

***In situ* Gas Conditioning in Fuel Reforming for Hydrogen Generation**

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Abstract

The production of hydrogen for fuel cell applications requires cost and energy efficient technologies. The Absorption Enhanced Reforming (AER), developed at ZSW with industrial partners, is aimed to simplify the process by using a high temperature *in situ* CO₂ absorption. The *in situ* CO₂ removal results in shifting the steam reforming reaction equilibrium towards increased hydrogen concentration (up to 95 vol%). The key part of the process is the high temperature CO₂ absorbent. In this contribution results of Thermal Gravimetric Analysis (TGA) investigations on natural minerals, *dolomites*, *silicates* and *synthetic absorbent materials* in regard of their CO₂ absorption capacity and absorption/desorption cyclic stability are presented and discussed. It has been found that the inert parts of the absorbent materials have a structure stabilising effect, leading to an improved cyclic stability of the materials.

Introduction

The production of hydrogen for fuel cell application requires cheap, efficient and reliable technologies. In order to produce a hydrogen-rich gas for fuel cell applications with today's technologies, several catalytically supported reaction steps are required. Furthermore, in order to obtain a CO₂-free hydrogen an additional purification step, e.g. PSA, is required. At ZSW a new fuel-to-hydrogen conversion process, the Absorption Enhanced Reforming (AER), has been developed, which simplifies the conventional three or four step process into a basically one or two step process, making the hydrogen production more easily and less costly. The process can be applied to conventional gaseous and liquid fuels (such as methane, alcohols, liquid hydrocarbons, etc.), or solid fuels, e.g. biomass. The process works at atmospheric pressure. In this paper experimental results of thermal gravimetric analysis (TGA) on different CO₂-absorbent materials in respect on their CO₂ absorption capacity and cyclic stability will be presented. The investigated materials were selected among natural minerals, such as *dolomites*, *silicates* and *silicate/carbonates* and *synthetic compounds*. The selection criterion was related to the different CO₂ active centre in the minerals. In the case of dolomites CaO is the active part whereas in the case of silicates other metal oxides take over this role. A special case represents spurrite, which contains silicate and carbonate as well. As synthetic compounds lanthanum carbonate and lithium silicates have been investigated. XRD and RFA analysis were carried out for some dolomite species.

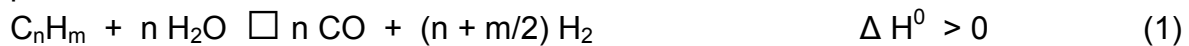
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Furthermore, typical steam reforming results with methane, obtained with a fixed bed AER reactor filled with dolomite and catalyst will be presented.

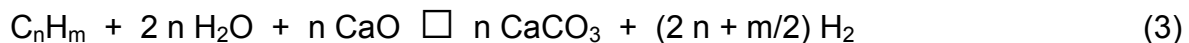
AER process

An important advantage of the AER process represents the integration of the CO₂ absorption and CO shift reaction enthalpy (both exothermic reactions) into the fuel-to-hydrogen conversion process, which is generally highly endothermic. The high temperature absorbent material removes CO₂ during the fuel reforming process, enhancing the hydrogen production by shifting the reaction equilibrium towards increased hydrogen concentration. Experiments with methane, methanol, hexane, etc. and dolomite revealed that hydrogen concentrations higher than 95 vol % can be achieved with this technology [Specht 2000; Weimer 2002]. The spent absorbed material has to be regenerated in a reforming subsequent step.

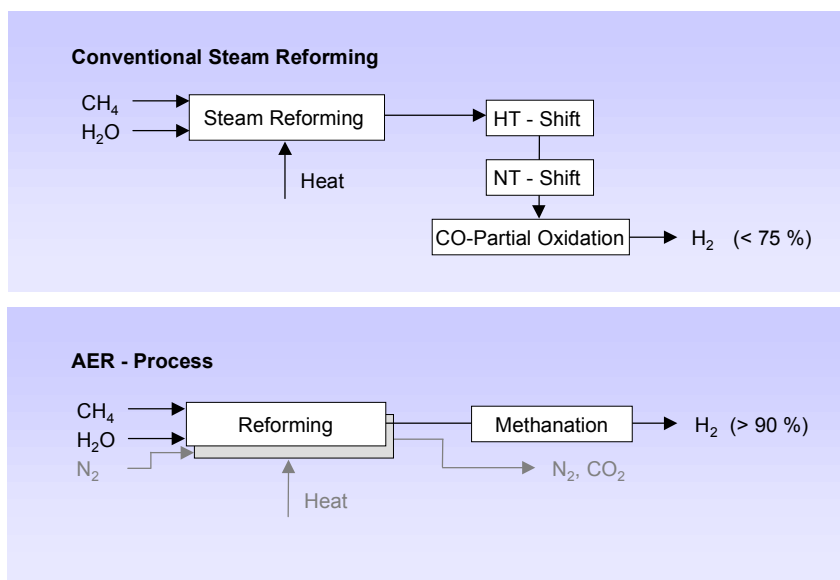
In a conventional steam reforming of hydrocarbons the following reactions take place:



In the presence of an absorbent, e.g. CaO, the overall steam reforming reaction will be:



Both, the CO₂ absorption reaction and the shift reaction are exothermic:



In the case of methane steam reforming ($\Delta H^0 = +206 \text{ kJ/mol}$) the overall reaction at 600-800°C is thermally neutral or slightly endothermic. A comparison of the two processes in the case of methane reforming, aiming to reveal the advantages of the AER process versus conventional reforming, is presented schematically in Fig. 1. In the AER process instead of a costly three step CO cleanup (conventional reforming), a simple selective methanation of CO can be applied. The core part of the AER process represents the absorbent. The

Fig 1: Comparison of reforming processes.

