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THE ZEOLITE HEAT PUMP AND ITS APPLICATION PROSPECTS IN MODERN HEATING SYSTEMS

The increasing range of the application of zeolites in various areas of technology bodes well for their use in heat pumps. This paper presents the concept of a zeolite application in a heat pump solution, operating with two absorber/desorber zeolite heat exchangers in conjunction with a heat distribution system. The expected gain in heating efficiency in the new solution is considerable in comparison with a conventional gas boiler, and even with a condensation boiler. The emission of CO_2 can be reduced by ca. 30% when compared with a regular gas boiler.

Heat pumps are a focus area for research institutes and the industry, and their practical application has been spreading worldwide. They provide a solution to the growing need for green energy reducing fossil fuel consumption and environmental pollution. We live in an environment abundant with energy, but whose energy level is not sufficiently high. The energy is found in air, water and in the ground. It could be applied for various purposes, provided that certain technical problems are solved.

The key issue is the transport of heat from a colder to a warmer body. In accordance with the second law of thermodynamics, heat cannot pass from a lower temperature body to one with a higher temperature spontaneously. This problem was solved as early as in the 19th century, when the energy of evaporation was utilised in the first ammonia cooler (1875). Ammonia as a cooling agent was very efficiently superseded by chlorofluorocarbons or CFCs also known as freons, discovered in 1931. During the last few years, focus has been primarily on compressor-driven heat pumps using chemicals with desirable thermodynamic properties as coolants, mainly freons and ammonia.

Despite their good thermodynamic properties both cooling agents have proved imperfect for two reasons: ammonia is hazardous to use and freon is even more danger-

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ous. They contribute to the hole in the ozone layer and to the greenhouse effect, causing global risk to humans. This is the reason why the development of heat pumps went into a dead-end.

In 1987, freons were added to the list of banned substances (Montreal Protocol). While ammonia has been recovering its former significance with the implementation of latest protection technologies, it cannot meet the demands fully. Other agents currently in focus include water, carbon dioxide, certain hydrocarbons, air, helium and hydrogen. Water seems to be the most promising of them all for technological and environmental reasons, especially in combination with zeolitic minerals included in the fundamental components of a heat pump, the condenser and the evaporator.

Zeolites are minerals. They consist of hydrated aluminosilicates, primarily sodium, calcium, strontium, barium, magnesium and manganese [1], [2]. They are characterised by a high concentration of water particles in the free spaces of the crystal lattice and a large capacity for positive ion exchange.

Known zeolites include: chabazite – $(Ca, Na)_2\,[Al_3Si_9O_{24}]\cdot 9H_2O$, stilbite – $Ca[Al_2Si_7O_{18}]\cdot 7H_20$, harmotome – $Ba[Al_2Si_6O_{16}]\cdot 6H_20$, heulandrite – $Ca[Al_2Si_7O_{18}]\cdot 6H_2O$, phillipsite – $KCa[Al_3Si_5O_{16}]\cdot 6H_2O$ and others. Generally, the zeolite composition can be summarised as follows: $M_{x/n}\,[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$; whereby n denominates the positive ionic charge, typically Na^+, K^+ or Ca^+, while z is the number of moles of the hydrated water.

Zeolites are formed as regular crystals or as fibrous, lamellate or radial clusters. Their characteristic feature is an internal structure of a network of empty channels and cavities with diameters ranging from 2 to $11\cdot 10^{-10}$ m. Zeolites are colourless or white, possibly with a yellowish, reddish, pinkish or greenish shade.

On Mohs' scale, zeolites rate from 3 to 5 and are resistant to abrasion. They are very rare and occur in small quantities. The largest European concentrations have been discovered in Russia and Bulgaria. In Poland they occur in Lower Silesia and in the Pieniny Mountains.

