

Recent developments and future prospects of sorption heat pump systems

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Abstract — Heat transformation with sorption systems has received increased attention in recent years. The intention of this review article is to discuss current as well as forthcoming applications along with the respective appropriate technology. This includes chillers and refrigerators which may be direct fired or waste heat driven. Emphasis is given to the improvement of efficiency on the one hand, as well as to adaptation to low temperature waste heat use on the other hand – two very different developments. The use of solar energy as heat source also belongs to this area. The second area of application is heat pumping for heating purposes. Systems with large capacity are being installed every once in a while, but the small-scale domestic market is not yet really covered with appropriate technology. Finally, industrial heat pumping involves the reverse cycle (heat transformer). This market has declined after a climax in the seventies. Nevertheless the heat transformer offers opportunities for enhanced process integration and will probably attract renewed interest in the future. © Elsevier, Paris.

review / absorption / adsorption / chemical reaction / chiller / refrigerator / heat pump / heat transformer / heat recovery

Résumé — **Développements récents et perspectives en matière de pompes à chaleur à sorption.** Au cours des dernières années, les transformateurs de chaleur à sorption ont fait l'objet d'une attention particulière. Dans cet article de synthèse, on présente des applications actuelles et prochaines avec les technologies associées. Ces applications recouvrent, tout d'abord, les machines à eau glacée et les réfrigérateurs utilisant la chaleur issue directement d'une combustion ou de rejets thermiques. L'intérêt est porté, d'une part, sur l'amélioration des rendements et, d'autre part, sur l'adaptation des systèmes aux basses températures dans le cas de l'utilisation des rejets thermiques. L'utilisation de l'énergie solaire comme source de chaleur fait partie de ce champ. Le second domaine d'applications concerne le pompage de la chaleur pour des besoins de chauffage. Des systèmes de grandes puissances seront installés dans un avenir proche. En revanche, il n'existe pas de technologies réellement appropriées au marché du secteur domestique. Dans le secteur industriel, le pompage thermique implique également les cycles réversibles (transformateurs thermiques). Ce marché est en déclin, après avoir connu un maximum dans les années 1970. Cependant, les transformateurs thermiques permettent l'intégration de processus améliorés et, de ce fait, feront probablement l'objet d'un regain d'intérêt dans le futur. © Elsevier, Paris.

inversion des déformations / problème de revue / absorption / adsorption / réaction chimique / refroidissement / réfrigération / pompe à chaleur / thermotransformateur / revalorisation de chaleur

Nomenclature

c	concentration of solution
COP	coefficient of performance
l	specific heat of solution..... $\text{kJ}\cdot\text{kg}^{-1}$
PE	primary energy kJ
PER	primary energy rate
Q	transferred heat..... kJ
r	specific heat of condensation..... $\text{kJ}\cdot\text{kg}^{-1}$

T	temperature..... $^{\circ}\text{C}$ or K
ν	efficiency

Indices

0, 1, 2, 3	temperature levels in rising order
5	five-effect
B	burner
bottom	bottoming cycle
s	strong solution
s	solar
top	topping cycle
w	weak solution

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1. INTRODUCTION

In the early years of this century, sorption refrigeration was quite frequently used. Later, with the development of cheap reliable compressors and electrical motors, the improvement in power station efficiency, and the introduction of the CFCs, sorption refrigeration became a niche technology. However, recent years have witnessed increasing interest in this technology for many different specific reasons. The main arguments in favour are that sorption systems are quiet, long lasting, cheap to maintain and environmentally benign. Of course this opinion is not universally held. There have been cases involving high maintenance costs and short life; the environmental impact consists of many different parts which cannot be summarized by the statement that sorption systems (normally) do not use CFCs or HCFCs. Nevertheless, the freedom from noise and vibrations and, above all, the possibility of using heat to energise the systems are convincing arguments in favour of sorption systems. The most often quoted drawbacks are heavy weight and large footprint, a lack of understanding the process, and, above all, the relatively high initial cost.

In this paper we review the state of the art and the current R & D. We will distinguish between the different possible areas of application because the respective pros and cons will differ quite considerably also. We want to give a view of where, and for what reason, sorption systems are being used today and what the future will be. We will cover chiller applications (gas cooling, solar cooling, waste heat cooling) as well as refrigeration, heat pumping and industrial waste heat recovery. We will not discuss very small systems (hotel room and camping refrigerators). We will also skip sorption-compression hybrids [1–4] which have interesting features but are much less developed. Moreover, we will exclude open sorption systems [5–8].

To begin with, we give a short introduction to the fundamentals. For more basic information the reader should refer to the literature [9–13]. Stephan [14], Burgett et al. [15], Fiskum et al. [16], and Furutera et al. [17] give history and contemporary evolution. In addition, current developments may also be traced by reading the Proceedings of the International Absorption Heat Pump Conferences, the most recent of which were held in New Orleans [18] and Montreal [19].

2. FUNDAMENTALS

Sorption systems transform latent heat of the phase change liquid–vapour or solid–vapour between different temperature levels. Sorption systems use two working

fluids, the refrigerant and the sorbent. Thus the temperature of phase transition can be manipulated not only by changing the pressure but also by changing the refrigerant concentration.

2.1. The basic cycle

One possible use of this physical principle is realised in the single-effect heat pump cycle which is depicted in figure 1.

The four most important components are the evaporator E, where cooling is provided, the generator G, where the driving heat is conveyed to, and the absorber A and condenser C, from which the pumped heat is disposed of. In the generator vapour is desorbed from the solution due to the heat input. The vapour is condensed, throttled and evaporated as in compression systems. After evaporation the vapour is absorbed in the solution which is cooled in the absorber. The solution is pumped to the generator to be regenerated and throttled back to the absorber. To improve efficiency a solution heat exchanger SHX is introduced into the solution circuit. For cooling applications, the efficiency (coefficient of performance, *COP*) is defined as the ratio of cooling output, Q_0 , to driving heat input, Q_2 .

$$COP = \frac{Q_0}{Q_2}. \quad (1)$$

Other performance measures, e.g. for heat pumping, may be defined accordingly.

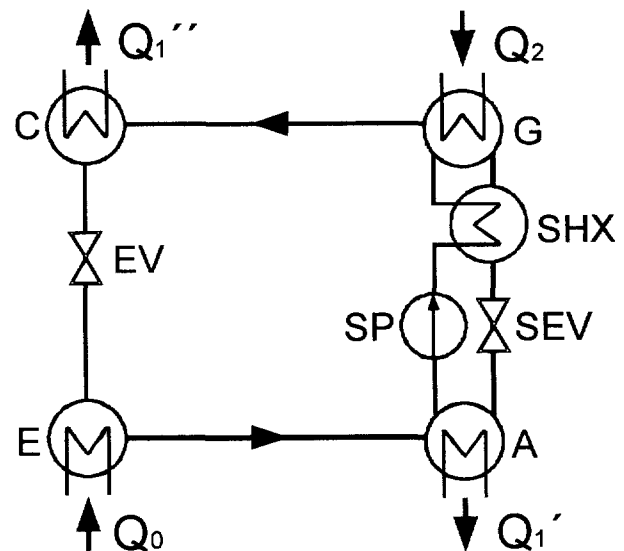


Figure 1. Flow sheet of a single-effect absorption chiller. A: absorber, C: condenser, E: evaporator, EV: expansion valve, G: generator, SEV: solution expansion valve, SHX: solution heat exchanger, SP: solution pump.

