



# The retrofit of the calcium chloride production by Pinch approach and process modifications

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## ABSTRACT

In this paper, the analysis of an existing calcium chloride evaporation unit was performed to cut primary energy use and harmful emissions. This paper proposes the use of several approaches for retrofit of existing calcium chloride production. The existing process's energy efficiency was examined to identify drawbacks and bottlenecks and provide the pathways for proper process modification. The methodology is based on a systematic analysis and step-by-step reduction of energy use. It uses a Pinch approach, process unit simulation and vapour recompression considering existing process constraints, e.g. product quality, process capacity etc. Two retrofit options of heat exchanger network were proposed with the simulation and design of additional equipment. Energy recovery was increased by identifying vapour recompression potential and its proper application and retrofitted exchanger network. All process changes were simulated by commercial software to prove the robustness of proposed energy-saving measures. The case study analyses a chemical plant that exploits the Solvay process and distilled liquid of ammonia production as a feedstock. In the result of retrofit, the energy cost was cut by about 400,000 USD/y and emissions reduction by 18,818 tCO<sub>2</sub>/y. Steam consumption was reduced by 51%, and the cooling water flow rate is decreased by 69%. The economic efficiency of proposed energy-saving measures demonstrates the payback period up to 1.5 years. The roadmap of the step-by-step application of process changes was proposed.

## 1. Introduction

Since the first energy crisis in the second part of the 20th century, the efficiency of process industries is still a huge problem worldwide. It is more and more complicated due to world population growth and as a result, a huge amount of emissions. Despite the application of different energy-saving measures, industrial energy use is around 30% of the global energy consumption (Fig. 1). This distribution has not much changed in the last 35 years [1]. The chemical and petrochemical industry is still one of the most energy-intensive production sectors that generate a considerable 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 [2].

Calcium chloride (CaCl<sub>2</sub>) is an inorganic salt, which is highly soluble

in water and hygroscopic in solid-state [3]. One of the most widespread uses of calcium chloride is the ice formation preventing and de-icing [4]. It is the most widely used non-sodium containing de-icing agent. CaCl<sub>2</sub> is more effective for de-icing at lower temperatures than sodium chloride. For anti-icing, preventive measures calcium chloride is used as small solid particles, and for de-icing it is used as water solution that has a freezing point low than -52 °C that corresponds to about 33% mass concentration of CaCl<sub>2</sub> in the solution. CaCl<sub>2</sub> is relatively harmless to plants and soil but corrosive to the transport, so it is recommended to use it with corrosion inhibitors [5]. Another wide application of CaCl<sub>2</sub> is the dust control in the surfacing of ground roads. This application is based on the hygroscopic properties of CaCl<sub>2</sub> hydrates and concentrated solutions [6]. In the food industry, calcium chloride is used as a firming agent and as a sequestrant. European Union permitted to use E509 as a firming agent [7]. A well-known application of CaCl<sub>2</sub> is an additive to

*Abbreviations:* C, cooler; CAPEX, capital cost; CC, Composite Curves; C1, C2, C3, cold streams; Ev, evaporator; Ex, heat exchanger; GCC, Grand Composite Curves; H, heater; HEN, heat exchanger network; H1, H2, hot streams; MINLP, Mixed-Integer Nonlinear Programming; MVR, mechanical vapour recompression; OPEX, operating cost.

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**Nomenclature***Variables*

A	heat transfer area, m <sup>2</sup>	Q <sub>C</sub>	compressor shaft power, kW
CP	heat capacity flow rate, kW/°C	Q <sub>Ev</sub>	heat duty of evaporator, kW
CP <sub>C</sub>	heat capacity flow rate of cold stream, kW/°C	Q <sub>F</sub>	heat load of feedstock, kW
CP <sub>H</sub>	heat capacity flow rate of hot stream, kW/°C	R	ratio of heat capacity flowrates
C <sub>p</sub>	specific heat capacity, °C	r	latent heat of evaporation, kJ/kg
<i>f(t)</i>	temperature correction factor	T	temperature, °C
F <sub>t</sub>	correction factor of countercurrent in the heat exchanger	TS	supply temperature, °C
h <sub>s</sub>	shell-side film transfer coefficient, kW/(m <sup>2</sup> °C)	TT	target temperature, °C
h <sub>T</sub>	tube-side film transfer coefficient, kW/(m <sup>2</sup> °C)	T <sub>inH</sub>	inlet temperature of hot stream, °C
i	fractional interest rate, %	T <sub>inC</sub>	outlet temperature of cold stream, °C
K <sub>S1</sub> , K <sub>S2</sub> , K <sub>S3</sub>	dimensional constants of shell side pressure drop correlation	t <sub>inEv</sub>	inlet temperature of evaporator feed, °C
K <sub>PT1</sub> , K <sub>PT2</sub>	dimensional constants of tube side pressure drop correlation	t <sub>Ev</sub>	evaporation temperature, °C
m	mass flowrate, kg	t <sub>mix</sub>	mixing temperature, °C
n	project lifetime, y	T <sub>outC</sub>	inlet temperature of cold stream, °C
P	thermal effectiveness of the exchanger	T <sub>outH</sub>	outlet temperature of hot stream, °C
Q	heat duty, kW	U	heat transfer coefficient, kW/(m <sup>2</sup> °C)
		ΔH	enthalpy difference, kW
		Δp	pressure drop, kPa
		ΔT <sub>min</sub>	minimum temperature difference, °C
		ΔT <sub>LM</sub>	logarithmic temperature difference, °C

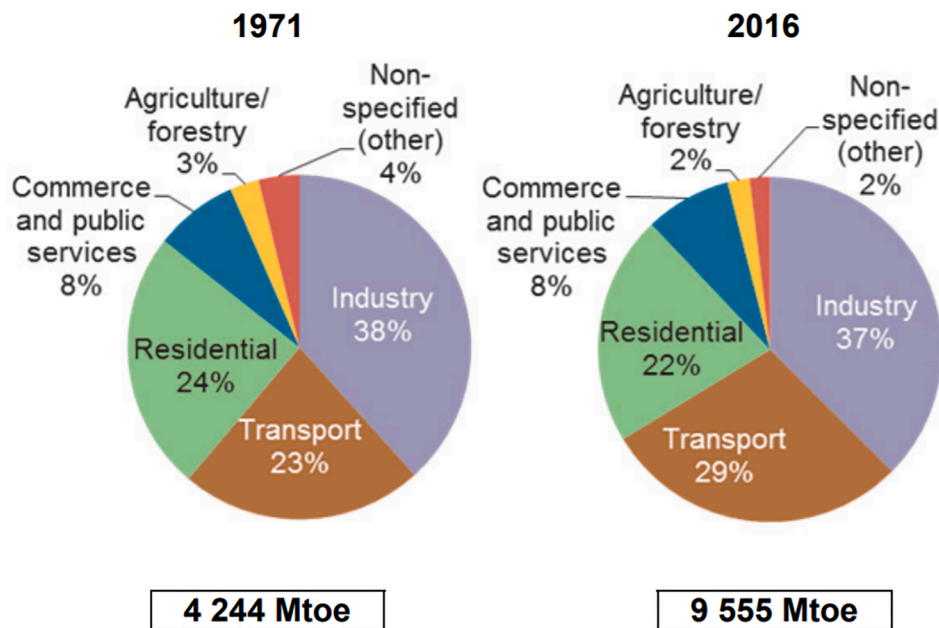


Fig. 1. World Energy Balances [1].

the cement to decrease the time of set and increase the strength of the resulting concrete. This property is used in oil and gas wells. CaCl<sub>2</sub> increases mud fluid densities of drilling fluids [8]. Innovative applications of calcium chloride are the use as the component of molten salts mixture in silicon nanowires [9], fine tungsten powder production [10] and CaCl<sub>2</sub> – formic solution for dry-spun silk fibers manufacturing [11].

There are two feedstocks of calcium chloride: the natural feedstock and industrial by-products. In nature, the CaCl<sub>2</sub> is contained in high salinity basinal brines and in high-salinity lakes. Calcium chloride minerals in the natural state are rare [12]. The main feedstock of calcium chloride is CaCl<sub>2</sub> solution as a by-product of the Solvay process of soda ash production. An additional quantity of CaCl<sub>2</sub> may be recovered from wastes of this process disposed of ponds or so-called “white seas”. Solvay Process is dominated in Europe and Asia [13]. Calcium chloride

product is produced as concentrated solutions with a mass concentration of 30–45%, flakes (72–78% mass) and granules (up to 98% mass). Taking into account that the feedstock of CaCl<sub>2</sub> is essentially a water solution with relatively low salt content, it is clear that the concentration process is necessary with the water evaporation and drying process.

Typical industrial processes are the Dow Chemical process of calcium chloride obtaining from natural brine and the process of Solvay Process by-product treatment. Dow Chemical process includes iodine and bromine separation, magnesium hydroxide precipitation and separation. The residual brine contained 24–25% CaCl<sub>2</sub> is sent to triple effect evaporators; the concentration of CaCl<sub>2</sub> after evaporators is 32–45%. Part of the concentrated solution is evaporated again and goes to crystallisation and drying to obtain CaCl<sub>2</sub> flakes or solid 90–94% of CaCl<sub>2</sub>.

Solvay process distilled liquid of ammonia production as a feedstock.

This liquid is a water solution of  $\text{CaCl}_2$  and  $\text{NaCl}$  containing  $\text{CaSO}_4$  and calcium hydroxide. Distilled liquid is supplied to sedimentation and carbonisation where  $\text{CaCO}_3$  is precipitated and then distilled liquid, with 11% mass of  $\text{CaCl}_2$ , goes to three effects evaporation unit where the solution is concentrated up to 28–45% mass. The concentrated solution is centrifugated, and solid  $\text{NaCl}$  is separated. The liquid  $\text{CaCl}_2$  is partly delivered as a final product and part is sent to additional evaporation under vacuum and then to crystallisation and drying.

Modern improvements in mentioned above processes are related mainly to the elimination of magnesium-containing and other impurities [14]. Environmental friendly perspective technologies of  $\text{CaCl}_2$  production are presented in [15] and [16]. The feedstock includes waste concentrated brine after seawater desalination and carbon dioxide containing in flue gases of nearby power plants.  $\text{CO}_2$  is captured from flue gases with amine solutions and mixed with brine salt solutions.

The main challenge in  $\text{CaCl}_2$  production processes mentioned above is a big energy consumption connected with evaporation on the stage of  $\text{CaCl}_2$  concentration. One of the ways to decrease energy consumption is the use of highly effective heat exchangers and evaporators. Alfa Laval plate evaporator was used at Kemira Kemi AB (Sweden) calcium chloride production. The installation of plate evaporator with titanium plates as the third effect lets to decrease the energy consumption of  $\text{CaCl}_2$  concentration. The cost of plate evaporator was half of the shell-and-tube one [17]. New generation heat pumps such as compression/absorption [18] and Stirling cycle based [19] may be integrated into  $\text{CaCl}_2$  production to obtain high-temperature streams and even for steam generation. In [19] described the possibility of steam generation up to 10 bar with the use of heat source and temperature potential 80–85 °C. The Process Integration approaches provide the considerable reduction of primary energy consumption in industrial systems, efficient use of heat transfer equipment and optimal network structure of process flowsheet [20]. Cucek et al. [21] reported that systematic approaches are 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, for example, in chemical [22]. Pavao et al. [23] 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. [24] 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. [25] proposed the ways to achieve the objectives of the retrofit in the context of administrative and technical restrictions considering different retrofit options of the existing design. Ahmetovic et al. solved a problem by a general superstructure and a Mixed-Integer Nonlinear Programming (MINLP) model for the synthesis and simultaneous optimisation and Heat Integration of Single- and Multiple-Effect Evaporation systems including Mechanical Vapour Recompression (MVR) and the background process [26]. Thermal and mechanical vapour recompression may be applied for low-grade energy reuse, but it should be appropriately targeted to make a synergy of all energy-saving measures. E.g. Walmsley et al. demonstrated general methodological aspects and application in milk evaporation [27].