The core part of the AER process represents the absorbent. The

most important requirements for the suitability of an absorbent for high temperature CO₂ removal are:

- *high reaction rate* (in temperature range of 600-700°C)
- *chemical stability* (reversible CO₂ uptake/release),
- *mechanical stability* and
- *thermal stability*.

Furthermore, the absorbent material should be largely available for a low price. CaO would be a suitable absorbent material, it is available in the nature in large quantities. However the absorption capacity decreases during repeated absorption-desorption cycles. The reversibility of the reaction $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ has been intensively studied. In /e.g. Baker 1973; Bhatia 1983; ZSW 1996/ is reported that the carbonate decomposes up to 100% to the oxide, while the ability of the oxide to regenerate the carbonate decreases strongly with the increasing number of cycles. By the thermal decomposition of calcium carbonate an oxide is formed, whose surface is roughly 50 times higher than that of the carbonate. The carbonate decomposition leads to an oxide structure with a large number of fine pores (diameter < 4 nm). The absorption process can be described with two mechanisms: at first a fast surface reaction takes place, which leads to the formation of a carbonate layer. The reaction advances with the diffusion of CO₂ through this carbonate layer into narrow pores. This reaction step controlled by the diffusion of CO₂ and its rate is significantly lower than that of the surface reaction. The reversibility of the absorption/desorption process with CaO/CaCO₃ decreases drastically during the first couple of cycles, thereafter the reversibility alteration becomes significantly slower. For the absorption capacity decrease two effects play a role: (I) the loss of pore volumes in the oxide and (II) the sintering of crystallites. One possibility to avoid these negative effects is the use of structure stabilising components for CaO, e.g. MgO, or other oxides, carbonates, silicates, etc., which do not participate in the CO₂ absorption reaction. Furthermore, the use of other CO₂ active centres others than CaO may contribute to the increase chemical, thermal and mechanical stability of absorbent materials.

Experimental

Methods

Thermogravimetric analysis were performed employing a Netzsch apparatus STA 409 and Shimadzu (TGA-50). Experiments were conducted in isothermal and quasi-isothermal manner. All experiments were carried out in controlled gas atmosphere: 70 vol% N₂, 10 vol% CO₂ and 20 vol% H₂O (if not differently shown). This gas atmosphere were selected as representative for the gas composition in a reforming reactor. In quasi-isothermal experiments the samples were cycled between 480 and 830°C. The cyclic experiments were conducted up to 20-120 cycles. The heating rate was 10°C/min. In isothermal experiments the samples were heated up to 830°C in N₂ for carbonate decomposition and then decreased the temperature to the isothermal value and kept constant switching the oven atmosphere to 70 vol% N₂, 10 vol% CO₂ and 20 vol% H₂O, or to 90 vol% N₂ and 10 vol% CO₂. In order to get more information about the cause of the absorption capacity decrease, XRD investigation were carried out with a Siemens D-5000 apparatus. Chemical analysis for selected samples have been carried out with RFA (EDAX/EAGLE XXL) and atomic absorption spectroscopy (Perkin-Elmer 2380). The pore distribution of samples has been

recorded in order to document the structure changes (porosity meter Carlo Erba 2000).

Materials

The first group of minerals consisted of different carbonates of the dolomite class, two types of dolomite (dolomite I and dolomite II), ankerite, barytocalcite, strontianite and huntite. In the class of nesosilicates bakerite, datolite, howlite, jasmundite and spurrite were investigated. In the class of inosilicates, cyclosilicates and phyllosilicates the following minerals were investigated: sugilite, spodumene, petalite, zinnwaldite and lepidolite. Dolomites have been supplied of quarries in Germany, Hufgard (dolomite I) and Schöndorfer (dolomite II). The other minerals were provided by Krantz GmbH, Germany. Originally the minerals stem from different regions of the earth. $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ was supplied by ABCR (Germany). Lithium orthosilicate was supplied of Aldrich and Toshiba. For comparison Calcit (Fluka, Aldrich) was also investigated. All samples were ground and sieved. For TGA experiments 20-50 mg samples (particle size $< 20 \mu\text{m}$) were employed in all cases, except Toshiba silicate, which was investigated with the original pore structure.

Characterisation tools

In order to characterise the thermal and chemical stability, the so called cyclic stability of the samples, the *absorption capacity* $C(n)$, has been defined as the ratio of the absorbed amount of CO_2 $m_{\text{CO}_2, \text{abs}}(n)$ at a certain cycle n to the amount of absorbed CO_2 $m_{\text{CO}_2, \text{abs}, 1}$ in the first cycle ($n = 1$):

$$C(n) = \frac{m_{\text{CO}_2, \text{abs}}(n)}{m_{\text{CO}_2, \text{abs}, 1}} 100\% = \frac{m_{\text{charged}}(n) - m_{\text{discharged}}(n)}{m_{\text{charged}, 1} - m_{\text{discharged}, 1}} 100\% \quad (6)$$

The *specific capacity*, C_S , is related to the ratio of the CO_2 amount in the 10th cycle to the initial weight of the sample. It can be calculated as:

$$C_S = \frac{m_{\text{CO}_2, \text{abs}, 10}}{m_{\text{initial}}} = \frac{m_{\text{charged}, 10} - m_{\text{discharged}, 10}}{m_{\text{initial}}} \quad (7)$$

The CO_2 *absorption rate*, v_{CO_2} , is calculated as the amount of CO_2 absorbed in one minute by 1 g of absorbent material, expressed with $\text{mg}/(\text{g} \cdot \text{min})$.

Results and discussions

Dolomites

An overview of the investigated materials of the dolomite class is presented in Table 1.

