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Sustainability Improvement of Kazakh Chemical Industry via Process Integration: A Case Study of Calcium Chloride Production

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This work presents the analysis of the calcium chloride concentration unit to reduce energy consumption and harmful emissions. The concentration of the calcium chloride in the raw materials is 14 % (mass) and a concentrated solution has 35 % of $CaCl_2$. Process Integration techniques were used for the analysis of the existing process to identify bottlenecks and disadvantages. A Pinch approach was executed to get real energy targets, energy gap and possible ways for process update. The authors proposed the solution for the process improvement using traced Grid Diagram and detailed simulation of the parameters of heat exchangers and evaporation units to get a feasible and economically beneficial retrofit. The representative case study of a Kazakh chemical factory was presented. There are some barriers to the development of the profitable and feasible solution, e.g. process constraints and limited performance of existing equipment. It forces developing a local methodology to apply the case study in an appropriate and most profitable way. The energy consumption of the inspected unit is 25 % higher than the target value. Nevertheless, the 1st feasible retrofit case with a detailed simulation of heat exchanger network parameters has only 17 % less energy consumption but, at the same time, the improved operating conditions of the evaporation unit were achieved. The 2nd retrofit option reduces the energy consumption by 22 % and more complicated network with additional operation changes was proposed. The results of this work may be used for the energy saving retrofit of the industrial evaporation units and decreasing the environmental impact of the chemical industry in Kazakhstan.

1. Introduction

The problem of energy efficiency in process industries is still a hot topic since the first energy crisis in the second part of the 20th century. Nowadays, this issue is becoming more complex accounting global warming and different kinds of wastes. The chemical and petrochemical industry is still one of the most energy-intensive production sectors that generate a huge amount of solid, liquid and gaseous wastes. The International Energy Agency has reported that the energy consumption in chemical & petrochemical is 28 % of final industrial consumption (IEA, 2017). Calcium chloride is one of the most used inorganic salts. It is the most widely used non-sodium containing de-icing agent (Nixon, 2008). It is also used as an additive to the cement to decrease the solidification time and to increase the strength of the concrete especially for oil and gas wells and to increase mud fluid densities in oil and gas wells drilling as reported by Al-Yami et al. (2017). Innovative applications of calcium chloride are the use as the component of molten salts mixture in silicon nanowires and fine tungsten powder production make it more important in future as reported by Tang et al. (2012). The main feedstock of calcium chloride is a by-product of the Solvay Process of soda ash production. An additional quantity of $CaCl_2$ may be recovered from wastes of this process disposed of ponds. Solvay Process is dominated in Europe and Asia as shown in the EC report (2007).

The last trend of sustainable development out to develop both new processes and retrofit in a new way accounting global environmental problems. One of the most applicable approaches for the retrofit of industrial

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heat systems is a Process Integration that was well described by Smith (2016). Cucek et al. (2019) reported that it is a systematic technique and is based on insights and optimisation. The method based on insights is unified and more or less simple for application in different industries. However, the real completed projects have shown the features and local methods for applications in different industries as for chemical production was shown by Boldyryev and Varbanov (2014). Pavao et al. (2019) proposed an alternative method based on a model derived from a broad superstructure solved with a meta-heuristic approach that is based on mathematical programming. Lal et al. (2018) used a Monte Carlo simulation to analyse the effect of stream data variation on the economic performance of retrofit designs. They solved a simple four-stream problem to compare retrofit designs and utility reduction. Ulyev et al. (2018) proposed the ways to achieve the objectives of the retrofit in the context of administrative and technical restrictions considering different retrofit options. Ahmetovic et al. (2018) solved an objective by a general superstructure and a Mixed-Integer Nonlinear Programming (MINLP) model for the synthesis and simultaneous optimisation and Heat Integration (HI) of Single- and Multiple-Effect Evaporation (SEE/MEE) systems including Mechanical Vapour Recompression and the background process.
The novelty of this paper is an application of the hybrid method for heat integration improvement during the retrofit of the existing unit. The method uses simultaneously the Pinch approach and process modification minimising the investment and maximising the overall profit. It presumes to find the energy gap and prospective process updates. The detailed simulation of heat exchange equipment and process changes were applied to get a technically feasible and economically beneficial retrofit option. The main constraints are the use of existing equipment and minimum process changes.

