Abstract

Electrocoagulation is an empirical (and largely heuristic) water treatment technology that has had many different applications over the last century. It has proven its viability by removing a wide range of pollutants. The approach to reactor design has been haphazard, however, with little or no reference to previous designs or underlying principles. This thesis reviewed these reactor designs, identifying key commonalities and synthesising a new design hierarchy, summarised by three main decisions:

1. Batch or continuous operation;
2. Coagulation only or coagulation plus flotation reactors, and;
3. Associated separation process if required.

This design decision hierarchy thereby provides a consistent basis for future electrocoagulation reactor designs.

Electrochemistry, coagulation, and flotation are identified as the key foundation sciences for electrocoagulation, and the relevant mechanisms (and their interactions) are extracted and applied in an electrocoagulation context.

This innovative approach was applied to a 7 L batch electrocoagulation reactor treating clay-polluted water. Structured macroscopic experiments identified current (density), time, and mixing as the key operating parameters for electrocoagulation. A dynamic mass balance was conducted over the batch reactor, for the first time, thereby enabling the extraction of a concentration profile. For this batch system, three operating stages were then identifiable: lag, reactive, and stable stages. Each stage was systematically investigated (in contrast to the previous ad hoc approach) with reference to each of the foundation sciences and the key parameters of current and time.

Electrochemical behaviour characterised both coagulant and bubble generation. Polarisation experiments were used to determine the rate-limiting step at each electrode’s surface. Consequently the appropriate Tafel parameters were extracted and hence the cell potential. At low currents both electrodes (anode and cathode) operated in the charge-transfer region. As the current increased, the mechanism shifted towards the diffusion-limited region, which increased the required potential. Polarisation experiments also define the operating potential at each electrode thereby enabling aluminium’s dissolution behaviour to be thermodynamically characterised on potential-pH (Pourbaix) diagrams. Active and passive regions were defined and hence the aluminium’s behaviour in an aqueous environment can now be predicted for electrocoagulation.
Novel and detailed solution chemistry modelling of the metastable and stable aluminium species revealed the importance of oligomer formation and their rates in electrocoagulation. In particular, formation of the positively trimeric aluminium species increased solution pH (to pH 10.6), beyond the experimentally observed operable pH of 9. Thereby signifying the importance of the formation kinetics to the trimer as the active coagulant specie in electrocoagulation.

Further leading insights to the changing coagulation mechanism in electrocoagulation were possible by comparison and contrast with the conventional coagulation method of alum dosing. Initially in the lag stage, little aggregation is observed until the coagulant concentration reaches a critical level. Simultaneously, the measured zeta potential increases with coagulant addition and the isoelectric point is attained in the reactive stage. Here a sorption coagulation mechanism is postulated; probably charge neutralisation, that quickly aggregates pollutant particles forming open structured aggregates as indicated by the low fractal dimension.

As time progresses, pollutant concentration decreases and aluminium addition continues hence aluminium hydroxide/oxide precipitates. The bubbles gently sweep the precipitate through the solution, resulting in coagulation by an enmeshment mechanism (sweep coagulation). Consequently compact aggregates are formed, indicating by the high fractal dimension.

Flotation is an inherent aspect of the batch electrocoagulation reactor via the production of electrolytic gases. In the reactor, pollutant separation occurs in situ, either by flotation or settling. From the concentration profiles extracted, original kinetic expressions were formulated to quantify these competing removal processes. As current increases, both settling and flotation rate constants increased due to the additional coagulant generation. This faster removal was offset by a decrease in the coagulant efficiency. Consequently a trade-off exists between removal time and coagulant efficiency that can be evaluated economically.

A conceptual framework of electrocoagulation is developed from the synthesis of the systematic study to enable a priori prediction. This framework creates predictability for electrocoagulation, which is innovative and original for the technology. Predictability provides insights to knowledge transfer (between batch and continuous), efficient coagulant and separation path, to name just a few examples. This predictability demystifies electrocoagulation by providing a powerful design tool for the future development of scaleable, industrial electrocoagulation water treatment design and operation process.
Acknowledgments

The guidance and support from both my supervisors, Cynthia Mitchell and Geoffrey Barton, was invaluable and has enabled me to develop professionally and personally. I genuinely admired your intellect, expertise, and experience. I have been privileged to have worked with you both. I also wish to extend my sincere thanks to Peter Linkson for his time, interest and energy that he committed to this project. I greatly appreciated the contributions of the undergraduate students that worked with me: Kate Burger, Owen Burton and Mary Wark.

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To my fellow postgraduate students and friends, your understanding of the challenges of research created a supporting and vibrant environment to work.

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Student declaration

I hereby certify that this thesis is my original work and that it has not been submitted to any other university or institution for the award of a degree.

Peter Holt
August 2002
List of Publications


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¹ Delivered as platform presentation at the Third World Water Congress, as a part of the Enviro2002 conference in Melbourne, 2002.

² Delivered as platform presentation at the Sixth World Chemical Engineering Congress conference in Melbourne, 2001.
Table of contents

Abstract
Acknowledgments
Student declaration
List of Publications
Table of contents
List of figures
List of tables
Nomenclature
   Alphanumeric notations
   Greek symbols
1 Introduction and literature review
   1.1 Introduction – water
      1.1.1 Global perspective
      1.1.2 Australian perspective
      1.1.3 Water management
   1.2 Electrocoagulation
      1.2.1 Pollutant removal mechanisms
      1.2.2 Electrochemistry
      1.2.3 Coagulation
         1.2.3.1 Coagulation by metal cations
         1.2.3.2 Eh - pH diagrams
      1.2.4 Flotation
   1.3 Reactor design and operation
      1.3.1 Interpreting reactor designs
      1.3.2 Batch and continuous
      1.3.3 Mixing pattern
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3.4</td>
<td>Reactor scale-up</td>
<td>31</td>
</tr>
<tr>
<td>1.3.5</td>
<td>Pollutant separation</td>
<td>33</td>
</tr>
<tr>
<td>1.4</td>
<td>Electrocoagulation: synthesis</td>
<td>33</td>
</tr>
<tr>
<td>1.5</td>
<td>Chapter conclusions</td>
<td>37</td>
</tr>
<tr>
<td>1.6</td>
<td>Thesis scope</td>
<td>38</td>
</tr>
<tr>
<td>1.7</td>
<td>Thesis structure</td>
<td>39</td>
</tr>
<tr>
<td>2</td>
<td>Electrocoagulation</td>
<td>40</td>
</tr>
<tr>
<td>2.1</td>
<td>Design</td>
<td>40</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Reactor design</td>
<td>40</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Electrode design</td>
<td>41</td>
</tr>
<tr>
<td>2.2</td>
<td>Experimental Methods</td>
<td>44</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Pollutant Characterisation</td>
<td>44</td>
</tr>
<tr>
<td>2.2.1.1</td>
<td>Particle sieve analysis</td>
<td>44</td>
</tr>
<tr>
<td>2.2.1.2</td>
<td>Particle size distribution</td>
<td>45</td>
</tr>
<tr>
<td>2.2.1.3</td>
<td>Zeta potential measurement</td>
<td>45</td>
</tr>
<tr>
<td>2.2.1.4</td>
<td>X-ray Diffraction</td>
<td>45</td>
</tr>
<tr>
<td>2.2.1.5</td>
<td>Settling column with image analysis</td>
<td>45</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Electrocoagulation experiment set-up</td>
<td>46</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Electrocoagulation mass balance</td>
<td>47</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Electrocoagulation experimental design</td>
<td>48</td>
</tr>
<tr>
<td>2.3</td>
<td>Experimental Results</td>
<td>51</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Pollutant characterisation</td>
<td>51</td>
</tr>
<tr>
<td>2.3.1.1</td>
<td>Zeta potential</td>
<td>51</td>
</tr>
<tr>
<td>2.3.1.2</td>
<td>Particle characterisation</td>
<td>52</td>
</tr>
<tr>
<td>2.3.1.3</td>
<td>X-ray diffraction results</td>
<td>53</td>
</tr>
<tr>
<td>2.3.1.4</td>
<td>Settling rate</td>
<td>53</td>
</tr>
<tr>
<td>2.3.1.5</td>
<td>Pollutant characterisation summary</td>
<td>54</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Electrocoagulation results</td>
<td>55</td>
</tr>
<tr>
<td>2.3.2.1</td>
<td>Classification into reaction stages</td>
<td>55</td>
</tr>
<tr>
<td>2.3.2.2</td>
<td>Reliability of results</td>
<td>56</td>
</tr>
<tr>
<td>2.3.2.3</td>
<td>pH response results</td>
<td>58</td>
</tr>
</tbody>
</table>
2.3.2.4 Conductivity - sodium chloride concentration results

2.3.2.5 Impact of pollutant loading

2.3.2.6 Electrocoagulation results summary

2.3.3 Operating parameter - current

2.3.3.1 Current results - Time basis

2.3.3.2 Current results - Aluminium basis

2.4 Chapter summary and thesis direction

3 Electrochemistry

3.1 Electrocoagulation reactor

3.1.1 Aluminium dissolution rate and hydrogen production rate

3.1.2 Theoretical cell potential

3.1.3 Operational cell potential of electrocoagulation reactor

3.1.4 Electrochemical kinetics

3.2 Electrochemical experimental method

3.2.1 Solution preparation

3.2.2 Experimental equipment

3.2.3 Experimental procedure

3.3 Electrochemical results

3.3.1 Aluminium anodic potentiodynamic polarisation curves

3.3.2 Stainless steel cathodic potentiodynamic polarisation curves

3.3.3 Solution pH

3.4 Comparison with electrocoagulation results

3.4.1 Basis for comparison

3.4.2 Combined polarisation curves

3.5 Tafel plots – charge transfer regions

3.6 Electrical power and energy requirements

3.7 Thermodynamics - Potential – pH diagrams

3.7.1 Modelling approach

3.7.2 Modelling results

3.8 Chapter conclusions
4 Coagulation

4.1 Solution chemistry

4.1.1 Modelling methodology

4.1.2 Results and Discussion

4.1.3 Section summary

4.2 Particle and aggregate characterisation

4.2.1 Experimental Methods

4.2.1.1 Aluminium analysis

4.2.1.2 Light microscopy

4.2.2 Experimental Results

4.2.2.1 Light microscopy results

4.2.2.2 Turbidity results

4.2.2.3 Particle size measurements

4.2.2.4 Aluminium analysis results

4.2.3 Fractal dimensional analysis

4.2.3.1 Fractal theory

4.2.3.2 Fractal results

4.2.4 Section summary

4.3 Electrocoagulation and chemical dosing

4.3.1 Experimental Method

4.3.2 Results and Discussion

4.3.2.1 Clay removal – Chemical dosing

4.3.2.2 Clay removal – Electrocoagulation

4.3.3 Zeta Potential

4.3.3.1 Zeta Potential for Chemical Dosing

4.3.3.2 Zeta Potential for Electrocoagulation

4.3.4 Electrocoagulation - shifting coagulation mechanisms

4.3.4.1 Reactive stage

4.3.4.2 Stable stage

4.3.5 Electrocoagulation – Change in current

4.3.6 Comparison of electrocoagulation and chemical coagulation – fixed aluminium concentration

4.3.7 Section conclusion
6.3 Technology advancement ................................. 177
6.3.1 Interaction of foundation sciences .................. 177
6.4 A conceptual model of electrocoagulation .......... 179
6.5 Technology future ...................................... 181

7 Conclusions and Recommendations .................. 184
7.1 Conclusions ............................................. 184
7.2 Recommendations .................................... 186
7.2.1 Recommendations for technology advancement 186
7.2.2 Recommendations for the research breadth ...... 187
7.3 The last word ........................................... 188

8 References ............................................... 189

Appendices .................................................. 200
List of figures

Figure 1-1 Water cycle with Australian consumption and uses detailed (numerical values from AWA (2002)). 3

Figure 1-2 Water cascade; relationship between water quality and potential usefulness. 4

Figure 1-3 Interactions occurring within an electrocoagulation reactor. 10

Figure 1-4 Venn diagram of main sciences underlining electrocoagulation. Note DAF – Dissolved Air Flotation. 11

Figure 1-5 Distribution diagram for Al-H2O considering only mononuclear species. 18

Figure 1-6 Solubility diagram of aluminium hydroxide Al(OH)3(s) considering only mononuclear aluminium species. 19

Figure 1-7 Potential-pH equilibrium diagram for the system aluminium-water at 25 °C (Pourbaix, 1974). 21

Figure 1-8 Summary of the electrocoagulation reactors and their separation processes. 27

Figure 1-9 Continuous reactor types; continuously stirred tank reactor (CSTR), plug flow reactor (PFR) and a differential side stream reactor (DSR) (Glasser and Hildebrandt, 1997). 30

Figure 1-10 Electrocoagulation’s relationship between scientific bases and operating parameter represented in a Venn diagram 34

Figure 1-11 Generic electrocoagulation reactor highlighting operating parameters relationship to underlying sciences. 36

Figure 2-1 Schematic diagram of electrode arrangement 42

Figure 2-2 Diagram of electrode dimensions 43

Figure 2-3 Experimental electrocoagulation reactor 46

Figure 2-4 Zeta potential of clay pollutant as a function of pH. 51

Figure 2-5 Particle size distribution of sieve fraction less than 53µm, d50=2.5µm. 52

Figure 2-6 Clay particle’s settling velocities measured in settling column. 54

Figure 2-7 Normalised turbidity and pH for electrocoagulation; [clay] = 0.8 g/L; I = 0.5 A; [NaCl] = 0.20 g/L. 56

Figure 2-8 Normalised turbidity; I = 1.0 A; [clay] = 0.8 g/L; [NaCl] = 0.20g/L; n= 4. 57
Figure 2-9: Cumulative mass collected at the surface; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L; I = 1.0 A; n = 4.

Figure 2-10: Normalised turbidity for various conductivities; [clay] = 0.8 g/L; [NaCl] = 0 – 0.32 g/L.

Figure 2-11: Turbidity as a function of pollutant loading; [clay] = 0.1, 0.4, 0.8, 1.6 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.

Figure 2-12: Normalised turbidity as a function of pollutant loading; [clay] = 0.1, 0.4, 0.8, 1.6 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.

Figure 2-13: Cumulative mass collected at the surface; [clay] = 0.1, 0.4, 0.8, 1.6 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.

Figure 2-14: Normalised turbidity and pH; I = 0.25, 0.5, 1.0, 2.0 A; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

Figure 2-15: Normalised turbidity as a function of current; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L; I = 0.25, 1.0, 2.0 A.

Figure 2-16: Cumulative mass collected at the surface as a function of current; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L; I = 0.25, 1.0, 2.0 A.

Figure 2-17: Normalised turbidity and pH as a function of equivalent aluminium; I = 0.25, 0.5, 1.0, 2.0 A; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

Figure 2-18: Cumulative mass collected at the surface per mg/L of available aluminium; I = 0.25, 1.0, 2.0 A; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

Figure 3-1: Measured E\text{CELL} for the batch electrocoagulation reactor; I = 0.25, 1.0, 2.0 A; [clay] = 0.1, 0.8, 1.6 g/L; [NaCl]=0.20g/L.

Figure 3-2: Pathway of general electrode reaction (based on Figure 1.3.6, Bard and Faulkner, 2001).

Figure 3-3: Diagram of the cell used during electrochemical experiments (PAR, 1974).

Figure 3-4: Relationship between standard hydrogen electrode (SHE) and saturated calomel electrode (SCE) (based on Figure E.1, Bard and Faulkner, 2001).

Figure 3-5: Potentiodynamic anodic polarisation; aluminium; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

Figure 3-6: Anodic polarisation of aluminium; [clay]=0, 0.8 g/L; [NaCl]=0, 0.20 g/L.

Figure 3-7: Cathodic polarisation of 316 stainless steel; [clay]=0.8 g/L; [NaCl] = 0.20 g/L.

Figure 3-8: Polarisation curves for aluminium anode and 316 stainless steel cathode; [NaCl] = 0.20 g/L; [clay] = 0.12 g/L.
Figure 3-9 Potential difference for individual Aluminium anode and 316 stainless steel cathode potentials from polarisation cell; [NaCl] = 0.20 g/L; [clay] = 0.12 g/L.  
Figure 3-10 Tafel plot for anodic polarisation of aluminium; [NaCl] = 0.20 g/L; [clay] = 0.8 g/L; $E_{\text{mixed}} = -560 \text{ mV (SCE)}$.  
Figure 3-11 Tafel plot for cathodic polarisation of 316 stainless steel; [NaCl] = 0.20 g/L; [clay] = 0.8 g/L; $E_{\text{mixed}} = -340 \text{ mV (SCE)}$.  
Figure 3-12 Power required for electrocoagulation; $A = 732 \text{ cm}^2$; [NaCl] = 0.20 g/L; [clay] = 0.12 g/L.  
Figure 3-13 Eh – pH diagram (SHE) for aluminium – water system with mononuclear species and Al(OH)$_3$(s) considered; $[\text{Al}] = 1 \text{ mg/L}$. Anode and cathode potentials for operating currents 0.341 mA/cm$^2$ (orange dash), 1.36 mA/cm$^2$ (green long dash) and 2.74 mA/cm$^2$ (red long dash dot); [clay] = 0 g/L. Electrocoagulation pH range (blue vertical dot).  
Figure 3-14 Eh – pH diagram (SHE) for Aluminium – water system with mononuclear species and Al(OH)$_3$(s) considered; $[\text{Al}] = 20 \text{ mg/L}$. Anode and cathode potentials for operating currents 0.341 mA/cm$^2$ (orange), 1.36 mA/cm$^2$ (green) and 2.74 mA/cm$^2$ (red); [clay] = 0 g/L. Electrocoagulation pH range (blue vertical).  
Figure 3-15 Eh – pH diagram (SHE) for Aluminium – water system with mononuclear species and Al(OH)$_3$(s) considered; $[\text{Al}] = 100 \text{ mg/L}$. Anode and cathode potentials for operating currents 0.341 mA/cm$^2$ (orange), 1.36 mA/cm$^2$ (green) and 2.74 mA/cm$^2$ (red); [clay] = 0 g/L. Electrocoagulation pH range (blue vertical).  
Figure 4-1 Speciation model for monomeric aluminium species, water and solid aluminium hydroxide only.  
Figure 4-2 Speciation model for monomeric and trimeric aluminium, aluminium hydroxide, and water only.  
Figure 4-3 Speciation model of monomeric, di-meric, tri-meric, $Al_{13}$ aluminium – water species and aluminium oxide.  
Figure 4-4 Speciation model for monomeric, di-meric, tri-meric, $Al_{13}$ aluminium, water, aluminium hydroxide, aluminium oxide and the inclusion of carbon dioxide and carbonate species.  
Figure 4-5 Microscopic image of clay particles prior to electrocoagulation (10X).  
Figure 4-6 Microscopic image of aggregates from electrocoagulation reactor at 12 minutes (10X).
Figure 4-7 Average particle length and shape factors; $I = 1.0 \, A$; $[\text{clay}] = 0.8 \, g/L$; 
$[\text{NaCl}] = 0.5 \, g/L$. 

Figure 4-8 Normalised turbidity for pollutant and no pollutant; $[\text{clay}] = 0, 0.8 \, g/L$; $I = 1.0 \, A$; $[\text{NaCl}] = 0.20 \, g/L$. 

Figure 4-9 pH for pollutant and no pollutant; $[\text{clay}] = 0, 0.8 \, g/L$; $I = 1.0 \, A$; $[\text{NaCl}] = 0.20 \, g/L$. 

Figure 4-10 Electrocoagulation’s medium diameter ($d_{50}$) measurements; $I = 1.0 \, A$; 
$[\text{clay}] = 0, 0.8 \, g/L$; $[\text{NaCl}] = 0.20 \, g/L$. 

Figure 4-11 Total Aluminium concentration; $[\text{clay}] = 0, 0.8 \, g/L$; $[\text{NaCl}] = 0.20 \, g/L$; $I = 1.0 \, A$. 

Figure 4-12 Fractal dimension for aggregates produced by electrocoagulation; $I = 1.0 \, A$; 
$[\text{clay}] = 0, 0.8 \, g/L$; $[\text{NaCl}] = 0.20 \, g/L$. 

Figure 4-13 Normalised turbidity at various chemical dosing levels; $[\text{clay}] = 0.8 \, g/L$; 
$[\text{Al}_2(\text{SO}_4)_3] = 0 – 200 \, mg-\text{Al}/L$. 

Figure 4-14 Zeta potential for solutions subjected to chemical dosing; $[\text{clay}] = 0.8 \, g/L$; 
$[\text{Al}_2(\text{SO}_4)_3] = 0, 2, 4 \, mg-\text{Al}/L$. 

Figure 4-15 Zeta potential for solutions subjected to chemical dosing; $[\text{clay}] = 0.8 \, g/L$; 
$[\text{Al}_2(\text{SO}_4)_3] = 10, 20 \, mg-\text{Al}/L$. 

Figure 4-16 Electrocoagulation reactor’s zeta potential and normalised turbidity; 
$[\text{clay}] = 0.8 \, g/L$; $I = 0.5 \, A$. 

Figure 4-17 Normalised turbidity from chemical dosing; $[\text{clay}] = 0.8 \, g/L$; $[\text{Al}_2(\text{SO}_4)_3] = 4 \, mg-\text{Al}/L$; $pH = 3.6 – 11.4$. 

Figure 4-18 Normalised turbidity from chemical dosing; $[\text{clay}] = 0.8 \, g/L$; $[\text{Al}_2(\text{SO}_4)_3] = 20 \, mg-\text{Al}/L$; $pH = 4.4 - 10.6$. 

Figure 5-1 Mass removal rate for clay pollutant; $I = 0.25, 1.0, 2.0 \, A$; $[\text{clay}] = 0.8 \, g/L$. 

Figure 5-2 Forces on a single settling particle. 

Figure 5-3 Mean settling time assuming Stokes Law. 

Figure 5-4 Reynolds number for particle as a function of particle diameter. 

Figure 5-5 Experimentally measured settling of clay pollutant with Stokes’ Law. 

Figure 5-6 Forces on a single rising bubble. 

Figure 5-7 Single collector efficiency ($\eta_T$) based on DAF model by Edzwald, 1995 vs particle diameter; $d_B = 20 \mu m$; $\rho_p = 1.77 \, g \, L^{-1}$. 

xv
Figure 5-8 Typical concentration profile during electrocoagulation; I = 1.0 A; [clay] = 1.6 g/L. 162

Figure 5-9 Bulk solution pollutant concentration; I = 0.25, 1.0, 2.0 A; [clay] 0.1 - 1.6 g/L. 163

Figure 5-10 Evaluation of $k_1+k_2$ for 2.0 A; [clay] = 1.6 g/L. 166

Figure 5-11 Evaluation of $k_2/k_1$ for 2.0 A; [clay] = 1.6 g/L. 167

Figure 5-12 Rate constants for surface ($k_1$) and base ($k_2$); [clay] = 1.6, 0.8, 0.1 g/L. 168

Figure 6-1 Systematic approach to research electrocoagulation. 173

Figure 6-2 Mechanistic summary of electrocoagulation. 177

Figure 6-3 Flowsheet of conceptual electrocoagulation model. 180

Figure 7-1 Flowsheet of conceptual model for electrocoagulation (reproduced Figure 6-4). 185
List of tables

Table 1-1 Summary of electrode properties and pollutant .......................... 7
Table 1-2 Comparison between batch and continuous systems. .................. 27
Table 1-3 Electrode surface area to reactor volume ratio (SA/V) and current density
(A m^{-2}) ........................................................................................................... 32
Table 2-1 Relationship between operating current and current density. ........ 47
Table 2-2 Summary – electrocoagulation experiments with reactor conditions and
experiment motivation ..................................................................................... 50
Table 2-3 Mass Percentage fraction at selected sieve sizes. ......................... 52
Table 2-4 Summary of X-ray diffraction results .................................. 53
Table 2-5 Conductivity versus sodium chloride concentration. ..................... 60
Table 2-6 Mass balance breakdown for mass added and collected; [clay] = 1.6 – 
0.12 g/L; I = 1.0 A. ...................................................................................... 63
Table 2-7 Mass balance breakdown for mass added and collected; I = 0.25 – 2.0 A;
[clay] = 0.8 g/L. .................................................................................................. 69
Table 3-1 Electrode surface area used in polarisation cell ........................... 80
Table 3-2 Matrix of polarisation experiments ................................................ 82
Table 3-3 Polarisation experiments final pH ................................................. 86
Table 3-4 Comparison between electrocoagulation and polarisation cell experimental
systems. .................................................................................................................. 87
Table 3-5 Potential differences (V) for electrocoagulation reactor and polarisation cell.
......................................................................................................................... 90
Table 3-6 Summary of experimental Tafel parameters ................................. 94
Table 4-1 Summary of species used in modelling .......................................... 105
Table 4-2 Species included in electrocoagulation thermodynamic model .......... 107
Table 4-3 Comparison of measured pH with calculated pH (using HSC) at increasing
alum concentrations .......................................................................................... 108
Table 4-4 Relationship between pixel length and objective lens used for Nikon E800
microscope. .......................................................................................................... 114
Table 4-5 Summary of comparative chemical coagulation and electrocoagulation
experiments. .......................................................................................................... 128
Table 4-6 Flocculation mechanisms and associated fluid regime .................. 136
Table 4-7 A summary of the properties of the clay and no clay experiments. 142
Table 5-1 Bubble volume concentration for $d_B = 20 \, \mu m; I = 0.25 - 2.0 \, A$. 157
Table 6-1 Electrocoagulation performance summary 179
# Nomenclature

### Alphanumeric notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AW</td>
<td>Atomic weight (g/mol)</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>Distance between the electrodes</td>
</tr>
<tr>
<td><strong>Base</strong></td>
<td>Base</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Concentration of specie $i$</td>
</tr>
<tr>
<td>$c_j$</td>
<td>Concentration of specie $j$</td>
</tr>
<tr>
<td>$c_k$</td>
<td>Concentration of specie $k$</td>
</tr>
<tr>
<td>$c_{\text{Base}}$</td>
<td>Theoretical “concentration” at the base</td>
</tr>
<tr>
<td>$c_{\text{Poll}}$</td>
<td>Concentration of the pollutant in the bulk solution</td>
</tr>
<tr>
<td>$c_{\text{Poll}}^0$</td>
<td>Initial pollutant concentration</td>
</tr>
<tr>
<td>$c_{\text{Poll}}^{t_{\text{lag}}}$</td>
<td>Pollutant concentration at $t_{\text{lag}}$</td>
</tr>
<tr>
<td>$c_{\text{Surf}}$</td>
<td>Theoretical “concentration” at the surface</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusivity of specie $i$</td>
</tr>
<tr>
<td>$d_b$</td>
<td>Bubble diameter ($\mu$m)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter ($\mu$m)</td>
</tr>
<tr>
<td>$E$</td>
<td>Actual potential supplied to cell</td>
</tr>
<tr>
<td>$E_o$</td>
<td>The equilibrium potential</td>
</tr>
<tr>
<td>$E_0^{\text{CELL}}$</td>
<td>Standard cell potential</td>
</tr>
<tr>
<td>$E_{\text{CELL}}$</td>
<td>Actual cell potential</td>
</tr>
<tr>
<td>$E_A^0$</td>
<td>Standard anode potential</td>
</tr>
<tr>
<td>$E_{\text{ANODE}}$</td>
<td>Actual potential required at the anode</td>
</tr>
<tr>
<td>$E_C^0$</td>
<td>Standard cathode potential</td>
</tr>
<tr>
<td>$E_{\text{CATHODE}}$</td>
<td>Actual potential required at the cathode</td>
</tr>
<tr>
<td>$E_h$</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>$E_{\text{loss}}$</td>
<td>Potential due to losses</td>
</tr>
<tr>
<td>$E_{\text{MIXED}}$</td>
<td>Mixed potential at equilibrium</td>
</tr>
<tr>
<td>$E_{\text{solution}}$</td>
<td>Potential required by the solution</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant ($96,486 \text{ C mol}^{-1}$)</td>
</tr>
<tr>
<td>$F_B$</td>
<td>Buoyancy force</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$F_D$</td>
<td>Drag force</td>
</tr>
<tr>
<td>$F_W$</td>
<td>Weight force</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational constant</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>Standard Gibb’s free energy of formation</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density (A cm$^{-2}$)</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density</td>
</tr>
<tr>
<td>$i_c$</td>
<td>Current density of cathode (A cm$^{-2}$)</td>
</tr>
<tr>
<td>$i_L$</td>
<td>Limiting current density (A cm$^{-2}$)</td>
</tr>
<tr>
<td>$I$</td>
<td>Current (A)</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Exchange current</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Flotation rate constant</td>
</tr>
<tr>
<td>$k_2$</td>
<td>Settling rate constant</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzman’s constant</td>
</tr>
<tr>
<td>$MW$</td>
<td>Molecular weight (g mol$^{-1}$)</td>
</tr>
<tr>
<td>$m_{Al}$</td>
<td>Mass of Al dissolving (g Al cm$^{-2}$)</td>
</tr>
<tr>
<td>Poll</td>
<td>Pollutant</td>
</tr>
<tr>
<td>$O$</td>
<td>Oxidant</td>
</tr>
<tr>
<td>$O_{bulk}$</td>
<td>Oxidant in the bulk solution</td>
</tr>
<tr>
<td>$O_{surf}$</td>
<td>Oxidant in the surface region</td>
</tr>
<tr>
<td>$O'$</td>
<td>Intermediate oxidant specie</td>
</tr>
<tr>
<td>$O'_{ads}$</td>
<td>Oxidant adsorbed on electrode’s surface</td>
</tr>
<tr>
<td>$Q$</td>
<td>Flowrate of water (L/min)</td>
</tr>
<tr>
<td>$R$</td>
<td>The gas constant (8.314 Jmol$^{-1}$K$^{-1}$)</td>
</tr>
<tr>
<td>$R$</td>
<td>Reductant</td>
</tr>
<tr>
<td>$R_{bulk}$</td>
<td>Reductant in the bulk solution</td>
</tr>
<tr>
<td>$R_{surf}$</td>
<td>Reductant in the surface region</td>
</tr>
<tr>
<td>$R'$</td>
<td>Intermediate reductant</td>
</tr>
<tr>
<td>$R'_{ads}$</td>
<td>Reductant adsorbed on electrode’s surface</td>
</tr>
<tr>
<td>$Re_b$</td>
<td>Bubble Reynolds number</td>
</tr>
<tr>
<td>$Re_p$</td>
<td>Particle Reynolds number</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SHE</td>
<td>Saturated hydrogen electrode</td>
</tr>
<tr>
<td>Surf</td>
<td>Surface</td>
</tr>
</tbody>
</table>
\( t \) Time (s or min)
\( t_{lag} \) Time lag
\( t_{\text{Rise}} \) Average rise time
\( T \) Temperature (K)
\( T^0 \) Absolute temperature (K)
\( u_b \) Bubble’s terminal velocity (m s\(^{-1}\))
\( u_p \) Particle’s terminal velocity (m s\(^{-1}\))
\( Z \text{ or } z \) Stoichiometric number of electrons
\( V_{AP} \) Applied electrical voltage (V)

**Greek symbols**

\( \Delta \) Change or difference
\( \Phi_b \) Bubble volume concentration
\( \alpha \) Flocculation collision efficiency
\( \alpha_A \) Anodic transfer coefficient
\( \alpha_C \) Cathodic transfer coefficient
\( \beta_A \) Anodic Tafel constant (mV/decade)
\( \beta_C \) Cathodic Tafel constant (mV/decade)
\( \beta(i,j) \) Collision frequency between particles of size i and j
\( \beta(i,j) \) Collision frequency between particles of size i and k
\( \delta \) Boundary layer thickness
\( \gamma_i \) Activities
\( \eta \) Overpotential (mV or V)
\( \eta_A \) Anode overpotential (mV or V)
\( \eta_{AI} \) Aluminium efficiency
\( \eta_C \) Cathode overpotential (mV or V)
\( \eta_{\text{CON}} \) Concentration overpotential (mV or V)
\( \eta_D \) Collector efficiency due to Brownian diffusion
\( \eta_I \) Collector efficiency due to interception
\( \eta_{IN} \) Collector efficiency due to inertia
\( \eta_S \) Collector efficiency due to sedimentation
\( \eta_{\text{SUR}} \) Surface overpotential (mV or V)
\( \eta_T \)  Total collector efficiency
\( \rho_B \)  Bubble density
\( \rho_P \)  Particle density
\( \rho_W \)  Water density
\( \mu \)  Viscosity of water
\( \nu_i \)  Stoichiometric coefficients
\( \sigma \)  Conductivity
1 Introduction and literature review

1.1 Introduction – water

1.1.1 Global perspective

Water provision will be a global challenge. Water is essential for all life. At the beginning of 2000, 1.1 billion people (one-sixth of the global population) were without improved water supply (WHO and Unicef, 2000). As the human population increases, to 8 billion by 2025 (Asmal, 2000) so does the demand for water. By this time, the Water Supply and Sanitation Collaborative Council (WSSCC) has set a target of universal coverage for water supply (WSSCC, 2000). To reach this target almost 3 billion people will need water supply (WHO and Unicef, 2000).

The Commonwealth Knowledge Network predicts that within 25 years at least 64 countries will be seriously short of water (Commonwealth Knowledge Network, 2000). The protection of water has the potential to be a source of conflict (Strong, 1999). Nations will seek to protect their water source to ensure they can meet future water demands. Wars may be waged over water (Fullerton, 2001). Clearly water will be a focal point in the future. Water is critical for life but is now influencing world peace and harmony.

The ethical right of all people to access water now and in the future is a challenge for the global community. Water is becoming not only a planning and technological issue but also increasingly a human rights issue. Consequently it is vital for all to have proper and sustainable water management strategies.

1.1.2 Australian perspective

Australia faces unique challenges for sustainable water management. Australia is the driest inhabited continent with an average of 455 mm rainfall per year (AWA, 2002). Yet the vast majority of Australians inhabit lush, coastal areas with plentiful rainfall. More importantly for Australians, there are huge variations in rainfall throughout the continent resulting in unpredictable water sources.
Australians desire a reliable, predictable water source as opposed to the variable water source nature provides. Australians have coped with this variability by using vast storages, for example, dams and aquifers. Dams were built to ensure water supplies. Irrigation systems were installed to water crops. Large catchment areas and river deviation has totally altered natural water flow patterns (Harris, 2002). This suits the immediate needs of Australian society and economy but the environment has suffered. Unknowingly at the time, these water management practices have contributed to environmental problems including salinity, turbidity increases, algal blooms break out and the degradation of rivers. Thus, anthropogenic alterations to natural water flows have had drastic and unpredictable environmental effects.

### 1.1.3 Water management

The link between water consumption and salinity problems faced throughout Australia is now apparent (Murray-Darling Basin Commission, 1999). Restoring vegetation and water flows to inland rivers will assist in lowering the water table. To increase water flow throughout the river system, consumption must be reduced or, at a minimum, stabilised. In addition, the demand on water increases as population increases. Thus the correct management of the entire water cycle is critical for a sustainable water supply and future. An integrated solution is required that accounts for all requirements and meets Australia’s demand.

The complex dynamics and interactions of water systems are only beginning to be understood. The interconnectedness of the water cycle is shown in Figure 1-1. Total consumption in Australia from the natural environment is 24,000 GL/year with irrigation the main use (72%). In order to reduce environmental degradation, water extraction from the natural environmental must be minimised.

Water extraction can be minimised by reducing the demand or increasing water’s useable life within the system, that is, the built environment. The longer water remains in the built environment, that is, its residence time within the system, the lower the overall consumption from nature. This is achieved by increased water reuse and recycling as indicated in Figure 1-1. Thus all forms of water, regardless of quality, must be recognised as a valuable and useable resource (Fullerton, 2001).
A sustainable water management system matches water quality to appropriate use. Potable water is used for drinking, while a lower water quality for example grey water (shower water), can be used to flush toilets. This cascading relationship between water quality and water use is shown in Figure 1-2. The greater the number of uses, the greater the useable life within the built environment. Clearly, as water is used, the quality decreases and its potential usefulness decreases. To reverse this step and increase water quality, the water must be treated (vertical arrows in Figure 1-2). This increases the residence time within the built environment. In order to achieve this, new science and new technologies are needed (Harris, 2002).

To increase water quality, that is, “fit for purpose” the technology must be able to operate over a wide pollutant range. Smaller, localised treatment technologies are preferable over centralised treatment. Centralised treatment requires transportation with associated infrastructure (pumping and piping). Transportation also requires energy to remove water, a valuable resource, from its potential usage point. Thus small, local
water treatment technologies are required that reduce consumption and transportation, and extend the water’s useable life.

![Water Cascade Diagram](image)

**Figure 1-2 Water cascade; relationship between water quality and potential usefulness.**

Electrocoagulation is an ideal technology to upgrade water quality. It is a stand-alone, portable treatment with the ability to remove a wide range of pollutants. A diversity of opinions exist in the literature for explaining both the key mechanisms and the best reactor configurations. Presently, the technology’s science and reactor design is empirical and heuristic. These empirical studies invariably prove the viability of the technology, but singularly fail to fully capitalise on its potential. This is due to a lack of fundamental understanding of the system and hence the inability to accurately predict performance. This thesis aims to quantitatively understand electrocoagulation’s pollutant removal mechanisms. This provides the scientific foundation to facilitate design and development of the water treatment technology.

### 1.2 Electrocoagulation

Electrocoagulation uses an electrochemical cell to treat polluted water. Sacrificial anodes corrode to release active coagulant cation, usually aluminium or iron, to solution. Accompanying electrochemical reactions are dependent on species present and usually evolve electrolytic gases. The coagulant’s delivery and its nature influence the coagulation and separation processes by its speciation, removal path and associated byproduct, electrolytic gases.
Electrocoagulation is currently experiencing a renaissance. During the late nineteenth century, it was seen as a promising technology - in fact, several water treatment plants were successfully commissioned in London at this time (Matteson et al., 1995; Vik et al., 1984). Another plant was built in Salford, England, at the same time using iron electrodes with seawater as the source for chlorine disinfection. Electrolytic sludge treatment plants were operating as early as 1911 in various parts of the United States of America (Vik et al., 1984), and in the following decades, plants were also commissioned there to treat municipal wastewater. By the 1930’s, however, all such plants had been abandoned due to perceived higher operating costs (Vik et al., 1984), and the ready availability of mass-produced alternatives for chemical coagulant dosing.

Electrocoagulation resurfaced periodically throughout the last century. During the 1940’s Stuart (1946) and Bonilla (1947) reported on an electrochemical water treatment process, but this was received with little enthusiasm. During the 1970’s and 1980’s significant interest was generated by Russian scientists researching the application of electrocoagulation for a variety of water treatment processes (Amosov et al., 1976; Kaliniichuk et al., 1976; Bochkarev et al., 1977; Osipenko and Pogorelyi, 1977; Vershinina and Rogovets, 1978; Gavrilyuk, 1981; Gavrya et al., 1981; Kharlamova and Gorokhova, 1982; Nikolaev et al., 1982; Novikova et al., 1982; Avetisyan et al., 1984; Pazenko et al., 1985), although again there seems to have been little in the way of industrial follow-up on this work.