Pinch approach is still one of the most used methods for energy-saving in different industries, and it was applied using features of particular processes. It can be used in combination with Exergy Analysis for a new process plant design of the diesel hydrotreating unit to get minimum energy consumption [28]. The pyrolysis of sugarcane integration was investigated in [29] to improve conventional ethanol production. Aspen Plus simulation and heat integration via Pinch Analysis rise in energy efficiency and product diversification. Equation-oriented simulators were also used in combination with Pinch Analysis for bioethanol production [30]. Better process integration has cut steam consumption by 12.8% and improved plant productivity. Another recent study presented the results of an integrated spatial and Pinch Analysis to

determine the minimum cost of the primary energy mix and greenhouse gas (GHG) emissions [31]. The method was proved by an industrial case study in Malaysia, and GHG emission was reduced by 30%. The novel approach that utilises chemical exergy and Pinch method was proposed for sugar mill plant to provide optimal pressure retarded osmosis and net power recovery [32]. Combination of Exergy and Pinch Analysis is widely used last time, e.g. the case study of big gas refinery site was investigated, and heat recovery was improved by 43% [33]. Unfortunately, there no many detailed case studies of evaporator integration; they are limited by milk production [27].

Despite different methods for retrofit of the processing system, different approaches were not used simultaneously, and their synergetic effect was not properly investigated. Additionally, there are limited applications of energy-saving technologies in calcium chloride production, especially for retrofit of existing facilities. The limited performance of existing equipment needs developing the local methodology to realise process changes in the most profitable way. The retrofit is more important last time when the economic growth slowed down, and the start-up of new facilities are not so impressive for investors.

This paper proposes simultaneous use of different approaches for retrofit of existing calcium chloride production to get low energy consumption within the existing plant layout with minimum changes. Pinch approach, MVR, process simulation, and detailed design of heat exchangers were used to get the best retrofit options that are proved by economic efficiency. In this work, an experimental and theoretical investigation of real calcium chloride production was performed to identify energy-saving potential and whether it can be achieved by proper process changes. Used combination of different approaches provides boundaries of energy targets and main barriers, e.g. additional changes of evaporation unit or mixing temperature of feedstock. The solution proposes the systematic and step-by-step energy reduction of existing evaporation unit, decreasing the investment optimising heat transfer equipment and associated capital investments. Presented above may prove both the scientific contribution and relevance of the paper goal.

The main constraints, such as existing equipment performance, minimum process changes and minimum payback of investments were considered when developing pathways for process modernisation.

## 2. Methods

### 2.1. Simulation of existing process

The proposed approach is grounded on the detailed simulation of process flowsheet, including stream thermophysical properties and operation mode of heat exchanger network (HEN). The nominal capacity of the evaporation unit and material balance remains unchanged. The simulation is done by UniSim Design software [34] applying HTRI Xist Heat Exchanger (HTRI Xist) option for the simulation of existing heat exchangers [35]. The properties of the brine  $\text{NaCl}/\text{CaCl}_2$  in the water were generated by VMGThermo methods with the next preferences:

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

The initial energy and mass balances were verified by plant operation data.

### 2.2. Energy targeting, potential definition and bottlenecks finding

Key instruments of Pinch technology were used to identify real energy targets of calcium chloride concentration unit and efficiency of utility distribution. Thermodynamically available heat, utility potential

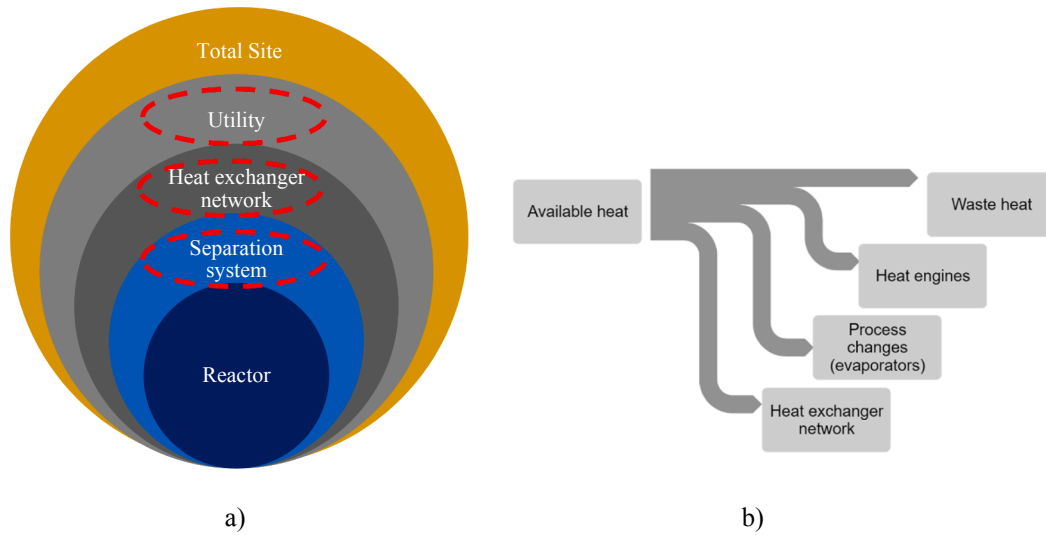


Fig. 2. (a) Onion diagram (developed after [20]); (b) Sankey diagram of energy reduction workflow.

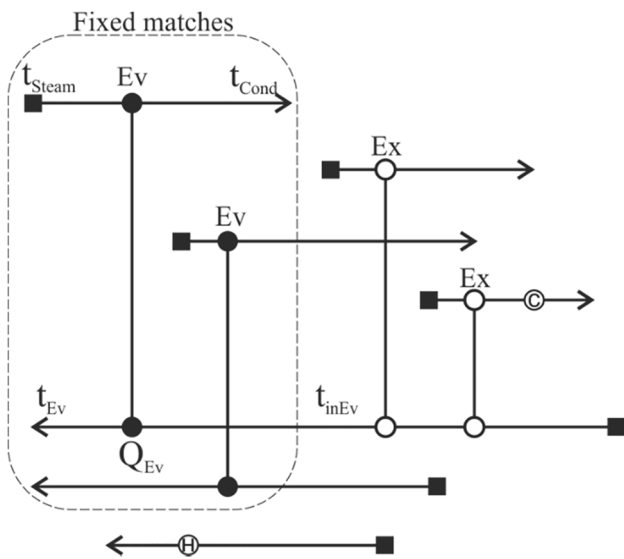


Fig. 3. HEN representation with fixed and flexible matches. Ev – evaporator; Ex – heat exchanger; C – cooler; H – heater.

and minimum temperature approach were identified by Composite Curves (CC) and Grand Composite Curves (GCC). Energy targets were compared with existing energy consumption, and the energy gap was analysed in terms of what process changes are required to get good saving. HEN, separation and utility systems were involved in analysis and further modernisation as shown in Fig. 2a. The thermodynamically available heat was analysed for further application of techno-economically feasible measures. Usually, when doing grassroots design, it goes from the core of the onion diagram to the external layer. In the current approach, the retrofit workflow starts from HEN, continues with the separation system and finishes at the utility system by applying heat engines (Fig. 2b). The main structural drawbacks of HEN are identified according to efficient energy use and heat recovery [36]. Energy targets and energy-saving potential were determined by HILECT software [37]. Usually, evaporation effects are placed on GCC against Composite Curve, but here, they are considered and analysed as process streams. It presumes to analyse a minimum temperature approach for the whole system and make appropriate process changes or units modernisation.

### 2.3. Retrofit design – Step 1 heat exchanger network

The retrofit option was developed accounting available waste heat, process changes, feasibility, investments and economic benefits. Existing heat exchangers have been placed according to the Pinch rules. The thermo-hydraulic regimes of heat exchangers were investigated to maximise their heat duty, at the same time, mixer of recycled final product and feedstock was optimised to get appropriate mixing temperature. Waste heat opportunities were used to satisfy remaining heating demands and applying minimum possible heat transfer unit. The retrofit options were checked for the feasibility of process flow diagram (PFD), process complications and safety reasons. Additional heat exchangers are selected, and its working conditions were analysed to avoid operational problems and improve performance.

Existing HEN is considered applying fixed matches for evaporators, and heat exchangers can be revamped (Fig. 3). The inlet temperatures of evaporators are considered as flexible variables to reduce steam consumption. The correlation for evaporator heat duty is based on Eq. (1):

$$\min Q_{Ev}(t_{inEv}) = \lim_{t_{inEv} \rightarrow t_{Ev}} (rm + C_p m(t_{Ev} - t_{inEv})) \quad (1)$$

The current problem includes the mixer of feedstock and recycled product; the feedstock is heated before mixing with hot recycle. The mixing temperature is considered as flexible variable as well and can be calculated by Eq. (2). The variables are shown in Figs. 4 and 5. The process streams associated with this part of flowsheet are demonstrated in Fig. 4a and the position of existing heat exchangers can be changed as shown in Fig. 4b.

$$t_{mix} = \frac{m_1 C_{p1} t_3 + m_2 C_{p2} t_2}{m_1 C_{p1} + m_2 C_{p2}} \quad (2)$$

The heat load of feedstock heating from  $t_1$  to  $t_4$ , assuming mixing with recycling is calculated from eq. (3):

$$Q_F = m_1 C_{p1} (t_2 - t_1) + m_3 C_{p3} (t_4 - t_{mix}) \quad (3)$$

Additional heat exchangers can be added for feedstock heating accounting moving of the existing unit or remain current. The efficiency of HEN modification is estimated by the capital cost of new units and utility reduction. When revamping an existing heat exchanger, the heat load is changed according to Eq. (4):

$$Q = UA \Delta T_{LM} F t \quad (4)$$

Parameters  $\Delta T_{LM}$  and  $F_T$  impact the heat transfer area of new unit and performance of existing ones, and they are considered from Eqs. (5) and

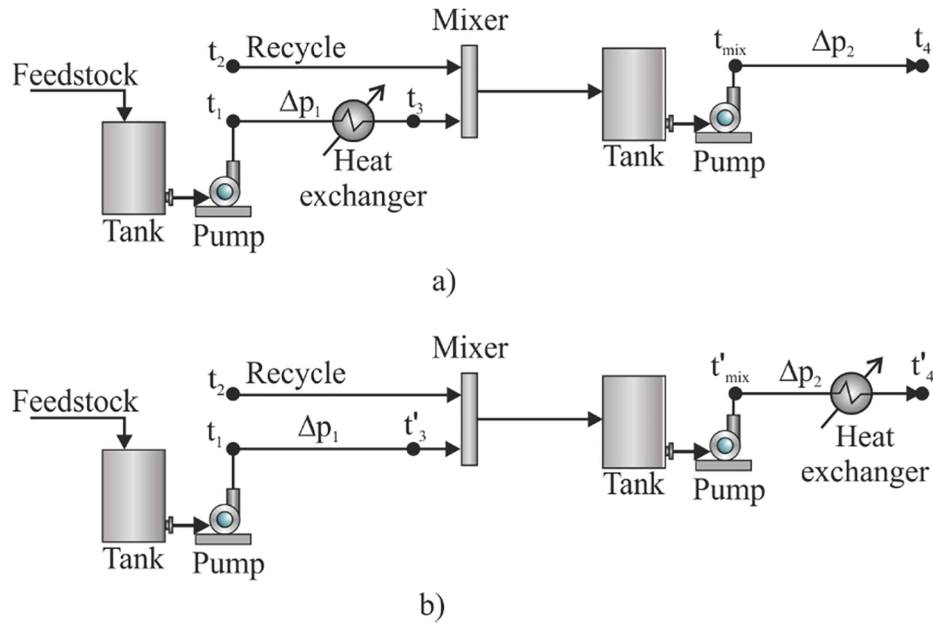


Fig. 4. PFD of feedstock and recycle mixing; (a) initial heat exchanger position; (b) revamped heat exchanger.

