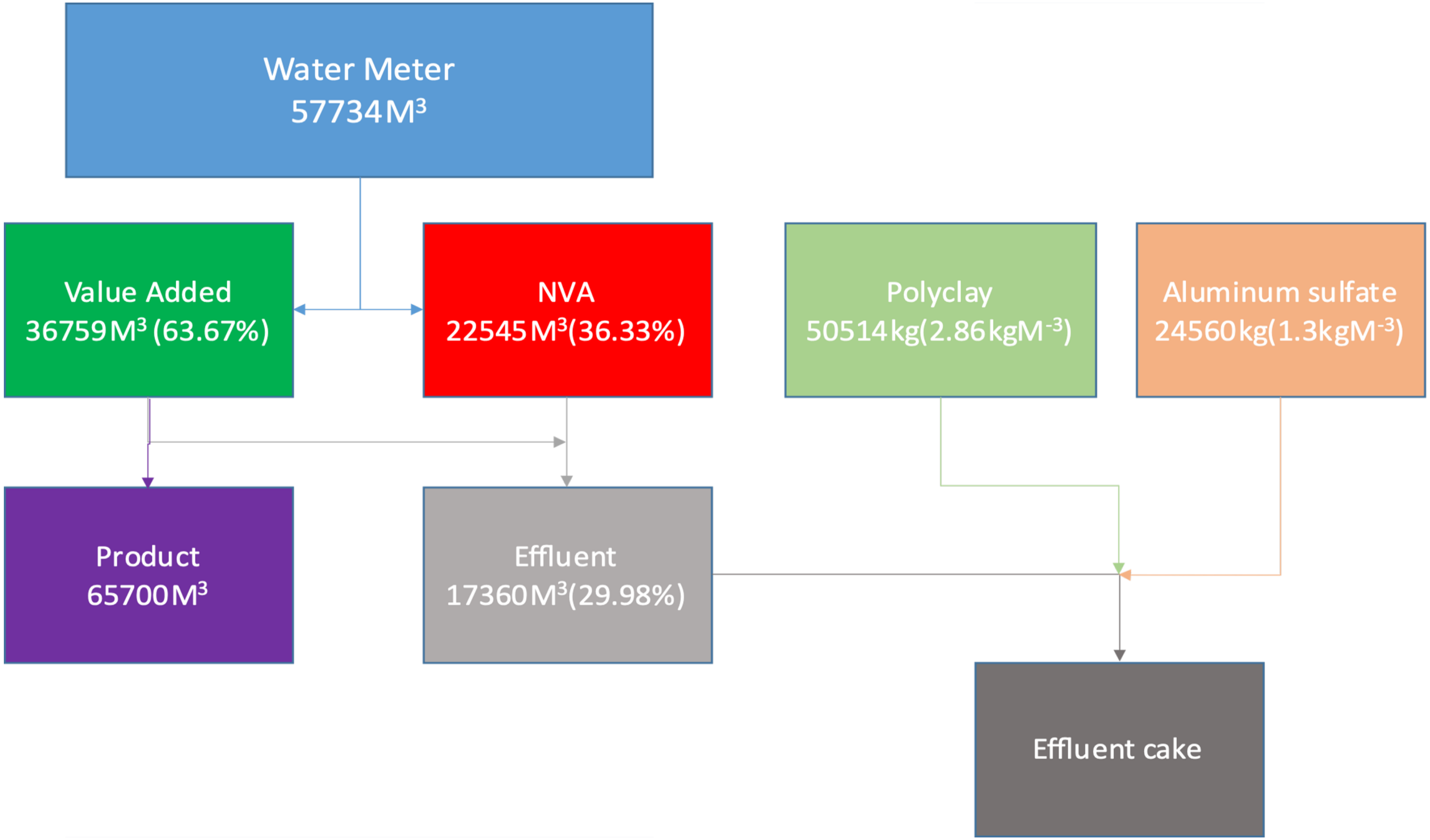


Figure 110: Value Stream map for Hull site 2014

3.5 Conclusions from the Value Stream Analysis (VSA) of Crown Paints effluent generation and treatment processes.

The purpose of the VSA was to provide a comprehensive evaluation of the generation of effluent and its treatment at Crown Paints Darwen and Hull manufacturing sites.

The VSA established the means to measure the quantity of effluent produced at both manufacturing sites. Identifying data sources to establish the sources of effluent and contextualise this quantity with respect to the Value Added component, VA (i.e. the water used within the product).

From this study, it was found that approx. 28% of the Darwen sites' influent water ultimately becomes effluent compared to approx. 30 - 40% of the Hull sites' influent. These figures are comparable, however the lower value for the Darwen process is likely to be due to greater automation of the process, both in terms of using a PLC system rather than manual additions of water within the formulations using batch cards (i.e., more accurate data and addition of material) and in a more automated washing process. Improvements to automate the process at the Hull site will likely improve this value. It is reasonable to suggest that the design of the plant at the Hull site; essentially operating as a "pipeless plant" (as explained in 2.2.4.) may also contribute to a greater washing of portable pumps and pipes. However, conversely careful production planning to use the same portable pipes for similar formulations (or shades) could be utilised to reduce the need for washouts.

This study has shown the use of a VSA within an industrial environment to estimate the generation of waste throughout the process, its resource value and also its treatment cost. This has provided the project with a valuable baseline to measure success against and identify potential areas to focus on. Academically, this study is unique within the literature and provides an interesting tool for use within industrial processes to identify areas of concern for maximum impact.

An idealised VSA of this process would include a mass and energy balance throughout potentially supported by chemical analysis at appropriate stages. This in turn could be included as a component within a LCA to fully understand the product lifecycle in a more holistic manner.

4 DISCUSSION OF POTENTIAL SOLUTIONS

After establishing the origin and scale of Crown Paints waste burden from their emulsion paint manufacturing processes in Chapter 3. the attention of this work is now drawn to identifying potential solutions to reduce this. This represents the third deliverable of KTP project as defined in (1.3.).

The Waste Hierarchy[114] establishes an order of preference system to reduce resource and energy wastage and to maximise the resource potential from this waste (a typical visual representation is provided in Figure 111.). The Waste Hierarchy has a philosophy similar to that of the circular economy with the aim to extend a resource's lifespan before eventual disposal for as long as possible.

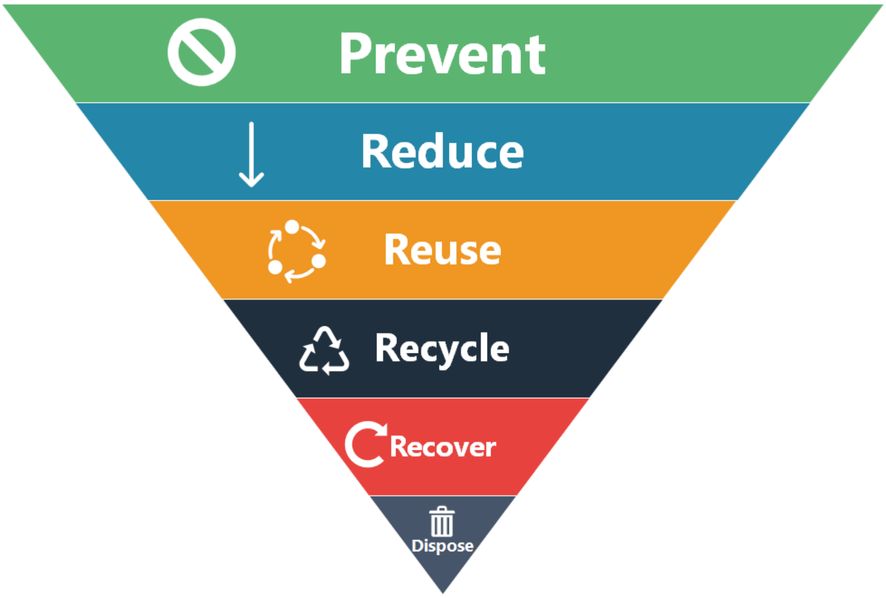


Figure 111: A typical representation of the Waste Hierarchy shown as a pyramid.

Using the waste hierarchy, the preferred action is to reduce and manage waste arising at source. If the generation of waste is inevitable, the focus should be on reusing the material in its present form. If this is not possible the recycling and recovery of any raw materials should then be considered.

Figure 112. illustrates a number of potential solutions (following the Waste Hierarchy) which could be used to maximise the resource potential within the effluent generated by Crown Paints emulsion paint manufacturing processes. The "Hierarchy of solutions" presented in Figure 112. appears as a rotated version of the typical "upside down pyramid" representation of the waste Hierarchy, however this perspective is not totally unique[115]. This is due to the aim of this work being to reduce effluent volumes from pain manufacturing at source rather than maximise the recyclability. The logical justification for this perspective that the highest risk, highest reward solutions are presented at the top of the pyramid

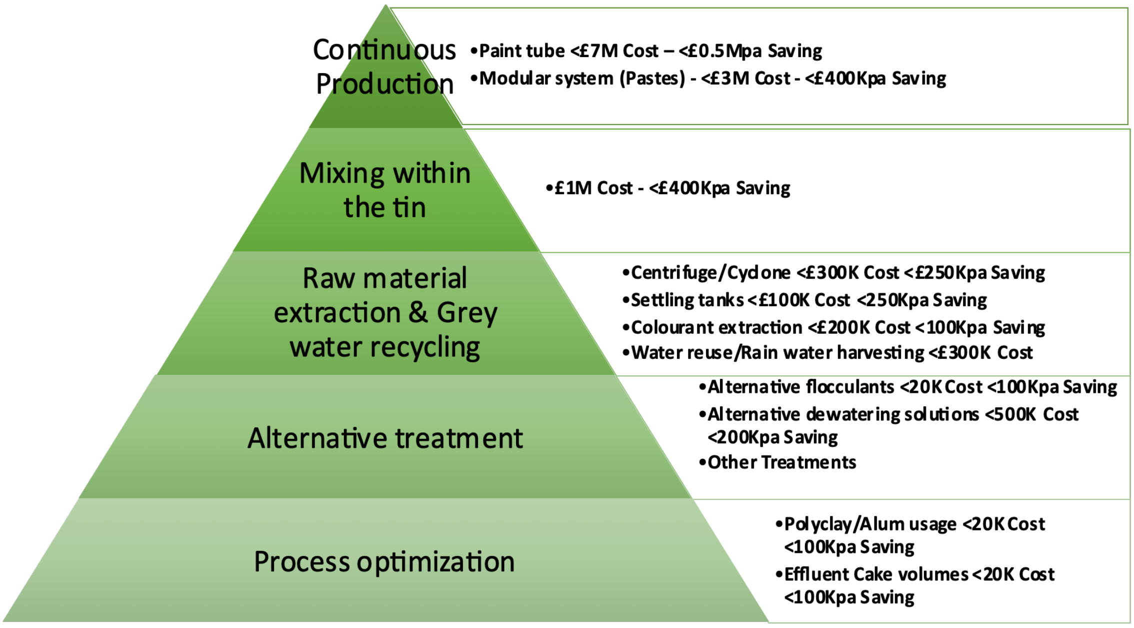


Figure 112: Hierarchy of solutions with estimated costs/savings associated with them.

Ideally, a waste management strategy to reduce the effluent stream should be attempted where possible. Perhaps the most obvious solution would be a reduction in the washing of production vessels, however this proves problematic due to the requirement of a paint manufacturing process to be conducted in a highly sterile environment. A move towards a continuous manufacturing process (or semi continuous modular system) could also be designed to reduce the need for regular cleaning and thus the volume of effluent generated (whilst still maintaining the necessary sterile environment). Such a system however would require a high initial capital investment to be implemented. Similarly adding colourants at the end of the process such as “mixing within the tin” would reduce the residence time of colourants within vessels and thus dramatically reduce the volume of water needed to cleanse residual material, which could adversely affect the products shade. A similar system would need a complex restructuring of the production process and would also require a large investment.

The next stage on the hierarchy would be to reuse the generated waste, with potential systems such as grey water recycling or rain water harvesting. Preliminary testing suggests that it is possible to slowly “bleed” raw effluent into paint formulations with the only significant effect being due to residual colourants. It may be possible however, to remove these contaminants (via a treatment process) or significantly reduce the effect (through a colour matching system). The reintroduction of effluent back into the paint manufacturing process is explored more in Chapter 7. of this thesis. Grey water harvesting could also potentially reduce the virgin water requirements of the plants substantially (by an estimated: Darwen 28%, Hull 33%, 2015). The high capital cost would most likely not be a sensible investment (due to the limited cost of virgin water), however the same techniques could be employed to utilise rainwater within the plant. The Darwen site is the obvious location for such a system where approximately 50% (2014) of the site’s virgin water requirement could be achieved through a rainwater harvesting system.

Systems to dewater and extract the raw material from the waste effluent, such as settling tanks or centrifuges/cyclones could return approximately £160,000 p.a. (Figure 113.) of raw material back within the paint manufacturing process. Despite a high initial expenditure and the difficulty of reintroducing the material into the production system, the financial savings would be enormous with additional savings in Flocculent/Coagulant dosages (up to approx. £100,000 p.a., 2014) and disposal (up to approx. £100,000 p.a.) due to a vastly reduced volume of “solid material” being treated by the effluent plant.

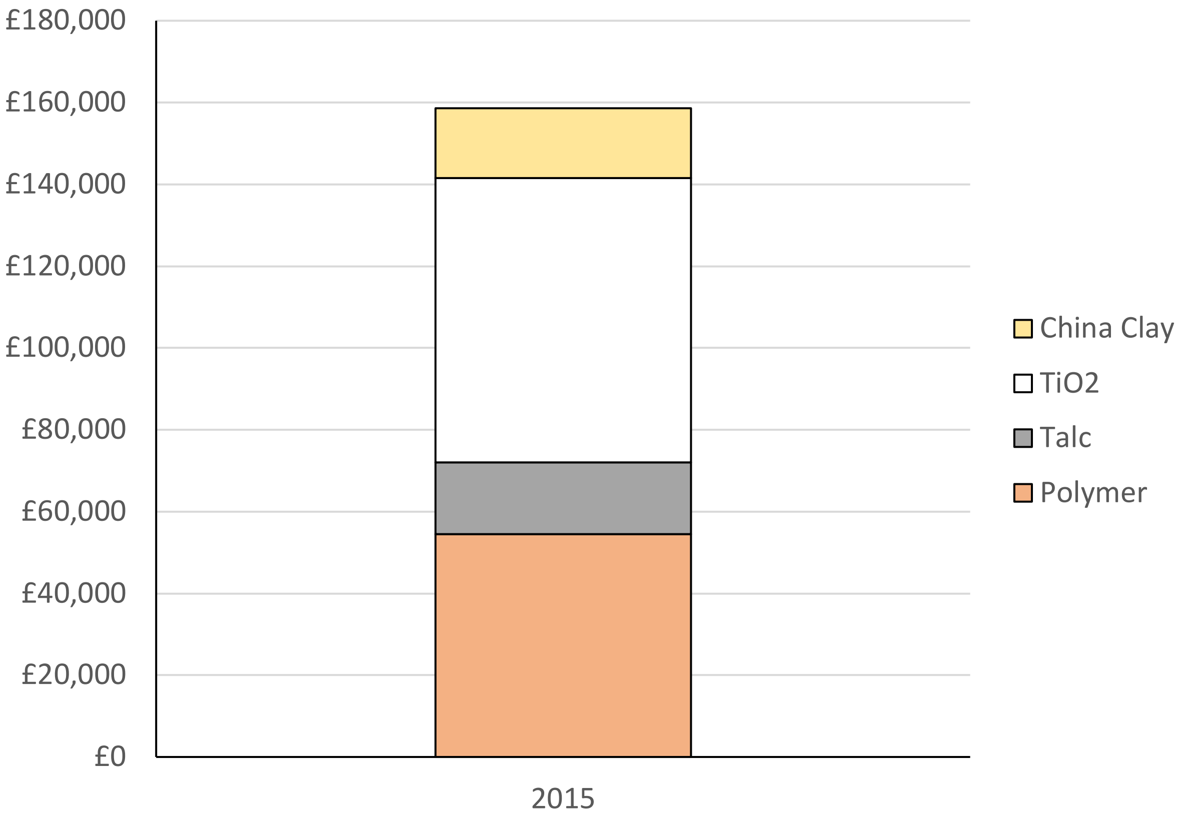


Figure 113: Raw Material Cost, 2015 at Crown Paints' Hull Site.

One of the large associated costs of Crown Paints' effluent treatment process is the cost of coagulants and flocculants, consumable chemicals which are utilised in the treatment plant. "PolyClay", the flocculent, costs over £60,000 p.a. at the Hull site alone (2015) with a further £8,900 p.a. at the Darwen site (Figure 114.). Utilising different flocculants could potentially reduce this figure. However, Crown Paints have attempted similar solutions in the past which have proved less suitable than their current system. Options exist to use different dewatering techniques to improve the effluent process such as dissolved air flotation (DAF), centrifugal dewatering, ultrasonic settling or potential modifications to their treatment/settling tanks. Solutions could be tailored to both reduce consumable consumption and produce a drier by-product for disposal. Whilst all these possible solutions are not fully considered in this work Chapter 6. provides a tool which could be utilised for comparative analysis of dewatering technologies.

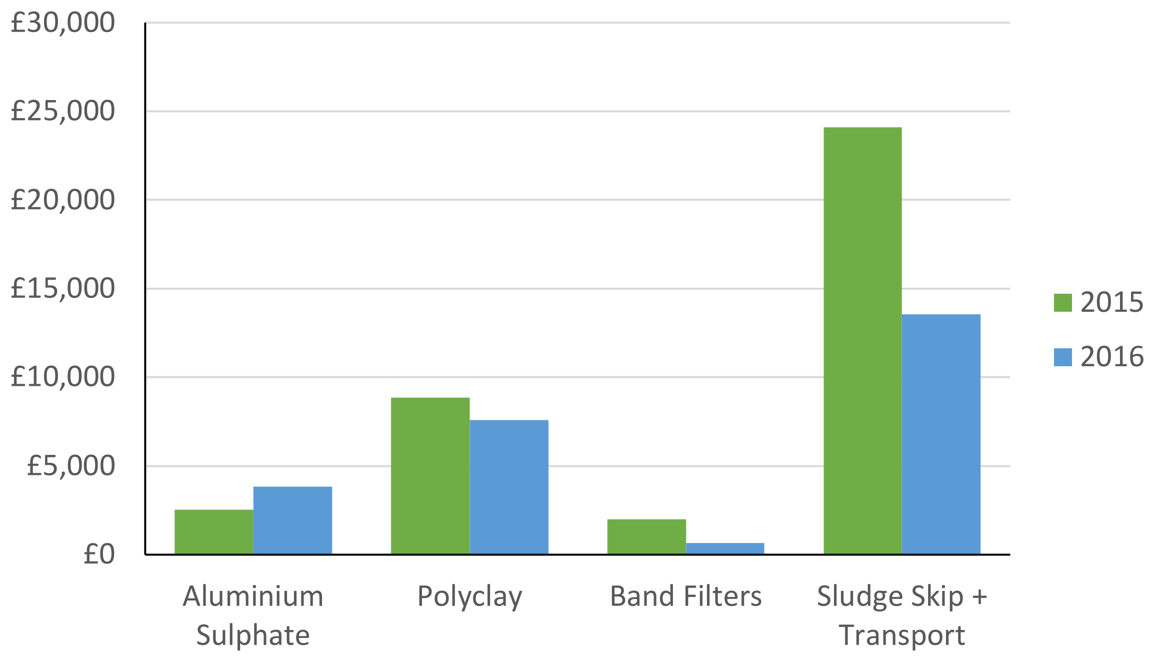


Figure 114: Costs of the Effluent Treatment process at Crown Paints' Darwen Site.

Finally, the lowest stage of the hierarchy would be to maximise the current process, to insure it runs as efficiently as possible. The principal method is to optimise the coagulant and flocculent dosages and thus reduce wastage through the system. Although this may be the lowest stage of the hierarchy (in respect to waste minimisation), process optimisation offers a reasonable starting point in the sense of "improving what is available, first", it also has the benefit of being relatively simple, quick and cheap (i.e. not requiring large amounts of planning or investment), whilst also offering invaluable insight into the process and waste material generated at each stage (raw effluent, treated effluent, filtercake and greywater). The optimisation of the current coagulation, flocculation and filtration process is detailed in Chapter 5. and Chapter 6.

5 OPTIMISATION OF CURRENT EFFLUENT PROCESS

Whilst representing the lowest stage of the Hierarchy of Solutions presented in Figure 112. the process improvement strategy with the lowest risk is the optimisation of the Crown Paints' current effluent treatment processes. The optimisation of the current effluent treatment process represents the third identified deliverable of the KTP project (from Section: 1.3.). This chapter presents a laboratory-based Jar Test study demonstrating a reduction of the currently used flocculant ("Polyclay") by up to 90 % with only a limited impact on the observed floc size. This method was then scaled up to a full-size batch trial for seven effluent batches at Crown Paints Hull manufacturing site, where the flocculant dose was conservatively reduced by 50 %. This showed limited effect on the process however the flocs did not settle within the Sludge Tank (i.e. they floated), reducing the speed of effluent treatment. Concerns were also raised on the impact of this reduced flocculant dosage within the Filter Press stage of the process. This limitation is further explored in Chapter 6. where a new apparatus was developed to study this impact further.

Basic Jar Tests have suggested that the effluent from Crown Paints emulsion paint processes may form small, flocculated particles (flocs) at a lower pH (approx. <6) without the need for additional "PolyClay". The aim of this subproject is to establish whether this effect could be scaled up and thus make a significant cost reduction for the company (circa £70,000 p.a., 2015).

It is important to understand that during the KTP project, there was a significant cultural shift at Crown Paints' Hull site, where the site became increasingly enthusiastic at reducing the burden of the effluent treatment process. Independently from this research, a significant drive towards waste reduction has been made. Resulting in a vast improvement to the efficiently of the site's effluent process (with strong investment, better housekeeping and a motivated staff) savings have been made across the board. Due to the site's increased awareness and reduction in waste, it was appropriate to establish a baseline that remains consistent despite the changing environment due to these improvements. The aim therefore was to reduce the average "PolyClay" dosed in each batch per m^3 of effluent (average costs demonstrated in Figure 115.).

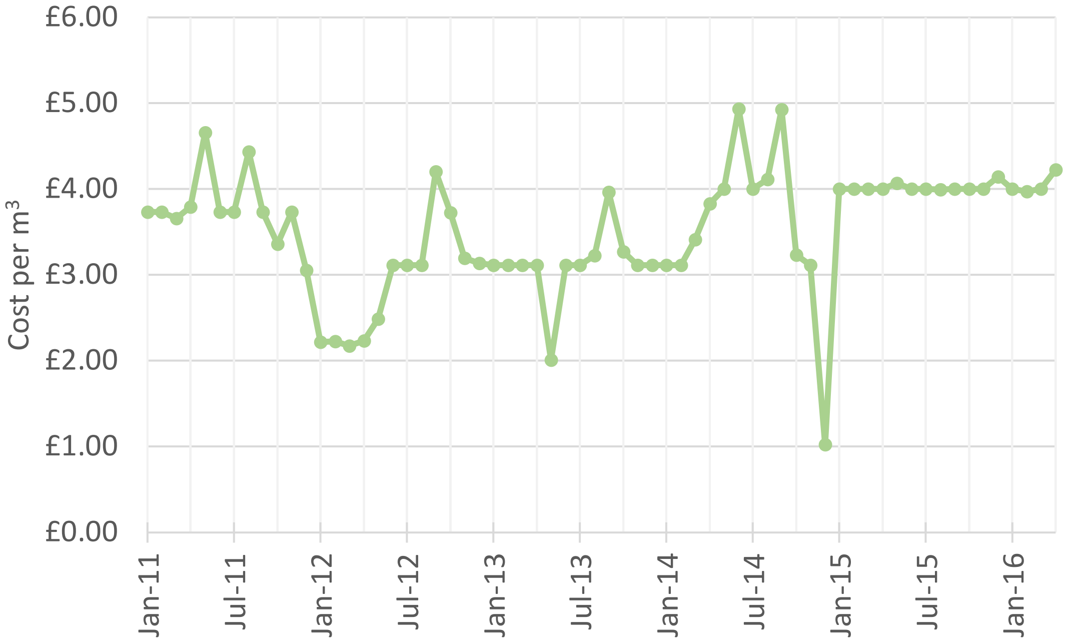


Figure 115: Average cost of "PolyClay" for treating 1 m^3 of effluent at Crown Paints' Hull Site.

A consistent data set of recording the treatment of each batch (from operator records) has been established at the Hull site since 2011, however recent improvements to the plant have included the installation of an automated reporting system. Despite a number of reporting issues (several instances where the system has failed to record any readings) the system acts as an invaluable tool to assess the quantity of effluent treated and the conditions placed on the plant. Figure 116. shows how the data compares to previous years. The data illustrates that although the mean "PolyClay" dose has decreased since 2015 (by a value of approximately £5,000) it is comparable to the values obtained in 2014.

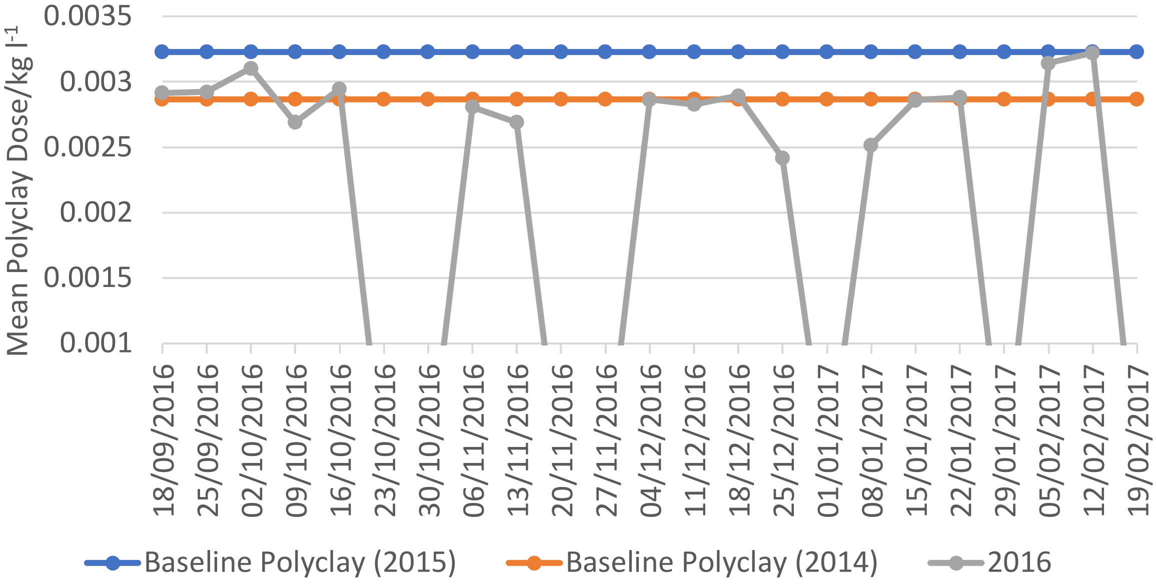


Figure 116: Mean "PolyClay" dose at Crown Paints' Hull Site.

5.1 Overview of Effluent Process

5.1.1 The Hull Process

The Effluent plant at the Hull manufacturing site (Figure 117.) is fitted with a semi-automatic wastewater system built by Colloid Treatment Technologies Ltd (CTECH).

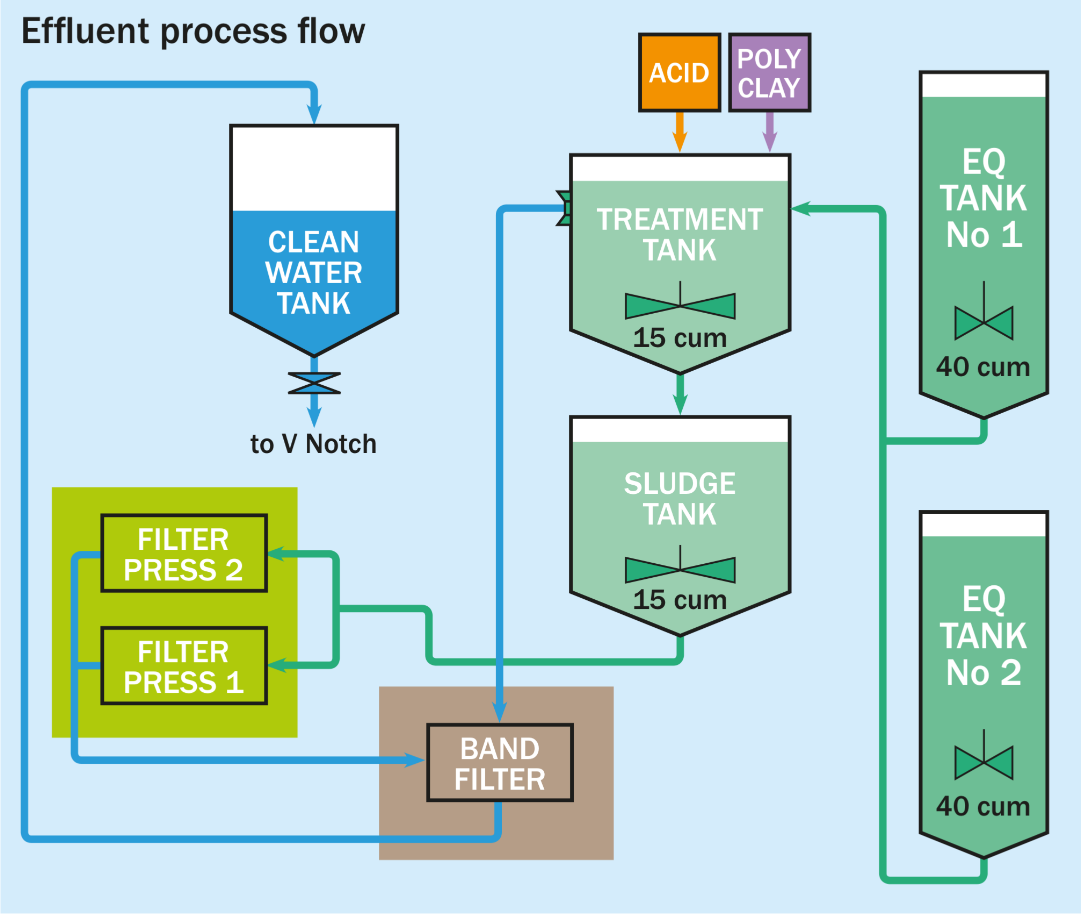


Figure 117: Illustration of the Effluent Process at Crown Paints' Hull Site (n.b. volumes are shown as cubic metres, cum).

Initially, the waste wash water is pumped into one of two Equalisation Tanks (EQ); both of which are of 40 m^3 capacity, and the level of effluent within these tanks is monitored through an ultra-sonic level control system. The purpose of these tanks is to homogenise the incoming waste and thus reduce the variability of the waste stream whilst also acting as holding tanks to allow the potentially continuous flow of waste to be treated via a batch process.

The Treatment Tank has a much smaller capacity (than the EQ tanks) of 15 m^3; it is here where the coagulant (colloquially known as "Acid") aluminium sulphate ($Al_2(SO_4)_3$) is added. The pH of the effluent in the treatment tank is monitored by an automatic probe situated in the base of the tank and the coagulant is continuously added until a stated pH is achieved, known as the "crack pH" (although variable this is currently set at 6.20) at which the effluent forms what is described as "micro flocs". A "post mix" is then activated to insure the homogenization of the solution (typically for 120 s).

The Flocculent is then added, Crown Paints use CTECH's own product, "PolyClay 656", which is primarily Bentonite (a volcanic clay), further aluminium sulphate, lime and an unknown (commercially sensitive) polymer. The flocculent binds the micro flocs, increasing their size to aid settling and filtration whilst slightly increasing the pH of the solution. The flocculated solution is mixed for a period (usually 300 s) and then left to settle (similarly also usually for 300 s), the addition of the flocculent (and also the mixing/settling cycle) can be repeated as necessary to achieve a suitably "good floc" (one which visually and through moulding through the operators hands rather subjectively, will hold its clay-like composition within the press) and thus suitable for dewatering within the filterpress.

The effluent is then pumped into the Sludge Tank, which also has a 15 m^3 capacity. The Sludge Tank is a typical conical cylinder Settling Tank with a vertical flow (Figure 118.). The inflow is in the centre of the tank and the slope at the base of the tank guides the sludge towards the extraction point forcing the less dense water to the top of the tank from which it can be extracted. This “clarified water” is then pumped to a Band Filter to catch any remaining suspended solids. The sludge is pumped from the Sludge Tank to the Filter Press for further water extraction.

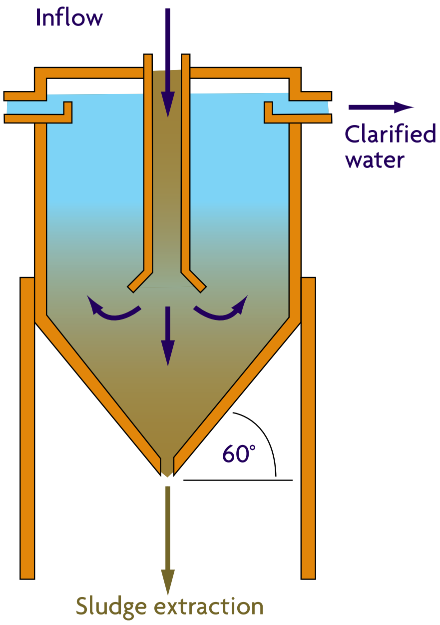


Figure 118: A typical Conical Cylinder Settling Tank such as the one at the Hull effluent plant, adapted from SNF Floerger[116].

The Filter Press is hydraulically driven and has the capacity to hold between 2-5 batches of effluent sludge. Despite the press running automatically, an operator must open and clean the filter press manually whenever filled. This pushes the filter cake through the bottom of the press into a skip.

Figure 119: The Hull effluent plant filter press dewatering.

