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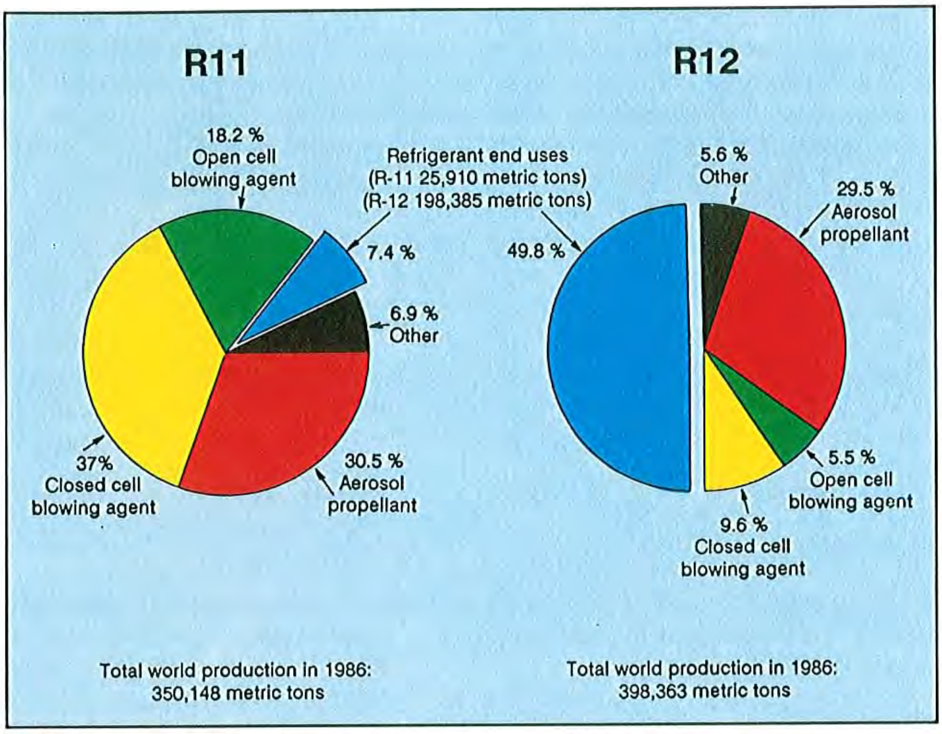

Worldwide R11 and R12 use (excluding Eastern Europe and China)
[Source: Chemical Manufacturers Association (CMA)]

This issue: Working fluids

Editorial*

People, especially technicians, have a tendency to classify things in an attempt to maintain some kind of order. This can be good because it provides a working structure; but it can also be bad because such classification may limit the imagination.

The topic of this issue of the Newsletter is "Working Fluids." And what are these? We will define these as various types of fluids present in heat pump plants which are necessary for their proper functioning and performance. Using this definition, we classify such things as refrigerants, absorbents, oils, brines, liquid heat sources and sinks, etc., as working fluids.

Working fluids have good and bad characteristics. The bad characteristics usually cause problems which cost time and money to solve. For example, their flow must be mass-controlled, and their chemical, thermophysical and thermodynamic properties must be known since they are of utmost importance for design and performance. Furthermore, they can react chemically, they can leak, and they can be dangerous to human life and environment.

It is, therefore, not surprising that this topic lends itself for an issue of the Newsletter. There are always new developments, connected directly or indirectly, to working fluids.

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Nevertheless, words have a tendency to get special emphasis depending on what is popular at the moment. At present, the CFC-ozone-environment problem is a commonly discussed theme; therefore "working fluids" for many people is synonymous with CFC refrigerants.

The increasing anxiety over the last few years concerning the influence of CFC's on the ozone layer and the earth's climate has led to international agreements to decrease the consumption of these working fluids. On September 16, 1987, the European Economic Community and 24 nations signed the "Montreal Protocol on Substances that Deplete the Ozone Layer" which becomes a part of the United Nations Environmental Programme (UNEP) *Vienna Convention for the Protection of the Ozone Layer*. (For more details about the Montreal protocol, see *ASHRAE Journal*, November 1987.)

Although the percentage of CFC usage for refrigeration and heat pumps is relatively small compared to total CFC usage (see cover figure), this situation presents one of the biggest problems to ever face the refrigeration and heat pump industry.

A number of countries have implemented programs to deal with the CFC problem in the manner outlined in the Montreal protocol. The article titled *Measures Taken Against CFC Problems in Japan* shows one approach to carry out the measures agreed to in Montreal. The two papers, *Measures to Minimize CFC Leakage* and *Thermophysical Properties Research on Refrigerant Mixtures and CFC Alternatives in Japan* are examples of how the scientific and technical community are dealing with this problem. The former paper discusses solutions which can be used in existing plants, whereas the latter paper is concerned with accurate property determinations of alternative working fluids to ultimately be used in designing new plants.

To keep up the exchange of information and to develop new approaches in dealing with the CFC problem, numerous meetings and workshops have been organized. Of particular interest to the heat pump community is the "IEA Seminar on the CFC Problem" which is mentioned in our News Briefs section. A detailed article describing the results of this seminar will be published in a future issue.

Papers will continue to be written on the CFC issue. We are following the developments with interest and will report on new information in upcoming issues of the Newsletter.

The influence of human activities on the environment is another common theme which also concerns heat pump technology. This is dealt with in two articles, *Environmental Consequences of Heat Pump Technology* and *Environmental Impact of CFC in Groundwater*. The conclusions from the first of these papers is that "natural heating systems" are the most environmentally friendly heating methods for large-scale use (disregarding the environmental effects of possible CFC leakage from heat pumps which utilize these sources). The second paper suggests that CFC leakage into groundwater is not hazardous. Instead, the CFC will most likely strip out of the groundwater without changing the water's chemistry. Eventually, though, this CFC will probably end up in the atmosphere which presents a different problem.

This latter paper should also be kept in mind when reading the paper *ECR's Direct Expansion Earth-Coupled Heat Pump System* to help answer some of the questions about the risk of refrigerant leakage into the ground from buried direct-expansion heat exchangers. The ECR paper also describes a very interesting refrigerant control system which can be utilized in all heat pumps using common fluorocarbon refrigerants. We are sure there will be other elegant solutions to this problem.

Of course, there are also many basic research projects going on in the field of working fluids. The papers *Nonazeotropic Refrigerant Mixtures* and *Thermodynamic Data of the Binary Mixture R22/R114* are summaries of two research projects on physical data of CFC mixtures. The former shows that binary refrigerants often have advantages over a single component refrigerant. For R22/R114 mixtures, the advantages were lower vapor pressure and higher oil solubility. This should be of particular interest to specialists in this field.

The same is true for the paper *World-wide Survey of Absorption Fluids Data* which identifies the "data gaps" requiring further research efforts. Even for common fluid pairs like ammonia/water these gaps exist.

Finally, the editorial staff has not limited the contents of this issue to working fluids only. The articles *Studies on the Basic Principles of a High Temperature Chemical Heat Pump* and *Carrier's Advanced Heat Pump*, which cannot be classified exclusively under working fluids, are nevertheless consistent with the overall aim of the Newsletter to show the trends of R&D in the field of heat pump technology.

Many articles in this issue use the following terms, which are defined here for clarity:

Azeotrope -- A refrigerant mixture which acts as a single component. One example is R500, which is an azeotropic mixture of R12 and R152a.

CFC -- Chlorofluorocarbon (such as R11, R12)

Chemical heat pump -- A heat pump which uses the latent heat of absorption or of chemical reactions as the primary heating mechanism

Direct-expansion -- A system in which the heating or cooling effect is obtained directly from the refrigerant without the use of an intermediate heat transfer fluid

Earth-couple -- A heat exchanger which is placed below ground to allow the extraction/rejection of heat from/to the ground

Nonazeotropic -- A refrigerant mixture which changes composition during boiling or condensation

Ozone layer -- A layer containing a high concentration of O_3 molecules located in the earth's stratosphere which absorbs a large portion of the sun's short wavelength radiation (240-320 nm).

We invite you to follow the flow of information about working fluids and hope it will encourage you to be imaginative in solving the problems faced by the heat pump industry.

**Editorial by IEA Heat Pump Center Staff, Karlsruhe, Fed. Rep. of Germany*

K. Yamagishi*

Measures Taken Against CFC Problems in Japan

In the early 1970's, chlorofluorocarbons (CFCs) were identified as harmful to the earth's ozone layer. Because of this, international attention has been focused on solving this problem. The U.S.A., Canada, and Scandinavian countries have taken steps prohibiting the use of CFC in aerosols. Decreased use of CFC for aerosol and the freezing of CFC-11 and CFC-12 production have been implemented in the European Economic Community (EC) countries. In Japan, the Japanese Government has been taking steps similar to those of the EC countries since December 1980. In March 1985, Japan signed the "Vienna Treaty for Protection of the Ozone Layer" and in September 1987, the "Montreal Protocol On Substances That Deplete the Ozone Layer." Thus, Japan decided to institute legal measures in order to conform to these agreements. The following is an outline of the legislation to be enacted, the present state of research on CFC countermeasures, and the steps taken by the industry.

Proposed legislation

In view of the global interest, the Japanese Government prepared a bill for legal control in order to positively promote the protection of the ozone layer. The "bill concerning the protection of the ozone layer through restriction on specific substances and other measures" was submitted by the Government in conformity with the Treaty and Protocol mentioned above. This bill stipulates that the annual consumption of CFC starting July 1989 shall be frozen at 1986 levels, then through gradual reductions, it will be reduced to one-half of the 1986 level by July 1998. The bill was deliberated during the current Diet session and passed in May of 1988. In short, this bill provides that the Government fix the upper limits of production and consumption of CFC, and that the manufacturers must be granted approval for CFC production every year by the Ministry of International Trade and Industry (MITI).

In conjunction with positive and smooth enforcement of the Vienna Treaty and the Montreal Protocol for the purpose of protecting the environment and human life, both of which might be adversely affected by the ozone layer destruction, the bill stipulates: (1) In conformity with the international rules, the Ministry of International Trade and Industry and the Ministry of State for Environment fix the upper limits of production and consumption of CFC; (2) The manufacturers must get approval for the production quantity every year by MITI; (3) Upon confirmation of the amount of CFC destroyed, the manufacturers can increase their production quantity by this amount; (4) Those who use or deal with CFC gas must endeavor to recover and recycle by sealing the containers hermetically so as to control the emissions; (5) The government can instruct and advise on how to use the gas and the means of emission control; and (6) Those manufacturers who produce CFC without an approval shall be given a jail sentence of up to three years or shall be imposed a fine not exceeding 1 million yen.

Present state of CFC gas consumption and its countermeasures in Japan

The 1987 production of CFC gas in Japan totalled 176,000 tons, accounting for about 15% of total world production. Consumption of gases to be controlled is estimated at about 137,000 tons, which includes 26,000 tons of CFC-11, 36,000 tons of CFC-12, 52,000 tons of CFC-113, and small amounts of CFC-114 and CFC-115. As for uses, CFC-11 and CFC-12 are used as refrigerants in household refrigerators and automobile air conditioners, or as an aerosol or foaming agent, while CFC-113 is mainly used as a detergent for semiconductors, precision parts, etc.

Since the Japanese bill, which conforms with the Montreal Protocol, will be effective from July 1, 1989, the Japanese Government and industry began examining countermeasures for decreasing CFC production and consumption along with the reduction time schedules. The MITI has launched the research and examination of CFC alternatives, including CFC-123 and CFC-134a, which are regarded as very promising alternatives for CFC-11 and CFC-12. This research is examining the basic physiochemical properties and applicable properties, as well as safety with respect to toxicity and flammability, necessary for refrigerants, foaming agents, detergents, solvents, and aerosols. The MITI also set about research and examination methods for reducing leakage and recovering CFC-11 and CFC-12 used in refrigerators, automobile air conditioners, etc. In the "super heat pump energy accumulation system" which is now under research and development, the alternatives (CFC-123 and CFC-134a) are being studied as heat pump refrigerants by measuring the basic physical and other applicable properties.

Industry is also planning to strengthen their measures. For example, in order to prevent gas leakage, some automobile air conditioner manufacturers are proceeding with the development of techniques for strengthening the rubber hoses, re-designing to shorten the hose length, and decreasing gas consumption by developing smaller heat exchangers. In addition, they will make an all-out effort to develop air conditioners which can use the alternative CFC-134a. As for CFC-113, which is massively used in the washing process for semiconductors and high precision parts, no promising alternatives have been discovered so far. However, while decreasing consumption and emission of CFC gas by developing a hermetically sealed device, early development of alternative substances will be pursued mainly by CFC manufacturers.

Since it is predicted that it will take time to develop CFC-113 alternatives, both industry and the academic circle are jointly proceeding with research and development of interim measures, for example: (1) rendering used CFC-113 harmless by reducing it to salt; (2) developing a process which, by absorption, can recover the used CFC-113 at a high rate; (3) developing a process in which the used CFC-113 is recycled to a high grade, etc.

Conclusion

The bill for protecting the ozone layer, drafted in conformity with the Montreal Protocol, was submitted to the current Diet session. After deliberation, it was passed in May 1988. As this bill is to be enacted starting July 1, 1989, the examination of countermeasures is already under way jointly by industry, government, and the academic circle. As one of the largest CFC producing and consuming countries, Japan will establish a system for positively contributing to the international countermeasures for protecting the ozone layer.

Kiichiro Yamagishi, Director for Development Program, Moonlight Project Promotion Office, Agency for Industrial Sciences and Technology (AIST), Ministry of International Trade and Industry (MITI), Japan

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L.-O. Glas*

Measures to Minimize CFC Leakage: Instructions for Refrigeration and Heat Pump Plant Personnel

This article provides an example of how to formulate general instructions for heat pump plant personnel in all plants in order to minimize chlorofluorocarbon (CFC) emissions. CFC emissions are, of course, not only expensive but have also been noted in recent years as environmentally hazardous. Swedish authorities have strongly recommended that companies and individuals who handle CFC take strict measures to prevent emissions. Authorities expect a 25% reduction in CFC emissions within a three-year period. Otherwise, direct intervention by the authorities is anticipated.

Sweden's refrigeration industry recently prepared a proposal for a new safety manual for refrigeration and heat pump plants which includes prevention measures for CFC emissions. Moreover, the Heat Pump Advisory Group of the Swedish Council for Building Research (BFR) has issued a publication on the hazards of CFC emissions in which it developed recommendations for appropriate actions with the assistance of outside experts. This publication is intended for government officials, journalists, and government agencies working for environmental protection.

The author has participated in both of the above projects, during which time he compiled the base material to prepare the above-mentioned instructions for personnel working in large heat pump plants delivered by Termoekonomi AB in Stockholm, Sweden.

1. Risks of CFC Type Refrigerants

Health hazards from direct contact with CFC

In the 1940's, increasing use of CFC media began to replace the significantly more poisonous working media, such as sulphur dioxide, methyl chloride and ammonia, in refrigeration and heat pump plants due to health hazards.

The boiling points of the most common CFC media, CFC 12, 22, and 502, at atmospheric pressure are -30°C, -42°C, and -46°C, respectively. This means that any CFC leakage from the liquid-filled parts of a plant normally evaporates immediately to the gaseous phase. Larger quantities of leaked CFC that touch an exposed part of the body may result in freeze injuries due to evaporation and the low temperature. However, such leakage is very unusual.

CFC normally leaks in the gaseous phase. The gas does not injure the skin but dissolves in the blood after having been inhaled into the lungs. As more CFC dissolves in the blood, heartbeat becomes more rapid and then irregular, resulting in possible cardiac arrest. The central nervous system is probably also affected. The hygienic limit that can be inhaled during an 8-hour period has been set at 500 ppm = 0.05% CFC in air by volume.

Values that lie over 10%, 100,000 ppm present an immediate danger. Guinea pigs were unconscious after inhaling 10% CFC 11 for one hour. Humans who inhaled 0.1%, 1,000 ppm, CFC 12 for 2.5 hours showed symptoms of CFC effect by scoring lower ratings in psychological tests. For comparison, it can be said that inhaling 1% ammonia is viewed as immediately life threatening. However, through its painful effect on the mucous membrane, ammonia induces panic reactions even at substantially lower contents.

CFC gases usually have no distinct smell, but higher contents have a smell that is reminiscent of trichloroethylene. The following symptoms may occur when inhaling higher CFC concentrations:

-- Dizziness and an intoxicating effect as from solvents
-- Impaired thinking and concentration ability
-- Increasing heartbeat, from a quicker but regular heartbeat to an increasingly more irregular heartbeat
-- Breathing difficulties

The intoxicating effect is particularly dangerous. With judgment blunted, there is a risk that one does not withdraw from the job premises when necessary. If CFC leakage reaches volume contents of over 10% = 100,000 ppm, loss of consciousness may occur followed by death caused by cardiac arrest. No known deaths due to this have occurred in Sweden so far.

Health hazards of decomposed CFC during a fire

An important risk that is frequently discussed regarding CFC leakage in connection with fire is phosgene, an extremely poisonous gas that is a product of decomposition of CFC. Concern stems from one case in Sweden some decades ago which indicated phosgene poisoning from decomposed CFC. However, it is claimed that water vapor, which usually occurs both naturally in air and builds up during fire, decomposes phosgene. Practical experience, too, seems to confirm this opinion.

Environmental effects of CFC

CFC in the atmosphere is considered as having two adverse environmental effects: (1) it produces a warmer climate; and (2) it increases the damaging ultraviolet radiation onto the earth's surface. The former effect could be caused by the fact that CFC media have a considerable ability to absorb low-temperature radiant heat from the earth's surface which they partially re-emit to the earth's surface. This produces the so-called "greenhouse effect," heat radiation from the earth decreases and its temperature increases. This absorption is currently dominated by carbon dioxide, for example from the combustion of coal, wood and oil, but also from volcanic eruptions and water vapor. Considering that all of these gases practically absorb different wavelengths of low-temperature radiation, and that carbon dioxide at prevailing contents in the atmosphere has reached relatively close to its maximum possible absorption, any given quantity of CFC 12 emitted to the atmosphere is estimated as producing a radiation absorption around 8,000 times higher than that produced by the same quantity of CO_2 emitted to the atmosphere. The corresponding figure for CFC 22 is approximately 4,000.

It should be observed in this context that the majority of heat pumps in Sweden utilize water and nuclear electricity replacing oil-firing. Present leakage of CFC from these heat pumps is substantially less than 1/8000th of the CO_2 emissions that are eliminated through oil substitution. Moreover, they also reduce emissions of other environmentally hazardous flue gases such as sulphur and nitrogen oxides.

The latter effect is thought to be due primarily to the decomposition by the sun's ultraviolet radiation of the more stable CFC compounds, for example 11 and 12, mostly after they have reached a distance of 20 km or more above the earth's surface. The major part of the earth's ultraviolet radiation-absorbing ozone layer occurs above this height. Chlorine from decomposed CFC there decomposes the ozone to oxygen, thus increasing the amount of ultraviolet radiation that reaches the earth's surface. The conditions governing the build-up and decomposition of ozone are very complicated and still not sufficiently known. For example, ultraviolet radiation from the sun, higher temperature, hydrocarbons, and certain nitrogen oxides are believed to increase ozone build-up, whereas bromine, dinitrogen oxide, and, as already mentioned, chlorine, decompose ozone. Ozone contents in the atmosphere vary widely in different parts of the earth and according to measurements, can rapidly oscillate between lower and higher values. Additionally, contributing to these variations, as exemplified by chemical effects, are strong atmospheric currents, that is to say, physical conditions that affect both the movement of ozone and the gaseous emissions from industrial and agricultural activities.

Calculations of the changes in the ozone content given present conditions and CFC emissions can be performed only by using very simplified models of the real processes. The so-called ozone hole over the Antarctic from September to October every year since about 1975, with a gradually lower ozone content, cannot as yet be explained with any certainty. The ozone content rises to nearly normal values during November and remains there until August. Simplified models presented by Wuebbles indicate that if CFC emissions continue at the current rate, the ozone content would be reduced by 4% by the year 2100. A 7% reduction in current CFC emissions would yield a return to nearly normal values within 100 years. On the other hand, an annual increase of 7% would deplete the ozone content very quickly, resulting in a 20% reduction by the year 2020. It should be noted that Wuebbles' prognoses are still only partially verified by few measurements of the distribution of ozone over the earth at different points in time.

Depending on their stability, different types of CFC are estimated to yield different chemical effects on the ozone. The less stable the refrigerant, e.g., CFC 22, the more rapid the decomposition due to the ultraviolet radiation from the sun and the lesser the risk that chlorine from the decomposition reaches the higher, denser layer of ozone. Wuebbles gives the following relative values calculated for a few CFC types that are applicable to refrigeration and heat pump plants(CFC 11 has the value 1):

CFC Type	Relative ozone Decomposition
12	0.86
22	0.05
502	0.18

Effects of ultraviolet radiation on organisms

Ozone efficiently absorbs the shortest wavelengths of solar radiation and constitutes the only gas in the atmosphere to absorb such radiation. The shorter the wavelength, the higher the risk of damage due to radiation penetrating through a thin layer on the surface of organisms. Thus there is a risk of injuring bare skin and eyes, algae, plankton and fish spawn close to the surface of the sea, and plant foliage and outer coat. If not for the absorption of the short-wave radiation by the current ozone belt, the injurious effect would increase on the order of one hundredfold in Scandinavia, and tenfold in the dry desert areas around the equator. Desert areas presently receive a damaging effect via ultraviolet radiation ten times larger than the Stockholm area, which is primarily due to the height of the sun and the path of the solar rays through the ozone layer.

A thinner ozone layer and reduced capability for absorbing the ultraviolet radiation not only means a greater total radiation effect, but also that even more of the dangerous short-wave radiation is not absorbed. Thus, approximately a 1% reduction in the ozone layer will mean a 2% increase in the risk of damage.

People who are able to protect themselves against short-wave ultraviolet radiation by wearing clothes and sunglasses may incur the following injuries upon long-term exposure to radiation:

-- Skin cancer of the squamous cell carcinoma type. In Sweden, the death rate of 0.2 per mil before reaching age 75 is very likely the effect of ultraviolet radiation. Thus, the occurrence of squamous cell cancer in outdoor workers and sun-exposed body parts is considerably higher than those in indoor workers and sun-protected body parts. Squamous cell cancer is very easily induced on the skin of furless parts on mice.

-- Skin cancer of the malignant melanoma type. In Sweden, the mortality rate of 2 per mil prior to reaching age 75 is still not proven to be caused by the effect of ultraviolet radiation. In contrast to squamous cell carcinoma cancer, the occurrence of malignant melanoma has not been more frequent in outdoor workers or sun-exposed body parts. In addition, it is very rare that malignant melanoma can be induced on experimental animals by means of ultraviolet light. Certain studies conducted in sunny climates closer to the equator, however, show higher frequency of malignant melanoma. 1.6 times more people die in Australia than in Sweden as a result of this type of cancer. For squamous cell cancer, this figure is about 5 times greater.

-- Snow blindness

-- Cataracts, though cause is not decisively proven.

Obviously, the risk of injury depends on the time of exposure and individual characteristics. The risks for dark complexioned humans are thus lower. Clothes and sunbathing habits must also have a very strong effect on the risk of injury.

In the case of plants and animals, the effect will also depend on the species. A substantial rise in the effect of short-wave ultraviolet radiation during experiments has been shown to cause injuries and growth-inhibiting effects, especially in species that are normally exposed to insignificant radiation of this kind. Of course, this is an outcome of the law of nature. Species that have not obtained the requisite characteristics to survive in a changed environment through continuing permutations are eliminated. A thinning ozone layer could also lead to the elimination or reduction of reproduction in many animal and plant species.

2. Indications of leakage

Relatively large quantities of oil circulate with the refrigerant in the refrigerant system. The oil separator can only separate liquid phase oil discharged by the compressor. The higher the compression temperature that rises with the difference between condensation and evaporation temperatures, the more oil leaves the compressor as oil vapor.

Oil leakage from the refrigerant system is, therefore, always an indication of refrigerant leakage, although this leakage could be minimal and impossible to localize using a leak detector. However, refrigerant leakage may occur without the occurrence of any marked oil leakage at O-rings or packbox-sealed valve spindles, for example.