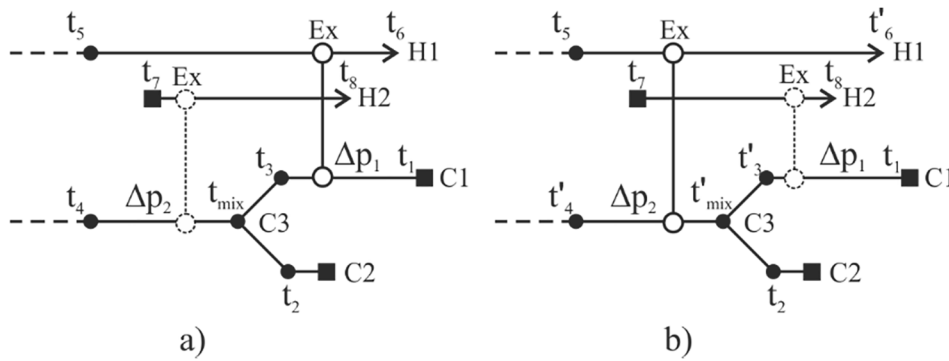


Fig. 5. HEN modification associated with feedstock stream.

(6):

$$\Delta T_{LM} = \frac{(T_{inH} - T_{outC}) - (T_{outH} - T_{inC})}{\ln \frac{(T_{inH} - T_{outC})}{(T_{outH} - T_{inC})}} \quad (5)$$

$$Ft = f(R, P) \quad (6)$$

$$R = \frac{CP_C}{CP_H} \quad (7)$$

$$P = \frac{T_{outC} - T_{inC}}{T_{inH} - T_{outH}} \quad (8)$$

The representation of HEN changes that are connected with a feedstock stream is demonstrated at a grid diagram in Fig. 5.

Apart this, both new and existing unit should satisfy the pressure drops of an existing process, these restrictions based on the performance of pumps (see Fig. 4). The pressure drop is estimated by correlations proposed in [38] for shell and tube sides of heat exchangers (Eqs. (9) and (10)):

$$\Delta P_S = K_{S1} h_S^{2.86} + K_{S2} A h_S^{4.42} + K_{S3} A h_S^{4.69} \quad (9)$$

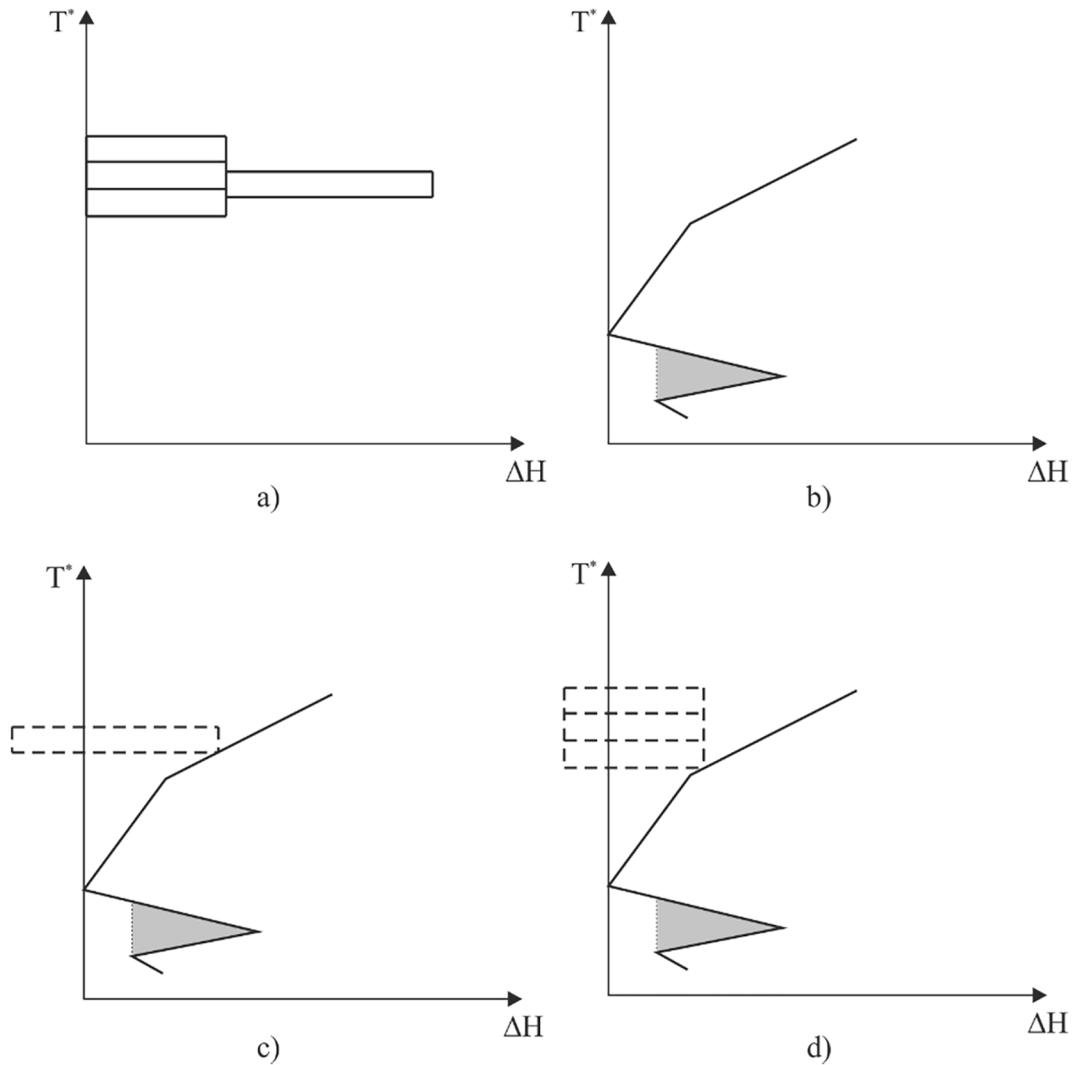
$$\Delta P_T = K_{PT1} A h_T^{3.5} + K_{PT2} h_T^{2.5} \quad (10)$$

#### 2.4. Retrofit design – Step 2 evaporation units and vapour recompression

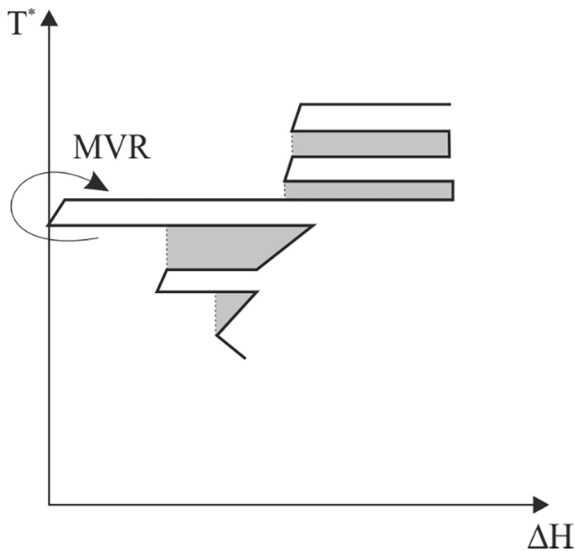
More substantial process changes are applied to get more energy-savings. Extra steam use of evaporation unit is analysed. The one effect vacuum evaporator is integrated with 3-effect evaporation unit, and extra vapour reuse is investigated. The integration of evaporation units is executed according to CC and GCC targets. The simulation of vapour recompression is performed by UniSim software to fulfil hot utility needs where appropriate. Temperature driving forces in evaporators after process changes are analysed to prove the performance of existing equipment.

The representation of 3-stage evaporator and 1-stage evaporator in the temperature-enthalpy diagram is shown in Fig. 6a. It is possible to integrate the 1-stage unit within 3-stage evaporator and, in retrofit case, it requires heat transfer area increase due to driving force changes. The evaporation temperatures and steam consumption are recalculated. It results in steam reduction but needs additional investments into the evaporator retrofit.

In Fig. 6b the GCC of process streams is demonstrated, and the existing evaporation units can be integrated with the process assuming initial evaporation temperatures. The maxim heat recovery between evaporation units and process stream is defined from GCC (Fig. 6c and d), wherein, higher of extra steam (Fig. 6c) increase a waste heat utilisation opportunity. Nevertheless, it is not always possible to utilise all



**Fig. 6.** Evaporator integration within the process (developed after [39]); (a) representation of 3-stage evaporator and 1-stage evaporator in the shifted temperature-enthalpy diagram; (b) GCC of process streams; (c) integration of 1 stage evaporator within the process; (d) integration of 3-stage evaporator within the process.



**Fig. 7.** Integration of evaporation units with process streams and MVR option.

waste heat of evaporation unit to process heating, and another approach can be used to increase recovery ratio. Evaporation unit stream may be considered with process streams together in GCC to identify an additional opportunity for energy reduction. GCC shows the targets for additional saving via MVR application accounting fixed temperatures of existing process and evaporation unit (Fig. 7). The shifted temperatures and heat load of MVR are identified from GCC and analysed with the use of a simulation environment of UniSim Design. First, the heat recovery opportunity within the HEN is applied and, second, the MVR is simulated, accounting the available amount of extra steam. The fresh steam flowrate is calculated from the mass and heat balance of the evaporation unit and MVR simulation.

