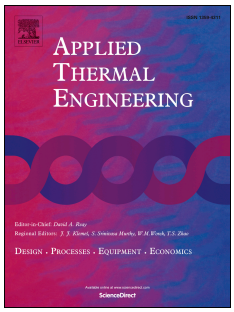
Accepted Manuscript



Performance analysis of a triple-effect absorption cooling cycle using aqueous (lithium, potassium, sodium) nitrate solution as a working pair

MaríaE. Álvarez, Xavier Esteve, Mahmoud Bourouis

PII: S1359-4311(15)00015-0

DOI: 10.1016/j.applthermaleng.2015.01.011

Reference: ATE 6279

To appear in: *Applied Thermal Engineering*

Received Date: 21 July 2014

Revised Date: 3 December 2014

Accepted Date: 4 January 2015

Please cite this article as: M. Álvarez, X. Esteve, M. Bourouis, Performance analysis of a triple-effect absorption cooling cycle using aqueous (lithium, potassium, sodium) nitrate solution as a working pair, *Applied Thermal Engineering* (2015), doi: 10.1016/j.applthermaleng.2015.01.011.

Performance analysis of a triple-effect absorption cooling cycle using aqueous (lithium, potassium, sodium) nitrate solution as a working pair

María E. Álvarez, Xavier Esteve, Mahmoud Bourouis*

Department of Mechanical Engineering, Universitat Rovira i Virgili, Av. Països Catalans No. 26, 43007 Tarragona, Spain

* Corresponding Author (Email: mahmoud.bourouis@urv.cat; Phone: +34 977 55 86 13; Fax: +34 977 55 96 91)

Abstract

A triple-effect absorption cooling cycle using aqueous (lithium, potassium, sodium) nitrate solution (Alkitrate) as a working fluid in the high temperature stage is simulated in this work. This cycle takes advantage of the thermal potential of high temperature heat sources and has a configuration consisting of a H_2O/LiBr double-effect cycle coupled with a single-effect cycle that uses Alkitrate as a working fluid. Heat is exchanged between the two cycles by thermal fluids which flow in the external circuits. The conventional working fluid H_2O/LiBr suffers from serious problems of corrosion and thermal decomposition at temperatures of over 180ºC, which restricts its use in the high temperature components of a triple-effect absorption cooling cycle. At the nominal operating conditions selected, namely a heat source temperature T_H of 250°C and a cooling-water temperature T_C of 30°C the coefficient of performance achieved with the Alkitrate topping cycle is 1.73. The correct operation of the cycle is demonstrated by drawing the cycle in the Duhring diagram, where the safety margin for the crystallization of the working fluid is adhered to.

Results show that the Alkitrate triple-effect cycle has a slightly higher efficiency as compared to the H_2O/LiBr triple-effect cycle at generator temperatures of over 180ºC. Moreover, the practical operation of a H_2O/LiBr triple-effect cycle at temperatures higher than 180ºC suffers from the abovementioned problems related to the thermal stability and corrosion of the working pair.

Keywords: triple-effect absorption cycle, aqueous nitrate solution, alkitrate, high-temperature heat sources.

Highlights

- A triple-effect absorption cooling cycle using Alkitrate as a working pair is simulated for high temperature heat sources.
- The cycle configuration consists of a H_2O/LiBr DE cycle coupled with a SE cycle using Alkitrate as a working fluid.
- The Alkitrate TE cycle has a slightly higher COP compared to H_2O/LiBr TE cycle at generator temperatures of over 180ºC.
- The Alkitrate triple-effect cycle represents a feasible and efficient configuration for high temperature heat sources

1. Introduction

Triple-effect absorption cooling cycles take advantage of the thermal potential of high temperature heat sources and can achieve a coefficient of performance (COP) of up to 50% more than the conventional cooling systems with double-effect cycles [1]. Several authors proposed different configurations of triple-effect absorption cooling cycles. These configurations were often characterized in terms of the number of thermal components. A multi-stage absorption cooling

system comprising several generator/condenser stages and at least one single-stage evaporator/absorber was patented by Mamiya [2]. Oouchi et al. [3] patented a triple-effect cooling system with three generators parallel with each other, in which the solution was supplied from the absorber directly to each of these three generators. Ziegler et al. [4] estimated the performance of seven different configurations of triple-effect cycles for chilling and refrigeration applications. These cycles were formed by the superposition of single-effect cycles and consisted of seven or eight thermal components. Grossman et al. [5] simulated several configurations of H_2O/LiBr triple-effect cycles in a wide range of operating conditions. The systems analysed included the three-condenser-three-generator cycle, to form an extension of the conventional double-effect cycle, and two cycles in which additional heat recovered from the condensate leaving the highest temperature condenser was supplied to the lowest temperature generator. These two cycles were called Double Condenser Coupled (DCC) cycles since heat recovered from the highest temperature condensed refrigerant was used to heat both the middle temperature generator (heat of condensation) and the lowest temperature generator (subcooling of the condensed refrigerant).

Garimella et al. [6] investigated a triple-effect absorption heat pump using NH_3/H_2O as a working fluid in the higher pressure cycle, while NH_3-H_2O and NH_3/NaSCN solutions were studied for the low pressure cycle. The cycle configuration was such that the heat duties of the absorber, condenser and rectifier of the high pressure cycle were rejected to the generator of the low pressure cycle.

Kaita [7] performed a simulation analysis of three configurations of the H_2O/LiBr triple-effect absorption cooling cycle, corresponding to different flow arrangements i.e. parallel-flow, series-flow and reverse flow.

Wang et al. [8] proposed the integration of an exhaust heat recovery generator with conventional gas-fired triple-effect H_2O/LiBr absorption cooling cycles to improve the energy efficiency of the system. The results showed that the coefficient of performance of the system was increased from

1.78 to 1.83. The authors concluded that this technology could be easily implemented and could provide desirable economic benefits, which would be feasible in the development of triple-effect absorption cycles.

Gebreslassie et al. [9] determined the coefficient of performance (COP), the exergetic efficiency, the exergy destruction rate and evaluated the effect of the heat source temperature for seven different configurations of simple, double, triple and half effect H_2O/LiBr absorption cycles. The COP obtained significantly increased from half-effect to triple-effect cycles. The exergetic efficiency showed a less pronounced variation between the different configurations. At higher heat source temperatures the COP decreased slowly. The same qualitative behavior was observed for the exergetic efficiency but the decrease at higher heat source temperatures was more significant. The exergy destruction rate of the heat exchangers increased with the heat source temperature for the absorber and generator, but was practically independent of the heat source temperature for the condenser and solution heat exchanger.

Gomri [10] investigated the potential of H_2O/LiBr single, double and triple-effect absorption cycles for chilled water production. The effects of different operation parameters on the coefficient of performance, exergetic efficiency and the ratio of refrigerant generated to the heat supplied in the generator were investigated by numerical simulation. The author concluded that the COP of the triple-effect cycle was almost three fold that of the single-effect cycle. The results also showed that when the evaporation temperature was varied between 4 °C and 10 °C and the condenser and absorber temperatures were varied from 33 °C to 39 °C the maximum COP values of the triple-effect absorption cycle were in the range 1.62-1.90.

Matsushima et al. [11] developed a dynamic simulation program to predict the transient behaviour of absorption chillers with different cycle configurations. This simulation program was used in the development phase of a high efficiency triple-effect absorption chiller. The results obtained showed

that this machine could be operated smoothly without significant problems and reached COP values of over 1.6.

Agrawal and Karimi [12] proposed a triple-effect cycle which combined the advantages of absorption cycle, ejector cycle and low temperature N_2O refrigerant based compression cycle. The authors concluded that the cycle configuration proposed could produce refrigeration output at different temperatures simultaneously.