The leakage of a refrigerant from a refrigerant system in most cases means that the evaporation temperature, measured at the compressor on the suction manometer, for instance, drops due to the lack of refrigerant liquid in the evaporator. An abnormally low evaporation temperature thus indicates possible refrigerant leakage. Vapor bubbles seen in a sight glass in the liquid line prior to the expansion valve constitute the same indication. Indications of sinking refrigerant levels in the sight glass, level indicators, etc., on the receivers at identical operating conditions usually mean refrigerant leakage. It must be observed, however, that the operating conditions for a refrigeration and heat pump plant generally vary considerably, which means wide variations in the levels mentioned. Higher heating loads or cooling output from the evaporator yield a higher vapor volume in the evaporator and more refrigerant liquid in other parts of the refrigerant system, whereas a higher condensation temperature and pressure causes a larger weight quantity of refrigerant vapor on the high pressure side and a lower quantity of refrigerant liquid in other parts of the refrigerant system.

If stationary equipment for indicating refrigerant leakage has been installed, then it should be able to give a warning signal when the refrigerant content in the air at the sensor exceeds the set value. Of course, the sensitivity to leakage indication increases with decreased distance between the sensor and the location of the leak and lower set level for alarm signal content. Thus, the possibility of presetting a lower level for alarm content may compensate for fewer sensors and greater distance from the potential leak locations. However, the following must be observed when selecting the sensor positions and alarm levels:

-- Large quantities of outdoor air are turned over in the machine room and in the spaces around air-cooled condensers or outdoor air heated heat pump evaporators, for example. Due to the draft effect of the air, any leaked refrigerant will be very thoroughly mixed with air. This may require an unreasonably large number of sensors to indicate possible leakage, especially in the two latter cases. As an example, we can say that a medium-sized machine room turns over 1,000 m^3/h = 1,200 kg/h = approx. 10^7 kg outdoor air/year. If a stationary leak finder is installed for an alarm level of 500 ppm = "allowable limit of hygienic safety" this means that a "diluted" CFC 12 leak is indicated only when the leakage exceeds $10^7 \times 500 \times 10^{-6} \times 121/29$ = 21,000 kg/yr. (PPM = parts of volume per million, and 121/29 = ratio of weight of CFC 12 to air per unit volume.) If the ventilation can be shut off for a few hours, outdoor air intake can be assumed to be reduced to 10% or 100 m^3/h and if the alarm level can be reduced to 10 ppm, then the indicated leakage quantity drops to $0.1 \times 10^7 \times 10 \times 10^{-6} \times 121/29$ = 40 kg/yr. Cooling coils may be needed in this case in order to cool the room when the refrigera-

Bibliographic Review

Listed below are excerpts from the results of a search in the ENERGY database of STN International. The search was limited to entries made in the database since the beginning of 1987. The terms used for this search included working fluids, refrigerants, CFC, environment, and ozone layer. Individuals from member countries may contact the HPC to obtain the complete results of this search, or to request a search on a specific heat pump topic. In addition, the HPC has a summary of important literature related to refrigerants for heat pumps in Japan. If you would like a copy of this information, please contact the HPC.

STN International, the Scientific & Technical Information Network, provides an on-line computer database service. This service is operated cooperatively by FIZ, Karlsruhe, Federal Republic of Germany; the American Chemical Society, Columbus, Ohio, USA; and the Japan Information Center of Science and Technology, Tokyo, Japan. STN offers over 30 separate databases on various subjects. The ENERGY database contains references of worldwide literature on energy research and technology for all kinds of energy sources. It contains more than 1.5 million citations from journals, reports, books, patents, and conference proceedings, and is updated bi-weekly. The database can be searched on subject terms, titles, authors' names, and other bibliographic information.

Ideal fluid properties for optimizing absorption heat pump performance. Perez-Blanco, H., M.R. Patterson, and J. Braunstein. Report ORNL/TM--10315, Oak Ridge National Lab, Oak Ridge, TN, USA, April 1987 (English).

This report focuses on defining the fluid properties that will optimize the performance of a heat pump cycle. A simple heat pump computer model in conjunction with a parametric binary solution model is coupled to a computer code that searches for optimum values. The code determines the values of the parameters that maximize the thermal performance of the heat pump. The set of parameters is thermodynamically consistent and describes an ideal fluid with which single-effect cycle performance of 90% of Carnot is possible. The ideal fluid properties are a guide toward the properties that real fluids must exhibit in order to enhance the thermal performance of single-effect cycles.

Thermodynamic properties of aqueous ternary solutions relevant to chemical heat pumps: final report. Ally, M.R. Report ORNL/TM--10258, Oak Ridge National Laboratory, Oak Ridge, TN, USA, March 1987 (English).

Polynomial expressions are developed that correlate experimental vapor-liquid-equilibrium (VLE) and specific enthalpy concentration data for a newly developed ternary absorption fluid (LiNO3-KNO3-NaNO3). The development of these expressions is an important step toward using existing ORNL computer software to evaluate heat pump performance. A canned least-square-fit program, (program name POLFIT.BAS), was invoked to obtain the polynomial coefficients. Results show that the maximum deviation between correlated and actual values is less than 3% for vapor pressure and enthalpy. This is considered sufficiently accurate for heat pump cycle performance studies.

Theoretical analysis of an absorption heat pump with continuous regeneration of working fluids by solvent extraction. Cheng, C.S. and Y.S. Shih. *Chem. Eng. Res. Des.*, United Kingdom, September 1987, v. 65(5), pp. 415-420 (English).

A new type of absorption heat pump is proposed by using a second liquid to extract the refrigerant from the dilute absorbent solution in the absorber. The proposed system gives a better thermodynamic efficiency eta, defined as eta chemically bonded (QA/QE + W), than the traditional absorption heat pump. The calculated eta value reaches as high as 0.73 which is about 50% higher than the conventional one. Using LiBr/H_2O/acetophenone as an example, this paper presents the thermodynamic feasibility, the concept design and the operation analysis of the proposed plant.

Thermodynamic design data for absorption heat pump systems operating on water-lithium-chloride. Part 1: cooling. Grover, G.S., M.A.R. Eisa, and F.A. Holland. *Heat Recov. Sys. CHP*, United Kingdom, 1988, v. 8(1), pp. 33-41 (English).

The free choice of operating temperatures in absorption systems is limited by the Gibbs phase rule and the thermodynamic properties of the working pair. For a given combination of temperatures, the concentrations in the absorber and the generator are fixed automatically. This determines the flow ratio. Therefore, for any particular working air, the coefficient of performance is related to the flow ratio. Tables of possible combinations of operating temperatures and concentrations, including flow ratios, Carnot coefficients of performance and enthalpy-based coefficients of performance have been presented for a water-lithium chloride absorption system for cooling. The interaction of operating temperatures has been illustrated graphically. The data obtained are also compared with published data for the water-lithium bro-

5. Measures to rectify refrigerant leaks

Many types of leakages, as mentioned in Section 3, often can be sealed immediately, such as at a flange joint and valve spindles. Small leaks from the pores or cracks in pipes, for example, normally require that the actual closeable section in the refrigerant system get its refrigerant transferred through suitable means to other parts of the system or outside containers. Prior to soldering or welding, the refrigerant pressure must be brought down to slightly over atmospheric pressure. The repair work must, of course, be performed by a qualified person.

In case of large leakages, e.g., broken pipes, large cracks in the cast material and broken seals at flange joints, close attention must be paid to the health hazards described in Section 1. Every single plant requires detailed and specific instructions as to the measures required. However, it is important to observe the following points:

-- Local emergency or fire department should be contacted to decide on the appropriate procedures in case of large refrigerant leakages and, additionally, suitable personal safety equipment must be provided for personnel. The use of various types of pressurized air and breathing apparatuses or face masks can be extremely risky if the equipment has not been handled competently and the user is not familiar with the correct handling procedures. In 1986, Sweden's National Board of Occupational Safety and Health issued a special publication on the requirements for personnel and equipment for working in a hazardous atmosphere. These requirements are so stringent that the fire department doubts if its part-time personnel would be allowed to perform such work. In many cases, the local fire department may have to be called in to assist with the personal safety equipment when larger leakages are involved. Contacts with the local fire department are also very important so that the latter will be able to take measures against explosions and leakages in case of fire.

-- In case of leakage on the plant's pressure side, the compressor should usually be shut off immediately. This does not normally have to be done in case of leakage on the suction side, since it would yield higher pressure and hence more leakage.

-- Special instructions are needed as to whether the different apparatuses ought to be kept in operation or shut off, how to manipulate the valves, etc., depending on the location of the leak.

-- A list must be set up with the phone numbers of the people and companies to contact in the event of different types of leakages.

6. Maintenance measures to prevent refrigerant leakage

The larger the quantities of refrigerant a plant uses, the more frequent the leak search and inspections of the conditions that may cause leakage should be (see Section 3 above). Faults and deficiencies observed during these inspections as well as the measures taken should be compiled in a journal in order to eliminate permanently any possible weaknesses in the plant. Special instructions and maintenance reports on the above-mentioned activities, therefore, need to be tailored to every individual plant.

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K. Watanabe*

Thermophysical Properties Research on Refrigerant Mixtures and CFC Alternatives in Japan

In this article, some of the ongoing research programs on thermophysical properties of nonazeotropic refrigerant mixtures in Japan are reviewed and, in addition, current state-of-the-art on similar thermophysical properties of CFC alternatives is discussed.

After two energy crises in the 1970s, most industrialized nations are concentrating on R&D of advanced technology for the efficient use of energy. This includes waste heat recovery from various industrial processes with moderate and/or lower temperature levels as well as the utilization of renewable energy resources such as solar, geothermal, ocean thermal, biomass, etc. Increasing attention is being given to heat pump systems to satisfy these demands, since they are able to take thermal energy from a lower temperature source, use mechanical work to upgrade the temperature and then reject both the heat from the lower temperature source and the mechanical work to the higher temperature sink. Without reliable information about basic thermophysical properties of working fluids, it becomes almost impossible to design, develop and operate a heat pump system with confidence. Moreover, it becomes more difficult to choose the optimum working fluid among the proposed candidates without compiling thermophysical properties of these candidates on a systematic and consistent basis.

With our present knowledge in engineering and chemical thermodynamics, the only reliable method of determining thermophysical properties of working fluids is by conducting experimental measurements. Although many predictive approaches have been proposed to describe some of the fundamental thermophysical properties, they are mostly restricted to predicting only the specified property in a very limited range of

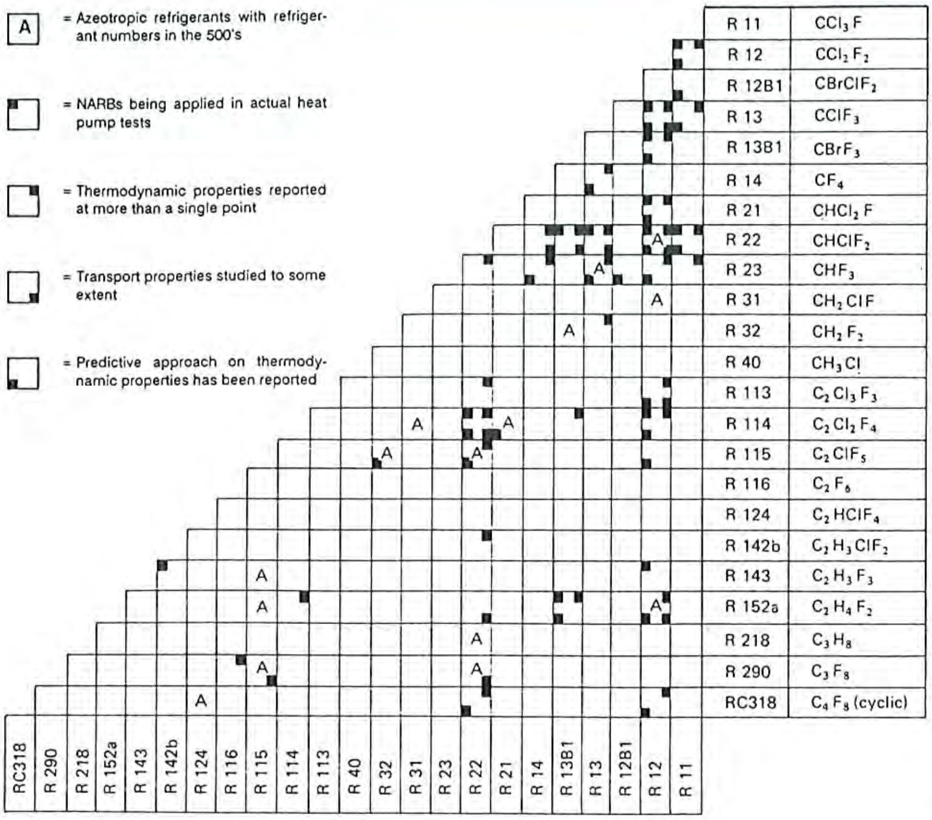

Figure 1. Possible blends ever proposed and/or studied for NARB's

validity with low accuracy. Hence, it is essential to perform the precise measurements of various thermophysical properties so as to obtain a set of reliable numerical data.

Thermophysical properties

Thermophysical properties of fluids, in general, are classified into three groups: equilibrium or thermodynamic properties, non-equilibrium or transport properties, and other miscellaneous properties including optical properties, radiation properties, and so on.

Available information about thermophysical properties of nonazeotropic refrigerant blends (NARBs) is limited in its quantity and quality in comparison with that of conventional pure refrigerants. This is due to the fact that the precise measurement of the thermophysical properties of NARBs with different compositions is elaborate and is accompanied by many difficulties.

Figure 1 summarizes the current state-of-the-art for the possible blends ever proposed and/or ever investigated, as far as the present author has surveyed with respect to thermophysical properties of NARBs. It is interesting to note that the proposed and/or investigated blends are composed of the most popular conventional refrigerants, such as R12, R22, R13B1 and R114, for their pure components. As can be clearly seen from Figure 1, there is much room for further examination of their possible application to advanced heat pump systems.

Equilibrium properties research on NARBs

A group of researchers, working under the author at Keio University, Yokohama, have been involved in an extensive research program on the experimental studies of equilibrium properties of NARBs since 1977. This activity was based on our past contributions in the field of thermodynamic property measurements for various pure halogenated hydrocarbons. At the very beginning of the program, we surveyed the proposed R&D projects on advanced heat pump systems and concluded that the most popular refrigerants being used worldwide were R12, R22, R114, R13B1 and R502. This survey led us to investigate binary blends using the first three refrigerants mentioned above, taking into account the scarcity of reliable and systematic measurements available at that time.

Currently, our research program on equilibrium properties of NARBs is composed of three projects closely interrelated to each other: pressure, specific volume, temperature and composition properties (PVTx) and vapor-liquid equilibrium (VLE) measurements, measurements of critical parameters and vapor-liquid coexistence curve near the critical point, and analytical studies for developing the equations of state together with some novel approaches toward prediction of thermodynamic properties of NARBS.

PVTx and VLE measurements

The experimental measurements on PVTx properties as well as vapor-liquid equilibria have been continued by using a constant-volume method coupled with isothermal expansion procedures of the sample with composition being kept unchanged. The NARBs we have studied up to the present are R12 + R22, R22 + R114, R13B1 + R114, R114 + R152a and R114 + R115 systems. Generally speaking, we have obtained several hundred sets of PVTx data for respective blends covering temperatures 280-440 K and pressures up to about 10 MPa, both in single phase and vapor-liquid coexisting phase. The uncertainties of our measurements are 8 mK, 2 kPa, 0.1% and 0.1%, in temperature, pressure, density and composition, respectively. Since we have measured PVTx properties both in the single and two-phase region, we were able to determine the composition and temperature dependences of bubble point and dew point pressures for the respective blends studied. Some of the results have been published.[1-6]

Measurements of critical parameters and coexistence curve

The second ongoing project is the measurement of critical parameters as well as of vapor-liquid coexistence curve near these critical points of different compositions of NARBs. The principle of measurements is direct observation of the vapor-liquid coexisting meniscus disappearance of the sample NARBs. In accordance with the measurements of saturated liquid and vapor densities for the range of reduced temperatures between around 0.96 and 1.0 (corresponds to critical temperature), the critical temperature and critical density of binary refrigerant mixtures have been directly determined with the aid of careful observation of meniscus disappearing level with critical opalescence. Most of our experimental determinations of the critical parameters have been achieved with estimated uncertainty of 10 mK and 2-3 kg/m^3, respectively. Up to the present, we have finished the measurements for NARBs including R12 + R22, R22 + R114, R13B1 + R114, and R152a + R114, respectively.[7-10]

Non-equilibrium properties research on NARBs

Non-equilibrium properties, in particular, transport properties such as viscosity and thermal conductivity of NARBs, play an essential role in the analysis of heat and mass transfer processes with phase change as well as in the optimum design of heat exchangers, i.e., evaporator and condenser for advanced vapor-compression heat pump systems. Despite their importance, however, the available information about non-equilibrium properties of NARBs is very limited in comparison with that for equilibrium properties as shown in Figure 1.

In the 1980s, some extensive and systematic research projects on non-equilibrium properties of NARBs have been started at two institutions in Japan. Makita and his colleagues at Kobe University, who have extensive experience in measuring various thermophysical properties of fluids and their mixtures, are currently devoted to measuring both thermal conductivity and viscosity of typical nonazeotropic refrigerant mixtures. Concerning their thermal conductivity measurements, they are using a coaxial cylinder method on a relative basis and they have reported the results on R22 + R152a for temperatures of 298-498 K and pressures up to 1.5 MPa as well as on R22 + R14 for 323-348 K with pressures up to 2.5 MPa.[11,12] They are currently measuring thermal conductivities of gaseous NARBs under room temperature conditions for R22 + R12, R22 + R13, R22 + R23 and R22 + R114 systems.

Another research project on viscosity measurements of NARBs is also in progress at Kobe University. The method that Makita and his colleagues are using is a rolling ball viscometer and the measurements have been performed at normal pressures for several compositions and isotherms. The results on three different mixtures including R290 (propane) + R22, R290 + R115 and R290 + R502 have been reported for temperatures of 273-348 K and pressures up to around 1 MPa with an error of less than 0.5%.[13] They have also finished their viscosity measurements recently on five different NARBs including R22 + R13, R22 + R13B1, R22 + R14 and R22 + R152a for temperatures of 298-323 K under atmospheric pressure.[14]

Another research activity is in progress at the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Senday, by Takahashi and his colleagues with respect to transport properties of NARBs. They have measured gaseous viscosity for systems such as R22 + R152a[15] and R12 + R22[16] by using an oscillating viscometer. The covered range of temperatures and pressures is 273-398 K and up to 5 MPa. They have an error of 0.3%, which is extremely precise in viscosity measurements of NARBs.

Thermophysical properties research on CFC alternatives

In accordance with the increasing concerns about the depletion of stratospheric ozone due to the atmospheric release of certain substances, it becomes an urgent task for thermophysicists to study some essential thermophysical properties of CFC alternatives. The Ministry of International Trade and Industry (MITI), Japan, is now planning to encourage basic research in this field together with the manufacturers of CFC products in Japan. A tentative task force on thermophysical properties of CFC alternatives has been established quite recently so as to make it feasible to examine various thermophysical properties of possible alternatives, R123 and R134a, extensively and systematically. The author has been requested to organize such a task force with several experts from different Japanese institutions.

Having discussed some preliminary programs, we now intend to make a series of precise measurements both on equilibrium and non-equilibrium properties of R123 and R134a. The objectives of our measurements include thermodynamic properties such as PVTx properties, vapor pressures, critical temperature and surface tension, as well as transport properties such as viscosity and thermal conductivity. The program will start within several months and hopefully we may be able to get some preliminary results within a year or so. It is essential to accumulate some reliable thermophysical property data through our program in order to evaluate the feasibility of applying the proposed CFC alternatives to various industrial applications.

Conclusion

Over the last several years, there have been many discussions on the prospective applications of NARBs in advanced heat pump technology. Most of these discussions and contributions, however, deal with performance evaluation of the heat pump systems on the basis of computer simulations using predicted and/or estimated thermophysical property data on different NARBs. In this connection, the author wishes to stress the importance of examining the predicted results on thermophysical properties more carefully in light of reliable measured information. It is not unusual to find some discrepancy between measured and calculated properties, and this fact may lead engineers to some unexpected results with respect to heat pump performance.

It is also noteworthy to point out that heat and mass transfer within the heat exchangers of advanced vapor compression heat pump systems is definitely playing a major role in controlling the cycle performance when using NARBs. For the purpose of more exact and concrete discussion on this problem, an extensive accumulation of reliable thermophysical property data is absolutely necessary. In particular, we must produce more reliable and systematic information about viscosity, thermal conductivity, surface tension, density and specific heat capacity.

Regarding the task of revealing some basic thermophysical properties of CFC alternatives, consistent sets of measured data should be produced. To achieve this, it is essential to build an international task group composed of experts from different nations, to accelerate international cooperation effectively and efficiently.

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Environmental Consequences of Heat Pump Technology

The following is a summary of the Swedish Council for Building Research (BFR) Report R28:1985 entitled "Environmental Consequences of Heat Pump Technology" (Vaermepumpteknikens miljoekonsekvenser) by Torbjoern Svensson, et al.

Introduction

A great deal of low temperature heat energy is temporarily stored on the surface of our planet by radiation from the sun. Heating systems based on extraction of this heat from the ground, from water or from air have rapidly become rather common. They are often referred to as natural heating systems. These systems usually include electrically driven heat pumps to increase the temperature of the heat energy extracted.

In the future, one-family houses are expected to use mostly outside air, surface ground and groundwater as a heat source. Apartment houses are going to use outside air and ventilation air. Heat pumps for district heating systems are supposed to use mostly cleaned sewage water and lake- and seawater.

Many different techniques, adapted to the local environmental circumstances, have been developed to extract the heat from these heat sources. In parallel with this technical development, a program for studying the consequences for the

Natural heat source	Ground (shallow)	Groundwater	Rock	Lake water (Open system)	Seawater (Closed system)
Design considerations	Earth quality Water content	Hydrogeology Test pumping Water chemistry	Rock quality Heat conductivity	Temperature Water volume	Temperature Sea bottom structure
Plant design technique	Known Account for risk of ground damage	Conventional well technique	Conventional rock drilling	Intake and outlet devices to be tested	Pipe anchorage methods
Possible operating problems	Leakage	Plugging Corrosion	Minimal	Low temperature Corrosion	Damages Leakage
Environmental effects	Leakage Effect on vegetation	Changes in water quality Surface water effects	Minimal	Changes in nourishment and oxygen balance	Effect on bottom fauna and flora close to the pipes
Competing interests	Ground for buildings Water supply	Water supply	Underground buildings	Water supply Fishing	Water supply Fishing
R,D&D needed	Cold carrying fluids Practical design methods Environmentally friendly installation techniques	Investigation of operating experience Water chemistry	Hole spacing Freezing and recharging	Ecological follow-up Water temperature and heat energy turnover Ice formation	Ecological follow-up Water temperature and heat energy turnover Ice formation

Table 1. Comparison of systems using natural heat sources

environment has been carried out in Sweden.

Closed and open systems

Extracting heat from these heat sources disturbs the natural sun-based heat turnover. This thermal influence on the environment is one of the subjects considered in this paper.

The techniques to utilize these heat sources can be divided into the use of closed and open systems. In closed systems a special heat exchanging circuit is used, consisting mostly of a piping system, to transfer the heat from the source to the heat pump. This circuit contains a circulating heat carrying fluid such as glycol, alcohol, or a brine, often mixed with components to eliminate corrosion and the growth of organisms. In the case of leakage, there is a risk of unacceptable fouling of the environment. This is another subject to be considered.

Problems such as noise, vibrations, and leakage of refrigerants (CFC) were not considered in this study.

Comparisons

A comparison of the qualities and problems of natural heat source use and natural heat store use is shown in Tables 1 and 2, respectively.