In recent years, however, smaller scale electrocoagulation processes have advanced to the point where they are seen as a reliable and effective technology. Numerous examples of water treatment systems have been reported in the recent literature, some of which are shown in Table 1-1. A wide range of reactors has been tried, with individual designs being largely determined by the (volumetric) scale and the nature of the pollutant being treated. This diversity in reactors has resulted in isolated advances being made in electrocoagulation technology.

To fully exploit electrocoagulation’s potential, a quantitative understanding of the interactions occurring between the fundamental process mechanisms is required. Surprisingly, research aimed at providing such a quantitative understanding of electrocoagulation's (relatively complex) pollutant removal mechanisms has only begun.
Chapter 1 – Introduction and literature review

quite recently (Holt et al., 1999). Thus, this chapter will begin by reviewing the available literature on electrocoagulation and its applications, introducing a structured approach to highlight commonalities and differences between the works reported.

1.2.1 Pollutant removal mechanisms

An electrocoagulation reactor is an electrochemical cell, where a sacrificial metal anode (usually aluminium, but sometimes iron) is used to dose polluted water with a coagulating agent (Matteson et al., 1995; Vik et al., 1984; Holt et al., 1999; Barkley et al., 1993; Mameri et al., 1998; Pouet and Grasmick, 1995). Electrocoagulation introduces metal cations in situ, rather than via external dosing. Simultaneously, electrolytic gases are generated (typically hydrogen at the cathode).

Electrocoagulation has the capability to remove a wide range of pollutants including suspended solids, heavy metals, dyes, organic material (such as sewage), FOG's (i.e. fats, oils and greases), ions and radionuclides. Table 1-1 presents pollutants removed by electrocoagulation and associated references. The pollutant's physicochemical properties influence its interactions within the system and eventual removal path. For example, ions are most likely electro-precipitated whilst charged suspended solids are adsorbed onto the charged coagulant. Electrocoagulation's ability to remove a wide range of pollutants is the reason for both its on-going industrial attraction, and its inherent complexity (via the wide range of possible pollutant removal mechanisms).

Previous researchers have taken a largely empirical approach to understanding electrocoagulation (Vik et al., 1984; Abuzaid et al., 1998; Barkley et al., 1993; Chen et al., 2000; Pouet and Grasmick, 1994). That is, they have recognised the technology's pollutant removal capability (under a restricted set of reactor design and operational conditions) but have failed to extract (and quantify) the key underlying mechanisms of pollutant removal. This has resulted in numerous electrocoagulation being systems designed and operated for specific pollutants.
Table 1-1 Summary of electrode properties and pollutant

<table>
<thead>
<tr>
<th>Reference</th>
<th>Pollutant</th>
<th>Current and/or Cell Voltage(^3)</th>
<th>Electrodes Anode/ Cathode</th>
<th>Electrode Type</th>
<th>Removal path</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SUSPENDED SOLIDS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abuzaid et al. (1998)</td>
<td>Bentonite</td>
<td>0.2, 0.5, 1 A</td>
<td>Stainless steel</td>
<td>6 electrodes</td>
<td>Settling implied</td>
<td>4L reactor</td>
</tr>
<tr>
<td>Avetisyan et al. (1984)</td>
<td>Carbon</td>
<td>120 – 170 Am(^{-2})</td>
<td>Al/Fe</td>
<td>Horizontal plate</td>
<td>Flotation</td>
<td>Continuous</td>
</tr>
<tr>
<td>Belongia et al. (1999)</td>
<td>Silica (SiO(_2)) and alumina (Al(_2)O(_3))</td>
<td>2.5 to 10.0 V/cm</td>
<td>304 stainless steel</td>
<td>Mesh</td>
<td>Settled</td>
<td>3L batch</td>
</tr>
<tr>
<td>Holt et al. (2001)</td>
<td>Clay</td>
<td>3.4 – 27 Am(^{-2})</td>
<td>Al/316 stainless steel</td>
<td>Parallel plates</td>
<td>Flotation and settling</td>
<td>Batch – 7L</td>
</tr>
<tr>
<td>Ivanishvili et al. (1987)</td>
<td>Suspended solids</td>
<td>5 – 50 Am(^{-2})</td>
<td>Al and Fe</td>
<td>Plates</td>
<td>Sedimentation</td>
<td>Continuous</td>
</tr>
<tr>
<td>Matteson et al. (1995)</td>
<td>Kaolinite</td>
<td>0.01 Am(^{-2})</td>
<td>Stainless steel</td>
<td>Mesh</td>
<td>Sedimentation</td>
<td>Stirred batch and series of batch</td>
</tr>
<tr>
<td>Syrbu et al. (1986)</td>
<td>Suspended solids</td>
<td>50 – 70 Am(^{-2})</td>
<td>Al/Stainless steel</td>
<td>Trapezoidal plate electrodes at 5-10° from base</td>
<td>Floated in separate chamber</td>
<td>Octagonal pyramidal baffled reactor at 3.3x10(^{-6}) m(^3)s(^{-1})</td>
</tr>
<tr>
<td><strong>HEAVY METALS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drondina et al. (1985)</td>
<td>Se and St</td>
<td>10 – 20 Am(^{-2})</td>
<td>Fe/Fe</td>
<td>Electroflotation chamber</td>
<td>Continuous</td>
<td>5.6x10(^{-6}) m(^3)s(^{-1})</td>
</tr>
<tr>
<td>Gnusin et al. (1985)</td>
<td>Cd(^{2+})</td>
<td>10 – 30 Am(^{-2})</td>
<td>Steel</td>
<td>Plane parallel plates</td>
<td>Settled</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

\(^3\) Current and/or Cell Voltage – current density is usually reported (A m\(^{-2}\)) but if not available, electrical requirements are reported in parameters as denoted by their units.
Osipenko and Pogorelyi (1977) Cr\textsuperscript{6+} 8.33 Am\textsuperscript{-2} Fe Parallel plate Settler Continuous with air for agitation 3.3x10\textsuperscript{-4} m\textsuperscript{3}s\textsuperscript{-1}.

Pozhidaeva et al. (1989) Ni, Cr 2000 Am\textsuperscript{-2} Steel Plate Settled – intermediate clarifier Continuous

| COLOUR | | | | | |
|--------|--------|------------|--------|---------------------------------|
| Do and Chen (1994) | Dye | 0.1 A | Fe and Al | Area 5cm\textsuperscript{2} | Centrifuge | Batch – 250 mL |
| Ibanez et al. (1998) | Dye | 9 V | Fe | Rod | Flotation and settling | Batch |

| ORGANICS | | | | | |
|----------|--------|------------|--------|---------------------------------|
| Baklan and Kolesnikova (1996) | Sewage | 120 Am\textsuperscript{-2} | Fe and Al | Plate |
| Maatta and Tabakov (1987) | Pesticides | 563 Am\textsuperscript{-2} | | Sedimentation | Continuous |
| Novikova et al. (1982) | Detergents | 100 Am\textsuperscript{-2} | Fe | Vertical plate electrodes | Flotation in cell then filtration | Continuous radial movement of water |
| Pouet and Grasmick (1995); Pouet et al. (1992) | Urban wastewater | 3.9 A | Al/Al | 15 plate electrodes | Flotation then DAF or micro-filtration | Continuous 2.7x10\textsuperscript{-4} m\textsuperscript{3}s\textsuperscript{-1} |
| Pouet and Grasmick (1994) | Municipal wastewater | 4 - 10 A | Al/Al | 21 plate electrodes | Flotation then micro-filtration | Continuous 2.7x10\textsuperscript{-4} m\textsuperscript{3}s\textsuperscript{-1} |
| Ramirez et al. (1977); Ramirez (1982) | Tannery & rendering waste | 1500 or 2940 A | “Duriron” | Electrofloation chamber | Continuous |
| Vik et al. (1984) | Aquatic humus | 6-12 V | Al/Al | 4 Parallel | Flotation | Continuous 2.8x10\textsuperscript{-6} m\textsuperscript{3}s\textsuperscript{-1} |

<p>| FATS, OILS AND GREASES | | | | | |
|------------------------|--------|------------|--------|---------------------------------|
| Amosov et al. (1976) | Solvar, alcohol | 80 – 130 Am\textsuperscript{-2} | Al/Al | Area 15m\textsuperscript{2} | Flotation | Continuous |
| Balmer and Foulds, (1986) | Oil | 200-781 mA | Fe/Pt | Mesh/gauze | Flotation then filtration | Continuous |
| Cames et al. (2001) | Oils | 20 – 400 Am\textsuperscript{-2} | Al/Al | Mono-, bi-, polar Al plate | Settler | Beaker and 50L pilot |</p>
<table>
<thead>
<tr>
<th>Authors (Year)</th>
<th>contaminant</th>
<th>Concentration</th>
<th>Electrodes</th>
<th>Treatment</th>
<th>Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen et al. (2000)</td>
<td>Restaurant Oil</td>
<td>1.67 - 9.95 F/m³</td>
<td>Fe and Al</td>
<td>Dipolar plate electrodes</td>
<td>Floated and settled</td>
</tr>
<tr>
<td>Clemens (1981)</td>
<td>Oily wastewater</td>
<td>300 A at 8V</td>
<td></td>
<td></td>
<td>Floated in separate basin</td>
</tr>
<tr>
<td>Kalinichuk et al. (1976)</td>
<td>Oil – refinery</td>
<td>35 Am⁻²</td>
<td>Al</td>
<td>Packed sheets</td>
<td>Floated and settled</td>
</tr>
<tr>
<td>Kharlamova &amp; Gorokhova, (1982)</td>
<td>Phenol</td>
<td>50 – 250 Am⁻²</td>
<td>Fe &amp; Al/graphite</td>
<td>Monopolar plate electrodes</td>
<td>Floated</td>
</tr>
<tr>
<td>Rubach and Saur (1997)</td>
<td>Oil, salt and chemicals</td>
<td>40-220 A</td>
<td>Al</td>
<td>Corrugated and plate</td>
<td>Flotation in separate tank</td>
</tr>
<tr>
<td>Sleptsov et al. (1988)</td>
<td>Detergents</td>
<td>50 – 100 Am⁻²</td>
<td>Al</td>
<td></td>
<td>Floated or settled</td>
</tr>
<tr>
<td>Weintraub et al. (1983)</td>
<td>Oil</td>
<td>100 Am⁻²</td>
<td>Fe</td>
<td>Sheet</td>
<td>Flotation in separate cell</td>
</tr>
<tr>
<td>Woytowich et al. (1993)</td>
<td>Hydrocarbons, metals, phosphates</td>
<td></td>
<td>Al and steel tubes</td>
<td>Concentric tubes</td>
<td>Settled in clarifier</td>
</tr>
<tr>
<td>IONS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barkley et al. (1993)</td>
<td>Zn²⁺; Cu²⁺; Ni²⁺; PO₄³⁻; F⁻</td>
<td>20 A</td>
<td>Al with S/S electrodes</td>
<td>Pellets in fluidized bed</td>
<td>Settled in clarifier</td>
</tr>
<tr>
<td>Gnusin et al. (1986)</td>
<td>Natural water (ions, etc)</td>
<td>10 – 500 Am⁻²</td>
<td>Steel (type St. 3), Al or duralumin.</td>
<td>Plane parallel plates</td>
<td>Settled</td>
</tr>
<tr>
<td>Groterud and Smoczynski (1992)</td>
<td>Phosphorus</td>
<td>50 - 200 mA</td>
<td>Al / Fe or Carbon</td>
<td>AC at 2-3 min</td>
<td>Settled then filtered</td>
</tr>
<tr>
<td>Grechko et al. (1982)</td>
<td>Pesticides</td>
<td>150 Am⁻²</td>
<td>Al/Al</td>
<td>Sheets</td>
<td>Settled then filtered</td>
</tr>
<tr>
<td>Mameri et al. (1998)</td>
<td>Fluorides</td>
<td>75 Am⁻²</td>
<td>Al/Al</td>
<td>Bipolar</td>
<td>Settled</td>
</tr>
<tr>
<td>Mameri et al. (2001)</td>
<td>Fluorides</td>
<td>53 Am⁻²</td>
<td>Al/Al</td>
<td>Mono and Bipolar</td>
<td>Settled</td>
</tr>
<tr>
<td>Pretorius et al. (1991)</td>
<td>Nutrients, N, P</td>
<td>15 – 300 Am⁻²</td>
<td>Fe/Fe</td>
<td>Bipolar</td>
<td>Settled</td>
</tr>
</tbody>
</table>

Note – blank indicates information was not available.
Figure 1-3 begins to show the complex, interdependent nature of the electrocoagulation process (Holt et al., 2001). Clearly, the coagulant and its hydrolysis products can have numerous interactions with the pollutant, with other ionic species or with the electrolytic gas bubbles. These interactions are neither understood nor quantified. A scientific centred approach is required to decipher electrocoagulation.

![Diagram of electrocoagulation process]

Figure 1-3 Interactions occurring within an electrocoagulation reactor.

It is possible to identify three basic sciences - electrochemistry, coagulation, and flotation - that interact to make electrocoagulation work. The fact that these sciences are difficult to investigate separately in an operational reactor goes some way towards explaining the lack of a detailed technical literature on electrocoagulation. These contributors can be conceptualised as a Venn diagram in which the combination of all three sciences results in electrocoagulation, as opposed to the combination of various pairs of sciences, which lead to other technologies (Figure 1-4).
Chapter 1 – Introduction and literature review

The perspective presented in Figure 1-4 recognises and defines the three foundations that underlie electrocoagulation. Each of these areas has been researched in depth over the last century or so. This chapter will now summarise what each area has to offer in terms of a quantitative understanding of the electrocoagulation process.

1.2.2 Electrochemistry

As noted, all electrocoagulation reactors are electrochemical cells. All such reactors consist of an electrode arrangement in contact with the polluted water, with coagulant production in situ being their distinguishing feature. To release the coagulant, an applied potential difference across the electrodes is required. Potential requirements for the electrodes can be deduced from the electrochemical half-cell reactions occurring at each electrode, which will vary according to the operational pH and the species present in the system.

Reported electrode designs are numerous - including aluminium pellets in a fluidised-bed reactor (Barkley et al., 1993), bipolar aluminium electrodes (Mameri et al., 1998), mesh electrodes (Matteson et al., 1995), bipolar steel raschig rings (Ogutveren et al., 1992), as well as simple plate electrodes (Vik et al., 1984; Mameri et al., 1998; Holt et al., 2001). Various electrode materials have also been reported - including aluminium,
iron, stainless steel and platinum. The electrode material used determines the coagulant type. Thus, regardless of the electrode design employed, the electrode material determines the electrochemical reactions occurring, and hence the coagulant cation. For this reason, electrochemistry is one of the foundations for electrocoagulation.

Aluminium, the most commonly used anode material, is used here as an exemplar (note that an analogous description can be developed for other metals). Equation E1-1 presents aluminium’s anodic dissolution.

$$\text{Al}_{3+} + 3e^- \leftrightarrow \text{Al} \quad E_A^0 = -1.66 \text{ V} \quad (E1-1)$$

Oxygen evolution is also possible at the anode (Equation 2) (Mameri et al., 1998), although this was not detected by Przhegorlinskii et al. (1987)’s analysis.

$$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad E_A^0 = -0.40 \text{ V} \quad (E1-2)$$

Simultaneously, an associated cathodic reaction, usually the evolution of hydrogen, occurs. The reaction occurring at the cathode is dependent on pH. At neutral or alkaline pH, hydrogen is produced via Equation E1-3,

$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad E_C^0 = -0.83 \text{ V} \quad (E1-3)$$

while under acidic conditions, Equation E1-4 best describes hydrogen evolution at the cathode.

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E_C^0 = 0 \text{ V} \quad (E1-4)$$

Reactors using both aluminium anodes and cathodes have repeatedly reported aluminium dissolution in excess of 100% (Przhegorlinskii et al., 1987; Donini et al., 1994; Mameri et al., 1998; Bozin and Mikhailov, 1990), where efficiency calculations were based on anodic dissolution following Faraday’s law (Equation E1-5). Faraday’s Law is used to relate the current passed (I) to the mass (m) of electrolytically generated material within the reactor, and hence in this case provides a theoretical estimate of the
amount of aluminium going into solution. Donini et al. (1994) and Przhgorlinskii et al. (1987) both point to the chemical dissolution of aluminium at both electrodes (Equation 6) as the likely source of the observed efficiency above that computed via Faraday's Law. It should be noted that Hulser et al. (1996) erroneously presents an electrochemical reaction to describe aluminium's cathodic corrosion (Equation E1-7). In reality, Equation E1-7 is simply the sum of Equations E1-3 and E1-6, with the aluminium ion being further hydrolysed (the issue of cationic speciation will be discussed later).

\[ m = \frac{I \times t \times MW}{Z \times F} \]  \hspace{1cm} (E1-5)

\[ Al + 3H_2O \rightarrow Al(OH)_3 + 1.5H_2 \]  \hspace{1cm} (E1-6)

\[ Al + 4H_2O + e^- \rightarrow Al(OH)_4^- + 2H_2 \]  \hspace{1cm} (E1-7)

Equations 1 – 4 are the dominant electrochemical half-cell reactions for reactors with aluminium anodes and inert cathodes. Operational reaction potentials will vary according to both the electrode material used and the aqueous environment. The Nernst equation (Equation E1-8) is used to calculate the equilibrium potential \( E \) for any half-cell reaction. Assuming ideality \( (\gamma_i = 1) \), concentrations \( (c_i) \), can be used in place of activities (Bard and Faulkner, 2001).

\[ E = -\frac{\Delta G^0}{nF} - \frac{RT}{nF} \Sigma v_i \ln c_i \]  \hspace{1cm} (E1-8)

The overall potential for a reactor is thus calculated as the sum of the anodic \( (E_a) \), cathodic \( (E_c) \), solution \( (E_{solution}) \) and loss \( (E_{loss}) \) potentials (Equation E1-9). The solution potential \( (E_{solution}) \) is a function of its conductivity \( (\sigma) \), the distance between electrodes \( (\Delta b) \), and the current density \( (i_c) \) (Equation E1-10). \( E_{loss} \) is generally included to account for potential losses such as the energy required to overcome the passivation layer. These last two terms make it clear that (in addition to anodic and cathodic potential
requirement), a reactor’s potential is dictated by solution characteristics, electrode geometry and the way in which the reactor is operated.

\[ E_{\text{cell}} = E_c - E_d - E_{\text{solution}} - E_{\text{loss}} \]  
(E1-9)

\[ E_{\text{solution}} = \frac{\Delta b_i}{\sigma} \]  
(E1-10)

**Electrochemical kinetics**

It should be noted here that thermodynamics yields the *conditions* under which various species are stable, but does not indicate the *rate* at which changes towards equilibrium occur. Thus, to predict any reactor's performance, all reaction kinetics must be quantified (Levenspiel, 1999). In the case of an electrocoagulation reactor, the coagulant addition rate is determined by the relevant electrode kinetics.

Electrode reactions are heterogeneous and take place in the interfacial region between the electrode and solution. Both potential and concentration gradients exist between the electrode surface and the bulk solution. Thus, the chemical species to be reduced or oxidised must diffuse from the bulk phase to the electrode surface (via a mass transfer process) before electron transfer can occur at the surface. Consequently, at the extremes, electrochemical reactions are either charge transfer or mass transfer limited. Clearly, in many practical cases, both charge and mass transfer are relevant in determining the overall rate of reaction.

The charge transfer reaction is commonly described by the Butler-Volmer equation (Equation E1-11), which relates the current to the electrode overpotential (\(\eta\)), the latter being the quantity that provides the "driving force" for the electrochemical reactions. The overpotential is a measure of the degree of polarisation, that is, the deviation from an electrode’s equilibrium value (\(E_0\)) (Equation E1-12). The Butler-Volmer equation describes the kinetics for single step, one-electron transfer processes where diffusion effects can be neglected.
\[ i = i_0 \left\{ \exp \left( \frac{\alpha_A nF \eta}{RT} \right) - \exp \left( -\frac{\alpha_C nF \eta}{RT} \right) \right\} \quad \text{(E1-11)} \]

\[ \eta = E - E_o \quad \text{(E1-12)} \]

For high overpotential systems, the term describing the backward (cathodic) reaction is approximately zero, and the Butler-Volmer equation can be simplified to the Tafel equation (Equation E1-13). Tafel parameters can be determined experimentally for both anodic and cathodic polarisation, whereby a potentiostat varies the potential and measures the resultant current density. The slope of the resultant polarisation curve is the Tafel parameter ($\beta$) relating the surface overpotential ($\eta_{\text{SUR}}$) to the current density.

\[ \eta_{\text{SUR}} = \beta \log \left( \frac{i}{i_0} \right) \quad \text{(E1-13)} \]

At equilibrium, where no net current flows, the resultant potential and current is known as the mixed potential ($E_{\text{MIXED}}$) and exchange current density ($i_0$), respectively and can be determined by the intersection of the anodic and cathodic polarisation curves.

If the experimentally determined potentiodynamic curve approaches a constant current density value, that is, a limiting current density ($i_L$), then the system is said to be diffusion (or concentration) polarised (Equation E1-15). In such cases, increasing the concentration overpotential ($\eta_{\text{CON}}$) will have minimal impact on the reaction rate, as the rate of diffusion from the electrode surface to the bulk phase is the rate-limiting step.

\[ \eta_{\text{CON}} = \frac{2.303RT}{nF} \log \left[ 1 - \frac{i}{i_L} \right] \quad \text{(E1-14)} \]

\[ i_L = \frac{nFD_i c_i}{\delta} \quad \text{(E1-15)} \]

The complexity of electrochemical reactions increases with multi-transfer step and multi-electron processes. Numerous interactions may occur before, during and after
electron transfer (including chemical reactions - such as protonation, dimerisation or other surface reactions such as adsorption or desorption). Any of these processes could prove to be the rate limiting step for a given electrocoagulation reactor (Bard and Faulkner, 2001).

Thus electrochemistry, the first of the foundations underpinning electrocoagulation, dictates both the species able to be produced and the cell potential required, with electrode kinetics describing the relationship between the operating potential and the coagulation generation rate.

**1.2.3 Coagulation**

Coagulation is a key feature of all electrocoagulation reactors, describing the interaction between the coagulant and any pollutant material. The coagulant’s role here is to destabilise the colloidal suspension by reducing any attractive forces, thereby lowering the energy barrier and enabling particles to aggregate. Depending on the physical and chemical properties of the solution, pollutant and coagulant, a number of coagulation mechanisms (e.g. charge neutralisation, double layer compression, bridging and sweep) have been postulated (Thomas et al., 1999; Letterman et al., 1999). For any given electrocoagulation reactor, the dominant coagulation mechanism will vary with the reactor's operating conditions, the pollutant type (and concentration), and the coagulant concentration.

Electrocoagulation has been compared to chemical coagulation to assess its efficiency and advantages. Chemical dosing delivers the coagulant as a salt that dissociates in solution with hydrolysis of the aluminium cation (and associated anions) determining solution speciation and pH. Alum (i.e. aluminium sulphate) addition, for example, acidifies the water. By contrast, aluminium added via electrocoagulation does not bring with it any associated salt anions, with the result that the pH typically stabilises in the alkaline range (Koparal and Ogutveren, 2002). However, it is worth noting that both Donini et al. (1994) and Musquere et al. (1983) claim that the coagulation mechanism for electrochemical and chemical dosing are very similar, yet neither author supports their claim with rigorous experimental evidence.
In electrocoagulation, a pollutant’s stability is determined by its physicochemical properties. Pollutants composed of similarly charged particles repel each other, with the repulsive forces creating a stable, colloidal system with oppositely charged ions, typically hydroxyl (OH\textsuperscript{−}) or hydrogen ions (H\textsuperscript{+}), being attracted to the charged pollutant particles. The attraction of counter ions to a charged pollutant forms an electric double layer - referred to as the Stern and diffuse layers (Letterman et al., 1999; Thomas et al., 1999; Hunter, 1993; Lyklema, 1978). Electrostatic repulsion between electric double layers drives particles apart, whilst van der Waals forces act to bring them together. The Deryaguin, Landau, Verwey and Overbeek (DLVO) theory describes the interactions between these forces of attraction and repulsion (Deryaguin and Landau, 1941; Verwey and Overbeek, 1948). The energetics are such that attraction dominates at small separations.

However, to reach a small separation, a repulsive energy barrier must first be overcome. The zeta potential is used as an experimental measure of the particle’s effective charge as it moves through the solution, thus providing a direct indicator of solution stability (Letterman et al., 1999). Holt et al., (2002) reported the isoelectric point’s coincidence with the greatest pollutant removal from measurements in a batch reactor. Hence, zeta potential measurement provides an important characterisation for any electrocoagulation system (Clemens, 1981; Ramirez, 1982) providing an indication of stability and an indication of possible coagulation mechanisms.

1.2.3.1 Coagulation by metal cations

Aluminium is the most frequently used sacrificial anode in an electrocoagulation reactor. The aluminium cation has a variety of paths available (depending upon the pollutant properties, solution pH and concentration) - it could directly interact with the pollutant, it could hydrolyse to form a hydro-aluminium complex, or it could precipitate. Thus, the speciation of the cation is vital to understanding a given electrocoagulation process.

Thermodynamics are used to determine (and quantify) the stable aqueous species. Using aluminium as our exemplar, mononuclear complexes are initially formed as described by Equations E1-16 to E1-19. Note that the presence of a superscript denotes the species as an ion and its value indicates the ion’s charge.
Considering only mononuclear speciation, the total aluminium present in solution (α) at a given pH can be calculated (Figure 1-5) (using data from Bertsch and Parker, 1996). This distribution diagram shows the extent of hydrolysis, which depends upon total metal concentration and pH. As the latter increases, so the dominant species shifts, in this case from the aluminium cation (Al$^{3+}$(aq)) to the aluminate ion (Al(OH)$_4^{-}$(aq)).

\[ \text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{AlO}H^{2+} + H^+ \quad (E1-16) \]

\[ \text{AlO}H^{2+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_2^+ + H^+ \quad (E1-17) \]

\[ \text{Al(OH)}_2^+ + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3^0 + H^+ \quad (E1-18) \]

\[ \text{Al(OH)}_3^0 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_4^- + H^+ \quad (E1-19) \]

**Figure 1-5** Distribution diagram for Al-H$_2$O considering only mononuclear species.

Figure 1-6 is the solubility diagram for aluminium hydroxide, Al(OH)$_3(s)$. The solubility boundary denotes the thermodynamic equilibrium that exists between the dominant
aluminium species in solution at a given pH and solid aluminium hydroxide. The minimum solubility (0.03 mg-Al/L) occurs at pH 6.3, with solubility increasing as the solution becomes either more acidic or alkaline (Letterman et al., 1999; Stumm and Morgan, 1962; Stumm and O'Melia, 1968).

So, the active metal cation (produced at the anode) reacts with the hydroxide ions (produced at the cathode) to form a metal hydroxide which then acts as a coagulant, with the pollutant particles and metal hydroxides forming larger aggregates which may either settle out or be carried to the surface by (hydrogen) bubbles produced at the cathode. In addition, any solid precipitate of aluminium hydroxide is a precursor for pollutant removal by sweep coagulation. The solubility diagram provides an insight into the likely importance of this latter mechanism for pollutant removal.

For a specified aqueous environment, the dominant species and solubility limits can be calculated on the basis of aqueous thermodynamic calculations. However, both the distribution and solubility diagrams shown here assume mononuclear aluminium species, while in reality this system is considerably more complex. As the aluminium species...
concentration increases and/or the solution "ages", polynuclear aluminium complexes are formed and aluminium hydroxide precipitates, as shown in Equation 20. Addition of polymeric species (with different protonation, charge and size) changes the aqueous environment considerably (Amirtharajah and Mills, 1982; Bertsch and Parker, 1996). Thermodynamic modelling packages (including HSC, MINTEAQ2, PHREEQC) assist in the calculation of equilibrium speciation but they are limited by the accuracy of the available data. Details of the aqua-aluminium system are neither completely understood nor completely quantified (Stumm and Morgan, 1962; Stumm and O'Melia, 1968), hence limiting the usefulness of such equilibrium modelling for electrocoagulation. A greater understanding of speciation kinetics is required to inform aluminium chemistry within electrocoagulation reactors.

\[ Al^{3+} \rightarrow Al(OH)_{n}^{(3-n)} \rightarrow Al_{2}(OH)_{4}^{2+} \rightarrow Al_{3}(OH)_{4}^{5+} \rightarrow Al_{13} \text{ complex} \rightarrow Al(OH)_{3} \quad (E1-20) \]

Aggregation after metal coagulant addition can occur via numerous coagulation pathways (Letterman et al., 1999), with each pathway describing a different interaction between the coagulant and the pollutant particles. Sorption involves the binding between coagulant and pollutant surface at specific surface sites. If this binding is by charge interaction, then the coagulation mechanism is charge neutralisation. Precipitation pathways describe the interaction of the pollutant with the metal hydroxide precipitate. As the coagulant precipitates, it can react with pollutant particles binding them to the precipitate. Any excess coagulant precipitates as metal hydroxide, forming a polymeric hydroxide floc that "sweeps" through the solution enmeshing pollutant particles. Alternatively, the coagulant may remain predominantly as a soluble hydrolysed species in solution. It is difficult to generalise here, with a particular pathway's dominance depending on the coagulant concentration, pollutant particle properties and the interaction between the coagulant and pollutant.

However, thermodynamic modelling provides a useful (if under-utilised) insight into the likelihood of alternative coagulation pathways.
1.2.3.2 **Eh - pH diagrams**

As noted, thermodynamics defines the relationship between electrochemistry and speciation, as articulated by the Nernst equation. Eh – pH diagrams map regions of thermodynamically stable species on potential versus pH axes, thereby describing the stability of metals in different aqueous environments (Pourbaix, 1974). Both chemical and electrochemical reactions are incorporated here, demonstrating the overlap of the electrochemical and coagulation lobes of the Venn diagram (Figure 1-4).

Electrocoagulation requires aluminium corrosion. The electrochemical equilibrium for the aluminium-water system is presented in Figure 1-7, where regions of immunity, passivation (*i.e.* formation of an oxide layer) and corrosion are identified. Thus, optimal corrosion conditions for aluminium (that is, the pH and potential conditions under which aluminium goes into solution) are readily apparent on such a diagram.

![Figure 1-7 Potential-pH equilibrium diagram for the system aluminium-water at 25°C (Pourbaix, 1974).](image)
Eh-pH modelling provides a useful insight to the stable, thermodynamically favoured species. Its usefulness is limited by the accuracy of the available thermodynamic data and its inability to account for any kinetics, thus should not be used in isolation.

In this context, passivation reduces electrocoagulation performance by inhibiting corrosion. Passivation of aluminium electrodes has been widely observed and recognised as detrimental to reactor performance (Novikova et al., 1982; Osipenko and Pogorelyi, 1977). This formation of an inhibiting layer, usually an oxide, on the electrode surface prevents metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Over time, the passivation layer typically increases, reducing the efficacy of the electrocoagulation process.

Novikova et al. (1982) investigated various methods of preventing and/or controlling passivation - including changing the polarity of the electrodes, introducing inhibiting agents, and hydro-mechanical cleaning of the electrodes. It was concluded that the most efficient and reliable method of electrode maintenance was to periodically clean the electrodes by mechanical means.

The presence of the chloride ion in solution has been reported to decrease passivation and thereby increase electrocoagulation's pollutant removal efficiency (Donini et al., 1994; Jiaqian, 1988; Ogutveren et al., 1992; Novikova et al., 1982; Velikaya and Baturin, 1983; Sleptsov et al., 1987; Weintraub et al., 1983). All authors attributed the increase in removal efficiency to the "pitting" corrosive action of the chloride ion on the metal surface. Alternatively, Mameri et al. (1998) postulated a mechanism for chloride ion reducing passivation of the oxide layer formed on aluminium, as shown in Equations E1-21 to E1-22. The precise mechanism by which chloride acts here is not completely understood, with the reader directed to the literature for recent developments (Szklarska-Smialowska, 1999; Pyun et al., 1999; Lee and Pyun, 1999).

\[ Al + 3HCl \rightarrow AlCl_3 + H_2 \]  \hspace{1cm} (E1-21)

\[ AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \]  \hspace{1cm} (E1-22)
Coagulation is the second of the foundations on which electrocoagulation is built, preparing as it does the pollutant for removal. The aggregated pollutant is now ready for separation.

1.2.4 Flotation

The production of electrolytic gases is an inevitable by-product of electrocoagulation (Equations 2 - 4, 6). These gases lift pollutant particles and coagulant aggregates to the surface by a flotation-like process, while encouraging contact between pollutant particles and coagulant by providing a certain amount of mixing action.

The main difference between this "electrolytic flotation" and more conventional flotation techniques is the method of bubble production and resultant bubble size. Expertise from other flotation techniques, including electroflotation, dissolved air flotation (DAF) and air-lift reactors, can be employed to understand the flotation process in electrocoagulation reactors. Electroflotation describes the production of electrolytic gases for the sole purpose of pollutant removal. In both batch and continuous processes, electrochemistry determines the rate and type of bubble production, and this synergy is represented by the overlap of the flotation and electrochemistry lobes in the Venn diagram (Figure 1-4).

One of the main advantages of flotation by electrolytic gases is the small size of the bubbles produced (Matis, 1995; Fukui and Yuu, 1980). Using inert electrodes, such as platinum or stainless steel, hydrogen is produced at the cathode and oxygen at the anode (Belongia et al., 1999; Kharlamova and Gorokhova, 1982; Syrbu et al., 1986) (refer to Table 1-1). For such systems, Matis (1995) studied the interaction of the gas bubbles with the aggregated pollutant material, showing that the electrolytic bubbles are typically small (less than 50 µm in diameter), close to neutral buoyancy, and present in low concentrations. For a given gas volume, a smaller bubble diameter results in both a greater surface area and more bubbles, thereby increasing the probability of collision and the ability to remove fine pollutant particles (Matteson et al., 1995). Also, as noted, electrolytic bubbles enhance mixing in the bulk solution via their overall upward momentum flux, increasing the likelihood of effective contact between coagulant and pollutant particles.
Bubble movement within a reactor is a function of the bubble density, bubble path and bubble residence time. Current density determines the production rate of electrolytic gas, and thus the bubble density, while reactor geometry (size, height, electrode positioning, effective electrode surface area to volume ratio) determines the bubble path. The average time a bubble spends in the reactor is referred to as its residence time, which is a function of bubble size and path length (the latter being largely determined by the extent of solution mixing and the depth of liquid to which the electrodes are immersed).

It should be noted that shear forces from any mixing source affect the growth of aggregates. Operation at a low current density produces relatively few bubbles, resulting in gentle agitation - conditions that are idea for aggregate growth and flocculation. As the current density increases, however, bubble density and the net upward momentum flux increases. These increases change the reactor’s hydrodynamic behaviour and the degree of mixing. High shear forces induced by mixing can damage and break flocs apart, reducing the effectiveness of pollutant removal. The effects of mixing (within the context of reactor design) are considered in more detail in the following section.

An extensive literature exists on most aspects of flotation, with the reader being directed to reviews by Dai et al. (2000), Matis (1995), and Ralston and Dukhin (1999) for specific information.

Electrochemistry, coagulation and flotation thus form the three foundation stones for electrocoagulation. Each component is a well-studied technology in its own right. However, it is clear from the published literature that what is lacking is a quantitative appreciation of the way in which these technologies interact to provide an electrocoagulation system, as will be demonstrated in the following section on reactor design and operation.

### 1.3 Reactor design and operation

The literature does not reveal any systematic approach to electrocoagulation reactor design and operation. Reported designs range through laboratory, pilot and industrial scales - both as stand alone reactors to fully integrated units within a wastewater purification system. Table 1-1 summarises this variety of reactors, and the associated
operating conditions. There is certainly no dominant “electrocoagulation reactor” in use today. For example, the electrodes used vary in material, design, and mode of operation, ranging from simple plate electrodes, through raschig rings (Ogutveren et al., 1992) and pellets in packed bed style reactors (Barkley et al., 1993). Similarly, reactor operation varies enormously; electrode current densities reported range from 0.01 to 2000 A/m².

The key driver for the development of a particular technology has generally been the removal of a particular pollutant (not the understanding of electrocoagulation in any general sense). For example, Vik et al. (1984) used aluminium plate electrodes in a continuous reactor to remove aquatic humus from a wastewater stream. The sludge formed in the reactor was floated to the surface by the hydrogen generated at the cathode, and then skimmed from the surface for disposal. For comparison, Woytowich et al. (1993) removed oil from ship’s bilge water in a continuous system employing concentric metal tubes as electrodes. Here, the stream passed through the tubes and then into a clarifier where the aggregated pollutant settled out. Although both were continuous operations, each system had quite distinct electrode designs, modes of reactor operation and separation processes, largely set by the properties of the pollutant in question. Each group used an electrocoagulation reactor and separation method suited to the particular pollutant type resulting in a pollutant centred design approach. Neither group seemed to base their design on published literature, in the sense that theirs was a refinement (or an incremental improvement) over previous studies.

These “pollutant centred” studies are typical of much of the published research into electrocoagulation. While solving a particular problem, the long-term disadvantage is that the knowledge gleaned is limited to a specific case, that is, to a given pollutant, reactor design and separation technology. This has resulted in the steady accumulation of a great deal of highly empirical information, all of which repeatedly proves the viability of electrocoagulation as a technology, but singularly fails to advance its potential as a generally applicable approach to pollutant removal. The latter requires that electrocoagulation be understood via a “scientific centred” approach.
What follows is a critical look at the key aspects of reactor design and operation, with an emphasis on how these apply to the electrocoagulation process. A generic set of design rules applicable to any electrocoagulation system are thereby developed.

1.3.1 Interpreting reactor designs

The first section of this chapter dealt with the technological bases for electrocoagulation. Regardless of the reactor design eventually employed, electrocoagulation’s bases do not change. It is a process built on the interactions between electrochemistry, coagulation and flotation (Figure 1-4). These bases can be combined to form a wide range of (seemingly unrelated) reactor designs. Hence, the general key to understanding reactor design and operation is the interactions between the electrochemistry, coagulation and flotation components. Specifically, the reactor design dictates the interactions between the species present.

Published electrocoagulation reactors were classified as shown in Figure 1-8. The first major distinction between alternative designs was whether a reactor was configured as a batch or a continuous system. The second distinguishing criterion employed was the role of flotation. The last criterion considered was the type of (pollutant) separation technology used. The resultant hierarchical structure succinctly summarises current electrocoagulation reactor design practice.

Reactors that ignore flotation effects are labelled as “coagulation only” processes, while reactors that integrate flotation into their design are classed as “coagulation and flotation” processes. If no additional separation process is required, that is separation occurs in situ within the electrocoagulation reactor, the references are cited directly below (being connected by a vertical arrow and dashed box). Otherwise, the (additional) separation processes are reported in bold with references grouped accordingly.

The hierarchical design decision framework developed can now be used to inform design decisions for new systems. Inductively this hierarchical structure provides a conceptual and useful approach for future electrocoagulation reactor designs. The myriad of reactor designs is reduced to three core design decisions. Regardless of details and individual features, reactor design decisions are summarised as follows:

1. Batch or continuous operation;
2. Coagulation only or coagulation and flotation reactors and;
3. Chosen separation process.

