Highlights

- Applied combination of computational and laboratory methods to design leachate treatment
- Solved the challenge of reducing ammoniacal nitrogen and solution conductivity to meet guidelines
- Combination of clarification, two cation resins and one anion resin recommended
- Economic calculations suggested viable process for industry

Process Design of a Treatment System to Reduce Conductivity and Ammoniacal Nitrogen Content of Landfill Leachate

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An innovative combination of computational modelling and laboratory testing was applied to address the challenge of reducing conductivity and ammoniacal nitrogen in landfill leachate. The hypothesis was that accelerated selection of an appropriate treatment process could be achieved by application of new water process engineering software termed AqMB. Several scenarios were investigated incorporating settling ponds, clarifiers, lime softening, ion exchange, pH adjustment and degassing unit operations. Settling ponds reduced the lime demand if a lime softening process was tested, albeit ponds involved greater expense and needed space. Alternately, a clarifier using aluminium chlorohydrate removed suspended solids. Use of a single cation resin bed in series with a strong base anion (SBA) resin column was not able to meet regulatory targets. However, employment of a weak acid cation (WAC) and strong acid cation (SAC) resin combination achieved very low ammoniacal nitrogen levels. To satisfy conductivity limits both a degassing unit and a strong base anion (SBA) resin were also necessary. Bench top testing of actual leachate confirmed that the software predicted the trends in water quality. Final solution conductivity of *ca.* 250 µS/cm and ammoniacal nitrogen content of <1 mg/l were recorded which were compliant with target values of <1600 µS/cm and <100 mg/l ammoniacal nitrogen. Process economics encompassing power, chemicals, and resin costs were calculated to be A$10.50 per kL leachate.

Key Words: landfill leachate; process design; ion exchange; simulation; softening

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1. Introduction

Waste disposal methods for municipal waste vary depending on geographical location and legislation. For example, in Japan a significant amount of municipal waste is treated by incineration [1], whereas in many countries such as USA, China and Australia, landfilling remains a popular practice [2, 3]. Landfills can be problematic in terms of their impact on local communities, especially in third world countries where landfills often do not have facilities to treat leachate or deal with biogas which is produced [4]. Khalil *et al.* [5] analysed a range of landfill leachates produced in Lebanon and noted that the Mediterranean sea received a substantial amount of this solution. Numerous species were found to be present, which not only exceeded the accepted discharge guidelines but also were also toxic, carcinogenic, and hazardous to health. Han *et al.* [6] similarly found that groundwater near landfill sites in China was typically highly contaminated with a wide range of substances and also that the concentrations present were dependent upon age of the landfill.

As such, there is not only a need to properly construct landfill sites to control the egress of contaminated leachates [7, 8] but also to manage the produced leachate [9]. The leachate is composed of a wide range of chemicals including organic matter, inorganic species, ammoniacal nitrogen, sulphate, phosphate, and heavy metals [10]. The precise leachate composition varies widely not only between landfill sites but also within the same landfill site due to changes caused by the age of the landfill [11]. Technologies developed for landfill leachate remediation include but are not limited to membranes [12, 13], advanced oxidation [14-16], coagulation [17], ion exchange [18], biological [19, 20], microbial fuel cells [21], wetlands/lagoons [22], and air stripping [23]. A particular challenge is the treatment of leachate from mature landfill sites as this solution is typically characterized by a low Biological Oxygen Demand/Chemical Oxygen Demand (BOD_5/COD) ratio and also a relatively high concentration of ammoniacal nitrogen [24].

The array of treatment technologies which can be applied for landfill leachate remediation invariably means that numerous process designs have been implemented. Complicating the process design for leachate treatment facilities is the fact that allowance for a water quality composition change over time must also be considered [25]. For example, Theepharaksapan *et al.* [26] described a treatment process for leachate from the Nonthaburi solid waste site in

Thailand. Leachate treatment was achieved by a process which included: stabilization pond; coagulation; sedimentation; sand & activated carbon filtration; micro-filtration and reverse osmosis (RO). Chemical coagulation with $FeCl_3$ combined with the sand filter eliminated a significant amount of organic species, the RO system reduced the dissolved ions. Ammoniacal nitrogen was noted not to be removed until the final treatment step and overall COD, ammoniacal nitrogen and heavy metals were reduced by at least 99, 97, and 90 %, respectively. In contrast, Smaoui *et al.* [27] evaluated a landfill leachate treatment system in Tunisia which encompassed coagulation/flocculation, Fenton oxidation, and air stripping pre-treatment strategies prior to the central anaerobic digester stage. Cingolani *et al.* [12] discussed a process for landfill leachate from a facility in Marche Region, Italy, which had the following unit operations: coagulation-flocculation; activated sludge with intermittent aeration; ultrafiltration, microfiltration, and pH adjustment with sulphuric acid prior to a disc-tube RO desalination plant.

As can be seen from the above illustration of the different process designs used for landfill leachate treatment, there does not exist a single solution for this problem. Factors which influence the process design include the level and nature of organic material presence, concentration of ammoniacal nitrogen, presence of heavy metal ions and solution pH [28]. For example, Hasar and Unsal [29] provided an outline of a treatment plant which comprised of both high organic and ammoniacal nitrogen content. In this case it was proposed that ammonia stripping, coagulation/flocculation, aerobic/anaerobic membrane bioreactor, and reverse osmosis should be employed to meet regulatory guidelines.

Due to the inherent situation where landfill leachate composition and physical properties varies greatly, it is necessary to develop a means to accelerate process design. Computational modelling is an approach which has been demonstrated to aid the creation of treatment streams for a range of contaminated water problems. Barbera *et al.* [30] used ASPEN Plus software to model the growth of the microalgal strain *Acutodesmus obliquus* in a leachate process incorporating both solar evaporation, and production of a concentrated ammonia solution. Costa *et al.* [31] applied an activated sludge model to predict the performance of an aerobic biological system for landfill leachate produced from northern-central Spain. Recently, Vedelago and Millar [32] described the use of a new software package termed

AqMB (Aqueous Material Balance) for the process design of a treatment system for coal seam gas (CSG) associated water. It was found that application of pH adjustment and chemical dosing technology was limited to only CSG associated water with a relatively low concentration of bicarbonate species. Thus, it was suggested that ion exchange resins may be a better approach to treating CSG associated water for beneficial reuse options such as irrigation, stock watering, and dust suppression. Wicks *et al.* [33] have also applied AqMB process design software to the challenge of identifying appropriate ion exchange strategies for desalination of CSG associated water. This study not only demonstrated that software predictions were in accord with published papers relating to water desalination but also that optimal combinations of synthetic resins, degassing, chemical addition and pH adjustment could be identified. Significantly, estimates of operational costs were calculated by AqMB which allowed screening of scenarios in relation to potential commercial viability.

It was evident from critical evaluation of existing literature that there was a knowledge gap relating to process design regarding landfill leachate. A significant number of technologies have been proposed as being beneficial to landfill leachate treatment, yet a means of rapidly deciding which process designs may be viable has not been presented. Therefore, the aim of this investigation was to design a process to treat an actual landfill sample, which was not discharge compliant. To exemplify the modelling approach a leachate produced in Queensland, Australia was investigated; the key parameters being solution conductivity and ammoniacal nitrogen. The hypothesis was that the use of computational methods may accelerate the design of landfill leachate treatment strategies and reduce the extent of laboratory testing and/or pilot plant trials required. Consequently, the following research questions were considered in relation to proving the hypothesis: (1) what is the predicted performance of treatment processes are effective for the removal of ammonium/ammonia in landfill leachates? (2) which process designs can satisfy both electrical conductivity and ammoniacal nitrogen effluent standards? (3) what are the techno-economics of the selected process? (4) How do the software modelling predictions compare to laboratory results? To answer the aforementioned research questions application was made of AqMB software to determine the viability of a range of leachate treatment process designs. In addition, bench scale tests were conducted to confirm the performance predicted by the simulation software.

2. Materials and Methods

2.1 Leachate Composition

A leachate composition from a landfill site in Australia was chosen (precise identity not disclosed due to confidentiality considerations) for demonstration of the computer simulation process [Table 1]. The total flow rate of leachate was 20 kL/h (480 kL/day).