Table 1. Dolomite class minerals

Sample	Molar ratio (RFA, chemical analysis)							General (empirical) formula
	Ca	Ba/Sr	Mg	Fe	Si	Al	Mn	
Dolomite I	1		0.97	0.03				$\text{CaMg}(\text{CO}_3)_3$
Dolomite II	1		0.83	0.02				$\text{CaMg}(\text{CO}_3)_3$
Ankerite	1		0.79	0.17				$\text{Ca}(\text{Fe, Mg, Mn})(\text{CO}_3)_2$
Barytocalcite	1	0.7			0.02	0.07	0.02	$\text{CaBa}(\text{CO}_3)_2$
Huntite	1		3.23					$\text{CaMg}_3(\text{CO}_3)_4$
Strontianite	1	0.9			0.03			$(\text{Ca, Sr})(\text{CO}_3)$

A typical shape of cyclic behaviour of all investigated dolomite minerals is presented in Figures 2 and 3 (dolomite I). Fig. 2 shows a number of cycles at the beginning of the cyclic experiment,

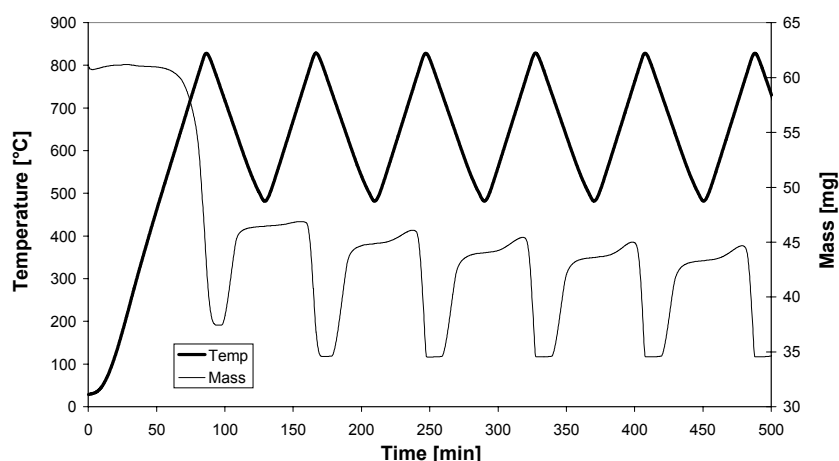


Fig. 2: Typical cyclic behaviour of dolomites (dolomite I) at the beginning of cycling experiments (70 vol% N_2 , 20 vol% H_2O and 10 vol% CO_2).

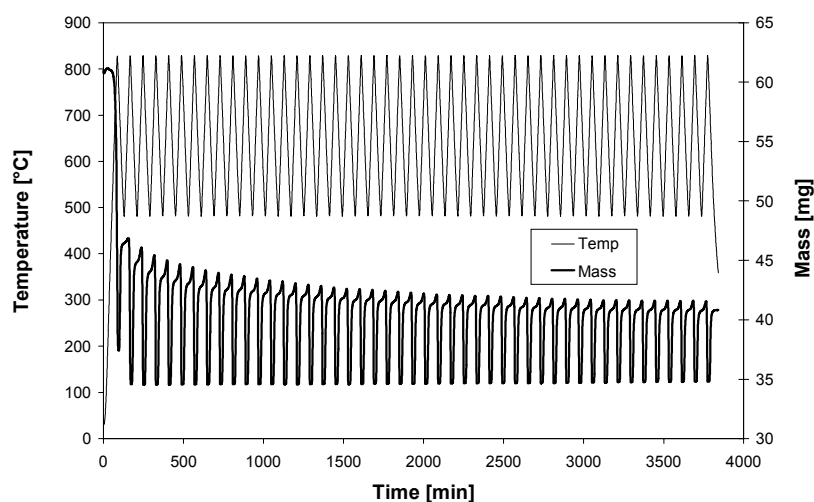


Fig. 3: Cyclic experiments with dolomite I (70 vol% N_2 , 20 vol% H_2O and 10 vol% CO_2).

whereas Fig. 3 shows the cyclic behaviour during the whole cyclic experiment. The first calcination step (Fig 2), according to the observed mass loss, produces the decomposition of both MgCO_3 and CaCO_3 . With the temperature reversal the carbonation starts and leads to $\text{MgO}\cdot\text{CaCO}_3$. The carbonation of MgO is thermodynamically possible however for kinetic reasons, at the given CO_2 partial pressure of 0.1 bar, does not take place.

The shape of the carbonation curve reveals that the CO_2 absorption occurs with two different mechanisms. The first one is a rapid surface reaction which leads to the major CO_2 uptake. The process continues with a diffusion controlled step, the CO_2

molecules diffuse through the surface carbonate layer in the narrow pores of the grains (similar to calcite reactions /Barker 1973, Bhatia 1983/. This process is highly enhanced by temperature increase, leading to absorption peaks. However, the MgO which doesn't absorb CO₂, has a structure stabilising effect, providing dolomites a higher cyclic stability compared to calcite (see Fig. 7).

XRD analysis with dolomite I revealed that the major part of the starting material consists of dolomite crystallites of ca. 60 nm size and a small amount of calcite with crystallite size of ca. 30 nm. After the first calcination the dolomite part is transformed in very small crystallites (< 5 nm) of CaO which has a large surface area. The inactive part of the sample consists of periclase, MgO with a size of ca. 40 nm. XRD records show that with increasing cycle number the CaO crystallites size increases steadily, the active surface shrinks, the absorption capacity becomes smaller and the

