

Development of a Process to Manufacture High Quality Refined Salt from Crude Solar Salt

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Abstract—This paper describes the research carried out to develop a process to increase the NaCl percentage of crude salt which is obtained from the conventional solar evaporation process. In this study refined salt was produced from crude solar salt by a chemico-physical method which consists of coagulation, precipitation and filtration. Initially crude salt crystals were crushed and dissolved in water. Optimum amounts of calcium hydroxide, sodium carbonate and Polyaluminiumchloride (PAC) were added to the solution respectively.

Refined NaCl solution was separated out by a filtration process. The solution was tested for Total Suspended Solids, SO_4^{2-} , Mg^{2+} , Ca^{2+} . With optimum dosage of reagents, the results showed that a level of 99.60% NaCl could be achieved. Further this paper discusses the economic viability of the proposed process. A 83% profit margin can be achieved by this process and it is an increase of 112.3% compared to the traditional process.

Keywords—Chemico-physical, Economic, Optimum, Refined, Solar Salt.

I. INTRODUCTION

SRI Lanka is a country, where the coastal areas, especially in the South, East, North and the North-western have easy access to sea water, long periods with dry weather and geographical factors such as flat land at low cost for solar salt production. Since sea water (the raw material) and the solar energy (energy source) are available free of charge, solar salt manufacturing is extremely profitable when compared with agriculture where land preparation, seeds, fertilizer, agrochemicals and man power requirements lead to a high cost of production.

During the solar salt manufacturing process, salt is crystallized from brine between the densities of 24 Be° and 29 Be°. Evaporation beds are made of soil and the brine is transferred between beds open canals. The flow is achieved by gravity by maintaining differential levels at the two ends. Therefore most of the time solar salt is contaminated with suspended solids throughout the process. CaSO_4 , MgSO_4 and MgCl_2 are identified as the main impurities of crude salt. With the excessive hydro attraction capacity, dried free flowing salt absorbs water because of these compounds [1].

The method used in traditional salt manufacturing process for removal of CaSO_4 and MgCl_2 is not efficient. After

harvest, crude salt is washed by a highly saturated brine solution to remove the impurities. Recycling brine solution is saturated with the impurities and also there is no purification system to remove Mg and Ca compounds from the system. The industrial practice is to discharge the recirculating brine solution after about 25-30 cycles. The impurities which are trapped inside the salt crystals do not get removed by washing with the brine solution [2], [3].

Despite the comparative advantage, it is unfortunate to note that solar salt production has not been developed in Sri Lanka due to lack of knowledge amongst industrialists and the public at large. Moreover, the quality of solar salt produced in Sri Lanka has very poor value due to which, many industries which require high quality salt in their manufacturing processes tend to import refined salt. Examples are confectionary, food, beverage, pharmaceutical, textile manufacturing, water purification and bottling industries. Therefore the industry demands for a cost effective and efficient process to upgrade the purity level of solar salt so that it can target high market prices.

The main objective of this research is to develop a chemico-physical process, to increase the quality of solar salt into high purity refined salt which has 99.6% NaCl, which will add value to solar salt and lead to socio-economic benefits to Sri Lanka. The existing process fails to obtain high purity levels and the resultant products are incapable of fetching high prices such as imported refined salt.

Kiln dried solar salt manufacturing, SALEX process [5], mechanical vapor recompression [4] and vacuum salt manufacturing are the leading processes used in worldwide. Although these processes are capable of delivering high purity salt, high energy consumption adversely affects the production cost.

This research study is focused on addressing these challenges in order to provide a cost effective process capable of manufacturing high purity refined salt.

II. PROCEDURE

A. Materials

Crude solar salt samples were collected from three salterns in Puttalam.

Ethylenediaminetetraacetic acid 99.5% (w/w), Calcium carbonate 97%(w/w), Hydroxynaphthol blue, Eriochrome black T, pH 9.2 buffer solution (MERCK chemicals), Hydrochloric acid 33% (w/w), Sodium hydroxide 98% (w/w) and Barium chloride were used for the salt analysis.

