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OPTIMIZATION OF ION EXCHANGE RESIN REGENERATION



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A strong acid cation resin has a low affinity to regenerated ion form (H^+). A conventional regeneration where fresh regenerant flows through the resin bed has proven to be inefficient. A large portion of H^+ ions in the regenerant flows through the resin bed without regenerating the resin. A different method to regenerate resin was evaluated to improve the resin regeneration efficiency.

The recycling of the spent regenerant was tested. Spent acid was recycled twice in regeneration before disposal. The recycling of regenerant reduced the consumption of fresh acid in half without a significant difference in the cycle length compared to conventional regeneration, although it caused a higher ion leakage during exhaustion. The ion leakage was caused by the unregenerated resin, which leaked during exhaustion. The co-flow regeneration led to the concentration of unregenerated resin near the column outlet.

A reverse flow regeneration was tested to reduce ion leakage. The regeneration decreased the leakage to a minimum, keeping the cycle length approximately the same. There was not a significant difference in the exhaustion length of the two regeneration methods. The outflow was collected during strong acid cation regeneration to determine a sufficient amount of rinsing water after regeneration. It was noted that extra rinsing did not have an impact on the water quality of the outlet.

Regenerant recycle was noted to be a possible solution to increase the regeneration efficiency. Decreasing chemical consumption could also be achieved by determining the sufficient amount of regenerant, which requires more studies. Reverse flow regeneration was noted to be a viable option to decrease ion leakage. In the study, only a few cycles were performed. Therefore, longer testing is required to examine the long-term impact of regenerant recycle and reverse flow regeneration on the resin and the exhaustion.

The study highlighted the importance of operating capacity in the ion exchange process. Even though the ion exchange line was exhausted, causing ions to leak through the resin, strong acid cation resin was more than half in regenerated ion form. The ion leakage was increasing between ion exchange cycles. Therefore, ion exchange tests should include multiple ion exchange cycles to obtain reliable data on the ion exchange.

KEYWORDS:

Ion exchange, Resin, Regeneration, Strong acid cation exchanger

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IONINVAIHTOHARTSIN ELVYTYKSEN OPTIMOINTI

Vahvan kationinvaihtajan affiniteetti elvytettyyn muotoon (H^+) on matala, mikä johtaa tehottomaan elvytykseen. Perinteinen elvytys, missä tuore elvytysliuos virtaa myötävirtaan hartsipedin läpi, on tehotonta. Elvytyksen aikana suuri osa elvytyskemikaalista kulkeutuu vahvan kationinvaihtajan läpi kaikkia vetyioneja hyödyntämättä. Erilaista elvytysmetodia arvioitiin elvytystehokkuuden parantamiseksi.

Elvytysliuoksen kierrättämistä testattiin elvytyksen tehokkuuden parantamiseksi. Käytetty elvytysliuos kierrätettiin kahdesti hartsipedin läpi ennen hävittämistä. Elvytysliuoksen kierrätys puolitti kemikaalin kulutuksen ilman ioninvaihtosyklin merkittävää lyhenemistä tavalliseen elvytykseen verrattuna, mutta se johti korkeampaan ionivuotoon. Myötävirtaelvytys jättää hartsin elvytyksen vajaaksi kolonnin ulostulon läheisyydessä, mitkä eluoituivat ajon aikana

Vastavirtaelvytystä testattiin ionivuodon vähentämiseksi. Vastavirtaelvytys vähensi ionivuodon minimiin säilyttäen ioninvaihdon sykclipituuden kuitenkin samana myötävirtaelvytykseen verrattuna. Elvytysliuoksen kierrätyksen ja perinteisen elvytyksen välillä ei ollut merkittävää eroa ioninvaihtosyklin pituudessa. Ulosvirtaus kerättiin elvytyksen ajan riittävän elvytyksen jälkeisen huuhteluvesimäärän määrittämiseksi. Ylimääräisellä huuhteluvedellä ei todettu olevan vaikutusta ulostulon veden laatuun.

Elvytysliuoksen kierrätys todettiin mahdolliseksi ratkaisuksi tehostamaan elvytyksen tehokkuutta. Tehokkuutta voidaan lisätä optimoimalla riittävä elvytyskemikaalin määrä ja tämä vaatii jatkotutkimuksia. Vastavirtaelvytys osoittautui tehokkaaksi tavaksi vähentää ionivuotoa. Tutkimuksissa tehtiin vain muutamia ioninvaihtosyklejä, joten pidempiaikaiset vaikutukset hartsiin ja ioninvaihtoon jäivät epäselviksi.

Tutkimukset osoittivat operointikapasiteetin tärkeyden ioninvaihtoprosessille. Ioninvaihdon jälkeen vahva kationinvaihtaja oli vielä yli puolet elvytettyssä muodossa, vaikka ioninvaihtolinja alkoi vuotamaan ioneja merkiksi kapasiteetin loppumisesta. Ioninvaihdon aikana tapahtuva ionivuoto lisääntyi syklien välillä. Näin ollen ioninvaihtotestien pitäisi kattaa useita syklejä saadakseen luotettavaa tietoa ioninvaihdosta.

ASIASANAT:

Ioninvaihto, Harts, Elvytys, Vahva kationinvaihtaja

CONTENT

LIST OF ABBREVIATIONS AND SYMBOLS	8
1 INTRODUCTION	6
2 ION EXCHANGE THEORY	9
2.1 The principle of ion exchange	11
2.1.1 The effect of concentration on the equilibrium	13
2.1.2 The effect of the degree of cross-linking to equilibrium	14
2.2 Donnan potential	14
2.3 Ion exchange resin	16
2.3.1 Strong acid cation resin	16
2.3.2 Weak acid cation resin	17
2.3.3 The strong and weak base anion resin	18
2.4 Degree of cross-linking	19
2.5 The function of ion exchange resin	20
2.5.1 Strong acid cation resin	20
2.5.2 The strong base anion resin	20
2.5.3 Weak acid cation resin	21
2.5.4 Weak base anion resin	22
2.6 Structure of resin	23
2.6.1 Gel	23
2.6.2 Macroporous	24
2.7 Resin stability	24
3 ION EXCHANGE AS A PROCESS	26
3.1 Ion exchange cycle	26
3.1.1 Backwash	26
3.1.2 Regeneration	27
3.1.3 Rinsing	29
3.1.4 Exhaustion	30
3.2 Expansion of a resin bead	30
3.3 Regeneration efficiency	32
3.4 Regenerant recycle	33
3.5 Regeneration chemicals	34

3.6 Cross and power regeneration	34
3.7 Optimization potential	35
3.8 Design of an ion exchange process	35
4 ION EXCHANGE STUDIES	36
4.1 Materials and methods	36
4.2 Regenerant recycle in co-flow regeneration	38
4.2.1 Results	38
4.2.2 Discussion	44
4.3 Regenerant recycle in reverse flow regeneration	45
4.3.1 Results	45
4.3.2 Discussion	50
4.4 SAC resin regenerant reduction	51
4.4.1 Results	51
4.4.2 Discussion	53
4.5 Rinsing in SAC regeneration	53
4.5.1 Results	53
4.5.2 Discussion	54
5 CONCLUSION	55
REFERENCES	58

APPENDICES

Appendix 1. Inorganic analysis of the outflow after co-flow regeneration.
Appendix 2. Inorganic analysis of the outflow after reverse flow regeneration.

FIGURES

Figure 1. Steps of ion exchange (Harland, 1994, p. 136).	9
Figure 2. A fictional membrane in ion exchange resin (SenGupta, 2017, p. 86).	15
Figure 3. Formation of strong acid cation resin (Harland, 1994, p. 26).	17
Figure 4. Formation of weak acid cation resin (Harland p.28).	17
Figure 5. Formation of styrenic anion exchange resin (Harland, 1994, p. 29).	18
Figure 6. Formation of acrylic anion exchange resin (Harland, 1994, p. 31).	19

Figure 7. Hoffman degradation of strong base anion exchange resin. (SenGupta, 2017, p. 113).	25
Figure 8. Co-flow and reverse flow regeneration (Harland, 1994, p. 176).	29
Figure 9. Regenerant recycle (Nachod & Schubert, 2013, p. 38).	33

EQUATIONS

Equation 1. Fick's first law of diffusion (Harland, 1994, p. 136).	9
Equation 2. Zero net charge (Harland, 1994, p. 137).	10
Equation 3. Electroneutrality (Harland, 1994, p. 137).	10
Equation 4. Fick's first law applied in particle diffusion (Harland, 1994, p. 137).	10
Equation 5. Ion exchange reaction (Harland, 1994, p. 105).	11
Equation 6. Separation factor (Harland, 1994, p. 106).	11
Equation 7. Selectivity coefficient (Harland, 1994, p. 106).	12
Equation 8. Relation of selectivity coefficient and separation factor in univalent ion exchange (Harland, 1994, p. 107).	12
Equation 9. Relation of selectivity coefficient and separation factor in multivalent ion exchange (Harland, 1994, p. 107).	12
Equation 10. Effect of concentration on multivalent ion exchange (SenGupta, 2017, p. 63).	13
Equation 11. Ion exchange reaction of strong acid cation resin (Harland, 1994, p. 51).	20
Equation 12. Ion exchange reaction of strong base anion resin (Harland, 1994, p. 51).	21
Equation 13. Reverse ion exchange of weak acid cation resin (Harland, 1994, p. 54).	21
Equation 14. Neutralization of weak acid cation resin (Harland, 1994, p. 54).	21
Equation 15. Ion exchange of weak acid cation resin (Harland, 1994, p. 54).	21
Equation 16. Hydration of weak base anion resin (Harland, 1994, p. 55).	22
Equation 17. Reverse ion exchange of weak base anion resin (Harland, 1994, p. 55).	22
Equation 18. Neutralization of weak base anion resin (Harland, 1994, p. 55).	22
Equation 19. Ion exchange of weak base anion resin (Harland, 1994, p. 55).	22
Equation 20. Ion exchange of weak base anion resin in free base form (Harland, 1994, p. 56).	23
Equation 21. Regeneration of weak base anion resin to its' free base form (Harland, 1994, p. 56).	23
Equation 22. Regeneration of resin (Harland, 1994, p. 174).	28
Equation 23. Ion leakage during the exhaustion phase (Harland, 1994, p. 175).	28
Equation 24. Exhaustion phase (Harland, 1994, p. 168).	30
Equation 25. Regeneration efficiency (Harland, 1994, p. 170).	32
Equation 26. The volume of the exhaustion phase (Harland, 1994, p. 172).	33

CHARTS

Chart 1. Co-flow regenerated ion exchange line during exhaustion (part 1).	39
Chart 2. Co-flow regenerated ion exchange line during exhaustion (part 2).	39
Chart 3. Cations during the exhaustion of co-flow regenerated resin.	41

Chart 4. Organic acids during the exhaustion of co-flow regenerated resin (recycled regenerant).	43
Chart 5. Organic acids during the exhaustion of co-flow regenerated resin (fresh regenerant).	44
Chart 6. Reverse flow regenerated ion exchange line during exhaustion (part 1).	45
Chart 7. Reverse flow regenerated ion exchange line during exhaustion (part 2).	46
Chart 8. Cations during the exhaustion of reverse flow regenerated resin.	46
Chart 9. Organic acids during the exhaustion of reverse flow regenerated resin (recycled regenerant).	48
Chart 10. Organic acids during the exhaustion of reverse flow regenerated resin (fresh regenerant).	49
Chart 11. The exhaustion of SAC resin regenerated with 3 and 4 BV of 5 w-% H ₂ SO ₄ (part 1).	52
Chart 12. The exhaustion of the ion exchange line where SAC resin was regenerated with 3 and 4 BV of 5 w-% H ₂ SO ₄ (part 2).	52

TABLES

Table 1. Analysis of the ion exchange feed.	36
Table 2. The cations of the ion exchange feed.	36
Table 3. The anions and organic acids of the feed.	37
Table 4. Regeneration capacities of the regenerants.	37
Table 5. Resins used in ion exchange study (Dow, 2006; Dow 2017.)	37
Table 6. Anions during the exhaustion of co-flow regenerated resin.	42
Table 7. Anions during the exhaustion of reverse flow regenerated resin.	47
Table 8. Exhausted strong acid cation resin.	49
Table 9. The regeneration efficiency of strong acid cation resin.	50
Table 10. The outflow during strong acid cation resin regeneration.	54

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation	Explanation of abbreviation (Source)
α_A^B	Separation factor between ions A and B (Harland, 1994, p. 106.)
BV	Unit of volume in proportion to used resin bed volume (Harland, 1994, p. 172.)
C_A	Concentration of ion A (Harland, 1994, p. 136.)
C_T	Total concentration (SenGupta, 2017, p. 63.)
D_A	Diffusion coefficient of A (Harland, 1994, p. 136.)
δ	Length of a film (Harland, 1994, p. 136.)
Eq/L	Unit of capacity, equivalent per liter
J_A	Flux of ion A (Harland, 1994, p. 136.)
K_A^B	Selectivity coefficient between ions A and B (Harland, 1994, p. 106.)
m_A	Molality of ion A (Harland, 1994, p. 106.)
Q	Ion exchange capacity (SenGupta, 2017, p. 63.)
R	Resin (Harland, 1994, p. 107.)
r_0	Resin bead radius (Harland, 1994, p. 137.)
SAC	Strong Acid Cation (Harland, 1994, p. 212.)
SBA	Strong Base Anion (Harland, 1994, p. 212.)
V	Volume (Harland, 1994, p. 172.)
WAC	Weak Acid Cation (Harland, 1994, p. 212.)
WBA	Weak Base Anion (Harland, 1994, p. 212.)

X_A	Ratio of ion A (Harland, 1994, p. 106.)
y_A	Fractional loading of ion A in the resin (SenGupta, 2017, p. 63.)
z_A	Electric charge of ion A (Harland, 1994, p. 137.)

1 INTRODUCTION

Ion exchange is a phenomenon where ions in aqueous solutions are replaced with a different counterion with an equal charge, which can be positive or negative. Ion exchange processes can be divided into four categories based on their primary purpose: purification and ion removal, recovery, metathesis, and separation (Harland, 1994, p. 166).

In purification and ion removal, the solution is purified from undesirable ions and impurities. Wastewater treatment and water purification are under this category. The purification is also used for analytical purposes to remove ions before the analysis. On the contrary, the product of a recovery process is the ions in the solution accumulated to the ion exchange resin. Ion exchange is used in the hydrometallurgy to recover ions from solutions. In metathesis, an ion is simply replaced by another ion with resin in specific ion form. In other words, the ions of a single electrolyte are substituted by another ion. Such a process is, for example, a softening process where calcium and magnesium ions are replaced with sodium ions. Ion exchange may also be used to separate ions. In the separation, ions are first attached to the resin and then eluted separately in order by their affinities. The separation method is called ion-exchange chromatography or ion chromatography (Bhattacharyya & Rohrer, 2012, p. 4). (Harland, 1994, p. 166.)

The ion exchange is rather old technology, and it was scientifically first discovered in 1850 by two chemists who studied the removal of ammonium ions by cation exchanging soil. Later, inorganic zeolites were used widely in the softening process. The zeolite-based ion exchanger lacked chemical stability and durability, which was achieved in 1935 when the first organic-based polymers for ion exchange purposes were found. By the year 1942, both strong and weak cation and anion exchange resins have been found. (Harland, 1994, p. 1–3.)

As ion exchange has been early discovered, much of the literature is old. In the 1960s was published the book “Ion Exchange” by Friedrich Helfferich (Helfferich, 1962) explaining the phenomenon and theory of ion exchange. Newer literature has been made on the ion exchange, but the theoretical foundation was already known in the 1960s. Another thorough and very practical book explaining the ion exchange phenomenon is “Ion exchange: Theory and practice” by C.E. Harland (Harland, 1994), published in 1994. The main source for the theory also included two other books, “Ion exchange technology”

by Nachod and Schubert (Nachod & Schubert, 2013) and “Ion exchange in environmental process” by SenGupta (SenGupta, 2017). Thus, newer literature was also used as the source material.

Ion exchange generates a great amount of wastewaters when regenerating the resin to proper ion form for the exhaustion phase. The regeneration efficiency of strong cation and anion exchange resin is low, leading to the usage of an excessive amount of regeneration chemicals. Ion exchange is a batch operation that consists of four steps: backwash, regeneration, rinsing, and exhaustion. During the exhaustion step, the raw material is treated in an ion exchange process. When performing the other steps, the production is stopped. This downtime should be minimized. Thus, it yields larger buffer tanks before and after the ion exchange line, greater volumes of resin required to meet the production capacity, and it may increase the need for multiple ion exchange lines to avoid bottlenecking of the production. The proportion of the downtime can also be decreased by increasing the length of the exhaustion step. The volume of treated solution in an ion exchange cycle can be increased by increasing the number of equivalents the ion exchange line can replace. This can be done by increasing the volume of the resin or increasing the operating capacity of the resin. The operating capacity is the difference between exhausted and regenerated resin expressed in equivalents per volume.