2.2. Consequences of solution field geometry

In order to get more information about the performance it is useful to discuss the reversible limit of the *COP* which is well-known and in a first order approximation proportional to the ratio of temperature thrust $T_2 - T_1$ and temperature lift $T_1 - T_0$:

$$COP < \frac{T_0(T_2 - T_1)}{T_2(T_1 - T_0)} \approx \frac{\text{Thrust}}{\text{Lift}} \quad (2)$$

The temperatures can be seen in *figure 2*, where the single-effect cycle is plotted over the pressure-temperature relationship of the solution field. The temperature of the evaporator T_0 and the temperature of the condenser, as well as that of the absorber outlet T_1 are in general fixed within a range of some degrees by the chilled water and cooling water temperature. The physical properties of the working fluids used, i.e. essentially the vapour pressure lines, determine the position of the cycle within the solution field. In principle this is equally valid for adsorption machines, i.e. those using solid sorbents to adsorb the refrigerant vapour. The equilibrium sorbate charge of the solid sorbent at given temperature and pressure yields equilibrium lines for the phase change which can be treated in the same way as the vapour pressure curves of the liquid absorption system.

The external conditions for chilled and cooling water determine the internal temperatures T_0 and T_1 , the pressure levels, and finally the temperature T_2' , which is

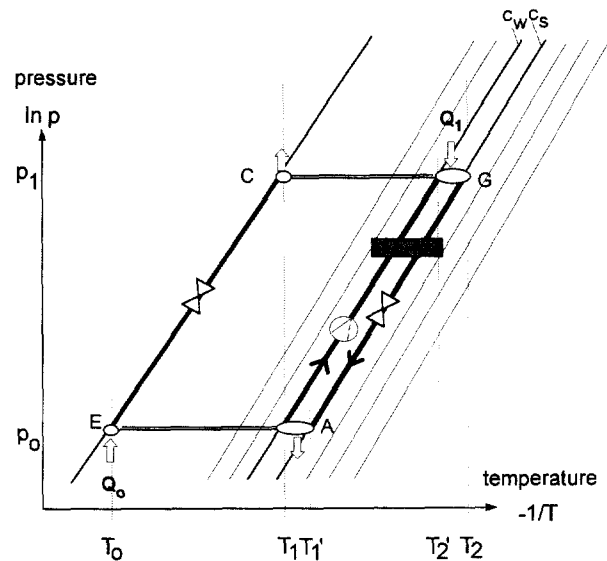


Figure 2. Schematic drawing of a single-effect absorption cycle in the pressure-temperature plot. E: evaporator, A: absorber, G: generator, C: condenser, c_w : weak solution, c_s : strong solution, Q: transferred heat.

the minimum driving temperature. Of course, during the desorption or regeneration process the solution changes concentration from strong, c_s , to weak, c_w , and the equilibrium temperature changes accordingly from T_2' to T_2 . In the absorber A, the concentration changes back from weak to strong with the equilibrium temperature gliding from T_1' to T_1 . So the temperature which is really required or attained in the generator G is T_2 , which only for infinite solution flow is equal to the minimum temperature T_2' . We want to elaborate briefly on the magnitude of this temperature.

The reciprocal temperature thrust, $1/T_1 - 1/T_2$, and the reciprocal temperature lift, $1/T_0 - 1/T_1$, due to the Clausius-Clapeyron equation, are related to the heat of solution, l , and condensation, r :

$$(1/T_1 - 1/T_2')/(1/T_0 - 1/T_1) = r/(r + l) \quad (3)$$

Classical liquid and solid sorbents do not vary strongly in the relation of the heat of solution to the heat of condensation. The heat of solution is in the order of 5 to 20 % of the heat of condensation. Because this ratio does not vary strongly with changes in the working pair, the minimum driving temperature T_2 for a given lift is independent of the working pair within a few degrees.

Moreover, comparing equation (3) with (2), we can write the *COP* also in the form:

$$COP < r/(r + l) \quad (4)$$

This also means that the maximum *COP* does not vary strongly with changes in the working pair.

From these very simple considerations we may draw two important conclusions: firstly, the *COP* cannot be raised above a limit in the order of one for a simple single-effect cycle. Secondly, the temperature of the driving heat cannot be lowered beyond a certain temperature which can be derived from chilled water and cooling water temperature for a simple single-effect cycle.

2.3. Multistage cycles

The two restrictions discussed above are very inconvenient. However, they have traditionally been overcome by the method of multistaging the single-effect cycle [9, 10, 20, 21, 22]. The basic idea is to repeat either the desorption-condensation processes or the evaporation-absorption processes at different pressures or temperatures as compared to the single-effect cycle. Three simple possibilities are shown in *figure 3*, which is a pressure-temperature plot with the solution field and the axes not shown. The circles represent the main exchangers, the arrows denote the heat flowing in or out of a component. Consequently, circles with arrows going to them represent evaporators or generators, circles with arrows leaving represent absorbers or condensers. The number of arrows qualitatively represents the respective

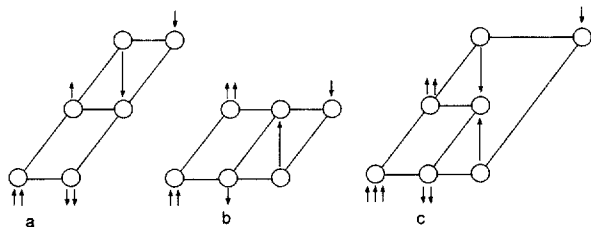


Figure 3. Schematic drawing of multi-effect cycles (a and b double-effect, c triple-effect) in the pressure-temperature plot. Arrows denote heat flow.

heat load. In *figure 3a* heat of condensation is used internally to regenerate the solution a second time. In *figure 3b* the same is accomplished using the heat of an absorber. In *figure 3c* both heat of condensation and absorption are used to regenerate the solution internally. This internal re-use of heat of condensation or absorption increases performance as is indicated by the number of the arrows. The first two cycles are of the double-effect type, whereas the third cycle is of the triple-effect type.

The same principle is possible also when the concentration difference between the solution leaving the absorber and that leaving the generator is increased so much that the temperature glide in absorber and generator overlap (*figure 4*). In the region of the overlapping temperature band, heat of absorption is utilised to regenerate the solution in the generator as was done in the case of *figure 3b*. Consequently, the cycle is of the double-effect type, although the heat recovered may be just a small fraction of the total heat of absorption [13]. Altenkirch [23] described this method using the name “cycle with overlapping temperatures”. Girsberger [24] called it “unechte Mehrstufigkeit” which may be translated as “false multistaging” or “quasi-multistaging”. Scharfe et al. [25] used the name “absorber generator heat exchange” (AGHX) and Radermacher [26] coined the name desorber/absorber heat exchange (DÁHX), which was later changed generator-absorber heat exchange (GÁHX or GAX), the name current today.

If solid sorbents are used as working material, the temperature overlap can also be utilised. GAX-performance is achieved with cycles using a so-called

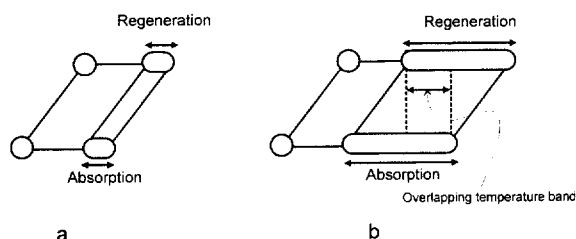


Figure 4. Schematic drawing of a single-effect cycle without (a) and with (b) overlapping temperatures (GAX) in the pressure-temperature plot.

thermal wave [27, 28] either in adsorption systems or using the multi-salt or multi-hydride process [29] with chemical reaction systems.

In the following sections, we will discuss the development of several kinds of multistage systems.

2.4. Working pairs

As was stated above, the main freedom in designing absorption systems lies in the principle of (true or quasi) multistaging. However, the choice of the working pair also has a large impact on technical questions and applicational concerns.

There are many rationales for the choice of a working pair: temperature and pressure range, thermodynamic efficiency (*COP*), experience, complexity in handling, safety, environmental concerns, etc.