In general, all the techniques considered can be used without any environ-

Natural heat store	Storage using rock caverns	Storage using drilled holes in rocks	Storage using in ground piping systems	Storage using ground water
Design considerations	Rock quality Cracks Hydrogeology	Rock quality Cracks Hydrogeology	Earth quality Water content Geotechnique	Hydrogeology Geology
Plant design technique	Known Rock cavern building	Known Rock drilling	Known	Known Well technique
Possible operating problems	Chemical precipitations Temperature layering	Chemical precipitations Flow distribution	Leakage Flow distribution	Plugging Corrosion
Environmental effects	Local temperature increase	Local temperature increase Building work	Vegetation damage Ground settling	Small
Competing interests	Surface area for storage	Building area	Building area	Water supply
R,D&D needed	Investigation of environment close to old rock caverns Cost decrease	Investigation of operating experience Cost decrease	Investigation of operating experience Ground settling The properties of peat	Investigation of operating experience Plugging Thermohydraulic

Table 2. Comparison of systems using natural heat stores

mental consequences worth mentioning if designed and applied according to accepted practices. It neither makes sense nor is it possible to rank the different systems from an environmental point of view. Furthermore, local conditions are decisive in determining the amount of heat which can be extracted or stored. The local competitive interests in water supply, environmental protection, and of other heat users, etc., must be considered in the design. The designer must also consider the capacity of the heat source and the environmental effects of the actual heat extraction and storage rates. The risk of leakage and other breakdowns should also be minimized by the design. These are minor design constraints to the use of natural heat sources and stores.

R,D&D, reports and references

The report also contains a list of ongoing R,D&D projects and a list of reports and other references used in the study.

Summary

By using natural heating systems, the use of other methods of heating, such as burning oil, solid fuels and coal, and direct electric heating is decreased. At the same time, the direct and indirect environmental influence from these heating systems, mainly in the form of air pollution, is also decreased. The environmental impacts connected to the natural heating systems, if they are carefully designed and operated, are small compared to the problems caused by the combustion of fuels, such as acid rain, risk for human health, influence on climate, and corrosion. The total load on the environment from heating systems is decreased when the application of natural heating systems is increased. In other words, natural heating systems are the most environmentally friendly of all means of heating available for large scale use.

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Environmental Impact of CFC in Groundwater - a Study Regarding Direct Expansion Ground-Coupled Heat Pumps

Direct expansion is a new step in the development of ground-coupled heat pumps (GCHP). Some installations already exist in Sweden, Austria, USA and Germany; systematic R&D in the IEA-framework is beginning. In Schwalbach GCHP Research Station, Fed. Republic of Germany, a prototype direct expansion heat pump with vertical borehole evaporator has been in operation since December 1987. Prior to this test installation, laboratory experiments were carried out to assess the environmental risk of CFC leakage. Beginning in April 1987, the working group on organic geochemistry in applied geosciences of Giessen University conducted the investigations. In September 1987 a meeting on this topic was held near Giessen with participants from Austria, Switzerland, Netherlands and Germany; initial findings were presented and discussed. Additional results are now available and are presented in this paper.

Analytic methods

All chemical analysis was done using a real groundwater, pumped from a borehole in Schwalbach. This water represents a regular, non-polluted groundwater and is considered as standard laboratory analysis water (SLAW) for the investigations. The experiments were restricted to difluor-monochlormethane (R22), which is best suited for GCHP applications. Some tests were also done with R12.

Each sample was divided into two parts, one to be treated with CFC and one to

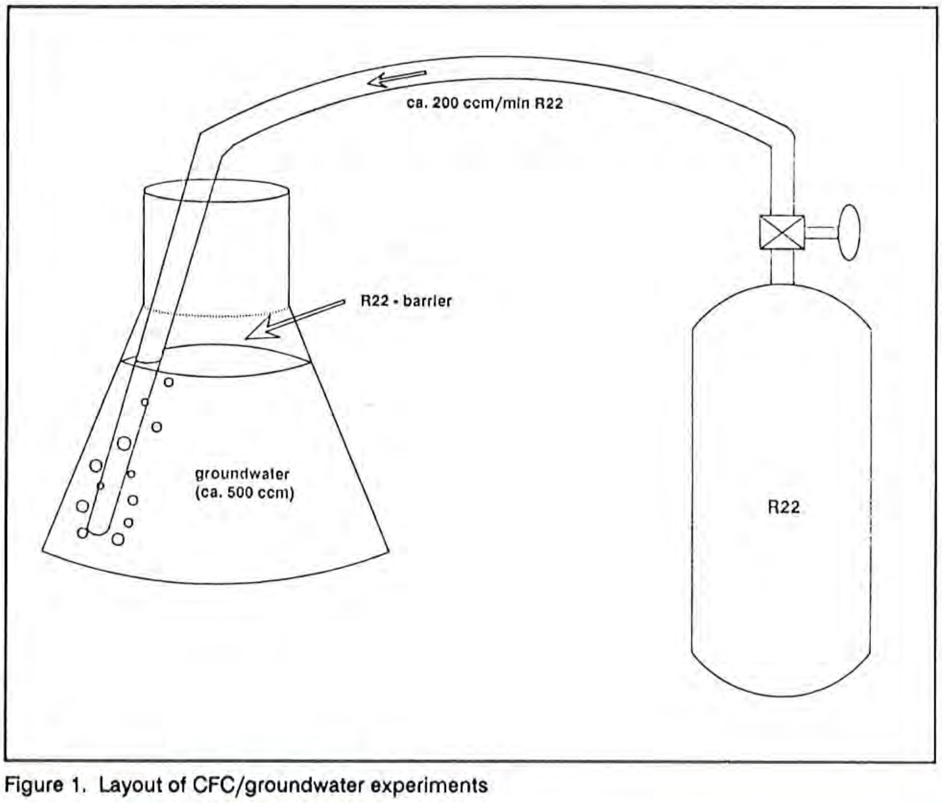

Figure 1. Layout of CFC/groundwater experiments

serve as an untreated sample. The untreated samples were prepared under the same conditions as the CFC-samples, to identify chemical changes not related to the CFC treatment. The samples were stored frozen until the very moment of the experiments.

A glass vessel was filled with 500 cm^3 of groundwater. The CFC was added as vapor at a rate of about 200 cm^3/min; this treatment lasted 6-8 hours (Figure 1). Measurement of physicochemical parameters was done in short timesteps in the beginning and longer periods after two hours of CFC treatment. This screening included assessment of pH-value, oxidation potential and electrical conductivity under controlled temperature. These parameters are sensible tracers for chemical alterations in the groundwater.

Following the same schedule, samples of 1 cm^3 each were drawn for gaschromatographic analysis. These specimens served for detection of light volatile hydrocarbons, which may originate in decomposition of CFC under the physicochemical conditions in groundwater. Decomposition or reassembling of CFC could result in toxic substances or those harmful to the environment. An occurrence of such reactions would limit the use of CFC in direct expansion heat pumps penetrating the groundwater table.

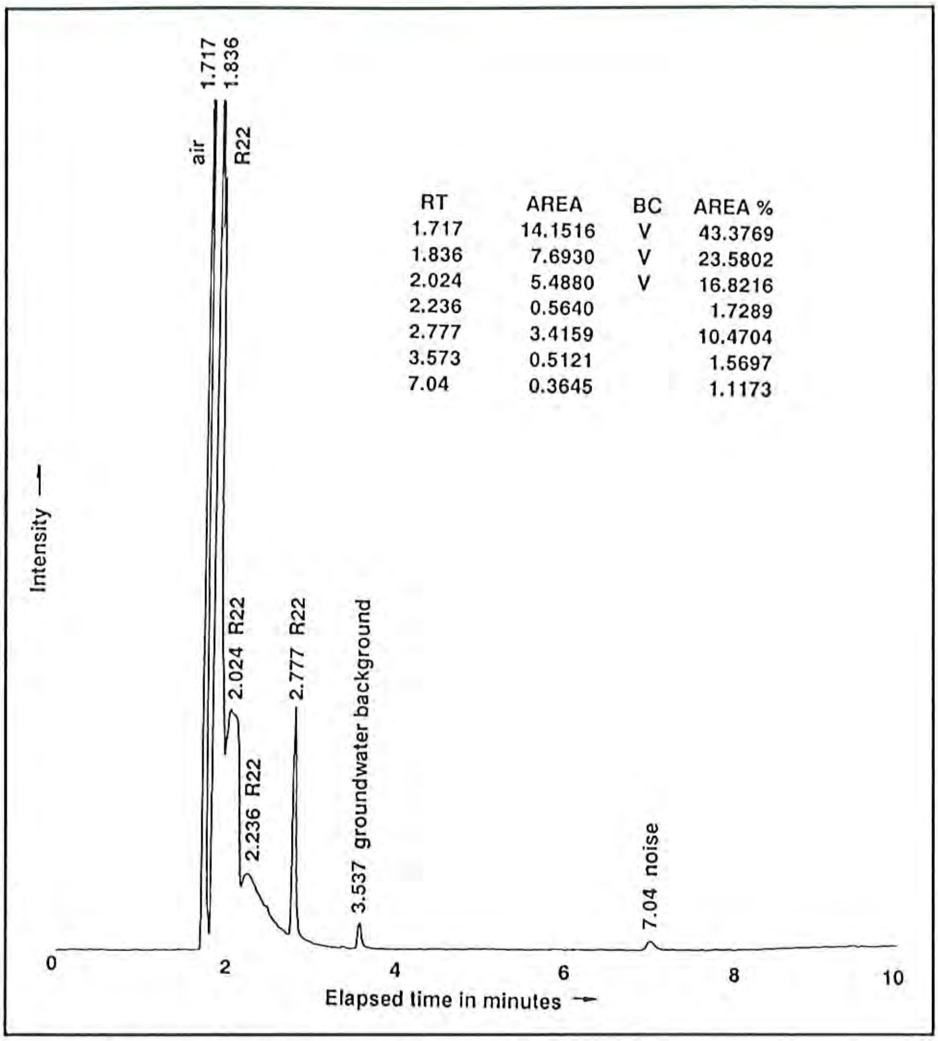

Figure 2. Gaschromatogramm of groundwater contaminated with R22

Investigations with pure groundwater (SLAW)

The most significant observation is an increase of the pH-value, which rises from 6.7 to 7.6 in the untreated sample. The increase can be observed in the CFC-treated groundwater as well as in the untreated sample. The reason for this is an expulsion of CO_2 due to the stirring of the water. There is a strong correlation between CO_2-content and pH-value in the SLAW. The oxidation potential (Eh-value) shows similar behavior. Stirring enables oxygen to dissolve in the water, and the Eh-value approaches 100%.

In the presence of R22 the increase of pH-value is higher, but the oxidation potential approaches 0%. The explanation is a CFC-barrier which forms above the water surface. R22 is less dense than water, but about four times denser than air under atmospheric conditions. Hence it strips out of the water and remains above the water table. The consequence is an easy upward path for light volatiles such as O_2 and CO_2, but no way back into the fluid. This results in the higher pH-value and lower Eh-value in the presence of CFC due to a loss of oxygen and carbon dioxide. Chemical reactions with CFC cannot be proven nor excluded by these observations.

The electrical conductivity as a tracer for decomposition reactions remains nearly constant. The slight variations are due to the resolution of the metering equipment and occur in both the CFC-treated and the untreated samples. This indicates a stable chemistry without reactions caused by the CFC.

The gaschromatography (more than 200 chromatogramms were produced) proved this not only when using the flame-ionization-detector, but even when employing the highest resolution electron-catcher-detector. Only peaks present in the background of the groundwater and those representing the unchanged R22 could be found (Figure 2). R22 is in solution in the groundwater, but it remains inert. This is proved for short periods of a few days. Samples of CFC-treated groundwater, which were stored over six weeks, were free of R22 in the fluid; the CFC seems to be stripped completely out into the air. Further investigations are necessary to show this function over time.

Experiments with soil suspensions in groundwater

In most cases natural groundwater is not clear, therefore, suspensions with the most important soil materials, i.e., clay and sand, were prepared. CFC-

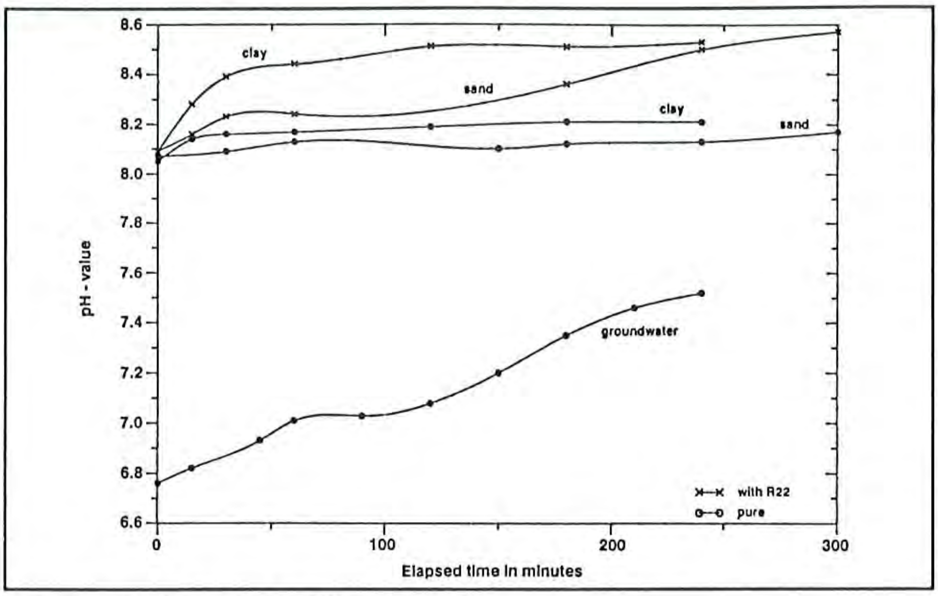

Figure 3a. pH-value vs. time in different suspensions

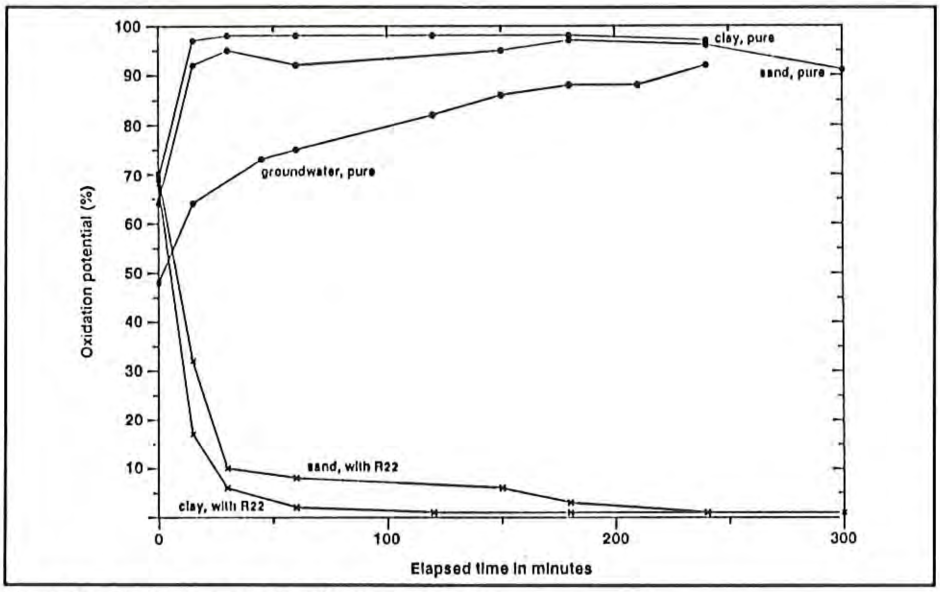

Figure 3b. Eh-value vs. time in different suspensions

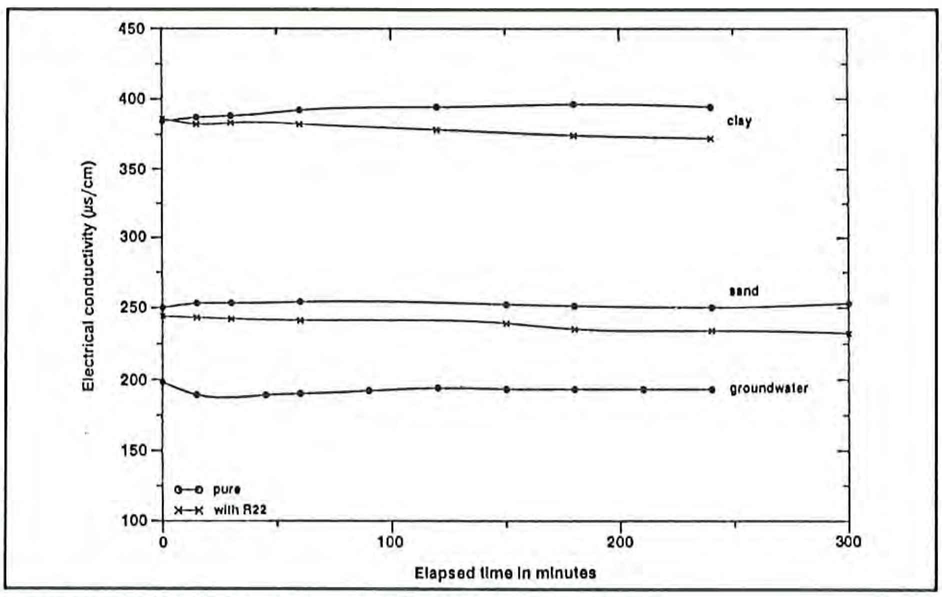

Figure 3c. Electrical conductivity vs. time in different suspensions

treated and untreated samples were analyzed as described above. The pH-value is highest in clayey suspensions with R22 (Figure 3a). The higher pH-value of clayey versus sandy material is a consequence of the adsorptive properties of clay. This is also responsible for the Eh-changes (Figure 3b). The development of the electrical conductivity is affected by the clay as well (Figure 3c).

In sandy suspensions, the detection of CFC with gaschromatography resembled the investigations in pure SLAW. In the presence of clay particles, a different behavior could be observed; no R22 could be detected in the water, even after hours of treatment with the CFC. The only explanation is the adsorption of R22 to the clay. This has to be verified and the amount of adsorptively held CFC and the corresponding clay minerals must be determined in future research.

Conclusions

For interpretation, one must consider that all tests were done under laboratory conditions, which do not necessarily represent the exact conditions in the ground (pressure, temperature). According to the current investigations, no evidence can be seen for a noxious impact of leakage of R22 in the groundwater regime. No new substances due to decomposition or conversion of CFC could be detected in the experimental timescale. R22 strips out of the groundwater without changing the water chemistry; only physicochemical alterations as a result of a CFC barrier above the groundwater table can be expected. The use of R22 in direct expansion systems seems to be no hazard for groundwater and soil.

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ECR's Direct Expansion Earth-Coupled Heat Pump System

The following is a summary of a report which was prepared by ECR Technologies, Inc., Lakeland, Florida, USA. For a complete copy of the report, please contact the Heat Pump Center.

Introduction

ECR's ground-source heat pump (GSHP) circulates refrigerant directly through its in-ground heat exchanger (direct expansion system). The heat exchanger only requires 1-1/4" (3.18cm) diameter bore-holes which can be drilled at a lower cost than the larger holes used for conventional GSHPs. A second feature of the unit is its patented refrigerant circuit control devices which are used to maintain optimum operating conditions for the evaporator, condenser and compressor, allowing the total system to operate at maximum efficiency. For these reasons, installation and operating costs are much lower than conventional GSHPs, and the installed cost is only slightly higher than air-source heat pumps (ASHP) currently sold on the market. At the end of 1987, units up to 5-ton capacity had been installed and are currently undergoing testing in various regions of the U.S. Initial results indicate higher COPs than ASHPs.

Unique direct expansion earth coupled heat pump system

ECR Technologies, Inc., of Lakeland, Florida, USA, has solved many of the problems associated with the installation and operation of GSHPs by developing a unique Direct Expansion Earth Coupled Heat Pump (DXHP). The name "Direct Expansion" derives from the direct expansion of the refrigerant in the buried heat exchanger (copper tube earth tap) without an intermediate heat transport fluid. In this system, refrigerant alone is circulated in the buried heat exchanger. ECR's system, which both heats and cools, is mechanically simpler and has also been proved more efficient than the standard Air Source Heat Pump (ASHP) on the market today.

The main features of the new ECR system are:

-- A simple direct-expansion buried heat exchanger (earth tap) design consisting of a specific number of vertical or diagonal coaxial copper tube earth taps, operating in parallel, inserted directly into the ground to depths up to 60', through which refrigerant circulates continually in a closed circuit that includes a heating/cooling unit (air handler) located in the building to be heated or cooled.

-- ECR's patented Refrigerant Controls consist of two simple devices that replace the conventional expansion valve and accumulator. These devices automatically adjust the refrigerant flow and system charge to changing requirements while simultaneously providing a non-subcooling condenser and a constantly flooded evaporator that assures near-zero superheat at the compressor inlet.

In conventional systems without ECR's controls, subcooling initially delivers more energy at the condenser, but the reduced condensing surface causes increased compressor output pressure resulting in increased input power and slight loss in throughput (mass flow). The result is that system capacity may increase slightly in the heating mode, but at the expense of system efficiency.

Similarly, superheat at the compressor inlet means more energy per unit of refrigerant mass flow, but mass flow will be reduced due to the reduced volumetric efficiency of the compressor and reduced output pressure from the evaporator (because less evaporator surface is being used to evaporate when part of the evaporator is used to superheat the vapor). The net result of superheat is a loss of capacity and efficiency.

Economical buried heat exchanger design

The ECR direct expansion buried earth tap design incorporates a specific number of small vertical or diagonal coaxial copper tube earth taps, operating in parallel, inserted into bore-holes having a 1-1/4" diameter (Figure 1). Each tap is composed of concentric copper tubes separated by a thermal buffer (Figure 2). The length of earth tap required for wet or saturated soil is approximately 180'/ton (16 m/kW) of compressor capacity. Vertical head losses and pressure drop limit the depth of each tap to about 70' (21 m).

An important economic advantage of the ECR DXHP is the significant reduction in drilling costs it affords. The ECR system requires about 1.8 times the length of bore-hole per ton or kW of other ground-source systems but 1-1/4" (3.18cm) diameter holes in the ECR system require drilling less than 8% of the volume of the 6" (15 cm) diameter holes in other GSHP's. This considerably reduces drilling costs.

ECR has developed its own drilling rig that economically drills 1-1/4" holes to 70' (21m). This drilling technology can be easily adapted for use with several small commercially available drill rigs. Using this drill rig, system-compatible 1-1/4" holes have been drilled in the state of Florida (USA) at a cost of $1.40/ft (4.60/m), including all labor, drill bits, drilling fluid, power, return on capital, and driller's profit. Figure 3 shows one of the units in operation drilling diagonal holes for the earth taps.