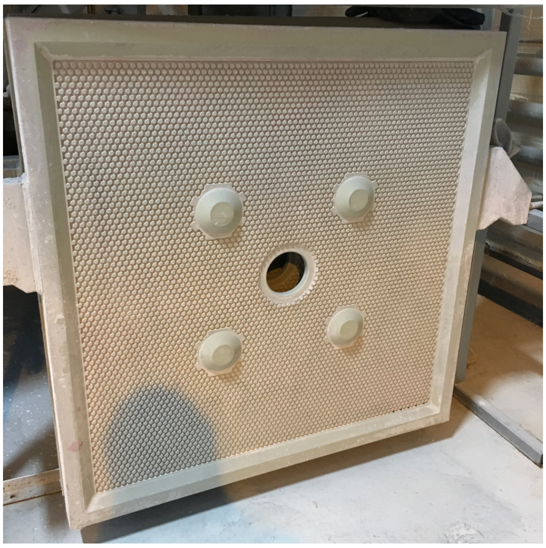


Figure 120: A filter press plate from the Hull effluent plant (approx. 1m^2).

5.1.1.1 Current Coagulant and Flocculent dosage at the Hull Site

At present an approximate 500 ml sample of effluent is taken from each of the two EQ tanks daily (ideally when full) and this is assumed to be representative of the incoming effluent for that day. The “solids content” is analysed gravimetrically via a solids analyser, once identified the dose can then be established according to the range as described in Table 12.

Table 12: “PolyClay” additions as provided at the Hull site.

Solid Range/ wt%	“PolyClay” Addition for 500ml Jar Test/g	“PolyClay” Addition for 14,000L Batch/kg	“PolyClay” concentration/kg m^{-3}
1.00-2.14	1	28	2.0
2.15-2.50	1.25	35	2.5
2.50-3.49	1.5	42	3
3.50+	1.75	49	3.5

n.b. The data in Table 12. is provided from an extensive 6-week trial to quantify a practical ideal dose of Flocculent according to the variability of effluent within the EQ tanks.

A Jar test is performed (Figure 121.) by lowing the pH of the 500 ml mixture to 6.2 through the addition of aluminium sulphate and monitored through a pH probe. The required “PolyClay” dose (from Table 12.) is added and the sample mixed for 5 minutes (approx. 650 rpm), before being allowed to settle for 5 minutes and finally mixed for a further 3 minutes before being allowed to settle.

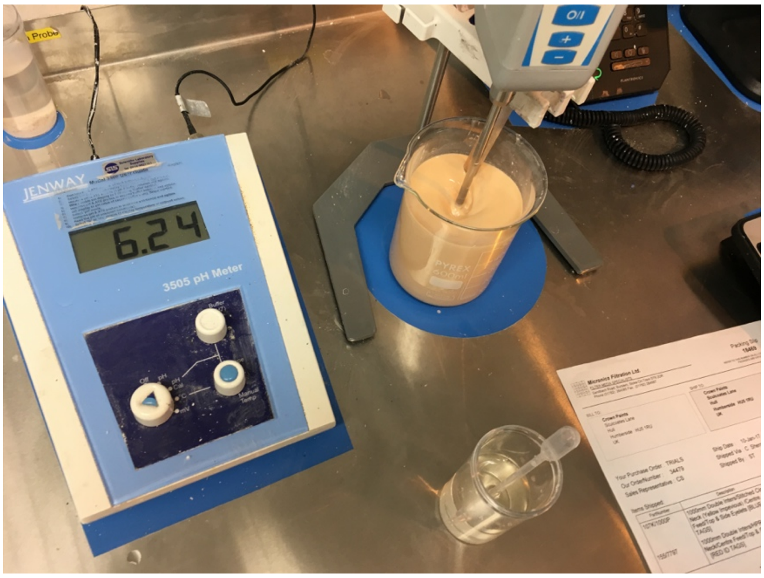


Figure 121: The Jar Test Equipment at the Hull Site (Beaker with sample. pH probe, mixer)

Once the sediment has settled, the supernatant is decanted from the container and the sludge removed and subjected to a simple “squeeze test” in which the operator manually tries to compact the sludge and dewater it through their fingers (supposedly mimicking the action of the filter press) to attempt to obtain a “dry cake” with a clay-like consistency, despite being relatively primitive, the test is remarkably effective at predicting how the cake will perform within the press (i.e. “sloppy” non-dryable sludges in a squeeze test will result in a wetter “sloppy” filtercake within the press with a high proportion of water and a potentially damaging effect on the filter press cloths through clogging). If the test is deemed successful (the sludge is dewatered sufficiently) the batches for the day will be treated with the same concentration of “PolyClay” however if not, the method is repeated with using the “PolyClay” dose corresponding to the next solids range.

5.2 Laboratory modelling of the Hull Effluent Treatment Process

5.2.1 Method

5.2.1.1 Sampling

Samples of effluent were taken from various locations throughout the effluent process

(Table 13. & Figure 122.).

Table 13: Effluent Sampling Points.

Sampling Point	Sample	Location
1	Raw Effluent	EQ Tank 1
2	Raw Effluent	EQ Tank 2
3	Treated Effluent	Treatment Tank (During post Mix)
4	Grey Water	After Band Filter

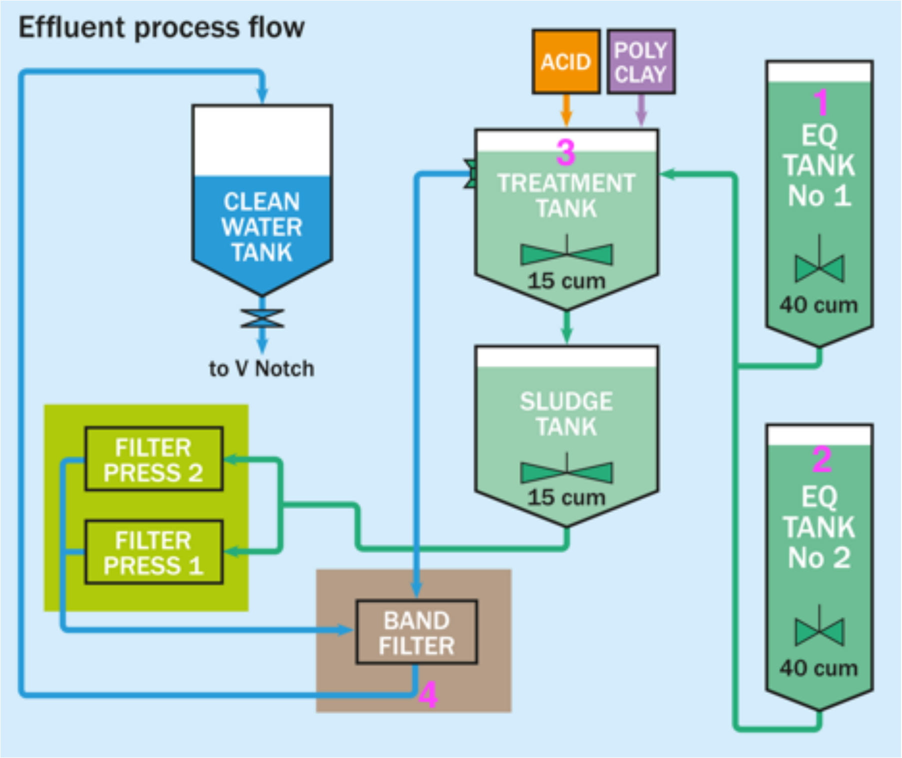


Figure 122: Illustration of the Effluent Process with marked Sampling Points.

Five samples of raw effluent (three from EQ Tank 1 & two from EQ Tank 2) were collected (shown on Figure 122. as Sampling Points 1. & 2.) with the corresponding (post-flocculation) treated effluent (Sampling Point 3.) and grey water (Sampling Point 4.) so that the whole effluent process could be compared from plant to laboratory scale.

5.2.1.2 Jar Tests

Because each of these raw effluent samples represents a treated batch (Table 14. details the specification for each batch) the Jar Test method was designed to match the treatment within the effluent plant. To simulate the Effluent treatment process accurately a flow chart of the process was produced through analysis of the effluent treatment reports provided by the plant's operating system for each sampled batch (Figure 123).

Table 14: Batch Data provided by Batch Reports.

Batch	**1**	**2**	**3**	**4**	**5**
EQ Tank	1	2	1	2	1
Date	03/11/2016	07/11/2016	07/11/2016	09/11/2016	10/11/2016
Time		07:57:16	15:57:30	06:59:23	08:41:43
Volume/m^3	14.2	11.36	14.2	14.2	14.2
Pre-Mix/s	60	60	60	60	60
Crack pH	6.2	6.2	6.2	6.2	6.2
Post Mix/s	120	120	120	120	120
"PolyClay" Dose/kg	42	35	35	42	42
Powder Dos Mix/s	300	300	300	300	300
Final Mix Time/s	120	120	120	120	120
Final pH	6.2	6.2	6.2	6.2	6.2
Settling Time/s	300	300	300	300	300
Solids Content/%		3.83	2.17	2.23	3.92
Water/m^3	0	2.84	0	0	0

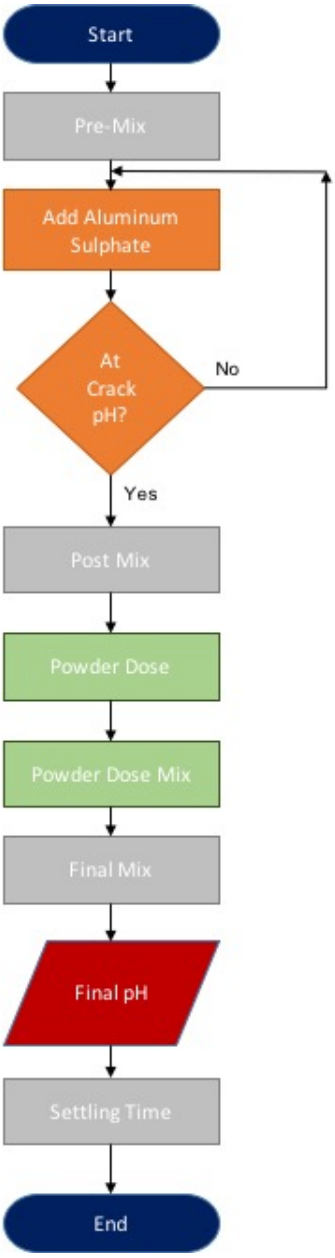


Figure 123: Flow Chart of Effluent Process.

Following the process detailed in Figure 123. a Jar Test method was developed:

1. 250 ml aliquots were taken of the Raw Effluent samples and decanted into a 400 ml beaker and “Pre-mixed” on a magnetic stirrer for the period recorded in the report data (Table 14.).
2. A 10% solution of the industrial coagulant (aluminium sulphate) was titrated against this effluent until the crack pH from the report data was reached (conveniently 6.2 with all samples tested).
3. The coagulated solution was then “Post Mixed” for the period defined in Table 14. (120s).
4. A dose of “PolyClay” was added.
5. The mixture was then “powder mixed” as stated in Table 14. (300s).
6. A “Final Mix” was then performed as stated in as stated in Table 14. (120s).
7. The “Final” pH was recorded.
8. The mixture was left to settle for as stated in Table 14. (300s).

This standardised process was repeated for each sample with only the “PolyClay dose” used to treat the batch in question (as in Table 14.) being varied. The different aliquots of each sample of “Raw Effluent” were dosed appropriately with a quantity of flocculent approximately equivalent to a 100%, 75%, 50%, 25% 10% and 0% proportion to the actual dose as treated in the plant (the calculated ideal values are expressed in Table 15.)

Table 15: "PolyClay" doses for each Jar Test.

		Batch				
		1	2	3	4	5
Batch Data	Effluent Volume/l	14,200	11,360	14,200	14,200	14,200
	"PolyClay" Dose/kg	42	35	35	0.00296	0.00296
	"PolyClay" Conc/kg l^{-1}	0.00296	0.00308	0.00246	0.739	0.739
Scaled "PolyClay" Dose for 250ml Jar Test/g	100%	0.739	0.770	0.616	0.555	0.555
	75%	0.555	0.578	0.462	0.370	0.370
	50%	0.370	0.385	0.308	0.185	0.185
	25%	0.185	0.192	0.154	0.074	0.074
	10%	0.074	0.0770	0.0616	0	0
	0%	0	0	0	0.00296	0.00296

Figure 124: An example of a flocculated Jar Test.

5.2.1.3 Settling Rate

The aim was then to use a simple sedimentation test to determine the rate of settling, clarity of the supernatant liquid and the final proportion of sludge. The sedimentation test method utilised is a standard test method used to aid in the selection of suitable dewatering equipment. Typically, a 1 l measuring cylinder would be used.

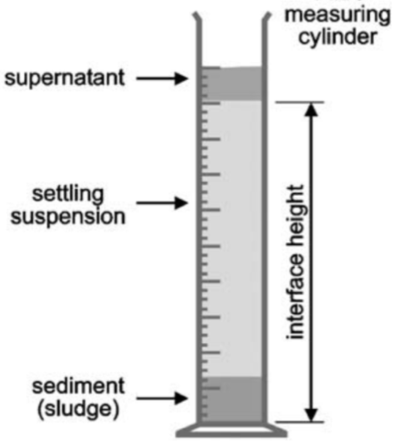


Figure 125: Idealised schematic of a Jar Sedimentation Test, adapted from Tarleton[117].

The method described in Tarleton[117] measures the interface height using a ruler at regular time intervals. This proved ineffective with the material in question (as explained in 5.2.2.2.). An attempt was made to improve this method using a "Go-Pro" camera to record the sedimentation test at a high frame rate (60 fps). However, this was not effective either. Experimentally, the method has been shown to not be practical for this purpose. Another option would be the use of a Turbiscan[118] a device that uses static multiple light scattering to detect particle migration as used in a similar study into different flocculants, Glover et al.[119].

5.2.2.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an analytical technique used for elemental analysis. Due to its sensitivity, it is heavily used within the water industry. Here it is used to determine any contamination of the clarified water following the Jar Tests.

Overview of the Technique

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a powerful analytical tool to determine trace elements within a variety of different samples. An ICP-OES system is composed of two parts the ICP torch (Figure 126.) and the Optical spectrometer. A radio frequency (RF) coil surrounds the ICP torch producing an intense electromagnetic field which excites a flow of gas (typically argon) to create a plasma. Liquid samples are converted into an aerosol; typically using a nebulizer and fed into the plasma. At the torches core a sustained temperature of 10,000 K is achieved (comparable to the surface of the Sun) vaporising the aerosol, which then rapidly collides with electrons and charged ions which excites the samples component atoms into ions and promoting them to excited states. These excited species may then return to the ground state by the emission of photons with a characteristic energy. Through observation of the wavelengths of these photons it is therefore possible to determine the element from which they originated; quantification is possible due to the total number of photons being directly proportional to the concentration of the element within the sample.

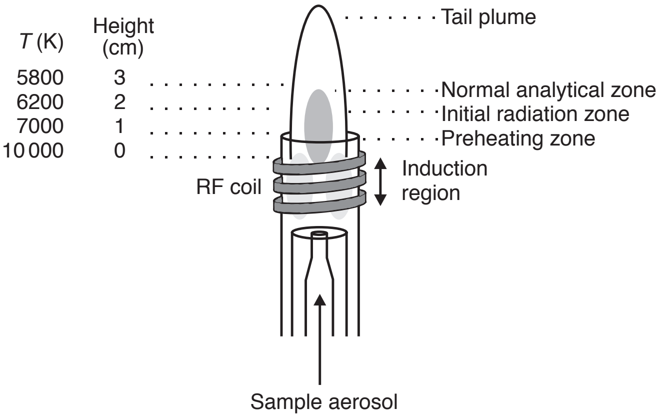


Figure 126: A schematic of an ICP Torch, from Fassel et al.[120].

Observation configurations

Two principle different viewing configurations exist for spectrometric measurements; the classical radial view with a side-on view of the plasma's normal analytical zone (NAZ) or an axial view where the NAZ is observed from the end of the plasma; additionally, in some systems it is possible to record measurements from both locations at once, in what is known as a dual view configuration. Both configurations are better suited to different tasks with a radial view limiting background interferences whilst the axial view has a much better sensitivity. Despite Lancaster's system having the capability for a dual view configuration all measurements were taken from the standard radial view.

Sample preparation

Whilst liquid and gas samples may be directly injected into an ICP (via a nebulizer) solid samples require a form of extraction or acid digestion to ensure any analytes are present in a solution. As the consent to discharge lists the "Toxic metals concentration" as dissolved and the samples are all liquid it was decided initially that acid digestion was unnecessary. However, the Raw effluent samples were centrifuged for 30mins to force the sedimentation of any particulates (Figure 128.). All samples were then filtered through a 0.45um filter before injection.

The calibration solutions were made through a serial dilution of a standard solution (Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, & Zn 10ppm, K 100ppm) in 98% Nitric Acid (Table 16.) These were then filtered through a 0.45um filter before injection.

Table 16: Concentration of Analytes in Standard Solutions.

	Blank	**Standard 1**	**Standard 2**	**Standard 3**	**Standard 4**	**Standard 5**
Al/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
As/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Ba/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Cd/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Cr/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Cu/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
K/ppm	**0**	**5**	**10**	**20**	**50**	**100**
Mn/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Mo/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Ni/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Pb/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Se/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Sr/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**
Zn/ppm	**0**	**0.5**	**1**	**2**	**5**	**10**

Figure 127: Lancaster University Chemistry Department's Agilent 5100 ICP-OES.

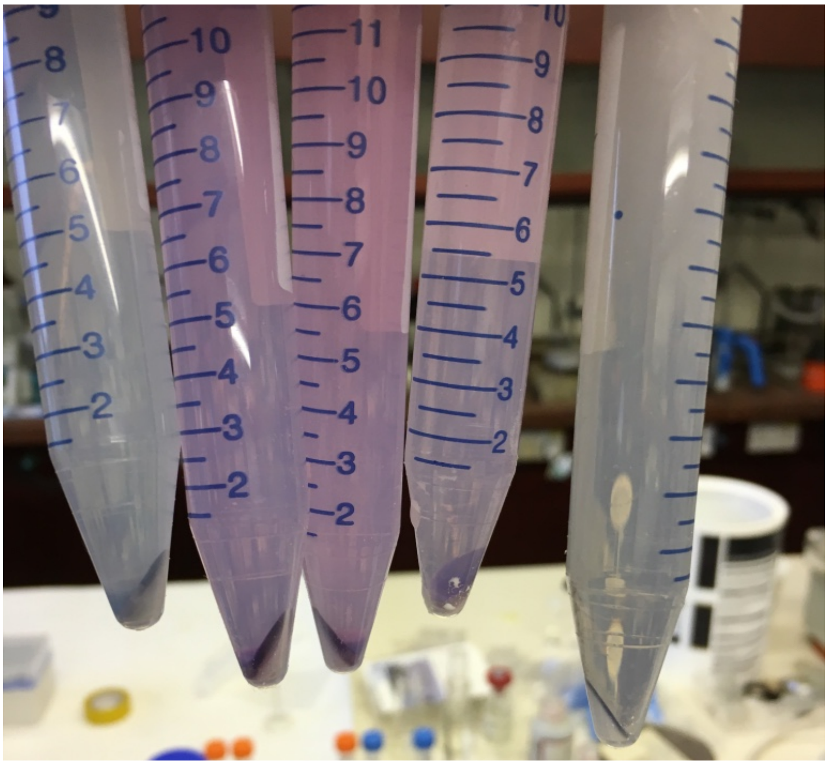


Figure 128: Samples of Raw Effluent after centrifugation.

Results

5.2.2.2 Jar Tests

Coagulant Dosing

Due to the nature of the data report provided by the Plant’s operating system (Table 14.) recording the “Crack pH” rather than the quantity of coagulant dosed. The corresponding volume of coagulant required to reach the target “Crack pH” for the Jar Tests is provided in Table 17. An example of a “cracked” Jar Test with micro flocs is also provided in Figure 129.

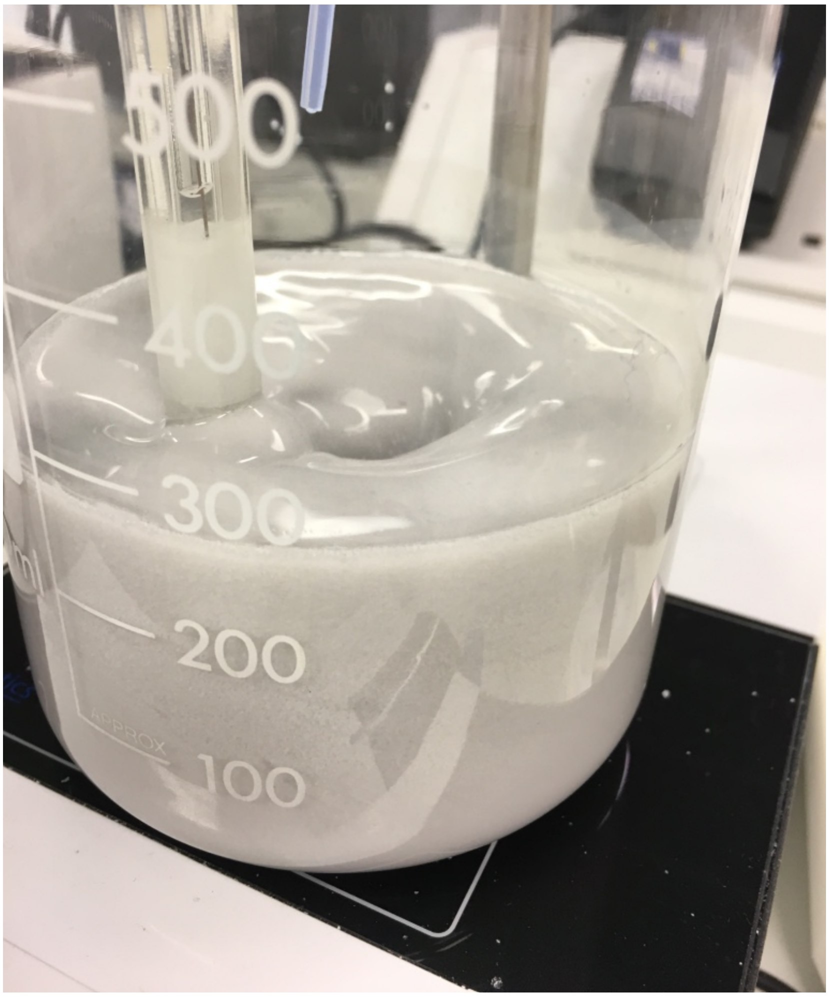


Figure 129: A "cracked" Jar Test at the target “Crack pH”.

Table 17: Volume of coagulant required to reach “Crack pH” for Jar Tests.

Batch	“PolyClay”	ml of 10% Alur	Final pH	l of Alum on Plant
1	100%	2.9	6.045	16.50
	75%	2.8	6.186	15.90
	50%	3.1	6.009	17.58
	30%	2.8	6.181	15.90
	10%	2.6	6.177	14.77
	0%	3.0	6.142	17.05
2	100%	1.4	6.199	6.36
	75%	1.5	6.157	6.82
	50%	1.4	6.173	6.36
	30%	1.5	6.173	6.82
	10%	1.5	6.16	6.82
	0%	2.1	6.179	9.54
3	100%	1.2	6.197	6.82
	75%	1.3	6.182	7.38
	50%	1.2	6.186	6.82
	30%	1.4	6.183	7.95
	10%	1.0	6.189	5.68
	0%	1.2	6.192	6.82
4	100%	1.0	6.151	5.68
	75%	0.9	6.193	5.11
	50%	1.0	6.172	5.68
	30%	0.8	6.198	4.54
	10%	0.7	6.185	3.98
	0%	1.2	6.194	6.82
5	100%	0.8	6.189	4.54
	75%	0.7	6.149	3.98
	50%	1.0	6.17	5.68
	30%	0.9	6.2	5.11
	10%	0.9	6.199	5.11
	0%	1.0	6.154	5.68

Visual observations

Small “micro-flocs” (Figure 129 & Figure 130.) were formed after the addition of the coagulant (aluminium sulphate) but without any addition of the flocculent (“Polyclay”). The addition of the flocculent increased these floc’s size until the dose of “Polyclay” reached approximately 50% of the plant treated batches dose. Beyond this point the floc size was visually indistinguishable from the 75% or 100% dose (Figure 131.). Similarly, the rate of settling of the flocculated particles appeared to be faster for Jartests with a higher addition of flocculent (Figure 132. & Figure 133.).

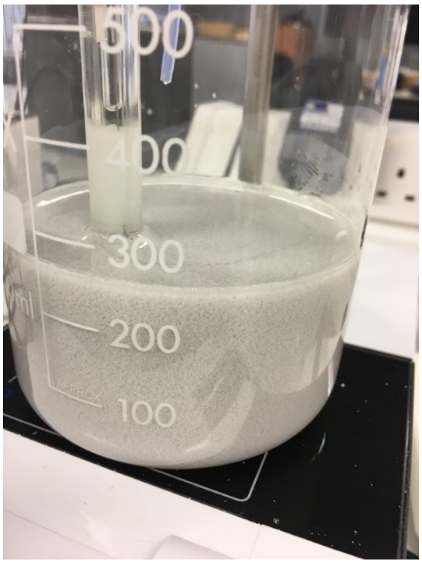


Figure 130: Example of "Floc" produced in a Jar Test with no "PolyClay" added.

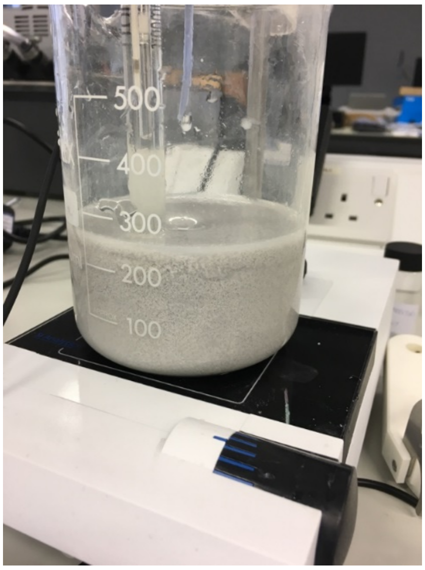


Figure 131: Example of "Floc" produced in a Jar Test with a full "PolyClay" dose.

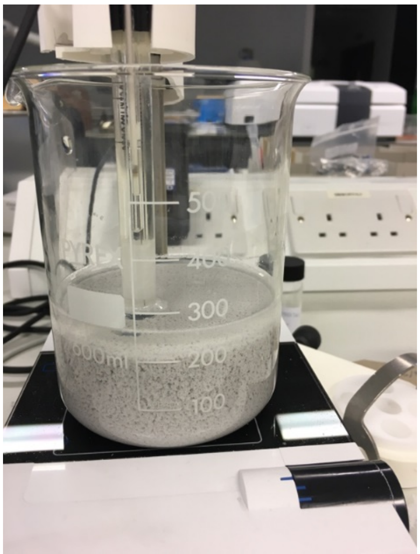


Figure 132: Example of settling within a Jar Test with no "PolyClay" added.

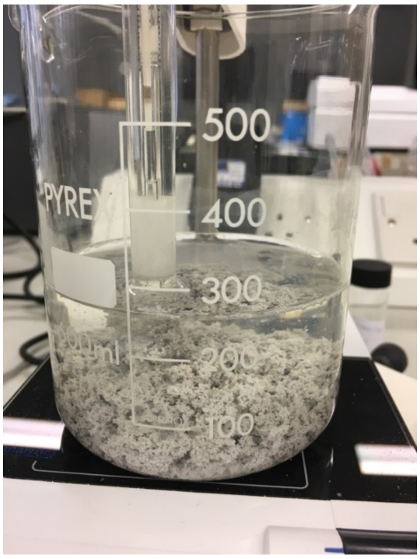


Figure 133: Example of settling within a Jar Test with a full "PolyClay" dose.

Settling Rate

The Jar Test Sedimentation method was found to be not suited to the material in question. Firstly, with all samples where "PolyClay" was added the "settling suspension" rose to the top of the measuring cylinder (Figure 134. & Figure 135.) rapidly (<2 s) at a virtually indistinguishable rate (i.e. no values for the rate were able to be recorded), the samples with no "PolyClay" dosed however, settled (Figure 136.) but at a much lower rate.

Figure 134: Photograph of a Jar Test sedimentation with a 100% "PolyClay" dose.

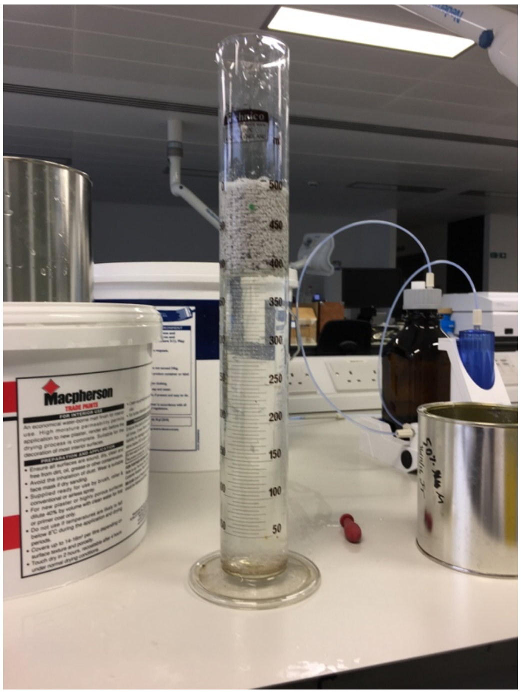


Figure 135: Photograph of a Jar Test sedimentation with a 50% "PolyClay" dose.

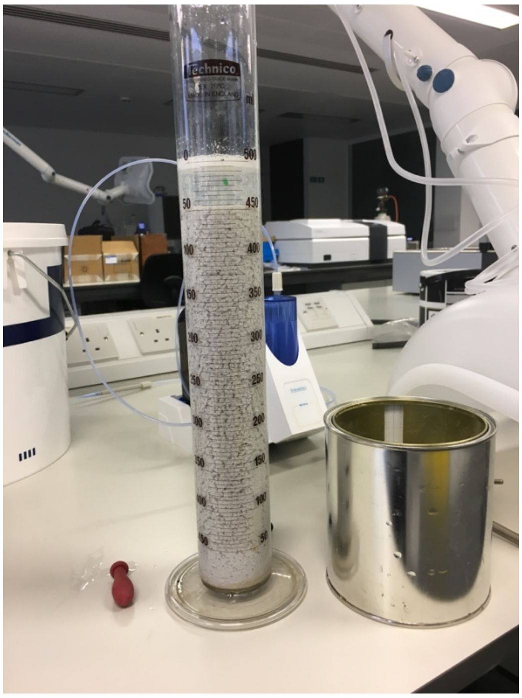


Figure 136: Photograph of a Jar Test sedimentation with no “PolyClay” added.

Other issues with the method include using a rod to mix the effluent which proved difficult to homogenize the effluent fully, it is possible that a motorized stirrer would improve this issue. However, this would likely introduce additional shear into the system and risk damaging the flocs. Video recording of the sedimentation process may also aid in recording the rate of sedimentation accurately. The author attempted to repeat the experiment using a “Go-pro” to video record the experiment, but the system wasn’t effective.

Conclusion

The ICP data suggested the concentration of all metals within all effluent samples were well below the consent level of “10,000 $\mu g\ l^{-1}$ individually or in total”. There was limited evidence of any effect (either chemically or physically) provided by the addition of “PolyClay”. Comparison of results with previous data suggest that the detected concentrations are particularly lower than expected. It was suggested that this is due to the filtration of the material before injection and thus the removal of the majority of the metals before analysis.

The analysis was therefore repeated with an amended method utilising an acid digestion within an aqua-regia solution (one-part nitric acid, three-parts hydrochloric acid) within a microwave digester to dissolve all the required metals before analysis. Such a method would also be suitable for filtercake analysis. Figure 137. illustrates a sample of raw effluent pre-treated via this method, notice the residual material at the base of the vessel which is believed to be talc (hydrated magnesium silicate), which can only be dissolved by hydrofluoric acid (HF). Due to the complexity and hazardous nature of microwave digesting a sample in HF at approximately 100°C when the composite elements of talc (i.e. silicone) are not of specific interest; this method is best avoided.

Figure 137: An acid digested solution of Raw Effluent.

Acid Digestion for ICP-OES analysis

Method

The method for acid digestion was adapted from the US Environmental Protection Agency (EPA) Method 3005A[121], for analysis of water samples:

1. A 10 ml aliquot of homogenised sample was transferred into a 35 ml microwave acid digestion vessel, 2 ml of concentrated HNO_3 and 5 ml of concentrated HCl was added. The vessel was then sealed with a pressure resistant cap.

2. The vessel was inserted inside a CEM Microwave Digester, and the temperature ramped to 100 °C over a period of 5 minutes, the temperature was held at a constant 100°C for a further ten minutes before being allowed to cool (Figure 138.).