Yabase and Makita [13] proposed a solar cooling system employing a steam-driven triple-effect absorption chiller. The cooling system consisted of a triple-effect absorption chiller, a solar thermal collector, a backup boiler, and accessory devices. The steam-driven triple-effect absorption chiller was based on the direct-fired triple-effect absorption chiller developed by Japanese manufacturers between 2001 and 2005 in which only the high temperature generator was modified from a boiler to a heat exchanger for steam heat recovery. The proposed solar cooling system was compared with existing solar thermal cooling systems including those using gas-fired and steam double-effect absorption chillers and gas-fired triple-effect absorptions chillers and its superiority was demonstrated.

Geng and Liu [14] performed an exergy analysis of a compressor assisted triple-effect absorption refrigeration cycle. The authors reported that the addition of a compressor between the low pressure generator and the condenser was an effective solution to reduce the heat source temperature required and to mitigate the corrosion problem in counter-series triple-effect H_2O/LiBr absorption refrigeration cycles.

Agrawal et al. [15] proposed a solar driven triple-effect absorption refrigeration cycle for the production of cooling at temperatures ranging from -80ºC to -50ºC. The cycle configuration integrated an ejector, absorption and cascaded refrigeration cycles. The effect of several design

parameters on energy and exergy performances of the proposed cycle was analysed. The authors concluded that their results could be used to perform a suitable thermodynamic design of solar-assisted triple-effect absorption refrigeration systems.

Therefore, different configurations can be obtained by changing the number of components or loops to establish different couplings between the components and thus allow the use of a different working fluid in each loop. Thereby, a corrosive absorbent can be restricted where it is required within a certain loop, while other working fluids can be employed in other loops [1].

The conventional working fluid H_2O/LiBr suffers from serious problems of corrosion and thermal decomposition at the operating conditions of the triple-effect absorption cooling cycles. The mixture H_2O/LiBr is corrosive at temperatures of over 180ºC and this makes it necessary to use high temperature corrosion inhibitors and specific construction materials which are costly and may affect the absorption process. The corrosion and thermal instability of the H_2O/LiBr working fluid restricts its use in the high temperature components of a triple-effect cycle.

On the other hand, Howe and Erickson [16] determined that the working fluid mixture called Alkitrate is compatible with austenitic stainless steel materials at high temperatures of up to approximately 260°C. This fluid mixture is composed of water as a refrigerant and the salt mixture $LiNO_3$+KNO_3+$NaNO_3$, as absorbent with mass compositions of 53%, 28% and 19%, respectively.

However, this working fluid mixture does not exhibit a wide range of solubility, and consequently its use at low temperatures is limited due to crystallization problems [1]. Therefore, Erickson et al. [1] suggested that Alkitrate could be used in the high temperature components of triple-effect absorption cooling cycles, while the conventional working fluid H_2O/LiBr could be used in the low temperature components.

The objective of this work is to investigate the possibility of improving the use of the thermal potential of high temperature heat sources, by simulating a triple-effect absorption cooling cycle using aqueous (lithium, potassium, sodium) nitrate solution as a working fluid in the high temperature stage. The operating principles of the selected absorption cooling cycles and the thermodynamic simulation methodology are described. The effect of the heat source temperature (T_H) and cooling-water temperature (T_C) on the performance of the Alkitrate triple-effect cycle is also analysed. Moreover, a comparative analysis of the theoretical performance of the Alkitrate triple-effect cycle is made with the H_2O/LiBr triple-effect cycle at different operating conditions.

2. Triple-effect absorption cooling cycle using aqueous nitrate solution as a working fluid

2.1. Cycle configuration

Erickson et al. [1] investigated different triple-effect cycle configurations. In their study, the most promising triple-effect cycle configurations were identified using qualitative selection criteria such as operating pressure, solubility requirements of the working fluids, generic values of the coefficient of performance (COP) estimated according to the superposition principle described by Alefeld and Radermacher [17], risks involved in the component design and the number of components exposed to a high corrosive environment. Based on their analysis, the authors [1] proposed a triple-effect cycle with a high temperature stage using the aqueous (lithium, potassium, sodium) nitrate solution (Alkitrate) as a working fluid. They considered this cycle, known as the "Alkitrate topping cycle", one of the best performing configurations. This triple-effect absorption cooling cycle consists of a H_2O/LiBr double-effect cycle in parallel flow configuration, and a single-effect cycle using Alkitrate as a working fluid. The aqueous nitrate solution is limited to use in the high temperature stage because it does not offer a wide solubility range. Its use at low temperatures is therefore non-viable due to crystallization problems. The triple-effect cycles require high operating temperatures at which the conventional working fluid H_2O/LiBr cannot operate without the addition of corrosion inhibitors or the

use of costly resistant materials, besides presenting problems of thermal instability. Therefore, Alkitrate could be used in the high temperature components, while the conventional working fluid H_2O/LiBr could be used in the lower temperature components of a triple-effect cycle.

In this study, a triple-effect absorption cooling cycle based on the configuration proposed by Erickson et al. [1] has been selected. In this cycle configuration none of the components are exposed to corrosion. The coupling details between the two cycles are discussed below.

2.2. Operating principles

In the conventional triple-effect cycles the heat rejected in the refrigerant condensation process is used to activate the low pressure generator. Based on this and in order to achieve the integration of the high temperature single-effect cycle and the double-effect cycle, two coupling loops are defined as shown in Figure 1 and described below:

- Coupling loop 1: the heat rejected in the high temperature condenser and absorber (Alkitrate single-effect cycle) is used to drive the middle temperature generator (high pressure level in the H_2O/LiBr double-effect cycle).
- Coupling loop 2: the heat rejected in the middle temperature condenser (high pressure level in the H_2O/LiBr double-effect cycle) is used to drive the low temperature generator and to evaporate the refrigerant in the evaporator of the Alkitrate single-effect cycle.

These two coupling loops are made to work by heat exchange of the thermal fluids flowing in the external circuits.

The Alkitrate topping cycle consists of 23 components and 56 streams. The absorber ABS(2) and the condenser CND(6) are cooled by means of external circuits, while the generator GEN(13) is externally heated by the high temperature heat source. Chilled water is produced in the evaporator

EVP(1). Heat rejected in the condenser CND(5) is divided into two streams. To drive the generator GEN(3) on the one side and on the other side to evaporate the refrigerant in the evaporator EVP(11). The coupling between these three components CND(5), GEN(3) and EVP(11) is achieved with a heat exchange circuit (coupling loop 2), in which the cooling water leaving the condenser is split into two streams that later flow through the external circuits of the generator and the evaporator. In the coupling loop 1 the heat rejected in the condenser CND(14) and the absorber ABS(12) of the Alkitrate single-effect cycle is used to drive the generator GEN(4) in the double-effect cycle. The cooling-water streams leaving the external circuits of the condenser and the absorber of the high temperature single-effect cycle are mixed and then sent to the external circuit of the high temperature generator of the double-effect cycle.

The configuration of the double-effect cycle forming part of the selected triple-effect cycle corresponds to the cycle configuration proposed by Grossman et al. [6] and consists of parallel flow alternatively coupled condensers (Figure 1). The hot condensate leaving the condenser CND(5) and the superheated steam from the generator GEN(3) are mixed together before entering the condenser CND(6). The solution rich in refrigerant leaving the absorber ABS(2) is divided into two streams before entering the generators GEN(3) and GEN(4) [6].