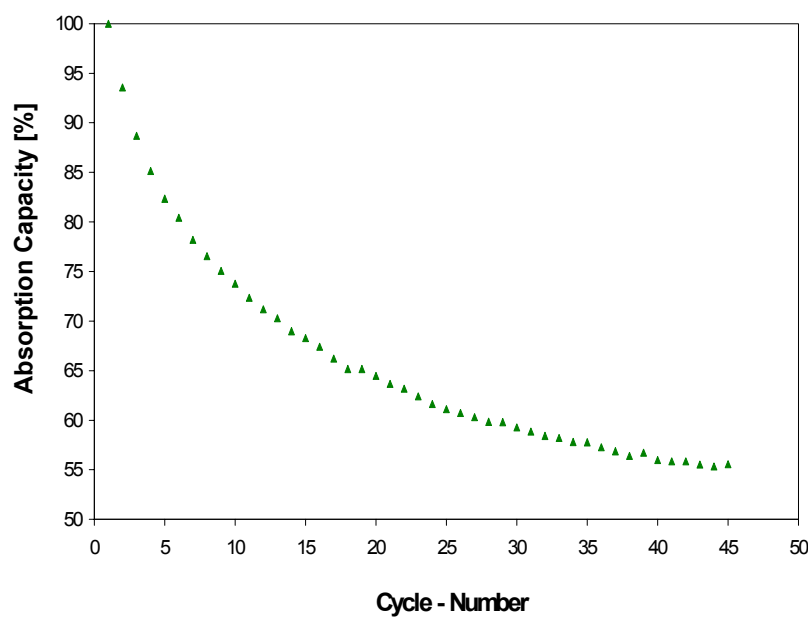


Fig. 4: CO₂ absorption capacity vs. Cycle number (dolomite I, 70 vol% N₂, 20 vol% H₂O and 10 vol% CO₂).

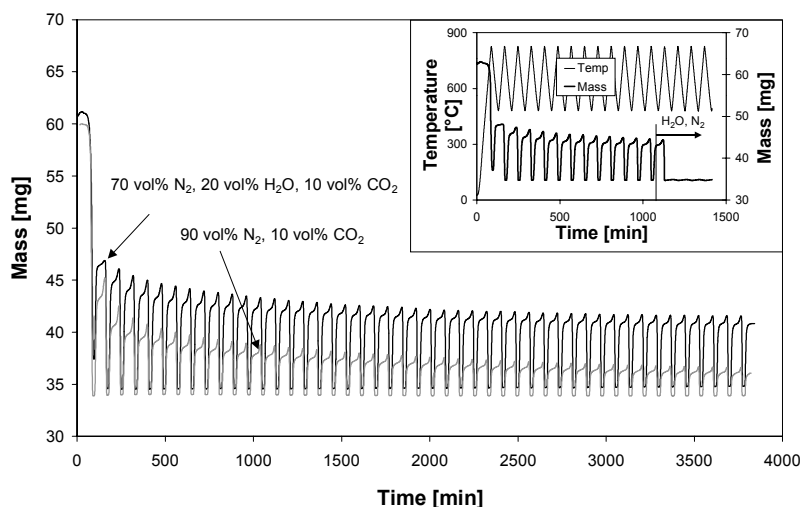


Fig. 5: Cyclic behaviour of dolomite I with water and without water.

pore structure changes. The MgO crystallites remain unchanged. With 120 cycles the adsorption capacity is only 20% of the initial capacity. Fig. 4 shows the absorption capacity decrease with increasing cycle number. The presence of water influence substantially the absorption capacity of all adsorbents below of ca. 500°C. A possible explanation could be the formation of hydrogen carbonates, which allows the binding of two CO₂ molecules to an adsorption centre (see Fig. 5). The presence of water has also a slightly positive effect on the cyclic stability of the dolomites if the absorption temperatures are below of ca. 500°C. Obviously the presence of water ameliorates the destructive effect of the CO₂ absorption process. Water without CO₂ doesn't show any

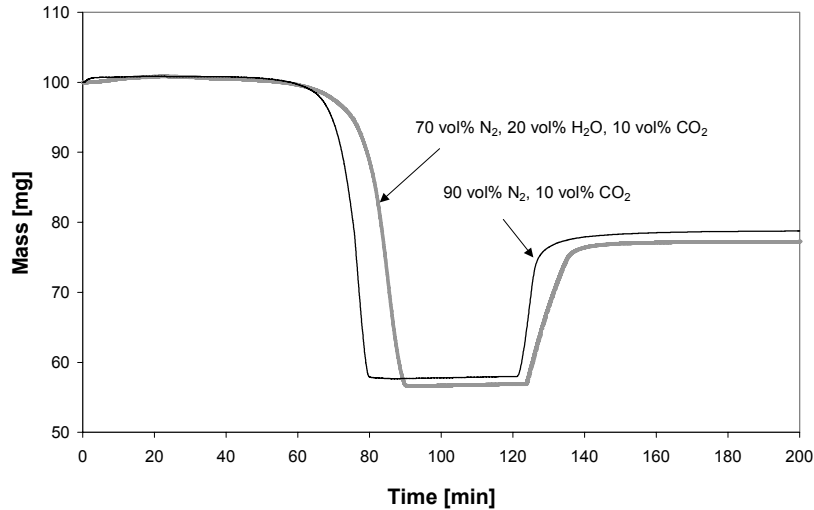


Fig. 6: Isothermal experiment with dolomite 1.

comparison with dry experiments. The CO_2 absorption rate calculated of the isothermal experiments for dolomite I and II at 575 and 625 °C are presented in Table 2.

Table 2: CO_2 absorption and desorption rates for dolomites I and II

	H_2O	CO_2 absorption rate (480°C) mg/g·min
Dolomite I	+	20
Dolomite I	-	40
Dolomite I	+	27
Dolomite II	+	17
Dolomite II	+	22

As seen with the isothermal experiments, the presence of water affects the kinetics of the CO_2 reaction with the absorbent. The rate for CO_2 absorption decreases when water was added to the gas atmosphere.

