CHEMICAL ENGINEERING TRANSACTIONS

VOL. 56, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim
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ISBN 978-88-95608-47-1; **ISSN** 2283-9216

DOI: 10.3303/CET1756040

Sensitivity Analysis for Optimisation of Brine Purification Process

Muhammed Anwar Abu Bakar[a,c], Arshad Ahmad*[,b,c], Mukri Harun[a]

[a]CCM Chemicals Sdn. Bhd., Kawasan Perindustrian Pasir Gudang, 81710 Pasir Gudang, Malaysia
[b]Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
[c]Department of Chemical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
arshad@utm.my

A two-stage brine purification process involving an ion exchange column and a secondary filter is an important process unit in a chlor-alkali plant. As part of the effort to increase the plant capacity, the throughput of this process has been increased, which has subsequently caused non-conformance to the production specifications unless the filter is changed more frequently. Investigations are then carried out to study the sensitivity of potential variables to be manipulated in order to optimise the process, and increase the filter life. The results obtained from plant tests show that by increasing Calcium to Magnesium ratio, and maintaining lower excess sulphate the filter life can be increased. Based on these findings, a recycle stream is introduced and better performance is obtained. Following this modification, better performance is obtained, however, due to some production issues, the target desired improvement level is not achieved

1. Introduction

A local manufacturer runs a chlor-alkali plant in the southern part of Malaysia. The plant is designed to produce 40,000 Mt/y of chlorine. Chlorine is produced together with its co-product, Sodium Hydroxide and derivatives such as Hydrochloric Acid and Sodium Hypochlorite. Few plants are integrated in the manufacturing of those products above. For example, the feed stock is prepared at primary and secondary brine purification plant. After that, the pure brine is fed into the electrolyser together with sodium hydroxide separated with a membrane in the centre. These two liquids are not mixed. After electrolysed the gas and also liquid, it will be process to the downstream operation.

One important part of the plant is the brine process where this is the important feed stock for electrolyser. The operation is very much depending to the consistency of supply and also its superior quality. The factor that affects the above is the operation of the brine filter. The brine filter is operated based on differential pressure. The increasing pressure at inlet of brine filter will reduce the flow leaving the filter. The operation needs a changeover to the second brine filter which is installed parallel. The first brine filter can be backwashed and made ready to take over after the second brine filter exhausted. The brine inventory should be maintained as much as practical possible. Increasing through put through the brine filter will reduce its operation hours.

The needs for increasing the production rate has cause the increase on brine flow from 35 m^3/h to 65 m^3/h. This increase in capacity has significant impact on the process performance. It is understood that the brine filter is not able to perform as per baseline life because of increasing throughput, lesser retention time and higher suspended solid carry over. It is therefore important to optimise the plant operating parameters to meet the intended production objectives with existing facilities. This sets the premise for the plant optimisation studies reported in this paper.

2. Problem Statement

2.1 Process Description

The primary brine purification stage includes salt saturation, chemical dosing, reaction and sedimentation processes. The objectives of the primary brine purification are:

Please cite this article as: Bakar M.A.A., Ahmad A., Harun M., 2017, Sensitivity analysis for optimization of brine purification process, Chemical Engineering Transactions, 56, 235-240 DOI:10.3303/CET1756040

1. To re-saturate the return brine with raw solid salt,
2. To remove impurities from the saturated raw brine, and
3. To produce brine with specifications required in the chlor-alkali plant in Southern Malaysia as summarised in Table 1 below.