3. Simulation methodology

The operation and performance of the triple-effect absorption cooling cycle with a high temperature single-effect stage using Alkitrate as a working pair were analysed using the ABSIM (Modular Simulation of Advanced Absorption Systems) program. ABSIM was selected as a simulation tool because it is a specific modular program for absorption systems and was successfully used by several researchers to simulate a variety of absorption systems with different multi-staged configurations and different working fluids [18]. New subroutines containing the thermophysical properties of the working fluids used in this work were developed and integrated into the ABSIM

properties database. The properties of the working fluid $H_2O/(LiNO_3+KNO_3+NaNO_3)$ with mass compositions in salts of 53%, 28% and 19%, respectively, were then incorporated into the ABSIM program. This program offers the possibility of updating the thermophysical properties of the working fluids already available in the database. The flexibility of ABSIM allowed for the modification of the aqueous nitrate solution properties in accordance with the research carried out by Alvarez in his doctoral thesis [19].

Figure 2 shows a schematic diagram of the Alkitrate triple-effect absorption cooling cycle created in the ABSIM environment. The external coupling loops can be appreciated in this diagram. The streams numbered 15, 16, 45, 46, 51 and 52, the mixer MIX(21) and the splitter SPL(20) form the coupling loop 1, while the coupling loop 2 consists of the streams numbered 10, 11, 48, 49, 54 and 55, the mixer MIX(23) and the splitter SPL(22).

3.1. Problem definition in the ABSIM environment

Since the operation of each absorption cooling cycle depends on a number of operating conditions and design parameters, the approach considered in the cycle simulations carried out in this work was to establish a reference operation point for the system and vary the relevant parameters around it. Furthermore, the design features, particularly the size of the heat exchange surfaces in the cycle components (evaporators, generators, condensers, heat exchangers and absorbers), are a determining factor in the cycle performance.

In previous studies Gommed and Grossman [20] selected a reference case consisting of a H_2O/LiBr single-effect absorption chiller and tested it extensively. An extension of this study was carried out by Grossman et al. [5] using the same approach for triple-effect absorption cooling cycles. Based on the above, a reference case was defined in this work for the triple-effect cycle with a high temperature stage operating with Alkitrate as a working fluid (Figure 2). The values for the size, expressed in

terms of UA values of the evaporator, absorber, condenser, generators, and heat exchangers, are those reported by Grossman et al. [5] and also for the external circuit flows, as well as for the components operating with the aqueous nitrate solution as a working fluid. Actually, this consideration is not completely correct, even if the heat transfer areas (A) remain constant, the overall heat transfer coefficients (U) characterizing the heat transfer process taking place in the thermal components vary depending on the working fluid and the operating temperatures. However, selecting the reference case makes it possible to obtain a good approximation of the real case, since the variation of the overall heat transfer coefficients (U) is relatively small in most cases and it also allows for comparison of the results obtained for the triple-effect cycle under study with other absorption cooling cycles. For a better understanding of the combined heat and mass transfer governing the absorption and desorption processes, the variation of the UA values with relation to the working fluid and operating temperatures should be considered [5].

Input data for simulating the triple-effect cycle with a high temperature stage using Alkitrate as a working fluid are listed in Table 1. They include the flow rates and temperatures in the external circuits, the chilled water flow rate, the flow rate of the solution rich in refrigerant leaving each absorber and the UA values.

The flow rate of the solution rich in refrigerant leaving the absorber ABS(2) is divided equally between the streams sent to generators GEN(3) and GEN(4), as established in Table 1. Based on this and in order to maintain the same solution flow rate at the generator entrance of each pressure stage, the flow rate of the solution leaving the Alkitrate absorber ABS(12) was set at 0.225 $kg.s^{-1}$.

With this input data, the simulation code calculated the internal temperatures, flow rates, concentrations, and other operating parameters at all the cycle streams at which the cycle performance parameters were calculated.

The independent variables selected for simulating the triple-effect absorption cooling cycle with a high temperature Alkitrate stage are as follows:

- The thermal activation energy is supplied to the upper stage generator GEN(13); hence the temperature of the stream 35 is known, T_{35} = 250 °C.
- The outlet temperature of the chilled water (stream 29) is set at 7.2 °C. The cooling effect (chilled water) takes place in the evaporator of the first stage EVP(1).
- The heat rejected in the thermal components is dissipated by means of cooling-water streams. Thus, the temperature of the cooling-water entering the condenser CND(6) and the absorber ABS(2) is known, $T_{23} = T_3$ = 30 °C.

3.2. Mathematical modelling

ABSIM was employed as a simulation tool in the present work. It incorporates a mathematical model based on mass and energy balances, heat and mass transfer equations, equilibrium considerations and the properties of the working fluids. Each component of the absorption cycle is treated as a control volume, with its own inputs and outputs that can be connected to other components. The governing equations applied to each component as well as the global equations are based on some or more of the following physical laws [5]:

a. Conservation of total mass:

$$\sum_i m_i = 0 \qquad (1)$$

where m_i is the mass flow rate (kg.s^{-1}) of the stream numbered (i) in the absorption cycle.

b. Conservation of absorbent:

$$\sum_i (m_i . x_i) = 0 \qquad (2)$$

where x_i refers to the total salt mass fraction of the stream (i)

c. Energy balance:

$$\sum_i [(m_i . h_i)_{in} - (m_i . h_i)_{out}] + Q_{component} = 0 \qquad (3)$$

h_i is the specific enthalpy of the solution ($kJ.kg^{-1}$) of the stream (i) and $Q_{component}$ is the heat duty of the component.

d. Heat transfer was expressed as follows:

$$Q_{component} - UA * LMTD = 0 \qquad (4)$$

where UA values were user-supplied inputs to describe the heat transfer characteristics. The heat duty and logarithmic mean temperature difference, namely $Q_{component}$ and LMTD were calculated according to the temperatures in each component of the absorption cycle.

e. Vapour-liquid equilibrium was defined by the pressure-temperature-concentration (P-T-X) relationship:

$$f(P_i, T_i, x_i) = 0 \qquad (5)$$

P_i and T_i refer to the equilibrium pressure and temperature of the stream (i) at salt mass fraction x_i.

f. Mass transfer expressed in terms of a temperature deviation from equilibrium (DEV):

$$T_i = T_{iE}(P_i, x_i) + DEV \qquad (6)$$

where T_{iE} is the equilibrium temperature and DEV is the parameter that measures the deviation of the vapour and liquid phases from the equilibrium conditions.

From the above equations of each component, a set of nonlinear equations was formed for the whole system and then solved simultaneously.

To carry out the simulation, a number of assumptions that allow for the evaluation of the selected absorption cooling cycles were considered. As mentioned before, the UA values of the thermal components were obtained from a H_2O/LiBr absorption cooling cycle. Additional assumptions, commonly made in this type of thermodynamic modeling, are:

- Steady state conditions are assumed,
- The kinetic and potential energies are negligible,
- Pressure drops along the pipelines and in components are neglected.
- Heat gains or losses to the surrounding along the pipelines and in components are neglected.
- Solution streams leaving the generators and absorbers are in saturated conditions,
- Refrigerant streams leaving the evaporators and condensers are in saturated conditions,
- Enthalpy of the fluid entering the expansion valve is equal to its enthalpy in the valve exit.

3.3. Operating parameters of the triple-effect absorption cooling cycle

The cycle analysis was performed in terms of the coefficient of performance (COP), cooling capacity (Q_E), circulation ratio (CR) and the risk of crystallization of the working fluid mixture.