The consequences of these reactor design decision for electrocoagulation reactors provide the basis for further discussion.

Figure 1-8 Summary of the electrocoagulation reactors and their separation processes.

1.3.2 Batch and continuous

It is clear that the majority of electrocoagulation reactors reported in the literature are continuous. All such reactors have a continuous pollutant feed, with the system operating under (pseudo) steady-state conditions. A key advantage for such reactor systems is their fixed coagulant requirements. Batch processes on the other hand typically have a fixed volume (rather than a fixed feed flowrate) with concentrations changing with time as the reaction(s) proceed. The defining features of continuous and batch systems are compared in Table 1-2.

Table 1-2 Comparison between batch and continuous systems.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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### Table 1.1: Comparison of Batch and Continuous Systems

<table>
<thead>
<tr>
<th>Condition</th>
<th>Batch Systems</th>
<th>Continuous Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flowrate – constant volume</td>
<td>Constant flowrate</td>
<td>Constant flowrate</td>
</tr>
<tr>
<td>Internal concentrations change with time</td>
<td>Internal concentrations constant</td>
<td></td>
</tr>
<tr>
<td>Performance related to reaction time (i.e. time in reactor)</td>
<td>Performance related to residence time (space-time) in reactor</td>
<td>Steady-state operation</td>
</tr>
<tr>
<td>Inherently dynamic operation</td>
<td>Mixing varies between extremes of well-mixed and plug-flow</td>
<td></td>
</tr>
<tr>
<td>Reactor contents are well-mixed (uniform composition)</td>
<td>Mixing varies between extremes of well-mixed and plug-flow</td>
<td></td>
</tr>
</tbody>
</table>

Electrocoagulation batch reactors exhibit time-dependent behaviour as the coagulant is continuously "fed" to the reactor as the aluminium anode corrodes. The aluminium is hydrolysed, as previously discussed, into a form capable of aggregating the pollutant. As a result, pollutant, coagulant, and pH concentrations shift over time - with both the solution speciation and the equilibrium state towards which the system is moving also changing with time. It is this inherently dynamic behaviour, coupled with the interplay between thermodynamic considerations (which define where a system is heading at a particular point in time) and kinetic considerations (which determine the rate at which a process is moving towards the thermodynamically stable state) that makes batch electrocoagulation reactors so difficult to model mathematically.

Continuous systems were perceived by Levenspiel (1999) as better suited to industrial processes for large quantities at high production rates, such as large-scale water treatment plants. Levenspiel also contends that for large volume processes, continuous processes have often been found to be more economical than batch systems. In contrast, batch reactors are perceived by both Levenspiel and Fogler (1992) as simple reactors suited to laboratory scale applications. The dominance of continuous systems is reflected in development and research of electrocoagulation reactors. Practitioners seem to assume that continuous is always better and thus continuous reactors have become the norm. It may be that this assertion has exerted itself in electrocoagulation design. Electrocoagulation design may benefit from some unpacking of this assertion.

In order to unpack this assertion, it is necessary to study the fundamentals of electrocoagulation. The fundamental species are the coagulant, pollutant and bubbles. The interactions between these species are critical. Firstly the species must contact each other. Mixing and flow determine this contacting pattern. This contact occurs within the
reactor. Hence the exploration of the relationship between reactor design and mixing pattern is critical for electrocoagulation.

1.3.3 Mixing pattern

Effective aggregation requires adequate contact between the coagulant and pollutant particles. Consequently, the transport mechanism and fluid regime are important. They determine the transportation and collisions between pollutant particles, coagulant and bubbles. Reaction kinetics then describes the reaction rate. The reaction kinetics quantifies the reaction dynamics, that is the time for pollutant removal. A combination of both contact pattern and reaction kinetics are pivotal to defining the reactors’ performance. These points are discussed further as follows.

The contact pattern is central to reactor design. Adequate contact between particles, coagulant and bubbles is required for effective aggregation. The contact is dependent on mass diffusion, transport mechanisms and fluid regime within the reactor. These have a significant impact on both the flocculation mechanism and the subsequent means of pollutant removal (Letterman et al., 1999). Contact patterns describe individual interactions whilst mixing describes an overall state. Mixing is a gross measure and describes the homogeneity within a reactor. Thus mixing strongly influences the performance and effectiveness of electrocoagulation reactors.

Batch reactors are usually well mixed. Mixing in a batch reactor is primarily a function of fluid flow and agitation. Agitation increases homogeneity throughout the reactor and is usually due to a mechanical source, such as a stirrer. In electrocoagulation batch reactors, electrolytic bubbles produced in situ can aid agitation. Rising bubbles create disturbances in the fluid resulting in eddy formation. These eddies aid mixing in the reactor (Holt et al., 2001). Thus mixing in a batch reactor may be induced by a variety of sources and is dependent on reactor design and operation.

Mixing in a continuous system is determined by the residence time and flow path. Residence time is a function of reactor geometry and flow rate. Complex geometries, such as the octagonal pyramidal baffled reactor reported by Syrbu et al. (1986) result in complex flow paths. Higher flow rate increases shear forces and radial dispersion thereby increasing homogeneity, which gives a well-mixed system. Generally, the
residence time and flow path combination, which is a function of reactor geometry and flow rate, governs the mixing regime.

Continuous reactors can be classified according to mixing regime. Design mixing regimes in continuous reactors vary along a spectrum between well-mixed continuously stirred tank reactors (CSTR) to plug flow reactors (PFR), with no radial dispersion. A further extreme mixing pattern is the differential side stream reactor (DSR), which is a PFR with multiple side stream feeding (Glasser and Hildebrandt, 1997). Thus for the continuous reactor, three mixing patterns are available, as shown in Figure 1-9.

![Figure 1-9 Continuous reactor types; continuously stirred tank reactor (CSTR), plug flow reactor (PFR) and a differential side stream reactor (DSR) (Glasser and Hildebrandt, 1997).](image)

For batch reactors, “impulse-fed” (or shot-fed) batch reactors are most common: they are fed instantaneously as the reactors are charged. Mathematically the impulse-fed batch reactor is identical to the plug-flow reactor (PFR). Both reactor performance equations were derived based on the residence time of chemical species in the reactor (Wong, 2002). Consider a particular chemical species in an impulse-fed batch reactor. The extent of its reaction is determined by the time in the reactor. This can be observed by changes in concentration gradients. Now consider the same chemical species in a PFR. The position along the reactor’s length determines the reaction’s extent. The position in the PFR is directly proportional to the time it has spent in the reactor. Thus the residence time for both scenarios is the key parameter. Similarly, a continuously fed-batch reactor (batch electrocoagulation reactors) is mathematically equivalent to a differential side stream reactor (DSR) (Wong, 2002). There is no batch analogy for the continuously stirred tank reactor, where composition is uniform throughout the reactor over time. Thus a fed-batch electrocoagulation reactor is mathematically equivalent to a continuous DSR reactor.
The above analogies suggest that research is transferable between batch and continuous systems. The differences between a batch and continuous reactor are not as great as one may assume. This is significant for research in electrocoagulation reactors. Batch, laboratory scale reactors can provide valuable mechanistic insights to continuous larger scale reactors. The converse is also applicable with industrial experience transferable to laboratory experiments. This knowledge transferability between batch and continuous systems enhances electrocoagulation’s technological development and advancement.

1.3.4 Reactor scale-up

Increased reactor size, or scale-up, is typically the result of an increased feed flowrate. In order to maintain similar performance between different size reactors, it is necessary that the key operational parameters (e.g. mixing patterns and reaction kinetics) be maintained at comparable levels. The most common engineering approach here is to correlate a unit's performance in terms of a set of appropriate dimensionless parameters. This approach, however, has not proved to be particularly successful for electrocoagulation - almost certainly because of the wide range of reactor types and pollutants to be handled, and the inherent complexity of the electrocoagulation process.

As an example, the United States EPA initially evaluated pollutant (here radionuclide waste) removal by electrocoagulation using a bench-scale reactor. A full-scale trial failed utterly for one key component (uranium) that had been successfully removed at the laboratory scale (USEPA, 1998). However, both the basic reactor design and operation conditions were quite different between the two systems, resulting in quite different hydrodynamic and kinetic behaviour.

In order to achieve similar flow patterns within a reactor system, dynamic, geometric and kinetic similarity must be maintained (Coulson and Richardson, 1996). Zolotukhin (1989) adopted this approach by scaling an electrocoagulation-flotation system from laboratory to experimental scale, and finally to industrial scale. The following scale-up parameters were employed (although values were not reported) to ensure correct sizing between reactor systems:

- Reynolds number (provides a measure of the fluid flow regime)
Chapter 1 – Introduction and literature review

- Froude number (provides a measure of the importance of gravitational forces in the system)
- Weber criteria (provides a measure of the importance of surface tension related forces in the system)
- Gas saturation similarity (related to the volumetric bubble density in the system)
- Geometric similarity

Surprisingly, few scale-up parameters are reported in the electrocoagulation literature. One basic scale-up design parameter would be the electrode surface area to reactor volume ratio (SA/V), which is a (crude) measure of the potential for delivering coagulant and bubbles to a system (on a volumetric basis). Current density, defined as the current per unit active electrode area, is another obvious scale-up design parameter.

Several values reported in the literature for the SA/V ratio and current density are presented in Table 1-3, where little in the way of consistency is discernible. The SA/V ratios are the same order of magnitude, but the associated current density values vary by orders of magnitude. It is perhaps worth noting that Mameri et al. (1998) reports that an optimal current density exists for a fixed SA/V ratio, on the basis that as the SA/V ratio increases so the treatment time decreases and consequently the optimal current density decreases. However, there is no real evidence that this general observation has been used as a design aid.

Table 1-3 Electrode surface area to reactor volume ratio (SA/V) and current density (A m⁻²)

<table>
<thead>
<tr>
<th>Reference</th>
<th>SA/V (m²/m³)</th>
<th>Current Density (A m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mameri et al. (1998)</td>
<td>6.9 - 34.6</td>
<td>5 - 300</td>
</tr>
<tr>
<td>Holt et al. (2001)</td>
<td>10.5</td>
<td>3.4 - 27</td>
</tr>
<tr>
<td>Osipenko and Pogorelyi (1977)</td>
<td>18.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Amosov et al. (1976)</td>
<td>30.8</td>
<td>80 -130</td>
</tr>
<tr>
<td>Novikova et al. (1982)</td>
<td>42.5</td>
<td>100</td>
</tr>
</tbody>
</table>

Given the complexity of the electrocoagulation process, it is highly doubtful if dimensionless number based correlations will ever prove to be useful in reactor design or scale-up, except for cases where the pollutant and reactor type are quite similar.
1.3.5 Pollutant separation

Pollutant separation is electrocoagulation’s primary objective. Electrocoagulation dosing has been combined with many separation technologies, including dissolved air flotation (DAF) (Pouet and Grasmick, 1995), electroflotation (Ramirez, 1982), filtration (Balmer and Foulds, 1986), and clarification (Woytowich et al., 1993). A more extensive list is shown in Figure 1-8. Basically, pollutant separation is either integrated into the reactor’s design, or else occurs in a separate (downstream) unit. This chapter only considers the former, as extensive literature exists on the design and operation of stand-alone separation processes (such as clarifiers).

Integrated units have two main pollutant removal paths - flotation and settling (Holt et al., 2001). Separation by settling is the more common option, with the fact that electrolytic gases are also being produced simultaneously with the dosing process, often viewed as an unnecessary complication (Mameri et al., 1998).

The prime driver between pollutant removal by settling or flotation would seem to be the current density employed in the reactor. A low current produces a low bubble density, leading to a low upward momentum flux - conditions that encourage sedimentation over flotation (Holt et al., 2002). As the current is increased, so the bubble density increases resulting in a greater upwards momentum flux and thus faster removal by flotation.

1.4 Electrocoagulation: synthesis

The key to progress in electrocoagulation is exploiting the obvious - that the foundation of any electrocoagulation process is based on electrochemistry, coagulation and flotation. Any electrocoagulation reactor can be viewed as a combination of these three foundation technologies. This starting point can be visualised by “mapping” electrocoagulation reactors onto the Venn diagram shown in Figure 1-4. Each reactor, depending on its design and operation characteristics, then occupies a unique region of this Venn diagram. One example is the integrated reactors (i.e. those that utilise coagulant dosage and electrolytic gases for separation into the design), sit within the intersection of the three lobes. In this region, flotation, coagulation and electrochemistry are all significant components in the pollutant removal process. By contrast, reactors
that are primarily electrochemical dosing devices (i.e. where flotation is not employed as a pollutant removal mechanism) are situated between the intersection of the coagulation and electrochemistry lobes (Barkley et al., 1993; Donini et al., 1994; Cames et al., 2001; Matteson et al., 1995).

Figure 1-10 Electrocoagulation’s relationship between scientific bases and operating parameter represented in a Venn diagram

This conceptual framework is extended and enhanced in Figure 1-10, where the interactions between the three main species (coagulant, bubbles and pollutant particles), are highlighted. Each foundation area brings a certain perspective to electrocoagulation, as represented by each lobe of the Venn diagram (Figure 1-10). Electrocoagulation’s (at times overwhelming) complexity can thus be broken down to manageable "chunks" according to this schematic diagram. Relevant phenomena, characterisation methods and tools are highlighted in each lobe. The information presented in the intersection
between two lobes represents knowledge that links the foundation sciences. For example, thermodynamically modelling the solution chemistry of hydrolysed metal cations links the electrochemistry and coagulation lobes, and consequently is represented in these lobes’ intersection.

Central to understanding electrocoagulation is the contact pattern (i.e. mixing) and kinetics. Contact pattern describes the interactions between the species (coagulant, pollutant particles, bubbles) and kinetics the rate at which these occur. Hence, these are placed in the intersection of all three lobes.

The combination of physico-chemical processes occurring within an electrocoagulation reactor shifts the dominant separation mechanism. There are two main forces that remove pollutant: gravity and buoyancy. These result in settling and flotation as the main pollutant removal paths, respectively. The vertical arrows in Figure 1-10 represent these removal paths. The combination of design and operating parameters shift the relative importance of these two separation paths. As an example, current density shifts the relative importance between the flotation and coagulation lobes in the Venn diagram. Current density (represented by a double-headed arrow at the base of Figure 1-10) determines the coagulant dosage rate and the bubble production rate, as well as influencing the fluid regime (mixing) within a reactor. As noted, a low current produces a low bubble density, leading to a low upward momentum flux, and thus low mixing within the reactor - conditions that encourage sedimentation over flotation. As the current is increased, so the bubble density and the amount of mixing increase – favouring flotation over sedimentation (Holt et al., 2001). Therefore, current density is not only a key operational parameter, but also a key factor in determining a pollutant's removal path. Similarly, contact time and the extent of mixing within a reactor can each alter the dominant pollutant removal path. Thus, for a given pollutant, the dominant removal path is a function of both reactor operation (e.g. current density) as well as reactor design.

Design decisions cannot be made in isolation due to the inherent complex nature of electrocoagulation. There is an inseparable link between design and operational parameters and hence also to the underlying sciences of electrocoagulation. The
mapping of processes and tools onto Figure 1-10 combines the hierarchical approach to design with the scientific basis. Combination of scientific basis, explored in each science with attention to the interactions and the reactor design and operation enables global optima to be determined rather than local optima.

The challenge with electrocoagulation is that all operating parameters are interrelated to some extent, and cannot be considered in isolation. For example, the operating parameters identified here are current density, time and mixing - as shown in Figure 1-11. A change in one operating parameter can influence the other parameters. Thus, a change in current density changes bubble density, which influences mixing. Furthermore, increased current density increases coagulant concentration, which (at a constant pollutant loading) decreases the necessary contact time.

![Figure 1-11 Generic electrocoagulation reactor highlighting operating parameters relationship to underlying sciences.](image)

It is these interactions that make electrocoagulation too complex a process to ever be adequately analysed by short-cut methods (such as via dimensionless analysis). Rather, electrocoagulation is a process for which mathematical modelling (of the underlying and inter-related mechanisms) is almost certainly required for the technology to progress beyond its present state of "enlightened empiricism". It is for this reason that this chapter has focussed so sharply on the key foundations that underpin
electrocoagulation (electrochemistry, coagulation and flotation) and the interactions between them.

1.5 Chapter conclusions

Electrocoagulation currently lacks fundamental understanding and this will continue to exist as long as a pollutant-centred approach dominates research in this field. This chapter advocates a scientific centred approach with electrochemistry, coagulation and flotation as the foundation sciences for all electrocoagulation processes. Understanding the interactions between these three sciences is critical for successful reactor design and operation. A mechanistic approach to electrocoagulation is required.

Individually the three foundation sciences of electrocoagulation are well understood, yet no attempt has been made to use this knowledge to construct a fundamental understanding of electrocoagulation. A conceptual framework for electrocoagulation synthesised from the underlying sciences was produced in this chapter. The interactions between the main species, coagulant, bubbles and pollutant particles, were explored. The relevance to electrocoagulation of specific scientific areas including operating variables, models and tools to electrocoagulation were evaluated (refer to Figure 1-10). Contact patterns and reaction kinetics were thus identified as central to reactor behaviour.

This chapter also classified electrocoagulation reactors according to batch or continuous operation, use of electrolytic flotation and separation process. Based on this classification a generic design hierarchy was developed which should be used for future reactor design decisions.

Combining a technology-centred approach based on fundamental sciences with a hierarchical design decision framework advances electrocoagulation technology. Operating parameters (current density, mixing and time) provide a dynamic link between electrocoagulation science, design and operation. Failure to make progress in this area will consign electrocoagulation to a future as haphazard (in terms of industrial acceptance and success) as the last hundred years. Electrocoagulation requires a mechanistic approach to ensure higher sophistication reactor designs.
1.6 **Thesis scope**

Presently electrocoagulation is an empirical, heuristic, pollutant centred technology. Ultimately a successful, reliable and scalable industrially applied technology is desired. Research path and technology evolution connect electrocoagulation’s present state and its application. This thesis redefines electrocoagulation and establishes a systematic path towards a fully understood technology.

This thesis develops a conceptual approach and understanding that is applicable to other pollutant types. Investigating electrocoagulation as a realistic water treatment process is the rationale of this thesis. Numerous pollutant paths are available resulting in pollutant removal but also a complex system due to the number of interactions. As such, a heterogeneous pollutant, a potter’s clay, is used as the pollutant in this study.

This chapter developed a scientific and mechanistic approach for electrocoagulation, which will be applied in the thesis. An engineering approach is utilised to identify the mechanisms, removal paths interactions and specific sciences of interest. This directs research into deciphering electrocoagulation. Central to the reactor’s performance is the contact pattern and reaction kinetics. Operational variables identified (time, mixing and current density) are interrelated and interconnected. This thesis examines the operational variables of time and current density explicitly. Whilst recognising the operating variables’ interconnectedness, the reactor is assumed well mixed.

This thesis explores the interaction and links between electrocoagulation’s foundation sciences. Related fields are called upon to inform electrocoagulation. Particularly, this thesis maintains electrocoagulation’s inherent complexity and investigates the relative phenomenon systematically. To reveal overall dominant mechanisms the focus is on the interactions and links between the sciences. Therefore, coagulation, electrochemistry and flotation are investigated to inform the electrocoagulation pollutant removal.

For industrial application, detailed scale up properties and geometric relationships need to be defined. This thesis employs simple reactor geometry on a laboratory scale. Additional reactor scales would be required to evaluate scale up properties. Detailed hydrodynamic studies would also be required to define scale up properties.
1.7 Thesis structure

This thesis uses the Venn diagram presented in Chapter 1 as a basis for its structure.

Electrocoagulation is explored on a macroscopic level in Chapter 2.

Electrochemistry forms the basis of all electrocoagulation reactors and is the basis for Chapter 3. Each electrode is examined on a mechanistic level. The electrodes are then examined as a pair and discussed in relation to the electrochemical behaviour of the electrocoagulation reactor.

The coagulation aspects of electrocoagulation are investigated in Chapter 4. The beginning of the chapter focuses the solution chemistry of the system using thermodynamic models. The next section examines the particles, characterising their behaviour throughout the electrocoagulation reaction. The final section compares electrocoagulation to the conventional water treatment practice of alum dosing.

Flotation is an inevitable by-product of electrocoagulation and provides an important removal path. Its interaction with the electrocoagulation system is considered in Chapter 5.

The main elements of electrocoagulation, coagulation, electrochemistry and flotation are synthesized in Chapter 6. Finally conclusions and recommendations are drawn in Chapter 7.
2 Electrocoagulation

This chapter describes the design and construction of an instrumented laboratory scale electrocoagulation reactor and investigates its response on a macroscopic level. As demonstrated in Chapter 1, electrocoagulation has been investigated in a wide range of mainly continuous, and often complex, reactors with disparate outcomes. Furthermore, technology advancement is associated with understanding the scientific basis of electrocoagulation. To decipher this scientific basis, controlled conditions were required. Thus simple reactor geometry was chosen in the context of a systematic study. This chapter focuses on developing such a simple but novel reactor design.

This chapter then characterises and quantifies this reactor’s response. The impact of conductivity (via sodium chloride concentration), pollutant loading and current are investigated. The overarching aim was to direct future research to specific scientific areas so as to help elucidate the dominant pollutant removal mechanisms.

2.1 Design

2.1.1 Reactor design

The experimental electrocoagulation reactor was designed using the systematic approach developed in Section 1.3.1. To summarise, the proposed design decision hierarchy for such reactors consists the following decisions:

1. Batch or continuous?
2. Coagulation only or coagulation and flotation?
3. Additional separation process?

The way in which these decisions were applied to designing a research reactor is explained below.

Research is transferable between batch and continuous systems (refer to Section 1.3.3). A continuous system operates under fixed conditions, specifically a fixed pollutant loading and flow rate. By contrast, a batch reactor’s dynamic nature enables a range of conditions to be examined during the course of a single run. The batch system provides a greater insight to the operational response range. Thus, a batch reactor design is preferable for research and is chosen for this study.
Flotation was identified as one of electrocoagulation’s key sciences. Consequently, the flotation effects occurring provide an important aspect of electrocoagulation and these effects were integrated into this reactor design for this thesis.

The final design decision concerns pollutant separation. In a batch reactor, pollutant separation is a function of time with separation occurring *in situ*. That is, the pollutant can either settle or float within the reactor. For research, the dominant separation path and its relationship to the operable variables was a focus of this study. Thus additional separation is unnecessary.

Overall, a batch reactor, which incorporates both coagulation and flotation with pollutant removal *in situ*, was desired. A rectangular reactor with external dimensions, height = 187 mm, width = 172, length = 322 mm and wall thickness = 10 mm, was constructed from Perspex (see Figure 2-3). Maximum fluid height is 165 mm and thus the batch electrocoagulation reactor has a 7.1 L maximum capacity. The instrumentation used in this reactor is described later in Section 2.2.2.

### 2.1.2 Electrode design

Electrode design determines coagulant release and bubble type, thereby influencing flotation, mixing, mass transfer and pollutant removal. Aluminium cations and their hydrolysed derivatives are the desired coagulant in this study and hence aluminium was used for the anode.

Flotation is a major separation mode, and hence electrolytic bubble production is required. Thus, an electrochemically inert electrode is needed. Stainless steel is effectively electrochemically inert and does not readily corrode especially as a cathode, thus such electrodes were chosen for the cathode.

In this study, predictable coagulant dosage and bubble generation rates were required to quantify electrocoagulation’s performance. Faraday’s law (Equation E1-5) defines these rates at a specific current density. Current density is determined by operating current and electrode surface area. For consistent and predictable anodic dissolution and hydrogen production rates, constant current density is essential.
An electrode with a known flat surface area, such as a plate electrode, and constant spacing from other electrodes ensures constant current density. To ensure consistent spacing, Perspex spacers evenly separated anode and cathode plates. Thus, for a given solution resistance, a constant density over the entire electrodes’ surface was maintained using flat monopolar electrodes.

In the literature, electrode surface area to volume ratio ranges from 6.9 to 43 m$^2$/m$^3$ (Section 1.3.4). The electrodes here were designed with a surface area to volume ratio of 10.5 m$^2$/m$^3$, which is within this cited range. Brass rods connect the parallel plate electrodes alternatively as shown in Figure 2-1 and Figure 2-2. These fittings were covered with latex during experimentation to prevent corrosion.

The final electrode design consisted of five stainless steel cathodes interspersed with four aluminium anodes, as shown in Figure 2-1. Electrode dimensions are shown in Figure 2-2. Thus the total aluminium active aluminium area is 732 cm$^2$.
The maximum operational current was 2A. This corresponds to a current density, defined as current divided by electrode active area, of 2.74 mA/cm². Again, this figure lies within range (0.5 to 300 mA/cm²) reported in the literature.

The combination of current and electrode placement determined bubble removal path rate and mixing. As current density increased, so did bubble production resulting in both greater upward momentum flux and increased mixing. Electrode arrangement and its physical placement within the reactor determined bubble dispersion throughout the reactor. Larger electrode surface area resulted in a greater dispersion of bubbles throughout the reactor, whereas a smaller electrode surface area resulted in a concentrated source of bubbles within the reactor. The electrode pack considered in this thesis covered 114 cm² (25%) of the reactor’s base area of 459 cm². This intermediate electrode coverage ensured sufficient bubble dispersion for removal by flotation but also enabled formation of eddies that induced agitation and hence also mixing.

Electrode passivation is the accumulation of an inhibiting layer (usually an oxide) on the electrode’s surface, as discussed in Section 1.2.3.2. Passivation was undesirable for aluminium dissolution and hence electrocoagulation operation. The primary control of passivation was the galvanostatic operation mode of electrocoagulation. That is, the current was set and the potential found its own value dependent on the system’s overall resistance. This ensured coagulant and bubble production at a predetermined rate defined by Faraday’s law. Any resistance from a passivating layer increased the cell potential but did not affect either coagulant or bubble production rates. Additionally, the
use of deionised water minimised the presence of contaminants such as carbonates, which can readily passivate electrodes. As an additional precaution, the electrodes were periodically mechanically cleaned to remove any passivating material. This maintained the integrity of the electrodes and helped ensure anodic dissolution at close to a constant rate.

Simple, reliable and predictable electrodes were constructed. This electrode pack is positioned on the reactor’s base. Thus to explore electrocoagulation’s scientific foundation, a simple reactor and electrode combination was constructed.

2.2 Experimental Methods

Various experimental methods were employed to characterise electrocoagulation and its response. Firstly, the heterogeneous pollutant, that is, the potter’s clay, was characterised. This establishes a basis for electrocoagulation’s performance evaluation. Thus, Section 2.2.1 explores the pollutant characterisation method followed by the electrocoagulation method in Sections 2.2.2 to 2.2.4.

2.2.1 Pollutant Characterisation

The pollutant was characterised using a combination of experiments; particle sieving, particle size distribution, zeta measurements, X-ray diffraction and settling analysis.

The clay’s average moisture fraction was measured at 15.5%. Clay density was measured at 1.8 g cm\(^{-3}\) on a dry basis.

2.2.1.1 Particle sieve analysis

Particle sieving was used to broadly classify the clay’s mass fractions. A known clay amount was dispersed in deionised water. Sodium chloride was added to a concentration of 0.20 g/L to increase conductivity and replicate electrocoagulation experiments. Conductivity’s effect is investigated in Section 2.3.2.4. The clay suspension was washed through a set of calibrated stainless steel Endecotts Ltd. test sieves. The particles were sieved with mesh sizes at 1.00mm, 710\(\mu\)m, 500 \(\mu\)m, 212\(\mu\)m and 53 \(\mu\)m. The mass collected in each sieve was backwashed into a beaker. Each beaker was then dried and the sample weighed.
2.2.1.2 Particle size distribution

The particle size distribution was measured by a Malvern Mastersizer S, which uses a light scattering technique to measure intensity patterns. Particle diameter and volume were calculated by the Mastersizer using the Rayleigh - Deybe and Mie theories. The Malvern has a range of 0.5 – 900 µm with the magnetically stirred sample cell.

The clay particle fraction smaller than 53 µm was measured in the Malvern Mastersizer to obtain its particle size distribution.

2.2.1.3 Zeta potential measurement

Zeta potential was measured using a Malvern Zetasizer. It uses a laser to determine the zeta potential by measuring the electrophoretic velocity through a combination of the Doppler effect and light diffraction. The Zetasizer takes a series of measurements and reports an average potential.

2.2.1.4 X-ray Diffraction

The heterogeneity of the potter’s clay was characterised using X-ray diffraction. Samples from each mass fraction extracted during the sieve analysis were analysed. Magnetic and nonmagnetic species were separated. Samples were heated to 105°C and 500°C to enable mineralogical species to be identified. Three samples (25°C, 105°C, 500°C) from each mass fraction were analysed in the X-ray diffractometer. This combination of mass fraction and mineralogical identification enabled a semi-qualitative assessment.

2.2.1.5 Settling column with image analysis

Settling velocities of clay particles were measured in a rectangular glass settling column (15mm x 30mm and 1.5m high). The column was filled with water maintained at a controlled temperature. Particles were introduced by pipette to minimise disturbance to the top of column. The particle’s movement was recorded by a charge-coupled device (CCD) camera and video system. Image analysis software (WiT) was used to measure settling velocity and particle size. The apparatus is described in detail by Nobbs et al. (2002). The apparatus can detect particles 2-240 µm in size and the maximum settling velocity recordable is 0.225 m s⁻¹.
2.2.2 Electrocoagulation experiment set-up

All experiments were conducted with deionised water (resistance = 13 M\(\Omega\)/cm). Clay pollutant was dispersed (sonicated or allowed to stand overnight) in the deionised water. Analytical grade sodium chloride was used to enhance conductivity.

Turbidity is an optical measurement and has been widely used as a performance indicator for water clarity. Turbidity is often related to suspended solids concentration, though this relationship is specific to individual pollutants. Turbidity was measured off-line using a Merck Turbiquant 1500T (tungsten lamp).

Power was supplied by a regulated power supply. The electrocoagulation reactor operated in a galvanostatic mode - that is, the current was held constant and the cell potential varied to maintain current requirements. Current was investigated from 0.25 to 2.0A, which linearly corresponds to 0.34 to 2.74 mA/cm\(^2\), as shown in Table 2-1. The current and cell potential across the electrodes were recorded using a computer based FC4 data logger.
Conductivity, total dissolved solids (TDS), salinity and temperature were all measured using a WTW LF340 probe. TDS and salinity were measured before and after the reaction. pH was measured by a calibrated pH probe, in a flow-through cell which draws water from the reactor at a rate of 0.30 L/min using a peristaltic pump. Solution pH was not controlled but monitored and recorded for all experiments. All experiments were conducted at ambient conditions and hence the temperature was approximately 25ºC. Conductivity, temperature and pH were measured online. Online parameters were recorded through the computerised data logging system.

The dispersed clay solution and sodium chloride were added to the reactor. The reactor was then filled with deionised water. The electrodes were connected to the power supply by coated copper wires. Prior to the reaction, all initial offline parameters were recorded including a 10 mL sample to measure turbidity. Additional turbidity measurements were taken by periodically extracting 10 mL samples from the sample port. Electrocoagulation commenced as current flows across the electrodes. This defined the beginning of the electrocoagulation reaction.

### 2.2.3 Electrocoagulation mass balance

A mass balance approach to examine the pollutant’s fate is novel to electrocoagulation. In this study, mass balance measurements were also employed to quantify the pollutants’ fate. Previously, performance indicators were used. Donini et al. (1994) used only turbidity as an optical measurement that provided a fast (but gross) water quality measurement. Alternatives used to investigate electrocoagulation include spectrophotometry (Chen et al., 2000; Matteson et al., 1995), optical and UV adsorption (Do and Chen, 1994; Vik et al., 1984), as well as chemical oxygen demand (COD) (Barkley et al., 1993; Chen et al., 2000; Pouet and Grasmick, 1995). All these methods focus on bulk water quality but none directly measures pollutant removal or type. There

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**Table 2-1 Relationship between operating current and current density.**

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.34</td>
</tr>
<tr>
<td>0.50</td>
<td>0.68</td>
</tr>
<tr>
<td>1.0</td>
<td>1.36</td>
</tr>
<tr>
<td>2.0</td>
<td>2.74</td>
</tr>
</tbody>
</table>

---
is certainly no differentiation between removal to the reactor’s surface or to its base. Nor is there differentiation between coagulant or pollutant removal. In other words, the pollutant’s fate is unknown in all these published works. Thus pollutant fate was the focus here.

The experimental set-up enabled mass (clay and coagulant) balances to be conducted over the reactor. The reactor was designed so that all instrumentations (multi-functional probe), sample point, and connections (electrical to electrodes, inlet/outlet for pH flow-through cell) were from the reactor’s sides. This ensured there were no obstructions on the reactor’s surface, thereby enabling mass to be collected.

A metal scraper was used to collect the froth/foam at the surface, which was then funneled to a beaker. Froth at the surface was collected at regular intervals (usually every five minutes), dried and weighed. At the conclusion of the experiment, the solid sludge at the reactor’s base was also collected, dried and weighed. This experimental set-up enables the pollutant’s fate to be quantified.

This batch reactor enables dynamic mass balances to be deduced. The customised reactor was designed and constructed to enable a thorough and systematic study. Using this reactor as the experimental platform a series of structured experiments were designed to quantify electrocoagulation’s performance.

2.2.4 Electrocoagulation experimental design

A systematic approach was utilised to investigate electrocoagulation. Experimental variables were identified to examine the system’s degrees of freedom. The experimental variables are:

- pollutant type and loading;
- coagulant type and loading;
- solution characteristics;
- temperature;
- reaction time and;
- power requirements (cell potential and current).

As previously discussed, design decisions determined pollutant type and coagulant type. All experiments were conducted at ambient conditions; hence the degrees of freedom were reduced.
The experimental variables were divided in two distinct categories. Firstly, those variables that were controlled. Secondly, those variables that were investigated. The experimental approach to investigate electrocoagulation is also divided in two sections to reflect the distinction above. Electrocoagulation experiments are summarised in Table 2-2.

The first experimental set (Set A - experiments 1 to 28) aimed to establish an experimental protocol. Set A quantified electrocoagulation using turbidity and mass balances as performance indicators. The system’s repeatability and reliability was assessed on a dynamic basis (Section 2.3.2.2). Solution characteristics were investigated by evaluating the effects of conductivity and pollutant loading on the system. This enabled the impact of a particular variable to be isolated.

The second set (Set B - experiments 29 to 64) examined the relationship between operating variables and parameters. Operating parameters, as distinct from experimental variables were identified in Chapter 1 as mixing, time, and current density (refer to Section 1.4). All three are inherently interconnected. Mixing, in this reactor, was a result of solution hydrodynamics due to bubble interactions and diffusion gradients and hence a function of the reactor. The dynamic nature of batch electrocoagulation incorporates the dimension of time. Thus experiments were conducted on a time basis. Consequently current was the critical operating variable.

Current determines both coagulant loading and bubble density, thereby influencing mixing. Thus, in experimental Set B, the impact of current investigated over time with the solution characteristics maintained, that is, the pollutant loading and sodium chloride concentration were maintained at constant values.
Table 2-2 Summary – electrocoagulation experiments with reactor conditions and experiment motivation

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Current (I) (A)</th>
<th>[clay] (g/L)</th>
<th>[NaCl] (g/L)</th>
<th>Performance indicator</th>
<th>Basis</th>
<th>Experimental motivation</th>
<th>Results Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.8</td>
<td>0.2</td>
<td>Turbidity &amp; pH</td>
<td>Time</td>
<td>Quantify electrocoagulation response</td>
<td>2.3.2.1</td>
</tr>
<tr>
<td>2 to 5</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Turbidity</td>
<td>Time</td>
<td>Assess electrocoagulation's reliability and repeatability</td>
<td>2.3.2.2</td>
</tr>
<tr>
<td>6 to 9</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Mass</td>
<td>Time</td>
<td>As above</td>
<td>2.3.2.2</td>
</tr>
<tr>
<td>10 to 13</td>
<td>0.35 - 2.0</td>
<td>0.8</td>
<td>0 - 0.32</td>
<td>Turbidity</td>
<td>Time</td>
<td>Evaluate conductivity's effect on performance by varying [NaCl]</td>
<td>2.3.2.4</td>
</tr>
<tr>
<td>14 to 21</td>
<td>1.0</td>
<td>0.1 - 1.6</td>
<td>0.2</td>
<td>Turbidity - normalised and actual</td>
<td>Time</td>
<td>Evaluate the system's response to change in pollutant loading</td>
<td>2.3.2.5</td>
</tr>
<tr>
<td>22 to 28</td>
<td>1.0</td>
<td>0.1 - 1.6</td>
<td>0.2</td>
<td>Mass</td>
<td>Time</td>
<td>As above on a mass basis</td>
<td>2.3.2.5</td>
</tr>
<tr>
<td>29 to 32</td>
<td>0.25 - 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Turbidity &amp; pH</td>
<td>Time</td>
<td>Evaluate the system's response to change in operating current</td>
<td>2.3.3.1</td>
</tr>
<tr>
<td>33 to 39</td>
<td>0.25, 1.0, 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Turbidity</td>
<td>Time</td>
<td>Δcurrent - evaluated over a longer time period</td>
<td>2.3.3.1</td>
</tr>
<tr>
<td>40 to 46</td>
<td>0.25, 1.0, 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Mass</td>
<td>Time</td>
<td>As above on a mass basis</td>
<td>2.3.3.1</td>
</tr>
<tr>
<td>47 to 53</td>
<td>0.25, 1.0, 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Mass</td>
<td>Time</td>
<td>Measure pollutant's fate - mass at reactor's surface &amp; base</td>
<td>2.3.3.1</td>
</tr>
<tr>
<td>54 to 57</td>
<td>0.25 - 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Turbidity &amp; pH</td>
<td>Aluminium</td>
<td>Evaluate the system's response to change in operating current</td>
<td>2.3.3.2</td>
</tr>
<tr>
<td>57 to 64</td>
<td>0.25, 1.0, 2.0</td>
<td>0.8</td>
<td>0.2</td>
<td>Mass</td>
<td>Aluminium</td>
<td>As above on a mass basis</td>
<td>2.3.3.2</td>
</tr>
</tbody>
</table>
2.3 Experimental Results

Pollutant characterisation results (Section 2.3.1) are presented first, followed by electrocoagulation performance results (Sections 2.3.2 to 2.3.3).

2.3.1 Pollutant characterisation

2.3.1.1 Zeta potential

The clay particles’ zeta potential measurements range from -34 to -60 mV (see Figure 2-4). Zeta potential of ±5 mV is considered small because it infers little attractive or repulsive forces. As zeta potential increases beyond this region, repulsive forces and thus dispersion stability gradually increases. Beyond the ±30 mV region, dispersions are considered stable. Figure 2-4 shows that the clay pollutant is well inside the stable range (beyond ± 30mV) where particles can be expected to settle. Thus over the pH range 2-12, clay colloids will be stable in solution.

The low ionic concentration ([NaCl] = 0.20 g/L) indicates that double layer compression was impossible in these conditions. This implies that depletion aggregation was also improbable.