Refrigerant flow and charge control system

Numerous heating and cooling apparatus, including straight air conditioning systems, heat pumps, and other refrigeration systems, use fluorocarbon refrigerants. To operate at optimum efficiency, the three major components in all such systems - compressor, condenser and evaporator - require the refrigerant to be in a certain ideal condition. The compressor requires a dry or totally evaporated refrigerant from the

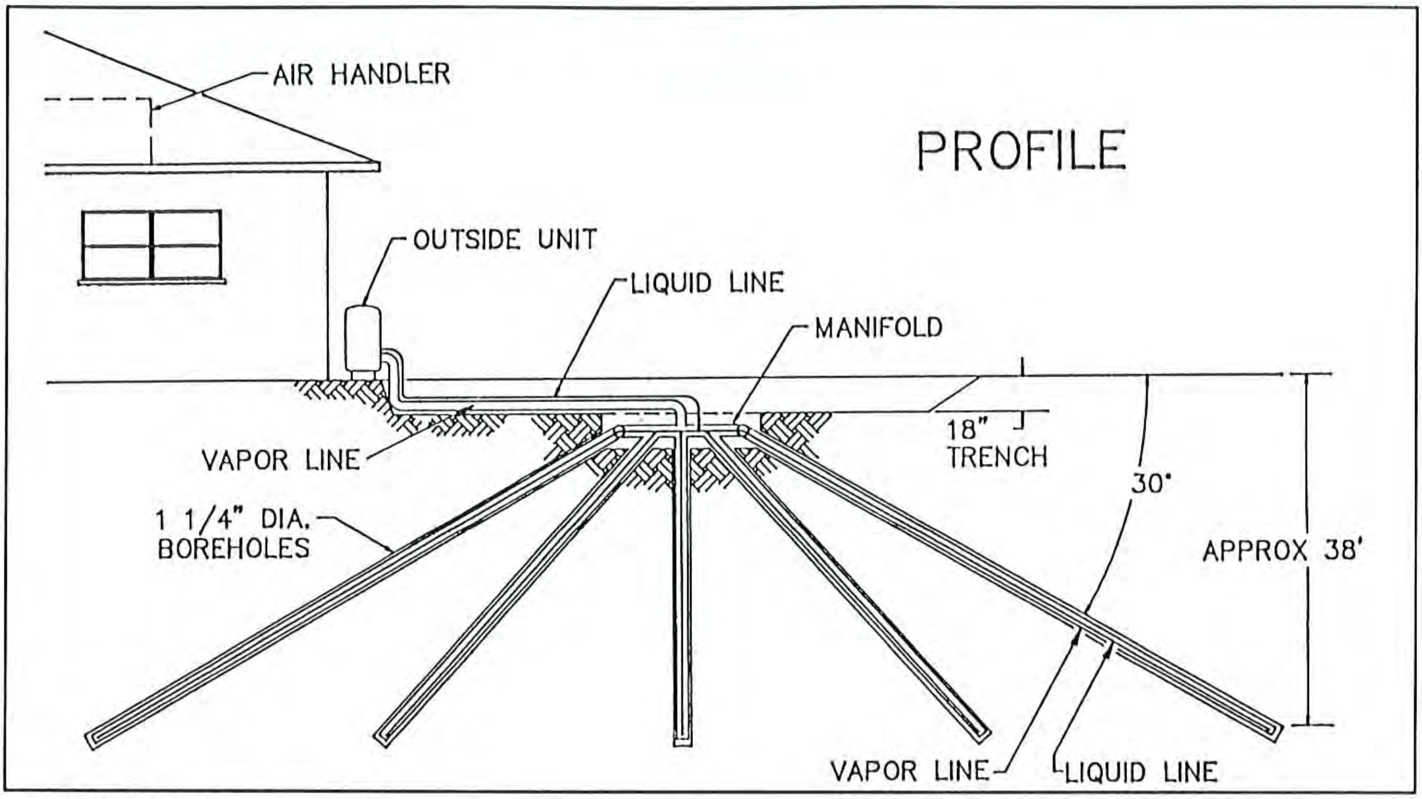

Figure 1. Buried earth tap arrangement

evaporator, containing little or no superheat at the compressor inlet. The condenser requires its outlet "back pressure" to be just sufficient to cause all refrigerant vapor to condense (become a liquid) before it reaches the condenser outlet. In contrast, the evaporator requires totally liquid refrigerant at its inlet, and the refrigerant should become completely evaporated just as it reaches the evaporator outlet. This is the "flooded" evaporator condition.

The new ECR Refrigerant Flow and Charge Control System is the first simple and reliable system to automatically produce ideal refrigerant conditions throughout the operating cycle in all three major system components, thereby permitting the refrigeration system to operate at optimum efficiency. These controls are automatic, efficient, effective, and reliable. Figure 4 shows the typical arrangement of the control system which consists of:

-- A Liquid Flow Control (LFC), replacing the thermal expansion valve, that controls the flow of refrigerant between the condenser and the evaporator.

-- An Active Charge Control (ACC), replacing the accumulator, operatively coupled between the evaporator and the compressor to regulate the active charge of refrigerant in the system in coordination with the LFC.

Liquid flow control

The Liquid Flow Control (LFC) operates together with the Active Charge Control (ACC) to provide optimum system efficiency by positively controlling the flow of refrigerant between the condenser and the evaporator. As shown in Figure 5, liquid refrigerant entering the LFC through the liquid inlet (top) is variably restricted from leaving the enclosed liquid/vapor reservoir through the liquid metering orifice (bottom) by the action of the hollow float and movable metering member relative to the outlet metering orifice. As the liquid refrigerant level in the reservoir increases, the float rises proportionately opening the liquid metering orifice a corresponding amount. Conversely, as the liquid level falls, the orifice closes correspondingly. Thus the rate of liquid flow through the liquid metering orifice is inversely proportional to the amount of vapor in the reservoir. Equilibrium is reached when

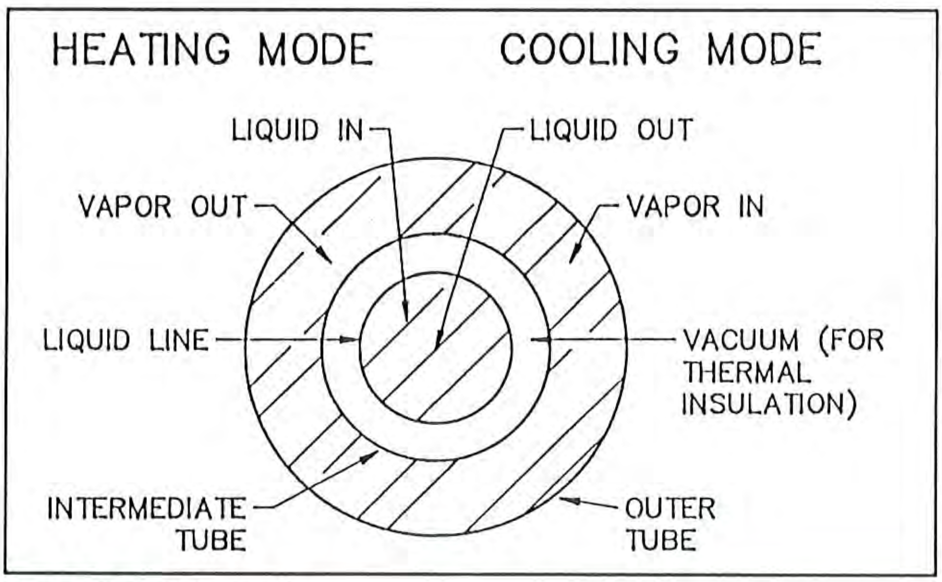

Figure 2. Earth tap cross-section

the rate of liquid flow through the liquid metering orifice equals the rate that refrigerant is condensed by the condenser. Thus the LFC passes liquid at exactly the rate it is produced in the condenser, and thereby "sets the pace" of refrigerant flow for the system, prevents back-up of liquid in the condenser and the associated loss of condensing surface (the subcooling condition), and prevents blow-through of vapor from the condenser to the evaporator.

Active charge control

The Active Charge Control (ACC) consists of a thermally-encapsulated, enclosed liquid/vapor reservoir (Figure 6). The inlet (bottom) of the ACC is connected to the outlet of the evaporator, while its outlet (top) is connected to the inlet of the compressor. Refrigerant reaching the inlet of the ACC from the evaporator is forced through the liquid refrigerant stored therein to : (1) trap any liquid refrigerant it may contain; or (2) evaporate a portion of the stored liquid refrigerant if the arriving vapor refrigerant contains superheat.

The ACC is configured for adequate liquid reserve in the lower section and proper vapor velocity in the upper section near the outlet. A vertical evaporator tube is coupled directly to the ACC inlet. The evaporator tube has a liquid entrance orifice located near its lower end, which provides a constant flow of liquid into the evaporator tube. The liquid level in the vertical evaporator tube thus tends to be substantially the same as in the reservoir. The evaporator tube serves to mix the incoming vapor with the liquid entering at the orifice, and to discharge the liquid/vapor mixture radially with the aid of a circular deflector plate. Any liquid in the mixture falls back into the reservoir, while vapor and entrained oil proceeds to the ACC's outlet. Thus the ACC serves to maintain an optimum charge of refrigerant in active circulation in the system while at the same time allowing oil and only evaporated refrigerant to reach the compressor.

Direct expansion ground-source heat pump

One very effective application of the ECR control system is in the ECR DXHP (Figure 7).

Figure 3. Drill rig for radial earth tap installation

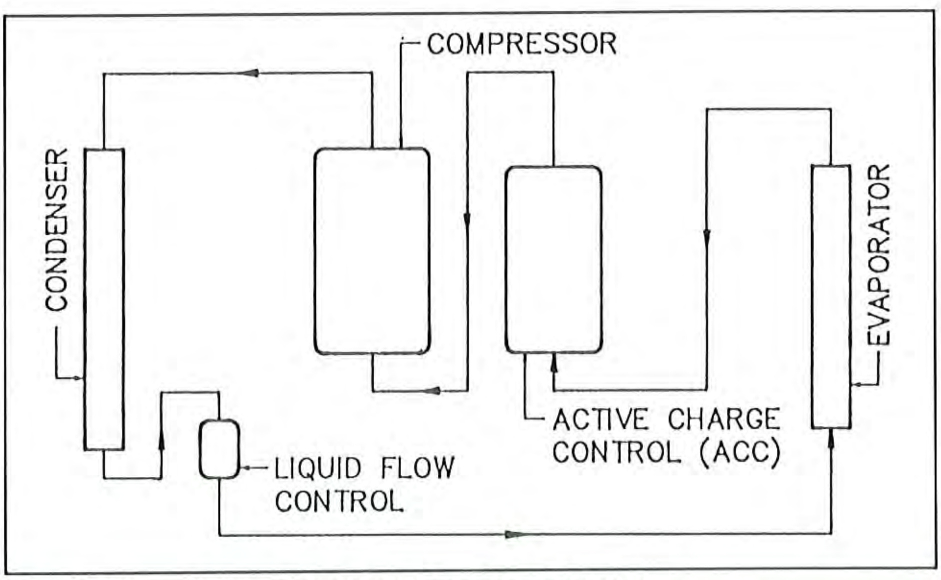

Figure 4. Refrigerant circuit schematic using the LFC and ACC devices

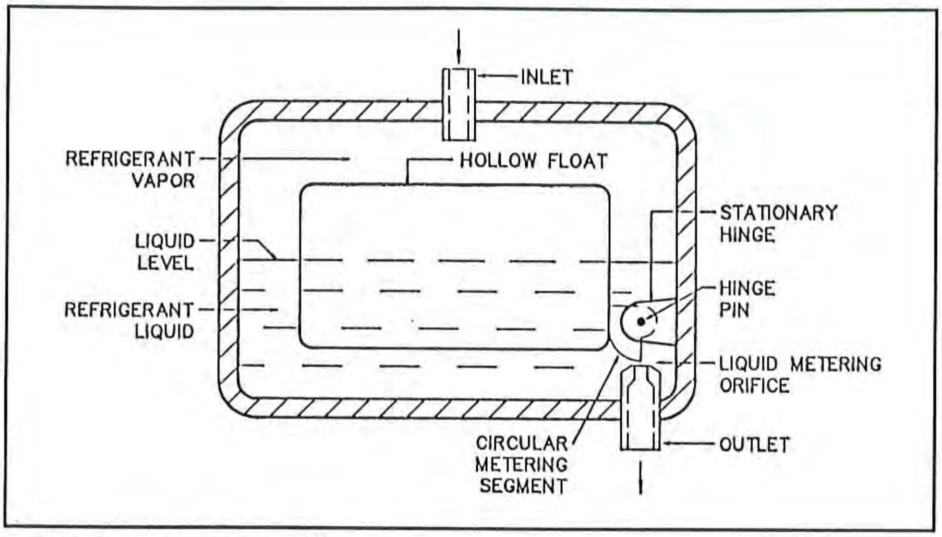

Figure 5. Liquid flow control (LFC)

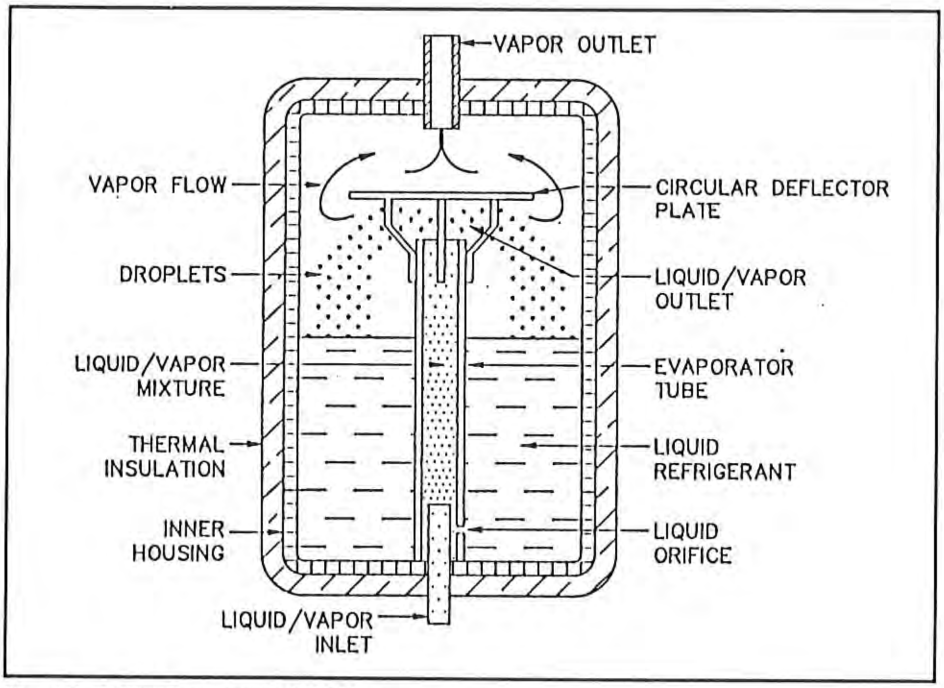

Figure 6. Active charge control (ACC)

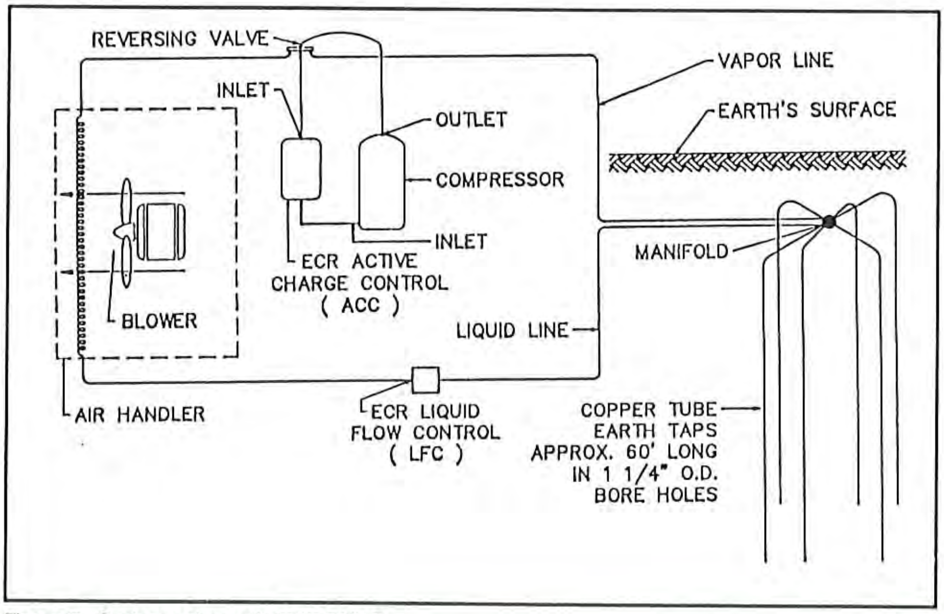

Figure 7. System schematic ECR DXHP

In contrast to ASHPs, ECR's direct expansion heat pump has the following advantages:

-- Extracts heat for space heating from the earth, which is relatively warm, and rejects heat for space cooling into the earth, which is relatively cool.

-- Is 20-30% more efficient in the heating and cooling cycle than a standard efficiency ASHP.

-- Eliminates the need for electric-resistance or other supplemental heating, even in colder climates, thereby reducing consumer operating cost and the additional peak demand placed upon electric utility systems.

-- Is mechanically simpler by eliminating the exterior condenser/evaporator coil, fan, fan motor and capacitor, defrosting controls, and ancillary wiring required by the standard ASHP.

-- Has a totally enclosed outside unit (containing the compressor) that is about one-half the size of the typical ASHP unit; it can also be located in a utility room or basement, or be combined with the air handler into a single unit.

-- Runs quieter because of total enclosure and elimination of the exterior fan.

-- By using the relatively constant temperature of the earth as its heat source and heat sink, reduces thermal stress to the compressor.

-- Exterior condenser/evaporator unit (fan coil in ASHP) is buried out of sight, protected from damage, theft, or clogging by leaves or snow.

-- Installed cost is only slightly more.

-- Cost recovery period is less than 18 months.

Demonstration projects

Beginning in October of 1985, a 3/4-ton, a 1-ton, and a 2-ton ECR DXHP were operated in bench tests at ECR's R&D facility in Lakeland, Florida, USA. These successful bench tests were followed by two electric-utility-sponsored field demonstrations of the ECR system during the summer of 1987. A 1.5-ton ECR system was installed in June of 1987 in a townhouse in New Castle, Delaware, USA, for a 12-month monitoring field test sponsored by Delmarva Power & Light Company. A 2.5-ton system, funded by the City of Lakeland Department of Electric & Water Utilities was installed in July of 1987 in a new, 1,368 sq ft single-family residence in Lakeland, Florida, for 12-month field test monitoring (see Figure 8).

The objectives of these currently operating demonstration projects are:

-- Prove the technical and economic viability of ECR's system in areas having differing subsurface temperatures and heating loads.

-- Prove the ECR system's capability to provide the sponsoring utility with an effective heat load building tool.

-- Quantify the number of kW's of peak electric capacity that can be eliminated by each ECR installation.

-- Provide a foundation for ECR and the sponsoring utility to develop a program for heat pump displacement of alternate heating fuels within its service territory.

System performance is being monitored continuously by instrumentation that includes an automatic monitoring and recording system. Output data are being analyzed to determine system efficiency and characteristic load profiles as a function of weather conditions. Testing schedules include both winter and summer peaks at each site to capture data for both heating and cooling months.

Preliminary efficiency tests were carried out in late August, 1987, at the New Castle, Delaware site. During continuous 8-hour run on heat the average efficiency of the ECR system was a CCP of 3.78. During the last three hours of this test run, the COP averaged 3.75 (12.8 BTUs/Watt). Over the entire 8-hour test period, the earth tap temperature only dropped to 40°F. At the beginning of the test run, the 1.5-ton ECR system was delivering 26,600 BTUs/hr (8kW) to the house, and the system was still delivering 23,600 BTUs/hr (7kW) after running continuously for 8 hours. Due to cooling of the earth tap field during long cold spells, the seasonal COP and capacity are expected to drop but not below a COP of 3.0 and a rated capacity of 18,000 BTUs (19kJ). Preliminary data from cooling mode operation indicate a COP of 3.9 upon system startup and approximately 3.5 for a season average.

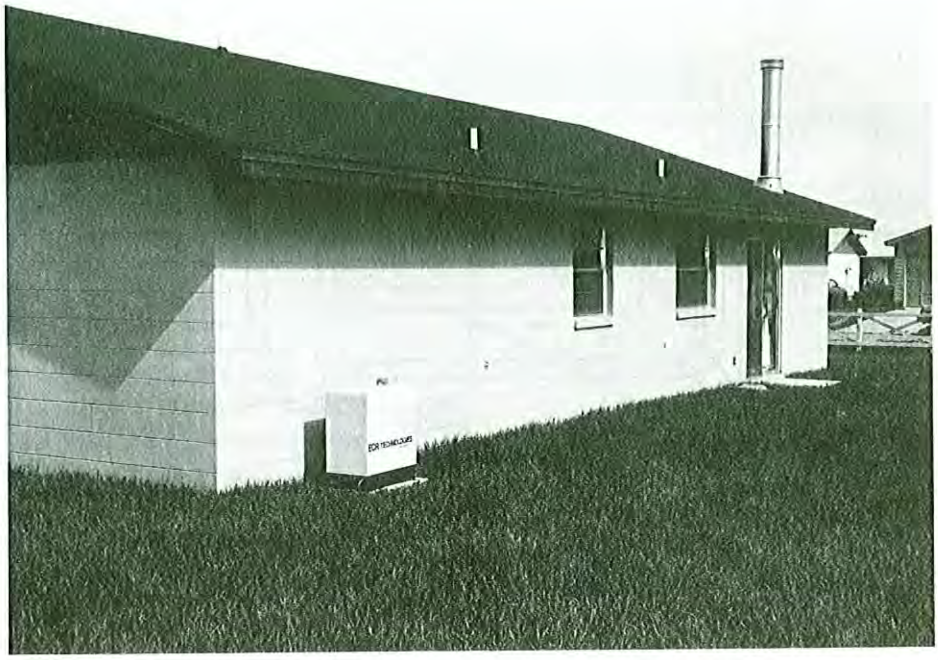

Figure 8. Outdoor unit of ECR's DXHP

A 5-ton ECR system was installed in December 1987, in a showcase home in Lakeland, to demonstrate state-of-the-art energy-saving technology. The installation included ECR's first radially drilled, diagonal earth tap system (16 taps in a conical configuration), which both decreased the time necessary to drill bore-holes and reduced installation costs. The earth tap system was intentionally oversized by 3 taps because it was the first unit produced by ECR larger than 2.5 ton capacity. The system is producing 6 tons of capacity with a 5-ton compressor.

Further demonstration projects include a 4-ton DXHP, and a 1.5-ton system for heating, cooling, and year-round hot water production. A 2.5-ton ECR system will be installed in a Michigan residence for field test monitoring during two heating seasons and one cooling season.

In addition, ECR's Refrigerant Flow and Charge Control System has been retrofit on a rooftop-mounted 15-ton commercial air conditioner unit to replace its standard thermal expansion valve and accumulator. Initial data indicates a 15-20% improvement in efficiency.

ECR Technologies, Inc., was formed in 1980 for the purpose of developing an efficient earth-coupled heat pump. A patent (U.S. Patent #4255936) was obtained on a preliminary unit in 1981. Continued research resulted in an improved Refrigerant Flow and Charge Control System (RFCC) on which a patent (U.S. Patent #4573327) was obtained in 1986. The technological improvements and competitive advantage provided by its RFCC System enabled ECR, in 1985, to produce the most energy-efficient heat pump water heater ever tested at the Florida Solar Energy Center at Cape Canaveral, Florida. A third patent (U.S. Patent #4665716) for heat pump technology was granted in 1987, and a continuation-in-part of this patent is pending. ECR has filed for international protection in various European countries, Japan, and Australia under the Patent Cooperation Treaty (International Application #PCT/US/87/00386) on which a foreign filing license was issued October 30, 1987. Canadian protection is pending under Application #539,471.

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Nonazeotropic Refrigerant Mixtures: Their Behavior in the Presence of Lubrication Oil

The following is a summary of a paper presented at the XVIIth International Congress of Refrigeration, Vienna, Austria, August 1987. A complete copy of this report is available from the Heat Pump Center.

Introduction

The use of nonazeotropic refrigerant mixtures for heat pumps and refrigeration systems has been proposed in the past.[1] The gliding temperatures of these refrigerant mixtures during evaporation and condensation and the possibility of loss-free capacity control by altering the mixtures' composition could be used for saving energy. Another field of application is the mixture cascade for low evaporation temperatures.

Since 1977, these possibilities have been described by several authors. The properties of the refrigerant mixtures were determined and now there are calculation methods to predict the behavior of the mixtures with high precision.

One field, however, where there is almost no information available is the behavior of the refrigerant mixture in the presence of oil or the influence of the mixture on the properties of the oil. In almost every compressor and compressor-driven system, the circulating fluid is a mixture of oil and refrigerant. Most of the thermophysical data of binary mixtures composed of one oil and one pure refrigerant are available. For mineral oils, this data can be determined rather exactly by calculations.[2]

In the past, there was only one investigation concerned with a ternary mixture of one oil and the nonazeotropic refrigerant mixture R12/R114.[3] It was a synthetic oil for use in heat pump screw compressors.