The coefficient of performance of the cycle (COP) was defined as the ratio of the thermal load (cooling capacity, Q_E) in the evaporator EVP(1) producing the desired cooling effect to the heat

supplied to the high temperature generator externally heated GEN(13) ($Q_{GEN(13)}$). The consumption of the solution pumps and heat losses were not considered. The mathematical formulation of this parameter for the absorption cooling cycle under study is:

$$COP = \frac{Q_E}{Q_{GEN(13)}} \quad (7)$$

The circulation ratio (CR) or flow ratio between the solution rich in refrigerant and the refrigerant entering the absorber is a parameter that provides information on the amount of solution which is needed to absorb 1 $kg.s^{-1}$ of refrigerant vapour in the absorber. A high value of CR indicates that mass concentrations of the rich and poor solutions are very close, and therefore it is necessary to circulate a high flow rate of the solution to absorb the refrigerant vapour mass flow rate of a given cooling capacity. A high value of CR is not suitable because it implies that more pumping power is required to circulate the solution and that the pipe diameters should be greater. It also indicates that sensible heat losses taking place in the solution heat exchangers are greater.

The risk of crystallization of the working fluid in an absorption cooling cycle is evaluated by the difference between the temperature (T_{44}) of the solution poor in refrigerant leaving the solution heat exchanger HEX(15) and the crystallization temperature corresponding to the solution concentration at this point (T_{crist} (X_{44})).

Indeed, the risk of crystallisation of the working fluid is higher at the heat exchanger exit of the circuit using the solution poor in refrigerant because this is where the solution with the highest concentration in salt is at its lowest temperature. A safety margin of 10 ºC was selected to prevent crystallisation at this point of the cycle.

4. Results and discussion

The simulation results of the Alkitrate topping cycle together with a comparison with the triple-effect cycle using H_2O/LiBr as a working fluid are presented in this paragraph.

4.1. Alkitrate topping cycle

We evaluated the performance of a triple-effect absorption cooling cycle formed by the coupling of two separate cycles, namely a double-effect cycle operating with the conventional working fluid H_2O/LiBr and a single-effect cycle that operates at high temperatures with the working fluid H_2O/($LiNO_3$+KNO_3+$NaNO_3$) with mass ratios in salts of 53:28:19, respectively.

The simulation results of the Alkitrate topping cycle represented in Figure 2 at the operating conditions specified in Table 1 are shown in the Duhring diagram of Figure 3. This diagram is very useful because it allows for visualization of the cycle circuits and the relative positions of the thermal components and facilitates the understanding of the cycle operation and direct observation if the operating conditions of the cycle violate the limits of the design. As observed in Figure 3, the Alkitrate topping cycle operates at 4 levels of pressure. Crystallization lines of the aqueous solutions of H_2O/LiBr [21] and nitrates (Alkitrate) [22] were included in the Duhring diagram in order to observe the areas for solubility of both working fluids. Indeed, a drawback of the Alkitrate working pair is its limited solubility. However, in the stream number 44 at the exit of the solution heat exchanger HEX(15) where the solution has the highest concentration in salt (91.01 wt%) and the lowest temperature in the whole circuit of the solution poor in refrigerant, no risk of crystallization is appreciated. The temperature of stream 44 is 11ºC above the crystallization temperature of the solution, as observed in Figure 3. These operating conditions ensure that the operation of the cycle is feasible, although the safety margin for salt crystallization in the cycle is narrow.

The results obtained for the reference case showed that the triple-effect cycle with Alkitrate has a coefficient of performance (COP) of 1.73, a cooling capacity of 55.39 kW and a circulation ratio of 18.57 for the H_2O/LiBr double-effect cycle (CR_{LiBr}) and of 19.09 for the Alkitrate single-effect cycle (CR_{Alk}) without risk of crystallization (T_{44}-Tcrist = 11.2°C).

Figure 4 shows the coefficient of performance (COP) of the Alkitrate topping cycle as a function of the heat supply temperature T_H (stream 35) in the externally heated generator GEN(13) at three different values of the cooling-water temperature T_C (streams 3 and 23), keeping the remaining parameters constant. The cycle performance curves exhibit typical behavior for absorption cooling cycles, the COP increases as the heat supply temperature T_H increases and decreases with the increase in the cooling-water temperature T_C. When the activation temperature reaches the minimum temperature required for the cycle operation, the COP increases sharply then stabilizes to a constant value at a higher temperature and even decreases slightly with a further increase in the heat supply temperature. The values of T_H for which an asymptotic trend of the COP curves was obtained are 170º, 190º and 250ºC at cooling-water temperatures T_C of 25º, 30º and 35ºC, respectively. Figure 4 represents the lines corresponding to the temperature of the solution poor in refrigerant at the exit of the solution heat exchanger HEX(15) (stream 44) and the crystallization temperature corresponding to the current concentration of this stream. These lines illustrate that an increase in the heat source temperature T_H reduces the difference between the current operation temperature of stream 44 and the corresponding crystallization temperature which, in turn, increases the risk of crystallization of the solution. Moreover, Figure 4 shows that the maximum temperature at which the generator can operate safely without the risk of the solution crystallizing is 260°C. The risk of crystallization is lower for the rest of the operating conditions.

4.2. Comparison with cycles employing H_2O/LiBr as a working fluid

The results obtained with the Alkitrate topping cycle were compared with the results obtained from previous studies for triple-effect absorption cooling cycles using H_2O/LiBr as a working fluid. Concretely, a comparison was made between the H_2O/LiBr triple-effect cycle proposed by Grossman et al. [5] (Figure 5) and the Alkitrate topping cycle in which the flow arrangement in the H_2O/LiBr double-effect cycle is in series (Figure 6).

The input data in Table 1 was adapted to each cycle configuration. The coefficient of performance (COP) and cooling capacity of each cycle were used as parameters for comparison. Figures 7 and 8 show the trends of the performance parameters in each cycle configuration depending on the heat source temperature T_H. The temperatures of the chilled water and cooling-water entering ABS(2) and CND(6) were set at 7.2° and 30°C, respectively. In all the cycle configurations investigated, the mass flow rate of the solution leaving the absorber ABS(2) was set at 0.45 $kg.s^{-1}$ and an equal distribution was used for the solution flow rate entering the middle temperature and high temperature generators.

According to the COP curves, the Triple-effect cycle using H_2O/LiBr as a working fluid shows COP values greater than those of the Alkitrate topping cycle up to T_H of 180°C, and from then on COP trends are slightly inverted as T_H increases leading to a higher performance of the Alkitrate topping cycle with a parallel flow configuration compared to the H_2O/LiBr triple-effect cycle. Likewise, the results obtained in previous studies regarding the flow arrangement are confirmed. The parallel flow arrangement represents an improvement of approximately 20% in the COP of the cycle as compared to the series flow arrangement.

Cooling capacity usually follows an opposite trend in behaviour to that of COP, therefore COP maximization actually results in a reduction of the cooling capacity. However, the reduction of the

cooling capacity in the Alkitrate topping cycle is more significant as compared to the H_2O/LiBr triple-effect cycle. On the other hand, the operation of H_2O/LiBr triple-effect absorption cooling cycles at temperatures of over 180°C suffers from serious problems related to thermal stability and corrosion of the working pair, so the feasibility of using H_2O/LiBr triple-effect cycles for high temperature heat sources depends on the development of new construction materials or corrosion inhibitors that allow for the above mentioned obstacles to be overcome.

Therefore, the triple-effect cycle with a high temperature Alkitrate stage represents a feasible and efficient option that allows for the thermal potential of high temperature heat sources to be taken advantage of.