The research question in this thesis focuses on the efficiency of ion exchange resin regeneration. The efficiency of regeneration varies between different resin types. Firstly, it needs to be determined which resin should be studied. The source material provides the answer for the determination and methods to improve the regeneration efficiency. The given methods need to be verified to determine whether they are viable options to improve the regeneration efficiency. The study includes performing ion exchange cycles and analyzing the outflow of exhaustion. The analyses contain pH, conductivity, concentration, color content, cations, anions and organic acids. The resin should also be analyzed to compare different regeneration methods. The resin analysis includes the determination of the ion form and resin capacity.

Other aspects related to poor regeneration efficiency, such as the amount of wastewater and the regeneration chemical consumption, should also be evaluated. The impact on the ion exchange product quality is a vital factor due to that is the whole purpose of the process – to produce purified ion exchange product. Ion exchange is usually only one step of a larger production. A viable method to improve the regeneration efficiency should

not decrease the capacity of an ion-exchange process leading to bottlenecking the larger production.

This thesis focuses on understanding the phenomenon of ion exchange. It explains the principle of ion exchange, the type of ion exchange resins available, and how they are formed. The difference between each type of ion exchange resin is explained and how they function. In the following chapter, the ion exchange process is explained, including each step. The regeneration efficiency and optimization potentials are covered in the own chapter and the basic information regarding the designing an ion exchange process. In the last chapter, before the conclusion, ideas from the theory are tested. The regeneration of strong cation and anion exchange resin is less efficient than weak cation and weak anion exchange resin. Often strong acid cation exchange resin is paired with weak base anion resin. Thus, the optimization potential is evaluated with strong cation exchange resin. The findings may also be implemented to strong base anion exchange resin due to the low regeneration efficiency of strong base anion resin.

2 ION EXCHANGE THEORY

In ion exchange, several smaller events occur, and the slowest step determines the overall rate. Figure 1 demonstrates three steps occurring in ion exchange: a film diffusion, a particle diffusion, and a chemical reaction. (Harland, 1994, p. 136.)

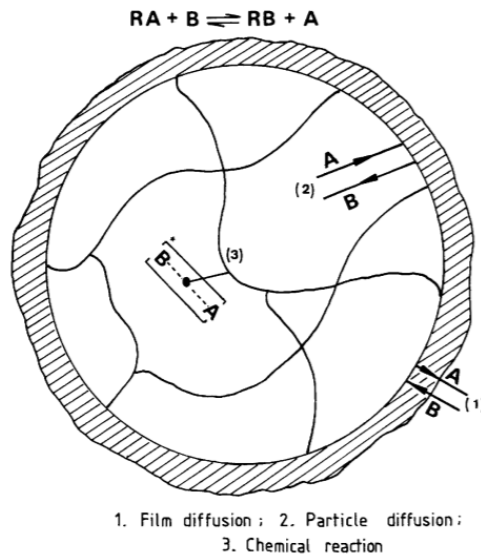


Figure 1. Steps of ion exchange (Harland, 1994, p. 136).

First, there is the diffusion of an ion through a stagnant solution or film. Even though a solution to be ion exchanged is fed to the resin fast, a stagnant liquid layer surrounds a resin bead. The mass needs to be transferred by diffusion through this layer to reach the solid resin particle. Equal diffusion of a counterion to the opposite direction is needed to preserve electroneutrality. Therefore, this film diffusion can be considered as a coupled mass transfer. Fick's first law applies to this diffusion expressed in equation 1. (Harland, 1994, p. 136.)

$$J_A = \frac{D_A \Delta C_A}{\delta}$$

Equation 1. Fick's first law of diffusion (Harland, 1994, p. 136).

In equation 1, the Fick's first law of diffusion describes the flux (J_A) of ions A^{z_A} ($\text{kmol m}^{-2} \text{s}^{-1}$) where z_A is the ionic charge of ion A. The diffusion occurs through a film δ (m) by a concentration difference ΔC_A (kmol m^{-3}), which acts as a driving force. D_A is a diffusion

coefficient of ion A^{z_A} ($\text{m}^2 \text{s}^{-1}$). As stated previously, electroneutrality is required, and therefore there is an opposite flux of ion B^{z_B} where z_B is the ionic charge of ion B. (Harland, 1994, p. 136.)

$$z_A J_A + z_B J_B = 0$$

Equation 2. Zero net charge (Harland, 1994, p. 137).

Where z_A and z_B are the ionic charges of ions A and B, and C is the total concentration (kmol m^{-3}). (Harland, 1994, p. 136-137.)

$$z_A C_A + z_B C_B = C$$

Equation 3. Electroneutrality (Harland, 1994, p. 137).

A continuation for ion A is to diffuse through a resin bead, which is called the particle diffusion. The mass transfers from the resin-solution interface through the interior of resin by the driving force of concentration difference in the resin bead radius r_0 (m). \bar{D}_A signifies an average diffusion coefficient of A in the resin bead, which is significantly smaller than typically in solution due to a solid copolymer matrix causing resistance for the mass transfer. (Harland, 1994, p. 137.)

$$\bar{J}_A = \frac{\bar{D}_A \Delta \bar{C}_A}{r_0}$$

Equation 4. Fick's first law applied in particle diffusion (Harland, 1994, p. 137).

The third event affecting the ion exchange rate is the chemical reaction occurring within the resin bead. The reaction occurs at the functional groups of the resin where ion A and B breaks and forms ionic, covalent or dative bond. The chemical reaction is not the slowest step in ion exchange as a simple reaction of aqueous ions is fast and, therefore, not the controlling event. The reactions can be neutralization of a strong functional group, association-dissociation of a weakly functional group, or complex formation with a co-ion. (Harland, 1994, p. 138–139.)

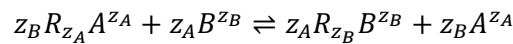
It has not solely been demonstrated what the slowest step in ion exchange controlling the actual rate is. There is only minor resistance for mass transfer in the solution-resin

interface for a clean resin, which is negligible. The resistance starts affecting the ion exchange rate when the resin fouling increases. (Harland, 1994, p. 141.)

2.1 The principle of ion exchange

The ion exchange resin uptakes aqueous ions from the solution to its solid structure and releases ions from its structure back to the solution. This exchange occurs towards the preferred equilibria of the resin. The relative affinity describes the preferred ion for the resin (Harland, 1994, p. 104). The relative affinity of the resin is usually greater towards a higher electrovalence of an ion, which applies to all cation and anion resins.

The ion exchange equilibrium can be described as in equation 5. The reaction is between ions A^{z_A} and B^{z_B} where z is the ionic charge, and R represents the resin with fixed ion (Harland, 1994, p. 106).



Equation 5. Ion exchange reaction (Harland, 1994, p. 105).

Equation 5 states that a divalent ion takes the place of two monovalent ions in the resin. To further open the equilibrium of two ions in resin, it can be expressed by a separation factor of α_A^B where concentrations of ions A^{z_A} and B^{z_B} in resin and solution are expressed in variables of molal (m), molar (C), and rational (X) (Helfferich, 1962, p. 153). For example, concentration in the resin structure is \bar{C} and in solution, it is C . The separation factor describes the preference of resin between two ions. The separation factor is dimensionless. Therefore, the concentration unit does not have an impact on the separation factor.

$$\alpha_A^B = \frac{\bar{m}_B m_A}{\bar{m}_A m_B} = \frac{\bar{C}_B C_A}{\bar{C}_A C_B} = \frac{\bar{X}_B X_A}{\bar{X}_A X_B}$$

Equation 6. Separation factor (Harland, 1994, p. 106).

If the separation factor α_A^B is higher than unity, the resin is favorable to ion B^{z_B} . When it is lower than unity, the resin is favorable to ion A^{z_A} . The same equilibrium can also be written as selectivity coefficient K_A^B which is expressed in the same variable as in

equation 7. The selectivity coefficient describes the ion exchange equilibrium (Helfferrich, 1962, p. 153.)

$$K_A^B = \frac{\bar{m}_B^{z_A} m_A^{z_B}}{\bar{m}_A^{z_B} m_B^{z_A}} = \frac{\bar{C}_B^{z_A} C_A^{z_B}}{\bar{C}_A^{z_B} C_B^{z_A}} = \frac{\bar{X}_B^{z_A} X_A^{z_B}}{\bar{X}_A^{z_B} X_B^{z_A}}$$

Equation 7. Selectivity coefficient (Harland, 1994, p. 106).

Selectivity coefficient expressed in any variables equals the same, and the relationship to separation factor can be expressed as following when exchanging ions of equal valency (Harland, 1994, p. 107).

$$K_{Am}^B = K_{Ac}^B = K_{Ax}^B = (\alpha_A^B)^{z_A}$$

Equation 8. Relation of selectivity coefficient and separation factor in univalent ion exchange (Harland, 1994, p. 107).

The previous equation expressed the relation between the selectivity coefficient and separation factor in univalent exchange. The equation 9 shows the relation of selectivity coefficient, and separation factor in a heterovalent exchange where z_B is higher than z_A and the equilibrium in the resin is favorable to ion B^{z_B} . In such equilibrium, the concentration of ion B^{z_B} is higher in resin than in external solution. (Harland, 1994, p. 107.)

$$(\alpha_A^B)^{z_B} = K_{Am}^B \left(\frac{\bar{m}_B}{m_B} \right)^{z_B - z_A} = K_{Ac}^B \left(\frac{\bar{C}_B}{C_B} \right)^{z_B - z_A} = K_{Ax}^B \left(\frac{\bar{X}_B}{X_B} \right)^{z_B - z_A}$$

Equation 9. Relation of selectivity coefficient and separation factor in multivalent ion exchange (Harland, 1994, p. 107).

Where z_B is higher than z_A , and the ion B concentration is higher in the resin than in the external solution. To change the equilibrium to more favorable to the ion with lower valency, the concentration in the external solution needs to be high. Equation 9 illustrates the importance of concentration when regenerating resin from multivalent ion form with monovalent regenerant such as hydrogen ion. The ionic valency has an impact on the ion exchange equilibrium of the resin. This is called electroselectivity (Helfferrich, 1962, p. 156). A general rule can be formed that the resin prefers ions with higher ionic valences, and the preference is increasing in a lower concentration (Helfferrich, 1962, p. 157). This can be explained with the Donnan potential, which is proportional to the

valences of the ions, where the counterion with a higher charge is more favorable for the resin. (Harland, 1994, p. 107–108.)

2.1.1 The effect of concentration on the equilibrium

According to the Le Chatelier principle, by increasing the monovalent ion concentration, the equilibrium can be moved from divalent ion towards the monovalent ion (Nachod & Schubert, 2013, p. 60). This has a significant impact on the utilization of ion exchange resin in desalination or softening processes as resins usually are regenerated with a monovalent regenerant. Removal of divalent ion from resin with monovalent regenerant in dilute concentration is inefficient, which can be changed by increasing the regenerate concentration.

The effect of concentration on the equilibrium in a heterovalent ion exchange is explained in equation 10. The equilibrium is between monovalent ion A^+ and divalent ion B^{2+} where y_A is fractional loading of A in the resin, X_A is the ratio of A in the solution, C_T is total concentration, and Q is ion exchange capacity.

$$K_{AC}^B = \frac{y_B X_A^2}{y_A^2 X_B} \times \frac{C_T}{Q} = \frac{\frac{y_B}{(1-y_B)^2}}{\frac{X_B}{(1-X_B)^2}} \times \frac{C_T}{Q}$$

Equation 10. Effect of concentration on multivalent ion exchange (SenGupta, 2017, p. 63).

The equilibrium changes to more favorable to monovalent ion when a total concentration in the solution increases. The separation factor α_A^B must decrease as the total capacity of resin and selectivity coefficient are constant, meaning the equilibrium is less favorable for ions with higher valences. The same idea can be considered as the total concentration is constant. When using resin with a higher total capacity, ion exchange is preferable to ions with higher valences. (SenGupta, 2017, p. 63–64.)

The same effect can be described when regenerating resin. The relative affinity of hydrogen ion for strong acid cation resin is low (Harland, 1994, p. 105). Resin prefers ions that are caught during the exhaustion phase, and the regeneration phase is towards the unfavorable ion form. Therefore, to change the separation factor to favor monovalent ion, a high concentration needs to be used. This also applies to strong base anion resin

but not for weak acid cation or weak base anions resins, which has the highest relative affinity in hydrogen and free base form.

2.1.2 The effect of the degree of cross-linking to equilibrium

The resin in its hydrated form contains water, which is often called a solvent. The water within the resin tries to even the concentration gradient caused by osmotic pressure. The water inside the resin structure causes swelling, controlled by divinylbenzene cross-linking in the copolymer matrix. A higher degree of cross-linking makes the resin structure stronger, and less swelling occurs. It can also be explained as a higher degree of cross-linking causes a higher elastic force in resin, which is a counter-force for osmotic force trying to expand the resin (SenGupta, 2017, p. 52). Hydrated resin swell due to there is water inside the resin structure. This elastic structure caused by cross-linking tends to relax and to do so, the resin can exchange the counterion to a smaller one or an ion with higher valency. Resin prefers a smaller equivalent volume. The preference increases even more when resin cross-linking increases. The selectivity coefficient is higher for ions with higher valences and a smaller radius. (Helfferich, 1962, p. 158.)

The degree of cross-linking determines the elasticity of the resin. Low percent of divinylbenzene cross-linking causes high expansion for the resin when ion form or external concentration changes. In time, this causes the resin to degrade into fragments, which decreases the service life of the resin. Low cross-linking increases the kinetics of ion exchange (SenGupta, 2017, p. 52). Therefore, a balance in the degree of divinylbenzene cross-linking should be found to optimize the ion exchange process.

2.2 Donnan potential

One phenomenon affecting ion exchange equilibrium is called the Donnan effect, which describes the sorption of ionic electrolytes through the solution-resin interface. The phenomenon can be illustrated by a cation exchanger introduced in a dilute solution of electrolytes. There is a concentration difference of cations and anion between the resin-solution interface meaning a high concentration of cations in the resin phase and a high concentration of anions in the solution phase. Diffusion would normally level out the concentration difference. Anions diffuse to the resin phase and cations to the solution phase creating a potential difference called the Donnan potential. The potential moves

positively charged cations back to negatively charged resin and negatively charged anion to the positively charged solution. Due to the formed Donnan potential, anions cannot diffuse from solution through a resin-solution interface to a solid resin. The inability for anions to diffuse through the resin-solution interface is presented in figure 2 as a fictitious semi-permeable membrane. A balance is formed where the drive of concentration difference to level out is in equilibrium with the electric field between interface. The Donnan potential prevents co-ion concentration from increasing above the equilibrium, which is usually smaller than the external solution concentration. Thus, making the external electrolyte partially excluded. (Helfferich, 1962, p. 134–135.)

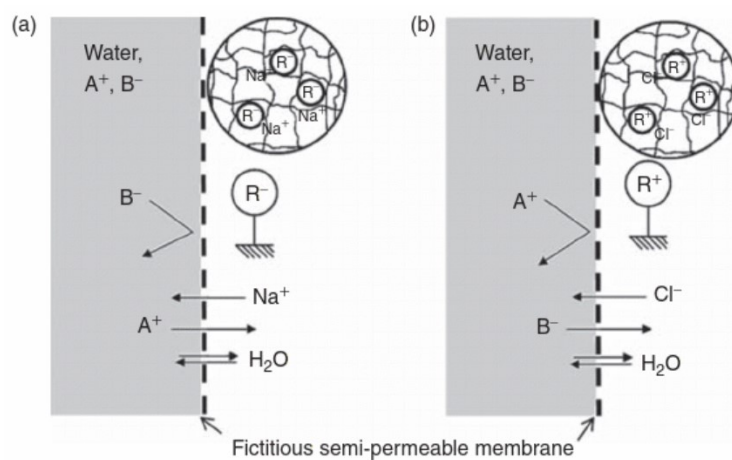


Figure 2. A fictional membrane in ion exchange resin (SenGupta, 2017, p. 86).

The Donnan potential depends on the concentration of the external solution and the ionic valences. There is formed an equilibrium between the potential and the tendency of a counterion to diffuse through the resin-solution interface. The electrolyte exclusion increases when the Donnan potential increases, and the potential increases with the increasing concentration of the external solution. The equilibrium can also be described between the exclusion of the electrolyte by the Donnan potential and the tendency of counterions to diffuse out of resin. Other aspects that impact the Donnan potential are the ion exchange capacity and the cross-linking of the resin. The co-ions are more excluded by the Donnan potential when the concentration difference between the resin and solution is high, meaning the internal concentration of the resin is higher than the external concentration of the solution. Therefore, the high ion exchange capacity of the resin increases the Donnan potential and co-ion exclusion. Resin swells in dilute electrolyte solution due to the difference in osmotic pressures. During swelling, the volumetric capacity (eq/L) decreases, allowing more electrolyte sorption. A high degree

of cross-linking increases the Donnan potential when the resin in a dilute solution cannot swell, keeping the concentration difference between resin and solution high. As does the increasing dilution of external solution. (Harland, 1994, p. 101–102; Helfferich, 1962, p. 136.)

