# The Development and Evaluation of a Donnan Dialysis Process for the Recovery and Reuse of Aluminium from Potable Water Treatment Residual Streams

Report to the
**Water Research Commission**

by

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# EXECUTIVE SUMMARY

## BACKGROUND

Aluminium (Al) salts, particularly aluminium sulphate (alum), are widely used as a coagulant in large scale potable water treatment plants. The resultant precipitate sludges are currently discarded to evaporation ponds or to landfill sites. There would be significant benefits to the costs of water treatment plants, the preservation and optimal use of natural resources, and the protection of the environment if Al could be recovered from the waste sludge, recycled and reused in coagulation. However, whilst there have been concerted efforts to do so over many years, the recycle and reuse of aluminium has proven to be extremely difficult. Digestion of the sludge to recovery Al, with an acid or a base, results in co-digestion of organics and hence the digested solution cannot be directly reused as a coagulant. Conventional pressure driven membrane processes have also been only partially successful, mainly due to the difficulties in separating small organics from the Al solution, and the obvious membrane fouling.

Donnan Dialysis (DD) is a relatively new technology in the water treatment field. DD uses a cation-exchange membrane, i.e. a membrane that will allow only positively-charged ions to pass through but blocks the passage of negatively-charged and un-charged species. Hence DD could potentially enable Al to be recovered from a waste stream that contains Al, organics, other contaminants, etc. without the recovered stream being contaminated with organics. In the simplest application of DD, the contaminated Al stream flows along one side of the membrane (feed), while an acid solution flows along the opposite side (sweep). Due to the difference in chemical potential, $Al^{3+}$ ions diffuse from the feed to the sweep, while $H^+$ ions diffuse from the sweep to the feed. Colloids or organics cannot pass through the membrane (in theory). The driving force is a difference in chemical potential, so there is no "pore fouling" like in UF/MF/RO (in theory). The evaluation and testing of a DD for Al recovery from water treatment residue streams forms the topic of this project.

## PROJECT AIMS

The Aims of this project were as follows:

(1) To investigate and identify the important engineering and geometric variables that determine Al recovery in a Donnan Dialysis (DD) cell. Hence, to determine a regime map of geometry and operating variables for a DD cell module that could be upscaled.

(2) To develop, construct and evaluate a design for an "industrial" DD cell module that could be upscaled for application in large scale potable water treatment works.

(3) To evaluate the performance of the new module design in terms of Al recovery, operability and fouling, and to estimate the cost benefits of recovering and reusing Al.

(4) To create expertise in DD in at least two South African universities.

## METHODOLOGY

Following a literature survey of the DD process, a test cell and an experimental rig were designed and constructed. The performance evaluation initially used a synthetic solution of aluminium sulphate as the feed, and sulphuric acid as the sweep. A v*alidation investigation* was conducted to validate the experimental apparatus, protocol and analytical methods in terms of concurrence with literature, repeatability and closure of mass balances. Thereafter a scanning *investigation* was performed at similar operating conditions to that reported in previous DD literature. From this the typical performance profiles for a DD were identified and confirmed, and effects of main operating variables were identified. Next, more realistic operating conditions were selected, based on what would be feasible for an industrial process. Then an o*ptimisation investigation* was performed to determine the maximum performance that could be obtained in terms of Al recovery and final Al concentration when operating at these 'realistic' conditions. Both the scanning and the optimisation investigations used a synthetic aluminium sulphate solution as the test feed, to facilitate direct control over the Al concentration and ensure repeatable feed streams for the investigations. Thereafter an *organics rejection* investigation was performed, to specifically answer the question of whether Al could be selectively recovered from a water treatment residual stream. The feed stream for this was obtained by acid digestion of dry water treatment residual sludge obtained from an evaporation pond. Subsequently a *fouling investigation* focussed on whether the presence of organics affected membrane performance in any way. Finally, the cost impact of current Al practices was briefly reviewed.

## RESULTS AND DISCUSSION

### Validation Investigation

Results were repeatable to within 5%, and mass balance closures were > 90%, validating the equipment, the operating protocol and the analytical procedures.

### Scanning Investigation

Scanning investigations were performed using relatively high feed Al concentrations (2000 mg/L to 3000 mg/L) and sweep acid concentrations (1 M to 2 M sulphuric acid). These scans were primarily to compare the form of feed and sweep concentration profiles with that reported in literature, and to identify the main operating parameters. It was found that osmotic transport of water from the feed side to the sweep side played an important role in the form of the sweep Al profile. Typically, the sweep Al concentration would increase rapidly, level off, and then decrease slightly, when the dilution effect of osmosis exceeded the transport of Al ions to the sweep. In most runs the sweep concentration profile appeared to be quite unstable just before it levelled off or decreased. Rather than being 'experimental error', it seems that this might be a real phenomenon, possibly arising from the osmotic effect. It was found that the feed flowrate, initial sweep acid concentration and initial feed Al concentration were the main parameters that controlled performance, with the sweep flowrate playing a lesser role.

### Determination of realistic operating conditions

The scanning runs were performed at high initial feed Al concentrations and high initial sweep acid concentrations in order to facilitate comparison with literature. However, these conditions were regarded as being too extreme for any real industrial process. In practice, the Al concentration of a read feed obtained from acid digestion of sludge would range from ~ 300 mg/L to about 600 mg/L. From the point of view of materials of construction and safety, acid concentrations should be kept below 0.5 M. A short investigation into the osmotic effect indicated that hydrochloric acid would result in less of an osmotic effect than sulphuric acid. Accordingly, it was decided that the next stage of the project should proceed under these 'realistic' conditions, i.e. an initial feed Al concentration of 200 mg/L to 700 mg/L, and initial sweep acid concentrations of 0.25 M to 0.75 M hydrochloric acid.

### Optimisation Investigation

A matrix of feed flowrate, initial feed Al concentration and initial sweep acid concentration were investigated to determine their effects on performance. The criteria selected as the performance variables were the final sweep Al concentration and the Al recovery, defined as the fraction of Al in the initial feed that was recovered to the sweep. In the optimisation investigation, the osmotic effect was negligible, and the concentration profiles were substantially more stable than the scanning investigation. The optimisation investigation indicated that feed flowrate and initial sweep acid concentration had marginal effects on Al recovery and final sweep Al concentration, but the initial feed Al concentration has a very noticeable effect on both Al recovery and final sweep Al concentration, with lower feed Al concentrations favouring higher performance. Al recoveries ranged from ~ 40% to ~ 95%, final Al concentrations ranged from 400 mg/L to 1400 mg/L, and Al concentration factors ranged from ~ 1.1 to 3, depending on the combination of operating conditions selected.

The effect of the three operating variables on Al recovery was statistically modelled, yielding the following relationship:

$$Y_{recovery} = 212.98 - 32.65X_1 - 0.17X_2 + 28.70X_3 + 3.40{X_1}^2 - 78.78{X_3}^2 + 0.0005X_1X_2 + 0.24X_1X_3 + 0.1X_2X_3$$

where: $X_1$ is the feed flowrate (ml/s)

$X_2$ is the initial feed Al concentration (mg/L)

$X_3$ is the initial sweep acid concentration (M)

The above statistical model can be used to determine an operating point to maximise Al recovery, if one variable, e.g. initial feed Al concentration, is specified.

## Rejection of Organics

All the above investigations were performed using a synthetic aluminium sulphate feed. The next investigation focussed on real feeds, to determine whether the membrane could selectively recover Al whilst rejecting organics. Dried Al sludge from a water works evaporation pond was obtained, and digested with two concentrations of hydrochloric acid, viz. 0.5 M and 0.05 M. These digested solutions were then used as feed in DD investigations. UV 254 absorption was used as an indicator of organics concentration since the low pH made the utilisation of TOC problematic. Based on UV 254 absorption, there was a passage of organics through the membrane, however > 95% of the organics in the feed were rejected. There was an indication that the passage of organics occurred after about 30 hours of operation. Al recoveries on these digested feeds were ~ 84% (0.05 M digested feed) and ~ 40% (0.5 M digested feed).

## Fouling of membranes

In theory, membrane processes where there is no bulk liquid flow through the membrane, e.g. Donnan Dialysis and membrane distillation, should not experience any fouling. This was tested as follows: - (a) three runs were performed with a synthetic Al solution at a fixed operating point (feed flowrate, initial feed Al concentration and initial sweep acid concentration) and gave very repeatable feed and sweep Al concentration profiles; (b) the same membrane was then run on the digested feeds, i.e. containing organics; (c) the membrane was the run on a synthetic Al feed at the same fixed operating point as in (a) above. The concentration profiles and Al recovery profiles were then compared. The profiles obtained from (c) were very unstable and not very repeatable, similar to profiles obtained in the earlier scanning runs. However, there are strong indications that the rate of transport of Al after the membrane was exposed to organics is less than the rate obtained before the membrane was exposed to organics. However, the results from this project are not conclusive, and further investigations into this are necessary.

**Cost impacts of Al usage**

The project concluded with a brief overview of the cost impacts of Al usage, in order to gauge the potential value of recovering and reusing Al. There are two costs to be considered, viz. the cost of alum procurement, and the cost of handling and disposing of the sludge. In terms of procurement, the cost of the alum solution is approximately R2200 per ton. Approximately 70 kg of alum solution is per ML of water produced. Hence, the unit cost of alum solution is approximately R150/ML of water produced. In some plants disposal of waste Al sludge is done via evaporation ponds. These occupy massive areas of land, and the dried sludge will eventually have to be dug out and disposed of, when the ponds reach their solids capacity. Hence the cost of sludge disposal is very significant but is currently not given consideration in 'Al accounting' by waterworks. Other plants dispose of the sludge to landfill. The cost of this disposal is approximately R160/ML water produced. Hence the combined cost of procurement and disposal is approximately R310/ML. Considering, e.g. a water treatment plant that produces 100 ML/day, the annual usage of alum will be approximately 2500 tons of alum solution. The cost of alum procurement and sludge disposal will be approximately R11m per annum. If, for example, 50% of the Al from the sludge could be recovered and reused, this will result in a direct cost saving of approximately R5.55m per annum per 100 ML plant. Alum has a negative impact on the country's balance of payments, since the trihydrate, a starting material for alum, is fully imported. Any direct impact on the environment is difficult to quantify. In principle there should be no leaching of Al into groundwater if the evaporation ponds are impermeable. However, the eventual disposal of the dried cake is likely to have a significant negative environmental effect if it is disposed of on land.

## CONCLUSIONS

The main questions that this study set out to answer, and the answers emanating from this project, are listed below:

(1) Can DD be used to recover Al from local water treatment residues, whilst rejecting organics?

This study found that DD could selectively recover Al ions whilst rejection > 95% of organics, using a feed stream obtained by digesting waste Al sludge with acid.

(2) What is the recovery of Al that can be obtained?

Using a synthetic feed, recoveries of up to 95% were obtained, whilst on a real feed a recovery of 84% was obtained. It is confidently believed that further optimisation on real feeds could increase the recovery to > 90%.

(3) What is the maximum concentration of Al that can be obtained?

For the 'industrially acceptable' sweep acid concentrations used here, concentrations of up to 1400 mg/L were achieved.

(4) Can the product (sweep) be directly re-used in water treatment?

No. The alum solution currently used in water treatment works has an Al concentration of ~ 40000 mg/kg. Hence, the product from DD would have to be concentrated up via e.g. nanofiltration, to obtain a solution that could be directly applied.

(5) What is the potential cost benefits of Al recovery?

The cost of alum procurement and sludge disposal is ~ R310/ML water produced. Considering a plant that produces 100 ML/day, this current cost is ~ R11m/year. If only 50% of the alum in the sludge was recovered and recycled, there would be a saving of ~ R5.5m per annum per plant. However, there is also a significant environmental benefit that should be considered. Evaporation ponds, which are currently used for management of the Al precipitate sludge in many water works have a significant capital cost associated with them. The ultimate environmental cost of sludge disposal is likely to be quite significant if the cake is disposed of on land.

(6) Based on the above, should further R&D effort be put into developing a DD process for the recovery and reuse of waste Al from waterworks sludges?

Technically, the DD process for recovery and reuse of Al looks very promising. It should be developed up to the point where an economic evaluation can be performed, to ultimately decide on its applicability.

## RECOMMENDATIONS

The DD process for recovery and reuse of Al from water works residuals appears to be technically attractive. Further development should be pursued to the point of a continuous pilot-plant, to obtain realistic data that would enable an economic evaluation of the process.

Particular aspects which future R&D should focus on include:

(i) Detailed investigation of the kinetics – This study focussed on the thermodynamic aspects, i.e. 'WHAT can be achieved?'. Future investigations should focus on the kinetics, i.e. 'HOW FAST does it occur?'. This is essential for scale-up and further optimisation. As most of the 'critical phenomena' occur between 6 hrs and 15 hrs from start up, consideration should be given to automated sampling to obtain frequent samples in this region.

(ii) Fouling – Contrary to expectations, there is a hint that organics may negatively affect the membrane. This needs to be investigated in detail, together with approaches to mitigate it.

(iii) Base digestion rather than acid digestion – If the feed to DD consisted of a hydroxide rather than an acid, the driving force for Al transport should increase in theory. This definitely warrants further investigation.

(iv) Scale-up of modules – An essential part of the process development is to establish whether the flat-sheet module can be easily scaled to larger membrane areas.

(v) Concentration of the sweep – Nanofiltration is a very promising option for the concentration of the sweep product from ~ 1400 mg/L to ~ 40000 mg/L. This should be investigated.

Concluding the above recommendations should yield sufficient information for a confident economic assessment of the process. If the economic evaluation looks positive, then the process should be pursued up to 'demonstration' scale.

Ultimately, if the process proves technically and economically attractive, a model should be developed to enable individual water works to evaluate the economic impacts of Al recovery and reuse for their unique circumstances.

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| Mrs S Freese | WaterScience cc |
| Mr S Ramphal | Rand Water |
| Ms Cl Phillips | ESKOM |
| Mrs M Hloyi | City of Cape Town |
| Dr R Magoba | City of Cape Town |
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# CHAPTER 1: **INTRODUCTION**

## 1.1 BACKGROUND TO THE PROJECT

Aluminium (Al) salts, particularly aluminium sulphate (alum), are widely used as a coagulant in large scale potable water treatment both internationally as well in South Africa. Alum combines with colloidal and organic contaminants to form a precipitate, which is subsequently removed in a clarifier or a sand-filter. The precipitated solids from these processes are further dewatered in a filter, yielding an aluminium-rich sludge. At present, the sludge invariably ends up on a land-fill / waste-disposal site. It would seem obvious that there would be significant benefits to the costs of water treatment plants, the preservation and optimal use of natural resources, and the protection of our Environment if Al could be recovered from the waste sludge, recycled and reused. However, whilst there have been concerted efforts to do so over many years, the recycle and reuse of Al have proven to be extremely difficult. Digestion with and acid or a base is the most promising method to recover Al from the Al sludges. However, the acid also digests a very high proportion of the organics. Hence, the recovered alum is highly contaminated with organics, defeating the purpose of adding alum to the raw water. It has also been postulated that the digested organics may be more reactive than "natural" organics, and form precursors for THMs. Hence it may be dangerous to use alum obtained by acid digestion for potable water treatment. Conventional pressure driven membrane processes have also been only partially successful, mainly due to the difficulties in separating small organics from the Al solution, and the obvious fouling. Hence, if Al could be recovered from WTRs, without being contaminated by organics, it would be a major step towards the recycling and reuse of Al as a coagulant.

Donnan Dialysis (DD) is a relatively new technology in the water treatment field. DD uses a cation-exchange membrane, i.e. a membrane that will allow only positively-charged ions to pass through but blocks the passage of negatively-charged and un-charged species. What this means in practice is that DD could potentially enable Al to be recovered from a waste stream that contains Al, organics, other contaminants, etc. without the recovered stream being contaminated with organics. In the simplest application of DD, the contaminated Al stream flows along one side of the membrane (feed), while an acid solution flows along the opposite side (sweep). Due to the difference in chemical potential, $Al^{3+}$ ions diffuse from the feed to the sweep, while $H^+$ ions diffuse from the sweep to the feed. Colloids or organics cannot pass through the membrane (in theory). The driving force is a difference in chemical potential, so there is no "pore fouling" like in UF/MF/RO (in theory). The development of DD towards an industrial process, and the evaluation thereof, forms the topic of this project.

## 1.2 PROJECT AIMS

The Aims of this project were as follows:

(1) To investigate and identify the important engineering and geometric variables that determine Al recovery in a Donnan Dialysis (DD) cell. Hence, to determine a regime map of geometry and operating variables for a DD cell module that could be upscaled.

(2) To develop, construct and evaluate a design for an "industrial" DD cell module that could be upscaled for application in large scale potable water treatment works.

(3) To evaluate the performance of the new module design in terms of Al recovery, operability and fouling, and to estimate the cost benefits of Al recovery.

(4) To create expertise in DD in at least two South African universities.

## 1.3 MAIN RESEARCH QUESTIONS

The application of the DD technology for water treatment is still at research stage. This project is primarily a scoping project, to determine whether the development of a DD-based Al recovery technology should be pursued further. Hence, the main questions that this study set out to answer were as follows:

(A) Can DD be used to recover Al from local water treatment residues, whilst rejecting organics?

(B) What is the recovery of Al that can be obtained?

(C) What is the maximum concentration of Al that can be obtained?

(D) Can the product (sweep) be directly re-used in water treatment?

(E) What are the potential cost benefits of Al recovery?

(F) Based on the above, should further R&D effort be put into developing a DD process for the recovery and reuse of waste Al from waterworks sludges?

## 1.4 APPROACH AND REPORT ORGANISATION

- **Chapter 2** – A **Literature Survey** of the DD process is reported in Chapter 2.
- **Chapter 3** – The **Experimental Apparatus and Protocol** used in this study is reported in Chapter 3.
- **Chapter 4** – The **Performance Evaluation** is reported in Chapter 4. Firstly, a *Validation Investigation* validated the experimental apparatus in terms of concurrence with literature, repeatability and closure of mass balances. Thereafter a *Scanning Investigation* was performed at similar operating conditions to that reported in previous DD literature. Then an *Optimisation Investigation* was performed to determine the maximum performance that could be obtained in terms of Al recovery and final Al concentration when operating at these 'realistic' conditions.
- **Chapter 5** – This Chapter reports on findings from an **Organics Rejection** investigation, performed to specifically answer the question of whether Al could be selectively recovered from a water treatment residual stream. The feed stream for this was obtained by acid digestion of dry water treatment residual sludge obtained from an evaporation pond.
- **Chapter 6** – A **Fouling Investigation** focussed on whether the presence of organics affected membrane performance in any way. This performance evaluation provided the answers for the 'Research Questions' and is detailed in Chapter 6. A brief overview of the **Cost Benefits** of Al recovery is outlined in Chapter 6.
- **Chapter 7** – Conclusions and recommendations

# CHAPTER 2: **LITERATURE SURVEY ON DONNAN DIALYSIS**

## 2.1 PROCESS DESCRIPTION

Donnan dialysis (DD) is a membrane-based separation process that exploits the counter diffusion of ions through an ion exchange membrane. The process is driven by an electrochemical potential gradient across the membrane (Prakash *et al.*, 2004). The process is performed counter currently with the objective of taking dilute solutions and concentrating them into a small volume. There are two types of membranes processes available for Donnan dialysis. The first is cationic exchange and the second is anionic exchange (Davis, 2000). Figure 2-1 below illustrates the cationic exchange process. The feed consists a water treatment residual sludge, and the swap side consists of dilute sulphuric acid. Only positive ions such as hydrogen and aluminium are permitted through the membrane, negative ions and organic matter are impermeable. Initially the feed side only contain water treatment residuals and the sweep side sulphuric acid. As time goes by, there is an ionic exchange of hydrogen ions to the feed side and aluminium ions the sweep side. This ionic exchange continues until equilibrium is reached, aluminium sulphate which is now concentrated in the sweep side is then recovered.

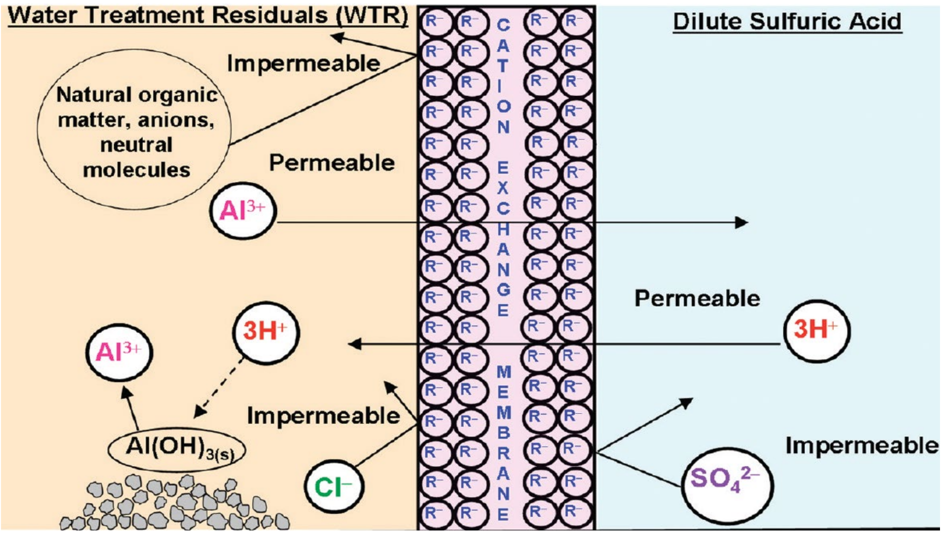


**Figure 2-1: Cation exchange membrane (Adopted from Sarkar *et al.*, 2010)**

The anionic membrane operates under the same principle as the cationic membrane, with the primary difference that positive charges are fixed in the membrane and the counter ions are negatively charged. This means that the membrane can interact with negative ions in both compartments (Davis, 2000). Ion exchange membranes used for the Donnan process have low electrical resistance, high permselectivity, high resistant to mechanical force and structural deformation, resistant to high chemical and thermal conditions (Strathmann, 2004). In both processes a membrane separates two compartments containing two different electrolytic solutions. The cationic membrane is essentially a plastic film with fixed negative charges dispersed uniformly within the film. The counter ions which are positively charged are free to exchange with other positively charged ions from the solutions in both compartments, while the negative counterparts of the positive ions in solutions are not permitted to interact with the membrane due to their charge (Davis, 2000). The Donnan equilibrium is established by the inability of the counter ions to permeate. The Donnan membrane process makes uses of the Donnan equilibrium concept in order to understand the relationship and effect of the concentrations of ions in solution in both compartments.

## 2.2 THEORY OF OPERATION

### 2.2.1 Development of transport equations

The Donnan equilibrium relationship may be explained using thermodynamics and may be derived as described by (Smith *et al.*, 2001). The first four fundamental thermodynamic properties are defined as;

$H = U + PV$ [1]

Where (H) is the enthalpy, (U) is the internal energy; (P) is the pressure and (V) the volume.

The second and third properties are the Helmholtz (A) and Gibbs (G) energies which are defined as follows;

$A = U - TS$ [2]

$G = H - TS$ [3]

Lastly the internal energy can also be expressed in terms of temperature (T), pressure, entropy(S) and volume;

$U = TS - PV$ [4]

Upon multiplying equation [1] as well as [4] by the number of moles in the system (n) and differentiating each equation, leads to;

$d(nH) = d(nU) + Pd(nV) + (nV)dP$ [5]

$d(nU) = Td(nS) - Pd(nV)$ [6]

Then, replacing $d(nU)$ in equation [5] with equation 6 yields

$d(nH) = Td(nS) + (nV)dP$ [7]

Combining equations [7] and [3] yields another expression for Gibbs energy;

$d(nG) = (nV)dP - (nS)dT$ [8]

Equation (8) is valid for a closed system. In order to provide an open system case of the Gibbs equation where material may enter and exit the system, a new function which provides a relation between the number of moles of chemical species and Gibbs is defined, the chemical potential.

$\sum[\frac{\partial(nG)}{\partial n}]_{T,P,n} = U_i$ [9]

Finally, for a system consisting of two phases in equilibrium, each individual phase is open to the other and thus mass transfer can occur between the phases. In cooperating equation [9] into [8] yields [Smith *et al.*, 2001];

$d(nG)^{\alpha} = (nV)^{\alpha}dP - (nS)^{\alpha}dT + \sum_i(\mu_i)^{\alpha}\, d(n_i)^{\alpha}$ [10]

$d(nG)^{\beta} = (nV)^{\beta}dP - (nS)^{\beta}dT + \sum_i(\mu_i)^{\beta}\, d(n_i)^{\beta}$ [11]

where $\alpha$ $and$ $\beta$ represent the two phases present.

The total change in Gibbs energy is obtained by summing the two systems as follows;

$$d(nG) = (nV)dP - (nS)dT + \sum_i (\mu_i)^\alpha \, d(n_i)^\alpha + \sum_i (\mu_i)^\beta \, d(n_i)^\beta \qquad [12]$$

When the two phases $\alpha \: and \: \beta$ are in a closed system and are at equilibrium, two things occur. Firstly, at equilibrium as there is constant pressure and temperature equation [12] simplifies to;

$$\sum_i (\mu_i)^\alpha \, d(n_i)^\alpha + \sum_i (\mu_i)^\beta \, d(n_i)^\beta = 0 \qquad [13]$$

Secondly, as the system is closed, mass must be conserved and it thus follows that;

$$d(n_i)^\alpha = -d(n_i)^\beta \qquad [14]$$

Therefore, from equations [13] and [14] it can be established that when two or more phases at the same temperature and pressure are in equilibrium with each other, then their chemical potential must be the same [Smith *et al*., 2001];

$$(\mu_i)^\alpha = (\mu_i)^\beta \qquad [15]$$

For the case of a system which is not at standard conditions of pressure and temperature and the chemical potential is still required, the chemical potential of the system at that temperature and pressure may be calculated with the use of equation [16] [Smith *et al*., 2001];

$$U_i = U_i{}^0 + RTlna_i \qquad [16]$$

(R) is the gas law constant;

(T) is the absolute temperature;

$(a_i)$ is the activity of species i.

Due to the solutions in Donnan dialysis being electrolytic and therefore having charge, electrochemical potential must also be considered when describing equilibrium. It is factored in with the chemical potential as follows;

$$\eta = U_i{}^0 + RTlna_i + \mathrm{Z}F\theta \qquad [17]$$

where $(\mathrm{Z})$ is the ionic charge, (F) is Faradays constant and $(\theta)$ is the electric potential.

Similarly to the chemical potential, when equilibrium is achieved between two phases, the electrochemical potential is the same (Davis, 2000).

$$\eta_1 = \eta_2 = RTlna_1 + \mathrm{Z}_1 F\theta = RTlna_2 + \mathrm{Z}_2 F\theta \qquad [18]$$

It should be recalled that, for a particular type of membrane (cationic or anionic), co ions of a solutions are not permitted to permeate through the membrane. If the concentration on both sides of the membrane is different there will be a potential difference across the membrane. This potential difference is termed the Donnan potential ($E_{Don}$ ) and may be calculated by rearranging equation [18] (Davis, 2000)

$$E_{Don} = \frac{RT}{Fln\left(\frac{a_1}{a_2}\right)^{\frac{1}{Z}}} \qquad [19]$$

Activities are a precise method in determining equilibria; however, molar concentrations are mostly used as they simplify the theory behind the Donnan membrane process (DMP). Since the Donnan potential is felt on all ionic species in solution, the value of $\left(\frac{a_1}{a_2}\right)^{\frac{1}{Z}}$ is the same for all counter ions in solution (Davis, 2000). This therefore means that if we were to have two dilute salt solutions of KCl and NaCl separated by a cationic membrane, of which KCl starts of in the feed compartment and NaCl in the sweep side, their Donnan equilibrium written in terms of concentration would be:

$$\left(\frac{[Na]^+{}_1}{[Na]^+{}_2}\right)^{\frac{1}{1}} = \left(\frac{[K]^+{}_1}{[K]^+{}_2}\right)^{\frac{1}{1}} \qquad [20]$$

Where Z=1 for both cationic species. The subscript 1 denotes the ions in the feed compartment and 2 denote the ions in the sweep side compartment. It can be seen from equation [20] that if the concentration of the sodium ion on the sweep side is increased, the end result is a higher concentration of potassium recovered.

Similarly, the equilibrium concentrations can be calculated and expressed as a function of the initial concentrations of the feed side ($C_1$), sweep side ($C_2$), volume, volume of feed side ($V_1$), volume of sweep side ($V_2$) and number of moles transported through the membrane (x) as follows;

$$\frac{\frac{(C_1-x)}{V1}}{\frac{x}{V1}} = \frac{\frac{x}{V2}}{\frac{(C_2-x)}{V1}} \qquad [21]$$

The above equation can then be rearranged and solved for x in order to determine the number of moles transported through the membrane at equilibrium.

Unlike other membrane processes such as nano-filtration, ultra-filtration and reverse osmosis, which make use of pressure driven systems, the Donnan membrane Process (DMP) does not. The DMP is only affected by concentration and electrical potential. This therefore means it is not affected by traditional membrane limitations such as fouling because large particulate matter does not concentrate on the membrane surface [Prakash, 2004]. It is however affected by a phenomenon known as concentration polarization which will be discussed at a later section. While a sound understanding of the thermodynamics behind the Donnan principle is essential as it offers knowledge towards the Donnan membrane equilibrium principle and species transported across the membrane at equilibrium, it simply is not enough. Kinetics also play an important role in any process, and as such, a parameter which describes the rate at which a process occurs is required. Such a parameter was found to be flux. The flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time [applied membranes.com].

Consequently, Fick came up with a law describing flux in terms of solution concentrations and diffusivity. Fick's law is written as follows (Ho *et al.*, 1993);

$$J_m = \frac{D_m}{\partial l}(C_m - C'_M) \qquad [22]$$

where $J_m$ is the flux, $C_m and\ C'_M$ are the metal ion concentrations in the bulk solution and interface on the feed side, $D_m$ is the diffusivity and *l* is the length of the membrane.

The disadvantage with Fick's law however is that it only accurately describes the flux through a membrane when the two counter ions have similar diffusion coefficients (Ho *et al.*, 1993). Planck and Nernst further built on the theory of Fick and established an equation called the Nernst-Planck equation. The following five assumptions are made in order to derive the Nernst-Planck equation (Ho *et al.*, 1993);

- The system is controlled by membrane diffusion.

- The number of co-ions in the membrane is negligible compared with its ion exchange capacity. No co-ions can also permeate the membrane
- Thermodynamic equilibrium exists at the membrane-solution interface.
- Osmotic water flow across the membrane can be ignored.
- The overall electro neutrality is preserved in the system.