The first zeolite, later named stilbite, was discovered more than two hundred years ago. Since then, more than forty natural zeolites have been discovered. Their valuable properties have attracted research on methods of artificial zeolite production. So far, more than one hundred synthetic zeolites have been developed, some with an entirely original composition and new properties. Artificial zeolites are produced using fly ash. In this way, otherwise useless waste can be turned productive and the synthetic zeolites can be used to clean up and dry up flue gases, to filter water and wastewater in chemical, refinery and other industries.

Due to their unique properties both natural and synthetic zeolites are used as adsorbents, catalysts and molecular sieves. Recently, zeolites have been used in cooling, heating and air conditioning, as well as new construction material technologies [3]–[5]. However, the relatively high price of zeolites restricts their general use.

In 2001, at an international heating technology fair in Frankfurt, Vaillant exhibited a prototype zeolite heat pump with the capacity of 10 kW for household and water heating. This zeolite heating device is being developed in cooperation with the Chair of Thermodynamics of the Aachen Technical College, Germany. It is expected that production units with the capacity of 5 to 25 kW will become available in Germany during the next few years [6]. Commercial versions of the zeolite heat pumps are currently undergoing large scale operating tests in natural conditions. Several hundred units are involved in Germany and Austria.

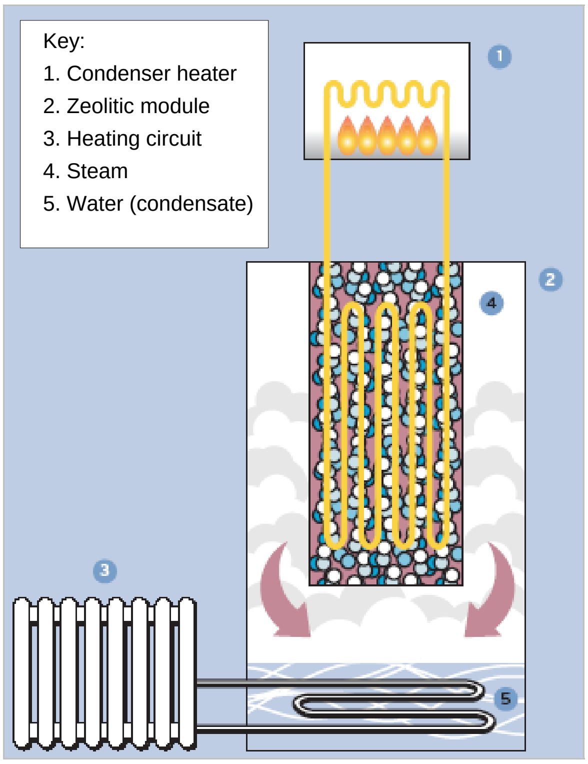

Fig. 1. Module 1: Zeolite drying (desorption)
by heating with condenser heater

The main component of a zeolite pump is a zeolite module (figures 1 and 2). Water is used as the cooling agent. The zeolite as an adsorbent agent is placed on the top of the modules, in the adsorbent/desorbent-type heat exchanger. At the bottom there is a second heat exchanger, this time the condenser/evaporator type. Both exchangers comprise ribbed piping, straight or spiralled, filled with granulated zeolite (figure 3). The modules are tightly sealed with 0.5 to 20 kPa vacuum inside.