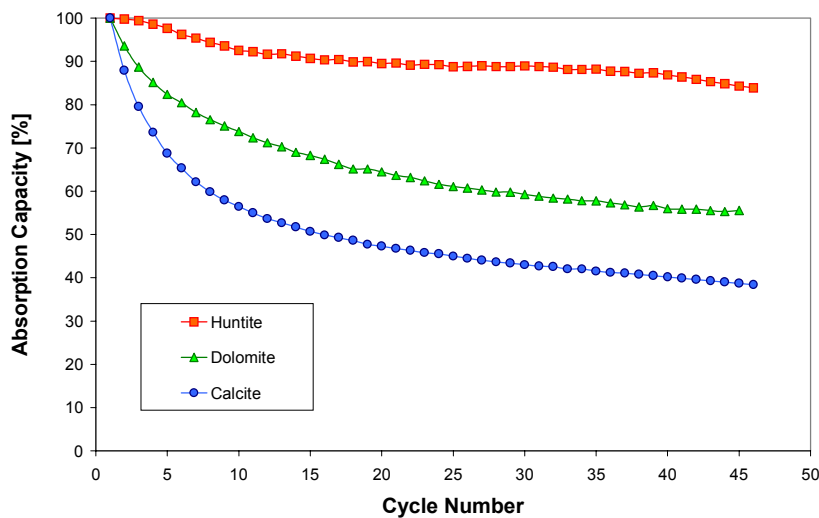


Fig. 7: Influence of the inert part (MgO) of the absorbent on the cyclic stability 70 vol% N_2 , 20 vol% H_2O and 10 vol% CO_2 .

mass change as presented in the small window diagram in Fig. 5. However, when the absorption temperature is high enough, e.g. 575°C, there is no difference between absorption capacities, as shown with isothermal experiments (Fig. 6). The presence of water influences merely the absorption kinetics. The rate of the CO_2 absorption is reduced in the presence of water in

A comparison of cyclic stability of different dolomites shows the positive effect of the molecular environment on the absorption capacity and cyclic stability. The more inactive material is

present in the absorbent, the higher is the chemical and thermal stability of the sample. The best examples are huntite and barytocalcite. In the case of huntite each CO₂ absorption centre is surrounded by 3 MgO molecules which doesn't participate in the absorption/desorption process, however stabilise the CaO centres. In the case of barytocalcite BaCO₃ is the inactive part. The decomposition temperature of this compound is higher than that of CaCO₃ and therefore doesn't participate in the reaction. Strontianite showed only a poor cyclic stability, the experiments were interrupted after a few cycles. Kutnahorite showed a very high cyclic stability but only a very low absorption capacity. However this dolomite presents interest as very stable structure and may serve as basis for a synthetic absorbent. The role of the inactive part in absorbent is illustrated in Fig. 7 which shows the absorption capacity change with the cycle number for calcite (0 % MgO, 100% CaO), dolomite I (50% MgO, 50% CaO) and huntite (75% MgO, 25% CaO). Calcite shows a poor stability, the absorption capacity decreases steadily with the increasing cycle number and after ca. 50 cycles it represents only 35% of the initial capacity. With increasing inactive part in absorbent, with dolomite I 50% MgO and huntite 75% MgO, the cyclic behaviour improves substantially. The disadvantage of absorbents with high inactive part is the increased energy demand for the regeneration as the inert part must be heated up during the absorbent regeneration. Fig 8 shows the amount of CO₂ (g) which can be absorbed by 1 g initial amount of absorbent (C_s). Herein are included the absorbents from the dolomite class and the synthetic materials. It is to be seen that absorbents with large molecules, e.g. natural silicates with complex structures, show less favourable CO₂/absorbent ratio. However, a rapid decrease of the absorption capacity results also in an unfavourable ratio. This material parameter reveals not sufficiently a prediction for applicability of a material as CO₂ absorbent, as a highly stable material but with low CO₂/absorbent ratio is preferred compared to one with more favourable mass ratio but low cyclic stability. The CO₂/absorbent mass ratio expresses merely the volume requirement for an absorbent. In thermochemical processes a large absorbent mass with high thermal capacity can influence positively the thermal balance of the process. As a general consequence of Fig. 8, the dolomite

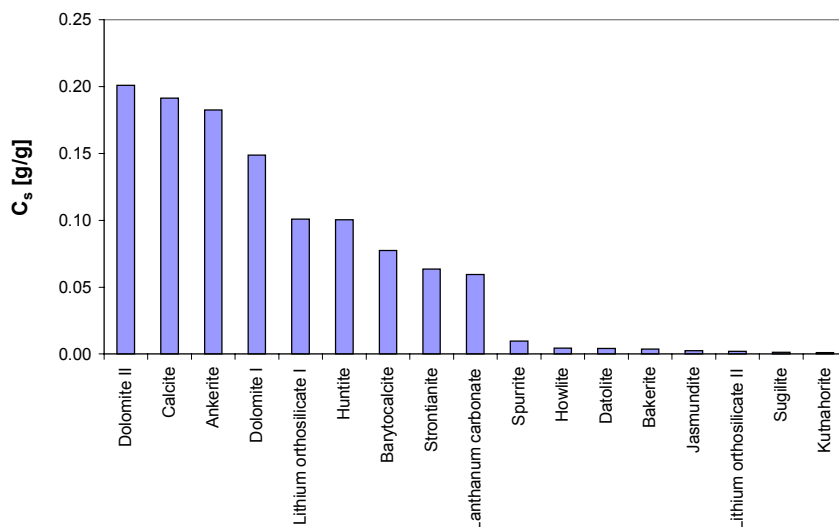


Fig 8: Comparison of different absorbent materials in regard of CO₂/absorbent mass ratio.

class materials and the Toshiba lithium orthosilicate seem to be appropriate absorbent for CO₂ in an industrial application.