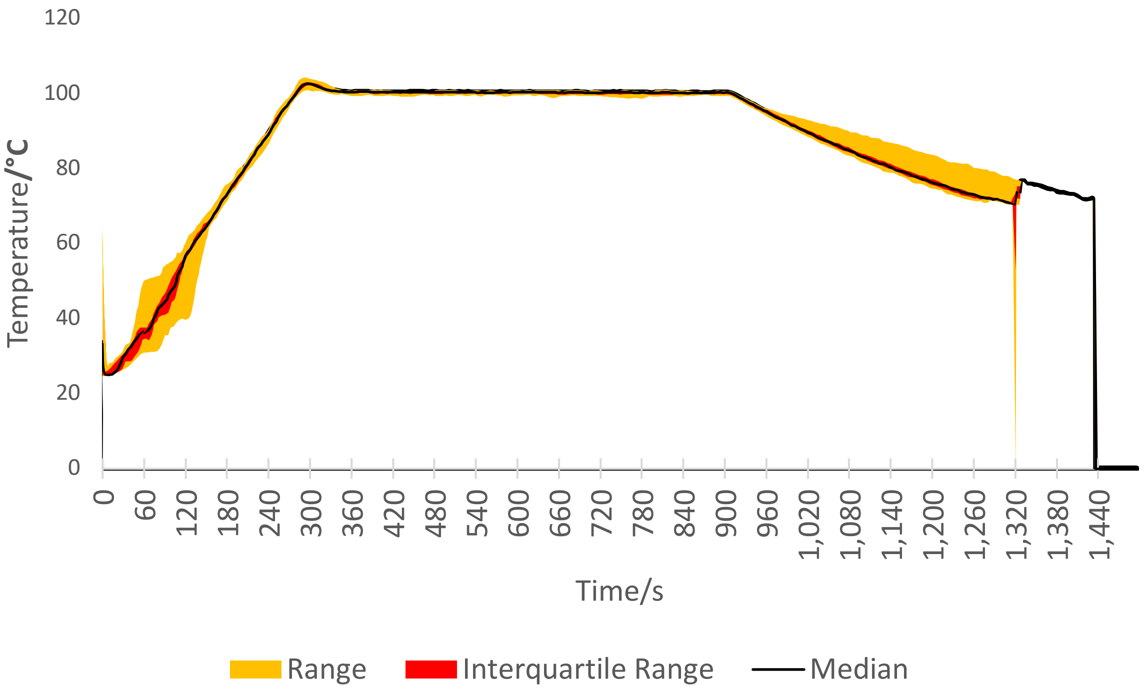


Figure 138: Acid digester temperatures during Jar Test and plant trial digestions.

3. The cooled solution was then decanted into a 100 ml volumetric flask and deionized water was added to adjust the final volume of the solution to 100 ml (an overall 10x dilution of the original sample).

4. An approximate 12 ml sample of the solution was decanted into a 15 ml centrifuge tube and centrifuged (Figure 139.) to remove any insoluble silicates (as in Figure 137.)which could clog the ICP's nebulizer.

5. The process was repeated for all samples, blanks and standards to matrix match the calibration standards.

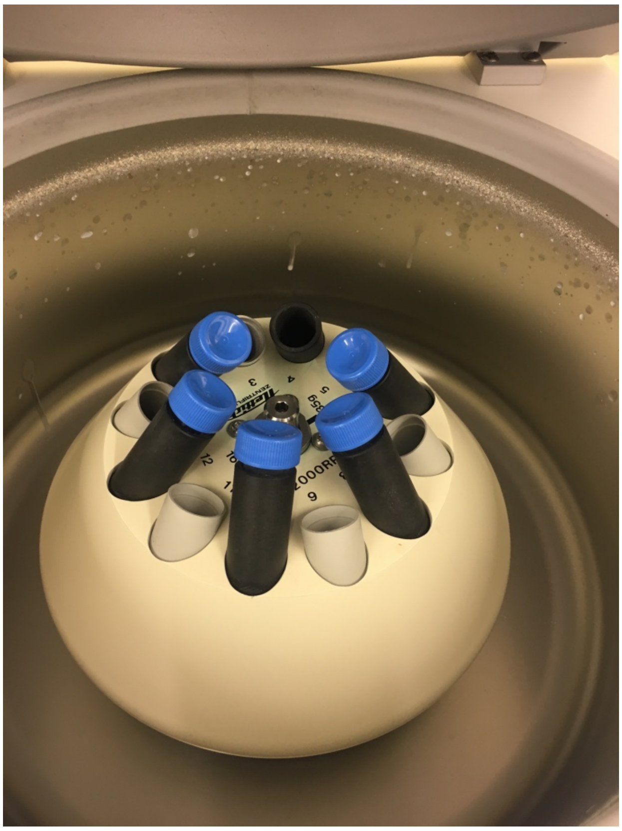


Figure 139: A series of samples in a centrifuge.

ICP-OES Analysis of Jar Test samples post Acid Digestion

Standards

Standard solutions (Table 18.) were produced by dilution of a 50 mg l^{-1} standard solution of the following elements (aluminium, arsenic, chromium, cobalt, copper, nickel, lead, selenium, strontium & zinc).

Table 18: Standard solutions for ICP-OES.

Standard	**Known Concentration, mg l^{-1}**									
	Aluminium	**Arsenic**	**Chromium**	**Cobalt**	**Copper**	**Nickel**	**Lead**	**Selenium**	**Strontium**	**Zinc**
Blank	0	0	0	0	0	0	0	0	0	0
Standard 1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Standard 2	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125
Standard 3	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Standard 4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Standard 5	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Standard 6	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Results

Notably, no quantity of the elements within the standard except for aluminium was detected in any of the effluent samples. Therefore, no trace of arsenic, chromium, cobalt, copper, nickel, lead, selenium, strontium or zinc was detected. Although Crown Paints' discharge consents (for either site) give a specific consent limit value for some of the metals listed above, aluminium contamination is not a concern within the either of the consents. Therefore, any reduction in flocculant dosage would not put Crown Paints at a compliance risk under their current discharge consents. On the caveat that the effluent complied with all other specification limits within the consents, for example the total suspended solids (TSS) and total dissolved solids (TDS).

Calculated concentration of aluminium in raw effluent samples

As aluminium is the only element detected within the samples the calculated concentration of aluminium is provided here. These values are for information and to record the findings of this work, however as noted above because the aluminium is not a concern in terms of the discharge consent, the impact of reduced flocculant dosage on aluminium concentration is of lower concern than would be of the other metals.

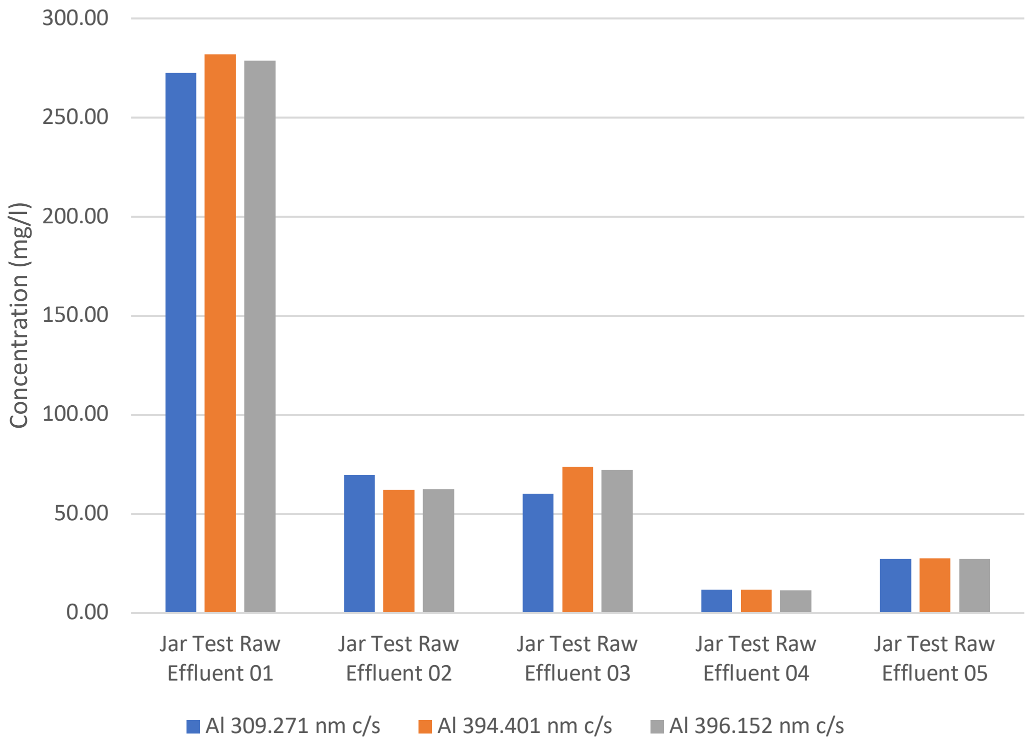


Figure 140: The aluminium concentration of Raw Effluent.

Table 19: The aluminium concentration of Raw Effluent.

	Al 309.271 nm c/s	**Al 394.401 nm c/s**	**Al 396.152 nm c/s**	**Mean**	**SD**
Jar Test Raw Effluent 01	272.40	281.94	278.82	277.72	4.86
Jar Test Raw Effluent 02	69.50	62.10	62.45	64.68	4.18
Jar Test Raw Effluent 03	60.19	73.89	72.18	68.75	7.47
Jar Test Raw Effluent 04	11.92	11.88	11.54	11.78	0.21
Jar Test Raw Effluent 05	27.45	27.65	27.24	27.44	0.21

Table 20: Changes in aluminium concentration.

		Al 309.271 nm c/s		Al 394.401 nm c/s		Al 396.152 nm c/s	
		Conc (mg/l)	**% Al Removed**	**Conc (mg/l)**	**% Al Removed**	**Conc (mg/l)**	**% Al Removed**
Plant Treated	**JT T01**	0.00	100.00	0.00	100.00	0.13	99.95
	JT T02	0.00	100.00	0.00	100.00	0.05	99.92
	JT T03	0.00	100.00	0.00	100.00	0.15	99.79
	JT T04	0.00	100.00	0.00	100.00	0.00	100.00
	JT T05	0.00	100.00	0.14	99.49	0.14	99.48
Batch 01	**JT 01 0%**	0.35	99.87	0.30	99.89	0.34	99.88
	JT 01 10%	2.12	99.22	1.85	99.32	1.95	99.30
	JT 01 30%	0.94	99.66	0.80	99.71	0.81	99.71
	JT 01 50%	0.00	100.00	1.15	99.58	1.10	99.61
	JT 01 75%	0.74	99.73	0.65	99.76	0.68	99.76
	JT 01 100%	0.00	100.00	0.00	100.00	0.08	99.97
Batch 02	**JT 02 0%**	1.32	98.10	1.25	98.21	1.29	97.94
	JT 02 10%	0.00	100.00	0.24	99.65	0.33	99.48
	JT 02 30%	0.43	99.38	0.30	99.56	0.36	99.43
	JT 02 50%	2.76	96.03	2.50	96.40	2.60	95.84
	JT 02 75%	10.80	84.46	10.74	84.54	10.61	83.02
	JT 02 100%	0.00	100.00	0.00	100.00	0.20	99.69
Batch 03	**JT 03 0%**	24.04	60.06	24.28	59.65	23.65	67.23
	JT 03 10%	1.67	97.22	1.60	97.34	1.59	97.79
	JT 03 30%	0.00	100.00	0.20	99.66	0.34	99.53
	JT 03 50%	0.78	98.70	0.74	98.77	0.86	98.80
	JT 03 75%	6.21	89.68	6.15	89.78	5.96	91.75
	JT 03 100%	0.00	100.00	0.38	99.36	0.35	99.52
Batch 04	**JT 04 0%**	39.18	-228.61	39.03	-227.32	38.47	-233.26
	JT 04 10%	10.77	9.66	11.28	5.37	11.09	3.92
	JT 04 30%	4.19	64.82	4.14	65.26	4.08	64.62
	JT 04 50%	0.89	92.54	0.99	91.70	0.93	91.92
	JT 04 75%	4.00	66.41	4.05	66.01	4.03	65.11
	JT 04 100%	1.06	91.07	0.96	91.95	1.04	90.99
Batch 05	**JT 05 0%**	60.26	-119.56	60.34	-119.86	59.65	-119.02
	JT 05 10%	18.96	30.92	18.93	31.03	18.46	32.20
	JT 05 30%	1.41	94.85	1.40	94.90	1.41	94.82
	JT 05 50%	0.00	100.00	0.00	100.00	0.20	99.26
	JT 05 75%	0.31	98.88	0.00	100.00	0.32	98.83
	JT 05 100%	1.22	95.56	1.49	94.57	1.53	94.39

Table 20. shows that the plant treated effluent removed 100% of the aluminium within the effluent. The Jar Test treated effluent was more inconsistent however, and the impact of “PolyClay” on the removal of aluminium is indeterminate based on the data from these Jar Tests.

In terms of this project the ICP-OES analysis provided confidence that any reduction in “PolyClay” dosing would not provide any risk of contamination of the discharged effluent by heavy metals and subsequent environmental issues. As the risk was seen to be low a plant trial to reduce the quantity of PolyClay used within the effluent process was scheduled.

For waste effluent streams containing more concerning metal contamination (e.g. As, Cd, Cr, Hg, Ni, etc.) the removal of this contamination would be of far greater interest and any attempt to vary the treatment process would necessarily require a greater focus on this.

5.3 Effluent Plant Optimisation Plant Trial

Following the laboratory-based Jar Testing, the experiment was scaled into a two-day plant trial at the Hull manufacturing site. This was organised for the 25th-26th January 2017, the aim was to match the plant's current method of work as closely as possible to observe any effect a significant decrease in “PolyClay” addition may have on the operation of the plant. The principal concern by plant operators and management at the commencement of the trial was the capability of the filter press to dewater the produced sludge effectively. This was highlighted as a limitation of the Jar Test methodology used within this chapter and resulted in the solution presented within Chapter 6.

5.3.1 Method

As the Effluent Plant’s standard method, once a volume of effluent substantial enough (>14,000 l) for a batch was built up within one of the EQ tanks a 500 ml sample was taken.

The sample was agitated to keep it homogenised and representative of the continuously mixed EQ tank. The “Solids” content of the sample was analysed through a solids analyser through a gravimetric method in which an approximately 5 g aliquot of the sample is dried at 130°C producing a calculated “percentage solids”. Using Table 12. the corresponding dosage of “PolyClay” was determined. A Jar test was then performed.

For this trial, once the suitable dose was determined the Jar test was repeated with an additional 500 ml sample. However, the pH was adjusted to 6.0 and the “PolyClay” dose reduced by approximately 50%. Squeeze tests were repeated on both Jar Tests, and the observations recorded.

The effluent was treated following the process detailed in Figure 123.:

n.b. whilst this method was idealistic it was necessary during the trial to amend the method slightly as detailed in the results section.

1. A 14,000 l batch of effluent was decanted into the Treatment tank and “Pre-mixed” for 60 s.
2. The aluminium sulphate was added to the solution until the crack pH of 6.0 was reached.
3. The coagulated solution was then “Post Mixed” for 120 s.
4. A dose of “PolyClay” was added approximately 50 % lower than the standard “Polyclay” dose as determined in Table 12..
5. The mixture was then “Powder Mixed” for 300 s to insure the hominization of the “PolyClay”.
6. A “Final Mix” was then performed for 120 s.
7. The “Final” pH was recorded.
8. The mixture was left to settle for a period of 300 s.

Following the Treatment process:

9. The supernatant was pumped from the Treatment tank and filtered through the Bandfilter.
10. The resulting settled sludge was pumped into the settling tank after which it was subsequently pumped into the filterpress.
11. Additional bathes were repeated until the filter press was filled (approximately 2-5 batches depending on the solids content of the effluent).
12. The filter press was activated compressing the sludge to form a filtercake.
13. The filtrate then was clarified through the Bandfilter.

A simplified process diagram of the Hull effluent plant optimisation trial is provided in Figure 141.

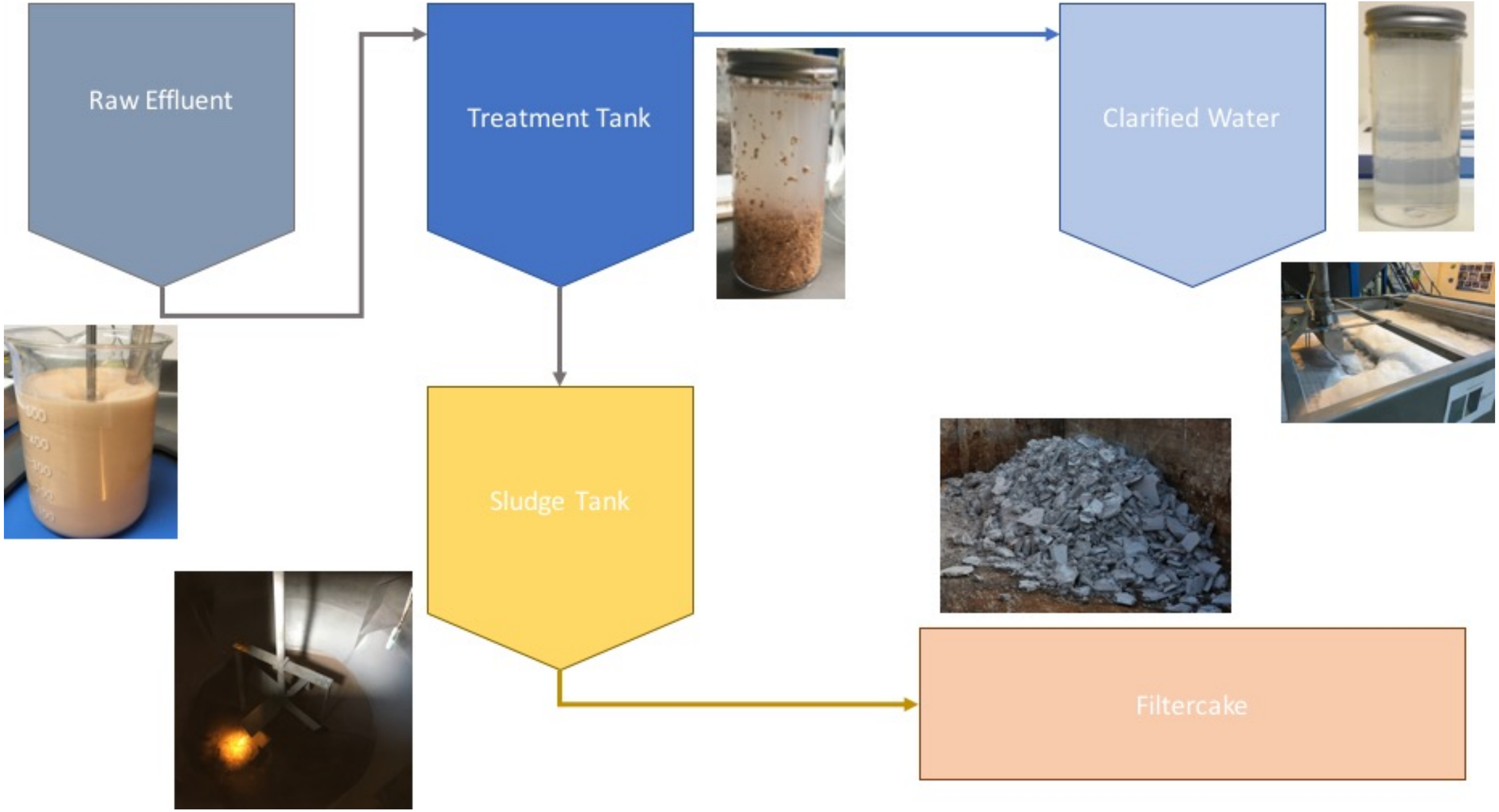


Figure 141: A simplified process diagram of the optimisation plant trial.

Results

Table 21: Overview of Treated Batches during the Trial.

Batch	Date	Start Time	Effluent volume/m^3	Water/m^3	% "Solids"	Standard Dose/ kg	Treated Dose/ kg	% of Standard "PolyClay" Dose	Approx. cost saving
1	25/01/2017	13:28:35	12.78	1.42	2.46	35	21	60	£16.80
2	25/01/2017	15:16:20	14.2	0	2.72	42	21	50	£25.20
3	26/01/2017	07:53:18	14.2	0	2.25	35	18	51	£20.40
4	26/01/2017	09:32:04	14.2	0	2.25	35	18	51	£20.40
5	26/01/2017	11:41:52	14.2	0	3.16	42	15	36	£32.40
6	26/01/2017	14:55:07	14.2	0	3.16	42	15	36	£32.40
7	26/01/2017	18:02:20	14.2	0	3.16	42	15	36	£32.40

Table 21. shows the data recorded through the effluent plant’s operating system during the trial period. The approximate cost saving for each batch is based on the assumption of 1,000 kg of “PolyClay” costing £1,200.

5.3.1.1 Batch 1

Very little effluent was available during the first day of the trial due to previous batches being treated earlier in the day and a relatively low stream of incoming effluent in the afternoon. Once a sufficient quantity of effluent for a batch (14,000 l) was obtained in one of the EQ tanks (this first occurred in EQ2) a sample could be taken.

The solid analysis of the first batch (2.46 %) corresponded to a standard dose of 35 kg (or 2 g in the 500 ml scale Jar Test) of “PolyClay”. However, following the “squeeze test”; where the material failed to form a dewatered clay, the plant operator suggested that a larger amount of “PolyClay” would normally be added (estimated to be 42 kg) through the standard method. The Jar test was then repeated with a dose equivalent to 42 kg (1.5 g) however the subsequent squeeze test also failed to form a suitable clay. It was then decided to dilute the batch with 10 % virgin water. This was suggested by the operator as a normal deviation from the standard method. Due to the potentially problematic nature of this batch it was decided to treat the effluent with a dose of 21 kg of “PolyClay” equivalent to 60 % of the recommend dose detailed in Table 12. Though as mentioned previously as in reality due to the Jar Test results the standard dose would normally be increased to 42 kg (making the trial dose equivalent to a 50 % of this dose).

Figure 142:Batch 1 Jar Test (raw effluent).

Figure 143: Batch 1 Jar Test (settled).

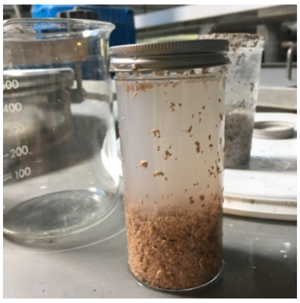


Figure 144: Batch 1 Final Mix.

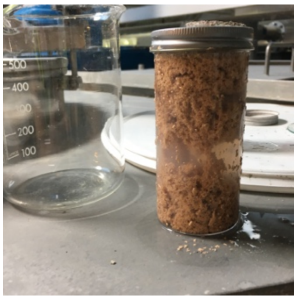


Figure 145: Batch 1 Final Mix (post agitation).

Figure 146: Batch 1 filtration of supernatant through the Bandfilter

Figure 147: Batch 1 sludge on the Bandfilter

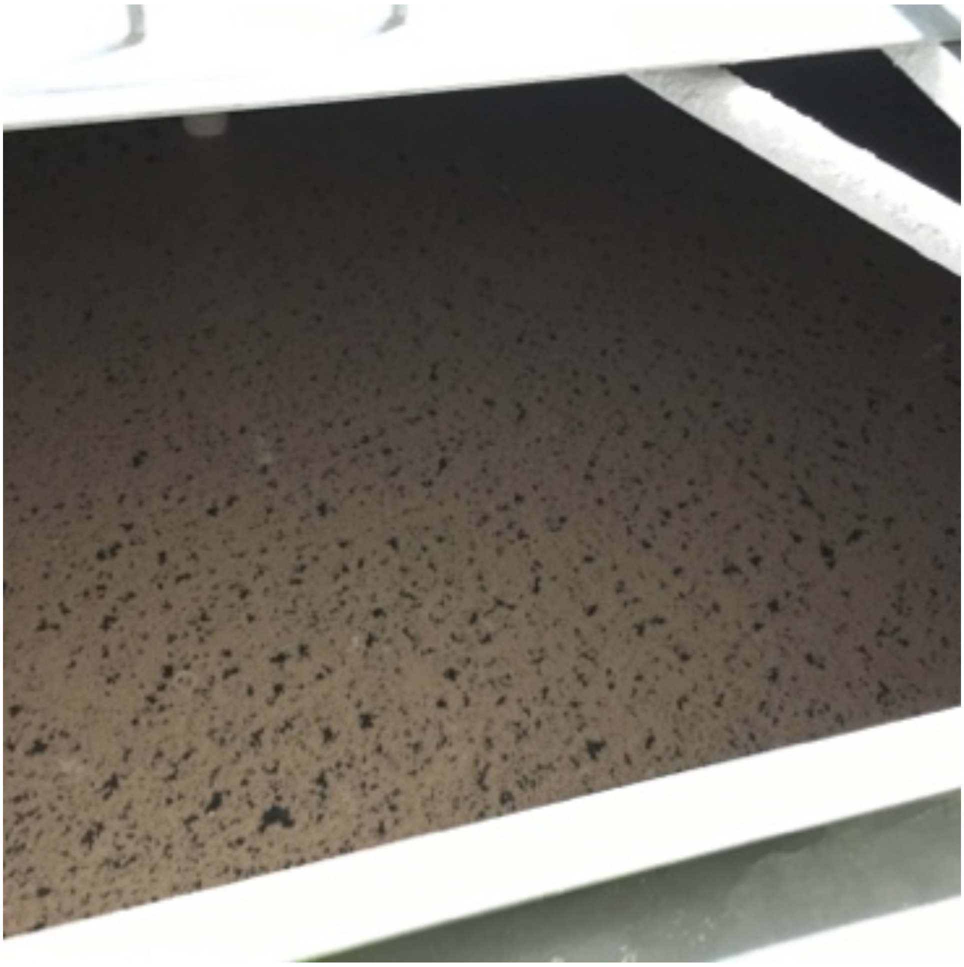


Figure 148: Batch 1 floating layer of flocculated material

Once flocculated within the treatment tank the “flocs” floated to the surface of the tank (Figure 148.) and it was noted by the operator that they also appeared smaller than normal. A sample (Figure 144.) of the treated effluent was taken before the final settling stage. This flocculated sample did settle as expected (contrary to what was observed within the treatment tank). However, when agitated (through simply shaking the container) a substantial quantity of flocculated material rose to the surface of the vessel (Figure 145.) presumably mirroring the effect within the treatment tank. Small bubbles were seen below the floating flocs suggesting pockets of air being trapped by these smaller flocs which is in turn lowering their relative density and causing them to float.

An issue then arose when the supernatant was decanted from the treatment tank. This floating layer was removed with the clarified water as seen in Figure 146., leaving a large deposit of sludge on the Bandfilter (Figure 147.). Through normal operation it is inevitable that some flocs will be decanted along with the supernatant (and the Band filter’s purpose is after all to remove these stray particulates), this quantity however was seen to be problematic by the operator.

Eventually, the supernatant ran clear (Figure 149.) once the whole of the “floating layer of floc” had been removed. A sample of this clarified water was taken (Figure 150.).

Figure 149: Batch 1 clear clarified water.

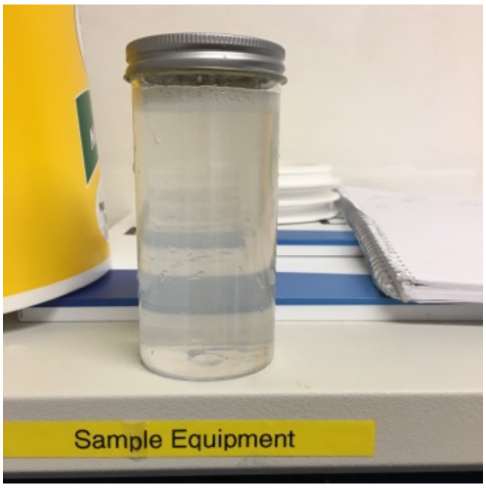


Figure 150: Clear clarified water sample.

Also, of note the distinctive terracotta colour of the effluent matched closely with the Standex masonry paint being produced on one of the lines. It is possible that this formulation may have a different effect to the standard matt effluent stream usually passing through the plant.

5.3.1.2 Batch 2

Following Batch 1, the trial remained limited by the volume of effluent available to treat and the thus the second batch moved to treat effluent from EQ tank 1.

The “PolyClay” dosage was far more simplistic for Batch 2 (compared to Batch 1); the solids content of 2.72 % corresponded to a standard dose of 42 kg which formed a good cake during the “squeeze test”. The treated dose was reduced by 50 % to 21 kg and subsequent Jar Test performed. The sludge produced (in the Jar test) with this reduced dose did not form a dry “claylike” cake during the “squeeze test” however the decision was made to continue to treat the batch with the reduced dose of “PolyClay”.

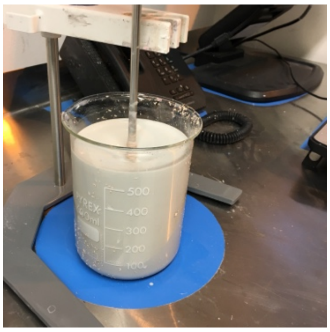


Figure 151: Batch 2 Jar Test (raw effluent).

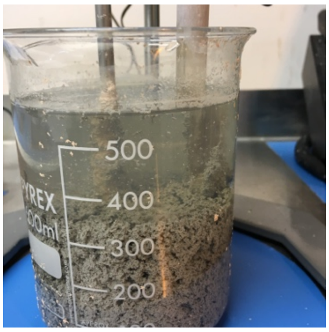


Figure 152: Batch 2 Jar Test (settled).

Figure 153: Batch 2 floating layer of flocculated material.

Figure 154: Batch 2 Final Mix (post agitation).

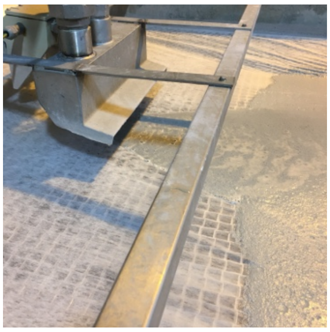


Figure 155: Batch 2 filtration of supernatant through the Bandfilter.

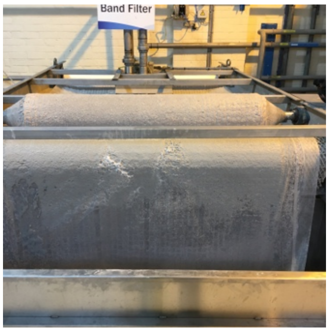


Figure 156: Batch 2 sludge on the Bandfilter.

Figure 157: Quantity of sludge being removed via the Bandfilter.

Similarly, to Batch 1., once treated within the treatment tank a substantial proportion of the flocculated particles floated to the surface of the vessel (Figure 153.). However, this appeared to be a much greater issue with this batch (Batch 2.) with a far larger volume of sludge decanted onto the Bandfilter (Figure 155. & Figure 156.) than with the previous batch (Batch 1.). This resulted in the skip used for collecting the used Bandfilter cloth to fill with sludge from the process (Figure 157.). Whilst this sludge eventually ended up being added to the effluent cake skip it still contained a high proportion of liquid (having not being fully dewatered itself). This would later have an adverse effect on quantity of effluent cake being disposed of. Another disadvantage of trying to decant this quantity of sludge and thus soiling the Bandfilter is the extra volume of cloth consumed. It is worth noting however that this extra cost would be minimal and that by even using a roll of filter cloth a day rather than a week (at the present consumable rate) would still have a lower cost than the potential saving of a 50% reduction in “PolyClay” useage.

As with Batch 1., eventually the decanted water ran clear (though with some discolouration Figure 158.); suggesting a stratified layer of floating material rather than this floating sludge being homogenized through the tank.

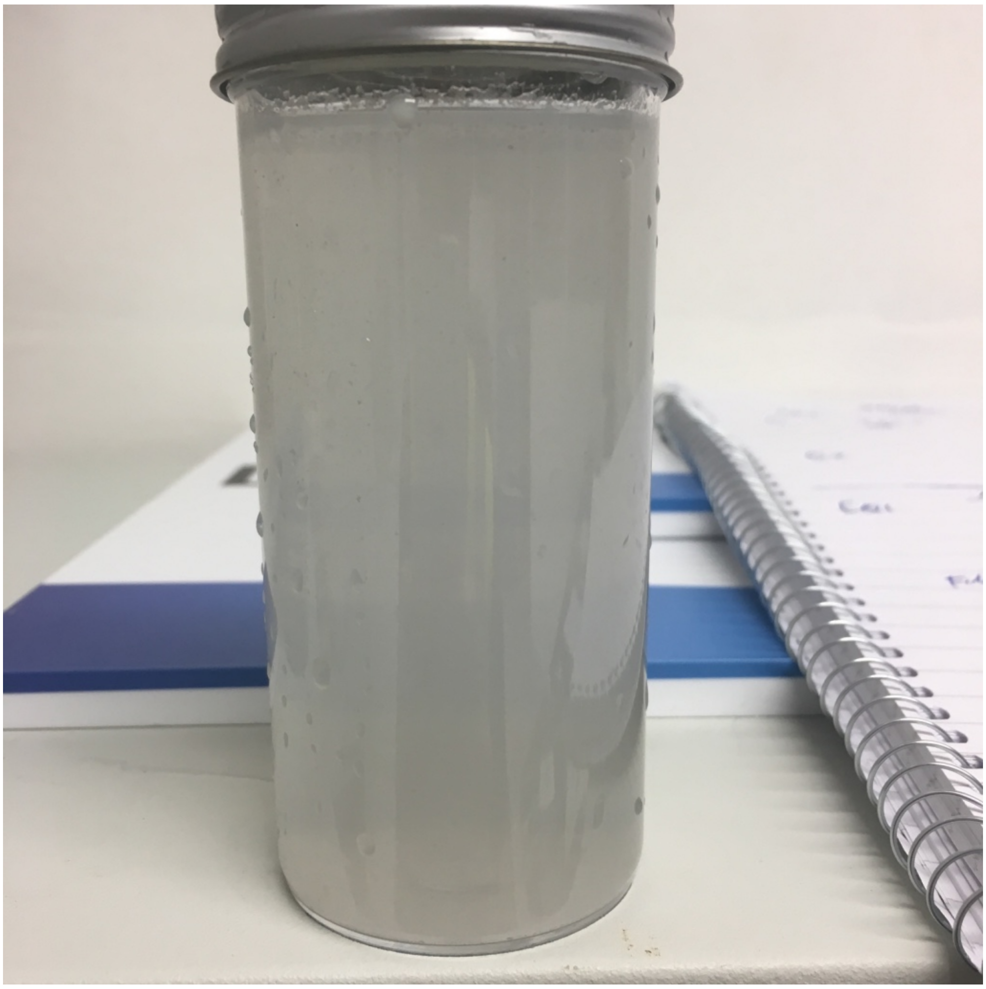


Figure 158: Slightly discoloured clarified water sample.