With these assumptions in mind, the Nernst-Planck equation may be written as;

$$J_m = -D_m(\frac{dC_m}{dl} + Z_i C_m \frac{F}{RT}\frac{d\emptyset}{dl}) \qquad [23]$$

### 2.2.2 Summary of critical equations for Donnan Dialysis

In summary, there are two essential equations that are crucial to the Donnan membrane process. The first is the Nernst-Planck equation which is used to describe the amount of permeate produced per unit area of membrane surface per unit time, also known as the membrane flux. The equation is provided below. Through this equation, the rate of transport of ions through the membrane can be determined. It can be seen that the higher the initial concentration and ionic charge are, the faster the rate of transport of ions across the membrane will be.

$$J_m = -D_m(\frac{dC_m}{dl} + Z_i C_m \frac{F}{RT}\frac{d\emptyset}{dl})$$

The second essential equation provides a way to understand the relationship between the initial concentration, and final solution concentration of both the feed and swap side.

$$\left(\frac{[Ca]^+{}_1}{[Ca]^+{}_2}\right)^{\frac{1}{Za}} = \left(\frac{[Cb]^+{}_1}{[Cb]^+{}_2}\right)^{\frac{1}{Zb}}$$

The subscript 1 denotes the ions in the feed compartment and 2 denote the ions in the sweep side compartment. $C_a$ And $Z_a$ are the concentrations and ionic charge of the target metal. $C_b$ And $Z_b$is the concentration and ionic charge of the species substituting the target metal. The implications of this equation are as follows;

- A high initial concentration of the substitute ion results in a high final concentration of the target metal ion.
- The higher the ionic charge of the target metal to be recovered and the lower the ionic charge of its substitute ion are, the higher the recovery and final concentration of the target metal will be.

## 2.3 PROCESS LIMITATIONS INHERENT TO DONNAN DIALYSIS

### 2.3.1 Concentration polarization

A major factor that influences the flux in Donnan dialysis exchange membranes and consequently their performance, is a phenomenon known as concentration polarization. It is illustrated in Figure 2-2 below. Concentration polarization is when a gradient occurs at the membrane and solution interface due to the selective permeation of ions at different rates. Polarization is generally known to occur when a significant boundary layer exists on the membrane surface (Baker, 2012). The concentration of the more selectively transported species is higher in the bulk phase, as it approaches the membrane interface and enters the boundary layer, the concentration decreases. The concentration gradient then increases across the membrane due to the rate of permeation of target species through the membrane. On the other side of the membrane the concentration then decreases with increasing distance from the membrane.

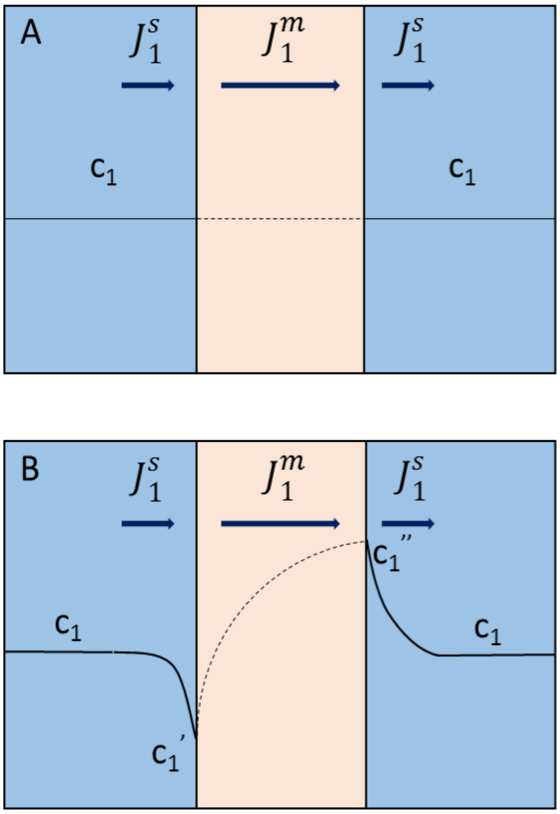


**Figure 2-2: Concentration polarization (adopted from Wikipedia). A = no concentration polarisation – concentrations are constant up to the membrane surface, B = concentration polarisation – steep concentration gradients near the membrane surface and hence the membrane 'sees' concentrations that are very different from the bulk concentrations.**

Figure 2b provides an illustration of a system with concentration polarization, while figure 2a illustrates an idealistic scenario of what would happen if concentration polarization did not exist. According to Baker (2012), concentration polarization in a membrane system can be reduced by promoting turbulent flow in the system. The objective of the turbulent flow is to reduce the boundary layer thickness by promoting uniform species concentration throughout the vessel. A state of turbulence can be achieved via two methods. The first one is by increasing the velocity of the flow over the membrane. The second method would be by manipulating the flow patterns of the solution with the aim of trying to produce a turbulent regime. Sheet or mesh spacers as well as baffles can be used to achieve this.

### 2.3.2 Osmosis effects

Osmosis is the transport of molecules of water through a semipermeable membrane from a region of less concentration to a more concentrated area. Over the years, two milestones in terms of studies towards the understanding of water transport characteristics of Nafion (a type of cation exchange membrane widely used in DD) membranes have been achieved. These studies are briefly discussed in this section.

The first study was conducted by Okada *et al*. in 1998. It was found that the number of moles of water transported across a Nafion 117 membrane is attributed to two main effects, namely; the electrostatic interactions between ions in solution and water dipoles; as well as an effect due to the size of the cation present in solution. Okada *et al*. observed that for hydrophilic cations, the transfer of water across a membrane increased as ionic radius of the cation decreased. For hydrophobic cations however, the transfer of water across the membrane increased with ionic radius. Electrostatic interactions in solution were found to aid the transport of water when dipole charges between cations and water molecules were dominant. The cations were found to attract water molecules around them and were seen to move in unison with those water molecules. Lastly, from experimentation the group observed that larger cations tended to also aid in the transport of water molecules by "pushing" water through membrane channels by volume exclusion.

Duan, Wang and Benziger (2012) built on the research of Eikerling and co-workers (1998) who hypothesized that water transport across Nafion membranes was due to driving forces such as capillary, pressure, osmotic pressure and an external pressure gradient. Duan *et al*. published their research and findings in 2012. The group experimentally investigated the effect of temperature and pressure on the flux of water through Nafion membranes. They found that the transport of water across the membrane increased with temperature and pressure. As the temperature was increased the viscosity of water decreased and the hydrophilic volume fraction increased and hence the increase in water transport across the membrane with temperature. In terms of pressure, the research is unclear as to what the reason for the increase in water flux across the membrane with pressure is. Lastly, Prakash *et al*. (2003 and 2004) further worked on research which utilized Nafion membranes. The objective of the research was to concentrate aluminium using Donnan dialysis. While their research was not targeted at investigating the effects of water transport through Nafion membranes, it was found to be useful because it demonstrated the effect of water transport through a Nafion membrane and the resulting effect. Prakash *et al*. demonstrated that the graph for the concentrating of Al using Donnan dialysis could be divided into three main regions, this is illustrated in Figure 2-3 below.

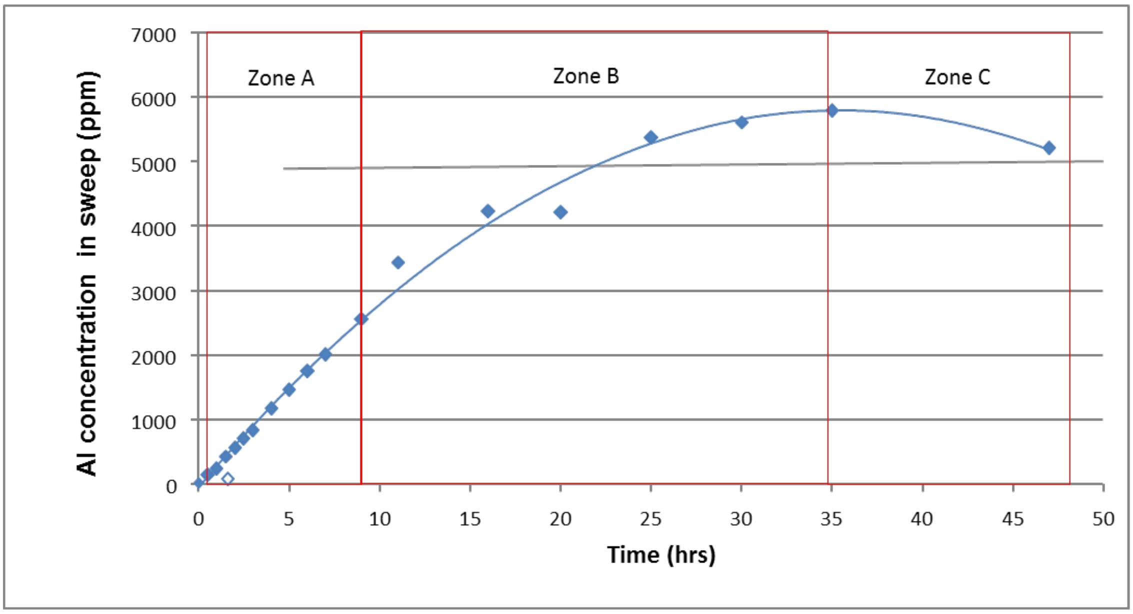


**Figure 2-3: Postulated 'zones' in a typical sweep Al concentration profile**

The first zone, which is zone A, displays a linear trend and is governed by a high electrochemical potential and is termed the "kinetically driven zone". As the concentration of aluminium decreases in the feed side and the electrochemical potential decreases, the rate of recovery of aluminium decreases. This can be seen by the decrease in the gradient, this is zone B and is termed the Donnan equilibrium zone. Lastly, when the aluminium recovered reaches a maximum it is seen to decrease again. This is Zone C and is predominantly characterized by hydrodynamic effects. Prakash *et al*. hypothesized that the water transport was due to osmosis and termed the zone as the "osmosis driven" zone. The transport effects of water become more visible here and the end result is a reduction in the concentration of aluminium due to water dilution.

## 2.4 CURRENT STATUS OF DONNAN DIALYSIS

Donnan dialysis is an extremely dynamic process which has uses both in the mineral processing industry, waste water treatment industry and near raw water feeds. Table 2-1 shows a few cited examples of the uses of the Donnan Membrane Process.

**Table 2-1: Selected Examples of Donnan Dialysis recovery application**

| Category | Researchers | Description of process | Scale | Motivation |
|---|---|---|---|---|
| Water Treatment Residue | Prakash and SenGupta (2003) | A method was formulated to selectively recover coagulants such as Alum (Aluminium Sulphate) from waste water treatment residuals using the Donnan Membrane Process. The process was found to selectively recover about 70% Alum and ferric chloride under the following conditions;<br>• 6.6 Litres of water treatment residuals on feed side.<br>• 1.5 Litres of 10% sulphuric acid on sweep side.<br>• pH between 3-3.5<br>• Nafion 117 membrane<br>• Duration of experiment was 24hrs | Laboratory | The motivation behind the recovery of Alum was to mitigate the improper disposal of Alum in landfill sites or water bodies because of its extremely hazardous nature. |
| | Prakash *et al*. (2004) | Two membranes, a homogeneous Nafion 117 and a heterogeneous Ionca 3470 was studied for recovery. An 80% selective concentration of Alum was achieved for homogeneous membrane under the conditions;<br>• 3 Litres of water treatment residuals on the feed side | Laboratory | This assesses the impact of different membranes morphology on recovery with respect to kinetics, permselectivity, osmotic and fouling effects and quality of Alum yield. |

| | | | | |
|---|---|---|---|---|
| | | • The sweep side contained 1.0L of 1M sulfuric acid solution.<br>• Duration of experiment was 9-24hrs | | |
| Industrial Effluent | Marzouk *et al*. (2013) | The removal of chromium (VI) from industrial waste water resulting from processes such as electroplating, dies and textiles was investigated. It was investigated under the following conditions;<br>• Cr(VI) concentration of 1 g/l<br>• At a pH of 4<br>• Using two anion exchange membranes, namely; Selemion AMV and Neosepta AFN.<br>• A NaCl concentration of 0.1M in sweep side. | Laboratory | The removal of chromium in waste streams was found to be essential due to chromium's deleterious impact on ecosystems and public health. |
| | Cengeloglu *et al*. (2003) | The recovery of titanium, Fe, Al and Na from red mud from aluminium plants using cation exchange membrane with the use of the Donnan Dialysis process under the following conditions;<br>• Feed and sweep compartment volume of 40 ml.<br>• Feed compartment was red mud and diluted 50% aqueous solution<br>• The stripping was HCl varied concentration ranges 0.05-1M<br>• ICE-450 (SA3T), Neosepta CMX and Neosepta CMB | Laboratory | The objective is to recover potential raw materials and valuable metals that are disposed through effluent waste. |
| | Hichour *et al*. (1999) | The removal of fluoride in drinking waters with the use of Donnan dialysis with an ionic exchange membrane was studied under the following conditions; | Laboratory | The objective was to reduce the fluoride content in water to make it suitable for human consumption. |

| | | | | |
|---|---|---|---|---|
| Saline water Spiked Feeds | | • A feed volume of 21.12 cubic centimetres.<br>• A sweep side volume of 410ml.<br>• NaCl in the sweep side at a concentration of 10 moles per Litre.<br>• pH of 5 | | |
| | Wiśniewski *et al*. (2005) | The Donnan dialysis was successfully used for denitrification, defluoridation and removal of bicarbonates using:<br>• Feed volume and concentration of 2.5-10 $dm^3$ and 5mM.<br>• NaCl was used as the stripping solution<br>• Membranes used were Selemion (AMV and DMV) and Neosepta (AFN and AMX) | Laboratory | The purpose is to improve deep desalination of water by avoiding scaling effect caused by anions during electrodialysis. |
| | Hamouda *et al*. (2017) | The removal of nitrate using Donnan dialysis was studied for various membranes and at a varied pH of at feed phase. The experimental design had;<br>• Feed and Sweep compartment of 25 ml.<br>• The stripping solution, NaCl, was varied at concentration ranges of 0.001-0.1 M<br>• Stirring of both solutions at 700 rpm | Laboratory | The objective was to reduce the nitrate content in water to acceptable thresholds. |
| | Zhao *et al.* (2012) | The removal of arsenate using a point of use (POU) Donnan dialysis system to achieve 80% removal was done under conditions of;<br>• Feed consist of 250-540 µg/l of As<br>• Stripping solution was 12 g/l of table salt | Laboratory | The removal of arsenate in ground water and raw streams was found to be essential due to environmental and health related issues associated arsenic contamination |

| | | | | |
|---|---|---|---|---|
| | | - POU device has a treatment capacity of 35 L per batch.<br>- Batch mode at a retention time of 24 hours and aeration at 4.7 $Lmin^{-1}$.<br>- pH of 7.0± 0.2 | | |
| Complexes | Akretche and Kerdjoudji (2000) | The efficiency of separating gold, silver and copper cyanide complexes was determined using Donnan dialysis. It was investigated under the following conditions;<br>- A feed solution of 250 cubic centimetres.<br>- A sweep solution of 250 cubic centimetres.<br>- NaOH of 6M used as stripping solution.<br>- Experiments performed for single ion metal component in presence of 0.2 M KCN at pH of 9. | Laboratory | The motivation for this was the potential of recycling reactants and thus making the process more cost efficient. An additional consideration was the harm that cyanide compounds do to the environment. |
| Electronic Waste | (Agarwal *et al.*, 2016) | The separation efficiency of Donnan Dialysis for the selective removal gold from complexes with copper and nickel in an aqua regia solution under experimental conditions;<br>- Micro pore grafted poly propylene membrane was used.<br>- A feed solution of 100 ml was used<br>- The sweep compartment contained 0.5 M NaCl | Laboratory | The purpose extract gold from growing electronic waste for potential reuse by demanding industries. |

### 2.4.1 Current Research and development of Donnan Dialysis.

The selectivity and transport of ions across a membrane depends on several factors such as ion exchange capacity of the membrane, concentration of electrolytic solution, self-diffusion coefficients (SDC) of ions in membrane, selectivity coefficient, ionic radius and membrane morphology (Agarwal *et al.*, 2012; Xue *et al.*, 1990). Current research and development still lacks in the complete understanding of the nature of the inter-diffusion process, however what is known thus far is that in Donnan dialysis, the inter-diffusion rate can either be controlled by the boundary layer or the membrane. At low metal ion concentrations or low rotating speeds, the transport is controlled by boundary layer diffusion. Conversely, at high metal ion concentration and high rotating speeds, process is controlled by membrane diffusion (Xue *et al.*, 1990). Xue *et al.* (1990) discovered that; the thinner the membrane being used, the higher the metal ion concentration required to shift rate control from boundary to membrane diffusion. The Levich equation provides a correlation for determining the membrane thickness, the equation is as follows;

$$\partial = 0.643V^{\frac{1}{6}}D^{1/3}w^{-1/2} \qquad [24]$$

where $\partial$ is the boundary layer thickness (in cm);

V is the kinematic viscosity $(cm^2s^{-1})$;

D is the diffusion coefficient $(cm^2s^{-1})$;

w is the rotational speed $(s^{-1})$.

Combining the Levich equation with Fick's first law provides a way to determine what the inter diffusion process is controlled by. The resultant equation is;

$$J_m = 1.555V^{\frac{-1}{6}}{D_m}^{2/3}w^{1/2}(C_m - C'_M) \qquad [25]$$

If the inter diffusion process is controlled by the boundary layer, then plotting $\frac{1}{J_m}$ Vs $w^{-1/2}$ results in a straight line through the origin. If however, the inter diffusion process is controlled by membrane diffusion, then a straight line with a Y-axis intercept is observed (Xue *et al.*, 1990).

Miyoshi (1998) investigated the effect of having different valence ions on the feed side and sweep side of a Donnan dialysis cell membrane. He discovered that in general, monovalent (those with an ionic charge of one) sweep side (in sweep side) paired with higher valence (valence greater than one) feed side ions have a larger driving force than equally charged feed and sweep side ions. Furthermore, feed and sweep side ions with equal valences have a larger driving force than a feed side solution with ions having lower valences than the sweep side. Miyoshi (1998) hypothesised that the reason for this was that monovalent ions were free to move from one fixed ion to near another fixed ion, however bivalent/trivalent ion need to migrate from two/ three fixed ions to another two/three, which is much more difficult to achieve. Miyoshi, (1997) study of the effect of having equal valence of ions on the feed and sweep side showed that, monovalent feed and sweep side ions had higher flux than divalent feed and sweep sides.

### 2.4.2 Limitations towards full-scale operation, and current R&D to overcome those limitations.

Donnan membrane principle is an emerging technology which is yet to be fully researched and its full potential not yet understood. There have been two notable periods in the history of the technology. Firstly, F.G Donnan's account of the equilibrium that occurred when a semipermeable membrane separated two solutions of electrolytes in 1924 signified the birth of Donnan Dialysis. The second milestone of Donnan dialysis was a few decades later in 2002 when Prakash and Sengupta patented a process for the selective recovery of trivalent metal coagulant compound from clarifier solution on the basis of the Donnan principle.

There is common consensus amongst researchers so far on two current limitations of the Donnan membrane process. The first limitation of this process is the extremely slow kinetics of ion transport across the dialysis membrane and the time taken for equilibrium to be achieved. This factor makes it undesirable to make Donnan dialysis an industrial application because the concentration and separation of metals and other ions takes too long to occur (Akretche and Kerdjoudji, 2000; Ben Hamouda *et al.*, 2012). Alternatively, to improve on separation kinetics, fully harness Donnan dialysis advantages and reduce the process limitations of other existing technologies, DD has been integrated with other treatment processes. This includes incorporation with reverse osmosis to reduce the scaling effect and increase the recovery kinetics (Vanoppen *et al.*, 2015) remove multivalent ions to reduce scaling and increase current density for electrodialytic desalination (Rozanska *et al.*, 2006; Wiśniewski and Rózańska, 2007) and reduce limitation of salt accumulation during microbial desalination(Ping *et al.*, 2015).

The second deterring factor of using Donnan dialysis as is the high purchasing cost of the membranes which has great impact on the operational expenditure (OPEX) (Keeley *et al.*, 2012; Vanoppen *et al.*, 2015). Most emerging technology, like DD often have to scale over the phenomenon of high cost of purchase. However, the research and development will also be geared towards finding the more cost-effective methods of manufacturing the membranes. In addition to this, as more companies start producing these membranes and the demand for them globally increases, the cost price will decline.

# 3 EXPERIMENTAL APPARATUS AND OPERATING PROTOCOL

## 3.1 INTRODUCTION

This chapter firstly discusses the development of the cell design and the construction of the cell. Next the design and construction of the experimental rig is discussed. Following this, details are presented of the membrane used, and directions for its management. Finally, the operating procedure for the rig is outlined.

## 3.2 DEVELOPMENT OF THE CELL DESIGN

### 3.2.1 Criteria for an industrial membrane module design

The main design criteria for an ‘industrial’ membrane module is that the module:

- (i) should promote high cross-flow velocities at low flowrates to minimise fouling and boundary layers;
- (ii) should have a high filtration area to volume packing ratio;
- (iii) should have sufficiently large flow paths to be able to handle fouling components, i.e. should not require extensive pre-treatment of the feed to remove problematic components of the raw feed; and
- (iv) should be scalable, i.e. easily upscaled to larger throughputs.

There are four types of membrane modules currently used in industrial membrane applications, viz. (Baker; 2004) plate and frame modules, tubular modules, spiral-wound modules and hollow fibre (including capillary) modules. The performance characteristics of these various modules are compared in Table 3-1. In the instance of DD, where it is desired that there should be separate solutions flowing on either side of the membrane, the possible options for a module are spiral, tubular or flat-sheet.

**Table 3-1: Performance characteristics of various module types**

| Module type | Promotion of high C/F velocity | Area/Volume packing ratio | Pretreatment required |
|---|---|---|---|
| spiral wound | excellent | excellent | high |
| hollow fibre (inside-out filtration) | poor | excellent | high |
| hollow fibre (outside-in filtration) | excellent (with air-scouring) | excellent | low |
| tubular | medium | medium | low |
| flat-sheet | low | low | low |

### 3.2.2 Previous Cell designs used in DD investigations

A survey was performed of the various DD membranes that could be available to the project, and this is summarised in Table 3-2. In general, most investigations used flat-sheet membranes, with the exception of Pozniak *et al.* (1989), who used a tubular module. Tubular membranes would be superior to flat-sheets, as discussed in Table 3-2.

**Table 3-2: DD cell designs reported in the literature**

| Researchers | Description of process | Setup |
|---|---|---|
| Wallace. R.W. (1967) | Concentrate uranyl ions from dilute solutions of uranyl nitrate. | Plate with membrane sandwiched between |
| Marzouk *et al*., (2013) | The removal of chromium (VI) from industrial waste water resulting from processes such as electroplating, dies and textiles was investigated. | Two compartment cell |
| Akretche and Kerdjoudj (1999) | The efficiency of separating gold, silver and copper cyanide complexes was determined using Donnan dialysis. | Three compartment cell |
| Pozniak and Trochimizuk (1989) | Produce sodium chloride from sodium hydroxide and hydrochloric acid using an anion exchange membrane | Tubular membrane |

### 3.2.3 Selection of module design

The ultimate factor which influenced the module design was the availability of DD membranes. It emerged that there were only two types of DD membranes that were available, viz. flat-sheets which have been used in compartmental cells, and tubular membranes. However, the tubular membranes are 'experimental' membranes that were not yet available to the public. Accordingly, the project is currently restricted to a module design based on flat-sheet membranes, simply due to availability.

There are two options for modules based on flat-sheets:

(i) a flat-sheet cell – the basic elements of this are two flat sheets which sandwich a membrane in between them. In order to obtain a greater membrane area, multiple flat-sheet cells have to be stacked in parallel to form a flat-sheet membrane pack. This is not ideal from the point of view of area/volume packing density.

(ii) a spiral module – a spiral module is, in principle, simply a rolled up flat-sheet membrane. However the technical challenges in doing this, especially with a DD membrane are likely to be considerable.

The main aim of the project at present is to establish whether the DD process is a viable option for Al recovery from water treatment residues. In view of this the project team decided to proceed with finalising a flat-sheet cell design. Down the line, if the process proves promising, consideration could be given to developing a spiral module for up-scaling of the process.

### 3.2.4 Module Construction

The DD module followed a standard ‘flat-sheet membrane format’, i.e. the membrane was sandwiched between two flat plate endblocks, with gaskets on each side of the membrane (Figure 3-1). Each sheet was fabricated from PVC, with appropriate holed drilled for holding bolts and for the inlet and outlet ports (Figure 3-2). The assembled module is shown in Figure 3-3, which indicates the inlet and outlet ports.

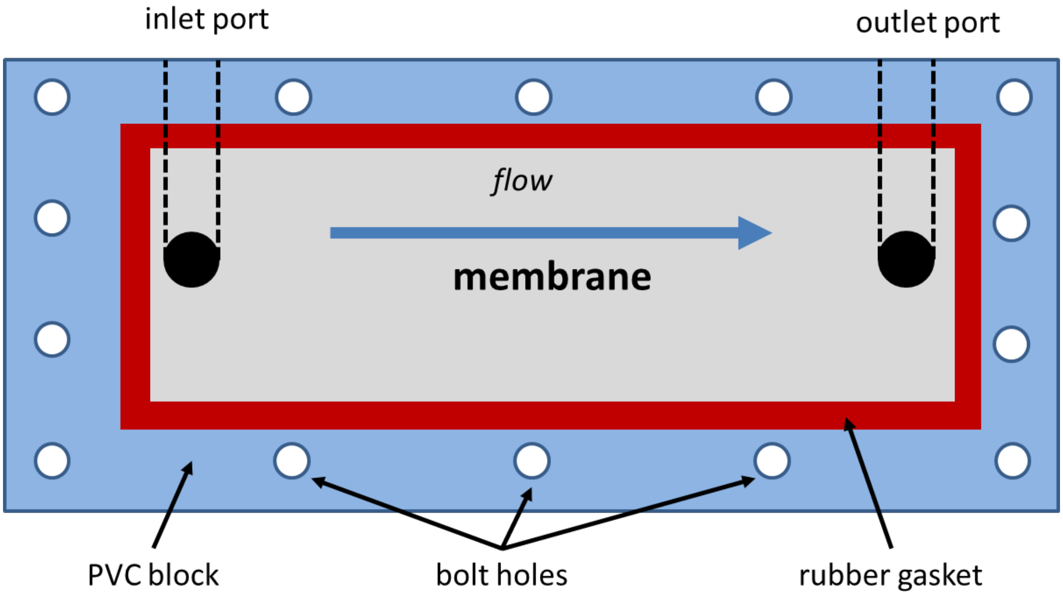


**Figure 3-1: Schematic of flat-sheet module**

**Figure 3-2: Graphic of an endblock**

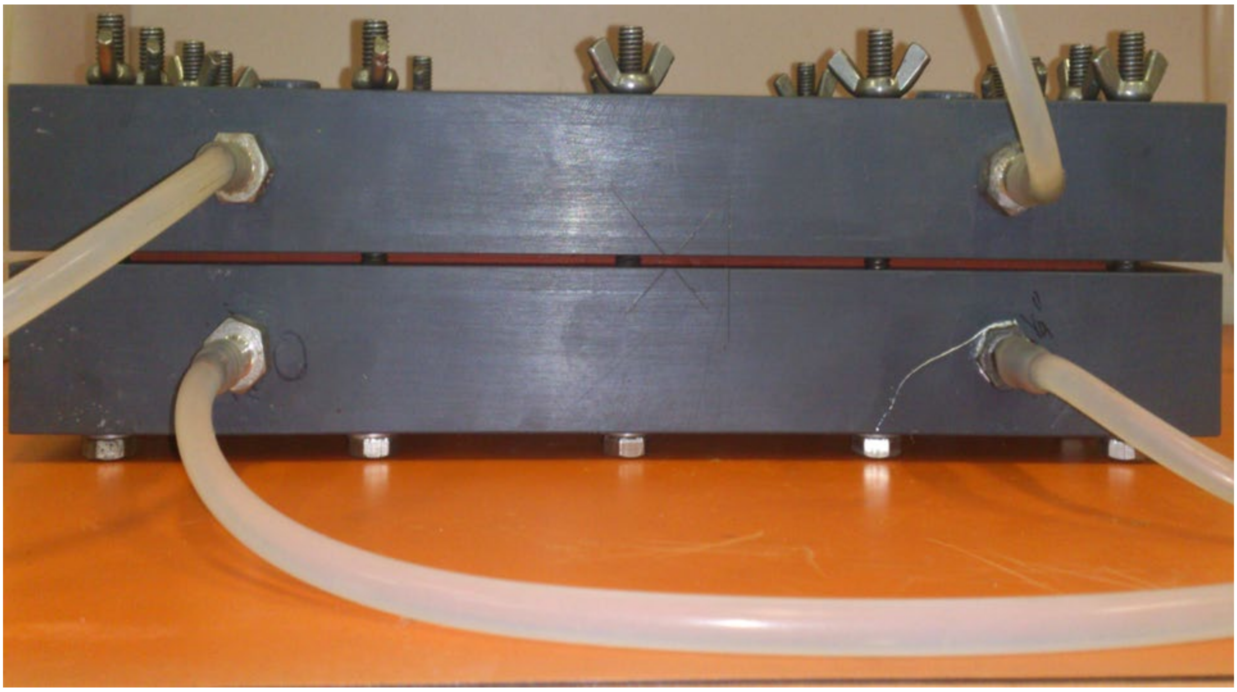


**Figure 3-3: Graphic of the assembled module**

### 3.2.5 Materials of construction

The above represents the final cell design. In the ‘version 1’ cell that was constructed and used for initial experiments (not reported here), it was found that there was a significant amount of Fe in the sweep stream, although there was no Fe present at the beginning of an experiment. Investigations indicated that the sweep acid was slowly dissolving the stainless-steel fittings that had been used at the inlet and outlet ports. In the final design shown above, all fittings and piping were replaced with either polypropylene or PVC. This solved the problem, and there were no further issues of Fe contamination.

## 3.3 DESIGN OF EXPERIMENTAL RIG

The important operating variables to be investigated include:

- Feed concentration – initial feed side concentration of aluminium sulphate
- Sweep concentration – initial sweep side concentration of the sweep (hydrochloric acid or sulphuric acid)
- Feed flowrate – flowrate of aluminium sulphate solution across the membrane
- Sweep flowrate – flowrate of the sweep solution to the cationic exchange membrane

All of the above requirements were achieved by a rig consisting of two reservoirs and two pumps. The experimental rig is shown in Figures 3-4 and 3-5 below.

