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Primernost reakcije magnezijevega oksida z vodo za uporabo v kemičnem hralnilniku toplote

The Suitability of Magnesium Oxide and Water for Use in Chemical Heat Storage

Yukitaka Kato - Boštjan Cerkvenik - Atsushi Minakami - Yoshio Yoshizawa

Zaradi velikih gostot energije lahko kemične toplotne črpalke uporabimo tudi kot hranilnike toplote. Z uporabo povračljivih kemičnih reakcij, s krmiljenjem toka tekočine, ki reagira, lahko toploto shranimo in sproščamo glede na zunanje potrebe. V primeru zadovoljive ponovljivosti lahko kemične reakcije uporabimo v hranilnikih toplote, ki se lahko vključijo v sedanje kogeneracijske sisteme. Z uporabo kemične toplotne črpalke lahko uravnotežimo obremenitev kogeneracijskih sistemov. Odvečno toploto v času manjšega odjema toplote s kemično reakcijo shranimo v hranilniku, v času koničnih obremenitev pa jo sprostimo s povratno reakcijo.

V tem prispevku je govor o izvedljivosti kemične toplotne črpalke, ki uporablja reakcijo magnezijevega oksida z vodo. V tem primeru lahko med reakcijo dehidracije magnezijevega hidroksida toploto shranimo pri temperaturi 300 °C do 400 °C, ali jo med hidracijo magnezijevega oksida oddamo pri temperaturi 100 °C do 200 °C. Da bi preverili uporabnost magnezijevega hidroksida kot reakcijskega sredstva za toplotne črpalke, smo eksperimentalno izvedli reakcijski postopek v območju tlakov med 30 kPa in 203 kPa. Kot reaktorsko sredico v valjastem reaktorju smo uporabili posebej pripravljen reaktant – $Mg(OH)_2$, z dobro večkratno ponovljivostjo reakcije. Krog delovanja naprave je sestavljen iz endotermnega postopka dehidracije magnezijevega hidroksida ter eksotermnega postopka hidracije magnezijevega oksida. Krog smo ponavljali v različnih obratovalnih razmerah, ki so značilne za delovanje hranilnika toplote v kogeneracijskem sistemu. Med postopkom reakcije smo v obeh smereh merili razporeditev temperature ter reagiran delež v reaktorski sredici. Na koncu smo preverili tudi dejansko izvedljivost reaktorja ter povprečno specifično moč reaktorja.

(Ključne besede: črpalke toplotne kemične, shranjevanje energije, oksidi magnezijevi, kogeneracija)

Because of their high energy density, chemical heat pumps are an interesting possibility for heat storage. With reversible chemical reactions the heat can be stored or released on demand by controlling the flow of the reactive fluid. If they prove to have satisfactory repeatability, the reversible reactions can also be used in a heat storage system for cogeneration systems. In this way it would be possible to even out the load of the cogeneration system: in a period of low heat demand the surplus heat is stored with the chemical reaction in the heat storage and during a peak load period it can be released with the reverse reaction.

In this paper we discuss the operation of a chemical heat pump that uses the reaction between magnesium oxide and water. In this case the heat can be stored with a dehydration process at about 300–400 ^{o}C and released with a hydration process at about 100–200 ^{o}C. In order to test the potential of magnesium hydroxide as a reactive medium for heat pumps we performed reaction experiments over a range of operation pressures between 30 kPa and 203 kPa. For the experiment, a specially prepared reactant with good properties for repetitive operation was packed in a cylindrical reactor. The experimental cycle consisted of an endothermic dehydration of the magnesium hydroxide for the heat storage, and an exothermic hydration of the magnesium oxide for the heat release. The cycle is repeated under various operating conditions that are characteristic for a heat-storage operation of a cogeneration system. Both directions of the reversible reaction were studied by measuring the reactor-bed temperature distribution and the reacted fraction changes. We conclude with a discussion of a practical application and the mean heat output rate of the reactor.

(Keywords: chemical heat pumps, heat storage, magnesium oxide, cogeneration)

0 UVOD

Prispevek poskuša predstaviti uporabnost povračljivih reakcij v kemičnih toplotnih črpalkah, ki bi jih uporabili za izkoriščanje presežkov toplot v kogeneracijskih sistemih ter za dvig energijske učinkovitosti tovrstnih sistemov. Kemična toplotna črpalka, s katero spreminjamo temperaturno raven toplote z uporabo kemičnih reakcij, je eden izmed načinov za shranjevanje in izkoriščanje toplote. Zaradi zadovoljive ponovljivosti ter razmeroma velike gostote energije smo naše delo osredotočili na povračljive reakcije kovinskih oksidov z vodo.

Osnove kinetike reakcij magnezijevega in kalcijevega oksida z vodo, ki sta v našem primeru najbolj zanimivi, je predstavil Hartman [1]. Fujii je opravil osnovne meritve primernosti kalcijevega oksida za shranjevanje energije [2]. Kasneje je za isto reakcijo objavil tudi eksperimentalne rezultate o dinamiki procesa hidracije in dehidracije [3]. Kinetiko kemične reakcije kalcijevega oksida z vodo, ki jo lahko uporabimo v kemični toplotni črpalki za izkoriščanje odvečne toplote, je predstavil tudi Kamimori [4]. Poleg tega je Ogura [5] reakcijo tudi eksperimentalno preveril za primer uporabe v sušilnem sistemu.

Nasprotno je Cerkvenik [6] uporabil reakcijo kalcijevega oksida z vodo za hlajenje. Zaradi nizkih delovnih tlakov, do 15 mbar, ki povzročajo manj intenziven prenos snovi do reakcijskih mest v reaktorju, in zaradi nizke toplotne prevodnosti kalcijevega oksida, je uporabil novo grafitno matrično strukturo. Zaradi grafita v matrici se toplotna prevodnost reaktorske sredice v primerjavi s samim oksidom poveča. Poleg tega je v drugih delih ([7] in [8]) predstavil uporabo kalcijevega oksida kot soli v krovnem postopku kaskadne sorpcijske naprave. S tem korakom lahko dosegamo višja toplotna grelno-hladilna števila (GHŠ - COP) kakor s samostojno napravo. Standardne delovne temperature so med dehidracijo 500 °C do 600 °C (shranjevanje energije) in med hidracijo 200 °C do 300 °C (uporabo energije).

Kinetika kemične toplotne črpalke z magnezijevim oksidom/vodo je bila že predstavljena [9]. Na podlagi ravnotežne krivulje je bilo ugotovljeno [9], da lahko toplotna črpalka z magnezijevim oksidom/vodo shranjuje odpadno toploto pri temperaturi 300 °C ter jo oddaja v večji količini pri temperaturah med 100 °C in 150 °C, če delujemo v podtlaku. Za boljšo ponovljivost reakcije je bil magnezijev oksid posebej pripravljen v zelo fini prašni obliki ([10] in [11]). Da bi preverili uporabnost tako pripravljenega magnezijevega oksida, smo izvedli laboratorijsko eksperimentalno napravo ([12] in [13]).

Da preverimo praktično uporabnost toplotne črpalke, je treba eksperimentalno napravo natančno pripraviti. Razlog je zahteven termodinamičen sistem v reaktorju zaradi poteka kemične reakcije, ki vključuje prenos toplote in snovi. Za delovanje eksperimentalne

0 INTRODUCTION

In this paper we attempt to show how it might be possible to use surplus heat and the reversible reaction in a chemical heat pump to enhance the energy efficiency of a cogeneration system. A chemical heat pump, which manages the heat transformation via a chemical reaction, is one of the possibilities for a heat-storage and heat-utilisation system. Because of the satisfactory repeatability of the reversible reactions between metal oxides and water and their relatively high heat density our work has focused on these reactions.

The basic reaction kinetics of the reactions between water and the oxides of magnesium and calcium have already been reported [1]. Fujii has performed basic measurements on calcium oxide as a heat-storage medium [2] and published the experimental results on hydration and dehydration process dynamics [3]. The reaction between calcium oxide and water as a heat-storage system for utilising surplus energy has also been discussed kinetically [4]. In addition, the same reaction was examined experimentally by Ogura et al. [5] as a drying system.

In contrast, Cerkvenik [6] used the reaction between calcium oxide and water for cooling purposes. Because of the low operating pressures of less than 15 mbar, which causes a less intense mass transport to the reaction sites in a reactor, and because of the low thermal conductivity of the calcium oxide, he used a novel graphite matrix structure. As a result of the graphite in the matrix the thermal conductivity of the reactor bed, which is low when only the salt is used, was increased. In other works ([7] and [8]) he used calcium oxide as a topping cycle in a cascading sorption device. With this step a higher heating/cooling ratio COP could be reached, similar to a stand-alone device. The standard operating temperatures are 500–600 °C for dehydration (heat storage) and 200°C for hydration (heat utilization).