The aim of this new investigation, initial results of which are presented here, is to give a better understanding and acknowledgment concerning the problems of such ternary mixtures.

Oil, refrigerant and methods

As a refrigerant mixture, the system R22/R114 was chosen, which is proposed for application in heat pumps or in two temperature refrigerators.

The oil is a synthetic lubrication oil based on a hydrocarbon of the alkyl benzene type. These kinds of oil show a good miscibility with refrigerants. They have nearly the same properties as mineral oils. Alkyl benzene is often used in the chemical industry where it is also a waste product of some processes. Therefore, alkyl benzene becomes a low-cost substitute for mineral oils.

The investigation of this ternary system included the determination of the thermophysical data viscosity, density, vapor pressure, and miscibility.

Results

Viscosity - Figure 1 shows the results of the viscosity measurements. The kinematic viscosity is displayed as a function of the temperature. The mass fraction of R22 at the refrigerant mixture is 0.5. The curves are lines of constant oil mass fractions of 0.7, 0.8, 0.9, and 1. In this diagram, the curves of constant concentration are nearly parallel and are straight lines. The distance of these lines to the line which represents the pure oil are nearly proportional to the additional mass fraction of both refrigerants in the ternary mixtures. This behavior of the ternary mixtures is like that of binary mixture made of one oil and a pure refrigerant.

Vapor pressure - Curves showing the bubble point pressure as a function of the temperature are also presented at differing oil, R22 and R114 mass fractions. The behavior of the ternary mix-

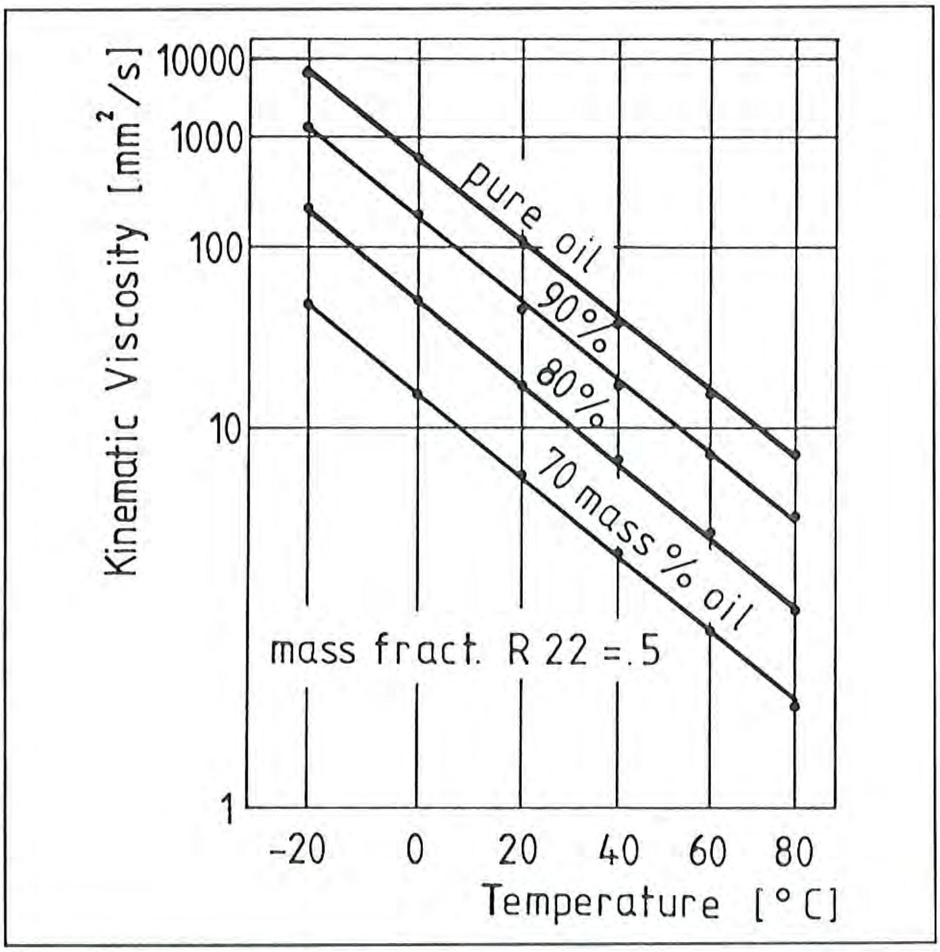

Figure 1. Kinematic viscosity of R22/R114-oil mixtures

ture is the same as that of a binary mixture with one oil and one refrigerant. It was also determined that at every refrigerant composition, the bubble point pressure of the mixtures with an oil mass fraction of 0.8 is nearly half the bubble point pressure of the refrigerant mixtures without oil (Figure 2). At these pressures, 20 mass % of the refrigerant is dissolved in the oil. Hence, the viscosity decreases. This, for example, is important for machines with the oil reservoir at the discharge side of the circuit, like screw compressors.

Density - The results of density measurements show that at constant R22/R114 concentrations, the curves are straight lines and they are nearly parallel for constant oil mass fractions (Figure 3). The dependence of density upon oil mass fraction was found to have a slightly different behavior than that of pure R22 or R114 refrigerant oil mixtures. This is known from other oils, too.[2]

Miscibility - The highest critical demixing temperature is for the binary mixture with pure R114. This temperature is lower than -50°C, subsequently, this oil is an oil of very high refrigerant solubility. The demixing temperature curve of R22 is about 10°C lower than that for R114. It is most remarkable that the demixing temperature of ternary mixtures with both refrigerants is about 20°C lower than of the binary mixtures. This effect of reducing the critical demixing temperature is nearly the same with different refrigerant compositions. This is shown in Figure 4, where the limiting temperature is displayed as a function of the refrigerant composition. The measured mixtures with mass fractions of 0.25, 0.5, and 0.75 R22 in the refrigerant mixture are nearly all at the same level.

Conclusion

The investigation of the ternary mixture of R22/R114 with oil gave the following results: Viscosity and density can be determined by a linear interpolation between the data of the binary oil/refrigerant mixtures. The behavior of the bubble point pressure is similar to that of the refrigerant mixture without oil. The limiting temperature of solubility is much lower than that of the binary mixtures. Therefore, this refrigerant mix-

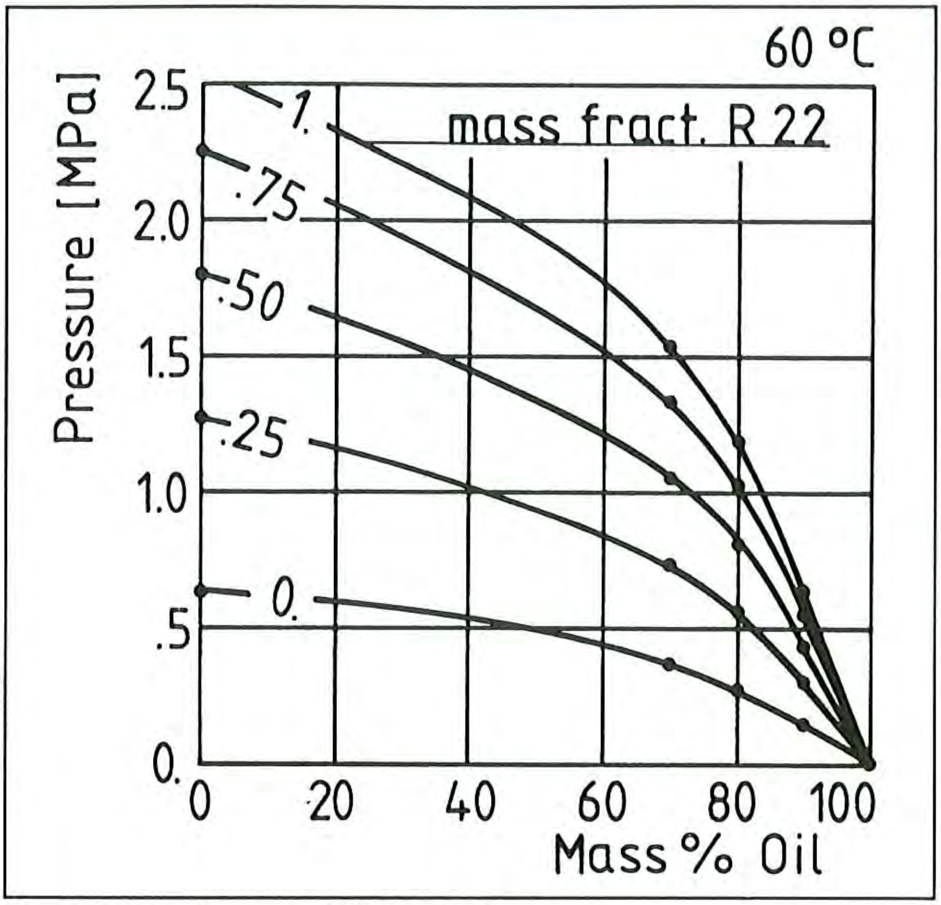

Figure 2. Bubble point pressure of R22/R114-oil mixtures

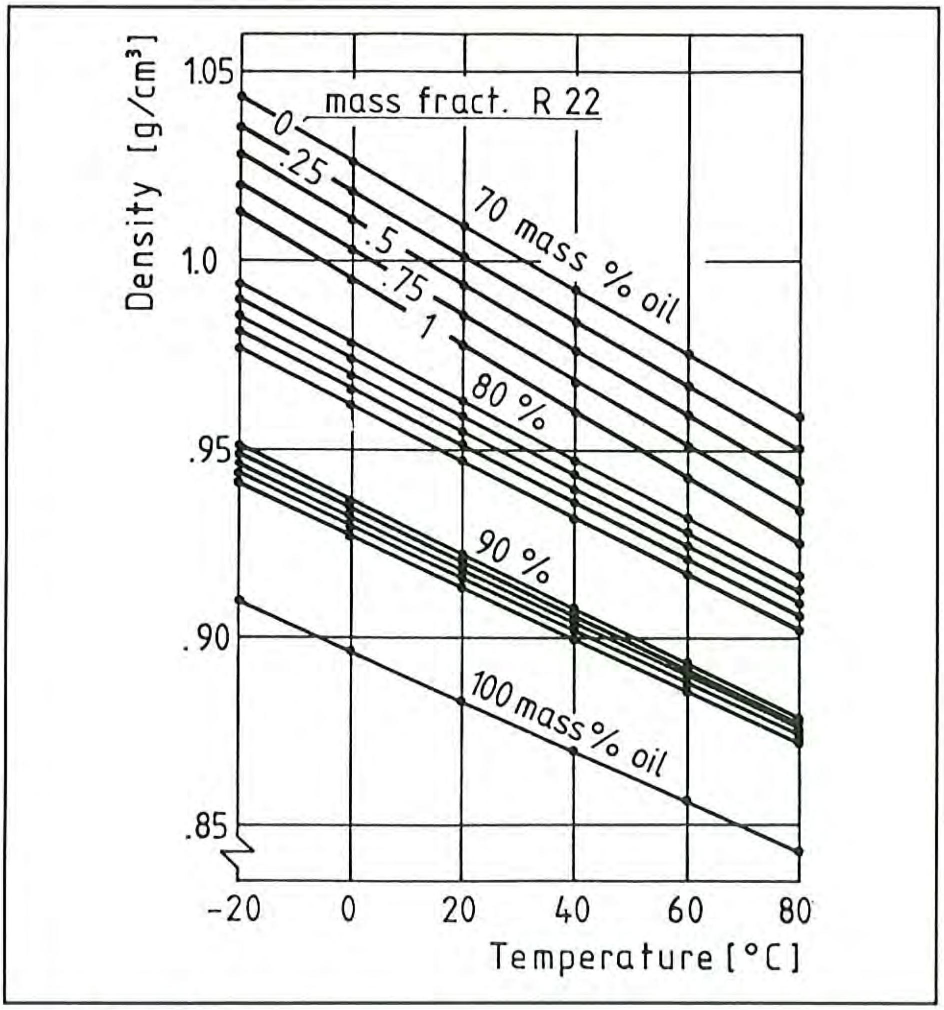

Figure 3. Density of R22/R114

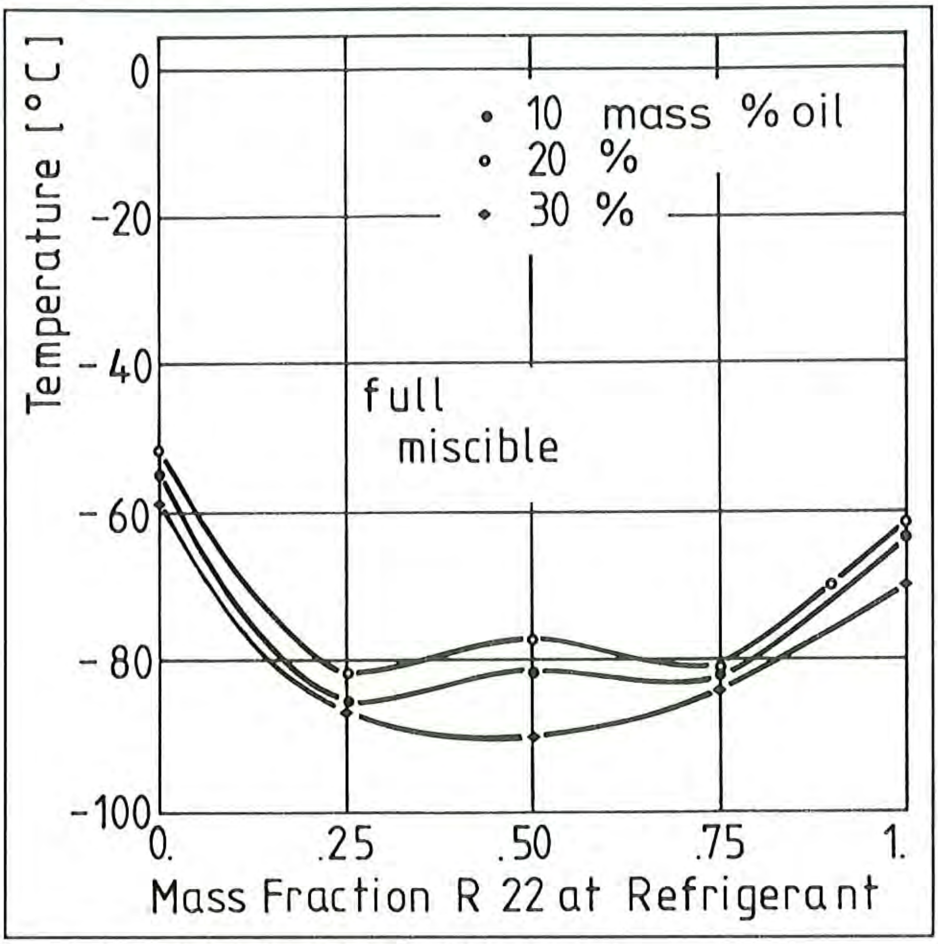

Figure 4. Critical demixing temperature of R22/R114-oil mixtures

ture offers better properties in the presence of oil than the pure refrigerants.

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Thermodynamic Data of the Binary Mixture R22/R114

The following is a summary of a paper presented at the XVIIth International Congress of Refrigeration, Vienna, Austria, August 1987. The complete report is available from the Heat Pump Center.

Introduction

In recent years, a growing interest in the application of nonazeotropic refrigerant mixtures could be observed, especially for the binary mixture R22/R114 which was examined in several types of vapor compression cycles. The application of this mixture is one way of improving the COP.[1] Nevertheless, there is a lack of information concerning the thermodynamic properties of this binary system.

Up to now, there are three publications on this topic. In 1976, Hackstein[2] measured vapor-liquid-equilibria data of five isotherms in the temperature range of -20°C up to 60°C. Valtz, et al,[3] measured bubble pressures of four isotherms from 25°C to 100°C; and Hasegawa, et al,[4] measured some isochorics especially at higher vapor densities. In this publication, vapor pressure measurements of the pure components and vapor-liquid-equilibria measurements were carried out and the results were analyzed.

Measurement equipment

The measurements were carried out in a p,v,T,x-arrangement, which was described earlier.[5] Temperatures were predicted with a platinum resistance thermometer with an accuracy of better than 10 mK. The pressure was determined by a compensation method with an accuracy of better than 100 Pa.

The samples of the liquid and vapor phase were analyzed by a gaschromatograph with an accuracy of about 0.4% by weight.

Pure component vapor pressure

The vapor pressure of R22 and of R114 was measured and compared with other publications and was found to agree within 0.2% in the temperature range from -40°C up to 90°C. Nevertheless, due to the presence of systematic error, the coefficients of the original Riedel's vapor pressure equation (1) were fitted to the measured data of all authors.

$$\ln\pi = A_o + A_1/v + A_2 \ln v + A_3 v \qquad (1)$$

The following coefficients were determined:

A_0 = 8.79002510438
A_1 = -9.02062083514
A_2 = -3.5335007434
A_3 = 0.23036752596

The average deviation was only 0.096% to all 69 data.

For R114, vapor pressure measurements were carried out in the temperature range of -20°C - 100°C. The data of this work, as well as that of others, were compared with equation (1) using coefficients from a German table of thermodynamic data of refrigerants.

A new fitting of equation (1) gave the following results:

A_0 = 9.21658169441
A_1 = -9.46708152114
A_2 = -3.91194418422
A_3 = 0.248127301434

The average deviation of all 73 data was 0.16%.

Vapor-liquid-equilibria data of R22/R114

Vapor-liquid-equilibria (VLE) measurements were carried out in the temperature range of -20°C - 60°C. The reliability of the data was tested by means of a thermodynamic consistency test and the results indicate that the data are consistent.

The Redlich-Kwong-Soave (RKS) equation of state was used to calculate VLE-behavior of the mixture. In a previous publication[6] the parameters of the RKS-equation as well as the applied mixture rules were given. The optimum value of the interaction parameter was found to be k_{ij} = 0.042 with an average deviation in bubble pressure calculation of 1.66%. As an example, Figure 1 shows calculated and experimental results for the 0°C isotherm.

The experimental bubble point pressures did agree very well with the results of Valtz, et al.[3] Valtz used the Peng-Robinson equation of state for VLE-calculation and found an optimum interaction parameter close to that determined by this work.

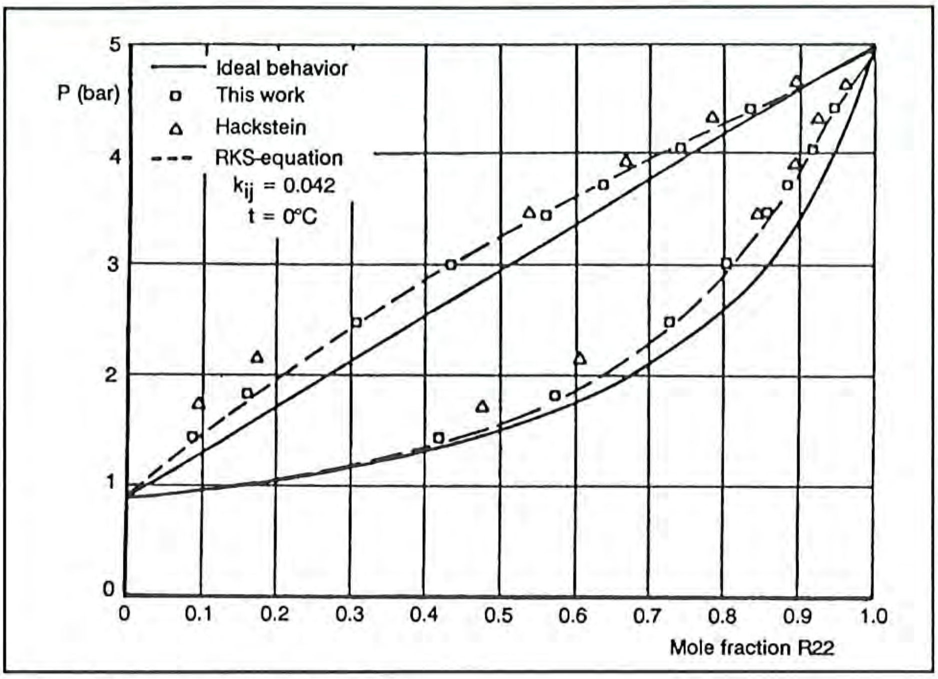

Figure 1. Pressure vs. composition diagram

Conclusions

The nonazeotropic refrigerant mixture R22/R114 is one of the most interesting to be applied in vapor compression cycles. Vapor pressures of the pure components were measured and the results were compared with other publications. The coefficients of Riedel's vapor pressure equation are presented. Experimental VLE-data is measured in the temperature range of -20°C - 60°C and the results compared with other publications. VLE-calculations were carried out using the RKS-equation of state and the optimum value of the interaction parameter was determined.

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Worldwide Survey of Absorption Fluids Data

The overall objective of this study has been to compile, catalog and coarse-screen the available worldwide data of known absorption fluids and publish it as a reference document to be distributed to manufacturers, researchers and others active in absorption heat pump activities. To this end, over 500 different worldwide publications containing data relating to properties of binary, ternary, and multi-component absorption fluids have been identified; from these publications, 278 were selected as primary sources of relevant data. Data coarse screening and evaluations were performed. Data gaps for key fluids are summarized and unresolved conflicts in data are noted. Results show that, with very few exceptions, all candidate fluids have data gaps that must be addressed. The most critical gaps concern diffusion rates, mass transfer additives, thermal and chemical stability, corrosion rates and inhibitors.

Introduction

Over the past 90 years, a wealth of physical and thermodynamic property data has been developed for fluid systems potentially applicable to the absorption refrigeration/heat pump cycle. A significant portion of the data is available in the literature, some still remain confined to in-house files for various reasons and others are proprietary.

Generally, published data have been generated in regions of temperature, pressure and composition of interest to designers of absorption chillers and heat pumps. Recent research has focused on developing efficient cycle configurations, using multi-effect or multi-stage concepts, for both space heating and cooling. These new designs operate at temperatures and pressures significantly higher than encountered in the conventional absorption cooling cycle. Other new concepts are based on the addition of a third component to the binary solutions normally used in the conventional cycle.

In an effort to define the availability and quality of existing data and, thereby, assist in the determination of needs for new data useful to advanced concepts, the Institute of Gas Technology (IGT) has performed a comprehensive literature search and a coarse and fine screening of existing literature data in order to identify potential conflicts or gaps in the data, with particular emphasis on certain key fluid systems. Assisted by Oak Ridge National Lab (ORNL), IGT has carried out liaison activities with foreign researchers at the Universities of Essen and Stuttgart (Federal Republic of Germany), French Petroleum Institute and Graz de France, Kansai University (Japan) and Ben Gurion University (Israel), known to possess other unpublished data that may be useful to this program.

These activities have helped to further demonstrate the importance of a centralized and well documented source of the available data to the timely development and introduction of advanced absorption heat pump technology for space conditioning and temperature boosting. Clear benefits are thought to be the identification of unresolved conflicts in data of known, important fluid systems, of data gaps for key fluids and properties, and of new, potentially useful fluid systems.

A first compilation covering data developed in the USA has been published (ORNL/Sub/84-4798/1). A second compilation covering mainly European and Japanese data has also been published (ORNL/Sub/84-4798/2). The information and data in this paper are from the recently published final (Worldwide) report (ORNL/Sub/84-4798/3).