5. Conclusions

The triple-effect absorption cooling cycle called the "Alkitrate topping cycle" which uses aqueous (lithium, potassium, sodium) nitrate solution as a working fluid is investigated here. This cycle permits the thermal potential of high temperature heat sources to be harnessed and used. The operation of triple-effect cycles with the conventional working fluid H_2O/LiBr is not feasible at temperatures of over 180°C due to the limited thermal stability and the high corrosiveness of the working pair at high temperatures. The Alkitrate topping cycle consists of a double-effect cycle in parallel flow with H_2O/LiBr as a working fluid coupled with a high temperature single-effect cycle using Alkitrate as a working fluid. The results obtained from the Alkitrate topping cycle are compared with those obtained from the triple-effect cycle using H_2O/LiBr as a working fluid.

At the nominal operating conditions selected, namely a heat source temperature T_H of 250°C and a cooling-water temperature T_C of 30°C the coefficient of performance achieved with the Alkitrate topping cycle is 1.73. The correct operation of the cycle is demonstrated by drawing the cycle in the Duhring diagram, where the safety margin for the crystallization of the working fluid is adhered to.

The Triple-effect cycle with H_2O/LiBr as a working fluid shows COP values greater than those of the Alkitrate topping cycle up to T_H of 180°C, when COP trends are inverted as T_H increases leading to a slightly higher performance of the Alkitrate topping cycle. Moroever, it is worth mentioning that the practical operation of H_2O/LiBr triple-effect cycles at temperatures of over 180 ºC is not feasible due to the limited thermal stability and the high corrosiveness of this working fluid at high temperatures.

Hence, the triple-effect cycle with a high temperature Alkitrate stage represents a feasible and efficient option to take advantage of the thermal potential of high temperature heat sources.

Acknowledgements

This study was part of an R&D project funded by the Spanish Ministry of Science and Innovation (ENE2007-65541/ALT). M. Álvarez acknowledges the receipt of scholarship award (BES-2008-006253) from the Spanish Ministry of Science and Innovation.

438 **References**

439 [1] Erickson D., Potnis S., Tang J., Triple effect absorption cycles, Proceedings of the 31st
440 Intersociety Energy Conversion Engineering Conference; 1996, Washington (USA), pp. 1072-1077.

441 [2] Mamiya, G. Multi-stage absorption refrigeration system. US Patent No. 3 831 397, 1974.

442 [3] Oouchi, T.; Usui, S.; Fukuda, T.; Nishiguchi, A. Multi-stage absorption refrigeration system. US
443 Patent No. 4 520 634, 1985.

444 [4] Ziegler F., Kahn R., Summerer F., Alefeld G, Multi-effect absorption chillers, International Journal
445 of Refrigeration 16 (1993), pp. 301-11.

446 [5] Grossman G, Wilk M, DeVault R., Simulation and performance analysis of triple-effect absorption
447 cycles. ASHRAE Transactions 100 (1994); pp.452-62.

448 [6] Garimella S., Lacy D., Stout R., Space-conditioning using triple-effect absorption heat pumps

449 Applied Thermal Engineering 17 (1997), pp. 1183-1197.

450 [7] Kaita Y., Simulation results of triple-effect absorption cycles, International Journal of Refrigeration
451 25 (2002), pp. 999-1007.

452 [8] Wang L., You S., Zhang H., Li X, Simulation of gas-fired triple-effect LiBr/water absorption cooling
453 system with exhaust heat recovery generator, Transactions of Tianjin University 16 (2010), pp. 187-
454 193.

455 [9] Gebreslassie B., Medrano M., Boer D., Exergy analysis of multi-effect water-LiBr absorption
456 systems: From half to triple effect, Renewable Energy 35 (2010), pp. 1773-1782.

457 [10] Gomri R., Investigation of the potential of application of single effect and multiple effect
458 absorption cooling systems, Energy Conversion and Management 51 (2010), pp. 1629-1636.

459 [11] Matsushima H., Fujii T., Komatsub T., Nishiguchi A., Dynamic simulation program with object-
460 oriented formulation for absorption chillers (modelling, verification, and application to triple-effect
461 absorption chiller), International Journal of Refrigeration 33 (2010), pp. 259-268.

462 [12] Agrawal B., Karimi, M., Thermodynamic performance assessment of a novel waste heat based
463 triple effect refrigeration cycle, International Journal of refrigeration 35 (2012), pp.1647-1656.

464 [13] Yabase H., Makita K., Steam driven triple effect absorption solar cooling system. International
465 Refrigeration and Air Conditioning Conference at Purdue, USA, 2363 (2012) pp. 1-8.

466 [14] Geng C., Liu Y., Exergy analysis of a compressor assisted triple-effect absorption refrigerating
467 cycle, Applied Mechanics and Materials 405-408 (2013), pp. 2975-2979.

468 [15] Agrawal S., Kumar R., Khaliq A., First and second law investigations of a new solar-assisted
469 thermodynamic cycle for triple effect refrigeration, International Journal of Energy Research 38
470 (2014), pp. 162-173.

471 [16] Howe L., Erickson D., Proof-of-Concept Testing of Alkitrate, Phase III. Final Report- Energy
472 Concepts Co., Annapolis, Maryland, USA, 1990.

473 [17] Alefeld, G.; Radermacher, R., Heat conversion systems, USA, CRC Press Inc, 1994.

474 [18] Grossman G., Zaltash A., ABSIM-modular simulation of advanced absorption, International
475 Journal of Refrigeration 24 (2001), pp. 531-543.

476 [19] Álvarez M.E., Theoretical and experimental study of the aqueous solution of lithium, sodium and
477 potassium nitrates as a working fluid in absorption chillers driven by high temperature heat sources
478 (in Spanish), PhD Thesis, Rovira i Virgili University, Tarragona, Spain, 2013.

479 [20] Gommed K., Grossman G., Performance analysis of staged absorption heat pumps: Water–
480 Lithium Bromide systems, ASHRAE Trans 1990, 96: 1590-1598.

481 [21] Boryta D., Solubility of lithium bromide in water between -50ºC and 100 ºC (45 to 70% lithium
482 bromide). Journal of Chemical Engineering & Data 15 (1970), pp. 142-144.

483 [22] Vargas P., Salavera D., Galleguillos H., Coronas A., Solubility of aqueous mixtures of alkaline
484 nitrates and nitrites determined by differential scanning calorimetry, Journal of Chemical Engineering
485 & Data 53 (2008), pp. 403-406.

486

487

488

Table 1. Input data for the simulation in ABSIM of the Alkitrate topping cycle [5]