A chemical heat pump using magnesium oxide and water was described in terms of reaction kinetics [9]. A thermobalance experiment showed that the magnesium oxide and water heat pump is capable of storing waste heat at around 300 °C and rejecting the stored heat between 100 and 150 °C for sub-atmospheric pressures. To improve the repeatability of the reaction a new reactant made from ultra-fine magnesium-oxide powder and purified water was prepared ([10] and [11]). A laboratory-scale heat pump was setup to observe the heat-storage ability for a particular type of reactant in the reactor ([12] and [13]).

A detailed bed-reactor experiment is necessary in order to evaluate the practical performance of the heat pump because the reactor bed is a complex thermodynamic system in which chemical reactions involving heat and mass transfer proceed simultaneously. The experimental heat-pump naprave v prejšnjih študijah ([12] in [13]) je bilo potrebno mehansko delo zaradi omejitve izvedbe kondenzacije med postopkom shranjevanja toplote. Da smo se izognili neekonomični rabi energije, smo rabo mehanske energije izločili. Poleg tega je nov preskus zasnovan pri visokih tlakih, ki so potrebni, če želimo kemično toplotno črpalko uporabiti v kogene-racijskem sistemu.

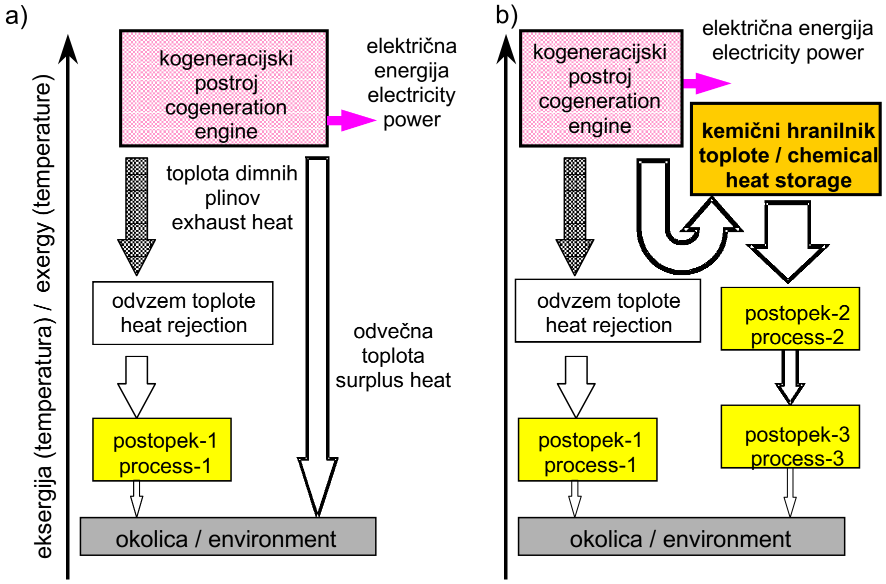
apparatus in the previous study ([12] and [13]) required mechanical work because of a design restriction on the condensation in the heat-storage process. To avoid uneconomical energy consumption, the use of mechanical work must be avoided. Moreover, a study of the heat-output operation under higher pressures is also required to expand the applicability of the heat pump for use with the cogeneration system.

1 SHRANJEVANJE ENERGIJE V KOGENERACIJSKEM SISTEMU

Namen raziskav kemičnih toplotnih črpalk je povečanje energijske učinkovitosti običajne kogeneracije z uporabo zmožnosti kemičnega shranjevanja energije. Običajni kogeneracijski postroj, ki je predstavljen na sliki 1a, uporablja dizelski agregat ali malo plinsko turbino za proizvodnjo električne energije ter toploto motorja in izpušnih plinov za proizvodnjo toplote. Ker se ponavadi poraba toplote ne ujema z enakomerno proizvodnjo električne energije, moramo večje količine odvečne toplote občasno odvajati v okolico.

1 HEAT STORAGE IN A COGENERATION SYSTEM

In our case the chemical heat pump is developed to enhance the energy efficiency of a conventional cogeneration system by using its chemical heat-storage ability. A conventional cogeneration system, which is shown in Figure 1a, uses a diesel engine or micro-gas-turbine for the electrical output and the heat from the engine or the exhaust gases for the heat output. However, because the demand for the electrical output is generally inconsistent with that of the heat output, a large amount of surplus heat is occasionally discharged into the environment.



Sl. 1. *Uporaba kemičnega toplotnega hranilnika v kogeneracijskem sistemu. (a) toplotni tokovi v običajnem kogeneracijskem sistemu, (b) toplotni tokovi v primeru kombiniranega sistema kogeneracije in kemičnega hranilnika toplote*

Fig. 1. *Application of a chemical heat-storage system in a cogeneration system: (a) thermal flow of a conventional cogeneration system, (b) thermal flow of a combined system for chemical heat storage and cogeneration*

Z uporabo kemičnega hranilnika toplote lahko povečamo učinkovitost porabe grelne toplote kogeneracijskega sistema. Predlagan sistem je predstavljen na sliki 1b. Hranilnik toplote deluje izmenično, v načinu shranjevanja in načinu sproščanja toplote. Ko poteka v reaktorju hranilnika toplote endotermni proces, hranilnik polnimo (način shranjevanja toplote) z uporabo odvečne toplote, ki je na voljo iz kogeneracijskega postroja. V načinu

With the use of chemical heat storage the energy efficiency of a cogeneration system could be enhanced. The proposed system is shown in Figure 1b. The heat storage is operated in batch mode between heat-input mode and heat-output mode. In the heat-input mode an endothermic dehydration reaction takes place in the heat-storage reactor by consuming the surplus heat that is generated in the cogeneration system. In the heat-output mode an praznjenja (sproščanje toplote) v reaktorju hranilnika toplote poteka eksotermna reakcija hidracije, zaradi česar se sprošča reakcijska toplota. Ker lahko kemični hranilnik shrani toploto za dalj časa v obliki ločenih kemičnih reaktantov in ker lahko spreminjamo temperaturo reakcije z izbiro reakcijskih pogojev, je omogočeno sproščanje toplote po potrebi na različnih temperaturnih ravneh. Rezultat tega je, da je toplota s kemičnim hranilnikom toplote bolj izkoriščena kakor z običajnim sistemom hranilnika toplote.

1. 1 Shranjevanje toplote z uporabo povračljivih reakcij

Učinkovitost sistema shranjevanja energije temelji na termodinamičnih lastnostih materialov, ki jih uporabimo za shranjevanje. V primeru uporabe reakcij v hranilnikih energije sta potrebni lastnosti velika gostota shranjevanja energije in povračljivost reakcij. Na sliki 2 smo pripravili primerjavo gostote energij fizikalnih in kemičnih sprememb, ki jih lahko uporabimo za shranjevanje energije. Pri primerjavi ne bomo upoštevali dejstva, da je gostota shranjevanja energije v vseh sistemih v veliki meri odvisna od zgradbe posod za shranjevanje energije. Vsaka dodatna masa, ki je potrebna za delovanje sistema, npr. masa prenosnika toplote ali masa sekundarne tekočine, zmanjša dejansko gostoto shranjevanja energije.

Gostota energije je v primeru kemičnih sprememb razmeroma večja od gostot v primeru fizikalnih sprememb. Kemične spremembe, npr. oksidacija, so nepovračljive ter tako težko uporabne za krožno delovanje hranilnika toplote. Zato je pričakovano, da imajo povračljive kemične reakcije potencial za shranjevanje energije v sistemih izkoriščanja energije prihodnosti.

Med fizikalnimi spremembami so adsorpcijski in absorpcijski postopki po gostoti shranjevanja energije najbolj zanimivi. Obstaja že več študij o uporabnosti zeolitov in podobnih materialov za shranjevanje grelne ali hladilne toplote ([14] in [15]). Zeoliti so zaradi relativno velike gostote energije okoli 3200 kJ/kg adsorbirane vode, dostikrat uporabljani v tovrstnih sistemih. Nasprotno je zanimanje za absorpcijski hranilnik toplote, v obliki ločenega topila in močne raztopine, manjše. V določenih primerih se ju uporablja za premagovanje nestalne razpoložljivosti pogonskega vira toplote ([16] in [17]). Da dosežemo povečanje celotne učinkovitosti kogeneracijskega sistema, lahko absorpcijski postopek uporabimo tudi drugače. Če absorpcijsko hladilno napravo uporabimo kot dopolnilni sistem k sedanjemu kogeneracijskemu sistemu ([18] in [19]), potem preraste sistem v zahtevnejši trigeneracijski sistem. Zanj je značilno, da lahko s hkratno porabo grelne toplote za ogrevanje in hlajenje, dosegamo večjo izkoriščenost razpoložljive toplote.