Despite the large number of possibilities, there are only two working pairs which are state of the art: $\text{H}_2\text{O}/\text{LiBr}$ for water chillers, and $\text{NH}_3/\text{H}_2\text{O}$ for refrigeration. Although well-known and mature, both pairs have drawbacks: in the case of $\text{H}_2\text{O}/\text{LiBr}$, the temperature lift is restricted due to crystallisation. In the case of $\text{NH}_3/\text{H}_2\text{O}$, toxicity and high working pressure as well as the need for rectification hamper use. Consequently, we can distinguish two lines of research: one line tries to change the characteristics of the well-known pairs in order to overcome the problems mentioned. The other line tries to come up with new working pairs. Information about liquid pairs has been collected systematically and published by Macriss et al. [30] and Macriss and Zawacki [31].

2.4.1. Changes in well-known working pairs

One of the most important directions in today's R & D is the quest for air-cooled chillers. To this end, several salt-mixtures, based on the LiBr-system, have been proposed [17, 32]. Up to now, the problems of corrosivity and bad heat transfer have not yet been solved. Nearly the same holds for the change from salt solutions to hydroxides [33–38].

In the case of refrigeration, one seeks to add ingredients into the solution which lower the vapour pressure of the water, thereby reducing the need for rectification [39–41]. Up to now, no commercial product is available.

2.4.2. New working pairs

In this situation of mature but not fully satisfactory technology, many other working pairs are under discussion. In order to cope with the freezing point of water, in the early days, a mixture with Glycol (Carol), and later the use of methanol as replacement, were proposed [42, 43]. Organic pairs [44–46] might have taken the

Type of cycle	<i>COP</i>	Improvement of <i>COP</i>	Specific energy demand	Reduction in energy demand
Single-effect	0,75		1.33 kW/kW cooling	
Double-effect	1.2	0.45	0.83 kW/kW cooling	38 %
Triple-effect	1.5	0.3	0.67 kW/kW cooling	19 %

place of $\text{NH}_3/\text{H}_2\text{O}$ if they had performed better and if the CFC-debate had not come along. Today they still do not play a significant part, if any.

A more radical solution is the switch to solid sorbents for water. Both well-known sorbents, silica-gel [47, 48] and zeolite [49-51], have a relatively wide solution field. Silica-gel chillers are commercially available, whereas zeolite chillers are not. Zeolite has the advantage of allowing reject heat temperatures of 80 °C or more, which makes it attractive for applications like automotive systems [52], but also for use as topping cycle in cascading multistage systems [53].

The situation of other solid sorption systems is quite similar, whether these be adsorption with carbon [54] or chemical reaction using complex compounds [55-57], hydrates [58], or hydrides [59, 60]. As stated above, they are suitable primarily for high temperature applications, because crystallisation is not a danger but a prerequisite. So far, two problems have prevented more widespread use: the discontinuous cyclic manner of operation necessitates the thermal cycling of a lot of thermal mass which brings down the *COP*, and the relatively (as compared to a liquid film) thick active beds exhibit bad heat and mass transfer characteristics. Some of the different technologies investigated recently have been compared in a European joint research project [61-65].

3. GAS COOLING

The most prominent area of application of sorption systems is providing chilled water for air-conditioning by $\text{H}_2\text{O}/\text{LiBr}$ absorption chillers. Here, the mainstream development has led from single-effect to double-effect systems and from steam-fired to direct gas-fired generators [15]. However, it must be kept in mind that the reason for using gas-fired double-effect chillers instead of compression chillers is most often not that they are favourable from the energy aspect: the increase in efficiency of power plants (above 60 % on LHV) as well as of turbocoolers (*COP* > 6) is dramatic and results in a *COP* on primary energy (primary energy rate) of 3.6, leaving an absorption chiller with a *COP* of 1.2 (on LHV) far behind. The push forward for absorption chillers stems from economic considerations: in many countries the mid-afternoon peak in electricity

supply which is created by compression chillers leads either to a shortage in electricity or to investment in electricity producing capacity which is not used for 20 hours a day and therefore is not economic. At the same time, the gas grid is idle. Consequently, in the scope of least cost planning it is very beneficial to use the gas grid for cooling. In this situation it is obvious that, although efficiency considerations are not first priority, it is important to bring the energy demand into the order of magnitude of compression systems. Consequently, this has a strong impact on developing absorption chillers with performances beyond double-effect.

Figure 5 is a schematic representation of the single-effect, the specific double-effect, and the specific triple-effect absorption cycles. By adding two further exchange units (a generator and a condenser) to a single effect cycle, double-effect performance can be attained. Two more exchange units lead to triple-effect performance. Many other cycle configurations are known which exhibit double, triple, or even higher effect performance [10, 21, 66-74]. If we compare the performance of these systems, we of course also have to consider a change in burner efficiency, and we have to be aware that the energy saving is only reciprocal to the increase in performance. From the figures given in table I it is immediately clear that competitiveness can be achieved

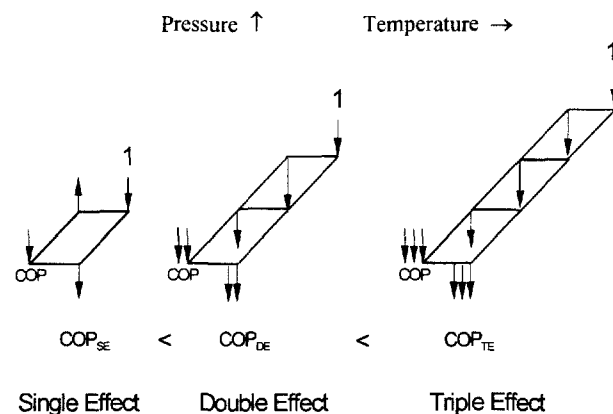


Figure 5. Schematic drawing of a single-effect, a double-effect, and a triple-effect cycle in the pressure-temperature plot. Arrows denote heat flow.

only with a very small cost increase when changing from double-to triple-effect: although the increase in COP (from 1.2 to 1.5) is quite considerable, the marginal reduction in energy demand (19 %) is much less impressive. The reduction in energy demand, on the other hand, has to pay back all the increase in first cost which is required to attain the increase in COP . Consequently, it is of paramount importance either that the high-performance system has only marginally higher cost or that the reduction in energy demand is considerably higher than that shown in the table.

Triple-effect chillers are not yet on the market, but in development in several laboratories. Most work seems to be concentrated on the very triple-effect cycle of *figure 5*. It is easy to handle from a conceptual point of view because it is a straightforward repetition of the double-effect principle. The problems arise from secondary properties: the working fluids and the construction materials have to stand temperatures in the vicinity of 200 °C. There, the solution is very corrosive, which necessitates expensive construction materials, or efficient corrosion inhibitors, or less corrosive mixtures. All three paths are not easy to walk. Moreover, the conventional heat transfer enhancing additives are not stable at the high temperatures.

Having taken notice of these inconveniences, it is interesting to consider the use of solid sorbents: corrosion is anticipated to be less severe, and no problems with decomposition of additives will arise. However, solid sorption chillers in most cases exhibit poor performance, even when built in multi-effect arrangement. Consequently, a cascading design with

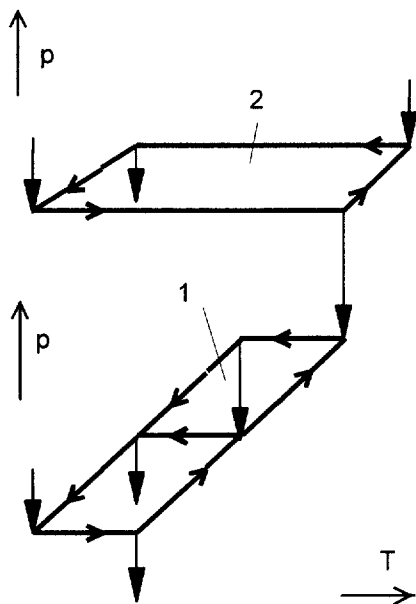


Figure 6. Schematic drawing of a triple-effect cycle, consisting of a double-effect bottoming stage (1) and a single-effect topping stage (2) in the pressure-temperature plot.

an effective liquid sorption bottoming stage and a temperature resistant topping stage seems to be an attractive compromise. An experiment of this kind has been performed in the early 80's, using the triple-effect principle of *figure 3c* [53]. The performance increase, however, was too small to outweigh the experimental difficulties and the initial cost. In recent years, an experiment was started with a double-effect $H_2O/LiBr$ bottoming cycle (2 and 3) and a chemical reaction topping stage (1) (*figure 6*) [73].