In multivalent ion exchange, the Donnan potential increases when a co-ion valency increases excluding more multivalent co-ions than monovalent co-ions. The tendency of a counterion diffusion from the resin to solution is smaller when the counterion has a higher valency. The Donnan potential and the tendency of counterion diffusion are in equilibrium resulting in a lower Donnan potential, which yields to lower exclusion. On the other hand, when co-ion has a higher valency, the Donnan effect excludes electrolyte more efficiently. For example, a strong cation exchanger excludes more Na_2SO_4 than NaCl because the co-ion SO_4^{2-} has a high valency, and NaCl is more excluded than CaCl_2 because of the counterion (Ca^{2+}) has a high valency. (Harland, 1994, p.102; Helfferich, 1962, p. 136.)

2.3 Ion exchange resin

2.3.1 Strong acid cation resin

Strong acid cation exchange resin is made by polymerizing styrene with divinylbenzene. The amount of divinylbenzene determines the degree of cross-linking in the resin. Polystyrene would form a linear polymer in the polymerization reaction, but when divinylbenzene is copolymerized with styrene, the polymers are cross-linked to other polymers forming a three-dimensional structure (Harland, 1994, p. 26). The resin is then treated with a solvent such as ethylene dichloride. During the solvent treatment, the resin swells. The resin is then treated with sulfuric acid at elevated temperature (80 °C), resulting in a sulfonated cross-linked polystyrene resin. Even though the resin is insoluble, the three-dimensional structure allows water to flow through a resin bead. (Rousseau, 1987, p. 697.)

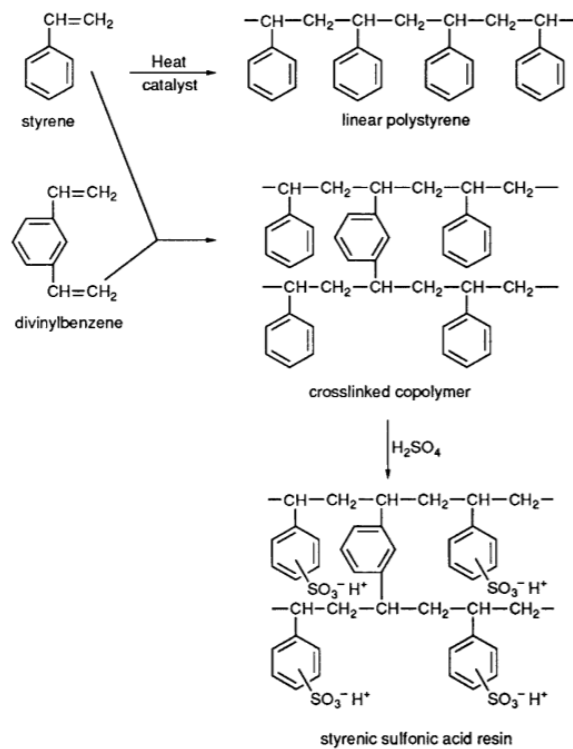


Figure 3. Formation of strong acid cation resin (Harland, 1994, p. 26).

2.3.2 Weak acid cation resin

The weak acid cation resin is made by copolymerizing methacrylic or acrylic acid and divinylbenzene (Rousseau, 1987, p. 697). Methacrylic and acrylic acid contains carboxylic acid, which is the functional group in weak acid cation resin. Other compounds, such as acrylonitrile or acrylic ester, can substitute methacrylic acid in copolymerization with divinylbenzene. In this case, the resin needs to go through acid hydrolysis to form the resin's functional group. (Harland, 1994, p. 27.)

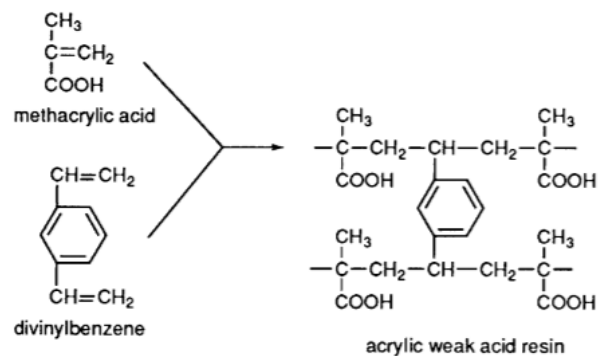


Figure 4. Formation of weak acid cation resin (Harland p.28).

2.3.3 The strong and weak base anion resin

Styrenic resin

Styrenic anion exchange resin is made by copolymerizing styrene with divinylbenzene as described information of styrenic cation exchanger. The formed copolymer will go through two steps. At first, the copolymer reacts with chloromethyl methyl ether introducing a chloromethyl group to a benzene ring. The reaction is sensitive to avoid secondary cross-linking through the methylene group. After this point, any amine group can be attached to the chloromethyl group. The second step is amination, where the type of amine impacts which type of base anion resin is formed. Trimethylamine forms a quaternary benzytrimethylammonium chloride group, which is a Type I strong base anion resin. Dimethylethanolamine forms Type II strong base anion resin, which has a quaternary benzydimethylethanolammonium chloride as the functional group. If methylamine or dimethylamine is used in a similar reaction, weak base anion resin is formed. (Harland, 1994, p. 29–30.)

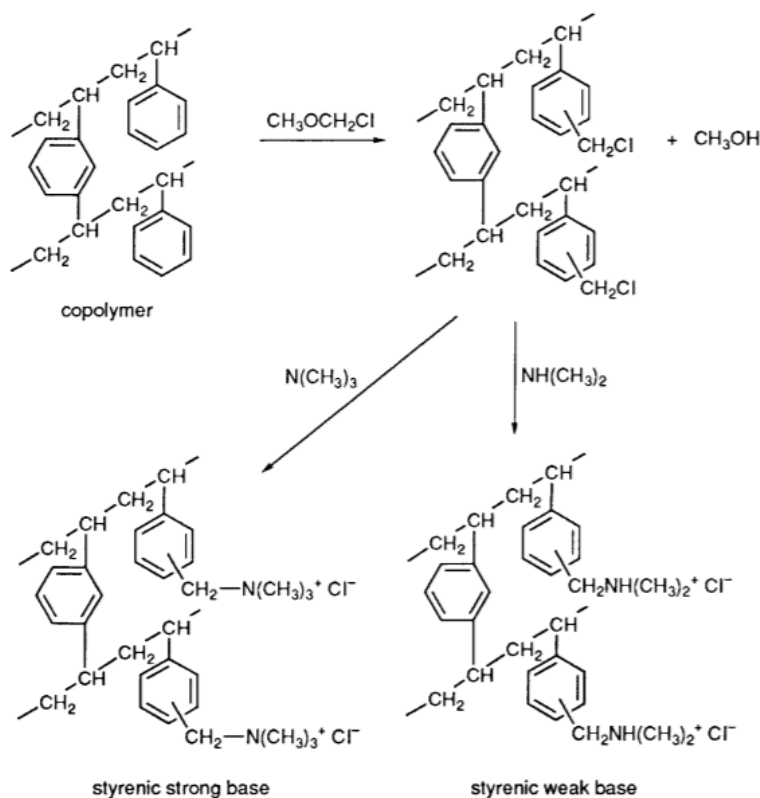


Figure 5. Formation of styrenic anion exchange resin (Harland, 1994, p. 29).

Acrylic resin

Methyl acrylate is copolymerized with divinylbenzene. The copolymer is then aminated with dimethyl aminopropylamine (DMAPA), resulting in a weak base functionality by a tertiary amine functional group. The acrylic weak base anion resin can go through quaternization where methyl chloride converts weak base resin to strong base resin with a quaternary ammonium chloride group. (Harland, 1994, p. 30.)

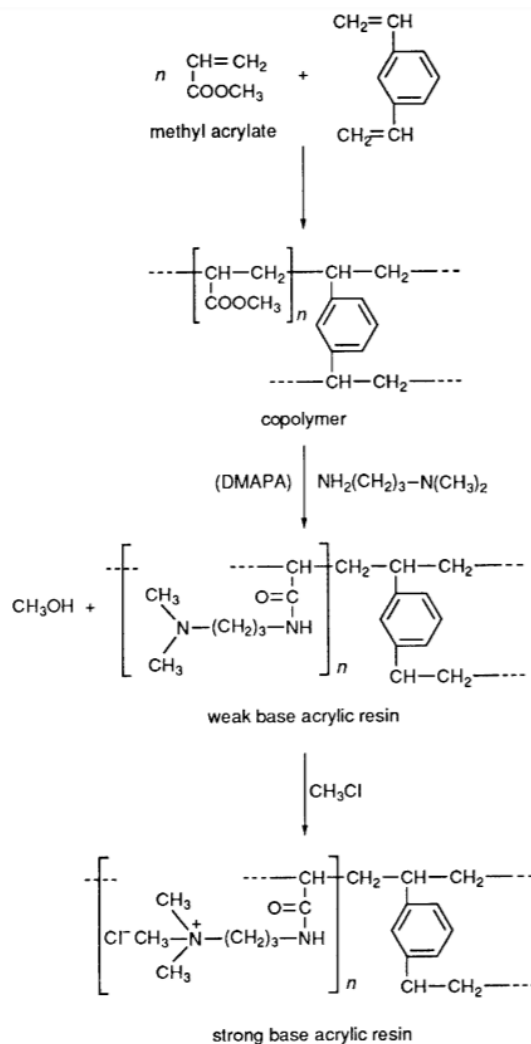


Figure 6. Formation of acrylic anion exchange resin (Harland, 1994, p. 31).

2.4 Degree of cross-linking

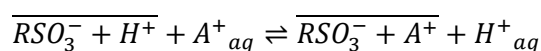
Resin is made by copolymerizing divinylbenzene with styrene or acrylic, where the degree of cross-linking means the number of divinyl-benzene in the copolymer matrix.

The degree of cross-linking is normally 8-12 %, and it determines the hardness of the resin structure. When the amount is low, the resin is softer, and the size changes more depending on the ion form and the osmotic pressure of the external solution. For example, when the resin is immersed in a dilute salt solution, the difference in osmotic pressure causes the resin to swell. The osmotic pressure inside resin is greater than outside. The resin with a lower degree of cross-linking, in this case, swells more. There is more external solution inside the resin, decreasing the difference in osmotic pressure. The same phenomenon occurs when the resin is immersed in a concentrated salt solution during resin regeneration. In this case, resin shrinks when trying to decrease the difference in osmotic pressure. (Kargel et al., 1973, p. 339; SenGupta, 2017, p. 90.)

2.5 The function of ion exchange resin

2.5.1 Strong acid cation resin

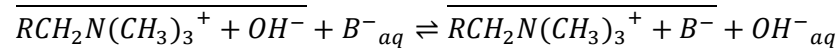
Strong acid cation resin, also known as SAC in acid form, contains hydrogen ion. When in contact with other cations, the resin exchanges its hydrogen ions to other cations. The released hydrogen ions can also reverse exchange back to the resin. The functional group of strong acid cation resin can dissociate completely at any pH. The dissociation of hydrogen ion occurs only when the resin is hydrated, and there are other counterions present in the solution. A strong acid cation resin requires strong acid to regenerate resin back to the acid form. In equation 11, $\overline{RSO_3^-}$ represents a copolymer matrix with a functional group. (Harland, 1994, p. 50.)



Equation 11. Ion exchange reaction of strong acid cation resin (Harland, 1994, p. 51).

2.5.2 The strong base anion resin

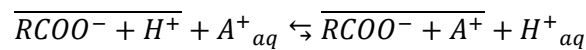
A strong base anion resin, also known as SBA in base form, contains hydroxide ion. The quaternary ammonium group of the strong base anion resin dissociates hydroxide completely when a counter anion is present in a hydrated environment. Strong base anion resin requires a strong base to regenerate the resin back to a base form. (Harald, 1994, p. 50.)



Equation 12. Ion exchange reaction of strong base anion resin (Harland, 1994, p. 51).

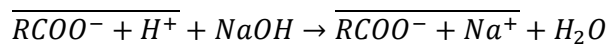
2.5.3 Weak acid cation resin

Differencing from strong acid cation resin, the dissociation of weak acid cation resin is not complete. The functional group of the resin, which is methacrylic or carboxylic acid, is favorable to hydrogen form. In other words, during an ion exchange of neutral solution, weak acid cation resin will reverse exchange a released hydrogen ion back to the resin. Therefore, the weak acid cation resin in acid form can be used to ion exchange alkaline solutions, neutralizing the hydrogen ion, and the reverse ion exchange cannot occur. (Harland, 1994, p. 53.)



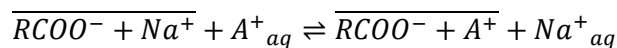
Equation 13. Reverse ion exchange of weak acid cation resin (Harland, 1994, p. 54).

The weak acid cation resin has a high tendency to H⁺ form. An ion A⁺ can replace H⁺ in the resin momentarily, and then it is replaced by the free H⁺ ion. (Harland, 1994, p. 54.)



Equation 14. Neutralization of weak acid cation resin (Harland, 1994, p. 54).

A neutralization is required for sodium to replace the H⁺ in the resin. After neutralization, the resin stays in Na⁺ form. (Harland, 1994, p. 54.)

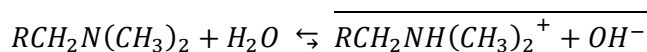


Equation 15. Ion exchange of weak acid cation resin (Harland, 1994, p. 54).

Ion exchange of neutral solution is possible with weak acid cation resin in process, for example, in a softening (Harland, 1994, p. 191).

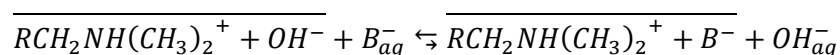
2.5.4 Weak base anion resin

A tertiary weak base anion resin ($RCH_2N(CH_3)_2$ or $RN(CH_3)_2$) remains in free base form when it is anhydrous. There is not clear dissociation path in the functional group of weak base anion resin as strong base anion resin has. The dissociation can be explained with the Lewis Theory of acid and base. In the hydration of the weak base anion resin, the amine protonation causes the lone pair of electrons of the nitrogen to form a bond with hydrogen ion of the water, and the resin forms ionized hydroxide form. The behavior of weak base anion resin can be expressed as the following. Even though it is not fully right, the expressed way is illustrative. (Harald, 1994, p. 54–55.)



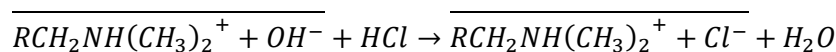
Equation 16. Hydration of weak base anion resin (Harland, 1994, p. 55).

The dissociation is weak, and any significant concentration of hydroxide converts the hydroxide form of weak base anion resin to an undissociated free base form. The ion exchange of neutral solution with weak base anion resin is unfeasible due to free hydroxide ion reverse ion exchange back to the resin. (Harald, 1994, p. 55.)

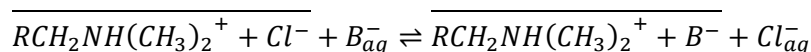


Equation 17. Reverse ion exchange of weak base anion resin (Harland, 1994, p. 55).

The neutralization of free hydroxide ion is the only way weak base anion resin can be utilized in the hydroxide form. The weak base anion resin can be used to exchange anions when it is in salt form. The pH should be low to maintain the protonated form of the amine nitrate atom. (Harald, 1994, p. 55.)

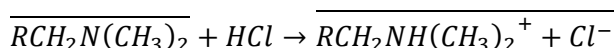


Equation 18. Neutralization of weak base anion resin (Harland, 1994, p. 55).



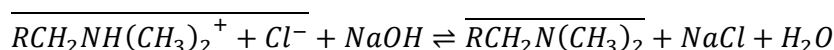
Equation 19. Ion exchange of weak base anion resin (Harland, 1994, p. 55).

The behavior of weak base anion resin is correctly expressed in equation 20. When a weak base anion in free base form is in contact with acid, the hydrogen ion protonates the resin. The weak base anion resin does not have a hydroxide form. The regenerated form is the free base form of the resin, which can remove anions only if the environment is acidic. (Harald, 1994, p. 55.)



Equation 20. Ion exchange of weak base anion resin in free base form (Harland, 1994, p. 56).

The weak base anion resin is regenerated with sodium hydroxide, where hydroxide ion neutralizes the hydrogen ion resulting in water and releasing chlorine from the resin. (Harland, 1994, p. 56.)



Equation 21. Regeneration of weak base anion resin to its' free base form (Harland, 1994, p. 56).

2.6 Structure of resin

Diffusion inside the resin structure plays a significant role in the kinetics of ion exchange. Particle diffusion is often bottlenecking the ion exchange, where the slowest step determines the rate of ion exchange. The other steps, which are often faster, are film diffusion and ion exchange reaction. The resin structure determines the resistance for ions to travel to the functional group of the resin. The most common resin structures are gel-type and macroporous bead resin. (SenGupta, 2017, p. 242.)