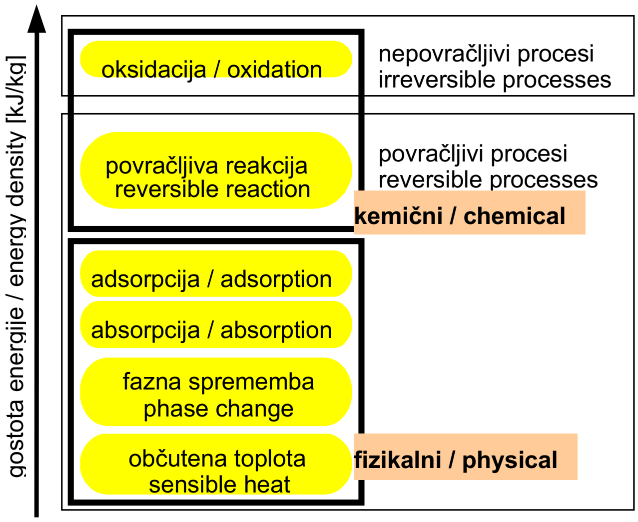
exothermic hydration reaction process takes place in the reactor generating a reaction heat output. Because the heat-storage system can store heat for a long period in the form of separated chemical reactants, and the heat-output temperature can be varied by choosing the reaction conditions, then the heat output can be supplied on demand at various temperature levels. As a consequence, the surplus heat in the chemical heat storage is utilized more efficiently than with a conventional heat-storage system.

1. 1 Heat storage using a reversible chemical reaction

The thermal performance of a heat-storage system depends on the thermodynamic properties of the heat-storage materials. The reactions in heat-storage systems require materials with a high heat-storage density and a reaction reversibility. In Figure 2 is a comparison of the energy densities of physical and chemical changes for heat storage. In this comparison we will not consider the fact that the density of the energy stored in all cases depends on the construction of the heat-storage vessels. Every additional mass that is required for the system's operation, i.e. the mass of the heat exchanger or the mass of the secondary fluid, diminishes the practical energy density.

The energy density of the chemical changes is higher than that of the physical changes. Chemical changes such as oxidation are irreversible and hard to apply in cyclic heat-storage operations. Thus, reversible chemical reactions are expected to have the most potential for heat storage in future energy-utilization systems.

Of the physical changes the adsorption and the absorption processes are, because of their high energy density, the most interesting for heat-storage systems. There were already several studies using zeolites and similar materials for hot or cold storage ([14] and [15]). Due to the relatively high energy densities of about 3200 kJ/kg of water, zeolites are often used in such systems. In contrast, the interest in absorption heat storage in the form of a separated solvent and a strong solution is less. There is, however, some research into using this kind of storage for overcoming the discontinuous availability of a driving heat source ([16] and [17]). The absorption processes can also be used in a different way to improve the overall efficiency of the cogeneration system. If they are used to complement a standard cogeneration system ([18] and [19]), the cogeneration system expands to become a more complex trigeneration system. With such systems a simultaneous heat consumption during heating and cooling, and an increased exploitation of available heat, could be achieved.



Sl. 2. *Primerjava gostote energije kemičnih in fizikalnih postopkov, ki se lahko uporabijo za shranjevanje toplote*
Fig. 2. *Comparison of the energy density of chemical and physical processes for heat storage*

Občutena toplota, ki pomeni občuteno segrevanje in ohlajanje snovi, in fazne spremembe so kot fizikalni postopki zelo razširjeni v običajnih sistemih shranjevanja toplote. Občutene toplote kot fizikalnega postopka ne moremo neposredno primerjati z drugimi postopki na sliki 2. Razlog je v tem, da je moč sistema, ki izkorišča občuteno toploto, odvisna od temperaturnega dviga toplote in ne od fizikalne ali kemične spremembe.

Pri vseh drugih fizikalnih in kemičnih postopkih je prav tako navzoč postopek občutenega segrevanja in hlajenja. Zato lahko za samostojen postopek občutene toplote predpostavimo, da je gostota energije nižja kakor pri drugih postopkih ter postopek kot tak manj primeren za velike sisteme shranjevanja toplote.

V nadaljevanju bo natančneje predstavljena povračljiva reakcija magnezijevega oksida in vode, ta se je izkazala kot najprimernejša za uporabo v kemičnem hranilniku toplote, ki bi ga lahko vezali na kogeneracijski sistem. Preostali kovinski oksidi, ki reagirajo z vodo [8], so zaradi previsokih delovnih temperatur v našem primeru neprimerni.

1. 2 Kemična toplotna črpalka z magnezijevim oksidom in vodo

Kemično toplotno črpalko, ki uporablja povračljivo reakcijo magnezijevega oksida z vodo za shranjevanje in izkoriščanje energije, je teoretično raziskovalo že več avtorjev ([9], [20] in [21]). Kemični postopek v tovrstni toplotni črpalki temelji na naslednjem ravnotežju:

Sensible heat (Fig. 2), which represents the sensible heating and cooling of matter, and the phase changes, is usually used in conventional heat-storage systems. Sensible heat, as a physical process, cannot be directly compared with the other processes in Figure 2. The reason is that the power of the system that uses the sensible heat depends on the temperature increase and not on a physical or chemical change.

In the same way, sensible heating and cooling are present in all other processes. Therefore, we can assume that for an independent sensible process that the energy density is low in comparison with the other processes and that the process is less suitable for larger storage systems.

In the following, the reversible magnesium oxide and water reaction, which is found to be the most appropriate for use in the heat-storage system as part of a cogeneration system, will be presented in more detail. This is due to the fact that the operating temperatures in the case of other metal-oxide reactions with water are far above the level that is required for a cogeneration system [8].

1. 2 A chemical heat pump using magnesium oxide and water

Chemical heat pumps that use a reversible magnesium oxide and water reaction to promote heat storage and energy utilisation have been examined by different authors ([9], [20] and [21]). The chemical process in such a heat pump is based on the following equilibrium:

$$MgO(s)+H_2O(g)\leftrightarrow Mg(OH)_2(s) \qquad \Delta H^\circ_1 = -81,0\ \mathrm{kJ/mol} \qquad (1),$$

$$H_2O(g)\leftrightarrow H_2O(l) \qquad \Delta H^\circ_2 = -40,0\ \mathrm{kJ/mol} \qquad (2).$$

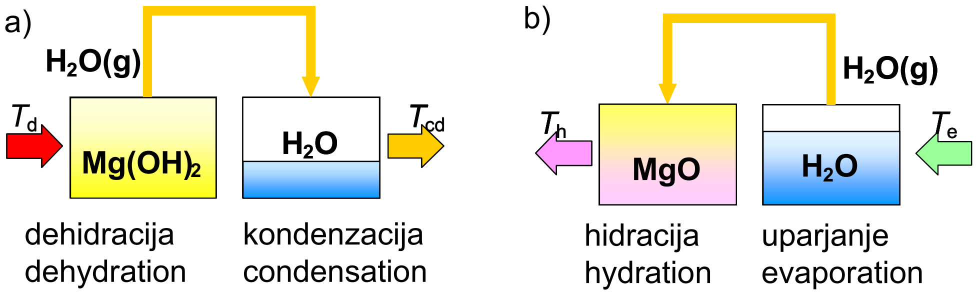
Toplotna črpalka omogoča shranjevanje grelne energije med postopkom dehidracije magnezijevega

The heat pump enables thermal energy to be stored via the dehydration of magnesium hidroksida (smer v desno, enačba 1) in glede na potrebe sproščanje shranjevane energije s hidracijo magnezijevega oksida (smer v levo, enačba 1). Načelo delovanja je predstavljeno na sliki 3. Toplotna črpalka v osnovi sestoji iz dveh delov, reaktorja z magnezijevo soljo ter hranilnika z vodo.

Med shranjevanjem toplote (sl. 3a) magnezijev hidroksid v reaktorju dehidriramo z odvečno toploto na temperaturni ravni T_d. Para, ki se sprošča med dehidracijo, kondenzira v hranilniku z vodo na temperaturni ravni T_{cd}. Med sproščanjem toplote (sl. 3b) poteka v reaktorju hidracija magnezijevega oksida, pri čemer se sprošča toplota na temperaturni ravni T_h. V uparjalniku – hranilniku z vodo, pa se voda uparja pri temperaturi T_{ev}, za kar lahko uporabimo nizkotemperaturno toploto, npr. toploto zunanjega zraka ali izpušnih plinov.

hydroxide (right direction, Equation 1) and then released on demand via the hydration of magnesium oxide (left direction, Equation 1). The principle of operation is shown in Figure 3. The heat pump consists of a reactor with a magnesium salt and a water reservoir.

In heat-storage mode (Figure 3a) the magnesium hydroxide ($Mg(OH)_2$) is dehydrated by surplus heat at the temperature T_d. The generated vapour is then condensed in the reservoir at T_{cd}. In heat-output mode (Fig. 3b) the magnesium oxide is hydrated. The water vapour that is used in the reaction evaporates in the reservoir at the temperature T_{ev}. A low-temperature heat source, which is required for the evaporation process, could be obtained from the surrounding air.



