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Brine Purification for Chlor-Alkalis Production Based on Membrane Technology

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Abstract

The experimental work is concerned to process and schematic methodology to reduce the percentage of sulfates and also to minimize the concentration of other impurities such as Calcium and Chlorate. The technology used in this study is a unique combination of primary and secondary treatment of raw brine to prepare a feed for the production of chlor-alkalis.

A series of experimentation was conducted for the determination of major constituents and other trace metals in the brine using ICP spectrophotometer. The major elements determined were sodium, calcium, magnesium, potassium, strontium, sulfur and chloride. The trace metals determined were iron, barium, silicon, nickel, manganese, chromium, copper and boron. The influence of different parameters like concentration, temperature, pressure, impurity, pH, resin capacity was studied experimentally. On the basis of data collected and their analysis it can be concluded that best results are obtained when the treating chemicals Na_2CO_3, NaOH and Flocculating agent (Anionic) may be added to brine as a separate addition point.

Key Words: Brine; Purification; Membrane Technology; Chlor-alkalis

1. Introduction

Many people think of salt as food seasoning, found on every dining table. It is that and far more. It is an essential ingredient in the diet of humans, animals, and plants and is one of the extensively used food preservative. It is used as an intermediate in the chemical industry to produce many other chemicals. Its uses are almost without number, it is almost involved in all aspects of human activity, In addition, large amounts of salt are consumed by meat and fish packers, in water softening, road stabilization, ice and snow removal, and recovery of bromine from seawater. It had also been used as a means of exchange in earlier times.

2. Historical Background

Brine is the life blood for Chlor-alkali industries. A passable supply of high quality brine on a continuous basis is invaluable for plants operation. The caustic soda (a Chlor-alkali) industry has vital importance because its per capita consumption is normally considered as an indicator of normal growth of a country, especially in the sector of derived chemicals, textiles, thermoplastics, polymeric products etc. Its need has been increasing substantially worldwide in last decades and will continue to increase in the coming times.

Three processes generally, mercury, diaphragm and membranes cell electrolysis are employed for the production of chlor-alkalis. Out of these, membrane cell electrolysis has received much attention being a modern as well as having overriding economic and environmental advantages [1, 2].Sodium chloride (brine) is the main input and caustic soda, chlorine and hydrogen gas are simultaneously produced in the membrane cell electrolytic process.

For membrane process, essentially high purity brine is required as the unwanted impurities (Ca^{+2}, Mg^{+2} and SO_4^{-1}) deteriorate membrane performance, therefore, purification of brine, settling, filtration, acidification, de-chlorination are auxiliary processes for the quality and efficient production of such alkalis. Chlor-alkali industry is power intensive and is considered as the second largest consumer of electricity [3,4].

Chlor-alkali industry, being red category industry, generate amount of amount of solid and liquid waste containing a number of contaminants such as calcium, magnesium, iron, and other metallic hydroxides depending on the nature, purity and source of sodium chloride rock and imparts a number of environmental issues [5].