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Polyaluminiumchloride 70% (w/w), Calcium hydroxide 98% (w/w) and Sodium carbonate 99.5% (w/w) were the reagents used for salt refining process.

B. Experimental Setup

A vacuum filter unit was set up with Whatman grade 1 (11µm) filter paper which frequently used for qualitative analytical separations for precipitates such as calcium carbonate.

Jar test apparatus was used to determine the optimum PAC dosage required to settle insoluble impurities present in the crude salt solution.

C. Preparation of EDTA Solution

4g of EDTA (Ethylenediaminetetraacetic acid, was dried for 1hour at 80°C and allowed to cool to room temperature in a desiccator. 3.8g of dried EDTA powder was added to 100ml volumetric flask and dissolved in distilled water to make a diluted solution. EDTA solution was standardized using calcium carbonate solution.

To produce calcium carbonate solution, primary CaCO_3 powder was dried overnight at 110°C. 0.25g of dried CaCO_3 was transferred to a 250ml volumetric flask and dissolved using 5ml of 1M HCl solution. Then the solution was diluted to a volume of 250 ml using distilled water. Concentration of the standard calcium solution was calculated. EDTA solution was titrated with standard calcium solution in the presence of hydroxynaphthol blue as the indicator at a pH of 12 (color change was pale red to blue).

D. Analysis of Salt Solution

50g of salt was weighed accurately and dried at 110°C until it gives a constant weight over the time. Then the weight of the dried salt was measured and moisture content was calculated in dry basis.

Then the salt was dissolved in distilled water using 1000ml volumetric flask. Salt solution was filtered using dried and pre-weighted filter paper. Then the filter cake was dried in an oven at 110°C until it gives a constant weight over the time and total suspended solids (TSS) content was calculated.

Filtered salt solution was used to determine the content of impurities such as Mg^{2+} , Ca^{2+} and SO_4^{2-} .

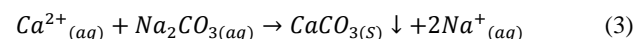
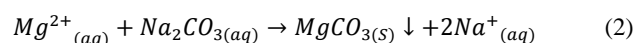
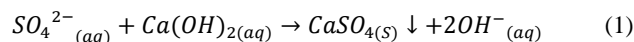
EDTA titration method was used to determine the Mg^{2+} and Ca^{2+} content. Ca^{2+} was determined in the presence of hydroxynaphthol blue as the indicator at pH 12 where Mg^{2+} was precipitated as $\text{Mg}(\text{OH})_2$ so that it would not react with EDTA. Then another sample of salt solution was titrated with EDTA solution in the presence of eriochrome black T as the indicator at pH10 to measure the amount of Ca^{2+} and Mg^{2+} present in the solution. pH 9.2 buffer solution was used to maintain the pH of the solution at 10.

In order to determine the SO_4^{2-} content, gravimetric precipitation was used. 250ml of the salt solution was transferred to a pyrex beaker and pH of the solution was adjusted below 3.0 using HCl solution. Equal amount of saturated BaCl_2 solution was added to the salt solution while it boiled. Then the solution was mixed well using magnetic stirrer and allowed to digest the solution for 2 hours at 90°C.

Digested solution was filtered using vacuum filter. Then the filter cake was dried in an oven at 110°C until a constant weight given over the time. BaSO_4 precipitate was then calculated.

E. Dosage Optimization

The precipitation of Ca^{2+} , Mg^{2+} and SO_4^{2-} is described by the following reactions.



According to the stoichiometry, the amounts of Na_2CO_3 and $\text{Ca}(\text{OH})_2$ were calculated (Table IV). But to completely precipitate the impurities, over dosage of reagents is needed [6]. Therefore, series of experiments were carried out to optimize the dosage of reagents.

Six saturated salt solution samples of 250ml were treated with following $\text{Ca}(\text{OH})_2$.