2.6.1 Gel

Gel resin bead has a high capacity, and it can be considered as a cross-linked polyelectrolyte. The cost of the production of gel-type resin is low, and it is still widely used today. The isoporous or microporous structure of the resin is functional groups covalently attached to a matrix. Free water molecules may flow inside the resin structure due to osmosis, and it is needed to hold the resin structure open. In the absence of water, the structure of the gel resin will collapse. (SenGupta, 2017, p. 242.)

2.6.2 Macroporous

A macroporous resin bead is a cluster of microgels connected in a macroporous structure. The resin is produced by suspension polymerization, where microgels form microspheres in the resin structure. All the functional groups exist inside the microgels, and the macroporous structure forms paths in the resin bead. The macroporous particle size is between 0.2 and 1.0 mm when the microgel is smaller than 100 μm . The size of the pores inside the resin structure is between 10 and 100 μm . (SenGupta, 2017, p. 243.)

2.7 Resin stability

In time the cross-linking resin and functional groups decompose, causing resin fragmenting and reduced operating capacity. Strong oxidative agents such as nitric acid, peroxide, chlorate ions, chromic acid, and halogens should be avoided due to the decross-linking of resin. Nitric acid in high concentration should never be used with anion exchange resin due to the explosive reaction between nitric acid and resin. (SenGupta, 2017, p. 112-114.)

Both strong and weak cation exchange resins are rather chemically and thermally stable when considering the ion exchange capacity. The main contributors to their service life are mechanical stress caused by swelling and shrinking and fouling of the resin. Anion exchange resin is more sensitive to thermal degradation. The strong base anion resin, especially in hydroxide form, is the most unstable, and it should not be exposed to a long period to elevated temperature (60 °C). The quaternary ammonium group degrades from the strong base anion resins approximately from 5 % to 10 % annually. In hydroxide form, strong base anion resin will go through Hoffman degradation resulting in cleavage of one carbon-nitrogen bond to form methanol. When losing a methyl group, the functionality changes from the strong base into a weak base functional group. The functional group of weak base anion functions only in an acidic environment, which strong base anion cannot provide. (SenGupta, 2017, p. 113–114.)

It should be noted that the reaction can also split the whole amine group causing total loss of ion exchange capacity. The Hoffman degradation breaks the covalent bond splitting off the whole amine group resulting a tertiary amine. It should be also noted that

tertiary amine group can undergo the same Hoffman degradation. (SenGupta, 2017, p. 113–114.)

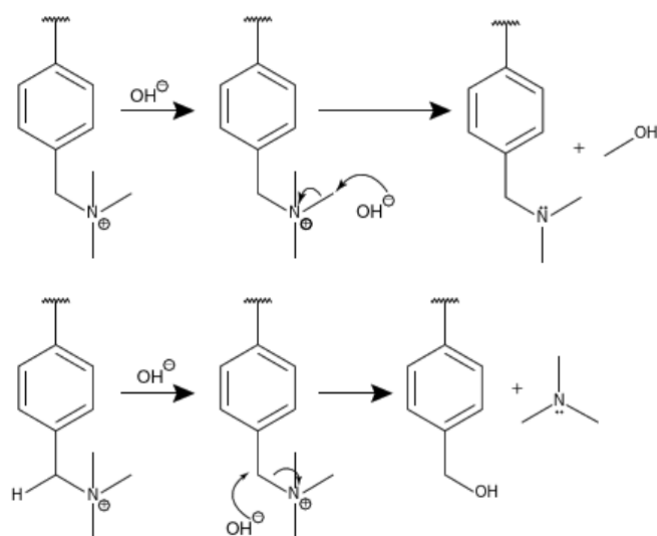


Figure 7. Hoffman degradation of strong base anion exchange resin. (SenGupta, 2017, p. 113).

The size expansion causes mechanical stress for the resin structure. Weak acid cation resin undergoes the greatest change in size. A rapid change in size causes an osmotic shock that yields premature resin fragmenting. This osmotic shock can be decreased by using a smaller concentration of regenerant or decreasing the flow rate during exhaustion and regeneration. The degree of cross-linking effects to the size expansion due to harder resin structure has a higher resistance to osmotic pressure. (SenGupta, 2017, p. 112–113.)

3 ION EXCHANGE AS A PROCESS

The most common way to perform ion exchange is to pack resin in columns. There are some processes where ion exchange resin is put into a tank with the solution to be treated. The solution is mixed with ion exchange resin and then filtrated to separate the resin from the solution. This is a rare type of ion exchange operation, and the subject is not covered in any more detail. As mentioned earlier, the ion exchange resin is normally packed in a column. The ion exchange process is operated in cycles. Each cycle consists of backwash, regeneration, rinsing, and exhaustion (Nachod & Schubert, 2013, p. 14).

3.1 Ion exchange cycle

3.1.1 Backwash

During backwashing, the ion exchange resin is washed upflow from the bottom of the column. The resin bed expands and resettles during the backwash. After backwash, the resin is more evenly distributed in the column, improving regeneration and the next exhaustion phase. Channeling is a phenomenon where solution flows certain paths through the resin bed, forming channels and causing inefficient exhaustions and regenerations due to the whole amount of resin is not utilized. (Harland, 1994, p. 168–169; Nachod & Schubert, 2013, p. 14.)

The resin bed act as a filter, so all solids introduced to resin, such as dirt and even formed precipitate, accumulate on resin, which can be removed in the backwash (Nachod & Schubert, 2013, p. 14). This reduces the pressure drop in the following loading phases. Not only precipitate formation decreases the flow rate, but it can also cause the resin to break and even harm internal components (Harland, 1994, p. 168).

The resin bead will break naturally in normal operation. These broken resin fragments can be removed during the backwash when carried to the top of the resin bed and removed by overflowing a small amount of resin (Harland, 1994, p. 169).

Lastly, the ions after the exhaustion phase are in layers in the resin. The ions which are easier to remove from the resin get replaced with the ions, which are harder to remove. Low-affinity ions are located at the bottom of the resin bed, and high-affinity ions are at

the top. Therefore, ions are distributed in sections which are mixed during the backwashing (Nachod & Schubert, 2013, p. 14).

In some cases, backwash is required before regeneration due to its purpose is to classify two different types of resin, for example, in a mixed bed column (Harland, 1994, p. 169). It may also be after regeneration or be left out completely if the distributions of ions are not wished to be changed before regeneration (Harland, 1994, p. 177). In this case, regeneration occurs in reverse flow.

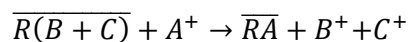
3.1.2 Regeneration

Cation exchange resins are regenerated with acid or salts, and anion exchange resins are regenerated with alkaline solutions. The strong exchange resins can only be regenerated with strong acids or bases. The regeneration of strong acid cation and strong base anion resin is inefficient and requires a large amount of chemicals above the equivalent number (SenGupta, 2017, p. 96). The regeneration of weak acid cation and weak base anion resin is more efficient than strong acid cation and strong base anion due to the high affinity of resin to the regenerated form (Harland, 1994, p. 105).

There are two ways to perform regeneration – co-flow and reverse flow (Harland, 1994, p. 174). In co-flow regeneration, the regenerant flows the same direction as during the exhaustion phase. In reverse flow regeneration, the regenerant flows the opposite direction than the solution during the exhaustion phase. Usually, the co-flow regeneration is performed from top to bottom or, in other words, downflow. Before regeneration, excess water on top of the column can be taken out. At the top of the resin bed, there is a higher number of ions to be removed by regeneration as the resin is more exhausted there. Also, the ions at the top of the resin bed have a higher affinity than the ion at the bottom of the resin bed (Harland, 1994, p. 175).

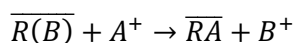
This can be illustrated with an example where A^+ is the ion in the regenerant. B^+ and C^+ are removable ions in the treated solution. B^+ has a lower affinity than C^+ . During the regeneration, the ions B^+ and C^+ are exchanged with A^+ . The co-flow regeneration can fully complete the regeneration at the top of the resin when there will be left B^+ ions left at the bottom of the resin after regeneration. When the next loading cycle is performed, the exchanged A^+ ion eluates B^+ ion at the bottom of the column, causing leakage of ions. The incomplete regeneration of the resin at the bottom of the column is more

common with co-flow regeneration than in reverse flow regeneration. R represents the resin. (Harland, 1994, p. 174–175.)



Equation 22. Regeneration of resin (Harland, 1994, p. 174).

The exhaustion phase causes leakage of ions B^+ at the bottom of the column. The exhaustion phase starts with leakage of ion B^+ . The leakage is only at the beginning of the cycle, and it decreases when B^+ ions are removed from the bottom of the resin bed. More constant outflow can be obtained if the resin bed is backwashed before loading (Nachod & Schubert, 2013, p. 18).



Equation 23. Ion leakage during the exhaustion phase (Harland, 1994, p. 175).

The other direction to regenerate is a reverse flow where the regenerant flows in the opposite direction than during the exhaustion phase. The regenerant is often introduced from the bottom of the column, where there is still partially regenerated resin and low-affinity ions, as described previously (B^+ ions). When the regenerant flows through the resin, A^+ ion releases B^+ ion, which flows through the upper part of the column where the resin is attached to C^+ ion. Due to lower affinity, B^+ does not impact the resin, and it flows out from the outlet at the top of the column. The ion C^+ is eluted from the resin by regenerant due to an excessive amount of A^+ ion. As described earlier, the resin containing ions with higher affinity is at the top of the resin bed. Therefore, before the ions are flowing out, the contact time is short, and displacement is more minor. (Harland, 1994, p. 176–177.)

The advantages of reverse flow regenerations are better regeneration efficiency and lower leaking of ions. The disadvantage is that the resin cannot be backwashed between the cycles because it disturbs the ionic distribution in the resin bed. When the resin needs to be backwashed higher amount of chemicals is needed to regenerate resin to ensure enough regeneration with low leakage during the next exhaustion phase. (Harland, 1994, p. 177.)

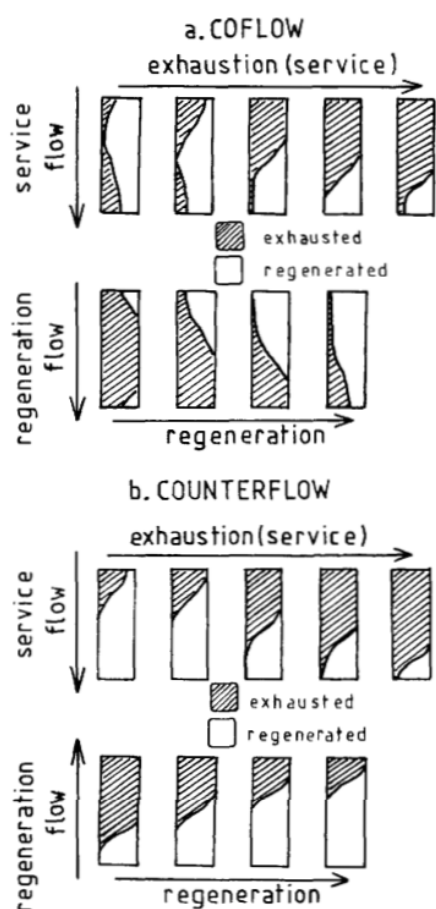


Figure 8. Co-flow and reverse flow regeneration (Harland, 1994, p. 176).

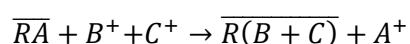
3.1.3 Rinsing

After the desired amount of regeneration chemical is used, the resin is rinsed clean from the regenerant. Regenerant removal by rinsing can be important since it may improve both product stability and quality. The first part is to displace resin from the regeneration chemical. During this phase, the same flow rate is used as in regeneration. When most of the regenerant is displaced, the flow rate is increased to reduce rinsing time. Only a minor improvement of the effluent quality is obtained in the final steps of rinsing. (Nachod & Schubert, 2013, p. 19.)

When the resin is washed enough, another backwash can be performed. The backwash is short, and it is performed only to avoid channeling and distributing residual ions in the resin bed evenly. (Nachod & Schubert, 2013, p. 18.)

3.1.4 Exhaustion

The feed contains ions B^+ and C^+ . The relative affinity is increasing from B^+ to C^+ , meaning that B^+ has a lower affinity, C^+ has a higher affinity. The feed is first introduced to the first ion exchange column. The outflow is going to waste until the concentration of the outflow starts increasing. Depending on the process, the dilute outflow can be collected as sweet water, which can be recycled back to the process or used to backwash the resin. If the product has a high value, extra dilution may be tolerated (Harland, 1994, p. 168). When the concentration is high enough, then the treated solution is collected in the product tank. The resin regenerated with A^+ is exchanging ions B^+ and C^+ with A^+ . (Harland, 1994, p. 173–175.)



Equation 24. Exhaustion phase (Harland, 1994, p. 168).

As B^+ has a lower affinity than C^+ , reverse exchange occurs. In the reverse exchange, ion C^+ displaces B^+ , which is already attached to the resin. Therefore, at the top of the resin bed, more ions with higher affinity are connected to the resin and the ions with the lowest affinity concentrate at the bottom of the resin. (Harland, 1994, p. 173–174.)

The solution is fed until the ion exchange resin is exhausted. This moment is when the resin cannot completely exchange ions present in the exhausting solution (B^+ and C^+), and B^+ with the lowest affinity starts leaking. The exhaustion can be seen in a change of outflow quality (Harland, 1994, p. 168). Typically, solution conductivity, pH or color level changes when resin gets exhausted. At this point, the solution is displaced with water. If the displacement cannot be accepted as a product, it can be fed back to the feed tank and treated in the next cycle or used as a sweetwater. The displacement is continued until the concentration is low enough. (Harland, 1994, p. 173–175.)

3.2 Expansion of a resin bead

Ion exchange resin has a high internal osmotic pressure, and it can be considered a cross-linked polyelectrolyte. The fixed ions of hydrated ion exchange resin are attached to the copolymer matrix and cannot diffuse out of the resin. The electroneutrality prevents diffusion of counterion even when there is a significant concentration difference. Water

can move inside the resin bead to decrease the osmotic pressure. The water moving into the resin bead dilutes the concentration causing the resin to swell. An equilibrium is formed between the osmotic pressure and so-called swelling pressure. The degree of cross-linking of the resin impacts the resin expansion. Lower cross-linking allows the resin to swell more, making the resin structure softer. (SenGupta, 2017, p. 51.)

The relative affinity of univalent ions is related to the swelling-shrinking of a resin. For strong acid cation resins, the relative affinity of monovalent ions is $K^+ > Na^+ > Li^+$ when resin sequence of swelling is to opposite direction $K^+ < Na^+ < Li^+$ (SenGupta, 2017, p. 53). The relative affinity with univalent ions has related the radius of the ion, which has an impact on the size expansion (SenGupta, 2017, p. 71).

The expansion can be explained in various situations. When the degree of cross-linking increases, the swelling decreases due to resin has a higher strength to resist the osmotic pressure. When ion exchange capacity increases, the swelling increases due to greater osmotic pressure. When the ionic concentration of the solution increases, the resin swelling decreases due to lower osmotic pressure difference between resin and solution. Resin size increases when the radius of the counterion increases. When a higher valency ion replaces counterion, the osmotic pressure decreases shrinking the resin. (SenGupta, 2017, p. 53.)

The change in resin size causes stress for the resin structure. A larger change increases the stress, which resin structure must tolerate. The stress causes the resin to break into fragments. Beyond a certain degree of cross-linking, the size expansion decreases significantly, causing less stress to the resin. The resin with a lower degree of cross-linking tends to have a lower service life. Different resin types have a varying change in size. For example, strong acid cation resin has a normally 1.5-2.0 eq/L capacity in hydrogen ion form when weak acid cation resin has above 4.0 eq/L capacity in hydrogen ion form. This means that weak acid cation resin will swell and shrink more when changing ion form. Lastly, a rate of swelling and shrinking is important when considering ion exchange resin. If the concentration of external solution changes too fast, meaning the concentration or flow rate is too high, the resin may break prematurely due to an osmotic shock. (Harland, 1994, p. 69.)

3.3 Regeneration efficiency

The regeneration efficiency is more related to strong acid and base resins, which have considerably lower regeneration efficiency than weak acid and base resins. During the exhaustion phase, the ion exchange is into a more favorable equilibrium. In other words, the regeneration reverse ion exchanges the resin towards the unfavorable equilibrium. This topic relates to the relative affinity of the resins. The favorable equilibrium of the resin is towards ion with the higher valency (Harland, 1994, p. 105). The same principle applies to weak acid and base resin except that the highest relative affinity is with H^+ or OH^- ions. A relatively high concentration of chemicals must be used in regeneration to overcome the preferred ion form of the resin. Equation 10 states that resin regeneration in multivalent ion form requires a higher concentration of monovalent regenerant to push the ion form of the resin to monovalent form. (Harland, 1994, p. 170.)