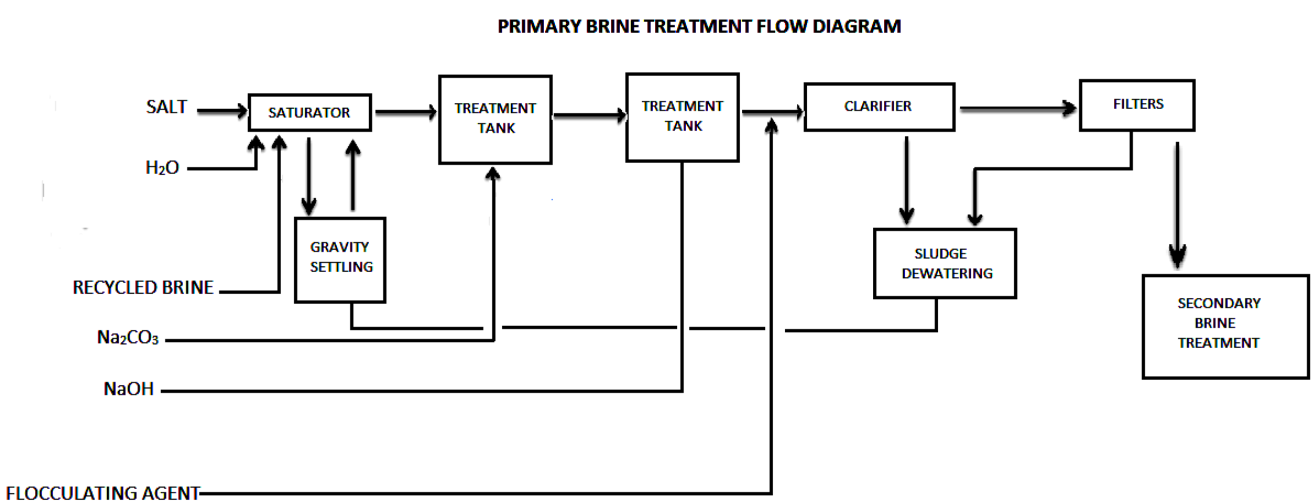
In the past decades much work is done and studies (such as waste filtration and recycling of supernatant, using single cell of large size, enhancing cathode and anode reaction by magnetic modification of electrodes surfaces and source reduction), are conducted and suggestion are made by researchers to evaluate the characteristics of effluent as well as to identify the prospective waste minimization approaches [6-9]. Studies show that magnetic modified electrode flux is larger than flux of non-magnetically modified electrodes [13, 14].

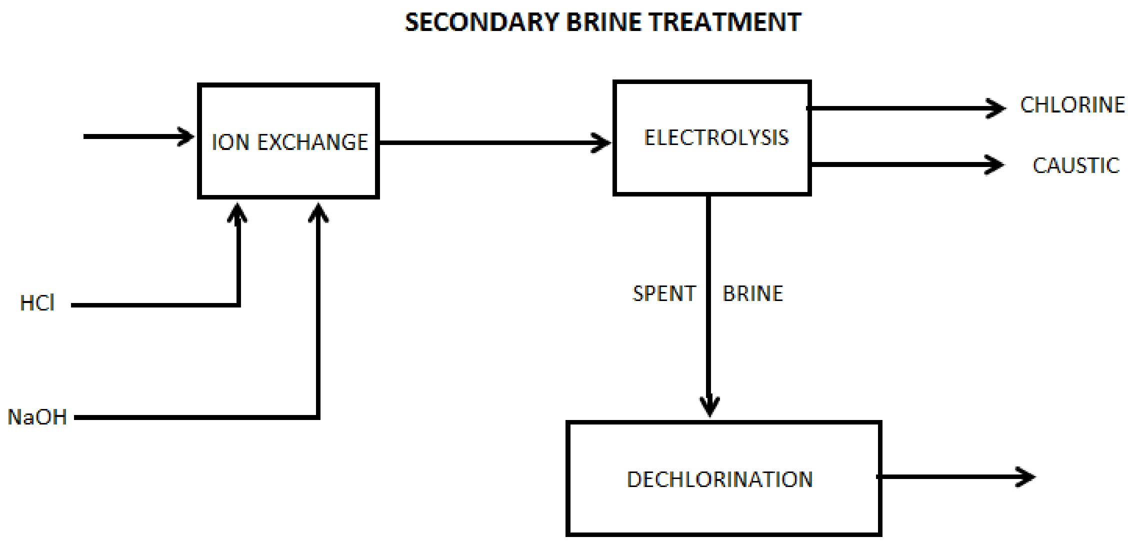
Out of all these approaches, source reduction are usually the lowest cost practical alternate to adopt for improving production process. A study show the maintenance cost is reduced to much extent while waste disposal cost is reduced by 55% [15].

Efforts are also made to properly use the waste products produced from this industry.