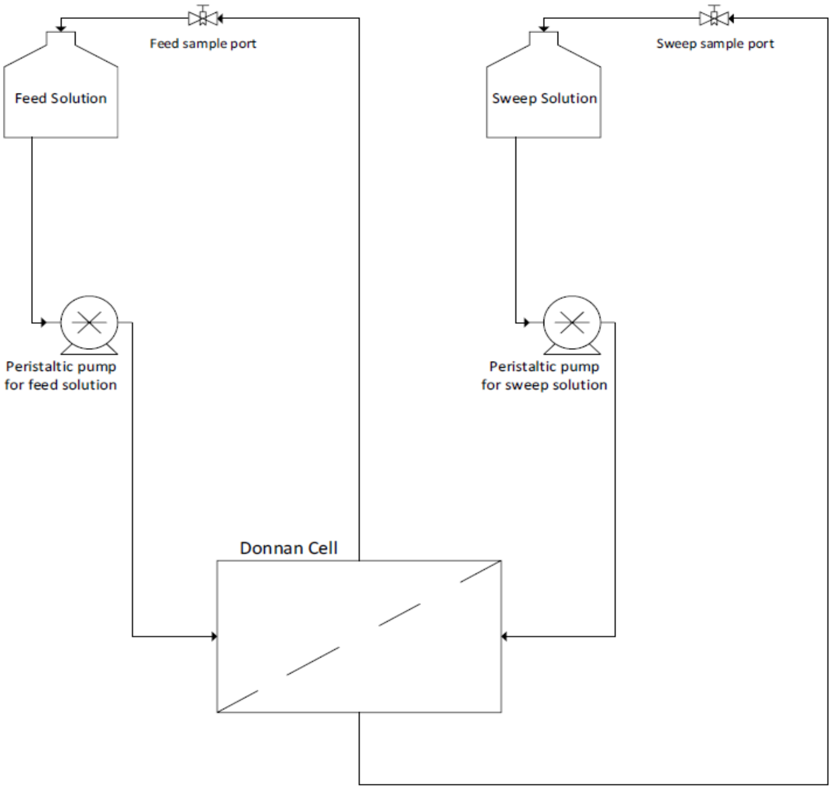


Figure 3-4: Flow diagram of experimental rig

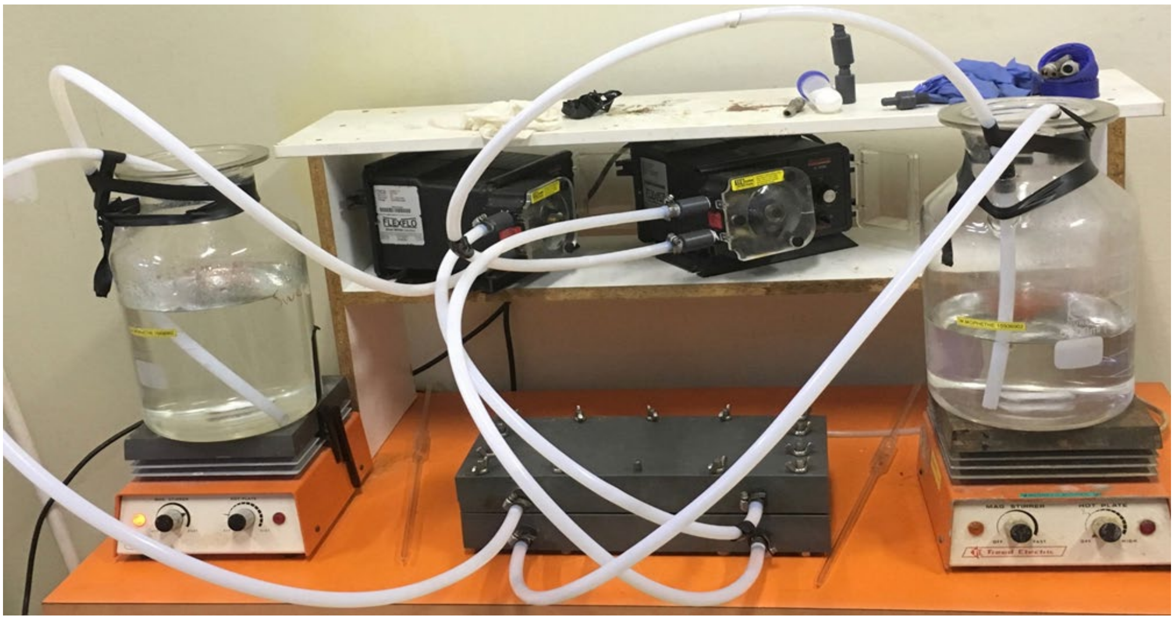
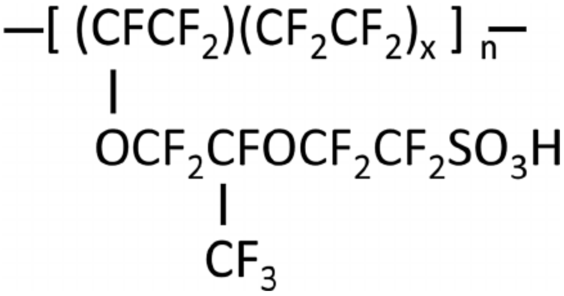


Figure 3-5: Graphic of experimental rig

## 3.4 DESCRIPTION OF THE DD MEMBRANE

### 3.4.1 The cationic exchange membrane – Nafion 117

The cationic exchange membrane that was used was a Nafion 117 membrane manufactured by Dupont industries, and obtained from Sigma Aldrich. The 117 denotes that the nominal thickness of the membrane is 183 microns. This specific membrane has an equivalent weight of 1100. The equivalent weight is a relation between two important parameters which determine the membranes ability to conduct and transport ions, it is the mass of dry membrane per mole of sulfonic acid groups (Napoli *et al*., 2013). The structure of the membrane is as follows; Perfluorinated polymer backbone which has sulfonic acid groups branching off of it. The sulfonic acid group is then surrounded by a hydrophobic matrix of a tetrafluoroethylene support and perfluorovinyl ether pendant side chains. The membrane provides the transport of protons through water sorption. The water sorption increases the size of the hydrophilic domains present, this then provides the necessary channels for ionic transport to occur (Napoli *et al*., 2013). The formula for the structure of the membrane is provided in Figure 3-6. It is also important to understand that the perfluorinated polymer backbone is responsible for the membranes stability and ability to operate over a wide operating range. From pH levels of 1 to 14 and temperatures ranging from 5 to 130 degrees Celsius.



$$\begin{array}{l} -[\,(\mathrm{CFCF_2})(\mathrm{CF_2CF_2})_x\,]_n- \\ \quad\;\; | \\ \quad\;\; \mathrm{OCF_2CFOCF_2CF_2SO_3H} \\ \qquad\qquad\; | \\ \qquad\qquad\; \mathrm{CF_3} \end{array}$$

**Figure 3-6: Structure of Nafion**

### 3.4.2 Activation of the membrane

Membrane activation is an essential part of Donnan dialysis, without this step very little hydration of the tortuous pathways is achieved and thus very little ionic transport will be observed. Although there are different schools of thought on how to go about this, the general consensus is that membrane conditioning through aqueous acid immersion is of the utmost important. To activate a new membrane, the first step was to ensure that all the impurities were removed from the surface of the membrane. This is done by conditioning the membrane in a 3% HCL warm solution at an elevated temperature of about 90 degrees Celsius. This is done for an hour, where after the membrane was then removed and rinsed off with deionized water for about 15min. After this step, the membrane was immersed in a dilute (1% HCL) solution for 3 hours further. This reportedly increases the inter-pore hydration of the membrane which in turn further increases ionic transport. The last step was to rinse off the membrane with deionized water for about 15min. The membrane was then regarded as *activated*, hydrated and ready to use. It should be noted that membrane activation only has to be performed for a new membrane. It does not have to be repeated between runs, after the membrane is cleaned.

### 3.4.3 Cleaning and storing of the membrane

Once experimentation was completed, the membrane was simply rinsed off with deionized water to remove any abrasive chemicals or compounds on its surface. It is then set out to dry and then stored away in an airtight container.

### 3.4.4 Membrane recovery

For reuse and further experimentation all that was done was to rehydrate the membrane again. This was a process similar to the activation of the membrane. The membrane was immersed in a 1% aqueous HCL solution for 3 hours. After this, it was rinsed off with deionized water for about 15 min.

## 3.5 TEST SOLUTIONS AND ANALYTICAL METHODS

### 3.5.1 Feed solution

In all investigations, unless otherwise stated, a synthetic aluminium sulphate feed solution was used. This was to ensure consistency and repeatability in the investigations into the effects of operating conditions on Al transport.

The Alum used had the formula $Al_2(SO_4)_3 18H_2O$ and was purchased from Kimix (97% assay).

### 3.5.2 Sweep acid solution

The hydrochloric acid (HCl) was also obtained from Kimix as a 36.46 wt % solution. It contained not more than 1 mg/L Fe.

### 3.5.3 Analysis for Al concentration

Al was analysed with an atomic absorption spectrophotometer (AAS) – AnalytikJena NovAA 400p.

The aluminium standard for the AAS was bought from Kimix, concentration 1000 mg/L.

## 3.6 EXPERIMENTAL PROCEDURE

### 3.6.1 Selection of operating parameters

#### *3.6.1.1 Flowrates*

Two flowrates were investigated in this study, viz. HIGH (75% pump speed) and LOW (25% pump speed). This corresponded to flowrates of 2.2 ml/s and 4.9 ml/s respectively. The thickness of the rubber gasket was 2.5 mm (0.0025 m) and the width of the flow path was 10 cm (0.1 m), giving a cross-sectional flow area of 0.00025 m$^2$. Hence the high and low linear velocities across the membrane were 0.02 m/s and 0.009 m/s respectively. Hence for each run the feed and sweep flowrates were set to either HIGH or LOW, depending on the investigation.

#### *3.6.1.2 Initial feed and sweep concentrations*

The feed solution was made up by dissolving the appropriate amount of laboratory grade aluminium sulphate in reverse osmosis water. The sweep solution was either laboratory grade sulphuric acid or hydrochloric acid of the required molarity.

### 3.6.2 Experimental procedure

#### *3.6.2.1 Start up*

(i) It was ensured that the silicone rubber gaskets were in place on either side of the Nafion membrane and PVC blocks in order to avoid leakages.

(ii) All the bolts holding together the two PVC blocks must be tight.

(iii) A **3 Litre** feed solution with the specified aluminium sulphate run concentration was prepared.

(iv) A **1 Litre** sweep solution with the specified hydrochloric acid or sulphuric acid concentration was prepared.

In order to check that the membrane was operating well and that there were no leaks in the cell, the feed solution was pumped through the module with no liquid on the sweep side. Hence, if the membrane was damaged or if there were any leaks, liquid would have leaked through to the sweep side. After 10 min of operation if there was still no liquid in the sweep side, then the membrane and module were regarded as operating correctly.

#### *3.6.2.2 Operation*

(i) Pump 1 (feed side pump) was set to the required setting.

(ii) Pump 2 (sweep side pump) was set to the required setting.

(iii) Both pumps were switched on.

(iv) The start time of the experiment was noted.

(v) Samples of the feed and sweep side were taken at 2-hour intervals.

#### *3.6.2.3 Shutdown*

(i) After a 48-hour operation, decided from initial experiments, both pumps were switched off.

(ii) The contents of the feed side and sweep side reservoirs were emptied and stored. Deionized water was then added into the empty reservoirs.

(iii) Pumps 1 and 2 were switched on, thus cleaning the membrane and module with water.

(iv) After 15min of running time, the pumps were switched off. The deionized water in the feed and sweep side containers was discarded.

(v) The Nafion membrane was immersed in 1% hydrochloric acid in order to saturate the membrane with hydrogen ions.

# 4 PERFORMANCE EVALUATION

## 4.1 INTRODUCTION

This section commences by addressing the validation of the experimental apparatus and results, in terms of repeatability and closure of Al mass balances. Thereafter the scanning investigations are discussed. The main purpose of the scanning investigations was to establish whether the form of the results from this investigation matched that reported in the literature, and to get an indication of the effects of the major operating parameters on Al transport. These scanning runs were performed at high feed and sweep concentrations similar to that reported in the literature. Hence, following the scanning runs, a decision was made on 'realistic' operating conditions that should be used for further investigations. The next stage involved an optimisation study, to investigate the effects of the important operating parameters on the recovery of Al. From this the capability and potential of the process are deduced.

## 4.2 VALIDATION OF EXPERIMENTAL RESULTS

To validate the module and the experimental protocol, the repeatability of concentration profiles and the closure of mass balances were investigated.

### 4.2.1 Repeatability

The feed and sweep concentration profiles for two experiments performed at similar operating conditions is shown in Figure 4-1.

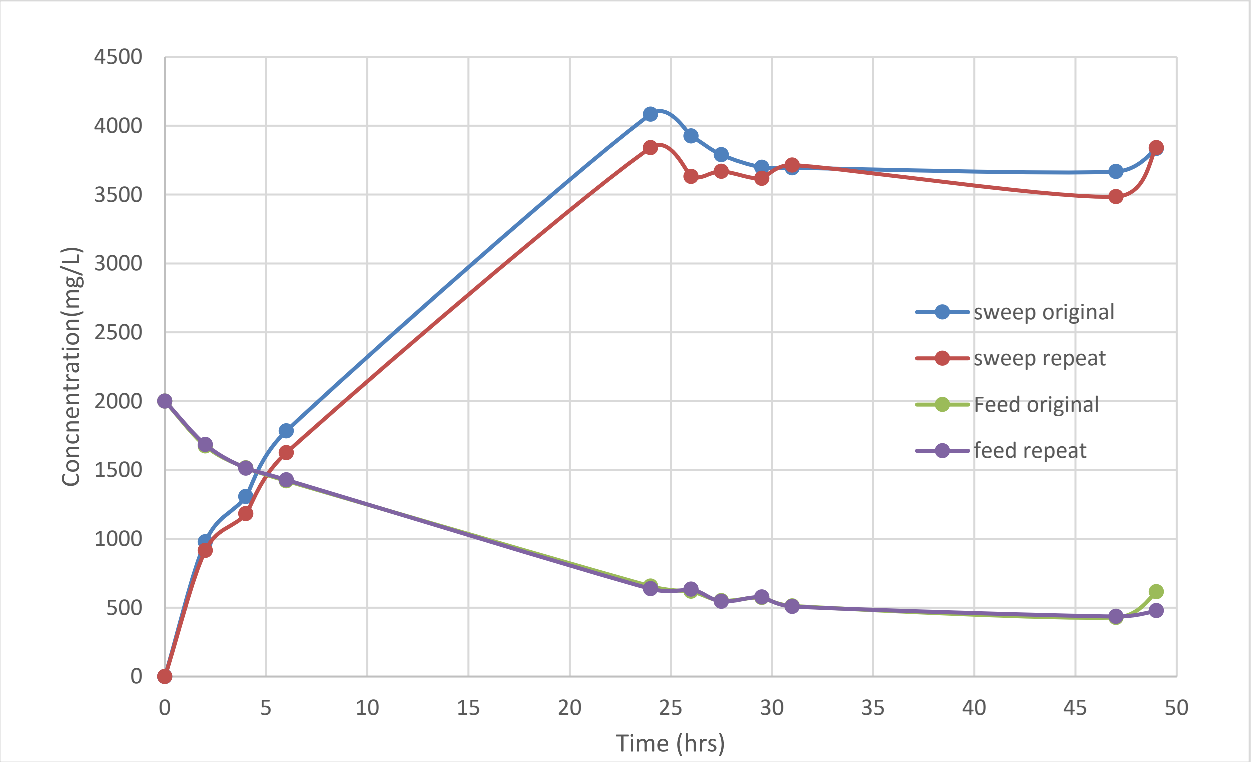


**Figure 4-1: Feed and sweep concentration profiles illustrating repeatability. (IFC = 2000 mg/L, ISC = 1M, FF = 75%, SF = 25%)**

It is clear that there was a very good repeatability. It is noted that there are gaps in the data taken between ~ 8 hours and ~ 20 hours. This was due to restricted access to the laboratory after hours, arising from security and health and safety concerns. However, the graph does follow the trend reported in literature. The forms of the profiles will be discussed in the next section.

### 4.2.2 Mass Balances

One validation of experimental results is to ascertain where there is closure of the mass balances, i.e. can the Al that was available at the start of the experiment be accounted for at the end of the experiment. In general, a mass balance closure of > 90% is regarded as acceptable, whilst low closures indicate leaks in the apparatus, errors with the analytical method, or similar failures. Mass balances were performed by measuring the volumes and the Al concentrations of the sweep and feed reservoirs before and after an experiment. Note that the feed volume decreased and the sweep volume increased during experiments, due to osmosis from the feed to the sweep, as discussed in Chapter 2. Two typical mass balances are shown in Tables 4-1 and 4-2. The variance observed was within the combined error expected from the analytical instruments, sampling, etc. For all experiments reported in this study, the mass balance closure was > 90%.

**Table 4-1: Mass closure 1**

| 3000 mg/L 2M 25% 25% | Mass of Al at start of experiment (mg) | Mass of Al at end of experiment (mg) |
|---|---|---|
| Feed | 9000 | 1299.7 |
| Sweep | 0 | 8400 |
| Total mass | 9000 | 9699.7 |
| | Mass difference (mg) | ~ 700 |
| | Variance | 7.7% |

**Table 4-2: Mass closure 2**

| 2000 mg/L 2M 25% 25% | Mass of Al at start of experiment (mg) | Mass of Al at end of experiment (mg) |
|---|---|---|
| Feed | 6300 | 325.035 |
| Sweep | 0 | 6025.36 |
| Total mass | 6300 | 6350.395 |
| | Mass difference (mg) | 50 |
| | Variance | 0.8 |

### 4.2.3 Limitations in Data Acquisition

In all results presented in this report, there are large gaps in data points. This was due to the difficulty in obtaining samples during the night, arising from security rules and OHS rules at SUN. The Project Team did investigate the option of an automated sampler, but this was way beyond the project budget. The ‘second best’ option was to take at least two to three samples a short period after each other, to eliminate outliers.

## 4.3 SCANNING INVESTIGATIONS

### 4.3.1 Overview

Most of the previous investigations into using DD for Al recovery used fairly high initial feed and sweep concentrations, i.e. feed concentrations of 2000 mg/L to 5000 mg/L Al, and sweep molarities of 1 M to 2 M. As discussed in Section 4.4, these concentrations are unrealistically high for an industrial process. Nevertheless, scanning experiments were conducted at these elevated concentrations with the following objectives:

(i) to establish whether the 'form' of the feed and sweep concentration profiles obtained in this investigation matched that reported in literature, and

(ii) to determine the influence of the various operating variables on Al transport. Operating at high concentrations would amplify phenomenon that might not be distinct at lower concentrations.

To improve the flow of this report, the detailed results of the scanning runs have been relegated to Appendix A, and the investigation into the influence of the operating variables has been relegated to Appendix B. A summary of the results, answering the above objectives, will be presented here.

### 4.3.2 Experimental Design

The feed consisted of an aluminium sulphate solution in water, whilst the sweep consisted of sulphuric acid.

Four operating parameters were investigated, viz.

(i) Initial feed Al concentration (IFC)

(ii) Initial sweep acid concentration (ISC)

(iii) feed flowrate (FF)

(iv) sweep flowrate (SF)

The high and low values for each parameter are shown in Table 4-3. A full factorial design was developed, i.e. all possible combinations of the above values. This required 16 experiments ($4^2$), and the combinations investigated are shown in Table 4-4.

**Table 4-3: Values selected for operating parameters**

| | Code | IFC | ISC | FF | SF |
|---|---|---|---|---|---|
| **LOW** | **-1** | 2000 mg/L | 1 M | 2.2ml/s | 2.2ml/s |
| **HIGH** | **1** | 3000 mg/L | 2 M | 4.9 ml/s | 4.9 ml/s |

**Table 4-4: Full factorial experimental design**

| Run | IFC | ISC | FF | SF |
|---|---|---|---|---|
| **1** | -1 | -1 | -1 | -1 |
| **2** | 1 | -1 | -1 | -1 |
| **3** | -1 | 1 | -1 | -1 |
| **4** | 1 | 1 | -1 | -1 |

| | | | | |
|---|---|---|---|---|
| **5** | -1 | -1 | 1 | -1 |
| **6** | 1 | -1 | 1 | -1 |
| **7** | -1 | 1 | 1 | -1 |
| **8** | 1 | 1 | 1 | -1 |
| **9** | -1 | -1 | -1 | 1 |
| **10** | 1 | -1 | -1 | 1 |
| **11** | -1 | 1 | -1 | 1 |
| **12** | 1 | 1 | -1 | 1 |
| **13** | -1 | -1 | 1 | 1 |
| **14** | 1 | -1 | 1 | 1 |
| **15** | -1 | 1 | 1 | 1 |
| **16** | 1 | 1 | 1 | 1 |

### 4.3.3 Typical form of results

A typical set of Al concentration profiles is shown in Figure 4-2. In this instance the effect of initial sweep acid concentration on feed and sweep Al concentration profiles was investigated.

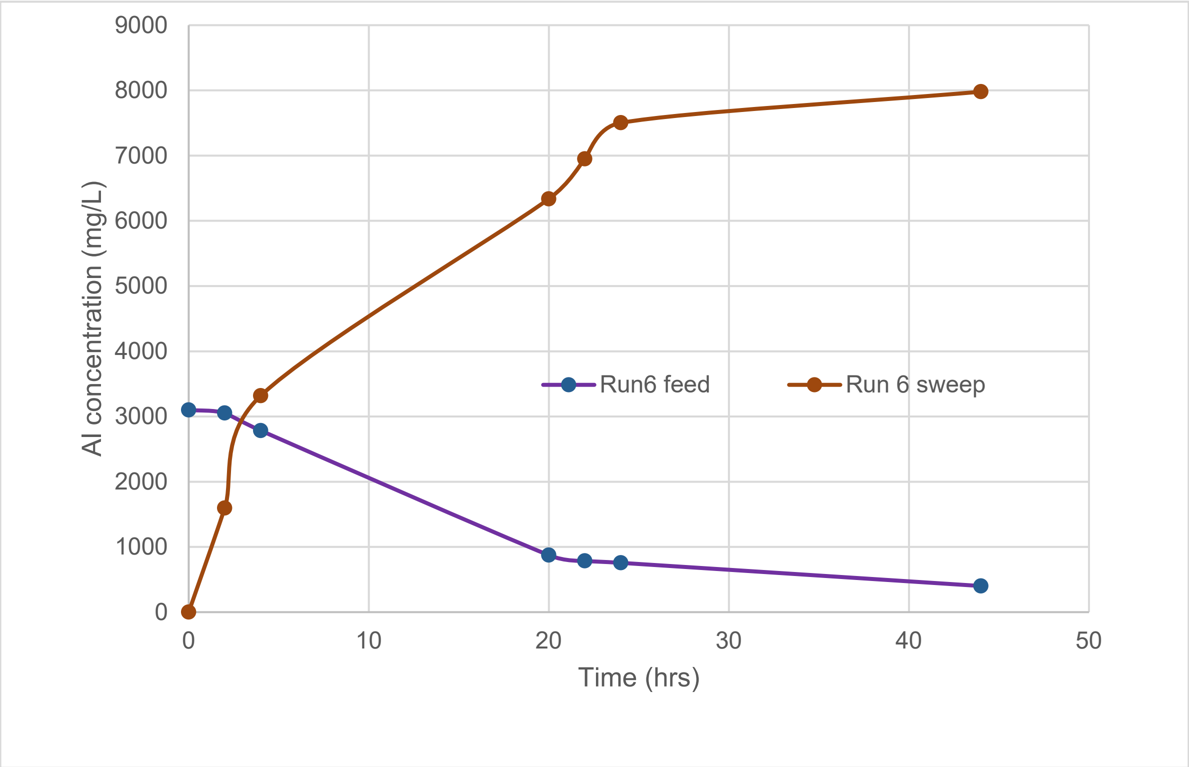


**Figure 4-2: Typical feed and sweep Al concentration profiles. (Run 6: IFC = 3000 mg/L, ISC = 2M, FF = 75%, SF = 75%)**

Observations from Figure 4-2:

(i) The sweep Al concentration increases rapidly, then levels out. In some runs, the sweep concentration reaches a maximum, and then decreases (Appendix B). Conversely the feed Al concentration decreases rapidly and then levels out. These observations are consistent trends reported in literature (see Chapter 2), where osmosis of water from the feed to the sweep progressively dilutes the sweep, resulting in the sweep concentration levelling out and possibly decreasing. In the above figure an 'equilibrium' appears to have been reached after about 28 hours.

(ii) Initially the feed Al concentration was 3000 mg/L and the sweep Al concentration was 0 g/L. When the curves level out the feed Al concentration is approximately 500 mg/L whilst the sweep Al concentration is about 8000 mg/L (Run 6).

In 'normal' closed loop mass transfer processes, an equilibrium is usually reached when the feed and sweep concentrations are similar. In this instance the 'equilibrium' sweep concentration is ~ 16 times the feed concentration. Further, the final sweep Al concentration is substantially higher than the initial feed Al concentration (8000 mg/L and 3000 mg/L).

This is one of the 'non-intuitive' behaviours of DD. An explanation of the processes that causes this is beyond the scope of this project. However, the reason for this arises from the fact that in DD, the driving force depends not only on the concentration of ions, but also on their ionic charge (see Chapter 2). In the present instance, the metal ion ($Al^{3+}$) has a charge of +3, and the substitution ion ($H^+$) has a charge of +1. Hence, an equilibrium (ignoring osmotic effects) will be reached when:

$$\left(\frac{[Al]^{+}{}_{feed}}{[Al]^{+}{}_{sweep}}\right)^{\frac{1}{3}}=\left(\frac{[H]^{+}{}_{feed}}{[H]^{+}{}_{sweep}}\right)^{\frac{1}{1}} \qquad \text{[20 rewritten]}$$

The above phenomenon is a major advantage of DD, i.e. that product concentrations of the metal ion can be significantly higher than the initial feed concentrations of the ion.

(iii) Around 25 hours, just before the 'equilibrium', the concentrations of both the feed and sweep appear to be 'unstable' and go through dips and peaks. Initially it was thought that this may be due to normal analytical errors. However, repeatability experiments indicated that these were seemingly real instabilities. Further, they appeared on most of the results obtained in the scanning runs (see Appendix A). An explanation for this is beyond the scope of this project.

(iv) Concerning the effect of initial sweep acid concentration on DD performance, the above figure indicated that for the 2 M solution significantly greater transport of Al occurs than for the 1 M sweep acid concentration. This is intuitively obvious, since a greater molarity implies a greater concentration of $H^+$ ions, and hence a greater driving force.

### 4.3.4 Effects of operating variables

#### *4.3.4.1 General trends*

The detailed results of the scanning investigation are presented in Appendix B. The important trends observed are summarised here:

(i) **Sweep Flowrate:** Varying the sweep flow rate was found to change the final sweep Al concentration by about 400 mg/L. This difference was found to be the least significant of the operating parameters.

(ii) **Feed Flowrate**: Varying the feed flowrate was found to have a significant impact on the final Al concentration in the sweep. Surprisingly however, it was found that a *lower* flow rate increased the final Al sweep concentration. The final Al sweep concentrations of Run pair 3 and 10 were found to differ by about 700 mg/L, while that of Run pair 2 and 9 differed by about 1200 mg/L, in favour of the lower flow rate.

(iii) **Initial Sweep Acid Concentration**: The effect of sweep concentration was found to be a pull and tug effect of two factors. Firstly, a higher sweep acid concentration was found to increase the volume of water transported across to the sweep side and hence dilute the concentration of aluminium recovered. Secondly, a higher sweep concentration was found to provide a higher electrochemical potential which resulted in a higher transport of aluminium to the feed. The final sweep concentration of Run 1 was found to be 6335 mg/L while that of Run 3 was 4950 mg/L. For the second pair of runs, Run 4's final concentration was found to be 3871 mg/L and Run 6 to be 7980 mg/L. The results of both of these pairs of runs demonstrated that the hydrodynamic effect was found to be smaller in relation to the ability of the acid to draw aluminium ions to the sweep via ionic exchange.

**Initial Feed Al Concentration**: The trend of the feed Al concentration was found to also be a function of the sweep acid concentration. A higher concentration of aluminium was recovered in the sweep for high feed concentrations only when high acid sweep concentrations were used. A higher aluminium concentration was recovered in the sweep using low feed concentration when low acid sweep concentrations were used. This trend was illustrated using enrichment ratios for Runs 1, 5, 2 and 4. Runs 1 and 5 yielded a ratio of 2.1 and 1.3. For Runs 2 and 4; 1.6 and 1.3 were obtained. The results of the first pair indicated that a higher feed concentration enriched the final aluminium concentration collected in the sweep more than a lower feed concentration. The second pair of runs suggested the opposite.

#### *4.3.4.2 Statistical Analysis*

In order to determine the relative importance of the four operating variables, a statistical analysis of the experimental data was performed. The maximum Al recovery was calculated for each run. A regression was then performed to determine the contributions of feed flowrate, feed concentration, sweep flowrate and sweep concentration to Al recovery. The details of the analysis are presented in Appendix C.

The analysis indicated that the relative importance of the four operating variables was as follows (in order of decreasing importance):

1. sweep concentration ***(high)***
2. feed concentration ***(medium)***
3. feed flowrate ***(low)***
4. sweep flowrate ***(negligible)***

Statistically the effect of sweep flowrate emerges as negligible, indicating that it did not have a major effect on Al recovery. The statistical analysis is supported by the visual trends reported in Section 4.3.4.1, i.e. that the sweep flowrate has the least effect on Al transfer. Accordingly, to simplify further investigations, it was decided that only sweep concentration, feed concentration and feed flowrate would be varied, whilst sweep flowrate would be kept constant.

### 4.3.5 Minimising the osmotic effect

In most of the scanning runs, the osmotic or hydrodynamic effect was very prominent, causing the sweep Al concentration to either level out or to decrease with time (Appendix B). This obviously negates the intention of having a final sweep product with a high Al concentration. This prompted a short investigation into the osmosis effect, with the intention of reducing it. The osmotic transport of water from the feed side to the sweep side results in the dilution of the sweep, manifesting as a sweep concentration that either levels out, or actually decreases with time Since the objective of Al recovery is to obtain a 'high concentration' sweep that can be reused in coagulation, the osmotic pressure effect obviously needs to be minimised.

The main chemical species used in the scanning runs were aluminium sulphate and sulphuric acid, each of which exerts an osmotic pressure that increases approximately linearly with concentration. An alternative sweep acid for the recovery of the Al would be hydrochloric acid. Both aluminium sulphate and aluminium chloride can be used as water treatment coagulants. The osmotic pressure of a chemical solution can be calculated from Van't Hoff's expression, i.e.

$$\pi = iMRT \qquad [26]$$

where $\pi$ is the osmotic pressure

*i* is the Van't Hoff factor

M is the molar concentration of species

R is the ideal gas constant

T is the temperature

The molar masses of aluminium sulphate, sulphuric acid and hydrochloric acid are given below:

| | |
|---|---|
| $Al_2(SO_4)_3$ | = 342.1 g/mol |
| $H_2SO_4$ | = 98.1 g/mol |
| HCl | = 36 g/mol |

The Van‘t Hoff factors are calculated from the number of ions that would be formed by complete ionization of the molecule. For the species under consideration here, these are as follows:

| | |
|---|---|
| $Al_2(SO_4)_3$ | = 5 ($2\ Al^{3+} + 3\ SO_4^{2-}$) |
| $H_2SO_4$ | = 3 ($2\ H^+ + SO_4^{2-}$) |
| HCl | = 1 ($H^+ + Cl^-$) |

Using the appropriate Van't Hoff factors, a graph of osmotic pressure as a function of molar concentration was generated (Figure 4-3). Note this is a theoretical graph, based on the assumption of complete ionisation. In practice, acids will not ionise completely at high concentrations, and hence the osmotic pressures for high acid concentrations will be less than Figure 4-3. Figure 4-3 is nevertheless adequate to illustrate the points raised below.

Observations arising from Figure 4-3:

(i) For the sulphuric acid concentrations used in the scanning runs, i.e. 1 M to 2 M, the theoretical osmotic pressure of the acid ranges from 75 atm to 150 atm.

(ii) The Van‘t Hoff factor for aluminium sulphate (5) is significantly greater than that of sulphuric acid (3). The Al concentrations encountered in the scanning runs (2000 mg/L to 8000 mg/L) are equivalent to aluminium sulphate concentrations of ~ 13000 mg/L to 51000 mg/L. This translates into aluminium sulphate molarities of ~ 0.03 M to 0.15 M. From Figure 12, the osmotic pressure of an aluminium sulphate solution at these low concentrations is less than 18 atm, and is hence significantly lower than the osmotic pressure of the sulphuric acid used.

(iii) The osmotic pressure of sulphuric acid is ~ 1.5 times the osmotic pressure of hydrochloric acid.