### 2.5. The operation, energy benefits and emissions reduction

The heat transfer area of new heat exchangers is optimised to reduce investment cost utilising maximum waste heat. The final retrofit design was checked for operation mode changes and the possibility of step-by-step implementation of the developed energy-saving measures. The retrofit investment cost, energy benefits and CO<sub>2</sub> savings are calculated. Discounted payback period of investments is calculated based on annualised capital cost 5 years project and fractional interest rate per year of 8%. The final retrofit design supposed to be energy efficient, simple, economically beneficial and suitable for further process updates

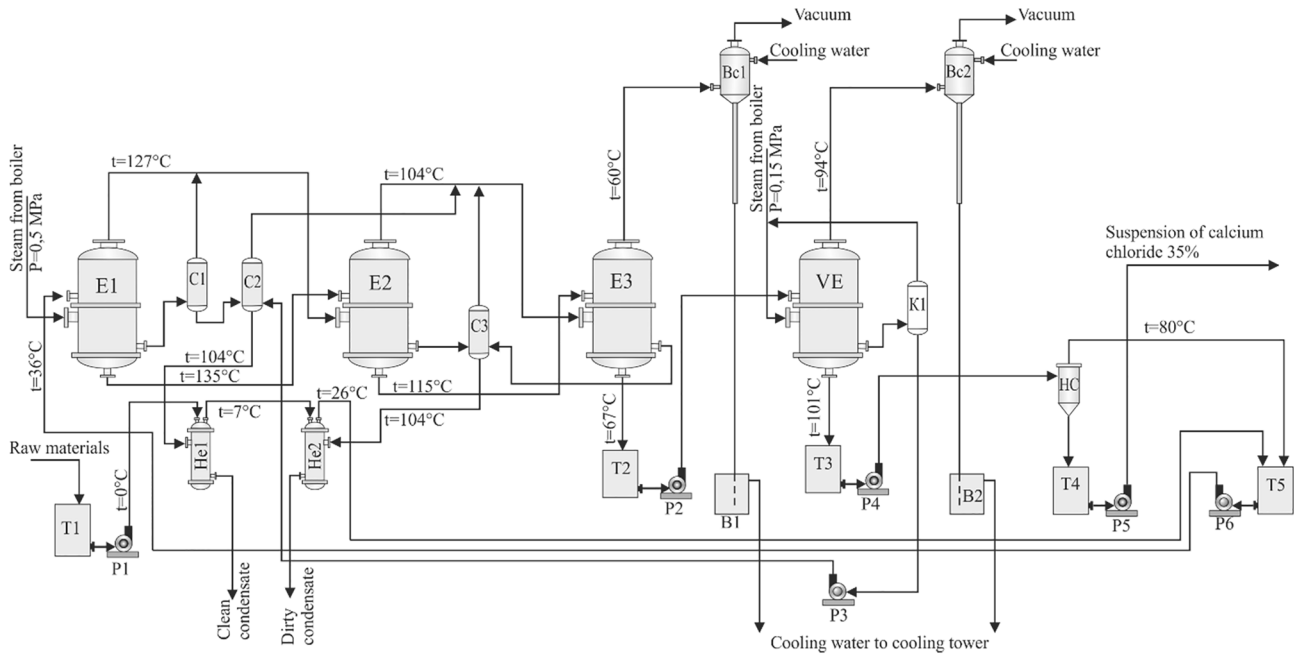


Fig. 8. PFD of calcium chloride evaporation unit. E1-E3 – evaporators; VE – vacuum evaporator; C1-C3 – separators; K1 – condensate trap; Bc1-Bc2 – barometric condensers; T1-T5 – tanks; B1-B2 – barometric tanks; P1-P6 – pumps; He1-He2 – heat exchangers; HC – hydrocyclone.

and control.

The capital cost of heat exchangers was calculated from the Hall method for stainless steel unit [40]:

$$Exchangercost = 10,000 + 324A^{0.91}(\text{USD}), \tag{11}$$

where A is a heat transfer area of the heat exchanger; 10,000, 324, 0.91 are coefficients for stainless steel units. This method provides an accuracy of 5% as proved by Taal et al. [41].

The capital cost of the compressor was estimated based on Chemical Engineering Indexes and Marshall and Swift by Eq. (12):

$$Compressorcost = 98,400 \left( \frac{Q_c}{250} \right)^{0.46} f(t)(\text{USD}), \tag{12}$$

The formulas (1) and (2) accounted cost of specific items of equipment as a function of size, materials of construction, design pressure and design temperature.

The correlation 11 is typically used for the estimation of heat exchanger cost, which is accepted by many researchers. This correlation was compared by Tal et al. 2003, with other correlation and proved as

more appropriate.

The compressors cost may vary a lot because of different working temperatures. Formula (12) was accepted as it considers the temperature factor of compressor cost. The accuracy of this correlation is  $\pm 10\%$  that is a typical target for capital cost estimation.

Annualised investment and payback period were calculated from Eqs. (13) and (14) [20]:

$$Annualised\ investment = Capital\ cost \frac{i(i+1)^n}{(i+1)^n - 1} (\text{USD}) \tag{13}$$

$$Payback\ period = \frac{Annualised\ investment}{Annual\ saving} n(y) \tag{14}$$

Formulas (13) and (14) are economic correlations that are used for annualised investment and payback period calculation (see, e.g. [42]). The results accuracy depends on capital cost calculation by formulas (1) and (2).

The evaluation of capital cost matches 4 AACE International Recommended Practice No. 18R-97 that is  $\pm 30\%$ .

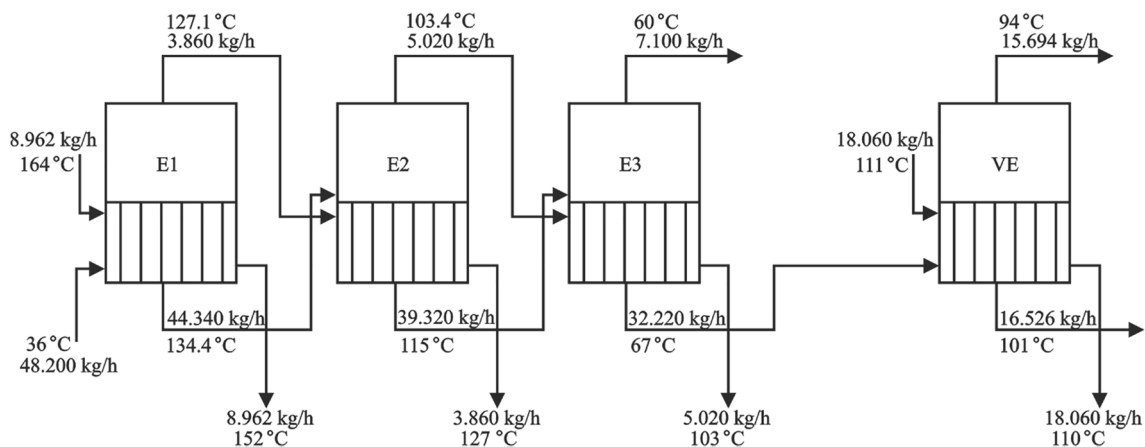


Fig. 9. The mass balance of calcium chloride production.

**Table 1**  
Stream data of calcium chloride concentration unit.

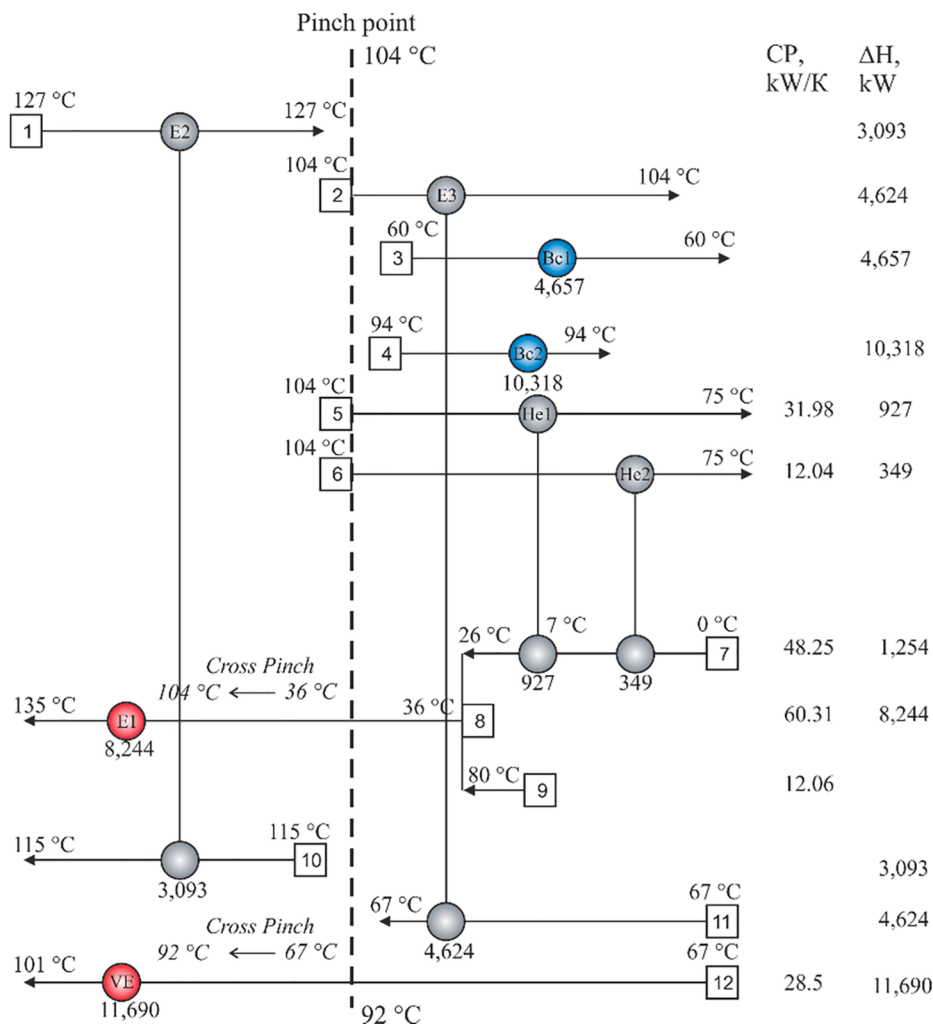
No	Stream name	Type	TS, °C	TT, °C	CP, kW/°C	ΔH, kW
1	Extra steam of 1st evaporator	Hot	127	127	-	3,093
2	Extra steam of 2nd evaporator	Hot	104	104	-	4,624
3	Extra steam of 3d evaporator	Hot	60	60	-	4,657
4	Extra steam of vacuum evaporator	Hot	94	94	-	10,318
5	Clean condensate	Hot	104	75	31.98	927
6	Dirty condensate	Hot	104	75	12.04	349
7	Raw material	Cold	0	26	48.25	1,254
8.1	Raw material + recycle	Cold	36	135	60.31	5,923
8.2	1st stage evaporation	Cold	135	135	-	2,321
9	Suspension of salts (CaCl <sub>2</sub> 35% mass)	-	80	80	-	-
10	2nd stage evaporation	Cold	115	115	-	3,093
11	3d stage evaporation	Cold	67	67	-	4,624
12.1	Calcium chloride in a vacuum evaporator	Cold	67	101	37.98	1,291
12.2	Vacuum evaporation	Cold	101	101	-	10,399

**3. Case study**

**3.1. The description of the existing process**

The production of liquid calcium chloride consists of 3-effect evaporation unit and vacuum evaporator, two shell-and-tube heat exchangers, hydrocyclone and several tanks and pumps (Fig. 8).

The capacity of the current unit is 16.5 t/h of CaCl<sub>2</sub> (14% mass). A cold feed enters the tank T1 to mix and set a calcium hydroxide concentration of 0.03%. The cold feedstock 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 a three-step evaporation unit with a heat transfer area of each unit of 250 m<sup>2</sup>. 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



**Fig. 10.** Grid Diagram – existing HEN of calcium chloride production. E1-E3 – evaporators; VE – vacuum evaporator; Bc1-Bc2 – barometric condensers; He1-He2 – heat exchangers.