From the economic point of view, the resin is never regenerated to complete 100 % conversion. It is possible, but it would take an excessive amount of chemicals, and therefore it is uneconomical. Regeneration of strong functional resins is not an efficient process. The used amount of chemicals as equivalents does not equal the conversion of resin in equivalents. The terms regarding the capacity of the resin should be explained. Resin has a total capacity, which is the total equivalents of ions connected to the resin, which is expressed equivalent per liter of resin (eq/L). Resin has an operating capacity, which is the capacity of regenerated ion form before and after exhaustion, expressed as $\Delta eq/L$. The regeneration efficiency describes the relation of consumed regenerant and total amount of passed chemicals. (Harland, 1994, p. 170.)

The regeneration efficiency can be determined by the ratio of how much regenerant was consumed in the regeneration and how much of regenerant was used in the regeneration (Harland, 1994, p. 170). The regenerant consumption equals the operating capacity, which is a useful ion exchange capacity. Equation 25 illustrates regeneration efficiency.

$$\text{Regeneration efficiency} = 100 \times \frac{\text{Regenerant consumed (keq)}}{\text{Total regenerant used (keq)}}$$

Equation 25. Regeneration efficiency (Harland, 1994, p. 170).

A larger amount of solution treated with a relatively small amount of used chemicals reduces ion exchange treatment cost. In equation 26, V_R is the volume of the resin (L),

Q is the operating capacity of the resin (eq/L), and C_T is the total ion concentration in the feed (eq/L), and V_S is the volume of treated solution (L). (Harland, 1994, p. 172.)

$$V_S = \frac{V_R Q}{C_T}$$

Equation 26. The volume of the exhaustion phase (Harland, 1994, p. 172).

Higher the total concentration of ions in the feed equals a smaller amount of treated solution each exhaustion, and at the same time, higher operating capacity equals the opposite. If resin needs to be regenerated more frequently, the higher amount of chemicals is used, and the downtime is longer in the process. The ion exchange is normally operated in batch mode, and therefore downtime must be considered (Harland, 1994, p. 172). In a continuous process, multiple ion exchange lines can be used to ensure that there is one ion exchange line in operation all the time or to build up a large enough feed tank, which can collect enough material when the ion exchange line is not in operation.

3.4 Regenerant recycle

Due to the regeneration of strong functional resin is inefficient, a large amount of regenerant flows through the column without releasing the attached ion from the resin. This leads to a large amount of unused chemical is wasted. Regenerant handling is normally managed by an online mixing system where concentrated acid or base is diluted to the desired concentration (Nachod & Schubert, 2013, p. 38). Another way is to build large enough dilution tanks where regenerant is diluted desired concentration.

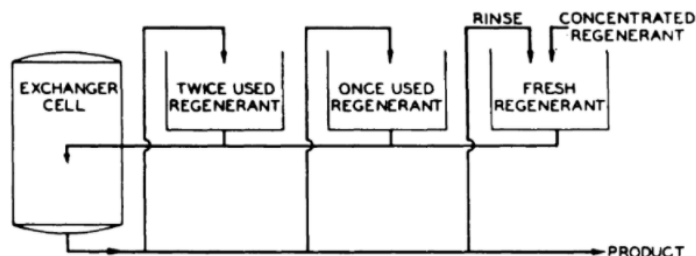


Figure 9. Regenerant recycle (Nachod & Schubert, 2013, p. 38).

The recycling of regenerant can be a viable option to increase regeneration efficiency by decreasing chemical consumption, as illustrated in figure 9. If regenerant is recycled twice, the regeneration is started with twice used regenerant, and the outflow will be wasted. The regeneration is continued with once used regenerant. When this starts to flow out, it will be collected to twice used regenerant tank. The regeneration will be finished with a fresh regenerant collected after the column to once used regenerant tank. After regeneration, the resin is washed with water. The displacement is collected to the once used regenerant tank, and then the first part of the water is collected to a fresh regenerant tank. When enough water is collected for one regeneration, then the rest of the washing water is put into waste. Water needed for dilution is in a fresh regenerant tank, and the concentrated chemical is dosed for the next regeneration. Often this type of regenerant handling is used to reduce chemical consumption. Acid and brine regenerations are done in three-stage regeneration and alkali in two-stage. (Nachod & Schubert, 2013, p. 38.)

3.5 Regeneration chemicals

The functional group of the resin determines chemicals suitable for regeneration of cation and anion exchange resins. Strong acid cation resin requires a strong acid for regeneration due to the least favorable ion form for strong acid cation resin is H^+ form. A weak acid cation can be regenerated with both strong and weak acids due to H^+ form has the highest affinity.

There is a larger amount of options when choosing an acid for a cation exchanger than a base for an anion exchanger. Normally sodium hydroxide is used to regenerate both strong and weak base anion resins. Other possible options are potassium or calcium hydroxide, but both contain hydroxide anion. Ammonia and sodium carbonate can be used to regenerate weak base anion resin. (Harland, 1994, p. 210.)

3.6 Cross and power regeneration

Ion exchange resin is fouled in time, which increases the resistance for intraparticle diffusion. Cross regenerations can be made to improve the operating capacity of the resin. Anion exchange resin is washed with acid to dissolve organic fouling before caustic regeneration. The operating capacity of heavily fouled anion exchange resin can be

restored by soaking in a mixture of caustic (2 w-%) and brine solution (10 w-%). Cross regeneration extends the service life of the resin. The acid cation exchanger is washed with caustic before acid regeneration. Extended regeneration should be made using a 1.5 times larger amount of regeneration chemicals from time to time. (Dow, 2013.)

3.7 Optimization potential

Quite often, ion exchange has been considered as a support process rather than a major process unit. Therefore, the focus has not been on the optimization of ion exchange. However, there can be great potential to reach significant savings if large enough volumes are treated, or the treated solution contains a great number of ions. Each ion-exchange cycle consumes a large amount of water and chemicals. If the costs of water and chemicals are high, the saving potential becomes even greater.

Depending on the process, the amount of resin is not normally large. The ion exchange resin price is roughly 1.5–5 €/L (Harland, 1994, p. 2). When an ion-exchange line contains, for example, 4 m³ of resin, the cost of renewing the resin is 6 000–20 000 €. If the resin service life is short, this cost may become significant, and optimization for prolonging the service life could be economical.

3.8 Design of an ion exchange process

For the ion exchange process design, one needs to know the concentration of ions in the solution to be purified. Column sizing needs to be planned to achieve maximal purification capacity with minimal investment and operating costs. Each ion-exchange cycle consumes a certain amount of chemicals and water and generates a certain waste stream volume. The concentration of removable ions with the volume of the resin determines the cycle length of the ion exchange at a given operating capacity. The regeneration leads to downtime in the process, which takes several hours to complete. This reduces the overall production capacity, impacting the column sizes or the number of ion exchange lines. The removable ions and the purity specification of the product stream determine the resin type used in the process. (Harland, 1994, p. 173)

4 ION EXCHANGE STUDIES

4.1 Materials and methods

The feed used in exhaustion contains neutral carbohydrates, salts, organic acids, and color compounds. The concentration of the solution was 21.8 g/100 ml based on the refractive index, pH was 6.1, conductivity was 4.9 mS/cm and color was 3174 ICUMSA unit.

Table 1. Analysis of the ion exchange feed.

	Concentration, g/100 ml	pH	Conductivity, μS/cm	Color, ICUMSA	Cations, eq/L	Anions, eq/L
feed	21.8	6.1	4930	3174	0.071	0.062

There was 303 mg/kg dry substance (DS) potassium, 10343 mg/kg DS calcium, 560 mg/kg DS magnesium, and 32 mg/kg DS iron in the ion exchange feed. The main impurity of cations was potassium, which covers 92 % of the total cations.

Table 2. The cations of the ion exchange feed.

Na ⁺ mg/kg DS	K ⁺ mg/kg DS	Ca ²⁺ mg/kg DS	Mg ²⁺ mg/kg DS	Fe ^{2+/3+} mg/kg DS
303	10343	43	560	32

There was 159 mg/kg DS acetate, 40 mg/kg DS formate, 82 mg/kg DS chloride, 13037 mg/kg DS sulfate, 173 mg/kg DS oxalate, 593 mg/kg DS phosphate, 315 mg/kg DS lactate, 944 mg/kg DS succinate and 156 mg/kg DS nitrate in the ion exchange feed. The main impurity of anions was sulfate, which covers 94 % of the total anions. Strong base anion is normally used to remove the organic content (Harland, 1994). Therefore, the organic acids are not expected to be removed well with weak base anion resin used in the testing.

Table 3. The anions and organic acids of the feed.

Acetate mg/kg DS	Formate mg/kg DS	Cl ⁻ mg/kg DS	SO ₄ ²⁻ mg/kg DS	Oxalate mg/kg DS	PO ₄ ³⁻ mg/kg DS	Lactate mg/kg DS	Succinate mg/kg DS	NO ₃ ⁻ mg/kg DS
159	40	82	13037	173	593	315	944	156

The regeneration chemicals were 95-98 w-% H₂SO₄ from Honeywell and 99.3 w-% NaOH pellets from Fischer Chemical diluted to proper concentration, 5 w-% H₂SO₄, and 4 w-% NaOH.

Table 4. Regeneration capacities of the regenerants.

Regenerant	Concentration, w-%	Regeneration capacity, eq/L
H ₂ SO ₄	5	0.53
NaOH	4	1.04

The strong acid cation resin was Dowex 88 by DuPont, and the weak base anion resin was Dowex 66 by DuPont, which were packed in glass columns with a 24-mm diameter. During the exhaustion and regeneration, the flow rate was 2 BV/h meaning 30 min passing time if resin void is 50 %. During rinsing, the flow rate was 2 BV/h for 30 min to displace the regenerant, and then it was increased to 4 BV/h. The rinsing volume varied between 10-14 BV of ion-exchanged water.

Table 5. Resins used in ion exchange study (Dow, 2006; Dow 2017.)

Resin name	Type	Capacity, eq/L	Volume, mL	ion exchange capacity, eq
Dowex 88	SAC	1.80	100	0.180
Dowex 66	WBA	1.35	100	0.135

Samples were collected from the testing and analyzed by refractive index, pH and conductivity, color, and inorganic content. The concentration during the exhaustion phase was calculated based on the relation between the refractive index and concentration. The color was calculated based on the absorbance in 420 µm wavelength and expressed in ICUMSA units (Poel, 1998, p. 94). The inorganic content was analyzed

with inductively coupled plasma mass spectrometry (cations) and ion chromatography (anions).

Resin analysis included eluting cations from the resins and analyzing the cations with inductive coupled plasma mass spectrometry. The cations were eluted by regenerating the resin with hydrochloric acid. The total capacity of the resin was determined by titration. Completely regenerated strong acid cation resin was fully exhausted with dilute NaCl solution. The outflow was collected, and the hydrogen content was determined by titration with 1 N NaOH solution.

4.2 Regenerant recycle in co-flow regeneration

4.2.1 Results

An ion-exchange process that consists of two resins in line was studied. The first resin was strong acid cation resin and the second weak base anion resin. Weak base anion resin has high regeneration efficiency meaning caustic used for regeneration converts close the stoichiometric number of equivalents in resin to free base form. Strong acid cation resin has lower regeneration efficiency, and therefore the study is focused on improving strong acid cation regeneration.

A great amount of acid flows through a strong acid cation resin bed unutilized during the regeneration. The used regenerant can be collected and recycled for the next regeneration. This would decrease the acid consumption in the regeneration of strong acid cation resin.

5 w-% of sulfuric acid was recycled twice before wasting. The regeneration was started with 2 BV of twice used acid, followed by 2 BV of once used acid, and lastly, 2 BV of fresh acid was used. The resin regenerated with recycled regenerant was compared with other strong acid cation resin, regenerated with 4 BV of fresh acid.

In chart 1 is presented the concentration and conductivity during the exhaustion phase. The ion leakage is higher when recycling acid in regeneration. This is caused by impurities left in the resin during the regeneration. The conductivities started increasing after 10 BV of product collection, indicating the exhaustion of ion exchange resin.

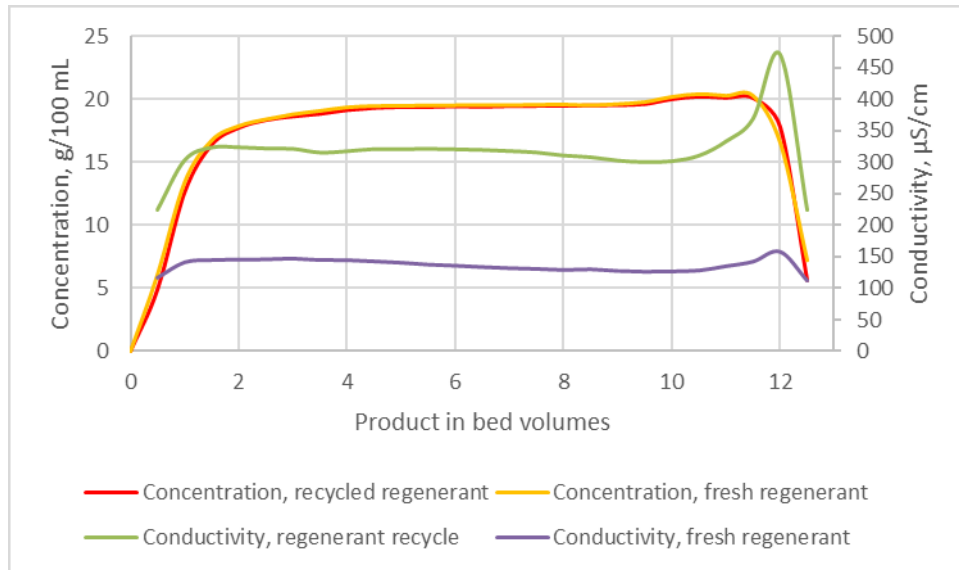


Chart 1. Co-flow regenerated ion exchange line during exhaustion (part 1).

Decreasing pH indicates that some of the hydrogen ions released from the strong acid cation resin flow through the weak base anion resin without protonating the resin. Close to decreasing pH and increasing conductivity, the color of the outflow starts increasing. The pH of the ion exchange line with fresh acid regenerated strong acid cation resin decreased rapidly between 8-11 BV of product collection, and after that, the decline was smaller. When the regeneration was done with recycled regnerant, the pH did not decrease in the same way. The decline was slower, and it increased towards the end. The feed has a brown color, which was removed in ion exchange.

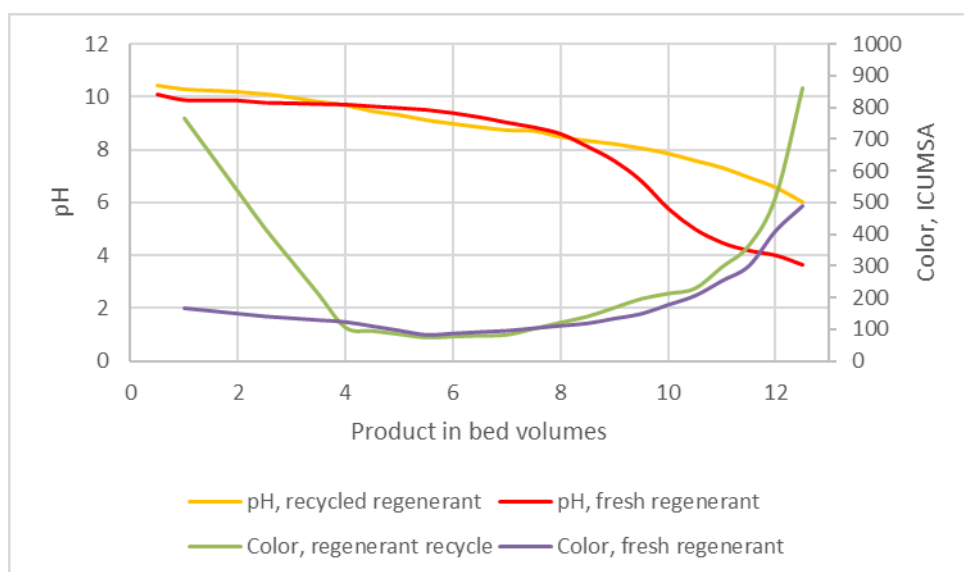


Chart 2. Co-flow regenerated ion exchange line during exhaustion (part 2).

In chart 3 is presented the cations analyzed from the outflow of co-flow regenerated resin. The feed contained 10343 mg/kg DS of K^+ , 303 mg/kg DS of Na^+ , 560 mg/kg DS of Mg^{2+} , 43 mg/kg DS of Ca^{2+} and 32 mg/kg DS of $Fe^{2+/3+}$. Strong acid cation resin was leaking potassium during the whole exhaustion. The leaking was higher from strong acid cation resin, which was regenerated with recycled regenerant. The leaking potassium content was between 590–1080 mg/kg DS from strong acid cation resin regenerated with recycled regenerant. In the end, the leaking of potassium was increasing, which indicated that the strong acid cation resin was exhausted. The sodium ions were also leaking during the exhaustion from the resin, which was regenerated with recycled regenerant. The strong acid cation resin has a high affinity to magnesium form, which can be seen as a low magnesium leakage. The magnesium leakage increased slightly at the end of exhaustion, and iron also started to leak. Calcium was not leaking from the resin regenerated with recycled acid.