REFRIGERANTS \ ABSORBENTS	ETFE	DMETEG	DMETrEG	DMEDEG	TEG	DMF	DMA	DMH	DMD	H_2O	LiBr	LiCl	LiSCN	$LiNO_3$	$LiClO_3$	NH_4I	NaSCN	$ZnBr_2$	$ZnCl_2$	LiBr: LiCl	LiBr: $ZnBr_2$	LiBr: LiSCN	CsF: RbF	
R-123a	1																							
R-133a	3																							
R-124a		1																						
R-134		1																						
R-11		2																						
R-30		1																						
R-31		1																						
R-12		1				1	1																	
R-21		6	1	1		4	1	2																
R-22	1	14	3	4		7	2	2																
R-123								1																
R-131a								1																
R-140a									1															
R-1112a								1																
R-1120									1															
R-1130								1	1															
SO_2		1				1	1																	
CH_3NH_2		1			2					2			3	1			2							
$(CH_3)_2NH$					1					1														
$(CH_3)_3N$					1																			
C_3H_7OH												1						1	1					
CH_3OH										1	13	2	1					7	1	1	9			
C_2H_5OH										1	3	1						1	1		1			
H_2O		1			1	2					22	4	1	1	1			1	1	4	3	5	1	
NH_3		1	1		1		1			32			2	2		2	2							

Figure 1. Number of references for vapor-liquid equilibrium data

Vapor-Liquid Equilibrium									
Fluid System	Data Type	Temp. Range (°C)	Pressure Range (atm)	Concentration Weight (%) X (R) Y (R)	Reference				
					No.	Author	Year	Country	Text
H_2O + LiBr	T,E,P	0 - 72	0.42 - 53 (1)	42.2 - 55.6	133	Matsuda	1980	Japan	Japanese
H_2O + LiBr	G,E,P	0 - 72	0.6 - 60 (1)	44.8 - 54.6	133	Matsuda	1980	Japan	Japanese
H_2O + LiBr	G,P	0 - 80	0.4 - 100 (1)	35.0 - 60.0	133	Matsuda	1980	Japan	Japanese
H_2O + LiBr	G,E,P	20 - 160	2 - 800 (1)	35.5 - 77.2	248	Uemura	1964	Japan	English
H_2O + LiBr	G,P	30 - 160	1 - 800 (1)	40.0 - 65.0	248	Uemura	1964	Japan	English
H_2O + LiBr	P	NA	NA	NA	232	Uemura	1977	Japan	Japanese
H_2O + LiBr	G,E,P	0 - 150	3 - 800 (1)	35.5 - 100.0	70	Hasaba	1959	Japan	Japanese
H_2O + LiBr	T,G,P	0 - 180	1 - 800 (1)	40.0 - 80.0	70	Hasaba	1959	Japan	Japanese
H_2O + LiBr	G,E	30 - 100	3.16 - 160 (1)	NA	92	Iyoki	1977	Japan	Japanese
H_2O + LiBr	G,S	- 20 - 190	0.1 - 1000 (1)	30.0 - 100.0	161	Oouchi	1985	Japan	Japanese
H_2O + LiBr	T,E,P	20 - 175	5 - 950 (2)	30.0 - 75.0	183	Renz	1981	Germany	German
H_2O + LiBr	G,S	0 - 180	1 - 1000 (2)	30.0 - 100.0	183	Renz	1981	Germany	German

X - Liquid Phase
Y - Vapor Phase
(1) - mmHg
R - Refrigerant
A - Absorbent(s)
(2) - mbar
c - ppm by weight of A in Vapor Phase
M - Mole, W - Weight
NA - Not Available

Table 1. Water binary and multicomponent absorption fluids properties data

Methodology

Both in-house-file and literature searches were undertaken to obtain available worldwide publications, dating back to the 1900's, with pertinent physical, thermodynamic and transport properties data for absorption fluids. Cross-checks of literature searches were also made, using available published bibliographies and literature review articles, to eliminate secondary sources for the data and only include original sources and manuscripts.

Fluid properties and data

The properties of the fluids relate to the liquid and/or vapor state, as encountered in normal operation of absorption equipment employing such fluids, and to the crystallization boundary of the liquid phase, where applicable. The actual data were systematically classified according to the type of fluid and property, as well as temperature, pressure and concentration ranges over which data were available. Data were sought for the 17 different properties listed in the next column.

Mixture properties:

1. Vapor-liquid equilibria
2. Crystallization temperature
3. Corrosion characteristics
4. Heat of mixing
5. Liquid-phase-densities
6. Vapor-liquid-phase enthalpies
7. Specific heat
8. Stability
9. Viscosity
10. Mass transfer rate
11. Heat transfer rate
12. Thermal conductivity
13. Refractive index
14. Entropy
15. Surface tension
16. Toxicity
17. Flammability

The type of available data was of importance, with raw experimental data considered to be highly desirable for use in actual process and equipment design and sizing, and for process design correlation development. For this reason, raw tabulated experimental data were given the highest possible ranking, with other forms of data following in importance, as shown in the next column:

DATA RANK

Form of Data	Symbol
RAW EXPERIMENTAL	(E)
-- Tabular	(T)
-- Graphical	(G)
SMOOTHED EXPERIMENTAL	(S)
-- Tabular	(T)
-- Graphical	(G)
EMPIRICAL POLYNOMIAL	(P)
EQUATIONS OF STATE	(C)

Empirical polynomial relationships based on raw or smoothed experimental data are often reported. Such correlations are at best as good as the experimental data and can help facilitate the use of the data in performance and design calculations through automation (computer software and terminals). In the absence of data, reliable methods of prediction were sought (equations of state, generalized correlations). These methods are expected to possess greater uncertainties than the previous forms of data.

Coarse-screening of literature data

Several approaches have been used in carrying out quality review and coarse screening of data from multiple sources, for each of several key or highest priority binary and ternary fluids. These alternative approaches include:

-- Consideration of the authors' statements concerning data quality

-- Assessment of the measurement technique and apparatus used in obtaining the data

-- Consideration of a given authors' reputation for measuring data, where a single authors' data were the only available for a fluid system.

A more reliable method used to compare data from various sources, for a given fluid and property, has been the plotting of data on a common basis. Such plots have also served to reveal the amount of scatter or internal consistency of a given author's data and, therefore, its quality.

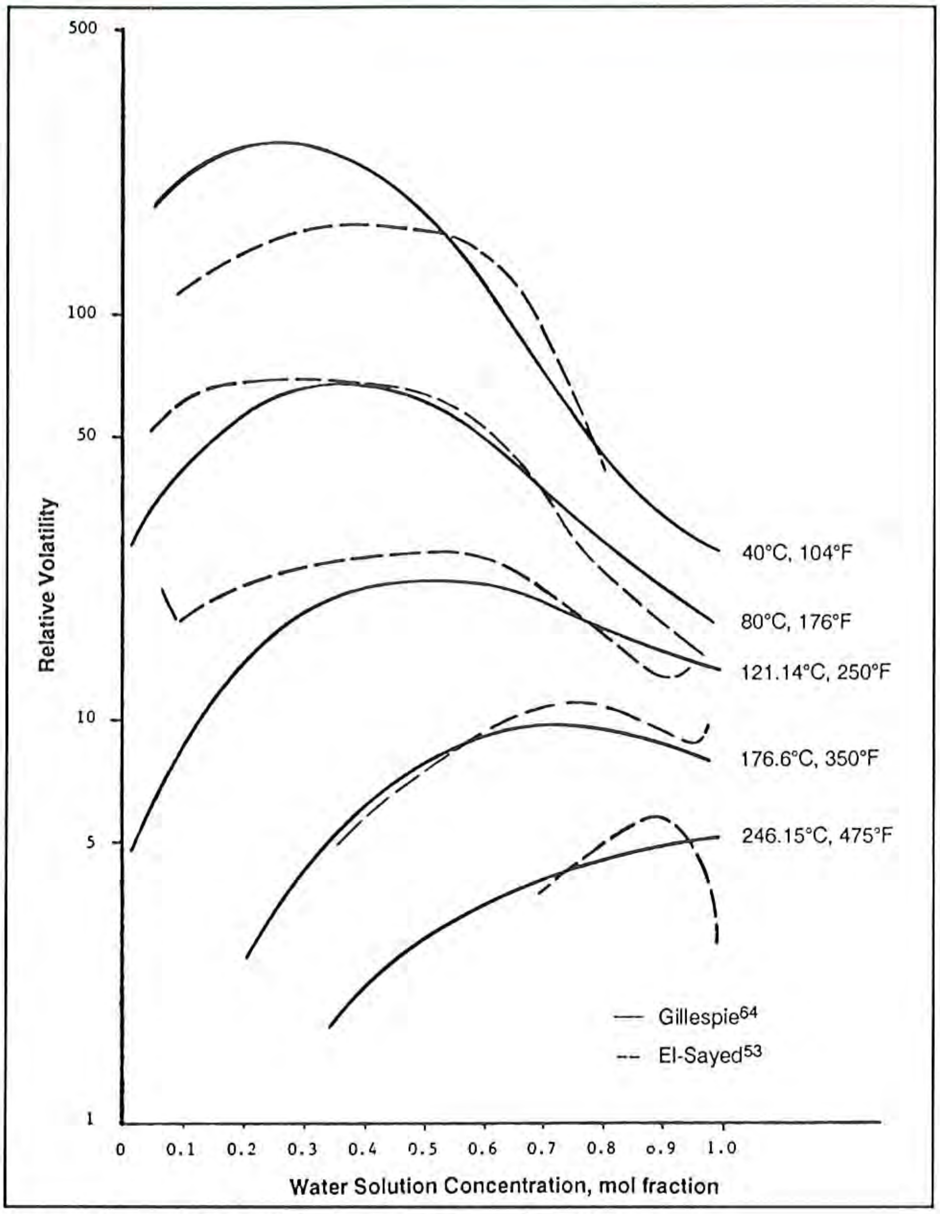

Figure 2. Comparison of projected and measured relative volatilities

Accomplishments

Over 500 different worldwide publications were identified with data relating to properties of binary, ternary and multicomponent absorption fluids. After elimination of duplication through cross-checking, a total of 278 primary sources of data were selected (see References) and the actual documents acquired, dating as far back as 1901, with nearly 90% of the documents published between 1960 and 1987. The texts of these manuscripts are mainly in English, German, Japanese, Russian or French.

The absorption fluids covered in the 278 documents are combinations of 38 different "refrigerant" compounds with 131 single, 42 binary and 14 ternary "absorbent" compounds. Generally, the 38 refrigerants are divided among the following categories of chemical compounds:

Refrigerants

INORGANIC	3
ORGANIC	35
-- Amines	4
-- Alcohols	5
-- Halogenated	25
-- Hydrocarbons	1

Likewise, the single absorbent compounds are generally subdivided as follows:

Absorbents

INORGANIC	48
ORGANIC	83
-- Alcohols	10
-- Ethers	5
-- Alcohol-Ethers	3
-- Amides	9
-- Amines	4
-- Amine-Alcohol	1
-- Esters	21
-- Ketones	5
-- Acids	4
-- Aldehyde	1
-- Others	20

The binary and ternary absorbents are various mixtures of two or more single absorbent compounds. Figure 1 presents examples of absorption fluid systems and the number of references that contain vapor-liquid equilibrium data for each fluid system. Similar charts have been prepared to cover other fluids, properties and relevant references.

In terms of absorption fluids properties, for which data are available in the 278 primary documents, the list shown below reveals that vapor-liquid equilibrium is the predominant property. Toxicity and flammability of fluids, on the other hand, are reported in only two documents.

Thermodynamic, Transport, and Other Data

Fluid Property	No. of References*
Vapor-liquid equilibrium	407
Enthalpy	87
Specific heat	59
Viscosity	56
Heat of mixing	102
Density	65
Crystallization	101
Surface tension	19
Corrosion (and inhibitors)	32
Thermal conductivity	12
Entropy	18
Stability	31
Refractive index	8
Heat transfer	8
Mass transfer	10
Toxicity	1
Flammability	1

*A given document may contain data relating to more than one property; therefore, the sum of the references is larger than 278.

For each fluid and property in this study, the type of data and the temperature, pressure and concentration ranges, to which the data correspond, and the reference access number, first author, year of publication and text language, are all included in tables as shown in Table 1.

Several key absorption fluids, currently of interest to researchers of advanced absorption heat pumps, are shown below:

Key Fluids

NH_3-H_2O	CH_3OH-LiBr-$ZnBr_2$
NH_3-H_2O-LiBr	TFE-NMP
NH_3-H_2O-$LiNO_3$	TFE-DMEDEG
NH_3-NaSCN	TFE-DMETEG
H_2O-LiBr	CH_3NH_2-H_2O-LiBr
H_2O-LiBr-LiCl	R21-DMETEG
H_2O-LiBr-LiSCN	R22-DMEDEG
H_2O-LiBr-$ZnBr_2$	R22-DMETEG
H_2O-NaOH-KOH-CsOH	R22-DMF
H_2O-$LiNO_3$-$NaNO_3$-KNO_3	R123a-ETFE
CH_3OH-LiBr	R124-ETFE
CH_3OH-$ZnBr_2$	R133a-NMP

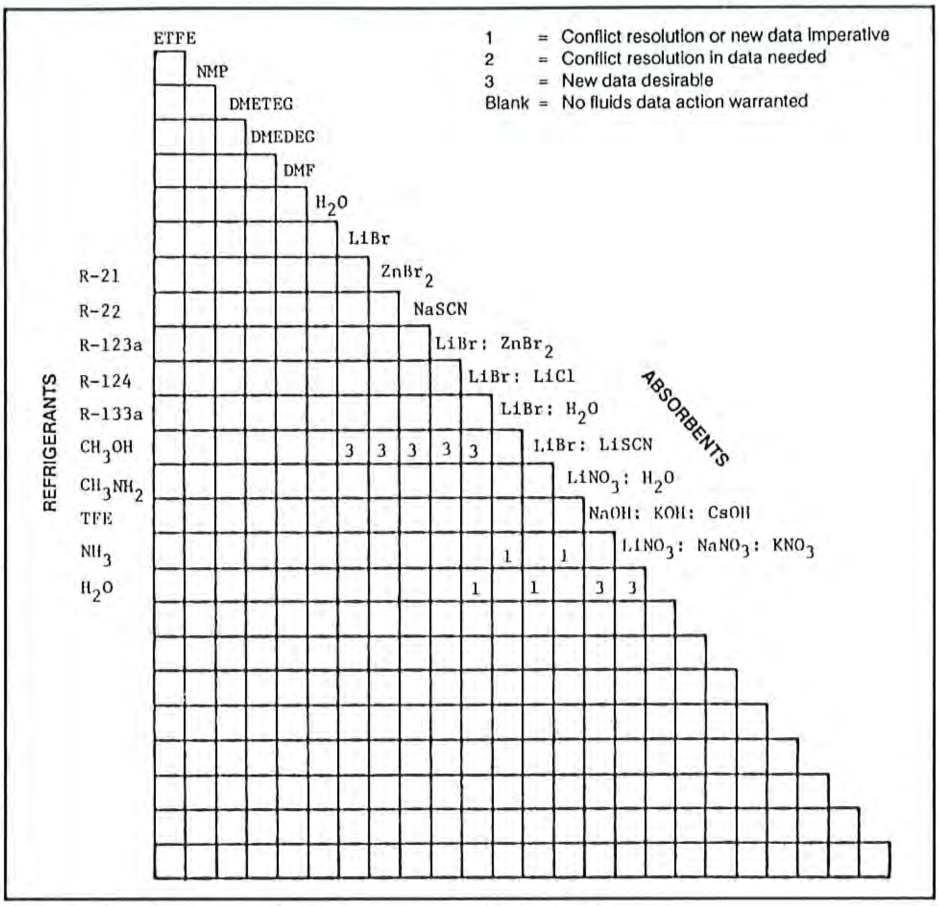

Figure 3. Gaps in crystallization temperature data for key fluids

Data coarse-screening and evaluations were carried out for the selected or key absorption fluids. The data screening indicated that the plethora of references for NH_3/H_2O may be misleading for the following reasons:

-- Most current research with the NH_3/H_2O fluid is concentrated in advanced cycle designs, with operating conditions (temperature, pressure) covered by data developed in the past 2-3 years.

-- Data for several important properties (heat and mass transfer rates, stability), and for operating conditions beyond present limits for other properties, are not available.

Unresolved conflicts in important data of various fluids and data gaps for key fluids were summarized. Figure 2 is an example of conflicting data for the vapor phase composition of the NH_3 + H_2O system at various temperatures. Data conflicts, lack of data for known key fluids at conditions beyond the limits of present data, and new fluids without property data constitute these summaries.

Figure 3 presents an example of absorption fluid systems with prioritized gaps in vapor-liquid equilibrium data.

With extremely few exceptions among key fluids and their properties, and with emphasis toward the current development activities dealing with advanced absorption heat pump concepts, nearly all candidate fluids have data gaps that need to be addressed in the near future.

References

There are 278 references for this article. The complete list of references is available from the Heat Pump Center upon request.

Robert A. Macriss and Thomas S. Zawacki, Institute of Gas Technology, Chicago, Illinois, USA

M. Hasatani, H. Matsuda, M. Miyazaki, and M. Yanadori*

Studies on the Basic Principles of a High Temperature Chemical Heat Pump Which Utilizes Reversible Thermochemical Reactions

There is a great deal of interest in heat pumps in Japan today. In view of this, the present study investigates the basis of a chemical heat pump which can provide temperature upgrading at high temperatures. This type of temperature upgrading has been difficult to accomplish with conventional technologies. Basically, the chemical heat pump uses a high- and low-temperature heat source, needs only a small amount of mechanical energy input, and, depending on which component element reactions are selected, can deliver useful heat at a desired temperature. A wide variety of combinations of working reactants are conceivable for chemical heat pumps. For this study the reversible thermochemical reaction of $CaO/Ca(OH)_2$ was used along with the evaporation and condensation of water to complete a heat pump cycle. Previous studies have indicated that this reactant is a good choice.[1,2] The laboratory scale heat pump constructed for this investigation has a normal working temperature above 800K. Experiments were conducted to determine some of its basic characteristics such as temperatures and their distribution within the equipment, reaction progress, and general effectiveness.

Principle of operation

The operation of this chemical heat pump consists of the reactions given in the following equations:

Equation 1:

$$CaO(s) + H_2O(g) = Ca(OH)_2(s) + 1.858 \times 10^3 \text{ kJ/kg}$$

Equation 2:

$$H_2O(g) = H_2O(1) + 2.316 \times 10^3 \text{ kJ/kg}$$

(average value of 293K to 641K)

Figure 1 shows the relationship between the reaction equilibrium pressure P_e and temperature for the reaction in Equation 1. This is given by line 2 - 4 in the figure. Also shown is the relationship between the saturated steam pressure P_s and temperature for Equation 2. This is given by line 1 - 3.

Heat release mode

Consider a hermetically sealed reaction system having a reactor and an evaporator filled with CaO and water, respectively. If heat (Q_M) is added to the evaporator from a medium temperature (T_M) heat source, the water in the evaporator becomes pressurized steam (path 1 - 3 in Figure 1). Due to the pressure difference between P_s and P_e, this steam enters the reactor to undergo an exothermic hydration reaction with CaO. This causes the temperature in the reactor to rise (2 - 4) to temperature T_H at which point high temperature heat (Q_H) becomes available.

Heat storage (regeneration mode)

In this case, heat Q_M from a medium-temperature (T_M) source is added to the reactor which contains $Ca(OH)_2$ formed as described above. At the same time, the condenser is cooled to a temperature T_L. Under these conditions, the $Ca(OH)_2$ undergoes an endothermic dehydration reaction to release steam. The steam shifts from the reactor to the condenser (2 - 1 in Figure 1) due to the pressure difference between the two chambers. There it condenses by releasing its latent heat of condensation to the low temp. heat sink (T_L).

Experimental unit

The experimental unit is shown in Figure 2 and its schematic diagram in Figure 3. The evaporator/condenser (1) and the reactor (2) are made of stainless steel and are cylindrical in shape, having both an inside diameter and a height of 150mm. Both containers are equipped with a cooling coil (4), thermocouple insertion tube (5), and an electric heater (6). Each of these items is arranged symmetrically about the center of the container. Both containers

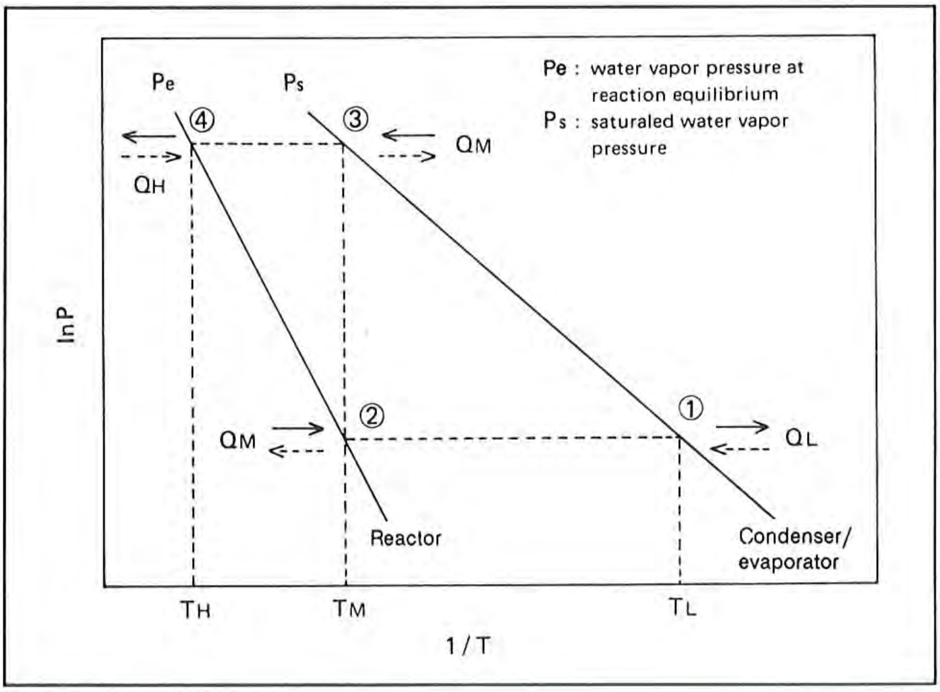

Figure 1. Operation lines

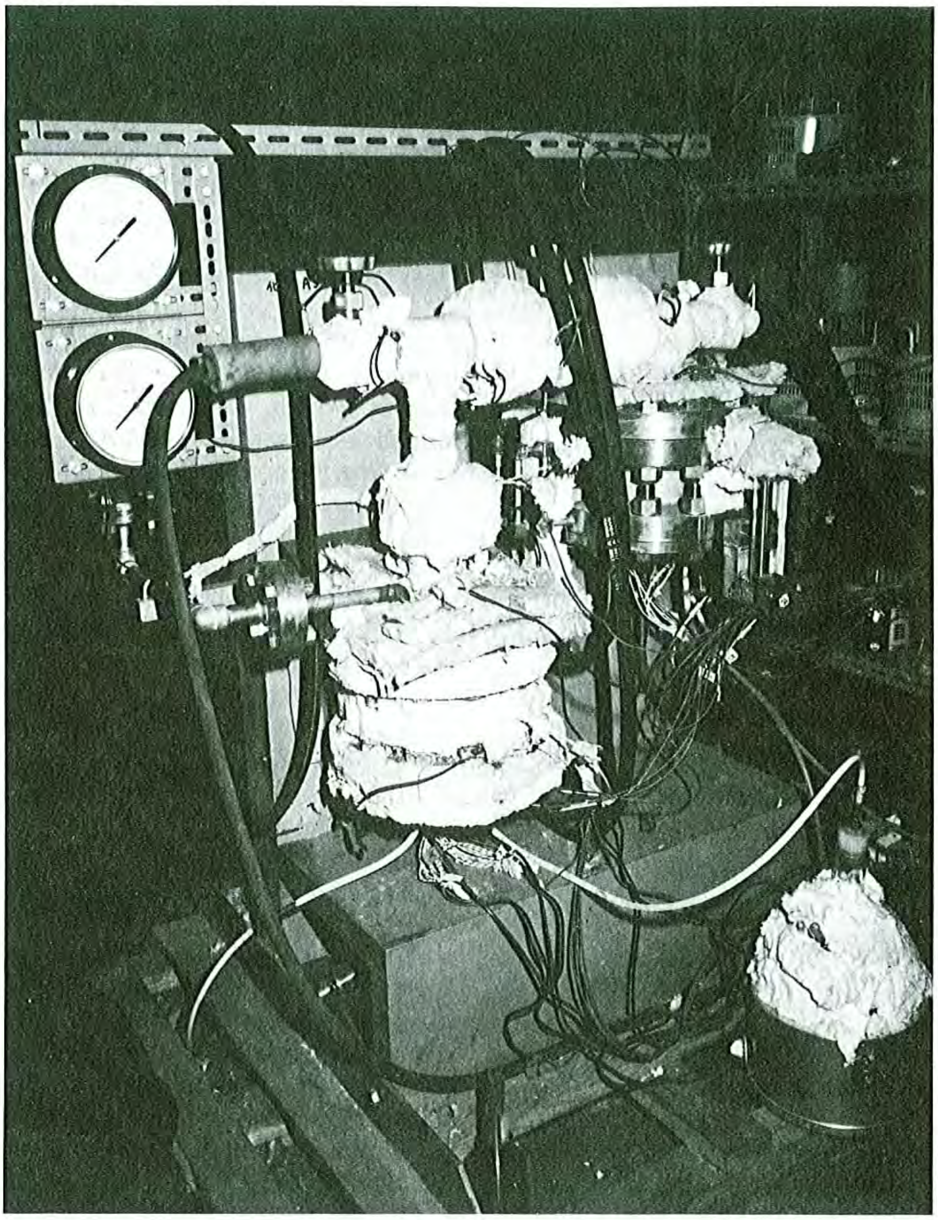

Figure 2. Experimental unit

are also equipped with a pressure gauge (7). In addition, the evaporator/ condenser has a water level gauge (8) and the reactor has an auxiliary external heater (9). The auxiliary heater consists of nichrome wire wound around the reactor's outer surface. The two containers are connected to each other by stainless steel piping via valve V2. A vacuum pump (3) is used to obtain the proper pressure level in the reactor. The equipment is insulated with an adiabatic material to reduce heat loss. Figure 4 shows details of the reactor's construction.