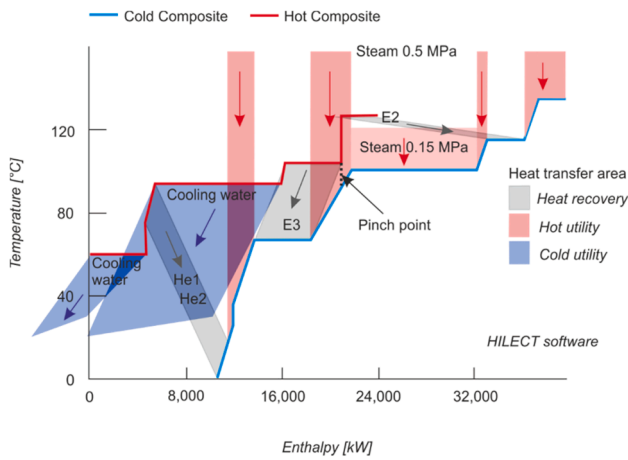


Fig. 11. Composite Curves, temperature driving forces and heat transfer area distribution of existing calcium chloride production.

where it is fed to the vacuum evaporator VE by the pump P2. The heat transfer area of the vacuum evaporator is 630 m<sup>2</sup> and it is heated by the steam (0.15 MPa) 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 Fig. 9.

3.2. Analysis of existing process

During the audit of the factory, more than 50 process and energy streams were considered. Twelve process streams were selected for further analysis and integration; they are collected in Table 1. The equilibrium concentration of NaCl/CaCl<sub>2</sub> brine simulated by HTRI property generator and presented in Appendix A.

Other process streams have remained unchanged as well as equipment associated. The hot utility in a particular process is saturated steam from the boiler house. There are two steam pressure levels 0.5 MPa and 0.15 MPa; the cold utility is cooling water. Cooling water is also used by the vacuum system with barometric condensers and vacuum pumps. Existing heat exchanger network is represented by Grid Diagram in Fig. 10. The energy consumption of the existing process is 19.9 MW for hot and 15.0 MW for cold utility; minimum temperature approach

( $\Delta T_{min}$ ) is 12 °C and it is located on 1st evaporator E1. CC for  $\Delta T_{min} = 12$  °C is shown in Fig. 11 and they demonstrate that the energy targets of particular  $\Delta T_{min}$  are 15.7 MW and 10.7 MW of hot and cold utility respectively. The energy consumption of an existing process is 22% and 28% higher than the target values. This energy gap is the result of the not efficient heat transfer and energy recovery, as demonstrated in Fig. 11. The feeds of the 1st evaporator and vacuum evaporator are under heated. From one side, it is a reason for high energy consumption, from another side, it leads to lower heat transfer coefficient in evaporators and, as a result, its low efficiency.

3.3. Energy-saving potential and pathways

Energy consumption of existing calcium chloride production is 19.9 MW of hot utility and 15 MW pf cold utility; it corresponds to  $\Delta T_{min} = 38$  °C assuming vertical heat transfer (Fig. 12a). Fig. 12 shows that the energy input can be reduced to targets of  $\Delta T_{min} = 12$  °C by 4.2 MW. It may be done by HEN improving without significant changes in the process. This segment decrease monotonically but further function behaviour is controversial; from 10 to 3 °C the energy consumption is constant, and from 3 to 2 °C it comes down dramatically by 5 MW (see Fig. 12b). The HEN improvement by reduction of  $\Delta T_{min}$  below 12 °C is useless, a sharp decrease in energy consumption can be achieved by changes in evaporation units. Pinch point location is not much changed

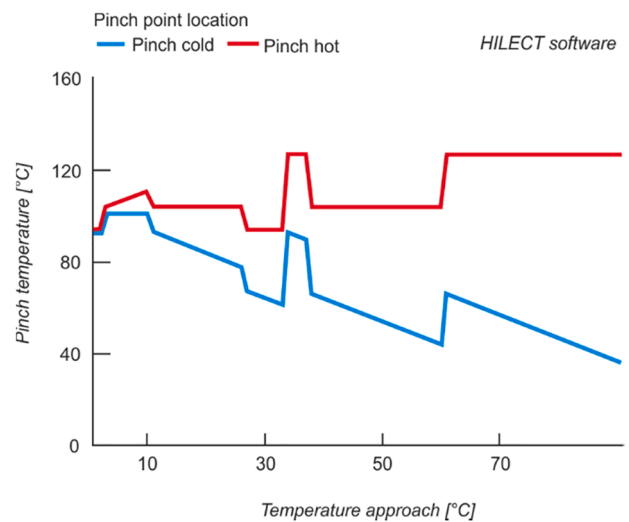


Fig. 13. Pinch point location from the temperature approach.

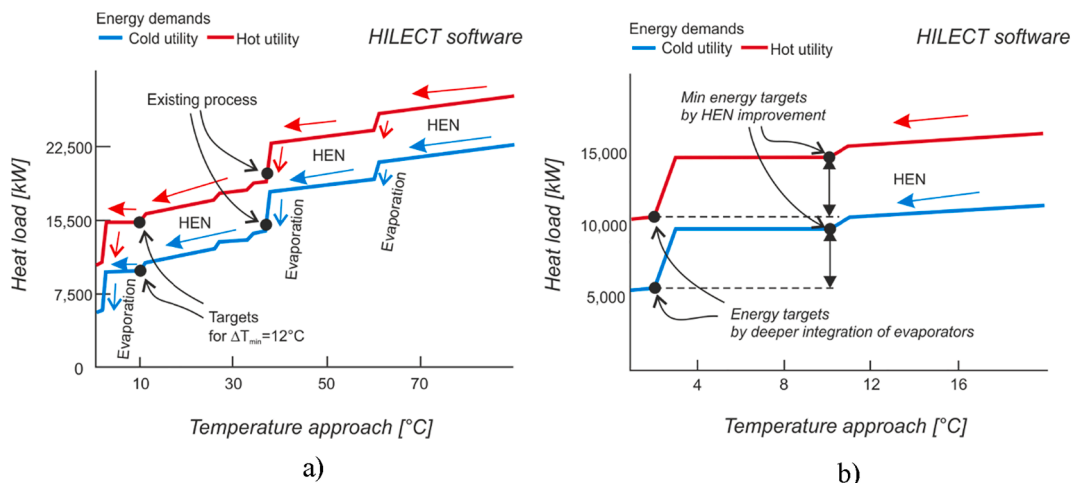


Fig. 12. Energy targets function from temperature approach. (a)  $\Delta T_{min} = 0 \dots 80$  °C; (b)  $\Delta T_{min} = 0 \dots 20$  °C.

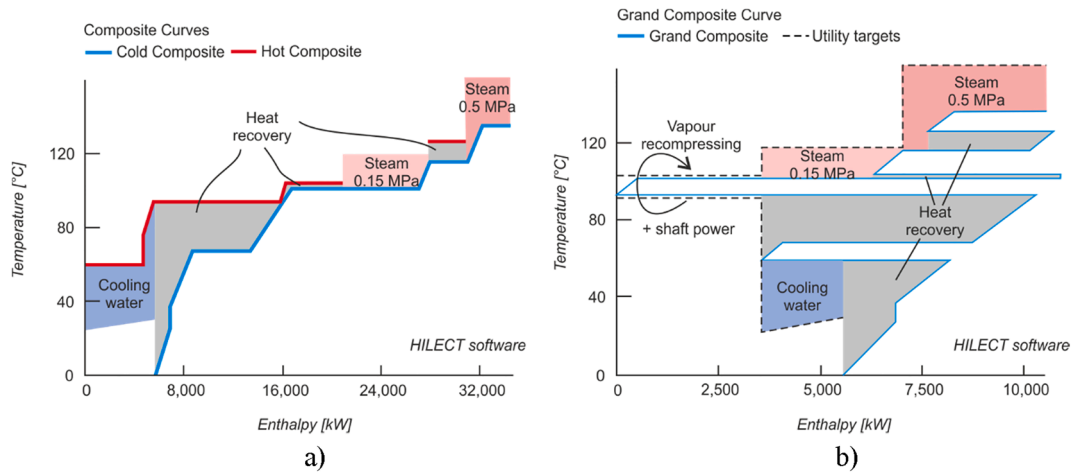


Fig. 14. Energy targets for calcium chloride production for  $\Delta T_{min} = 2^\circ C$ . (a) CC; (b) GCC.

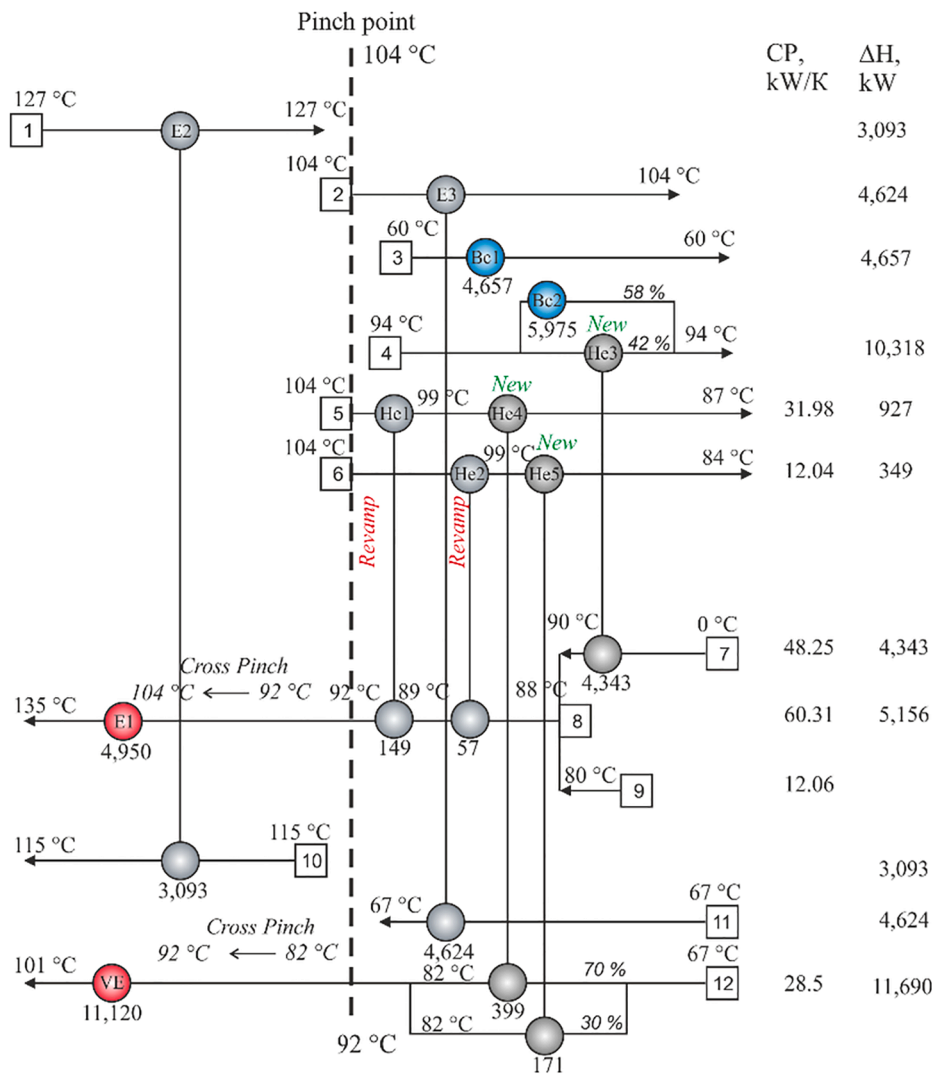


Fig. 15. Grid Diagram – retrofitted HEN (option 1). E1-E3 – evaporators; VE – vacuum evaporator; Bc1-Bc2 – barometric condensers; He1-He2 – existing heat exchangers; He3-He5 – new heat exchangers.

(Fig. 13), and the structure of HEN above and below the Pinch remains the same and simplifies the retrofit design. CC in Fig. 14a demonstrates the possibility of deep heat integration of the investigated process,

which can be assisted by MVR. It will lead to a reduction of heat energy consumption below the targets but with additional electrical energy input. This is well demonstrated by GCC in Fig. 14b.