Table 1: Composition and physical properties of leachate samples for computational analysis and laboratory testing

	Units	Typical Leachate Composition used for Simulation	Actual Leachate used for Laboratory Testing	Target Value
pH Value	pH	7.57	7.05	6.5 - 9.0
Electrical Conductivity @ 25°C	µS/cm	5430	5820	<1600
Total Dissolved Solids @180°C	mg/L	4066		<5000
Suspended Solids (SS)	mg/L	395.8		
Total Alkalinity as $CaCO_3$	mg/L	1965		
Bicarbonate	mg/L	2335		
Carbonate	mg/L	20.16		
Carbon Dioxide	mg/L	79.1		
Bromide	mg/L	8.48	1.569	
Sulphate as SO_4^{2-}	mg/L	0	13.0	
Chloride	mg/L	627	573.2	
Calcium	mg/L	191	177.6	
Magnesium	mg/L	62	60.9	
Sodium	mg/L	530	558.3	
Potassium	mg/L	89	85.2	
Aluminium	mg/L	0.06	0.018	<100
Arsenic	mg/L	0.002	0	<0.5
Chromium	mg/L	0.016	0.016	<3
Copper	mg/L	0.037	0.003	<5
Zinc	mg/L	0.03	0.014	<1
Iron	mg/L	0.2	0.29	<10
Fluoride	mg/L	0.4	1.30	<30
Ammonia as N	mg/L	239	278.8	<100
Total Organic Carbon	mg/L	183	158	

Table 1 provides compositional data for the generic leachate used for modelling studies ("typical leachate composition") and that for an actual leachate sample collected from the landfill site ("actual leachate for testing"). The target values were supplied by the landfill site operators.

2.2 Process Modelling

AqMB (Aqueous Material Balance) is a process modelling software developed by Salt Water solutions [34]. The software incorporates a wide range of unit operations and was written to accelerate the design of water processing treatment facilities, while minimising expensive pilot tests.

2.2.1 Settling Pond

Settling ponds are often used in water treatment facilities to store wastewater prior to treatment [35]. For simulation purposes the settling pond had the following characteristics: net zero evaporation rate per annum; 10 mg/L increase in organics per annum; solids removal of 80 %; 5 m vertical wall height; and 240 hours residence time.

2.2.2 Chemical Coagulation

The coagulant aluminium chlorohydrate (ACH) was employed when using the clarifier unit for reduction in suspended solids. A 40.2 wt% solution of ACH was dosed in order to create 100 mg/L ACH in the leachate.

2.2.3 Solids Contact Clarifier/Thickener

The solids contact clarifier had the following design properties: overflow solids 10/mg/L; minimum underflow solids (0.5 w/v %); surface loading rate 3 m/h; floc/contact zone detention 5 min; clarifier area 6.66 m^2; and rake drive torque of 594.2 Nm. Due to the high solids content of the pH adjusted feed when lime was added, a thickener was also modelled. The solids contact thickener used in the process simulations had: overflow solids 10/mg/L; minimum underflow solids (5 w/v %); surface loading rate 10 m/h; and floc/contact zone detention 20 min.

2.2.4 Ultrafiltration

The ultrafiltration unit was equipped with Suez ZeeWeed (ZW1500-550) ultrafiltration membranes of 51 m^2 area per module. These membranes were made of polyvinylidene fluoride (PVDF) and were comprised of 0.02 micron pores. 6 modules were simulated in one train and the design flux was 68 L/m^2/h.

2.2.5 Ion Exchange Resins

Three resins were assessed: (1) DOW MAC 3 weak acid cation (WAC) resin in the H$^+$ form which had an operating capacity of 1.8 eq/L. The service velocity was 30 m/h and regeneration was designed to occur once every 48 hours. Regeneration was achieved by using 5 wt % hydrochloric acid (HCl) solution in reverse flow mode and a stoichiometric equivalent ratio of 2:1; (2) DOW Marathon C strong acid cation (SAC) resin in the H$^+$ form was also tested and it was assumed that the operating capacity was 1.2 eq/L. The service velocity was kept at 30 m/h and regeneration was again designed to occur once every 48 hours. Similar to the WAC resin, regeneration involved using 5 wt % hydrochloric acid (HCl) solution in reverse flow mode and a stoichiometric equivalent ratio of 2:1; It is noted that the cationic resins were in the acid form due to the requirement to decompose the bicarbonate/carbonate species in the leachate sample to meet regulatory discharge guidelines; (3) DOW Marathon A strong base anion (SBA) resin in the OH$^-$ form which had an operating capacity of 0.6 eq/L. The service velocity was maintained at 30 m/h and regeneration was designed to occur once every 48 hours to synchronize with the cation resins. Regeneration was achieved by using 4 wt % sodium hydroxide (NaOH) solution in reverse flow mode and with a stoichiometric equivalent ratio of 2:1.

2.2.6 Degassing Unit

Air stripping was performed through using a packed column gas adsorption tower. The leachate entered the top of the tower, wherein the solution was distributed over the packing material and air forced up through the packing medium and leachate. The process conditions were: temperature 30°C; pressure 101.3 kPa; gas water ratio of 5 kg gas/kg liquid; and air as the stripping gas.

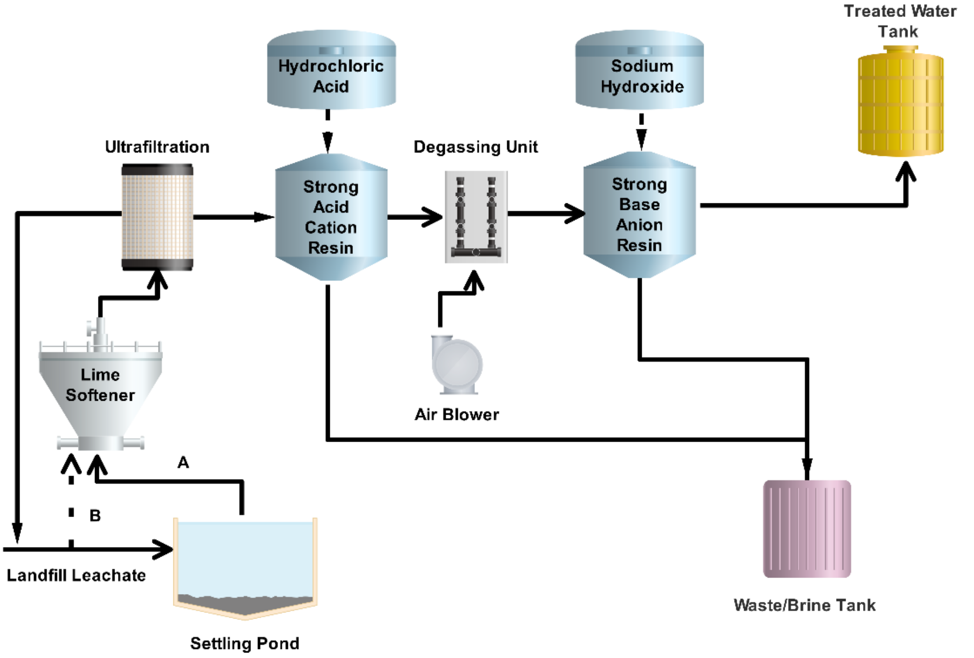
2.3 Process Designs

One constraint placed upon the design of the leachate process was that a reverse osmosis unit could not be employed as the landfill site owner had already confirmed that fouling of the membranes was a problem. Inspection of the leachate analysis indicated that the hardness was 732 mg/L $CaCO_3$, which was in the very hard water range. Consequently, a softening strategy was deemed worthy of evaluation as this should reduce solution conductivity and stabilize operation of downstream unit operations [36]. Common softening methods include lime softening [37] and softening using a cation resin [38, 39]. Process designs also included the option of a leachate stabilization pond prior to the softening step [26]. Selection of the pond in reality depends upon the space available and cost considerations. The level of suspended solids was also relatively high (395.8 mg/L) and thus a clarification stage utilizing addition of a coagulant was potentially advantageous in the case where lime softening was not implemented. An ultrafiltration membrane was used for modelling purposes to ensure that no particulate matter remaining after the clarification or lime softening stages entered the resin beds. In practice, the ultrafiltration system may be replaced by microfiltration. Passage of the leachate through the first acidic cation bed was expected to release significant amounts of carbon dioxide gas [32] due to the reactions shown in Equations 1 & 2.