For the reaction system employed, the temperature T_M shown in Figure 1 is in principle about 640K. At this temperature, the pressure of the saturated steam in the evaporator is 27.5MPa. The present experimental apparatus was not designed for such high pressures. For this reason the evaporator temperature was kept below about 430K for this experiment.

Experimental procedure

The following items were done to prepare the equipment for the experiment. First the evaporator and reactor were filled with water and CaO, respectively. The CaO was in the form of grains having an average diameter of 1mm. The CaO layer in the reactor was 110mm thick and rested on a 30mm thick asbestos insulating sheet. With valve V2 closed, the reactor was evacuated to the proper pressure using the vacuum pump. Finally the evaporator/condenser was heated with valve V3 open until steam had displaced all air present in the container.

For the heat release experiment, the specimen layer temperature and the steam pressure within the evaporator were adjusted to their proper values using heaters 6 and 9 shown in Figure 3. Valve V2 was then opened to allow pressurized steam from the evaporator to enter into the reactor causing an exothermic hydration reaction. For some experiments 358K steam was also passed through the reactor's cooling coil (4) to recover part of the reaction heat. During the reaction period, the temperature changes in time which took place within the specimen layer

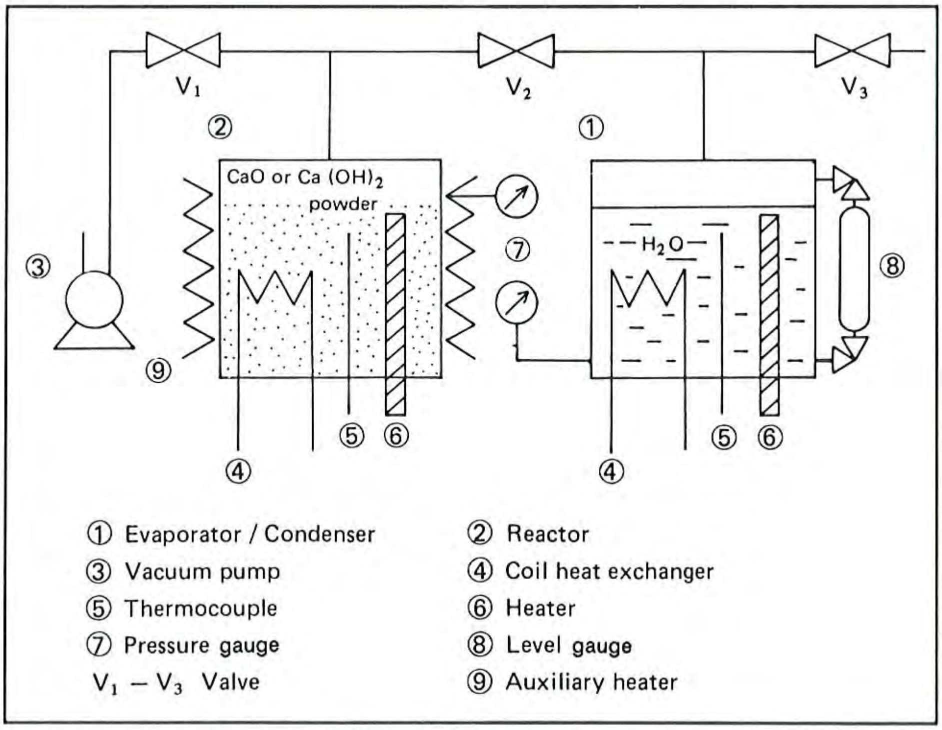

Figure 3. Schematic diagram of the experimental unit

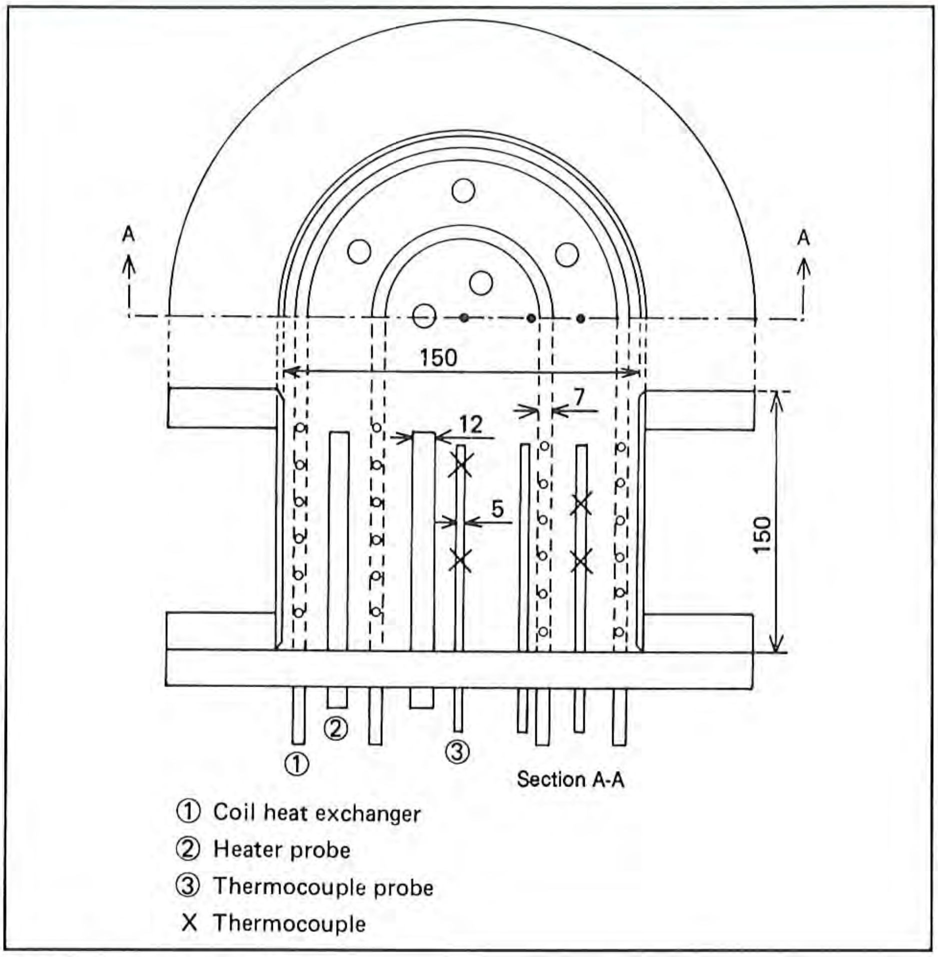

Figure 4. Details of the reactor

were measured with a thermocouple and recorded automatically. Changes in the evaporator/condenser water level were also recorded.

In the experiment on storing heat, cold water was passed through the condenser/evaporator cooling coil (4) to maintain a temperature of T_L. At the same time, the reactor was heated by heaters (6) and (9) to cause $Ca(OH)_2$ to undergo an endothermic dehydration reaction. The steam produced by this reaction was condensed in the condenser/evaporator and as before the temperature change in time within the specimen layer and the change in water level within the condenser were measured and recorded.

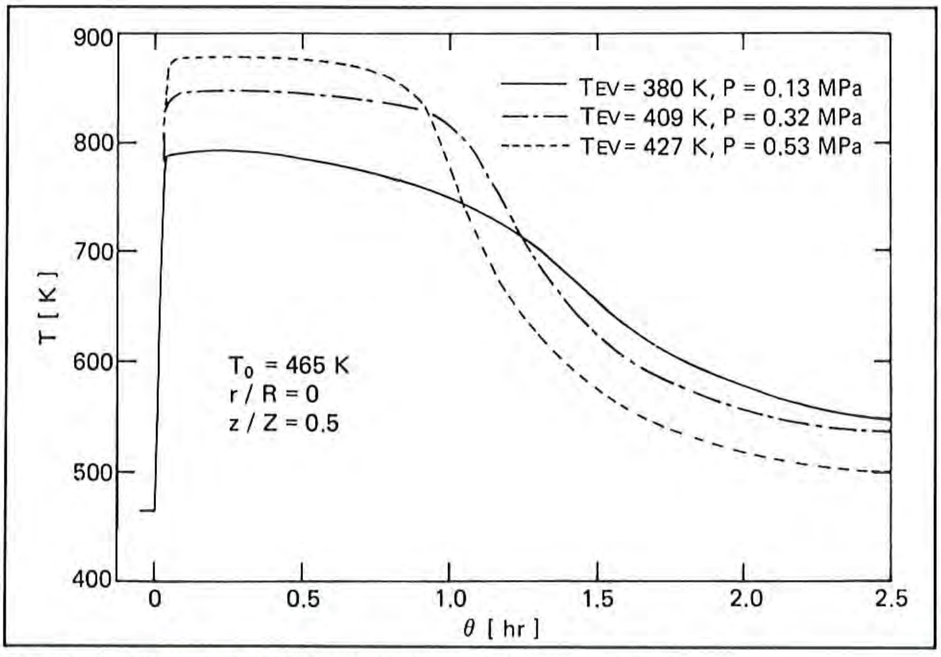

Figure 5. Temperature changes in time during heat release (hydration)

Experimental results

Heat release (hydration) process

Figure 5 shows the temperature changes in time which occurred in the specimen layer during the exothermic hydration reaction. The steam pressure (P) and temperature (T_{EV}) within the evaporator are used as parameters. As seen in Figure 5, as soon as pressurized steam is introduced into the reactor, the temperature rises instantaneously and maintains a fairly constant temperature (fictitious equilibrium temperature) for 40 to 60 minutes, after which it slowly decreases to its initial temperature.

Temperature changes in time at various radial positions in the specimen layer were also measured. It was determined that after the temperature of each part of the specimen layer rose uniformly and instantaneously up to the fictitious equilibrium temperature, it eventually dropped, beginning first at points closest to the container wall. The general reaction ratio based on the reactor's total contents were also measured.

Process of storing heat

Figure 6 shows the temperature changes occurring in the reactor at various radial positions during the endothermic dehydration reaction of $Ca(OH)_2$. The condenser water temperature (Tc) in this case is 297.7K. After an initial temperature rise in the specimen, the temperature eventually levels off at about 693K. At this point, the reaction is taking place and progressing most rapidly at points closer to the container wall and the heating coil. Completion of the reaction is signified by the temperature once again increasing. As in the case of the heat release process, the radial temperature distributions in the reactor at various times and the reaction ratio during dehydration were also measured. It was found that the endothermic dehydration reaction deviates from equilibrium conditions as the steam pressure becomes lower. This agrees with results described in preceding reports.[1,2]

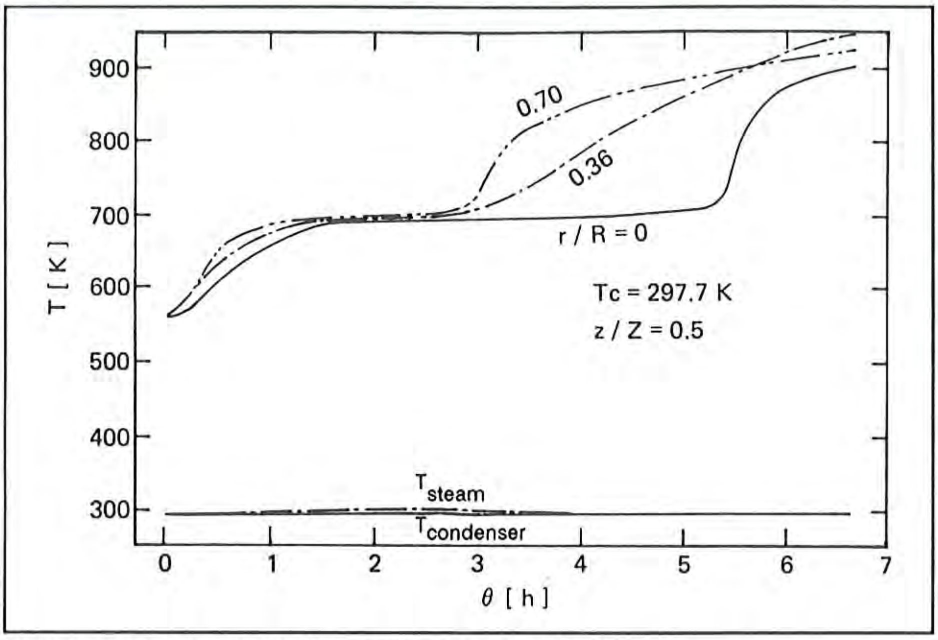

Figure 6. Changes in time (θ) of temperature (T) during dehydration

Summary

Experiments with a laboratory scale chemical heat pump using CaO/ $Ca(OH)_2$ reactions have been conducted. Work included experimental examination of the relationship between the non-steady state heat transferring behavior and the general reaction speed for the hydration and dehydration reactions of CaO and $Ca(OH)_2$, respectively.

References

1. Matsuda, et al: Kagaku kogaku Ronbunshu 11, 542 (1985)
2. Lee, et al : Kagaku kogaku Ronbunshu 12, 165 (1986)

M. Hasatani, H. Matsuda, M. Miyazaki, Department of Chemical Engineering, Nagoya University, Nagoya, Japan; M. Yanadori, Mechanical Engineering Research Laboratory, Hitachi Ltd., Tsuchiura, Japan

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T. Moore*

Carrier's Advanced Heat Pump

The following is a summary of an article written by Taylor Moore which appeared in the EPRI Journal, March 1988. Used by permission of the author.

Five years of joint funding and development by the Electric Power Research Institute (EPRI) and the Carrier Corporation, a U.S. heat pump manufacturer, have resulted in the EPRI-Carrier advanced heat pump. This product has cooling and heating energy efficiencies 30 to 40% higher than the average model sold in the U.S. today, and it integrates water heating with space heating and cooling in a package suitable for new construction and retrofitting. Increased comfort, reduced noise, and a better electric utility load factor are some of the additional benefits of this new product which will be marketed early next year. This electric heat pump will be sold in 2-, 3-, and 5-ton capacity for use in residential and small commercial buildings.

Features

Figure 1 shows the three components of the EPRI-Carrier advanced heat pump. The unit consists of an outdoor fan coil, an indoor compressor section, and an indoor fan coil to supply warm or cold air to various parts of the house. Refrigerant lines interconnect the three units. The compressor section is also connected to the hot tap water supply tank. Figure 2 shows the separate units and their interconnections.

The outdoor unit is designed to operate at 1/8th the noise level of a conventional unit. The compressor section consists of an inverter-driven compressor, a refrigerant-to-water heat exchanger, a small pump to circulate hot water, and the electronic controls. The indoor fan coil section connects to the house ductwork and consists of a variable speed fan electronically linked to the compressor. A supplemental heat source, either gas or electric, is also included for use when the compressor is operating at maximum speed.

Performance

The variable speed compressor and indoor fan of the EPRI-Carrier advanced heat pump give it a number of advantages over constant speed units. These include improved operating efficiency and comfort. The unit's heating seasonal performance factor (HSPF) is 9.0 and its seasonal energy efficiency ratio (SEER) is 12. Both ratings are 30% better than the 1987 average for heat pumps manufactured in the U.S. In addition, the SEER rating method does not account for the additional energy saved through water heating with waste heat from the house during cooling operation. Performance analyses for climates as varied as Chicago, St. Louis, and San Antonio show that operating costs will range from U.S. $700 to U.S. $1,000 per year.

Comfort is improved by the variable speed indoor unit's fan. With it, the system can operate so that during heating operation the indoor fan starts up slowly as the coil heats up, avoiding any cold drafts which usually occur with conventional heat pumps. By being able to adjust the compressor speed to the actual heating or cooling load, indoor temperature variations can be kept to less than 1°F.

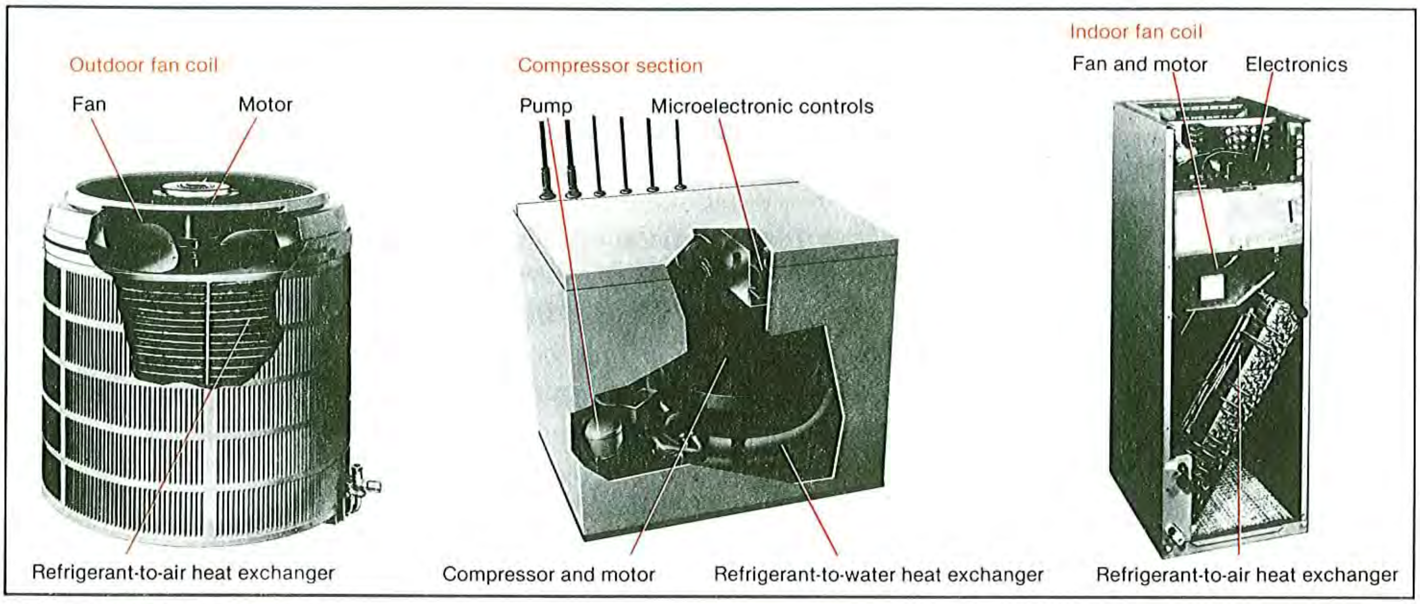

Figure 1. Heat pump components

Utility benefits

The design of the advanced heat pump's microelectronic controls allows utilities to control demand of the unit during peak consumption periods via a radio or powerline signal. This is especially useful during the hottest days of the summer cooling season. The advanced heat pump will also allow the utility to expand its customer base in the three main areas of energy use in the home: heating, cooling and hot water.

Economics

The advanced heat pump will cost approximately 50% more than the average conventional heat pump, giving it an estimated payback period of about four to five years. A 15-year service life is expected from the unit. Presently extensive testing is being carried out by Carrier, including running the unit through 80 to 90 million cycles at the company's test facilities. During 1988 a total of 37 units will be in operation in residences across the U.S.

Development

The development of the EPRI-Carrier advanced heat pump is unique in that it is a joint project funded by EPRI, an association of public utilities, and Carrier, a large U.S. manufacturer of HVAC equipment. This is probably the first time that utilities are involved in the development of an electric appliance. When the heat pump finally becomes available on the market, utilities are expected to encourage its use as part of their conservation programs.

Taylor Moore, EPRI Journal senior feature writer; additional technical background information provided by Arvo Lannus, Energy Management and Utilization Division, Electric Power Research Institute, Palo Alto, California, USA.

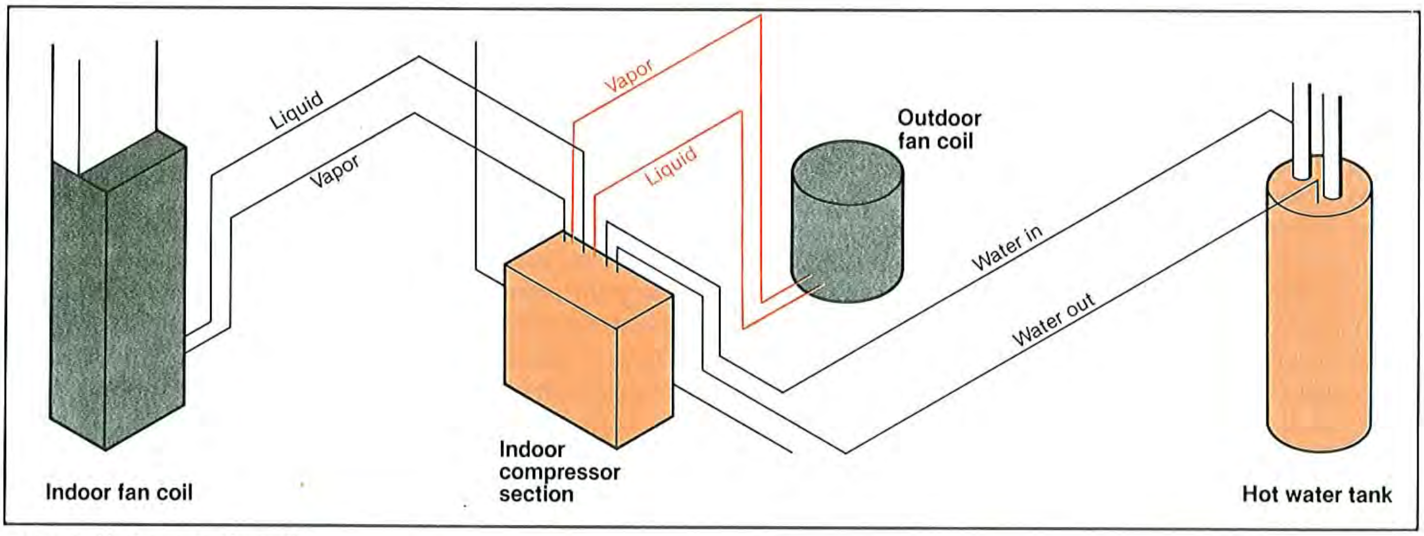

Figure 2. Heat pump schematic

Bibliographic Review

Listed below are excerpts from the results of a search in the ENERGY database of STN International. The search was limited to entries made in the database since the beginning of 1987. The terms used for this search included working fluids, refrigerants, CFC, environment, and ozone layer. Individuals from member countries may contact the HPC to obtain the complete results of this search, or to request a search on a specific heat pump topic. In addition, the HPC has a summary of important literature related to refrigerants for heat pumps in Japan. If you would like a copy of this information, please contact the HPC.