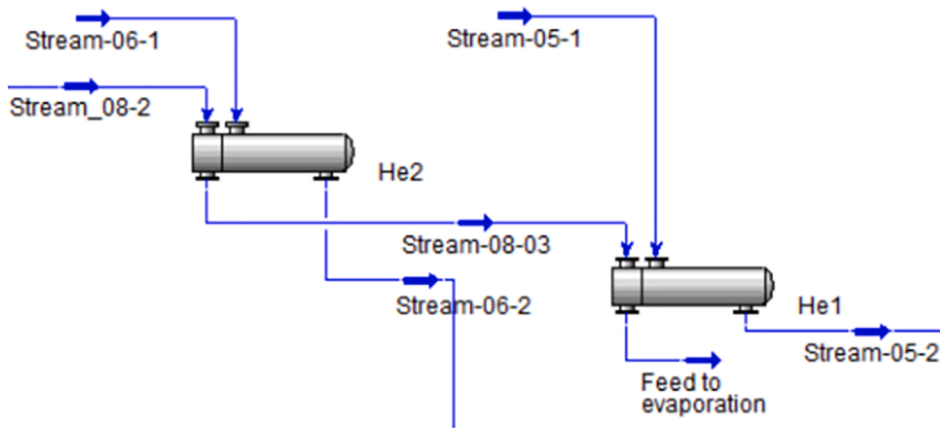


Fig. 16. Simulation PFD for investigation of operation conditions of existing heat exchangers.

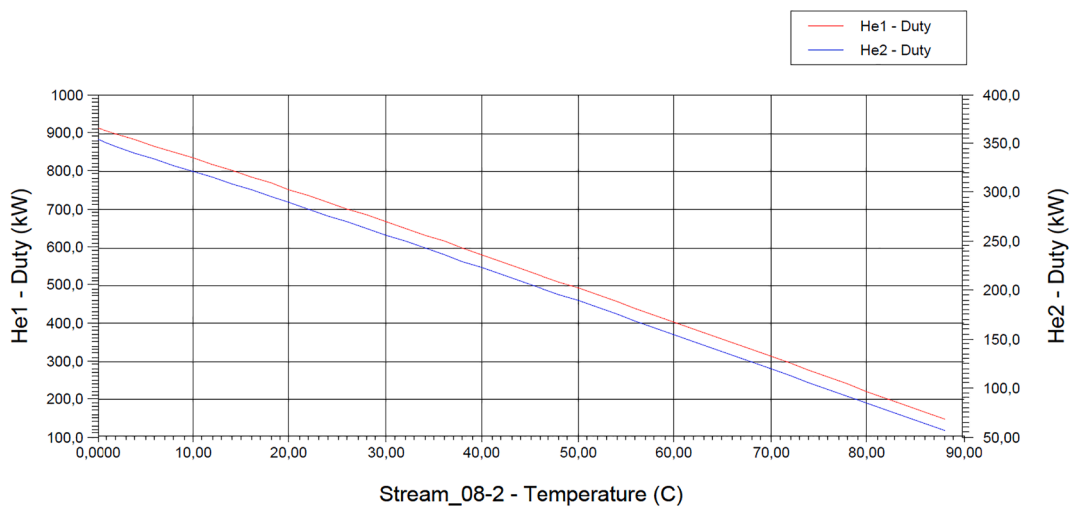


Fig. 17. Correlation of He1 and He2 heat duty from the temperature of mixed feed.

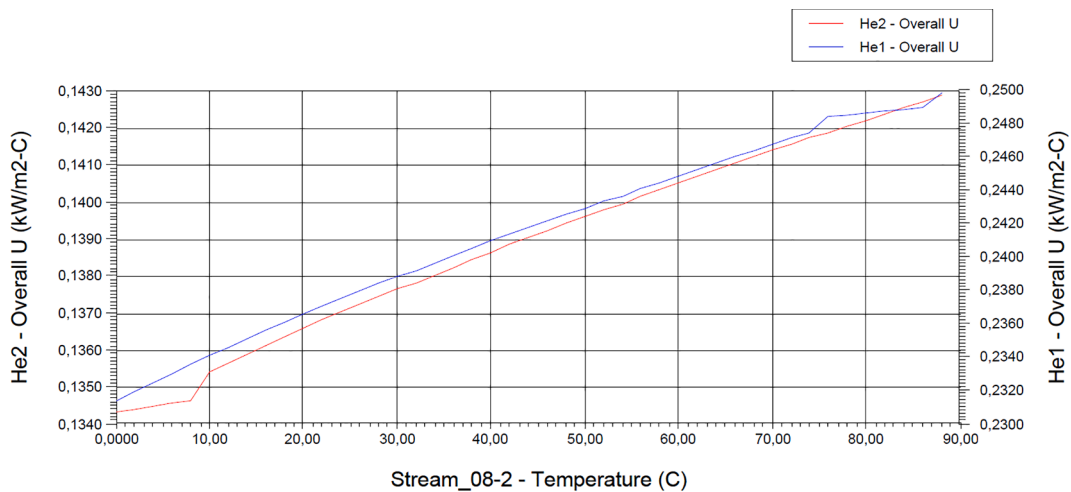


Fig. 18. Correlation of He1 and He2 heat transfer coefficients from the temperature of mixed feed.

Such small temperature approach at Pinch point could be a potential problem for shell-and-tube heat exchangers but can be deployed by other higher efficient units.

### 3.4. Retrofit design – Heat exchanger network

#### 3.4.1. Retrofit option 1

The first retrofit option was applied to eliminate the use of hot utility below the Pinch point. Stream 8 may be heated up to Pinch temperature

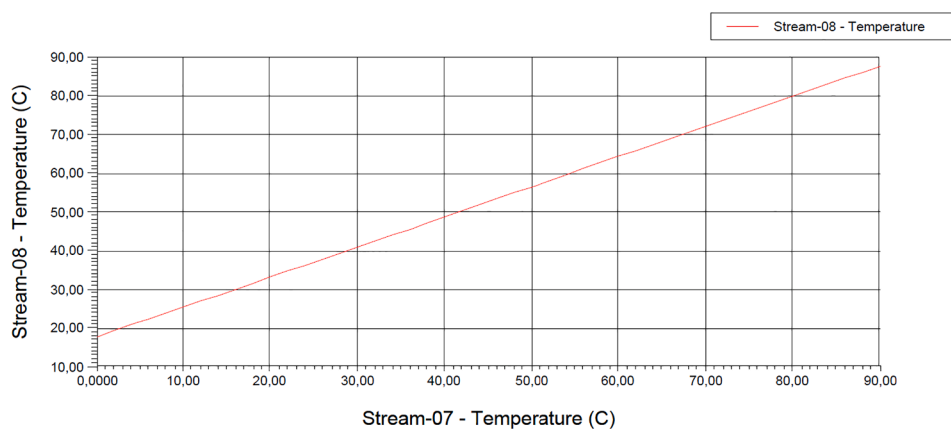


Fig. 19. Simulation results of mixing temperature.

Table 2

Simulated parameters of new heat exchanger He3 for retrofit option 1.

$\Delta p$ , kPa	Stream 7 outlet temperature, °C	Heat recovered, kW	Heat transfer area, m <sup>2</sup>	No of tube passes/baffles	No of shells	Ft factor
5	90	4425	56.02	6/3	1	0.933
10	90	4444	68.23	4/7	1	0.825
15	90	4440	68.23	4/7	1	0.771
20	90	4448	98.25	2/3	2	0.956

only by stream 5 and 6. Existing heat exchangers He1 and He2 may be used for this and placed after the mixer, but it should be first proved by the simulation of operation parameters. The retrofitted heat exchanger network is presented in Fig. 15.

The UniSim simulation PFD of He1 and He2 is shown in Fig. 16.

The working conditions of He1 and He2 heat exchangers were calculated, changing the inlet temperature of feedstock (stream 8) to He2. Fig. 17 demonstrates that the heat duty of both heat exchangers is reduced with temperature grow while the heat transfer coefficients are increased (see Fig. 18). It is demonstrated that the feed of evaporation station (stream 8) may be heated by existing He1 and He2 with the use of clean (stream 5) and dirty (stream 6) condensates from 88 °C to Pinch temperature 92 °C. So, the total energy recovery of two heat exchangers is 306 kW. The mixing temperature of streams 7 and 9 is 88 °C and appropriate temperature of stream 7 were calculated. The temperature of stream 9 is fixed, and it is 80 °C. Fig. 19 shows the simulation results of the mixing of streams 7 and 9, and the final temperature of stream 7 is 90 °C.

Stream 7 is heated in a new additional heat exchanger (He3) by extra steam of vacuum evaporator. The detailed simulation of this heat exchanger was performed, and its construction was optimised to reduce capital investments. The calculation was done for shell-and-tube heat exchangers limited by the maximum shell diameter 800 mm, tube length 4 m and pressure drop of 50 kPa for tube side. Shell side pressure drop varied from 5 to 20 kPa. Pressure drop below 5 kPa is not possible due to crossflow in the shell-side flow model, it is less than 30% and give poor heat transfer. The results of He3 simulation is presented in Table 2.

The most suitable option is the first one with a minimum heat transfer area and acceptable Ft factor. There is still excess heat of

streams 5 and 6 that may be utilised to heat the feed of vacuum evaporator (stream 12). Two more heat exchangers (He4 and He5) were added, and their constructions were selected optimising stream splitting to recover maximum energy and capital investments. The process constraints are the maximum shell diameter 800 mm, tube length 4 m, the pressure drop of tube side 20 kPa and shell side 30 kPa. The simulation results of He4 and He5 are presented in Table 3.

#### 3.4.2. Retrofit option 2

The second option of calcium chloride production retrofit presumes remaining existing heat exchangers at the initial positions. Such an approach remain high non-vertical heat transfer that violates Pinch design principles but recovers maximum energy by the existing heat exchangers. The heat of stream 4 (extra steam of vacuum evaporator) is used to heat both streams 8 and 12 (Fig. 20). The selection of heat exchangers for these purposes is limited by pressure drops 10/20 kPa for shell and tube sides, respectively. The constructions are optimised to get acceptable working conditions and maximum heat recovery. The main restriction here is an Ft factor of the designed heat exchangers and low bound of Ft = 0.75. Therefore, the objective is maximum heat transfer and outlet temperature of the cold stream while Ft factor is higher of 0.75. Parameters of the selected construction of new heat exchangers He3 and He4 are presented in Table 4.

#### 3.5. Retrofit design – Evaporation units

The reduction of the hot utility consumption up to 15 MW is possible by HEN modernisation and decreasing of  $\Delta T_{\min}$  as shown in Fig. 12. Nevertheless, when  $\Delta T_{\min}$  reaches 3 °C, the abrupt utility reduction is observed. It is explained by deeper heat integration of evaporation station that presumes the revamp of steam mains; this is illustrated by CC in Fig. 14a. GCC (Fig. 14b) demonstrated that more integration options and utility targets might be reduced below the values obtained from Pinch point analysis. Though the revamp of extra steam mains is needed to get these targets. Such modification is not viable due to decreasing of temperature driving forces in VA and limited heat transfer area of this unit. In addition, the risk of deposit formation on the heat exchange surface increases, which may lead to a performance reduction of the existing unit. Therefore, the expected energy savings by lowering the minimum temperature difference are highly questionable. Consequently, additionally to HEN improvement, the MVR may be applied to

Table 3

Simulation results of heat exchangers He4 and He5 for retrofit option 1.