![Figure 2-4 Zeta potential of clay pollutant as a function of pH.](image-url)
2.3.1.2 Particle characterisation

The mass fraction at each sieve size is summarised in Table 2-3. The bulk of the mass (69%) exists as silt and clay (particles smaller than 53µm). The remaining mass exists as sand and gravel (particles greater than 53 µm). The mass of particles greater than 500µm is virtually insignificant.

Table 2-3 Mass Percentage fraction at selected sieve sizes.

<table>
<thead>
<tr>
<th>Size Fraction</th>
<th>Mass Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1.00 mm</td>
<td>0.29%</td>
</tr>
<tr>
<td>710 µm - 1.00 mm</td>
<td>0.17%</td>
</tr>
<tr>
<td>500-710 µm</td>
<td>0.29%</td>
</tr>
<tr>
<td>212-500 µm</td>
<td>16.6%</td>
</tr>
<tr>
<td>53 -212µm</td>
<td>13.4%</td>
</tr>
<tr>
<td>&lt;53 µm</td>
<td>69.3%</td>
</tr>
</tbody>
</table>

![Figure 2-5 Particle size distribution of sieve fraction less than 53µm, d_{50}=2.5µm.](image)

The particle size distribution of particles smaller than 53µm is shown in Figure 2-5. The clay’s multi-modal distribution indicates the range of particle sizes within the clay. For
this size fraction, the $d_{50}$ was 2.5µm. This fraction exhibited colloidal properties and remained suspended in solution by the electrostatic repulsion between the negatively charged clay particles.

**2.3.1.3 X-ray diffraction results**

Analysis of each mass fraction at specific temperatures identified the mineralogical species present. Semi-quantitative approximation is possible by combining the mass balance results from Sections 2.3.1.2 with the X-ray diffraction analysis.

**Table 2-4 Summary of X-ray diffraction results**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Substance</th>
<th>Semi-quantitative approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay (settled - &lt; 2.4µm)</td>
<td>Kaolinite</td>
<td>~95%</td>
</tr>
<tr>
<td>(consistent with all samples)</td>
<td>Mica (Illite)</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>0</td>
</tr>
<tr>
<td>-212µm +53µm (Non magnetic)</td>
<td>Quartz</td>
<td>80-85%</td>
</tr>
<tr>
<td></td>
<td>Feldspar (XAl(<em>{1-2}) Si(</em>{3-2}) O(_8))</td>
<td>~10%</td>
</tr>
<tr>
<td></td>
<td>Mica (Illite)</td>
<td>Trace amounts</td>
</tr>
<tr>
<td></td>
<td>Kaolinite</td>
<td>Trace amount</td>
</tr>
<tr>
<td>-212µm +53µm (Magnetic)</td>
<td>Feldspar (plagioclase)</td>
<td>Trace amounts</td>
</tr>
<tr>
<td></td>
<td>Magnetite (iron oxide)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maghemite</td>
<td></td>
</tr>
</tbody>
</table>

Thus the clay consisted of kaolinite (67%), quartz (25%), illite/mica (3%), feldspar (3%) and other trace elements (2%) as shown in Table 2-4. Detailed analysis is presented in Appendix A.

**2.3.1.4 Settling rate**

The settling rates of eighty (80) particles were analysed in the settling column (Figure 2-6). Here the average particle diameter was measured at 7.0 µm and average settling velocity was $1.51 \times 10^{-4}$ m s\(^{-1}\). This corresponds to an average particle’s unhindered settling time of 8 minutes in the electrocoagulation reactor. In contrast, the Malvern particle sizer measured significantly larger number of fine particles, reporting a $d_{50}$ =
2.5 µm (Figure 2-5). These fine particles account for a large proportion (79% less than 7.0 µm) by volume and hence also by mass of the total. Clearly the different detection limits (settling column–2 µm; Malvern particle sizer–0.5 µm) influences the measured particle sizes and settling velocities. The smaller particles (less than 2 µm) consisting of 44% total mass were not seen by the settling column. Thus settling velocity measured by the settling column was based on a particle diameter that was not representative of the pollutant. Consequently the settling rates are further investigated in Chapter 5.

![Graph showing settling velocities vs particle diameter](image)

Figure 2-6 Clay particle’s settling velocities measured in settling column.

### 2.3.1.5 Pollutant characterisation summary

Pollutant characterisation provides a comparative basis to evaluate electrocoagulation’s performance. The clay pollutant was diverse with a wide multi-modal distribution. The dominant pollutant particle size fraction consisted primarily of clay and silt. These small negatively charged particles do not readily settle. Larger particles, a minority albeit still significant, settled faster. Pollutant removal and aggregation could now be evaluated against the primary particle’s characteristics.

A dilemma exists between ensuring adequate connection to reality whilst providing sufficient control to distinguish between phenomena. The connection to reality occurs
with the pollutant’s heterogeneity that replicated a pollutant typically encountered in real water treatment processes. In addition, the pollutant’s heterogeneity created an electrocoagulation system whereby a variety of different mechanisms could be exhibited. To distinguish between these mechanisms, sufficient control over the pollutant was required. The pollutant characterisation provided this control, albeit complex, whilst maintaining electrocoagulation’s connection to reality.

### 2.3.2 Electrocoagulation results

Turbidity and mass balance results were used to evaluate electrocoagulation’s dynamic response, repeatability, and also the impact of changing solution characteristics, specifically conductivity and pollutant loading.

#### 2.3.2.1 Classification into reaction stages

The normalised turbidity (i.e. turbidity at some time, t, divided by the initial turbidity value) and pH profiles for a typical electrocoagulation run (experiment 1) are shown in Figure 2-7. The response observed in this study is similar to the “reverse S” turbidity response observed by Matteson et al. (1995) when removing kaolinite using stainless steel electrodes in a batch cell.

The initial clay concentration was 0.8 g/L and the operating current was kept constant at 0.5A (0.68 mA/cm²). Three stages can clearly be identified - namely, a lag, a reactive and a stabilising stage. Little or no turbidity change is observed in the lag stage, with the majority (~ 95%) of turbidity removal occurring during the reactive stage. As time progresses, the rate of turbidity reduction decreases, with the turbidity eventually levelling out at a value above zero.

Clearly, the behaviour and the removal mechanisms shift as the run proceeds through these stages. This time dependent behaviour is examined in more detail in Section 2.3.3.
Figure 2-7 Normalised turbidity and pH for electrocoagulation; [clay] = 0.8 g/L; I = 0.5 A; [NaCl] = 0.20 g/L.

2.3.2.2 Reliability of results

Normalised turbidity for a set of repeat experiments (experiments 2 – 5) (n = 4) at current 1 A (note that n is the number of repetitions) is shown on a semi-log plot in Figure 2-8. Again, all experiments have an initial lag (first 5-8 minutes) in their turbidity response, before a rapid decrease. Turbidity then slowly decreases until approximately 50 minutes, where it stabilises to approximately 10 NTU (nephelometric turbidity units).

The results shown indicate considerable repeatability particularly in the first 90% of reduction. As the reaction progressed, the standard deviation remained less than 3.6%. The value of this particular model system, as observed here, is high repeatability. Therefore the effect of key operating parameters can be investigated with a greater degree of confidence.
Chapter 2 - Electrocoagulation

Figure 2-8 Normalised turbidity; \( I = 1.0 \, A; [\text{clay}] = 0.8 \, g/L; [\text{NaCl}] = 0.20g/L; n= 4 \).

Considering the same experimental conditions (experiments 6 – 9), the cumulative mass collected at the surface is shown in Figure 2-9 as a percentage of total mass removed. Note that the total mass includes that added as feed (clay pollutant) and mass generated (coagulant) in the reactor, with no mass removed in the first five-minute interval.

Mass was collected at the surface and base of the reactor. Thus, the mass balance is:

\[
\text{Mass IN (FEED)} + \text{Mass IN (GENERATED)} = \text{Mass OUT (SURFACE)} + \text{Mass OUT (BASE)} + \text{Mass REMAINING (BULK SOLUTION)}
\]

\[
\begin{align*}
\text{aluminium}^0 & \quad \text{clay}^0 \\
\text{hydroxide} & \quad \text{collected} \\
\end{align*}
\]

After 20 minutes, the removal rate slows, as indicated by the decrease in the slope of the removal curve. All data points lie within \( \pm 2 \) standard deviations of the mean, indicating acceptable experimental reproducibility. The mass remaining "in solution" consistently accounted for less than 2% of the total mass (clay and coagulant), indicating tight closure of the mass balance. Operating at 1.0 A, approximately 55% of the total mass is
collected at the surface (and hence removed by flotation) with the remaining mass settling out to the bottom of the reactor. This split is discussed further in Section 2.3.3.1 and Chapter 5.

![Cumulative mass collected at the surface]

**Figure 2-9** Cumulative mass collected at the surface; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L; I = 1.0 A; n = 4.

### 2.3.2.3 pH response results

The pH stabilised at about 8.5 after some 10 minutes of operation (Figure 2-7). Additional pH profiles for varying operating currents (0.25 to 2.0 A) are presented in Figure 2-14 and Figure 2-17 on a time and aluminium basis, respectively. As noted in Chapter 1 (Section 1.2.2), the amount of aluminium entering solution can be calculated as a function of time and current using Faraday’s law. That is, operation at 1.0 A for 60 minutes was equivalent to 46 mg/L of aluminium added to an operating volume of 6 L. Thereby enabled the system’s response to be investigated on a time or equivalent aluminium basis, which is further explored in Section 2.3.3.2.
To summarise, regardless of initial pH, the pH stabilised to an alkaline value between 8 and 9 after the lag stage. Note that while the system pH was monitored, it was not controlled for any electrocoagulation experiments. Thus, the observed stabilisation of the pH is a characteristic of the batch electrocoagulation reactor.

For this clay pollutant, batch electrocoagulation resulted in a stable alkaline pH, which might be taken as implying stable speciation within the solution. Yet the process was inherently dynamic, with aluminium continuously entering the system, being hydrolysed in a complex manner, and then being removed from the system. Simultaneously, water was reduced, adding hydroxyl ions to solution. The stable pH belies the addition of hydroxyl ions to solution through water reduction at the cathode. Obviously, a kinetic balance was achieved between hydroxyl production and consumption. Such dynamic changes in concentration affect both the solution speciation and the equilibrium state towards which the system is moving at any one time.

A detailed analysis of the solution chemistry for an electrocoagulation system has not been reported in the literature. Previous researchers (Donini et al., 1994; Musquere et al., 1983) have assumed the solution chemistry was similar to conventional chemical dosing coagulation systems. That assumption is questioned in this thesis and is further investigated in Section 4.1.

### 2.3.2.4 Conductivity - sodium chloride concentration results

The sodium chloride concentration was varied to evaluate the impact of solution conductivity on electrocoagulation in this section. Sodium chloride also reduces passivation (Pourbaix, 1974):

Table 2-5 shows the relationship between sodium chloride concentration and measured conductivity. Normalised turbidity for runs (experiments 10 – 13) with varying sodium chloride concentrations is shown in Figure 2-10. Initial clay concentration remained constant at 0.8 g/L in all runs.
Table 2-5 Conductivity versus sodium chloride concentration.

<table>
<thead>
<tr>
<th>Conductivity (µS/cm)</th>
<th>[NaCl] (g/L)</th>
<th>Voltage (V)</th>
<th>Measured Current (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0</td>
<td>24</td>
<td>0.35</td>
</tr>
<tr>
<td>48</td>
<td>0.015</td>
<td>24</td>
<td>0.60</td>
</tr>
<tr>
<td>90</td>
<td>0.031</td>
<td>24</td>
<td>1.30</td>
</tr>
<tr>
<td>350</td>
<td>0.15</td>
<td>7</td>
<td>2.0</td>
</tr>
<tr>
<td>660</td>
<td>0.32</td>
<td>3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Throughout each experiment, the measured conductivity remained constant. At low sodium chloride concentrations (i.e. low conductivity), a slower turbidity reduction response was observed. Greater solution resistance from low conductivity means a higher cell potential was required. The maximum voltage difference available from the power supply was 24 V, and thus limited the available current. As the sodium chloride concentration increased, so did the system’s response rate. Above 0.15 g/L of sodium chloride, the responses were essentially identical.

![Figure 2-10 Normalised turbidity for various conductivities; [clay] = 0.8 g/L; [NaCl] = 0 – 0.32 g/L.](image-url)
Clearly above 350 $\mu$S/cm, which was equivalent to 0.15 g/L of sodium chloride, there was no change in the system’s response. Measured conductivity and total dissolved solids (TDS) remained constant even at high operating currents. The sodium chloride concentration was significantly greater than ions produced from electrochemical reactions. Consequently, to remove the influence of conductivity on further experiments conductivity must be above this level. Thus a standard concentration of 0.20g/L sodium chloride in deionised water was used for all subsequent electrocoagulation experiments.

### 2.3.2.5 Impact of pollutant loading

![Figure 2-11 Turbidity as a function of pollutant loading; [clay] = 0.1, 0.4, 0.8, 1.6 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.](image)

In experiments 14 to 21, pollutant loading was varied from 0.1 to 1.6 g/L at a constant current of 1.0A (equivalent to density of 1.36 mA/cm$^2$). Absolute turbidity results are presented in Figure 2-11: for all pollutant levels the three reaction stages are apparent. The highest pollutant loading (1.6 g/L) takes a longer time, and hence greater coagulant
addition, to reduce turbidity. However within 30 minutes, all turbidity levels had reached the same order of magnitude and by 50 minutes, all runs were below 20 NTU.

Figure 2-12 presents the same data as in Figure 2-11 but with the results normalised and plotted on a semi-log basis. No discernible trend exists between different pollutant loadings during the lag and reactive stages. The response for all pollutant loadings was similar with differences noticed in residual turbidity levels. Using normalised turbidity results, the lowest load gave the highest residual turbidity and the highest load gave the lowest residual. For 1.6 g/L and 0.1 g/L pollutant loading, absolute residual turbidity levels were almost identical at 4.3 and 3.6 NTU respectively. Thus given sufficient time and coagulant, ultimate turbidity removal is independent of initial pollutant load. Thus electrocoagulation response or removal mechanism appears independent of pollutant loading.
Figure 2-12 also shows similar time dependent trends for normalised turbidity reduction, independent of pollutant load. The slight variation in the stabilising stage for the lowest pollutant load could be an artefact of the sensitivity of the turbidity measurements and removal units: a change of just one NTU represents a 1% change for the low load as opposed to a 0.1% change in normalised turbidity of high load. Thus, in normalised terms the precision decreased at low pollutant loading.

Dynamic mass balance results are presented for experiments 22 to 28 in Figure 2-13. These experiments corresponded to the range of pollutant loading (0.1 – 1.6 g/L) investigated for turbidity. Again, the highest pollutant loading (1.6 g/L) has a slightly slower response in the reactive phase (i.e. in the 10-20 minutes region). These mass balances were based on the total mass including aluminium hydroxide (coagulant) generation, as was discussed in 2.3.2.2.

Table 2-6 Mass balance breakdown for mass added and collected; [clay] = 1.6 – 0.12 g/L; I = 1.0 A.

<table>
<thead>
<tr>
<th>Pollutant loading g/L</th>
<th>Mass In (t = 0 min)</th>
<th>Mass Out (t = 60 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total g</td>
<td>Total clay g (% total)</td>
</tr>
<tr>
<td>1.6</td>
<td>12.00</td>
<td>11.03 (92%)</td>
</tr>
<tr>
<td>0.8</td>
<td>6.49</td>
<td>5.52 (85%)</td>
</tr>
<tr>
<td>0.4</td>
<td>3.76</td>
<td>2.79 (74%)</td>
</tr>
<tr>
<td>0.1</td>
<td>1.82</td>
<td>0.85 (47%)</td>
</tr>
</tbody>
</table>

The breakdown of the overall mass balances is presented in Table 2-6. The mass added to the reactor was a combination of coagulant addition and initial pollutant loading. In
fact, operation at 1 A for 1 hour generated 0.97 g of aluminium hydroxide. At a low pollutant loading (0.1 g/L), a greater proportion of total mass was due to the coagulant generated (53%) compared to higher pollutant loading. This distorted the mass balance results. That is, at low pollutant loading, the majority of mass removed was generated by the reactor (coagulant) whereas at high pollutant loading, the clay was the dominant specie. Thus a mid-range pollutant loading (0.80 g/L) provided sufficient sensitivity and pollutant quantity, for measurement.

![Graph showing cumulative mass removed at surface for different clay concentrations](image)

**Figure 2-13** Cumulative mass collected at the surface; [clay] = 0.1, 0.4, 0.8, 1.6 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.

### 2.3.2.6 Electrocoagulation results summary

To decipher the complexity of electrocoagulation the system’s degrees of freedom must be decreased. This experimental set (Set A) demonstrated that pollutant loading had minimal impact on electrocoagulation’s performance. Slight differences were noticed and these variations were explained by variation in the initial turbidity for normalised turbidity results and similarly, the relative amount of coagulant generated to pollutant
removed. Therefore variation of pollutant loading was not a critical experimental variable in the batch reactor and also for this thesis.

Pollutant loading can be investigated in a batch system. The dynamic nature, and hence the change in pollutant concentration over time, enables a range of pollutant concentrations to be investigated with each individual run. In addition this research is transferable from a batch system to a continuous system as was discussed in Section 1.3.2.

Batch electrocoagulation was classified into three stages to assist with analysis: lag, reactive and stable stage. Experimental variables, specifically conductivity and pollutant loading, were evaluated. From an experimental perspective their influence is controllable and easily quantified. Experiments demonstrated that their influence could be controlled and thereby fixed in further runs. Henceforth conductivity was maintained at 0.20 g/L greater than 0.15 g/L level identified. A mid-range pollutant loading of 0.8 g/L provided a concentration proven to be repeatable with high measurement precision. Sufficient measurement sensitivity was attained at this concentration including the coagulant addition from electrocoagulation. Thus for the following experimental set, conductivity was maintained at 0.20 g/L and pollutant loading at 0.8 g/L.

### 2.3.3 Operating parameter - current

Current is the only operational parameter left that can be directly controlled in batch electrocoagulation runs. It is significant because it directly determines both coagulant dosage and bubble generation rates. It also influences both mixing and mass transfer at the electrodes, as discussed in Section 1.4. Here, experimental Set B explores the impact of current on a dynamic and equivalent aluminium concentration basis.

#### 2.3.3.1 Current results - Time basis

A higher current is expected to produce a higher pollutant removal rate due to the increased coagulant production and bubble density. Figure 2-14 shows pollutant removal behaviour when current was varied from 0.25 to 2.0 A (Experiments 29 to 32). For all cases, regardless of the initial value, the pH stabilises within 15 minutes to somewhere in the range 8.3 to 8.8, as discussed in Section 2.3.2.3. The highest current (2 A) produced the shortest lag (10 minutes) and the quickest response, with a 90%
turbidity reduction occurring between 10 - 15 minutes. As the current density decreased, the duration of each electrocoagulation stage increased.

Normalised turbidity profiles were also examined over a longer time period at 0.25, 1, and 2 A to achieve comparable residual turbidity levels, and are shown in Figure 2-15. Higher current certainly led to a faster reduction in turbidity. At the highest current (2.0 A) investigated, turbidity dropped at 46 NTU/min during the reaction phase, compared to 31 and 15 NTU/min, respectively, for 1.0 and 0.25 A. At 2.0 A, Faraday’s law predicts that the aluminium and hydrogen generation rates double those at 1.0 A. This infers that coagulant addition and bubble density would also double, resulting in the doubling of turbidity reduction rate. This was not observed in these results as the removal rate increased by only 50%. In addition, when current was reduced by a quarter (1.0 to 0.25 A), the removal rate was only halved (31 to 15 NTU/min). Clearly, the
relationship between current and turbidity reduction requires clarification. Thus, this question was also examined from a mass balance perspective.

![Figure 2-15 Normalised turbidity as a function of current; [clay]= 0.8 g/L; [NaCl] = 0.20 g/L; I = 0.25, 1.0, 2.0 A.](image)

The cumulative mass collected at the surface as a percentage of total mass removed for each current (Experiments 40 – 46) is shown in Figure 2-16. All responses achieved a stable stage after the reactive stage, where a constant mass was removed in each time interval. During the reactive stage, the highest current, 2.0 A, had the fastest response and essentially no time lag, with 31% (2.3g) floated to the surface in the first 10 minutes of operation. This corresponded to a removal rate of 0.23 g/min for 2 A. At the lowest current, 0.25 A, a much slower removal rate was observed. The highest removal rate was 0.03 g/min. That occurred in the 30-40 minute interval, much later than the 2.0 A’s peak removal. Current decreased by an eighth (2.0 to 0.25 A) and the peak pollutant removal rate followed likewise. Thus the pollutant removal rate followed the expected trend with changes in the current during the reactive stage.
The mass balance method followed expected removal rate trends as current changed that were not clearly explained by the preceding turbidity results. The use of the mass balance approach quantified mass removal rates to the surface. Whereas turbidity results provided a gross indication of the water clarity with a non-linear relationship between itself and mass removed. Mass balances, as employed in this thesis, provided a definitive answer rather than using a performance indicator, such as turbidity, solely by itself. Past studies have used a variety of performance indicators as discussed in Section 2.2.3, all of which focused on a particular water quality aspect. The mass balance approach was thus proven to be reliable and effective to evaluate electrocoagulation’s mass removal.

Figure 2-16 Cumulative mass collected at the surface as a function of current; [clay]= 0.8 g/L; [NaCl] = 0.20g/L; I = 0.25, 1.0, 2.0 A.

The mass balance approach also quantified the pollutant mass at the surface and the base. At 0.25 A, a total of only 1.68g (26% - see Table 2-7) was recovered after four hours of operation. The remaining 74% of the mass was collected at the reactor’s base.
Settling was clearly the dominant removal mechanism at low currents where fewer bubbles are produced resulting in a decrease in mixing and material uplift. In addition, the coagulant dosage rate decreased with current, another factor that favoured the settling of coagulated material. Conversely, the highest current, 2.0 A, produced the greatest mass reporting to the surface (63% of total) for a one hour reaction time. Flotation was favoured by the higher bubble density and coagulant dosage occurring at this current and resulted in mass removal to the surface.

Table 2-7 Mass balance breakdown for mass added and collected; \( I = 0.25 - 2.0 \) A; [clay] = 0.8 g/L.

<table>
<thead>
<tr>
<th>Current A</th>
<th>Time min (hr)</th>
<th>Total Mass In clay g (% total)</th>
<th>Total Mass In Al(OH)(_3) g (% total)</th>
<th>Mass Out At surface g (% total)</th>
<th>Mass Out At base g (% total)</th>
<th>Mass Out In bulk solution g (% total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>240 (4)</td>
<td>6.49 (85%)</td>
<td>0.97 (15%)</td>
<td>1.68 (26%)</td>
<td>4.76 (73%)</td>
<td>0.05 (1%)</td>
</tr>
<tr>
<td>1.0</td>
<td>60 (1)</td>
<td>6.49 (85%)</td>
<td>0.97 (15%)</td>
<td>3.59 (55%)</td>
<td>2.63 (41%)</td>
<td>0.27 (4%)</td>
</tr>
<tr>
<td>2.0</td>
<td>60 (1)</td>
<td>7.48 (74%)</td>
<td>1.94 (53%)</td>
<td>4.70 (63%)</td>
<td>2.93 (39%)</td>
<td>-0.15 (-2%)</td>
</tr>
</tbody>
</table>

Removal time must also be considered with operating current for evaluation of the pollutant’s fate (see Table 2-7). At higher current (2.0A), the removal time was shorter (see Figure 2-16) due to the greater upward momentum flux induced by the increased hydrogen production rate. Conversely at low current (0.25 A), removal time was longer due to slower coagulant addition and decreased upward momentum flux, thereby enabled aggregates to settle. Thus the combination of current and time determine pollutant removal.

Faradays’ law (Equation E1-5) related both current and time. This law also calculated the aluminium, that is coagulant, delivered to the solution. Current and time were the only variables required to calculate aluminium concentration. The product of current
and time was the charge as recognised by Chen et al. (2000). All other parameters in Faraday’s law for aluminium calculation were constant. Thus the total aluminium was used as a basis, which combines current and time (i.e. the charge) for comparison in the proceeding section.

2.3.3.2 Current results - Aluminium basis

The system’s turbidity response was monitored as a function of the available coagulant based on aluminium (Experiments 54 to 57). In Figure 2-14, the independent variable was time. In Figure 2-17, the independent variable was equivalent aluminium, which was a combination of time and current. Thus the total amount of aluminium electrochemically added to the solution, up to a given point in time, provided the basis for evaluation.

![Figure 2-17 Normalised turbidity and pH as a function of equivalent aluminium; I = 0.25, 0.5, 1.0, 2.0 A; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.](image-url)
Reactor behaviour is clearly a strong function of aluminium concentration. However, the order of turbidity reduction has reversed relative to the time-based data (see Figure 2-14). The lower the current, the less aluminium is used to achieve an equivalent turbidity reduction. For low currents (0.25 and 0.5 A) the responses were similar, with lag, reactive and stable stages coinciding. Here, settling dominated and coagulant addition appeared to be the rate-limiting factor. As current increased, the characteristic stages, that is, lag, reactive and stabilising stages for each current occurred at different aluminium levels. Here, flotation became significant and resulted in a change in the relationship between pollutant fate and coagulant usage. Thus as the aluminium concentration increased the dominant removal paths and coagulant use altered implying a shifting mechanism.

To investigate this shifting mechanism, cumulative mass removal profiles (Experiments 57 to 64) were presented on an equivalent available aluminium basis in Figure 2-18. Current was varied from 0.25 to 2.0 A. It is clear that the response profiles were similar at the higher currents when observed on an aluminium basis. That is, the shape of the curves are similar, after the initial rapid increase in mass removed, the removal rate stabilises for each current level used.

The response order was somewhat counter-intuitive. As expected, the lowest current removed the least mass to the surface as aluminium concentration increased, primarily due to the dominance of settling. Operation at 2.0 A, which produced more coagulant and more hydrogen would be expected to achieve the greatest mass removal. Yet as current increased, and hence also the bubble density, the mid-range current of 1.0 A removed the greatest mass percentage to the surface on an aluminium basis.

In other words, efficiency appeared greatest at 1.0 A, where efficiency was defined as the pollutant mass removed divided by the available coagulant concentration. Conversely, if efficiency was defined as the pollutant mass removed divided by time (see Figure 2-16), operation at the highest current would be the most efficient. So far, this analysis has failed to discuss the time constants for each removal process.

The time constants for each process, settling and flotation, are different. Time taken to settle is far greater than time taken to float. Settling can be increased with larger
aggregates, which require a greater coagulant dosage. Likewise, flotation can be increased with increased bubble density. Both require increased current. The paradox is that current and time control both these processes. Current determines not only coagulant production rate but also the bubble generation rate. Both the coagulant concentration, bubble density, and time influence pollutant removal.

![Figure 2-18](image)

**Figure 2-18** Cumulative mass collected at the surface per mg/L of available aluminium; \( I = 0.25, 1.0, 2.0 \) A; \([\text{clay}] = 0.8 \) g/L; \([\text{NaCl}] = 0.20 \) g/L.

The relationship between operating current and pollutant removal cannot be considered in isolation. Pollutant removal is both a function of coagulant addition and pollutant removal path. Both processes are a combination of both operating current and time. These two processes are not synergistic, hence resulting in the apparent contradiction in results. To gain insight into these interactions, the combination of coagulation, flotation and removal paths, are examined in greater detail in this Chapter 5.
2.4 **Chapter summary and thesis direction**

Electrocoagulation involves a combination of pollutant removal paths and mechanisms that operate synergistically. The complexity of electrocoagulation was explored by examining the experimental variables. The effect of conductivity was controlled and pollutant loading’s effect was shown to be inconsequential. This thereby reduced the degrees of freedom. Consequently experimentation on a macroscopic level has identified the key operating parameters as current and time.

Current determines coagulant dosage and bubble production rate. Generation and production of coagulant and bubbles is determined by the electrochemical behaviour of anode and cathode. Electrocoagulation’s electrochemistry is researched in more detail in Chapter 3.

Additionally current determines coagulant addition resulting in the aggregation of particles. Effective aggregation and hence pollutant removal relies on coagulation. Coagulant addition results in various possible coagulation mechanisms. Thus the relationship between coagulation mechanisms and electrocoagulation’s reaction stages are explored in Chapter 4.

Clearly current and time determine removal mechanism, but the relationship between the competing removal paths (i.e. to surface or base) and operating parameters is not well understood. This phenomenon is further investigated in Chapter 5.
3 Electrochemistry

Electrochemistry is the foundation science common to all electrocoagulation reactors. Dissolution of the aluminium anode delivered coagulant into solution. Simultaneously reduction of water at the cathode determined hydrogen gas generation. Both these electrochemical processes occurred at the electrodes as potential was applied. Hence electrochemical reactions and phenomena governed the coagulant and bubble generation. This chapter explores the electrochemistry of electrocoagulation.

This chapter examines the electrocoagulation reactor’s relationship with the possible electrochemical processes occurring at the electrode’s surface (Section 3.1) using a dedicated electrochemical polarisation experimental rig (Section 3.2 and 3.3). Fundamental electrochemical experiments combined with the electrocoagulation experiments provide a basis for comparison. Consequently, Section 3.4 compares and evaluates the performance of the electrocoagulation reactor. Finally the implications for electrocoagulation reactor operation are evaluated in Sections 3.6 and 3.7. This approach is novel, with no electrochemical mechanistic studies reported for electrocoagulation in the literature.

3.1 Electrocoagulation reactor

The electrochemical reactions occurring in the electrochemical reactor were dependent on the electrodes, the aqueous environment and the applied potential. Possible electrochemical half-cell reactions have been previously discussed in Section 1.2.2. This analysis considers the desired electrochemical reactions for electrocoagulation: primarily aluminium dissolution (Equation E1-1) and hydrogen generation from the reduction of water in an alkaline environment (Equation E1-3). Aluminium dissolution delivered the active aluminium cation in situ to act as the coagulant. Hydrogen production released small bubbles into solution providing uplift for pollutant removal by flotation.

3.1.1 Aluminium dissolution rate and hydrogen production rate

In this thesis, each electrocoagulation run was conducted galvanostatically, that is, at constant current (as described in Section 2.2.2). This resulted in constant aluminium dissolution rate and hydrogen generation rate. Faraday’s Law has been experimentally
shown to accurately describe aluminium dissolution in electrocoagulation reactors (Koparal and Ogutveren, 2002; Vik et al., 1984). Additionally, the aluminium analysis conducted in Section 4.2.2, also followed Faraday’s Law. Thus, the rate of aluminium dissolution, and hence also the rate of coagulant production, was described by Equations E3-1 or E3-2 on either a mole or mass basis, respectively.

\[
\begin{align*}
\frac{r_{\text{Al}^{3+}}}{A} &= \frac{l}{ZF} \text{ mol Al}^{3+} \text{ s}^{-1} & (E3-1) \\
\frac{r_{\text{Al}^{3+}}}{A} &= \frac{l(\text{AW})}{ZF} \text{ g Al}^{3+} \text{ s}^{-1} & (E3-2)
\end{align*}
\]

Where \( I \) was the current (A), \( Z \) the number of electrons, \( F \) was Faraday’s constant (96,486 C mol\(^{-1}\)) and \( \text{AW} \) the atomic weight. Similarly, the hydrogen generation rate was calculated. Thus, operation at constant current density ensured constant aluminium dissolution and hydrogen generation rates.

### 3.1.2 Theoretical cell potential

The primary half-cell equations considered here were Equations E1-1 (anode) and E1-3 (cathode) for the electrocoagulation system. Thus the standard equilibrium potential (Equation E3-3) was +0.83 V (at 298.15K, 1 atm, 1 molar solution). Note that these values were relative to the standard hydrogen electrode (SHE).

\[
E_{\text{CELL}}^0 = E_C^0 - E_A^0
\]

The electrocoagulation reactor operated at conditions other than standard, particularly with respect to the aluminium concentration and solution pH. Aluminium concentration of 0-200 mg/L and pH 6-9 spanned the batch electrocoagulation reactor’s operable region. The Nernst equation (Equation E1-8) related these experimental conditions to standard cell potential \( (E_{\text{CELL}}^0) \) with the potential ranging from +1.13 to +1.31 V. The predominant effect was due to pH where the cathodic potential \( (E_C^0) \) ranged from -0.35 to -0.53 V for pH 6 – 9, respectively. Note variations in solution conditions (pH and total aluminium concentration) resulted in values predicted greater than the standard conditions. This provides a minimum cell potential for the electrocoagulation reactor.
The actual cell potential \( E_{\text{CELL}} \) was the difference between the actual cathodic and anodic potentials. This value included the overpotential required by the anode and cathode, solution resistance and losses (see Equation E1-9). The actual operational potentials are presented in the following section.

### 3.1.3 Operational cell potential of electrocoagulation reactor

For the electrocoagulation reactor, the actual cell potential \( E_{\text{CELL}} \) was measured and recorded at various fixed currents. The resultant potential difference was measured as shown for a range of conditions in Figure 3-1.

![Figure 3-1 Measured \( E_{\text{CELL}} \) for the batch electrocoagulation reactor; \( I = 0.25, 1.0, 2.0 \) A; \([\text{clay}] = 0.1, 0.8, 1.6 \) g/L; \([\text{NaCl}]=0.20 \) g/L.](image)

Initially a higher cell potential was observed in all cases. This high potential overcame initial solution and surface resistances. However, the cell potential stabilised within a minute’s operation under a wide range of conditions. Overall, the cell potential increased as the current increased, as expected; though for each current a cell potential range was observed. Average cell potentials are presented in Appendix B.
Little additional information was provided concerning the mechanistic electrochemical reactions at each electrode. The total cell potential ($E_{\text{CELL}}$) was the result of a combination of processes occurring at each electrode and the bulk solution (refer to Figure 3-2). That is, the interactions occurring at the metal – solution interface, which determine the dissolution behaviour (as previously discussed in Section 1.2.2).

There has only been one study examining the electrochemistry of electrocoagulation by Chen et al. (2002). This study examined a range of resistances (electrode spacing, conductivity, surface resistance) and quantified their effect. They failed to examine the processes occurring at surface of the electrode and its implications to electrocoagulation reactor operation. Thus a study here, of electrode kinetics provided an important insight into the rate limiting processes. The two limiting reactions considered here in more detail, relate to charge transfer and diffusion processes.

3.1.4 Electrochemical kinetics

Electrode reactions are heterogeneous in that they take place in the interfacial region between the electrode and solution. To make the overall process more understandable, consider a generic electrochemical reaction (Equation E3-4) that is expanded schematically in Figure 3-2.

\[
O + ne \leftrightarrow R
\]  
(E3-4)

The oxidant ($O_{\text{bulk}}$) diffused through bulk solution to the electrode surface region (i.e. $O_{\text{surf}}$). Consequently a potential and a concentration gradient exist between the electrode surface and the bulk solution. These species could then chemically react forming an intermediate labelled $O^\prime$ before adsorption on to the electrode’s surface ($O'_{\text{ads}}$). At the surface, electron transfer occurs and the specie is reduced to form $R'_{\text{ads}}$. A similar process, in reverse order, described the reductant’s diffusion into the bulk solution.

The overall reaction rate is governed by the relative speed of the mass transfer (from bulk solution to electrode surface) and electron transfer (at the surface) processes. Hence, the rate limiting processes may be either the charge-transfer or diffusion process. The rate-limiting step determines the overall electrochemical reaction kinetics.
The measured cell potential was an absolute difference and not relative to a reference potential. The experimental measurements of the electrocoagulation reactor ($E_{\text{CELL}}$) did not distinguish between electron and diffusion limiting reactions. These electrode processes and their kinetics dictate coagulation generation and bubble production rates. Thus a fundamental study of the electrochemical characteristics of the system was required to gain some insight to the electrochemical mechanisms of electrocoagulation. The individual potentials of both the anode and cathode were required to characterise their electrochemical behaviour.

### 3.2 Electrochemical experimental method

Electrochemical polarisation experiments were used to characterise each electrode individually. The aim was to determine the rate limiting process at each electrode. A dedicated electrochemical cell was used to polarise each electrode under controlled conditions. Potentiodynamic anodic polarisation techniques characterised each metal specimen electrode by its polarisation curve (i.e. current-potential relationship). This polarisation curve enabled electrochemical parameters ($E_{\text{mixed}}, i_0, i_L$ - as identified in Section 1.2.2) to be extracted that characterise the system’s kinetic behaviour. Potentiodynamic polarisation experiments (explained below) were conducted and their interpretations used to characterise each electrode’s response under the same aqueous environment experienced in the electrocoagulation reactor.

### 3.2.1 Solution preparation

Aqueous solutions were prepared from deionised water, with sodium chloride added to give a concentration of either 0 or 0.20 g/L. Clay concentrations varied from 0.1 to
1.6 g L$^{-1}$. These clay and sodium chloride concentrations are based on those used for the electrocoagulation experiments performed on the 7.1 L batch electrocoagulation reactor (refer to Section 2.2.2). The initial and final solution pH was measured using a calibrated pH electrode.

### 3.2.2 Experimental equipment

An electrochemical cell, as illustrated in Figure 3-3, was used for these electrochemical experiments. The polarisation cell contained five necks, with four housing electrodes and the fifth neck was used for purging and pH measurement. The role of each electrode is now considered.

![Diagram of the cell used during electrochemical experiments (PAR, 1974)](image)

The centre neck housed the working electrode and specimen electrode (i.e. the electrode of interest). The specimen electrode was tightly secured to the working electrode’s base. A Teflon gasket was used to ensure a tight seal between the glass-housing rod and the specimen electrode. Table 3-1 lists the specimen electrodes used in this study and their surface area (dimensions measured using digital calipers).
Table 3-1 Electrode surface area used in polarisation cell

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Area (cm²)</th>
<th>Height (mm)</th>
<th>Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430 stainless steel</td>
<td>4.52</td>
<td>11.37</td>
<td>9.35</td>
</tr>
<tr>
<td>Aluminium</td>
<td>4.47</td>
<td>8.84</td>
<td>12.37</td>
</tr>
<tr>
<td>316 stainless steel</td>
<td>5.07</td>
<td>9.59</td>
<td>12.70</td>
</tr>
</tbody>
</table>

The smaller neck at the front housed the reference electrode. A saturated calomel electrode (SCE) was used as the reference electrode and its relationship to the saturated hydrogen electrode (SHE) is shown in Figure 3-4. A saturated KCl salt bridge separated the reference electrode from the bulk solution whilst ensuring excellent conductivity between the reference electrode and the working electrode. A porous frit enabled the close measurement of working electrode’s surface potential.

Finally, the adjacent necks housed the graphite counter electrodes. The counter electrodes conducted the resultant current for the desired potential between the reference and working electrodes.

```
E vs SHE       E vs SCE
SCE  0.24      0.0
   Hg/Hg₂Cl₂ KCl (saturated)
SHE  0.0       -0.24
   Pt/H₂/H⁺
```

Figure 3-4 Relationship between standard hydrogen electrode (SHE) and saturated calomel electrode (SCE) (based on Figure E.1, Bard and Faulkner, 2001).

The polarisation cell was situated above a magnetic stirrer to ensure the contents were well mixed.