5.3.1.3 Filter cake 25th January

The two batches (Batch 1. & Batch 2.) conducted on the 25th January, approximately filled Filterpress 2. and it was decided to activate the filterpress to dewater the sludge produced. Despite initial reservations from the production team, the cake formed reasonably well, and a relatively dry non sticky filtercake was produced. Visual comparison between the cake produced during the trial batches and the filtercake from Press 1 (not used in the trial) suggested a slightly drier filtercake from Press 1, however this difference was negligible. Samples of the two filtercakes were homogenized and their percentage solids analysed using the same method as with the liquid effluent (Table 22.). The solids content was shown to be lower in the filtercake produced by the trial (Batch 1. & Batch 2.) than with the previous batches with a standard dose of “Polyclay” (44.38 % and 55.5 % respectively), however it was noted that because the press was not totally full the pressure placed onto the filtercake would be less and thus the dewatering couldn’t be totally representative. A sample was then taken from the filtercake produced at the front of Filterpress 2., where the pressure would be greatest which had a solids content higher than the homogenized sample from Press 1. (unfortunately, a front of press sample for Press 1 was unavailable for comparison).

Table 22: Solid content of Filtercake from trial on 25th January 2017.

	Press 1 Homogenized	**Press 2 Homogenized**	**Press 2 (Front of press)**
% Solid	55.5	44.38	57.75

Whilst these results may be inconclusive, they did show that an adequate cake may be produced with a reduced “PolyClay” dose without any of the feared dramatic effects on the press.

5.3.1.4 Batches 3 & 4

The following day a far larger volume of effluent was available for treatment within the EQ tanks. A 500 ml beaker sample from EQ 2.’s solid content was found to be 2.25 % corresponding to a standard 35 kg “PolyClay” dose. Results from the Jar test and “squeeze test” were positive and the actual dose was reduced to 18 kg (51 % of the standard dose. Following a repeat of the Jar Test with this new dose, the “squeeze test” was not as successful and the cake remained sloppy.

Figure 159: Batch 3 samples of the Treated Effluent (final mix) and clarified water.

Instead of decanting the clarified water through the Bandfilter it was decided to pump all the sludge out and divert the mixture through the Filterpress (in a process known simply as “diverting through the press”). This prevented the issues associated with the Bandfilter however the process’s time was greatly increased. Although unusual the operators confirmed that this method was sometimes used in the plant at present.

As Batch 4 was taken from EQ2 immediately after Batch 3 had been pumped into the sludge tank it was assumed to be identical and treated in exactly the same manner.

Figure 160: Batch 4 Final Mix

(post agitation).

Figure 161: Clarified Water samples

(left Batch 3., right Batch 4.)

5.3.1.5 Batches 5,6 & 7

Following Batches 3 & 4, the operator hypothesised that perhaps the floating floc effect was caused by too much “PolyClay”, although this was deemed unlikely a decision was made to lower the “PolyClay” dose even further.

Solids analysis of the effluent in EQ 1. (3.16 %) suggested a standard “PolyClay” dose of 42 kg it was however decided to treat the effluent with a dose of 15 kg (equivalent to 36 % of the standard dose). Notably the shifts changed whilst Batch 5 was being treated and the process resulting in a flocculated sludge that again didn’t settle (Figure 162.), the new effluent plant operator was reluctant to divert the whole treatment tank’s contents through the Filterpress and offered an alternative solution: the addition of defoamer (Dispelair CF 515- a mineral oil) to cause the flocculated particles to sink. The mixture was agitated for a further 3 minutes and approximately 8 l of Dispelair was added into the treatment tank, the result was startling with none of the previous floating floc layer remaining at the surface.

The same process was then repeated for Batches 6 & 7.

Figure 162: Batch 5 Final Mix (post agitation).

5.3.1.6 Comparison of Water samples

Figure 163: Treated Effluent (final mix) Batches 1-5 (left to right).

Figure 164:Clarified water samples Batches 1-5 (left to right).

5.3.1.7 Filtercake 27th January

Following the trial both Filterpress were emptied the following morning. The filtercake produced was very sludgy and described as oily with fine flocs, which were subsequently difficult to be cleaned off the press (Figure 165.). As this cake was notably more difficult to remove it would suggest that the dosage used with batches 5,6 & 7 (36 % of the standard dose) generated a floc with a size sufficiently small to cause clogging issues with the filter's pores. The oily effect it is suggested is most likely due to the addition of the defoamer (a mineral oil), which should ideally be avoided.

Figure 165: Sludgy & oily Filtercake, 27/01/17.

5.3.2 Conclusions from Hull trial

The trial at Crown Paints Hull effluent plant showed that it was feasible to lower the “PolyClay” to approximately 50 % of its current dosage without any catastrophic effect on the Effluent Plant or Filterpress. However, it also showed that adverse effects do occur due to this lower flocculant dose; predominantly the floating of the flocculated particles however this can be mitigated through diverting the sludge directly through the Filterpress (although this has an adverse effect on the speed of the process).

Unknowns highlighted through this trial include the effect of this reduced “PolyClay” on the solids concentration and thus volume of filtercake produced, the impact on additional Bandfilter cloth useage and the actual time constraint of having to divert all the material through the Filterpress. To quantify these unknowns, the recommendation was to conduct the trial over a longer period (of at least a week however a period of 4-6 weeks was identified as preferable). This would enable the recording of the number of batches, quantity of cake, number of used Bandfilter clothes used etc. and the effect to the holistic process ascertained. Crown Paints however were concerned with the increased time pressures the change in the process may place onto the plant and thus there was limited motivation to continue the “Polyclay” reduction trial further.

As a point of note, observation of the batch data from across the week beginning 23/1/17 (the week of the trial) suggest despite the increased time pressure of diverting both the supernatant and the sediment through the Filterpress (for two batches during the morning) did not appear to have any impact on the number of treated batches that day. Figure 166. shows that five batches of effluent were treated on the 26thJanuary (the only day where the decanting stage was bypassed) as opposed to four on the other days (where data was available). Figure 167. shows a lower total discharge volume from the plant on the 26th January (50,690 l) compared to 25th (55,530 l) but slightly higher than the 23rd and 24th (48,570 l & 49,240 l respectively). The apparent discrepancy between the two values is likely due to residual batches being left in the treatment tank/sludge tank overnight for the next shift to process in the morning thus varying the time at which the water is actually discharged.

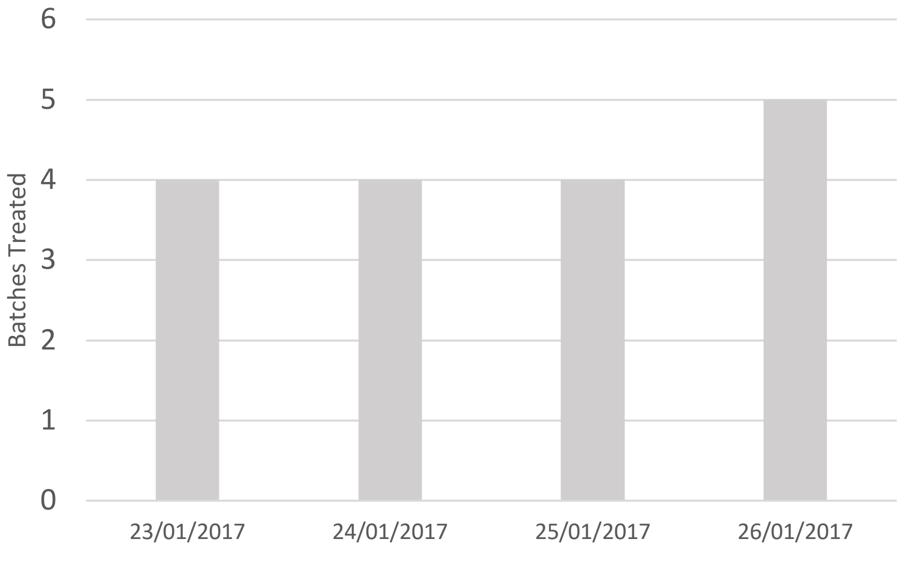


Figure 166: Number if treated batches week beginning 23/01//17

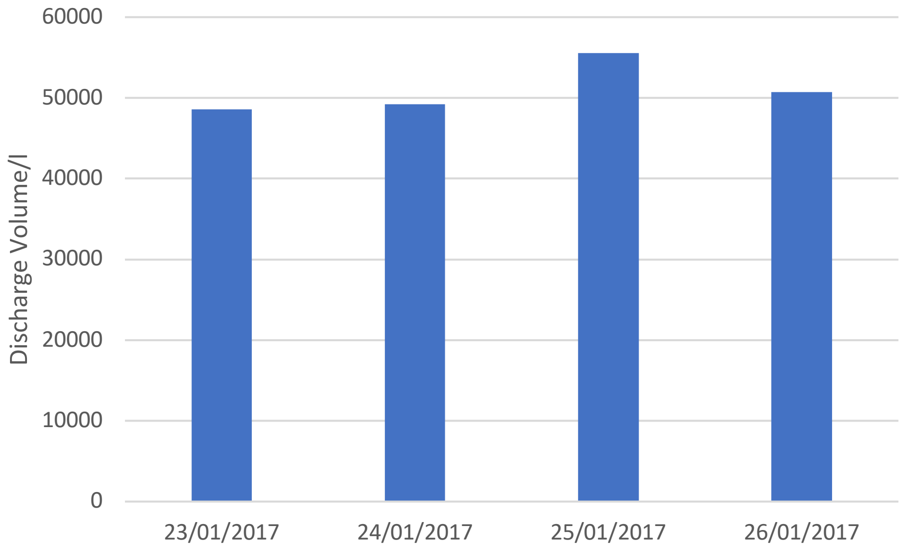


Figure 167: Volume of discharged water week beginning 23/01//17

Although the bypassing of the decantation stage of the process is obviously more time consuming the data available does not suggest this additional time pressure had a significant effect on the volume of effluent treated during this trial.

5.4 Conclusions of optimisation project.

The Jar Tests suggested that it is possible to form flocs following coagulation with aluminium sulphate without the need for an additional flocculent (“PolyClay”) however this does visibly reduce the size of the flocs, which resulted in a reduced settling time and potential Filterpress issues. Before the plant trial the impact on the filtration of the material was the biggest concern for the production team at Crown Paints Hull site. Reduction of the dose of flocculent to approximately 50% does not have a significantly visible effect on the particle size or its settling time in a Jar Test environment. However, the scale up of the process to a full-scale plant trial suggested an increase in the volume of a “buoyant floc” which presented a challenge within the settling tank. Alternatively, this “buoyant floc” can be dewatered directly within the Filter Press, however this additional change to the process increased the concerns of the production team.

Ultimately, there was limited motivation to continue this optimisation trial due to the perceived impact of the reduction of flocculant on the Filterpress process and a fear of increased process time.

Although it was decided not to continue to optimise the process further, the “buoyant floc” may have a positive effect if Dissolved Air Floatation (DAF) dewatering systems were to be explored[122,123].

Importantly, the scale up of the process from a laboratory-based Jar Test to a full-size plant trial demonstrated some limitations of the Jar Testing methodology with this material (aqueous based paint effluent). Settling rate measurements were not possible and the Jar Test methodology didn’t provide any evidence of the ability to dewater the suspension. Therefore, any concerns regarding the impact on the filtration process could not be addressed before the plant trial. A significant improvement of the Jar Test methodology is described in Chapter 6., using a bespoke stepped filtration device (essentially a scaled down filter press) and subsequent analysis of the physico-chemical parameters observed. This methodology directly aimed to minimise the limitations of the Jar Test system observed here.

6 STEPPED FILTRATION METHOD

This chapter is based on the preprint Wardrop et al.[1] describing a novel stepped filtration method (the graphical abstract is shown in Figure 168.). Additionally, an overview of the background of stepped pressure filtration is provided in Section 2.2.6.2.

The work described in this chapter aims to provide three objectives. It presents a new simple design of a benchtop pressure filtration apparatus. Additionally, this equipment can be used relatively easily to predict a filtration process, for both Jar Test experiments and the evaluation of a process at plant scale. Finally, a mathematical model is presented to demonstrate how the compressive yield stress, ***Py(c)*** and resistivity, ***r(c)*** of a filtration process can be determined in a single experimental run, thus improving on the two test run method described by De Kretser et al.[101]. Ultimately, these three outcomes provide a method which has significant opportunity to aid both academia and wider industry in understanding filtration processes.

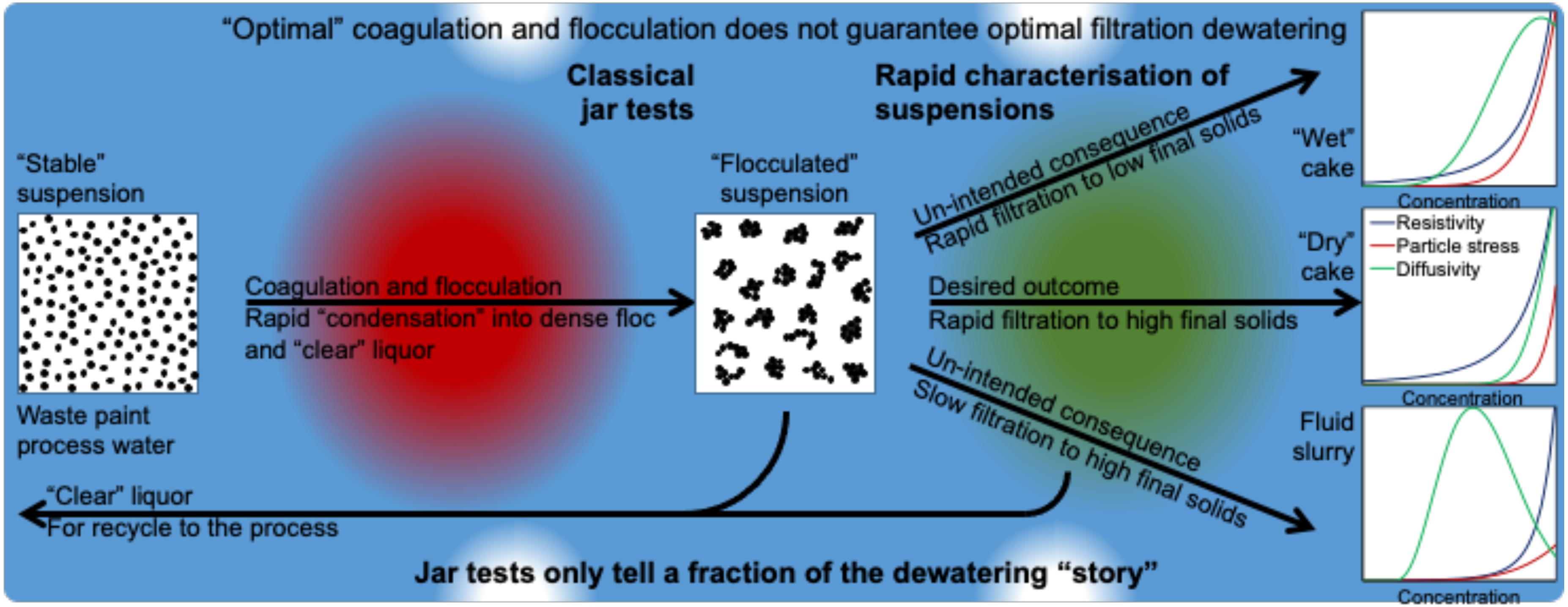


Figure 168: The Graphic Abstract accompanying Wardrop et al. [1]

6.1 Overview

To model the impact of the trial described in Chapter 5. a simple device to conduct stepped pressure filtration measurements was developed. A significant limitation identified of the optimisation trial described in Chapter 5. was that the Jar Test methodology proved to be extremely subjective in understanding the behaviour of generated flocs, whilst the effluent plant trial identified a key area of concern regarding the pressure filtration stage of the effluent treatment process. A method to readily simulate the filtration process on a smaller scale was therefore highly valuable. An analytical device based on similar equipment devised by in Green et al[100] and De Kretser et al [101] was developed for this purpose. This proved an effective means to fully characterise the filtration process for samples (approx. 80 ml) produced at Jar Test size scale (500 ml). From the perspective of the KTP project, this Chapter provides a solution for the third identified deliverable of the KTP project (from 1.3) as a method to study the filtration process which was neglected in the trial described in Chapter 5.

The advantage of the method described is that it presents a laboratory simulation of the filtration process while providing detailed monitoring of the filtration properties. Unlike the devices of Green et al[100] and De Kretser et al [101] the device described here is also gravitationally driven which provides advantages by avoiding pressurised systems. Multiple runs of a pressure filtration experiment can be arduous. Mathematically, this method also combines the need for two separate runs to determine ***Py(c)*** and ***r(c)*** into a single run.

The work described in this Chapter (and additionally in Wardrop et al[1]) represents the second highlighted novel outcome of this research (1.1.1.), which could arguably be separated into three separate "contributions to knowledge". The unique design for the stepped pressure filtration apparatus is especially innovative, utilising a precise gravity driven pressure system unlike the air pressurised systems of previous work. Additionally, the method presented to characterise the compressive yield stress, ***Py(c)*** and resistivity, ***r(c)*** of a filtration process using only a single experimental run is a completely original element of this research. Finally, no literature could be identified with the application of stepped-pressure filtration or any characterisation of effluent containing emulsion paint. And thus, a study into the filtration parameters of paint based effluent is unique to this work.

Returning to the "Hierarchy of Solutions" presented in Figure 112. this device was primarily used to statistically justify any optimisation of the current process. It also has a potential application in comparing physico-chemical parameters (e.g. compressive yield stress) of other dewatering technologies with pressure filtration such as centrifugation with a methodology such as described in Yeow & Leong[124].

The design of this unique apparatus is described together with methods for making the empirical measurements and interpreting the data obtained. The data interpretation method applies a multi-step systematic approach, with each step supported by statistical justification, to characterise filter cake particle stress, filtration diffusivity and cake hydraulic resistivity from a single stepped pressure experiment. The methods enable different flocculant materials to be more rapidly and more appropriately screened than conventional jar tests and large-scale filtration trials. The methods are applied to the characterisation of a paint residue treated with aluminium sulphate and “PolyClay”.

The work shows that the addition of “PolyClay” as a filter aide reduces the hydraulic resistivity at lower solids concentrations but increases it at higher concentrations whilst simultaneously increasing the particle stress. Together these have a combined deleterious effect on the time and energy required to dewater the residues to high solids concentration by filtration. The results also show that a significant change in suspension behaviour occurs between the “PolyClay” doses of 140 mg l^{-1} and 660 mg l^{-1} and that further changes up to “PolyClay” doses of 1600 mg l^{-1} are more modest. The results indicate the existence an opportunity to reduce “PolyClay” dose into a range between 10% and 50% of current practice. In addition, the results provide evidence that alternative, centrifuge based, technology is worthy of investigation.

6.2 Background

Particulate suspensions are a common by-product or process intermediate in many industrial processes. It can often be advantageous to separate these suspensions into their constituent raw materials to increase the economic viability of a process. Multiple processes exist to enable this such as filtration, evaporation, and centrifugation. Worldwide the coatings industries make extensive use of “engineered” suspensions whose properties make any wastes or residues arising difficult to treat or successfully recycle. Water borne paints have helped to reduce the environmental impact associated with solvents but achieved little with regard to the solid polymers, pigments and adjuncts. The costs of disposal of treated wastes are typically levied in accordance with the wet mass. “Aggressive” treatment processes designed to maximise the elimination of water typically have the coincident effect of rendering both the solids and the water more difficult to recycle.

Crown Paints is a major UK based decorative paints manufacturer. As is typical for large fast moving consumer goods, “FMCG”, manufacturing processes are generally batch or short run continuous. Such operations typically give rise to high volumes of waste from cleaning and product change over activities. Continuous, commodity, minerals processing operations also give rise to substantial quantities of waste materials in the form of suspensions. These residuals by their nature and quantity must be safely disposed of in the environment. This activity necessitates understanding the characteristics of the suspensions in order to cost effectively dewater and subsequently safely store the resultant cake. A key waste stream arising from Crown Paints’ manufacture of water based paints is process washings. The company currently dewaters this material via a conventional coagulation using aluminium sulphate followed by flocculation with a modified bentonite clay, "PolyClay" and finally a pressure filtration process.

6.2.1 Characterise the resistance of a flocculated suspension

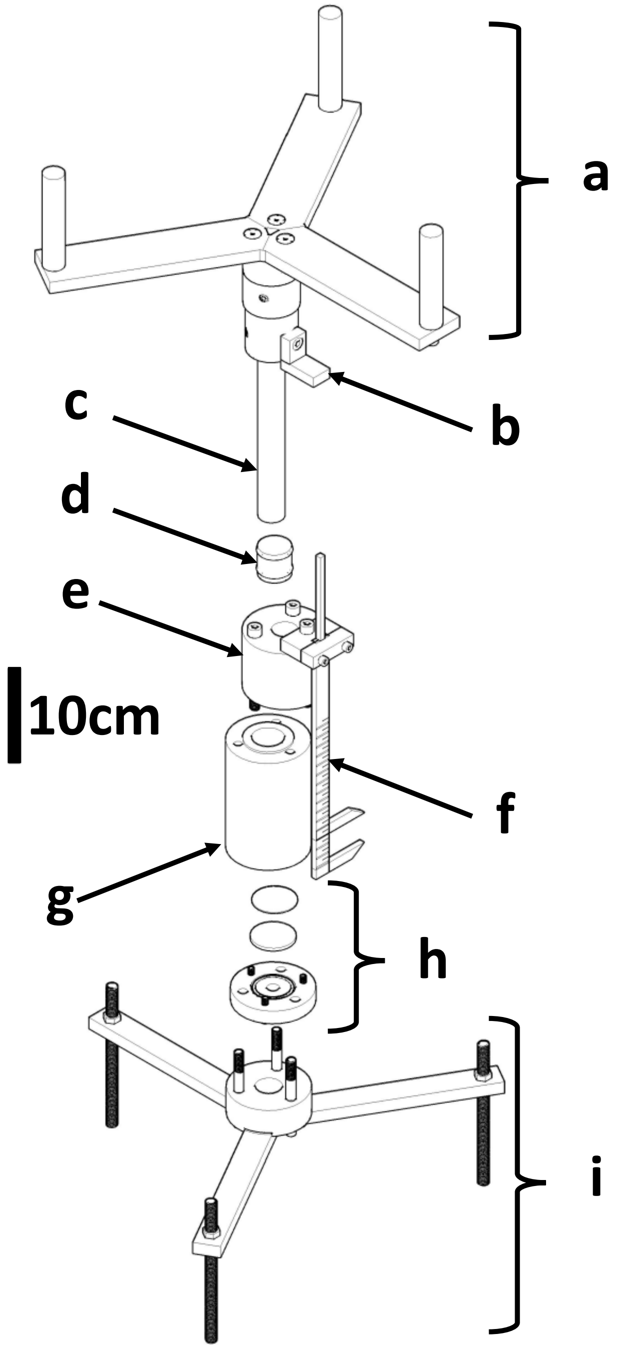
Buscall and White[95] developed the idea of compressive yield stress, ***Py(φ)*** to characterise the resistance of a flocculated suspension to further compression. It defines the minimum pressure required to obtain a filter cake of specific volumetric concentration, ***φ***. ***Py(φ)*** was expected to be dependent on the arrangement of interparticle interactions. In this work the volumetric concentration, ***φ***, is substituted for the mass concentration analogue, ***c***. A sample suspension of concentration, ***φ*** or ***c*** is contained within a device comprising a cylinder closed at top with a piston and at the bottom with a porous membrane to yield an initial suspension height, h_0 . A differential, filtration pressure, ***ΔP*** is applied to the piston driving the filtration process (typically in specific pressure steps hence "stepped pressure filtration"), forcing the liquid through the filtration membrane. After a sufficient time period the system reaches an equilibrium condition where the pressure from the piston is fully supported by the structure of the filter cake. Replicating this process over multiple pressures is used to characterise the ***Py(c)*** curve. The hydraulic resistivity, ***r(c)*** whose reciprocal is commonly termed the "permeability" is characterised by the product of the hydrodynamic drag on an isolated particle, r_0, and the so-called hindered settling function. this parameter characterises hydrodynamic resistance to flow through the suspension network structure as a function of solids concentration. Established methods to determine ***Py(c)*** and ***r(c)*** experimentally are variously described by De Kretser et al [101], Kynch [125] and Landman and White [98].

As performing multiple experiments to determine ***Py(c)*** and ***r(c)*** is arduous and time consuming, a stepped filtration method to reduce characterisation time was proposed by De Kretser et al [101] and validated by Usher et al[126] (as described in 2.2.6.2). A typical stepped pressure filtration method requires two runs to fully characterise a sample (one to determine ***Py(c)*** of the sample at a range of pressures and the other the permeability/hydraulic resistivity, ***r(c)***. The method described here, takes the next logical step to simplify the method into a single filtration test.

A filtration device was designed and built based on the designs in Green et al[100] and De Kretser et al[101]. Modifications to those designs include the accurate delivery of a specific pressure gravitationally (via water dosing) rather than via a pneumatic cylinder.

6.3 Filtration apparatus

The filtration device was designed and built by J. Wardrop & P. R. Fielden.



Where:

a, barrel assembly;

b, digital calliper stop;

c, plunger;

d, piston;

e, plunger guide;

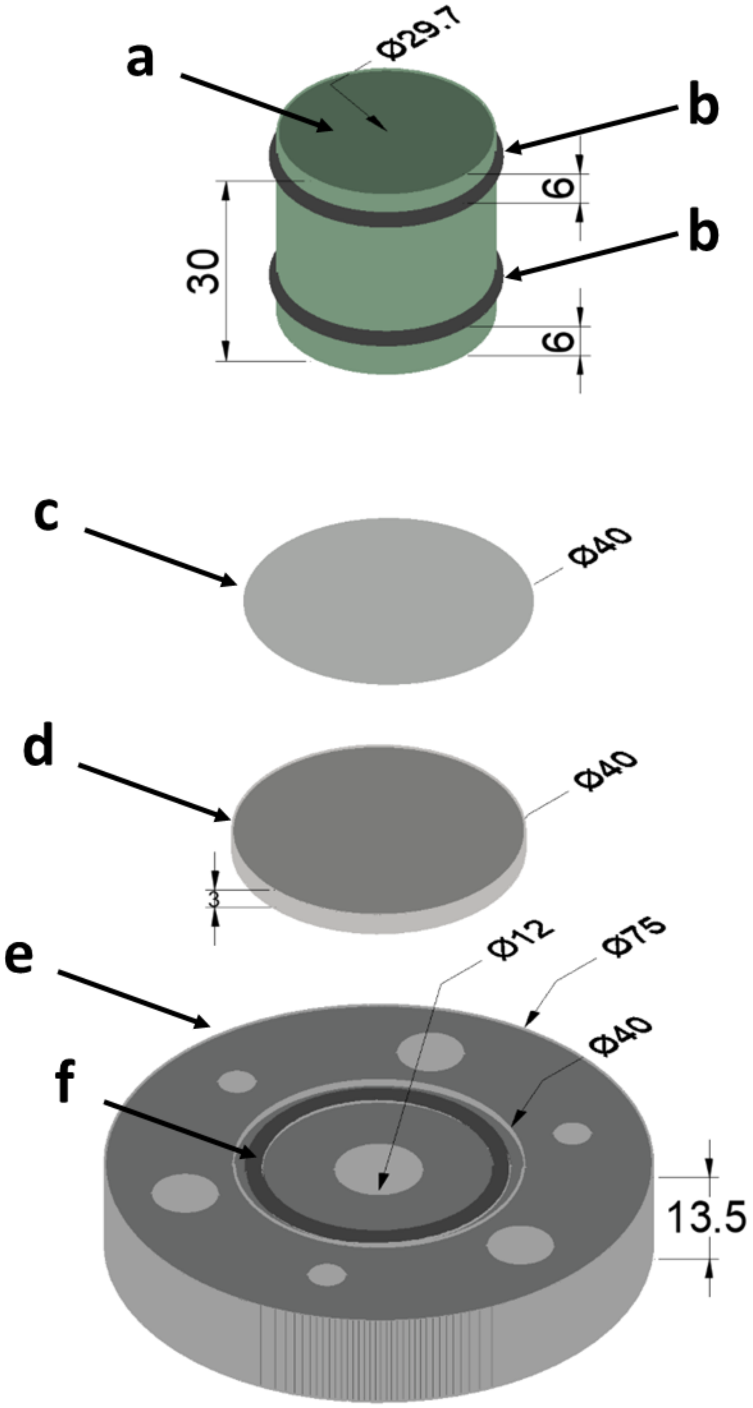
f, digital calliper;

g, piston cylinder;

h, filter assembly;

I, support tripod assembly.

Figure 169: Schematic diagram of bench filter-press.



Where:

a, is the Delrin® piston;

b, is a Nitrile 70 O-ring;

c, is a circle of filter press membrane fabric;

d, is a porous sintered stainless-steel support;

e, is the piston cylinder endcap;

f, is a Nitrile 70 O-ring.

Figure 170: Detailed schematic of the filter assembly (dimensions in mm).

Figure 169. shows a schematic of the lab-scale filter press apparatus. The device is gravity driven to provide controlled and programmed pressure to the flocculated wastewater. The barrel assembly supports a 40 l plastic barrel (load reservoir) which receives programmed doses of water from a charge vessel in 1 l aliquots to add weights with a resolution of 0.997 kg. The assembly is fabricated from aluminium arms and nylon upright guides to hold the barrel in a fixed and centralised position. The linear movement of the barrel assembly, as the sample is forced through the filter assembly (h), is measured against the digital calliper stop (b). A plunger fabricated from a brass bar (c) drives the Delrin® piston (d) through the piston cylinder (g). A perfect seal is provided by a pair of O-rings. The plunger guide (e) is fabricated from 303 stainless steel to ensure perpendicular drive between the plunger and piston. The linear progression of the piston is monitored using a USB-linked digital calliper (Moore and Wright “Digitronic” digital vernier calliper, with USB connectivity. With an accuracy of 0.02 mm and precision of 0.01 mm). The piston cylinder (g) is fabricated from 303 stainless steel, and is precision bored to 30 mm. The filter assembly (h) is shown in a detailed schematic in Figure 2. The apparatus is supported by an adjustable tripod arrangement (i), which is adjusted to ensure the bore of the piston cylinder is vertical. Additionally, a circular bubble gauge was used to level the apparatus and to ensure the piston cylinder was set vertically.

Figure 170. shows the detailed design and dimensions of the filter assembly and piston. The filter press membrane used throughout this study is a Polypropylene Filtercloth (PP-365-OM, Lathams International, Newcastle-under-Lyme, UK). Alternatively, the device is specifically designed to hold a standard 40 mm filter membrane if required. The sintered stainless steel support disc (Powder Filter Disc) was a sample supplied by Porvair Filtration Group Ltd. (Fareham, Hampshire, UK). The endcap is fabricated from 303 stainless steel. The O-rings (2 mm x 33 mm bore; nitrile 70 rubber) were procured from Simply Bearings Ltd., (Leigh, Lancashire, UK) The arrangement of the endcap is mirrored in the base of the piston cylinder, which includes an identical recess and sealing O-ring.

In operation, the piston cylinder was separated from both the support tripod assembly and components “a” to “e” (see Figure 169.). The piston was placed into the top end of the piston cylinder and the whole unit inverted. The sample was then loaded, and the piston manually pushed until the sample liquor was at the level of the O-ring seal in the base of the piston cylinder. The filter assembly was then carefully introduced, and the endcap added and secured with three M6 303 stainless steel hex-bolts. The bolts were tightened until the O-rings were fully compressed within their recesses, which was designed to coincide with the tight clamping of the endcap onto the base of the piston cylinder. The piston unit was then inverted into its correct orientation, slipped onto the three support prongs of the support tripod assembly. The plunger, with the barrel assembly was carefully added such that the only force applied to the piston was the weight of the components of the assembly above the piston cylinder. Finally, the 40 l plastic water barrel was placed securely within the barrel assembly.

The digital calliper was linked with a laptop and was designed to transmit the length information directly into an Excel spreadsheet. The transmission would usually be triggered by a manual footswitch, which in our experiments was replaced by a CMOS analogue switch (CD4066) which itself was triggered by a switchable quartz crystal oscillator and frequency divider that gave a choice of 2; 1; 0.5; or 0.1 Hz. The experiment was initiated with the simultaneous activation of the trigger oscillator, such that the spreadsheet generated included the timeframe data in the vertical cell number, with the length data in each timeframe cell.

The weight added to the piston, via the plunger and weight of water held in the 40 l plastic barrel, was added by a programmable charge vessel that delivered exactly 1 l (0.997 kg) of water at a time determined by a simple time loop program executed from an Arduino UNO microcontroller. The microcontroller was pre-programmed according to the experiment design of the programmed plunger weight sequence.