Heat exchanger	Stream 12 outlet temperature, °C	Heat recovered, kW	Heat transfer area, m <sup>2</sup>	Number of tube passes/baffles	No of shells	Ft factor
He4	82.41	454	7.97	1/16	1	1.000
He5	82.29	193	3.82	1/38	1	1.000

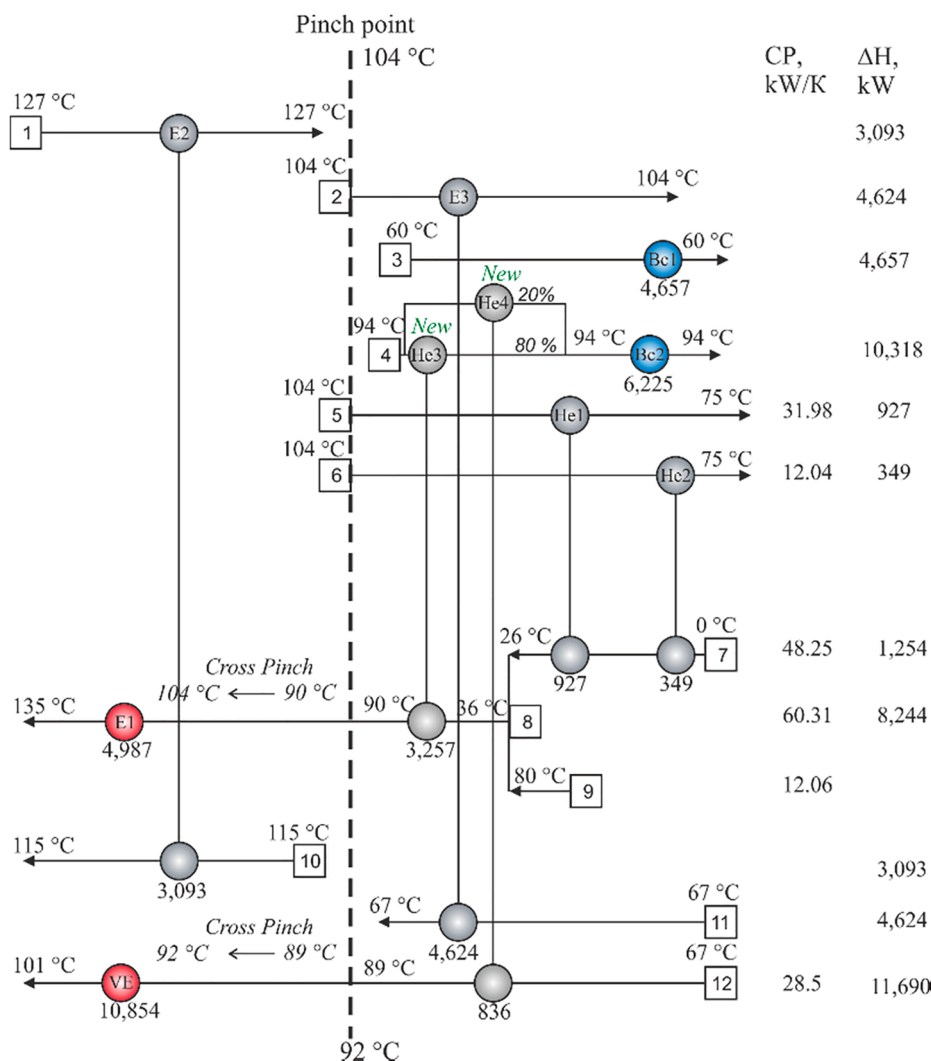


Fig. 20. Retrofitted HEN (option 2) of calcium chloride concentration unit. E1-E3 – evaporators; VE – vacuum evaporator; Bc1-Bc2 – barometric condensers; He1-He2 – existing heat exchangers; He3-He4 – new heat exchangers.

Table 4  
Parameters of additional heat exchangers for HEN retrofit option 2.

Heat exchanger	Stream 8/12 outlet temperature, °C	Heat recovered, kW	Heat transfer area, m <sup>2</sup>	No of tube passes/baffles	No of shells	Ft factor
He3	90	3,285	62.34	4/4	1	0.785
He4	89	926	21.34	2/13	1	0.807

cut the consumption of steam (0.15 MPa) in a vacuum evaporator (VE). Part of VE extra steam goes to HEN developed in Sections 3.4.1 and 3.4.2, and the remain feeds to MVR (K1) where it is compressed and sent to the steam header. The simulation of MVR and steam distribution were executed by UniSim software [34] to get compressor power load, steam (0.15 MPa) flowrate and parameters of steam after the steam header. The simulation PFD, parameters of units and streams are shown in Fig. 21. The final steam (0.15 MPa) consumption is reduced on 2.65 kg/s by MVR that needs additional power of 363 kW. The PFD after proposed process modifications is presented in Fig. 22 and both options of retrofitted HEN can be applied together with the modified process.

#### 4. Results and discussion

##### 4.1. HEN retrofit

Both developed HEN retrofit options of calcium chloride production

need installation of additional exchangers to utilise the waste heat. The retrofit option also needs revamping of He1 and He2; the revamping cost assumes 2,000 USD per shell. Heat exchangers He1 and He2 were revamped within option 1, but the heat carriers in these heat exchangers remain the same. The only changes are that the cold stream goes to new heat exchanger He3, mixes with recycled stream and enter to He2. The revamp cost was accepted as 2 k\$ per unit, and it was selected based on the previous retrofit of similar equipment at an inspected chemical plant. The first option was developed applying more vertical heat transfer that resulted in low additional heat transfer area while the second option has less additional unit numbers. The investment cost for HEN retrofit is presented in Table 5.

The capital cost is different by 21%, but the cost of heat exchangers (He3, He4) of 1st option can be reduced by lowering installation cost. Both exchangers heat feed of vacuum evaporator by condensate and common basement, piping and control devices can be used.

From the other side, the performance of heat exchangers of option 2

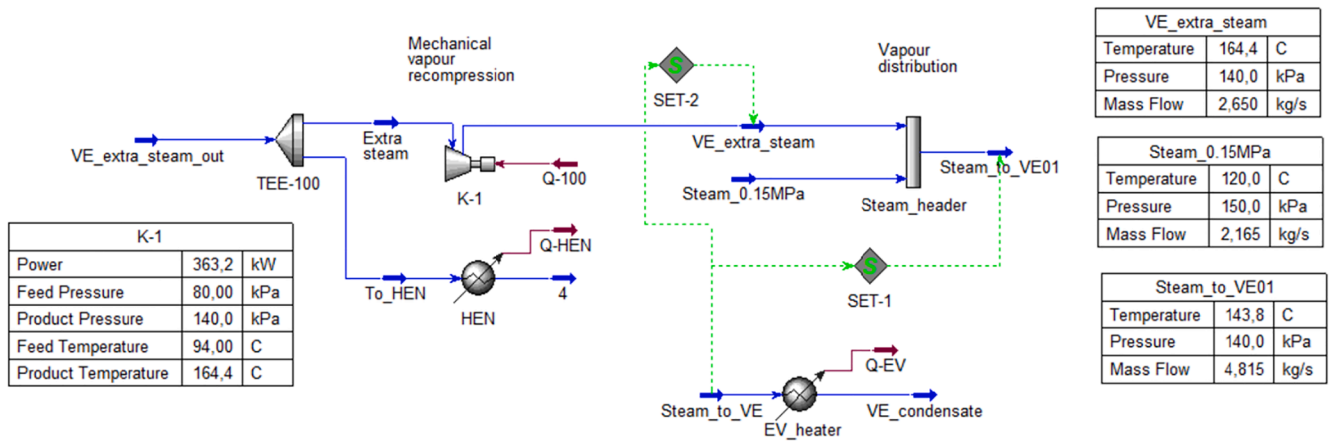


Fig. 21. Simulation PFD of MVR and steam distribution of vacuum evaporator.

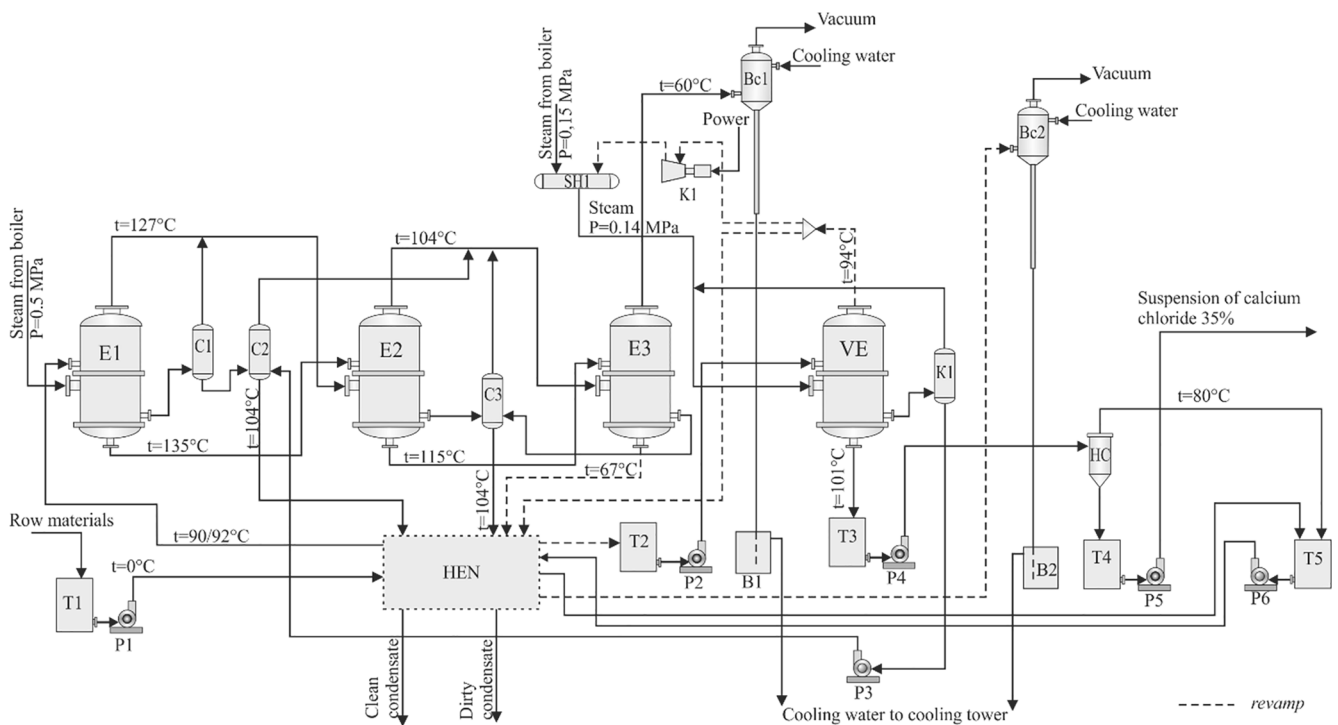


Fig. 22. PFD of calcium chloride concentration with process modifications. E1-E3 – evaporators; VE – vacuum evaporator; C1-C3 – separators; K1 – condensate trap; Bc1-Bc2 – barometric condensers; T1-T5 – tanks; B1-B2 – barometric tanks; P1-P6 – pumps; He1-He2 – heat exchangers; HC – hydrocyclone; HEN – heat exchanger network; K1 – compressor; SH1 – steam header.

Table 5  
The capital cost of retrofit options.