3. Scope of Present Work

Researchers have been engaged in developing unconventional and innovative processes that are inexpensive, yet achieve highest levels of brine purity. Present research work describes the prediction methods of the process performance and presents results obtained in Chlor-alkali plant commissioned recently. The prime objective is to explore the technical possibility and economic feasibility to introduce a simple technique for the purification of raw brine. The purification operation is designed to avoid unwanted components (i.e., purification of calcium, Barium, Magnesium and other trace elements). These operations are classified as primary stage includes precipitation, purification, and filtration. Secondary purification unit is comprised of an ion-exchange membrane circuit to perform high quality of separation of impurities like Sr, SiO_2, heavy metals. Whereas the 3rd step high temperatures and high pressure liquefaction systems need cryogenic system to store liquid chlorine is very expensive and advanced process. The present work is an effort to bridge the gap for the development of an economical and efficient method which can be applied at chlor-alkali industries.





4. Experimental Setup and Experimentation

The systematic block diagram for the primary and secondary refinement of brine solution is given in fig 1 and 2.

A series of experiments were performed to study the effects of order and amount of addition of chemicals and of various variables on the settling rate and removal of suspended particles. Their graphical representation is presented in the subsequent figures. The amounts of both major contaminant components and trace metals in the brine were calculated a using ICP spectrophotometer DR/4004U.

Additionally a Turbiditimeter-2100N and inductively coupled plasma optical emition spectrometry were also used to analyze the data's

5. Order of Inputs

1. Addition of all chemicals together.
2. Separate addition with Na_2CO_3,ahead of NaOH and flocculating agent.
3. Separate addition with NaOH, ahead of Na_2CO_3 and flocculating agent.
4. Separate addition with Na_2CO_3,ahead of NaOH and a separate addition point of flocculating agent

6. Discussion of Results

As is often the case, there is both art and science at work in making a specific brine treatment system work. Figre-1 reveals the results of order of inputs ((Na OH & Na_2 CO_3) and flocculating agent to remove the suspended particles. It shows that option-4 provides the best results. Formation of and settling rate of contaminants suspended particles (Ca CO_3& Mg $(OH)_2$) and their settling rate depends upon inputs in excess and temperature of brine. It is observed that excess inputs and higher temperature reduce the solubility of contaminants and increase the crystal size and settling rate as shown in Figure-2, 3. The effect of imputes i.e. of magnesium content on the size of crystals and their settling rate is revealed in Figure-4 which shows that the brine with higher content will have lower settling rate of contaminates, thereby resulting into a process difficulty. The effect of pressure and temperature on the contaminants settling rate and their removal is shown in Figures-5, 6. It is observed that higher pressure and temperature significantly increase the settling rate and removal of contaminants. Figures-7, 8 expose the effect of PH and temperature on the calcium ions breakthrough. Figure-7 shows that pH in between 8 to 11 favours to remove the calcium efficiently. However, PH greater than 11.