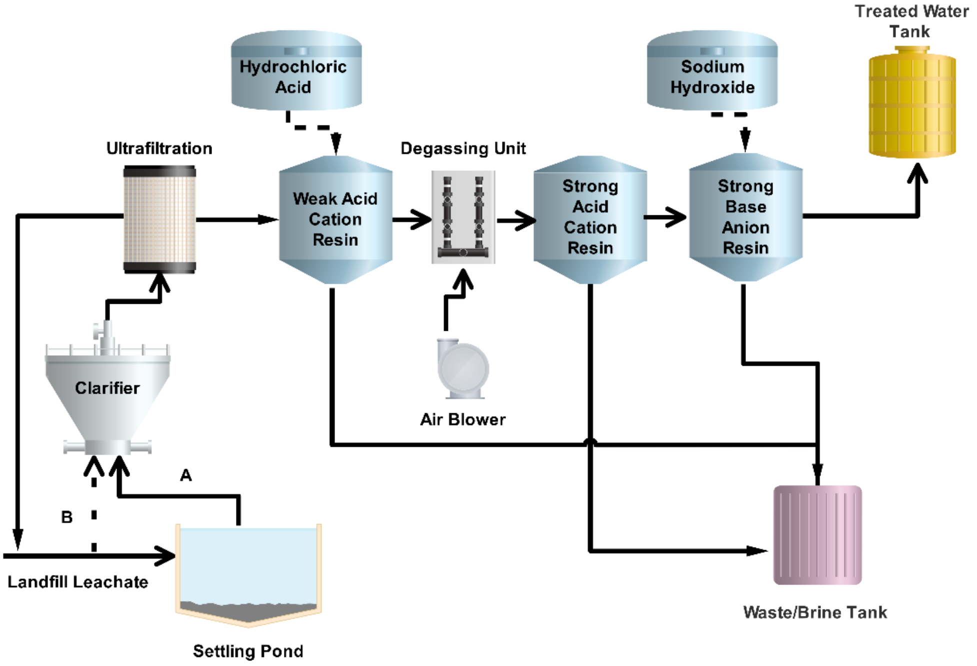
Equation 1: $CO^{2}{}_{3}^{-} + H^{+} \leftrightarrow HCO_{3}^{-}$

Equation 2: $HCO_{3}^{-} + H^{+} \leftrightarrow CO_{2} + H_{2}O$

Therefore, a degassing unit operation was necessary to remove dissolved carbon dioxide as this not disrupted the integrity of the resin bed but also could form bicarbonate species on the downstream anion resin surface [40]. A strong base anion resin was chosen as it can operate at all pH values whereas a weak base anion resin requires acidic conditions to be effective. The resultant two general process options are shown in Figure 1.



(a) Design 1: Lime softening followed by SAC & SBA resins



(b) Design 2: clarification followed by WAC, SAC & SBA resins

Figure 1: Process design concepts for landfill leachate remediation

2.4 Lime Softening by Addition of Calcium Hydroxide (Slaked Lime)

Three 250 mL samples of leachate were stirred at 250 rpm in a suitable container whereupon calcium hydroxide was added until the target pH was achieved (pH 9, 10, and 10.5). The solutions were then left undisturbed to allow any solids to settle before an aliquot was removed for analysis.

2.5 Laboratory Scale Demineralization/Dealkalization/Ammoniacal Nitrogen Removal using Synthetic Resins

To validate the process modelling using AqMB software it was necessary to confirm predictions using a bench top laboratory system. Consequently, Leachate was passed initially through a u-PVC column (2.54 cm diameter) filled with WAC resin (Purolite SST104). A degasser was not equipped to the laboratory set-up and instead the column was pressurized to avoid disruption to the resin bed integrity. It was also not necessary to install pre-filtration for the short term column tests as no sign of water flow problems were recorded. The flow rate was controlled *via* a Masterflex II pump which was regularly calibrated. Subsequently, the solution was degassed by use of a hydrophobic membrane contactor (Liquicel) to minimise void formation in the downstream resin beds. The effluent from WAC resin column was collected in a holding tank prior to passage through the SAC resin (Purolite SST60) column. Again the effluent was collected in a storage vessel before finally flowing through a column of SBA resin (Dow Marathon A). pH and conductivity were measured throughout the experiment and samples were collected periodically for analysis. Bed characteristics and experimental conditions are shown in Table 2.

Table 2: Experimental parameters for WAC; SAC; SBA resin column test

Material Identity	**Column 1 (WAC)**	**Column 2 (SAC)**	**Column 3 (SBA)**	**Units**
	Purolite SST104 (H^+)	Purolite SST60 (H^+)	DOW Marathon A (OH^-)	
Material Loaded	136.2	189.3	125	g
Height of Material Bed	0.342	0.467	0.397	m
Bed Volume	0.17	0.24	0.20	L
Flow Rate	0.0069	0.0089	0.0072	m^3/h
Flow Rate	39.82	37.61	35.79	BV/h
Linear Velocity	13.62	17.56	14.21	m/h
Empty Bed Contact Time	0.025	0.027	0.028	hours

2.6 Analysis

2.6.1 Ammoniacal Nitrogen

Ammoniacal nitrogen content was measured by a Thermo Fisher Gallery Discrete Analyser instrument. The apparatus was calibrated using a certified standard from Australian Chemical Reagents.

2.6.2 pH and Conductivity

The solution parameters of pH and conductivity were recorded using a Labchem-CP benchtop conductivity/TDS - pH/mV - temperature meter obtained from TPS Australia. The pH meter was calibrated using pH buffer 4.00, 7.00 and 10.06 standard solutions. Whereas, the conductivity meter (sensor K=10) was calibrated using a 58.00 mS/cm conductivity standard again supplied by TPS Australia.

2.6.3 Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

A Perkin Elmer Optima 8300 DV ICP-OES instrument was employed to determine the concentrations of various elements. Internal standardisation and auto dilution was conducted by integration with an ESI SC-4DX auto sampler and PrepFAST 2 sample handling unit. ICP-MS grade single element solutions supplied by High-Purity Standards, Charleston, USA were used to calibrate the ICP-OES instrument. Samples were filtered with a 0.45 µm filter and also diluted in a 1:10 ratio using purified nitric acid to decrease the solution pH to 2.

2.7 Process Economics

Plant availability was set at 350 days per annum. It was assumed that the price of cation and anion resins was A$5 per L [34]. Hydrochloric was supplied as 32 % solution with a cost of A$297 per tonne [34]. Electricity price was set to A$0.1 per kWh. Aluminium chlorohydrate coagulant was costed on the basis of a concentration of 40.2 % and price of A$450 per tonne [34]. Resin was assumed to have a lifetime of 3 years before replacement was required. Sodium hydroxide (50 % solution) was estimated to be A$960 per tonne based upon quotes from local suppliers (A$614 per tonne on 32 % basis modelled by AqMB).

3. Results and Discussion

3.1 Pre-Treatment Options

3.1.1 Lime Softening by Addition of Calcium Hydroxide (Slaked Lime)

As indicated above in Section 2.3 reduction of the leachate hardness was deemed to be an important step in the remediation process. As mentioned by Amiri *et al.* [41] both hot and cold lime softening are common industrial unit operations which are employed when significant concentrations of alkaline earth ions are present in solution. Therefore, a lime softener was simulated at feed pH values of 9, 10, and 10.5 to determine the impact upon leachate quality [Table 4]. One important prediction was a substantial decrease in solution conductivity by pH 10 (whereupon further lime addition reduced the conductivity slightly). Ordóñez *et al.* [42] added lime to a brine solution from a reverse osmosis plant and also noted a reduction in solution conductivity. Depending upon the experimental design the conductivity decreased by 40 to 60 %, which was in accord with the data in Table 4 that 41 % conductivity reduction occurred at pH 10.5. The lime softening process also effectively removed suspended solids with only 10 mg/L of this material recorded regardless of feed pH. In general, the bicarbonate concentration decreased significantly as feed pH was elevated and carbonate species likewise increased in concentration (in agreement with the reverse of Equation 1). Bouchahm *et al.* [43] described similar trends when they added lime to aquifer water. Indeed, up to 85 % reduction in bicarbonate concentration was recorded. Carbon dioxide solubility also decreased as more lime was added. Calcium ions were greatly removed by the softening step with only 25.2 (86.8 % removal), 8.2 (95.7 % removal), and 7.95 (95.8 % removal) mg/L remaining at pH 9, 10, and 10.5, respectively. It is noted that the pH was not adjusted in this study to higher values as O'Donnell *et al.* [44] showed that dissolved calcium ion actually concentrations increased at a pH of 11.

In contrast, magnesium ions were not removed to any notable extent until a feed pH of 10.5 wherein 42.9 mg/L Mg remained in solution (30.8 % removal). This behaviour was consistent with previous reports that magnesium ions do not majorly precipitate until pH values in excess of 10 [42]. The extent of Mg removal by lime addition to 10.5 was consistent with the data of O'Donnell *et al.* [44] who recorded less than 20 % magnesium ion removal when softening well water with lime. Overall, the solution hardness decreased to 317, 275, & 196 mg/L $CaCO_3$ for feed pH values of 9, 10, & 10.5, respectively. In conjunction, lime consumption naturally increased as the feed solution pH was raised. Ammoniacal nitrogen concentration was not predicted to change as a result of lime addition to the leachate [Table 4]. Nurul Hanira *et al.* [45] discovered up to *ca.* 45 to 48 % removal of ammonia from a scheduled waste leachate sample when they used either lime of sodium hydroxide to raise solution pH. However, it was necessary to increase pH to 12.4 to 12.8, which were values considerably in excess of the maximum pH of 10.5 used in this current simulation. An interesting finding was that lime was preferred compared to caustic soda as significantly mess material was required to be added to the leachate. Thus, the economics was improved while the degree of ammonia removal was not impacted significantly. The study of Nurul Hanira *et al.* [45] supported the lime in this investigation and not alternate alkaline chemicals such as sodium hydroxide. Lime softening was also predicted to remove >99 % of the total organic carbon content of the leachate. Cho and Gorczyca [46] demonstrated that lime softening was indeed capable of reducing the amount of dissolved organic carbon in a water treatment plant.