The performance of this cycle will surpass the pure double-effect performance, albeit with a substantial increase in first cost. But if the principle is successful and easy control can be achieved, the path is open for developing cycles with significantly higher COP , e.g. the quintuple-effect cycle of *figure 7* [74]. The COP which can be achieved depends largely on the efficiency of the topping stage (1), COP_{top} . Approximately it holds for the quintuple-effect COP_5 :

$$COP_5 = COP_{bottom} * (1 + COP_{top}) + COP_{top} \quad (5)$$

With a double-effect performance of $COP_{bottom} = 1.2$ of the bottoming cycle, the quintuple-effect performance will be:

$$COP_5 = 1.2 + 2.2 * COP_{top} \quad (6)$$

With a topping stage performance of 0.1 the performance increase against double-effect will only be marginal. With a topping stage performance of 0.3 the

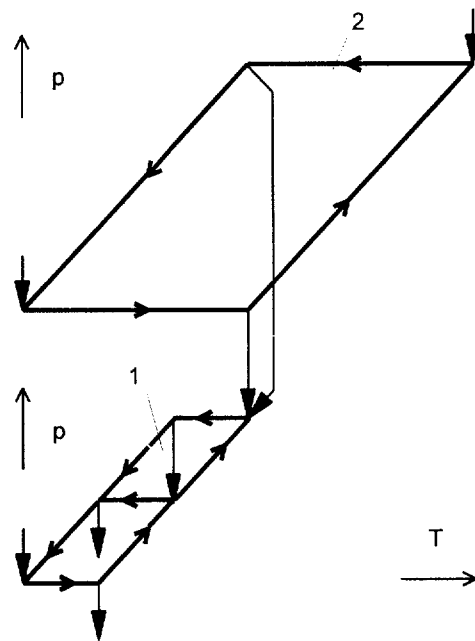


Figure 7. Schematic drawing of a quintuple-effect cycle, consisting of a double-effect bottoming stage (1) and a single-effect topping stage (2) in the pressure-temperature plot.

performance increase will be 50 %, which is tremendous and hard to achieve with any other design. Moreover, the construction of the high-efficient cycle from a state-of-the-art double-effect cycle and a topping cycle allows for retrofiting, which is an important benefit on the marketing side.

The reported development is done mainly for large capacities (MW). There are almost no H₂O/LiBr chillers available with a capacity in the range of a few tens of kW. There is, however, a direct-fired single-effect chiller with NH₃/H₂O which is now being upgraded to improved performance by employing the GAX-principle. Using NH₃/H₂O of course is beneficial in two aspects: it gives more freedom in choice of the chilled water temperature which can be lower than 0 °C also (ice slurry), and it gives some freedom regarding the heat sink temperatures. Still, NH₃/H₂O chillers are not competitive at larger capacities due to the lower COP and the higher initial cost.

4. SOLAR COOLING

The driving force behind research on multi-effect cycles is primary energy saving. This can also be achieved when regenerative energy is used as input, in part or in total. In the US around the year 1976 some 500 solar air-conditioners had been installed [75, 76]. They ran about 75 to 80 % on solar. The rest of the time the chillers were operated with electricity or fuel oil. This is important to reconsider in the light of an energy comparison: a single-effect chiller with a COP of 0.7 operated on electricity requires about 5 times the primary energy required by a compression chiller with a COP of 3.5. Consequently, all the energy saving by solar operation will be compensated by a 20 % share of electrical operation. We may conclude that a significant fraction of the above mentioned installations were no big energy savers at all.

If, on the other hand, a gas-fired single-effect chiller is operated half of its running hours on solar, its fossil energy demand is comparable to that of a typical triple-effect chiller [77]. This is shown in figure 8, where the primary energy rate PER of different sorption chillers is shown. The primary energy rate is the primary energy PE required to produce a given amount of cooling Q₀:

$$PER = \frac{PE}{Q_0} \quad (7)$$

The abscissa of figure 8 is the solar fraction *f* which is attained when collectors are installed to operate a solar assisted single-effect (solid line) and double-effect absorption chiller (broken line). The solar fraction is defined as the ratio of solar input Q_S and total energy input required, (Q_S + PE)

$$f = \frac{Q_S}{Q_S + PE} \quad (8)$$

The primary energy demand PE is related to the driving heat input, Q₃, via the burner efficiency η_B:

$$Q_3 = Q_s + PE \eta_B \quad (9)$$

Then, the primary energy rate of solar assisted absorption chillers can be given as a function of solar fraction and COP:

$$PER = \frac{1}{\eta_B + \frac{f}{(1-f)}} \frac{1}{COP} \quad (10)$$

The solid line gives the primary energy rate of single-effect absorption chillers with a COP of 0.75 and a burner efficiency of 0.85 for the fossil operation: with a solar fraction of 0.3 to 0.6 the primary energy rate is comparable to that of a compression chiller with a COP of 3. The dotted line is valid for a double-effect solar assisted absorption chiller with a COP of 1.2 and a burner efficiency of 0.85 again. A triple-effect chiller (square symbol ■) with a COP of 1.6, totally fossil fired (*f* = 0) with burner efficiency of 85 % again still requires somewhat more primary energy than a compression chiller with COP of 3 combined with a power station with 50 % efficiency, a compression chiller with COP of 5 combined with a power station with 30 % efficiency, a double-effect absorption chiller with 30 % solar input, or finally, as stated above, a single-effect absorption chiller with 50 % solar input.

From these numbers, it follows that the solar option has to be evaluated carefully: the use of solar heat reduces the fossil energy demand of sorption chillers, but this is not always enough to cope with compression chillers. This problem has been addressed several times. Recently, in a Joule-project sponsored by the Commission of the European Communities [78], a dedicated two-stage chiller (double-effect/single-effect) was developed. The objective of this work is to market

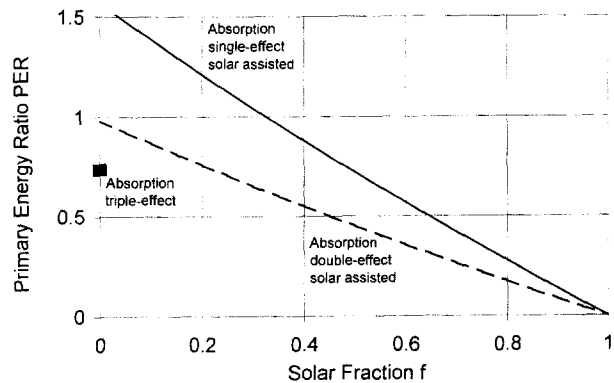


Figure 8. Comparison of the primary energy ratio for different solar-assisted sorption systems as function of the solar fraction *f*.

an absorption cooling machine which can use either solar energy from medium temperature thermal collectors or natural gas with a higher *COP* than standard single effect chillers. To this end a gas-fired double-effect absorption chiller is being tested which is modified in such a way that it can be operated partly or totally by hot water from thermal collectors at the middle pressure generator (figure 9).