The strong acid cation resin regenerated with fresh regenerant was also leaking potassium during the exhaustion, although the leaking was lower than resin regenerated with recycled acid. When a fresh regenerant was used to regenerate the resin, the leaking potassium was between 300–470 mg/kg DS. Sodium, magnesium and iron started leaking from the resin at the end of exhaustion. Calcium was not leaking from the resin regenerated with fresh acid.

Higher ion leakage occurred when using recycled regenerant, meaning there was a higher amount of unregenerated resin after the regeneration. Lower ion leakage of fresh acid regenerated resin indicated that the regeneration was more complete. The numeric data can be found in appendix 1.

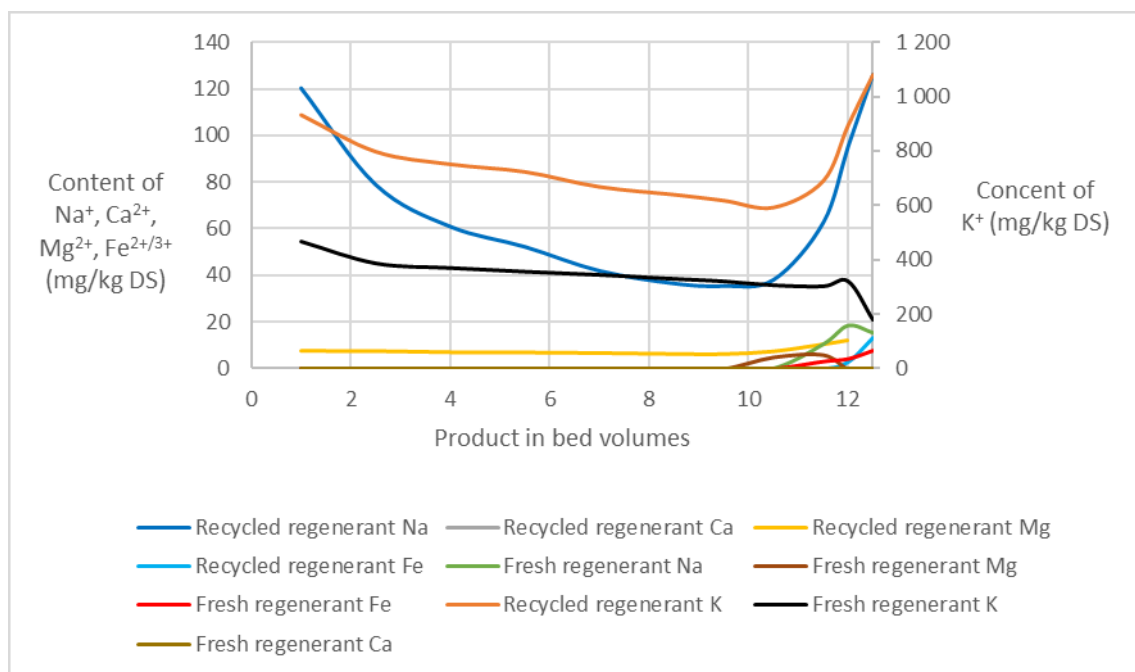


Chart 3. Cations during the exhaustion of co-flow regenerated resin.

In table 6 is presented anions of the ion exchange outflow. The feed contained 13037 mg/kg DS sulfate, 593 mg/kg DS phosphate, 156 mg/kg DS nitrate and 82 mg/kg DS chloride. Both weak base anion resins were regenerated with 2 BV of 4 % NaOH. The weak base anion resin was able to remove all anions well. There was some minor leaking of chloride and sulfate from the line containing strong acid cation resin regenerated with recycled acid and sulfate from the line containing strong acid cation regenerated with fresh acid was noted. The leaking was not significant. In appendix 1, page 2 can be found the data used in table 6.

Table 6. Anions during the exhaustion of co-flow regenerated resin.

Regenerant	Product	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻
	BV	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	< 1	13	< 40	< 40
	2.5	< 3	10	< 30	< 30
	4	< 4	< 5	< 30	< 25
	5.5	6	< 3	< 30	< 30
	7	7	< 3	< 3	< 25
	8.5	6	7	< 3	< 25
	9.5	6	< 3	< 3	< 25
	10.5	5	< 3	< 3	< 25
	11.5	4	< 2	< 4	< 25
	12	5	11	< 4	< 30
	12.5	< 8	< 8	< 10	< 80
Fresh	1	< 3	10	< 35	< 35
	2.5	< 3	< 4	< 25	< 30
	4	< 3	< 3	< 25	< 25
	5.5	< 2	< 4	< 25	< 25
	7	< 2	< 3	< 25	< 25
	8.5	< 2	< 5	< 25	< 25
	9.5	< 3	< 4	< 3	< 25
	10.5	< 2	< 2	< 3	< 25
	11.5	< 2	< 3	< 3	< 25
	12	< 3	< 3	< 3	< 30
	12.5	< 6	< 7	< 7	< 70

The removal of organic acids was not unambiguous. The feed contained 159 mg/kg DS acetate, 40 mg/kg DS formate, 173 mg/kg DS oxalate, 315 mg/kg DS lactate and 944 mg/kg DS succinate. The weak base anion resin was able to remove oxalate fully, but the removal of acetate, formate, lactate, and succinate was hard to follow due to great variance. The acetate content varied between 75–270 mg/kg DS. In the beginning, it was above 250 mg/kg DS. After 2.5 BV of product collection, it decreased to 75 mg/kg DS, which was achieved at 9.5 BV. The formate content varied between 20–130 mg/kg DS even though there was only 40 mg/kg DS of formate in the feed. The lactate content was close to 50 mg/kg DS initially, and it started increasing at 4 BV of product collection. The lactate content varied between 50–180 mg/kg DS. Succinate was removed in the beginning, and after 2.5 BV of product collection, it started leaking. The succinate content varied between 0–950 mg/kg DS. The dry substance was decreasing at 12 BV of product

collection, and it may have impacted the analysis due to acetate, formate, lactate, and succinate contents were increasing at the same time in the end.

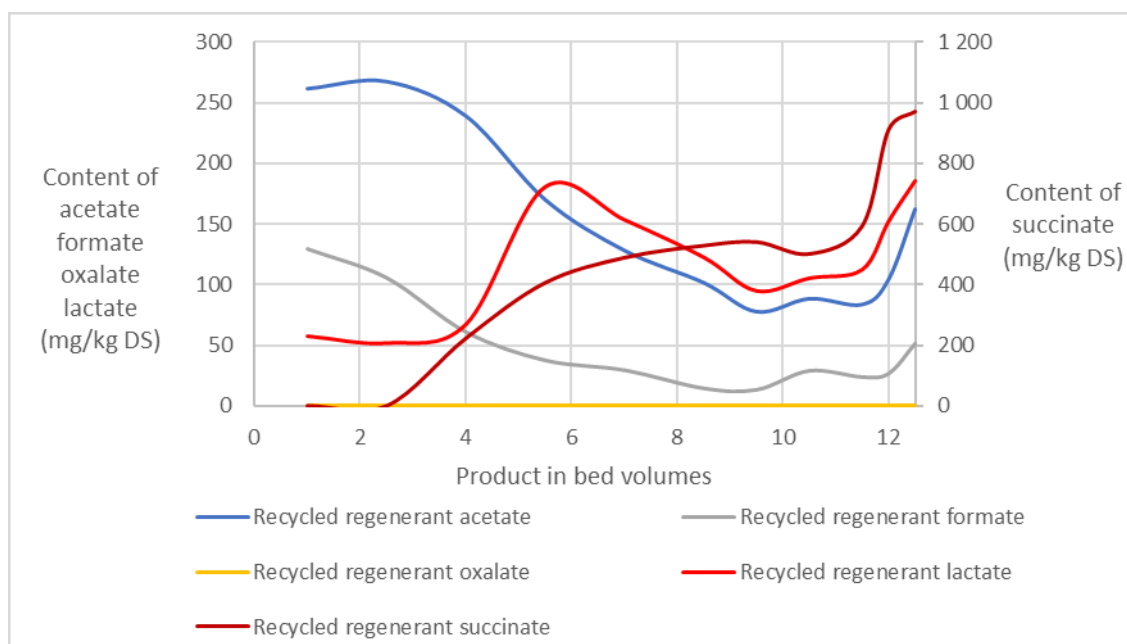


Chart 4. Organic acids during the exhaustion of co-flow regenerated resin (recycled regenerant).

The weak base anion resin was able to remove oxalate fully, but the removal of acetate, formate, lactate, and succinate was hard to follow due to great variance. The acetate content varied between 40–220 mg/kg DS. In the beginning, it was above 175 mg/kg DS. After 4 BV of product collection, it decreased to 40 mg/kg DS, which was achieved at 9 BV. The formate content varied between 20–130 mg/kg DS even though there was only 40 mg/kg DS of formate in the feed. The lactate content was close to 50 mg/kg DS initially, and it started increasing at 4 BV of product collection. The lactate content varied between 0–75 mg/kg DS. Succinate was removed in the beginning, and after 5.5 BV of product collection, it started leaking. The succinate content varied between 0–1300 mg/kg DS. A similar increase of acetate, formate, lactate and succinate contents were noted after 12 BV of product collection. In appendix 1, page 2 can be found the numeric data of organic acids.

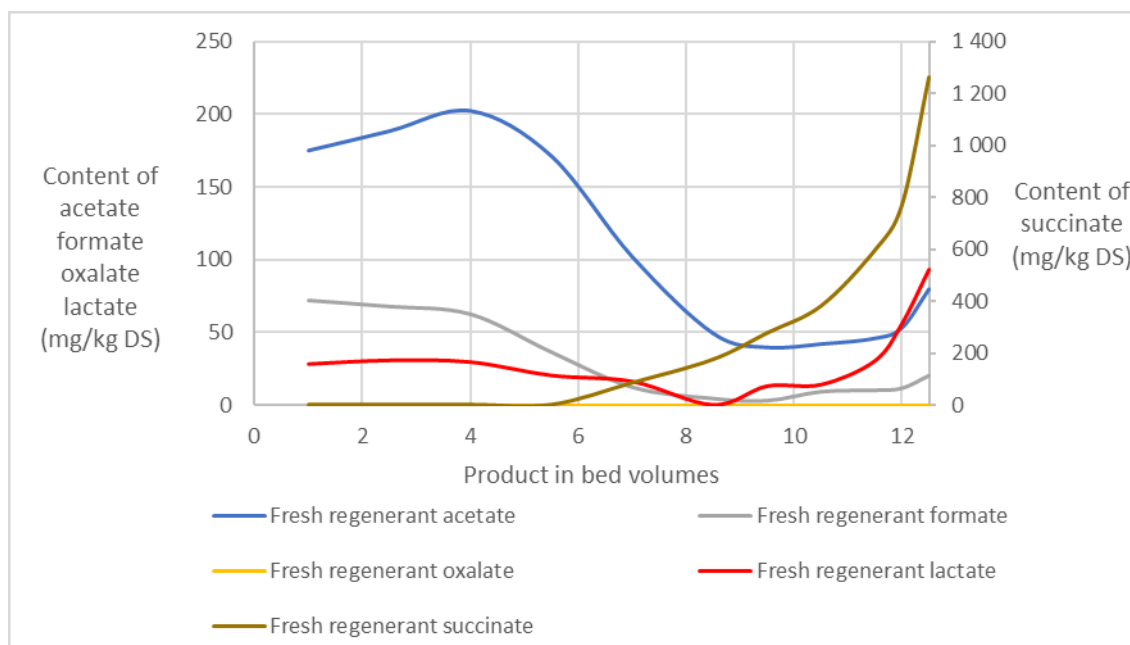


Chart 5. Organic acids during the exhaustion of co-flow regenerated resin (fresh regenerant).

4.2.2 Discussion

Both ion exchange lines, regenerated with fresh regenerant or recycle regenerant, have close to the exact length of the exhaustion phase. The determination became difficult due to the ion leakage was increased when recycling regenerant, and the pH did not decrease as it did when using only fresh regenerant. Even when strong acid cation was regenerated with 4 BV of fresh 5 w-% sulfuric acid, the minor ion leakage during exhaustion caused pH to decline slower than when reverse flow regeneration was used.

Surprisingly, anions did not start leaking as suspected at the end of exhaustion when monitoring the pH. The decreasing pH indicated that the strong acid cation resin was still releasing hydrogen ions, but the weak base anion was not able to take all of them when the resin was protonating. The content of sulfate, phosphate, nitrate, and chloride was low during the whole exhaustion.

The study contained only a few cycles, and the long-term impact on the regeneration was not tested. When the resins have more cycles, the operating capacity may decrease, causing a shorter exhaustion length. In the long-term, the recycled regenerant may have to be discharged periodically and start collecting recycled regenerant again.

4.3 Regenerant recycle in reverse flow regeneration

4.3.1 Results

It was noted that regenerant recycle increased the conductivity during the exhaustion phase, which was caused by a greater ion leakage from the resin. There was also conductivity leaking when using only a fresh regenerant, meaning there was ion leakage from the resin. All the earlier regenerations had been performed with co-flow. Reverse flow regeneration was used for both strong acid cation and weak base anion resin. The strong acid cation resin was regenerated in reverse flow with recycled regenerant, and, in parallel, fresh regenerant in reverse flow was tested as a comparison. The reverse flow regeneration decreased ionic leakage to a minimum. The conductivity started increasing in the outflow of both ion exchange lines after 8 BV of product collection. The increase was lower when using fresh regenerant.

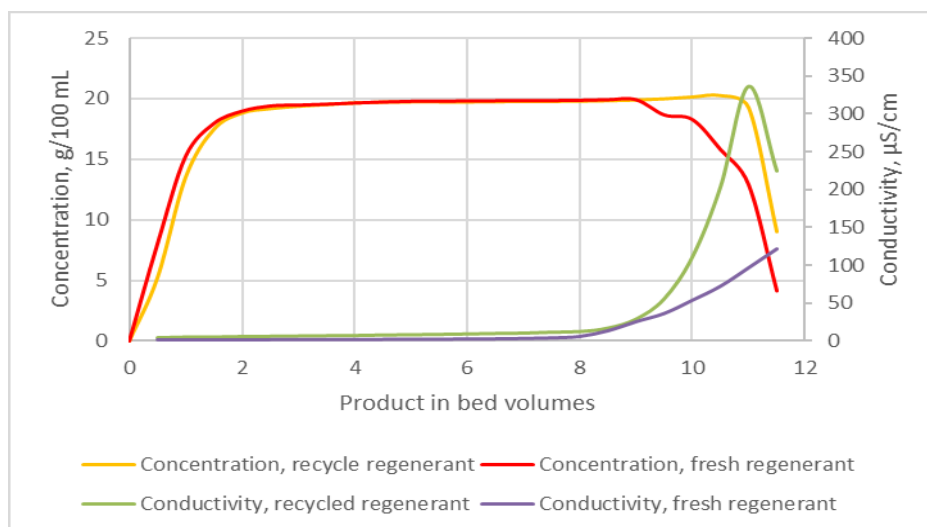


Chart 6. Reverse flow regenerated ion exchange line during exhaustion (part 1).

The pH decreased in the outflow of both ion exchange lines indicating the exhaustion of the ion exchange line. When using fresh regenerant, the moment was after 6 BV of product collection. When using recycled regenerant, the moment was after 7 BV of product collection. The color started to leak at the same moment when pH started to decrease.

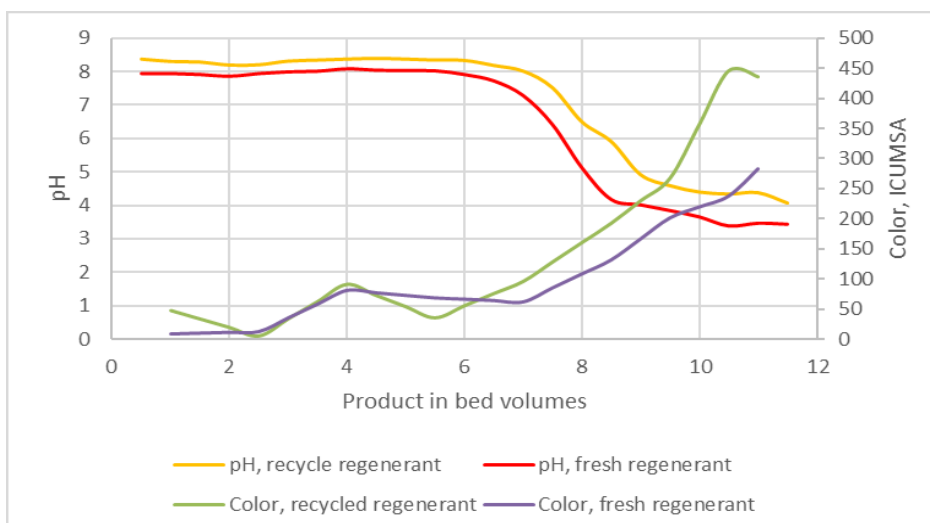


Chart 7. Reverse flow regenerated ion exchange line during exhaustion (part 2).