It was estimated at a feed pH of 9 that calcium carbonate (240.6 mol/h) and gibbsite ($Al(OH)_3$) were precipitated due to the lime softening process. The results here are in agreement with the findings of previous studies [47]. At a feed pH of 10 the amount of calcium carbonate produced was substantially greater (553.1 mol/h). In addition, ferrihydrite (FeOOH) was also precipitated in agreement with the noted reduction in iron solubility [Table 4]. Instead of gibbsite formation aluminium ions became incorporated in a hydrotalcite material (0.022 mol/h). Finally, at pH 10.5 precipitation of $Mg(OH)_2$ (brucite) precipitation was predicted by AqMB at a rate of 15.98 mol/h; which corresponded with the increasing insolubility of magnesium ions [Table 4]. As more calcium was removed at pH 10.5 compared to pH 10.0, the calcium carbonate formation rate also increased to 636.3 mol/h. Ferrihydrite (0.07 mol/h) and hydrotalcite (0.022 mol/h) were also present in the precipitated solids.

Table 3: Predicted performance data for: Option 1; lime softening of leachate using a thickener and Option 2; removal of suspended solids using a clarifier and ACH coagulant addition

	Unit	Feed water	Option 1: Lime Addition			Option 2: Clarifier
pH Value of Feed	pH	7.57	9.0	10.0	10.5	
Overflow pH	pH		8.37	9.71	10.09	7.36
Underflow pH	pH		9.98	10.55	11.76	7.12
Flow Rate of Overflow	kL/h	20.0	19.23	18.36	18.1	17.82
Flow Rate of Underflow	kL/h		0.77	1.64	1.9	2.18
Electrical Conductivity	µS/cm	5430	5059	3512	3204	5380
Total Dissolved Solids	mg/L	4066	3475	2336	2063	4115
Suspended Solids (SS)	mg/L	395.8	10	10	10	10.0
Total Alkalinity as $CaCO_3$	mg/L	1965	1527	1506	1425	1871
Bicarbonate	mg/L	2335	1640	478.7	221.7	2241
Carbonate	mg/L	20.16	56.5	297.9	301.1	11.49
Carbon Dioxide	mg/L	79.1	9.3	0.1	0.02	123.3
Bromide	mg/L	8.48	8.48	8.48	8.48	8.48
Chloride	mg/L	627	627	627	627	647
Calcium	mg/L	191	25.2	8.2	7.95	163.9
Magnesium	mg/L	62	62	62	42.9	62
Sodium	mg/L	530	530	530	530	530
Potassium	mg/L	89	89	89	89	89
Aluminium	mg/L	0.06	0.006	0.000	0.000	0.56
Iron	mg/L	0.2	0.23	0.005	0.004	0.2
Fluoride	mg/L	0.4	0.4	0.4	0.4	0.4
Ammonia as N	mg/L	239	239	239	239	239
Total Organic Carbon	mg/L	183	0.95	0.44	0.38	3.3
???	?					
Lime Consumption (kg/h)			12.2	35.9	42.05	
ACH Consumption (kg/h)						4.975

Overall, the materials predicted to precipitate agreed with the study of lime sludge characteristics by Korchuganova *et al.* [48] who indicated the sediment comprised of a mixture of calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$), aluminium hydroxide ($Al(OH)_3$), various iron hydroxide materials and organic contaminants.

3.1.2 Leachate Settling Pond then Lime Softening by Addition of Calcium Hydroxide (Slaked Lime)

In this example a stabilization pond was included prior to the lime softening stage [Table 5]. Indicated in section 2.2.1 ponds are often employed to collect wastewater and ensure the water flow is relatively uniform in a water treatment facility [35]. Based upon the data in Table 4 only a feed pH of 10 was evaluated as this was considered optimal in terms of performance and cost. When leaving the pond the solution pH had notably increased from 7.57 to 9.10 as did carbonate concentration. Simultaneously, there was a decrease of conductivity, dissolved carbon dioxide, bicarbonate, calcium, aluminium and total dissolved solids. In addition, a portion of the suspended solids appeared to settle to the bottom of the pond (58.6 % reduction).

The data was consistent with replacement of dissolved carbon dioxide with oxygen from the air during the period the leachate resided in the stabilization pond. Reduction in the presence of the acidic carbon dioxide increased the pH, which accordingly caused the ratio of bicarbonate to carbonate to adjust according to the reverse of Equation 1. Kirby *et al.* [49] described similar behaviour when mine drainage was aerated. In this case, the pH increased by 1.9 pH units, dissolved oxygen became saturated (8.9 mg/L), iron precipitated (<0.03 mg/L remained), and carbon dioxide was degassed (192 to 5 mg/L). The higher pH in the pond also promoted the precipitation of a fraction of the calcium ions as calcium carbonate (26.69 mol/h), aluminium to hydrotalcite (0.004 mol/h) and iron to ferrihydrite (0.011 mol/h). Lime addition to raise the pH to 10 further induced the precipitation of $CaCO_3$ (calcite) at a rate of 226.0 mol/h (of which 224.6 mol/h were transferred to the underflow stream and 1.34 mol/h to the overflow stream). A small amount of ferrihydrite (FeOOH) was also predicted to form as the dissolved iron species became increasingly insoluble (0.021 mol/h). An almost imperceptible amount of hydrotalcite-CO_3 was also potentially present in the solid phase (0.005 mol/h).

Table 4: Predicted performance data for leachate settling pond then: Option 1; lime softening or Option 2; ACH coagulant addition to clarifier

		Feed water	Exit of Pond	Option 1: Lime Addition	Option 2: Clarifier
pH Value of Feed	pH	7.57	9.10	10.0	8.99
Overflow pH	pH			9.85	8.80
Underflow pH	pH			10.66	9.59
Flow Rate of Overflow	kL/h			19.34	17.47
Flow Rate of Underflow	kL/h			0.65	2.52
Electrical Conductivity	µS/cm	5430	4248	3404	4257
Total Dissolved Solids	mg/L	4066	2863	2251	2826
Suspended Solids (SS)	mg/L	395.8	164.0	10	10.0
Total Alkalinity as $CaCO_3$	mg/L	1965	1641	1506	1325
Bicarbonate	mg/L	2335	1160	373.6	1192
Carbonate	mg/L	20.16	217.3	317.7	84.84
Carbon Dioxide	mg/L	79.1	1.20	0.07	2.52
Bromide	mg/L	8.48	8.48	8.48	8.48
Chloride	mg/L	627	627	627	647.5
Calcium	mg/L	191	61.8	8.0	12.7
Magnesium	mg/L	62	62	62	21.3
Sodium	mg/L	530	530	530	530
Potassium	mg/L	89	89	89	89
Aluminium	mg/L	0.06	0.01	0	0.06
Iron	mg/L	0.2	0.06	0.004	0.06
Fluoride	mg/L	0.4	0.4	0.4	0.4
Ammonia as N	mg/L	239	239	239	239
Total Organic Carbon	mg/L	183	36.9	0.49	0.75
Lime Consumption (kg/h)				15.4	
ACH Consumption (kg/h)					4.97

Due to the decrease in calcium content in the leachate caused by a stabilization pond and higher pH of the leachate prior to the thickener; a significant reduction in lime demand was predicted (*c.f.* 15.4 to 35.9 kg/h). This saving equated to 492 kg per day or 162.36 tonnes per annum (based upon 330 days per annum operation). Assuming that slaked lime cost was A$297 per metric tonne [34], then the annual saving was estimated as *ca.* A$48221. Further economic analysis is required to determine if the savings in lime addition compensate for the additional cost of a storage pond and the availability of sufficient land to accommodate a storage pond. Such considerations are beyond the scope of the current study but should be pursued by companies interested in implementing the outcomes of this study.

3.1.3 Clarification of Leachate by Coagulant Addition

A process variant was also analysed wherein a lime softener was not included, instead a standard solids contact clarifier was installed in order to reduce suspended solids content [Table 4]. ACH coagulant was dosed to the clarifier unit at 100 mg/L which corresponded to an addition rate of 4.975 kg/h. As a consequence, suspended solids were majorly removed from the leachate (*c.f.* 395.8 to 10 mg/L) as was total organic carbon (*c.f.* 183 to 3.3 mg/L). In contrast the aluminium content of the leachate increased to 0.56 mg/L due to addition of the aluminium based coagulant. Hydrolysis of the ACH according to Equation 3 resulted in the formation of 22.97 mol/h gibbsite.

Equation 3: $$Al_2(OH)_5Cl.H_2O \rightarrow 2\ Al(OH)_3 + \ H^+ + Cl^-$$

Calcium carbonate which was unstable in the leachate was also removed by the clarifier (13.77 mol/h) which explained the decrease in calcium ions from 191 to 163.9 mg/L [Table 6].