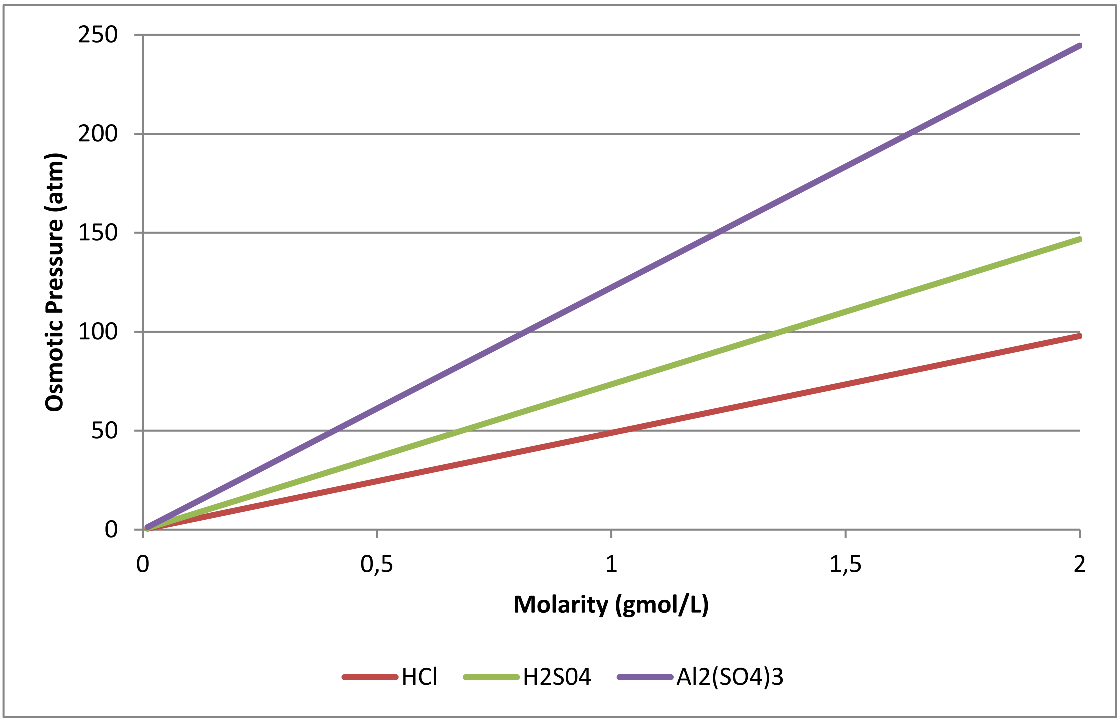


**Figure 4-3: Feed and sweep concentration profiles illustrating repeatability**

Accordingly:

(i) Sulphuric acid dominated the osmotic effect, 'dragging' water molecules from the feed to the sweep side.

(ii) The osmotic effect could be reduced by operating at lower sweep sulphuric acid concentrations. This will reduce the osmotic effect but will also reduce the driving force for Al transport.

(iii) Possibly the best option is to use hydrochloric acid instead of sulphuric acid. Hydrochloric acid has a low osmotic pressure and hence will have a lower osmotic effect than sulphuric acid.

Hence, it was decided that hydrochloric acid would replace sulphuric acid as the sweep acid in subsequent investigations. A change from sulphuric acid to hydrochloric acid does not affect the objectives of this project, since $AlCl_3$ can be used as a coagulant instead of $Al_2(SO_4)_3$ – the active ion in coagulation is the $Al^{3+}$ ion, and not the $SO_4^{2-}$ ion or the $Cl^-$ ion.

## 4.4 DECISION ON 'REALISTIC' OPERATING CONDITIONS

This project aims to eventually lead to a practical process for the recovery of Al from water treatment residuals. The scanning investigations were performed at feed Al concentrations of 2000 mg/L and 3000 mg/L, and sweep acid concentrations of 1 M to 2 M.

Previous literature indicates that the concentration of Al that can be obtained by digestion of Al precipate sludges is generally 200 mg/L to 400 mg/L. According the Al concentrations used in the scanning runs were not applicable to any real process.

Using 1 M to 2 M acids as the sweep solutions requires highly chemically resistant tanks, pipes and fitting, and poses a significant safety hazard to operators. In any industrial process, the acid molarity would have to be < 0.5 M to be manageable. A further point affecting the choice of sweep acid concentration is the osmotic effect mentioned above. Operating at high sweep acid concentrations increases the transport of Al, but also accelerates the transport of water due to osmotic effects. A further point disfavouring the use of high acid concentrations in the sweep is that the sweep product will have to be corrected for pH before it can be used as a coagulant in water treatment.

Taking all the above into account, it was decided that subsequent investigations would be based on the following more realistic concentrations:

- Initial Feed Al concentration: 300 mg/L to 700 mg/L
- Initial Sweep acid concentration: 0.25 M to 0.75 M

## 4.5 EVALUATION AND OPTIMISATION OF ALUMINIUM RECOVERY

### 4.5.1 Overview

In all investigations performed in this study the primary information produced was Al concentration profiles of the feed and sweep streams, i.e. concentration vs time. Concentration profiles are of limited value in deciding whether the DD process for Al recovery is viable or not.

Accordingly, two 'practical' performance indicators were extracted from the concentration profiles:

(i) The Al recovery, defined as follows:

$$Al\ recovery\ (t) = \frac{(Sweep\ concenentration)(t) * (Sweep\ volume)(t)}{(Inital\ Feed\ concentration) * (Initial\ feed\ volume)}$$

This indicates the % of Al in the initial feed that was actually recovered in the sweep.

(ii) The Final Al concentration – this is of importance in determining whether the final sweep stream can be directly reused, or whether further processing is required.

The scanning investigation identified the main operating parameters as feed flowrate (FF), initial feed Al concentration (FC) and initial sweep acid concentration (SC). An investigation was them performed, to evaluate these parameters on Al recovery and final sweep Al concentration, using the 'realistic' operating conditions stated in Section 4.4.

### 4.5.2 Experimental Design

While a full factorial design is very accurate because it takes into account all the possible combinations of the system, it is also very expensive to run all the experiments.

Another option to consider is the Box Behnken design approach. The Box Behnken design utilizes three factors at three different levels to evaluate the relationship between variables and their effects. The design has twelve points on the centre of the edges of the cube and 3 points in the centre of the cube as can be seen in Figure 4-4. An added bonus of the three points in the centre of the cube lies in the fact that they can be used to evaluate the repeatability of the experiment. The major advantage of the Box Behnken is that it requires the least number of experiments to be performed in order to determine the relationship between the variables of importance and their effects.

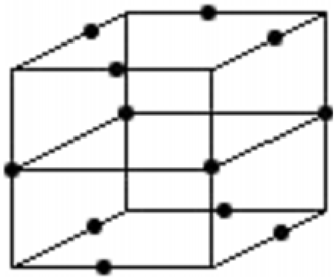


Figure 4-4: Box Behnknen cube and points

Table 4-5 below shows the way in which the combinations of points are calculated by varying the low, medium and high points of every variable. Table 4-6 shows the actual values to be used.

**Table 4-5: Box Behnken combinations**

| Test no | FF | IFC | ISC |
|---|---|---|---|
| 1 | -1 | -1 | 0 |
| 2 | 1 | -1 | 0 |
| 3 | 0 | 0 | 0 |
| 4 | -1 | 1 | 0 |
| 5 | 1 | 1 | 0 |
| 6 | -1 | 0 | -1 |
| 7 | 1 | 0 | -1 |
| 8 | 0 | 0 | 0 |
| 9 | -1 | 0 | 1 |
| 10 | 1 | 0 | 1 |
| 11 | 0 | -1 | -1 |
| 12 | 0 | 1 | -1 |
| 13 | 0 | -1 | 1 |
| 14 | 0 | 1 | 1 |
| 15 | 0 | 0 | 0 |

**Table 4-6: Box behnken values**

| Condition | Symbol | FF | IFC | ISC |
|---|---|---|---|---|
| Low | -1 | 55% | 300 mg/L | 0.25 M |
| Medium | 0 | 75% | 500 mg/L | 0.5 M |
| High | 1 | 95% | 700 mg/L | 0.75 M |

### 4.5.3 Results

#### *4.5.3.1 Overview*

When the performance of a system is dependent on three operating parameters, it is extremely difficult to represent 'system performance' in a few simple graphs. Hence, in the sub-sections below, an attempt is made to illustrate the effect of each of the operating variables, followed by an attempt to model their combined effects.

#### *4.5.3.2 Typical form of Al recovery plots*

A typical set of feed and sweep Al concentration profiles is shown in Figure 4-5.

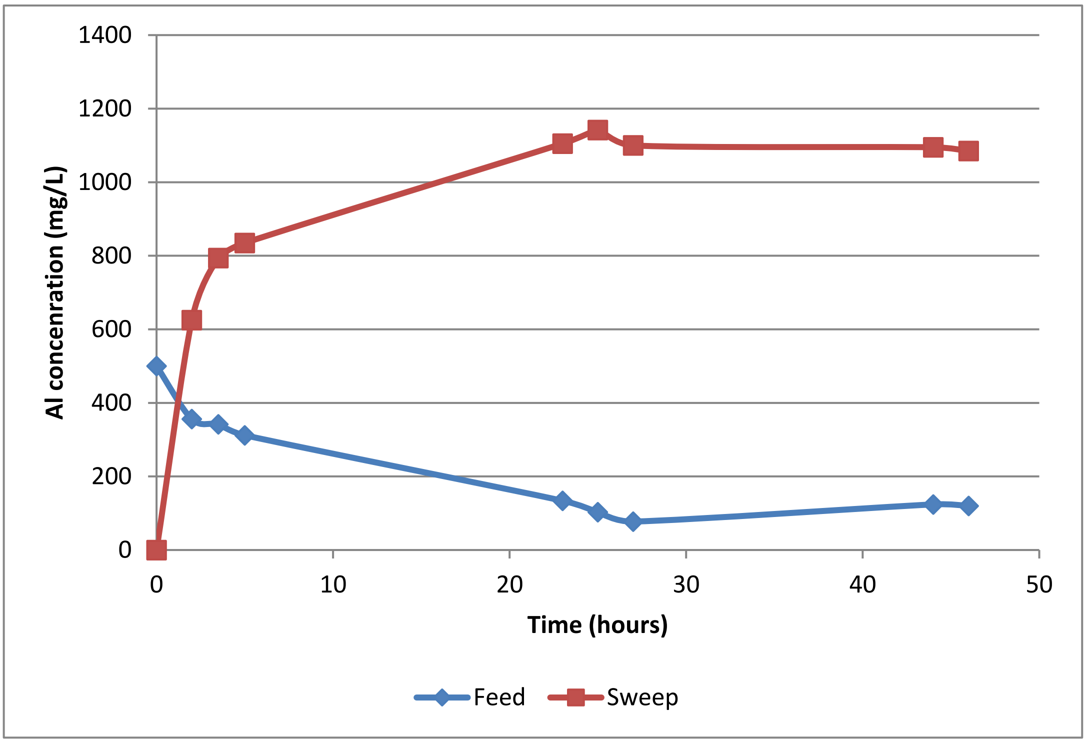


**Figure 4-5: Typical form of feed and sweep concentration profiles. (IFC = 500 mg/L, ISC = 0.25M, FF = 55%, SF = 75%)**

Observations from Figure 4-5:

(i) Similar to the scanning runs, the sweep Al concentration increases and then levels out, whilst the feed concentration decreases and then levels out. Due to the gaps in data it's difficult to state when the curves level out, but if smooth curves were fitted to the above data it would appear that the levelling out occurs between 15 and 20 hours.

(ii) Contrary to the scanning runs, no significant osmotic effects were observed in these runs, i.e. there was no significant change in the volumes of the feed and sweep reservoirs during the investigation. This was most likely due to operating at low initial sweep acid concentrations and replacing sulphuric acid with hydrochloric acid.

(iii) Contrary to the scanning runs, there was no indication of 'instability' close to the 'equilibrium'. This may indicate that the 'instabilities' experienced in the scanning runs may have the osmotic effect as their base cause.

The Al recovery profile for the above investigation is shown in Figure 4-6. The Al recovery increases rapidly, and then levels out between 15 and 20 hours. Note that the recovery is fairly constant after about 25 hours, supporting the interpretation that the levelling out of the sweep Al concentration curve (Figure 14) is due to some form of equilibrium being reached, and not to any osmotic effect.

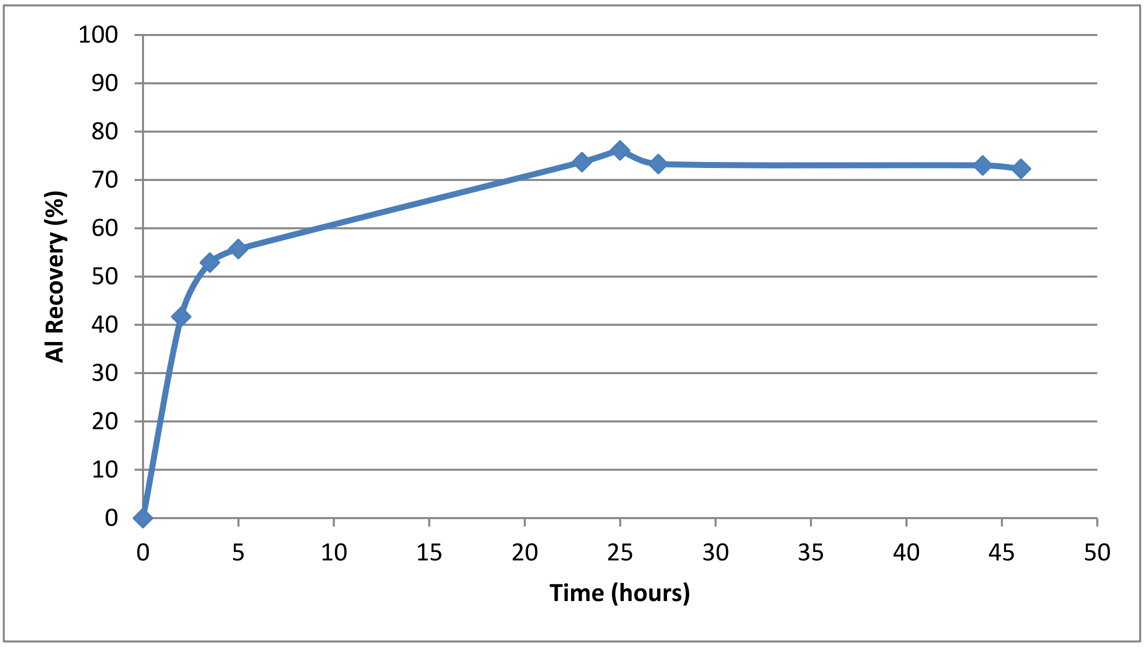


**Figure 4-6: Typical form of Al recovery profile. (IFC = 500 mg/L, ISC = 0.25M, FF = 55%, SF = 75%)**

### *4.5.3.3 Repeatability*

Three runs at a feed concentration of 500 mg/l, feed flow rate of 75% and sweep concentration of 0.5M were conducted in order to test for repeatability. The runs were conducted randomly in between other runs. Figure 4-7 shows the Al recovery plots for these repeated runs.

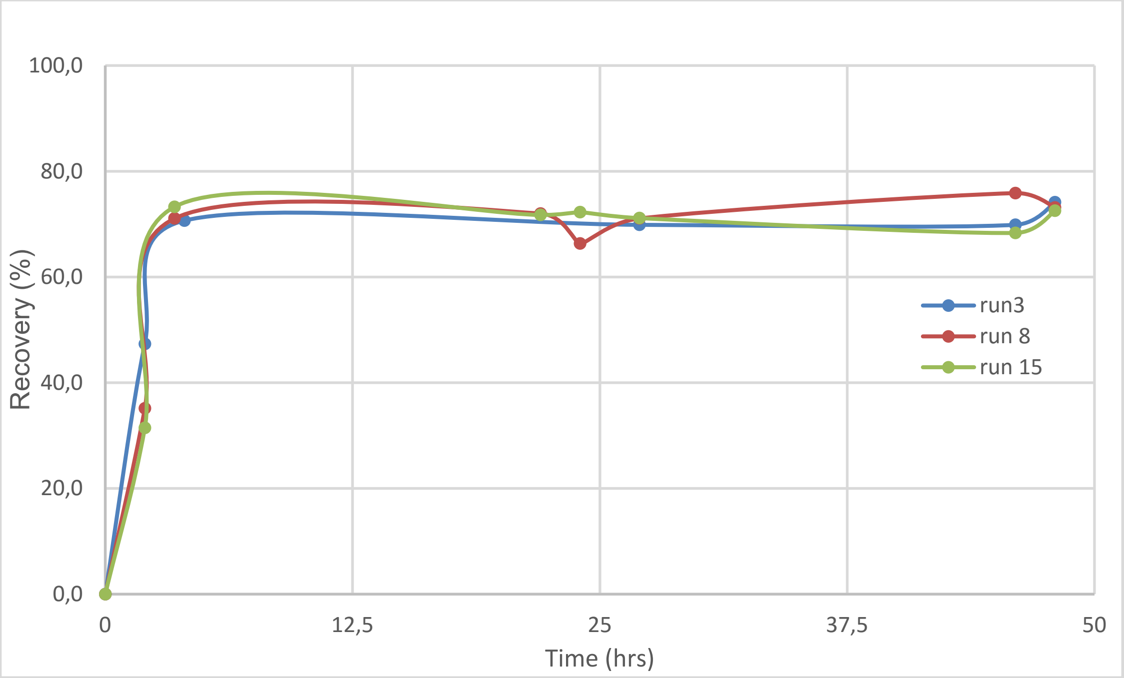


**Figure 4-7: Repeatability – Al recovery. (IFC = 500 mg/L, ISC = 0.5 M, FF = 75%)**

Figure 4-8 gives the final sweep Al concentrations. It is clear that repeatability was good, with a repeatability error of about 5% in the Al recovery plots, and an error of about 25 mg/L in the concentration plots.

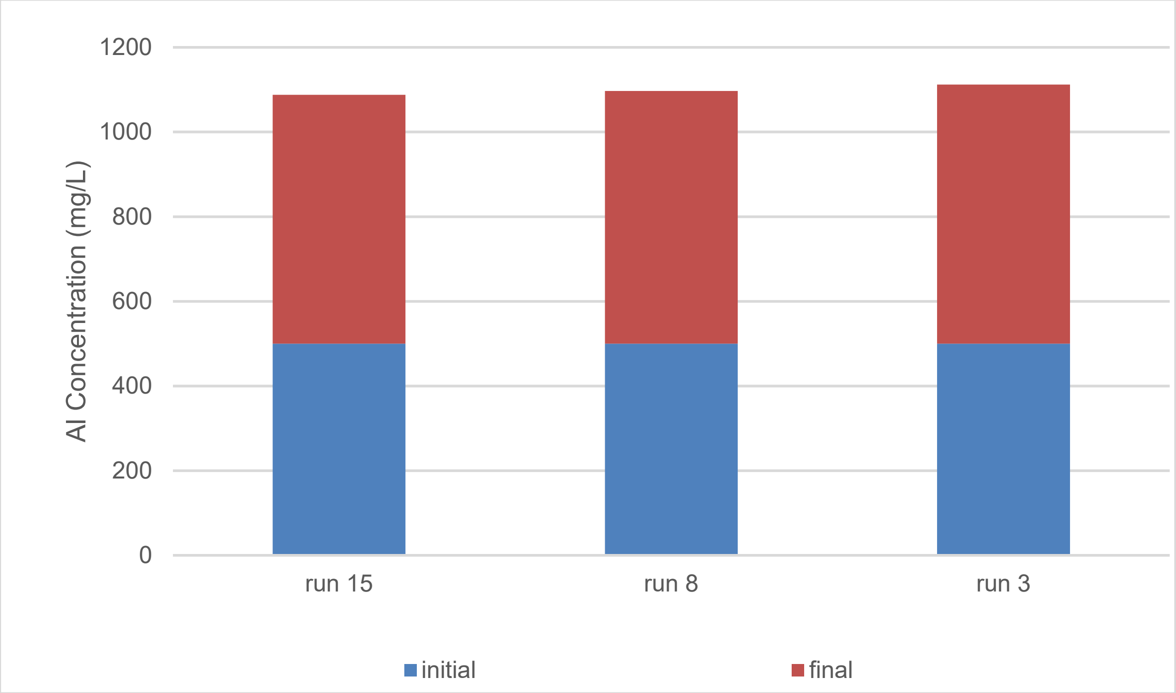


**Figure 4-7: Repeatability – Al concentrations. (IFC = 500 mg/L, ISC = 0.5 M, FF = 75%)**

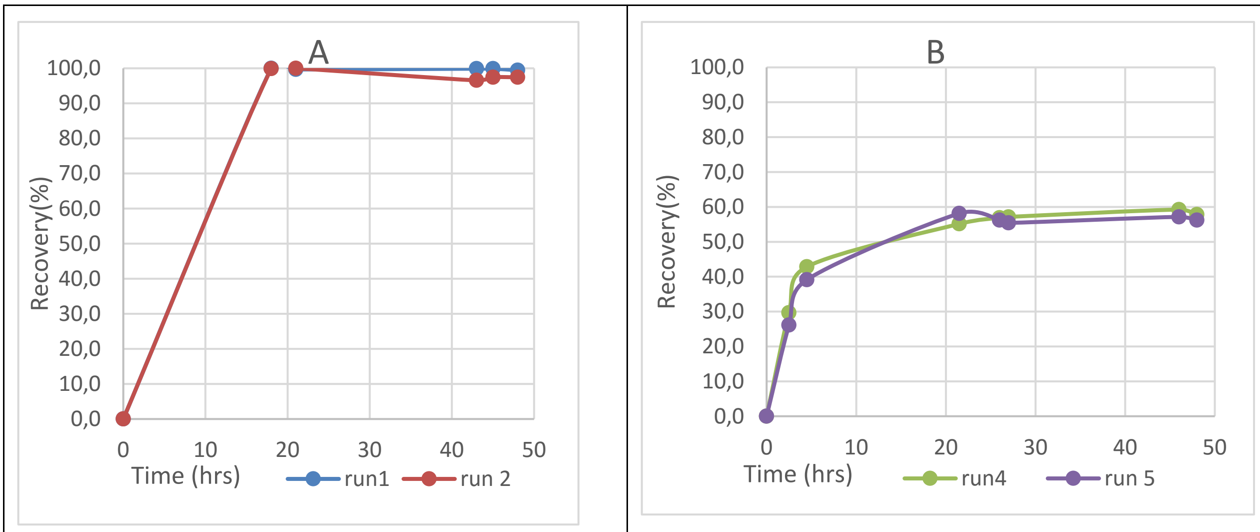
#### *4.5.3.4 Effect of feed flowrate*

The effect of feed flowrate on the recovery of aluminium is presented in this section. Table 4-7 shows the runs that were paired for comparison.

**Table 4-7: Run pairs selected to illustrate the effect of feed flowrate**

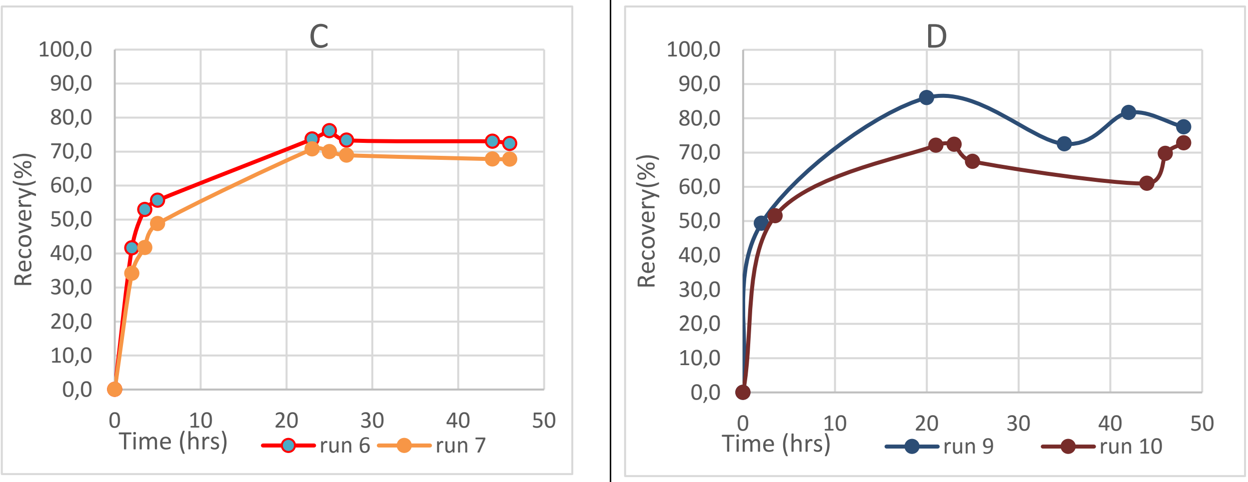
| **Runs** | **Description** |
|---|---|
| 1 and 2 | Medium feed Al concentration, medium initial sweep acid concentration, varying feed flowrates |
| 4 and 5 | High feed Al concentration, medium sweep acid concentration, varying feel flowrates |
| 6 and 7 | Medium feed Al concentration, low sweep acid concentration, varying feed flowrates |
| 9 and 10 | Medium feed Al concentration, high sweep acid concentration, varying feed flowrates |

The comparison is shown in Figure 4-9, which is divided into 4 graphs in order to illustrate the effect of feed flowrate at selected combinations of the other operating variables. The operating conditions for each run have been repeated below the figure.



(a) Low feed Al concentration, medium sweep acid concentration

(b) High feed Al concentration, medium sweep acid concentration



(c) Medium feed Al concentration, low sweep acid concentration

(d) Medium feed Al concentration, high sweep acid concentration

**Figure 4-8: Effect of feed flowrate on Al recovery**

| Run | Conditions (IFC, FF, ISC,) |
|---|---|
| 1 | 300 mg/l; 55%; 0.5M |
| 2 | 300 mg/l; 95%; 0.5M |
| 4 | 700 mg/l; 55%; 0.5M |
| 5 | 700 mg/l ; 95%; 0.5M |
| 6 | 500 mg/l; 55%; 0.25M |
| 7 | 500 mg/l; 95%; 0.25M |
| 9 | 500 mg/l; 55%; 0.75M |
| 10 | 500 mg/l; 95%; 0.75M |

Observations from Figure 4-9:

(i) The Al recovery increases rapidly in the first 5 hours or so. Thereafter the rate of recovery decreases up to about 15 to 20 hours. Following ~ 20 hours, there is no significant change in the Al recovery.

This would indicate that there is only marginal value in operating a process past 20 hours.

(ii) The recovery is not strongly dependent on the feed flowrate, over the range considered here. However, the recovery appears to be strongly dependent on the combination of the other operating parameters, particularly initial sweep acid concentration and initial feed Al concentration.

(iii) It does appear that lower flowrates favour a higher recovery. In most mass transfer processes, increasing flowrates resulting in increasing mass transfer, due to reduction of the concentration boundary layer. Hence, this contradicts ‘normal’ mass transfer processes, but any viable explanation for this is beyond the scope of this project.

(iv) Al recoveries range from ~ 60% to close to 100%, depending on the combination of operating parameters chosen.

The effect of feed flowrate on final Al concentration in the sweep is shown in Figure 4-10.

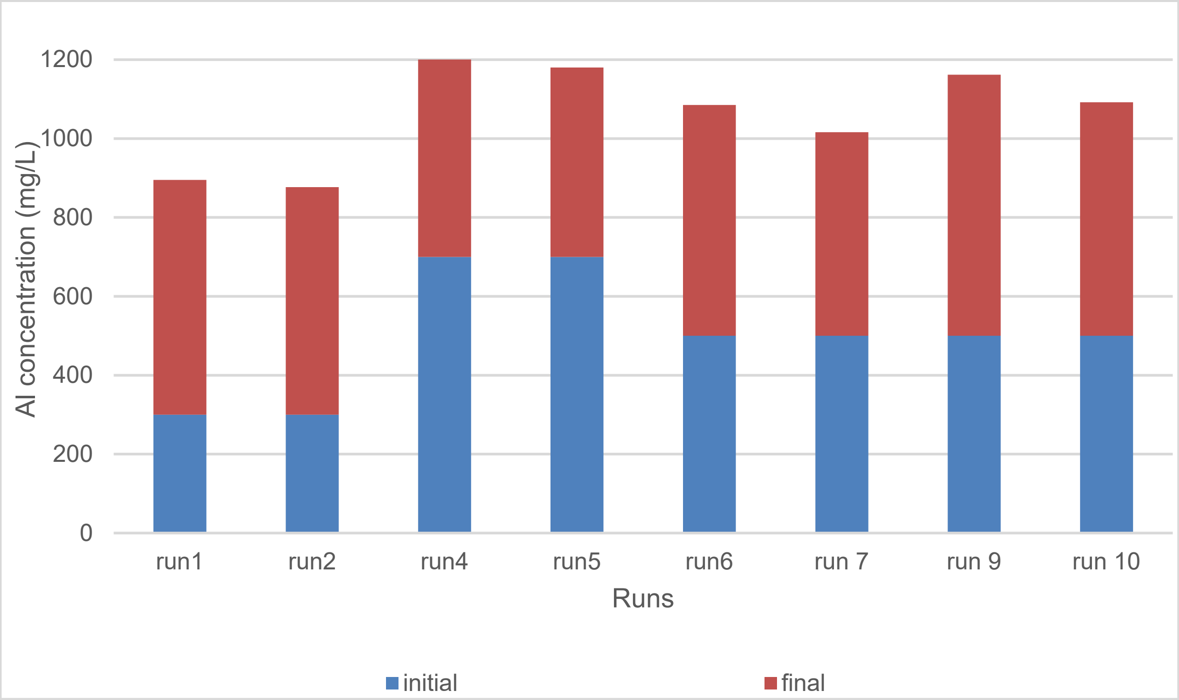


Figure 4-9: Effect of feed flowrate on final sweep Al concentration

Observations arising from Figure 4-10:

(i) Similar to the Al recovery, the final sweep Al concentration is only slightly dependent on feed flowrate. Once again, an unexpected effect is observed, with lower feed flowrates giving marginally higher final sweep Al concentrations.

(ii) For feed Al concentrations of 300 mg/L to 750 mg/L final sweep Al concentrations of ~ 800 mg/L to 1100 mg/L can be achieved.

(iii) Once again, the final sweep Al concentration is not a strong function of the feed flowrate. However, once again, the surprising result obtained is that lower feed flowrates result in higher final sweep Al concentrations.

(iv) Concentration factors, i.e. (final sweep Al concentration/initial feed Al concentration) range from ~ 1.5 to 3, with lower initial feed concentrations favouring higher enrichment factors.