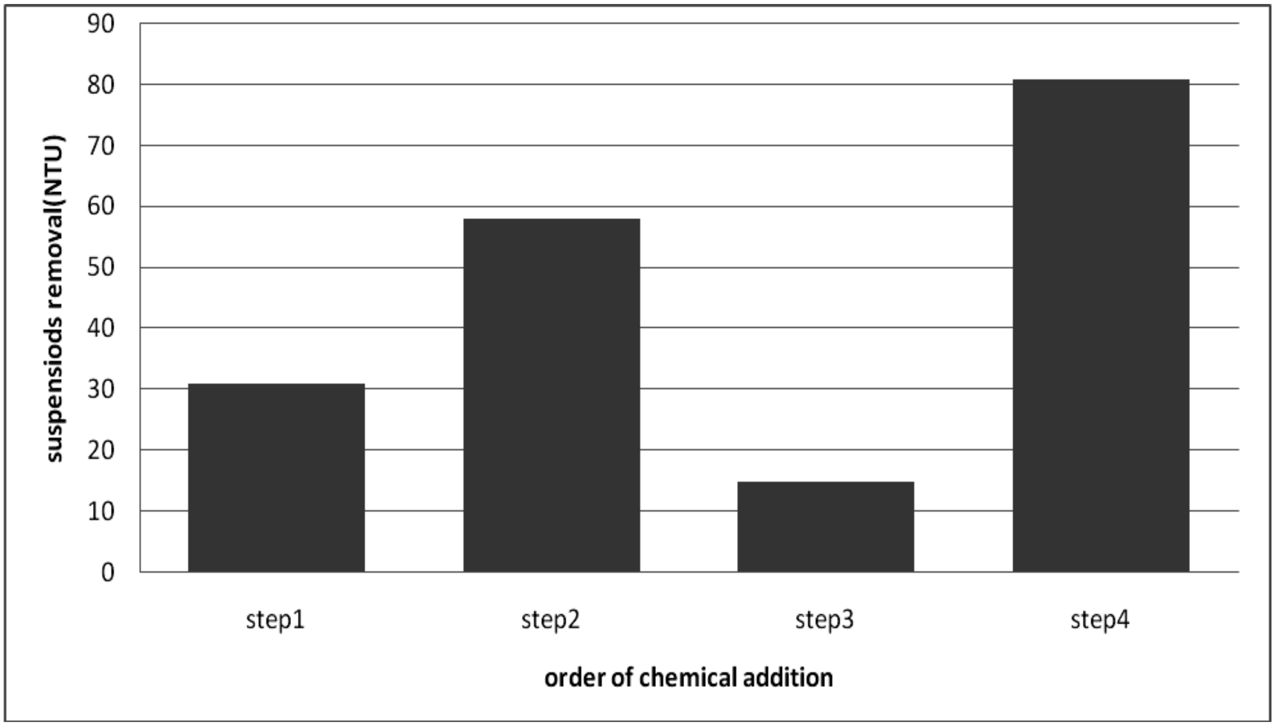


Fig. 1 Order of Chemical Addition vs Suspensoids Removal in Saturated Brine

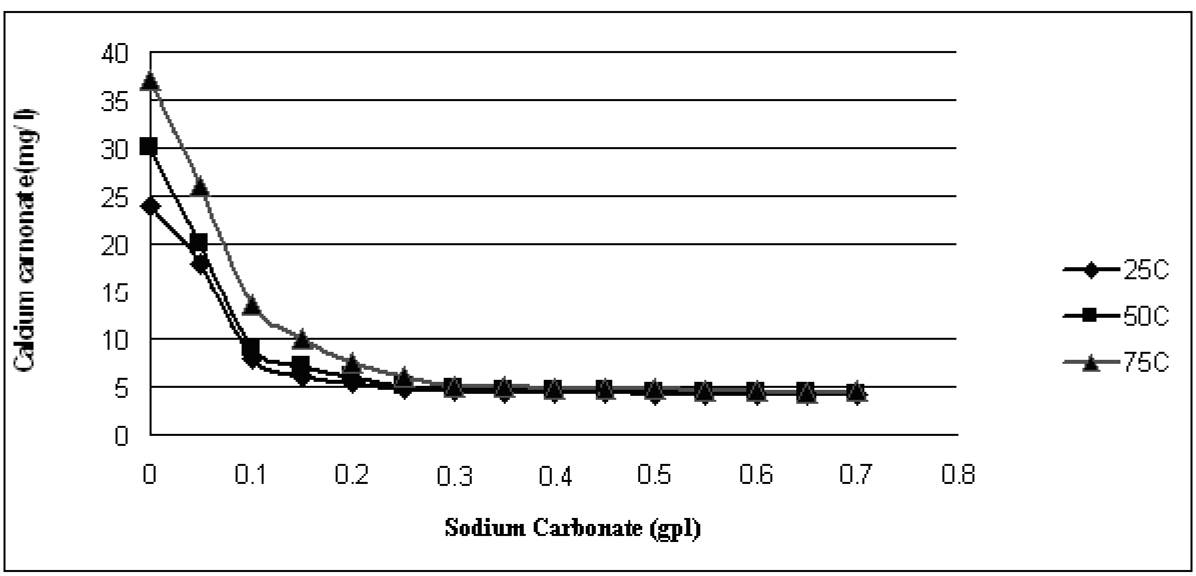


Fig. 2 Concentration of $CaCO_3$ vs. Na_2CO_3 in Saturated Brine.