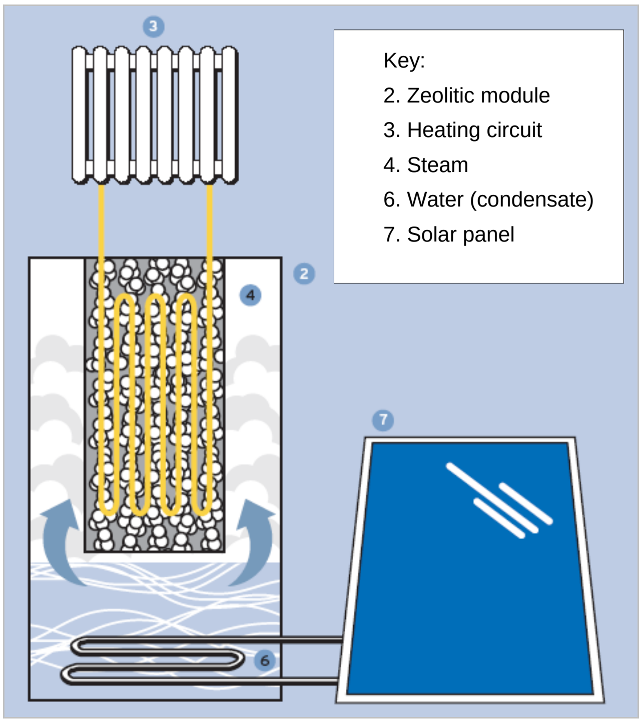

Fig. 2. Module 2: Wetting of zeolite (adsorption) – heating with ambient heat

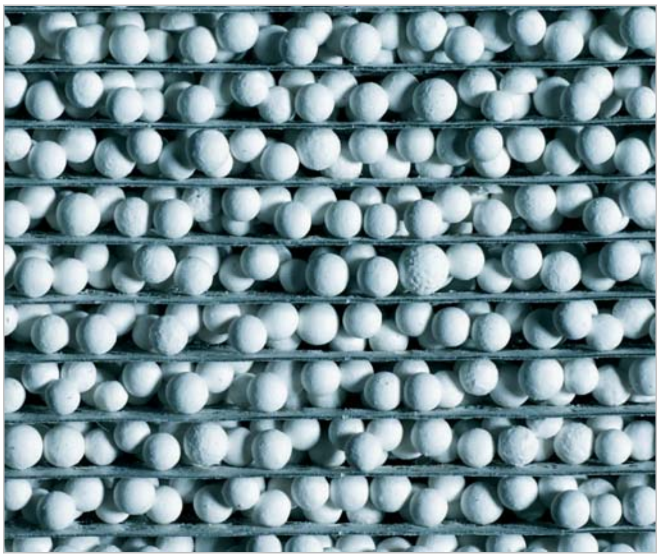

Fig. 3. A fragment of a zeolite heat exchanger

A zeolite heat pump consists of two modules operating in turns and controlled with an electronic switching array. Two modules are employed due to their cyclic operating nature and designed to ensure continuous exchange of the internal heat, to improve the pump efficiency and to maximise the utilisation of the free ambient energy. The latter may come from the air, ground or ground water. Also solar energy can be utilised by zeolite heat pumps. Other components, alongside the modules, include condenser heater, a chain of three heat exchangers, circulation pumps and the control automation (figure 4).