2. Methods

The proposed methodology is based on the detailed simulation of process flowsheet maintaining the operation mode and remain unchanged the capacity or improve it. The analysis of all process streams was executed including thermophysical properties of the brine $NaCl/CaCl_2$ in the water. To generate the brine properties the next VMGThermo methods were used:

- Flash Method: Integral;
- Critical Method: Local liquid pseudo critical;
- Liquid and vapour method: UNIQUAC/Ideal/Chemical;
- Bulk liquid-liquid properties: Mass weighted average.

The energy targets, Pinch temperatures and thermodynamic limits were obtained by Composite Curves. Another Process Integration approach, namely Grid Diagram, were used to identify the structure of the heat exchangers network and the bottlenecks finding (Klemes et al., 2018). The calculations were done by HILECT software (Boldyryev et al., 2017). The retrofit options were considered accounting Pinch principles, process changes, feasibility, investments and economic benefits. All changes in the process flow diagram (PFD) were done systematically by Pinch technology to achieve energy targets. Some process constraints as a mixers position and the brine concentration prior to the evaporation unit were considered as soft with minor changes.
All retrofit options were checked on the feasibility, flowsheet complications, safety reasons and operation mode changes. From another hand, the economic attractiveness of retrofit options was checked in term of the investment. The selected project should be energy efficient, simple, economically beneficial and suitable for further PFD improvement.

3. Case study

This case study provides an analysis of existing calcium chloride unit which uses a sludge of salts mixture as a feedstock.

3.1 Process description

The production of liquid calcium chloride consists of 3-stage evaporation and vacuum evaporation units, two shell-and-tube heat exchangers, hydrocyclone and several tanks and pumps (Figure 1). The capacity of the current unit is 16.5 t/h of $CaCl_2$ (14 % mass).
A cold feed enters the tank T1 to mix and set a calcium hydroxide concentration of 0.03 %. The cold feed is heated in two shell-and-tube heat exchangers He1 and He2 by dirty and clean condensate. The mixed raw material is fed by the pump P1 into the tank T5 through He1 and He2 for mixing with the recycled product from the hydrocyclone. The mixed feed with the recycled product is fed to three-step evaporation unit with a heat transfer area of 250 m^2 each. Mass fraction of calcium chloride solution entering the first evaporator is 14 %. The first evaporator is heated by the steam from the boiler house, the second and third ones are heated by the extra steam. The extra steam of the third evaporator is gone to the barometric condenser Bc1 where it is condensed by the cooling water. The condensate of the first evaporator is collected to pure condensate pipelines

and the condensate of the second and third evaporators is collected to dirty condensate pipelines. The first and second evaporators are operated under pressure and the third one is by vacuum. The solution of calcium chloride with a concentration of 19 % goes from the third evaporator to the tank T2, from where it is fed to the vacuum evaporator VE by the pump P2. The heat transfer area of the vacuum evaporator is 630 m^2 and it is heated by the steam from the boiler house. The product of vacuum evaporator is a calcium chloride solution with a concentration of 35 %. It is collected in the tank T3 and then pumped by P4 to the hydrocyclone HC. The upper layer from the hydrocyclone is returned to the process and the main product goes to the centrifuge to separate the calcium chloride solution and sodium chloride. The mass balance of current calcium chloride production is presented in Figure 2.