Sl. 3. *Delovanje kemične toplotne črpalke: (a) shranjevanje toplote, (b) sproščanje toplote*
Fig. 3. *Operation of chemical heat pump: (a) heat-storage mode, (b) heat-output mode*

Prednosti pred običajnim hranilnikom toplote sta višja temperatura in večja gostota shranjevanja odvečne toplote ali toplote dimnih plinov, zanesljivost, cenovna in ekološka sprejemljivost reaktantov ter dolgotrajno shranjevanje toplote. Pri tem 'toploto' hranimo v obliki ločenih reaktantov, npr. magnezijevega oksida in vode, ki sta ob ponovnem stiku po daljšem obdobju zmožna takojšnje reakcije.

2 PRESKUS

Eksperimentalna, toplotno gnana kemična toplotna črpalka, ki je bila sestavljena v Raziskovalnem laboratoriju za nuklearne reaktorje na Japonskem, je predstavljena na sliki 4. Toplotna črpalka se sestoji iz reaktorja (1) v reakcijski komori in vodnega rezervoarja (10). Posodi sta povezani z gibljivimi cevmi (6) in zapornim ventilom (8). Temperaturi v obeh posodah krmilimo z električnimi grelniki (4) in (12) in dodatnim cevnim prenosnikom toplote (11). Para potuje med posodama samo zaradi tlačne razlike. Reakcijska komora je dodatno izolirana in ogrevana, kar omogoča krmiljenje zunanje temperature reaktorja.

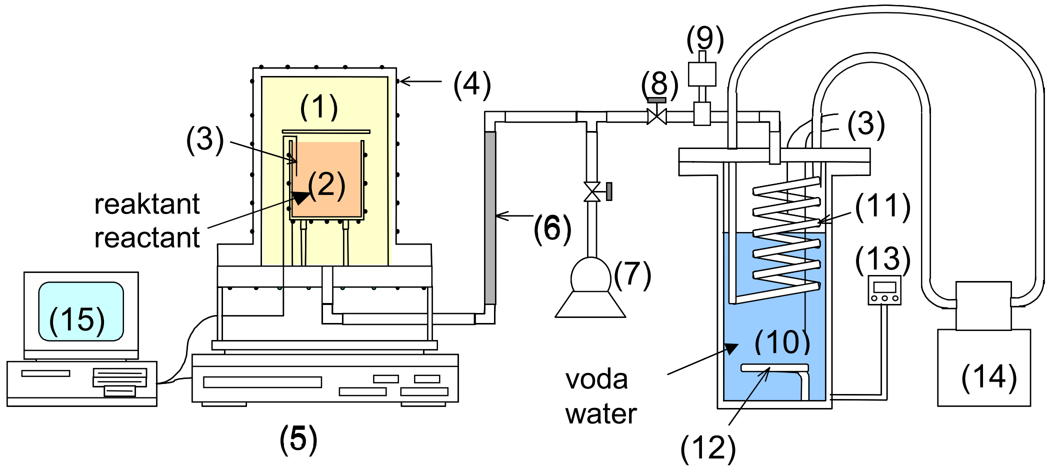
S spreminjanjem tlaka se spreminja tudi togost gibljive cevi (6), kar vpliva na merjenje teže reaktorja.

The advantages of a chemical heat pump are the higher temperatures and energy densities of the stored heat; this is combined with reactant materials that are safe, economical and environmentally friendly. Besides this, a longer-term heat storage is possible than with conventional heat storage. This means that the 'heat' is stored in the form of separated reactants, e.g. magnesium oxide and water, which are capable of instant reaction when they are brought into contact after a long period.

2 EXPERIMENT

A schematic diagram of our experimental, thermally driven chemical heat pump, which was built at the Research Laboratory for Nuclear Reactors, in Japan, is shown in Figure 4. The heat pump consists of a reactor (1) in a reaction chamber and a water reservoir (10). Both vessels are connected with a flexible tube (6) and a stop valve (8). The temperatures in the vessels are controlled with electric heaters (4) and (12). In addition, the temperature and thus the pressure in the reservoir are controlled with an additional heat-exchanger tube (11). The vapour is transported between the vessels through the stop valve by the pressure difference alone. The reaction chamber is additionally insulated and externally heated, which allows us to control the external temperature of the reactor.

By changing the pressure the stiffness of the hose (6) changes and influences the weight



Sl. 4. *Shema eksperimentalne toplotno gnane kemične toplotne črpalke z magnezijevim oksidom in vodo: (1) reaktor v reakcijski posodi, (2) reaktant - reaktorska sredica, (3) termoelementi, (4) grelnik, (5) tehtnica, (6) gibljiva cev, (7) vakuumska črpalka, (8) zaporni ventil, (9) varnostni ventil, (10) hranilnik vode, (11) grelna cev, (12) grelnik, (13) tlačni pretvornik, (14) termostatirana kopel, (15) računalnik*

Fig. 4. *Schematic diagram of an experimental, thermally driven, magnesium oxide and water, chemical heat pump: (1) reactor in a reaction chamber, (2) reactant – reactor bed, (3) thermocouples, (4) electric heater, (5) balance, (6) hose, (7) vacuum pump, (8) stop valve, (9) safety valve, (10) water reservoir, (11) heating tube, (12) electric heater, (13) pressure transducer, (14) thermostat bath, (15) computer*

Da smo se izognili dodatni merilni negotovosti, smo v prejšnjih meritvah določili odvisnost med spremembo teže ter obratovalnim tlakom. Reagiran delež smo izračunali po popravku izmerjene teže glede na obratovalni tlak.

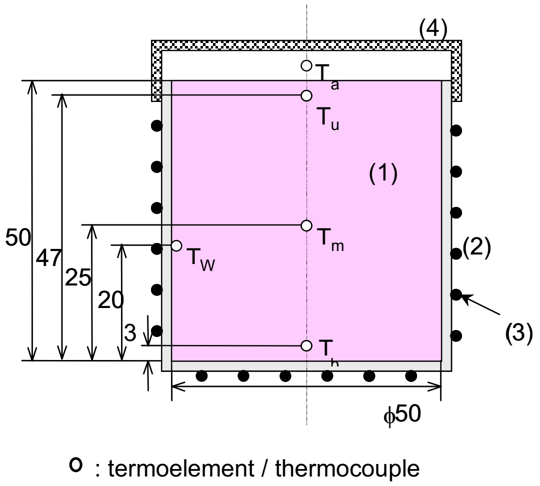
Na sliki 5 je predstavljen valjasti reaktor z reaktorsko sredico (2). Reaktor je narejen iz nerjavnega jekla, z notranjim premerom 50 mm ter višino 50 mm. Ob postavitvi je bilo v reaktorju 53g $Mg(OH)_2$ s povprečnim premerom zrn 1,5 mm. Temperaturo v reaktorju smo vzdrževali z električnim grelnikom, ki je nameščen na zunanji površini reaktorja (3 na sliki 5). Termoelementi so nameščeni na različnih mestih v reaktorski sredici, kakor je prikazano na sliki 5. Za zmanjšanje toplotnih izgub smo reaktor pokrili z izolacijskim pokrovom. Tlak v reaktorju oz. tlak pare, ki smo ga merili s tlačnim pretvornikom, smo vzdrževali s krmiljenjem temperature v hranilniku z vodo. Zato smo uporabili dodaten prenosnik toplote in grelnik (11 in 12 na sliki 4). Da smo lahko določili hitrost reakcije, smo med meritvami s tehtnico merili spremembe teže reaktorja (5 na sliki 4).

Magnezijev hidroksid, ki smo ga uporabili ob postavitvi preskusne naprave, smo pripravili iz zelo drobnega magnezijevega oksida v obliki prahu (povprečen premer delcev: 10nm, UBE Materials Co. Ltd.) ter vode. Prah magnezijevega oksida smo hidrirali s prečiščeno destilirano vodo ter zmleli v krogelnem mlinu. Po postopku hidracije smo gosto zmes posušili ter nastale kosmiče presejali.

measurement. To eliminate the additional measurement uncertainty we separately determined the weight change that is induced by a pressure change and by operational pressure in earlier measurements. The reacted fraction is calculated after the weight change is corrected with regard to the operational pressure.