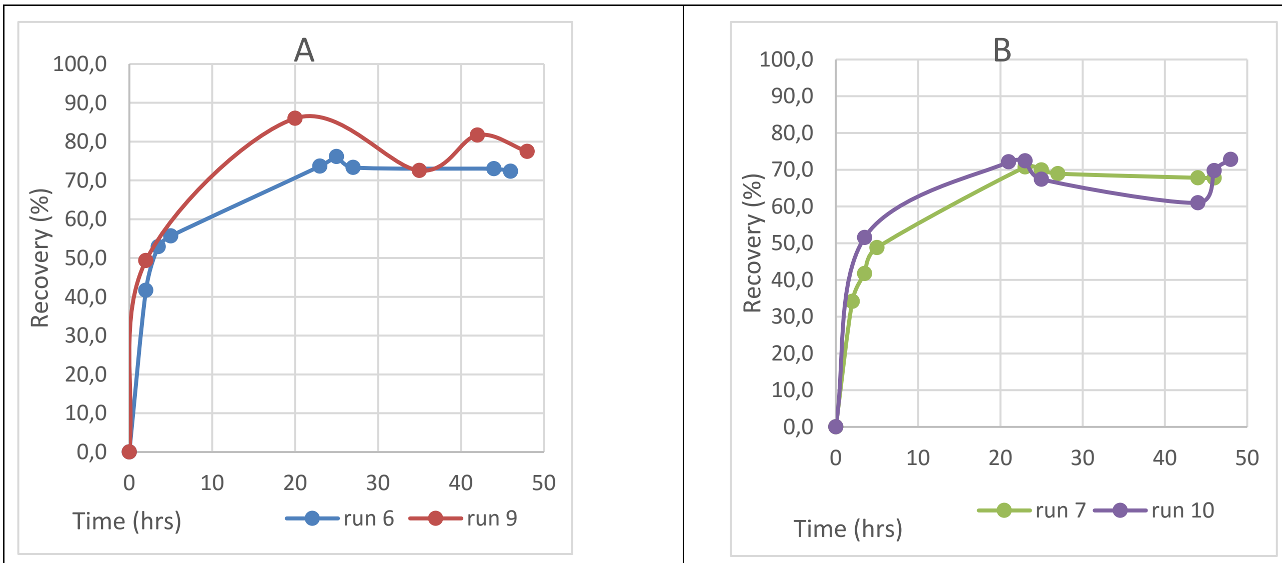
#### *4.5.3.5 Effect of initial sweep acid concentration*

The effect of initial sweep acid concentration on the recovery of aluminium and final sweep Al concentration is discussed in this section. Table 4-8 shows the runs that are paired for comparison.

**Table 4-8: Run pairs selected to illustrate the effect of initial sweep acid concentration**

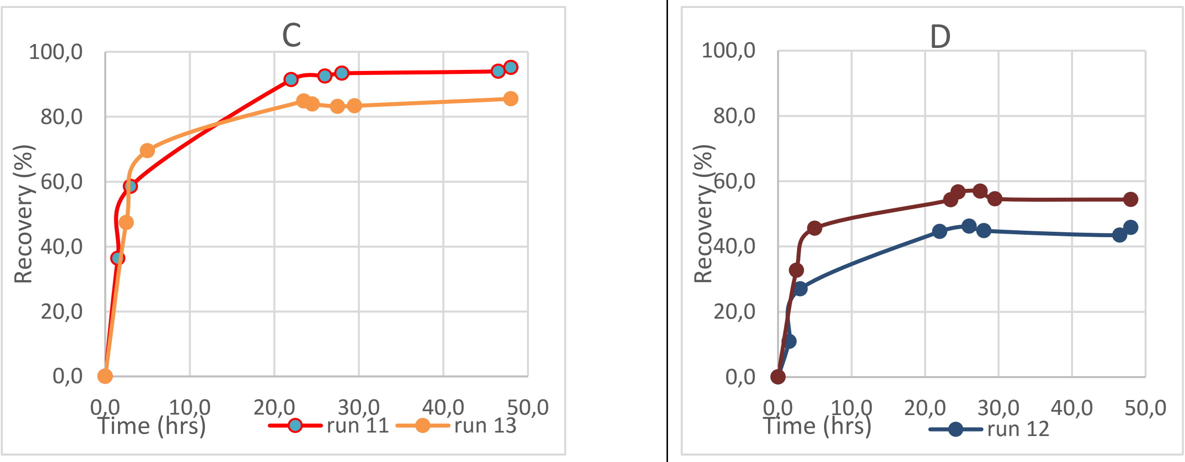
| **Runs** | **Description** |
|---|---|
| 6 and 9 | Medium initial feed Al concentration, medium feed flowrate, varying initial sweep acid concentration |
| 7 and 10 | Medium initial feed Al concentration, high feed flowrate, varying initial sweep acid concentration |
| 11 and 13 | Low feed Al concentration, low feed flowrate, varying initial sweep acid concentration |
| 12 and 14 | High initial feed Al concentration, medium feed flowrate, varying initial sweep acid concentration |

The effect of initial sweep acid concentration on Al recovery is shown in Figure 4-11. This has been divided into four graphs in order to assess the effect of sweep concentration at selected combinations of the other operating parameters. The operating conditions for each run have been provided below the figure.



(a) Medium initial feed Al concentration, medium feed flowrate, varying initial sweep acid concentration

(b) Medium initial feed Al concentration, high feed flowrate, varying initial sweep acid concentration



(c) Low feed Al concentration, low feed flowrate, varying initial sweep acid concentration

(d) High initial feed Al concentration, medium feed flowrate, varying initial sweep acid concentration

**Figure 4-10: Effect of initial sweep acid concentration on Al recovery**

| Run | Conditions (IFC, FF, ISC) |
|---|---|
| 6 | 500 mg/l; 55%; 0.25M |
| 9 | 500 mg/l; 55%; 0.75M |
| 7 | 500 mg/l; 95%; 0.25M |
| 10 | 500 mg/l; 95% ; 0.75M |
| 13 | 300 mg/l; 75%; 0.75M |
| 11 | 300 mg/l; 75%; 0.25M |
| 12 | 700 mg/l; 75%; 0.25M |
| 14 | 700 mg/l;75%; 0.75M |

Al recoveries range from ~ 40% to about 90%, depending on the combination of operating parameters. The initial sweep acid concentration does have an effect on Al recovery, with higher initial sweep acid concentrations resulting in higher recoveries. This is particularly noticeable with high initial feed Al concentrations and medium feed flowrates (Figure 4-11d). The effect of improved Al recovery with higher initial sweep acid concentration is consistent with expectations from normal mass transfer theory and the theory of transport in DD. A higher initial sweep acid concentration provides a higher driving force, which should increase both the rate of Al transfer and the final equilibrium sweep Al concentration. It is difficult to see any significant difference in transfer rates in Figure, but there does appear to be a positive effect on final Al recovery, as discussed above.

The effect of sweep concentration on final Al sweep concentration is shown in Figure 4-12. Final sweep Al concentrations range from ~ 750 mg/L to about 1100 mg/L, with concentration factors of ~ 1.25 to ~ 2.1. Similarly, to the effect on Al recovery, the initial sweep acid concentration has a positive, though marginal, effect on final sweep Al concentration.

In the scanning runs the higher driving force that results from higher initial sweep acid concentrations was offset by the increase in osmotic transport. However, at the reduced acid molarities used in these runs, the osmotic effects were seemingly negligible.

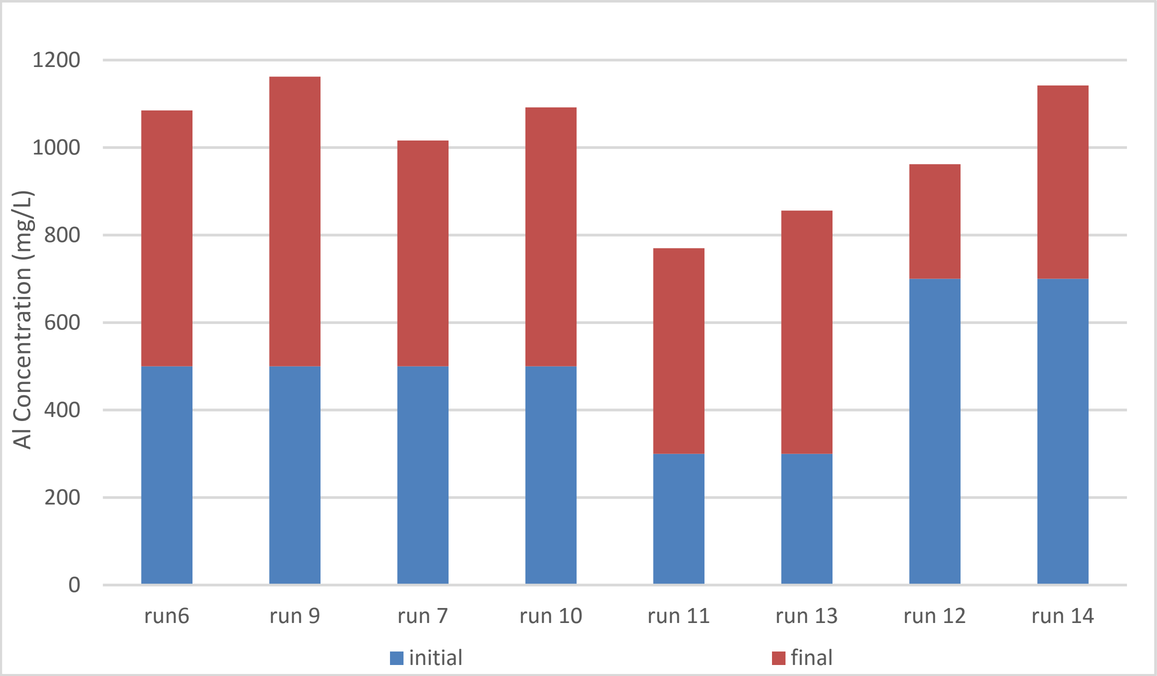


**Figure 4-11: Effect of initial sweep acid concentration on final sweep Al concentration**

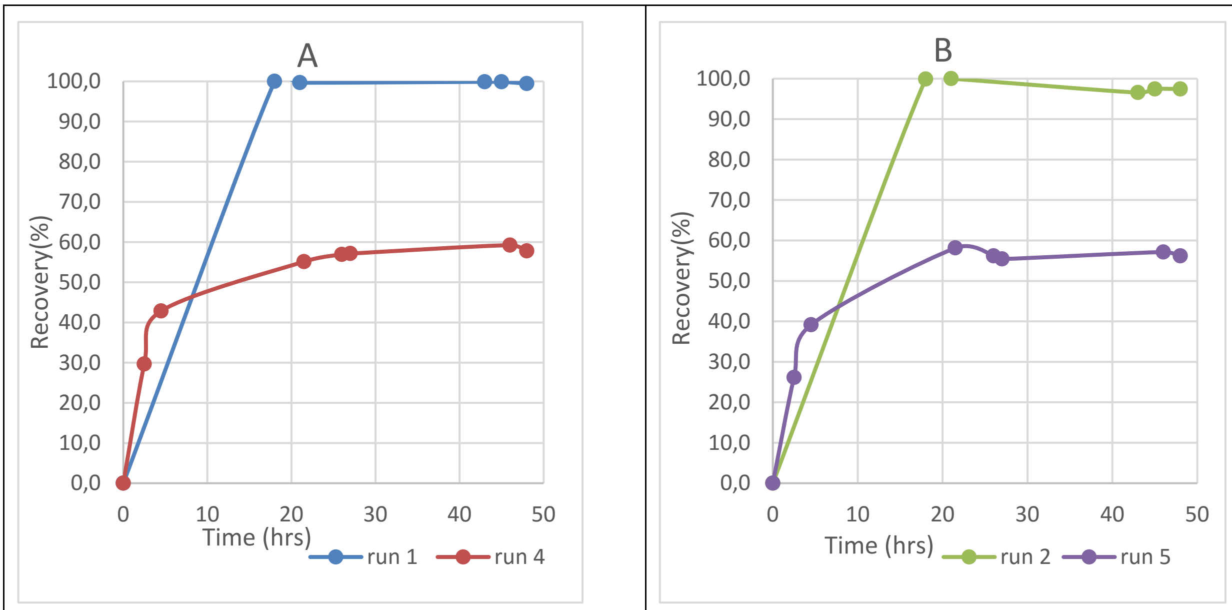
#### 4.5.3.6 *Effect of initial feed Al concentration*

The effect of initial Al feed concentration on both Al recovery and final sweep Al concentration are discussed in this section. Table 4-9 indicates the runs that were paired for comparison.

**Table 4-9: Run pairs selected to illustrate the effect of initial feed Al concentration**

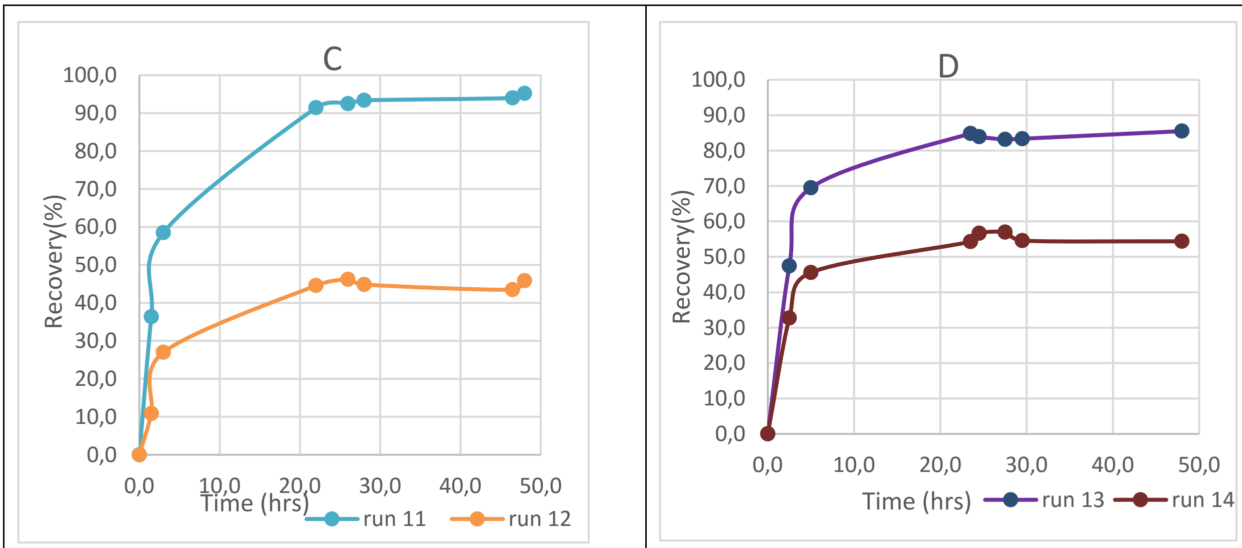
| Runs | Description |
|---|---|
| 1 and 4 | Medium feed flowrate, medium initial sweep acid concentration, varying initial feed Al concentration |
| 2 and 5 | High feed flowrate, medium initial sweep acid concentration, varying initial feed Al concentration |
| 11 and 12 | Medium feed flowrate, low initial sweep acid concentration, varying initial feed Al concentration |
| 13 and 14 | Medium feed flowrate, high initial sweep acid concentration, varying initial feed Al concentration |

The effect of initial feed Al concentration on Al recovery is shown in Figure 4-13, divided into four graphs in order to illustrate the effect of feed concentration at selected combinations of the other operating parameters. Recoveries range from about 40% to around 95%. It is clear that the initial feed Al concentration has a very significant effect on Al recovery, with lower initial feed Al concentrations strongly favouring Al higher recoveries. This is consistent with theoretical expectations, since a lower initial feed Al concentration would imply a higher driving force for Al transport, for equivalent initial sweep acid concentrations.



(a) Medium feed flowrate, medium initial sweep acid concentration, varying initial feed Al concentration

(b) High feed flowrate, medium initial sweep acid concentration, varying initial feed Al concentration



(c) Medium feed flowrate, low initial sweep acid concentration, varying initial feed Al concentration

(d) Medium feed flowrate, high initial sweep acid concentration, varying initial feed Al concentration

**Figure 4-12: Effect of initial feed Al concentration on Al recovery**

| Run | Conditions (IFC, FF, ISC) |
|---|---|
| 1 | 300 mg/l; 55%; 0.5M |
| 4 | 700 mg/l ; 55%; 0.5M |
| 2 | 300 mg/l; 95%; 0.5M |
| 5 | 700 mg/l ; 95%; 0.5M |
| 11 | 300 mg/l; 75%; 0.25M |
| 12 | 700 mg/l; 75%; 0.25M |
| 13 | 300 mg/l; 75%; 0.75M |
| 14 | 700 mg/l; 75%; 0.75M |

The effect of initial feed Al concentration on the final sweep Al concentration is shown in Figure 4-14. Final sweep concentrations range from ~ 750 mg/L to ~ 1200 mg/L, with concentration factors ranging from about 1.2 to about 3. Similar to Al recovery, lower feed concentrations strongly favour higher concentration factors.

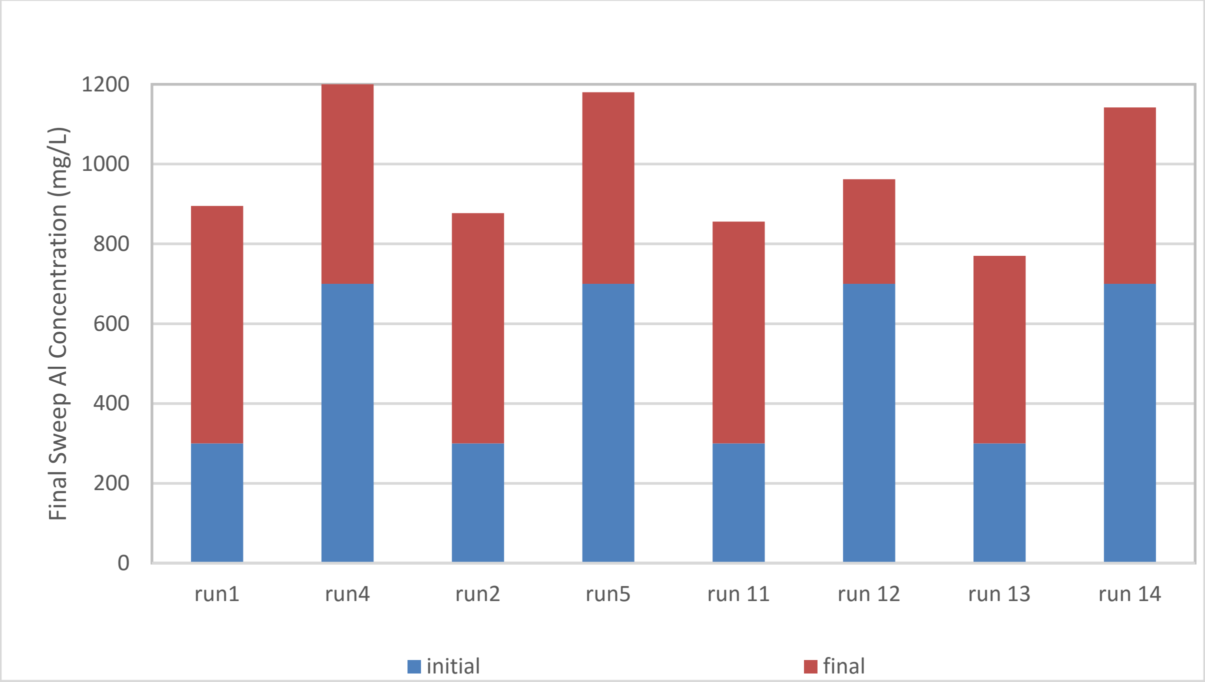


**Figure 4-13: Effect of initial feed Al concentration on final sweep Al concentration**

### *4.5.3.7 Statistical modelling and Optimisation*

There is significant value in being able to represent experimental results in the form of a mathematical equation. Where a phenomenon is well known and has previously being successfully modelled mathematically, experimental results can be fitted to these models. In the instance of DD, it is still a field under research, and there are no practical predictive models available to date. An attempt was made to model the experimental results obtained here in terms of the equations reported in the Literature Survey, but it emerged that there were too many unknown parameters. From a practical point of view, and alternative approach is a statistical model, which develops an equation relating the 'measured values' to the 'independent variables'.

From the final Box Behnken design of experiments and recoveries obtained above, a statistical model using least squares methods was constructed to represent and model the data. In matrix form the expression can be written as;

Y=BX+E

Where Y is the matrix of measured values, X is independent variables and E is a coefficient of errors. Further expanding this equation results in the below second order quadratic equation.

$$Yrecovery = \beta o + \beta 1X1 + \beta 2X2 + \beta 3X3 + \beta 11X1^2 + \beta 22Xx^2 + \beta 33X3^2 + \beta 12X1X2 + \beta 13X1X3 + \beta 23X2X3$$

Where $\beta$ii coefficients are quadratic coefficients, $\beta$ij are interacting coefficients and $\beta i$ are the main effects. These coefficients are found through regression and least square analysis. $X_1$ Is the feed flowrate, $X_2$ is the initial feed Al concentration and $X_3$ is the initial sweep acid concentration. The final model was in the form of a quadratic function with interacting parameters. The model obtained is given below;

$$Y_{recovery} = 212.98 - 32.65X_1 - 0.17X_2 + 28.70X_3 + 3.40{X_1}^2 - 78.78{X_3}^2 + 0.0005X_1X_2 + 0.24X_1X_3 + 0.1X_2X_3$$

The above equation has potential value in determining an optimized set of operating conditions to maximize recovery. If, for example, an initial feed Al concentration is specified, the above equation is then used to develop a surface plot of Al recovery as a function of both feed flowrate and initial sweep acid concentration. From this the optimal feed flowrate and initial sweep acid concentration to maximize Al recovery can be selected.

#### *4.5.3.8 Summary*

(i) For all combinations of operating parameters investigated, Al recovery increases rapidly, attaining about 60% to 70% of its final value within the first 5 hours of operation. Thereafter the rate of recovery gradually decreases, and levels off after about 15 to 20 hours of operation. Past 25 hours of operation, there is no significant change in Al recovery.

(ii) At the 'industrially realistic' operating conditions investigated in this section, the osmotic effect appears to be negligible. This is most likely due to the lower acid concentrations and the switch from sulphuric acid to hydrochloric acid.

(iii) Al recoveries of ~ 40% to ~ 95% can be achieved, and final sweep concentrations of 800 mg/L to 1200 mg/L can be achieved, depending on the combination of operating parameters. Concentration factors achievable range from 1.25 to 3.

# 5 REJECTION OF ORGANICS

## 5.1 INTRODUCTION

This section evaluates the claimed advantage of DD over other approaches to Al recovery, that DD allows Al to be recovered whilst rejecting organics. Obtaining samples of real water treatment residues proved to be a major bottleneck in the project. In a previous study performed at SUN settled sludge and the associated liquor was obtained from a Western Cape water treatment plant. However, that water works, and various others, were not in operation due to the water crisis in the Western Cape. Another operational Western Cape water treatment works uses alum and was operational. However, major modifications would have to be made to the piping to obtain samples of the settled sludge. Eventually it was decided to use dried sludge from the evaporation ponds at Blackheath as the source of waste water Al residues.

## 5.2 FEED PREPARATION

Water treatment residuals were obtained in the form of sludge from the Black heath water treatment plant in the Western Cape. Due to the water treatment residuals being in solid form, acid digestion was done before experimentation could get under weigh. 30 grams of sludge was digested in a 1L and 0.5M HCL solution. 3 Litres were made for the feed solution. Another digestion was also done with 30grams of sludge, however the sludge was digested in 1L of 0.05M HCL solution. Again, a 3L feed solution was made up. The reasoning behind having two digestive solutions differing by an order of magnitude was to determine two effects. Firstly, if increasing or decreasing acid concentration had an effect on the amount of organics and aluminium released from the sludge into solution. Secondly, if the acid concentration affected the kinetics and recovery of aluminium as well as rejection of organics in the Donnan dialysis experiment.

## 5.3 INVESTIGATIONS

Both feed solutions were at 75% feed flow and sweep flow rates. The sweep solution consisted of 1L of 0.5M HCL. Figure 5-1 shows the feed solution after digestion and before experimentation took place. Its dark brownish colour is indicative of a high concentration of dissolved organics.

Figure 5-1: Liquor from the digestion of waste Al sludge

Figure 5-2 shows feed and sweep samples of the 0.5M and 0.05M after 48 hours of Donnan dialysis run time. The feed side was found to still be a brown colour and the sweep side was unchanged in its transparent colour. The 0.5M digested sludge was also found to be a darker colour than the 0.05M.

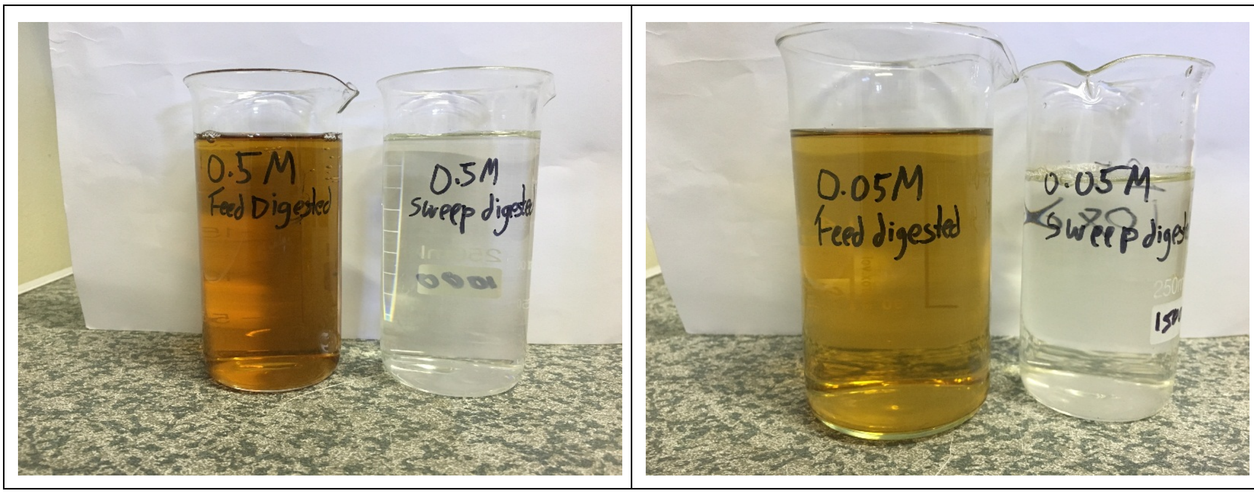


**Figure 5-2: Differences between feed and sweep solutions after DD runs**

## 5.4 RESULTS

### 5.4.1 Rejection of organics

Total Organic carbon (TOC) analyses would be the preferred method of quantifying organics in the feed and sweep streams. However, laboratory personal raised concerns at using 0.05 M to 0.5 M samples in their TOC instruments. Hence, eventually UV 254 absorbance was used as an indicator of organics. A UV analyzer was used and set at wavelength of 254nm in order to try and determine if any organics from the feed were transferred into the sweep side. UV analysis does not give absolute quantitive figures, but rather changes in concentration of organics. Figure 5-3 provides the results for both the 0.5M and 0.05M HCL feeds.

Firstly, the difference in absorbance of the two feeds indicates that a higher concentration of acid was able to breakdown the sludge more successfully, as more organics were found to be in solution. This is seen as the starting absorbance for the 0.5M feed is 20.6abs/cm and that of 0.05M is 19.2abs/cm. The sweep absorbances were however the same as at the beginning as there were no organics present in solution. The reason the absorbance reading was 12abs/cm and not 0abs/cm for both sweeps is that; the UV254nm wavelength doesn't just pick up humics and cyclic organics, but other compounds as well. However, as the main interest here is the organics 12abs/cm can be taken as a concentration of zero for the sweep, as there were no organics present initially.

At the end of the run it can be seen that there is a slight decrease in absorbance of the feed and a slight increase in the sweep. This signifies that some organic transportation to the sweep took place. The 0.5M feed started at 20.6abs/cm and ended up at 19.3abs/cm indicating that about 6% of organics were transported from the feed to the sweep. Most of this transport can be seen to take place from 40 hours. If the experiment were to be stopped at the 40 hours mark, only 3.4% of organics would be transported. The decision of whether or not to stop at 40 hours hinges on the profile of the recovery of the aluminium which will be discussed in the next section. The 0.05 M feed was found to also have a similar value of 6.8% of organic transport, however the 40 hours mark was found not to be as crucial as that of the 0.5 M.

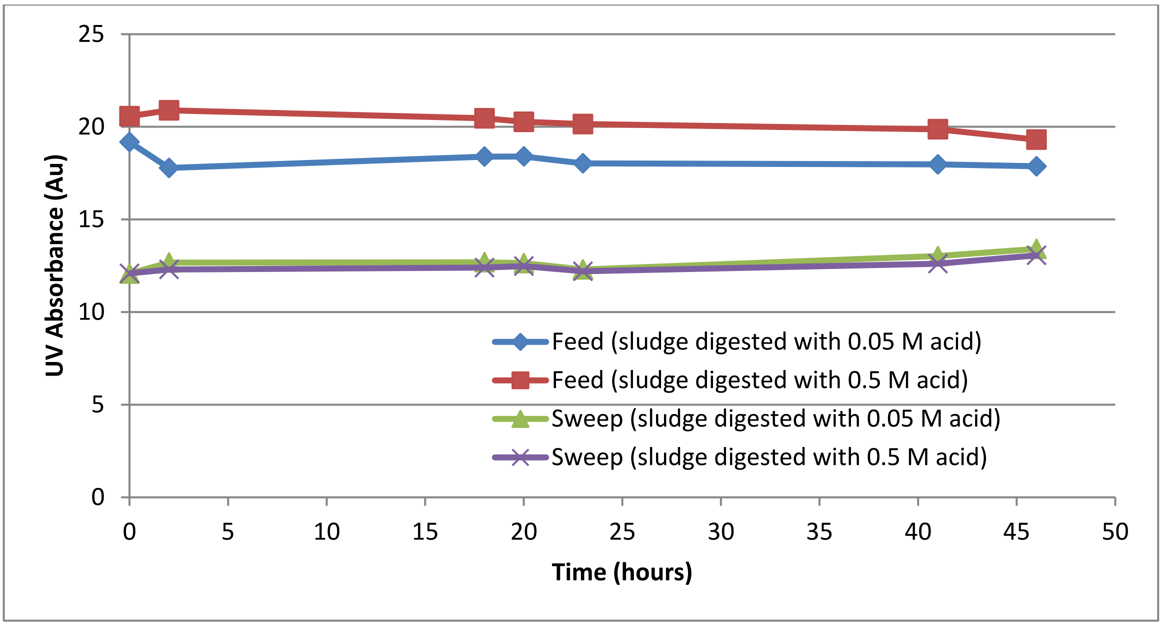


**Figure 5-3: UV 254 absorbance profiles for feed and sweep solutions**

### *5.4.2* Aluminium concentrations

Atomic Absorption Spectroscopy was used to analyze the aluminium concentrations of both the sludges digested at 0.5 M and 0.05 M as well as the Donnan dialysis runs performed on both these feeds. The total aluminium which was able to be extracted from the sludge into solution was found to be 600 mg/L for the 0.5 M HCL digestion and 300 mg/L for the 0.05 M digestion. These findings corroborate those found with organics in the previous stating that a higher acid concentration works better at breaking the sludge matrices and thus releasing more organics and aluminium into solution. For the specific case of concentration, it would seem that a change in magnitude of acid concentration results in the doubling of aluminium released into solution. Figure 5-4 illustrates the concentration of Al in the feed with time as the Donnan dialysis investigation was conducted.