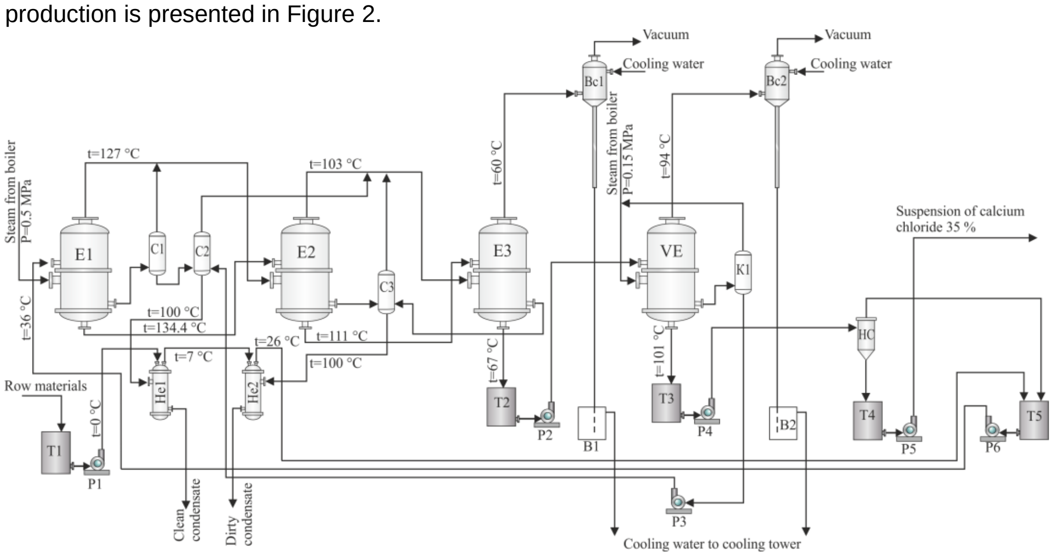

Figure 1. PFD of calcium chloride production. E1-E3 – evaporators; VE – vacuum evaporators; C1-C3 – separators; K1 – condensate trap; Bc1-Bc2 – barometric condensers; T1-T5 – tanks; B1-B2 – barometric tank; P1-P6 – pumps; He1-He2 – heat exchangers; HC – hydrocyclone.

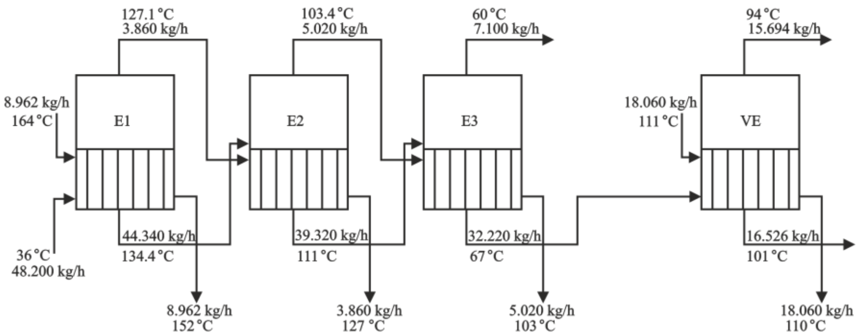

Figure. 2. Mass balance of current calcium chloride production.

3.2 Analysis of existing process

The plant expertise identified more than 50 streams both process and energy but only 12 of them may be considered while the heat integration. Other streams remain unchanged as well as equipment associated. Selected process streams and its process parameters were presented in Table 1. Targeting procedure shows that the utility requirements for heating and cooling of the current process are 14.7 MW and 10.7 MW. It is well demonstrated by Composite Curves shown in Figure 3. The minimum temperature approach of the current process is 12 ºC and it is placed on 1st evaporator E1. The Grid Diagram of existing calcium chloride production built according to Composite Curves shows some bottlenecks. The energy consumption of the existing process is 19.1 MW and 15.0 MW that is much higher than energy targets. The Grid Diagram (Figure 4) shows that some basic Pinch principles are violated, this is one of the main reasons of high energy consumption. Besides, the solution is fed to the 1st evaporator with a temperature of 36 ºC that is much lower than the boiling point of the first stage. Concluding mentioned above, the energy gap of existing calcium chloride production is due to design and operation mode reasons. Nevertheless, the retrofit option must avoid process traps and remain the quality of the product.

Table 1: Stream data of calcium chloride production.

No	Stream name	Type	T_S, ºC	T_T, ºC	CP, kW/ºC	ΔH, kW
1	Extra steam of 1st evaporator	Hot	127	127	-	3,093
2	Extra steam of 2nd evaporator	Hot	104	104	-	4,624
3	Extra steam of 3d evaporator	Hot	60	60	-	4,657
4	Extra steam of vacuum evaporator	Hot	94	94	-	10,318
5	Clean condensate	Hot	104	75	31.98	927
6	Dirty condensate	Hot	104	75	12.04	349
7	Row material	Cold	0	26	48.25	1,254
8.1	Row material + recycle	Cold	36	135	60.31	5,923
8.2	1st stage evaporation	Cold	135	135	-	2,321
9	Suspension of salts ($CaCl_2$ 35% mass)					
10	2nd stage evaporation	Cold	115	115	-	3,093
11	3d stage evaporation	Cold	67	67	-	4,624
12.1	Calcium chloride in vacuum evaporator	Cold	67	101	37.98	418
12.2	Vacuum evaporation	Cold	101	101	-	10,399