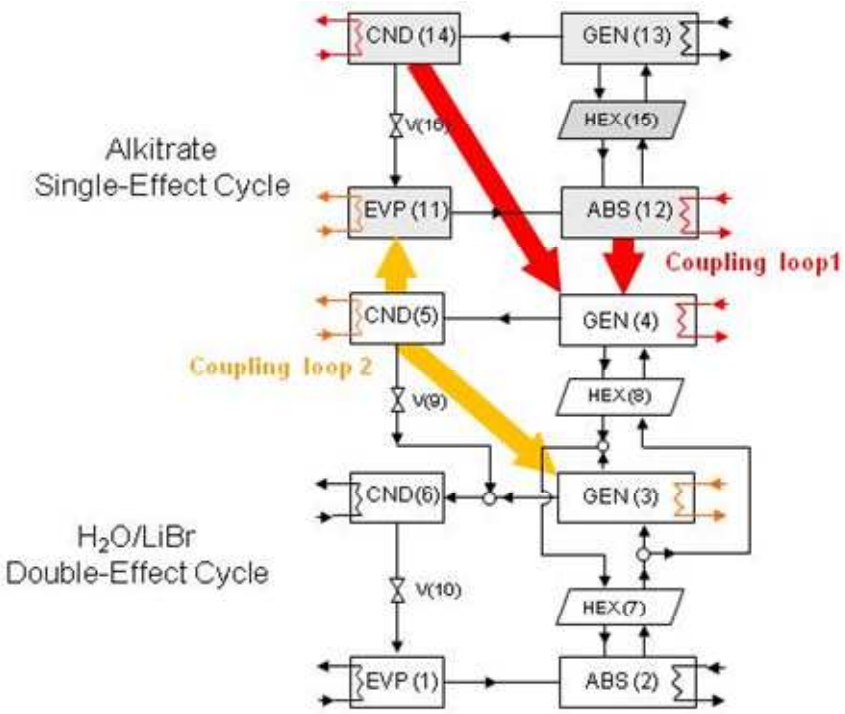
Input data	
Heat transfer characteristics (UA), kW.ºC^{-1}	
Absorbers: ABS(2) and ABS(12)	6.11
Generators: GEN(3), GEN(4) and GEN (13)	17.88
Condensers: CND(5), CND(6) and CND(14)	8.48
Evaporators: EVP(1) and EVP(11)	11.90
Heat exchangers: HEX(7), HEX(8) and HEX(15)	2.03
Mass flow rates, kg.s^{-1}	
Absorbers (cooling-water): m_3 and m_{52}	3.65
Condensers (cooling water): m_{11}, m_{23} and m_{46}	2.96
Evaporator (chilled water): m_{28} and m_{54}	2.27
Solution leaving the absorber ABS(2): m_5	0.45
Solution entering each generator: m_8, m_{13} and m_{33}	0.225
Temperatures, ºC	
Heat source in GEN(13): T_{35}	250.00
Inlet cooling-water: T_3 and T_{23}	30.00
Outlet chilled water: T_{29}	7.20

Table caption

Table 1. Input data for the simulation in ABSIM of the Alkitrate topping cycle [5]

518

519



520

521 Figure 1. Configuration of the triple-effect absorption cooling cycle with a high temperature Alkitrate

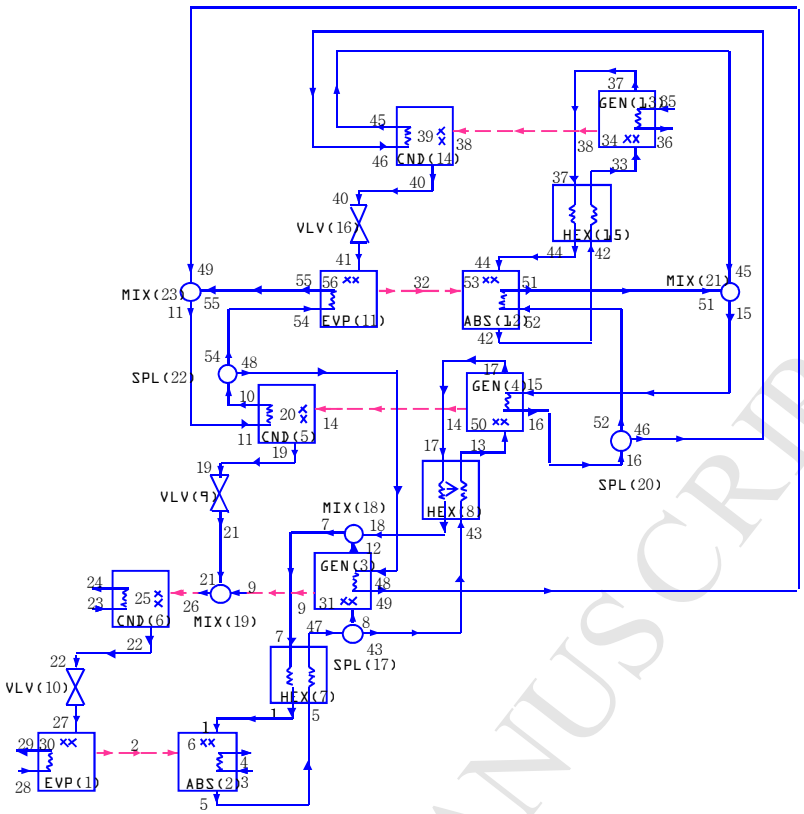
522 stage

523

524

525

526



527

528 Figure 2. Configuration in ABSIM of the triple-effect absorption cooling cycle formed by a H_2O/LiBr

529 parallel flow double-effect cycle and a single-effect cycle using Alkitrate as a working fluid