Table 1: Product Specifications for Primary Brine Purification Process (Asahi Chemical Industry Co., Ltd, 1996)

NaCl (g/L)	Temperature (°C)	pH	Max Ca^{+2} (mg/L)	Max Mg^{+2} (mg/L)	Max SO_4 (g/L)	Free Cl_2	Max solid salt (mg/L)
305 ± 5	60	11	10	1	6.5	None	10

The saturated raw brine from the Brine Storage Pit is pumped into the reactor, where NaOH, $CaCO_3$ and $BaCO_3$ are added in order to form precipitates with the impurities for removal. Approximately 8 wt% $BaCO_3$ suspension is prepared with water and around 8 wt% light $CaCO_3$ solution is prepared with dilute brine in stirred tank. The doses are fed to the reactor by dosing pump. $BaCO_3$ is added to the reactor react with Ba^{2+} to form $BaSO_4$, and simultaneously produces Na_2CO_3. The precipitation process is completed in the reactor by adding light $CaCO_3$ solution and NaOH solution.
The reactions involved in the process are as follows:
Sulphates, which are precipitated as BaSO4 by reaction with $BaCO_3$

$$\mathrm{SO_4}^{2-} + \mathrm{BaCO_3} \rightarrow \text{Precipitate } \mathrm{BaSO_4} + \mathrm{CO_3}^{2-} \tag{1}$$

Calcium, which is precipitated as

$$\mathrm{Ca^{2+}} + \mathrm{Na_2CO_3} \rightarrow \text{Precipitate } \mathrm{CaCO_3} + 2\mathrm{Na^+} \tag{2}$$

Magnesium, which is precipitated as

$$\mathrm{Mg^{2+}} + 2\mathrm{NaOH} \rightarrow \text{Precipitate } \mathrm{Mg(OH)_2} + 2\mathrm{Na^+} \tag{3}$$

Strontium, which is precipitated mainly as

$$\mathrm{Sr^{2+}} + \mathrm{CO} \rightarrow \text{Precipitate } \mathrm{SrCO_3} \tag{4}$$

In the chlor-alkali plant, the process of precipitation typically takes about 7 h, and during this process, pH of the brine is maintained at 10.5 by adjusting NaOH flow rate fed to the reactor. The brine is then fed out to the clarifier from the reactor in order to remove the precipitates to a target value of lower than 12 NTU. The precipitates are allowed to settle in the clarifier to form sludge. The clarified brine is sent to the secondary brine purification process, while the slurry collected at the bottom of the clarifier is pumped to the slurry tank for brine recovery, leaving the remaining solids as waste.

2.2 New Operating Requirement and its implication

The plant has been operating well based on the baseline condition shown in Table 2, giving a filter life of 45 h. As the need for higher flow rate arises, the flow rate has been increased from 35 m^3/h to 65 m^3/h. This has caused plant upset in terms of pure brine production to be fed to the electrolyser. The entire brine inventory has reduced to a level where it is insufficient for the operation.

Table 2: Operating Conditions of the Brine Purification Process.

	Brine Flow (m^3/h)	Inlet Calcium (ppm)	Inlet Magnesium (ppm)	Outlet Suspended Solid (NTU)	Retention Time (h)	Brine Filter Life (h)
Baseline condition	35	68.9	39.9	9.2	7.5	45
New condition	65	68.9	39.9	19.8	4.11	5.4

Increasing the flow rate from 35 m^3/h to 65 m^3/h has reduced the total retention time from 7.5 h to 4.11 h at the brine reactor affecting the reaction process. As a result of shorter retention time, there has been a significant carry-over of suspended solid (from 9.2 NTU to 19.8 NTU), leading to significantly shorter filter life of 5.4 h. Optimal filtration cycle time is also an important factor for optimal filtration performance. Filter sizing depends on filtration cycle time. Small filter has to be cleaned frequently while larger one needs longer cycles. Long filtration cycle causes the filter cake to become thick, hence reducing the flow rate per filter area. Very short filtration cycle causes longer downtime for cleaning which in turn reduces the filter capacity. It is very crucial to find an optimal cycle time which leads to highest overall throughput and lowest overall cost (Ripperger et al., 2012). Hence the needs for more frequent back washing and changeover of filter occur. This has significantly impacted the brine inventory, and supply to the electrolyser. Massive losses of productions were experienced, as the plant cannot operate at maximum loading. In some occasions, the plant operators were not able to control the low brine inventory situation, leading to plant shutdown.