The Princeton Applied Research (PAR) electrochemical equipment used was comprised of several modules. Different combinations and settings allowed various experimental techniques to be used. For potentiodynamic polarisation experiments, the PAR Model
173 Potentiostat/Galvanostat controlled the applied potential. The potential between the working electrode and the reference electrode was controlled by a PAR Model 178 Electrometer probe, connected to the Model 173 Potentiostat (refer to PAR, 1974 for details). The PAR 175 Universal Programmer generated the signal for the potential function.

The PAR potentiostat regulated the applied potential between the working and reference electrodes, with current measured between working and counter electrodes. Two analogue outputs were produced; the applied cell potential, relative to the reference electrode, and the resultant current. A dedicated PC using a data acquisition card and software recorded these outputs. A specialised software program was constructed to record analogue data outputs for post processing.

### 3.2.3 Experimental procedure

The cell was filled to cover the working electrode with ~750 mL of desired solution. The aqueous system was then purged with nitrogen for some 45 minutes to remove any dissolved carbon dioxide and oxygen from the solution.

The specimen electrode was carefully prepared immediately before the experiment. The electrode was cleaned with wet 240-grit SiC paper until the surface appeared smooth. The surface was then wet polished with 600-grit SiC paper to remove any coarse scratches. The electrode was then rinsed with acetone to remove grease and oil, before finally being rinsed with deionised water.

Potentiodynamic measurements of the anodic and cathodic potentials were conducted separately. The potentiostat (Model 173) controlled the potential between the working and reference electrode. Initially, the mixed potential was measured as detailed in PAR, 1974. The potentiostat then scanned the specimen at a sweep rate of 1 mV s\(^{-1}\) from the mixed potential. For anodic polarisation, the applied potential increased from the mixed equilibrium potential to a predetermined set point. For cathodic polarisation the applied potential was decreased from the mixed equilibrium potential.

The equipment was calibrated according to the ASTM Standards ((ASTM), 1985) using a 430 stainless steel electrode in a 0.5M sulfuric acid. Accurate and precise calibration
was achieved with these results reported in Appendix C. Following this calibration test, a series of anodic and cathodic polarisation experiments were carried out as detailed in Table 3-2.

### Table 3-2 Matrix of polarisation experiments

#### Anodic experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[clay] (g/L)</th>
<th>[NaCl] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.6</td>
<td>0.20</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.20</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>0.20</td>
</tr>
<tr>
<td>D</td>
<td>0.8</td>
<td>0.20</td>
</tr>
<tr>
<td>E</td>
<td>0.12</td>
<td>0.20</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>G</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>I</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>J</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>K</td>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

#### Cathodic Experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[clay] (g/L)</th>
<th>[NaCl] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>1.6</td>
<td>0.20</td>
</tr>
<tr>
<td>U</td>
<td>1.6</td>
<td>0.20</td>
</tr>
<tr>
<td>V</td>
<td>0.8</td>
<td>0.20</td>
</tr>
<tr>
<td>W</td>
<td>0.12</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### 3.3 Electrochemical results

Potentiodynamic polarisation curves for the aluminium anode and stainless steel cathode are presented here, followed by the solution pH results.

#### 3.3.1 Aluminium anodic potentiodynamic polarisation curves

A typical potentiodynamic anodic polarisation curves is presented in Figure 3-5. Two main regions can be identified: a charge-transfer region and a mass diffusion region. The charge transfer or Tafel region is labelled in Figure 3-5 following a primarily linear relationship. The second region, that is, the mass diffusion limited region, occurred as the limiting current was attained. That was when current density remained essentially constant with increasing potential. Between these regions, clearly both charge transfer and diffusion effects were significant.
Figure 3-5 Potentiodynamic anodic polarisation; aluminium; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

The curve’s shape provided an indication of aluminium’s dissolution behaviour in the same solution as in the electrocoagulation reactor. Passivation was not observed, with the aluminium surface remaining active. In the solution condition there was no evidence of a critical passivation potential (in contrast to the calibration curve in Appendix C). Thereby implying that aluminium, in these solution conditions, does not readily passivate.

A change was observed outside the Tafel region. The applied potential increased more rapidly for individually measured anode. Here, the diffusion processes at the electrode’s surface influenced current density.

Potentiodynamic anodic polarisation curves for different pollutant loadings and sodium chloride concentrations are presented in Figure 3-6. Sodium chloride’s presence had a significant influence on the anodic polarisation. Without sodium chloride present, the polarisation curve shifted to the left. The Tafel region was reduced and diffusion processes at the electrode became significant at lower current densities. Inclusion of chloride ions, as in electrocoagulation experiment, increased surface activity. Various
mechanisms have been postulated for the activation of aluminium by chloride with the exact mechanism still elusive (Babic et al., 1995; Kolics et al., 1998; Lee and Pyun, 1999; Paul et al., 1992; Pyun et al., 1999; Pyun and Lee, 2001). Regardless of the mechanism, the presence of chloride ions clearly enhanced aluminium dissolution (Pourbaix, 1974).

The pollutant’s presence had a modest influence on polarisation. The clay’s presence reduced the mass transfer limiting current density as shown in Figure 3-6. This was congruent with the results from electrocoagulation reactor experiments evaluating the pollutant in Section 2.3.2.5. Additional anodic polarisation curves are presented in Appendix D.

![Figure 3-6 Anodic polarisation of aluminium; [clay]=0, 0.8 g/L; [NaCl]=0, 0.20 g/L.](image)

3.3.2 Stainless steel cathodic potentiodynamic polarisation curves

Typical potentiodynamic cathodic polarisation curves for 316 stainless steel curves are shown in Figure 3-7. Two regions were identifiable; charge transfer (Tafel region) and a region where diffusion processes are also significant. Hydrogen evolved at the cathode as water was reduced. The cathodic polarisation curve primarily characterises the
hydrogen evolution behaviour with a stainless steel electrode and given solution conditions. In effect, it experimentally quantifies the hydrogen overpotential in an aqueous environment equivalent to that of the electrocoagulation reactor.

Figure 3-7 Cathodic polarisation of 316 stainless steel; [clay] = 0.8 g/L; [NaCl] = 0.20 g/L.

Additional cathodic polarisation curves, for other pollutant loadings and sodium chloride concentrations are presented in Appendix E.

3.3.3 Solution pH

The solution pH values for polarisation experiments are summarised in Table 3-3, with detailed results given in Appendix F. For all systems, the pH was not controlled and observed changes were due to electrochemical reactions, the same as in the electrocoagulation reactor.

The initial pH varied from 5.2 to 8.9, with the clay consistently contributing to the alkaline nature of the solution (refer to Section 2.3.1 for clay’s characterisation). The final pH ranges from 5.6 to 7.9 for anodic polarisation scans. This corresponds to the observed electrocoagulation reactor’s pH range of 6 to 9 (Section 2.3.2.3). Solutions containing clay were at the higher end of this range (pH 7.0 – 7.9), as also observed in
electrocoagulation. Without clay, a neutral or slightly acidic pH (range of 5.6 to 7.1) was observed.

Table 3-3 Polarisation experiments final pH

<table>
<thead>
<tr>
<th>Polarisation experiment</th>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode - All</td>
<td>5.2 to 8.9</td>
<td>5.6 to 7.9</td>
</tr>
<tr>
<td>- With clay</td>
<td>6.8 to 8.9</td>
<td>7.0 to 7.9</td>
</tr>
<tr>
<td>- Without clay</td>
<td>5.2 to 6.9</td>
<td>5.6 to 7.1</td>
</tr>
<tr>
<td>Cathode – All with clay</td>
<td>6.6 to 7.6</td>
<td>6.1 to 6.9</td>
</tr>
</tbody>
</table>

For most cathodic polarisation scans, the pH decreases slightly with the final pH in the range 6.1 to 6.9. Thus, cathodic polarisation under controlled conditions occurs in a slightly acidic environment.

The relationship between the solution chemistry and the electrochemistry is further explored when Potential-pH diagrams are discussed in Section 3.7. The following section compares the polarisation cell experimental results and the electrocoagulation reactor.

### 3.4 Comparison with electrocoagulation results

Polarisation experiments were conducted to aid the understanding of the electrochemical processes occurring in the electrocoagulation reactor. A basis for comparison between polarisation and electrocoagulation reactor experiments is defined in Section 3.4.1. Then the polarisation results are related to the performance of the electrocoagulation reactor in Section 3.4.2 and their implications to power and energy requirements are discussed in Section 3.6. Using the reference conditions experimentally determined, the electrocoagulation reactor’s operable region could then be plotted on a Potential – pH diagram (also known as a Pourbaix diagram) (see Section 3.7). This enabled a priori prediction of behaviour in changing aqueous and electrochemical environments.
3.4.1 Basis for comparison

Electrochemical polarisation experiments were conducted under controlled conditions to elucidate surface chemistry mechanisms, while electrocoagulation experiments were conducted to replicate a realistic water treatment process. These two systems are compared in Table 3-4.

Table 3-4 Comparison between electrocoagulation and polarisation cell experimental systems.

<table>
<thead>
<tr>
<th>Electrocoagulation reactor</th>
<th>Polarisation cell</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not purged.</td>
<td>Purged.</td>
<td>Conditions were controlled in the polarisation cell.</td>
</tr>
<tr>
<td>Combined electrodes.</td>
<td>Separate electrodes.</td>
<td>Each electrode was investigated separately in the polarisation cell.</td>
</tr>
<tr>
<td>Potential satisfied required current set point (galvanostatic).</td>
<td>Applied potential was controlled and varied (potentiostatic).</td>
<td>Polarisation experiments examined a range of applied potential rather than a set point (as in electrocoagulation).</td>
</tr>
<tr>
<td>Current controlled and constant.</td>
<td>Resultant current measured.</td>
<td>Changes in current density relate to anode dissolution behaviour.</td>
</tr>
</tbody>
</table>

Solution characteristics were similar between the electrocoagulation reactor and the polarisation cell. The sodium chloride and clay concentrations were the same in each system. Changes in the polarisation cells’ aqueous environment, that is the pH, were solely due to the electrochemical reaction(s) occurring for an individual electrode (anode or cathode). In the electrocoagulation reactor, by comparison, solution changes were due to electrochemical reactions occurring at both the anode and the cathode. Thus polarisation experiments were designed with solution and electrode conditions similar to the makeup of the electrocoagulation reactor.

Polarisation cell experiments separated the electrochemical effects from other external influences, as much as possible (see Table 3-4). This enabled the desired individual electrochemical reactions to be investigated. This knowledge and insight can then be applied to the overall electrocoagulation reaction. The electrochemical experiments
provided a firm scientific basis for investigation of electrocoagulation and their relevance is examined in the following section.

### 3.4.2 Combined polarisation curves

To evaluate the performance of the electrocoagulation reactor, relevant polarisation curves were combined. That is, the anodic and cathodic polarisation curves for identical solution conditions, specifically pollutant and sodium chloride concentrations, were plotted on the same figure. This plot related the anodic and cathodic polarisation behaviour, with a typical example for clay pollutant loading of 0.12 g/L shown in Figure 3-8. The electrode combination, specifically aluminium anode and 316 stainless steel cathode, was the same as in the electrocoagulation reactor. Thus the performance of the electrocoagulation reactor could then be evaluated against the potentiodynamic polarisation curves.

![Figure 3-8 Polarisation curves for aluminium anode and 316 stainless steel cathode; [NaCl] = 0.20 g/L; [clay] = 0.12 g/L.](image)

The electrocoagulation reactor operated at 0.25, 1.0 and 2.0 A, which corresponded to 0.34, 0.64 and 2.74 mA/cm² respectively. These current densities were then plotted on the same figure and were represented by the vertical lines in Figure 3-8. For each
current density of interest, the anodic and cathodic potential was determined against the SCE. Additional results for pollutant loading of 0.8 and 1.6 g/L are given in Appendix G.

From the combined polarisation curves the behaviour of each electrode could be isolated with three main implications apparent. Firstly, the individual potential was identified for each electrode, which enabled thermodynamic modelling, specifically Potential – pH diagrams, to be constructed. Secondly, the potential differences between the electrodes were deduced for each operating current of interest. Thirdly, the rate-limiting step at each electrode’s surface was deduced. Each implication and its consequence are discussed in the proceeding sections.

1. Individual potential established

Potentials measured against a standard reference (SCE) for each electrode were used to define operable regions in Potential – pH diagrams. These diagrams presented in Section 1.2.3, combine thermodynamic and electrochemical data to characterise the metal’s behaviour in an aqueous environment (Pourbaix, 1974). From these diagrams, thermodynamically favourable species can be deduced under a range of solution conditions (pH) and electrode potentials ($E_h$)$^4$. This is discussed further in Section 3.7.

2. Potential differences - polarisation results compared to electrocoagulation

For each current density of interest, the potential difference was deduced. That is, the difference between the anode and cathode potential as highlighted in Figure 3-8 can be calculated for the entire current density range as shown in Figure 3-9. This difference determined the minimum applied potential required for electrocoagulation based on the results of the polarisation experiments. This process was repeated for all pollutant loadings. These values were compared to the measured potential difference from the electrocoagulation reactor (see Figure 3-1 in Section 3.1) in Table 3-5. The operating current density primarily dictated potential requirement and as current density increased, the potential difference increased accordingly.

$^4$ Note on nomenclature. For potential-pH diagrams, the potential will be referred to as $E_h$ as per the notation used by Pourbaix (1974). This is equivalent to the potential described as $E_0$. 
Figure 3-9 Potential difference for individual Aluminium anode and 316 stainless steel cathode potentials from polarisation cell; [NaCl] = 0.20 g/L; [clay] = 0.12 g/L.

Table 3-5 Potential differences (V) for electrocoagulation reactor and polarisation cell.

<table>
<thead>
<tr>
<th>POTENTIAL (V)</th>
<th>[clay] (g/L)</th>
<th>0.341 mA/cm² (0.25 A)</th>
<th>1.36 mA/cm² (1.0 A)</th>
<th>2.74 mA/cm² (2.0 A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarisation cell</td>
<td>0.12</td>
<td>0.9</td>
<td>1.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Electrocoagulation reactor</td>
<td>0.12</td>
<td>1.8</td>
<td>4.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Polarisation cell</td>
<td>0.8</td>
<td>1.1</td>
<td>2.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Electrocoagulation reactor</td>
<td>0.8</td>
<td>1.8</td>
<td>2.8 to 4.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Polarisation cell</td>
<td>1.6</td>
<td>1.1</td>
<td>2.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Electrocoagulation reactor</td>
<td>1.6</td>
<td>1.5</td>
<td>4.9</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The cell potential measured from the electrocoagulation reactor ($E_{CELL}$) was consistently larger than the potential difference from the polarisation cell experiments ($E_{ANODE-E_{CATHODE}}$). At an equivalent current density, the electrocoagulation reactor consistently required a greater (up to a factor of 3) cell potential. This large variance was due to a number of effects including:

- Controlled versus uncontrolled conditions
- Surface resistance
- Junction potential
- Inter-electrode gap
- Solution resistance.
Solution resistance was minimised in both systems by the addition of sodium chloride that enhanced conductivity.

Differences between the reactors contributed to the observed variance in potential requirements and were previously discussed in Section 3.4.1. The polarisation cell operated in controlled conditions being purged with nitrogen. This removed any dissolved gases and thereby minimised any other possible electrochemical reactions and hence the potential was indicative of the desired electrochemical reaction (either aluminium dissolution or hydrogen production). Whereas the electrocoagulation reactor was unpurged with dissolved gases remaining in solution (e.g. oxygen) to replicate a more realistic water treatment process. This increased the possibility for additional and undesirable electrochemical reactions and hence the increased total applied potential required. Consequently the electrocoagulation reactor reported a significantly greater operating potential than the results from the polarisation experiments predicted.

Electrodes used in the polarisation experiments were meticulously cleaned before each experiment and hence surface resistance effects minimised (refer to Section 3.2.3). Surface resistance in the electrocoagulation reactor contributed to increased potential requirement. The solution in the electrocoagulation was not purged and hence oxygen was present. Oxygen is a strong oxidant and has the possibility of forming an oxide layer on the metal surface and hence increasing the surface resistance and overall potential required.

Additionally the electrodes used in the electrocoagulation reactor were only cleaned periodically to remove this passivating layer. This periodic cleaning aimed to replicate a realistic process but resulted in the increased surface resistance and hence also potential requirements. Passivation did not affect coagulant or bubble generation rates (as reactor was operated galvanostatically) but increased the required potential, as observed in Table 3-5. The result was increased power and energy requirements.

Junction potential resistances were greater for the electrocoagulation reactor’s electrodes. Contact area between adjacent electrodes was limited to the cross-sectional area of the electrode and the connecting brass rod (refer to electrode design in Section 2.1.2). In contrast, the specimen electrode used in the polarisation cell was connected
via a precisely designed and engineered thread ensuring adequate contact. Clearly, redesign of the electrocoagulation reactor’s electrodes will reduce junction potentials and hence the overall applied potential.

The applied potential must be sufficient to overcome all the resistances discussed above. The rate limiting mechanism at the electrode’s surface also has a strong influence on the required overpotential and is considered in the following section.

3. Electrocoagulation’s electrode mechanisms

It is clear that the operating current densities (of the electrocoagulation reactor) investigated corresponded to the charge transfer-limited region for both the anode and cathode (see Figure 3-8) until high current densities. In the charge transfer limiting region, Tafel parameters can be extracted from the polarisation curves to enable prediction of the required overpotential as examined in the next Section.

At high current densities, diffusion processes were also significant. Regardless of pollutant loading, similar results were obtained. Thus as operating current density increased greater cell potential ($E_{\text{CELL}}$) was required. This resulted in increased potential requirements and hence also power and energy, which are discussed in Section 3.6.

3.5 Tafel plots – charge transfer regions

Tafel parameters enable $a$ priori prediction of the overpotential required at each individual electrode (see Section 1.2.2). Tafel parameters were extracted from the polarisation curves. Hence the combination of the anode and cathode Tafel expression predicts the required cell potential. Consequently, Tafel plots were extracted from the experimental anodic and cathodic polarisation curves for example as shown in Figure 3-10 and Figure 3-11, respectively.

A Tafel region is defined as a linear region spanning a minimum of two (PAR, 1978). The charge transfer region was fitted with a line, with its slope the Tafel parameter. The results for all polarisation curves are summarised in Table 3-6.
Figure 3-10 Tafel plot for anodic polarisation of aluminium; [NaCl] = 0.20 g/L; [clay] = 0.8 g/L; $E_{MIXED} = -560$ mV (SCE).

Figure 3-11 Tafel plot for cathodic polarisation of 316 stainless steel; [NaCl] = 0.20 g/L; [clay] = 0.8 g/L; $E_{MIXED} = -340$ mV (SCE).
Each Tafel plot demonstrated the influence of the diffusion processes at the electrode’s surface as the applied potential approached a constant value (Figure 3-10 and Figure 3-11). The limiting current density ($i_L$) was approached but not achieved in both the anode and cathode polarisation curves and hence was not reported. Determination of the limiting current density enables the appropriate equation (e.g. Equation E1-14) to determine the overpotential.

Table 3-6 Summary of experimental Tafel parameters

<table>
<thead>
<tr>
<th>Anodic experiments</th>
<th>Tafel parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment [clay] (g/L) [NaCl] (g/L)</td>
<td>(mV/decade)</td>
</tr>
<tr>
<td>A 1.6 0.20</td>
<td>350</td>
</tr>
<tr>
<td>B 1.6 0.20</td>
<td>333</td>
</tr>
<tr>
<td>C 1.6 0.20</td>
<td>456</td>
</tr>
<tr>
<td>D 0.8 0.20</td>
<td>415</td>
</tr>
<tr>
<td>E 0.12 0.20</td>
<td>125</td>
</tr>
<tr>
<td>F 0 0.20</td>
<td>353</td>
</tr>
<tr>
<td>G 0 0.20</td>
<td>390</td>
</tr>
<tr>
<td>H 0 0.20</td>
<td>1137</td>
</tr>
<tr>
<td>I 0 0.20</td>
<td>908</td>
</tr>
<tr>
<td>J 0 0.20</td>
<td>1007</td>
</tr>
<tr>
<td>K 0 0.20</td>
<td>108</td>
</tr>
<tr>
<td>L 0 0</td>
<td>452</td>
</tr>
<tr>
<td>M 0 0</td>
<td>266</td>
</tr>
<tr>
<td>N 0 0</td>
<td>713</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cathodic Experiments</th>
<th>Tafel parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>T 1.6 0.20</td>
<td>-542</td>
</tr>
<tr>
<td>U 1.6 0.20</td>
<td>-233</td>
</tr>
<tr>
<td>V 0.8 0.20</td>
<td>-403</td>
</tr>
<tr>
<td>W 0.12 0.20</td>
<td>-201</td>
</tr>
</tbody>
</table>

Electrode kinetics are influenced by a range of processes that interact with the electrode surface properties (such as adsorption or desorption) (refer to Section 1.2.2). The measured Tafel parameters were high (>400 mV/decade) and variable compared to typical Tafel parameters possessing values of around 118 mV/decade (Pletcher, 1991). The heterogenous nature of the clay pollutant results in a large number of possible impurities present. These impurities, albeit at very small concentrations, could adsorb onto the electrode surface, thereby altering the electrode kinetics. Alternatively, intermediate species, such as aluminium oligomers (see Section 4.1), could also adsorb onto the electrode surface. Adsorption may explain the high Tafel parameters obtained. To further investigate adsorption’s influence on the electrode surface, capacitance and cyclic voltammetry studies are recommended.
Extraction of the Tafel parameters is useful for the prediction of the system’s response to changing aqueous conditions and application of different electrodes. This methodology developed can be applied to assess the electrochemical response of the electrodes in electrocoagulation reactor designs and hence also the power and energy requirements.

3.6 Electrical power and energy requirements

Power and energy requirements of the electrocoagulation cell are dependent on the potential and current. The power was calculated with Equation 3-5, which for t hours of operation enabled energy to be deduced (Equation 3-6). Using the potential-current relationship for the polarisation experimentation results (Figure 3-9), the power requirement was calculated and is shown in Figure 3-12.

\[
\text{Power} = I \times E_{\text{CELL}} \ (\text{Watts}) \tag{E3-5}
\]

\[
\text{Energy} = \frac{I \times E_{\text{CELL}} \times t}{1000} \ (\text{kW.hr}) \tag{E3-6}
\]

Figure 3-12 Power required for electrocoagulation; \( A = 732 \ \text{cm}^2 \); \([\text{NaCl}] = 0.20 \ \text{g/L} \); \([\text{clay}] = 0.12 \ \text{g/L} \).
Clearly as the current density increased, the power requirements also increased (see Figure 3-12). For the bench scale electrocoagulation reactor, the power consumption was greater (up to a factor of 3), corresponding to the greater cell potentials. As current density increased, the diffusion processes at the electrodes became more important. This increased the overpotential required and consequently the power. Power determined electrical cost and increased likewise. So, the current density determined the rate limiting electrochemical process, which then determined power and hence electrical cost.

In the batch electrocoagulation reactor considered in this thesis, the shift in electrochemical mechanisms had a strong influence on the potential and hence also power required. In this case, it did not affect coagulant generation rates, determined primarily by current (density) and time. The reactor operating decisions, specifically the decision to operate galvanostatically, ensured constant current and hence also constant coagulant addition. This was an artefact of this particular system.

If reactors are operated potentiostatically, the electrode rate-limiting reactions will have a dramatic influence on reactor performance both aluminium dissolution and electrolytic gases generation rates. In this operation mode, experimental determination of diffusion-limited region and the limiting current density ($i_L$) will be critical to establish appropriate operating conditions. A similar approach, as outlined in this chapter, could be employed. Thus the generic approach outlined here could be used for specific electrocoagulation designs to determined operating parameters.

### 3.7 Thermodynamics - Potential – pH diagrams

The electrochemical cell measurements provided individual potential measurements for each electrode. These measurements enabled thermodynamic models, specifically Potential-pH diagrams, to be revisited (refer to Section 1.2.3.2). In this section, thermodynamic modelling was used to explore the behaviour of aluminium metal in an aqueous environment. The solution chemistry, that is the interaction of the hydrolysed aqueous species produced, specifically the aluminium cation and its derivatives, is explored in the following chapter (Section 4.1).
The intersection of the pH and potential ranges established the operable region for electrocoagulation. Pourbaix (1974) defined various regions in the potential-pH diagram as previously explained. For example the region where precipitate formed is defined as the passivation region. Thus Potential-pH diagrams are used here to examine the stability of aluminium in solution and their dissolution behaviour. In the case of electrocoagulation, aluminium dissolution was desirable hence this approach aided *a priori* prediction of aluminium’s behaviour.

### 3.7.1 Modelling approach

A thermodynamic aqueous modelling package (HSC) was used (Outokumpu, 1999). This analysis considered an aluminium-water system with mononuclear species and aluminium hydroxide precipitate. HSC was used to construct the $E_h – pH$ diagrams. Experimentally determined operable ranges were then plotted over the $E_h – pH$ diagrams to define regions of interest.

Electrocoagulation has an operable pH range of 6-9, with the pH stabilising to approximately 8.5. For each electrocoagulation reactor current density of interest, the anodic and cathodic potentials were known (from Section 3.4.2) and plotted over the $E_h – pH$ diagrams. Thus the operable region was defined on the $E_h$-$pH$ diagrams and the thermodynamic stable species identified.

### 3.7.2 Modelling results

Thermodynamic modelling is equilibrium based and cannot elucidate reaction kinetics. To encapsulate changes over an electrocoagulation run, three broad ranges were considered. The low (<4 mg-Al/L), medium (4-40 mg-Al/L) and high (>40 mg-Al/L) aluminium concentrations considered corresponded to the lag, reactive and stable stages and are presented as Figure 3-13 to Figure 3-15 inclusive. Additional Figures are presented in Appendix H.

For all cases, the cathodic potential is below the stability of water (diagonal blue dotted line staring from 0 V at 0 pH). That is, hydrogen evolution was thermodynamically favourable, that reflected electrocoagulation behaviour. In effect the cathode polarisation curves evaluated the hydrogen overpotential.
The anodic reaction defined the upper electrochemical boundary. At higher current densities, the anodic potential lay above the stability of water. Consequently, it was thermodynamically possible for oxygen gas to evolve. No bubbles were observed at the aluminium anode in the electrocoagulation reactor nor were any detected by Przhegorlinskii et al. (1987). Thus to gain a better understanding of and to establish thermodynamic conditions for oxygen evolution, dedicated experimentation of the oxygen overpotential is required. Regardless for this electrocoagulation application, the anodic polarisation curve’s shape was not consistent with the oxygen formation and is not further considered.

Each concentration range (low, medium and high) is discussed in more detail following.

**Low aluminium concentration - 1 mg-Al/L**

Figure 3-13 is the Eh – pH diagram for total aluminium of 1 mg-Al/L, which corresponded to the beginning of an electrocoagulation process. The anode and cathode potentials were plotted over the Eh-pH diagram to identify the operable region for the electrocoagulation reactor. If a range was calculated for the individual potentials, then two lines represented this range is shown on the figure.

At low concentrations (lag stage), for the electrocoagulation reaction no turbidity reduction or pollutant removal occurred (refer to Figures 2-17 and 2-18). During this lag stage, coagulant concentration and solution pH both increased. Coagulant concentration due to aluminium dissolution and solution pH increased as water was reduced to hydrogen and the hydroxide ion. Even at this early stage, aluminium hydroxide was thermodynamically stable as predicted by the Eh-pH diagram (Figure 3-13).
Medium aluminium concentration – 20 mg-Al/L

As the electrocoagulation reaction proceeded, aluminium concentration increased as mass removal rates and turbidity reduction increased. In the reactive stage, aluminium hydroxide became the dominant species present, implying that the electrode passivated. Experimental results proved otherwise, with the continued activation and hence dissolution of the aluminium electrode. Literature reports that the chloride ion reduces the formation of a passivation layer (Pourbaix, 1974), yet inclusion of chloride ion in the thermodynamic model (results not shown) did not alter the thermodynamic boundaries. Thermodynamic model predicts the final stable species at equilibrium but does not consider the reaction kinetics for electrode passivation. Consequently, over a long period of time the electrodes would be expected to passivate.
The operating pH of electrocoagulation stabilises at approximately pH 8.5. This corresponds to the interface between solid aluminium hydroxide and the aluminate ion (\(\text{Al(OH)}_4^-(\text{aq})\)) predicted in Figure 3-14. The close proximity of this interface to the electrocoagulation’s operating pH implies that the negatively charged aluminate ion may deteriorate the performance. The consequence of aqueous speciation and the charge (zeta potential) is further investigated in Chapter 4.

![Eh – pH diagram (SHE) for Aluminium – water system with mononuclear species and Al(OH)_3(s) considered; [Al] = 20 mg/L. Anode and cathode potentials for operating currents 0.341 mA/cm\(^2\) (orange), 1.36 mA/cm\(^2\) (green) and 2.74 mA/cm\(^2\) (red); [clay]=0 g/L. Electrocoagulation pH range (blue vertical).](C:\HSC4\Al31.iep)

**Figure 3-14 Eh – pH diagram (SHE) for Aluminium – water system with mononuclear species and Al(OH)_3(s) considered; [Al] = 20 mg/L. Anode and cathode potentials for operating currents 0.341 mA/cm\(^2\) (orange), 1.36 mA/cm\(^2\) (green) and 2.74 mA/cm\(^2\) (red); [clay]=0 g/L. Electrocoagulation pH range (blue vertical).**

**High aluminium concentration - 200 mg-Al/L**

At a high aluminium concentration (200 mg-Al/L), the aluminium hydroxide region was larger and again was the dominant region as shown in Figure 3-15. The operable region for electrocoagulation corresponded to aluminium hydroxide precipitation. Over this range considered, the aluminium hydroxide area increased with the total aluminium concentration.
Figure 3-15 Eh – pH diagram (SHE) for Aluminium – water system with mononuclear species and Al(OH)₃(s) considered; [Al] = 100 mg/L. Anode and cathode potentials for operating currents 0.341 mA/cm² (orange), 1.36 mA/cm² (green) and 2.74 mA/cm² (red); [clay]=0 g/L. Electrocoagulation pH range (blue vertical).

Indeed if aluminium oxide (Al₂O₃(s)) was included in the thermodynamic model (refer to Chapter 4) its precipitation also coincided with the electrocoagulation’s operable region. Thus thermodynamically an aluminium hydroxide/oxide precipitate was predicted. Yet thermodynamically modelling does not consider the reaction kinetics for precipitate formation. Kinetic issues and the interaction of aqueous species are considered in the following chapter.

3.8 Chapter conclusions

This chapter outlined a methodology to investigate the electrochemical behaviour of electrocoagulation reactors. Polarisation studies revealed the rate limiting processes at each electrode and its relationship to operating current density. Electrocoagulation in
this thesis operated in the charge transfer (Tafel region) at low current densities. As the current density increased, diffusion processes at the electrode increased the potential required for electrocoagulation. This increased both the anode and cathode overpotential requirements and consequently the cell potential.

During galvanostatic operation, as in the case of the batch electrocoagulation reactor considered in this thesis, the result was increased power and energy requirements. Potentiostatic operation would have a greater operational impact on electrocoagulation performance and would benefit from experimental analysis.

Electrochemical studies defined individual operating potential and thereby enabled their operable regions to be defined on an E\textsubscript{h} – pH diagram. This operable region corresponded to the aluminium hydroxide or aluminium oxide precipitate formation. This implied that precipitate formation was a prerequisite for electrocoagulation. This hypothesis is investigated in the proceeding chapter, which explores the solution chemistry and resultant coagulation mechanisms.
4 Coagulation

Coagulation is central to effective pollutant aggregation and removal. Chapter 1 (see Section 1.2.3) acknowledged coagulation’s importance in the study of electrocoagulation. Chapter 2 demonstrated that the coagulation mechanisms are presently ill defined. This chapter aims to decipher, as far as possible, electrocoagulation’s coagulation mechanisms.

The dominant coagulation mechanism(s) vary with a reactor’s operating conditions, pollutant type (and concentration) and coagulant concentration. The three electrocoagulation stages, each with distinctly different removal characteristics, imply shifting mechanisms over time. To elucidate these coagulation mechanisms, a clearer understanding of the particles and aggregates is required. Consequently, the first section (Section 4.1) investigates electrocoagulation’s solution chemistry and how it relates to coagulation performance. Section 4.2 characterises the pollutant particles and the resulting aggregates. The final section (Section 4.3) examines and compares electrocoagulation and chemical coagulation (alum dosing).

4.1 Solution chemistry

Solution chemistry links coagulant production (electrochemistry) and pollutant aggregation (coagulation). Thermodynamic modelling of the solution chemistry is employed here to explore the behaviour and interaction of the coagulant and its hydrolysed metal cations with the pollutant. Chapter 2 identified an apparent contradiction in the solution chemistry behaviour of the electrocoagulation reactor. That is, electrocoagulation’s inherent dynamic nature due to the continual addition of the coagulant from the anode implied continual shifting concentration levels. In contrast, the measured pH was stable indicating constant aqueous speciation implying the system had attained equilibrium. Thus the experimental results imply stable speciation but knowledge of the system’s nature implies otherwise. Consequently, this section explores the relationship of the solution chemistry to the electrocoagulation process.

The Nernst equation (Equation E1-8) related the thermodynamic properties, specifically the Gibbs free energy, to the species’ activity, as discussed in Section 1.2.3. Both electrocoagulation and chemical coagulation were very dilute, with total aluminium
concentration less 0.05 mol/L. Hence interactions between ions were negligible and the systems were assumed to be ideal. Thus, all activity coefficients were assumed to be unity. This simplified the Nernst equation to Equation E4-1 where $K$ was the equilibrium constant and $\Delta G^0_R$ was the reaction’s standard Gibbs free energy of formation. Thus, the species equilibrium concentration could be determined simply from the temperature and the Gibbs free energy.

$$\ln K = \frac{\Delta G^0_R}{RT} \quad \text{(E4-1)}$$

In Chapter 3, only mononuclear species were considered because the focus was on the electrode and its immediate proximity. Speciation equations for mononuclear ions were presented as Equations E1-16 to E1-19 in Section 1.2.3. Mononuclear species adequately describe the system encountered at the electrode and its dissolution characteristics. The focus of this section is the aqueous chemistry of the bulk solution. The cation diffuses from the electrode surface to the bulk solution with possible polynuclear formation. As the systems ages more complex polynuclear aqueous species form (see Equation E4-20). Hence the progression of mononuclear to polynuclear aqueous species is important and both mononuclear and polynuclear aqueous species are considered in this section.

### 4.1.1 Modelling methodology

Again, the HSC thermodynamic aqueous modelling package was used that quickly and easily calculates thermodynamic equilibrium (Outokumpu, 1999). HSC draws on extensive thermodynamic data to calculate the equilibrium composition of aqueous species. It has the ability for additional customised species and their thermodynamic data to be added to the core database. Thus a specialised database was constructed with specialised aluminium species to investigate electrocoagulation.

Mononuclear and polynuclear aqua-aluminium ions have been reported in the literature (Bertsch and Parker, 1996). Table 4-1 lists the aluminium based species considered. Detailed thermodynamic data are presented in Appendix I.
Table 4-1 Summary of species used in modelling

<table>
<thead>
<tr>
<th>Group</th>
<th>Species considered&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H(+a), OH(-a), H2O(l)</td>
</tr>
<tr>
<td>Monomeric aluminium</td>
<td>Al(+3a), AlOH(+2a), Al(OH)2(+a), Al(OH)3(a), Al(OH)4(-a)</td>
</tr>
<tr>
<td>dimeric aluminium species</td>
<td>Al2(OH)2(+4a)</td>
</tr>
<tr>
<td>Trimeric aluminium specie</td>
<td>Al3(OH)4(+5a)</td>
</tr>
<tr>
<td>Al 13 specie</td>
<td>Al13O4(OH)24(+7a)</td>
</tr>
<tr>
<td>Aluminium hydroxide</td>
<td>Al(OH)3</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>Al2O3</td>
</tr>
<tr>
<td>Sulphate species</td>
<td>SO4(-2a), HSO4(-a)</td>
</tr>
<tr>
<td>Carbonate species</td>
<td>CO2(g), CO2(a), CO3(-2a), HCO3(-a), H2CO3(a)</td>
</tr>
</tbody>
</table>

Thermodynamics modelling predicts the thermodynamically stable state (minimised Gibbs free energy) and hence the final equilibrium composition. It provides no indication of the path or the rate to attain this equilibrium. For electrocoagulation, concentration gradients are continually shifting as aluminium continues to dissolve and release aluminium into solution. Therefore the sole use of thermodynamic modelling to describe the solution chemistry of electrocoagulation is insufficient.

A modelling approach was developed to account for the reaction kinetics. The modelling approach incorporated the thermodynamics and reaction kinetic phenomena into the model in two methods; firstly, by the species selection and secondly, by the stepwise addition of coagulant. This produced a series of pseudo steady-state equilibrium models that investigated electrocoagulation’s solution chemistry. Each method is discussed in more detail following.

<sup>5</sup> *Note on nomenclature:*

Phase of each specie was identified by either g (gas), l (liquid), a (aqueous) in the brackets proceeding its molecular formula with the charge identified by number and sign. No identification indicated solid species. E.g. Al3(OH)4(+5a) was the tri-meric aluminium ion, while Al(OH)3 was the solid aluminium hydroxide.
Firstly, the species included in the model determined its relevance and applicability to electrocoagulation. Inclusion of such species and kinetics estimates from literature are presented in Table 4-2. This kinetic information provided a structure for different solution chemistry models. Aluminium hydrolysis occurred rapidly to form all monomeric species and possible aluminium hydroxide formation hence all these species were included in all models (refer to Table 4-1). This provided the base case for all models (Case 1).

Aluminium-water speciation changed as the solution aged, with typically larger species formed at slower rates (Bertsch and Parker, 1996). Additional aluminium species were then cumulatively and progressively added to the model to replicate the dynamic kinetic changes. To account for slow formation kinetics, a series of “scenarios” were considered by the inclusion of various species. Initially, electrocoagulation was modelled with only mononuclear species, then with oligomers (polynuclear species included), and finally with the inclusion of aluminium oxide.

Additionally, oligomers formed in conditions were formed in experimental conditions similar to those experienced in electrocoagulation. Previous alum dosing experiments, where addition of a base such as sodium hydroxide was added to aluminium ions, reported formation of oligomers. In particular, the Al\textsubscript{13} complex was detected in systems (Bertsch and Parker, 1996). In electrocoagulation, the hydroxyl ion was continually added at the cathode as water was reduced. It would seem reasonable to infer that oligomers also form during electrocoagulation. Thus the nature of electrocoagulation inferred the likely formation of polynuclear species.

Secondly, electrocoagulation’s dynamic nature was approximately modelled by the stepwise addition of coagulant. Stepwise addition of Al\textsuperscript{3+}(aq) and OH\textsuperscript{−}(aq) in the stoichiometric ratio 1:3, replicated (in some measure) the electrochemical processes. This replicated the \textit{in situ} dissolution of the sacrificial aluminium anode and reduction of water to the hydroxide ion. At each such addition of Al\textsuperscript{3+}(aq) and OH\textsuperscript{−}(aq), HSC calculated the equilibrium concentrations, thereby producing a pseudo steady-state profile to replicate electrocoagulation’s dynamic concentration profile on an equivalent aluminium basis (analogous to the results presented in Section 2.3.3 Chapter 2).
Overall, a cumulative set of case studies was modelled to evaluate the solution chemistry of electrocoagulation as presented in Table 4-2.