In Figure 5 a detail of the cylindrical, packed-bed reactor (2) is presented. The reactor is made of stainless steel with an inner diameter of 50 mm and a height of 50 mm. At the beginning 53 g of $Mg(OH)_2$ (average grain diameter of 1.5 mm) was charged in the reactor. The reactor's temperature was maintained independently by the electric heater, which is mounted on the outer surface of the reactor (depicted as (3) in Fig. 5). Thermocouples were installed at various points in the reactor bed in order to measure the change in the bed temperature. The positions and notations of the thermocouples are depicted in Figure 5. A cap (4) was installed to enhance the thermal insulation of the upper bed surface. The reaction pressure, i.e. the pressure of the vapour, was monitored by a pressure transducer. The pressure level was maintained by controlling the temperature of the reservoir water using a heat-exchanger tube and an electric heater: (11) and (12) in Fig. 4. The weight change of the reactor during the measurements was measured directly with a balance: (5) in Fig. 4.

The magnesium hydroxide that was used during the setting-up of the experimental device was produced from an ultra-fine magnesium-oxide powder (avg. particle diameter: 10 nm, UBE Materials Co. Ltd.) and water. The ultra-fine oxide powder was hydrated with purified water in a ball mill. After the hydration process, the pasty product was dried and the resulting flakes were sieved.



Sl. 5. *Skica reaktorja: (1) reakcijska sredica - reaktant, (2) posoda reaktorja, (3) električni grelnik, (4) izolacijski pokrov*

Fig. 5. *Packed bed reactor: (1) reactor bed - reactant, (2) reactor, (3) electric heater, (4) insulation cap*

2. 1 Preskusni postopek

Vsaka meritev je bila sestavljena iz večkratnega ponavljanja kroga delovanja hranilnika toplote, postopkov dehidracije in hidracije. Zaradi poprej preverjene stabilne reaktivnosti izbranih snovi, smo se pri vsaki meritvi omejili na 24 zaporednih postopkov dehidracije in hidracije. Ker smo v prvih petih postopkih izmerili manjši padec reaktivnosti, smo v analizi rezultatov primerjali reaktivnosti med 6. in 20. postopkom meritve. Meritve smo izvedli v različnih razmerah reakcije.

Razen za začetno vakuumiranje preostalih plinov iz naprave, sistem ni potreboval dodatnega mehanskega dela za črpanje.

V načinu shranjevanja toplote smo $Mg(OH)_2$ v reaktorju dehidrirali. Zaporni ventil (8 na sliki 4) je bil na začetku zaprt. S kroženjem hladilne vode prek prenosnika toplote v rezervoarju z vodo smo krmilili tlak vodne pare v krmilniku ter posredno tudi tlak dehidracije. Temperaturo reaktorja smo krmilili z električnim grelnikom na zunanji strani reaktorja. Kot rezultat dehidracije sta nastala MgO in voda. Po odprtju zapornega ventila smo nastalo vodno paro kondenzirali v hranilniku z vodo. Na koncu reakcije smo zaprli zaporni ventil. Napredovanje reakcije in razmere v napravi smo merili s tehtnico in vgrajenimi termoelementi.

Pri načinu praznjenja hranilnika (faza hidracije), smo hranilnik z vodo greli, zato da smo dosegli načrtovano tlačno raven reakcije. Temperaturo reaktorja in njegove okolice smo vzdrževali pri načrtovani temperaturi hidracije, ki je bila za 25 °C višja od temperature nasičenja vode, zato da smo se izognili kondenzaciji pare v napravi. Ko sta temperaturi reaktorja in hranilnika dosegli ustaljeno stanje, smo z odprtjem zapornega ventila omogočili prenos pare iz rezervoarja do reaktorja. Magnezijev oksid je reagiral s paro, pri čemer se je sprostila reakcijska toplota.

2. 1 Experimental procedure

Each measurement consisted of an operational cycle: the dehydration and hydration process. Because the chosen reactants were found to be stable [11], we limited the experiment to 24 successive cycles of dehydration and hydration. Because we measured a slight reactivity drop during the first 5 cycles we compared the reactivities of the 6th to the 20th cycle. The measurements were conducted for different reaction conditions.

Apart from an initial removal of residual gases from the device using a vacuum pump, the system did not require any additional mechanical pump work.

In heat-storage mode the $Mg(OH)_2$ is dehydrated. The stop valve, (8) in Fig. 4, was initially closed and a water coolant was circulated in the heat-exchanger tube in the water reservoir. The dehydration pressure was controlled with the water-vapour pressure in the reservoir. The reactor temperature was controlled with an external electric heater. As a result of the dehydration process, MgO and water are generated. When the stop valve was opened, the generated vapour condensed in the water reservoir. At the end of the reaction the stop valve was closed. The reaction progress and the conditions in the device were measured with the balance and the thermocouples.

In the heat-output (hydration) mode the water reservoir was heated to generate a specified reaction vapour pressure. The reactor and reaction-chamber temperatures were maintained at a predetermined hydration temperature, which is 25°C higher than the vapour temperature, in order to avoid vapour condensation. After the reactor and the reservoir attained a steady state the steam generated in the reservoir was introduced into the reactor. The magnesium oxide reacted with the steam and the heat output was generated.

Sprememba teže reaktorja Δm je posledica reakcijskega postopka v reaktorju. To je količina vodne pare, ki reagira, ali se sprosti v reakcijski posodi. Tako je reagirani molski delež x za postopek dehidracije določen kot:

The reactor weight change Δm is due to the reaction process in the reactor. It represents the quantity of water vapour that is reacted or released in the reactor. Thus, the molar reacted fraction x is, for the dehydration process, defined as follows:

$$x = 1 + \frac{\left(\Delta m / M_{\mathrm{H2O}}\right)}{\left(m_{\mathrm{Mg(OH)2}} / M_{\mathrm{Mg(OH)2}}\right)} \qquad (3),$$

kjer je $m_{\mathrm{Mg(OH)2}}$ količina magnezijevega hidroksida ob polnjenju reaktorja. Dehidracija vzorcev ni potekala do x=0,0, temveč do x=0,2, zaradi strukturne vode v reaktantu. Fazi dehidracije je sledila faza hidracije. Konec hidracije je bila pri vrednostih reagiranega deleža okoli x=0,8. Da smo reaktivnost magnezijevih soli objektivno prikazali, smo določili razliko v reagiranem deležu Δx:

$m_{Mg(OH)2}$ is the initial charged weight of magnesium hydroxide in the reactor bed. The dehydration of samples did not proceed to x=0.0 due to the existence of structural water in the reactant. The reacted fraction at the end of the dehydration process, which is also the starting point for the hydration process, is around x=0.2. In order to obtain an objective value for the reactivity of the magnesium salts a molar reacted fraction change Δx is defined:

$$\Delta x = x - x_{\mathrm{ini}} \qquad (4),$$

kjer je x_{ini} začeten reagiran delež soli v določenem reakcijskem ciklu.

The x_{ini} is the initial reacted fraction of the reaction cycle.

3 ANALIZA REZULTATOV MERITEV

3.1 Postopek dehidracije

Notranjo temperaturo stene reaktorja T_w smo krmilili z zunanjim električnim grelnikom na nastavljeno temperaturno raven dehidracije T_d. Na sliki 6 so prikazani rezultati meritev temperatur in razlike reagiranega deleža Δx v reaktorju med postopkom dehidracije: pri temperaturi dehidracije 400°C, temperaturi kondenzacije T_{cd}=20°C ter temperaturi v reakcijski komori T_{rc}=100°C. Tlak reakcije P_d smo s parnim tlakom v rezervoarju vzdrževali pri vrednostih pod 3 kPa.

Temperatura na notranji steni reaktorja T_w se je relativno hitro povišala do vrednosti 400 °C. Zaradi nizke toplotne prevodnosti reaktanta se pojavi temperaturna razlika med steno T_w in notranjostjo sredice T_m in T_b. Začetek procesa dehidracije je pri temperaturi 280 °C. Po preteku 35 minut od začetka faze je opazno zmanjšanje gradientov temperatur v notranjosti sredice, ker je temperatura stene reaktorja T_w dosegla krmiljeno vrednost. Ko se postopek dehidracije bliža koncu, se toplota ogrevanja porablja bolj ali manj za občuteno gretje reaktorske sredice. Tako sta temperaturi v notranjosti reakcijske sredice proti koncu že višji kakor temperaturi na vrhu reaktorja T_a in T_u, ki nista pod neposrednim vplivom ogrevanja z grelnikom.