Considering the problem of the mid-afternoon peak in electricity consumption due to electric chillers, the idea of solar chilling is intriguing from demand-side considerations: the chilling demand at least to a significant extent runs parallel to the availability of solar radiation. Therefore, the interest in solar cooling by sorption systems has been prevalent for several decades. Quite a few systems have been installed all over the world and operate satisfactorily. However, no really cost-competitive system for widespread application exists today, although the demand is acutely pressing. A step forward can only be expected through the innovative design of collectors, chillers, or both, including open systems [8, 79]. Moreover, there could be more than just solar cooling for building air-conditioning: there is a review by the IIR which compares different technologies for solar refrigeration [80]. An example in the field of sorption is the solar icemaker which operates on $\text{NH}_3/\text{H}_2\text{O}$ [81].

5. COOLING WITH LOW-GRADE OR WASTE HEAT

In central and northern Europe especially, the use of heat from combined heat and power production in dis-

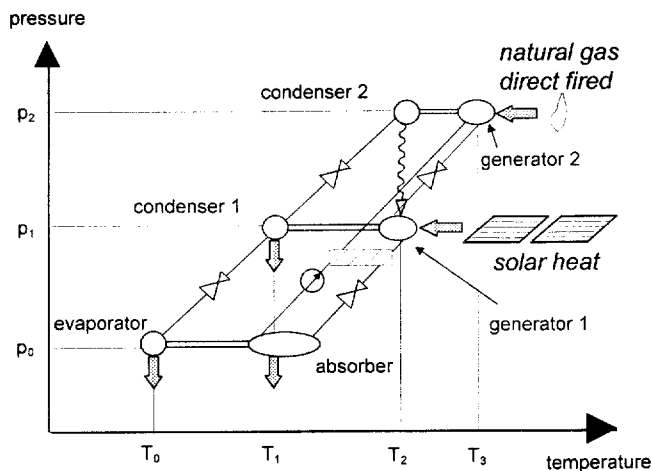


Figure 9. Schematic drawing of a solar-assisted double-effect sorption cycle with solar energy input at the middle pressure generator 1 at temperature T_2 .

trict heating systems for cooling purposes has attracted much interest. During summertime exploitation of this energy source for air conditioning with the consequence of increased utilisation of the district heating networks contributes to both energy savings and economics. One common feature of stations supplying combined heat and power is that the performance of the heat supply system increases when the temperature of the heat which is delivered to the user is lowered. Therefore, there is a distinct need to develop sorption cooling systems with low driving temperature, e.g. between 60° to 80°C or even lower.

There are three principal possibilities to lower the input temperature of a sorption chiller if the temperature of heat sink and heat source are fixed by the application (chilled water, cooling tower). The first one is to decrease the driving temperature differences at the external exchangers. This can be done by increasing the exchange surfaces (or decreasing the capacity). This method is expensive, but is done in commercial applications because it is simple and safe. Increasing the transfer coefficients would yield the same result but is hard to accomplish: often, the transfer coefficients increase with the specific load on the exchanger. Consequently, they rather decrease in the case of low temperature application where the driving temperature differences are small. Even the step from pool boiling desorbers to falling film desorbers, which is often considered in this respect, is not always beneficial because the heat transfer coefficients may be very different [82].

The second option is a change in working pair. For instance, silica-gel chillers are marketed with the argument that they are operational with low-grade heat [48]. However, as discussed above and in more elaborate form in earlier papers [83, 84] the choice of the working fluid influences only to a small extent the lowest possible driving temperature.

In the following, the third option, which is to use advanced cycles, will be highlighted. The concept is very similar to the concept of increasing the efficiency by staging. However, in the case of multistaging for increasing the temperature lift or – what is in principal the same – reducing the driving heat input temperature, the performance decreases: the temperature thrust becomes smaller than the temperature lift (equation (2)). On the other hand, the amount of exchangers, pipes, and controls has to be increased. So, the so-called multi-lift cycles are expensive and perform less well at the same time. Normally, they are only competitive if the driving heat is for free or very cheap and/or if both products (heat and cold) can be sold.

An example for this kind of system is the double-lift refrigerator [85, 86], which is depicted schematically in figure 10. It uses $\text{NH}_3/\text{H}_2\text{O}$ and produces cooling at temperatures as low as, e.g. -50°C . The refrigerant vapour is produced first at an intermediate pressure level and resorbed again in a second solution circuit. The second regeneration is done at the appropriate

pressure of the condenser. The effect is that both regeneration steps take place at a reduced temperature compared to a single-effect chiller. In spite of the low *COP* which may come down to the order of 0.3 to 0.2, the plant is competitive in relation to compression refrigerators, especially if driven with steam from grids or cogeneration.

In figure 11 a cycle is shown which is a superposition of the above-mentioned double-lift cycle with a single-effect cycle: the single-effect/double-lift cycle (SEDL). It has been designed for producing chilled water in district heating networks with $\text{H}_2\text{O}/\text{LiBr}$. The boundary conditions are in general low temperature (down to 80°C) of the district heating water supply and a high temperature spread between supply and return (about 20 to 30 K). The resulting very low return temperatures down to 50°C could be used in a double-lift cycle, the *COP* of which is about 0.4 with $\text{H}_2\text{O}/\text{LiBr}$ under the given circumstances. To take advantage of the relatively high supply temperature of the district

heating water of 80°C and in order to realise the large temperature spread which is required, the double-lift cycle was integrated into a single-effect cycle. The district heating water releases heat first in the generator of the single-effect stage and then in the two generators of the double-lift stage, leading to the high temperature spread. Depending on the distribution of the heat exchanger areas within the three generators, as well as on the temperature of the district heating water input, the *COP* will vary between the *COP* of the double-lift and single-effect cycle, 0.4 and 0.8 respectively [87–89]. In Germany, five of those machines are now in operation or in construction. A large fraction of single-effect performance is very important for the economics of these machines.

Finally, in order to operate chillers with even lower input temperature near the heat sink temperature, a triple lift cycle using silica-gel as adsorbent was designed as a laboratory plant [90]. In order to be competitive even with free waste heat as input, it is of paramount importance to design this system in a very simple and cheap way. This is one of the objectives of the research effort described where continuous triple-lift performance is attained with six silica-gel containers which are connected to a loop, so that the effort for vapour phase switching is minimised. However, in judging the economics, it has to be kept in mind that the *COP* will be very low, in the order of 0.1 to 0.2. Consequently, 10 to 20 times the refrigeration load has to be rejected to the ambient, which is a big investment and also causes considerable running cost, e.g. for cooling water. We think that a *COP* below 0.2 will not be competitive, even if the systems are fired with free waste heat. Things may change if the user of waste heat gets a refund.

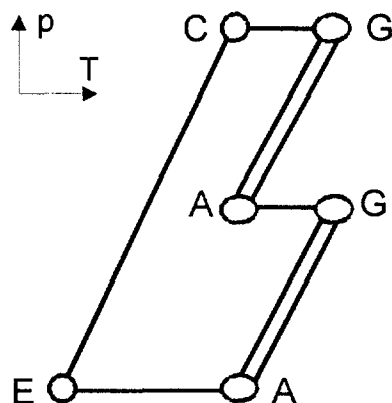


Figure 10. Schematic drawing of a double-lift cycle. A: absorbers, C: condenser, E: evaporator, G: generators.

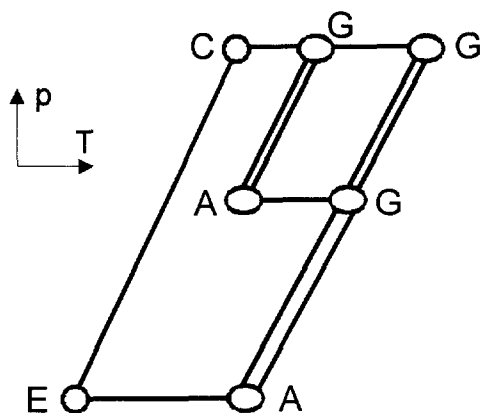


Figure 11. Schematic drawing of a single-effect/double-lift cycle. A: absorbers, C: condenser, E: evaporator, G: generators.