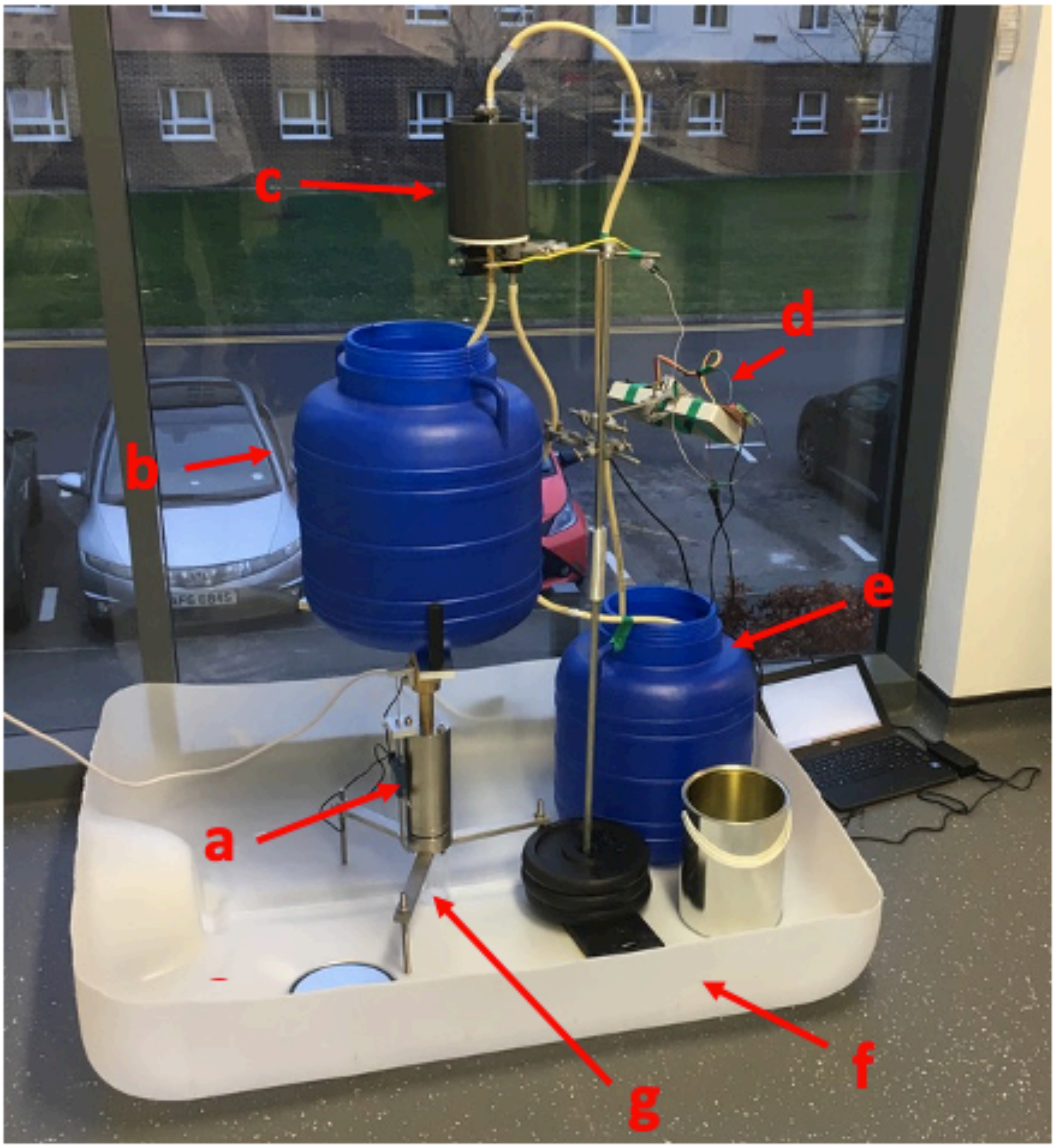


Figure 171: Photograph of the apparatus.

Where:

a, Filter Press;

b, 40 l vessel;

c, 1 l programmable charge vessel (0.997kg);

d, Arduino microcontroller;

e, 40 l reservoir ;

f, secondary containment (bund);

g, support tripod assembly.

6.4 Method

6.4.1 Sample preparation

Similar to the method described in Chapter 5. Mixtures, representative of paint residues, comprising 4% by volume paint were created using 20 ml (approx. 26.8 g) of Crown Retail Matt Emulsion Paint in 500 ml of DI water. The mixtures were agitated continuously to prevent sedimentation. A SI Analytics TitroLine 7750 & a 700 ml beaker was used to simulate a batch treatment tank. The pH of the residue mixtures were adjusted from approx. 8.4 to 6.3 using 3 g l^{-1} aluminium sulphate (Sigma-Aldrich) to model the treatment process (typically requiring approx. 3-5 ml of aluminium sulphate solution). "PolyClay" flocculant was then dosed to each agitated mixture to achieve concentrations of 140 mg l^{-1}, 660 mg l^{-1} and 1600 mg l^{-1}. These doses represented approximately 10%, 50% and 125% of the "PolyClay" dose typically used to treat residues from paint manufacture.

The treated suspension was slowly agitated for 300 seconds (Figure 172). After which a core sample (approx. 80 ml) was extracted using a syringe.

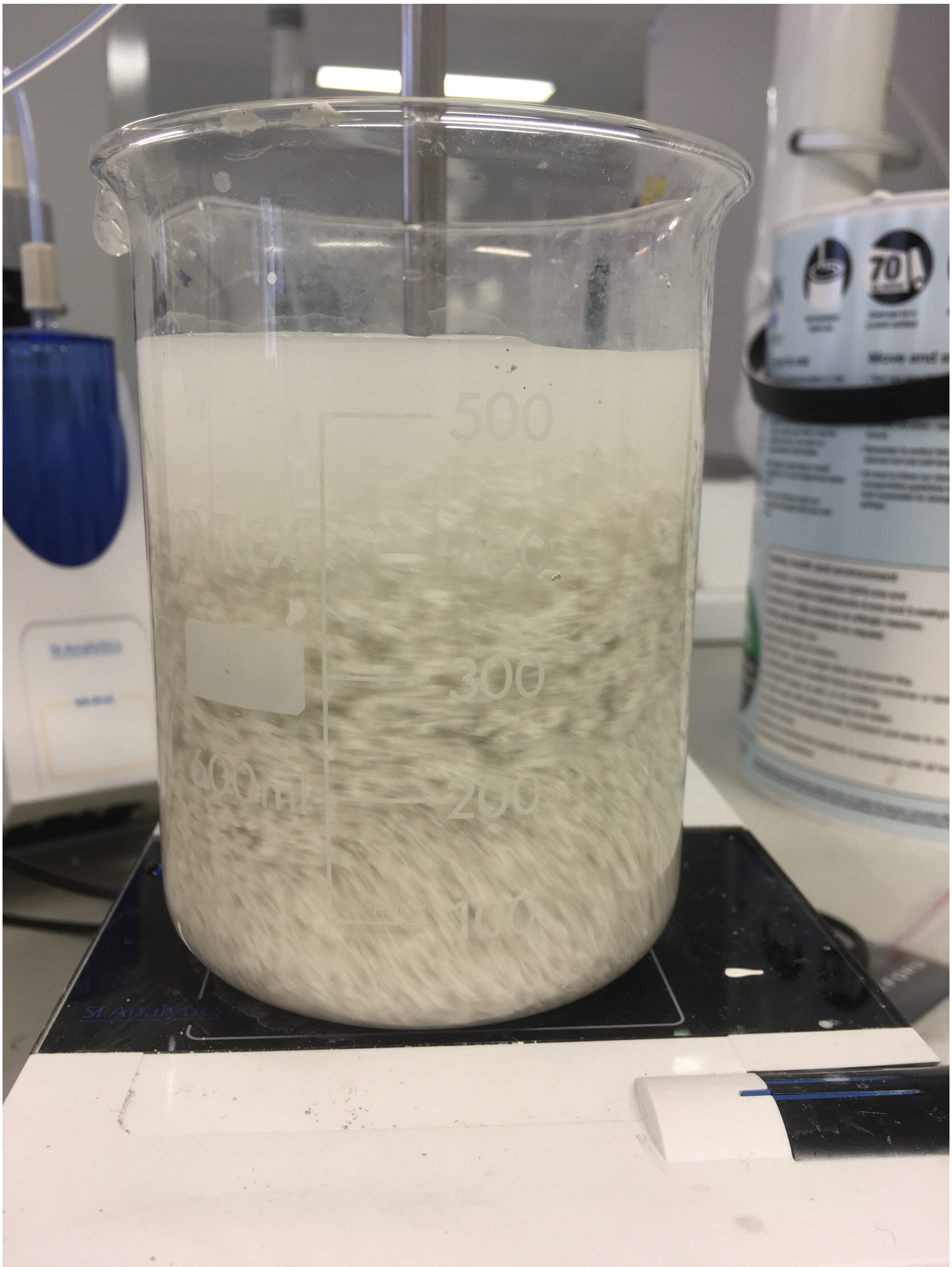


Figure 172: Photograph of flocculated material simulating a batch treatment tank.

6.4.2 Stepped filtration method

The filter cylinder and piston assembly was inverted and overfilled with approximately 80 ml of treated suspension to prevent the inclusion of air pockets before final closure by fitting of the filter membrane and support sinter. The closed filter assembly was then positioned into the tripod.

The stepped pressure filtration process was then initiated, following the pre-programmed sequence indicated in Figure 173.

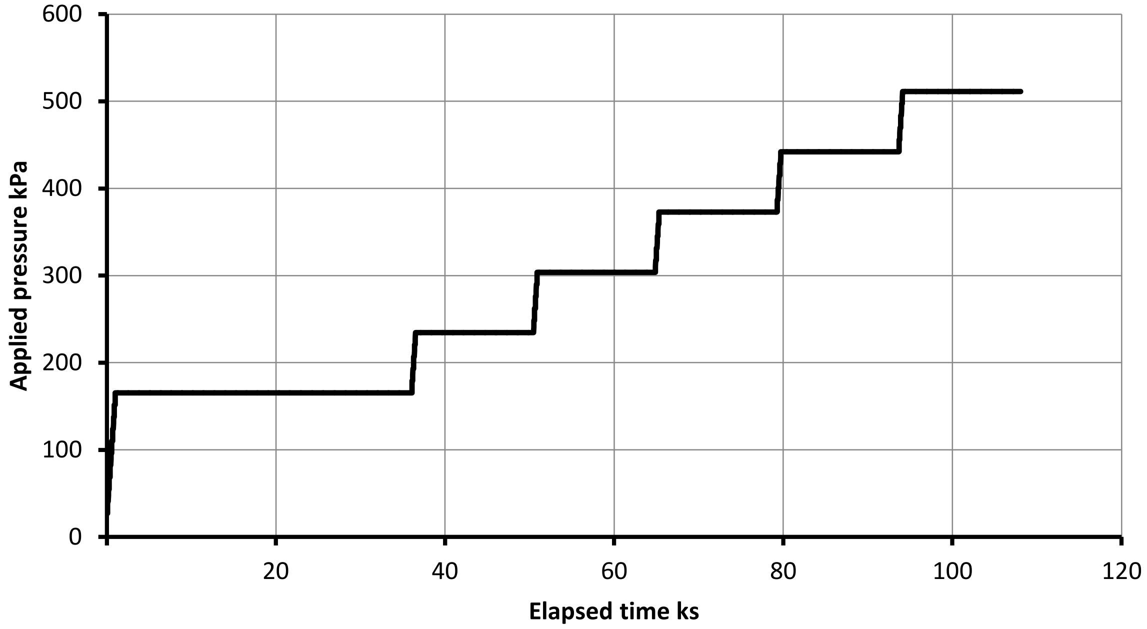


Figure 173: Stepped pressure program.

At the start of each pressure step the pressure was increased in a sequence of 5 sub-steps. Each sub-step comprised of 2 phases: charge and ramp. The charge phase, lasting 80 seconds, comprised of the filling of the calibrated charge vessel with a fixed mass (0.997 kg) of water, whilst the ramp phase, lasting 20 seconds, comprised of draining the charge vessel into the load reservoir mounted on the piston assembly. During the ramp phase the fluid transfer was assumed to proceed at a constant rate leading to an assumed linear ramp of the applied pressure. Whilst this assumption is not correct it is of no consequence to the data collection. Throughout the “run” the piston height above datum was recorded every 0.5 s to yield height vs time data sets of the type shown in Figure 174.

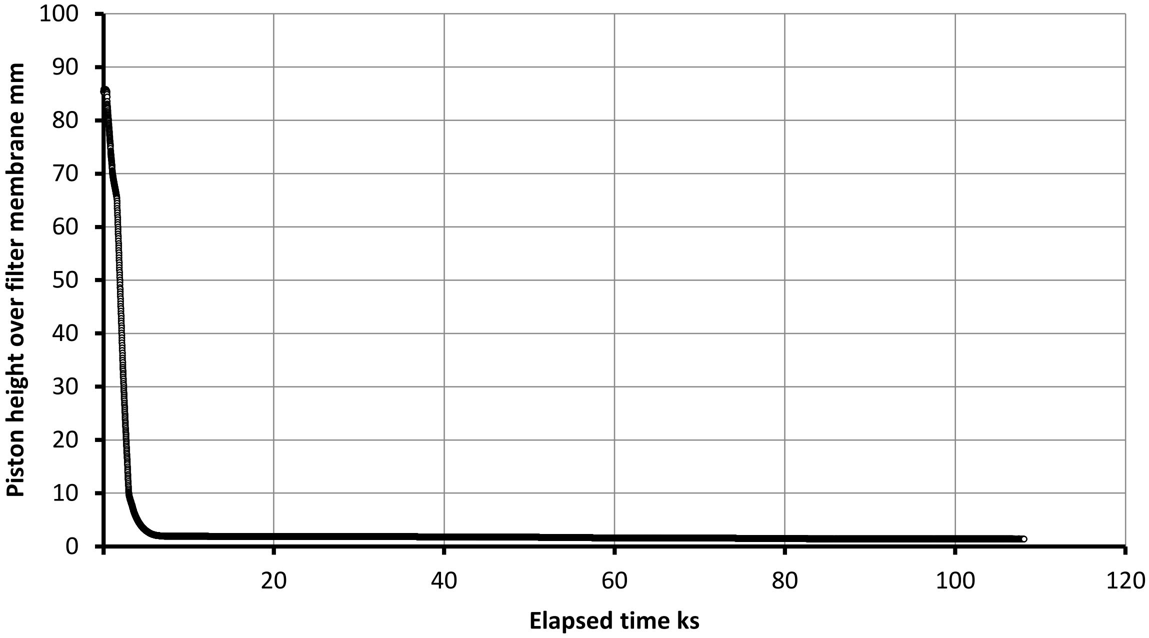


Figure 174: Typical height as a function of time data for a stepped filtration "run".

6.4.3 Interpretation of the data

The data interpretation was developed by A. Martin. and applied by Wardrop & Martin.

The height vs time data for each period of constant pressure was interpreted using a three-step process.

Step 1: Cleaning of the data

Step 2: Interpretation of height versus time data for each applied pressure

Step 3: Interpretation of height versus time parameters as functions of concentration

6.4.3.1 Step 1

In the first step, the raw height versus time data were cleaned to remove “rogue” data pairs arising from electrical interference and to remove data when the pressure was unsteady or deviated from the set value. The clean data set was then subsampled at a frequency of 1:20 simply to improve the manageability.

Rogue data were identified by considering “frames” of subsamples of the raw data comprising 11 data pairs. The mean and standard deviation of these subsamples was calculated, and the central data pair subjected to a significance test at the 0.95 level. A central data pair failing this test was flagged for subsequent removal before the sampling “frame” was advanced by 1 data pair.

6.4.3.2 Step 2

In the second step, the cleaned data were regressed to a sequence of increasingly detailed models the equations of which are set out in Table 23. Each increase in complexity is characterised by the addition of one or more parameters. Progress through the sequence of models was determined by the “incremental F test” with a rejection criterion of 0.95.

N	Fitting parameters	Material properties accessible	Model	Equation reference
1	h_∞	c_∞, $Py(c_\infty)$,	$\hat{h} = h_\infty$	26
3	h_∞, M_L, t_{offset},	c_∞, $Py(c_\infty)$, $D(c_\infty)$, $r(c_\infty)$,	$\hat{h} = \widehat{h_L} = h_\infty + (h^* - h_\infty)\sum_{n=1}^{5} B_{L,n} e^{-(n-1/2)^2 M_L (t_R - t_C)}$ **Where:** $B_{L,n} = \dfrac{\dfrac{4}{\pi^{3/2}(n-1/2)\,\mathrm{erf}(\alpha)} \int_0^\alpha e^{-z^2} \cos\left\{(n-1/2)\dfrac{\pi z}{\alpha}\right\} dz}{(n-1/2)\pi}$ $h^* = \dfrac{h_\infty + \sqrt{\pi}\alpha e^{\alpha^2}\,\mathrm{erf}(\alpha)\, h_0}{1 + \sqrt{\pi}\alpha e^{\alpha^2}\,\mathrm{erf}(\alpha)}$ $t_C = \dfrac{\pi^2}{4 M_L \alpha^2} + t_{offset}$ **α is constrained to a fixed value of 2.69702**	27 28 29 30
4	h_∞, M_L, t_{offset}, α,	c_∞, $Py(c_\infty)$, $D(c_\infty)$, $r(c_\infty)$, $r(c^*)$,	$\hat{h} = \begin{cases} t < t_C & \widehat{h_E} = h_0 + C_E - \sqrt{{C_E}^2 + M_E(t_R - t_{offset})} \\ t \geq t_C & \widehat{h_L} = h_\infty + (h^* - h_\infty)\sum_{n=1}^{5} B_{L,n} e^{-(n-1/2)^2 M_L (t_R - t_C)} \end{cases}$ **Where:** **$B_{L,n}$, h^* and t_C are defined as for the 3-parameter model plus** $C_E = -(h_0 - h_C)\dfrac{\left((h_0 - h_C) + 2 M_L t_C \sum_{n=1}^{5}(n-1/2)^2 B_{L,n}\right)}{2\left((h_0 - h_C) + M_L t_C \sum_{n=1}^{5}(n-1/2)^2 B_{L,n}\right)}$ $M_E = \dfrac{(h_0 - h_c + C_E)^2 - {C_E}^2}{t_C}$ $h_C = (h^* - h_\infty)\sum_{n=1}^{5} B_{L,n}$ **α is variable subject to the following constraint: $0 < \alpha < 2.69702$**	31 32 33 34
5	h_∞, M_L, t_{offset}, α, M_E,	c_∞, $Py(c_\infty)$, $D(c_\infty)$, $r(c_\infty)$, $r(c^*)$	$\hat{h} = \begin{cases} t < t_C & \widehat{h_E} = h_0 + C_E - \sqrt{{C_E}^2 + M_E(t_R - t_{offset})} \\ t \geq t_C & \widehat{h_L} = h_\infty + (h^* - h_\infty)\sum_{n=1}^{5} B_{L,n} e^{-(n-1/2)^2 M_L (t_R - t_C)} \end{cases}$ **Where:** **$B_{L,n}$, h^*, h_C and α are defined as for the 4-parameter model plus** $t_C = \dfrac{(h_0 - h_c + C_E)^2 - {C_E}^2}{M_E}$ **$M_E$is variable subject to the following constraint: $0 < M_E$** **C_E is constrained to a fixed value of zero**	35 36

Table 23: Filter piston height versus time models.

The simple 1-parameter model permits the concentration dependent particle stress, **$Py(c_{\infty})$,** to be estimated even when there has been little or no filtration under the applied stage pressure.

The 3-parameter model permits the interpretation of the data in terms of late or compression phase behaviour. The complementary 3-parameter model interpreting the data in terms of early or Darcian phase behaviour was not found necessary in this work. The late phase model facilitated the estimation of the filtration diffusivity at the asymptotic concentration, **$D(c_{\infty})$**, in addition to the particle stress. Interpretation of **$Py(c_{\infty})$** estimates as a function of concentration permitted subsequent estimation of the cake resistivity, **$r(c_{\infty})$** under the same asymptotic conditions.

The 4 and 5 parameter models permit the estimation of the cake resistivity at the diffusivity weighted mean cake concentration at cake completion, **$r(c^{*})$**. The key difference between the two models lies in the consideration of the moment of cake completion, **t_c**. Both models consider the piston height, **h,** to be a continuous function of time. However, the 4-parameter model also considers the function to be “smooth” through the transition, i.e., the first derivative is also continuous.

The 5-parameter model relaxes this constraint which, where statistically justified permits the model to describe the data more precisely with a concomitant development of a distinctive “kink” at cake completion and narrower confidence intervals for the estimated parameters.

A potential final model introducing a 6th parameter by relaxing the constraint on C_E was not considered, although this remains an opportunity for future work.

The models were implemented in Excel™ workbooks supported by additional VBA coding to systematically configure and run “SOLVER”. The squared unexplained residual, $\boldsymbol{E_U^2}$, was characterised by a linear sum of the un-weighted scalar differences between the estimated height, $\boldsymbol{\hat{h}}$ and the measured value, $\boldsymbol{h}$ squared.

$$\boldsymbol{E_U}^2 = \sum \left(\boldsymbol{h} - \boldsymbol{\hat{h}}\right)^2 \qquad \textbf{\textit{37}}$$

SOLVER was configured to minimise $\boldsymbol{E_U^2}$ subject to the parameters and constraints of the specific model under consideration. Initially the unexplained residual around the 1 parameter model was established which is also known as the total variation and here temporarily denoted $\boldsymbol{E_U^2}_{\boldsymbol{N-1}}$. Then commencing with the 3 parameter model a test fit was made to establish the unexplained residual for this model, $\boldsymbol{E_U^2}_{\boldsymbol{N}}$ and the improvement was statistically tested using an incremental F statistic, $\boldsymbol{F_{stat}}$, where:

$$\boldsymbol{F_{stat}} = \frac{\boldsymbol{DoF_N}}{\boldsymbol{E_U}^2{}_{\boldsymbol{N}}}\left\{\frac{\boldsymbol{E_U}^2{}_{\boldsymbol{N-1}} - \boldsymbol{E_U}^2{}_{\boldsymbol{N}}}{\boldsymbol{DoF_{N-1}} - \boldsymbol{DoF_N}}\right\} \qquad \textbf{\textit{38}}$$

The calculated value of F_{stat}, was then compared with the critical F statistic at the 0.95 level, F_{crit}, and the more complex model accepted when $F_{stat} > F_{crit}$ This procedure was then repeated for the 4 and 5 parameter models. When $\mathrm{F}_{\mathrm{stat}} \leq \mathrm{F}_{\mathrm{crit}}$ the simpler model was accepted and the fitting procedure terminated.

Once the preferred model had been established and the "best fit" estimates of the parameters made the confidence limits of the estimates were made using the method of Kemmer and Keller[127].

The confidence intervals for the derived material properties were then estimated using standard methods for the propagation of uncertainty.

This procedure was repeated for each set pressure to yield concentration dependent values for the material properties: $Py(c_{\infty})$, $D(c_{\infty})$, and $r(c^{*})$.

6.4.3.3 Step 3

The three material properties estimated during the course of step 2 are not fully independent as the diffusivity, ***$D(c_\infty)$***, is a function of the gradient of the particle stress and the cake resistivity. However, at the asymptotic concentration it is the diffusivity that can be independently measured. Rather than the cake resistivity. In addition, it is the particle stress, ***Py(c)***, and the resistivity, ***r(c)***, that are conventionally correlated with particle concentration. The interpretation proceeds according to 3 sub steps:

Step 3a: Interpretation of the ***Py(c)*** data as a function of solids concentration

Step 3b: Interpretation of the ***r(c)*** data as a function of solids concentration

Step 3c: Correlation of filtration diffusivity, ***D(c).***

6.4.3.4 Step 3a Interpretation of ***Py(c)*** data

N	Coefficients	Form	Equation reference
1	$\mathcal{R}^*$	$\mathbf{Py} = \mathcal{R}^*\mathbf{Tc}$	*39*
2	$\mathcal{R}^*\mathcal{D}^*, \mathbf{n_v}$	$\mathbf{Py} = \mathcal{R}^*\mathbf{T}\mathcal{D}^*\mathbf{c}^{\mathbf{n_v}}$	*40*
3	$\mathcal{R}^*,\ \tilde{\mathbf{c}}_{\mathbf{gel}}, \mathbf{n_v}$	$\mathbf{Py} = \mathcal{R}^*\mathbf{T}(\mathbf{c}+\mathcal{B}^*\mathbf{c}^2 + \mathcal{D}^*\mathbf{c}^{\mathbf{n_v}})$ Where: $\mathcal{B}^* = -\frac{(\mathbf{n_v}-1)}{(\mathbf{n_v}-2)\tilde{\mathbf{c}}_{\mathbf{gel}}}$ $\mathcal{D}^* = \frac{1}{(\mathbf{n_v}-2)\tilde{\mathbf{c}}_{\mathbf{gel}}{}^{\mathbf{n_v}-1}}$	*41* *42* *43*

Table 24: Models of Particle Stress

The 1 parameter model is analogous to an ideal osmotic pressure relationship and the ideal gas law, however with the concentration or reciprocal molar volume being expressed in terms of mass per unit volume the universal gas constant must be replaced by an analogous “specific gas constant”, R^*. The 2-parameter model permits some description of non-ideal behaviour analogous to an equation of state of the form:

$$Pv^n = \mathcal{R}T \qquad 44$$

Finally, the 3-parameter model is analogous to a simple virial equation of state. The number of parameters being minimised by arbitrarily constraining the particle stress to pass through a minimum at $c = \tilde{c}_{gel}$ where the gel stress, $Py = \tilde{P}_{gel} = 0$**.** The choice of this functional form is quite arbitrary; however it represents a simple continuous function which admits the possibility of a gel concentration and the coexistence of a dense particulate phase or floc and a rarefied suspension, a configuration routinely observed when conducting "jar testing" of coagulants and flocculants. However, in this work observations of the particle stress at concentrations less than $\tilde{\mathbf{c}}_{\mathbf{gel}}$ are not anticipated, thus the shape of the function in this region is not expected to carry any quantitative significance.

A method analogous to that used in the height versus time data is applied to the selection and fitting of the models to the data. The confidence band for the correlation and limits for the estimated parameters were calculated using the method of Kemmer and Keller[127].

*Step 3b Interpretation of the **r(c)** data*

A “measurement” of cake resistivity data, ***r(c)***, can be derived from 2 sources:

From the early-stage filtration using the following expression:

$$\boldsymbol{r(c^{*}) = \left\{\frac{(\Delta P - \Pi)}{M_E}\frac{(c^{*} - c_0)}{c_0}\right\}} \tag{45}$$

Where $\boldsymbol{c^{*}}$ is calculated from $\boldsymbol{h^{*}}$ using the following expression: $\boldsymbol{c^{*} = c_0\, h_0/h^{*}}$, and from late-stage filtration where,

$$\boldsymbol{\frac{r(c_\infty)}{\rho_s} = \frac{Py'(c_\infty)}{M_L}\frac{\pi^2}{{h_\infty}^2}} \tag{46}$$

The data was interpreted using a modified Richardson-Zaki[128] functional form:

$$\boldsymbol{r(c) = r_0\left\{1 - \frac{c}{\rho_s}\right\}^{-n_{RZ}}} \tag{47}$$

Where $\boldsymbol{r_0}$, $\boldsymbol{\rho_s}$ and $\boldsymbol{n_{RZ}}$ are candidate fitting parameters. Under the circumstances of the work reported here it is not possible, *a priori*, to assign a value to $\boldsymbol{\rho_s}$, so it must be retained as a fitting parameter. This situation presents an additional difficulty in the regression analysis, in particular with the calculation of the residual, $\sum \boldsymbol{e^2}$.

Three options were considered:

Residual option 1

$$\sum \boldsymbol{e^2} = \sum_{\mathbf{1}}^{\boldsymbol{n_1}} \left(\boldsymbol{r}(\boldsymbol{c}^*) - \widehat{\boldsymbol{r}(\boldsymbol{c})}\right)^2 + \sum_{\mathbf{1}}^{\boldsymbol{n_2}} \left(\boldsymbol{r}(\boldsymbol{c}_\infty) - \widehat{\boldsymbol{r}(\boldsymbol{c})}\right)^2 \tag{48}$$

Residual option 2

$$\sum \boldsymbol{e^2} = \sum_{\mathbf{1}}^{\boldsymbol{n_1}} \left(\boldsymbol{r}(\boldsymbol{c}^*) - \widehat{\boldsymbol{r}(\boldsymbol{c})}\right)^2 + \sum_{\mathbf{1}}^{\boldsymbol{n_2}} \left\{\frac{\boldsymbol{r}(\boldsymbol{c}_\infty)}{\boldsymbol{\rho_s}} - \widehat{\left\{\frac{\boldsymbol{r}(\boldsymbol{c})}{\boldsymbol{\rho_s}}\right\}}\right\}^2 \tag{49}$$

Residual option 3

$$\sum \boldsymbol{e^2} = \sum_{\mathbf{1}}^{\boldsymbol{n_1}} \left\{\frac{\boldsymbol{r}(\boldsymbol{c}^*)}{\boldsymbol{\rho_s}} - \widehat{\left\{\frac{\boldsymbol{r}(\boldsymbol{c})}{\boldsymbol{\rho_s}}\right\}}\right\}^2 + \sum_{\mathbf{1}}^{\boldsymbol{n_2}} \left\{\frac{\boldsymbol{r}(\boldsymbol{c}_\infty)}{\boldsymbol{\rho_s}} - \widehat{\left\{\frac{\boldsymbol{r}(\boldsymbol{c})}{\boldsymbol{\rho_s}}\right\}}\right\}^2 \tag{50}$$

Option 1

Option 1 is the intuitive selection and is mathematically reasonably rigorous. However, its calculation requires the multiplication of the “measured” variable by one of the fitting parameters, ρ_s. This introduces significant un-intended consequences in the fitting process, which is simply the minimisation of, $\sum e^2$ as a function of r_0, ρ_s and n_{RZ}. In effect the set of the “measured” values pertaining to $r(c_\infty)$ is multiplied by a variable weight, ρ_s, who’s magnitude depends on the success of the fitting process.

Option 2

Option 2, whilst the simplest to implement, it has the effect of strongly biasing the fitting process towards the $r(c^*)$ data sub-set. As a consequence of the potential for systematic but variable bias Option 2 was rejected.

Option 3

Option 3 is broadly similar to Option 1, however all the residuals are down-weighted by the solids density. This option suffers from the same issues as Option 1 and additionally it is susceptible to the floc density being set to zero during the course of the solution process. This final potential problem led to its rejection as a method.

Each of the options considered is based on a “scalar” characterisation of the residual. Such a characterisation implicitly assumes that the magnitude of the residual is independent of the measured value. Exploration of the impact of this assumption is warranted but is beyond the present scope.

Based on the Option 1 residual, the fitting process proceeded in a stagewise fashion. Commencing with $\boldsymbol{n_{RZ}}$ constrained to be zero and $\boldsymbol{\rho_s}$ constrained to an arbitrary value greater than the maximum concentration, 10^4, for computational convenience. This calculation yields the summed residuals around the mean. A test fit with $\boldsymbol{n_{RZ}}$ constrained to 4.5 was then performed. The constrained value for $\boldsymbol{n_{RZ}}$ was arbitrarily chosen as the most commonly reported value in the engineering literature and has no physical significance beyond that in this context. The test fit was checked for its statistical significance using a standard “F” test at the 0.95 level. If accepted a further test fit with the constraint on the value of $\boldsymbol{n_{RZ}}$ was performed and the incremental statistical significance checked for significant improvement.

Step 3c

The filtration diffusivity is related to the coefficient on the exponent of the late phase model through the following expression

$$\boldsymbol{D(c_\infty) = M_L \frac{{h_\infty}^2}{\pi^2}} \qquad \textbf{\textit{51}}$$

The functional form for the filtration diffusivity is defined by the combination of the first derivative of the particle stress, ***Py′(c)*** model with the cake resistivity, ***r(c)*** as follows:

$$\boldsymbol{D(c) = \frac{\rho_s Py'(c)}{r(c)}} \qquad \textbf{\textit{52}}$$

The fitting processes outlined in sections 3a and 3b fully define the functional form and coefficients for the above expression. Therefore, only the residual around the proposed model is calculated in order to estimate the confidence band for the correlation of ***D(c)*** versus ***c***.

Parameter		**Poly clay dose**					
Poly clay dose		**140 mg l^{-1}**		**660 mg l^{-1}**		**1600 mg l^{-1}**	
		Best fit value	**Confidence limit (95%)**	**Best fit value**	**Confidence limit (95%)**	**Best fit value**	**Confidence limit (95%)**
Hydraulic resistivity							
$\mathbf{r_0}$	TPa s m^{-2}	110	2.6 747	2.5	0.4 14	2.4	0 1650
$\boldsymbol{\rho_s}$	kg m^{-3}	3170	2393 4387	1520	1420 1675	1790	1540 4590
$\mathbf{n_{RZ}}$	-	4.5	-	4.5	-	4.5	-
Particle stress							
$\mathbf{n_v}$	-	4	2 5	7	6 8	6	2 10
$\mathbf{B}^*$	kJ m^3 kg^{-2} K^{-1}	-		-		-	
$\mathcal{D}^*$	kJ $m^{3(\mathbf{n_v}-1)} kg^{-\mathbf{n_v}} K^{-1}$	9.93×10^{-14}	9.09×10^{-14} 1.08×10^{-13}	3.39×10^{-22}	3.30×10^{-22} 3.48×10^{-22}	1.67×10^{-19}	1.45×10^{-19} 1.90×10^{-19}

Table 25: Estimated parameter and material property values.

r_0, represents the hydraulic resistivity of a single isolated floc, equivalent to an infinitely dilute suspension. In sedimentation this can be related to the settling velocity of the isolated floc. ***r_0*** is estimated with a poor degree of certainty. This arises principally from the relatively high and rather narrow range of concentrations which characterise the asymptotic filter cakes in conjunction with the very strong concentration dependence of the cake resistivity, ***$r(c_\infty)$*.**

ρ_s represents a limiting concentration or "pole" at which the hydraulic resistivity of the cake goes to **∞,** i.e. the cake becomes completely impervious and no further filtration can take place. The magnitude of ***ρ_s*** is bounded at the lower limit by the density of the suspending fluid and at the upper limit by the density of the floc forming solids. ***ρ_s*** is estimated with somewhat greater certainty than ***r_0,*** being approximately +/- 20% at the 0.95 confidence level for the 140 mg l^{-1} dose diminishing less than to +/- 10% at the 660 mg l^{-1} dose.

Despite the low confidence in the individual estimates of $\boldsymbol{r_0}$, the best fit values can be seen to diminish significantly as the "PolyClay" dose is raised from 140 to 660 mg l^{-1}. This is indicative of a change in floc morphology towards the formation of "tighter" structures which are generally more dense and less fractal. However, as the "PolyClay" dose is increased through the same range it can also be seen that the magnitude of $\boldsymbol{\rho_s}$ diminishes significantly too. This implies that the internal structure of the floc has become less permeable. At low cake concentrations the internal permeability of the floc is not significant only becoming dominant during the late, "compression" phase, when the inter floc spaces have diminished. The transition from a dense "pole" to a less dense "pole" is indicative of the properties of the filter cake moving from domination by the paint properties to domination by the "PolyClay" properties. The limiting density at high "PolyClay" doses estimated here is consistent with the range of values found for bentonite[129] "dumped" under natural ambient conditions of 1500 – 1800 kg m^{-3}.