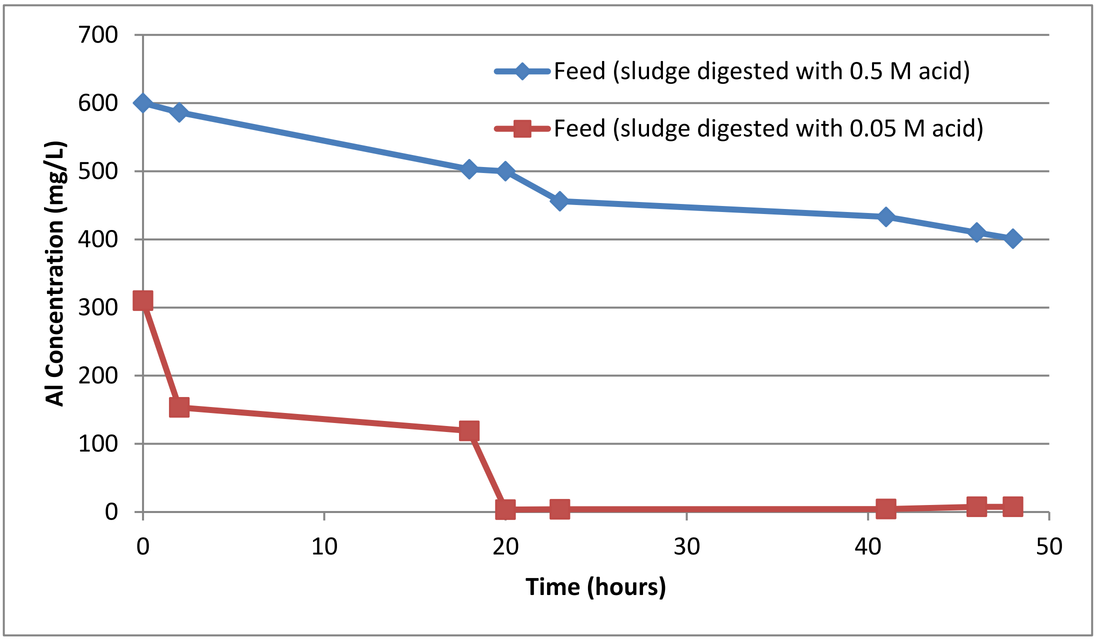


**Figure 5-4: Al concentration profiles of feed solutions obtained for sludge digestion at different acid concentrations**

Although though the 0.5M digested feed solution starts off at a higher concentration of 600 mg/L, the final concentration the feed ends off at is still more than half (402 mg/L) of what it was originally. The 0.05 M digested feed starts off at a much lower concentration (300 mg/L) but unlike the 0.5M feed, most of the aluminium is transported to the sweep side. Figure 5-5 below makes this much clearer by providing this in terms of recoveries. The final recovery of the 0.5 M digested sludge was found to be 44% while that of the 0.05 M digested sludge was 84%, almost double. The reason for such poor performance with the 0.5 M is attributed to the high hydrogen ion concentration in the digested feed sludge. The Donnan dialysis process work by transferring aluminium ions in the feed for hydrogen ions in the sweep. If the feed and sweep both contain the same concentration of hydrogen ions (0.5 M acid was used for the sweep), then the electrochemical potential between the two sides of the membrane becomes similar, this is turn reduces and slows down both kinetics and thermodynamic limits. The feed from the 0.05 M digested sludge can still yield high recovers because a driving force off at least an order of magnitude difference (0.05M hydrogen ion is feed and 0.5M in sweep) still exists.

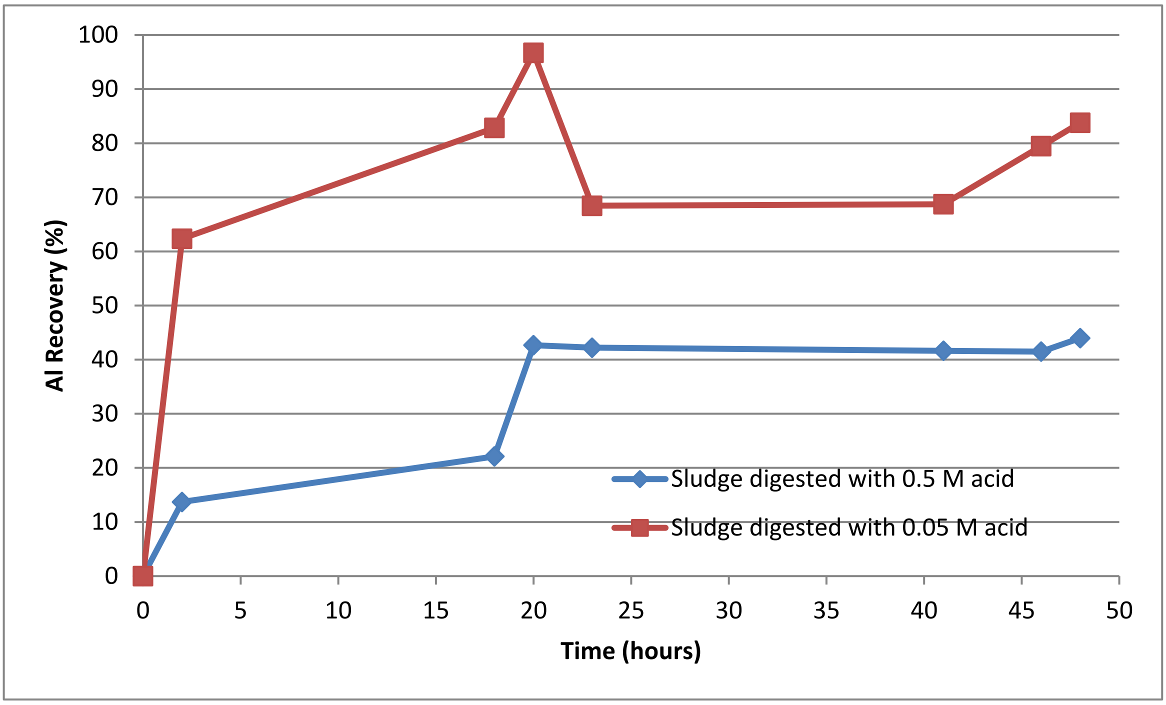


**Figure 5-5: Al recovery profiles for sludge digestion at different acid concentrations**

## 5.5 SUMMARY

(i) Two acids concentrations were used for digesting the sludge, namely 0.5 M and 0.05 M HCL. The stronger acid was found to breakdown the sludge more efficiently. The starting concentration of aluminium in the 0.5 M sludge was 600 mg/L while that of the 0.05 M acid was 300 mg/L. The concentration of organics in the stronger concentration digestion was also higher than that of the weaker.

(ii) Using the digested product from the 0.5 M acid gave a recovery of 42% after 20 hours and 44% after 48 hours. The digested product from the 0.05M acid gave a 97% recovery after 20 hours and 85% after 48 hours. The large difference was found to be due to the lack of an electrochemical potential driving force in the 0.5 M digestion as it was the same concentration of acid used to drive the reaction from the sweep side. The membrane was found to reject about 97% of organics for the first 24 hours of the experiment and 94% for the next 24 hours (until 48 hours).

# 6 FOULING OF DD MEMBRANES

## 6.1 INTRODUCTION

This section briefly addresses the issue of whether organics can result in fouling of DD membranes. A major drawback of pressure driven membrane processes is fouling, i.e. the accumulation of rejected material on the membrane surface and in the membrane pores, leading to an increased hydrodynamic resistance. This results in an increase in the transmembrane pressure (TMP) or a decrease in the product flowrate. In reverse osmosis, nanofiltration, ultrafiltration and microfiltration, fouling arises because of the flow of liquid through the membrane. This flow convects rejected material to the membrane surface and into the membrane pores, causing fouling. In some membrane processes, e.g. membrane distillation (MD) and Donnan Dialysis (DD), there is no flow of liquid through the membrane (ignoring the very slow osmotic effect). In the instance of DD, the only species that move through the membrane are cations. Hence, there is a perception in the literature that these membranes cannot foul since there is no bulk convection of fouling species to the membrane surface. This assumption is tested in this section.

## 6.2 ASSESSMENT OF ORGANIC FOULING IN DD

In pressure driven membrane processes, fouling can be identified by measuring the permeate flux profile with time (constant pressure operation) or the TMP with time (constant flux operation). If the flux or TMP changes with time, this indicates fouling. Clearly this approach to identifying fouling cannot be applied to DD. An alternative approach used in pressure driven membranes is to determine whether the pure water flux of the membrane has changed with time. The pure water flux of a new membrane is measured. After a period of use, the pure water flux is measured again. A decrease in pure water flux would indicate fouling of the membrane. This approach was adapted to assess organic fouling in DD, as discussed below.

All the scanning and optimisation runs under ‘realistic’ conditions were performed with a pure aluminium sulphate solution as the feed. There were no organics in those feeds, and repeatability was good. Subsequently, the same membranes were run on feeds obtained by digesting alum residue sludges. These feeds contained organics. If these organics had any detrimental effect on the membrane, i.e. the DD equivalent of ‘fouling’, this would show up as a change in Al transport through the membrane. This was implemented as follows:

(i) An operating point was selected from the ‘optimisation’ runs reported in Section 4.5. The ‘optimisation’ runs had been performed before the membrane was operated on a feed containing organics.

(ii) Three runs were then performed on this membrane at the same operating conditions, after the membrane had being exposed to organics (according procedure stated in Section 5.3).

## 6.3 RESULTS

Accordingly, comparison of the concentration profiles obtained before and after the membrane was exposed to organics would indicate whether exposure to organics did in fact affect membrane performance. The comparison is presented in Figure 6-1 and Figure 6-2. The runs performed before the membrane was exposed to organics are referred to as ‘Pre-organics 1, Pre-organics 2 and Pre-organics 3’, whilst the runs after the exposure to organics are referred to as ‘Post-organics 1, Post-organics 2 and Post-organics 3’.

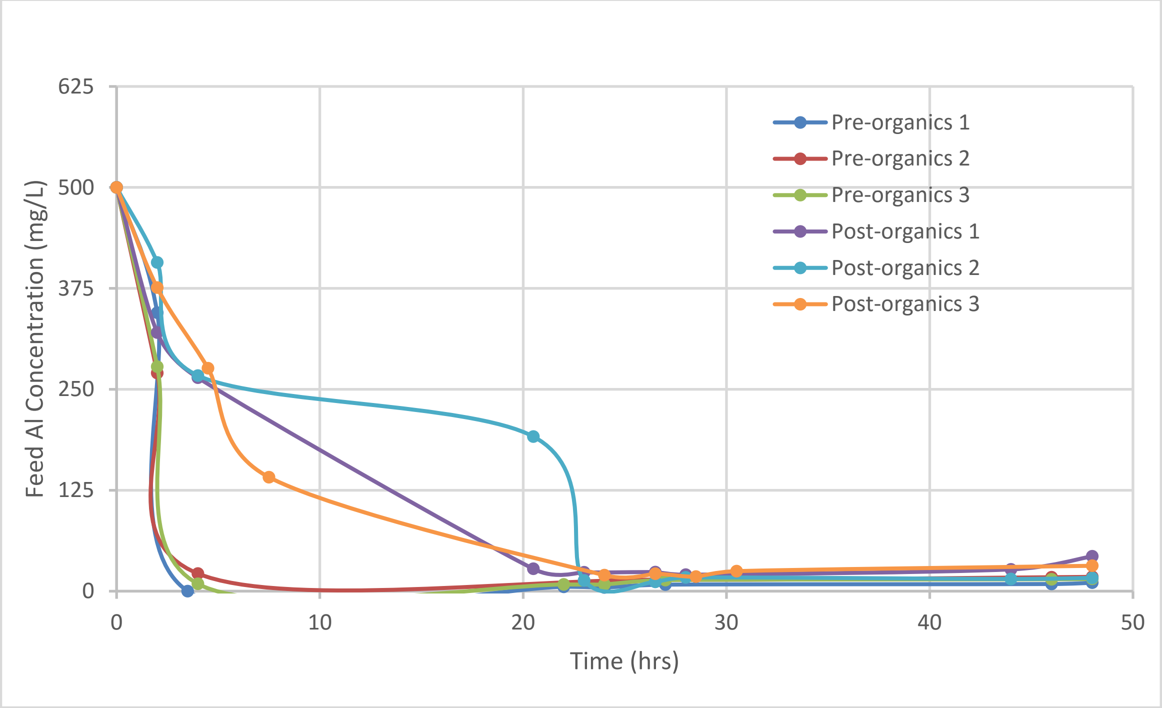


Figure 6-1: Feed Al recovery profiles before and after exposure to organics

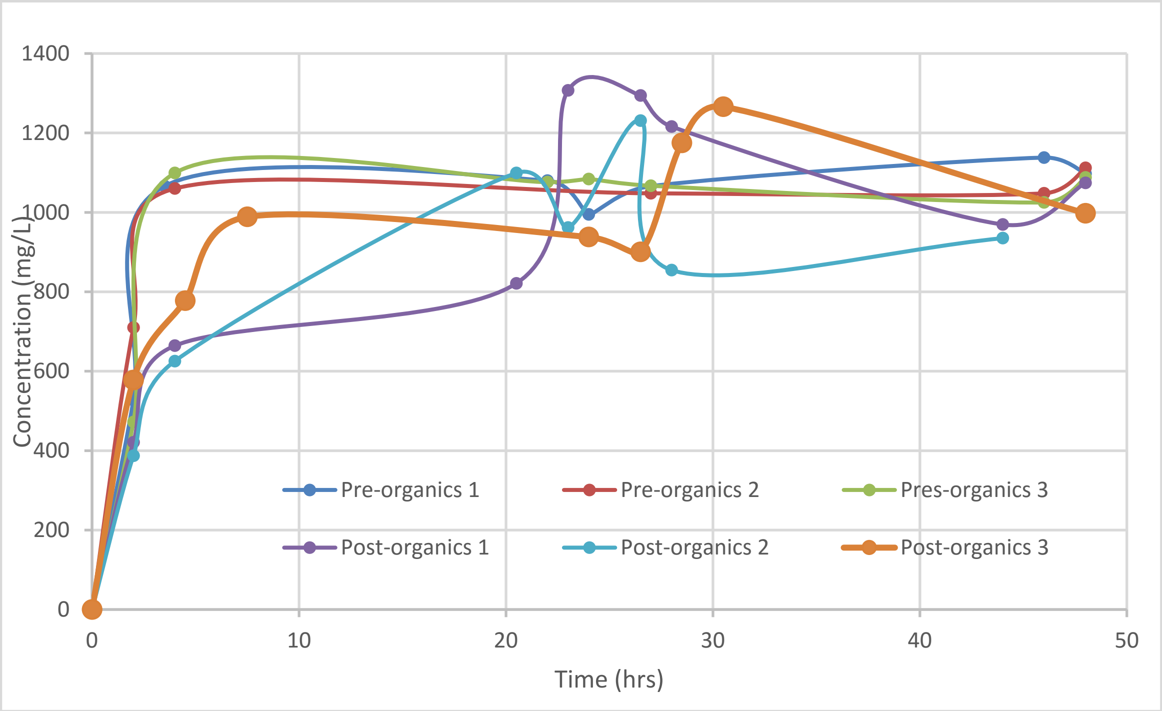


Figure 6-2: Sweep Al recovery profiles before and after exposure to organics

Observations arising from the above figures:

(i) The runs performed before the membrane was exposed to organics were very repeatable and very stable. Conversely, the runs performed after the membrane was exposed to organics are unstable and not very repeatable. Unfortunately, data does not exist for the ‘critical region’, viz. 8 hours to 20 hours, due to logistical difficulties in taking samples overnight.

(ii) Notwithstanding point (i) above, there appears to be a trend that the feed concentration after exposure to organics is decreasing slower than before exposure to organics (5 to 20 hours). Similarly, the sweep concentration after exposure to organics appears to increase at a slower rate than before the membrane was exposed to organics.

## 6.4 SUMMARY

There appears to be an indication that Al transport thorough the membrane has possibly decreased after the membrane was exposed to organics. An unequivocal conclusion cannot however be drawn from the above data and needs to be investigated further.

The issue of organic fouling of DD membranes has not been reported in any literature that this study had access to. If it is found that organics negatively affect Al transport through a DD membrane, some very interesting questions arise, which have significant implications for the practical application of DD for Al recovery:

(i) What is the nature of this ‘fouling’ since DD membranes don’t have ‘pores’? Do organics de-activate sites on the surface of the membrane, or is it that some organics which are being transported through the membrane matrix are ‘stuck’ in the matrix, thus reducing transport paths for Al and H ions?

(ii) Will exposure to organics result in a progressive decline in Al passage, or will there be an initial decline followed by stability?

(iii) Can this process be reversed by some form of physio-chemical treatment?

It is recommended that this should form a priority for future research on DD development.

# 7 COST BENEFIT ASPECTS

## 7.1 OVERVIEW

This section addresses the cost benefits of Al recovery and reuse. The DD process for the recovery of Al from water works residues is still at an early research stage. Accordingly, it is not feasible to perform an assessment of the economic viability of DD for Al recovery at this stage. This section briefly summarises the current cost factors around Al use, summarises the findings of this study, and hence draws a broad conclusion regarding whether the DD route for Al recovery should be pursued further.

## 7.2 COSTS TO WATER WORKS OF CURRENT ALUM USAGE

There are two costs associated with using alum as a coagulant, viz.:

(i) the cost of alum procurement; and

(ii) the cost of disposal of the sludge that results from precipitation.

### 7.2.1 Direct cost of alum procurement

Alum is used as a coagulant in many water treatment works around South Africa, particularly those that experience the challenge of significant organics but low turbidity. It's difficult to define a 'general' cost of alum in terms of R/ML since this seems to change depending on the raw water quality and the water treatment process employed. Figures obtained from a local Western Cape water treatment works are shown in Table 7-1 (private communication). It appears that the cost of alum for this specific plant ranges from ~ R110/ML to R185/ML. For the purposes of further discussion an average alum cost of R150/ML water produced will be assumed.

**Table 7-1: Recent direct costs of alum for a WC water treatment works**

| Month | R/Ton | Alum Used ( Tons) | Ml/Month | (R/month) | Cost of Alum (R/ML) |
|---|---|---|---|---|---|
| Jan-17 | R2 109.05 | 232.14 | 2647.65 | 489594.87 | 185 |
| Feb-17 | R2 219.05 | 109.24 | 2175.61 | 242409.02 | 111 |
| Mar-17 | R2 219.05 | 180.32 | 2280.98 | 400139.1 | 175 |
| Apr-17 | R2 219.05 | 131.8 | 2153.26 | 292470.79 | 136 |
| May-17 | R2 219.05 | 102.18 | 2252.28 | 226742.53 | 101 |
| Jun-17 | R2 219.05 | 189.98 | 2781.23 | 421575.12 | 152 |

### 7.2.2 Cost of disposal of alum sludges

When added to raw water, alum forms precipitates with the colloids and organics present in the water. This precipitate settles out in the settling tanks. The underflows from the settling tank are pumped to a further settler, where the alum precipitate thickens to form a 'water treatment residue sludge'. The supernatant, which contains some dissolved alum, is returned to the process, but the sludge has to be disposed of in some way. The cost of disposal of this sludge is difficult to quantify, due to different practices amongst waterworks.

The two current practices are as follows:

#### *7.2.2.1 Disposal to local evaporation ponds*

Many waterworks send their treatment residue sludges to evaporation ponds, and hence regard the cost of sludge disposal as ‘negligible’. However,

(i) Water treatment works utilise prime real estate, since they are generally situated at the top of hills. A visit to many waterworks in the Western Cape will verify this. The evaporation ponds that are used to dispose of waterworks sludges generally occupy a significantly larger area than the water treatment works itself. These are also generally based on prime real estate.

(ii) At some stage, the evaporation ponds will have to be dug out, and the Al rich sludge disposed of in some way.

Sludge disposal is seemingly not currently considered by these water works in terms of their regular ‘Al accounting’. However, if the cost of land and evaporation ponds is amortised over the volume of potable water produced, this is likely to be a significant cost.

#### *7.2.2.2 Disposal to Landfill*

Some water works which don’t have evaporation ponds load their dewatered sludges into dump trucks, and the sludge is subsequently transported to landfill sites for final disposal. The costs incurred in disposal of waste sludges do not include the overall environmental cost of landfill disposal but are nevertheless a good starting point to quantify the ‘minimal direct cost’ of disposal. Figures obtained from a Western Cape Water Treatment Works indicate that the cost of sludge disposal to landfill is ~ R11.5m for an average production of 196 ML/day. Assuming 100% uptime, this translates to a sludge disposal cost of R160 /ML water produced. This is the *minimal* sludge disposal cost, since in practice there will never be a 100% uptime. For the purposes of the cost benefit determination, a sludge disposal cost of R160/ML water produced will be assumed.

### 7.2.3 Estimated potential cost benefits of Al recovery and reuse

#### *7.2.3.1 Current practice – no Al recovery and reuse*

**BASIS**: A Water Works that produces 100 ML/day.

Cost of Alum procurement = R150/ML = R15 000 per day

Cost of sludge disposal = R160/ML = R16 000 per day

TOTAL COST of Al usage = R310/ML

= R31 000 / day

= R930 000 / month

= R11.1m / year

#### *7.2.3.2 Potential scenario – implementation of Al recovery and reuse*

**ASSUMPTION**: 50% of Al can be recovered from sludges and reused

Potential Cost Savings: ~ R5.5m per year, per 100 ML/day water treatment plant. This does not take into account the ‘environmental’ cost of current sludge disposal practices, and this cost is likely to be highly significant.

## 7.4 IMPACT ON TRADE BALANCE

Aluminium sulphate is produced according to the following exothermic reaction:

$$2Al(OH)_3 + 3H_2SO4 + 8H2O \rightarrow Al_2(SO4)_3 .14H2O$$

Aluminium trihydrate is purified from bauxite. Commercial bauxite (30-75% Al2O3) deposits occur in Australia, Jamaica, France, Guyana, Guinea, the USA and Brazil. Bauxite ore is dissolved in strong caustic soda to form sodium aluminate. The aluminium trihydrate is then precipitated by neutralisation (usually with carbon dioxide) or by auto precipitation. In South Africa the trihydrate is imported, and the conversion to alum is done locally. Hence, the importation of the trihydrate is a negative input on SA's trade balance.

### 7.4.1 Impact on the environment

Al is known to be a cause of, *inter alia*, Alzheimer's Disease. Accordingly, any release of Al into either surface- or groundwater poses a significant health threat. Whilst water works claim that their sludge handling will not result in Al leaching into water sources, some questions that need to be answered are:

(i) Can water works guarantee that there is no leaching of Al from evaporation ponds into surface or ground water sources?

(ii) When evaporation ponds have to eventually be dug up and the sludge disposed of, where/how will the sludge be disposed of?

### 7.4.2 Summary

(i) The direct cost of alum usage is ~ R110 /ML to R185/ML, depending on water quality.

(ii) Where evaporation ponds are used to dispose of alum sludges, the cost of sludge disposal is normally regarded as 'negligible'. However, these ponds do have a major cost associated with them, since they occupy large areas of valuable real estate and since they would need to be 'de-sludged' at some stage.

(iii) Where the current practice is to dispose of sludge by transporting it o landfills, the cost of disposal is ~ R160 /ML water produced.

(iv) Accordingly, the total cost of alum usage, taking into account both procurement and sludge disposal, can be averaged as R310/ML of water produced.

(v) The direct and indirect environmental effects of current Al sludge management practices are not yet known.

## 7.5 WHAT CAN THE DD AL RECOVERY PROCESS ACHIEVE, AND IS IT WORTH PURSUING?

This project has demonstrated that:

(i) DD can selectively recover Al from digested water works sludges, whilst rejecting > 90% of the organics.

(ii) DD can recover up to 95% of Al from a digested feed.

(iii) DD can achieve concentration factors of up to three times the initial feed Al concentration.

(iv) The above could result in significant savings in the cost of water treatment, in terms of both alum procurement and sludge disposal costs and could have a significant impact on reducing environmental contamination arising from the disposal of alum sludges.

Accordingly, it would appear that there could be value in pursuing the development of DD for Al recovery, at least up to the point where a practical technology has been established enabling an economic assessment to be performed.

# 8 CONCLUSIONS AND RECOMMENDATIONS

## 8.1 CONCLUSIONS

### 8.1.1 Scanning Investigations

Osmotic transport of water from the feed side to the sweep side played an important role in the form of the sweep Al profile. Typically, the sweep Al concentration increased rapidly, levelled off, and then decreased slightly, when the dilution effect of osmosis exceeded the transport of Al ions to the sweep. In most runs the sweep concentration profile appeared to be quite unstable just before it levelled off or decreased. Rather than being 'experimental error', it seems that this might be a real phenomenon, possibly arising from the osmotic effect. The feed flowrate, initial sweep acid concentration and initial feed Al concentration were the main parameters that controlled performance, with the sweep flowrate playing a lesser role.

### 8.1.2 Realistic Operating Conditions

Based on expectations for an industrial process, and taking into account the osmotic effect, 'realistic' conditions were defined as an initial feed Al concentration of 200 mg/L to 700 mg/L, and initial sweep acid concentrations of 0.25 M to 0.75 M hydrochloric acid.

### 8.1.3 Optimisation Investigation

The osmotic effect was negligible, and the concentration profiles were substantially more stable than the scanning investigation. Feed flowrate and initial sweep acid concentration had marginal effects on Al recovery and final sweep Al concentration, but the initial feed Al concentration has a very noticeable effect on both Al recovery and final sweep Al concentration, with lower feed Al concentrations favouring higher performance. Al recoveries ranged from ~ 40% to ~ 95%, final Al concentrations ranged from 400 mg/L to 1400 mg/L, and Al concentration factors ranged from ~ 1.1 to 3, depending on the combination of operating conditions selected. The effect of the three operating variables on Al recovery was statistically modelled, yielding the following relationship:

$$Y_{recovery} = 212.98 - 32.65X_1 - 0.17X_2 + 28.70X_3 + 3.40{X_1}^2 - 78.78{X_3}^2 + 0.0005X_1X_2 + 0.24X_1X_3 + 0.1X_2X_3$$

where: $X_1$ is the feed flowrate (ml/s)

$X_2$ is the initial feed Al concentration (mg/L)

$X_3$ is the initial sweep acid concentration (M)

The above statistical model can be used to determine an operating point to maximise Al recovery, if one variable, e.g. initial feed Al concentration, is specified.

### 8.1.4 Rejection of Organics

Based on UV 254 absorption, there was a passage of organics through the membrane, however > 95% of the organics in the feed were rejected. There was an indication that the passage of organics occurred after about 30 hours of operation. Al recoveries on these digested feeds were ~ 84% (0.05 M digested feed) and ~ 40% (0.5 M digested feed).

### 8.1.5 Fouling of membranes

There are strong indications that the rate of transport of Al after the membrane was exposed to organics is less than the rate obtained before the membrane was exposed to organics. However, the results from this project are not conclusive, and further investigations into this are necessary.

### 8.1.6 Economic impacts of Al usage

Procurement of alum solution costs around R150/ML water produced. Sludge disposal costs are approximately R160/ML of water produced. Hence, the total direct cost of alum usage is approximately R310/ML of water produced. The cost of sludge disposal infrastructure is very significant but is currently not given consideration in 'Al accounting' by waterworks that dispose of sludges via evaporation ponds. Alum has a negative impact on the country's balance of payments, since the trihydrate, a starting material for alum, is fully imported. Any direct impact on the environment is difficult to quantify. In principle there should be no leaching of Al into groundwater if the evaporation ponds are impermeable. However, the eventual disposal of the dried cake is likely to have a significant negative environmental effect if it is disposed of on land.

## 8.2 ANSWERS TO THE RESEARCH QUESTIONS

The main questions that this study set out to answer, and the answers emanating from this project, are listed below:

(1) Can DD be used to recover Al from local water treatment residues, whilst rejecting organics?

This study found that DD could selectively recover Al ions whilst rejection > 95% of organics, using a feed stream obtained by digesting waste Al sludge with acid.

(2) What is the recovery of Al that can be obtained?

Using a synthetic feed, recoveries of up to 95% were obtained, whilst on a real feed a recovery of 84% was obtained. It is confidently believed that further optimisation on real feeds could increase the recovery to > 90%.

(3) What is the maximum concentration of Al that can be obtained?

For the 'industrially acceptable' sweep acid concentrations used here, concentrations of up to 1400 mg/L were achieved.

(4) Can the product (sweep) be directly re-used in water treatment?

No. The alum solution currently used in water treatment works has an Al concentration of ~ 40000 mg/kg. Hence, the product from DD would have to be concentrated up via e.g. nanofiltration, to obtain a solution that could be directly applied.

(5) What is the cost benefit of Al recovery?

a. The direct cost of Al usage is ~ R150/ML. The direct cost of disposal of waste sludge to landfill is ~ R160/ML. Hence, the total direct cost of Al usage is ~ R310/ML.

b. Considering, for example, a 100 ML/day plant, the annual cost for alum solution procurement and disposal of the sludge would be ~ R11m. If at least 50% of the waste Al could be recovered and reused, this will represent a direct annual saving of R5.55m per year.

c. Evaporation ponds, which are currently used for management of the Al precipitate sludge in many water works have a significant capital cost associated with them. The ultimate environmental cost of sludge disposal is likely to be quite significant since the sludge cake is disposed of on landfill sites. Hence, the long term environmental cost saving of recovering and recycling Al is likely to be substantially higher than the 'direct costs' associated with alum usage.

(6) Based on the above, should further R&D effort be put into developing a DD process for the recovery and reuse of waste Al from waterworks sludges?

Technically, the DD process for recovery and reuse of Al looks very promising. It should be developed up to a pilot scale, which will provide the necessary data for an economic evaluation to be performed. This will determine whether the technology should be pursued to the 'demonstration' scale.

## 8.3 RECOMMENDATIONS

The DD process for recovery and reuse of Al from water works residuals appears to be technically attractive. Further development should be pursued to the point where an economic evaluation of this process becomes feasible.

Particular aspects which future R&D should focus on include:

(i) Detailed investigation of the kinetics – This study focussed on the thermodynamic aspects, i.e. 'WHAT can be achieved?'. Future investigations should focus on the kinetics, i.e. 'HOW FAST does it occur?'. This is essential for scale-up and further optimisation. As most of the 'critical phenomena' occur between 6 hrs and 15 hrs from start up, consideration should be given to automated sampling to obtain frequent samples in this region.

(ii) Fouling – Contrary to expectations, there is a hint that organics may negatively affect the membrane. This needs to be investigated in detail, together with approaches to mitigate it.

(iii) Base digestion rather than acid digestion – If the feed to DD consisted of a hydroxide rather than an acid, the driving force for Al transport should increase in theory. This definitely warrants further investigation.

(iv) Scale-up of modules – An essential part of the process development is to establish whether the flat-sheet module can be easily scaled to larger membrane areas.

(v) Concentration of the sweep – Nanofiltration is a very promising option for the concentration of the sweep product from ~ 1400 mg/L to ~ 40 000 mg/L. This should be investigated.

Concluding the above recommendations should yield sufficient information for a confident economic assessment of the process.

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# APPENDIX A – CAPACITY BUILDING

One of the aims of the project was to develop capacity in Donnan Dialysis at two South African Universities.

Two postgraduate students were employed on the project, one at Stellenbosch University and one at the Durban University of Technology. Their details are given below:

(i)

Name: Mr Moletsane Mophethe
Institution: Dept of Process Engineering, Stellenbosch University
Degree registered for: MEng (Process Engineering)
Race (BICW): Black
Sex: M
Nationality: Lesotho
Expected graduation: 2018

(ii)

Name: Mr Dennis Asante-Sackey
Institution: Dept of Chemical Engineering, Durban University of Technology
Degree registered for: MTech (Chemical Engineering)
Race (BICW): Black
Sex: M
Nationality: Ghana
Expected graduation: 2019

# APPENDIX B: SCANNING INVESTIGATIONS

## Introduction

The objective of this section is to investigate the effects of; feed concentration, sweep concentration, feed flow rate and sweep flow rate on the amount of aluminium which can be concentrated through the Donnan Dialysis process. The variables and their respective operating conditions were chosen as a good starting point for this investigation after numerous consultations from literature. An experimental run time of 46-48 hours was also decided upon for the same reason. A full factorial design with 4 factors and 2 levels was used to carry out this investigation. In addition to previous studies from literature pointing out the selected variables and their operating conditions were a suitable start for this investigative, the selection of the extreme operating conditions chosen would also provide a more noticeable effect on the recovery of aluminium.