530

531

532

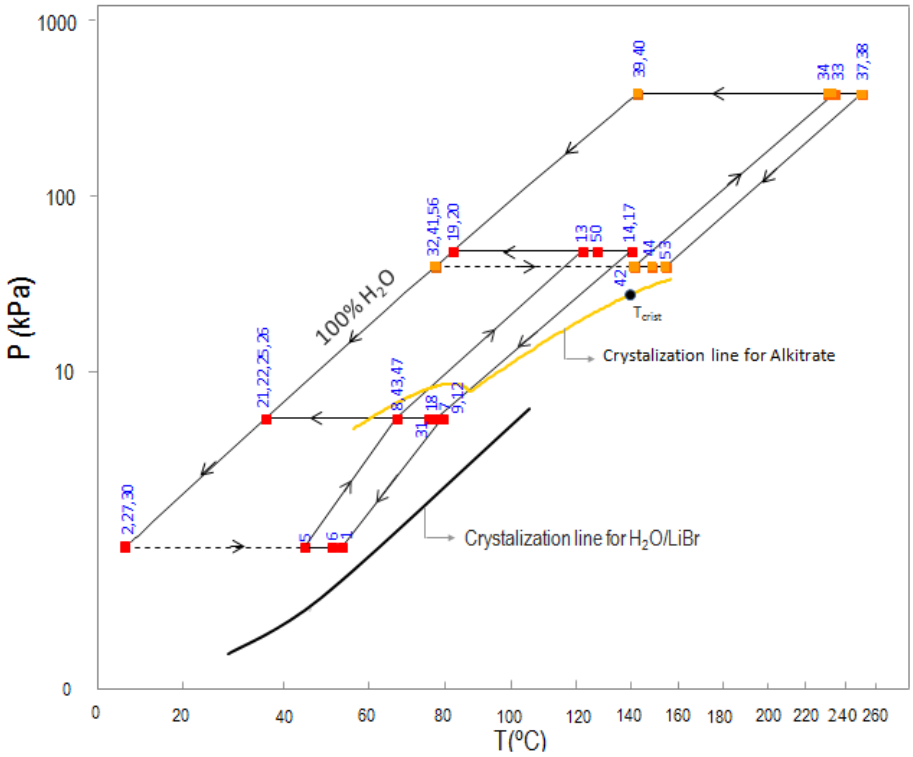
533

534

535

536

537

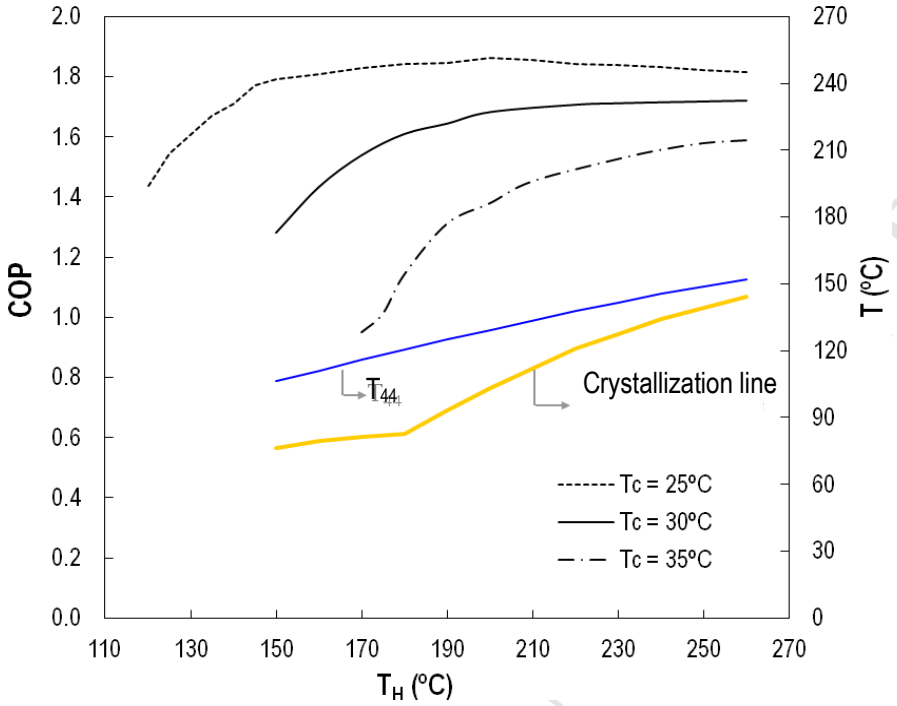


538 Figure 3. Dühring diagram (P-T-X) of the triple-effect absorption cooling cycle with a high

539 temperature Alkitrate stage at the operating conditions listed in Table 1

540

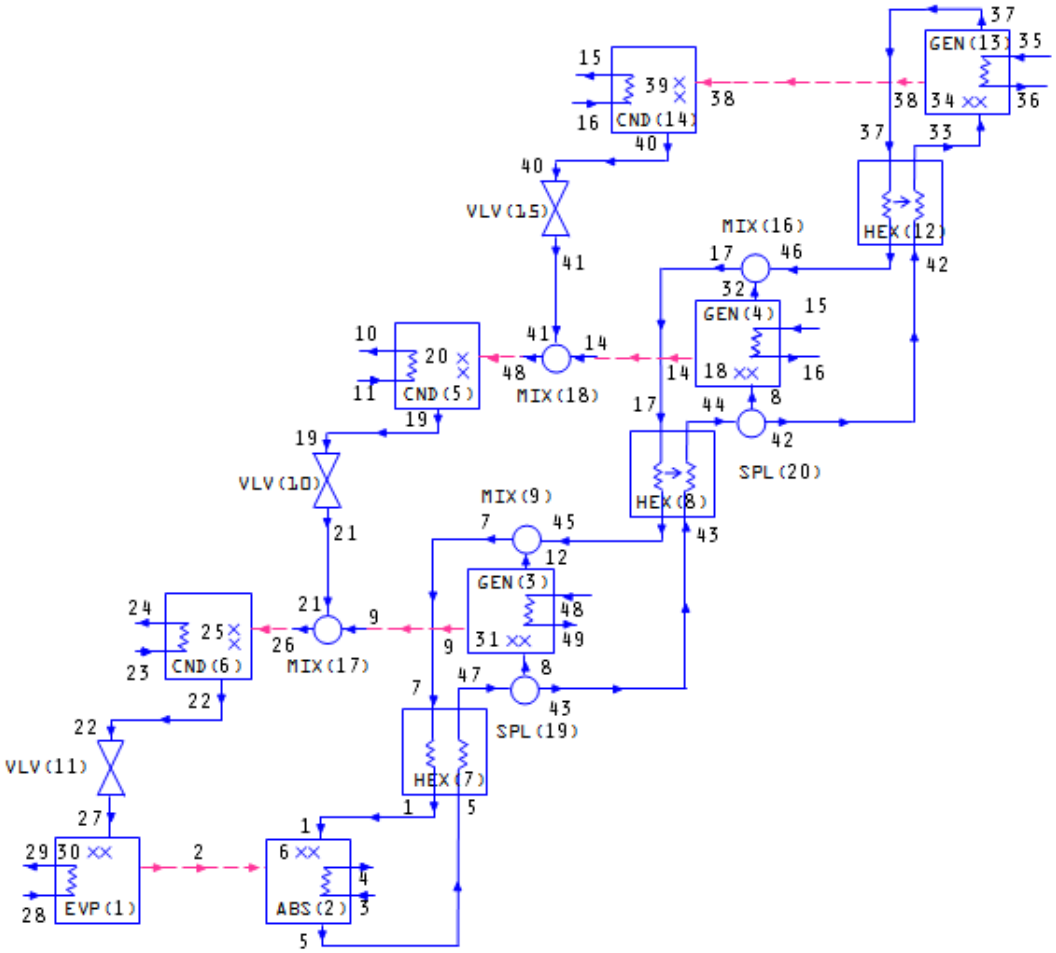
541



542

543 Figure 4. Coefficient of performance and crystallization line of the triple-effect absorption cooling
544 cycle with a high temperature Alkitrate stage, versus the temperatures of the heat source (T_H) and
545 cooling-water (T_C)