In appendix 2 are the inorganic analysis of the exhaustion phase after reverse flow regeneration. On page 1 can, be seen that no cations were leaking in the middle of exhaustion. In the end, potassium and sodium started leaking from both ion exchange lines. The analysis suggested that magnesium and iron started also leaking at the end. On page 2 can be seen the analysis of anions and organic acids. Sulfate, phosphate, nitrate, and chloride were not leaking even at the end of the exhaustion phase. Acetate, formate, oxalate, and succinate seemed to be removing better when using reverse flow regeneration.

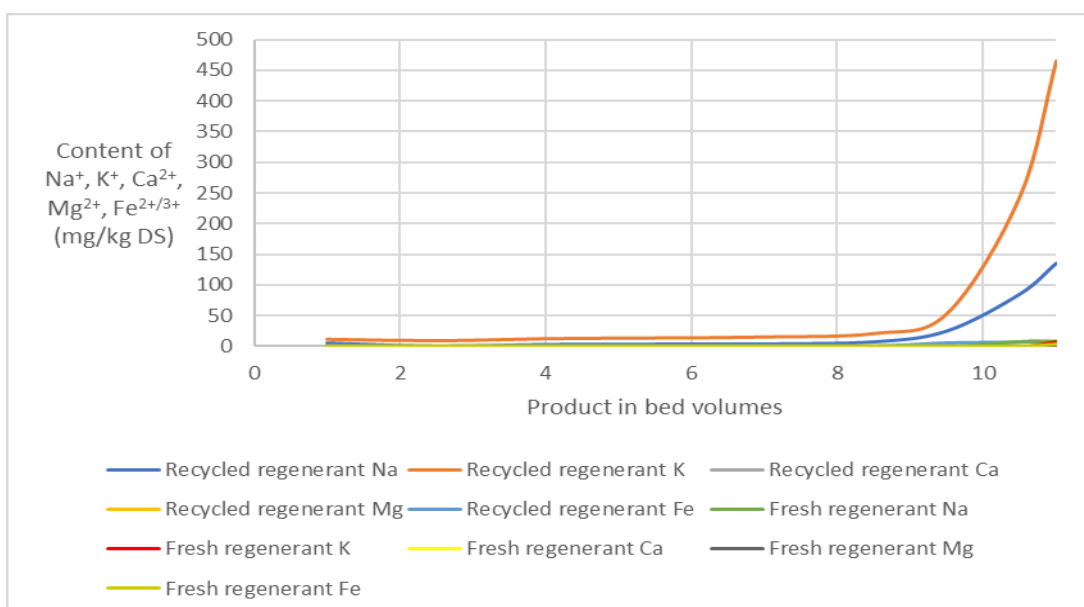


Chart 8. Cations during the exhaustion of reverse flow regenerated resin.

In table 7, anions of the ion exchange outflow are presented. The removal of anions was good with reverse flow regenerated weak base anion resin. Minor leaking of chloride and sulfate, which occurred from co-flow regenerated weak base anion resin, was not detected when changing the flow direction in regeneration. In appendix 2, page 2 can be found the data used in table 7.

Table 7. Anions during the exhaustion of reverse flow regenerated resin.

Regenerant	Product	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻
	BV	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	< 20	< 3	< 4	< 30
	2.5	< 15	< 2	< 2	< 25
	4	< 10	< 3	< 2	< 25
	5.5	< 10	< 2	< 2	< 25
	7	< 10	< 2	< 2	< 25
	8.5	< 10	< 2	< 3	< 25
	9.5	< 10	< 2	< 3	< 25
	10.5	< 10	< 2	< 4	< 25
	11	< 15	< 2	< 4	< 25
Fresh	1	< 15	< 3	< 3	< 30
	2.5	< 15	< 3	< 3	< 25
	4	< 15	< 3	< 3	< 25
	5.5	< 10	< 2	< 2	< 25
	7	< 10	< 2	< 3	< 25
	8.5	< 15	< 2	< 3	< 25
	9.5	< 15	< 2	< 4	< 5
	10.5	< 15	< 4	< 4	< 30
	11	< 20	< 4	5	< 40

In chart 9, the organic acids are presented. Acetate, formate, oxalate, and succinate seemed to be removing better when using reverse flow regeneration. Acetate content was below 20 mg/kg DS until 7 BV of product collection. After that point, acetate content was increasing steadily. Formate was removed well initially, and the content started increasing at 7 BV of product collection. The oxalate content varied between 20-30 mg/kg DS. Succinate started to leak after 7 BV of product collection.

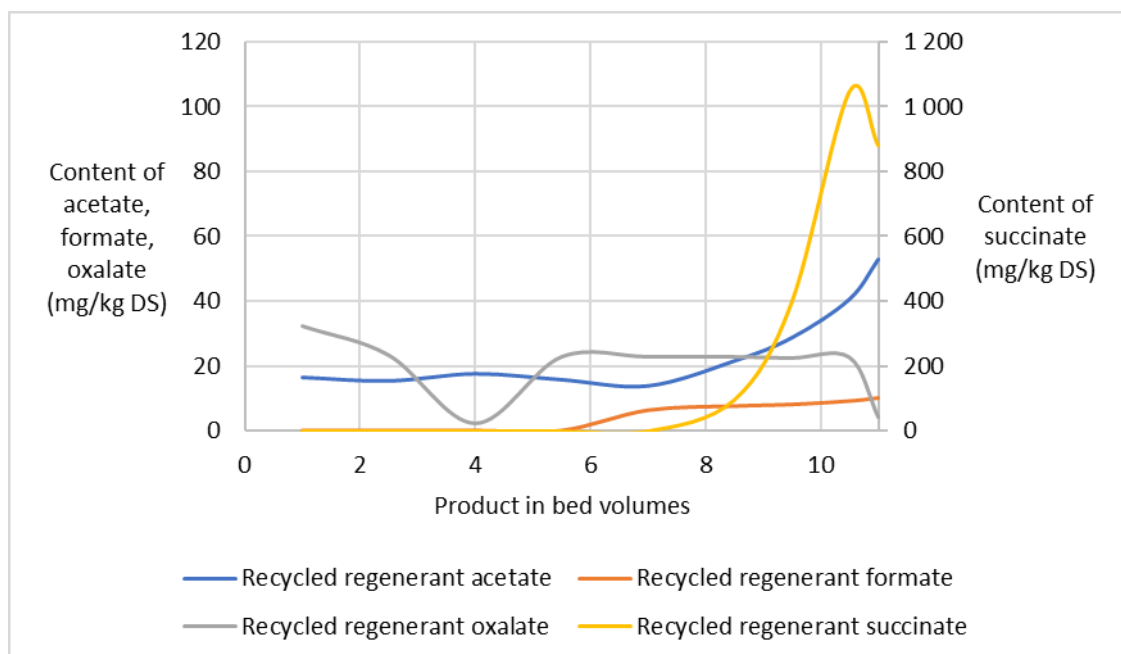


Chart 9. Organic acids during the exhaustion of reverse flow regenerated resin (recycled regenerant).

In chart 10, the organic acids are presented. Acetate content varied between 15–30 until 9.5 BV of product collection. After this point, the content was increasing to 50 mg/kg DS. The dry substance was decreasing in these samples, which may have impacted the increase. The formate was removed well initially, and the content started increasing at 7 BV of product collection. The oxalate content varied between 20–30 mg/kg DS. In the last sample point, the content increased to 36 mg/kg DS, which may also be due to decreasing dry substance. Succinate started to leak after 7 BV of product collection. In appendix 2, page 2 can be found the numeric data of organic acids.

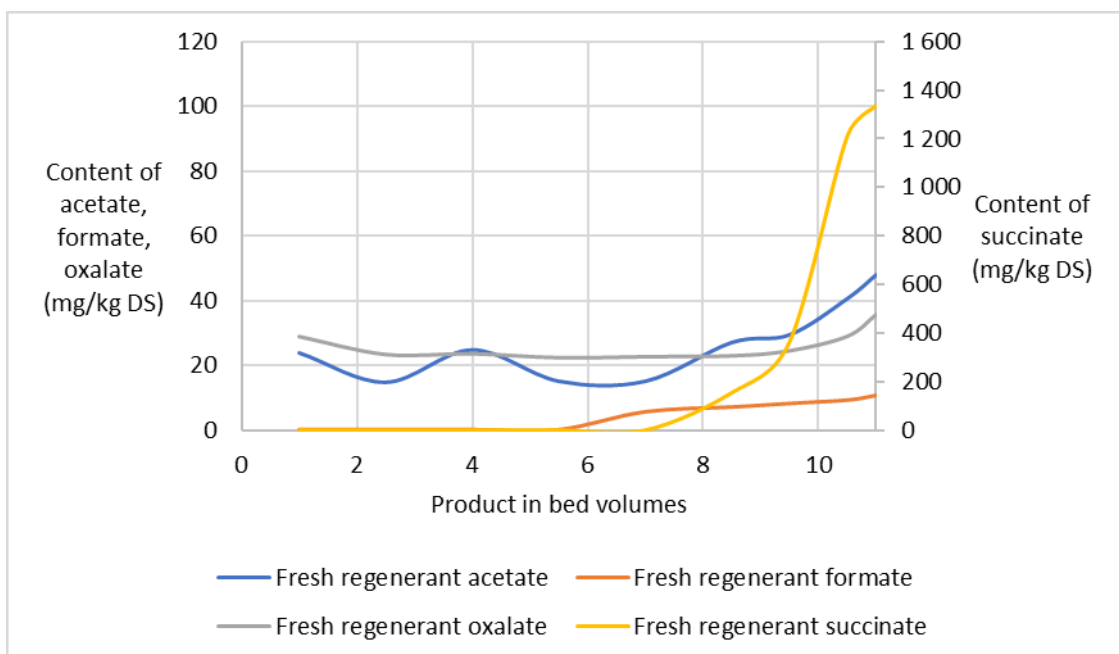


Chart 10. Organic acids during the exhaustion of reverse flow regenerated resin (fresh regenerant).

The strong acid cation resin was not analyzed after regeneration. The exhausted resin analyses are summarized in table 8. The largest impurity in the resin was potassium and the second largest was magnesium. There was also a small amount of sodium in the resin. There was only a small amount of calcium and iron in the feed presented in table 2.

Table 8. Exhausted strong acid cation resin.

		Capacity	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe ^{2+/3+}	H ⁺
SAC recycled regenerant	%		0.5	7.0	1.3	30.3	0.1	60.8
	eq/L	1.73	0.01	0.12	0.02	0.52	0.00	1.05
SAC fresh regenerant	%		0.5	5.6	1.2	25.3	0.1	67.3
	eq/L	1.72	0.01	0.10	0.02	0.43	0.00	1.15

If 100 % conversion to acid form is assumed, then the operating capacity of the SAC resin, which was regenerated with recycled regenerant, was 0.68 eq/L, and the efficiency of the regeneration was 64.2 % (2 BV of 5 w-% H₂SO₄ contains 1.06 eq/L of H⁺). Similarly, the operating capacity of the SAC resin, which was regenerated with fresh regenerant, was 0.57 eq/L, and the efficiency of the regeneration was 26.9 % (4 BV of 5 w-% H₂SO₄ contains 2.12 eq/L of H⁺).

Table 9. The regeneration efficiency of strong acid cation resin.

Regeneration method	Consumed regenerant, BV	Regeneration capacity, eq/L	Regenerated to H ⁺ form, eq/L	Regeneration efficiency, %
Regenerant recycle	2	1.06	0.68	64.2
Fresh regenerant	4	2.12	0.57	26.9
Fresh regenerant	3	1.59	0.57	35.9

2 BV of 5 w-% fresh acid was used in each regeneration when recycling regenerant. The lower H⁺ concentration in the resin indicates that the resin has a lower H⁺ concentration in regenerated form than resin regenerated with fresh regenerant. The higher ion leakage in the co-flow regenerated test also suggested that the strong acid cation resin after recycled acid regeneration was less in H⁺ form than when only fresh acid was used. Therefore, the operating capacity and regeneration efficiency would be lower. The normal regeneration consumed 4 BV of fresh regenerant. If the resin was regenerated with only 3 BV of fresh 5 w-% H₂SO₄ instead of 4 BV, and the result was the same regarding the conversion, then the regeneration efficiency would have been 35.8 % (3 BV of 5 w-% H₂SO₄ contains 1.59 eq/L of H⁺).

4.3.2 Discussion

The exact moment when exhaustion occurred was easier to detect when there was not ion leakage during exhaustion. This issue can especially be seen when regenerant recycle was used in co-flow regeneration. The strong acid cation resin was surprisingly much in H⁺ form after the exhaustion. Weak base anion resin should also be sampled to see the ion form before and after regeneration. Even though pH decreased at the end of exhaustion, the weak base anion resin did not start to leak anions. The strong acid cation resin appears to be the limiting factor here regarding the operating capacity.

The reverse flow regeneration decreases the ion leakage considerably even when a fresh regenerant is used. The regeneration of strong acid cation resin fully to acid form requires an excessive amount of acid, making it economically unprofitable. If reverse flow regeneration is not an option, a similar impact can be made by dividing strong acid cation resin into multiple columns. The regeneration should be done in reverse order.

Therefore, the last strong acid cation column is the best regenerated and not leaking cations. Dividing the strong acid cation resin into multiple columns decreases the ion leakage when all the resin does not have to be fully regenerated. The last column of strong acid cation resin is regenerated the best. Strong acid cation resin can be paired with weak acid cation resin to improve the regeneration efficiency. The acid regenerant flows through strong acid cation resin and then through weak acid cation resin. (Harland, 1994, p. 213.)

The case is the same as in the previous study. The long-term impact on the ion exchange cycle length was not covered, which requires further testing. Backwashing disturbs the distribution of ions in the resin. When ion exchange is operated longer, the resin requires backwashing eventually. The impact of backwashing on reverse flow regeneration was not tested. Although the proper distribution of ions should be obtained in the following ion exchange cycle.

4.4 SAC resin regenerant reduction

4.4.1 Results

Strong acid cation regeneration was studied to minimize acid consumption in the regeneration phase. The strong acid cation resin was regenerated with 5 w-% sulfuric acid. In comparison was 3 and 4 BV of regenerant. The strong acid cation resin was the first column of an ion exchange line, consisting of weak base anion resin as the second resin.

When 3 BV of 5 w-% H_2SO_4 was used to regenerate strong acid cation resin, there was a higher ion leakage during exhaustion than when 4 BV was used. The conductivity started increasing after 8-9 BV of product collection.

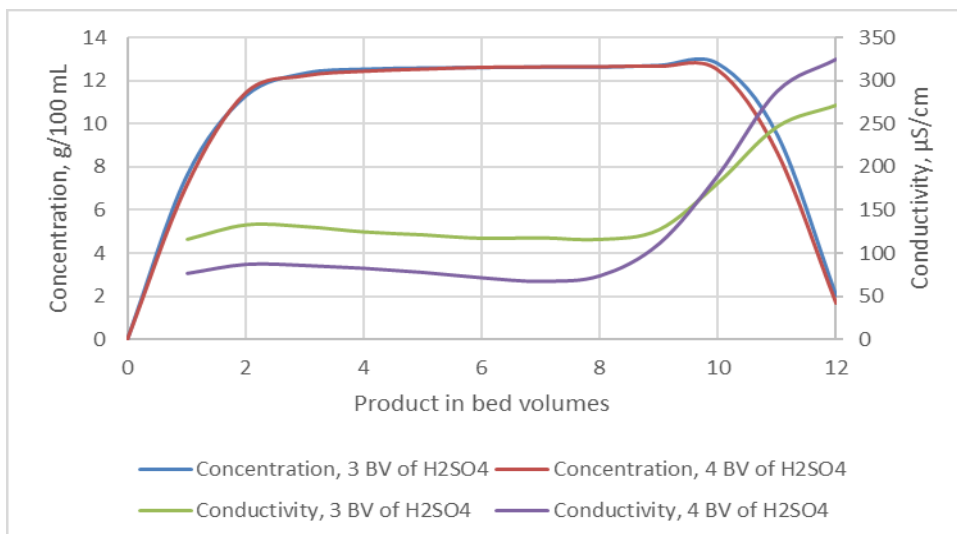


Chart 11. The exhaustion of SAC resin regenerated with 3 and 4 BV of 5 w-% H_2SO_4 (part 1).