STN International, the Scientific & Technical Information Network, provides an on-line computer database service. This service is operated cooperatively by FIZ, Karlsruhe, Federal Republic of Germany; the American Chemical Society, Columbus, Ohio, USA; and the Japan Information Center of Science and Technology, Tokyo, Japan. STN offers over 30 separate databases on various subjects. The ENERGY database contains references of worldwide literature on energy research and technology for all kinds of energy sources. It contains more than 1.5 million citations from journals, reports, books, patents, and conference proceedings, and is updated biweekly. The database can be searched on subject terms, titles, authors' names, and other bibliographic information.

Ideal fluid properties for optimizing absorption heat pump performance. Perez-Blanco, H., M.R. Patterson, and J. Braunstein. Report ORNL/TM--10315, Oak Ridge National Lab, Oak Ridge, TN, USA, April 1987 (English).

This report focuses on defining the fluid properties that will optimize the performance of a heat pump cycle. A simple heat pump computer model in conjunction with a parametric binary solution model is coupled to a computer code that searches for optimum values. The code determines the values of the parameters that maximize the thermal performance of the heat pump. The set of parameters is thermodynamically consistent and describes an ideal fluid with which single-effect cycle performance of 90% of Carnot is possible. The ideal fluid properties are a guide toward the properties that real fluids must exhibit in order to enhance the thermal performance of single-effect cycles.

Thermodynamic properties of aqueous ternary solutions relevant to chemical heat pumps: final report. Ally, M.R. Report ORNL/TM--10258, Oak Ridge National Laboratory, Oak Ridge, TN, USA, March 1987 (English).

Polynomial expressions are developed that correlate experimental vapor-liquid-equilibrium (VLE) and specific enthalpy concentration data for a newly developed ternary absorption fluid (LiNO3-KNO3-NaNO3). The development of these expressions is an important step toward using existing ORNL computer software to evaluate heat pump performance. A canned least-square-fit program, (program name POLFIT.BAS), was invoked to obtain the polynomial coefficients. Results show that the maximum deviation between correlated and actual values is less than 3% for vapor pressure and enthalpy. This is considered sufficiently accurate for heat pump cycle performance studies.

Theoretical analysis of an absorption heat pump with continuous regeneration of working fluids by solvent extraction. Cheng, C.S. and Y.S. Shih. *Chem. Eng. Res. Des.*, United Kingdom, September 1987, v. 65(5), pp. 415-420 (English).

A new type of absorption heat pump is proposed by using a second liquid to extract the refrigerant from the dilute absorbent solution in the absorber. The proposed system gives a better thermodynamic efficiency eta, defined as eta chemically bonded (QA/QE + W), than the traditional absorption heat pump. The calculated eta value reaches as high as 0.73 which is about 50% higher than the conventional one. Using LiBr/H_2O/acetophenone as an example, this paper presents the thermodynamic feasibility, the concept design and the operation analysis of the proposed plant.

Thermodynamic design data for absorption heat pump systems operating on water-lithium-chloride. Part 1: cooling. Grover, G.S., M.A.R. Eisa, and F.A. Holland. *Heat Recov. Sys. CHP*, United Kingdom, 1988, v. 8(1), pp. 33-41 (English).

The free choice of operating temperatures in absorption systems is limited by the Gibbs phase rule and the thermodynamic properties of the working pair. For a given combination of temperatures, the concentrations in the absorber and the generator are fixed automatically. This determines the flow ratio. Therefore, for any particular working air, the coefficient of performance is related to the flow ratio. Tables of possible combinations of operating temperatures and concentrations, including flow ratios, Carnot coefficients of performance and enthalpy-based coefficients of performance have been presented for a water-lithium chloride absorption system for cooling. The interaction of operating temperatures has been illustrated graphically. The data obtained are also compared with published data for the water-lithium bromide absorption system under identical conditions.

Energy storing absorption heat pump process. Lourdudoss, S. and H. Stymne. *Int. Journal Energy Res.*, United Kingdom, Apr-Jun 1987, v. 11(2), pp. 263-274 (English).

A novel process, named the super solution field absorption process, for storing and pumping heat is described. This makes use of a solid-salt-solution transformation through the absorption of a suitable fluid. Six working pairs are considered and are analyzed using their enthalpy-concentration diagrams. Although their heat pumping COPs are slightly lower than those of the corresponding conventional systems making use of an (unsaturated) solution 1-solution 2 transformation (through fluid absorption), their storage densities are high enough to be compared to those of the systems using solid 1-solid 2 transformation (through fluid absorption). The operation parameters of the pairs considered suggest that four of them can pump heat from natural thermal sources of a cold climate for space heating, although all six can be regenerated by means of solar collectors.

Development and testing of an absorption-type boiler. Grabenhenrich, H.B. *Ki, Klima, Kaelte, Heiz.*, Fed. Rep. of Germany, March 1987, v. 15(3), pp. 130-134 (German).

The Department of Technical Thermodynamics of Aachen Technical University has been working on a cost-efficient synthesis of heating boilers and absorption-type heat pumps for several years. The functional principle of an "absorption-type" heating boiler is explained, and the influence of the working fluids is discussed. The performance of the first 10kW prototype using methanol and water/lithium bromide is reviewed and discussed.

Double-effect absorption heat pump. Phase 3 final report, August 1984-December 1986. Cook, F.B., et al. Columbia Gas System Service Corp., Columbus, OH, USA, PB--87-232195/XAB, 30 June 1987 (English).

The RD&D program resulted in design, development, and testing of a packaged prototype double-effect generator-cycle absorption gas heat pump for the residential and small commercial markets. The 3RT heat-pump prototype demonstrated a COP_c of 0.82 and a COP_h of 1.65 at ARI rating conditions. The heat pump prototype includes a solid-state control system with built-in diagnostics. The absorbent/refrigerant solution thermophysical properties were completely characterized. Commercially available materials of construction were identified for all heat-pump components. A corrosion inhibitor was identified and tested in both static and dynamic environments. The safety of the heat pump was analyzed by using two analytical approaches. Pioneer Engineering estimated the factory standard cost to produce the 3RT heat pump at $1,700 at a quantity of 50,000 units/year. One U.S. patent was allowed covering the heat-pump technology, and two divisional applications and three continuation-in-park applications were filed with the U.S. Patent and Trademark Office. Corresponding patent coverage was applied for in Canada, the EEC, Australia, and Japan. Testing of the prototype heat pump is continuing, as are life tests of multiple pump concepts and long-term dynamic corrosion tests. Continued development and commercialization of gas-absorption heat pumps based on this technology are recommended.

Development of an absorption heat pump. Manago, A. *Enerugi, Shigen*, Japan, 5 May 1987, v. 8(3), pp. 77-81 (Japanese).

Absorption water cooling/heating machines that employ water and lithium bromide as refrigerant and absorbent, respectively, have been widely used in air conditioners (conventional type). The present study is aimed at developing an air-cooled condenser and absorber (for cooling) and a heat pump that uses air as heat source (for heating) in an effort to provide an energy-saving type air conditioner. The use of concentrated absorbent liquid in a conventional type machine may appear to be effective, but it results in the problem that crystallization occurs at low temperatures. Here, an aqueous solution containing lithium bromide and zinc chloride is developed to be used as absorbent liquid. With the new absorbent liquid, the COP (coefficient of performance) of air-cooled refrigeration cycle is 1.0, which is equal to that for the conventional type, while the COP of double-effect heat pump cycle is 1.56, which is about two times as high as the heating performance coefficient of 0.8 for the conventional type. A study for improving the corrosion resistance and testing of prototype machines are currently under way.

ORNL research programs related to chlorofluorocarbon (CFC) alternatives. Fairchild, P.D. Oak Ridge National Laboratory, Oak Ridge, TN, USA, DOE/OR/21400--T306, 13 May 1987 (English).

Testimony covered: uses and control impacts; federal/Department of Energy role; and relevant DOE research and development: absorption cycle technology, advanced insulation, novel thermodynamic cycles, fluid substitutes and recovery technology, development of replacement chemicals, development of recycling and recovery practices, development of alternative technologies, and resource requirements and schedules for accomplishments.

New compression heat pump media for medium and high temperature application. Narodoslawsky, M., F. Windisch and F. Moser. *Heat Recov. Sys. CHP*, United Kingdom, 1988, v. 8(1), pp. 23-31 (English).

A systematic method for looking for the best working fluids for a compression heat pump system has been developed. With the help of a commercial flowsheet program, a simulation routine of the heat pump has been established. This routine was used to screen all substances in the attached data bank in respect to their applicability as working media. In all, 940 substances have been investigated. From the substances, 42 show favorable properties as working fluids for the application in three cases, namely with a temperature of the heat source of 20°C and of the heat sink of 70°C, respectively, 60°C source temperature and 120°C at the heat sink, and of 90°C source temperature and 150°C at the heat sink. A further investigation of these 42 substances with respect to toxicity and stability left four of them as the ultimate proposal for operable compression heat pump fluids.

Ultrasonic speeds in the liquid phase of the azeotropic mixture refrigerant R502 under high pressure. Takagi, T. and H. Teranishi. *J. Chem. Eng. Data*, U.S.A., April 1987, v. 32(2), pp. 133-135 (English).

The ultrasonic speeds in the liquefied fluorocarbon azeotropic mixture refrigerant R502 were measured over the ranges of temperature from 283.15 to 323.15K and pressures from near-saturated vapor pressure to about 50 MPa by using a sing-around technique operated at a frequency of 2 MHz. The results, which showed smooth change with pressure for each isotherm, were used to estimate the values at the saturated liquid. The isentropic compressibilities were determined from experimental values.

Heat pump assisted distillation. Part 4 - an experimental comparison of R114 and R11 as the working fluid in an external heat pump. Supranto, S., et al. *Int. J. Energy Res.*, United Kingdom, Jan-Mar 1987, v. 11(1), pp. 21-33 (English).

A study has been carried out on a continuously operated pilot fractional distillation column equipped with an external heat pump. Theoretical and measured Rankine coefficients are higher for R11 than R114. A maximum actual coefficient of performance of 5.3 was obtained using R11 as the working fluid with a gross temperature lift of 38.4°C. The relative thermal instability of R11 compared to R114 has not apparently affected the performance of the system.

Nonazeotropic mixture for compression type heat pump. Nakaiawa, M. and S. Kawasaki. *Kagaku Kogyo Shiryo (Tsukuba-gun)*, May 1987, v. 22(1), pp. 19-28 (Japanese).

Compression type pump is now popular for air conditioning application, and is expected to expand its application both in household and industry areas because of its energy-saving characteristics. Although there are problems, the first consideration is the use of high performance fluid. In the past, halogenated hydrocarbons (e.g., Freon R11 or R113) were developed and used under the respective conditions. Other promising fluid is a nonazeotropic refrigerant which is now attracting the attention. This report outlines a heat pump cycle (Lorentz cycle) whose effectiveness was pointed out already in the 1950's, but has been made practical only recently, concerning its principle, effectiveness, problems and applications.

Utilization of new refrigerants for high temperature heat pumps. Blaise, J.C. and T. Dutto. *Rev. Gen. Froid*, France, September 1987, v. 77(9), pp. 485-488 (French).

This paper presents experimental results obtained with high temperature heat pumps working with new refrigerants: a pure fluid R142b and nonazeotropic mixture of R12 and R114, all these fluids being CFC's. The results are encouraging in the case where for R142b, the experimental values are in agreement with the theory and enable one to envisage energy production at 95°C and where for nonazeotropic mixtures, experiences reveal the mysteries which prevail upon their behavior in the presence of system leaks of the heat pumps.

Laboratory testing of a heat pump system with water-to-water, counterflow heat exchangers using various compositions of an R13B1/R152a nonazeotropic refrigerant mixture. Vineyard, E.A. ASHRAE Winter Meeting, January 1988 (English).

Testing was performed with a nonazeotropic refrigerant mixture of R13B1/R152a to determine its ability to achieve capacity, relative to R22, at low ambient temperatures. The selection of such a mixture could improve the efficiency of a heat pump by decreasing the cycling losses, which account for approximately 7-12% of the annual energy use, along with decreasing the amount of resistance heat required at low ambient temperatures. Results for the mixture show a potential capacity modulation from 12431 Btu/hr (343 W) at 17°F (-8.3°C) to 8550 Btu/hr (2506 W) at 47°F (8.3°C) in heating and from 7451 Btu/h (2184 W) at 82°F (27.8°C) to 9188 Btu/h (2693 W) at 95°F (35°C) in cooling. An analysis of the coefficients of performance for the mixture and its pure components is presented along with a comparison against results obtained with R22. The comparison is based on maintaining equivalent inlet and exit water temperatures in the evaporator and condenser for both R22 and the mixtures.

Power plant and heating cycles with nonazeotropic working fluids. [Kraftwerks und heizprozesse mit nichtazeotropen arbeitsmittelgemischen] Hansen, K. *VDI-Verl.*, 1987 (German)

Nonazeotropic binary fluids are investigated with a view to their applicability as working fluids in ORC and heat pump systems utilizing low-temperature heat. The various steps to be taken comprise: the choice of an equation of state for thermodynamic binary systems, the energetic calculation and optimization of real cycles with pure substances and nonazeotropic binary fluids as working fluids, and the economic optimization of energy conversion systems. ORC systems are analyzed by comparing the minimum power generation costs and optimum dimensions of system variants.

U.S. participation in international negotiations on ozone protocol. Hearing before the subcommittee on human rights and international organizations of the committee on foreign affairs, House of Representatives, One Hundredth Congress,-first session, 5 March 1987. U.S. Government Printing Office, Washington, D.C., 1987 (English).

Richard Benedick of the U.S. Department of State testified on the status of international negotiations in a hearing aimed at reviewing the United States' position on international environmental problems caused primarily by chlorofluorocarbon (CFC) pollutants. The negotiations seek a cooperative international research, monitoring and information exchange effort among the 27 countries which have signed the convention. The area of principal concern is the increase in skin cancers and other biological effects on both plants and animals. The economic impact of regulatory controls would be widespread. A scheduled plan for reducing CFC emissions would allow affected industries to find safer substitutes and adopt recycling procedures that would be less socially and economically disruptive. Additional material submitted by the witness for the record follows his testimony.

News Briefs

IEA Seminar on the CFC Problem

As mentioned in Newsletter Vol. 6, No. 1, a seminar on the CFC problem was held in Rome, May 30-31, 1988. This seminar was organized by Professor Thore Berntsson from Chalmers University of Technology, Sweden, on behalf of IEA Advanced Heat Pumps. Twelve countries were represented. The aims of the seminar were:

-- To discuss advantages and drawbacks of various future solutions
-- To define needs for further R&D activities
-- To propose R&D projects suitable for international cooperation within IEA

A preliminary report on questionnaires, which were previously completed by the member countries, was distributed to the attendees.

Each country gave a presentation on its current and planned CFC situation regarding regulations, norms, recommendations, etc., as well as ongoing and planned R&D activities. There were ten presentations on possible future measures. Finally, the need for further R&D activities and possible new IEA annexes was discussed.

Full proceedings will be available at a future date and will be distributed to the delegates. A summary report of the conclusions and suggested further activities and new annexes, written by Professor Berntsson, will be published in a future issue of the Newsletter.

Heat Pump Development and Application in China

A symposium on Heat Pump Development and Application in China was held March 9-11, 1988, at the Guangzhou Institute of Energy Conversion. This symposium, jointly sponsored by the Institute and Tianjin University, was backed by the Energy Bureau of the State Economic Commission, the Energy Bureau of the Chinese Academy of Sciences, and the Science-Technology Bureau of the State Education Commission. As the largest symposium of its kind ever held in China, it was attended by over 130 specialists from 81 universities, research institutes, design institutes, manufacturers, and user organizations. Included among the extensive subjects discussed at the symposium were the feasibility of heat pump development and application in China, and experiences using heat pumps in drying, evaporation, distillation, space heating, and hot water supply. It was also mentioned that more research is needed in the areas of gas-driven heat pumps, steam ejection heat pumps, and absorption and chemical heat pumps.

The resulting summary of the symposium declared that heat pumps of various kinds have bright prospects in China, and proposed that heat pump development requires a more organized approach. To that end, appeals were made to various authorities, especially government organizations at different levels, to give importance to and support heat pump development.

Beginning in the 1980's, economic development in China has been rapid. Such factors as the expansion of the refrigeration industry, increasing awareness of energy conservation, innovations in low-grade energy utilization, and improvements in living standards provide a favorable environment for heat pump development. This symposium will help further heat pump use in China.

(Courtesy of Li Song-Zhe, He Rong-Zhi, Ling Yi-Cheng, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, People's Republic of China)

Call for Papers

The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) has announced a call for papers for IAQ 89, the organization's fourth annual symposium on design solutions to indoor air quality problems, which will be held in San Diego, California, USA, April 17-20, 1989. The theme of IAQ 89 is "The Human Equation: Health and Comfort." The symposium will cover comfort issues and health effects, control, and survey protocols of specific contaminants such as microorganisms, combustion products, radon, volatile organic compounds, environmental tobacco smoke, odors and bioeffluents in residential and commercial environments.

Those wishing to submit papers should send abstracts of 300 words or less by August 10, 1988, to Jim Norman, Manager of Technical Services, ASHRAE, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA. Papers can be either case studies or reports on research. Abstracts for both should demonstrate new data of significant interest. For papers presenting research, include title, author, findings, and the name of the institution where the research was performed. Authors will be advised of acceptance of abstracts by August 31, 1988, and manuscripts will be due for peer review by November 15, 1988. Reviewers' comments will be returned to each author by January 16, 1989. Papers will be published in the symposium proceedings.

ASHRAE has also issued a call for papers for its 1989 Annual Meeting in Vancouver, British Columbia, June 24-28, 1989. The submission deadline is October 21, 1988.

Membership in ASHRAE is not a prerequisite for participation, and papers from outside the United States are welcome. All papers and presentations must be in English with units in rational inch-pound (I-P) followed by separate system international (SI) in parentheses. Papers accepted for presentation will be published in *ASHRAE Transactions*. To receive a copy of the submission procedures and the author's guide, contact: Continuing Education and Chapter Programs, ASHRAE, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA, telephone 01-404-636-8400.

Schedule of Conferences and Trade Fairs

July 18-21, 1988

West Lafayette, Indiana (USA); **1988 International Compressor Engineering Conference - at Purdue.** Sponsored by the Ray W. Herrick Laboratories, School of Mechanical Engineering, Purdue University, the International Institute of Refrigeration (IIR), and other cooperating groups. Contact: Ms. Vicki Delaney, Conference Secretary, Ray W. Herrick Laboratories, Purdue University, West Lafayette, Indiana 47907, USA, telephone (317) 494-2132, telex 4930593 PHERLUI.

September 12-14, 1988

Gothenburg (Sweden); **IEA Workshop on Air Quality, Heating and Cooling of Buildings.** Sponsored by the Swedish Council for Building Research acting on behalf of the International Energy Agency. Contact: Mr. T. Bostroem, Swedish Council for Building Research, Sankt Goeransgatan 66 S-11233 Stockholm, Sweden, telephone 46-8-540640, telex 10398 S.

September 14-17, 1988

Wilmington, Delaware (USA); **International Symposium on Energy Options for the Year 2000: Contemporary Concepts in Technology and Policy.** Sponsored by the U.S. Department of Energy, Argonne National Laboratory, and the Government of Finland. Contact: University of Delaware, Center for Energy and Urban Policy Research, Attention: Dr. J. Byrne, Newark, Delaware 19716, USA.

September 26-29, 1988

Graz (Austria); **2nd Workshop on Research Activities on Advanced Heat Pumps.** (Part of the Austrian-Italian-Yugoslav Chemical Engineering Conference.) Sponsored by the University of Graz. Contact: Technische Universitaet Graz, Inst. fuer Verfahrenstechnik, z.Hd. Dr. H. Schnitzer, Inffeldgasse 25, A-8010, Graz, Austria.

Sept. 29-October 1, 1988

Nuernberg (Fed. Rep. of Germany); **Internationale Fachmesse Kaelte-Klimatechnik (IKK '88).** [International Trade Fair for Refrigeration and Air Conditioning] Contact: Nuernberger Messe- und Ausstellungsgesellschaft m.b.H., Messezentrum, D-8900 Nuernberg 50, Fed. Rep. of Germany.

October 3-7, 1988

Madrid (Spain); **11th International Congress of Electrical Heating.** Sponsored by the Spanish Committee of the International Union of Electrical Heating (U.I.E.). Contact: UIE Kongress 1988, c/o Comité Español de Electrotermia, Francisco Gervas, 3, E-28020 Madrid, Spain, or Viajes Iberia, San Bernardo, 20-3.° Dcha., E-28015 Madrid, Spain.

October 17-20, 1988

Versailles (France); **JIGASTOCK 1988 Thermal Exploitation of Underground Resources and Storage.** Sponsored by the European Community Commission (ECC) and the International Council for Thermal Energy Storage (ICTES). Contact: JIGASTOCK 88 Office, c/o Agence Française pour la Maîtrise de l'Energie (AFME), Madame M. Leblanc, 27, rue Louis-Vicat, 75737 Paris Cedex 15, France, telephone 33-(1)47652182.

November 22-26, 1988

Brussels (Belgium); **European Exhibition on Heating, Ventilation, Refrigeration and Air-Conditioning.** Contact: Foire Internationale de Bruxelles A.S.B.L., Parc des Expositions, B-1020 Bruxelles, Belgique.

January 16-18, 1989

Gothenburg (Sweden); **Third Workshop on Solar Assisted Heat Pumps with Ground Coupled Storage.** Contact: Jan-Olof Dalenbaeck, CTH/Installationsteknik, S-412 96 Gothenburg, Sweden.

January 28-February 1, 1989

Chicago, Illinois (USA); **1989 ASHRAE Winter Meeting.** Sponsored by the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE). Contact: Judy Marshall or Judith Breese, ASHRAE International Headquarters, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA, telephone 01-404-636-8400, telex 705343.

January 30-February 2, 1989

Chicago, Illinois (USA); **International Air-Conditioning, Heating and Refrigerating Exposition.** Sponsored by the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) and ARI. Contact: International Exposition Company, 200 Park Avenue, New York, New York 10166, USA, telephone 01-212-986-4232.

June 24-28, 1989

Vancouver (Canada); **1989 ASHRAE Annual Meeting.** Sponsored by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE). Contact: ASHRAE International Headquarters, 1791 Tullie Circle, N.E., Atlanta, Georgia 30329, USA, telephone 01-404-636-8400, telex 705343.

August 28-September 1, 1989

Sarajevo (Yugoslavia); **CLIMA 2000** (The 2nd World Congress on Heating, Ventilating, Refrigerating and Air Conditioning). Sponsored by the Federation of Representatives of European Heating and Ventilating Associations (REHVA), ASHRAE, and IIR. Contact: Organizing Committee of CLIMA 2000, Masinski fakultet, Prof. Dr. E. Kulic, 71000 Sarajevo, Omladinsko setaliste bb, Yugoslavia, telephone 071/642071, telex 41 529 IPES YU.

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Reports

The following reports are available from the HPC:

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HPC-WR2*	Proceedings of the Workshop on Ground-Source Heat Pumps (1987), 245 pages	DM 50,--/U.S. $30
HPC-WR3	National Reports on the Status of Heat Pumps (1987), 105 pages	DM 40,--/U.S. $25
HPC-R2-1*	Heat Pump RD&D Projects Summary Report, Edition 2 (Dec. 1986), 514 pages	DM 75,--/U.S. $45
HPC-LR-3*	HPC Bibliography - Sorption Heat Pump Systems (Oct. 1986), 372 pages	DM 40,--/U.S. $25
HPC-LR-2*	HPC Bibliography - Industrial Heat Pumps (July 1986), 378 pages	DM 40,--/U.S. $25
HPC-LR-1*	HPC Bibliography - Environmental Aspects of Heat Pump Applications (May 1986), 105 pages	DM 25,--/U.S. $15
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Vol/No	Topic	Deadline for Contributions
6/3	10th Anniversary of the IEA Implementing Agreements	July 15, 1988
6/4	Absorption Heat Pumps	October 7, 1988

If you would like to contribute an article on any of these topics, please send it to the Heat Pump Center.

Our regular features (bibliographic review, news briefs, and schedule of conferences and trade fairs) will also be included.

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