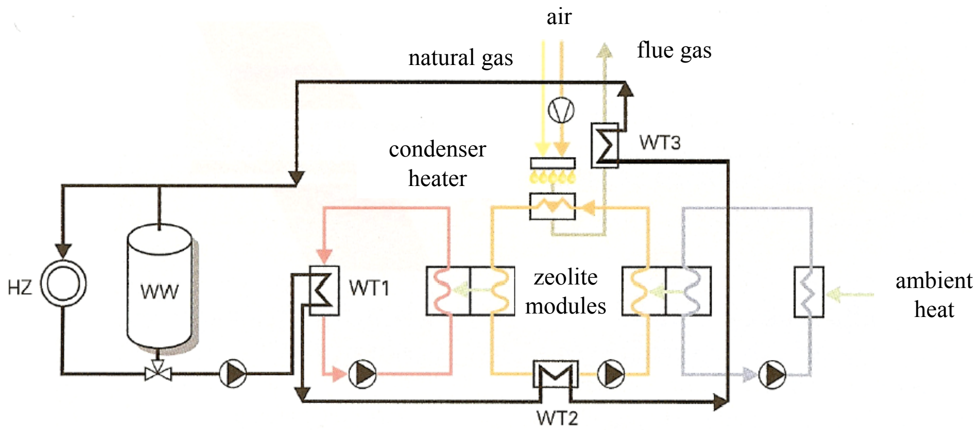

Fig. 4. Hydraulic schematic of a heating system with a zeolite heat pump

Inside a zeolite pump the cyclic process consists of two phases. The first phase begins in the adsorber/desorber (figure 1) where heat from the condenser heater causes a desorption (evaporation) of the coolant, i.e., water contained in the zeolite. The resulting steam is then condensed in the bottom part of the module, at the same time releasing the condensation heat as the useful heat in the WT1 exchanger (figure 4). The condenser heater keeps heating the desorber until the temperature in the condenser stops raising.

When this happens the zeolite has been dried completely and the entire volume of the cooling agent is contained in the condenser. At that point, the first phase of the process ends, the condenser heater is switched off, the module radiates useful heat and cools down. The zeolite temperature drops. The heat of the condenser heater flue gas is also put to use and passed on to the heating circuits through the WT3 exchanger (figure 4).

The second phase begins as the ambient heat raises the temperature of the coolant (figure 2), contained in the lower part of the module, which is evaporated and the steam is adsorbed again by the zeolite in the top part. This produces a certain amount of adsorption heat, which is passed on to the circulation in the form of useful heat in the WT2 exchanger (figure 4). The adsorption of steam by the zeolite raises its temperature to ca. 150 °C. When the liquid coolant is evaporated and absorbed by the zeolite until full saturation, the second phase ends and the process starts anew.

Useful heat is, therefore, collected in three independent heat exchangers, WT1, 2 and 3, serially connected in the heating system marked with a thick line on the schematic (figure 4). The useful heat is then transferred to the HZ heating circuit and to the WW hot water boiler.

The zeolite heat pump has the potential of becoming another milestone of heating technology. The physical efficiency barrier of gas condenser boilers of 111% has been breached. The devices will supply heat for indoor and water heating purposes at the average annual efficiency of 135% in relation to the combustion heat in the condenser heater (figure 5). This is a huge leap ahead in comparison to the central heating boilers operating at 93% efficiency [7]. At the same time, only 75% of the heating energy produced will come from the natural gas supplied to the device, the remaining 25% coming from the surroundings at no cost. Alongside a considerable energy conservation factor, zeolite heat pumps also emit by 30% less carbon dioxide (figure 5). They utilise water as the cooling agent, as opposed to the earlier generation equipment, the absorption and condenser coolers, which ran using freon or ammonia known to be environmentally harmful.

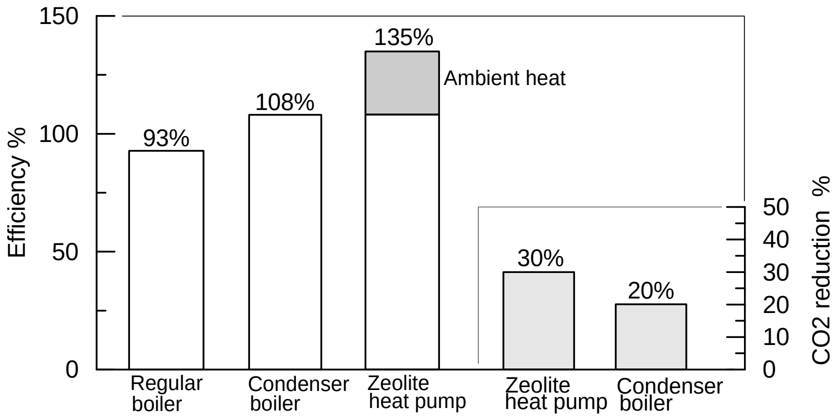

Fig. 5. New dimension in heating efficiency

In addition to its high energy efficiency benefits, the zeolite heat pump is characterised by a simple installation in heating systems and low installation requirements. It can be successfully applied in newly built low heat-loss buildings, as well as in older, but refurbished and insulated buildings. The zeolite heat pump can be fitted quickly and smoothly in any heating system. Also, the zeolite modules require no servicing. Only the heating device, i.e., the condensing boiler requires, just as any other gas boiler, a regular annual technical checkup. Figure 6 shows a photograph of zeolite heat pump components.