The advantage of this strategy was that it avoided the use of a lime softener and associated issues when handling and disposing of lime sludge [50]. However, disadvantages included higher concentrations of alkaline earth ions and bicarbonate species; and higher solution conductivity.

3.1.4 Leachate Settling Pond then Clarification by Coagulant Addition

A final pre-treatment strategy prior to the resin beds which was considered, was the addition of a settling pond to collect the leachate prior to removal of suspended solids using a solids contact clarifier [Table 5]. In this instance, the solution conductivity was less than when there was no settling pond present (*c.f.* 4257 to 5380 µS/cm), and the concentration of calcium and magnesium were notably lowered (*c.f.* 12.7 and 163.9 mg/L for calcium, and 21.3 and 62 mg/L for magnesium).

3.2 Demineralization/Dealkalization using Synthetic Resins

3.2.1 Stabilization Pond – Lime Softening to pH 10 – SAC resin – SBA resin

The first point to answer was if a single cation resin bed in conjunction with an SBA resin was sufficient to meet the discharge water quality for the landfill leachate. Hence, a treatment process was designed wherein leachate was pre-treated by stabilization in a pond followed by lime softening to pH 10 and removal of residual solids by an ultrafiltration unit. A combination of a strong acid cation resin, degasser, and strong base anion resin was then analysed for performance [Table 6].

Table 5: Predicted performance data for leachate clarification using Stabilization Pond – Lime Softening to pH 10 – SAC resin – Degasser - SBA resin

		Exit of UF	Exit of SAC resin	Exit of SBA resin
pH	pH	9.85	1.95	6.02
Flow Rate	kL/h	17.99	17.99	17.99
Electrical Conductivity	µS/cm	3400	6468	1282
Total Dissolved Solids	mg/L	2251	1414	839.4
Suspended Solids (SS)	mg/L	0	0	0
Total Alkalinity as $CaCO_3$	mg/L	1499	0	195.4
Bicarbonate	mg/L	373.2	0.03	237.8
Carbonate	mg/L	314.0	0	0.017
Carbon Dioxide	mg/L	0.07	499.3	499.4
Bromide	mg/L	8.48	8.48	0.04
Chloride	mg/L	627	627	7.23
Calcium	mg/L	5.25	0.008	0.008
Magnesium	mg/L	62	0.16	0.16
Sodium	mg/L	530	69.8	69.8
Potassium	mg/L	89	6.44	6.44
Aluminium	mg/L	0	0	0
Iron	mg/L	0.004	0.003	0.003
Fluoride	mg/L	0.4	0.4	0.05
Ammonia as N	mg/L	239	189.8	189.8
Total Organic Carbon	mg/L	0.14	0.14	0.14
HCl Consumption (kg)			3470	
NaOH consumption (kg)				2047
Resin volume (L)			23790	25590

Passage of the leachate through the SAC resin bed reduced the pH from 9.85 to 1.95. The pH of a 1259 mg/L sodium chloride solution when treated by a column of H^+-SAC resin was recorded to decrease to less than 1.5 due to release of protons from the resin surface sites as a result of sorption of sodium ions [Equation 4] [51]. Similarly, potassium ions have also been shown to readily exchange with protonated sites on SAC resin with a maximum loading slightly greater than that reported for sodium ions [52]. This latter observation suggested that potassium ions were preferred by the SAC resin than sodium ions. In agreement the concentration of sodium and potassium were reduced by 86.8 and 92.8 %, respectively [Table 6].

Equation 4: $R-H+Na^{+}(K^{+})\leftrightarrow R-Na(K)+\ H^{+}$

Calcium and magnesium ions were almost completely removed from the leachate by the SAC resin (>99 %) which was consistent with the greater affinity of the resin for alkaline earth ions compared to alkali metal ions. For example, Strelow [53] reported that the selectivity of SAC resins was as follows: $H^+ < Na^+ < Mg^{2+} < Ca^{2+}$. The exchange of alkaline earth ions with SAC resin sites is illustrated in Equation 5.

Equation 5: $2\,R-H+Ca^{2+}(Mg^{2+})\leftrightarrow R_2-Ca(Mg)+\ 2\,H^{+}$

Millar *et al.* [54] investigated the interaction of both sodium chloride and sodium bicarbonate species in aqueous solution with a SAC resin. It was found that sodium ions associated with bicarbonate species were sorbed on the resin exchange sites in preference to those associated with chloride ions. This phenomenon was linked to the thermodynamically favourable secondary decomposition of bicarbonate species to create dissolved carbon dioxide [Equation 6].

Equation 6: $R-H+NaHCO_3\leftrightarrow R-Na+H_2O+CO_2$

Hence, it can be seen that the alkalinity of the leachate was eliminated due to the acid decomposition process exemplified in Equation 6 and also the accumulation of substantial concentrations of carbon dioxide was evident as predicted in Table 6.

A fraction of the ammonium species present in the leachate was also predicted; albeit, only a 20. 6 % reduction was estimated. Previous studies revealed that the selectivity of a SAC resin was $NH_4^+/K^+ > Na^+ > H^+$ and that the identity of the resin used was important [53]. Indeed SAC resin significantly outperformed WAC resin in their tests. However, as indicated by Malovanyy *et al.* [55] ammonium ion uptake on SAC resin is inhibited in real wastewater samples as more strongly bound ions such as calcium and magnesium are invariably present.

Notably the key criteria of solution conductivity and ammoniacal nitrogen content were both in substantial excess than the limits imposed in Table 1. Introduction of an SBA resin bed after the SAC column had a beneficial impact upon the solution conductivity which was reduced from 6468 to 1282 µS/cm. However, ammoniacal nitrogen concentration was not affected by the SBA resin due to the lack of an anionic species to remove. In contrast chloride and fluoride ions were reduced in concentration by 98.9 and 87.5 %, respectively [Equation 7].

Equation 7: $$R - OH + Cl^{-}(F^{-}) \leftrightarrow R - Cl(F) + OH^{-}$$

A previous study by Samadi *et al.* [56] confirmed that fluoride uptake from aqueous solution occurred using a strong base anion resin. When solutions of sodium chloride were tested the loading capacity was 13.7 g F/kg resin in the best case. However, it was noted that the co-presence of chloride ions inhibited uptake of fluoride. This finding was in agreement with equilibrium sorption data reported by Lopez *et al.* [57] for fluoride ion exchange with Cl^- - SBA resin revealed that an unfavourable (concave) isotherm profile was present. Therefore, it was inferred that chloride ions were preferred rather than fluoride ions on SBA resin. It is noted that the “chromatography effect” would be observed if the simulation allowed higher loading of the SBA resin to occur [58]. When the resin has not attained monolayer exchange capacity essentially all ions in the solution may load on the exchange sites. However, at monolayer capacity the resin will continue to exchange preferred ions and displace weaker ions. In this case fluoride ions would be ejected from the resin surface by chloride ions.

3.2.2 Stabilization Pond – Lime Softening to pH 10 – WAC resin – Degasser – SBA resin

A second resin combination was designed wherein leachate pre-treatment was the same as illustrated in Section 3.2.1 but in this case a weak acid cation resin was evaluated instead of a strong acid cation resin. The degasser and strong base anion resin were the same as in Section 3.2.1 [Table 7].

Table 6: Predicted performance data for leachate clarification using Stabilization Pond – Lime Softening to pH 10 – WAC resin – Degasser – SBA resin

		Exit of UF	Exit of WAC resin	Exit of Degasser	Exit of SBA resin
pH	pH	9.85	2.25	2.25	9.49
Flow Rate	kL/h	17.99	17.99	17.99	17.99
Electrical Conductivity	µS/cm	3400	4862	4862	863.6
Total Dissolved Solids	mg/L	2251	1581	1083	447.8
Suspended Solids (SS)	mg/L	0	0	0	0
Total Alkalinity as $CaCO_3$	mg/L	1499	0	0	538.6
Bicarbonate	mg/L	373.2	0.06	0	0.98
Carbonate	mg/L	314.0	0	0	0.2
Carbon Dioxide	mg/L	0.07	499.3	0.85	0.85
Bromide	mg/L	8.48	8.48	8.48	0.04
Sulfate as SO_4	mg/L	0	0	0	0
Chloride	mg/L	627	627	627	6.61
Calcium	mg/L	5.25	0.04	0.04	0.04
Magnesium	mg/L	62	1.39	1.39	1.39
Sodium	mg/L	530	109.6	109.6	109.6
Potassium	mg/L	89	89	89	89
Aluminium	mg/L	0	0	0	0
Zinc	mg/L	0.03	0.001	0.001	0.001
Iron	mg/L	0.004	0.004	0.004	0.004
Fluoride	mg/L	0.4	0.4	0.4	0.05
Ammonia as N	mg/L	239	239	239	239
Total Organic Carbon	mg/L	0.14	0.14	0.14	0.14
HCl Consumption (kg/h)			3765		
NaOH consumption (kg/L)					2049
Resin volume (L)			13590		25610

Again the pH was substantially reduced when the leachate was treated by the WAC resin, although the decrease was not as great compared to when SAC resin was employed (*c.f.* 2.25 & 1.95 for SAC and WAC, respectively). In accord with the affinity of WAC resin for alkaline earth ions [39, 59], substantial reduction in the concentration of calcium and magnesium ions in the leachate was evident [Equation 8].