3. Brine Flowrate Optimisation

There are few factors that involve in this brine optimisation sensitivity analysis investigation. The factors are namely as in below Table 3. In order for brine filter to run longer hours, the criteria will be low in suspended solid and also lower Calcium and Magnesium content after the reaction process in the brine reactor. Both Suspended Solid and Calcium / Magnesium reaction takes place at different area of the process. Based on below methodology, the factors are being varied in the process and the output is being measured accordingly. The output, in this case for all the input factors will be the brine filter operating life in hours. The Table 4 below summarises the factors variety during the investigation

Table 3: Factors involves in brine optimisation investigation

Factors
Sulphate Level in Brine
Calcium / Magnesium Ratio in D021
Suspended Solid Content
Slurry recirculation

Table 4: Summary of Factors Varieties in Investigation

Factors	Min	Max
Sulphate Level in Brine	2 mg/L	4 mg/L
Calcium / Magnesium Ratio in D021	1.3	2.5
Suspended Solid Content	5 NTU	40 NTU
Slurry recirculation	None	8 m^3/h

3.1 Methodology

One of the simplest and most common approaches is that of changing one-factor-at-a-time (OFAT or OAT), to see what effect this produces on the output (Campbell, 2008). OAT customarily involves;

- Moving one input variable, keeping others at their baseline (nominal) values (Bailis et al., 2005), then,
- Returning the variable to its nominal value, and then repeating for each of the other inputs in the same way (Murphy et al., 2004).

Sensitivity may then be measured by monitoring changes in the output, e.g. by partial derivatives or linear regression. This appears a logical approach as any change observed in the output will unambiguously be due to the single variable changed. By changing one variable at a time, one can keep all other variables fixed to their central or baseline values. This increases the comparability of the results (all 'effects' are computed with reference to the same central point in space) and minimises the chances of computer programme crashes, more likely when several input factors are changed simultaneously. OAT is frequently preferred by modellers because of practical reasons. In case of model failure under OAT analysis the modeller immediately knows which the input factor responsible for the failure is (Saltelli and Annoni, 2010).
Despite its simplicity, this approach does not fully explore the input space, since it does not take into account the simultaneous variation of input variables. This means that the OAT approach cannot detect the presence of interactions between input variables (Czitrom, 1999). For this chlor-alkali process, the interaction changes will not be as significant as the dynamic of the volume are not so large. The changes in flow are almost zero.

4. Results and Discussions

The result for each sensitivity analysis is explained in following sections.

4.1 Effect of Sulphate level on Brine Filter Life

Based on Figure 1, it is observed that lower Sulphate content will improve the performance of brine filter life. The brine filter average life is 20 h at Sulphate level 2 ppm where else 14 h at Sulphate level 4 ppm.

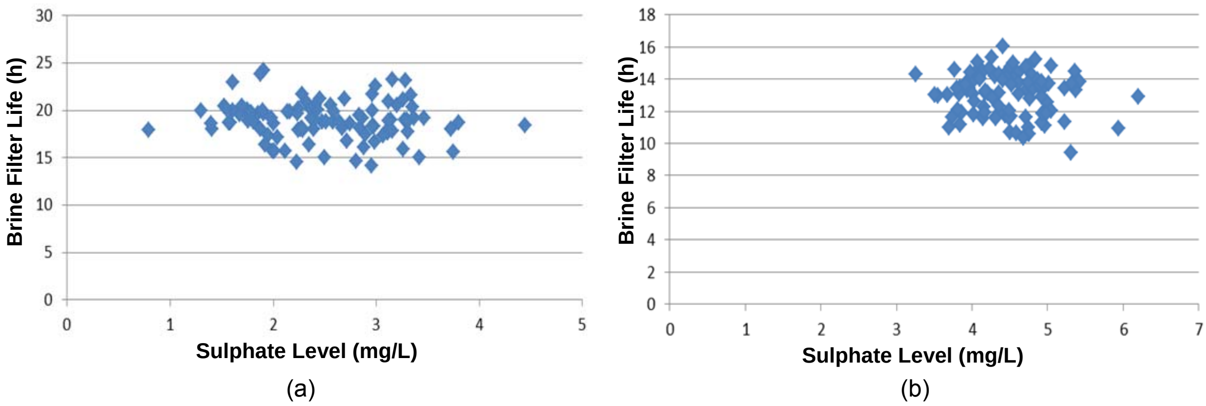


Figure 1: Effect of Sulphate level in brine on Brine Filter Life at (a) 2 ppm, (b) 4 ppm