TABLE I
DOSAGES OF $\text{Ca}(\text{OH})_2$ USED DURING OPTIMIZATION

| Sample Number | $\text{Ca}(\text{OH})_2$ dosage (mg) |
|---------------|--------------------------------------|
| 01 | 400 |
| 02 | 500 |
| 03 | 600 |
| 04 | 700 |
| 05 | 800 |
| 06 | 900 |

Considering the amount of sludge produced, optimum dosage of $\text{Ca}(\text{OH})_2$ was determined.

After treating with $\text{Ca}(\text{OH})_2$ following dosages of Na_2CO_3 were added to six samples of 250 ml salt solution.

TABLE II
DOSAGES OF Na_2CO_3 USED DURING OPTIMIZATION

| Sample Number | Na_2CO_3 dosage (mg) |
|---------------|--------------------------------------|
| 01 | 3300 |
| 02 | 3400 |
| 03 | 3500 |
| 04 | 3600 |
| 05 | 3700 |
| 06 | 3800 |

The optimum dosage of PAC was determined by the jar test method. Six samples of 500ml were treated with following PAC dosages maintaining pH of 8.

TABLE III
DOSAGES OF PAC USED DURING OPTIMIZATION

| Sample Number | PAC dosage (ppm) |
|---------------|------------------|
| 01 | 05 |
| 02 | 15 |
| 03 | 25 |
| 04 | 40 |
| 05 | 50 |
| 06 | 60 |

Considering the amount of sludge produced, optimum PAC dosage was determined.

F. Method

The salt used in this experiment was collected from Puttalam saltern in North Western Province of Sri Lanka. Salt water collected from Puttalam lagoon is used as the raw material for the crude solar salt production process in North Western Province.

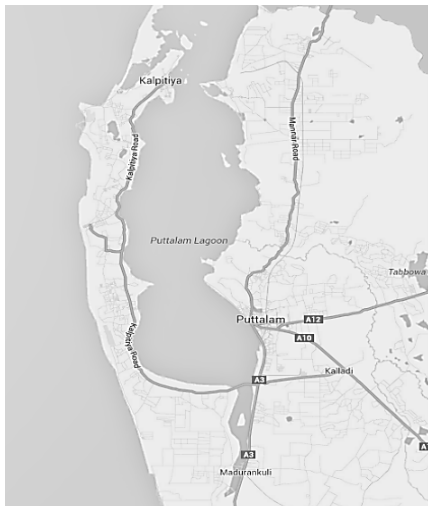


Fig. 1 Puttalam, North Western Province, Sri Lanka

Collected crude salt samples were initially analyzed in the laboratory to determine the impurities and their contents.

According to the results summarized in Table V, salt sample C had the lowest purity level of 98.02% NaCl and was used for the further refining process.

Crude salt was crushed and dissolved to get a saturated solution. Initially it was treated with 670ppm (Table IV) $\text{Ca}(\text{OH})_2$ and allowed to react with impurities in the solution. Then the solution was treated with optimum amount of Na_2CO_3 (Table IV) to react with existing impurities of the solution.

Finally, pH of the solution was adjusted to 8 using diluted HCl solution and Polyaluminiumchloride was added to settle the remaining impurities.

Once the refined salt solution was produced, it was analyzed for impurities and the results are given in Table VI.

The summarized process is in Fig. 2.