Declining pH indicates the exhaustion of the ion exchange line. The pH started decreasing after 6 BV of product collection. The pH declined faster when strong acid cation resin was regenerated with 4 BV of 5 w-% H_2SO_4 . The color also started increasing after 6 BV of product collection.

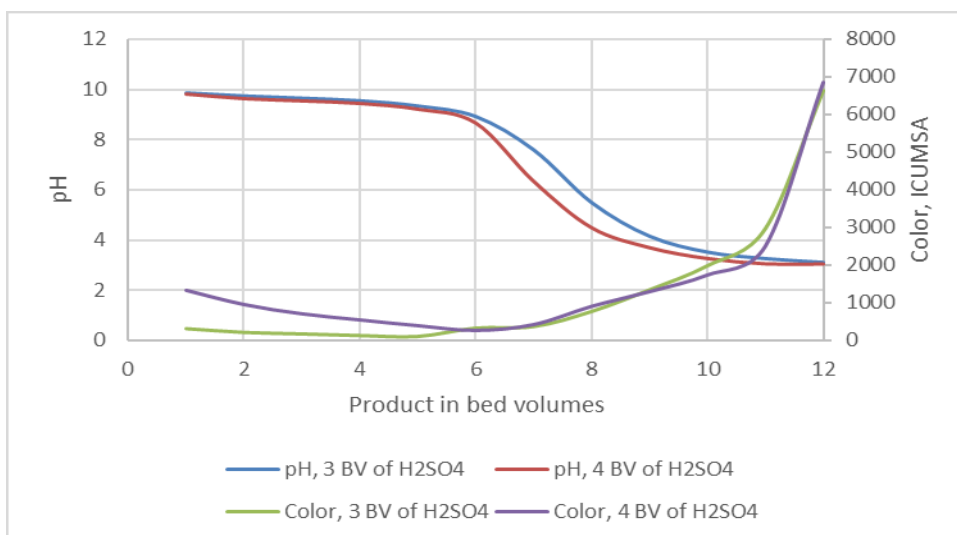


Chart 12. The exhaustion of the ion exchange line where SAC resin was regenerated with 3 and 4 BV of 5 w-% H_2SO_4 (part 2).

The strong acid cation resin can be regenerated sufficiently with 3 BV of 5 w-% H_2SO_4 . However, it causes higher ion leakage if using co-flow regeneration.

4.4.2 Discussion

The conductivity in the ion-exchanged product is from the ion leakage due to incomplete regeneration. The co-flow regeneration leaves impurities close to the column outlet, which leaks during the next exhaustion. The conductivity was higher when less regenerant was used, meaning a smaller amount of regenerant results in higher ion leakage. When the ion exchange line was exhausted, the pH started decreasing. Higher ion leakage caused a slower decreasing pH.

4.5 Rinsing in SAC regeneration

4.5.1 Results

The outflow was collected during regeneration to determine the sufficient amount of rinsing. Table 10 presents Brix value based on the refractive index of sucrose, pH, and conductivity of the regenerant used in the test (5 w-% H_2SO_4) and the outflow during the regeneration. The collection was started at the beginning of the regeneration. The strong acid cation resin was regenerated with 4 BV of 5 w-% H_2SO_4 . There was not a significant change in the outflow between 7-14 BV. Therefore, the sufficient amount of rinsing water was 2 BV deionized water after the regenerant.

The flow rate was kept constant during the whole regeneration (2 BV/h). Normally a rinsing step contains a slow rinsing step (2 BV/h) followed by a fast rinsing step (4 BV/h) to reduce the production downtime. (Harland, 1994, p. 169.)

Table 10. The outflow during strong acid cation resin regeneration.

SAC resin regeneration	Brix g/100g	pH	Cond mS/cm
5 w-% H ₂ SO ₄	4.3	0.8	198.0
0-1 BV	1.5	1.8	26.8
1-2 BV	4.6	1.1	101.9
2-3 BV	4.8	0.8	162.1
3-4 BV	4.6	0.7	180.8
4-5 BV	4.5	0.7	191.9
5-6 BV	1.3	1.1	60.9
6-7 BV	0.0	2.7	0.62
7-8 BV	0.0	3.8	0.08
8-9 BV	0.0	3.8	0.06
9-10 BV	0.0	3.9	0.05
10-11 BV	0.0	4.0	0.05
11-12 BV	0.0	3.9	0.04
12-13 BV	0.0	3.8	0.08
13-14 BV	0.0	4.0	0.05

4.5.2 Discussion

Acid is relatively easy to rinse from the resin after regeneration. The issue is with caustic used to regenerate anion exchange resins. An economical way to reduce the rinsing water consumption is to recirculate water through a cation and anion exchange resin in a closed system. After most regenerant is displaced from the resin, rinsing water is circulated through the ion exchange line. The remaining regenerant consumes the capacity of the opposite resin slightly, but the reduction of water consumption could be significant. Higher flowrate may be used during the final rinsing to save time (Harland, 1994, p. 169). The required rinsing water increased when the resin ages, especially with a weak base anion resin. Good quality rinsing water can also be reused as rinsing water or diluting thick regenerant to proper concentration. (Dowex, 2013.)

5 CONCLUSION

Recycling regenerant was tested for a strong acid cation exchanger. The used regenerant was 5 w-% sulfuric acid for strong acid cation resin. The acid was recycled twice and then wasted. It was noticed that 2 BV of fresh regenerant was sufficient to regenerate the resin as good as 4 BV of fresh regenerant when the regenerant was recycled twice. In table 8, the resin analysis stated that after exhaustion, the resin which had recycled regenerant was 61 % in hydrogen ion form, and the other regenerated with fresh regenerant was 67 % in hydrogen ion form. The capacity of the strong acid cation resin was 1.73 eq/L on average. In table 9 was presented the regeneration efficiencies. If it is assumed that the resin was fully in hydrogen ion form after regeneration, then the regeneration efficiency was 64 % when recycling regenerant and 27 % when using fresh regenerant. 3 BV of fresh regenerant may be sufficient to reach almost full conversion without decreasing the cycle length, which would yield 36 % regeneration efficiency.

The regenerant recycling led to increased conductivity, which indicated ion leakage in the exhaustion phase, meaning not all the cation impurities were released during regeneration. There was also conductivity leaking from the ion exchange line where the strong acid cation resin was regenerated with 4 BV of fresh regenerant in co-flow regeneration. Thus, 4 BV of fresh regenerant was not sufficient to fully regenerate resin either. Resin samples after regeneration would have aided to evaluate how well the resin was regenerated. It was noted that strong acid cation resin was the limiting factor, which was seen in the increasing cation leakage at the end of exhaustion. Also, pH started decreasing, indicating that weak base anion resin could not take all the released hydrogen ions when protonating. Resin samples from weak base anion resin before and after regeneration would give extra knowledge regarding the regeneration.

Further testing should be made with recycled regenerant to optimize the amount of fresh acid, which is recycled to further regenerations. Long-term impact on the cycle length was not tested when using regenerant recycle. Therefore, it is unknown could impurities accumulate in the resin, causing decreased cycle length or higher ion leakage during the exhaustion step. If this type of issue was faced, the resin could be regenerated only with the fresh regenerant and start recycling the regenerant again.

The regeneration was tested in reverse flow for both fresh regenerant and recycled regenerant. The reverse flow regeneration decreased the ion leakage to a minimum, and

it is recommended for the processes that requires low ion leakage. The cycle length could be slightly shorter when using reverse flow in regeneration, but the change is not significant.

In table 9, it was stated that the regeneration efficiency was 27 % when using 4 BV of 5 w-% sulfuric acid in an ion exchange process, which consists of strong acid cation resin in the first column and weak base anion resin in a second column. It was tested whether 3 BV of 5 w-% sulfuric acid is enough to regenerate the resin without decreasing the cycle length. There was no difference in the cycle length when using 3 or 4 BV of 5 w-% sulfuric acid to regenerate strong acid cation resin. There was higher conductivity when 3 BV of 5 w-% sulfuric acid was used to regenerate the resin, meaning there was a higher amount of residual ions after regeneration. Future studies should also include resin analysis before and after regeneration to understand the regeneration efficiency. The resin analysis should include the ionic form of the resin before and after the regeneration to determine the operating capacity of the resin. As it was noted in table 9 that the strong acid cation resin was still mostly in H^+ form when the resin started leaking cations. Water regain should also be analyzed if performing long-term testing. The water regain tells how much water one gram of resin can take. Decreasing water regain indicates the resin is fouling from impurities such as precipitate. Fouling decreases the operating capacity of the resin resulting in shorter ion-exchange cycles. If water regain has increased, the resin divinylbenzene crosslinking has been breaking. It is also possible that both phenomena take place which can be difficult to detect.

The importance of operating capacity was noticed in the study. Even though the ion exchange started leaking ions of the feed indicating the exhaustion of the resin, strong acid cation remained more than half in regenerated ion form. This plays a vital role when designing an ion exchange process. For example, the operational capacity of strong acid cation resin was more than half smaller than the total capacity in this case.

The ion leakage was increasing between the ion exchange cycles. A study covering only one or a few ion exchange cycles lacks vital information on how a continuous process with hundreds of cycles performs. Due to limited resources, long-lasting studies are not practical, but it should be noted when planning an ion exchange study that the testing should include more cycles to find how the increasing number of cycles impacts ion exchange the product and the length of exhaustion.

The impact of decreased chemical consumption would lower the cost of regeneration, making the production more profitable. The reduced acid consumption and wastewater would make the ion exchange a more environmentally friendly, easing wastewater treatment. Implementing reverse flow regeneration would allow producing low conductivity ion exchange product. The regenerant recycle requires tanks which are used to collect spent regenerant. After regeneration, water used to rinse could also be collected and used to dilute regeneration chemicals to proper concentration, decreasing the amount of produced wastewater and freshwater consumption.

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Inorganic analysis of the outflow after co-flow regeneration

Regenerant	Product	RI DS	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	Fe ^{+2/3}	Si
	BV	%	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	12.2	120	933	< 3	7	< 1	< 4
	2.5	17.3	79	798	< 2	7	< 1	8
	4	18.0	61	752	< 1	7	< 1	18
	5.5	18.2	52	724	< 1	7	< 1	7
	7	18.3	42	670	< 1	6	< 1	4
	8.5	18.3	36	641	< 1	6	< 1	4
	9.5	18.4	35	619	< 1	6	< 1	4
	10.5	18.9	38	594	< 1	7	< 1	4
	11.5	18.8	63	691	< 2	10	< 2	4
	12	16.8	95	895	< 2	12	3	4
	12.5	5.6	126	1 080	< 5	< 11	13	12
Fresh	1	12.9	< 5	465	< 2	< 4	< 1	< 1
	2.5	17.3	< 4	386	< 1	< 4	< 1	< 1
	4	18.2	< 5	369	< 1	< 4	< 1	< 2
	5.5	18.3	< 3	355	< 1	< 4	< 1	10
	7	18.3	< 2	344	< 1	< 4	< 1	13
	8.5	18.3	< 2	329	< 1	< 4	< 1	8
	9.5	18.5	< 2	320	< 1	< 4	< 1	5
	10.5	19.1	< 4	306	< 1	5	< 2	4
	11.5	18.9	10	302	< 1	6	3	4
	12	15.7	18	320	< 2	< 6	4	5
	12.5	7.1	15	180	< 4	< 3	8	8
Feed		20.2	303	10 343	43	560	32	3

Regenerant	Product	RI DS	Acetate	Formate	Cl ⁻	SO ₄ ⁻²	Oxalate	PO ₄ ⁻³	Lactate	Succinate	NO ₃ ⁻
	BV	%	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	12.2	262	129	< 1	13	< 4	< 40	58	< 40	< 40
	2.5	17.3	268	105	< 3	10	< 3	< 30	52	< 20	< 30
	4	18.0	240	61	< 4	< 5	< 3	< 30	68	223	< 25
	5.5	18.2	171	37	6	< 3	< 3	< 30	181	406	< 30
	7	18.3	129	29	7	< 3	< 2	< 3	154	488	< 25
	8.5	18.3	102	14	6	7	< 3	< 3	123	528	< 25
	9.5	18.4	78	13	6	< 3	< 3	< 3	95	540	< 25
	10.5	18.9	89	29	5	< 3	< 3	< 3	106	501	< 25
	11.5	18.8	84	24	4	< 2	< 2	< 4	113	593	< 25
	12	16.8	105	27	5	11	< 6	< 4	152	911	< 30
	12.5	5.6	163	51	< 8	< 8	< 8	< 10	186	970	< 80
Fresh	1	12.9	175	72	< 3	10	< 3	< 35	28	< 40	< 35
	2.5	17.3	189	68	< 3	< 4	< 3	< 25	31	< 30	< 30
	4	18.2	203	62	< 3	< 3	< 3	< 25	30	< 30	< 25
	5.5	18.3	171	36	< 2	< 4	< 2	< 25	20	< 30	< 25
	7	18.3	102	12	< 2	< 3	< 2	< 25	16	84	< 25
	8.5	18.3	49	4	< 2	< 5	< 2	< 25	< 2	175	< 25
	9.5	18.5	40	3	< 3	< 4	< 5	< 3	13	277	< 25
	10.5	19.1	42	9	< 2	< 2	< 2	< 3	14	381	< 25
	11.5	18.9	46	10	< 2	< 3	< 2	< 3	30	597	< 25
	12	15.7	53	11	< 3	< 3	< 3	< 3	56	771	< 30
	12.5	7.1	80	20	< 6	< 7	< 6	< 7	93	1 263	< 70
Feed		20.2	159	40	82	13 037	173	593	315	944	156

Inorganic analysis of the outflow after reverse flow regeneration

Regenerant	Product	RI DS	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	Fe ^{+2/3}	Si
	BV	%	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	13.0	5	12	< 1	< 1	< 1	< 1
	2.5	18.0	< 2	10	< 1	< 1	< 1	< 3
	4	18.4	3	13	< 1	< 1	< 1	4
	5.5	18.5	3	14	< 1	< 1	< 1	5
	7	18.5	4	16	< 1	< 1	< 1	4
	8.5	18.6	7	21	< 1	< 1	< 3	4
	9.5	18.7	25	54	< 1	< 1	5	4
	10.5	18.9	86	244	< 1	7	6	3
	11	18.1	136	466	< 1	9	7	4
Fresh	1	14.5	< 2	< 2	< 1	< 1	< 1	< 1
	2.5	18.2	< 1	< 2	< 1	< 1	< 1	< 2
	4	18.4	< 1	< 2	< 1	< 1	< 1	3
	5.5	18.5	< 1	< 2	< 1	< 1	< 1	6
	7	18.5	< 1	< 2	< 1	< 1	< 1	6
	8.5	18.6	< 2	< 3	< 1	< 1	< 2	4
	9.5	17.5	< 3	< 3	< 2	< 1	< 3	4
	10.5	15.0	7	< 6	< 2	< 1	< 3	4
	11	12.4	7	7	< 2	< 1	4	5
Feed		20.2	302	10 379	43	561	32	3

Regenerant	Product	RI DS	Acetate	Formate	Cl ⁻	SO ₄ ⁻²	Oxalate	PO ₄ ⁻³	Lactate	Succinate	NO ₃ ⁻
	BV	%	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS	mg/kg DS
Recycled	1	13.0	16	< 3	< 20	< 3	32	< 4	ND	< 35	< 30
	2.5	18.0	15	< 4	< 15	< 2	23	< 2	ND	< 34	< 25
	4	18.4	18	< 3	< 10	< 3	2	< 2	ND	< 25	< 25
	5.5	18.5	16	< 5	< 10	< 2	23	< 2	ND	< 25	< 25
	7	18.5	14	6	< 10	< 2	23	< 2	ND	< 25	< 25
	8.5	18.6	22	8	< 10	< 2	23	< 3	ND	96	< 25
	9.5	18.7	29	8	< 10	< 2	22	< 3	ND	399	< 25
	10.5	18.9	41	9	< 10	< 2	23	< 4	ND	1 046	< 25
	11	18.1	53	10	< 15	< 2	4	< 4	ND	880	< 25
Fresh	1	14.5	24	< 3	< 15	< 3	29	< 3	ND	< 30	< 30
	2.5	18.2	15	< 2	< 15	< 3	23	< 3	ND	< 25	< 25
	4	18.4	25	< 3	< 15	< 3	24	< 3	ND	< 25	< 25
	5.5	18.5	15	< 5	< 10	< 2	23	< 2	ND	< 25	< 25
	7	18.5	15	6	< 10	< 2	23	< 3	ND	< 23	< 25
	8.5	18.6	27	7	< 15	< 2	23	< 3	ND	154	< 25
	9.5	17.5	29	8	< 15	< 2	25	< 4	ND	364	< 5
	10.5	15.0	41	9	< 15	< 4	29	< 4	ND	1 211	< 30
	11	12.4	48	11	< 20	< 4	36	5	ND	1 336	< 40
feed		20.2	148	43	80	12 820	150	391	ND	877	147