Vpliv temperature kondenzacije T_{cd} na reaktivnost pri enaki temperaturi 400 °C je predstavljen na sliki 7. Tlak postopka dehidracije P_{cd} ustreza temperaturi kondenzacije T_{cd}. Sprememba reagiranega deleža Δx je hitrejša pri nižjih T_{cd}, zaradi večje tlačne razlike med ravnotežnim tlakom in tlakom kondenzacije. Kljub temu je dolžina faze dehidracije v vseh treh primerih podobna ter zato razlika v reaktivnosti premajhna za praktično uporabo. Višje

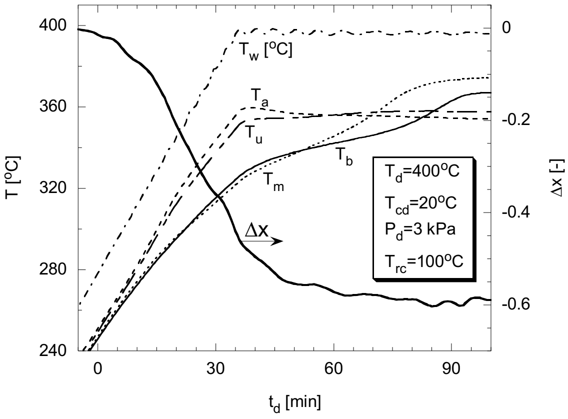
3 ANALYSIS OF MEASUREMENT RESULTS

3. 1 Dehydration process

During the dehydration process the inner wall temperature T_w was controlled with the electric heater at the dehydration temperature of T_d. In Figure 6 are the results for the temperatures in the reactor bed and for the difference in the reacted quantity Δx. The measurement conditions were: dehydration temperature T_d of 400°C, condensation temperature T_{cd} of 20°C and inner temperature of reaction chamber T_{rc}=100°C. The reaction pressure P_d was kept below 3 kPa by the vapour pressure in the reservoir.

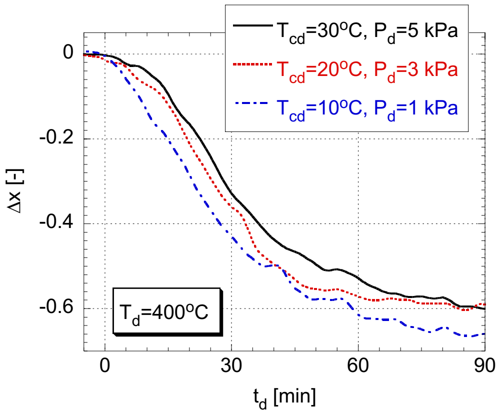
The inner wall temperature T_w rose to a T_d of 400°C relatively rapidly. Because of the low thermal conductivity of the reactant, a temperature difference arose between the wall T_w and inner bed T_m and T_b. The dehydration process started at around 280°C. The inner-bed temperature change slowed down after the first 35 minutes because the temperature of the reactor wall T_w reached the controlled value. As the dehydration approached completion the electric heating was greater than the heat consumed for the dehydration. As a result, the inner-bed temperature rose and eventually finally became higher than the upper-bed temperatures T_a and T_u.

The effect of condensation temperature T_{cd} on the reactivity under the same dehydration temperature of 400°C is shown in Figure 7. The dehydration pressure P_{cd} corresponds to the condensation temperature T_{cd}. The Δx change is faster at lower T_{cd}, due to a greater difference between the equilibrium and condensation pressures. However, the duration of the dehydration phase was in all three cases similar and thus the reactivity difference between them is too small to be of



Sl. 6. *Eksperimentalni rezultati dehidracije magnezijevega hidroksida pri temperaturi dehidracije reaktorja 400 °C, temperaturi kondenzacije 20 °C*

Fig. 6. *Experimental result for the magnesium hydroxide dehydration process, dehydration temperature of 400°C, condensation temperature of 20°C*



Sl. 7. *Vpliv tlaka dehidracije na reaktivnost pri temperaturi 400 °C*

Fig. 7. *Effect of dehydration pressure on the reactivity at 400 °C*

temperature kondenzacije imajo prednost za praktično obratovanje. V primeru temperature kondenzacije okoli 40 do 60 °C bi bilo mogoče kot nizkotemperaturni vir toplote uporabiti tudi sproščeno toploto kondenzacije.

Če pogledamo rezultate meritev pri T_{cd}=10 °C, ki je nižja od temperature okolice 20 °C, lahko ugotovimo odstopanje reagiranega deleža od pričakovane vrednosti. Proti koncu postopka dehidracije (t_d=60 do 90 min, slika 7) se pojavi odstopanje glede na preostale meritve, zaradi nestabilnih razmer pri kondenzaciji v hranilniku z vodo. Da smo se temu izognili, smo upoštevali le rezultate meritev do 60 minut delovanja.

3. 2 Postopek hidracije

Postopek hidracije, katerega rezultati meritev so predstavljeni na sliki 8, je potekal pri temperaturi uparjanja 100 °C, temu ustreznemu tlaku P_h=101,3 kPa ter začetni temperaturi reaktorja T_h=125 °C. Temperaturo notranje stene reaktorja T_w in notranjo atmosfersko temperaturo T_a smo krmilili na temperaturno raven T_h. V začetku faze hidracije je para hitro prodirala v reaktorsko sredico, zaradi velike tlačne razlike med P_d in P_h. Reakcija poteka hitro, kar je razvidno iz velikih količin reakcijske toplote ter hitrega dviga temperature reaktorja. Ker para, ki je relativno hladnejša kakor reakcijska sredica, vstopa z vrha posode in se med potjo k dnu posode segreva, sta temperaturi v spodnjem in srednjem sloju T_b in T_m višji od temperature v zgornjem sloju reaktorske sredice. Dodaten razlog za razliko v temperaturi je tudi slabša toplotna izoliranost pokrova posode. Če podrobneje pogledamo, lahko opazimo, da najvišjo

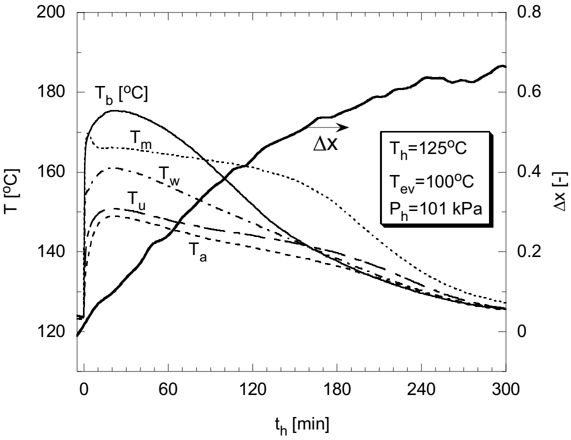
any practical use. A high condensation temperature is better for practical operation. With a condensation temperature of 40–60 °C it could be possible to utilize the heat of condensation as an additional low-temperature heat source.

If we look at the results for T_{cd}=10 °C, which is lower than the ambient temperature of 20 °C, a deviation of the reacted fraction from the expected results can be seen. At the end of the dehydration phase (t_d= 60-90 min., Figure 7) the deviation from the other measurements occurs as a result of the unstable condensation condition in the water reservoir. To avoid this, we only considered the results obtained during the initial 60 minutes of operation.

3. 2 Hydration process

The results of the hydration process are presented in Figure 8. The measurement was taken at the evaporation temperature T_{ev} of 100°C, the corresponding vapour pressure P_h of 101 kPa and an initial reactor-bed temperature T_h of 125°C. The initial temperature of the inner wall of the reactor T_w and the atmospheric temperature in the reactor T_a are controlled at T_h. At the beginning of the hydration phase the vapour diffuses rapidly into the bed due to a large pressure difference between P_d and P_h. The reaction occurs rapidly, which results in a large heat of reaction and a quick rise in the reactor temperature. Because the vapour, which is colder than the bed, enters from the top of the bed and heats up when it is transported by the diffusion to the lower layers, the temperatures T_b and T_m are higher than the temperature of the upper layer T_u. Another reason for the difference in the temperatures is the less effective thermal insulation of the reactor cover.

temperaturo dosežemo najprej v zgornjem sloju. To lahko razložimo z dinamiko reakcijskega postopka v različnih slojih reaktorske sredice [6]. Zaradi dodatnega upora prenosu snovi v navpični smeri sredice, lahko sklepamo, da para najprej v večjih količinah reagira v zgornjih plasteh. Kakor je tudi razvidno s slike 8, se temperatura v spodnji plasti T_b hitreje bliža zunanji temperaturi reaktorja T_h kakor temperaturi v srednji ali zgornji plasti reaktorske sredice. To lahko pripišemo namestitvi termoelementov. S slike 4 je razvidno, da je termoelement v spodnji plasti bližje zunanji steni reaktorja.