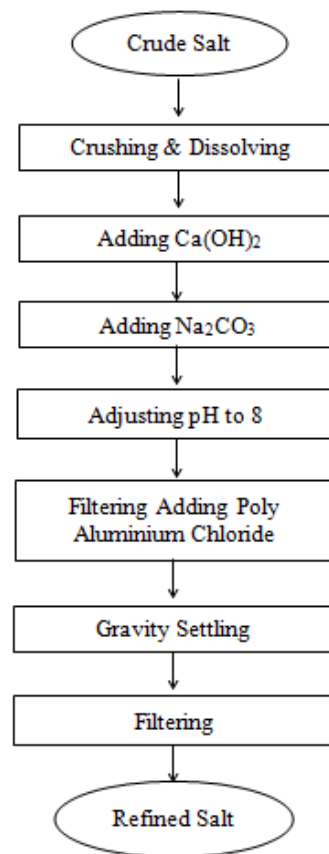


Fig. 2 Process flow chart

III. RESULTS AND DISCUSSIONS

A. Influence of $\text{Ca}(\text{OH})_2$ on Dissolved Solids Removal

According to the stoichiometric calculations, required dosage of $\text{Ca}(\text{OH})_2$ was 621.6 ppm. But, practically this amount is not sufficient to precipitate maximum amount of SO_4^{2-} present in the salt solution and therefore overdose was needed. Fig. 3 summarizes the variation of dissolved solid removal with respect to the dosage of $\text{Ca}(\text{OH})_2$. According to the results, optimum dosage of $\text{Ca}(\text{OH})_2$ was determined as 670 ppm.

B. Influence of Na_2CO_3 on Dissolved Solids Removal

According to the stoichiometric calculations, required dosage of Na_2CO_3 was 3392ppm. Since over dosage was needed the optimum Na_2CO_3 amount needed to be determined. Fig. 4 summarizes the variation of dissolved solid removal with respect to the dosage of Na_2CO_3 and the optimum dosage was determined as 3730ppm.

C. Influence of PAC on Suspended Solids Removal

Fig. 5 summarizes the variation of suspended solid (SS) removal with respect to PAC dosage for crude salt. Amount of SS removed increased gradually with the PAC dosage and eventually got constant. Therefore optimum PAC dosage for the crude salt sample was determined as 42ppm.

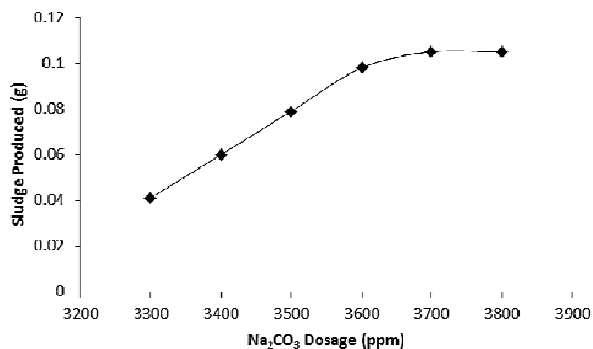
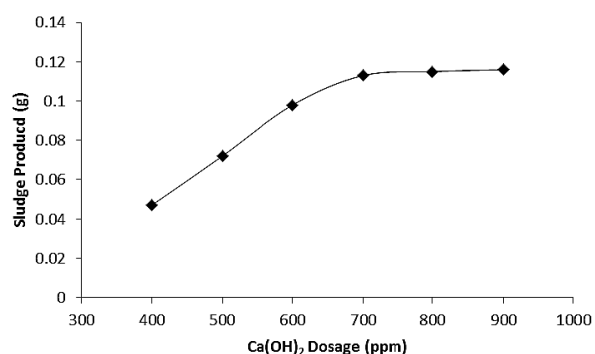
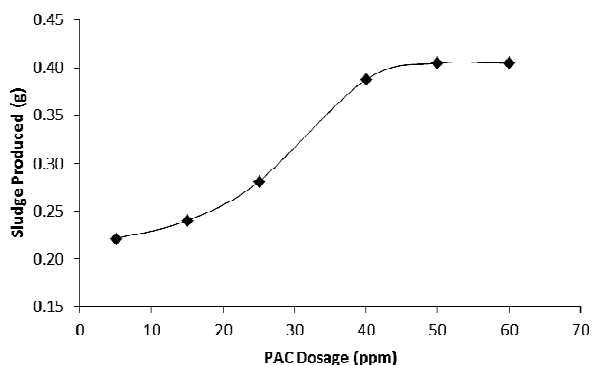
Fig. 3 Effect of Na₂CO₃ on dissolved solids removalFig. 4 Effect of Ca(OH)₂ on dissolved solids removal

Fig. 5 Effect of PAC on suspended solids removal

TABLE IV
DOSAGES OF REAGENTS

| Reagent | Theoretical dosage (ppm) | Experimentally optimized dosage (ppm) |
|---------------------------------|--------------------------|---------------------------------------|
| Ca(OH) ₂ | 621.6 | 670 |
| Na ₂ CO ₃ | 3392 | 3730 |
| PAC | - | 42 |