It is noted that both the paint solids and bentonite have distinct plate like structures. Thus, it is expected that at low concentrations of "PolyClay" the paint solids will tend to orientate with increasing concentration to form cakes of relatively high hydraulic resistivity. However, the addition of higher concentrations of "PolyClay" will tend to disrupt the formation of orientated layers to some extent and where "PolyClay" is added in excess the residual, "un-reacted" bentonite would be expected to orientate and form similar cakes for which the hydraulic resistivity rises sharply over a relatively narrow concentration range.

Equations of state, EoS, have their origins in describing the relationship between temperature, pressure and specific volume of an idealised substance, typified by the ideal gas. Here the concepts are adapted to describe the behaviour of the suspensions of solids. The virial EoS is applied as, at a mathematical level, it is a simple polynomial. Three terms have been used the first, linear, term describes "ideal" behaviour whilst the remaining pair describe deviation from the ideal. The coefficient of the linear term is then simply the product of the absolute temperature with a specific gas constant, $\boldsymbol{R^*}$**.** The second term, parabolic in concentration, provides the opportunity to create a minimum in the particle stress, ***Py***. The degree of final term, greater than 2, was determined by regression. The form of the EoS was further, arbitrarily, constrained to yield a minimum with a particle stress equal to zero. This minimum is termed the gel concentration. Once a value for $\boldsymbol{R^*}$ has been established it is a simple matter to establish an indicative molecular weight for the solid flocs. The virial model proposed here can be considered to have an encapsulated power law model and the linear ideal model. The nature of the power law model however precludes the estimation of $\boldsymbol{R^*}$ and thus an indicative molecular weight. The data collected in this work are such that the increment from the power law model to the 3 term virial model was not statistically significant and the latter was rejected making it impossible to determine values for the indicative molecular weight and gel concentration. Despite these limitations it can be seen that the exponent of the power law models increases significantly as the "PolyClay" dose steps from 140 to 660 g m^{-3}. This result reflects the changes in the hydraulic resistivity over the same range. The floc formed with the higher doses of "PolyClay" are generally "stronger" or better able to resist compression.

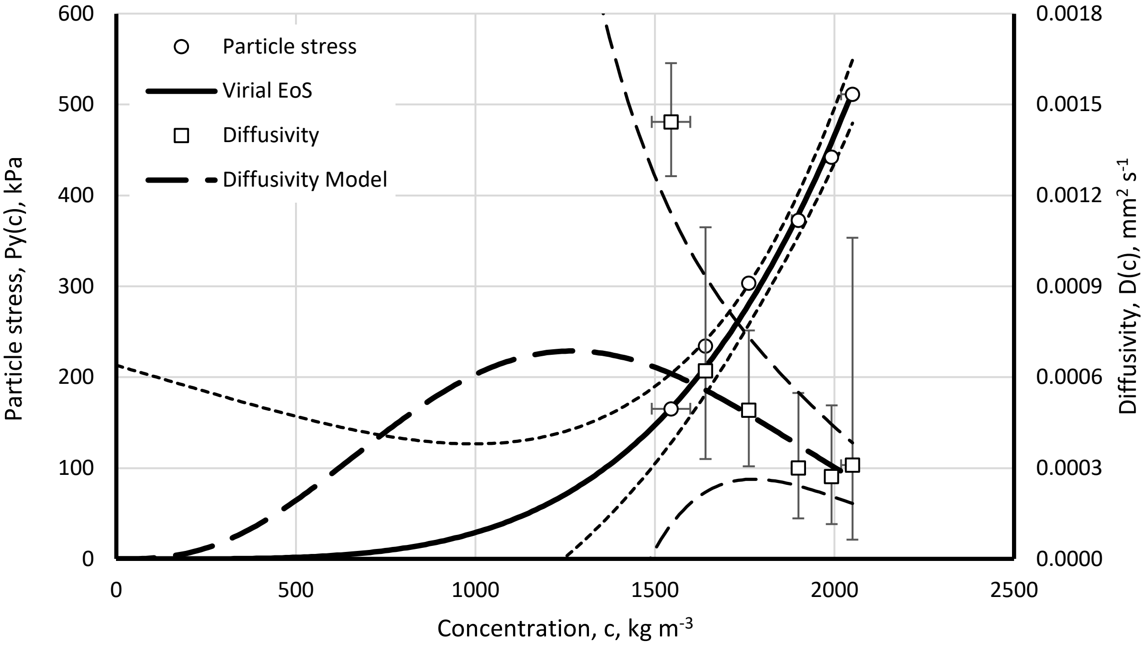


Figure 175: Particle stress and filtration diffusivity as functions of solids concentration for 4% paint residue adjusted to pH 6.3 with aluminium sulphate and dosed with 140 g m^{-3} "PolyClay".

Where: Heavy lines indicate the results of systematic regression analysis and the light dashed lines indicate the 0.95 confidence bands of correlation to the models. Horizontal and vertical error bars indicate the 0.95 confidence intervals in the data estimates.

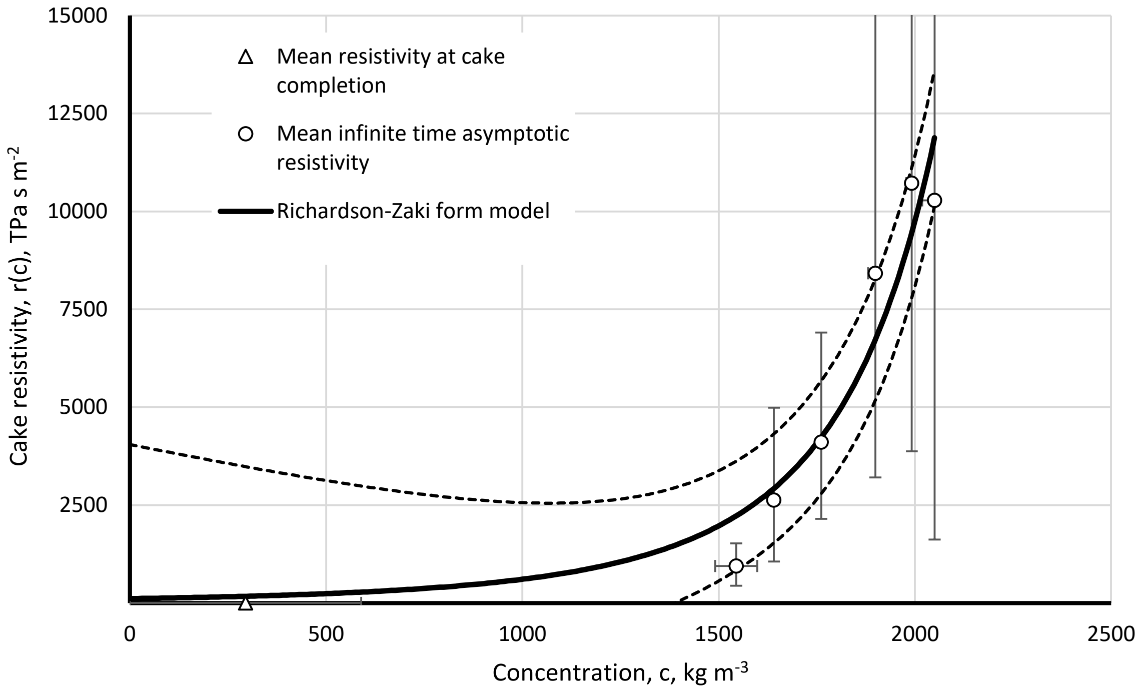


Figure 176:Filter cake resistivity as a function of solids concentration for 4% paint residue adjusted to pH6.3 with aluminium sulphate and dosed with 140 g m^3 "PolyClay".

Where: Heavy continuous line indicates the results of systematic regression analysis and the light dashed lines indicate the 0.95 confidence band of correlation to the model. Horizontal and vertical error bars indicate the 0.95 confidence intervals in the data estimates.

From Figure 175. showing the particle stress and the filtration diffusivity as functions of concentration, it can be seen that the measured stress is determined to a high degree of confidence due entirely to the method by which the load is applied to the press. However, there is hidden uncertainty in this determination potentially arising from “stiction” in the piston mechanism, as the load transmitted to the suspension was not measured directly. The horizontal error bars indicating uncertainty in the determination of the asymptotic solids concentration arise from the propagation of uncertainty in the determination of the asymptotic piston height in Step 2. of the regression process. The certainty in the determination of this parameter improves as the inter step travel of the piston diminishes. The indicated confidence is much lower for the filtration diffusivity than the particle stress. This arises from its dependence on both the estimate of the asymptotic piston height and on the exponential, “rate” term, M_L (Step 3c. Equation 51.). Confidence in the estimation of M_L diminishes with decreasing inter step piston travel. Thus, for the final pressure increment, where the piston travel was approximately 40 μm, the 0.95 confidence interval is particularly large. The estimated filtration diffusivity can be seen to pass through a maximum of approximately 0.007 mm^2 s^{-1} at a solids concentration of approximately 1250 kg m^{-3}, below the range of the collected data. Maximising the filtration diffusivity can be used as an objective of the addition of flocculants. In this work the qualitative effect of the addition of “PolyClay” is to increase the maximum value of ***D(c)*** but this is achieved at the cost of decreasing the concentration at which the maximum occurs and in the range for which data were collected the effect of “PolyClay” addition is to reduce the filtration diffusivity thus making the dewatering process less effective.

Over the concentration range of interest (>1250 kg m^{-3}) ***D(c)*** can be seen to decrease with increasing concentration. This is an indication that a technology which is counter current in character, i.e. water and solids move in opposite directions, may be more suitable for this dewatering process. In this case, should the required forces be achievable, centrifugation represents a candidate, counter current technology.

Figure 176. shows the hydraulic resistivity of the cake as a function of concentration fitting the Richardson-Zaki form model reasonably well. However, the large confidence intervals characterising the data show a very high degree of uncertainty. This arises from the dependence of the data values on ρ_s and the first derivative of the EoS, ***Py'(c),*** in addition to both M_L and h_∞. It is notable that the mean infinite time asymptotic resistivity is derived from experimental data but not measured directly and at higher concentrations the uncertainty increases dramatically. Interestingly, at the highest concentration levels the piston travel, Δh is very small (circa. 0.01 mm) and thus resolution of the measuring equipment (i.e. the “Digitronic” calliper with accuracy of 0.02 mm and precision of 0.01 mm) would likely be the cause of this increased uncertainty. To increase certainty at these levels a larger filtration device could be designed with a larger value of, Δh at these concentrations (or indeed similarly a higher concentrated mixture resulting in a larger interface height above the filter membrane, h) or a higher resolution calliper (e.g., circa. 0.001mm resolution) may be used.

Table 25. shows that ρ_s is characterised by relatively wide 0.95 confidence limits, particularly the upper confidence limit.

6.5 Summery and Conclusions

This work presents a novel design of a device to apply stepped pressure filtration on a suspension of aqueous paint waste. The device provided an effective method to evaluate the filtration process of an industrial effluent plant in a laboratory scale. Also reported is a method to use Microsoft Excel™ to use the data collected to model established filtration characteristics compressive yield stress, ***Py*** and the hydraulic resistivity, ***r*** uniquely in a single run rather than the usual two.

From the perspective of the material in question (i.e. the paint manufacturing effluent), this method has been tailored to optimise the current process (as shown in the "Hierarchy of Solutions" presented in Figure 112.) with an aim to demonstrate a suitable simulation of the filtration process. This work has shown that the addition of "PolyClay" as a filter aide for paint waste reduces the hydraulic resistivity at lower concentrations and increases it at higher concentrations, whilst simultaneously increasing the particle stress. Together these have a combined deleterious effect on the time and energy required to dewater the waste to high solids concentration by filtration. The results also show that a significant change in suspension behaviour occurs between the "PolyClay" doses of 140 mg l^{-1} and 660 mg l^{-1} and that further changes up to "PolyClay" doses of 1600 mg l^{-1} are more modest. It may be concluded that there is an opportunity to reduce "PolyClay" dose into a range between 10% and 50% of current manufacturing practice. In addition, this work indicates that alternative, centrifuge based, technology is worthy of investigation. The data interpretation method enables different flocculant materials to be more rapidly screened and more appropriately screened than conventional jar tests and large-scale filtration trials.

6.5.1 Evaluation of method and potential future research

The device proved effective at collecting large volumes of filtration data, which resulted in the need to subsample data from 0.5 s intervals to 10 s intervals. Even with 95% of the data removed it proved sufficient to model the process effectively. Modelling the process on Excel using VBA was a simple solution initially but proved extremely difficult to debug and implement any modifications or improvements to the code. An idealised system would monitor the data live as they readings are made and add the potential to control certain variables (i.e. pressure), the suggested improvement to the apparatus is the use of a stepper motor to drive the piston and an internal pressure sensor to monitor the filtration pressure directly. VBA wouldn't be an easy system to implement this, using LabView would make the activity significantly easier. The water delivery system worked as intended, giving controlled increases in pressure at a set time interval. A prototype system was also constructed using manual increases of 5 kg weights, but the time interval was near impossible to control effectively. Some good data sets were recorded from this prototype but will require a more arduous level of "cleaning" before any results could be obtained. Given the complexity involved it is far easier to use the automated system. Another area of interest is to remove the distinct pressure steps (which significantly aid in identifying and computing the data) and running a single "ramped pressure filtration" with exponentially larger sets of $\boldsymbol{\Delta P}$ values. This was not explored in this work due to limitations of the gravitational device and computational ease. However, such an experiment would certainly be possible with a device driven by a stepper motor. Any modification to the device to measure piston travel, $\boldsymbol{\Delta h}$ with the greatest resolution would be advantageous to increase certainty in the model, this could potentially include increasing the height of the sample and thus ***h*** directly or an alternative measuring equipment (i.e. replacing the callipers with an alternative).

Whist this method was specifically designed to aid in the optimisation of Crown Paints' effluent processes the method could also be used to compare "Alternative Treatments" (as shown in Figure 112.). As compressive yield stress, ***Py*** has already been established for other technologies (e.g. centrifugation[124]) comparative analysis with other dewatering technologies would be very useful in establishing the most effective technique for specific materials. This presents an exciting application of this method.

Several studies[101,126] use Zirconia suspensions as a controlled system, however the purpose of this study was to investigate flocculated paint suspensions. Zirconia is clearly a useful control to test the apparatus and model and provides a logical next step. Another element to investigate would be organic sludges. Additionally, the author currently manages several electroplating effluent treatment processes, from chrome, cadmium, and zinc nickel plating processes. Each of these streams potentially have very different particle shapes and properties and the application of this work with these materials would demonstrate its value to a diverse range of processes. The necessity to fully remove these often toxic or environmentally hazardous metals would add an additional complexity to this work. An interesting extension to this research could include the packing of specifically shaped particles under pressure filtration and subsequent filtercake formation, the deformation processes of these particles under high pressures may be an area of interest also.

7 RETURN OF WASH WATER INTO THE PRODUCTION PROCESS

7.1 Introduction

With approximately 50% of emulsion paint formulations consisting of water it seems appropriate to explore the recycling of wash water from the paint manufacturing process back into the paint formulation. The aim of this chapter is to present a study to ascertain the feasibility of reintroducing raw (i.e. untreated) effluent back into the manufacturing process and thus move towards a more circular economic production model. In terms of the “Hierarchy of Solutions” presented in Figure 112. the reintroduction of the effluent material would be an example of water recycling, however this solution could also simultaneously be introduced with other solutions such as mixing within the tin or alternative treatments depending on the complexity of the chosen solution.

This Chapter presents a study to return emulsion paint effluent back into the production process. In terms of the KTP project, this Chapter describes a solution to the final defined deliverable of the KTP project (1.3) in ascertaining the feasibility of returning washwater into the paint manufacturing process to create a circular economy within paint manufacturing. It also represents the final innovative element of the research described in this thesis as no previous example of returning waste material into FMCG processes (coatings or otherwise) could be found.

Although no relevant literature on the reintroduction of waste product into FMCG processes could be identified, previous experiments by Wardrop have suggested that effluent could be reintroduced into paint formulations with limited effect on the paint properties. These studies have suggested a potential positive effect on scrub resistance, when reintroducing effluent at concentrations circa 0.5 wt% (solids). Residual colourant was however seen to be the major issue when considering the reintroduction of wash water into the process.

The Hull site's Line 1 produces the most standardized stream of effluent and thus presented the most obvious material to attempt to reintroduce into a product. The line focuses on white and magnolia shades and thus colourant contamination within this effluent is minimal.

The effluent's concentration can be highly variable, ranging from 0.5 wt% - 35 wt% solids concentration., therefore any reintroduction of this material would require some basic solids analysis and adjustment of the formulation to take into account these extra solids (with the added benefit of raw material savings). Solids analysis already occurs within the site's effluent plant to appropriately dose the coagulant/flocculant system and a similar method is suggested to be used here to identify the "concentration of solids" within the effluent, $\boldsymbol{Solids_{RW}}$.

A Crown Vinyl Retail Matt formulation (LFW7047) was chosen as being a likely candidate formulation most susceptible to any changes in the raw material. Therefore, any issues experienced during this study would be seen by Crown Paints as “the worst case scenario”.

For this study virgin water within the formulation (Crown Vinyl Retail Matt) would be replaced by a volume of raw effluent (from Hull site’s Line 1). This new formulation would undergo standard laboratory testing as is typical of paint formulation at Crown Paints before a 9,000 l trial batch would be generated. To minimise risk this trial batch was quarantined for 90 days to allow sufficient testing of the product. Following successful testing the product entered the market.

7.2 Laboratory Testing

7.2.1 Introduction

As with the development of any new paint formulation at Crown Paints the formulation of interest was first made within Crown Paints Research and Development (R & D) laboratory at a smaller scale (typically 250 ml -5 l) and would undergo paint testing as described in 2.1.6. before a plant trial would be organised.

Washings from Crown Paints Hull Site’s Line 1 production processes were reintroduced into a Crown Vinyl Retail Matt formulation (LFW7047) in the place of virgin water, the concentration of the effluent was considered too high to directly input into the formulation (8 %-27 % solids) and thus the formulation was adjusted to take into account the additional solids (Table 26. & Table 27.).

Initially, all the virgin water was replaced with effluent (Samples: A, B & C), however later it was decided to only replace the virgin water in the letdown phase of the process (D & E). This minimised the risk of affecting the initial dispersion of the powders, whilst also being more representative of the potential volumes of effluent which could practically be reintroduced in this manner.

All samples (A, B, C, D & E) were tested against two standards (Std 1& Std 2) generated on the same day as the samples. Testing included standard QC specification methods, scrub resistance, opacity, whiteness and mud crack. Samples D & E then undertook applications testing.

7.2.2 Experimental

Wash water samples were taken from Line 1 at the Hull site, these were then analysed gravimetrically to determine their solids concentration, $\boldsymbol{Solids_{RW}}$. This was to maintain the total solids concentration of the original formulation, $\boldsymbol{Solids_{F}}$ and identify any savings in raw materials.

The first samples (A, B & C) were used to replace all the virgin water within a Crown Vinyl Retail Matt formulation (LFW7047). These 1 kg samples were tested against a standard for scrub, opacity, whiteness and mud crack. The intention was to perform applications testing on these samples however the size of the samples was deemed insufficient (< 2 kg) and when eventually this issue was identified the original water samples had become contaminated (after several weeks).

Table 26: Formulations adjusted for additional effluent (Samples: Std 1, A,B, C).

n.b the ingredients in the formulations have been redacted for commercial confidence,

			Sample	Std 1	A	B	C
			% Solids	0%	22%	27%	8%
Millbase	1	7Z006	Water/g	341.11	0	0	0
	2		Effluent/g	0	341.11	341.11	341.11
	3	8T39E	[redacted]	1.01	0.93	0.91	0.98
	4	8POAE	[redacted]	4.4	4.10	4.02	4.31
	5	8FAAK	[redacted]	1.5	1.39	1.37	1.47
	6	809376	[redacted]	3.80	3.50	3.43	3.68
	7	8J826	[redacted]	1.55	1.41	1.38	1.49
	8	936I3K	[redacted]	0.95	8.76	8.60	9.23
	9	037HKL	[redacted]	11.41	105.25	103.24	110.88
	10	UK0638	[redacted]	36.97	36.59	35.89	38.55
	11	60PLH	[redacted]	112.09	111.51	109.37	117.47
	12	97HLS	[redacted]	1.89	17.43	17.09	18.36
Letdown	13	DNL938	[redacted]	1.09	0.93	0.91	0.98
	14	7Z006	Water/g	124.49	0	0	0
	15		Effluent/g	0	124.85	124.85	124.85
	16	EJDH08	[redacted]	85.05	83.48	81.89	87.95
	17	80093	[redacted]	52.72	52.79	51.78	55.62
	18		Water/g	34.10	0	0	0
	19	7Z006	Effluent/g	0	34.10	34.10	34.10
	20	K55JS8	[redacted]	14.51	13.90	13.64	14.65
	21	8U09JK	[redacted]	8.00	7.41	7.27	7.80
	22	7Z006	Water/g	1.28	0	0	0
	23		Effluent/g	0	12.78	12.78	12.78
Total Mass/g				1000g	1000g	1000g	1000g

Table 26. shows the Crown Vinyl Retail Matt formulation (LFW7047) (for Standard 1., Samples A, B & C), where all the virgin water within the formulation (Std 1.) is replaced with a sample of raw effluent (Samples A, B & C.). Whilst the formulation cannot be fully disclosed due to commercial confidence it demonstrates that the samples matched the original formulation in all other respects other than the water/effluent content.

Two more 2.5 kg samples (D & E) were obtained from the same source (the Hull site's Line 1 process), these were much more dilute than the first range of samples, it was decided that rather than to add the effluent throughout the production process it would be more sensible to add it during the letdown phase (representing 17% of the total product), this was mainly because this minimised any issues with dispersion (which were believed to be responsible for an increased viscosity of the original set of samples), whilst also being more representative of the realistic volumes of effluent on the plant. These were then also tested for scrub, opacity, whiteness and mud crack. These larger samples and the second standard were then applied onto wallpaper via brushes and rollers by a professional decorator (a subject matter expert, SME) within Crown Paints applications lab. This testing was done blind with no information given as to the material in question.

Table 27: Formulations adjusted for additional effluent (Samples: Std 2, D, E).

n.b the ingredients in the formulations have been redacted for commercial confidence

			Sample	Std 2	D	E
			% Solids	0%	5%	6%
Millbase	1	7Z006	Water/g	852.78	852.78	852.78
	2		Effluent/g	0	0	0
	3	8T39E	[redacted]	2.53	2.48	2.47
	4	8POAE	[redacted]	11.10	10.90	10.87
	5	8FAAK	[redacted]	3.78	3.71	3.70
	6	809376	[redacted]	9.48	9.31	9.27
	7	8J826	[redacted]	3.83	3.76	3.74
	8	936I3K	[redacted]	23.75	23.33	23.25
	9	037HKL	[redacted]	285.25	280.22	279.22
	10	UK0638	[redacted]	99.18	97.43	97.08
	11	60PLH	[redacted]	302.20	296.87	295.81
	12	97HLS	[redacted]	47.23	46.39	46.23
Letdown	13	DNL938	[redacted]	2.53	2.48	2.47
	14	7Z006	Water/g	312.13	0	0
	15		Effluent/g	0	312.13	312.13
	16	EJDH08	[redacted]	226.25	222.26	221.46
	17	80093	[redacted]	143.08	140.55	140.05
	18	7Z006	Water/g	85.25	0	0
	19		Effluent/g	0	85.25	85.25
	20	K55JS8	[redacted]	37.68	37.01	36.88
	21	8U09JK	[redacted]	20.08	19.72	19.65
	22	7Z006	Water/g	31.95	0	0
	23		Effluent/g	0	31.95	31.95
Total Mass/g				2500	2500	2500

As with Table 26., Table 27. shows the Crown Vinyl Retail Matt formulation (LFW7047) (for Standard 2., Samples D & E). However, the virgin water addition remains the same as the original formulation for the milbase stage. Following dispersion, (i.e. within the letdown phase) all the virgin water is then replaced with a sample of raw effluent (Samples D & E).

7.2.3 Results

7.2.3.1 QC Testing, Samples: A, B & C

The first set of samples (Std 1, A, B & C) had noticeably high viscosities and none of them (including the standard) would have passed QC testing. This issue could be solved through basic adjustments of the added thickeners at the end of the process.

Table 28: QC Testing of Samples, Std 1, A, B & C.

	QC Spec	Std 1	A	B	C
Rotoball/cP	12.5-16.5	17.7	18.2	17.6	17.5
C & P/cP	0.7-1.0	1.2	1.78	1.24	1.35
pH	8.8-9.2	8.9	7.62	8.49	8.36

7.2.3.2 Scrub Resistance, Samples: A, B & C

Scrub resistance was similar for the first set of samples (Std 1, A, B & C) with A, B & C failing after 35 runs compared to 40 for Std 1. This was seen to be representative of the expected low scrub resistance of the retail matt formulation.

Table 29: Scrub resistance testing of Samples, Std 1, A, B & C.

	Std 1	A	B	C
Average Number of Scrubs	40	35	35	35

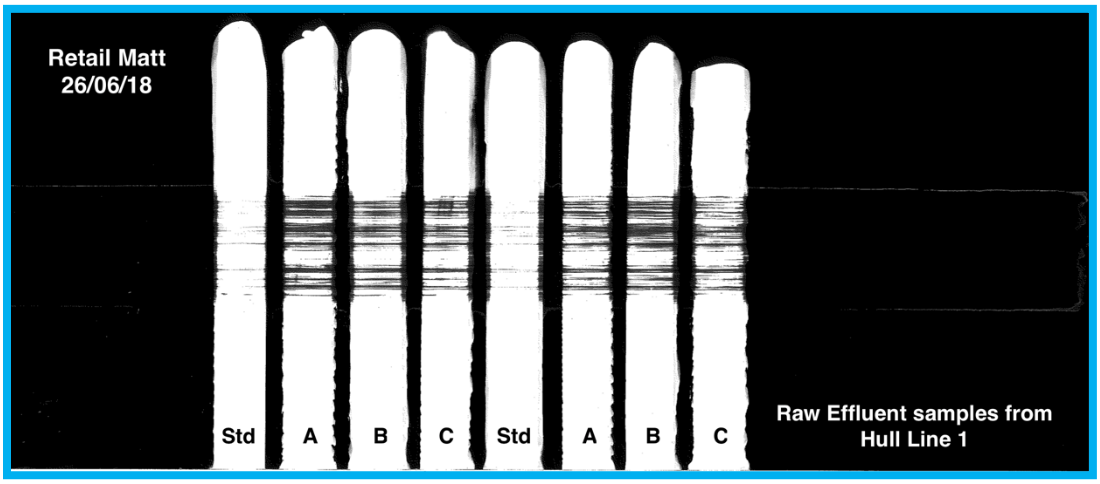


Figure 177: Scrub resistance of Std 1 and Samples A, B & C.

Opacity, Samples: A, B & C

Wet opacity appeared to be lower for samples A, B & C compared to the standard however the dry opacity was visibly better for samples A & C. All the samples with effluent (A, B & C) had a higher contrast ratio compared to the standard when dry.

Table 30: Contrast Ratio for Samples, A, B & C compared with Std 1.

	A		**B**		**C**	
	Std 1	**A**	**Std 1**	**B**	**Std 1**	**C**
CR	94.88	99.59	94.45	95.02	94.64	96.85

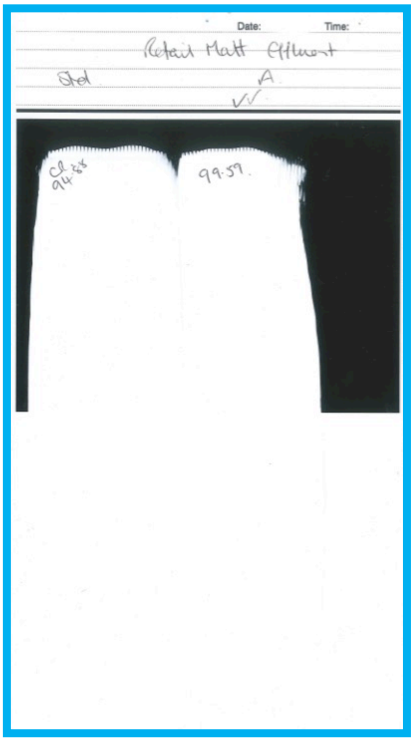


Figure 178: Retail Matt Std 1 & A.

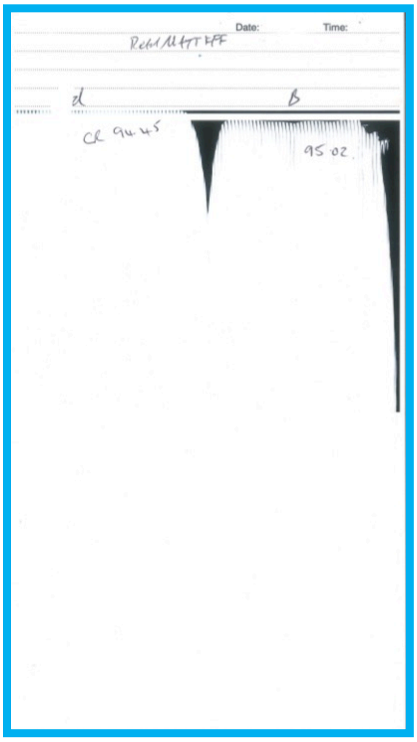


Figure 179: Retail Matt Std 1 & B.

Figure 180: Retail Matt Std 1 & C.

7.2.3.3 Whiteness, Samples: A, B & C

Visually Std 1 appears slightly duller than the other samples (with C appearing the brightest) and with the exception of A & B. All the samples could be visually distinguished against each other with some effort. The CIE whiteness was similar for all samples with Std 1 being slightly whiter.

Table 31: Whiteness Measurements for Samples, Std 1, A, B & C.

	Std 1	**A**	**B**	**C**
CIE	83.09	82.57	82.76	82.28
L	95.86	96.25	96.27	96.3
b	1.46	1.79	1.76	1.88

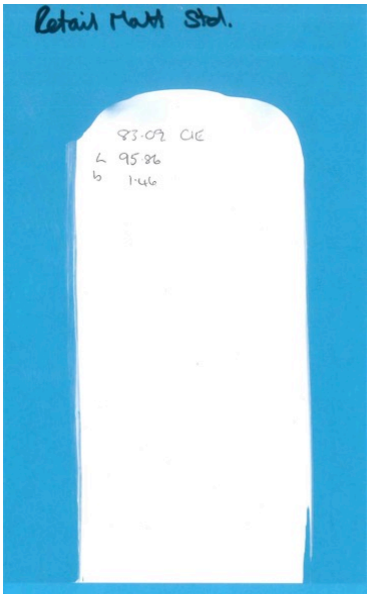


Figure 181: Retail Matt Std1.

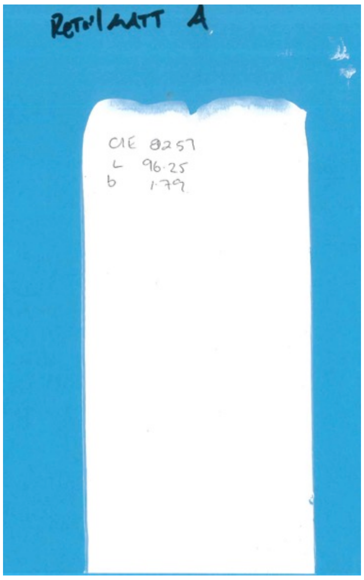


Figure 182: Retail Matt Sample A.

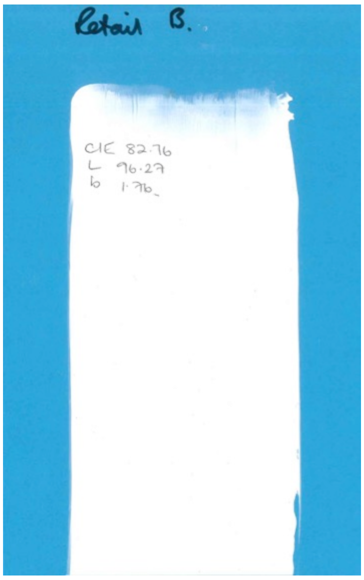


Figure 183: Retail Matt Sample B.

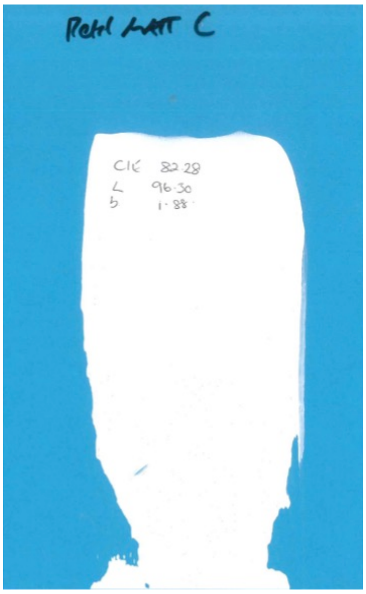


Figure 184: Retail Matt Sample C.

7.2.3.4 Mud Crack, Samples A, B & C

After two weeks no cracking was visible on any of the mud crack samples.

7.2.3.5 Overall Results, Samples: A, B & C

The additional effluent appeared to have little effect on the properties of the Retail Matt formulation. Due to the issues with the increased viscosity (which could indirectly account of the greater opacity) it was decided to repeat the process with two further samples (D & E).

7.2.3.6 QC Testing, Samples: D & E

The second set of samples (D & E) were within QC specification (Std 2 was had a slightly lower viscosity than QC specification).

Table 32: QC Testing of Samples, Std 2, D & E.

	QC Spec	**Std 2**	**D**	**E**
Rotoball/cP	12.5-16.5	10.4	12.6	13.4
C & P/cP	0.7-1.0	0.67	0.79	0.85
pH	8.8-9.2	8.9	9.1	8.8

7.2.3.7 Scrub Resistance, Samples: D & E

The scrub resistance was identical for the second set of samples (Std 2, D &E) all failing after 45 scrubs. There was no identified impact on scrub resistance.

Table 33: Scrub resistance testing of Samples, Std 2, D & E.