546
547

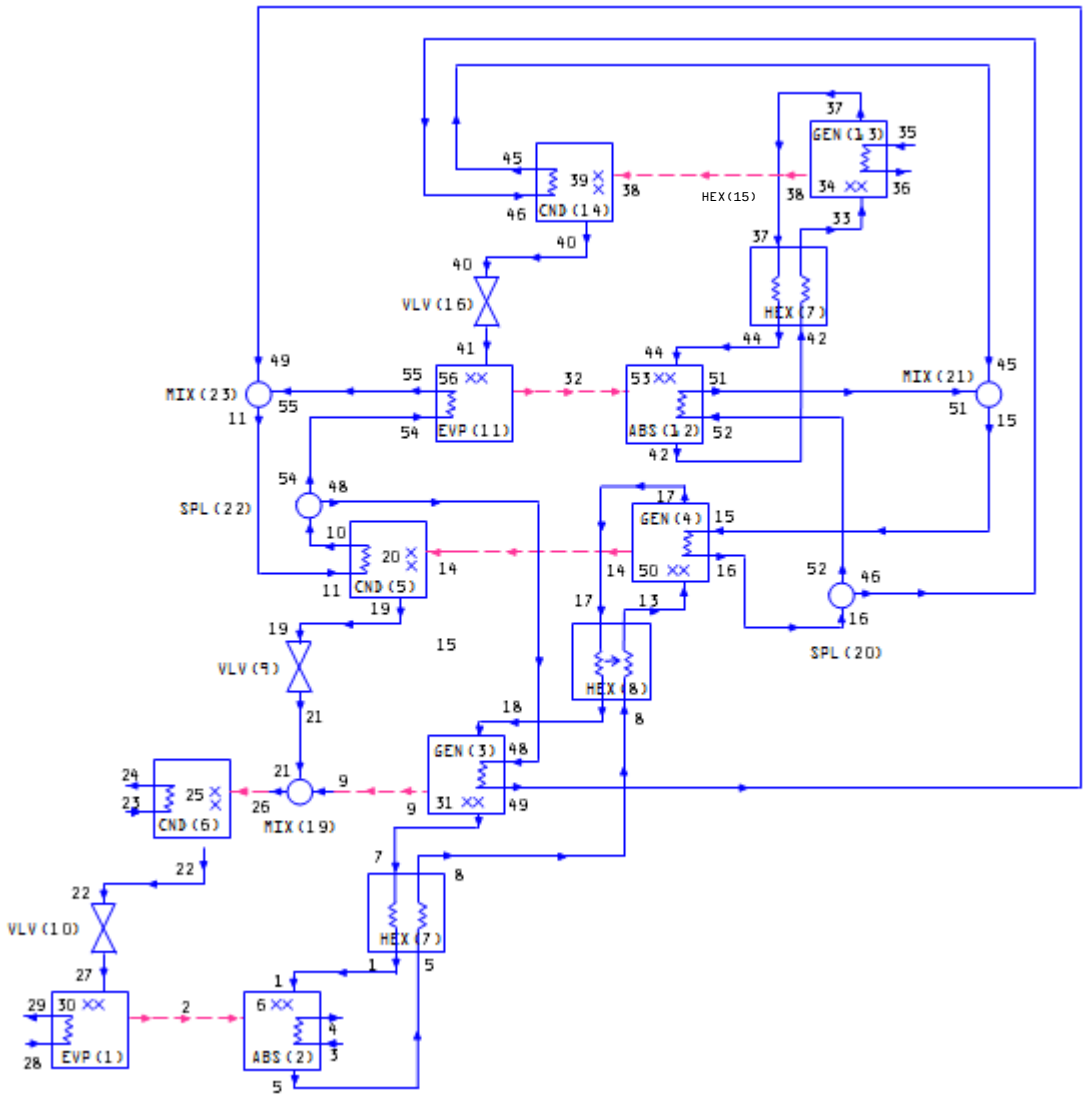


548

549 Figure 5. Configuration in ABSIM of the triple-effect absorption cooling cycle with two condensers

550 coupled alternatively in parallel flow [5]

551



552

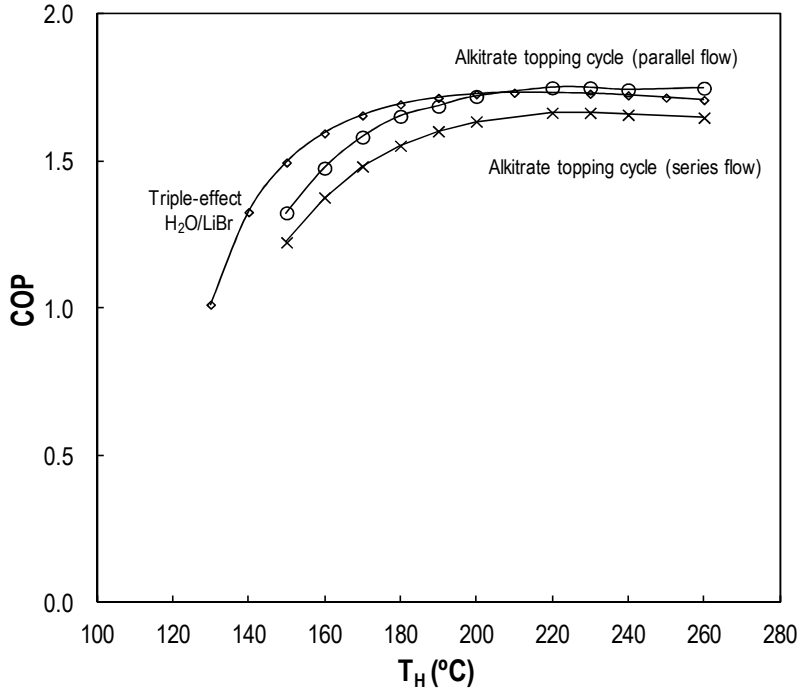
553 Figure 6. Configuration in ABSIM of the triple-effect absorption cooling cycle formed by a H_2O/LiBr

554 series flow double-effect cycle and a single-effect using Alkitrate as a working pair

555

556

557



558
559

560 Figure 7. Coefficient of performance of the simulated absorption cooling cycles, H_2O/LiBr triple-effect

561 cycles and parallel flow and series flow Alkitrate topping cycles, versus the heat source temperature

562 T_H

563

564

565

566

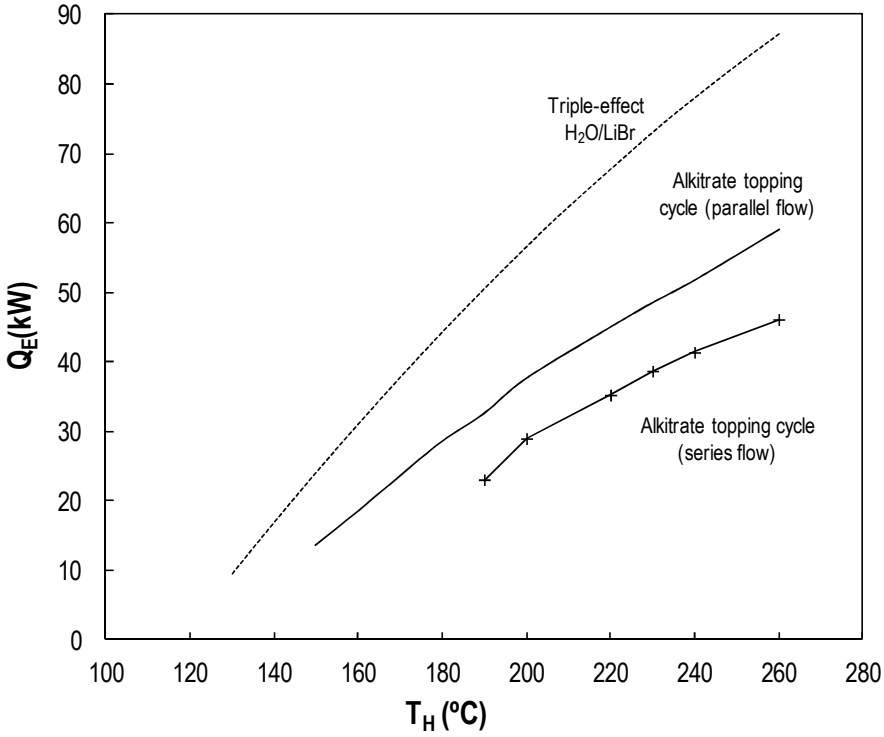
567

568

569

570

571



572

573 Figure 8. Cooling capacity of the simulated absorption cooling cycles, H_2O/LiBr triple-effect cycles

574 and parallel flow and series flow Alkitrate topping cycles, versus the heat source temperature T_H

575

576

577

578

579

580 **Figures caption**

581 Figure 1. Configuration used in the present work for the triple-effect absorption cooling cycle with a
582 high temperature Alkitrate stage

583 Figure 2. Configuration in ABSIM of the triple-effect absorption cooling cycle formed by a H_2O/LiBr
584 parallel flow double-effect cycle and a single-effect cycle using Alkitrate as a working fluid

585 Figure 3. Dühring diagram (P-T-X) of the triple-effect absorption cooling cycle with a high
586 temperature Alkitrate stage at the operating conditions listed in Table 1

587 Figure 4. Coefficient of performance and crystallization line of the triple-effect absorption cooling
588 cycle with a high temperature Alkitrate stage, versus the temperatures of the heat source (T_H) and
589 cooling-water (T_C)

590 Figure 5 Configuration in ABSIM of the triple-effect absorption cooling cycle with two condensers
591 coupled alternatively in parallel flow [5]

592 Figure 6. Configuration in ABSIM of the triple-effect absorption cooling cycle formed by a H_2O/LiBr
593 series flow double-effect cycle and a single-effect cycle using Alkitrate as a working pair

594 Figure 7. Coefficient of performance of the simulated absorption cooling cycles, H_2O/LiBr triple-effect
595 cycles and parallel flow and series flow Alkitrate topping cycles, versus the heat source temperature
596 T_H

597 Figure 8. Cooling capacity of the simulated absorption cooling cycles, H_2O/LiBr triple-effect cycles
598 and parallel flow and series flow Alkitrate topping cycles, versus the heat source temperature T_H

599