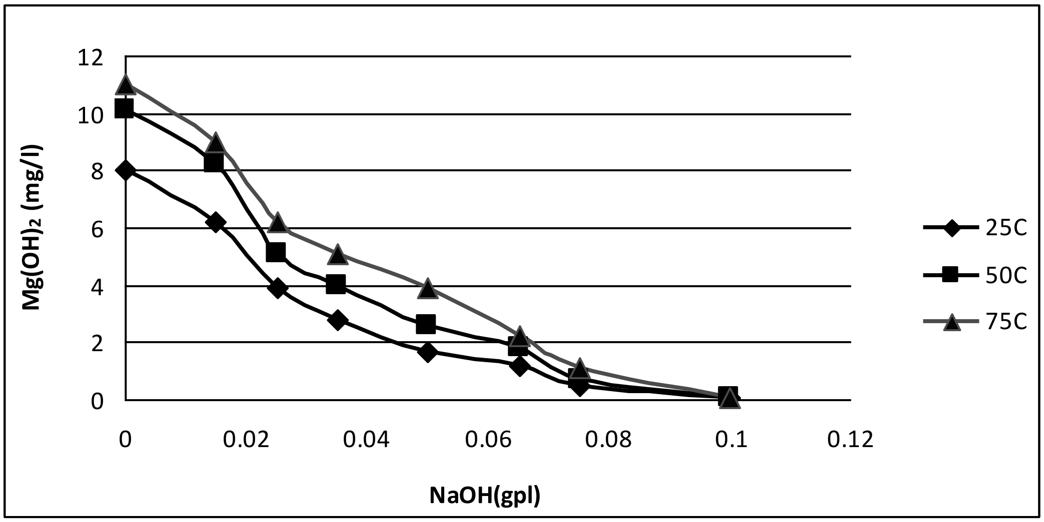


Fig. 3 Concentration of $Mg(OH)_2$ vs Caustic Concentration in Saturated Brine

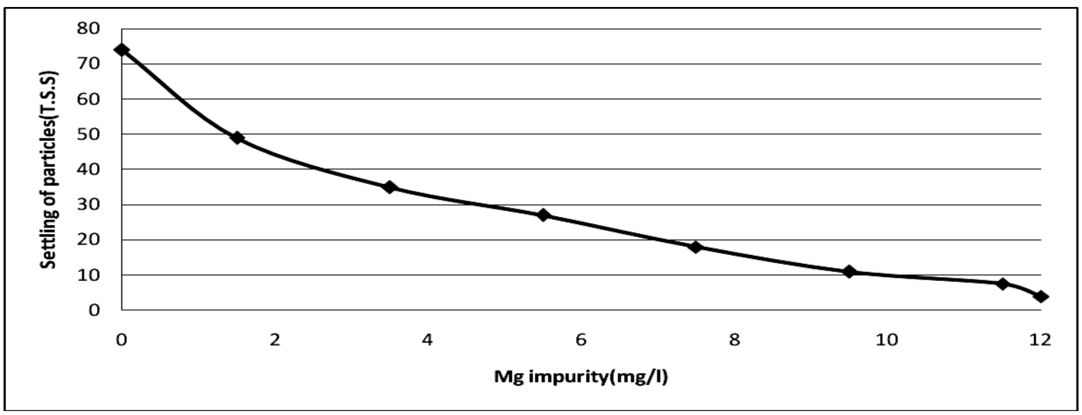


Fig. 4 Effect of Mg Impurity on Setting of Particles

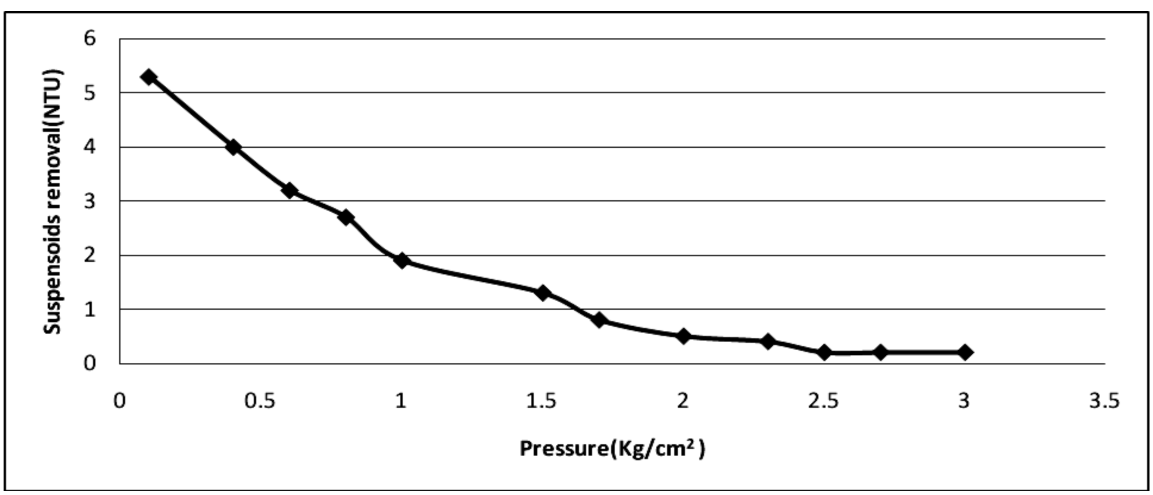