**Table 4-2 Species included in electrocoagulation thermodynamic model**

<table>
<thead>
<tr>
<th>Case</th>
<th>Species included</th>
<th>Reaction kinetics</th>
<th>Comments</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mononuclear aluminium species and Al(OH)$_3$(s)</td>
<td>Very fast – rate constant 4.4x10$^9$ (Holmes et al., 1968) and 1.1x10$^5$ s$^{-1}$ (Fong and Grunwald, 1969) for Equation E1-16.</td>
<td>Base case – Al$^{3+}$ rapidly hydrolyses</td>
<td>Figure 4-1</td>
</tr>
<tr>
<td>2</td>
<td>+ one oligomer specie (trimer)</td>
<td>Variable – rapid to months (Bertsch and Parker, 1996)</td>
<td>Oligomers – expected to form in system with continual base addition.</td>
<td>Figure 4-2</td>
</tr>
<tr>
<td></td>
<td>+ all oligomer species (dimer and trimer) Al$_{13}$ complex</td>
<td>As above</td>
<td>Inclusion of dimer and Al$_{13}$ complex does not alter equilibrium model</td>
<td>Results not shown</td>
</tr>
<tr>
<td>3</td>
<td>+ Al$_2$O$_3$(s)</td>
<td>Slow – months to years (Bertsch and Parker, 1996)</td>
<td>Very slow formation – not likely in electrocoagulation</td>
<td>Figure 4-3</td>
</tr>
</tbody>
</table>

Finally, the systems were extended to include carbon dioxide and sodium chloride to evaluate their impact. Carbon dioxide is present in the atmosphere and dissolved in water to form carboxylic acid, decreasing the pH as show in Equations E4-2 to E4-4.

\[
CO_2(g) \leftrightarrow CO_2^0(aq) \tag{E4-2}
\]

\[
CO_2^0(aq) + H_2O \leftrightarrow HCO_3^-(aq) + H^+(aq) \tag{E4-3}
\]
Chapter 4 - Coagulation

\[ HCO_3^{(aq)} + H_2O \leftrightarrow H_2CO_3^{(aq)} + H^+(aq) \]  
(E4-4)

4.1.2 Results and Discussion

To validate the thermodynamic modelling approach, the pH of alum dosing experiments (from Section 4.3.2) were compared to calculated values from HSC (see Table 4-3). A high correlation is observed between the experimentally measured and the calculated values indicating that the latter was quite accurate for such systems.

Table 4-3 Comparison of measured pH with calculated pH (using HSC) at increasing alum concentrations

<table>
<thead>
<tr>
<th>Alum Dose (mg/L)</th>
<th>Measured pH</th>
<th>Calculated pH (HSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.4</td>
<td>4.22</td>
</tr>
<tr>
<td>10</td>
<td>4.2</td>
<td>4.05</td>
</tr>
<tr>
<td>20</td>
<td>4.1</td>
<td>3.92</td>
</tr>
<tr>
<td>200</td>
<td>3.6</td>
<td>3.60</td>
</tr>
</tbody>
</table>

For both electrocoagulation and chemical dosing systems, including sodium chloride in the HSC model did not alter equilibrium concentrations, and hence the impact of these ions was not reported.

Electrocoagulation Case 1

Aluminium hydroxide was precipitated and was the dominant species formed (see Figure 4-1). All species’ concentrations level out as the aluminium hydroxide added increased. The pH stabilised to a slightly acidic pH (6.6), which was lower than experimentally observed (~8.5) (see Figures 2-7 and 2-14).


Electrocoagulation Case 2

Inclusion of the aluminium trimeric species \( \text{Al}_3(\text{OH})_4^{+5} \) had a significant impact. The dominant species were the aluminate ion \( \text{Al(OH)}_4^{-} \) and trimer \( \text{Al}_3(\text{OH})_4^{+5} \) ions. Inclusion of this trimer \( \text{Al}_3(\text{OH})_4^{+5} \) increased pH to 10.6, compared to measured pH ~8.5.

Note that no solid aluminium hydroxide precipitation was predicted. Furthermore, the inclusion of the dimer \( \text{Al}_2(\text{OH})_2^{+4} \) and the \( \text{Al}_{13} \) complex were calculated to have negligible impact to the system (results not shown).
Figure 4-2 Speciation model for monomeric and trimeric aluminium, aluminium hydroxide, and water only.

Electrocoagulation Case 3

Figure 4-3 Speciation model of monomeric, di-meric, tri-meric, Al13 aluminium – water species and aluminium oxide.
The model was again extended to include all aluminium species and aluminium oxide. Again, the model predicted a higher pH of 10.6 than experimentally observed pH. This scenario predicted precipitation of aluminium hydroxide and oxide at an equivalent aluminium dosage of 33 mg/L corresponding to 40 minutes of operation (at 1 A). This occurred in the stable phase. Precipitation corresponded to the point where aluminium levels (without pollutant present) (see Figure 4-11) and residual turbidity levels (see Figure 4-8) stabilised, both discussed in more detail in Section 4.2.

**Impact of CO₂ on modelling**

Carbon dioxide varies from 0.3% to 0.4% in the atmosphere. The calculated pH of pure water is 5.32 for 0.3% CO₂ in the atmosphere, decreasing to 5.26 as the CO₂ increases to 0.4%. Carbon dioxide’s inclusion in the electrocoagulation system is shown in Figure 4-4. Inclusion of carbon dioxide had a minimal impact on this system, although there was some evidence of an increased lag before the system stabilised. This corresponded to the time lag observed in Figure 4 for turbidity reduction.

![Figure 4-4 Speciation model for monomeric, di-meric, tri-meric, Al₁₃ aluminium, water, aluminium hydroxide, aluminium oxide and the inclusion of carbon dioxide and carbonate species.](image-url)

**Note:** key order reflects species concentration order.
The increasingly comprehensive thermodynamic models described here constructed a stepwise insight to the kinetics and dynamic behaviour of the batch electrocoagulation reactors. The nature of the species included in the model, particularly the solids and oligomers, strongly influences concentration profiles. The inclusion of the solids, specifically aluminium oxide and hydroxide, resulted in predicted precipitate formation at levels comparable to those observed experimentally. Exclusion of the trimeric specie resulted in a calculated pH of 6.6, and inclusion increased pH to 10.6. This provided a lower and upper prediction for the operational pH range of the electrocoagulation reactor. Speciation kinetics determined the trimeric species formation rate and hence overall pH. The measured pH of the electrocoagulation reactor is in the middle of this range at ~8.5. Thus suggesting partial production of this positively charged ion, with the speciation kinetics required to further refine the insights gained from the thermodynamic model.

### 4.1.3 Section summary

Electrocoagulation’s inherent dynamic nature was investigated from a solution chemistry perspective. To account for kinetics, a series of increasingly comprehensive models were constructed. The system’s character, particularly the addition of base (hydroxyl ions via water’s reduction at the cathode) to the aluminium infers formation of oligomers. These oligomers, specifically the trimeric aluminium specie \((\text{Al}_3(\text{OH})_4^{+5(aq)})\), were critical to span electrocoagulations operable pH region.

Co-precipitation of aluminium oxide and hydroxide occurs only with inclusion of the oxide. Its formation occurs in the stable stage and corresponds to turbidity, pH and aluminium stabilisation. The lag time increased with carbon dioxide inclusion in the model but neither it nor sodium chloride had a significant impact on solution chemistry modelling outputs.

The solution chemistry modelling provided a detailed insight of the hydrolysis processes after aluminium generation. The next stage in electrocoagulation is aggregation and hence the proceeding section focuses on particle and aggregate characterisation.
4.2 Particle and aggregate characterisation

In electrocoagulation, particles are expected to agglomerate and aggregate. The fastest pollutant removal occurred during the reactive stage, regardless of pollutant loading, as was identified from macroscopic experiments in Chapter 2. In order for effective aggregation, particles must bond and hence their interactions are important. Literature on particle – particle interactions is abundant with a variety of aggregation mechanisms discussed in detail. To differentiate between aggregation mechanisms, the particles’ behaviour must first be characterised. Thus, this section aims to characterise the pollutant particles and their aggregates.

4.2.1 Experimental Methods

Initially, light microscopy was used to provide images of clay particles and aggregates. A comparative basis on which to assess aggregation was required. Consequently, electrocoagulation experiments were conducted both with and without pollutant present. The procedure was the same as described in Section 2.2. The electrocoagulation experiments were conducted with initial clay pollutant loading 0.8 g/L and 0 g/L, in 6 L of de-ionised water, with 0.20 g/L sodium chloride to enhance conductivity. The experiments with no pollutant present provided a basis. Samples were extracted at regular intervals to measure turbidity, particle size, and aluminium concentration.

Other methods employed in this section include particle sizing and turbidity measurements, as previously described in Chapter 2.

4.2.1.1 Aluminium analysis

Aluminium concentration was measured using a Varian Atomic Absorption Spectrophotometer.

4.2.1.2 Light microscopy

Photomicrography was used to magnify and photograph clay particles and aggregates. A Nikon E800 light microscope with an attached 12 bit cooled charged-coupled device (CCD) digital colour camera (Sensicam) was used.

The electrocoagulation reactor was operated at 1 A for 1 hour. Clay concentration was 0.8 g/L and sodium chloride concentration was 0.5 g/L. There was no turbidity drop.
during the lag stage, and the majority of particles were removed by the beginning of the stable stage as reflected by the stable turbidity (refer to Figure 2-7 in Section 2.3.2). Hence, the image analysis experiments focused on primary clay particles and aggregates formed in the reactive phase. Samples were taken before reaction commenced (i.e. at 0 mins) and then every two minutes throughout the reactive stage (i.e. for the 10 – 20 min time period).

From each sample, a pipette was used to extract solution (containing particles and aggregates) onto a glass slide and a cover slip was placed on top. The light microscope was focused using objective lens of 4X, 10X and 20X, recording images at each magnification. The particles’ length and width were measured using the software package Adobe Photoshop with the pixel length defined in Table 4-4.

<table>
<thead>
<tr>
<th>Objective Lens</th>
<th>µm/pixel</th>
</tr>
</thead>
<tbody>
<tr>
<td>4X</td>
<td>1.61</td>
</tr>
<tr>
<td>10X</td>
<td>0.62</td>
</tr>
<tr>
<td>20X</td>
<td>0.33</td>
</tr>
</tbody>
</table>

### 4.2.2 Experimental Results

#### 4.2.2.1 Light microscopy results

A typical magnified photograph of the clay pollutant is shown in Figure 4-5. The clay’s heterogeneous nature was apparent and this image reinforced the pollutant’s diverse particle size and shape characterised in Chapter 2. The numerous dots in the background are the smaller pollutant particles (pollutant majority) and were difficult to observe at this magnification. Overall the particles were disparate implying a stable pollutant with colloidal behaviour at lower particle sizes.
Figure 4-5 Microscopic image of clay particles prior to electrocoagulation (10X).

The aggregates formed after 12 minutes of electrocoagulation operation at 1.0 A are shown in Figure 4-6. Clearly, coagulant addition aggregated the clay particles to form larger clusters. The primary clay particles can be seen bonded together forming larger aggregates. In fact, individual particles that constitute the aggregate can be readily seen. The aggregates formed possessed an irregular shape and varied in size. Generally, the aggregates formed were elongated with “irregular branching”.

The microscopic images examined 3-dimensional aggregate structures on a 2-dimensional focal plane. Approximated aggregate dimensions are also shown on Figure 4-6. Measurements along the x-axis (referred to as width) and along the y-axis (referred to as length) enabled an aspect ratio to be calculated (Equation E4-5). For each image, an average shape factor and length was calculated with results shown in Figure 4-7.

\[
\text{Aspect ratio} = \frac{\text{length (μm)}}{\text{width (μm)}}
\]  

(E4-5)
Using this basic particle characterisation method, the aggregates increased in length over time (see Figure 4-7). Increased reaction time resulted in increased coagulant addition. The greater amount of coagulant (and its hydrolysed species) resulted in a greater number of reactive and binding sites in solution. This thereby enables more pollutant particles to bind, hence forming aggregates. These aggregates can then in turn bind with one another to form larger aggregates. Aggregation mechanisms are further explored throughout this chapter.

The aggregates formed in the reactive stage are approximately twice as long as wide and increased in length over time. Larger aggregates would be expected to settle more readily, assuming shape and structure do not alter the aggregates’ drag coefficient significantly. Alternatively, the aggregates’ irregular shape and larger size (relative to primary clay particle) increased the probability of interaction with rising bubbles and thus removal by flotation. Hence aggregation resulted in pollutant removal by either
sedimentation or flotation, as observed by the turbidity reduction and mass removal in Figures 2-12 and 2-13 in Chapter 2.

![Graph](image)

**Figure 4-7** Average particle length and shape factors; I = 1.0 A; [clay] = 0.8 g/L; [NaCl] = 0.5 g/L.

The photomicrography image analysis qualitatively and semi-quantitatively evaluates aggregate formation. Yet it provides little information on aggregation or coagulation mechanism. Further experimentation was completed to investigate and characterise aggregation and is reported in the following section.

### 4.2.2.2 Turbidity results

Residual turbidity levels were examined by operating the electrocoagulation reactor both with and without clay present. The normalised turbidity results for initial clay loading of 0.8 g/L and without clay present are shown in Figure 4-8. The pH values for both cases were recorded and are shown in Figure 4-9. A slower response was observed without any clay present but both runs converged during the stable stage to a pH of approximately 8.5 indicating similar solution conditions.
Figure 4-8 Normalised turbidity for pollutant and no pollutant; [clay] = 0, 0.8 g/L; I = 1.0 A; [NaCl] = 0.20 g/L.

The most interesting point to note was the increase (during the reactive stage) in turbidity level over time when no clay was present. In this case, the only solution changes were due to the dissolution of the aluminium anode and the cathodic reduction of water. So this turbidity increase is best explained by the production of a solid precipitate, as predicted by thermodynamic modelling (see Section 4.1). During the stabilising stage, turbidity and pH levels in the two cases converged. This suggested that the residual turbidity observed in electrocoagulation runs with clay was due to the electrocoagulation process itself and not the clay. That is, the turbidity rise in the “no pollutant” case represented the establishment of a steady-state between the production and flotation of hydrolysed aluminium hydroxide flocs.

With clay present, these particles appear to act as nucleation sites for aggregate formation. Without clay present, a gelatinous aluminium poly-hydroxide was formed.
and is discussed in more detail in Section 4.3. Thus, the pollutant’s presence alters the coagulant’s behaviour.

4.2.2.3 Particle size measurements

As just noted, the electrocoagulation reactor was operated for comparison purposes with clay loading of 0.8 g/L and then without clay. On both occasions, samples were taken at regular time intervals and the particle sizes were measured using the Malvern Mastersizer S. The clay particles had a medium diameter ($d_{50}$) of 5 µm (at 0 minutes) in this analysis. Note that this was higher than recorded in Figure 2-5 in Section 2.2.1.1, which only considered the particle fraction less than 53 µm. Consequently, a smaller diameter of 2.5 µm was reported. Here, the larger medium diameter was indicative of the entire pollutant’s size distribution.
Here, the particles generally increase in size as time and hence aggregate as coagulant concentration increases. This occurs until 40 minutes, where the aggregates’ size stabilises at 25-30 µm. At this point in the reaction (stable stage), turbidity reduction stabilised (Figure 4-8) and the bulk of the pollutant has already been removed either by flotation or sedimentation (Table 2-6 in Section 2.3.2).

Without clay present, the Malvern particle sizer did not detect any particles in the first 10 minutes. Insufficient particles were detected with the sizer reporting an extremely low obscuration reading (<1%). This period corresponded to the lag stage. During the reactive stage (10 to 30 mins), the aggregates were generally larger (by 10µm) than corresponding aggregates with clay present. At the corresponding aluminium concentration, thermodynamics predicted aluminium precipitation (refer to solubility
diagram in Section 1.2.3.1 and Section 4.1). This size increase might then be attributed to the formation of aluminium hydroxide or oxide. At 40 minutes, their size decreased to 25-30 µm. At this point, turbidity and mass removed has stabilised (Figure 4-8 and also Figure 2-13 in Section 2.3.2.5). Also at this time, turbidity reduction, mass removal and particle size had stabilised when clay was initially present.

Convergence of particle size analysis results supported the assertion that the residual turbidity observed was due to the establishment of a steady-state between the production and flotation of hydrolysed aluminium hydroxide flocs. This assertion was further explored by measurements of total aluminium both in solution and as a precipitate, with and without clay.

**4.2.2.4 Aluminium analysis results**

![Graph showing Aluminium concentration over time](figure)

Figure 4-11 Total Aluminium concentration; [clay] = 0.8, 0 g/L; [NaCl] = 0.20 g/L; I = 1.0 A.
Aluminium analyses are shown in Figure 4-11. Faraday’s Law provided a theoretical amount for the total amount of aluminium put into solution.

The total bulk solution aluminium concentrations for runs with and without clay are shown in Figure 4-11. They all consistently remained below the level predicted by Faraday’s law. When clay was present, the total aluminium concentration was consistently below 5 mg/L. Thus the bulk of the coagulant must be bound to the clay pollutant and hence removed with the pollutant. This observation indicated a binding interaction exists between the coagulant and the pollutant, supporting a sorption style mechanism.

Without clay, the total aluminium concentration increased to 30 mg/L before levelling out. Presumably this occurred when the rates of formation and removal of the hydrolysed aluminium precipitate converge. The clay provided binding sites and was removed with the coagulant, yet when no clay is present, and hence there was an absence of binding sites, the added aluminium formed a colloidal suspension of microcrystalline aluminium hydroxide and oxide flocs (Letterman et al., 1999). This contributed to a residual turbidity level, observed during the stable phase, and the difference in measured aluminium concentration (as seen in Figure 4-11). Absence of binding sites, that is, the clay pollutant, resulted in electrocoagulation’s quite different behaviour. Thus the convergence of turbidity levels for the two scenarios considered (with and without clay) was somewhat coincidental with the aluminium and clay properties dictating the residual turbidity levels in the two cases.

Particle characterisation techniques were used to describe the system and detail its dynamic response. Aggregates were formed as coagulant was added, that is, as the aluminium electrode corroded. During the stable stage, aluminium hydroxide and oxide was formed contributing to a residual turbidity. Thus, the system was quite well characterised, but the aggregation mechanism was still not determined. Fractal dimensional analysis was employed next to assess the aggregates structure and hopefully infer their aggregation mechanism.
4.2.3 Fractal dimensional analysis

Aggregation and flocculation transformed the pollutant into a different form. Fractal aggregates can be formed from various aggregation mechanisms including; depletion, bridging, diffusion or reaction limited aggregation mechanisms (Bushell et al., 2002; Tang and Raper, 2002; Gregory, 1997).

Depletion flocculation occurs at high ionic concentration due to compression of the electrical double layer. A high ionic concentration was not present in electrocoagulation and hence depletion flocculation was not considered.

Bridging flocculation usually occurs with addition of a high molecular weight polymer. No polymer was present in the electrocoagulation system and hence bridging flocculation was not possible here.

Electrocoagulation adds the coagulant directly into the solution as a metal cation and hence could be considered similar to a salt induced aggregation mechanism. The nature of electrocoagulation limits the aggregation mechanisms to diffusion or reaction limited aggregation. Thus for electrocoagulation only diffusion or reaction limited aggregation were possible and consequently considered in this analysis.

Both loosely bound and tightly bound aggregates were possible. If fractal, these structures correspond to different aggregation mechanisms. Fractal dimensional analysis can differentiate between loosely bound and tightly bound aggregates and this can infer an aggregation mechanism.

4.2.3.1 Fractal theory

Fractals are defined as disordered systems with a non-integral dimension (Tang and Raper, 2002). It is a measure of how an object occupies and is distributed in space. The criterion for an aggregate to be fractal is that it obeys a power-law relationship, which relates the fractal (or cluster) mass, \( m(R) \), to its radius (R) and mass fractal dimension (\( D_f \)). The resulting fractal dimension provides an indication of the aggregate’s structure. The fractal dimension varies from 1 (a straight line) to 3 (a solid spherical structure).
If the relationship holds over a wide range, the aggregates are referred to as self-similar if they have the same structure, independent of magnification (Gregory, 1997). Commonly the fractal dimension is used to characterise the aggregates’ mass density, $\rho(R)$.

$$\rho(R) \propto R^{(D_F - 3)}$$  (E4-7)

where again $1 < D_F < 3$

Therefore, the fractal dimension provides a useful way of describing an aggregate relating its packing arrangement and structure.

Defining the aggregate’s structure often enables the aggregation mechanism to be deduced. Considering a collision between two clusters, (i.e. cluster-cluster aggregation) a loosely or tightly bound aggregate could be formed, which in turn infers diffusion- or reaction-limited aggregation mechanisms.

Diffusion-limited aggregation implies there is no repulsion between colliding particles and that each collision leads to attachment. Here, the clusters collide and bond on contact resulting in a loosely bound structure. A low fractal dimension is indicative of a loosely bound structure. Thus, a low $D_F (<1.8)$ indicates an open configuration formed by diffusion-limited cluster-cluster aggregation (DLCA) (Gregory, 1997).

Reaction-limited aggregation implies there is reduced collision efficiency due to inter-particle repulsion as indicated by the aggregates zeta potential (discussed in the proceeding Section 4.3.3). Increased numbers of collisions are required before clusters bond generally resulting in tightly bound aggregates. A higher $D_F$ indicates a more tightly bound structure. Hence, a high fractal dimension ($D_F >2.1$) indicates compact aggregates that are the results of reaction-limited cluster-cluster aggregation (RLCA) (Gregory, 1997).
Consequently, to characterise the aggregation mechanism in electrocoagulation, the fractal dimension was measured using small-angle light scattering (Amal et al., 1990). Fractal calculations are in Appendix J.

### 4.2.3.2 Fractal results

![Graph showing fractal dimension over time](image)

Figure 4-12 Fractal dimension for aggregates produced by electrocoagulation; $I = 1.0$ A; $[\text{clay}] = 0$, 0.8 g/L; $[\text{NaCl}] = 0.20$ g/L.

The fractal dimension ($D_F$) for aggregates produced from electrocoagulation are presented in Figure 4-12. With no clay present, the $D_F$ was generally higher (in the range 2.6 – 2.4) over the course of the reaction period indicating a dense aggregate structure. With clay present (at 0.8 g/L), the fractal dimension ($D_F$) was approximately 1.9 during the lag and reactive stages (the first 30 minutes). This indicated that loosely bound aggregates present and hence diffusion-limited cluster-cluster mechanism
(DLCA) where the clay pollutant particles acted as nucleation sites resulting in high collision efficiency.

With clay present, the $D_F$ increased after 30 minutes to reach approximately 2.4 at 50 minutes - implying the aggregates became more tightly packed. At this time, however, the majority of the pollutant had been removed (52% - refer to Figure 2-13). Aggregates detected would primarily be precipitated aluminium hydroxide as the pollutant is no longer in suspension. That is, the aggregates observed were similar to those produced without clay present.

The fractal dimension also indicated the more appropriate flocculation model to use. The Smoluchowski equation (Equation E4-8) has formed the basis of flocculation modelling (Thomas et al., 1999):

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta(i,j)c_i c_j - \sum_{i=1}^{\infty} \beta(i,k)c_i c_k$$

(E4-8)

where $\beta(i,j)$ is the collision frequency between particles of size i and j (similarly $\beta(i,j)$ is the collision frequency between particles of size i and k) with $c_i$, $c_j$ and $c_k$ the concentration of particles of size i, j and k, respectively.

The overall equation defines the rate of change in the number concentration of particles of size k. Generally the rate successful collision can be mathematically described between particles of size i and j (Thomas et al., 1999):

$$r_{floculation} = \alpha \times \beta(i,j) \times c_i \times c_j$$

(E4-9)

where $\alpha$ is the collision efficiency, $\beta(i,j)$ is the collision frequency between particles of size i and j with $c_i$ and $c_j$ are the concentration of particles of size i and j, respectively. The collision frequency ($\beta$) is a function of the mode of flocculation i.e. perikinetic, orthokinetic or differential sedimentation. The collision efficiency ($\alpha$, where $0<\alpha<1$) is a function of the degree of the particle destabilisation. Thus $\beta$ is a measure of the
transport efficiency leading to collisions while $\alpha$ represents the percentage of those collisions leading to attachments (Thomas et al., 1999).

A rectilinear approach assumes flocculation is not influenced by the bulk fluid properties and particles move in a linear path after collision (Lee et al., 2000). A curvilinear approach assumes that as the particles collide, fluid is “squeezed” out between them causing the particles to rotate relative to one another. Thus, particles move in a curved path after collision (Thomas et al., 1999). The latter authors noted that it has been generally observed that systems with higher collision efficiency tend to form flocs with a lower fractal dimension. Thus, considering these electrocoagulation results, it would seem that a rectilinear approach is more appropriate.

### 4.2.4 Section summary

This section photographed both primary clay particles and the aggregates formed during electrocoagulation. Generally, the aggregates increased in size over time remaining longer than wider. The coagulant was actively consumed in the presence of the pollutant contributing to aggregate formation. Without pollutant present, aluminium addition generally followed Faraday’s Law, until a stable stage was attained where a precipitate was formed that contributed to the residual turbidity.

Shifting aggregation mechanisms, that is, from diffusion-limited in the reactive stage to reaction-limited in the stable stage were quantified using fractal dimensional analysis. This inferred that a rectilinear approach appropriately described particles behaviour during electrocoagulation although it could be fair to say that a detailed coagulation mechanism is still elusive.

### 4.3 Electrocoagulation and chemical dosing

Donini et al. (1994) and Musquere et al. (1983) claim, while providing no evidence, that coagulation mechanisms in electrocoagulation are similar to those in chemical coagulation. Thus there is a perception that electrocoagulation is simply chemical dosing by another name, with the only difference being the way in which the coagulant is delivered. The objective in this section is to quantitatively compare chemical dosing and electrocoagulation to determine the dominant coagulation mechanisms. The two approaches were evaluated by monitoring key solution characteristics (such as
coagulant level, pH and zeta potential) in a series of chemical dosing jar tests and electrocoagulation runs.

### 4.3.1 Experimental Method

Chemical coagulation was evaluated using an adaptation of the standard jar testing technique (Riddick, 1964), with AR grade (99.8% pure) aluminium sulphate as the chemical coagulant. Sodium hydroxide and hydrochloric acid solutions were added for any subsequent pH adjustment. Clay was used as the pollutant.

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Conditions</th>
<th>pH</th>
<th>Parameter</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical dosing</td>
<td>[alum] = 0 – 200 mg/L</td>
<td>Not controlled</td>
<td>Turbidity</td>
<td>Figure 4-13</td>
</tr>
<tr>
<td>2</td>
<td>Chemical dosing</td>
<td>[alum] = 0, 2, 4 mg/L</td>
<td>Controlled</td>
<td>Zeta potential</td>
<td>Figure 4-14</td>
</tr>
<tr>
<td>3</td>
<td>Chemical dosing</td>
<td>[alum] = 10, 20 mg/L</td>
<td>Controlled</td>
<td>Zeta potential</td>
<td>Figure 4-15</td>
</tr>
<tr>
<td>4</td>
<td>Electrocoagulation</td>
<td>I = 0.5 A</td>
<td>Not controlled</td>
<td>Zeta potential and turbidity</td>
<td>Figure 4-16</td>
</tr>
<tr>
<td>5</td>
<td>Chemical dosing</td>
<td>[alum] = 4 mg/L</td>
<td>Controlled</td>
<td>Turbidity</td>
<td>Figure 4-17</td>
</tr>
<tr>
<td>6</td>
<td>Chemical dosing</td>
<td>[alum] = 20 mg/L</td>
<td>Controlled</td>
<td>Turbidity</td>
<td>Figure 4-18</td>
</tr>
</tbody>
</table>

A concentrated aluminium sulphate solution (1 mg-Al/mL) was added to a clay mixture (at 0.8 g/L) and the mixture was rapidly mixed (at more than 140 RPM) for a period of 30 seconds to ensure adequate contact between coagulant and pollutant. The solution was then left to settle (Bratby, 1980). No further mixing occurred. In the runs carried out, the initial clay concentration was always 0.8 g/L, while aluminium sulphate and pH were varied. Once rapid mixing had ceased (this being defined as time zero), samples were taken at 0, 1, 3, 5, 10, 15, 20, 25, 30, 45 and 60 minutes. Zeta potential was
measured off-line using a Malvern Zetasizer. All experiments were conducted at ambient temperature (nominally 20 °C).

Electrocoagulation experiments were carried out as detailed in Section 2.2.2. The current was held constant for each run. Current was investigated over the range 0.25 to 2.0 A (0.34 to 2.74 mA/cm²). Again, turbidity and zeta potential were measured off-line using a Merck Turbiquant 1500T (tungsten lamp) and Malvern Zetasizer.

All electrocoagulation experiments were conducted with an initial clay pollutant loading of 0.8 g/L, in 6 L of de-ionised water, with 0.20 g/L sodium chloride added to enhance conductivity. All experiments are summarised in Table 4-5.

4.3.2 Results and Discussion

Three broad aluminium concentration ranges – low (less than 4 mg-Al/L), medium (4-40 mg-Al/L) and high (greater than 40 mg-Al/L) – were used as a basis for comparing the effectiveness of chemical dosing and electrocoagulation at equivalent aluminium concentrations.

4.3.2.1 Clay removal – Chemical dosing

Normalised turbidity values as a function of settling time, that is, since the cessation of rapid mixing, for the dosage range 0-200 mg-Al/L studied are presented in Figure 4-13. Intermediate aluminium concentrations (4-40 mg-Al/L) produced effective (and very similar) turbidity reduction profiles. Overdosing (i.e. above 200 mg-Al/L) or underdosing (<4 mg-Al/L) produced less effective turbidity removal. Poor coagulation performance at low alum concentrations (0 and 2 mg-Al/L) suggested insufficient coagulant for pollutant destabilisation. At the highest alum dosage tested (200mg-Al/L), turbidity reduction was less effective than at lower dosages, most likely indicating some measure of colloidal restabilisation was occurring (Stumm and O'Melia, 1968).
Figure 4-13 Normalised turbidity at various chemical dosing levels; [clay] = 0.8 g/L; [Al$_2$(SO$_4$)$_3$] = 0 – 200 mg-Al/L.

The pH for these runs was monitored but not controlled. In these modified jar tests, the initial pH for all runs was 5.5 with the pH decreasing rapidly upon alum addition (as shown in legend for Figure 4-13). At an alum dosage level of 4 mg-Al/L, the measured final pH was 4.4, while at 200 mg-Al/L the pH was 3.6. Alum dosing acidifies the solution, with the pH dropping as the dosage level increases.

4.3.2.2 Clay removal – Electrocoagulation

This discussion refers to the electrocoagulation results from Section 2.3. The turbidity reduction, pH and mass removal response were discussed in detail. Three reaction stages (lag, reactive and stable) stages were defined and used as a basis for comparison.

For this clay pollutant, batch electrocoagulation approaches a stable alkaline pH (refer to Section 2.3.2.3), which might be taken as implying stable speciation within the solution. Yet the process is inherently dynamic, with aluminium continuously entering the system, being hydrolysed in a complex manner, and being removed from the system. Simultaneously, water was reduced, adding hydroxyl ions to solution. Such dynamic changes in concentration affect both the solution speciation and the
equilibrium state towards which the system was moving at any one time, as discussed in
detail in Section 4.1. Although jar tests (using alum) may also be seen as a time-varying
process, the dynamics (to a first approximation) might be regarded as less severe, with
coagulant addition occurring just once, and thus the system moving towards a constant
equilibrium state.

The important point here is that in a jar test the coagulant addition was a discrete event,
with the system behaving as a (shot-fed) batch reactor moving towards a defined final
equilibrium state. The (non-continuous flow) electrocoagulation reactor behaves more
like a fed-batch system with coagulant being added continuously, at a rate dependent on
electrode/solution properties and the applied current. As a result, the equilibrium
towards which such a reactor moves is itself constantly shifting. These differences in
dynamic behaviour contribute significantly to the distinction between chemical dosing
and electrocoagulation.

4.3.3 Zeta Potential

As previously discussed (Section 1.2.3), colloids are maintained in suspension by
electrostatic repulsion between particles. The zeta potential provides an effective
measurement of the charge on a particle. Addition of aluminium coagulant could
suppress the electric double-layer around colloidal particles, thus reducing repulsion and
encouraging aggregation of the pollutant (Letterman et al., 1999).

4.3.3.1 Zeta Potential for Chemical Dosing

Figure 4-14 shows the zeta potential in jar tests at low alum concentrations (0, 2 and 4
mg-Al/L) for pH adjusted from 3 to 11. The colloidal clay system (with no alum
addition) was always stable, with the particles being negatively charged. Alum addition
(2 and 4 mg-Al/L) increased the zeta potential, although it remained below zero. At
these concentrations, there was insufficient coagulant to effectively reduce the
pollutant’s electric double layer to enable destabilisation. The ineffective destabilisation
was reflected by the sub-optimal turbidity removal at 0 and 2 mg-Al/L alum (Figure
4-13). At an alum concentration of 4 mg-Al/L, particles approached the isoelectric point
and coagulation performance improved markedly (also see Figure 4-14). Generally, the
zeta potential decreased with increasing pH. This was probably due to an increase in
negatively charged ions, specifically the hydroxyl ion added to increase the pH, and the
aluminate ion, $\text{Al(OH)}_4^{-}(aq)$, which was dominant above pH ~ 9 (Letterman et al., 1999; Stumm and O'Melia, 1968) (also refer to Section 4.1).

Figure 4-14 Zeta potential for solutions subjected to chemical dosing; [clay] = 0.8 g/L; $[\text{Al}_2(\text{SO}_4)_3] = 0, 2, 4\text{mg-Al/L}$.

Figure 4-15 Zeta potential for solutions subjected to chemical dosing; [clay] = 0.8 g/L; $[\text{Al}_2(\text{SO}_4)_3] = 10, 20\text{mg-Al/L}$. 
At intermediate alum concentrations (10 and 20 mg-Al/L), the zeta potential increased from -3.5 mV at low pH values, to a maximum of +14.5 mV at a pH ~ 5.1, before decreasing as the solution became more alkaline. Figure 4-15 shows that the suspension passes through two isoelectric points at approximate pH values of 4.0 and 7.8. Effective turbidity removal was only observed at approximately pH 4.1, which corresponded to the isoelectric point (see Figure 4-13). At this pH, the highly charged aluminium(III) cation, \( \text{Al}^{3+} \), is expected to be the dominant species (Letterman et al., 1999; Bertsch and Parker, 1996) that binds to the negatively charged clay pollutant. Thus, the solution was destabilised by a charge neutralisation mechanism at alum concentrations of 10 and 20 mg-Al/L.

### 4.3.3.2 Zeta Potential for Electrocoagulation

![Zeta potential and normalised turbidity](image)

Figure 4-16 Electrocoagulation reactor’s zeta potential and normalised turbidity; [clay] = 0.8 g/L; \( I = 0.5 \text{ A} \).
Figure 4-16 presents the zeta potential measurements for the electrocoagulation reactor as a function of time for an applied current of 0.5A, along with normalised turbidity measurements relative to the initial value. Initially, there was no change observed in the zeta potential – a response that mirrored the lag stage in the reactor. As the amount of coagulant dissolved at the anode increases, a point was reached where there is a sudden decrease in turbidity and the zeta potential increases rapidly, passing through the isoelectric point. The pH stabilises at approximately 8.5 before the reactive stage (refer to Figure 2-7 in Chapter 2). As the run progresses, turbidity, zeta potential and pH stabilise.

4.3.4 Electrocoagulation - shifting coagulation mechanisms

The nature of the coagulant, a hydrolysed metal cation, in low ionic concentrations limits the possible coagulation mechanisms. As discussed in Section 4.2.3, depletion aggregation is not possible at low ionic concentrations nor is bridging flocculation due to the absence of high molecular weight polymer. Electrocoagulation adds the coagulant directly into the solution as a metal cation and hence could be considered similar to a salt induced aggregation mechanism. The nature of electrocoagulation limits the coagulation mechanisms to a sorption type mechanism without precipitation or a sweep mechanism if precipitation occurs.

4.3.4.1 Reactive stage

The beginning of the reactive stage may be defined as the point where a rapid decrease in turbidity commenced. Figure 4-16 shows that the isoelectric point occurred during this reactive stage. This isoelectric point occurs at about pH 8.5 which was comparable to results obtained from chemical coagulation with the occurrence of an isoelectric point at pH ~8 (see Figure 4-15). Assuming mononuclear aluminium speciation, the aluminate ion, \( Al(OH)_4^- \) (aq), is the dominant aqueous species at pH 8.5 (see Section 4.1). The negatively charged clay could not be destabilised by such a negative aluminium ion, hence coagulation by charge neutralisation appeared implausible. Nevertheless, the aluminium solution chemistry model initially assumed the presence of mononuclear species only. Extension of this model included polynuclear species,
specifically the aluminium trimeric specie, $Al_3(OH)_{14}^{5+}(aq)$, as detailed in Section 4.1. This specie shifted the calculated pH from 6.6 to 10.7. The measured pH lay in the middle of this pH range, thus suggesting partial production of this positively charged ion and that this highly charged positive ion could be responsible for colloid destabilisation and coagulation. Thus suggesting charge neutralisation may be a plausible coagulation mechanism.

Regardless of the exact speciation, the overlap, that is the correspondence of the isoelectric point and the rapid turbidity reduction, together with the nature of the aluminium coagulant and clay pollutant, strongly suggests that some type of sorption mechanism was the primary coagulation mechanism here (Stumm and O'Melia, 1968; Letterman et al., 1999).

4.3.4.2 Stable stage

As the system moved into the stable stage (i.e. $t > 30$ minutes), the rate of turbidity reduction continued to decrease, while the zeta potential increased above the isoelectric point before stabilising (see Figure 4-16). Increase in zeta potential indicated re-stabilisation of the solution. Thus any sorption coagulation mechanism was not possible during the stable stage.

For the stable stage precipitation was experimentally observed. The pH ranges from 8.3 to 8.8, and thermodynamics predicts precipitation of aluminium hydroxide and oxide when the total aluminium concentration exceeds 2.1 to 6.7 mg-Al/L, respectively (refer to solubility diagram Figure 1-6 in Chapter 1 and solution chemistry modelling in Section 4.1). Thus aluminium hydroxide and/or oxide precipitation occurs (as proved in Sections 4.1 and 4.2).

The combination of precipitate formation, zeta increase and continued pollutant removal (both on a mass and turbidity basis) would seem to indicate a gradual shift to sweep flocculation (or enmeshment) as the dominant pollutant removal mechanism in the stable stage. Thus sweep flocculation is the dominant aggregation mechanism during the stable stage.
4.3.5 Electrocoagulation – Change in current

As discussed in Chapter 2 (Section 2.3.3), the applied current in electrocoagulation not only determined the coagulant dosage rate but also the bubble production rate and thus the fluid regime (mixing) within the reactor. Hence, collisions between particles, floc growth, and the potential for material removal (both pollutant and coagulant) by flotation were largely determined by the current.