Fig. 6. A view of a commercial zeolite heat pump with front cover panel removed:
1 – condenser heater, 2 – switch of zeolitic module, 3 – membrane container of zeolitic circuit,
4 – zeolitic circuit pump, 5 – heat exchanger; zeolitic circuit – CH circuit,
6 – heat exchanger, zeolitic circuit – condenser heater, 7 – solar circuit pump, 8 – circulation switch valve

The global climate change, especially the rise of the average temperature of the atmosphere, as a result of the greenhouse effect caused by exhaust gas emissions, combined with the hole in the ozone layer over the Antarctic, and the ozone layer depletion over the rest of the Earth calls for efforts to develop more efficient heat sources. Conventional heat production does not only result in high pollution emission, but uses up the valuable and expensive fossil fuels, such as natural gas, coal and oil. The greenhouse effect can be reversed. The heat contained in the air, ground and water, as well as the solar radiation provide a boundless source, which, through the development of heating technologies, can be tapped to produce useful heat.

REFERENCES

[1] TRACY M.M.J., RANDALL K.H., RAO S., *The search for new zeolite frameworks*, [in:] Proceedings of the twelfth International Zeolite Conference, M.M.J. Tracy, B.K. Marcus, M.E. Bisher and J.B. Higgins (Eds.), Materials Research Society, Warrendale, U.S.A., 1999, Vol. 1, pp. 517–532.
[2] *Zeolite Molecular Sieves*, John Wiley and Sons 1974, Donald W. Breck.
[3] ANIELAK A.M., PIASKOWSKI K., *Zeolity naturalne i ich zastosowanie w oczyszczaniu ścieków*, Ekologia i Technika, 2000, Vol. VIII, No. 2, pp. 31–41.
[4] OSZCZUDŁOWSKI J., CHOMA J., *Strukturalne i adsorpcyjne właściwości zeolitów naturalnych modyfikowanych chromem*, Materiały XXXV Ogólnopolskiego Kolokwium Katalitycznego, Kraków, 2–4 April, 2003, pp. 133–134.
[5] *Database of Zeolite Structures*, Swiss Federal Institute of Technology Zurich, Switzerland, Database of Copyright © 2000 International Zeolite Association, http://www.iza-structure.org/database
[6] *Entwicklungsziele und Produktmerkmale, Einsatz in Einfamilienhaus*, Copyright © 2006 Vaillant GmbH, Remscheid. http:/www.vaillant.de/Privatkunden/Systeme&Produkte/Entwicklung/Zeolit-Heizgeraet/article
[7] Vereinigung Deutscher Elektrizitaetswerke e.V. (VDEW), Frankfurt und Berlin.

ZEOLITOWA POMPA CIEPŁA – PERSPEKTYWY ZASTOSOWANIA W NOWOCZESNYCH SYSTEMACH GRZEWCZYCH

Wzrastające zastosowanie zeolitów w różnych obszarach techniki i technologii rokuje nadzieje na wykorzystanie tego materiału w pompach ciepła.

Przedstawiono koncepcję wykorzystania zeolitów w pompie ciepła pracującej w podwójnym układzie dwóch zeolitowych wymienników ciepła absorber–desorber, jak również w instalacji do ogrzewania współpracującej z tą pompą. Spodziewany wzrost sprawności ogrzewania dzięki nowemu rozwiązaniu w porównaniu ze sprawnością zwykłego kotła gazowego, a nawet kotła kondensacyjnego, jest znaczny. Emisja CO_2 w porównaniu z emisją podczas spalania gazu w zwykłym kotle gazowym zostanie zredukowana o około 30%.