Fig. 5 Effect of pressure on Suspensoids Removal in a Vertical Tubular Backwash filter

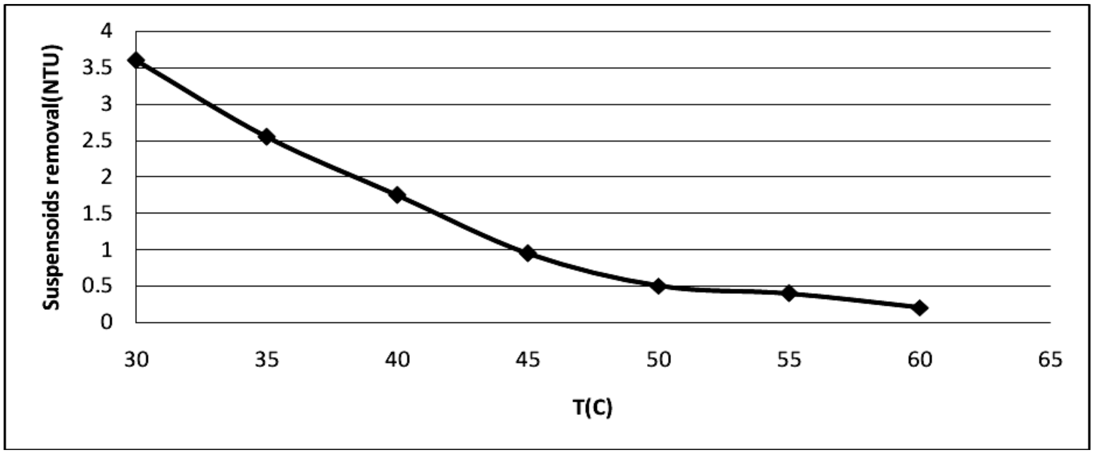


Fig. 6 Effect of Temperature on Suspensoids Removal in a Vertical tubular Backwash Filter