	Std 2	**D**	**E**
Average Number of Scrubs	45	45	45

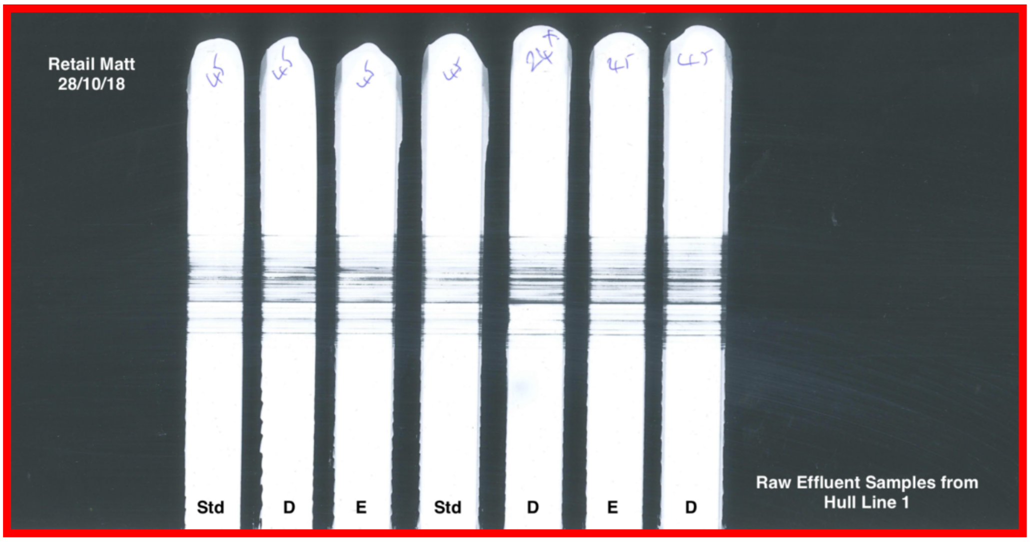


Figure 185:Scrub resistance of Std 2 and Samples D & E.

7.2.3.8 Opacity, Samples: D & E

Visually it was virtually impossible to distinguish between any of the second set of samples (both wet and dry). There was no significant difference in contrast ratios between these samples.

Table 34:Contrast Ratio for Samples, D & E compared with Std 2.

	D		E	
	Std 2	**D**	**Std 2**	**E**
CR	94.52	94.46	94.45	94.41

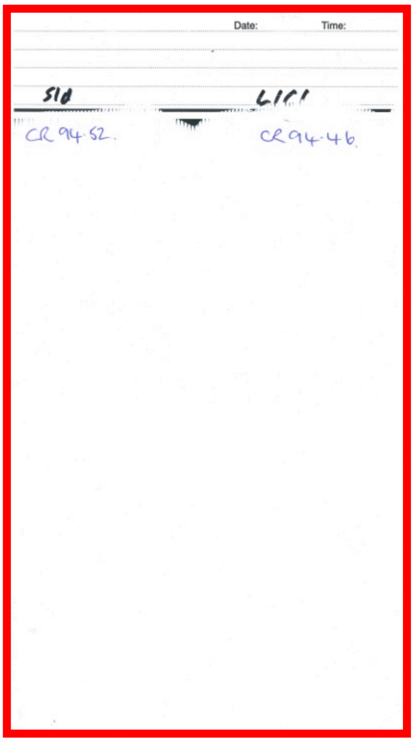


Figure 186: Retail Matt Std 2 & D.

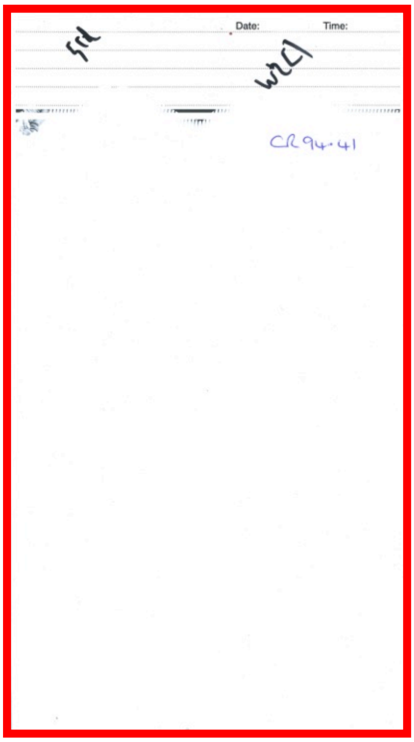


Figure 187: Retail Matt Std 2 & E.

7.2.3.9 Whiteness, Samples: D & E

The whiteness measurements were similar for all these samples (Table 35.).

Table 35: Whiteness Measurements for Samples, Std 2, D & E.

	Std 2	**D**	**E**
CIE	96.08	96.28	96.26
L	1.54	1.8	1.99
b	83.27	82.58	81.71

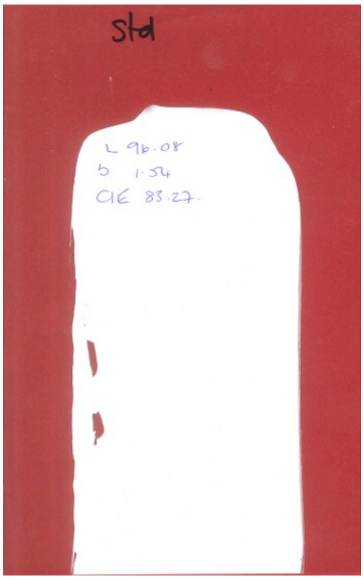


Figure 188: Retail Matt Std 2.

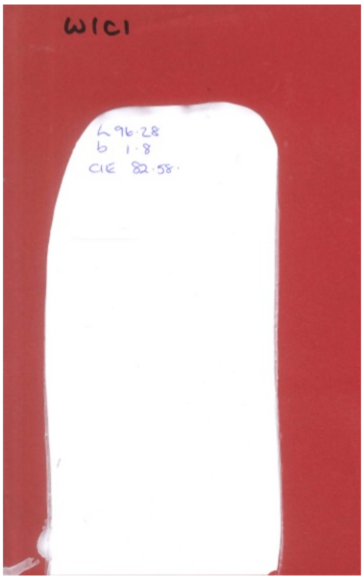


Figure 189: Retail Matt Sample D.

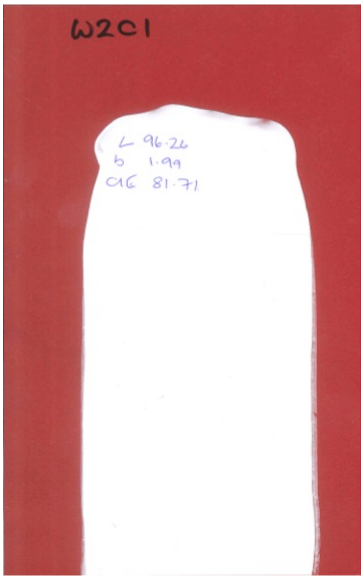


Figure 190:Retail Matt Sample E.

7.2.3.10 Mud Crack, Samples Std 2, D & E

Similarly, to the original samples after two weeks no cracking was visible on any of the mud crack samples.

7.2.3.11 Overall Results, Samples: D & E

Overall Samples D & E were virtually indistinguishable to the Std 2.

7.2.3.12 Applications testing, Samples Std 2, D & E

Applications testing was consistent with the other results for samples D & E. However, there was a slight difference in the weight of material applied to the wallpaper (D & E being higher, E more significantly so) although the paints were indistinguishable otherwise (Figure 191.).

Figure 191: Applications Testing of Std 2 and Samples D & E.

7.2.3.13 Microbe Testing Samples Std 2, D & E

None of the samples showed any microbial activity after being incubated for 3 days.

7.2.4 Conclusions

The results show it is possible to return the washings from Hull's Line 1 back into a formulation at a laboratory scale with limited effect on the properties of the product.

Samples A, B & C had all the virgin water within the formulation replaced with washings. Samples A, B & C performed similar to Std 1 in all testing however were visibly different to Std 1. The opacities were noticeably higher compared to Std 1 and the viscosity of Std 1 and Samples A, B, & C were all out of QC specification.

To mitigate any risk to the dispersion of the powders a more conservative approach was decided upon, where the washings would only be added within the letdown phase of the process.

Samples D & E were then made with all the virgin water from the letdown phase being replaced with washings. Samples D & E were not significantly different to Std 2 in any of the testing.

An estimation of the potential reduction of raw materials (depending on concentration of washings) as a result of the reintroduction of material is provided in Figure 192. based on the concentrations of effluent samples A, B, C & D and the total additional solid material the reintroduction of these samples would represent.

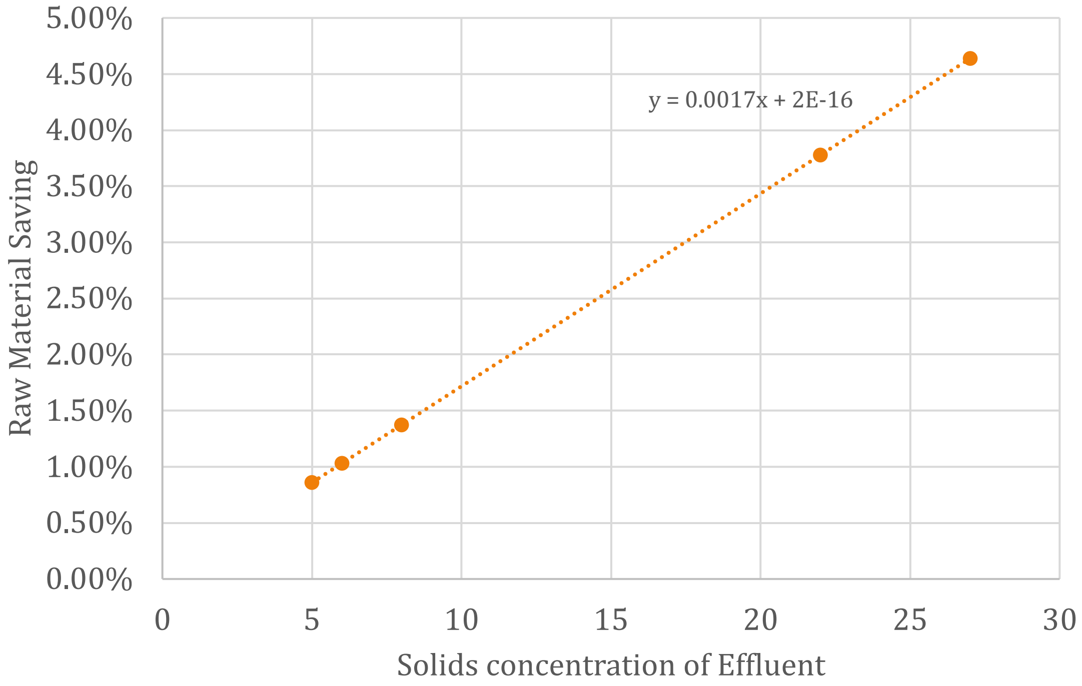


Figure 192: Estimated raw material savings for re-introduced washings into retail matt production.

7.3 Plant Trial

7.3.1 Feasibility and Suggested Methodology

Following the laboratory testing, the production of a 9,000 l trial batch of Crown Retail Matt Magnolia Low Cost Extender with all the virgin water within the letdown phase being replaced with raw effluent was approved. Initially, the aim was to compensate for the additional solids contained within the effluent using the method described in 7.3.1.1. however, an alternative method was decided on during the trail as explained in 7.3.4.

7.3.1.1 Compensating for the addition of solids during the return of reclaimed water

The laboratory testing showed that the concentration of wash water variability could present difficulties if the water was to be returned within manufacturing due to an increased solids concentration of the final product. A basic mathematical solution was identified to mitigate against this excess material.

$$\boldsymbol{Total\ \ Water\ in\ Product = Virgin\ Water + Reclaimed\ Water} \tag{53}$$

To pass the QC testing the water in the product must be equal to the water in the formulation however if the reclaimed water contains any additional material (which will be inevitably the case) the product will contain too much “solid” material, impacting on the products properties.

$$\boldsymbol{Total\ "Solids" = \ Raw\ Material\ "Solids" + Reclaimed\ "Solids"} \tag{54}$$

Because most of the formulations on that Line are approximately the same, we can assume that they have the same ingredients (on the scales in which we are operating under, the effects of any variation in these formulations are massively reduced). This assumption provides us with:

$$\boldsymbol{Solids_F = Solids_{RM}'' + ([Solids_{RW}] \; x \; Quantity \; of \; Reclaimed \; Water)} \qquad \textbf{55}$$

Where:

Solids$_F$, Total "Solids" in a formulation,

Solids$_{RM}$, Total Solids in Raw Materials,

Solids$_{RW}$, Total Solids in Reclaimed Water,

This allows us to mitigate the addition of the extra "solids" into the product via adjusting the quantity of raw material solids thus providing a small but significant additional saving in raw materials (as estimated in Figure 192.).

7.3.1.2 Suggested Trial Batch process

A basic process for the trial batch was devised:

1. A 9,000 l trial batch would be scheduled.
2. The batch card referring to the required batch would be isolated (to prevent the batch from being made prematurely).
3. Washings from the Line 1 hopper would be collected in an IBC.
4. The solids concentration of the IBC would be analysed.
5. The batch card's raw material quantities would be adjusted according to the solids concentration and volume of washings.
6. The batch's milbase will be prepared using virgin water (as normal).
7. The reclaimed water would be added (directly from the IBC) within the letdown phase.
8. The Batch would continue as normal through tinting (if necessary) and Quality Control (QC) testing.
9. The batch would be isolated for a period to allow for a suite of laboratory testing (approx. 90 days).

The aim was to focus on a single variable (the addition of reclaimed water within the letdown phase) and to minimise any risk to the final product, brand, or customer. The use of an IBC for storage was chosen for ease and transportability, it is notable however that the site did have the capability to pump the washings to an additional holding tank before returning them to the product, although this system was not at present compatible with the site's PLC system.

7.3.2 Chosen batch

A 9,000 l trial batch of Crown Retail Matt Magnolia Low Cost Extender was organised to occur on Friday 23rd November 2018 (Sefi: 4039108, Batch No: P05384815800). The week preceding the batch had at least two potential sources for reclaimed water (thus presenting some redundancy if required). The batch also had the advantage of potentially being able to be quarantined for up to three months if required. This provided an adequate time period to perform any detailed QC testing.

7.3.3 Effluent Sampling

The Effluent was collected in an IBC (Figure 193.) from the hopper on Line 1 from two separate batches (on Monday 19th and Wednesday 21st November 2018), it was not mixed or added to until the Friday (23rd November 2018). The scale on the side of the IBC suggested it was approximately full, with 1,000 l of effluent. The mixture was visibly dilute and slightly milky in appearance with a very faint magnolia film (almost like a skin) only visible at the surface (Figure 194.). A core sample of this IBC was taken, and the solids content analysed.

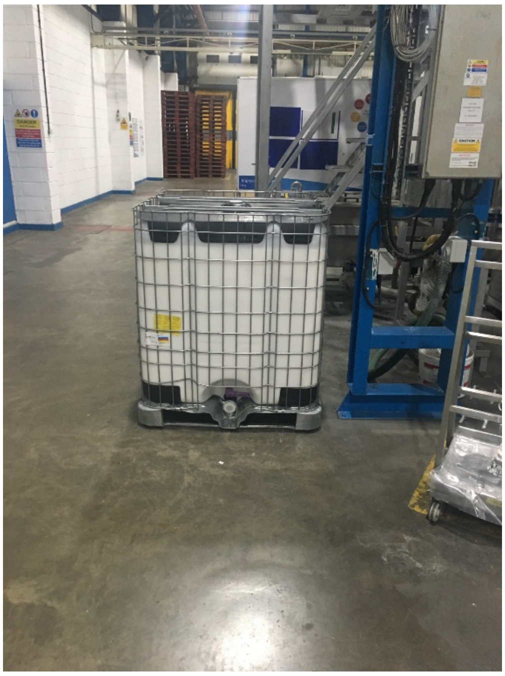


Figure 193: The IBC containing samples.

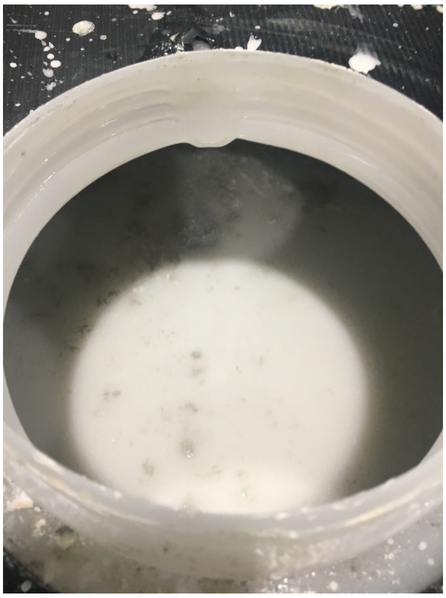


Figure 194: View of the surface of sample.

7.3.3.1 Solids content

The solids content was found to be lower than expected (approx. 5 wt%), this presented a significantly easier material to return to the batch than some previous samples (<40 wt%).

7.3.4 Revised plan

Due to the relatively low solids concentration of the sampled effluent, it was deemed easier to return the effluent directly into the batch without the additional modification of the formulation batch card. The trial therefore would rely on the extra addition of virgin water during the QC stage to effectively provide the same system.

Whilst certainly easier to manufacture, a criticism of this method could be that the overproduction of product (here by 400 l) is considered wasteful from a lean manufacturing perspective (3.1.1.1.).

7.3.5 Milbase

The formulation milbase was produced as normal. Notably, there were issues with the dispersion of the low cost extenders into the product, this had been a recently recurring issue with this raw material.

Figure 195: Weigh tank containing milbase.

7.3.6 Letdown

The washings were returned within the letdown phase directly from the IBC without any issues. In total, 800 kg of reclaimed water was added to the batch (to be extra conservative on volumes).

Figure 196: The full IBC of Reclaimed water being pumped into the Letdown Tank.

7.3.7 Tinting and QC

The product's viscosity was found to be high, as expected due to the additional solid material having yet to be accounted for. An additional 200 l of virgin water was then added to the batch to compensate for this. The addition of this volume of extra water corresponded very well with the concentration of additional materials from the reclaimed water within the batch. This essentially matched the suggested mathematical alteration in raw material quantities (given in Equation 55.). The final batch was approx. 4% larger than the 9,000 l required.

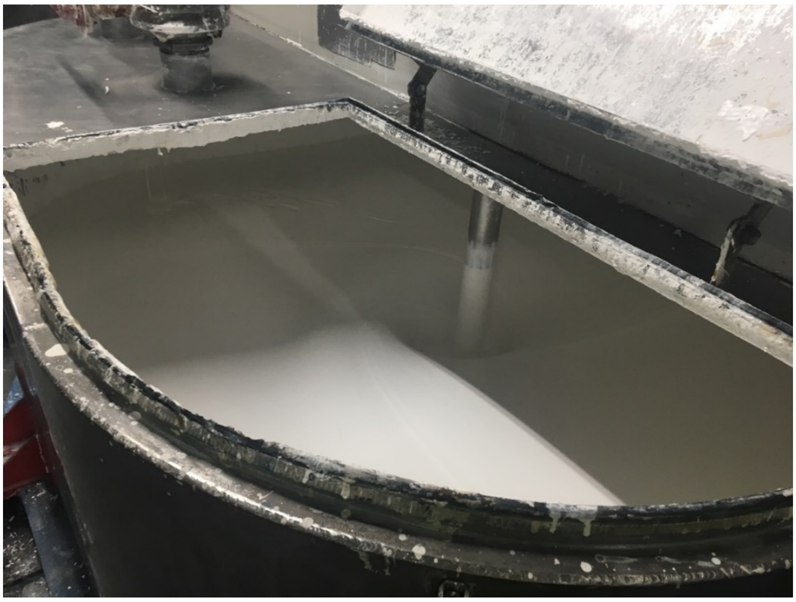


Figure 197: The trial Batch within the Tinting Tank.

Samples of the Batch pre-QC and after tinting were taken.

7.3.8 Laboratory testing of Trail batch

A non-tinted (Std 1) and tinted (Std 2) Retail Matt Magnolia low cost extender standard were sourced from previous batches. The Trial batch was tested against the standards in the same tests as the previous laboratory made paints.

7.3.8.1 Scrub Resistance, Std 1, Std 2, Batch 1, Batch 2

Scrub resistance was notably poor for all samples with each film failing after 5 scrubs. This was also seen to be representative of the lower scrub resistance of the retail matt formulation, which apparently is particularly poor with the addition of the lower cost extender.

Table 36: Scrub resistance testing of Samples, Non-tinted Std 1, Tinted Std 2, Batch 1 (Non-tinted) & Batch 2 (Tinted).

	Std 1	**Std 2**	**Batch 1**	**Batch 2**
Average Number of Scrubs	5	5	5	5

7.3.8.2 Opacity, Std 1, Batch 1,

Table 37: Contrast Ratio for Std 1 and Batch 1.

	Std 1	**Batch 1**
CR	94.75	95.23

The contrast ratio (CR) was similar for both paints, with Batch 1 having visibly better wet opacity, however this visual difference faded when dry.

7.3.8.3 Whiteness, Std 1, Batch 1,

Table 38: Whiteness Measurements for Std 1 and Batch 1.

	Std 1	Batch 1
CIE	81.82	82.02
L	95.97	96.00
b	1.94	1.77

Whiteness measurements showed the trial batch to be slightly whiter than the Std but not significantly.

7.3.8.4 Mud Crack, Std 1, Std 2, Batch 1, Batch 2

As with previous results after two weeks no cracking was visible on any of the mud crack samples.

7.3.8.5 Applications testing, Std 1, Std 2, Batch 1, Batch 2

Applications testing was consistent with the other results for the samples. There was seen to be no significant difference between the Standards and the Trial Batch (Figure 198. & Figure 199.).

Figure 198: Applications testing of Non-tinted Std 1 and Non-Tinted Batch 1.

Figure 199: Applications testing of Tinted Std 2 and Tinted Batch 2.

7.3.8.6 Microbe Testing, Std 1, Std 2, Batch 1, Batch 2

None of the samples showed any significant microbial activity after being incubated for 3 days. The only sample which showed any sign of contamination was Batch 2 (the Tinted Sample) which showed a single bacterial spore (Figure 202.) on both tests, however this was not seen to be a significant result.

Figure 200: Bacterial Growth Batch 1.

Figure 201: Fungal Growth Batch 1.

Figure 202: Bacterial Growth Batch 2.

Figure 203: Fungal Growth Batch 2.

7.3.9 Discussion of the results from the Plant Trial.

As the viscosity of the product as expected was higher than the QC requirement due to the increased solids provided by the effluent an additional 200 l of virgin water was required to bring the batch within the QC specification, resulting in a final batch size approximately 4% larger.

The laboratory testing of the quarantined trial batch (7.3.8.) showed no significant difference between the properties of the trial batch and a standard (Crown Retail Matt Magnolia Low Cost Extender) paint in any of the standard paint tests.

7.3.10 Conclusions from Plant Trial

The plant trial on 23rd November 2018 showed the relative ease in which washings from the Line 1 Hopper at the Hull Site may be returned to the letdown phase of a retail matt formulation. Testing of the trial batch (7.3.8.) has shown no significant difference between the trial batch and the standard paint. As a result, the trial batch was no longer quarantined and approval was given for the batch to enter the market.

The addition of extra solids within the reclaimed water was mitigated against through dilution at the tail end of the production process producing an extra 4% of product. This method proved easier than amending the batch cards (as suggested in 7.3.1.1.) given the circumstances experienced within the trial. However, this solution may prove problematic with higher concentrations of washings (which in some circumstances could require an additional phase where the reclaimed water is diluted to a more manageable concentration).

Estimates of the potential savings from the implementation of this process are circa. £45,000 p.a. (£20,000 Raw Materials, £25,000 Effluent Treatment) based on the volumes and concentrations of washings experienced on the week of the trial. It is notable that much greater effluent concentrations have been observed and there is scope for that value to increase.

7.3.11 Suggested next steps

This work has shown that it is possible to implement the return of this reclaimed wash water into the production process at present. Initially, it is suggested to routinely start collecting effluent from the Line 1 Hopper and to return this into the letdown phase of several select batches, which could be quarantined for paint testing. This could be achieved currently utilising an IBC as this trial has demonstrated until the PLC system can be modified for a longer-term solution (using already available storage tanks). The advantage of a phased approach at least initially would initiate a cultural shift within the organisation towards the return of waste material into the process (across the whole company), whilst minimising the required financial investment and potential risk to the brand.

Whilst the IBC based system is sufficient for delivery of the washwater, the PLC for the identified pipework and vessels should be updated before the process becomes normalised. This restricts the handling of the material and results in a more efficient process.

Whilst a significant step, the Hopper from Line 1 represents a much smaller (in terms of volume but not of concentration) source of effluent than the filter washout process. Further investigations should continue to explore the potential to return this material into the process, whilst potentially presenting some issues with particle size (which could require an additional filter system of its own) the estimated savings are very significant at approx. £200,000 p.a. This return would probably be more complex and require a significant investment but with continued momentum the feasibility of such a process could realistically be identified in 6-9 months.

The final issue would be the return of coloured effluent into the processes, which has been shown throughout this project to be a more complex process. The saving potential is high circa. £100,000 p.a. however it appears to require either (or indeed both) colourant removal or masking of the residual colourants. This may present itself as a much longer-term goal going forward

The method described in this chapter has the potential to be applied throughout the emulsion paint manufacturing industry worldwide. With the potential to increase the efficiency of the processes of the whole sector and significantly reduce raw material useage. Additionally, the reintroduction of waste material into a FMCG manufacturing process is an important development in creating a circular economic system. This simple methodology could be applied to a wide range of processes and presents a wealth of research opportunities.

8 CONCLUSIONS

8.1 Review of the research project

The research described in this thesis is the culmination of a three-year research project based at Crown Paints (KTP 10134[3]). This KTP was built off the success of a one-year MSc by research also based at Crown Paints in collaboration with Nimtech and Lancaster University's Centre for Global Eco-Innovation (CSG). Following the success of that project a collaborative partnership was formed between Lancaster University's departments of Chemistry and Chemical Engineering and Crown Paints. The stated objective of the project is provided in Quote 1.

From the partnership's conception it was intended that the research would be summarised in a thesis for submission for a PhD. Specifically, the aim of the KTP was to reduce the waste burden of Crown Paints' processes. However, it is noted that the research reported in this thesis is targeted at a more general audience within industry and academia. It may be of particular interest in considering FMCG processes, especially those involving the dispersion of material or those with high plant hygiene requirements due to higher concentrations of organic materials. The study into effluent optimisation (Chapter 5.) and stepped pressure filtration (Chapter 6.) may also have a great influence in any process that requires solid/liquid separation via filtration or other means.

8.2 Review of problem

Crown Paints is a world-renowned decorative paint manufacturer based in the North of England, UK. Crown Paints’ total effluent volumes are estimated to be approx. 30,000,000 l (equivalent to 12 Olympic swimming pools) annually of typically 2-5 wt% solid paint. This potentially is a large resource that Crown Paints currently pays to internally treat, dewater, and later disposes from its sites.

The five key deliverables of this work were defined in Section 1.3.:

1. Identify the source of the wash water within the paint manufacturing process and characterise the quantity & composition of the material (detailed within Chapter 3.).
2. Identify potential solutions specifically for the process defined in Deliverable 1. without any commercial, logistic, or financial limitations (Chapter 3.5.).
3. Optimisation of the current effluent treatment process with a view of reducing consumable useage by 50% (Chapter 5.).
4. Develop a new method to study the filtration process which was neglected within Deliverable 3. (Chapter 6.).
5. Ascertain the feasibility of returning washwater into the manufacturing process and create a circular economy within the paint manufacturing process (Chapter 7.).

The following sections will evaluate how this research achieved these deliverables.

8.3 Value stream mapping with an environmental bias

Chapter 3. provides a detailed evaluation of the current paint manufacturing process and characterises the quantity & composition of the washwater and effluent streams.

This work demonstrated the application of the value stream analysis (VSA) mapping tool to a process with a unique perspective. The application of standard continuous improvement tools (such as a value stream analysis) considering “sustainability metrics” (e.g. energy, pollution, resource consumption, waste, etc.) has been an research area in its infancy throughout this project. This work has shown the ability to adapt the VSA tool to use considering different priorities in a unique setting and represents the first novel element of this research.

Specifically, it has shown that basic recording of production data can be used to estimate with some accuracy the composition of generated Effluent Cake
(i.e. Hull 2015: 5.45 “PolyClay”, 2.42% Alum & 92.13% Effluent). It also demonstrated that most of the Effluent is a result of washing of vessels and represents approximately a third of the total water consumption by Crown Paints’ sites (e.g. Darwen: 30.3%,
Hull 2013: 34.06%).

The project has highlighted the value in utilising production data for this purpose and the relative ease such a study may be performed using historic records. This methodology could be readily adapted to various processes providing a VSA with an environmental perspective and thus identifying targeted areas for improvement.

8.4 Identifying of potential solutions

Once the waste was comprehensively evaluated a series of potential solutions was presented in Chapter 4. and an estimate of approximate costs/savings was given (Figure 112.). This provided a hierarchy of solutions giving structure to the project which wasn't constrained by any commercial, logistic, or financial limitations.

In practice the project couldn't possibly focus on all the possible solutions and thus attention was focused on areas where the impact would be maximised given practicalities and resource availability. The optimisation of the current equipment was the area focused on first and this is described within Chapter 5. & Chapter 6. The recycling of reclaimed water into the manufacturing process was then studied as detailed in Chapter 7.

Of the solutions not investigated further within this work, the continuous production model is an area of particular interest for coatings manufacturing. In fact Crown Paints' parent company Hempel invested heavily into specific research in this area during the life of the KTP project. This unfortunately brought the solution with the greatest potential reward out of scope of this research; however, it is worth noting the impact this project has had on drawing the business' attention to the potential advantages of such a production model.

Outside of Crown Paints or indeed within wider industry this hierarchy could be applied when designing plants as an optioneering tool to maximise desired attributes of a given process with the cost/benefit of each solution provided in a simplistic manner.

8.5 Optimisation of current equipment

The potential optimisation of the current effluent process was demonstrated in Chapter 5. through laboratory-based Jar Testing and a full-scale plant trial.

Laboratory (via Jar Tests) and plant trials have demonstrated an ability to reduce the flocculant (“PolyClay”) dose by approximately 50% with no negative impact on water quality. From a chemical perspective this was a complete success however the physical characteristics of the flocculated material (ie. floating, sludgey filtercake) made the processing of this dewatered material difficult in practice. The limitations of the Jar Test methodology made the study of the physical characteristics of the flocculated material impossible via this method.

Sedimentation testing proved extremely difficult to conduct with the rapid settling (and floating) rate of the flocculated material. This would suggest centrifugal and/or dissolved oxygen floatation (DAF) technologies may be worth considering for similar materials.

Within the plant trial, concerns were raised as to the impact on the filtration process. While no significant impact was observed the concern was sufficient to prevent the optimisation study from continuing.

Whilst this work has suggested that further optimisation is certainly possible, due to the concerns raised into the filtration process. Any chemical optimisation should be done in conjunction with the new stepped filtration method (described in Chapter 6.) to characterise the filtration parameters.

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8.6 Stepped filtration method

The new automated stepped pressure filtration method presented in Chapter 6. provides a unique method to characterise the filtration process. Characterising the physico-chemical parameters that revealed how the variations within the coagulation/flocculation process would influence the “yield stress” and “resistivity” of the solid waste “cake” formation.

The design of the apparatus was uniquely simple and provided a vast amount of high-quality data. To aid the data analysis the removal of 95% of the data points was performed. However, this still resulted in sufficient data to model the process effectively.

Practically, the data showed that the material dewaters easier at higher concentrations of “PolyClay” however there is not a significant decrease in hydraulic resistivity of the cake, $\boldsymbol{\rho_s}$ between 50% (1520kgm^{-3}) and 100% (1790kgm^{-3}) “PolyClay” doses. This would suggest limited impact on the filtration process by decreasing the “PolyClay” dose by 50%. However, a limitation of this study was that it was conducted with a standardised “effluent” rather than with a homogenised mixture of various different paints.

For Crown Paints this study suggested no impact on the filtration process from a 50% reduction in “PolyClay” dosing. A recommendation from this work is that the plant trial be repeated with a sample of each flocculated batch being characterised live within this new apparatus.

Chapter 6. provides a method which is innovative from multiple perspectives. It describes a new design for a benchtop filtration apparatus, with pressure provided by gravitational additions of water. It also builds off previous work of De Kretser et al [101] and Usher et al[126] to combine two separate runs to determine compressive yield stress, ***Py(c)*** and resistivity, ***r(c)*** into a single experimental run. Additionally, it represents the first identified reporting of stepped pressure filtration of a flocculated emulsion paint effluent.

The scope of this method is vast and could be applied in any solid liquid dewatering process. Initially a controlled Zirconia suspension should be characterised by this method to compare the results with previous work[101,126]. Following this standardisation, other solid liquid separation processes could also be evaluated via this method.

Within industry this equipment could easily be operated by a standard plant operator and provide an assessment of potential filtration behaviour before the material enters a filter press.

Improvements to the device as described in 6.5.1. would improve the ease for operating the device and potentially dramatically improve the experimental run time (depending on the real time analysis of filtration parameters).

Eventually the study would ideally evolve into developing the online instrumentation of filtration parameters within an active filterpress giving comparable data to the benchtop model presented within this work.

8.7 Return of washwater back into the production process

Chapter 7. evaluates the feasibility of returning reclaimed washwater into the paint manufacturing process without any additional pre-treatment. The study has shown that the effluent generated from Crown Paints’ manufacturing processes can be easily returned to the production process with limited identifiable impact on the quality of the product.

A series of sample paints of a general paint formulation were made containing untreated effluent within a laboratory environment and showed no significant difference with standard paints. Following this testing a 9,000 l trial batch of Crown Vinyl Retail Matt was generated with 800 l of reclaimed water. This product entered the market with no negative consequences. Through the addition of additional solids within the effluent the batch size was increased by 4% at no additional cost to Crown Paints.