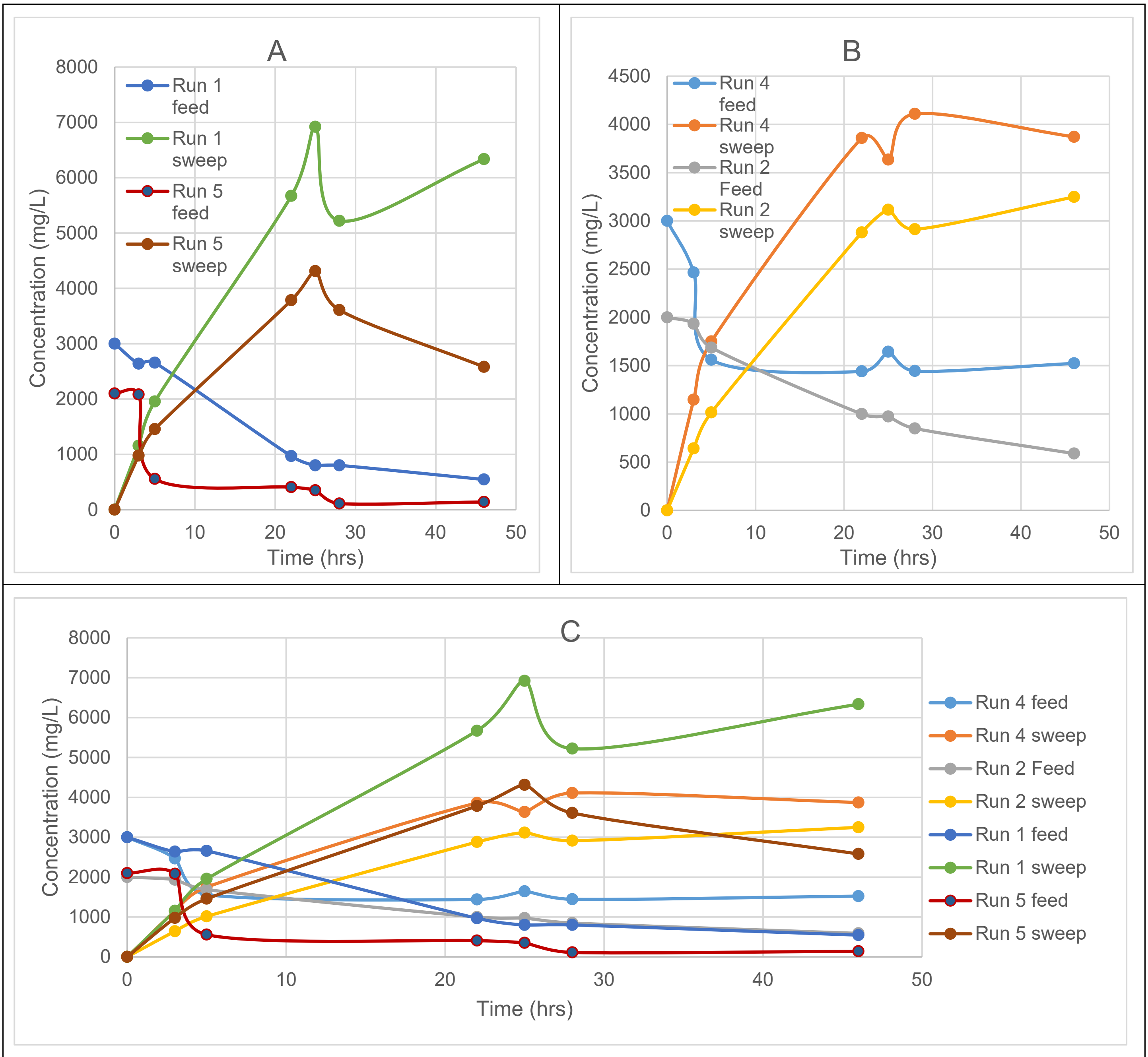
In order to assess both the effect of these variables on hydrodynamic transport as well as the amount of aluminium recovered, concentration was chosen as the response factor. Lastly, in order to represent the trends of the four variables, eight of the possible graphs will be used for comparison in each section. The remaining data for the runs can be seen in the Appendices section. Table AB-1 may be used as a key for the runs which will be used throughout this section and their corresponding conditions.

**Table AB-1: Key for runs to be used:**

| Run | Conditions |
|---|---|
| | Feed conc, sweep conc, feed flow rate, sweep flow rate |
| 1 | 3000 mg/l 2M 25%,25% |
| 2 | 2000 mg/L 1M 75%,75% |
| 3 | 3000 mg/L 1M 25%,25% |
| 4 | 3000 mg/L 1M 75%,75% |
| 5 | 2000 mg/L 2M 25%,25% |
| 6 | 3000 mg/L 2M 75%,75% |
| 7 | 2000 mg/L 1M 25%, 25% |
| 8 | 2000 mg/L 1M 75%, 25% |
| 9 | 2000 mg/l 1M 25%,75% |
| 10 | 3000 mg/L 1M 75% , 25% |
| 11 | 2000 mg/L 2M 75% 25% |
| 12 | 3000 mg/L 2M 75%, 25% |

## Effect of Feed concentration

In order to assess the effect of feed concentration, Runs 1 and 5 will be compared as well as Runs 2 and 4. For Runs 1 and 5, the sweep concentration, feed flow and sweep flow were held constant at 2M, 25% and 25% while the feed concentration was varied from 2000 mg/L to 3000 mg/L. For Run 2 and 4, the sweep concentration was fixed at 1M, feed flow rate at 75% and sweep flow rate at 75%. The feed concentration was also varied from 2000 mg/L to 3000 mg/L. The results may be seen plotted in Figure AB-1.



| Run | Conditions(feed conc, sweep conc, feed flow, sweep flow) |
|---|---|
| 1 | 3000 mg/l 2M 25%,25% |
| 5 | 2000 mg/L 2M 25%,25% |
| 4 | 3000 mg/L 1M 75%,75% |
| 2 | 2000 mg/L 1M 75%,75% |

**Figure AB-1: Effect of feed concentration**

Figure AB-1 A displays the trends of the feed and sweep concentrations of Runs 1 and 5. Starting off with the sweep of Run 1; it can be see that in 5 hrs of operation, the sweep side obtains a concentration of 2000 mg/L. From 5 hrs until 25 hrs the sweep further increases by 4920 mg/L to a maximum concentration of 6920 mg/L. Then in the last 23 hours of operation, the final concentration which is obtained decreases to 6335 mg/L. looking at the sweep concentration of Run 5, after the first 5 hours of operation the concentration can be seen to be 1457 mg/L. From 5 hrs to 25 hrs the concentration increases to a maximum of 4313 mg/L. From 25 hrs until the end of the experiment the concentration of the sweep then decreases to 2581 mg/L.

The feed concentrations of Run 1 and 5 display an opposite trend to the sweep. Run 1 starts off with a feed concentration of 3000 mg/L, after 5 hours of operation the concentration has decreased to 2650 mg/L. At 25 hours which is when the sweep concentration reaches a maximum, the feed concentration can be seen to be 801 mg/L. At the end of the investigation, the final feed concentration is even lower and found to be 545 mg/L. The feed of Run 5 starts off at 2000 mg/L and after 5 hours is found to be 557 mg/L. At 25 hours of operation which also corresponds to the maximum sweep concentration, the feed has a concentration of 349 mg/L. The final concentration at the end of the investigation was found to be 139 mg/L.

Looking at Figure AB-1 A, it would seem that a higher initial feed concentration yields a higher final sweep concentration, intuitively this is true, but not completely accurate. Run 1 operates with an initial feed of 3000 mg/L and has a final sweep concentration of 6335 mg/L. Run 5 operates with an initial feed concentration of 2000 mg/L and the final sweep concentration is 2581 mg/L. Starting with a higher concentration if the initial volumes of Run 5 and Run 1 are the same equates to starting off with a higher mass of aluminium in Run 1. More mass at the beginning will result in a larger amount of mass being recovered at the end. If instead, the final concentration of the sweep is divided by the initial concentration of the feed, the ratio obtained becomes more useful and provides us with a good idea of how much the final stream of aluminium can be enriched by. Doing this for Runs 1 and 5 yields 2.1 and 1.3 respectively. This means that starting off with a higher initial feed concentration favours ending up with a higher concentrating factor in the sweep.

Another trend which can be seen from the sweep results is that the graphs can be divided into three main sections. The first section takes place from 0 to about 5 hours and has the steepest gradient of all. The second section has a less steep incline and tapers off at about 25 hours. The last section has a decrease in concentration of the sweep. Prakesk *et al.* investigated this previously and postulated that; the first section is governed by a high electrochemical potential due to both the aluminium and acid being in abundance in the feed and sweep sides respectively. He defined this steepest section as the kinetically driven zone (this is why both Runs 1 and 5 had the highest increase in concentration in the first 5 hours). As the concentration of aluminium decreases in the feed side and the electrochemical potential decreases, the rate of recovery of aluminium decreases. This can be seen by the decrease in the gradient, this section is termed the Donnan equilibrium zone and is governed by the Donnan dialysis equation described in detail in the theory section (Runs 1 and 5 still increase in concentration but not as rapidly as in the time period of 0-5hrs). Lastly, when the aluminium recovered reaches a maximum it is seen to decrease again. This section is predominantly characterized by hydrodynamic effects. Prakesh *et al.* hypothesized that water transport from the feed to the sweep side was due to osmosis and termed the zone as the "osmosis driven" zone. The sweep concentrations of Runs 1 and 5 decrease in concentration after 25 hours of operation because dilution of the sweep is taking place due to this osmosis phenomenon.

The hydrodynamic transport behavior also servers to explain why the maximum sweep concentration at 25 hours for Runs 1 and 5 didn't correspond to a minimum in the feed section at that time. Looking at both the feed trends of Run 1 and 5, aluminium is still being transported from the feed to the sweep at this time hence the continued decrease in concentration in the feed. However, while the sweep is still receiving aluminium and the concentration should thus increasing, more water from the feed is reporting in the sweep due to hydrodynamic effects, and as a result further dilutes the concentration of aluminium in the sweep faster than more aluminium can be transported from the feed to the sweep side to counter this.

Figure AB-1 B compares Runs 2 and 4.From inspection of the sweep of Run 4 it can be seen that; for the first 5 hours of investigation Run 4 reaches a sweep concentration of 1686 mg/L. The concentration continues to rise for the next 23 hours and at 28 hours into the investigation reaches a maximum of 4109 mg/L. After this, the concentration decreases until the end of the investigation where it reaches a final value of 3871 mg/L. The trend of the sweep of Run 2 is similar. After 5 hours of operation Run 2 reaches a concentration of 1015 mg/L, the maximum concentration is reached 25 hours into the experiment and was found to be 3115 mg/L. By the end of the investigation, the final concentration of Run 2 was found to be 3248 mg/L. Similarly to Runs 1 and 5, the graph can be divided into the three zones discussed above. Namely, the kinetically driven zone from 0-5 hours, the Donnan dialysis zone from 5-25hours, and the osmosis driven zone from 25 hours onward.

In terms of the feed concentrations; Runs 2 was found to decrease from 2000 mg/L to 1774 mg/L in the first 5 hours of experimentation. After 25 hours of operation the concentration further decreased to 973 mg/L, by the end of the experiment Run 2 was found to have a final feed concentration of 589 mg/L. Run 4 started off with a feed concentration of 3000 mg/L and after 5 hours decreased to 1750 mg/L. At 28 hours of operation which corresponds to the maximum concentration reached in the sweep, the feed concentration was found to be 1444 mg/L. lastly, between 28 and 46 hours the concentration slightly increased to 1523 mg/L. For Runs 2 and 4, the concentrating factors obtained were 1.6 and 1.3 respectively.

Figure AB-1 C compares all of the runs on one graph. The results of the first pair (Runs 1 and 5) indicate that a higher feed concentration enriches the final aluminium concentration collected more than a lower feed concentration. The results from the second pair of runs (Runs 2 and 4) suggest the opposite. This may appear confusing at first, but all it means is that the effect of feed concentration is heavily intertwined with the acid concentration of the sweep. Recall previous investigations which concluded that the acid concentration in the sweep is linearly proportional to the amount of water transported from the feed to the sweep. The run pair 1 and 5 were conducted at 2M acid while run pair 2 and 4 were conducted at 1M acid. This means more water was pulled across and thus diluted the sweep side of Runs 1 and 5 more than Runs 2 and 4. Given this, the differences in dilution amounts in the respective sweeps played a critical role in the outcome of whether or not a high initial feed concentration resulted in a higher concentrating factor or not.

This difference in acid concentrations used and thus water transported across the membrane also serves as a possible explanation as to why the sweep of Run 2 increased from 3115 mg/L at 25 hours to 3248 mg/L by the end of the run. The usual trend of the sweep observed for all runs was for it to decrease after 25 hours as the run entered the osmosis driven zone. It is hypothesized that the water transported across to the sweep for Run 2 was much less since 1M acid was used and was thus not enough to dilute the sweep at a faster rate than aluminium was being transported from the feed to the sweep.

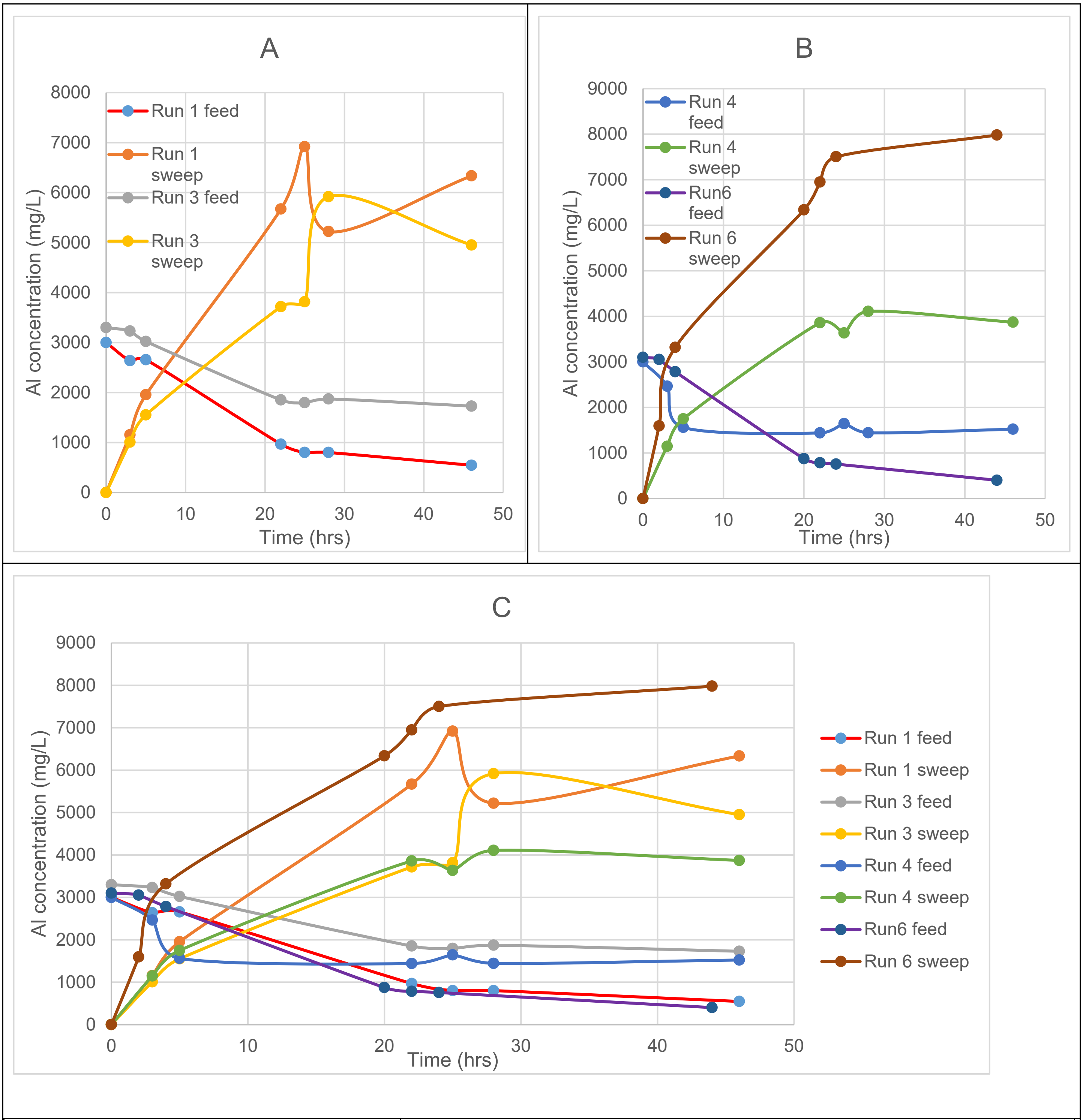
The effect of acid concentration on the amount of aluminium recovered will be discussed in the next section in order to fully understand this.

Effect of sweep concentration

The effect acid concentration in the sweep has on the recovery of aluminium is a balance between two forces. The first is hydrodynamic transport which is linearly dependent upon the concentration of acid used. A higher acid concentration results in more water being transported across the membrane to the sweep, thus decreasing the aluminium concentration.

On the other hand, a higher acid concentration provides faster kinetics and a higher aluminium exchange (due to more hydrogen ions being present). This is because a higher concentration firstly provides a higher electrochemical potential for section one of the graph (kinetically driven zone), as well as a higher ability to withdraw aluminium ion density from the feed to the sweep in the Donnan equilibrium driven zone (section 2 of the graph).

Ultimately, whichever net forces is larger will determine if a higher or lower concentration increases or decreases the final concentration of aluminium. For this investigation, Runs 1 and 3 were paired together as well as Runs 4 and 6. The Run 1 and 3 pair was operated at a 3000 mg/L feed concentration, 25% feed flow and 25% sweep flow. Run 1 was conducted at a sweep concentration of 2M and Run 3 at 1M. The run pair 4 and 6 was also operated at a 3000 mg/L feed concentration, with a 75% flow in both the feed and the sweep. Run 4 had 1M acid and Run 6 had 2M. The results of this investigation are displayed in Figure AB-2.



| Run | Conditions(feed conc, sweep conc, feed flow, sweep flow) |
|---|---|
| 1 | 3000 mg/l 2M 25%,25% |
| 3 | 3000 mg/L 1M 25%,25% |
| 4 | 3000 mg/L 1M 75%,75% |
| 6 | 3000 mg/L 2M 75%,75% |

**Figure AB-2: Effect of acid concentration on Al concentration**

From Figure AB-2 A, the following can be seen; the sweep concentration of Run 3 increases to 1552 mg/L of aluminium in the first 5 hours of operation (this is the kinetically driven zone). As the process switches into the Donnan equilibrium zone between 5 and 28 hours a maximum concentration of 5918 mg/L is reached. From 28 hours the concentration starts to taper off as osmotic effects become significant. The final sweep concentration at the end of the investigation was found to be 4950 mg/L. In terms of the sweep of Run 1; the kinetically driven zone (0-5 hrs.) yielded an aluminium concentration of 1955 mg/L, the Donnan equilibrium zone (5-25 hrs.) was found to further concentrate aluminium ions to a maximum concentration of 6920 mg/L. The osmosis driven zone (25-46 hrs.) was found to dilute the aluminium concentration in the sweep to a final value of 6335 mg/L.

In terms of the trend of the feed concentrations, for Run 1 the feed concentration was found to decrease by 343 mg/L from 3000 mg/L in the first 5 hours of operation. After 25 hours of operation which corresponds to the time the maximum concentration in the sweep occurred, the feed concentration was found to be 801 mg/L. The aluminium concentration continued to decrease and by the end of the run, the final feed concentration was found to be 545 mg/L. In comparison, the feed concentration of Run 3 decreased by 200 mg/L in the first 5 hours. At the 28 hour mark, the feed concentration had dropped to 1872 mg/L and by the end of the investigation the final concentration was found to be 1729 mg/L.

Analyzing Figure AB-2 B the trends which can be seen are as follows; the sweep concentration of Run 6 increased to 3318 mg/L of aluminium in the first 4 hours of operation (this is the kinetically driven zone). As the process switched into the Donnan equilibrium zone between 4 and 24 hours, a concentration of 7503 mg/L was reached. From 24 hours the concentration started to increase slightly. The final sweep concentration at the end of the investigation was found to be 7980 mg/L. In terms of the sweep of Run 4; the kinetically driven zone (0-5 hrs.) yielded an aluminium concentration of 1750 mg/L, the Donnan equilibrium zone (5-28 hrs.) was found to further concentrate aluminium ions to a maximum concentration of 4109 mg/L. The osmosis driven zone (28-46 hrs.) was found to dilute the aluminium concentration in the sweep to a final value of 3871 mg/L.

Upon evaluating the feed concentration; the concentration of Run 6 was found to decrease to 2784 mg/L during the first 5 hours of operation. After 24 hours of operation which corresponds to the time the maximum concentration in the sweep occurred, the feed concentration was found to be 756 mg/L. The aluminium concentration continued to decrease and by the end of the run, the final feed concentration was found to be 401 mg/L. In comparison, the feed concentration of Run 4 was found to decrease to 1750 mg/L in the first 5 hours. At the 28 hour mark, the feed concentration had dropped to 1444 mg/L and by the end of the investigation the final concentration was found to slightly increase again, the final value was 1523 mg/L.

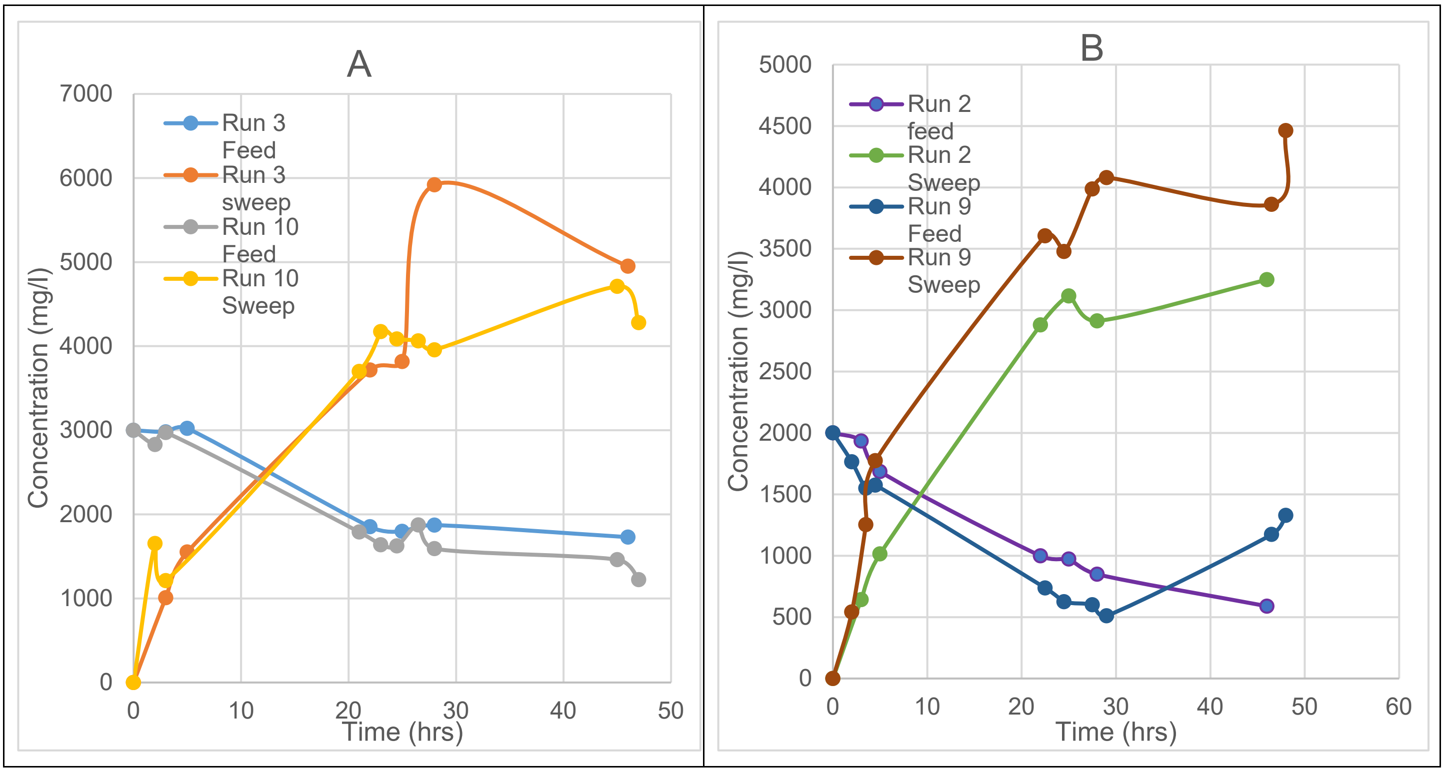
Figure AB-2 C compares all the runs on one graph for ease of reference. The final sweep concentration of Run 1 was found to be 6335 mg/L while that of Run 3 was 4950 mg/L. For the second pair of runs, Run 4's final concentration was found to be 3871 mg/L and that of Run 6 to be 7980 mg/L. These results illustrate that a higher initial sweep concentration favours a higher final aluminium concentration. Moreover, it demonstrates that the hydrodynamic effect is smaller in relation to the ability of the acid to draw aluminium ions to the sweep via ionic exchange. This however is not to say the hydrodynamic effect is not significant, on the contrary, it is. This is seen at a period around 25-28 hours (transition from Donnan equilibrium to osmotic transport zone) where most of the runs sweep aluminium concentration on average slowly tapers off until the end of the run. Given this, it would be prudent to have a future investigation at much lower acid concentrations in order to see if the hydrodynamic transport phenomenon can be mitigating and thus increase the final concentration of aluminium. If this proves to be unsuccessful, despite the thermodynamic limit of the experiment being around 46-48hours, there is no point continuing the experiment as the highest concentration obtainable will be at around 25-28 hours.

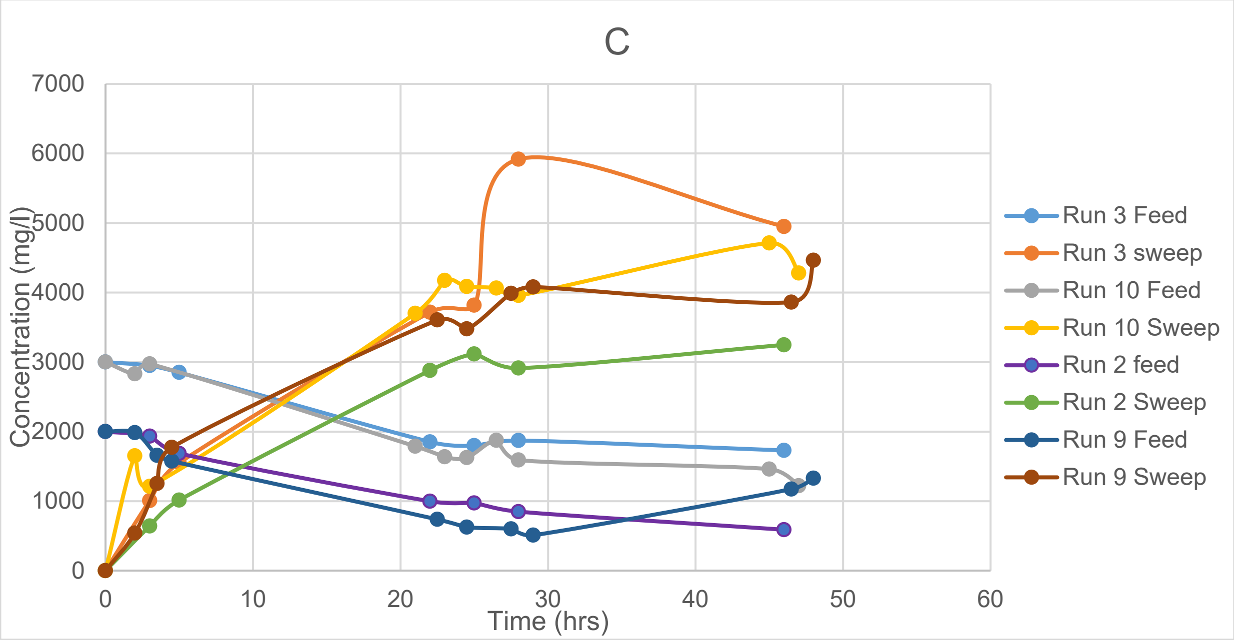
Runs 1 and 6 differ by about 1645 mg/L and yet they both were run with the same feed concentrations and sweep concentrations. Similarly Runs 3 and 4 were also run with the same feed and sweep concentration and yet they differ by about 1079 mg/L. This difference of at least 1000 mg/L of aluminium indicates that feed flow rate and/or sweep flow rate also play an important role in aluminium transfer and transport. Those are the only two factors that differentiate the runs. Consequently, the effect feed flow rate and sweep flow rate has on aluminium transport and the final concentration will be investigated in the next section.

Lastly, Given the possible coupling behaviour of the feed and sweep flow rates with the sweep concentration, it is hypothesized that the anomalous behaviour of Run 4 further increasing in concentration from 1444 mg/L to 1523 mg/L after 28 hours (into osmotic driven zone) of operation is due to the interactions of the flow rates of the sweep and feed with the sweep concentration.

**Effect of feed flow**

The effect of flow rate was investigated with run pairs 3 and 10 as well as 2 and 9. For Runs 3 and 10, the feed concentration was held constant at 3000 mg/l, sweep concentration at 1M and sweep flow rate at 25%. The feed flow rate was varied from 25% (Run 3) to 75% (Run 10). Runs 2 and 9 were operated at a feed concentration of 2000 mg/L, 1M sweep concentration and 75% sweep flow. Feed flow was varied from 25% (Run 9) to 75% (Run 2). The results are displayed in Figure AB-3.





| Run | Conditions(feed conc, sweep conc, feed flow, sweep flow) |
|---|---|
| 3 | 3000 mg/L 1M 25%,25% |
| 10 | 3000 mg/L 1M 75% 25% |
| 2 | 2000 mg/L 1M 75% 75% |
| 9 | 2000 mg/L 1M 25%, 75% |

**Figure AB-3: Effect of feed flow on Al concentration**

Figure AB-3 A displays the trends of the feed and sweep concentrations of Runs 3 and 10. Starting off with the sweep of Run 3; it can be see that in 5 hrs of operation, the sweep side obtains a concentration of 1800 mg/L. From 5 hrs until 28 hrs the sweep further increases by 4118 mg/L to a maximum concentration of 5918 mg/L. Then in the last 18 hours of operation, the final concentration which is obtained decreases to 4950 mg/L. looking at the sweep concentration of Run 10, after the first 3 hours of operation the concentration can be seen to be 1800 mg/L as well. From 3 hrs to 23 hrs the concentration increases to 4173 mg/L. From 23 hrs until the end of the experiment the concentration of the sweep then increases slightly to 4280 mg/L.