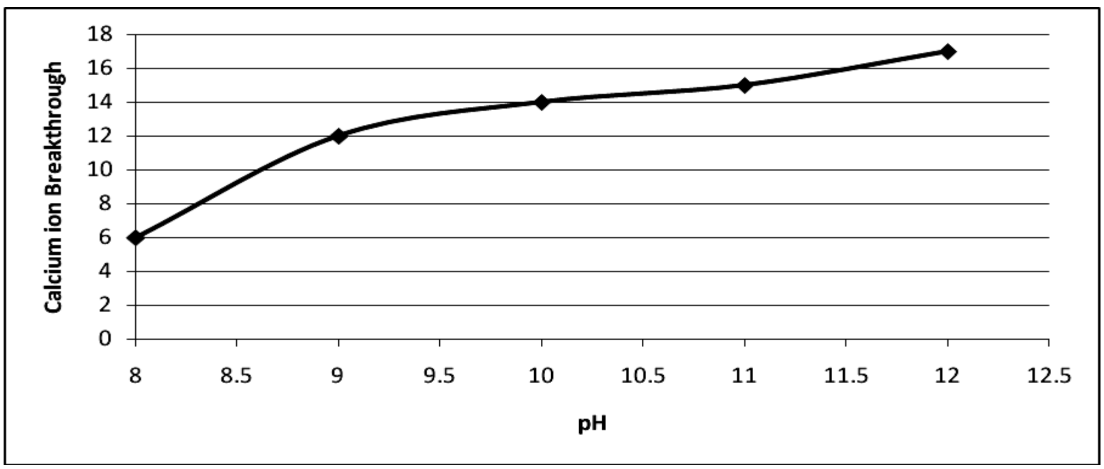


Fig. 7 Effect of Temperature on Suspensoids Removal in a Vertical tubular Backwash Filter