Fig. 9 summarises the cyclic behaviour of the investigated absorbents in the dolomite class and lanthanum carbonate. As it can be seen from Fig. 9, huntite and ankerite show the highest cyclic stability. Especially the huntite CO₂ capacity changes not significantly up to the cycle number 45. The large inert mass of MgO in huntite influence

very positive the cyclic stability. Ankerite keeps a high capacity value but shows from the beginning a steady decrease of the capacity. Dolomite I and II are very similar but dolomite I reaches a more stable cyclic behaviour by 45 cycles than dolomite II. Baritocalcite, which contains as inert part a carbonate group, has a good cyclic stability and shows less capacity loss than dolomites at the beginning of experiments.

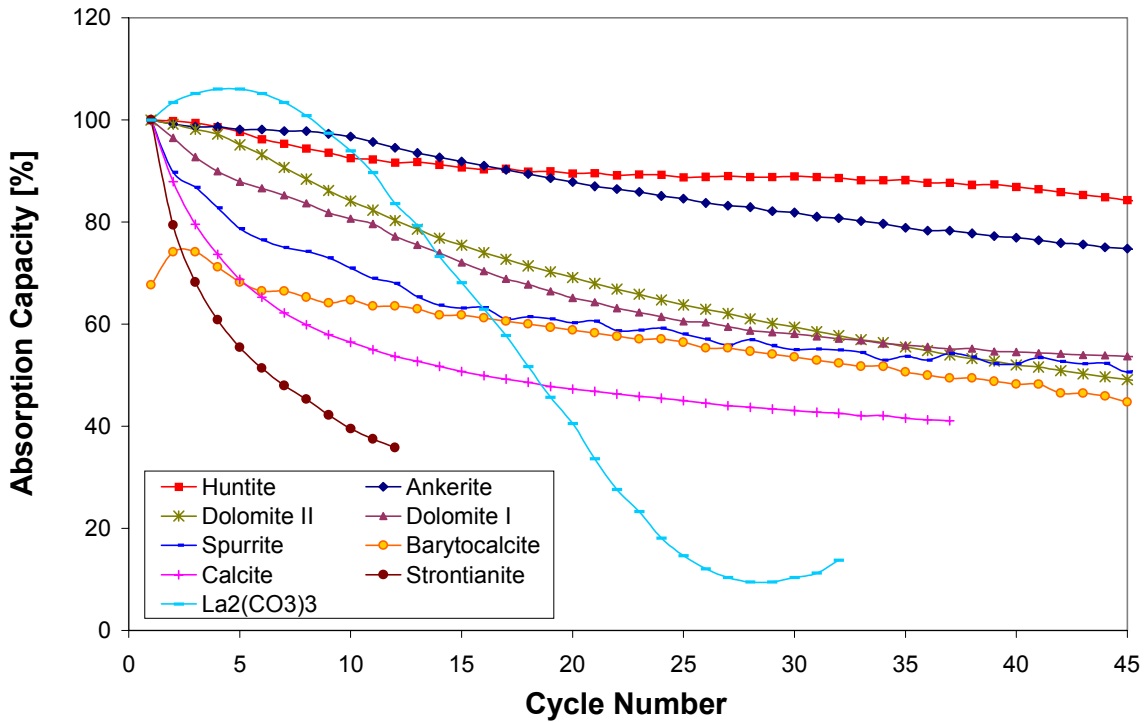


Fig. 9: Cyclic behaviour of dolomite class absorbents, spurrite and lanthanum carbonate.

Although, it shows a permanent decrease of capacity, the high stability of this material is evident. Lanthanum carbonate and strontianite are unsuitable as CO₂ absorbent materials.

Silicates

Spurrite

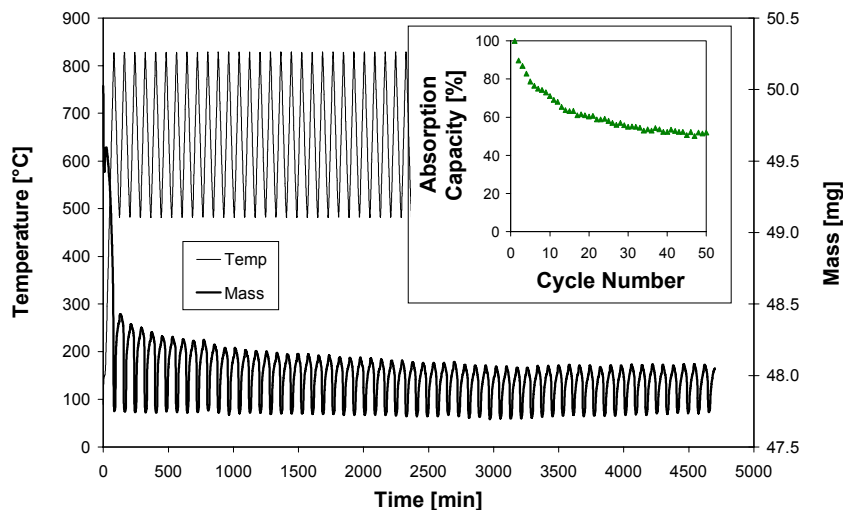


Fig. 10: Spurrite cyclic behaviour and capacity change with cycle number (70 vol% N₂, 20 vol% H₂O and 10 vol% CO₂).

A special attention was given to the mineral spurrite, which is a calcium silicate-carbonate mineral. The general (empirical) formula of this mineral is: Ca₅(SiO₄)₂CO₃. The composition is: 63.1 % CaO, 27.0 % SiO₂ and 9.90 % CO₂ /<http://webmineral.com/data/Spurrite.shtml>, 2002/. Some spurrite related

minerals, such as e.g. fukalite or chelyabinskite could be stable absorbent and will be tested in the future. Fig. 10 shows the results of TGA cycling experiments with spurrite and the absorption capacity change with cycle number. The absorption capacity change is pronounced at the beginning of the experiment but it becomes almost negligible after cycle number 35. This is a typical feature for absorbents based on CaO as CO₂ absorption centre. The results indicate that silicate ions around CaO as CO₂ absorbent, can improve even more the stability than MgO. One possible drawback of spurrite could be the unfavourable CO₂/absorbent mass ratio (see Fig. 8). However, in thermochemical processes an absorbent with high molecular weight is not necessarily an disadvantage as it can help to improve the heat distribution/balance of the system.