Equation 8: $2\,R - COOH + Ca^{2+}(Mg^{2+}) \leftrightarrow R_2 - COOCa(Mg) + 2\,H^{+}$

Removal of 79.3 % of sodium ions was achieved using the WAC resin [Equation 9], whereas it was indicated that the amount of potassium ions would not be notably reduced. This may be tentatively explained on the basis of the research by Kunin and Barry [44]. These authors described the exchange of potassium ions from aqueous solution with WAC resin as being very slow with 7 days required to achieve equilibrium uptake (albeit, similar data for sodium ions was not provided). In contrast, equilibrium with calcium ions was only 2 minutes.

Equation 9: $R - COOH + Na^{+} \leftrightarrow R - COONa + H^{+}$

The acidic sites on the WAC resin reduced the presence of bicarbonate ions due to the low pH conditions generated [Table 7] and ultimately formed dissolved carbon dioxide [Equations 10 & 11].

Equation 10: $R - COOH + NaHCO_3 \leftrightarrow R - COONa + H^{+} + HCO_3^{-}$

Equation 11: $HCO_3^{-} + H^{+} \leftrightarrow CO_2 + H_2O$

A degasser was again necessary to remove the dissolved carbon dioxide by air stripping. Passage of the leachate through the SBA resin resulted in a leachate conductivity (863.6 µS/cm), which was less than the target value of <1600 µS/cm. However, the ammoniacal nitrogen level was in excess of the discharge target of <100 mg/L. Examination of the effluent from the SBA resin revealed that the pH was alkaline (9.49) which was potentially attractive in relation to the idea of using air stripping as a subsequent unit operation to reduce ammoniacal nitrogen concentration (see Section 3.2.3).

3.2.3 Clarifier – WAC resin – Degasser – SBA resin

As WAC resin is well known for its ability to soften water the utilization of a lime softener before the resin may not be required. Therefore, a simulation was completed wherein a clarifier was initially used to remove suspended solids from solution and then the filtered effluent was flowed through a WAC resin – degasser – SBA resin set of unit operations [Table 8].

Table 7: Predicted performance data for leachate clarification using – Clarifier – WAC resin – Degasser – SBA resin

		Exit of UF	Exit of WAC resin	Exit of Degasser	Exit of SBA resin
pH	pH	7.36	5.63	7.66	12.07
Flow Rate	kL/h	16.57	16.59	16.57	16.57
Electrical Conductivity	µS/cm	5378	3189	2746	2992
Total Dissolved Solids	mg/L	4115	3000	1483	662.4
Suspended Solids (SS)	mg/L	0	0	0	6.9
Total Alkalinity as $CaCO_3$	mg/L	1866	362.6	363.0	1269
Bicarbonate	mg/L	2240	441.9	424.1	0.52
Carbonate	mg/L	11.49	0.02	1.68	43.4
Carbon Dioxide	mg/L	123.2	1427	0.89	0.89
Bromide	mg/L	8.48	8.47	8.47	0.06
Chloride	mg/L	647.3	646.7	646.7	10.3
Calcium	mg/L	163.4	1.26	1.26	1.26
Magnesium	mg/L	62	1.35	1.35	1.35
Sodium	mg/L	530.3	114.6	114.8	114.8
Potassium	mg/L	89	89	89	89
Aluminium	mg/L	0	0	0	0
Zinc	mg/L	0.03	0.02	0.02	0.02
Iron	mg/L	0.2	0.2	0.2	0.2
Fluoride	mg/L	0.4	0.4	0.4	0.07
Ammonia as N	mg/L	239	239	150.7	150.7
Total Organic Carbon	mg/L	0	0	0	0
HCl Consumption (kg/h)			4439		
NaOH consumption (kg/L)					2685
Resin volume (L)			16020		33560

As expected from Equations 8 to 10 the leachate pH was reduced and the concentrations of sodium, calcium and magnesium all diminished in value by passage through the WAC resin bed. Similarly, the degasser removed the dissolved carbon dioxide formed according to Equation 11 and increased the solution pH to 7.66. The leachate quality after the SBA resin stage was not compliant in terms of either conductivity or ammonia content. However, it was noted that the solution pH was 12.07 and thus potentially ideal for ammonia stripping. Hence, an additional degassing unit was modelled post the SBA resin column. The main findings were: ammoniacal nitrogen was reduced to 16.2 mg/L; solution conductivity was increased to 4723 µS/cm; and solution pH was raised to 12.3. As the leachate composition did not satisfy regulatory discharge conditions a final pH adjustment to pH 9 by hydrochloric acid was added to the simulation. This process did reduce conductivity but only to 2273 µS/cm, which may be a result of the additional chloride ions added from the acid dosing strategy.

3.2.3 Clarifier – WAC resin - degasser – SAC resin – SBA resin

The aforementioned modelling indicated that use of a two resin system (cation then anion) was not sufficient to satisfy the major process targets of conductivity less than 1600 µS/cm and ammoniacal nitrogen concentration < 100 mg/L. Therefore, in this instance the application of three resins in series was evaluated (WAC: SAC: SBA) [Table 9].

As indicated by Kunin and Barry [44] placement of a WAC resin prior to a SAC resin has the advantage of reducing the bicarbonate concentration more economically than with a SAC resin alone. This fact relates to the greater ease of regeneration of WAC resin with acid solutions, relative to SAC resin. Compared to the data displayed in Table 8, adding the SAC resin stage after the degasser further reduced the leachate pH to 2.18, which concomitantly removed alkalinity according to Equation 6. Major cations present (Na, K, Ca & Ca) were also removed in substantial amounts in agreement with Equations 4 & 5. The addition of the extra cation bed allowed the exchange of ammonium ions to occur to the extent that the concentration was significantly less (19 mg/L) than the 100 mg/L discharge limit. However, the solution conductivity was still in excess of the 1600 µS/cm target (3892 µS/cm). Passage of the effluent from the SAC resin column into the SBA resin bed not only raised the solution pH to 9.69 but also majorly removed chloride and fluoride from the leachate. As a consequence, the TDS was reduced and importantly the solution conductivity was now compliant with discharge limits (550.2 µS/cm). To make the treated water completely compliant with discharge regulations pH regulation using HCl was modelled by inserting a chemical doser immediately after the SBA resin column. Upon achievement of pH 9 in the leachate the solution conductivity became 610.5 µS/cm, the total alkalinity 409 mg/L $CaCO_3$, and TDS was 563.5 mg/L. An extra 3.27 kg/h of 32 w/w % HCl was required for the pH adjustment stage.

Table 8: Predicted performance data for leachate clarification using – Clarifier – WAC resin – Degasser – SAC resin - SBA resin

		Exit of UF	Exit of WAC resin	Exit of Degasser	Exit of SAC resin	Exit of SBA resin
pH	pH	7.36	5.63	7.66	2.18	9.69
Flow Rate	kL/h	16.57	16.59	16.57	16.57	16.57
Electrical Conductivity	µS/cm	5378	3189	2746	3892	550.2
Total Dissolved Solids	mg/L	4115	3000	1483	1031	497.9
Suspended Solids (SS)	mg/L	0	0	0	0	0
Total Alkalinity as $CaCO_3$	mg/L	1866	362.6	363.0	0	501.2
Bicarbonate	mg/L	2240	441.9	424.1	0.03	340.5
Carbonate	mg/L	11.49	0.02	1.68	0	101.6
Carbon Dioxide	mg/L	123.2	1427	0.89	320.1	320.2
Bromide	mg/L	8.48	8.47	8.47	8.48	0.04
Chloride	mg/L	647.3	646.7	646.7	647.5	7.62
Calcium	mg/L	163.4	1.26	1.26	0.002	0.002
Magnesium	mg/L	62	1.35	1.35	0.003	0.003
Sodium	mg/L	530.3	114.6	114.8	19.57	19.58
Potassium	mg/L	89	89	89	8.43	8.43
Aluminium	mg/L	0	0	0	0	0
Zinc	mg/L	0.03	0.02	0.02	0.001	0.001
Iron	mg/L	0.2	0.2	0.2	0.2	0.2
Fluoride	mg/L	0.4	0.4	0.4	0.4	0.06
Ammonia as N	mg/L	239	239	150.7	19.0	19.0
Total Organic Carbon	mg/L	0	0	0	0	0
HCl Consumption (kg/h)			4439		1680	
NaOH consumption (kg/L)						1948
Resin volume (L)			16020		11520	23450

3.3 Process Validation

3.3.1 Pre-Treatment using Slaked Lime Addition

Table 910 shows the analysis of leachate samples adjusted to *ca*. pH 9, 10, and 10.5. Calcium removal appeared to be practically complete by *ca*. pH 9.2, whereas magnesium precipitation was more difficult unless a higher pH value was employed. However, there was a performance trade-off as calcium in the treated water actually increased as further lime was added to the leachate. This result was in agreement with the data from the study by O'Donnell *et al.* [44] which also found that dissolved calcium ion concentrations increased as solution pH approached 11. In addition, the amount of lime required was naturally greater when raising the pH above 9. As outlined in Section 3.1.1 calcium was precipitated in the form of calcium carbonate and magnesium as magnesium hydroxide (brucite).