TABLE V
CRUDE SOLAR SALT ANALYSIS

| CRUDE SOLAR SALT ANALYSIS | | | | |
|---------------------------|-------------------|-------------------|----------|----------|
| Characteristic | | Weight Percentage | | |
| | | Sample A | Sample B | Sample C |
| Moisture Content | | 3.46 | 4.07 | 7.35 |
| Suspended solid | | 0.14 | 0.07 | 0.29 |
| Calcium Sulphate | CaSO ₄ | 0.45 | 0.44 | 0.51 |
| Magnesium Sulphate | MgSO ₄ | 0.09 | 0.21 | 0.35 |
| Magnesium Chloride | MgCl ₂ | 0.22 | 0.50 | 0.83 |
| Sodium Chloride | NaCl | 99.10 | 98.78 | 98.02 |

TABLE VI
REFINED SALT ANALYSIS

| Characteristic | Weight Percentage |
|--------------------|-------------------|
| Moisture Content | 0.7294 |
| Suspended solid | 0.0995 |
| Calcium Sulphate | 0.2750 |
| Magnesium Sulphate | 0.0057 |
| Magnesium Chloride | 0.0157 |
| Sodium Chloride | 99.6041 |

D. Comparison of Crude Salt with Refined Salt

According to Fig. 7, suspended solid content of crude salt sample has been reduced from initial value of 0.291% to 0.099% which is a percentage reduction of 65.98.

Reduction of CaSO₄ content from crude solar salt to the refined salt is from 0.506% to 0.275% and it is a percentage reduction of 45.65.

According to Fig. 8, reduction of MgSO₄ and MgCl₂ content from crude salt to refined salt is significant and over 90% reduction has been recorded.

E. Comparison of Conventional Process and Proposed Process

Two samples of crude salt were purified using traditional method and proposed refining process separately. Then, they were analyzed for impurities and results are summarized in Fig. 8.

According to the results, reductions in impurity levels are significantly higher in the proposed process than that in the traditional process. Proposed process reduces suspended solids content by 65.98%, MgSO₄ by 98.37% and MgCl₂ by 98.11% while traditional process reduces by 18.67%, 46.47% and 60.36% respectively.

Furthermore, it is noted that CaSO₄ content of the traditionally processed salt is slightly higher than that of crude salt. This is one of the drawbacks associated with the existing process since it recycles the same brine solution for washing crude salt over a long period of time.

Fig. 6 shows how the NaCl percentage of the crude salt has been increased by traditional washing and refining. According to the results traditional method is able to increase NaCl percentage of crude salt from 98.023 to 98.734, while the proposed system is able to upgrade NaCl percentage from 98.023 to 99.604.