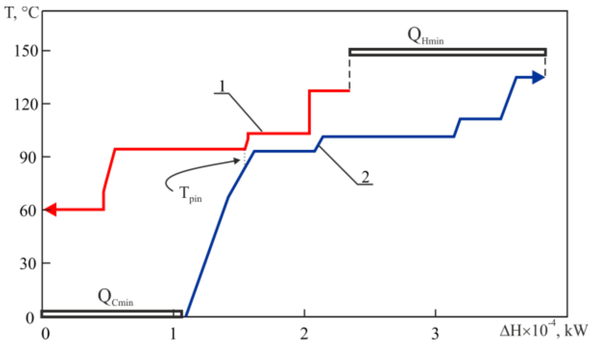

Figure. 3. Composite Curves of calcium chloride production. ΔT_{min} = 12 ºC; 1 – hot Composite Curves; 2- cold Composite Curves; T_{pin} – Pinch temperature.

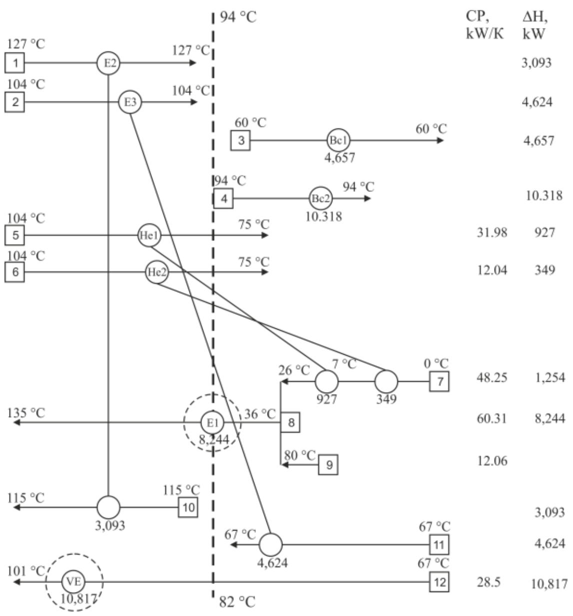

Figure. 4. Grid Diagram of existing calcium chloride production. CP – heat capacity flowrate; ΔH – enthalpy.

3.3 Retrofit options.

The retrofit options of the calcium chloride production were developed considering the detailed simulation of heat exchange equipment and changes of mixer position to get the feasibility and economic benefits. The present case study demonstrates the most appropriate retrofit options that arepresented by the Grid Diagrams in Figure 5. The proposed retrofit option 1 supposes to use one new heat exchanger He3 to avoid cross-Pinch by heat exchangers He1 and He2. Besides, the mixing of raw materials and recycle stream is placed before the heat exchangers He1 and He2 to increase the driving forces in these heat exchangers. It makes possible to utilise additionally 2.6 MW of the low potential waste heat and to use existing heat exchangers. The inlet temperature of the 1st evaporator is increased up to 80 ºC that improves the operation mode and reduce energy input from the boiler house. From the other hand, the use of low potential heat of extra steam of vacuum evaporator reduces the consumption of cooling water and power for pumping. This issue is very important in terms of water scarcity in Kazakhstan. The second retrofit option can utilize 1.5 MW more waste heat, but the investment is 3 times higher than option 1 (see Table 2).