Heat exchanger	Additional area, m <sup>2</sup>	Capital cost, USD	Revamping cost, USD
<i>Option 1</i>			
He1	–	–	2,000
He2	–	–	2,000
He3	56	22,630	–
He4	8	12,150	–
He5	4	11,144	–
Subtotal		45,923	4,000
<b>Total</b>	<b>68</b>	<b>49,923</b>	–
<i>Option 2</i>			
He3	62	23,855	–
He4	21	15,173	–
<b>Total</b>	<b>83</b>	<b>39,029</b>	–

can be decreased due to lower Ft factors. In case of process parameters fluctuation, such as flowrate of heat carriers, the operation of these heat exchanger can be stressed, and more utility may need. It should be noted that the heat recovered by these heat exchangers is limited by Ft factor. Increasing heat transfer area gives small increment of cold stream outlet temperature but results in higher capital cost. The correlations of the cold stream outlet temperature from the heat transfer area of exchangers He3 and He4 for retrofit option 2 are presented in Fig. 23.

There are 2 heat exchangers with a small area in retrofit option 1. The loop (He2-5-4-1) can be broken, and the unit smallest duty He2 is eliminated. In this case, the additional cooler is needed to stream 6 that presumes installation and revamping cost. If one of two new heat exchanger (He4, 5) was excluded from the same loop, it would lead again to an additional cooler at stream 5 or 6, capital cost and utility increase. The heat duty of existing heat exchangers He1, 2 cannot be increased without  $\Delta T_{LM}$  changing that presumes moving them to

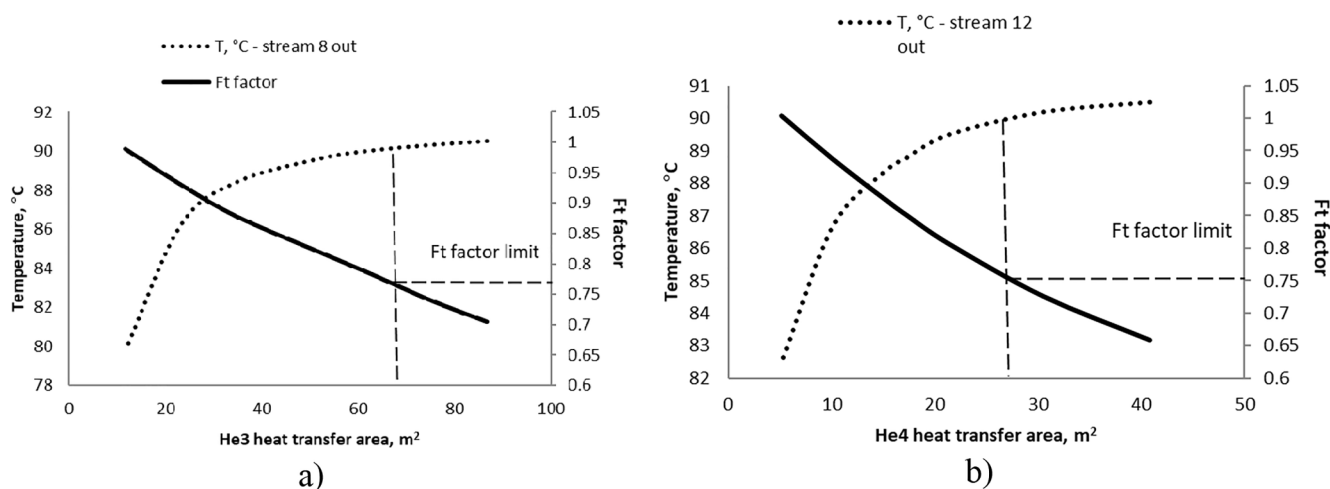


Fig. 23. The correlations of heat transfer area, cold stream outlet temperature and Ft factor: (a) He3; (b) He4.

Table 6

Investment and additional operating cost for process modification.

Item	Units	Value
Compressor cost	USD	186,952
Operating cost (electricity)	USD/y	95,832

another process stream. It again rises up a revamping cost. Small areas' exchangers He4, 5 recover 470 kW of energy, which is not possible to utilise by existing units and other HEN configuration in retrofit option 1. The retrofit 2 provides better hot utility saving but less cold utility saving.

#### 4.2. Process modifications with MVR

The process modifications are shown in Fig. 22 are targeted to the reduction of primary energy; it requires new additional equipment and 363 kW of electricity. The assessment of capital investment and energy needs for the application of the modified process of calcium chloride production is presented in Table 6. The price of electricity was accepted by 264 USD/kWy based on Russian Federation rates. The temperature correction factor of the compressor is accepted at 1.6.

The heat load of recompressed steam is higher than the targets illustrated by GCC (Fig. 14b). It is due to the use of 2nd effect extra stream remain unchanged for heat up 3<sup>d</sup> effect. It was considered as process constrain that increases the size of the processing unit needed for MVR and, as a result, the investment and electricity input. It is possible to avoid excess investments when designing a new unit. From the other side, the temperature difference between 2nd effect extra steam and solution in an additional vacuum evaporator (VA) is very small, and additional heat transfer area is needed that also increase investment.

#### 4.3. Economic efficiency of the retrofit

The application of proposed retrofit options provides utility saving that corresponds to the reduction of steam and cooling water consumption. The utility saving was transformed into financial benefits that may be achieved in the results of the retrofit. The price of hot utility (steam) was accepted of 44 USD/kWy that corresponds to the gas price of Russian Federation accounting 8200 working hours per year and the efficiency of steam boilers of 91%. The cold utility (cooling water) price was accepted by 10% of hot utility prices. The economic calculations were performed assuming project lifetime 7 years and interest rate 12%. Energy-saving measures result in emission reduction, and assessment of CO<sub>2</sub> saving for all retrofit options was done. CO<sub>2</sub> reduction was

Table 7

Economic results of retrofit of calcium chloride production.

Retrofit option	Utility saving hot/cold, %	Investments, USD	OPEX saving, USD/y	CO <sub>2</sub> saving, t/y	Discounted payback, years
HEN 1	19/29	49,923	189,125	7,604	0.40
HEN 2	21/27	39,029	198,101	8,055	0.30
MVR	31/42	186,952	205,458	10,763	1.40
HEN1 + MVR	51/71	236,875	394,099	18,347	0.92
HEN2 + MVR	52/69	225,981	403,075	18,798	0.86

estimated, assuming that the gas-burning generates 0.24 kg CO<sub>2</sub>/kWh [43] and electricity generation corresponds to 0.5 kg CO<sub>2</sub>/kWh [44]. All retrofit options reduce emissions due to utility saving, but MVR application generates it because of additional electricity consumption. Main economic results are presented in Table 7.

HEN retrofits need less investment for comparable OPEX saving that may be more interesting for implementation, but MVR option shows considerable utility saving that converted to high environmental impact. Besides, MVR option can be realised jointly with one of the HEN retrofits that increase economic and environmental benefits. On the first stage, the HEN may be retrofitted and obtained cost saving can be invested to process modification by MVR. As a result, the OPEX saving and environmental benefits will be doubled, as presented in Table 7.

The steam consumption for MVR may be decreased, and, as a result, the capital investments are saved. It is possible by the modernisation of the heating chamber of vacuum evaporator and the use of 2nd effect extra steam as a heating media. In this case, the heat transfer area of the heating chamber should be increased, and steam mains revamp is needed. In result, part of VE extra steam goes to 3<sup>d</sup> effect for heating and balanced amount feeds to MVR. However, this option is more complicated in terms of operation and control and should be investigated in details. Furthermore, the trade-off between these options should be analysed to select more economically beneficial measure.

Additional analysis of other environmental footprints, such as SO<sub>x</sub>, NO<sub>x</sub> etc., should be performed. For these purposes, the steam boilers and power generation system needs to be studied to get more details about fuel composition and efficiency of utility generation and transition. The reduction of fossil fuel consumption and the use of electricity in the process provides the possibility for the transition of the chemical industry to clean energy use. This aspect should be additionally analysed accounting geographical positioning and infrastructure availability of

**Table A1**The equilibrium concentration of NaCl/CaCl<sub>2</sub> brine simulated by VMGThermo.

Mole Fractions, 120.0 kPa														
Temperature	120.00C		124.78C		131.81C		136.46C		142.05C		148.70C		156.51C	
	x	y	x	y	x	y	x	y	x	y	x	y	x	y
NaCl Brine	0.394	6.08E-09	0.437	9.91E-09	0.483	1.93E-08	0.507	2.93E-08	0.530	4.74E-08	0.552	8.18E-08	0.572	1.51E-07
CaCl <sub>2</sub> Brine	0.208	2.59E-09	0.230	4.37E-09	0.254	8.83E-09	0.267	1.37E-08	0.279	2.25E-08	0.291	3.96E-08	0.301	7.41E-08
WATER	0.398	1.000	0.333	1.000	0.263	1.000	0.226	1.000	0.191	1.000	0.158	1.000	0.127	1.000

Mole Fractions, 120.0 kPa											
Temperature	163.63C		171.55C		180.25C		189.74C		200.00C		
	x	y	x	y	x	y	x	y	x	y	
NaClBrine	0.586	2.58E-07	0.598	4.55E-07	0.609	8.29E-07	0.618	1.55E-06	0.625	2.95E-06	
CaCl <sub>2</sub> Brine	0.309	1.28E-07	0.315	2.28E-07	0.321	4.18E-07	0.325	7.85E-07	0.329	1.50E-06	
WATER	0.106	1.000	0.087	1.000	0.070	1.000	0.057	1.000	0.045	1.000	

**Table A2**

Comparison of simulated and measured parameters.

Stream	Parameters	Units	Measured	Simulated
Solution after 1st evaporator	Temperature	°C	136	134.4
Solution after 2nd evaporator	Temperature	°C	116	115
Solution after 3d evaporator	Temperature	°C	68	67
Solution after vacuum evaporator	Temperature	°C	102	101
Extra steam of 1st evaporator	Temperature	°C	128	127.1
Extra steam of 2nd evaporator	Temperature	°C	105	103.4
Extra steam of 3d evaporator	Temperature	°C	61	60
Feedstock (after mixing)	CaCl <sub>2</sub> concentration	% mass	14	14.4
Product	CaCl <sub>2</sub> concentration	% mass	35	35.8
Feedstock before (mixing)	Temperature	°C	25	26
Feedstock (after mixing)	Temperature	°C	36	36.8

studied production facilities.

The final payback period of the proposed retrofit may be increased when implementing in the industry due to additional cost for the development of new documentation for process regulation, mechanical design and supporting guides.

## 5. Conclusions

The results of the current paper demonstrated high energy-saving potential of calcium chloride production. The analysis of process flow-sheet by thermodynamically based approaches identified several drawbacks and potential findings for energy recovery. The combination of different retrofit options was considered. The retrofit of HEN and process modifications with the use of MVR leads to steam usage reduction by 52% and cooling water capacity decreasing by 69%. For the realisation of developed retrofit needs 2 new heat exchangers, compressor and additional electricity consumption of 363 kW. The investment in retrofitting is about 220,000 USD and payback time no more than 1.5 years.

Besides economic benefits, which are about 400,000 USD/y, the retrofit provides reduction of environmental pressure and saving of 18,818 tCO<sub>2</sub>/y.

The results of this paper may be used for the analysis of different processes along with chemical, food, pharmaceutical and other industries that use the evaporation units. The findings could be potentially useful for chemical companies to prove feasibility study of different

energy-saving measures and improve sustainability.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A

See Tables A1 and A2.

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