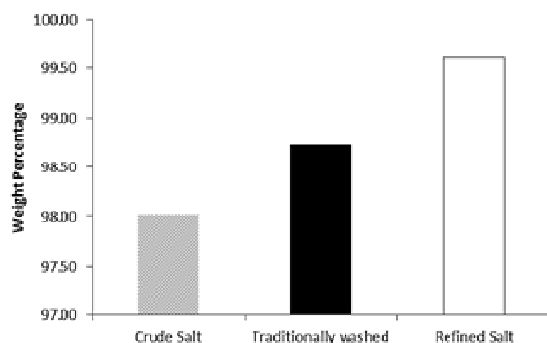


Fig. 6 Comparison of NaCl percentage

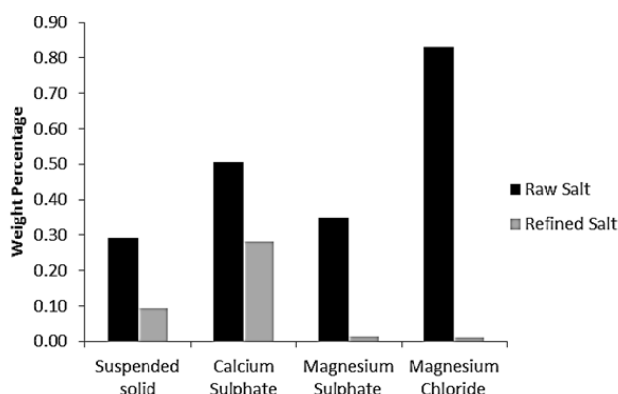


Fig. 7 Reduction of Suspended solids

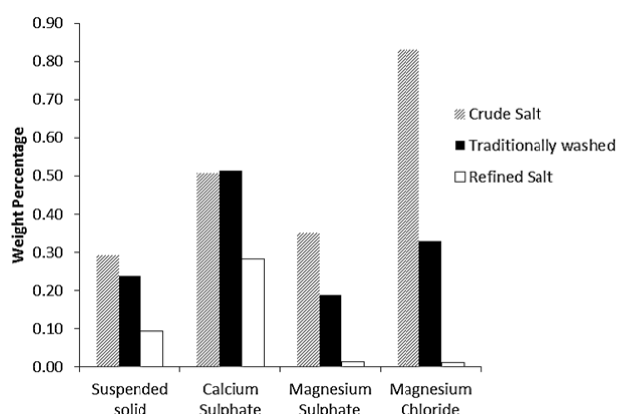


Fig. 8 Comparison of impurities present in crude and purified salt

F. Economical Viability of the Process

Economical viability of any research is a key factor that determines whether the proposed process will success or fail. The proposed process would cost 12.10 USD per 1MT of crude salt. The cost breakdown is summarized in Table VII.

TABLE VII
COST BREAKDOWN OF THE PROCESS

| Chemical cost breakdown (per 1MT of crude salt in USD*) | | | |
|---|---------------------------------|-------------|----------------------------------|
| Chemical name | Price per 1kg of chemical (USD) | Dosage(ppm) | Cost per 1MT of crude salt (USD) |
| PAC | 0.79 | 42.00 | 0.18 |
| Ca(OH) ₂ | 0.46 | 670.00 | 1.21 |
| Na ₂ CO ₃ | 0.61 | 3730.00 | 8.63 |
| HCl | 1.07 | 182.50 | 2.09 |
| Total | | | 12.10 |

*1USD = 131.15LKR = 6.09 Chinese Yuan

IV. CONCLUSION

In this study, we were able to develop a chemico-physical process to upgrade the quality of solar salt. The results of this study show that a purity level of 99.6% can be achieved by this process with optimum dosages of Ca(OH)₂, Na₂CO₃ and Polyaluminiumchloride.

Once the required dosage of each reagent was calculated theoretically, it was optimized experimentally in order to use the chemical reagents in an economically feasible manner. This technology can be implemented without making any modifications to the existing evaporation beds. Regardless of the amount of impurities present in the salt, this process is capable of upgrading the quality of crude salt with minor adjustments to the chemical dosage.

Furthermore, according to Table VIII, a profit margin of 83% can be achieved and it is a 112.3% increase compared to the existing process.

TABLE VIII
PROFIT COMPARISON

| Profit comparison existing process Vs developed process (per 1MT of salt in USD*) | | | |
|---|------------------|--------------|-------------------|
| | Existing process | | Developed process |
| Selling price | | 122.00 | 457.49 |
| Cost of salt before washing | 53.37 | | 53.37 |
| Chemical cost | 0.00 | | 12.10 |
| labor cost | 15.25 | | 7.62 |
| Iodine and Silica cost | 6.10 | | 6.10 |
| Production cost | | (74.72) | (79.20) |
| profit | | 47.27 | 378.29 |
| Profit margin | | 39% | 83% |

*1USD = 131.15LKR = 6.09 Chinese Yuan

For a climate which is favorable to solar salt production, this process would help to gain the comparative advantage and achieve the industrial purity levels. Since this process consumes low amount of energy compared with high energy intensive processes, it can be concluded that this process is a cost-effective method to refine crude solar salt and meet higher market prices. Therefore, this technology can be recommended to the solar salt producers who cannot afford the advanced refinery techniques to overcome the technological barriers and meet the higher purity levels.

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