4.2 Effect of Calcium and Magnesium Ratio and Suspended Solid at Brine Flow at 35 m^3/h on Brine Filter Life

Figure 2 visualises the effect of Ca/Mg Ratio towards brine filtration performance. At 35 m^3/h brine flow, it seems the ratio is above 1.5 to 2.0. For suspended solids content, 16 NTU and below will give tremendous filtration hours at 35 m^3/h brine production.

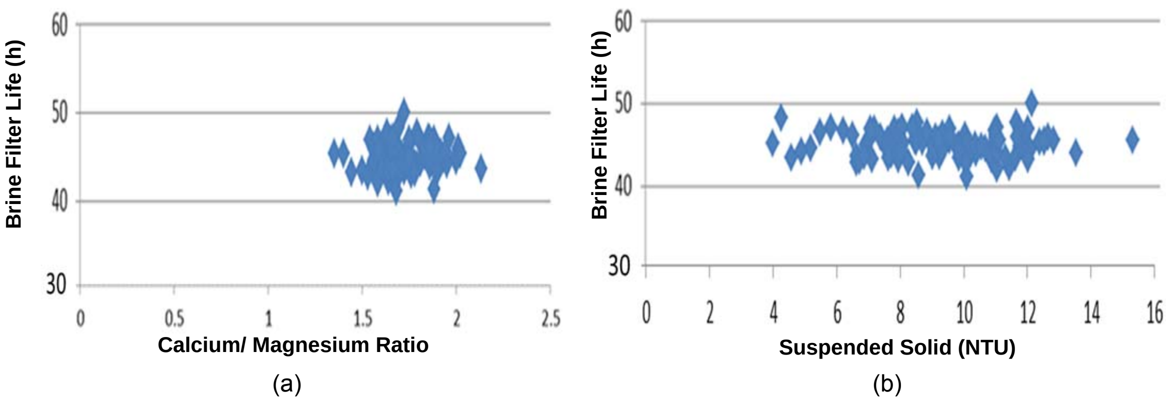


Figure 2: Effect of (a) Calcium and Magnesium ratio and (b) suspended solid, at brine flow at 35 m^3/h on Brine Filter Life

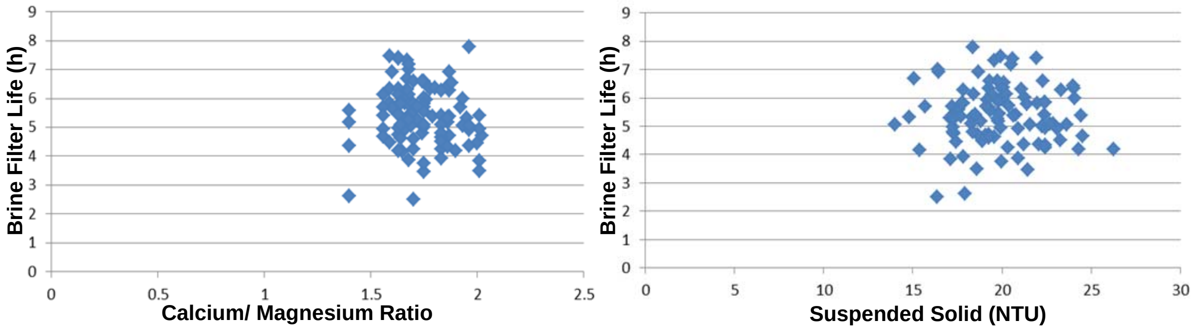
4.3 Effect of Calcium and Magnesium Ratio and Suspended Solid at Brine Flow at 65 m^3/h without slurry recirculation on Brine Filter Life

After increasing the brine flow requirement to 65 m^3/h, effects are visualized as in Figure 3. At 65 m^3/h brine flow, it seems the ratio is still at 1.5 to 2.0 but suspended solids content, increased from 16 NTU to 25 NTU and gives tremendous impact to brine filtration hours. The filter life is shortening from 48 h to minimum 4 h.