6. REFRIGERATION

In the field of low-temperature refrigeration, the situation is different from chillers: the competing compression systems are much less performant as compared to the water chillers because their *COP* is more or less proportional to the temperature lift according to the Carnot-*COP*. On the contrary, it has been stated above that the *COP* of sorption systems does not benefit strongly from a small lift, which means in other words that the *COP* does not deteriorate as much as that of compression systems with increasing lift. Consequently, for a high temperature lift, absorption systems compete not too badly against compression systems. This is true even though the driving heat is often not extremely cheap: if the temperature lift is large, then the temperature thrust must also be large, and in consequence the temperature of the heat input may be quite high.

Another difference from chillers is that the only working pair currently used for refrigeration purposes

Type of cycle	<i>COP</i>	Improvement of <i>COP</i>	Specific energy demand	Reduction in energy demand
Direct	1.0		1 kW/kW heating	
Single-effect	1.5	0.5	0.67 kW/kW heating	33 %
Double-effect	1.8	0.3	0.56 kW/kW heating	16 %

is $\text{NH}_3/\text{H}_2\text{O}$ and these machines do not come in large series but with large capacities (MW). For many years this business was done in the style of plant design of chemical engineers. Only in recent years have there been trials to standardise systems with capacities of some 100 kW using plate heat exchangers as very compact components.

In contrast to most other working pairs, in the case of $\text{NH}_3/\text{H}_2\text{O}$ the vapour pressure of the sorbent, water, is not negligible as compared to the vapour pressure of the refrigerant, ammonia. This fact necessitates the installation of a rectification device to reduce the water content in the vapour leaving the generator [91, 92]. By heat and mass exchange in a counterflow of liquid and vapour, the refrigerant is enriched in the vapour, and the sorbent is stripped of the vapour and enriched in the liquid reflux to the generator. In order to produce this reflux, some condensate has to be sacrificed. This means that a small part of the heat input to the generator is used to produce the reflux and not to produce refrigeration. The more water is contained in the solution the more water is contained also in the generated vapour and the more input heat is required to produce an appropriate amount of reflux: consequently the *COP* deteriorates. This can culminate in such a way that a double-lift cycle (figure 11) exhibits better performance than a single-effect cycle. Consequently, for very large temperature lifts, double-lift cycles are being used. Of course, they have the other benefit of requiring a lower temperature for the input.

If high input temperatures are available, it is beneficial to optimise the rectification process in order to regain the basic superiority in performance of the single-effect over the double-lift cycle. To investigate the thermodynamic possibilities, an experiment has been performed in which a 50 % increase in *COP* was achieved by re-arranging the solution flow so as to reduce the rectification requirement [93-95].

7. HEAT PUMPING

The economics of heat pumps are more difficult than those of cooling equipment, because heating is a very simple technology. In addition, even when

the machine itself is cheap, the cost of the external heat source often reduces the competitiveness. In this respect absorption technology has an advantage over compression technology: due to the lower *COP*, the ratio of the required capacity of the heat source to the heating capacity is smaller for absorption systems, i.e. the cost for the heat source tends to be smaller.

Another point worth mentioning is that, of course, the heating *COP* of a heat pump is always above 1. For an absorption system the single-effect *COPs* range from 1.3 to 1.6. As can be seen from table II, the relative increase in energy saving by using double-effect is much smaller than in the case of a chiller. Consequently there are almost no double-effect heat pumps being developed. An exception is the flexible double-effect/double-lift heat pump which, as a pilot project, was designed to supply two different heating systems of an exhibition hall [96].

7.1. Large capacities

There are a few large heat pump installations using $\text{H}_2\text{O}/\text{LiBr}$ in single-effect cycles, especially in Scandinavian countries. They are applied in district heating systems with geothermal heat sources, urban waste water, or seawater [97, 98].

Another very special system was installed in Erding, Germany. In the same way as is done with $\text{NH}_3/\text{H}_2\text{O}$ refrigerators, sometimes the evaporator/absorber pair is doubled and operates at two different pressures [113]. Consequently, the two evaporators and the two absorbers can each be connected in serial flow, in order to be matched to the large glide in heat sink and heat source. In this way the operational range can be enlarged on the one hand and the performance is increased on the other hand.

7.2. Small capacities

As for the chillers, there are almost no absorption heat pumps using $\text{H}_2\text{O}/\text{LiBr}$ available for small capacities of some 10 kW. This again is the domain of single-effect systems with using $\text{NH}_3/\text{H}_2\text{O}$. For example, there is a German manufacturer who provides such

machines typically for heating of large swimming pools and the like.

In the US large development programs were dedicated to machines for domestic heating and cooling using the GAX-principle [16, 99]. The operational parameters in heating and cooling modes are quite different from each other. Consequently, the flexibility of the GAX-principle allows for adaptation (*figure 12*): in the cooling mode (*figure 12a*) the machine may work with a large overlap in temperature thus operating in GAX-mode with double-effect performance. In the heating mode (*figure 12b*) the temperature lift $T_1 - T_0$ is much larger and the overlap will diminish or even vanish. Then the performance of the machine will be reduced to that of a single-effect cycle. However, the development of the machine has been much more complicated than anticipated and the cost goal has not been achieved, so that the machine is not yet on the market today. It is, however, for capacities in the range of 100 kW and more [100].

In the domestic market in Central Europe, the stress is much more on pure heating systems than on chilling/heating. For this reason, the R & D efforts in this region aim at simple apparatuses which should nevertheless be able to use quite cold ($-15\text{ }^\circ\text{C}$) ambient air as heat source and provide a large temperature lift (up to 60 K). Under these conditions, only single-effect systems have been proposed.

One of the most interesting developments is the scaling up of the $\text{NH}_3/\text{H}_2\text{O}/\text{H}_2$ diffusion-refrigerator used in campers or as mini-bar in hotels into a pumpless heat pump with 3 kW capacity [101, 102]. After decades

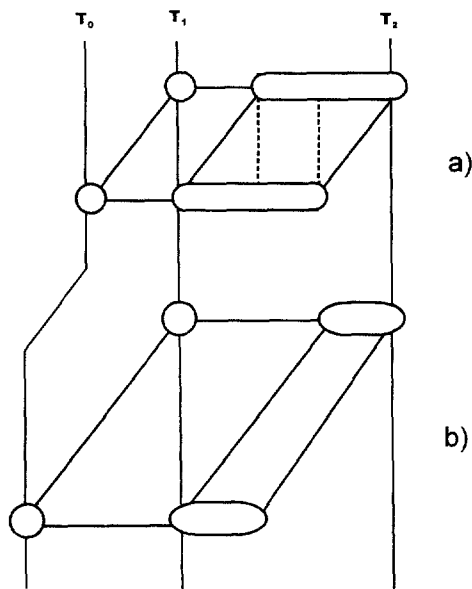


Figure 12. Schematic drawing of a cycle with GAX-performance in chilling operation (a) and with single-effect performance in heat pump operation (b).

of R & D, the system is now at last in a pre-market stage. There are not many competitors: an Austrian company is developing an oil-fired heat pump [103], and a system based on the water/zeolite pair has been developed [104]. There are also developments with hydroxides as absorbents and innovative heat exchanger design like rotary systems [37, 105] or spray absorption [106, 107]. All these systems still are not marketed.