Sl. 8. *Rezultati meritev postopka hidracije magnezijevega oksida pri temperaturi uparjanja 100 °C in začetni temperaturi reaktorja T_h=125 °C*

Fig. 8. R*esults for a magnesium-oxide hydration process at an evaporation temperature of 100°C and initial bed temperature of 125°C*

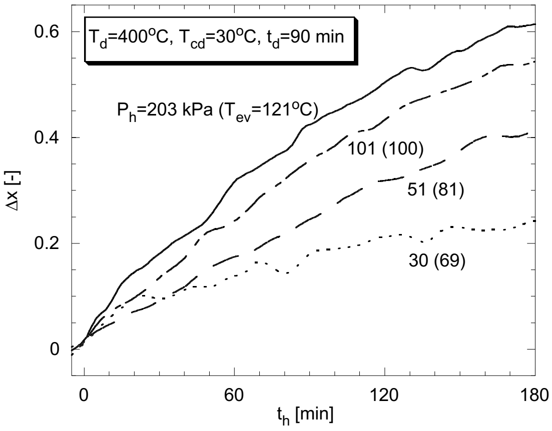
Vpliv tlaka hidracije na reaktivnost v enakih razmerah hidracije je predstavljen na sliki 9. Kakor lahko vidimo, je z višjim tlakom hidracije gradient spremembe reagiranega deleža Δx večji. To pomeni, da se postopek hidracije pri višjih tlakih odvija hitreje. Podobno kakor prej je pri višjem tlaku razlika med ravnotežnim in tlakom vodne pare večja, kar vpliva na hitrost reakcije.

Temperaturo v srednjem sloju T_m lahko vzamemo kot reprezentativno za celotni reaktor, zato jo bomo označili s T_h. Na sliki 10 je predstavljena odvisnost povprečne temperature reaktorske sredice T_h od tlaka hidracije P_h. Opazimo, da je z višjim tlakom temperatura v notranjosti reaktorja višja.

Pri tlaku 203 kPa smo dobili toploto na temperaturni ravni 190 °C. To toploto lahko npr. uporabimo za pogon absorpcijskega hladilnika z dvojnim učinkom. Pri nižjem tlaku 30 kPa pa smo dobili toploto pri 100 °C, ki jo lahko uporabimo kot vir toplote za sistem daljinskega ogrevanja.

Temperaturni dvig, razlika med temperaturo hidracije in temperaturo uparjanja, znaša med 40 in 70 K ter dosega vrednosti preostalih toplotnih črpalk.

A closer look reveals that the maximum temperature is reached in the upper layer first. This can be explained by the reaction process dynamics in the different layers of the reactor bed [6]. Due to the additional mass-transfer resistance in the vertical direction we can assume that the vapour reacts in larger quantities in the upper layers first. Figure 8 shows that the temperature of the bottom layer T_b tends to increase more quickly than the temperature of the middle layer T_m to the external temperature of the reactor T_{rc}. This is mainly because the position of the thermocouple in the bottom layer is closer to the reactor wall than the other two thermocouples (T_m, T_u, Figure 4).



Sl. 9. *Vpliv tlaka hidracije na reaktivnost v enakih razmerah hidracije*

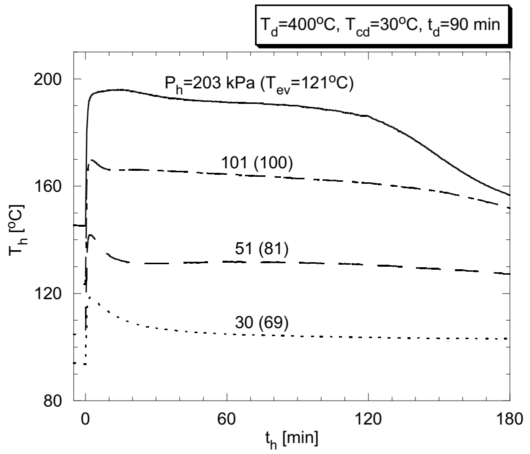
Fig. 9. *Effect of hydration pressure on the reactivity under the same dehydration condition*

The effect of the hydration pressure on the reactivity under the same dehydration condition is shown in Figure 9. It is clear that a higher hydration pressure represents a higher reacted fraction change Δx, which means that the reaction process occurs more quickly at higher pressures. Like before, at higher pressures the difference between the equilibrium and hydration pressure is greater, which has an influence on the reactivity.

The temperature in the middle layer T_m could be taken as a representative temperature for the whole reactor. In Figure 10 the dependency of the representative bed temperature on the hydration pressure is shown. A higher temperature of the reactor bed is attained at a higher pressure.

We can see that at a pressure of 203 kPa heat at over 190 °C is generated. This heat flow can be used, for example, as a driving heat source for a double-effect absorption chiller. At a lower pressure of 30 kPa a heat output at 100 °C is produced. In this case the heat output could be the source for a district-heating system.

The temperature rise, the difference between the temperature of hydration and the temperature of evaporation, amounts to 40–70 K, which is similar to



Sl. 10. *Vpliv tlaka hidracije na temperaturo, ki smo jo merili v srednjem sloju sredice*
Fig. 10. *Effect of hydration pressure on hydration temperature, measured in the middle part of the reactor bed*

Razvidno je, da lahko s postopkom hidracije pridobivamo toploto v širokem temperaturnem razponu s spreminjanjem tlaka v uparjalniku kemične toplotne črpalke. To lahko dosežemo s spreminjanjem temperaturni ravni vira toplote za uparjalnik, za kar lahko še dodatno izkoristimo toploto izpušnih plinov.

other heat pumps. It is clear that the heat that is rejected from the hydration process could be generated over a wide range of temperatures simply by varying the pressure in the evaporator of the chemical heat pump. This can be achieved by varying the heat-source temperature of the evaporator, where heat from the exhaust gases could also be used.

3. 3 Učinkovitost reaktorske sredice

3. 3 Thermal performance of the reactor bed

Učinkovitost toplotne črpalke kot hranilnika toplote, ki temelji na meritvah reaktorske sredice, smo ocenili z določitvijo povprečne specifične toplotne moči reaktorja w_{mean}. Najprej smo določili toploto iz reaktorja na enoto teže Mg(OH)$_2$, ki smo ga na začetku vstavili v reaktor q. Ta je določena z enačbo:

The thermal performance of the heat pump as a heat store, which is based on measurements of the reactor bed, was evaluated to determine the reactor's mean heat-output rate w_{mean}. First, the heat-output from the reactor per unit weight of initially charged Mg(OH)$_2$ q is determined. It is defined as:

$$q = (\Delta H_1^\circ / M) \int_0^{t_\mathrm{h}} x dt_\mathrm{h} \qquad (5).$$

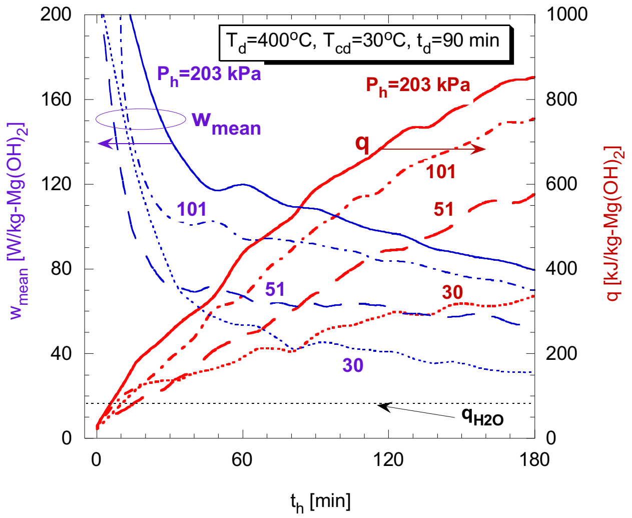
Povprečna specifična toplotna moč reaktorja w_{mean} je določena kot:

The mean heat output rate w_{mean} is expressed as:

$$w_\mathrm{mean} = \frac{q}{t_\mathrm{h}} \qquad (6).$$

Časovna odvisnost q in w_{mean} pri različnih tlakih hidracije je predstavljena na sliki 11. Za prvih 60 minut smo pri tlaku 203 kPa določili povprečno specifično toplotno moč reaktorja w_{mean}=119 W/kg ter skupno q=430 kJ/kg toplote. Če bi shranili toploto v obliki občutene toplote med 70 °C in 90 °C v vodnem hranilniku toplote, bi znašala specifična toplotna moč q_{H2O}=83 kJ/kg (črtkana črta na sliki 11). Kakor je razvidno, je gostota shranjevanja energije kemične toplotne črpalke z magnezijevim oksidom okoli 5-krat večja od običajnega vodnega hranilnika toplote, če bi trajanje postopka hidracije omejili na 60 minut. Poleg tega je tudi temperaturna raven toplote iz kemične toplotne črpalke okoli 170 °C do 200°C, kar je tudi do dvakrat višje od običajnih vodnih hranilnikov. Prednost kemične toplotne črpalke je tudi možnost shranjevanja toplote za daljše obdobje v obliki ločenih

The result of changing q and w_{mean} during the operation and for different hydration pressures is shown in Figure 11. At a pressure of 203 kPa, a mean heat-output rate of w_{mean}=119 W/kg and a gross heat output of q=430 kJ/kg are calculated for the initial 60 minutes. When the heat is stored in a conventional, sensible heat water-storage system between 70°C and 90°C, the heat output q_{H2O} amounts to about 83 kJ/kg (dashed line in Figure 11). This means that the heat-storage density of the measured chemical heat storage is about five times that of the water-storage system if the hydration process is limited to 60 minutes. The output temperature of the chemical heat pump is around 170–200 °C, which is more than twice as high as standard water-storage systems. The chemical heat pump can also store heat for a longer period in the form of separated reactants: magnesium oxide and



Sl. 11. *Toplotna učinkovitost postopka hidracije v kemični toplotni črpalki*
Fig. 11. *Hydration performance of the chemical heat pump*

reaktantov, magnezijevega oksida in vode. Poleg tega lahko toploto dobavljamo na različnih temperaturnih ravneh, odvisno od tlaka uparjanja.