4.4 Effect of Calcium and Magnesium Ratio and Suspended Solid at Brine Flow at 65 m^3/h with slurry recirculation on Brine Filter Life

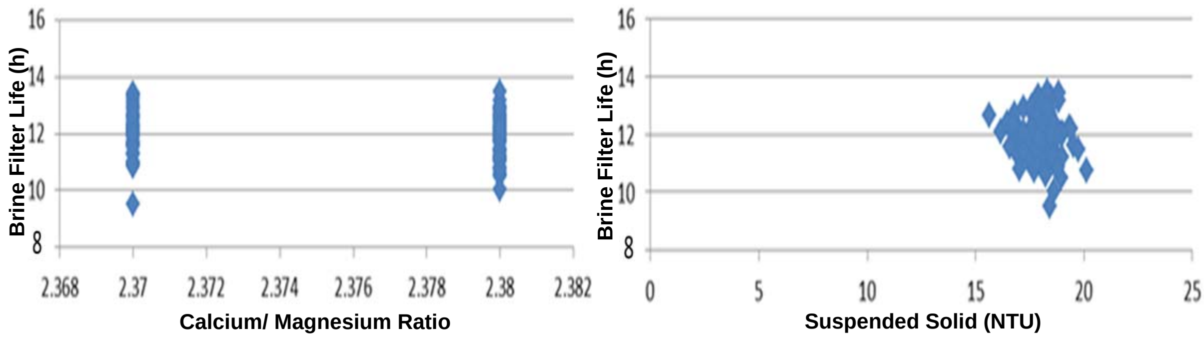
Figure 4 shows the filter performance after slurry recirculation introduced from the bottom of clarifier to the brine reactor. At 65 m^3/h brine flow, it seems the ratio of Calcium and Magnesium increased from 1.5 to 2.0 to

2.0 to 2.3. There is no significant increment of suspended solids content, only that it became more stable rather than give high fluctuation. The improvement in process variance can be observed before and after slurry recirculation process introduced. The filter life has slightly improved from minimum 4 h to 12 h maximum.



(a) (b)

Figure 3: Effect of (a) Calcium and Magnesium ratio and (b) suspended solid at brine flow at 65 m^3/h without slurry recirculation on Brine Filter Life



(a) (b)

Figure 4: Effect of (a) Calcium and Magnesium ratio and (b) suspended solid at brine flow at 65 m^3/h with slurry recirculation on Brine Filter Life

5. Conclusion

From the overall sensitivity analysis methodology and approach, the results show that the brine filters performance can be optimised with changes affecting the upstream of brine filtration process. The optimum running hours at the end of this analysis is ranging from 10 to 12 h. The factors that contributed most during the analysis are the slurry recirculation process. This process has significantly increase the Calcium to Magnesium ratio in brine hence improve the clarification process in brine clarifier. Another independent factor which also contributed in the performance of filtration is the Sulphate content in brine. By reducing the dosing of Barium Carbonate, the excess of Sulphate in brine will be reduced. But this is a double edged sword which will cause Barium carry over to the downstream of the process. The Barium carry over to the electrolyser section is very much harmful and costly. The damage is not recoverable. The Sulphate content will be maintained at 4 ppm minimum in brine to ensure there is no carry over Barium to the downstream of the process.

Acknowledgments

The author would like to acknowledge the Ministry of Higher Education (MOHE) of Malaysia, University Technology of Malaysia and CCM Chemicals Sdn Bhd for their kind heart to sponsor and help during the entire effort taken to research on and produce this analysis and undertaking the program as a whole. The author would also like to special acknowledgment the financial supports provided by University Technology of

Malaysia through the Research University Grants with vot number of Q.J130000.2509.07H12 and Q.J130000.2509.13H95.

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