Table 9: Analysis of leachate samples following pH adjustment to 9, 10 and 10.5: 250 mL sample volume

Parameter	Feed Water	Lime Addition		
pH Value of Feed	7.05	9.22	9.97	10.78
Electrical Conductivity	5820	3890	3340	3340
Calcium	177.6	1.695	2.244	15.98
Magnesium	60.9	27.61	0.7881	0.0255
Sodium	558.3	551.5	549.6	555.5
Potassium	85.23	86.99	86.93	88.18
Aluminium	0.0182	0.0152	0.0025	0.0032
Iron	0.292	0.0403	0.0032	0.0016
Lime Consumption (kg/h)		52.8	62.4	69.6

The reduction trend in calcium content of the leachate was similar for both the real and simulated leachate and in general it appeared that the computational predictions were conservative with respect to the actual data. Simulation did not indicate that magnesium would be removed at pH values of 9 & 10. However, as discussed by Wang *et al.* [60] co-precipitation of magnesium and calcium ions can occur under alkaline conditions. Depending upon the ratio of magnesium to calcium ions various morphologies and sizes of precipitates were observed using electron microscopy imaging. The software correctly indicated that both iron and aluminium species should be removed from solution at high pH conditions due to the formation of ferrihydrite (FeOOH) and gibbsite ($Al(OH)_3$).

It was observed that calculated and measured conductivity values agreed well especially for pH values of *ca*. 10 & 10.5. The measured lime consumption was notably higher than the corresponding quantity predicted using the AqMB software [Table 4]. One possible explanation was that the laboratory scale (250 mL of leachate) was considerably smaller than the volume present in an industrial lime softener. Hence, another test was conducted wherein the leachate volume was increased to 12 L and lime was again added to raise the pH to *ca*. 9. In this case the recorded lime dosage was significantly reduced to 33.3 kg/h (*c.f*. 52.8 kg/h for the 250 mL leachate sample). Another aspect was that the leachate received was slightly different in composition than the modelled sample (which was based upon historical data). For example, the initial pH of the sample was lower with the real leachate sample and this in turn would also increase the amount of lime required compared to computational simulation data.

3.3.2 Demineralization & Ammoniacal Nitrogen Removal of Landfill Leachate using WAC-SAC-SBA Resins

Computational predictions indicated that a WAC-SAC-SBA resin combination would satisfy discharge regulations for the leachate of interest in this study [Table 9]. Hence, actual leachate solution was flowed through the outlined series of resin columns [Figures 4 to 6]. The leachate pH initially reduced from 7.05 to 3.5 when less than 10 BV of leachate was processed by the WAC resin column [Figure 4]. As further leachate was treated the effluent pH increased to *ca*. 5.75 after 19.9 BV treated. This pH value was in agreement with the predicted pH of 5.63 in Table 9. We note that with the software full loading of the resin was not assumed, instead the working capacity for the WAC resin was 1.80 eq/L. Similarly, the solution conductivity was reduced to 1280 µS/cm after 6.6 BV of leachate was remediated and this value stabilized at *ca*. 3350 µS/cm as more leachate was processed. AqMB software estimated that the conductivity was approximately 3189 µS/cm which was again in accord with the experimental data.

With respect to the softening of the leachate by the WAC resin, the removal efficiency for calcium and magnesium ions was >99.9 in both instances. These values corresponded well to the simulation predictions of >99 and 97.8 % for calcium and magnesium, respectively.

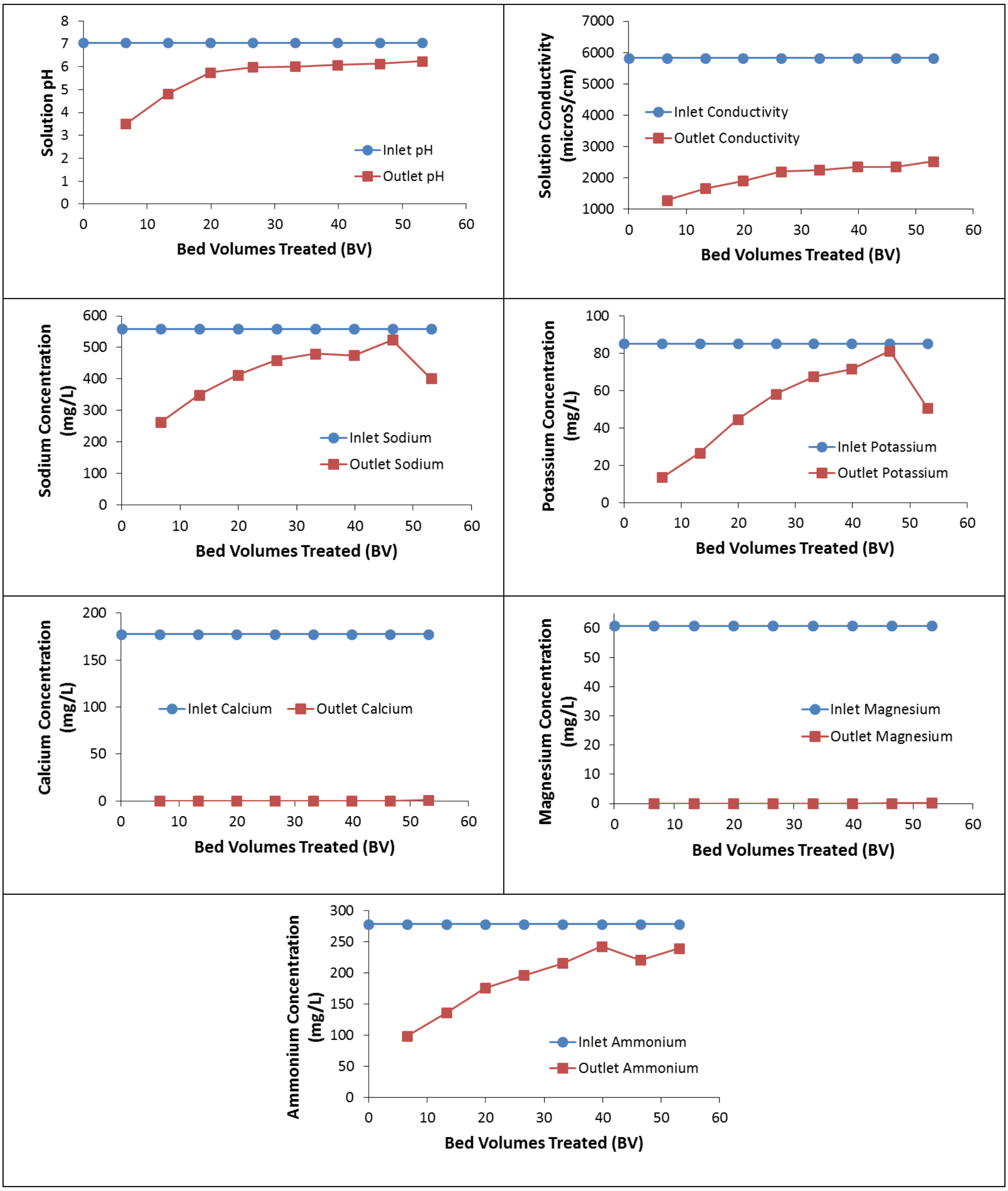


Figure 2: Breakthrough curves for landfill leachate treatment using combination of WAC, SAC & SBA resins: WAC resin influent and effluent data

Removal of ammoniacal nitrogen by the WAC resin was only partially achieved (168.5 mg/L in treated leachate storage vessel). This value was in good agreement with the simulation (150.7 mg/L) measured at the exit of the degassing unit immediately after the WC resin bed.

Treatment of the effluent from the WAC column with a SAC column further reduced the solution pH to *ca*. 2, which was similar to that of 2.18 predicted by AqMB.