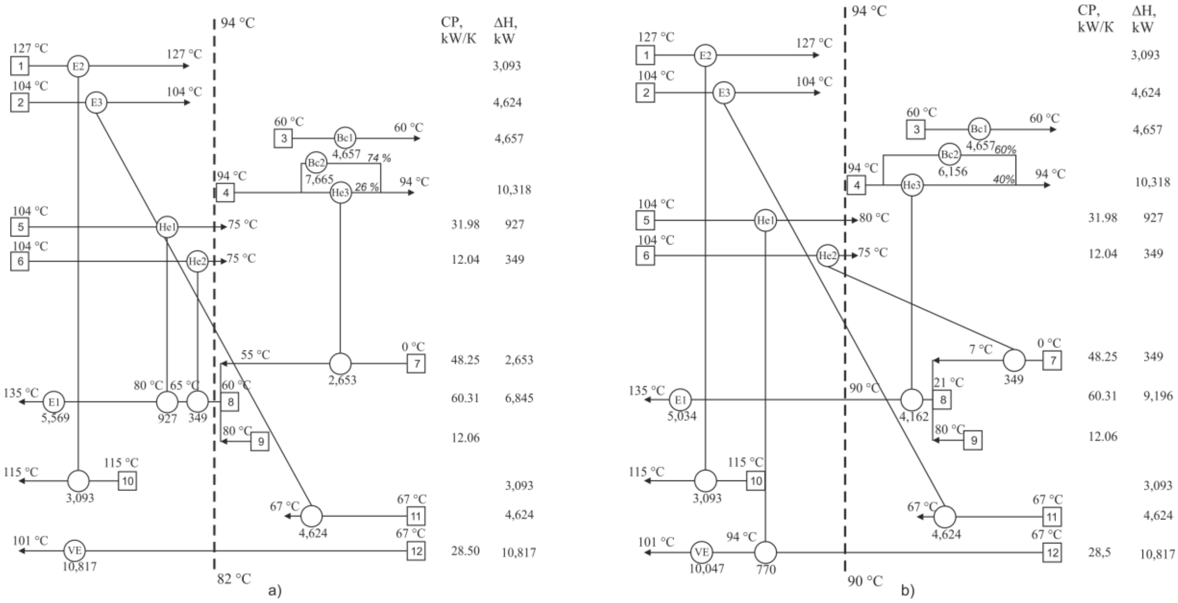

Figure. 5. Grid diagram of retrofitted calcium chloride production. a) – case 1; b) – case 2; He3 – new heat exchanger; CP – heat capacity flowrate; ΔH – enthalpy.

4. Discussion

The proposed retrofit 1 of calcium chloride production saves more than 2.5 MW of waste heat not considering the power of pumps but it still below the target value (see Table 2). The heat load of new heat exchanger He3 cannot be increased due to driving forces of He1 and He2. If the He3 heat load and heat transfer area are increasing the efficiency of He1 and He2 will be reduced and 1st evaporator inlet temperature reduced too. So, such changes would be useless.

Table 2: Energy consumption of calcium chloride production.

Option	Hot utility, MW	Cold utility, MW	Investments, EUR	Total saving, EUR/y
Base case	19.1	15.0	-	-
Targets	14.7	10.7	not estimated	-
Retrofit 1	16.4	12.3	52,197	127,609.72
Retrofit 2	15.0	10.8	184,000	193,777.73

Nevertheless, there is a potential of the 1st evaporator inlet temperature increasing but it presumes to utilise more energy to heat inlet stream. There are two options, the first one is adding the additional heat transfer area that requires the additional pumping of P6; the second option supposes enhancing the heat transfer of existing heat exchangers He1 and He2. Both options need additional investments and detailed research of heat transfer, hydrodynamic and pressure drops. Another one important point that should be discussed is a safety issue of

vacuum due to the installation of heat exchanger He3 on the vacuum line. The mechanical part of this work should be double checked because it may lead to the deterioration of the vacuum at the vacuum evaporator VE, and, as e result, to reduce the unit capacity and profit. To avoid such risks, it is recommended to use two heat exchangers in parallel at the position of He3.
There is an additional potential for energy efficiency at the hot stream 12. This stream could be heated between evaporators to reduce the consumption of steam at vacuum evaporator (Figure 5b). Nevertheless, again it needs additional investment as the installation of heat exchanger (see Table 2) leads to higher pressure drops in this line. The additional pump is needed otherwise it impairs the heat transfer in the vacuum evaporator and losses of the unit capacity. However, the potential of further improvement of current calcium chloride production is possible as was demonstrated in this case study. The pathways should be additionally analyzed in detail from the technical and economical point of view to be feasible and more attractive for investors.

5. Conclusions

The results of this work demonstrate the potential of waste heat recovery of the retrofit of calcium chloride production. It was shown that even such simple process requires the development of local methods and detailed simulation of process flowsheet to get a feasible and economically viable solution in a systematic way. The energy saving retrofits of the current process shown by the case study reduce the heat demands by 17 % and 22 % but it is a space for further process improvement as the energy gap was defined as 25 %. The proposed retrofit may be achieved by the minor process changes and remain unchanged the operation mode of the current calcium chloride unit. The results of this work may contribute to the environmental situation of the South Kazakhstan region for energy and water savings and may also be used for retrofitting of other productions with evaporation stations.

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