The feed concentrations of Run 3 and 10 display an opposite trend to the sweep. Run 3 starts off with a feed concentration of 3000 mg/L, after 5 hours of operation there is no change in concentration. At 28 hours which is when the sweep concentration reaches a maximum, the feed concentration can be seen to be 1872 mg/L. At the end of the investigation, the final feed concentration is even lower and found to be 1729 mg/L. The feed of Run 10 starts off at 3000 mg/L as well, and after 3 hours is found to be 2973 mg/L. At 28 hours of operation the feed has a concentration of 1638 mg/L. The final concentration at the end of the investigation was found to be 1222 mg/L.

The sweep concentrations of run pair 3 and 10 differ by about 700 mg/L, with Run 3 having the higher final concentration. This result indicates that a lower feed flow rate provides a higher final sweep concentration of aluminium. Moreover, from the difference of 700 mg/L it highlights that the effect of feed flow rate on the final sweep concentration of aluminium is quite significant. Baker (2004) investigated the effects of flow rate on membrane systems. He found that there were four distinct fluid regions across a membrane system. He termed the first region the bulk layer and found that this region was characterized by a high concentration of selectively transported species. As the distance to the membrane interface decreased, a new zone termed the boundary layer existed. Here the concentration of the selectively transported species was found to decrease. The concentration gradient then increased across the membrane due to the rate of permeation of target species through the membrane (third zone). On the other side of the membrane the concentration then decreased with increasing distance from the membrane (fourth zone). He termed this phenomenon as concentration polarization. He found polarization to happen when a gradient occurred at the membrane and solution interface due to the selective transport of certain species faster than others. Baker found that creating turbulence in the system by either increasing the velocity or via tortuous flow paths drastically increased the rate of transport of species from one side of the membrane to the other. In the case of aluminium and this investigation however, the opposite was found to be true. Decreasing the flow rate was found to favour a higher final concentration of aluminium in the sweep side.

Figure AB-3-B compares Runs 2 and 9.From inspection of the sweep of Run 2 it can be seen that; for the first 5 hours of investigation (kinetic zone) Run 2 reaches a sweep concentration of 1015 mg/L. The concentration continues to rise for the next 20 hours and at 25 hours (Donnan equilibrium zone) into the investigation reaches 3115 mg/L. From here (osmotic transport zone), the concentration increases slightly until the end of the investigation where it reaches a final value of 3248 mg/L. The trend of the sweep of Run 9 is similar. After 5 hours of operation (kinetic zone) Run 9 reaches a concentration of 1774 mg/L. At 29 hours into the experiment, the final Donnan equilibrium concentration was found to be 4080 mg/L. By the end of the investigation, the final concentration of Run 9 was found to be 4463 mg/L.

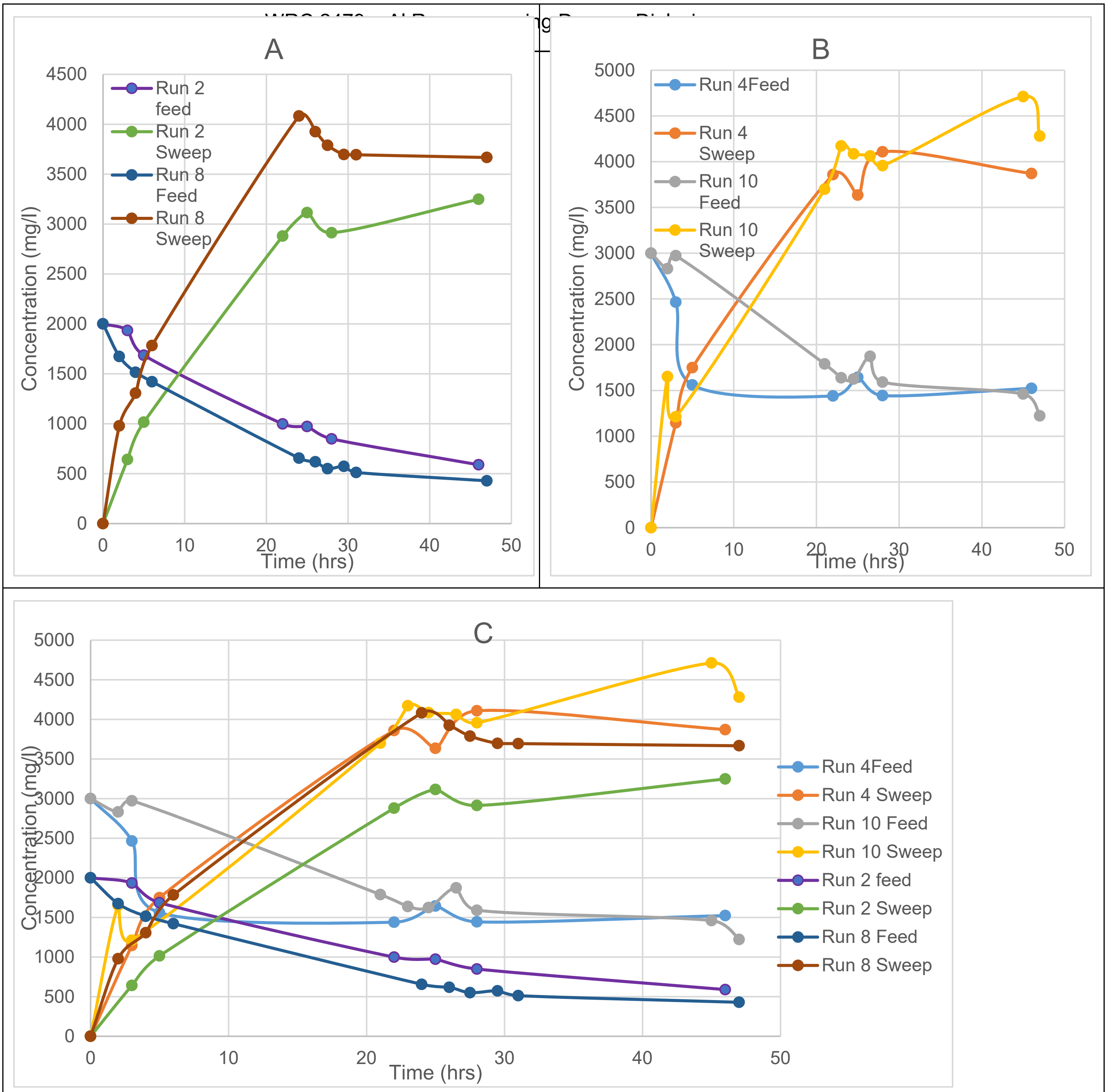
In terms of the feed concentrations; Runs 2 was found to decrease from 2000 mg/L to 1774 mg/L in the first 5 hours of experimentation. After 25 hours of operation the concentration further decreased to 973 mg/L, by the end of the experiment Run 2 was found to have a final feed concentration of 589 mg/L. Run 9 started off with a feed concentration of 2000 mg/L and after 5 hours decreased to 1575 mg/L. At 29 hours of operation, the feed concentration was found to be 509 mg/L. lastly, between 29 and 48 hours the concentration increased to 1329 mg/L.

The concentrations of run pair 2 and 9 differ by about 1200 mg/L of aluminium in favour of the lower flow rate. Similarly to Runs 3 and 10, these results also indicate that a lower feed flow rate provides a higher final aluminium sweep. Figure 42C compares all of the runs on one graph for convenience.

Lastly, as a final note, Runs 2, 9 and 10 serve as proof that the results displayed by the sweep of Run 6 in Figure AB-3 B were not anomalous. The sweep concentration of Run 6 was found to be 7503 mg/L at the end of the Donnan equilibrium zone, instead of decreasing as the run went into the osmotic driven zone, the concentration was found to increase to 7980 mg/L by the end of the investigation. Similarly, the sweep concentration of Run 2 was found to be 3115 mg/L at the end of the Donnan equilibrium zone, and then increased to 3248 mg/L by the end of the experiment. Runs 9 and 10 were also found to increase from 4080 mg/L and 4173 mg/L at the end of the Donnan equilibrium zone to 4463 mg/L and 4280 mg/L at the end of the osmotic driven zone respectively. These trends serve to show that using a combination of variables at specific operating conditions can mitigate the effects of osmotic transport towards the end of the investigation. This means that the rate of water transport to the sweep can be made smaller than the rate of transport of aluminium to the sweep, thus increasing the overall aluminium concentration in the sweep. The specifics of this will be investigated further in the optimization section.

**Effect of sweep flow rate**

The last variable, sweep flow rate was then investigated in order to determine its relationship with the final aluminium concentration recovered in the sweep side. For the investigation, run pairs 10 and 4 as well as 8 and 2 were utilized. Runs 4 and 10 were operated at a feed concentration of 3000 mg/l, sweep concentration of 1M, feed flow rate of 75%. The sweep flow rate was varied from 25% (Run 10) to 75% (Run 4). Runs 2 and 8 were operated at a feed concentration of 2000 mg/L, 1M sweep concentration and 75% feed flow rate. Similarly, the sweep flow rate was varied from 25% (Run 8) to 75% (Run 2). The results obtained are displayed with the aid of the Figure AB-4.



| Run | Conditions (feed conc, sweep conc, feed flow, sweep flow) |
|---|---|
| 2 | 2000 mg/L 1M 75%,75% |
| 8 | 2000 mg/L 1M 75%, 25% |
| 10 | 3000 mg/L 1M 75% 25% |
| 4 | 3000 mg/L 1M 75%,75% |

**Figure AB-4: Effect of sweep flow on Al concentration**

Figure AB-4 A compares Runs 2 and 8. From inspection of the sweep of Run 8 it can be seen that; for the first 6 hours of investigation Run 8 reaches a sweep concentration of 1783 mg/L. The concentration continues to rise for the next 18 hours and at 24 hours into the investigation reaches a maximum of 4083 mg/L. After this, the concentration decreases until the end of the investigation where it reaches a final value of 3667 mg/L. The trend of the sweep of Run 2 is similar. After 5 hours of operation Run 2 reaches a concentration of 1015 mg/L, the maximum concentration is reached 25 hours into the experiment and was found to be 3115 mg/L. By the end of the investigation, the final concentration of Run 2 was found to be 3248 mg/L. As with the graphs investigating feed concentration, sweep concentration and feed flow rate, the figure can be divided into the three zones as well, namely, the kinetically driven zone from 0-6 hours, the Donnan equilibrium zone from 6-25hours, and the osmosis driven zone from 25 hours onward.

In terms of the feed concentrations; Runs 2 was found to decrease from 2000 mg/L to 1774 mg/L in the first 5 hours of experimentation. After 25 hours of operation the concentration further decreased to 973 mg/L, by the end of the experiment Run 2 was found to have a final feed concentration of 589 mg/L. Run 8 started off with a feed concentration of 2000 mg/L and after 6 hours decreased to 1421 mg/L. At 24 hours of operation which corresponds to the maximum concentration reached in the sweep, the feed concentration was found to be 655 mg/L. lastly, between 28 and 46 hours the concentration was found to decrease to 1523 mg/L.

From Runs 2 and 8 it was found that a lower sweep flow rate yielded a higher final aluminium concentration in the sweep. Based on the research and findings of Baker in regard with concentration polarization discussed in the “effect of feed flow rate” section, these findings were contrary to what was expected to happen. Bakers research pointed out that more turbulence (in the form of a higher flow rate or tortuous flow path) was found to promote rapid transfer of species across the membrane, due to the turbulence reducing the effect of concentration polarization.

Figure AB-4 B further investigates the effect of sweep flow rate with the use of Runs 4 and 10. Looking at the sweep concentration of Run 10, after the first 3 hours of operation the concentration can be seen to be 1800 mg/L. From 3 hrs to 23 hrs the concentration increases to 4173 mg/L. At 23 hrs until the end of the experiment the concentration of the sweep then increases slightly to 4280 mg/L. In terms of the sweep of Run 4; the kinetically driven zone (0-5 hrs.) yielded an aluminium concentration of 1750 mg/L, the Donnan equilibrium zone (5-28 hrs.) was found to further concentrate aluminium ions to a maximum concentration of 4109 mg/L. The osmosis driven zone (28-46hrs.) was found to dilute the aluminium concentration in the sweep to a final value of 3871 mg/L.

The feed concentrations of Run 4 and 10 are discussed here. The feed of Run 10 starts off at 3000 mg/L, and after 3 hours is found to be 2973 mg/L. At 28 hours of operation the feed has a concentration of 1638 mg/L. The final concentration at the end of the investigation was found to be 1222 mg/L. In comparison, the feed concentration of Run 4 was found to decrease to 1750 mg/L in the first 5 hours. At the 28 hour mark, the feed concentration had dropped to 1444 mg/L and by the end of the investigation the final concentration was found to slightly increase again, the final value was 1523 mg/L.

Similarly, to Runs 2 and 8, a low sweep flow rate was found to favour a higher final aluminium concentration in the sweep side.

Run pairs 10 and 4 as well as Runs 2 and 8 which investigated the effect of sweep flow rate were found to differ by about 409 and 419 mg/L respectively. Run pairs 2 and 4 as well as 1 and 5 which investigated the effect of feed concentration were found to differ by 623 mg/L and 3754 mg/L respectively. The investigation of the effect of feed flow rate utilized run pairs 2 and 9 as well as 3 and 10. The aluminium sweep concentration differences of each pair were found to be 670 mg/L and 1215 mg/L respectively. Lastly the investigation on the effect of sweep concentration on the final aluminium concentration in the sweep made use of run pairs 1 and 3 as well as 4 and 6. The final concentration differences of the pairs were found to be 1385 mg/L and 4109 mg/L. Looking at these values it is evident that the effect of varying sweep flow rate on the final aluminium concentration is the least significant as the final concentration differences between each pair is not as large. The other investigations of the effects yielded concentration differences of at least a magnitude (looking at the largest difference in the pairs) in difference compared to the effect of sweep flow rate. Putting this into percentages. Using the largest concentration difference of the pairs; the effect of varying sweep flow rate only produced 11% ($100 * \frac{419}{3754}$ ) of the difference in varying the feed concentration. Similarly when comparing the sweep flow rate to the effect of varying sweep concentration, the effect of varying sweep flow rate only produced 10% $(100 * \frac{419}{4109})$ of the effect of varying the sweep concentration. Lastly, when comparing varying the sweep flow rate to the effect varying the feed flow rate had on the final aluminium concentration, the sweep flow rate yielded 34% $(100 * \frac{419}{1215})$ of the effect of varing the feed flow rate. Given this, the effect of varying the sweep flow rate was found to be the least significant parameter towards increasing the final aluminium concentration in the sweep.

**Summary**

To summarize this section, an investigation to determine the effects of feed concentration, sweep concentration, feed flow rate and sweep flow rate on the concentration of aluminium in the sweep was carried out. A full factorial design with two levels was used to assess this. The feed at 2000 mg/L and 3000 mg/L of aluminium, the sweep at 1M and 2 M HCl as well as feed and sweep flow rates at 25% and 75% pump speeds. An experimental runtime of46-48 hour was selected with guidance from literature, as this was found to be the time in which the thermodynamic limit of the process would be reached.

Varying the sweep flow rate was found to change the sweep concentration by about 400 mg/L. This difference was found to be the least significant in the process.

Varying the feed flow rate was found to have a significant impact on the concentration of aluminium in the sweep. It was found that a lower flow rate increased the aluminium concentration. The sweep concentrations of Run pair 3 and 10 were found to differ by about 700 mg/L, while that of Run pair 2 and 9 differed by about 1200 mg/L of aluminium in favour of the lower flow rate.

The effect of sweep concentration was found to be a pull and tug effect of two factors. Firstly, a higher sweep concentration was found to increase the volume of water transported across to the sweep side and hence dilute the concentration of aluminium recovered. Secondly, a higher sweep concentration was found to provide a higher electrochemical potential which resulted in a higher transport of aluminium to the feed. The final sweep concentration of Run 1 was found to be 6335 mg/L while that of Run 3 was 4950 mg/L. For the second pair of runs, Run 4's final concentration was found to be 3871 mg/L and Run 6 to be 7980 mg/L. The results of both of these pairs of runs demonstrated that the hydrodynamic effect was found to be smaller in relation to the ability of the acid to draw aluminium ions to the sweep via ionic exchange.

Lastly, the trend of the feed concentration was found to also be a function of the sweep acid concentration. A higher concentration of aluminium was recovered in the sweep for high feed concentrations only when high acid sweep concentrations were used. A higher aluminium concentration was recovered in the sweep using low feed concentration when low acid sweep concentrations were used. This trend was illustrated using enrichment ratios for Runs 1, 5, 2 and 4. Runs 1 and 5 yielded a ratio of 2.1 and 1.3. For Runs 2 and 4; 1.6 and 1.3 were obtained. The results of the first pair indicated that a higher feed concentration enriched the final aluminium concentration collected in the sweep more than a lower feed concentration. The second pair of runs suggested the opposite.

# APPENDIX C – DETERMINATON OF IMPORTANT OPERATING PARAMETERS

## OBJECTIVE

In order to turn the standard design into a robust process, it is important to establish the significant independent factors that largely affects the process through a scanning experiment. The objective of this section is to investigate the effect of the main operating variables on the recovery and concentration of aluminium through the Donnan dialysis process. The variables under study are feed concentration, sweep concentration, feed flowrate and sweep flowrate. These variables and their respective operating conditions are chosen as a good starting point for this investigation after numerous consultations from literature.

## METHODOLOGY

Extreme level conditions was chosen to provide more noticeable effect on the recovery of aluminium. An experimental run time of 46-48 hours was also decided upon for the same reason. However, in the analysis, a 28 hrs time was selected for maximum yield (Figure AC-1). A comparison on recoveries for both feed and sweep ends using Run 8 and 14 shows that maximum yield is obtained between 24-28hrs, and any change observed after is marginal: equilibrium has been achieved.

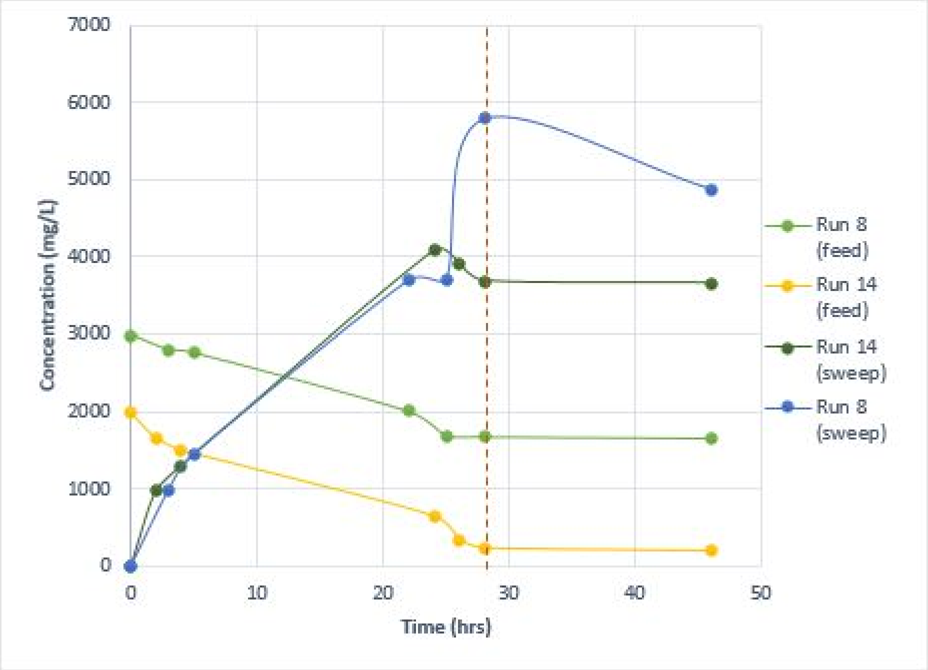


**Figure AC-1: Al-Recovery profiles at Feed and Sweep phase**

Also, to establish the maximum aluminium flux and reduce effects that can be observed at the sweep phase, recovery analysis was performed at the feed phase of the DD. System.

The removal rate of aluminium was calculated as

$$Y_{Al}(\%) = \left(\frac{C_oV_o - C_eV_e}{C_oV_o}\right) \times 100 \qquad (1)$$

where: $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/l) and $V_o$ and $V_e$ are volume of feed at initial and equilibrium respectively

A full factorial design with 4 factors and 2 levels was used to carry out this investigation. The full factorial matrix with 16 experiments was determined by ($N^x$) design where N= the factors and x= the level.The choice of the full factorial design is to enable the study of all possible combinations of variables at their discretized levels (lower and upper bounds). Minitab® (version 18) was used to design the experiment matrix (Table AC-1) at random condition and perform an ANOVA.

**Table AC-1: Full factorial experimental and random design**

| Run | Factors | | | |
|---|---|---|---|---|
| | Feed Conc. (mg/L) | Sweep conc. (M) | Feed flow (%) | Sweep flow (%) |
| 1 | 2000 | 1 | 75 | 75 |
| 2 | 3000 | 1 | 25 | 25 |
| 3 | 3000 | 1 | 75 | 25 |
| 4 | 3000 | 2 | 25 | 25 |
| 5 | 2000 | 2 | 25 | 75 |
| 6 | 2000 | 2 | 75 | 75 |
| 7 | 3000 | 1 | 75 | 75 |
| 8 | 3000 | 1 | 25 | 75 |
| 9 | 3000 | 2 | 75 | 75 |
| 10 | 3000 | 2 | 25 | 75 |
| 11 | 3000 | 2 | 75 | 25 |
| 12 | 2000 | 2 | 25 | 25 |
| 13 | 2000 | 2 | 75 | 25 |
| 14 | 2000 | 1 | 75 | 25 |
| 15 | 2000 | 1 | 25 | 25 |
| 16 | 2000 | 1 | 25 | 75 |

The calculated Al recoveries at the different operating combinations of operating variables are shown in Table AC-2. This table was used for the regression analysis.

**Table AC-2: Full factorial experimental matrix and recovery yield**

| Run | Feed Conc. (mg/L) | Sweep conc. (M) | Feed flow (%) | Sweep flow (%) | Al-Recovery (%) |
|---|---|---|---|---|---|
| 1 | 2000 | 1 | 75 | 75 | 62.56 |
| 2 | 3000 | 1 | 25 | 25 | 32.40 |

| Run | Feed Conc. (mg/L) | Sweep conc. (M) | Feed flow (%) | Sweep flow (%) | Al-Recovery (%) |
|---|---|---|---|---|---|
| 3 | 3000 | 1 | 75 | 25 | 75.90 |
| 4 | 3000 | 2 | 25 | 25 | 67.50 |
| 5 | 2000 | 2 | 25 | 75 | 90.05 |
| 6 | 2000 | 2 | 75 | 75 | 76.42 |
| 7 | 3000 | 1 | 75 | 75 | 57.00 |
| 8 | 3000 | 1 | 25 | 75 | 43.87 |
| 9 | 3000 | 2 | 75 | 75 | 71.80 |
| 10 | 3000 | 2 | 25 | 75 | 76.90 |
| 11 | 3000 | 2 | 75 | 25 | 76.20 |
| 12 | 2000 | 2 | 25 | 25 | 81.05 |
| 13 | 2000 | 2 | 75 | 25 | 93.56 |
| 14 | 2000 | 1 | 75 | 25 | 87.98 |
| 15 | 2000 | 1 | 25 | 25 | 63.96 |
| 16 | 2000 | 1 | 25 | 75 | 73.59 |

## RESULTS AND DISCUSSION

Despite the availability of several DOE plots, the Pareto Chart was specifically used to show the standardized effects for the most significant factor to the less significant. The reference line on the graph depends on the significance level, which was set at alpha (α) = 0.05 and at a forward selection method. The alpha level is the probability of making a wrong decision when the null hypothesis is true.

The significant main and interaction between factors that influences the recovery of aluminium (Al) using the DD process was determined by an analysis of variance (ANOVA). The ANOVA helps to accept or reject the null hypothesis at the set alpha value. The rejection of a null hypothesis shows that the model and factors are significant. Table AB-3 shows the full factorial regression at a 95% confidence level.

Table AC-3: Analysis of Variance for full quadratic interaction

| Source | DF | SS | MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Model | 9 | 3819.21 | 424.36 | 21.60 | 0.001 |
| Linear | 4 | 2545.68 | 636.42 | 32.40 | 0.000 |
| Feed Conc | 1 | 1017.61 | 1017.61 | 51.80 | 0.000 |
| Sweep conc | 1 | 1159.74 | 1159.74 | 59.04 | 0.000 |
| Feed flow | 1 | 324.90 | 324.90 | 16.54 | 0.007 |

| Source | DF | SS | MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Sweep flow | 1 | 43.43 | 43.43 | 2.21 | 0.188 |
| 2-Way Interactions | 4 | 1178.85 | 294.71 | 15.00 | 0.003 |
| Feed Conc*Sweep conc | 1 | 57.15 | 57.15 | 2.91 | 0.139 |
| Feed Conc*Feed flow | 1 | 146.17 | 146.17 | 7.44 | 0.034 |
| Sweep conc*Feed flow | 1 | 281.74 | 281.74 | 14.34 | 0.009 |
| Feed flow*Sweep flow | 1 | 693.80 | 693.80 | 35.32 | 0.001 |
| 3-Way Interactions | 1 | 94.67 | 94.67 | 4.82 | 0.071 |
| Feed Conc*Sweep conc*Feed flow | 1 | 94.67 | 94.67 | 4.82 | 0.071 |
| Error | 6 | 117.87 | 19.64 | | |
| Total | 15 | 3937.08 | | | |

The statistically significant effect in the model is determined from the P-value. This is to provide stronger evidence against the null hypothesis. Lower probabilities indicates greater significance. Main and interactional effects with P-values less than α=0.05 or closer to zero indicates greater significance. Values obtained in Table 2 suggest that the main factors reportedly feed concentration, sweep concentration and feed flowrate are statistically significant. The other significant interactions are Feed concentration and feed flow rate; sweep concentration and feed flowrate; feed flowrate and sweet flowrate.

The absolute values of the main effects and their interactions on a Pareto chart (Figure AC-2) at sixteen degrees of freedom shows a t-value = 2.262. The minimum level as indicated by the red-vertical line denotes that Sweep flowrate (D) attributed the least to the recovery process. Table AC-3 indicates that, sweep flowrate has a P-value = 0.188. From Table AC-3, it can also be confirmed that, 3-way interaction of all the main factors is significant with P-values less than 0.071.

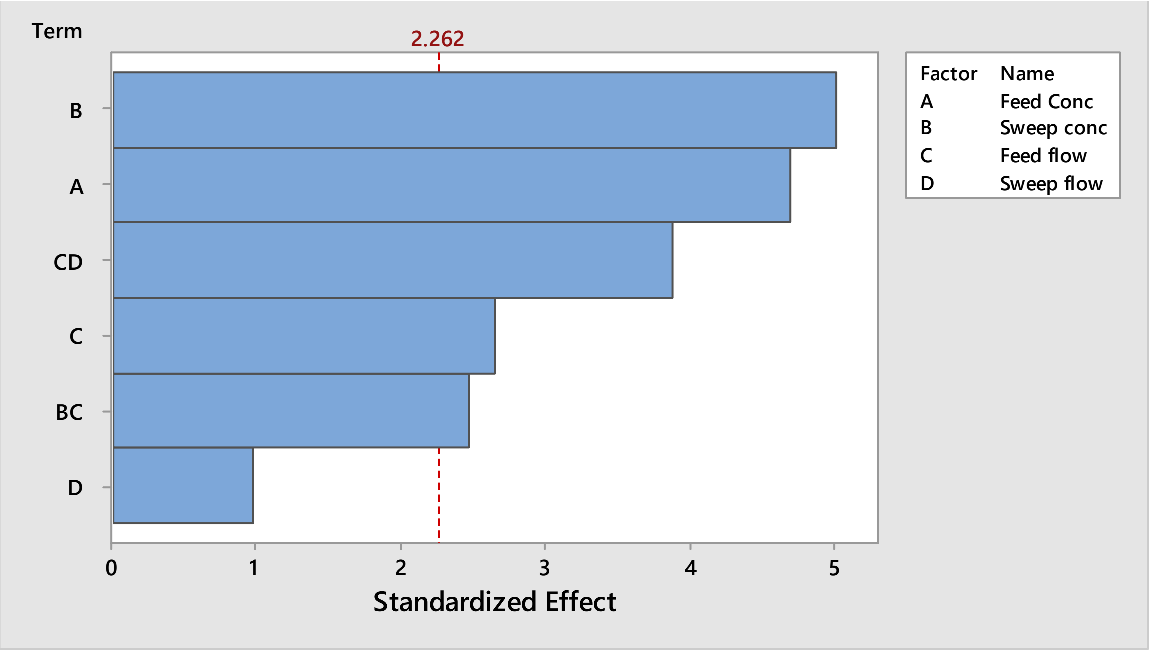


**Figure AC-2: Pareto chart for standardized effects for Al-recovery**

To clearly show the effect of the main factors, the Terms for the ANOVA was reduced to one term. The results is shown in Figure AC-3.

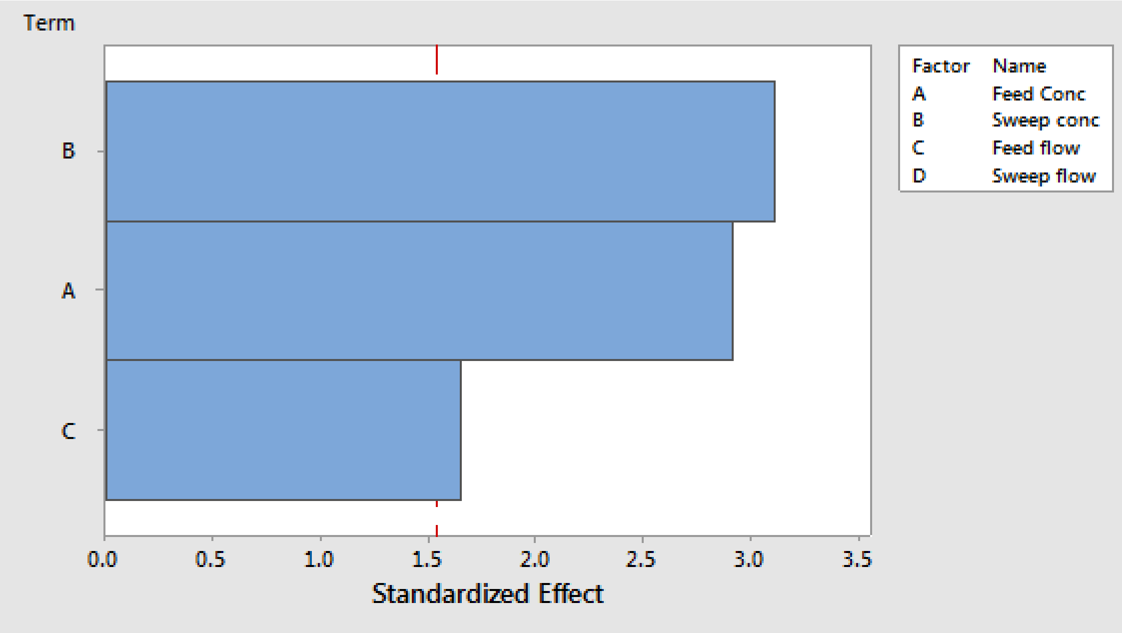


**Figure AC-3: Pareto Graph for a One Term ANOVA**

NB: the t-value will change due to the change in terms for ANOVA

**CONCLUSION**:

This study shows that the main factors that affect the recovery of aluminium using the DD process are feed concentration, feed flowrate and sweep concentration. The factor with a least effect is the sweep flowrate.