7.3. Heat transformers

There is an idea which dates back to Altenkirch [108] of using a heat transformer (type II), the reverse absorption heat pump for domestic heating (*figure 13*). The details of the cycle are described in the paragraph about industrial heat recovery, where heat transformers will find their main field of application (*figure 14*). The domestic application, however, is interesting to discuss mainly because it shows the variability of sorption systems. Usually, as depicted in *figure 13a*, primary energy is utilised in order to energise a heat pump which lifts heat from an abundant reservoir like sea water at a decent low temperature around $0\text{ }^\circ\text{C}$ to the room temperature. In the second case (*figure 13b*), the heat source at the decent low temperature serves both evaporator and desorber around $0\text{ }^\circ\text{C}$. The low temperature heat sink (condenser of the transformer) may then be cold air in winter (e.g. $-20\text{ }^\circ\text{C}$), and the high temperature heat sink (absorber) will be the heating system. For effective use with a heating temperature of $30\text{ }^\circ\text{C}$ or more, a double-lift transformer [109, 110] may be appropriate. The system has one outstanding favourable feature: the colder the outside air becomes, the larger the capacity and the temperature lift of the heat transformer will be. The economics

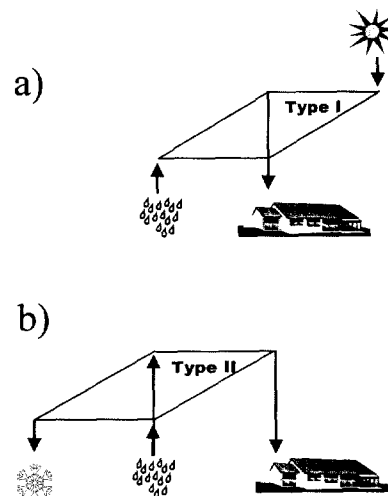


Figure 13. Sorption cycles for house heating purpose. a: heat pump (type I); b: heat transformer (type II).

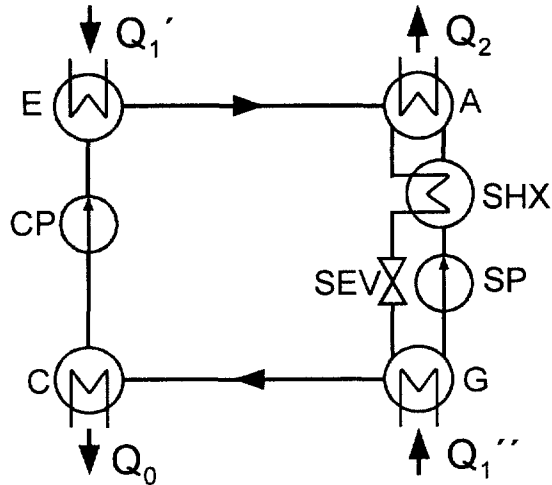


Figure 14. Flow sheet of a single-effect absorption heat transformer. A: absorber, C: condenser, CP: condensate pump, E: evaporator, EV: expansion valve, G: generator, SEV: solution expansion valve, SHX: solution heat exchanger, SP: solution pump.

however normally look dull, but in special circumstances an application may be possible. Experiments are performed for an installation in polar regions recently [111].

8. INDUSTRIAL HEAT RECOVERY

Industrial heat pumps are not series products similar to low-temperature refrigeration systems. Engineering companies find in them interesting possibilities, because they normally come in large capacities (several MW) and thus can be tailor-made. On the other hand, they produce just heat as output which often has not enough value to recover the initial cost. This is true even if the heat input to the system is waste heat. Consequently, there are not so many examples of installations. We will report in brief on some concepts which originate mainly from the late seventies when energy saving seemed to have a tremendous future.

8.1. Heat pumps (type I)

Of course the chiller or heat pump cycle as described above can be used for recovering heat. However, not many attempts have been reported. One pilot plant is known where a double-effect chiller is used in heat pumping mode as heat supply system to a water desalination plant. The idea is to operate the water desalination in a temperature range where scaling problems are less severe and still use high input temperatures effectively [112]. The fresh water output

is doubled for a given heat input. It was intended to reduce first cost by integrating the water desalination and the heat pump: the vapour which is produced in the second stage generator is used for heating the first desalination stage directly.

A very recent example involving the use of an absorption heat pump is upgrading waste heat of a fuel cell [113]. However, this is not strictly an industrial application and it is due to a shortcoming of today's fuel cells which hopefully will be overcome in the near future.

The main reason for industrial sorption heat pumps of the first kind not being widespread is probably that the required temperatures normally are well above those experienced in chiller operation. So the corrosion and stability problem obstructs the use of the proven technology.

8.2. Heat transformers (type II)

The reverse heat pump, the heat transformer (heat divider, temperature amplifier, heat pump type II), has been addressed briefly in the chapter about heat pumping above. The main field of application is not domestic but industrial heat recovery. The flow scheme is shown in *figure 14*. It consists of the same components as the chiller cycle; only due to the reverse flow direction of heat and mass as compared to the chiller, a pump, instead of an expansion device, is required between evaporator and condenser. The heat which is to be upgraded is conveyed at an intermediate temperature to generator and evaporator. The upgraded part is released from the absorber at a higher temperature, which is the useful effect. It is brought about due to the fact that another part of the heat input is degraded to the temperature of the condenser where it is given to an appropriate heat sink (cooling tower). In such a simple single-effect system about half of the heat input is upgraded and the other half is degraded: the *COP* of the system is about 45 %.

About a dozen installations have been reported on all over the world with a stress on Europe [97]. Most of the transformers are out of operation today, due mainly to a change in their industrial environment and not due to failure. The systems operate properly but payback of the initial cost is difficult to achieve.

There are several advanced concepts regarding heat transformers: multi-effect and multi-lift cycles have been discussed [109, 110, 114] and different working fluids are being studied [115]. No such systems have been incorporated commercially into a real plant up to today. The reason for this is different for the two different kinds: multi-effect transformers are able to upgrade more than just a half of the waste heat input, which is a very desirable feature. However, this is only possible by reducing the ratio of temperature lift to temperature thrust. If waste heat of 80 °C is to be upgraded using a

heat sink of about 30 °C (cooling tower) with a single-effect transformer, the lift will be smaller than about 40 K. Consequently, the achievable lift with multi-effect transformers will be too small for most applications.

On the other hand, the lift can be increased by multi-lift concepts. Then, of course, the fraction of upgraded heat is less than half of the waste heat input. If the waste heat is abundant and really for free or very cheap (including investment for installing the heat source), there still remains the requirement for a cooling tower for rejecting an amount of heat which is, e.g. for a double-lift cycle, about twice the amount of recovered heat. This cooling tower adds on to the investment and, additionally, causes running costs which are not negligible. So again we find that the economics of advanced concepts are not always more favourable than those of the basic cycle.

If the costs of the heat input and of the heat sink are negligible, the only energy costs to pay are those for the pumps. This is an important element in the case of high-pressure working fluids like $\text{NH}_3/\text{H}_2\text{O}$. In the case where the refrigerant water is used, this is less relevant. Still the pumps are parts which need to be maintained and sometimes cause trouble. In order to get rid of this cost a heat transformer has been tested with self-circulation using the concept of bubble pumps as in camping refrigerators or some chillers [36, 116].

8.3. Heat pump transformers (type III)

Naturally it is also possible to combine the two types of absorption cycles. One class of this so-called heat pump transformer which combines features of a chiller or refrigerator with those of a heat transformer (heat pump type IV) has been described by Arh [117]. Here we will concentrate on another industrial type (heat pump type III) which allows for quite high *COPs* beyond those of conventional multi-effect cycles [118-120]. The type III heat pump is composed of a heat pump type I topping a heat transformer (type II), whereas in the case of the type IV heat pump the situation is exactly reverse.