Other natural silicates

The experimentally tested silicates are listed in Table 3. All minerals listed in Table 3 have been tested on cyclic stability.

Table 3: Silicate class minerals

Sample	General (empirical) formula
Bakerite	Ca ₄ B ₄ (BO ₄)(SiO ₄) ₃ (OH) ₃ ·H ₂ O
Datolite	CaBSiO ₄ (OH)
Howlite	Ca ₂ B ₅ SiO ₉ (OH) ₅
Jasmondite	Ca ₁₁ (SiO ₄) ₄ O ₂ S
Sugilite	KNa ₂ Li ₃ (Fe, Mn, Al) ₂ Si ₁₂ O ₃₀
Spodumene	LiAlSi ₂ O ₆
Lepidolite	KLi ₂ Al(Al, Si) ₃ O ₁₀ (F, OH) ₂
Petalite	LiAlSi ₄ O ₁₀
Zinnwaldite	K Li Fe Al (AlSi ₃) O ₁₀ (OH, F) ₂

The TGA experiments revealed that all examined silicates show very stable cyclic behaviour. However the CO₂ absorption capacity is very poor (< 1 %) and therefore they are not suitable for a practical application. Most of the silicates show a pronounced mass loss in the first calcination, where after in the next cycles only a slight increase of mass can be observed. This is specially true when the original mineral contains OH groups.

The only exception is datolite which shows, compared to other silicates, a relative high absorption capacity and a good cyclic stability. However not comparable with spurrite. One important result of these investigations on silicates is the knowledge about the chemical composition of a potential synthetic absorbent which conveys the best cyclic stability. An crystallographic analysis will be certainly an important completion for understanding of the CO₂ absorption processes and to find an appropriate absorbent.

Synthetic absorbents

La₂(CO₃)₃·8H₂O

Earlier isothermal experiments performed at ZSW, Germany, [ZSW 1996] revealed that La₂O₃ is an excellent absorbent for CO₂. The calculated CO₂ absorption rate at 600°C was about 160 mg/g·min. However, as found with more recent experiments [ZSW 2001], the cyclic stability of the material is very poor. The result of cyclic

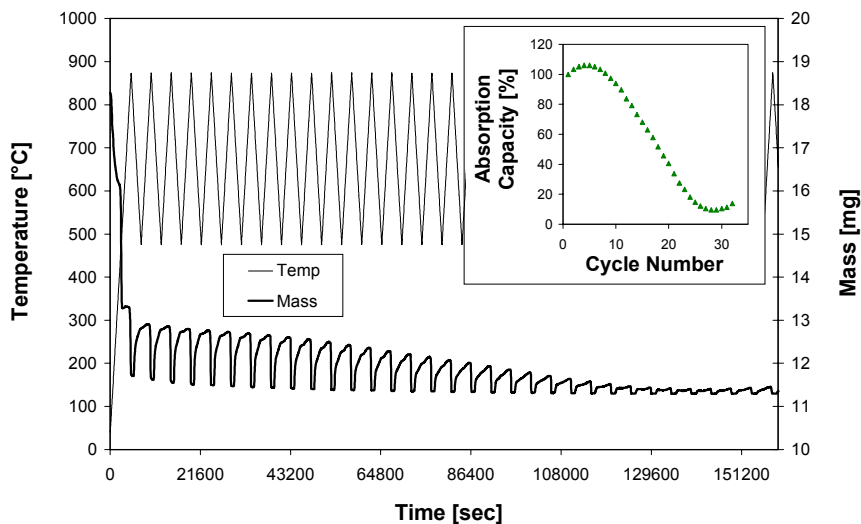


Fig. 11: Cyclic behaviour and capacity decrease with cycling of lanthanum carbonate (70 vol% N₂, 20 vol% H₂O and 10 vol% CO₂).

experiments and the change of the absorption capacity with the cycle number is presented in Fig. 11. As can be seen, the absorption ability of La₂O₃ diminishes rapidly with increasing cycle number and after ca. 30 cycles leads to an almost inactive material. The high rate of CO₂ uptake is coupled with a rapid destruction of the crystal structure.

After the first calcination step (water desorption and carbonate decomposition) La₂O₃ is formed, which doesn't rebuilt the original carbonate form in the next cycles. The decomposition and carbonation reactions can be described as follow:



The carbonation reaction reaches only the oxocarbonate stage. XRD analysis carried out with the carbonated compound showed the following sample composition: La₂O₂CO₃ 80%, La(OH)₃ 20% and traces of La₂O₃. The calcined samples showed only La₂O₃ [ZSW 2001].

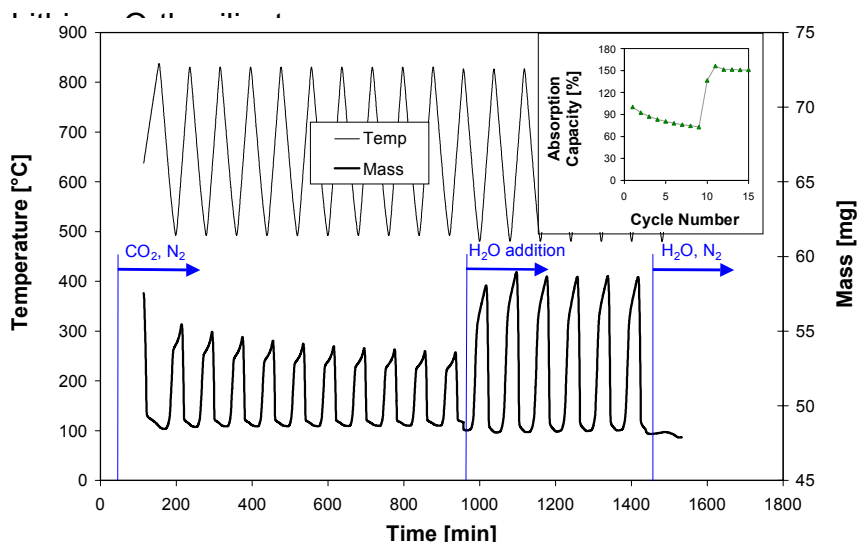


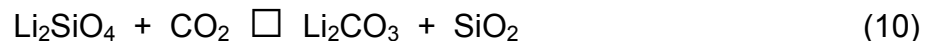
Fig. 12: Cyclic behaviour of Toshiba lithium orthosilicate.