V primeru uporabe naprave za pridobivanje hladilne toplote, kar bi kogeneracijski sistem dogradilo v trigeneracijski sistem, bi bilo treba napravo izvesti z dvema reaktorjema, v katerih bi potekala nasprotni reakciji ([17] in [22]). Poleg tega bi morali obe reakciji trajati približno enako dolgo, da bi lahko sistem deloval čim učinkoviteje ter omogočal toploto shranjevati in uporabljati ves čas delovanja. V našem primeru bi bilo treba postopek hidracije dodatno pospešiti, kar lahko dosežemo s spremembo v izvedbi reaktorske sredice.

4 SKLEP

V tem delu je eksperimentalno preverjena izvedljivost toplotno gnane kemične toplotne črpalke. S toplotno črpalko smo želeli povečati možnosti za izkoriščanje odvečne toplote iz kogeneracijskih postrojenj. Pričakujemo, da se bodo kemične toplotne črpalke uporabljale za izravnavanje obremenitev običajnih kogeneracijskih sistemov, ker pokrivajo temperaturno področje dimnih plinov kogeneracijskega postrojenja. Odvečna toplota bo v času manjše porabe grelne toplote shranjena pri temperaturi 300 °C do 400 °C. V času koničnih obremenitev, bi toploto hidracije po potrebi sprostili pri temperaturi okoli 150 °C do 200 °C.

Iz izmerkov smo ugotovili, da lahko pri tlaku uparjanja 203 kPa s postopkom hidracije pridobivamo toploto pri temperaturi okoli 190 °C. V primeru višjih tlakov bi lahko dosegli še višje temperaturne ravni, vendar samo pod pogojem, da imamo na voljo dodaten toplotni vir za uparjanje vode.

Kakor je razvidno iz rezultatov, traja faza hidracije vsaj dvakrat dalj kakor faza dehidracije. Če želimo kemični hranilnik toplote praktično uporabiti,

water. In addition, this heat can be supplied at various temperatures, depending on the evaporation pressure.

When using the device for continuous cold production, which would upgrade the cogeneration system to a trigeneration system, the device should have two reactors, which would operate with opposite reactions ([17] and [22]). In addition, the duration of both reactions should be similar, so that the cold can be produced more effectively over the whole operating time. In our case the hydration phase should be additionally intensified, which could be done with a change to the reactor bed.

4 CONCLUSION

In this paper the operation of a thermally driven heat pump is demonstrated experimentally. The heat pump is expected to make better use of the surplus heat that is generated in the cogeneration system. The proposed chemical heat pump is expected to act as a heat-storage system to even out the load of a common cogeneration system because it can cover the temperature range of exhaust gases from the cogeneration engines. The surplus heat, which is generated during the period of low heat demand, would be stored at 300 °C to 400 °C, whereas the heat from the hydration process would be released during the peak-load periods at a temperature of about 150–200 °C.

At a hydration pressure of 203 kPa a heat output above 190 °C is measured experimentally. In the case of higher pressures, higher temperature levels would be achieved, but only if an additional heat source is available for the evaporation process.

As we can see from the results, the hydration process is at least twice as long as the decomposition process. Therefore, to make practical use of the chemical heat storage, the dynamics of the heat storage and heat utilisation have to be better optimised. A proper je treba dinamiko shranjevanja in sproščanja toplote optimirati. S pravilno izvedbo sredice, kar je izhodišče za nadaljnje raziskave, je mogoče oba postopka v napravi uravnovesiti ter tako upravičiti namembnost naprave.

Po okvirni primerjavi z običajnim vodnim hranilnikom toplote smo ugotovili okoli 5-krat večjo gostoto shranjevanja energije, višje temperaturne ravni razpoložljivih toplot ter možnost shranjevanja toplote brez izgub na daljši časovni rok. Zaradi teh prednosti pred običajnimi sistemi je uporaba kemičnih reakcij v hranilnikih toplote več ko primerna.

Pri preračunu nismo upoštevali zmanjšanja gostote shranjevanja energije zaradi vpliva dodatnih mas, npr. mase prenosnika toplote, ki ne sodelujejo aktivno pri postopku shranjevanja toplote. To je odlično izhodišče za nadaljevanje raziskav v smeri izboljšanja prenosnih površin v reaktorjih kemičnih toplotnih črpalk z namenom povečanja gostote shranjevanja energije.

realisation of the reactor bed represents a starting-point for further research work. In this way both processes could be better balanced and research on the use of a chemical heat pump as a storage system would be justified.

In comparison with a classical water heat-storage system the improvement in the energy density is about a factor of five. In addition, higher temperatures could be reached with a chemical heat-storage system. The most interesting advantage is the possibility of on-demand heat utilisation, without any heat losses to the environment. Because of this advantage over classical systems the chemical reactions are more appropriate for use in heat storage systems.

In the calculation process the reduction in the energy density due to the influence of the additional mass, i.e. the mass of the heat exchanger, which does not play an active part in the heat storage process, is not included. This represents an excellent starting-point for the continuation of research in the direction of improving heat-exchange areas, which are used in the reactors of chemical heat pumps, with the intention of an increase in the heat-storage energy density.

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5 OZNAKE
5 NOMENCLATURE

specifična toplota	C	kJ/kmolK	specific heat
standardna reakcijska toplota	ΔH^o	kJ/kmol	standard heat of reaction
začetna teža magnezijevega hidroksida	L_i	kg	initial weight of loaded magnesium hydroxide
molska masa magnezijevega hidroksida	M	kg/kmol	molecular mass of magnesium hydroxide
začetna teža	m	kg	initial charged material weight
tlak reakcije	P	kPa	reaction pressure
sproščena toplota med hidracijo	q	kJ/kg	hydration heat output
občutena toplota vode	q_{H2O}	kJ/kg	sensible heat output of water
temperatura	T	°C	temperature
čas reakcije	t	s	reaction time
srednja specifična moč hidracijske toplote	w_{mean}	W/kg	mean heat output rate during a hydration process
reagiran molski delež	x	-	mole reacted fraction
sprememba reagiranega molskega deleža	Δx	-	mole reacted fraction change amount

Indeksi:		**Subscripts:**
reakcija magnezijev oksid/voda	1	magnesium oxide and water reaction system
fazna sprememba vode, kapljevina/plin	2	water liquid/gas phase change
prazen prostor v reaktorju	a	in-bed atmosphere
spodnji del reaktorske sredice	b	the bottom part of the bed
kondenzacija	cd	condensation
dehidracija $Mg(OH)_2$	d	dehydration of $Mg(OH)_2$
uparjanje	ev	evaporation
plin	g	gas

voda	H_2O	water
hidracija MgO	h	hydration of MgO
ogrevanje	he	heating
začetno stanje reakcijskega cikla	ini	the initial state of the reaction cycle
magnezijev hidroksid	$Mg(OH)_2$	magnesium hydroxide
srednji del reaktorske sredice	m	middle part of the bed
notranjost reaktorske komore	rc	inner reaction chamber
zgornji del reaktorske sredice	u	upper part of the bed
notranja stena reaktorja	w	inner wall of the reactor

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Naslova avtorjev: doc.dr. Yukitaka Kato
prof.dr. Yoshio Yoshizawa
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
O-okayama, Meguro-ku
Tokyo 152-8550, Japonska
yukitaka@nr.titech.ac.jp

dr. Boštjan Cerkvenik
Univerza v Ljubljani
Fakulteta za strojništvo
Aškerčeva 6
1000 Ljubljana
bostjan.cerkvenik@fs.uni-lj.si

mag. Atsushi Minakami
NSK Ltd.
1-5-50, Kugenuma Shinmei
Fujisawa-shi 251-8501, Japonska

Authors' Addresses: Doc.Dr. Yukitaka Kato
Prof.Dr. Yoshio Yoshizawa
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
O-okayama, Meguro-ku
Tokyo 152-8550, Japan
yukitaka@nr.titech.ac.jp

Dr. Boštjan Cerkvenik
University of Ljubljana
Faculty of Mechanical Eng.
Aškerčeva 6
1000 Ljubljana, Slovenia
bostjan.cerkvenik@fs.uni-lj.si

mag. Atsushi Minakami
NSK Ltd.
1-5-50, Kugenuma Shinmei
Fujisawa-shi 251-8501, Japan

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