In *figure 15* the concept of using a heat pump of type I, II, or III for heat recovery is depicted on a temperature axis [72]. Imagine that waste heat Q_1 is available with the temperature T_1 . It should be upgraded to the temperature T_2 where heat Q_2 is required by some arbitrary process (*figure 15a*). This upgrading can be accomplished by a heat pump (figure 15b), which recovers at least a part of the waste heat at T_1 and is driven by primary energy at T_3 . The upgrading is also possible using a transformer (type II, figure 15c) which rejects part of the heat input at T_0 and recovers the other part. A remainder of input is required at T_2 in the process. If both heat pumps are combined (figure 15d), the transformation system is operated with heat input at T_3 , it conveys heat to the process at T_2 , it recovers

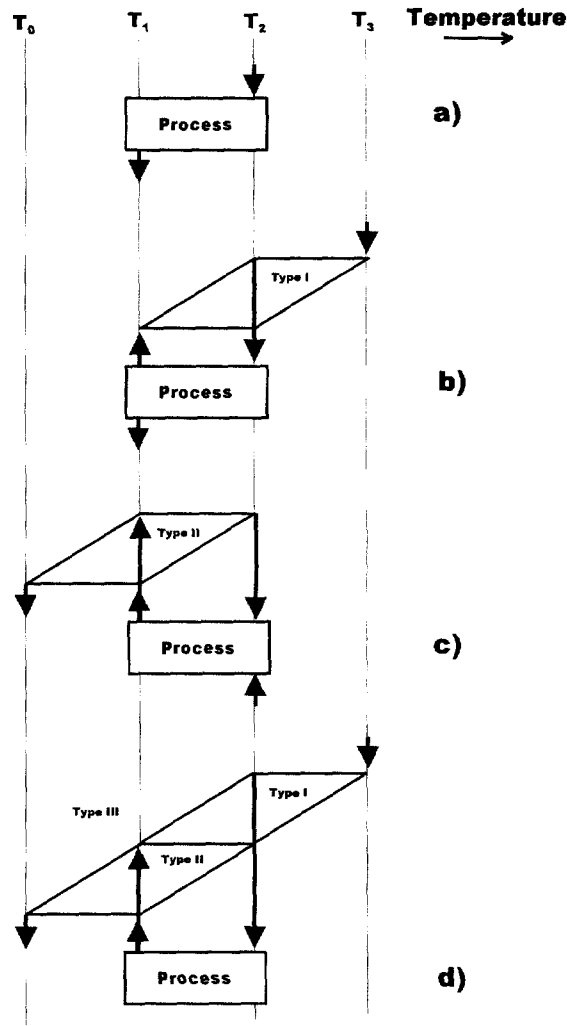


Figure 15. Schematic drawing of different heat systems to recover waste heat of a process. a: no heat recovery. b: heat recovery with a single-effect absorption heat pump (type I). c: heat recovery with a single-effect absorption heat transformer (type II). d: heat recovery with a two stage system composed of an absorption heat pump and a transformer (type III).

heat from the process at T_1 , and it rejects heat to a sink at T_0 . This is the most effective recovery system.

Let us discuss further the special case where Q_1 equals Q_2 . The heat Q_0 is rejected, and the heat Q_3 is required as primary energy, in order to add heat to the process in the case of the transformer (II) or in order to operate the heat pump (I) or heat pump transformer (III). Several cycles are evaluated in *table III*. The cycles have been identified by the type (heat pump I, heat transformer II and heat pump transformer III) and by the number of effects (single or double-effect). In the case of the heat pump transformer, the number of

TABLE III
Energy saving of several types of heat recovery heat pump cycles.

Type of cycle	Temperature Lift	<i>COP</i>	Relative energy saving
No heat recovery	--	--	0 %
a: Heat Pump (I), single-effect	40 K	1.7	41 %
b: Heat Pump (II), single-effect	40 K	0.45	45 %
c: Heat Pump (III), single-effect I + single-effect II	40 K	2.5	60 %
d: Heat Pump (III), double-lift I + single-effect II	40 K	2.1	52 %
No heat recovery	--	--	0 %
e: Heat Pump (I), double-effect	20 K	2.0	50 %
f: Heat Pump (II), double-effect	20 K	0.6	60 %
g: Heat Pump (III), double-effect I + double-effect II	20 K	4.0	75 %
h: Heat Pump (III), single-effect I + double-effect II	20 K	3.2	69 %

effects of the topping heat pump (I) and the bottoming transformer (II) are both given. Two cases have been distinguished: one with a temperature lift of about 40 K between T_2 and T_1 and one with about half that lift.

It is immediately seen that the energy saving of the heat pump transformer drastically surpasses that of all the other concepts. That is due to the synergetic effect of using both the heat pump and the heat transformer principle in one device. The heat pump transformer (c) is composed of the single-effect heat pump (a) and the transformer (b). So it combines the virtues but also the problems of both cycles. In order to show the flexibility of the concept a heat pump transformer, (d) has been added. Due to the use of a double-lift cycle for the topping heat pump, the maximum temperature in the generator can be lower than in case (c). So corrosion and stability problems are less severe than in the sole heat pump (a), and still the energy saving is much more than in the case of both pure heat pump and pure heat transformer. Analogously the heat pump transformer (g) is composed of the heat pump (e) and the transformer (f). Again the heat pump transformer (h) requires lower operation temperatures and still performs very satisfactorily.

It has to be stated that the numbers representing the heat pump transformer systems (c), (d), and (h), are based on numerical simulations. The numbers for system (g), however, which are the best in that table, have been realised experimentally [119, 120].

To conclude, both types of heat pump transformers (III and IV) have been realised in laboratory experiments. They have not seen industrial application yet. Again, the high initial costs have prohibited commercial use up to now. But it has to be kept in mind that the initial cost of a simple kind of heat pump type III will be comparable to that of a multi-effect cycle of the types I or II, but the *COP* will be much higher. So we think that the economics of a heat pump transformer type III

can be superior to that of a single-effect transformer or even to that of a single-effect heat pump for heat recovery. Thus it might be concluded that the chances of an application in industrial heat recovery in chemical engineering, waste treatment, food industry, and the like are best for this advanced cycle as compared to the other concepts we have discussed in this chapter.

9. CONCLUSION

There are many other possibilities for applications of sorption systems which, however, have not reached a significant state of maturity up to the present. One of the evergreens, for instance, is the waste heat driven air-conditioner for mobile application. In the open literature we find only laboratory experiments. In most cases they have faded away due to the fact that the systems become too bulky and too heavy [62]. In the recent years, an additional problem arose: with engines getting more efficient year by year, the waste heat available to operate the sorption chiller becomes too small and the whole idea may become obsolete.

Of course, sorption systems can also be applied for storing cold. There are reasons for considering this application, e.g. in firemen's cloths [122]. Other investigations are being made for pumping heat at very unusual temperatures, e.g. for topping cycles in power stations. For the time being however, all these ideas remain in a very premature stage.

We will conclude this review with a very personal view on the future of sorption systems: sorption chilling will stay strong where it is strong today, i.e. in the countries which suffer from a heavy mid-afternoon peak. There, sorption systems compete against engine driven systems and for this reason will make a transition

to, e.g. triple-effect soon. Sorption systems will not become mainstream in other countries or applications but will fill large niches, e.g. in total energy systems, in industrial heat recovery, in solar cooling, and of course in refrigeration. Large selling numbers may be attained for heating systems when the step beyond the condensing boiler happens. But one has to be aware that in the domestic market the all-electric low energy house is a strong competitor and here a heat pump will suffer from long payback periods.

As for the technology, we think that the classical working pairs $H_2O/LiBr$ and NH_3/H_2O are here to stay with us. Improvements by additives are more likely than a changeover to completely new pairs, except for special applications. On the other hand, the conventional shell and tube design will prevail only for very large capacities. For small capacities we will see more compact heat exchangers, like plates. Of course, control will be improved and bad experience with, e.g. crystallisation, will be a reminder of the past.

Finally we want to invite the reader who is interested into hearing more news about recent R & D in the field to attend the International Sorption Heat Pump Conference from March 24th to 26th in Munich, Germany (<http://www.zae.physik.tu-muenchen.de/konferenz/infoishp.htm>) or to consult the proceedings of this conference [123].

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