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silicate powder supplied with courtesy by Toshiba, first calcination step the at room temperature and l. 600°C. Then occurs a 30°C. The follow cycles relevance for a practical silicate are presented in increase is about 20% in ; the mass increase is

somewhat reduced and tends to level with increasing cycle number. After 11 cycles, water was added to the gas atmosphere (10 vol% CO₂, 20 vol% water and 70 vol% N₂). The presence of water produces a tremendous change in the absorption characteristics of the sample, the absorption capacity increases drastically and remain constant for a number of cycles. Removing CO₂ from the gas after 18 cycles there is no mass change observable. This proves that in the presence of water CO₂ is bonded differently as in dry atmosphere. However in order to clarify the water influence further investigations are needed. The calculation of the absorption capacity according formula (6) carries some uncertainty for this absorbent as there is no CO₂ contain in the initial material, which has been taken as reference in the calculation for all other absorbents tested. The chemical reactions which take place can be represented with the following equations /Yoshikawa 2001, Kato 2001, Kato 2002/:



The cyclic stability of this absorbent is still in investigation in a long term test. These preliminary results qualify the lithium orthosilicate produced at Toshiba as a very promising absorbent material for CO₂.

Experimental result to methane reforming with dolomite I and Ni catalyst.

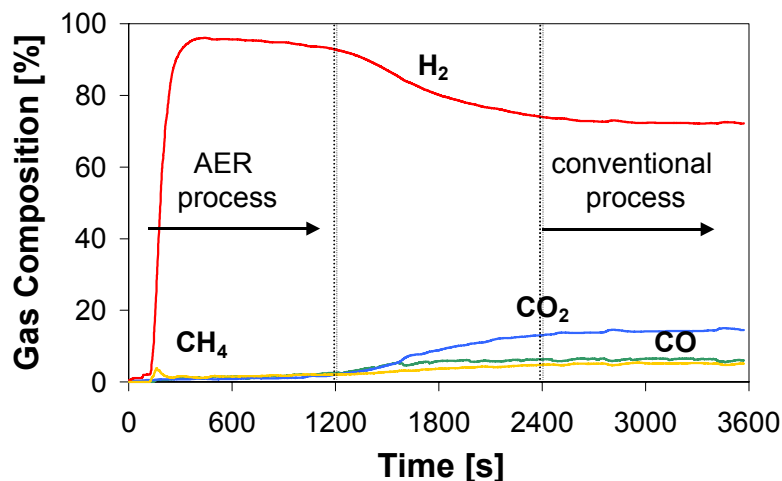


Fig. 11: Methane steam reforming with AER and conventional process (1.5 mol/h CH₄; s/c = 4; 60 g dolomite I; 6.6 g NiO catalyst).

from 2400 to 3600 sec, with spent absorbent), the hydrogen concentration remains below 75 vol% with ca. 15 vol% CO₂ and 5-7 vol% CO and CH₄ respectively. The product gas stream was ca. 120 NI/h. It is worth to note that with the AER process generally the reforming temperature can be reduced below that which is characteristic for conventional steam reforming.

Conclusions

Natural carbonates from the dolomite group, as cheap materials, are promising high temperature CO₂ absorbents in fuel-to-hydrogen processes. The cyclic stability is highly dependent on the chemical composition. An increased concentration of inert part in absorbent influences positively the cyclic stability. This is exemplary illustrated with huntite which contains 2 MgO more for each CaO than the ordinary dolomites.

Fig 13 illustrates the difference between methane steam reforming with AER process and the conventional steam reforming at 600°C. In the AER process a hydrogen concentration up to 95 vol% has been obtained (the first 1200 sec), with very low CO, CO₂ and CH₄ content. In the conventional steam reforming part of the process (reforming

Its cyclic stability is considerable higher than that of other absorbents of dolomite class. Dolomites I and II with 1 MgO for each CaO show a rapid decrease of capacity with increasing cycle number, but by cycle 45-50 the capacity change becomes minimal and it is to expect that it remains at this level for several hundred cycles. Ankerite and baytocalcite are also promising absorbents of the dolomite class. Dolomites as cheap natural absorbents are altogether attractive for industrial biomass processing toward hydrogen production, wherein periodically purging of absorbent is a process requirement due to the inherent ash and inert material accumulations in reactor. Natural complex silicates show a very poor ability for CO₂ absorption, but the cyclic stability can be qualified as very good. The stable crystalline and chemical structure of these materials can be a good indicator for future synthetic absorbents. Exception is spurrite as a silicate/carbonate shows a high cyclic stability and also apparent good mechanical stability. Mechanical stability is an other requirement for an absorbent, especially when used in fluidised or circulating bed reactors (not discussed here). Among the tested synthetic CO₂ absorbents, the Toshiba lithium orthosilicate showed promising cyclic behaviour. Long time cyclic tests are going on with this material. Using dolomite I in a lab-scale methane steam reformer a hydrogen concentration in product gas of ca. 95 vol% has been obtained.

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