After the colloidal suspension has been destabilised, effective aggregation required adequate contact between the coagulant and pollutant particles. Consequently, the transport mechanism was important as this determined collisions between, particles coagulant and bubbles. Thus, the fluid regime clearly had a significant impact on both the flocculation mechanism and the subsequent means of pollutant removal. Table 4-6 describes flocculation mechanisms and associated transport properties (Letterman et al., 1999).

<table>
<thead>
<tr>
<th>Flocculation Mechanism</th>
<th>Transport Mechanism</th>
<th>Forces on particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perikinetic flocculation</td>
<td>Brownian fluid motion</td>
<td>Random motion</td>
</tr>
<tr>
<td>Orthokinetic flocculation</td>
<td>Laminar flow</td>
<td>(Low) Shear</td>
</tr>
<tr>
<td>Turbulent conditions</td>
<td>Fluctuating flows and eddies</td>
<td>(High) Shear</td>
</tr>
<tr>
<td>Differential settling</td>
<td>Unequal settling velocities</td>
<td>Gravity</td>
</tr>
</tbody>
</table>

Figure 2-14 showed pollutant removal behaviour when current was varied from 0.25 to 2.0 A. For all cases, however, regardless of the initial value, the pH stabilised within 15 minutes to somewhere in the range 8.3 to 8.8. The highest current (2.0 A) produced the shortest lag period (10 minutes) and the quickest response, with a 90% turbidity reduction occurring between 10 and 15 minutes. As the current decreased, so the length of each electrocoagulation stage increased, implying a change in the transport mechanism and hence also flocculation mechanism.

The results of mass balances performed on the electrocoagulation reactor were presented in Table 2-7 in Chapter 2. Pollutant loading was constant for all experiments,
while current was varied. At 0.25A, 26% of the total pollutant was recovered at the surface after four hours of operation with the remaining mass recovered as sludge at the reactor base. Conversely, the highest current, 2.0 A, produced the largest pollutant recovery at the surface (63% of the total). Low current produced low (hydrogen) bubble density, leading to a low upward momentum flux, and thus poor mixing within the reactor - conditions that encouraged sedimentation over flotation. As the current was increased, the bubble density and the amount of mixing increased – favouring flotation over sedimentation (Holt et al., 2001). Hence, the operational current had a strong influence on the dominant pollutant removal path, that is, flotation (surface) or settling (base).

At high current, the coagulant dosage rate increased resulting in a greater amount of precipitate in the stable stage. Likewise, the bubble density increases resulting in a greater upwards momentum flux and thus faster removal of pollutant and coagulant by flotation (Holt et al., 2001). At higher current densities, more coagulant (aluminium) is available per unit time but there is a decrease in its residence time in the reactor. Hence there is a reduction in the probability of collision and adhesion between the pollutant and coagulant. This results in the observed decrease in efficiency on an aluminium basis. Consequently the electrocoagulation reactor operational current must be determined by a trade-off between reaction time, aluminium efficiency and desired pollutant removal path (flotation or settling).

4.3.6 Comparison of electrocoagulation and chemical coagulation – fixed aluminium concentration

A direct comparison between electrocoagulation and chemical coagulation was not practicable. The systems did not operate on an equivalent basis. In chemical coagulation, coagulant addition was a discrete (shot-fed) event with equilibrium determining aluminium speciation and pH. In electrocoagulation, the coagulant addition was a function of current and time. Concentrations continually shifted as the aluminium electrode corroded yet the pH stabilised at 8.3-8.8, depending on current (see Figure 2-14 in Chapter 2). Pollutant separation processes were also different with settling the only removal path for chemical coagulant while a combination of flotation/settling was possible for electrocoagulation. Thus, it is important to compare turbidity reduction on a more consistent basis, that is, on an aluminium basis.
A new set of chemical coagulation runs were carried out in which the pH was varied by addition of hydrochloric acid or sodium hydroxide solution. The alum dosages chosen for these runs (4 and 20 mg-Al/L) were significant for chemical dosing because they span the range of optimal turbidity reduction without pH adjustment (see Figure 4-13), and for electrocoagulation because they span the stage during which most turbidity reduction occurs (see Figure 2-17 in Chapter 2). Thereby enabling comparison at comparable pH values and aluminium concentrations. Normalised turbidity response curves for the chemical dosing jar tests at a range of pH values are presented in Figures 4-17 and 4-18 for 4 and 20 mg-Al/L alum dosage levels, respectively.

![Figure 4-17 Normalised turbidity from chemical dosing; \([\text{clay}] = 0.8 \text{ g/L}; [\text{Al}_2(\text{SO}_4)_3] = 4 \text{ mg-Al/L}; \text{pH} = 3.6 – 11.4.](image)

Alum dosing at 4 mg-Al/L produced mediocre performance and is presented in Figure 4-17. A high residual turbidity was observed: after 60 minutes, residual turbidity remained greater than 10% of initial turbidity for all pH values studied. The best turbidity reduction achieved was at an unaltered (ie no acid or base addition) pH of 4.1 where the zeta potential was closest to zero (Figure 4-14). As the pH increased, zeta
potential moved away from zero indicating an increase in solution stability and hence also turbidity removal performance declined. Indeed, under strongly basic conditions (pH ~ 11.4), settling performance was so poor as to indicate substantial restabilisation of the colloidal clay (Stumm and O'Melia, 1968). This sub-optimal turbidity removal performance was more noticeable in the electrocoagulation results.

![Figure 4-18 Normalised turbidity from chemical dosing; [clay] = 0.8 g/L; [Al₂(SO₄)₃] = 20 mg-Al/L; pH = 4.4 - 10.6.]

Considering the electrocoagulation results in Chapter 2 Figure 2-17, by 4 mg-Al/L no turbidity removal had occurred regardless of the current used. Turbidity removal began at 7 mg-Al/L for 0.25 A, with the concentration necessary for the start of turbidity reduction increasing as the current increased. At 4 mg-Al/L, the pH was far higher (8.3-10.1) than the optimal (acidic) pH of 4.2 identified for chemical dosing with alum where charge neutralisation was identified as the dominant coagulation mechanism (Stumm and Morgan, 1962). As the pH increased, zeta potential decreased and performance deteriorated. The two sets of results were thus consistent with the lag stage observed in electrocoagulation being characterised by a low coagulant level and a high
pH – a combination where both chemical coagulation and electrocoagulation were far from optimal with insufficient coagulant present for destabilisation of the solution.

In the electrocoagulation reactor at 20 mg-Al/L, pH levelled out to 8.3-8.8, which was towards the upper end of the range identified by alum dosing (see Chapter 2 Figure 2-17) as leading to "good" turbidity reduction. For 2.0 A, the system was still in the reactive stage at 20 mg-Al/L with the turbidity still dropping rapidly as the aluminium concentration increased. On an equivalent aluminium basis, efficiency had declined due to the higher bubble production rate resulting in the domination of flotation, as previously discussed. At low current the coagulant release was slow, bubble production low and hence resultant gentle agitation favoured removal by settling. This more closely resembled those conditions experienced in chemical coagulation jar tests. Thus a closer comparison was possible between chemical coagulation and electrocoagulation at low currents.

The normalised turbidity for alum dosage at 20 mg-Al/L is presented in Figure 4-18. Here, pH adjustment improved turbidity reduction with good performance demonstrated over pH 5.2 – 9.3, where residual turbidity fell to between 5-7% after 60 minutes. This region coincided, to a first approximation, to the pH range of 4 to 8 spanning the isoelectric points identified in chemical coagulation (Figure 4-15). Thus implying the clay solution was destabilised, to a certain extent, and coagulated by a sorption mechanism. Outside this range, however, zeta potential decreased, resulting in a stable solution reflected by a decline in turbidity removal performance. At a highly alkaline pH (~10.6) little change in turbidity was observed, due to restabilisation of the colloidal clay and the dominance of the aluminate ion in solution (Stumm and Morgan, 1962; Stumm and O'Melia, 1968). Thus at alum concentration of 20 mg-Al/L turbidity removal performance is better and occurs over a wider pH range than at 4 mg-Al/L.

For low currents (0.25 and 0.5 A) and at aluminium concentration of 20 mg-Al/L, the electrocoagulation system operated in the final (stable) stage. Aluminium hydroxide precipitated and removed the remaining clay particles by sweep coagulation, resulting in a small change in turbidity. In comparison to chemical coagulation at 20 mg-Al/L, the electrocoagulation reactor achieved better pollutant removal (than alum dosing) with
normalised turbidity being reduced to about 3% for both 0.25 and 0.5 A. Differences between systems (chemical coagulation and electrocoagulation) were minimised by operating at low currents. Specifically due to the resultant low bubble density and low removal by flotation. The remaining differences between the systems were due to the presence of the sulphate ion from alum (chemical coagulation) and the reaction time for equivalent aluminium levels (electrocoagulation). The presence of the sulphate anion, $SO_4^{2-}$ (aq), from alum has been suggested to improve sweep coagulation by destabilising positively charged ions (usually hydrolysis products) and adsorption into the Stern layer (Letterman et al., 1999). In this case, it appeared that electrocoagulation produced a better result than chemical coagulation. Hence the absence of sulphate anions and presence of hydroxyl ions, $OH^-$ (aq), formed at the cathode, appeared to improve overall performance. However, to achieve equivalent levels of coagulant dosage on an aluminium basis for 0.25 and 0.5 A, the reactor was operated for 85 and 43 minutes, respectively. This reaction time has a direct impact on the settling time. It appears that operation at 0.25 A had a longer time to allow clay pollutant to settle but this was not the case at 0.5 A. Thus, the governing influence, that is, either the absence of sulphate ions or the increased settling time, that resulted in the better performance of electrocoagulation at 20 mg-Al/L is questionable.

4.3.7 Section conclusion

The dynamic nature of batch electrocoagulation was characterised by lag, reactive and stable stages. During the lag stage, no turbidity reduction occurred and the pH (after an initial increase) stabilised in the range 8.3 - 8.8. During the reactive stage, the isoelectric point was reached and turbidity decreased rapidly, while in the stable stage turbidity approached an asymptote. The colloidal clay pollutant was destabilised and removed at a critical aluminium concentration that was dependent on the applied current. The results indicated that a sorption removal mechanism was dominant during the reactive stage. Further turbidity reduction in the stable stage was attributed to a sweep coagulation mechanism.
4.4 Chapter synthesis

The aggregation and coagulation mechanisms were identified and quantified in this chapter. To decipher these mechanisms, two approaches were used. The first approach was the evaluation of electrocoagulation with and without pollutant present. The other approach was to compare electrocoagulation and chemical coagulation. The main outcomes from the evaluation of electrocoagulation with and without pollutant present is summarised in Table 4-7.

Table 4-7 A summary of the properties of the clay and no clay experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>[clay] = 0.8 g/L</th>
<th>[clay] = 0 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>Decreases logarithmically until 40 min where level stabilises at ~20 NTU</td>
<td>Turbidity increases to 20 NTU at 40 min where it stabilises.</td>
</tr>
<tr>
<td>Aggregate size</td>
<td>Increases to 25-30 µm over 40 minutes before stabilising</td>
<td>Increases to 35-40 µm between 20 to 40 min and then decreases to 30 µm at 55-60 mins.</td>
</tr>
<tr>
<td>pH</td>
<td>Initial pH was 7.5 - increases to 8.5 in first 10 mins</td>
<td>Initial pH was 5.3 - increases gradually to 8.5 stabilising by 45 mins.</td>
</tr>
<tr>
<td>Al concentration</td>
<td>Constant at 3ppm.</td>
<td>Increases (just below Faraday’s law) stabilising after 45 minutes to 30 ppm.</td>
</tr>
<tr>
<td>Al(OH)₃ solubility</td>
<td>3.4 ppm at pH 8.5</td>
<td>Passes through minimum solubility (0.03 ppm) at pH 6.4 (~5 min) to then increase with pH to 3.4 ppm (45 min)</td>
</tr>
<tr>
<td>Nucleation</td>
<td>Sites available</td>
<td>No sites available</td>
</tr>
<tr>
<td>Fractal Dimensions</td>
<td>Increased fractal dimensions from 1.9 to 2.3 during reactive stage</td>
<td>Higher fractal dimensions – 2.4-2.6</td>
</tr>
<tr>
<td>Aggregation mechanism</td>
<td>Range spans diffusion limited to reaction limited aggregation</td>
<td>Reaction limited aggregates</td>
</tr>
</tbody>
</table>
Pollutant presence had a significant effect on the reactor’s performance, shifting the dominant removal mechanisms to suit the operating conditions within the reactor. Nucleation sites (the pollutant) enabled coagulation as evidenced by the coagulant (aluminium) consumption and diffusion-limited aggregation mechanism. This resulted in formation of larger branched aggregates.

Residual turbidity, in both cases, was explained by the formation of aluminium hydroxide and oxide, which was also supported by solution chemistry modelling results. Results for both systems converged during the stable stage (where bulk of pollutant was removed) inferring the residual turbidity is an artefact of the system and not its operation.

This chapter also provided a quantitative comparison between electrocoagulation and chemical coagulation to decipher electrocoagulation’s coagulation mechanisms. For electrocoagulation, the greatest turbidity reduction coincided with the isoelectric point. This indicated aggregation by a sorption mechanism (compared to charge neutralisation in chemical coagulation). During the stable stage, continued precipitation of aluminium hydroxide and a decrease in turbidity indicated a sweep coagulation mechanism.

4.5 Chapter conclusion

This chapter identified electrocoagulation’s coagulation and aggregation mechanisms. These mechanisms are summarised below for each reaction stage.

- Lag stage: no reaction – coagulant concentration increases until a critical coagulant concentration is reached.
- Reactive stage: sorption coagulation mechanism and diffusion-limited aggregation.
- Stable stage: sweep coagulation and reaction-limited aggregation.

Various modelling and experimental tools were employed to examine the dynamic electrocoagulation process. No tool in isolation could have provided a comprehensive overview of electrocoagulation’s coagulation mechanism. The novel synthesis of thermodynamic modelling, comparative experiments (with and without pollutant;
electrocoagulation and chemical dosing), and fractal analysis enabled coagulation mechanisms to be postulated.

Following coagulation and aggregation, the final phase of pollutant removal was separation. For electrocoagulation, the applied current determined the dominant pollutant removal path. At low currents, settling dominated. As the current increased, so the pollutant fraction that was removed by flotation increased, although the coagulant appeared to be used less effectively. Chapter 5 investigates flotation and the pollutant’s separation.
5 Flotation

Sedimentation and flotation occur simultaneously in the electrocoagulation reactor. Flotation is reliant on adequate coagulant addition for pollutant aggregation and bubble concentration for pollutant removal. Settling is also reliant on adequate coagulant dispersion followed by still conditions for settling. This chapter examines the pollutant separation in electrocoagulation with a focus on flotation.

As discussed in Chapter 2, the relationship between operating current and time determines the pollutant split between the reactor’s base and surface. Flotation and settling have different pollutant removal “time constants”, flotation being faster than settling. Yet the coagulant and bubble production rates are linked stoichiometrically by the electrochemical reactions. Hence, the current determines both coagulant addition and bubble production rates. Both processes are not necessarily synergistic for a specific pollutant removal path. This chapter’s overarching aims are to investigate these competing removal mechanisms, to quantify pollutant separation (between flotation and settling) and determine the role of current and time.

The electrocoagulation reactor’s macroscopic response and pollutant removal rate to the surface is quantified in Section 5.1. These results reveal the trends in overall removal, that is, that flotation is favoured at high currents (1.0 and 2.0 A) and sedimentation at low currents (0.25 A). Consequently, research is directed so as to investigate the individual settling and flotation behaviour that occurs in electrocoagulation. Initially the pollutant settling behaviour is investigated on an individual particle basis, and then on an overall basis to establish a baseline for interpretation in Section 5.2. Then the role of flotation (for individual bubbles) is examined in Section 5.3 and its relationship to electrocoagulation is evaluated. In order to combine the flotation and settling removal paths, existing models developed for dissolved air flotation (DAF), electroflotation and electrocoagulation are reviewed in Section 5.4. The differences between these systems are evaluated with the deficiencies of present flotation models highlighted for this application. Consequently in Section 5.5, a mathematical analysis is conducted to quantify the competing removal kinetics for the pollutant removal in the batch
electrocoagulation reactor. Finally, the pollutant separation mechanisms and paths are discussed in Section 5.6.

5.1 Pollutant removal in a batch electrocoagulation reactor

Pollutant removal occurred \textit{in situ} by flotation or settling. The operating current had numerous effects including coagulant addition, bubble generation, and the degree of mixing. Clearly, these aspects were interconnected, and their combination determined the dominant pollutant removal path and rate, as discussed in Section 1.4. To evaluate pollutant removal and its relationship to electrocoagulation, the role of flotation, time and removal rates are each discussed in the following sub-sections.

5.1.1 Flotation due to electrolytic gas production

Flotation was an inseparable aspect of this batch electrocoagulation reactor by design. Electrolytic hydrogen gas production occurred as water was reduced at the cathode, simultaneously as coagulant was delivered by the sacrificial anode. As discussed in Section 1.4, electrolytic bubble production had two main influences in the batch electrocoagulation reactor - mixing and pollutant removal by flotation. The bubbles created an upward momentum flux, if sufficient bubbles were present to create a large enough upward momentum, the aggregated pollutant particles floated to the surface. Bubble production also induced mixing within the reactor. Bubbles displaced fluid as they rose to the surface. This fluid displacement created agitation and eddies that induced contact between particles (both coagulant and pollutant), as well as between bubbles and particles. Thus, electrolytic gas production provided a source of both agitation (mixing) and a separation path (flotation). These effects must be considered in terms of their relationship to removal and contact time in electrocoagulation reactors.

5.1.2 Time for pollutant removal

For both pollutant removal paths (flotation and settling), the consideration of time was significant. To facilitate this discussion, two “descriptions of time”, removal and contact time, were important. Removal time described the time for the pollutant aggregate to report to the surface or the base. Contact time described the contact between a particular
coagulant and pollutant particles. Adequate contact time is required for aggregation and the formation of larger particles, which were easier to remove (especially via settling).

The link between operating current and pollutant removal path is discussed in Section 2.3.3. There, two distinct separation paths became evident:

1. Predominantly settling – at low current, and;
2. Predominantly flotation – at high current.

One of this chapter’s objectives is to interpret the consequences of each operating mode with respect to both removal and contact times.

Separation by flotation is expected to occur faster than separation by gravitational sedimentation. Faster removal decreases the contact time between coagulant and pollutant particles decreasing the coagulant efficiency. Overall pollutant removal rates to the surface provide a decent starting point for this investigation.

5.1.3 Pollutant removal kinetics and operating current

Operation at high current densities (1.0 and 2.0 A) resulted in “fast removal” on both a turbidity reduction (refer to Figures 2-14 and 2-15) and mass removal basis (refer to Figure 2-16). Mass (other than water) in the reactor comes from either the clay added initially or from material generated by the electrodes. The analysis in this thesis assumed all mass generated at the electrodes precipitated as aluminium hydroxide and could be calculated using Faraday’s law. Thus, over time, the coagulant mass increased and this dynamic change was incorporated in the total mass.

The total mass removal rate is thus defined as total mass (that is, both coagulant and clay) collected at the surface over a defined time period (typically 5 minutes). The removal rate for an initial pollutant loading of 0.8 g/L is shown in Figure 5-1. The highest rate of 0.32 g min⁻¹ was recorded for 1.0 A in the 5-10 minute interval - although the average removal rate over the first 10 minutes was 0.23 g min⁻¹ for 2.0 A compared to 0.16 g min⁻¹ for 1.0 A. As current was increased to 1.0 and thence to 2.0A, the bubble density, and therefore the upward momentum flux increased, removing a greater mass of coagulated pollutant to the surface.
As the current increased, so the coagulation addition also increased. This also increased the upward momentum associated with a higher bubble density. Hence, the contact time between individual coagulant molecules and pollutant particles was reduced. Thus, the opportunity for coagulant to collide with pollutant was reduced and removal efficiency decreased. So on an equivalent aluminium basis, the performance decreased in terms of both turbidity reduction (see Figure 2-17) and mass removal (see Figure 2-18).

Conversely, operation at low current (0.25 A) resulted in slower pollutant removal with a peak removal rate of 0.04 g min\(^{-1}\) (in the 30 – 40 minutes interval). At 0.25 A, settling was the dominant removal path. The slow release of coagulation occurred with little agitation (i.e. little mixing). This resulted in a longer contact time between coagulant molecules and hence the more efficient use of the coagulant. The removal path was longer and this resulted in an increased removal time.

To summarise, an increased current increased the degree of mixing in the reactor but this effect was overshadowed by the decreased coagulant efficiency due to faster
removal by flotation. Thus, the flotation and settling removal paths were in some sense competing. These competing processes are now examined separately.

5.2 Settling in the electrocoagulation reactor

A force balance enables the settling velocity of a particle or aggregate to be estimated. Combined with the measured particle size distribution, the average pollutant removal time can be calculated. The time constant for particle separation can then be determined. This is compared to the experimentally measured settling profile for the heterogeneous clay pollutant and hence also the removal times.

This settling velocity also influences the fluid regime. Hence, the particle’s Reynolds number is also calculated to provide an indication of the fluid flow around the particle. This analysis characterises the settling behaviour and provides a basis for comparison with the flotation separation path.

5.2.1 Forces on a single particle

Firstly, consider a single rigid spherical particle in solution. The force balance on this particle is due to weight ($F_W$), drag ($F_D$) and buoyancy ($F_B$), as shown in Figure 5-2.

\[
F_D + F_B = F_W
\]

Figure 5-2 Forces on a single settling particle.

Thus, the force balance at terminal velocity is:

\[
F_W = F_B + F_D \quad \text{(E5-1)}
\]
Assuming laminar flow, that is for the particles Reynolds number ($Re_p$) less than 0.1, the force balance reduces to Stokes’ Law (Clift et al., 1978) and hence the terminal velocity can be calculated,

$$u_p = \frac{gd_p^2(\rho_p - \rho_W)}{18\mu}$$  \hspace{1cm} (E5-2)

where $u_p$ is the particle’s terminal velocity (m s$^{-1}$), $d_p$ is the particle diameter ($\mu$m), $\rho_W$ density of water, $\rho_p$ particle density, $\mu$ viscosity of water and $g$ is the gravitational constant.

![Figure 5-3 Mean settling time assuming Stokes Law.](image)

Using this particle velocity, the mean settling time in the electrocoagulation reactor (mean height of reactor, $h = 78$ mm) for a range of particle sizes was calculated and is presented in Figure 5-3. Clearly for larger particles ($d_p > 25 \mu$m), settling occurred rapidly (less than 5 minutes). As pollutant particle diameter decreased, so settling time increased exponentially.
To assess the applicability of Stokes Law, the particle Reynolds number was calculated at the terminal settling velocity using Equation E5-3 (Perry et al., 1997).

\[
\text{Re}_p = \frac{\rho_w u_p d_p}{\mu}
\]  

(E5-3)

As the pollutant particle diameter increased, so the settling velocity increased, as did the Reynolds number. This relationship is shown in Figure 5-4. For particle diameters greater than 55 µm, the flow regime around the particle shifted from laminar to intermediate (also referred to as transitional). The drag coefficient changed and hence also the settling velocity. Clearly the larger sized particles from the heterogeneous clay have the potential to change the fluid characteristics. A heterogeneous pollutant with poly-dispersed particle size range (0.5 µm < d_p < 2.0 mm) was used in this thesis (refer to Section 2.3.1). Thus a significant proportion of the clay pollutant, regardless of electrocoagulation, would settle rapidly due to its larger particle diameter. Clearly an
individual particle approach is limited for electrocoagulation. This fraction is investigated in the following section.

Additionally, for particle diameters greater than 100 µm, particles could no longer be considered as rigid spheres, and shape factors should be incorporated (Clift et al., 1978). Non-spherical geometry alters the drag force and hence the drag coefficient. Particle characterisation results from Section 4.2 clearly revealed the non-spherical shape of the aggregates.

Here, mono-dispersed latex spheres would be an ideal pollutant for particle characterisation in contrast to the heterogeneous clay used in this thesis. Nevertheless, the choice of a realistic pollutant (i.e. clay) required a realistic solution. Latest developments in fractal dimension research aims to link the fractal characteristic of the aggregates to its settling behaviour (Bushell et al., 2002). Presently, this theory is being developed for well characterised systems. Thus its application to the heterogenous clay pollutant was limited and not appropriate here. Hence, an experimental approach was used to link the multi-modal particle size distribution of the clay pollutant to its settling characteristics because its impacts are not predictable from simplified assumptions in theory.

5.2.2 Experimental settling results

To establish a baseline for the electrocoagulation reactor, a series of settling experiments were carried out. Solution conditions were the same as those in the electrocoagulation reactor - that is, deionised water was used with a sodium chloride concentration of 0.20 g/L but no coagulant was added.

For each run, approximately 20 g of clay was dispersed in the sodium chloride solution. The dispersed clay was then transferred to a measuring cylinder. The level of water in the measuring cylinder was filled to the same height as the reactor (155 mm). The clay solution was shaken ensuring well-mixed conditions. The solution was then allowed to settle for 0, 15, 30, 45, 60, 120, 180 and 240 minutes.

After the requisite settling time, the top layer of water was decanted and the mass settled at the base was collected, dried and then weighed.
The particle size distribution of the clay had previously been measured using a Malvern Mastersizer S, with any coarser particles ($d_p > 53 \, \mu m$) separated using sieves, as discussed in Section 2.2.1.

The settling velocity was then calculated from Stokes’ Law (assuming laminar flow and spherical particles) with a particle density of 1.8 g cm$^{-3}$ (refer to Section 2.2.1). This enabled the calculation of the percentage mass settled for the electrocoagulation reactor, with no coagulant addition. This settling prediction is compared with settling results for clay without coagulant additions in Figure 5-5.

![Figure 5-5 Experimentally measured settling of clay pollutant with Stokes' Law.](image)

There is good agreement between the mass of clay settled (experimental data points) and that predicted by Stokes law (based on the previously measured PSD). Typical electrocoagulation experiments began approximately five minutes after the addition of clay, allowing any large particles to settle. The fraction $d_p > 24 \, \mu m$ settled in less than 5 minutes. Hence, approximately 41% of the mass of clay added settled before
electrocoagulation actually commenced. Further settling occurs in an approximately linear region of the settling curve and hence can be characterised by a linear relationship.

The settling characteristics of clay shown in Figure 5-5 provide a base line for comparison with the effect of electrocoagulation. For electrocoagulation at 0.25 A, the mass at the base of the reactor increased compared to the base case (as shown in Table 2-7) indicating enhanced settling. At higher currents, 1.0 and 2.0 A, the settling of clay is hindered compared to results at 0.25 A, thereby resulting in less mass settling and a greater amount recovered at the surface.

Additionally, mass (as coagulant) was continuously added to the electrocoagulation reactor. Assuming that all this aluminium precipitated as either aluminium hydroxide or oxide, the total mass that could be removed increased. Obviously, this additional coagulant mass changes with current and also affects the removal process. These dynamic changes are incorporated into the mass removal rates when considering the electrocoagulation process.

5.3 Flotation in the electrocoagulation reactor

Flotation competes with gravitational sedimentation as the pollutant separation path in batch electrocoagulation. Electrolytic gas produced at the cathode creates a source of bubbles that enables flotation by creating an upward momentum flux to remove pollutant to the surface. This section examines bubble characteristics and quantifies their effect in electrocoagulation.

The science of flotation is well established and researched (Dai et al. (2000), Matis (1995), and Ralston and Dukhin (1999)). The main difference between electrolytic flotation, as occurs in the electrocoagulation reactor, and conventional flotation based separation methods, is the bubble size, as recognised in Section 1.2.4. Bubbles produced in electroflotation cells are typically smaller than conventional processes (Gregory et al., 1999). Matis and Zouboulis (1995) reported a mean bubble size of 50 µm for electrolytic bubble production for combined oxygen and hydrogen evolution. Sillen et al. (1980) reported that hydrogen bubbles produced in alkaline environments at the cathode (similar conditions to the electrocoagulation reactor in this thesis) were
consistently smaller than oxygen bubbles from the anode. Fukui and Yuu (1980) reported that electrolytic hydrogen bubbles, such as those produced here, were typically less than 20 µm. Thus, a bubble diameter of 20 µm was considered appropriate for any preliminary analysis of this electrocoagulation reactor.

### 5.3.1 Forces on a single bubble

Initially a bubble rising in solution is examined to determine the average rise velocity and hence the bubble residence time. This enables the average number of bubbles in the reactor at any given time and the flow regime around the bubble to be calculated. The contact time, fluid regime and mean number of bubbles describe, to a first approximation, the bubble behaviour in the reactor, and hence provide an insight into the overall flotation process in electrocoagulation.

Consider a single bubble - the three main forces being drag ($F_D$), weight ($F_W$) and buoyancy ($F_B$), as shown in Figure 5-6.

![Figure 5-6 Forces on a single rising bubble.](image)

Thus, the force balance at its terminal velocity is:

$$F_B = F_W + F_D$$  \hfill (E5-4)

Bubbles with diameter ($d_b$) 100 µm or less rise as rigid spheres and thus Stokes’ Law was used to calculate the rise velocity assuming $Re_b < 0.1$ (Clift et al., 1978; Edzwald, 1995),
Chapter 5 - Flotation

\[ u_b = \frac{g d_b^2 (\rho_W - \rho_B)}{18 \mu} \]  

(E5-5)

where \( u_b \) is the bubble’s terminal velocity (m s\(^{-1}\)), \( d_b \) is the bubble diameter (\( \mu \)m), \( \rho_W \) is the density of water, \( \rho_B \) bubble density, \( \mu \) viscosity of water and \( g \) is the gravitational constant. To provide an indication of the flow around the bubble, the bubble Reynolds number (\( Re_b \)) was calculated using Equation E5-6. The \( Re \) was 5.5x10\(^{-3}\) for a 20 \( \mu \)m bubble was determined. This Reynolds number is significantly less than 0.1, indicating laminar flow around the bubble (Perry et al., 1997). Hence, the laminar assumption is valid and Stokes’ Law is applicable with a drag coefficient (\( C_D \)) equal to \( 24/Re \).

\[ Re_b = \frac{\rho_W u_b d_b}{\mu} \]  

(E5-6)

The terminal rise velocity was 2.5x10\(^{-4}\) m s\(^{-1}\) for a 20 \( \mu \)m hydrogen bubble. The mean bubble path, that is, from the middle of the electrode to the surface, was 130 mm, and hence the average rise time (\( t_{\text{rise}} \)) was 8.9 minutes for an “unhindered” bubble. The total number of bubbles can be calculated using the mean rise time, the hydrogen mass generation rate (from Faraday’s Law) and a bubble diameter of 20 \( \mu \)m - remembering that hydrogen generation rate is directly proportional to current according to Faraday’s Law (Equation E1-5).

The bubble volume concentration (\( \Phi_b \)), defined as the total bubble volume divided by the solution volume, was also calculated and is shown in Table 5-1. The bubble volume concentration provided an indication of the collision probability between bubbles and particles in the reactor. After collision, the bubbles could attach to the pollutant particle, and then help lift the pollutant to the surface. A higher \( \Phi_b \) indicated a higher collision probability. That is, the chances of a pollutant particle, aggregate and/or coagulant colliding with a bubble increases as the number of bubbles increases. For electrocoagulation, the bubble volume concentration was directly proportional to current, assuming constant bubble diameter and hence constant rise time (see Table 5-1).
Table 5-1 Bubble volume concentration for $d_b = 20 \, \mu m; I = 0.25 – 2.0 \, A$.

<table>
<thead>
<tr>
<th>Current (I) (A)</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble volume concentration ($\Phi_b$) v/v%</td>
<td>0.25%</td>
<td>0.50%</td>
<td>1.00%</td>
<td>2.01%</td>
</tr>
<tr>
<td>Mean number of bubbles ($N_b$)</td>
<td>$3.7 \times 10^9$</td>
<td>$7.4 \times 10^9$</td>
<td>$1.5 \times 10^{10}$</td>
<td>$2.9 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Greater flotation removal occurred at higher currents (1.0 and 2.0 A) (refer to Section 2.3.3) resulting in a higher mass removal rate to the surface, as observed in Figure 5-1. The bubble residence time is a function of the bubble diameter only. So as the current increased, the number of bubbles increased proportionally as this analysis assumed a constant bubble diameter ($20 \, \mu m$). Hence electrocoagulation operation (i.e. current) has a direct positive influence on the bubbles number in the reactor and consequently the interception and probability of collision.

This section and the previous settling analysis considered the settling and flotation aspects of electrocoagulation separately. Flotation and settling occurred simultaneously in the electrocoagulation reactor. Thus their interactions as competing separation processes is important. Reported techniques to combine these processes are investigated next.

5.4 Flotation models

To provide an insight into the competing removal processes in electrocoagulation, a number of existing approaches to flotation were evaluated. Numerous approaches have been developed for modelling flotation separation, as noted in Section 1.2.4. Initially, dissolved air flotation (DAF) models are considered in Section 5.4.1, an assessment of electroflotation models follows in Section 5.4.2, and finally electrocoagulation models are evaluated in Section 5.4.3.

5.4.1 Dissolved air flotation (DAF) models and their relationship to the batch electrocoagulation reactor

The leading dissolved air flotation (DAF) models reported in the literature are:

- The white water collector collision model by Edzwald et al. (1990), and;
- The population balance turbulence (PBT) model by Fukushi et al. (1995).
Each model describes DAF by a different approach. Edzwald’s approach models each bubble as a collector of particles and then considers all the bubbles as a white water blanket. The PBT approach described the collisions between bubbles and particles via population balance kinetic expressions (Gregory et al., 1999). Both models divide the DAF unit in two zones: reaction and separation. The reaction zone encourages contact between bubbles and particles. The separation zone is the clarification zone where particle-bubble aggregates float to the surface. Each model and its possible relevance to understanding separation processes occurring in electrocoagulation are now considered.

The population balance model assumes turbulent flow. The low value of the Reynolds number for \( d_b = 20 \ \mu m \) and \( d_p < 55 \ \mu m \) for the electrocoagulation reactor indicated laminar flow around the bubbles and particle. As the particle diameter increased (\( d_p > 55 \ \mu m \)), the flow regime in the reactor became intermediate as Re increased beyond 0.1, but was significantly less than Re of 500 associated turbulent flow. Thus for electrocoagulation, the population balance model was not appropriate.

Additionally, both the white water collector collision model and the population balance turbulence model considered the addition of the coagulant prior to flotation. Both models assumed all coagulation and flocculation processes were complete before flotation started. Hence, each assumed that the floc particle size was then constant in the reaction and separation zones of the DAF process. Whereas in the electrocoagulation reactor, coagulant addition occurred continuously as the sacrificial anode corroded. Thus electrocoagulation resulted in the growth of aggregates and flocs over time (see Section 4.2.2), and clearly the electrocoagulation process is more complex than either DAF model, with the continual coagulant addition occurring simultaneously with pollutant removal. Thus, neither DAF model will be able to accurately describe electrocoagulation. Nevertheless, the white water collector efficiency model provides an insight to the separation mechanisms that may be occurring in electrocoagulation.

Consider the single collector collision model for dissolved air flotation put forward by Edzwald et al. (1990) (see also Edzwald, 1995 and Gregory et al., 1999). Here it was assumed that separation in a DAF reactor took place in two distinct zones - reaction and separation (whereas the reaction and separation zones in a batch electrocoagulation
reactor are one and the same). Hence, the entire electrocoagulation reactor was considered here as comprising the “reaction zone” and Edzwald’s model was applied to electrocoagulation’s conditions. This model described the transport mechanisms of an individual particle to a bubble. Thus, Edzwald’s approach to DAF modelled the bubbles as collectors of particles. The total single collector bubble efficiency ($\eta_T$) described particle transport to the bubble surface. This total efficiency was comprised of Brownian diffusion ($\eta_D$), interception of the bubble and particle ($\eta_I$), sedimentation ($\eta_S$) and inertia ($\eta_{IN}$) (Equation E5-7).

$$\eta_T = \eta_D + \eta_I + \eta_S + \eta_{IN} \tag{E5-7}$$

$$\eta_D = 6.18 \left( \frac{k_B T}{g \rho_W} \right)^{2/3} \left( \frac{1}{d_P} \right)^{2/3} \left( \frac{1}{d_B} \right)^2 \tag{E5-8}$$

$$\eta_I = \frac{3}{2} \left( \frac{d_P}{d_B} \right)^2 \tag{E5-9}$$

$$\eta_S = \left( \frac{\rho_P - \rho_W}{\rho_W} \right) \left( \frac{d_P}{d_B} \right)^2 \tag{E5-10}$$

$$\eta_{IN} = \frac{g \rho_P \rho_W d_B d_P^2}{324 \mu^2} \tag{E5-11}$$

The single collector collision efficiency for the electrocoagulation conditions ($d_b = 20 \mu m$ and $\rho_p = 1.77 \text{ g cm}^{-3}$) was calculated using Equations E5-8 to E5-11 and the results (as a function of particle diameters) are shown in Figure 5-7 where $k_B$ is Boltzman’s constant (1.38x$10^{-23}$ J K$^{-1}$) and $T$ is the absolute temperature.

These efficiency equations may be used instructively for the electrocoagulation reactor. For the system considered in this thesis, the bubble diameter was smaller and the particle density greater than conditions considered by Edzwald for DAF. Thus, the
inertia effect was not significant for bubbles and particles less than 100 µm (Clift et al., 1978), as shown in Figure 5-7 and hence was ignored.

Figure 5-7 Single collector efficiency ($\eta_T$) based on DAF model by Edzwald, 1995 vs particle diameter; $d_B = 20$ µm; $\rho_P = 1.77$ g L$^{-1}$.

For electrocoagulation $\eta_T$ was dominated by Brownian diffusion for particles below 0.8 µm. Above this level, both interception and sedimentation together controlled particle removal for the electrocoagulation conditions - as indicated by the close proximity of $\eta_I$ to $\eta_S$ in Figure 5-7. Whereas Edzwald (1995) ignored sedimentation, these efficiency results showed that sedimentation is important in electrocoagulation.

Note also that for the conditions in the electrocoagulation reactor, the majority of the clay pollutant was within the 0.5 - 15 µm range (refer to particle size distribution in Figure 2-5). This corresponds to the particle size range identified by Edzwald’s model for which the sedimentation and interception mechanisms are important.
Chapter 5 - Flotation

The white water collector collision model provided a useful insight to the governing mechanisms involved in electrocoagulation, identifying both sedimentation and interception as important. However, neither this model nor the population balance model provided an adequate description for the separation processes observed in electrocoagulation. Hence an alternative approach was required and electroflotation was examined.

5.4.2 Electroflotation models in literature

The only mathematical model of electroflotation was reported by Matis and Zouboulis (1995) who employed a macroscopic approach to evaluate the overall kinetics for paint removal in an electroflotation cell. They only considered pollutant removal to the surface using a first-order kinetic expression to describe the flotation process. No consideration was given to sedimentation, as the pollutant was a colloidal suspension. For electrocoagulation, both flotation and sedimentation were significant pollutant removal paths.