Practically, the largest quality concern when considering the reintroduction of raw effluent into a product appears to be the residual colourants within the effluent and thus the impact on the colour of the final product. At concentrations of less than 4% solid material the variability of this colour can cause visible differences within white paint formulations. Colourant removal is certainly an option however this increases the complexity of the process. The solution presented here was to mask any residual colour with additional colourants shading the paint to a magnolia colour. This method was chosen as it didn’t require any significant investment from the business to implement (such as new plant etc.) however the opportunity to remove colourant contamination remains possible and should be the subject of future investigation.

Long term the process should be designed to separate different colours (or at least similar colours). The eclectic colour mix of the present homogenised effluent could then be avoided as much as possible. White paint represents the bulk of demand and white washings could easily be isolated and recirculated back into production with limited impact. Using a standardised base and in-can mixing of the colourants (such as currently conducted within stores) would also remove the colourant issue.

Implementing this across similar industries should be possible especially where similar formulations are repeated on the same production lines. The reintroduction of washwater would certainly be possible in many FMCG processes. Quality control (QC) concerns would need to be considered and thus this method is unlikely to be adapted within food or pharmaceutical industry however it is likely it could be applied within many consumer goods manufacturing processes

8.8 Overall impact of project

In terms of impact the success of the project was highlighted in an Impact Case Study for REF 2021, titled: " Lancaster University research improves the monitoring, control and optimisation of paint wastewater processing at one of the UK's largest paint manufacturing companies"[2]. The case study provides a context of this project and previous projects with the same academic team whilst providing evidence to support estimates of the financial impact of the research. The case study highlights the following impacts of the work described in this thesis:

1. An approx. £113,000 per annum saving on the cost of regents used within the effluent plant at both of Crown Paints production sites (Darwen and Hull). This is primarily due to the work described in Chapter 5. & Chapter 6.
2. An investment of £145,000 into the construction and commissioning of new waste paint processing plant at the Darwen and Hull manufacturing sites following recommendations of this work. The case study specifically details the investment in metering at the Darwen site necessary for the Value Stream Analysis work in Chapter 3. It is worth noting that much of this investment occurred at the Hull site and it was very beneficial to this project to have been implemented before the effluent plant trial described in Chapter 5. (as it provided significantly better process control methods).
3. The return of recycled water into the paint manufacturing process described in Chapter 7. The impact case study states that this is currently being adopted into the manufacturing process and thus into the market.
4. The novel method to determine yield stress and resistivity detailed in Chapter 6.

5. Additionally, but not detailed within this thesis was a study using Field-Emission Scanning Electron Microscope to understand the formation of paint films. The finds of which were presented to Crown Paints' parent Hempel Group to assist in diagnosing the failure of paint formulations.

The impact on Crown Paints of this research has been clearly demonstrated however further work is necessary to implement the findings of this work into other businesses and industries.

9 REFERENCES

List of references:

1. Wardrop, J, Baldock SJ, Coote, I, Demaine, R, Fielden, PR, Martin A. Rapid Characterisation of Suspensions for Waste Treatment and Resource Recovery. ChemRxiv. Cambridge: Cambridge Open Engage (2020). doi: 0.26434/chemrxiv.13385429.v1. Available at: https://chemrxiv.org/articles/preprint/Rapid_Characterisation_of_Suspensions_for_Waste_Treatment_and_Resource_Recovery/13385429. This content is a preprint and has not been peer-reviewed.

2. Fielden, P. & Martin, A. Lancaster University research improves the monitoring, control and optimisation of paint wastewater processing at one of the UK's largest paint manufacturing companies. REF 2021 Impact case study database (2022). Available at: https://results2021.ref.ac.uk/impact/02278c1b-3d17-492f-86eb-c46e848d148a?page=1. (Accessed: 7th July 2022).

3. KTP Online. Knowledge Transfer Partnership 10134- details. Available at: https://info.ktponline.org.uk/action/details/partnership.aspx?id=10134. (Accessed: 3rd April 2022).

4. Satyro, W. C., Sacomano, J. B., Contador, J. C. & Telles, R. Planned obsolescence or planned resource depletion? A sustainable approach. J. Clean. Prod. 195, 744–752 (2018). doi:10.1016/j.jclepro.2018.05.222.

5. United Nations Department of Economic and Social Affairs Population Division. World population prospects 2019. Department of Economic and Social Affairs. World Population Prospects 2019. (2019). ISBN: 9789211483161.

6. United Nations. Goal 12: Ensure sustainable consumption and production patterns. (2021). Available at: https://www.un.org/sustainabledevelopment/sustainable-consumption-production/. (Accessed: 10th September 2021).

7. European Commission. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. A new Circular Economy Action Plan For a cleaner and more competitive Europe. (2020). Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1583933814386&uri=COM:2020:98:FIN (Accessed: 10th September 2021).

8. EPEA. Cradle to Cradle. C2C TW (2020). Available at: https://www.c2cplatform.tw/en/c2c.php?Key=1. (Accessed: 5th August 2022).

9. Soldal, O. Circular Bricks: Getting the circular construction industry to shore. A scenario analysis of building material streams through the Port of Oslo. (2019). doi:10.13140/RG.2.2.18343.70569.

10. Lawlor, R. Delaying Obsolescence. Sci. Eng. Ethics 21, 401–427 (2014). doi:10.1007/s11948-014-9548-6. ISSN: 14715546.

11. Agrawal, V. V. & Ülkü, S. The role of modular upgradability as a green design strategy. Manuf. Serv. Oper. Manag. 15, 640–648 (2013). doi: 10.1287/msom.1120.0396. ISSN: 15234614.

12. Proske, M. & Jaeger-Erben, M. Decreasing obsolescence with modular smartphones? – An interdisciplinary perspective on lifecycles. J. Clean. Prod. 223, 57–66 (2019). Available at: https://doi.org/10.1016/j.jclepro.2019.03.116. doi: 10.1016/j.jclepro.2019.03.116. ISSN: 09596526.

13. Mishra, J. L., Hopkinson, P. G. & Tidridge, G. Value creation from circular economy-led closed loop supply chains: a case study of fast-moving consumer goods. Prod. Plan. Control 29, 509–521 (2018). doi: 10.1080/09537287.2018.1449245. ISSN: 1366587.

14. Niero, M. & Kalbar, P. P. Coupling material circularity indicators and life cycle based indicators: A proposal to advance the assessment of circular economy strategies at the product level. Resour. Conserv. Recycl. 140, 305–312 (2019). doi:10.1016/j.resconrec.2018.10.002. ISSN: 18790658.

15. Environment Agency. Technical Guidance WM3: Waste Classification - Guidance on the classification and assessment of waste. (2015). Available at: https://www.gov.uk/government/publications/waste-classification-technical-guidance. (Accessed: 10th September 2021).

16. Dursun, D. & Sengul, F. Waste minimization study in a solvent-based paint manufacturing plant. Resour. Conserv. Recycl. 47, 316–331 (2006). doi: 10.1016/j.resconrec.2005.12.004. ISSN: 09213449.

18. Salihoglu, G. & Salihoglu, N. K. A review on paint sludge from automotive industries: Generation, characteristics and management. J. Environ. Manage. 169, 223–235 (2016).doi: 10.1016/j.jenvman.2015.12.039. ISSN: 10958630.

19. Performance Review Institute. Nadcap. (2019). Available at: https://p-r-i.org/Nadcap/. (Accessed: 11th September 2021).

20. United Kingdom Environmental Law Association (UKELA). Landfill waste disposal. (2017). Available at: http://www.environmentlaw.org.uk/rte.asp?id=243. (Accessed: 11th September 2021).

21. European Commission. Pinasseau, A., Zerger, B., Roth, J., Canova, M., Roudier, S., JRC Science for Policy Report: Best Available Techniques (BAT) Reference Document for Waste Treatment Industries (Draft). (2015). Available at: https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/JRC113018_WT_Bref.pdf (Accessed: 11th September 2021). ISBN: 9789279940385.

22. Almesfer, N., Haigh, C. & Ingham, J. Waste paint as an admixture in concrete. Cem. Concr. Compos. 34, 627–633 (2012). Available at: http://linkinghub.elsevier.com/retrieve/pii/S0958946512000212. doi: 10.1016/j.cemconcomp.2012.02.001. ISSN: 09589465.

23. Khezri, S. M., Shariat, S. M. & Tabibian, S. Evaluation of extracting titanium dioxide from water-based paint sludge in auto-manufacturing industries and its application in paint production. Toxicol. Ind. Health 29, 697–703 (2013). Available at: https://pubmed.ncbi.nlm.nih.gov/22474031/. (Accessed: 01st December 2014). doi: 10.1177/0748233711430977. ISSN: 1477-0393.

24. Mahayan, D. FMCG companies join hands to protect environment. afaqs! (2019). Available at: https://www.afaqs.com/news/mktg/fmcg-companies-join-hands-to-protect-environment. (Accessed: 11th September 2021).

25. Unilever. Rethinking plastic packaging. (2021). Available at: https://www.unilever.com/planet-and-society/waste-free-world/rethinking-plastic-packaging/. (Accessed: 11th September 2021).

26. Montagnino, K. Johnson & Johnson Consumer Aligns to Big Goals In Environmental Sustainability, Signs New Plastics Economy Global Commitment. (2018). Available at: https://www.jnj.com/johnson-johnson-consumer-aligns-to-big-goals-in-environmental-sustainability-signs-new-plastics-economy-global-commitment. (Accessed: 11th September 2021).

27. Procter & Gamble. Reducing Virgin Plastic: P&G’s Commitment to Sustainability. (2020). Available at: https://www.pggoodeveryday.com/good-news/how-pg-is-reducing-plastic-in-packaging/. (Accessed: 11th September 2021).

28. The Coca-Cola Company. SUSTAINABLE PACKAGING. (2021). Available at: https://www.coca-colacompany.com/sustainable-business/packaging-sustainability. (Accessed: 11th September 2021).

29. Males, J. & Van Aelst, P. Did the Blue Planet set the Agenda for Plastic Pollution? An Explorative Study on the Influence of a Documentary on the Public, Media and Political Agendas. Environ. Commun. 1–15 (2020). doi:10.1080/17524032.2020.1780458.

30. Tatum, M. How big is the problem with greenwashing?: Fmcg brands are under pressure to be green. That’s brought about a large number of dubious claims - but UK regulators are now getting on the case. Grocer 22 (2021). Crawley: NLA Media. ISSN: 0017-4351.

31. McCarthy, J. & Sánchez, E. 5 Plastic Alternatives Doing More Harm Than Good — and What to Use Instead. Global Citizen (2019). Available at: https://www.globalcitizen.org/en/content/plastic-alternatives-doing-harm/. (Accessed: 11th September 2021).

32. Alternatives to chemicals used in plastic containers are equally harmful, says study. Progress. Digit. Media Packag. News (2015). London: GlobalData plc.

33. Green Alliance. Plastic promises What the grocery sector is really doing about packaging. (2020). Available at: https://green-alliance.org.uk/resources/Plastic_promises.pdf. Accessed: 11th September 2021). ISBN: 9781912393459.

34. OED Online. paint, n. Oxford University Press (2021). Available at: www.oed.com/view/Entry/136077. (Accessed: 11th September 2021).

35. The Council of the European Union. Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations. Official Journal of the European Union 42, (1999). Available at: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=OJ:L:1999:085:FULL&from=EN.

36. Chemiewinkel Enterprise Ireland, W. EC DG Environment Tender E1/ETU/980084 DECOPAINT: Study on the Potential for Reducing Emissions of Volatile Organic Compounds (VOC) Due To The Use Of Decorative Paints and Varnishes for Professional and Non-professional Use. (2000). Available at: http://ec.europa.eu/environment/archives/air/pdf/paint_solvents/decopaint.pdf. (Accessed: 11th September 2021).

37. Eastman. Eastman Texanol (TM) Ester Alcohol. Safety Data Sheet 0, (2018). Available at: http://ws.eastman.com/ProductCatalogApps/PageControllers/MSDS_PC.aspx?Product=71000148 (Accessed: 11th September 2021).

38. Encyclopædia Britannica Inc. Copolymers and polymer blends. Encyclopædia Britannica (2021). Available at: https://www.britannica.com/topic/industrial-polymer-chemistry-468716/Organometallic-catalysis. (Accessed: 26th September 2021).

39. Zhao, L., Zhu, W., Papadaki, M. I., Mannan, M. S. & Akbulut, M. Probing into Styrene Polymerization Runaway Hazards: Effects of the Monomer Mass Fraction. ACS Omega 4, 8136–8145 (2019). doi:10.1021/acsomega.9b00004. ISSN: 24701343.

40. US Chemical Safety Board. Hazard Investigation Improving Reactive Hazard Management. CSB (2002). Available at: https://www.csb.gov/assets/1/20/reactivehazardinvestigationreport.pdf?13865 (Accessed: 11th September 2021).

41. Sales, J., Mushtaq, F., Christou, M. D. & Nomen, R. Study of major accidents involving chemical reactive substances analysis and lessons learned. Process Saf. Environ. Prot. 85, 117–124 (2007). doi: 10.1205/psep06012. ISSN: 09575820.

42. Lovell, P. A. & Schork, F. J. Fundamentals of Emulsion Polymerization. Biomacromolecules 21, 4396–4441 (2020). doi: 10.1021/acs.biomac.0c00769. ISSN: 15264602.

43. Jensen, A. T. et al. 8 - Synthesis of polymer/inorganic hybrids through heterophase polymerizations. in Recent Developments in Polymer Macro, Micro and Nano Blends (eds. Visakh, P. M., Markovic, G. & Pasquini, D.) 207–235 (Woodhead Publishing, 2017). doi:https://doi.org/10.1016/B978-0-08-100408-1.00008-X. ISBN: 978-0-08-100408-1.

44. Harkins, W. D. A General Theory of the Mechanism of Emulsion Polymerization. J. Am. Chem. Soc. 69, 1428–1444 (1947).doi: 10.1021/ja01198a053. ISSN: 15205126.

45. Smith, W. V. & Ewart, R. H. Kinetics of emulsion polymerization. J. Chem. Phys. 16, 592–599 (1948). doi: 10.1063/1.1746951. ISSN: 10974628.

46. Firesine. Schematic diagram of emulsion polymerization. (2006). Available at: https://commons.wikimedia.org/wiki/File:Emulsion_Polymerization_Cartoon_3.svg. (Accessed: 11th September 2021).

48. Reusch, W. Visible and Ultraviolet Spectroscopy. (2013). Available at: https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/uv-vis/spectrum.htm. (Accessed: 1st July 2020).

49. LAKSHMI. LIGHT AND COLOUR. (2015). Available at: https://scijournallakshmi.wordpress.com/category/additive-and-subtractive/. (Accessed: 1st July 2015).

50. Mahroo, O. A. et al. Do twins share the same dress code? Quantifying relative genetic and environmental contributions to subjective perceptions of “the dress” in a classical twin study. J. Vis. 17, 29 (2017). doi: 10.1167/17.1.29. ISSN: 1534-7362.

51. Kuriki, I. A Novel Method of Color Appearance Simulation Using Achromatic Point Locus With Lightness Dependence. Iperception. 9, 1–16 (2018). doi: 10.1177/2041669518761731. ISSN: 20416695.

52. Logvinenko, A. D. An object-color space. J. Vis. (Charlottesville, Va.) 9, 5.1--5 (2009). ISSN: 1534-7362.

53. Bertolino, M. Etude de la procédure de stimulus fading dans l ’ apprentissage d ’ une discrimination visuelle Étude de la procédure de stimulus fading dans l ’ apprentissage d ’ une discrimination visuelle. (Université de Lille, Français. 2019). Available at: https://tel.archives-ouvertes.fr/tel-02569402.

54. British Standards Institution. BS EN ISO 11664-4:2011 Colorimetry Part 4: CIE 1976 L*a*b* Colour space. (2011). ISBN: 978 0 580 72262 2.

55. British Standards Institution. BS 3900-D10:1986, ISO 7724-3:1984: Methods of test for paints. Determination of colour and colour difference: calculation. (1986). ISBN: 0 580 15363 0.

56. Uzeda, G. How to create lab color chart using opencv. Stack Overflow (2018). Available at: https://stackoverflow.com/questions/52741742/how-to-create-lab-color-chart-using-opencv. (Accessed: 26th September 2021).

57. X-Rite PANTONE. X-Rite Colour Blog: LAB Colour Values. Available at: https://www.xrite.com/blog/lab-color-space. (Accessed: 13th July 2020).

58. Carter, E. C. et al. COLORIMETRY. (Commission Internationale de l'Eclairage, CIE, 2018). doi:10.25039/TR.015.2018. ISBN: 978-3-902842-13-8.

59. Hunt, R. W. G. & Pointer, M. R. Measuring Colour. (John Wiley & Sons, Incorporated, 2011). Available at: http://ebookcentral.proquest.com/lib/lancaster/detail.action?docID=693754. ISBN: 9781119975731.

60. Choudhury, A. K. R. 9.5 Topology of Whiteness. in Principles of Colour Appearance and Measurement 355–364 (Elsevier, 2014). doi: 10.1533/9780857099242.344. ISBN: 9780857099242.

61. Dey, S., Ricciardo, R. A., Cuthbert, H. L. & Woodward, P. M. Metal-to-metal charge transfer in AWO4 (A = Mg, Mn, Co, Ni, Cu, or Zn) compounds with the wolframite structure. Inorg. Chem. 53, 4394–4399 (2014). doi: 10.1021/ic4031798. ISSN: 1520510X.

62. Rogers, D. M. & Johansson, J. O. Metal-to-metal charge-transfer transitions in Prussian blue hexacyanochromate analogues. Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 227, 28–38 (2018). doi: 10.1016/j.mseb.2017.10.003. ISSN: 09215107.

63. Hradil, D., Grygar, T., Hradilová, J. & Bezdička, P. Clay and iron oxide pigments in the history of painting. Appl. Clay Sci. 22, 223–236 (2003). doi: 10.1016/S0169-1317(03)00076-0. ISSN: 01691317.

64. Müller-Wille, S. Marianne Sommer, Bones and Ochre: The Curious Afterlife of the Red Lady of Paviland. Cambridge, MA and London: Harvard University Press, 2007. Pp. xii+398. ISBN 978-0-674-02499-1. Br. J. Hist. Sci. 42, 619–620 (2009). ISBN 978-0-674-02499-1. ISSN: 0007-0874.

65. KREMER PIGMENTE. Yellow Ochre, from Andalusia. (2022). Available at: https://www.kremer-pigmente.com/en/shop/pigments/11272-yellow-ochre-from-andalusia.html. (Accessed: 5th July 2022).

66. Lesso, R. Red Ochre: The Colour of Survival. Fabrics store blog (2020). Available at: https://blog.fabrics-store.com/2020/04/28/red-ochre-the-colour-of-survival/. (Accessed: 5th July 2022).

67. Christie, R. M. Colour chemistry. 2nd Edition. (Royal Society of Chemistry, Cambridge, UK, 2015).ISBN: 9781680158045. ISSN: 9781849733281.

68. Dey, B. ., Hashim, M., Hasan, S. & Sen Gupta, B. Microfiltration of water-based paint effluents. Adv. Environ. Res. 8, 455–466 (2004). doi: 10.1016/S1093-0191(02)00122-3. ISSN: 10930191.

69. Health and Safety Executive. Approved Code of Practice and Guidance L8. Legionnaires ’ disease: The Control of Legionella Bacteria in Water Systems. (2013). Available at: https://www.hse.gov.uk/pubns/priced/l8.pdf. (Accessed: 9th July 2020).

70. Hydro X. Microbiological Dipslides. Available at: https://www.hydro-x.co.uk/hxstore/microbiological-dipslides/. (Accessed: 5th September 2021).

71. REYNOLDS, P. A. The Rheology of Coatings. in The chemistry and physics of coatings (ed. Marrion, A. R.) 26–45 (Royal Society of Chemistry, 2007). doi: 10.1016/j.cemconcomp.2012.02.001. ISSN: 09589465.

72. SOLVAY. Solutions for Improved Flow Profiles in Coatings. (2022). Available at: https://www.solvay.com/en/solutions-market/building/coatings/architectural-industrial/rheology. (Accessed: 5th July 2022).

73. Bieleman, J. H. Organic thickeners for water-borne paints. Chimia (Aarau). 56, 163–169 (2002). doi:10.2533/000942902777680504. ISSN: 00094293.

74. SpecialChem. Rheology Modifiers Selection for Paints & Coatings. (2021). Available at: https://coatings.specialchem.com/selection-guide/rheology-modifiers-selection-for-waterborne-and-solventborne-coatings. (Accessed: 26th September 2021).

75. British Standards Institution. BS EN ISO 2884-1-2006: Paints and varnishes — Determination of viscosity using rotary viscometers. 3, (BSI, 2006). ISBN: 0 580 42257 7.

76. ASTM. D2486-06: Standard Test Methods for Scrub Resistance of Wall Paints 1. ASTM Int. 06, 6–9 (2015). doi: 10.1520/D2486-06R12E01.2.

77. Haynes, W. CRC handbook of chemistry and physics : A ready-reference book of chemical and physical data. (CRC Press, 2010). ISBN: 9781439820773.

78. British Standards Institution. BS EN ISO 2884-2:2006:Paints and varnishes Determination of viscosity using rotary viscometers Part 2: Disc or ball viscometer operated at a specified speed. 3, (2006).ISBN: 0580422577.

79. International Organization for Standardization (ISO). ISO 7724-2:1984: Paints and varnishes - Colorimetry - Part 2: Colour measurement. (1984).ISBN: 7723/2.

80. Hunter, R. S. Photoelectric Tristimulus Colorimetry with Three Filters. J. Opt. Soc. Am. 32, 509–538 (1942). doi: 10.1364/JOSA.32.000509.

81. British Standards Institution. BS EN ISO 2814:2006 BS 3900-D4:2006 Paints and varnishes — Comparison of contrast ratio (hiding power) of paints of the same type and colour. 3, (2006). ISBN: 978 0 580 50069 5.

82. British Standards Institution. BS EN ISO 11998:2006 Paints and varnishes. Determination of wet-scrub resistance and cleanability of coatings. 3, (2006). ISBN: 978 0 580 55354 7.

83. Dören, K., Freitag, W. & Stoye, D. Water-Borne Coatings. (Hanser Gardner Publications, 1994). ISBN: 978-1569901397.

84. BYK Additives & Instruments. Wetting and Dispersing Additives. Tech. Inf. PVC-TI 2, (2009). Available at: https://www.byk.com/en/product/wetting-and-dispersing-additives. (Accessed: 9th July 2020).

85. Rotstein, G., Shah, N., Sorensen, E., Macchietto, S. & Weiss, R. A. Analysis and design of paint manufacturing processes. Comput. Chem. Eng. 22, 279–282 (1998). doi: 10.1016/s0098-1354(98)00065-9. ISSN: 00981354.

86. Reuters Staff. Akzo Nobel completes ICI takeover | Reuters. Reuters (2008). Available at: https://uk.reuters.com/article/uk-ici/akzo-nobel-completes-ici-takeover-idUKWEB129220080102. (Accessed: 27th May 2022).

87. Crown Paints. Colour Matching Service. (2022). Available at: https://www.crownpaintsprofessional.com/specification-services/colour-service/colour-matching-service/. (Accessed: 27th May 2022).

88. Jones, E. R., Van Vliet, M. T. H., Qadir, M. & Bierkens, M. F. P. Country-level and gridded estimates of wastewater production, collection, treatment and reuse. Earth Syst. Sci. Data 13, 237–254 (2021). doi: 10.5194/essd-13-237-2021. ISSN: 18663516.

89. Sathya, K., Nagarajan, K., Carlin Geor Malar, G., Rajalakshmi, S. & Raja Lakshmi, P. A comprehensive review on comparison among effluent treatment methods and modern methods of treatment of industrial wastewater effluent from different sources. Appl. Water Sci. 12, 1–27 (2022). doi: 10.1007/s13201-022-01594-7. ISBN: 1320102201594. ISSN:21905495.

90. Bostock, J. Pliny the Elder. The Natural History. (Taylor and Francis, London, 1855). Available at: http://www.perseus.tufts.edu/hopper/text?doc=urn:cts:latinLit:phi0978.phi001.perseus-eng1:35.5289. (Accessed: 9th July 2020).

91. Pernitsky, D. J. COAGULATION 101. Available at: https://www.rmwea.org/docs/Coagulation_DavidPernitsky_Nov2020.pdf. (Accessed: 9th July 2020).

92. Howe, K. J., Hand, D. W., Crittenden, J. C., Trussell, R. R. & Tchobanoglous, G. Chapter 5. Coagulation and Flocculation. in Principles of Water Treatment (John Wiley & Sons, 2012). ISBN: 978-0-470-40538-3.

94. Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. 9.6.1.3 Differential Settling. in MWH's Water Treatment - Principles and Design (3rd Edition) (John Wiley & Sons, 2012). ISBN: 978-0-470-40539-0.

95. Aragonés-Beltrán, P., Mendoza-Roca, J. A., Bes-Piá, A., García-Melón, M. & Parra-Ruiz, E. Application of multicriteria decision analysis to jar-test results for chemicals selection in the physical-chemical treatment of textile wastewater. J. Hazard. Mater. 164, 288–295 (2009). doi: 10.1016/j.jhazmat.2008.08.046. ISSN: 03043894.

96. ASTM. D4287: Standard Test Method for High-Shear Viscosity Using a Cone / Plate Viscometer 1. Astm 00, 1–3 (2015). doi: 10.1520/D4287-00R19.

97. Sengupta, S. Water Treatment: Theory and Practice. (2017). ISBN: 9781606505724. ISSN: 23753625.

98. Buscall, R. & White, L. R. The consolidation of concentrated suspensions. Part 1.—The theory of sedimentation. J. Chem. Soc.{,} Faraday Trans. 1 83, 873–891 (1987). doi: 10.1039/F19878300873.

99. Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. 10.2.1 Settling Velocity of Discrete Particles. MWH's Water Treatment - Principles and Design (3rd Edition) (2012).ISBN: 978-0-470-40539-0.

100. Sparks, T. & Chase, G. 4.7.1 Filter Press. in Filters and Filtration Handbook (6th Edition) (Elsevier, 2016). ISBN: 978-0-08-099396-6.

101. Landman, K. A. & White, L. R. Solid/liquid separation of flocculated suspensions. Adv. Colloid Interface Sci. 51, 175–246 (1994). doi:10.1016/0001-8686(94)80036-7. ISSN: 00018686.

102. Landman, K. A. & White, L. R. Predicting Filtration Time and Maximizing Throughput in a Pressure Filter. AIChE J. 43, 3147–3160 (1997). doi: 10.1002/aic.690431204. ISSN: 00011541.

103. Green, M. D., Landman, K. A., De Kretser, R. G. & Boger, D. V. Pressure filtration technique for complete characterization of consolidating suspensions. Ind. Eng. Chem. Res. 37, 4152–4156 (1998). doi: 10.1021/ie970544i. ISSN: 08885885.

104. De Kretser, R. G., Usher, S. P., Scales, P. J., Boger, D. V. & Landman, K. A. Rapid filtration measurement of dewatering design and optimization parameters. AIChE J. 47, 1758–1769 (2001). doi: 10.1002/aic.690470808. ISSN: 00011541.

105. Pyzdek, T. & Keller, P. The Six Sigma Handbook. (Mc Graw Hill Education, 2014). ISBN: 978-0-07-184053-8.

106. Ramana, P. What is Six Sigma? Six Sigma Study Guide Available at: https://sixsigmastudyguide.com/what-is-six-sigma/. (Accessed: 18th January 2021).

107. Skhmot, N. The 8 Wastes of Lean. THE LEAN WAY BLOG (2017). Available at: https://theleanway.net/The-8-Wastes-of-Lean. (Accessed: 18th January 2021).

108. Shou, W., Wang, J., Wu, P., Wang, X. & Chong, H. Y. A cross-sector review on the use of value stream mapping. Int. J. Prod. Res. 55, 3906–3928 (2017). doi: 10.1080/00207543.2017.1311031. ISSN: 1366588X.

109. Belekoukias, I., Garza-Reyes, J. A. & Kumar, V. The impact of lean methods and tools on the operational performance of manufacturing organisations. Int. J. Prod. Res. 52, 5346–5366 (2014). doi: 10.1080/00207543.2014.903348. ISSN: 1366588X.

110. Lai, J., Harjati, A., McGinnis, L., Zhou, C. & Guldberg, T. An economic and environmental framework for analyzing globally sourced auto parts packaging system. J. Clean. Prod. 16, 1632–1646 (2008). doi: 10.1016/j.jclepro.2008.01.011. ISSN: 0959-6526.

111. Torres, A. S. & Gati, A. M. Environmental Value Stream Mapping (EVSM) as sustainability management tool. in PICMET ’09 - 2009 Portland International Conference on Management of Engineering Technology 1689–1698 (2009). doi:10.1109/PICMET.2009.5261967. ISSN: 2159-5119.

112. Roosen, T. J. & Pons, D. J. Environmentally Lean Production: The Development and Incorporation of an Environmental Impact Index into Value Stream Mapping. J. Ind. Eng. 2013, 298103 (2013). doi: 10.1155/2013/298103. ISSN: 2314-4882.

113. Dhingra, R., Kress, R. & Upreti, G. Does lean mean green? J. Clean. Prod. 85, 1–7 (2014). doi: 10.1155/2013/298103. ISSN: 2314-4882. ISSN: 09596526.

114. Faulkner, W. & Badurdeen, F. Sustainable Value Stream Mapping (Sus-VSM): Methodology to visualize and assess manufacturing sustainability performance. J. Clean. Prod. 85, 8–18 (2014). doi: 10.1016/j.jclepro.2014.05.042. ISSN: 09596526.

115. Davies, E., van der Merwe KR. Methodology to produce a Water and Energy Stream Map (WESM) in the South African manufacturing industry. 27, 219–229 (2016). doi: 10.7166/27-3-1657. ISSN: 2224-7890.

117. Zhang, Y., Wang, H. P. & Zhang, C. Green QFD-II: A life cycle approach for environmentally conscious manufacturing by integrating LCA and LCC into QFD matrices. Int. J. Prod. Res. 37, 1075–1091 (1999). doi: 10.1080/002075499191418. ISSN: 1366588X.

118. UK Government. Guidance on Applying the Waste Hierarchy. Dep. Environ. Food Rrual Aff. 1–14 (2011). ISBN: 9781782561361.

119. Young, L. Improving sustainability through effective waste management: Scottish Power Energy Networks (SPEN) the case study. (THE UNIVERSITY OF EDINBURGH, 2019). doi:10.13140/RG.2.2.21877.12008.

120. S N F Floerger. Coagulation flocculation. Available at: https://snf.com.au/downloads/Coagulation_Flocculation_E.pdf. (Accessed: 3rd February 2016).

121. Tarleton, E. S. & Wakeman, R. J. Data acquisition, analysis and scale-up. Solid/liquid separation equipment selection and process design (Butterworth-Heinemann, 2007). doi:10.1016/b978-185617421-3/50004-3.

122. FORMULACTION. TurbiscanLAB THE WORLD REFERENCE STABILITY ANALYZER. Available at: https://www.formulaction.com/en/products-and-technologies/product-range/turbiscan-lab. (Accessed: 28th January 2021).

123. Glover, S. M., Yan, Y. de, Jameson, G. J. & Biggs, S. Dewatering properties of dual-polymer-flocculated systems. Int. J. Miner. Process. 73, 145–160 (2004). doi: 10.1016/S0301-7516(03)00070-X. ISSN: 03017516

124. Fassel, V. A. & Kniseley, R. N. Inductively Coupled Plasma-Optical Emission Spectroscopy. Anal. Chem. 46, 1110A-1120A (1974). doi: 10.1021/ac60349a722. ISSN: 15206882.

125. USEPA. SW-846 Test Method 3005A: Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by Flame Atomic Absorption (FLAA) or Inductively Coupled Plasma (ICP) Spectroscopy. ReVision (1992). Available at: https://www.epa.gov/hw-sw846/sw-846-test-method-3005a-acid-digestion-waters-total-recoverable-or-dissolved-metals. (Accessed: 11th October 2017).

126. Henderson, R. K., Parsons, S. A. & Jefferson, B. Surfactants as bubble surface modifiers in the flotation of algae: Dissolved air flotation that utilizes a chemically modified bubble surface. Environ. Sci. Technol. 42, 4883–4888 (2008). doi: 10.1021/es702649h. ISSN: 0013936X.

127. Al-Shamrani, A. A., James, A. & Xiao, H. Destabilisation of oil–water emulsions and separation by dissolved air flotation. Water Res. 36, 1503–1512 (2002). ISSN: 0043-1354.

128. Yeow, Y. L. & Leong, Y. K. Compressive yield stress from multiple-speed centrifuge measurements. AIChE J. 47, 2798–2806 (2001). doi: 10.1002/aic.690471217. ISSN: 00011541

129. Kynch, G. J. A theory of sedimentation. Trans. Faraday Soc. 48, 166–176 (1952). doi: 10.1039/tf9524800166. ISSN: 00147672.

130. Usher, S. P., De Kretser, R. G. & Scales, P. J. Validation of a new filtration technique for dewaterability characterization. AIChE J. 47, 1561–1570 (2001). doi: 10.1002/aic.690470709. ISSN: 00011541.

131. Keller, S. & Kemmer, G. Nonlinear least-squares data fitting in Excel spreadsheets. Nat. Protoc. 5, 267–281 (2010). ISSN: 1754-2189.

132. Richardson, J. F. & Zaki, W. N. Sedimentation and fluidisation: Part I. Chem. Eng. Res. Des. 75, S82–S100 (1997). doi: 10.1016/s0263-8762(97)80006-8. ISSN: 02638762.

133. Sipag Bisalta. Bentonite EC No. 215-108-5, CAS No. 1302-78-9. Available at: http://www.bentonite.it/what-is-bentonite.php#:~:text=Its density when dry varies,to 1.8 g%2Fcm 3. (Accessed: 1st January 2021).