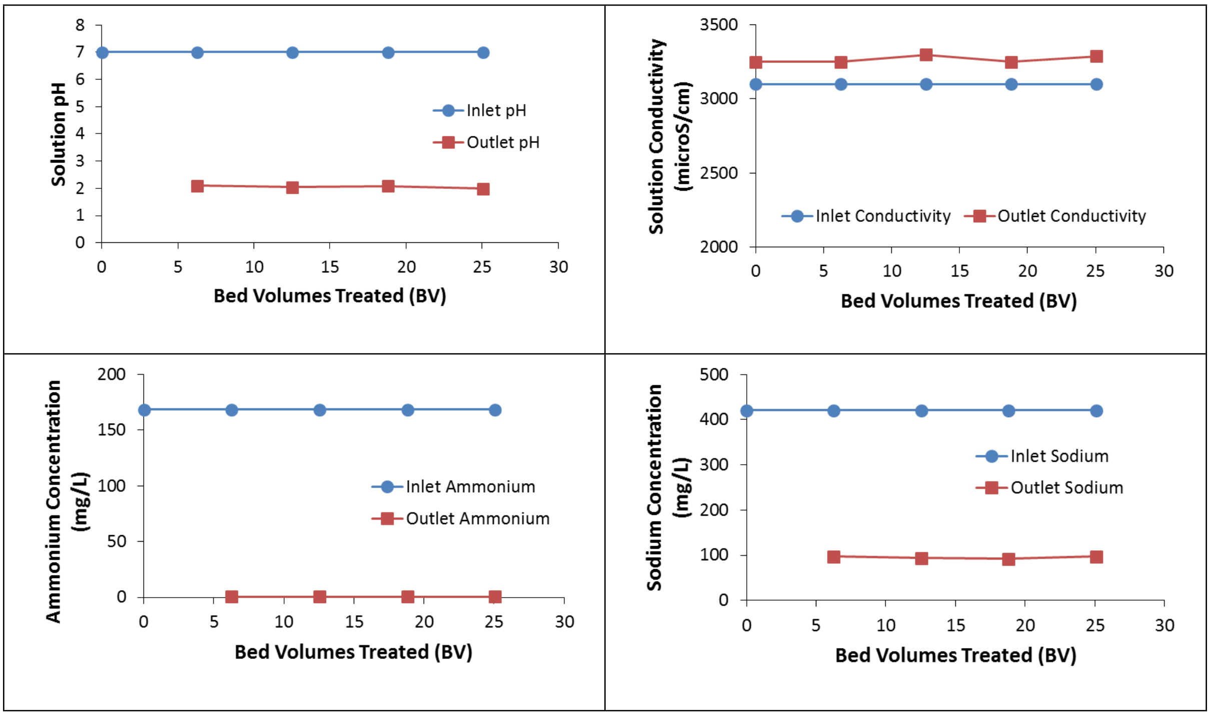


Figure 3: Breakthrough curves for landfill leachate treatment using combination of SAC & SBA resins: SAC resin influent and effluent data

Correspondingly, the solution conductivity increased from *ca*. 3100 to 3300 µS/cm which reflected the modelling data that indicated conductivity should become greater after SAC resin treatment. Ammonium ions were substantially removed by the SAC resin bed (< 2 mg/L) with minimal sign of breakthrough occurring which again was predicted by the software model (19 mg/L of ammonia after SAC resin). Sodium ions were also majorly removed by the SAC resin (77.9 %) which reflected in Table 9.

Error! Reference source not found. shows the pH, conductivity and chloride data when the effluent from the SAC resin column was treatment by SBA resin. The outlet pH was initially high (ca. 13.2) due to the exchange of chloride ions from the leachate with hydroxyl species on the resin surface. As the sites became saturated the pH dropped to 8.3. The higher value of 9.69 estimated by AqMB may be ascribed to the difference in breakthrough points in the simulation and laboratory experiment.

Final electrical conductivity measurements were below the discharge limit (< 500 µS/cm) as predicted by AqMB. Chloride levels were also significantly reduced, which was again supported by software simulation [Table 9].

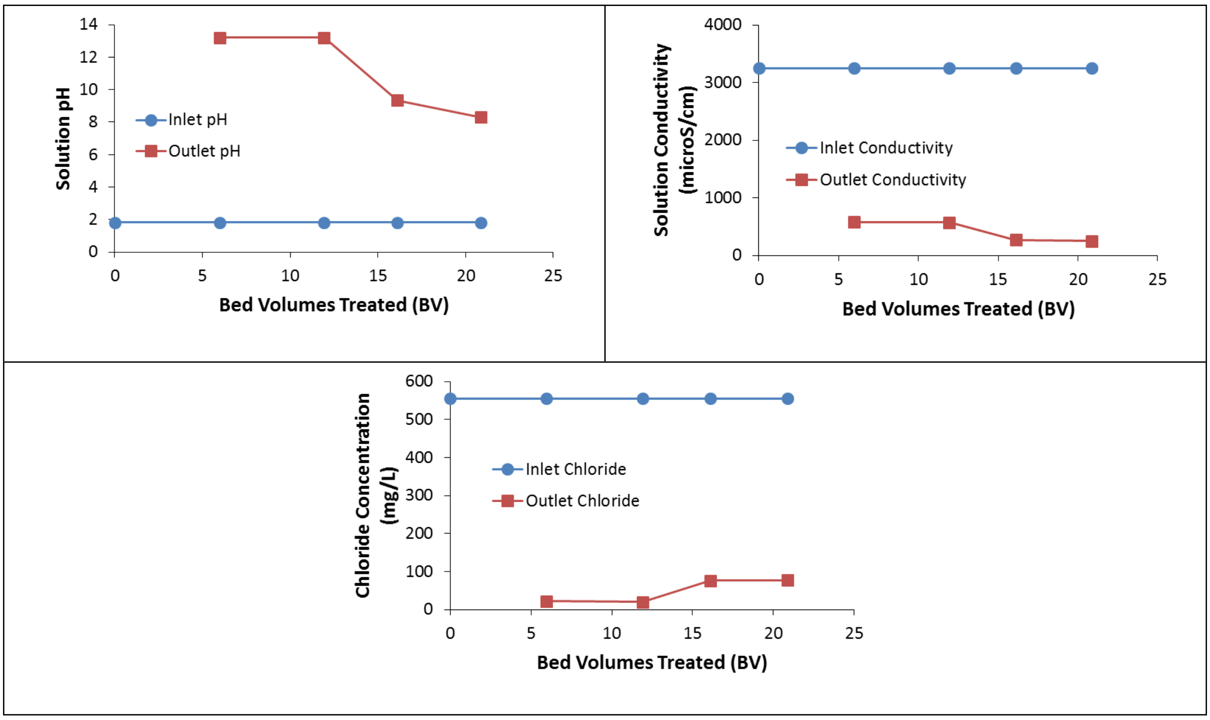


Figure 4: Breakthrough curves for landfill leachate treatment using combination of SAC & SBA resins: SBA resin influent and effluent data

3.4 Process Economics

A pertinent point is an estimation of the process economics for the leachate treatment designs considered. For the preferred process option using a WAC-SAC-SBA resin combination and no lime softening stage, the cost of resins, coagulant, and chemicals was calculated as well as the demand/cost for electricity. AqMB suggested that the total power consumption was 4.72 kWh per kL of leachate treated. This figure encompassed the demand of pumps (feed, recycle, sludge, regen/displacement, backwash, and effluent), flocculation mixer, rake drive motor, air scour blower, and air blower. Coagulant cost was A$0.115 per kL and hydrochloric acid for final pH adjustment was A$0.17 per kL. Annualized resin costs were A$21,111 for WAC resin, A$32,089 for SAC resin and A$15,181 for SBA resin. On a per kL of leachate treated basis the resin costs were A$0.13, A$0.19 and A$0.09, respectively. Regeneration costs were the major expenditure with the ion exchange process. HCl cost for regeneration of the WAC and SAC resins was estimated as A$4113 (for 4.434 tonnes 100 % acid basis or 13.85 tonnes 32 % basis) and A$1559 (for 1.680 tonnes 100 % acid basis or 5.25 tonnes 32 % basis), respectively every 2 days. Similarly, the cost for sodium hydroxide to regenerate the SBA resin was A$3740 (for 1.948 tonnes 100 % alkali basis or 3.896 tonnes 50 % basis) each 2 day cycle. As the number of regenerations was 175 per annum then these figures can be converted to a cost per kL of water treated (based upon 168,000 kL per annum leachate treated); A$9.80 per kL for regeneration chemicals. In summary, the estimated cost of leachate treatment was A$10.50 per kL.

4. Conclusions

Computational simulation has been demonstrated to allow rapid evaluation of options to treat a landfill leachate, which was characterized by excessive solution conductivity and ammoniacal nitrogen content. The hypothesis that the use of computational methods reduced the extent of laboratory testing was proven; as a wide range of process configurations were tested and predictions in agreement with literature generated. The preferred plant configuration to meet discharge guidelines was selected (three resin bed system (WAC:SAC:SBA)) as this not only facilitated ammonium uptake on the cation resin surface but also was necessary to achieve low solution conductivity. Laboratory experiments confirmed the usefulness of the computer simulation as the real leachate when treated by the 3 resin bed process design was indeed compliant with discharge regulations. In terms of economics, the treatment cost was estimated to be A$10.50 per kL, which may be potentially unattractive for commercial implementation (with the caveat that competing technologies need to also meet regulatory requirements).

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