Clearly, no literature approach adequately describes the processes occurring in electrocoagulation and an alternative model is required.

5.4.3 Electrocoagulation models in literature

An investigation by Matteson et al. (1995) focused on the coagulation aspects of electrocoagulation. They recognized the production of electrolytic gases were significant at both electrodes but did not include flotation effects in their second-order kinetic model. Mameri et al. (1998) derived a first-order kinetic model for the removal of fluoride from water, and similarly did not include flotation effects. These modelling approaches neglected flotation and only considered the coagulation process and removal by settling. Consequently a novel approach was required to describe electrocoagulation as developed in the proceeding section.

5.5 Mathematical description of electrocoagulation

This section presents a mathematical approach that includes both flotation and coagulation. It is based on a mathematical analysis of batch electrocoagulation and uses experimental data. A concentration profile of the pollutant within the electrocoagulation reactor was required to develop the kinetics.
The concentration profiles used were derived from the dynamic mass balances (refer to Section 2.2.3). Using these results, combined with the settling experiments described earlier in this chapter, enabled concentration profiles to be estimated.

Concentrations within the electrocoagulation reactor as a function of time were calculated assuming clay settled linearly over the reaction time and all aluminium hydroxide precipitated. A typical concentration profile is shown as Figure 5-8. The total mass (clay and coagulant) floated was collected at the surface. This measured concentration is denoted $C_{\text{Surf}}$ (g/L) in the concentration profile. The mass concentration of the bulk solution ($C_{\text{Poll}}$) reflected the mass remaining in solution - that is, the difference between the mass removed, either by flotation or settling, and the mass added, either initial clay pollutant loading or precipitated aluminium hydroxide.

Figure 5-8 Typical concentration profile during electrocoagulation; $I = 1.0$ A; [clay] = 1.6 g/L.
As noted previously, approximately 41% of the pollutant mass settled before an electrocoagulation run was commenced. This mass accounted for the difference between the reported initial pollutant concentration, that is, the dry clay added to solution, and the concentration recorded at $t = 0$ in Figure 5-8 and Figure 5-9. Electrocoagulation then either enhanced or hindered settling (refer to Table 2-7) from the base case presented in Figure 5-5. As such, a linear approximation was assumed for the mass settled and denoted as $c_{\text{Base}}$ (g/L) as shown in Figure 5-8.

![Figure 5-9 Bulk solution pollutant concentration; $I = 0.25, 1.0, 2.0$ A; [clay] 0.1 - 1.6 g/L.](image)

Once again, the three electrocoagulation stages (lag, reactive and stable) are observed. During the reactive stage, the greatest change in the bulk solution is observed with the majority of the pollutant reporting to the surface. The removal rate to the surface decreases during the stable stage.
Dynamic concentration profiles for a range of pollutant loadings and operating currents were produced, as shown in Figure 5-9. The mass remaining “in solution” consistently accounted for less than 2% of the total mass, indicating tight closure of the mass balances. At low initial pollutant loading (0.1 g/L), the concentration profile in Figure 5-9 was essentially flat.

The dynamic concentration profiles extracted from the electrocoagulation reactor’s experimental data provided the basis for the kinetic analysis in the following section.

### 5.5.1 Development of kinetic analysis of electrocoagulation

In this electrocoagulation reactor, the clay pollutant was either removed by sedimentation or flotation. Various kinetic approaches are available that could describe electrocoagulation. These include irreversible reactions occurring in parallel, shifting-order kinetics (e.g. Monod kinetics) and autocatalytic kinetics for various reaction orders (Levenspiel, 1999). A shifting order kinetic expression describes a change in the order of the reaction kinetics, with the system behaving differently at different concentrations. This produces a similar concentration profile to the surface concentration ($c_{\text{surf}}$) in Figure 5-8 but fails to include a congruent process, such as settling, observed in electrocoagulation. The autocatalytic approach assumes a synergistic interaction between the species, which does not occur in electrocoagulation.

Pollutant removal in electrocoagulation is a competitive process between flotation and settling and the removal kinetics need to reflect this competition. The relationship between separation processes can then be mathematically described by two irreversible reactions in parallel (Levenspiel, 1999): flotation (Equation E-12 - removal to the surface) and sedimentation (Equation E-13 - removal to the base). The controlling parameter here was the electrical current, as it determined both the production of coagulant (for aggregation) and bubbles (for flotation) (Holt et al. 2001).

$$\text{Pollutant}(c_{\text{Poll}}) \xrightarrow{k_1} \text{Surface}(c_{\text{Surf}}) \quad (E5-12)$$

$$\text{Pollutant}(c_{\text{Poll}}) \xrightarrow{k_2} \text{Base}(c_{\text{Base}}) \quad (E5-13)$$
Assuming the pollutant in the bulk solution (\( C_{\text{Poll}} \)) follows first-order removal kinetics to either the surface (\( C_{\text{Surf}} \)) or the base (\( C_{\text{Base}} \)) of the reactor, rate equations for each process can be expressed in terms of their concentrations:

\[
-r_{\text{Poll}} = -\frac{dc_{\text{Poll}}}{dt} = k_1 c_{\text{Poll}} + k_2 c_{\text{Poll}} \quad (E5-14)
\]

\[
= (k_1 + k_2) c_{\text{Poll}} \quad (E5-15)
\]

\[
r_{\text{Surf}} = \frac{dc_{\text{Surf}}}{dt} = k_1 c_{\text{Poll}} \quad (E5-16)
\]

\[
r_{\text{Base}} = \frac{dc_{\text{Base}}}{dt} = k_2 c_{\text{Poll}} \quad (E5-17)
\]

where \( c_{\text{Poll}} \) is the concentration of the pollutant in the bulk solution while \( c_{\text{Surf}} \) and \( c_{\text{Base}} \) are the theoretical “concentrations” at the surface and at the base, respectively. “Concentrations” at the surface and base were not realistic quantities but rather describe the time variation at the two “collector stations” – surface and base. Thus, a series of ordinary differential equations can be used to describe the separation behaviour of the electrocoagulation reactor.

Before any electrocoagulation induced removal can occur, the coagulant must reach a critical concentration (Holt et al. 2001). This lag time (\( t_{\text{lag}} \)) is dependent on current, and was identified in Section 2.3.2 as the lag stage. Thus integrating Equation E5-15 from \( t_{\text{lag}} \) to \( t \) and \( c_{\text{Poll}} t_{\text{lag}} \) (pollutant concentration at \( t_{\text{lag}} \)) to \( c_{\text{Poll}} \) produced Equation E5-18.

Note that during the lag stage there is minimal change from the concentration at \( t = 0 \).

\[
-\ln \left( \frac{c_{\text{Poll}}}{c_{\text{Poll}} t_{\text{lag}}} \right) = (k_1 + k_2) (t - t_{\text{lag}}) \quad (E5-18)
\]

Dividing Equation E5-16 by E5-17 gives,
while integrating Equation E5-19 gives,

\[
\frac{c_{\text{Surf}} - c_{\text{Surf}_{\text{lag}}}}{c_{\text{Base}} - c_{\text{Base}_{\text{lag}}}} = \frac{k_1}{k_2}
\] (E5-20)

Thus, using the available experimental data, rate constants \((k_1 \text{ and } k_2)\) could be determined from Equations E5-18 and E5-20.

### 5.5.2 Determination of rate constants

Plotting the left-hand side of Equation E5-18 against \((t-t_{\text{lag}})\), and fitting a linear regression to the data, estimates \((k_1+k_2)\), as shown in Figure 5-10. Figure 5-11 plots the “concentration” at the base against that at the surface, and by fitting a linear regression to the data estimates \((k_2/k_1)\). The combination of these two results enabled the rate constants \((k_1 \text{ and } k_2)\) to be determined.

![Figure 5-10 Evaluation of \(k_1+k_2\) for 2.0 A; [clay] = 1.6 g/L.](image)
Chapter 5 - Flotation

Figure 5-11 Evaluation of $k_2/k_1$ for 2.0 A; [clay] = 1.6 g/L.

Note that the change in slope evident in Figure 5-11 for the evaluation of $k_2/k_1$ occurred as the process switched from a reactive to stable stage.

The calculated rate constants for pollutant removal to the surface, $k_1$, and to the reactor base, $k_2$, are presented in Figure 5-12. Reproducibility of the results is shown by the four repetitions at 1.0 A and 0.8 g/L loading (triangles) and is more than acceptable to a first approximation given the challenges in obtaining concentration data as functions of time within the reactor.

Current had several effects on the electrocoagulation reactor. Firstly, it determined the coagulant addition rate through the sacrificial anode. Secondly, current determined the production rate of electrolytic gases and hence also the bubble volume concentration ($\Phi_b$). Finally, current also influenced mixing within the reactor and hence also the contact possible between individual pollutant particles, coagulant and bubbles. Thus, as
current increased, the pollutant removal rates, by both flotation and settling, were expected to increase accordingly.

![Plot showing rate constants for surface \( k_1 \) and base \( k_2 \); [clay] = 1.6, 0.8, 0.1 g/L.]

**Figure 5-12 Rate constants for surface \( k_1 \) and base \( k_2 \); [clay] = 1.6, 0.8, 0.1 g/L.**

### 5.6 Discussion of results

Generally, removal by flotation was significantly faster than by settling especially as current increased. Thus, overall the flotation constants \( (k_f) \) were approximately an order of magnitude greater than the settling constants \( (k_s) \), as seen in Figure 5-12 - the exception being at low current, where the settling constant \( (k_2) \) at 0.25 A appeared to be a function of pollutant loading. Consequently, the discussion of the estimated rate
constants is separated into two sections: low current (0.25 A) and high current (1.0 and 2.0 A).

5.6.1 Pollutant separation at low current (0.25A)

At low current the settling constants ($k_2$ ranged from $1.5 \times 10^{-4}$ to $1.5 \times 10^{-2}$) were comparable to the flotation constants ($k_1$ ranged from $5.7 \times 10^{-3}$ to $7.2 \times 10^{-3}$) - see Figure 5-12. These comparable reaction rate constants implied the removal time to either the base or surface was similar. Thus, the competing removal mechanisms occurred at a similar rate and over a similar time scale.

At low current, the number of bubbles was also low - thereby decreasing the probability of collision and interception between particles and aggregate. This low bubble number reduced the overall upward momentum flux in the reactor, resulting in reduced pollutant removal to the surface. In fact, the mass removed by flotation was small: 26% for 0.8 g/L of clay and 15% for 1.6 g/L.

At 0.25 A, separation occurred primarily via settling, and was therefore largely dependent on pollutant aggregate size. The slow hydrogen generation rate resulted in gentle mixing within the reactor and a low upward momentum flux. The low upward flux enabled the pollutant particles and coagulant to remain in solution for a longer period of time. This increased the contact time between them and enabled the growth of larger aggregates. The aggregate size was a function of both coagulant and pollutant concentrations, and the probability of collision and attachment between these two as described by the Smoluchowski equation (see Section 4.2.3). Thus, as the pollutant concentration increased (from 0.1 to 1.6 g/L), the probability of collision between pollutant particle and coagulant increased. Consequently, larger aggregates formed and settled faster, resulting in a faster removal rate as pollutant loading increased and hence an increase in the settling removal constant ($k_2$) at low currents.

5.6.2 Pollutant separation at high current (1.0 and 2.0 A)

Increased current has two impacts, that is, the formation of larger aggregates and increased removal by flotation. For an initial pollutant loading of 1.6 g/L, the settling rate constant ($k_2$) increased from $7 \times 10^{-3}$ to $1 \times 10^{-2}$ as the current doubled from 1.0 to 2.0 A. For the same pollutant loading (1.6 g/L), the rate constant at the surface ($k_1$)
increased from 0.05 to 0.16 as current was doubled (from 1.0 to 2.0 A). Thus the reaction rate constants increased as current increased, as expected.

For pollutant separation at these higher currents, the measured flotation rate constants ($k_1$) were approximately an order of magnitude greater than the settling constants ($k_2$) (see Figure 5-12). At higher currents, flotation was the dominant removal path as also observed in the mass balance results in Section 2.3.3.

Electrolytic bubble production rate increased as current increased. This increased the bubble volume concentration ($\Phi_b$), which in turn increased the probability of a bubble intercepting an aggregate. Also as current increased, so did the coagulant addition rate, thereby increasing the collision probability between coagulant and pollutant particles resulting in the formation of larger aggregates, which could then be removed more easily. Thus both, settling and flotation occurred more quickly due to the increased coagulant concentration and bubble concentration.

Flotation did not differentiate between the mass removed. Thus both coagulant and pollutant were floated to the surface. As current increased, not only did the coagulant addition concentration rate increase but also its removal rate increased. This decreased the contact time available between the coagulant and pollutant species (both primary particles and aggregates) and hence also the coagulant’s efficiency. Operation at higher currents thus resulted in faster removal time but decreased efficiency.

Critical parameters can be related to cost. Operating current determined power consumption that is electricity, and electrode consumption rates and hence operating costs. A longer removal time requires larger reactor volume and hence higher capital plant equipment cost. A trade-off exists between and current and time to design the most economical solution for a specific application.
5.7 Chapter conclusions

Conventional flotation models, such as for DAF units, were inadequate to describe pollutant removal by this electrocoagulation reactor. Thus a novel method using ordinary differential equations was developed to describe the pollutant’s settling and flotation behaviour respectively.

At low current (0.25A), sedimentation dominated with slow release of coagulant and gentle agitation provided by low bubble production. Removal was slow and hence the low rate constants calculated were appropriate. At high currents (1.0 and 2.0 A) faster removal occurred due to greater bubble density. This resulted in greater mass floated to the surface and higher rate constants were observed. Thus the developed rate equations successfully quantified the reactor’s performance over a variety of conditions.

Here, pollutant removal paths were investigated and quantified. Previously and separately, electrochemical mechanisms (Chapter 3) and coagulation and aggregation mechanisms (Chapter 4) were investigated in detail. The next chapter synthesises these into the overall electrocoagulation process.
6 Synthesis

Electrocoagulation has evolved in the course of this thesis from an empirical (and largely heuristic) technology to one with a firm scientific understanding and a promising future. It would be fair to say that for most (if not all) previous workers were limited by a lack of understanding of its fundamentals. This thesis has examined the technology’s status and developed a methodology to identify and unravel the scientific basis of electrocoagulation (Chapter 1). This methodology was then implemented throughout Chapters 3 – 5, with each foundation science (electrochemistry, coagulation and flotation) examined for a batch electrocoagulation reactor. The interactions of these sciences describe electrocoagulation. This chapter seeks to synthesise the understandings from each foundation science to enable the future development of electrocoagulation as a water treatment technology.

The technology status and the methodology developed for understanding and advancing electrocoagulation are reiterated in Section 6.1. The key impacts of each scientific basis on electrocoagulation are highlighted in Section 6.2 and synthesised in Section 6.3. A new conceptual framework for the model of electrocoagulation is then presented and its implications discussed in Section 6.4.

6.1 Technology status

Electrocoagulation has been repeatedly discovered, forgotten, and then rediscovered. Along the way, electrocoagulation has been successfully applied to a wide range of pollutant types (Section 1.2.1) in an even wider range of reactor designs (Section 1.3). These independent demonstrations prove the viability of the technology but fail to understand its underlying mechanisms and consequently also fail to advance the technology. Electrocoagulation’s evolution to date can thus be categorised as essentially empirical and heuristic.

This thesis identified the present empirical approach and its failure to advance electrocoagulation. A systematic and mechanistic approach was advocated as the only way to advance electrocoagulation. A methodology based on a firm scientific foundation was developed to evolve the technology. This distinguishes from past
research of electrocoagulation, marking the beginning of new phase in the research evolution of electrocoagulation.

6.2 Technology understanding

This thesis has stressed that a fundamental understanding of electrocoagulation was required. To gain this, a systematic approach was developed to examine the mechanisms controlling electrocoagulation based on its fundamental sciences, as shown in Figure 6-1.

![Diagram of systematic approach to research electrocoagulation]

Initially a macroscopic experimental approach was used to identify the key parameters in a batch laboratory-scale electrocoagulation reactor. This reduced the degrees of freedom for investigation to current and time. These two parameters were then investigated with respect to each of the foundation sciences.

Each foundation science (electrochemistry, coagulation and flotation) was studied separately. This examination of electrocoagulation’s fundamentals enabled the
dominant mechanisms to be identified in each case. The key results are briefly explored in the following sections.

6.2.1 Electrochemistry

Electrochemistry forms the basis of all electrocoagulation reactors and hence is the key foundation science. Coagulant and electrolytic gas generation rates are both determined by the electrochemical reactions occurring at the relevant electrodes. Both production rates are a function of current and time as described by Faraday’s Law.

The electrochemical studies enabled prediction of coagulant and bubble generation, as well as the cell potential required. The batch electrocoagulation reactor was operated galvanostatically, that is, at constant current with the potential varying as required. The cell potential is a function of the total resistance (i.e. that due to the solution, junctions, surface, etc), as well as the overpotentials required. The latter is primarily a function of the rate limiting processes at the electrode surface.

Polarisation experiments revealed a shifting mechanism at the electrode’s surface. Potential requirements within the charge transfer-limited region were predicted from experimentally measured Tafel parameters. As current density increased, diffusion processes at the electrode surface became more significant. This increased the overpotential required for a desired current density, and hence the power and energy requirements.

Thermodynamic speciation modelling characterised the aluminium behaviour and the solution speciation. Coagulant generation occurred at the anode with the subsequent step being aluminium hydrolysis. Formation of polynuclear species and solution pH determined the active coagulant species released \textit{in situ} to interact with the pollutant. Application of thermodynamic modelling to electrocoagulation is novel providing a unique insight to the active coagulant species.

6.2.2 Coagulation

Coagulation describes the aggregation of pollutant particles and growth of such aggregates. Larger aggregates are easier to remove (either by flotation or sedimentation), and hence coagulation was desirable. Electrocoagulation behaviour was
not merely alum dosing with an alternative coagulant addition method. The continued aluminium addition and hydrolysis kinetics contributed to active coagulant delivered *in situ*. For electrocoagulation, the coagulation mechanisms were dependent on the coagulant concentration, as determined by current and time, the solution characteristics, pollutant concentration and its physical chemical properties, and their interactions. The very nature of electrocoagulation, that is, only the addition of a hydrolysed metal cation, limited the possible aggregation mechanisms to being diffusion or reaction limited. Here diffusion refers to the formation of loose aggregates that are limited by diffusion processes in the bulk solution. Reaction refers to the attachment and adhesion of the pollutant and coagulant as the rate limiting step, resulting in the formation of compact aggregates.

Electrolytic bubbles produced at the cathode induced mixing and flotation in the batch reactor. Contact between coagulant and pollutant particles is essential for adequate aggregation. This contact was largely determined by the solution mixing and coagulant concentration, induced by electrolytic gas formation also a function of current. As current increased, removal time decreased due to faster pollutant removal (and hence also coagulant). This decreased the contact time between the coagulant and pollutant, which resulted in decreased coagulant efficiency.

Three reaction stages (lag, reactive and stable) were identified in the batch reactor. No pollutant removal was observed in the lag stage while the coagulant (that is hydrolysed aluminium) concentration increased with time. The majority of the pollutant removal occurred during the reactive phase. During this phase, the fractal dimension of the aggregates indicated an open structure, inferring that the aggregates were formed via a diffusion limited cluster-cluster aggregation mechanism. Also during the reactive stage, the isoelectric point was attained. Together, that is, the loose structure of the floc (low fractal dimension) and the isoelectric point; infers a sorption coagulation mechanism, most likely charge neutralisation.

As time progressed and the stable stage began, the pollutant removal rate decreased. The zeta potential increased and the aggregates were characterised as being more compact (higher fractal dimension of 2.4), inferring a reaction limited cluster-cluster mechanism was dominant. Precipitation of the coagulant as aluminium hydroxide/oxide
was thermodynamically favourable and hence predicted in this stage as pollutant removal continued. A sweep coagulant mechanism was postulated as the dominant coagulation mechanism in this last stage.

These studies identified key mechanisms for the coagulation behaviour. The relationship between the reaction time, reaction stage and the coagulation were explicit hence enabling a predictive mathematical expression, such as the Smoluchowski equation, to describe the aggregation behaviour.

### 6.2.3 Flotation

The final step of electrocoagulation is pollutant removal. This is a function of the aggregate’s size and structure, and the reactor conditions particularly the mixing and uplift. In this batch electrocoagulation reactor, separation occurred *in situ*, so aggregated pollutant either floated or settled. Flotation was an inherent aspect of this reactor, with the production of hydrogen at the cathode an integral aspect of the electrochemical reactions. Hydrogen generation released bubbles into the reactor proportional to operating current. Hence, the potential for flotation was directly proportional to the operating current.

Pollutant removal by flotation is a function of the bubbles formed and their interaction with the aggregate. Operation at low current suited settling with the slow release of coagulant in quiescent conditions. As the bubble volume concentration increases with current density, the probability of interception between aggregates and bubbles also increases. This interception results in pollutant removal by flotation to the surface. Additionally, higher current also increased the coagulant concentration. This trend was reflected in the increased of both the flotation and settling rate constants ($k_1$ and $k_2$) calculated when electrocoagulation was analysed as a pair of parallel competing reactions.

Overall, the operating current and removal time were again identified as key parameters, determining both the coagulant and electrolytic gas production rates. This in turn determined the “availability of coagulant to the pollutant” and the bubble volume concentration in the reactor. Current and time thus interlink the removal paths and mechanisms creating an inherently interconnected system.
### 6.3 Technology advancement

This section examines the interactions between each foundation science, with the aim of developing the technology. All three sciences, electrochemistry, coagulation and flotation, are intrinsically connected. Two key parameters, operating current and time (both removal and contact time) are critical for all sciences in this batch electrocoagulation reactor.

#### 6.3.1 Interaction of foundation sciences

This thesis characterises electrocoagulation as a technology at the intersection of three foundation sciences (electrochemistry, coagulation and flotation).

To examine the interactions occurring within batch electrocoagulation, the path of a single aluminium cation was examined - as is shown schematically in Figure 6-2. The aluminium cation is electrochemically generated in situ from the sacrificial anode. The electrode processes at the surface determine the rate limiting process (charge transfer or diffusion) for the generation of this cation.

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**Figure 6-2 Mechanistic summary of electrocoagulation.**
The aluminium cation hydrolyses in the bulk solution, with its speciation dependent on pH and total aluminium concentration. Over time, it has the possibility to form various mono- and poly- nuclear species. The longer an aluminium cation remains in solution, the greater the probability of oligomer formation (the base unit of any polynuclear species) – noting that the oligomer has quite slower formation kinetics. Eventually, over time and as total aluminium concentration increases, so the aluminium precipitates as a hydroxide or oxide. The dynamic changes in the aqueous speciation of aluminium dictates the coagulant’s availability and its physical form, and hence the dominant coagulation mechanism.

The introduction of the aluminium cation induces coagulation through a variety of mechanisms. Larger aggregates are formed as the aluminium coagulant, in its hydrolysed form, interacts with the pollutant. Aluminium cations added during the reactive phase also contribute to the charge neutralisation of pollutant particles as the isoelectric point is attained. Here a sorption coagulation mechanism exists resulting in formation of loose aggregates.

Aluminium cation added during the stable stage precipitates, which contributes to pollutant aggregation via an enmeshment mechanism (sweep coagulation). This mechanism entraps the pollutant particles in the amorphous aluminium hydroxide/oxide and results in the formation of tightly bound aggregates. So the coagulant’s role changes over time as the pollutant concentration decreases.

The final stage is pollutant removal - where the coagulated aggregates interact with bubbles or settle. If sufficient bubbles are present and attach to the aggregate, then the aggregate floats to the surface. Otherwise the aggregate settles to the reactor base.

The sequential explanation of electrocoagulation assists the understanding of the overall process and exemplifies electrocoagulation’s inherent interconnectedness. The common links here are the operating current and operating time. All pollutant removal mechanisms and stages are dependent on operating current and/or time as highlighted in Figure 6-2. The dominant removal mechanisms shift with current, time and pollutant concentration.
6.4 A conceptual model of electrocoagulation

Analysis of each foundation science identified the relevant mechanisms, and hence an appropriate mathematical model or description. Electrocoagulation performance can thus be described mathematically (at least to a first approximation). As current density increases, so the pollutant removed per unit of coagulant added (i.e. efficiency) decreases. These changes can now be described mathematically. To conceptualise the interactions the relationship between the change in the reactor’s performance and the relevant mathematical descriptors is made explicit in Table 6-1.

Table 6-1 Electrocoagulation performance summary

<table>
<thead>
<tr>
<th>Operating current density</th>
<th>Coagulant &amp; bubble concentration</th>
<th>Potential requirements</th>
<th>Probability of coagulant &amp; pollutant contact</th>
<th>Removal rate &amp; path</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Fast (Flotation)</td>
</tr>
<tr>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>Slow (Settling)</td>
</tr>
<tr>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Mathematical description</td>
<td>Faraday’s Law</td>
<td>Tafel expression</td>
<td>Smoluchowski equation - (probability of collision $\beta$)</td>
<td>DAF models, Stokes’ Law and path removal kinetics</td>
</tr>
<tr>
<td>→</td>
<td>Law</td>
<td>&amp; diffusion limiting expression</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This is the first fully integrated mechanistic approach of electrocoagulation. As the current density increases, so do the bubble and coagulant concentrations, and the cell potential required – and hence the probability of collisions between coagulant and particles. Also flotation is favoured as the removal path with a higher rate constant. This table highlights how the mechanisms combine. Thus Table 6-1 builds a framework for the development of a conceptual model of electrocoagulation.

A conceptual model of electrocoagulation is now possible and is presented as a flowsheet in Figure 6-3.
Faraday’s Law adequately describes the coagulant and bubble generation rates, while the overpotential required can be predicted from Tafel expressions. Hence, the power and energy consumption can be predicted for a given set of electrochemical equations.

From the coagulant concentration and the operating potential, thermodynamic modelling based on the Nernst equation details the electrode’s surface behaviour. Thermodynamics provides an insight to the electrode chemistry and hence the dissolution characteristics of the anode. It also provides an equilibrium-based description of the solution chemistry. The dominant hydrolysed aluminium species (or an aluminium precipitate) then acts as a coagulant, aggregating the pollutant.

**Figure 6-3 Flowsheet of conceptual electrocoagulation model.**

<table>
<thead>
<tr>
<th>Generation</th>
<th>Hydrolysis</th>
<th>Flocculation</th>
<th>Settling</th>
<th>Combination</th>
<th>Flotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faraday’s Law</td>
<td>Nernst Equation</td>
<td>General Equation</td>
<td>Stokes’ Law</td>
<td>e.g. overall kinetics</td>
<td>e.g. DAF model</td>
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<tr>
<td>$r_{H_2} = \frac{l \times MW}{ZF}$ g H$_2$ s$^{-1}$</td>
<td>$E = -\frac{\Delta G^0}{ZF} - \frac{RT}{ZF} \sum \nu_i \ln c_i$</td>
<td>$r_{\text{flocculation}} = \alpha \times \beta(i,j) \times c_i \times c_j$</td>
<td>$u_p = \frac{gd_p^2(p_p - p_W)}{18\mu}$</td>
<td>$-r_{\text{Poll}} = \frac{dc_{\text{Poll}}}{dt} = c_{\text{Poll}} (k_1 + k_2)$</td>
<td>Populaton balance turbulent model</td>
</tr>
<tr>
<td>$r_{\text{Al}^{3+}} = \frac{l \times AW}{ZF}$ g Al$_3^+$ s$^{-1}$</td>
<td></td>
<td>Smoluchowski equation</td>
<td></td>
<td>$r_{\text{Surf}} = \frac{dc_{\text{Surf}}}{dt} = k_1 c_{\text{Poll}}$</td>
<td>White water collector collision model</td>
</tr>
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<td></td>
<td></td>
<td>$\frac{dn_k}{dt} = \frac{1}{2} \sum \beta(i,j) n_i n_j - \sum \beta(i,k) n_i n_k$</td>
<td></td>
<td>$r_{\text{Base}} = \frac{dc_{\text{Base}}}{dt} = k_2 c_{\text{Poll}}$</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Probability of collision between coagulant and pollutant particles.</td>
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</table>
Once a coagulant is present, aggregation and flocculation occur. Particle aggregation can be described by collision and attachment probability expressions such as the classical Smoluchowski equation (Thomas et al., 1999). These aggregates can then be removed by flotation, setting, or a combination.

The systematic study of electrocoagulation, its foundation sciences and their interactions enabled the development of this framework. The separation of the electrocoagulation into its foundation sciences and the subsequent extraction of key mechanisms enabled relevant mathematical expressions to be proposed. This conceptual framework links (for the first time) these key mechanisms of electrocoagulation together. This enables the mathematical description and consequently evaluation of each aspect and each interaction. Thus the key outcome of this chapter is the development of the conceptual framework of electrocoagulation.

6.5 Technology future

Electrocoagulation can now be examined systematically and (semi-) quantitatively. The complexity of the system is recognised but is no longer as great a hindrance as in the past. This complexity is being understood by a reductionist approach advocated and developed in this thesis. This removes the mystic from electrocoagulation.

Electrocoagulation is now becoming a predictable technology. Predictability requires the relationship between operating parameters and impact on performance to be known. The conceptual framework provides the foundations for the development of a generic electrocoagulation model by establishing the links between the operating parameters and performance.

This newfound predictability enables insights for the future design and operation of electrocoagulation reactors. Several key insights include:

- Ability to transfer knowledge from a batch to a continuous system;
- Efficient use of coagulant, and;
- Desired separation – flotation or settling.
This is no coincidence that the key insights reflect similar issues as the design hierarchy developed for electrocoagulation in Section 1.3.1. To recap, the reactor design decision hierarchy are summarised as follows:

1. Batch or continuous operation;
2. Coagulation only or coagulation and flotation reactors and;
3. Chosen separation process.

Each design decision can now be revisited in light the advances from this thesis and the conceptual framework of electrocoagulation. These issues can now be treated *a priori*, at least at a semi-quantitative level. This is a tremendous advance on the development of electrocoagulation. Each issues is now considered in more detail.

Previously, it has been difficult to scale from batch to continuous electrocoagulation systems. By systematically breaking electrocoagulation into segments, it is now far easier to transfer batch information and apply the key results to a continuous system. For example, optimal operational operating conditions can be obtained from the batch reactor’s dynamic concentration profile. In the batch system investigated, maximum pollutant removal rate occurs during the reactive phase that corresponds to the isoelectric point. These criteria identify and establish the optimal operating conditions for a continuous reactor hence providing useful and practical insights for continuous operation.

As demonstrated the knowledge transfer (from batch to continuous systems) is applicable even without a detailed mathematical model. If a validated model is available, then the mathematical analogy between batch and continuous systems is even easier.

The relationship between coagulant usage and the role of electrolytic gases was not fully understood or appreciated in the past. Often researchers were more interested in the apparent novelty of an electrocoagulation system than the actual manner the coagulant was used. The research in this thesis has shown that efficient coagulant usage is dependent on the coagulant’s contact time within the reactor. Contact time is directly related to the operating current, which also determines the production of electrolytic bubbles and hence influences both flotation and mixing. For efficient coagulant usage, electrocoagulation reactors should be designed for high contact times and thus operated
at low currents. This slowly releases coagulant into a virtually still reactor ensuring adequate contact time and hence high coagulant efficiency. Once again, prediction of electrocoagulation’s response informs the reactor design.

Earlier designs for pollutant separation were ad hoc and often an afterthought. Frequently an additional unit operation was added to remove the pollutant. By quantifying the trade-off for the competing removal processes (i.e. flotation and settling) within the batch reactor and their relationship to the operating current, the desired pollutant removal path can be predicted. Hence the electrocoagulation can be designed to removal predominately the surface or the base, as desired, and an additional separation unit operation may be unnecessary.

Additional design issues, such as selecting the most appropriate coagulant and hence electrode material, economic analysis (trade-off between operating cost (electrical energy) and reactor volume), or evaluation of a pretreatment step (e.g. adjust influent pH) can now be more readily evaluated.

An understanding of all these interconnected issues outlined in the discussion above is required for successful scale-up and hence industrial application. By treating electrocoagulation as a set of interacting processes, informed and predictable (at least to some degree) reactors can be designed. The conceptual framework of electrocoagulation provides a useful design tool to inform construction of advanced reactors.
7 Conclusions and Recommendations

7.1 Conclusions

Electrocoagulation is a compact and reliable technology that has considerable potential for water reuse, which is vital for a sustainable future. As a first step, the technology status was reviewed, revealing an empirical (and largely heuristic) approach to the study of electrocoagulation. This approach failed to explain its key features, thereby limiting the technology’s advancement. This thesis developed a new methodology within which to research electrocoagulation. A systematic approach was advocated based on electrocoagulation’s foundation sciences:

1. Electrochemistry;
2. Coagulation, and;
3. Flotation.

Each science provides a firm basis for the mechanistic study of some key element of electrocoagulation. The interactions of all these sciences constitute electrocoagulation. The complexity of electrocoagulation lies within these interactions, which are only now beginning to be understood.

A conceptual framework of the overall electrocoagulation process was developed that synthesises the key mechanisms (see Figure 7-1). This conceptual framework links coagulant generation, coagulant hydrolysis, pollutant aggregation, and pollutant removal (either by flotation or settling). This framework forms the basis for a scientific understanding of electrocoagulation and a way forward for its use in a diversity of situations.

The methodology developed in this thesis was systematically implemented on a 7 L batch electrocoagulation reactor. Dynamic mass balances were conducted over the reactor leading to the construction of a concentration profile of the batch process. These profiles were used to unravel the dominant separation mechanisms as a function of time and current.
Coagulant generation occurred \textit{in situ} by the dissolution of the aluminium anode at a rate predicted by Faraday’s Law, while cell potential increased as the operating current density increased. This resulted in a shift from a charge transfer limited process, to one where diffusion processes at the electrode’s surface were also significant. Coagulation mechanisms also shifted, from a sorption to an enmeshment mechanism as time progressed and pollutant concentration decreased. A pair of kinetic expressions was developed to quantify the pollutant separation paths. Reaction rate constants were calculated on the basis of two irreversible reactions occurring in parallel (that is, settling and flotation) within the batch reactor.
As noted, it is the interactions between all these mechanisms that constitutes electrocoagulation. Consequently, the contact patterns within the reactor between all species greatly influence pollutant removal effectiveness. As the operating current increased, so the coagulant and bubble volume concentrations increased. This resulted in faster removal (as evidenced by higher rate constants as the current increased), a trend that was offset by decreased coagulant efficiency. Consequently, a trade-off existed between the removal time and coagulant usage – a situation that can be optimised (using economic analysis) for each electrocoagulation reactor design.

This thesis thus provides the conceptual development and experimental justification that has begun to unravel the science behind electrocoagulation. For the first time, the foundation sciences are explicitly linked to provide a sequential explanation of the processes occurring in electrocoagulation.

Advanced electrocoagulation reactor designs can now be produced from a firm scientific basis. This scientific basis can now be used to continue the technology of electrocoagulation to advance.

### 7.2 Recommendations

Recommendations for future research into electrocoagulation are divided between two sections. The first examines the potential for technology advancement (depth), while the second section considers the research required for technology applications (scope).

#### 7.2.1 Recommendations for technology advancement

This thesis has demonstrated that the interactions between all species within the reactor are vital to understanding electrocoagulation. To improve this understanding, further refinement and development of the conceptual model presented in this thesis is required. This should aim to further quantify both the key mechanisms in electrocoagulation and their interactions.

For example, the pollutant removal kinetics developed only described the competing removal processes to a first approximation. The kinetic behaviour appears to shift between the reactive and stable stages. Additionally, the rate constants extracted appear to be a strong function of the current and hence the kinetic expression should be refined.
This study also recognised the importance of the contact patterns within the electrocoagulation reactor. Bubble driven mixing determines the contact pattern within the reactor and this can be examined in more detail, for example, using a computational fluid dynamic (CFD) modelling package (such as CFX) to solve the Navier-Stokes equations. Hence, optimal fluid conditions (and also optimal current) within the reactor can be established.

Reactor design now has a far firmer scientific framework to build upon. To develop more sophisticated reactor designs, a greater understanding of the contact patterns is required. This can be also undertaken by study computational fluid dynamic (CFD) where complex flow patterns can be quantified and associated contact patterns can be assessed. This enables the interaction with reactor geometry to be assessed and thus optimal geometric designs to be determined for electrocoagulation reactors.

For successful industrial application of electrocoagulation, quantitative scale-up from batch laboratory scale is required. Key independent scale-up parameters must be identified to ensure dimensional consistency between small and large-scale processes. Development of dynamic and geometric models, as recommended, will assess this evaluation. Additionally the detailed understanding and knowledge gained from batch systems can be applied to continuous systems as advocated throughout this thesis.

7.2.2 Recommendations for the research breadth

To refine the operable regions for electrocoagulation, a sensitivity analysis will refine the system’s response to current and pH. A change in the operating current may affect coagulation mechanisms and thus the relationship between changing currents to coagulation mechanisms may provide valuable insights to the system’s response. Additionally, investigation at defined pH values (rather than allowing electrocoagulation to vary pH) will further refine the operable pH range relationship to associated coagulation mechanisms.

The experimental methodology developed in this thesis can be applied to assess the suitability and gain an insight to the mechanistic processes for other pollutant types. Consequently the generic framework for a model of electrocoagulation can be used to
assess electrocoagulation suitability to other pollutants (types and concentrations) and hence advance the technology’s application.

Development of advanced electrode materials and application of different electrode types (e.g. bipolar electrodes) brings a new dimension to electrocoagulation. Different electrode material can be used to assess different coagulant types for specific pollutants. For example the use of iron will produce ferric ions that are readily used in the water industry. Electrode operation, such as periodic polarity reversal, controls passivation formation \textit{in situ}. Development of sophisticated electrode arrangements and associated operation programs lead to significant developments for passivation control.

There is also ample opportunity for additional electrochemical characterisation of electrocoagulation. For example, experimental determination of oxygen overpotential will establish the operating cell anodic potential limit. This will refine the operable electrocoagulation region.

Pollutant removal efficiency by flotation is influenced by the bubble size. The assumption of a constant bubble diameter should be investigated along with the bubble size distribution as a function of operating current. The bubble size may influence the flotation mechanism (entrapment or entrainment). This determines how the bubbles interacts with the pollutant and consequently directs future reactor design and operation to improve separation efficiency. Additionally, the bubbles charge or the zeta potential should be quantified with time and its interaction with applied electric field. The charge of the bubble and its interaction with the system may also have some bearing of pollutant removal by flotation. Detailed knowledge of bubble characteristics will enable a better evaluation of the role of electrolytic bubbles in pollutant removal and hence enable the design of a more effective electrocoagulation reactor.

\section{The last word}

Prior to this study, electrocoagulation was largely characterised by a very disparate collection of processes and designs. The quantitative understanding produced in this thesis has progressed electrocoagulation from an empirical process to one based on a much firmer scientific foundation with the result that it now has a promising future as a viable alternative in the field of water treatment.
8 References


Outokumpu (1999) Outokumpu HSC Chemistry for Windows; Chemical reaction and equilibrium software with extensive thermochemical database., Outokumpu Research Oy, Finland.


Appendices