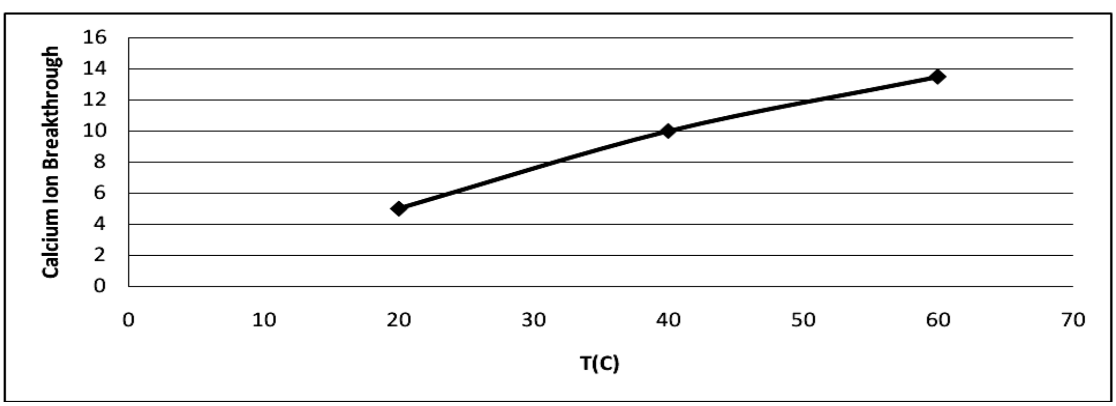


Fig. 8 Effect of Temperature on Calcium Ions Breakthrough

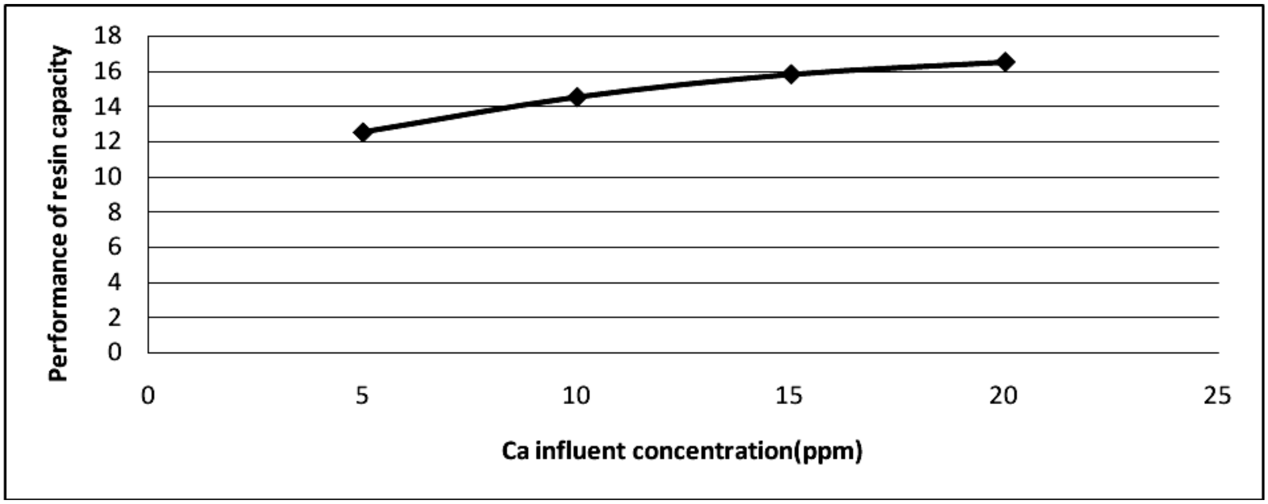


Fig. 9 Effect of Resin Capacity on Calcium Concentration

promote the formation of metal hydroxide precipitates that are in soluble and may cause padding of the resin bed and higher pressure drop across the column. However, higher temperature of brine results in efficient removal of calcium, higher rate and longer service runs are achieved at 60 °C.

However, the temperature of bine above 75 may cause irreversible resin damage. The effect of calcium concentration on resin performance is shown in Figure-9. It shows that resin performance increase when the calcium concentration is above 5ppm.

6. Conclusions

1. Best results are obtained when the treating chemicals Na_2CO_3, NaOH and Flocculating agent (Anionic) are added to brine as a separate addition point.

2. An anionic flocculating agent should be used for brine having alkaline nature.

3. The elimination of magnesium impurity should be of prime concern because the presence of magnesium impurity results into longer settling and poor brine quality as shown in graph #4.

4. The temperature of brine during the addition of treating chemicals should be about 0^0C-55^0C as shown in graph # (2 and 3) for efficient settling of impurities and improved clarity.

5. After primary brine treatment, an increase in temperature of the brine at about 55^0C-60^0C, as shown in the graph # 6, prior to secondary brine treatment is found to be beneficial to accomplish efficient sub-micron filtration. This is because higher temperature increases the particle size thereby increasing the cake thickness which results into efficient removal of suspended solids.

6. Longer service runs can be achieved if the temperature of the brine to ion-exchange columns as shown in the graph # 7 is maintained at about 60^0C-70^0C. However a further increase in temperature, as shown in the graph, is considered to be detrimental for the resin and will result into breakthrough of hardness not appropriate for membrane cells.

7. For efficient calcium removal a brine pH of 8-9 should be maintained as shown in the graph # 8.However, a pH of less than 8 drastically reduces calcium removal capacity. Similarly, as shown in the graph # 8, a pH greater than 11 though has no significant effect on resin performance but it does promote the formation of metal hydroxide precipitate has low solubility. These insoluble solids will eventually plug the

resin bed, creating an excessive pressure drop across the column and thus results into breakthrough of hardness not desirable for membrane cells. Calcium concentration in brine should be lowered up to l0ppm prior to entering in ion-exchange columns for longer service runs and efficient calcium removal.

6. References

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