Seasonal Thermal Energy Storage with Aqueous Sodium Hydroxide – Experimental Methods for Increasing the Heat and Mass Transfer by Improving Surface Wetting

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Abstract

Using thermochemical storage based on water absorption/desorption in a fluid with high volumetric energy density like sodium hydroxide solution ($NaOH$-H_2O) is an effective method for developing seasonal thermal energy storage. For the desorption process step which takes place in summer, a high renewable energy fraction can be reached by using solar thermal collectors. The system efficiency is influenced by the residence time of concentrated $NaOH$ in the water vapor and the surface wetting behavior of the heat and mass transfer unit. This strongly depends on the solid surface characteristics and on the thermo-physical properties of sodium hydroxide, especially the high surface tension of the concentrated $NaOH$ solution from the absorption process. An improved wetting of the concentrated $NaOH$ was achieved by modifying liquid's properties (e.g. surface tension) or by changing the solid surface structure and chemistry.

Keywords: *seasonal thermal energy storage, sodium hydroxide, surface wetting, surfactant, surface texturing*

1. Introduction

Almost half of the final energy demand in Europe is needed for heating and cooling applications. An important percentage can be supplied from sustainable heat sources like waste heat or renewables. However, the energy production is most of the times not synchronized with the energy demand. Seasonal heat storage/long-term storage of heat makes the energy available when it is needed. Moreover, these "heat batteries" are very advantageous when stand-alone systems are involved and when the security of supply is required.

Current research is focused on compact thermal energy storage (TES) technologies with high energy density like phase change materials (PCM) and thermochemical materials (TCM) or sorption processes. These concepts were investigated by researchers in different projects like the IEA joint Task/Annex 42/29 or the European financed COMTES project (Cabeza, 2015; Daguenet-Frick et al., 2015a; Navarro et al., 2016). Although considerable efforts were made to find and improve thermal energy storage materials, the seasonal/long term heat storage systems are still at lower technology readiness levels.

Water absorption/desorption in a high volumetric energy density sorbent as aqueous solutions like LiCl, LiBr, KOH or NaOH were successfully reported (Cabeza, 2015; Daguenet-Frick et al., 2015b; Navarro et al., 2016). Sodium hydroxide has the advantage of having high-energy density as well as low cost. Nevertheless, the challenges are related to process engineering and transferring the materials thermo-physical properties to a running system with the expected performance (Daguenet-Frick et al., 2015a; Fumey et al., 2014; Olsson et al., 1997).

Previous experiments made in the EU funded COMTES project have indicated a lower power compared with the theoretical value during the absorption (storage discharging) phase. This can be explained by the poor wetting of the concentrated sodium hydroxide over the tube bundle from the absorber/desorber unit

(Daguenet-Frick et al., 2014; Fumey et al., 2014). The tube bundle made from stainless steel (AISI 316L) was not efficiently wetted with the sorbent fluid. The sorption process of water in sodium hydroxide is influenced by the residence time, while the heat transfer is strongly influenced by the fluid surface wetting.

The focus of our work is to develop a 1 kW absorption/desorption demonstrator unit using the falling film working principle. One of the first steps is to optimize the heat and mass transfer at the tube bundle surface by improving wetting of the NaOH-H_2O (sorbent-sorbate) pair (see Fig. 1). In this paper, we present several experimental methods used for increasing the surface wetting of the stainless steel tubes with the concentrated sorbent. As wettability is depending on the surface roughness, surface oxygen content and the polar components, different surface modifications (structuring, annealing) and fluid properties tuning (use of surfactants) were investigated.

2. Working principle of a thermochemical storage using sodium hydroxide

The aim of the work is to develop a seasonal heat storage based on water absorption/desorption in sodium hydroxide solution. The main objective of our lab-scale system (1kW, Fig. 1) is to develop and improve the power unit. There are two main processes in such a system: charging and discharging. The charging process occurs in the desorber unit under reduced pressure. The thermal energy produced by the solar collectors in summer is used to partially vaporize the water contained in a diluted sodium hydroxide solution. The water vapors are condensed in the condenser unit, which is connected to a heat sink, e.g. a borehole. Water and sodium hydroxide are stored at room temperature in separate tank. The storing tank is giving the storage capacity, while the heat and mass exchangers are the power unit. This closed sorption heat storage system has the advantage of power and storage capacity separation.
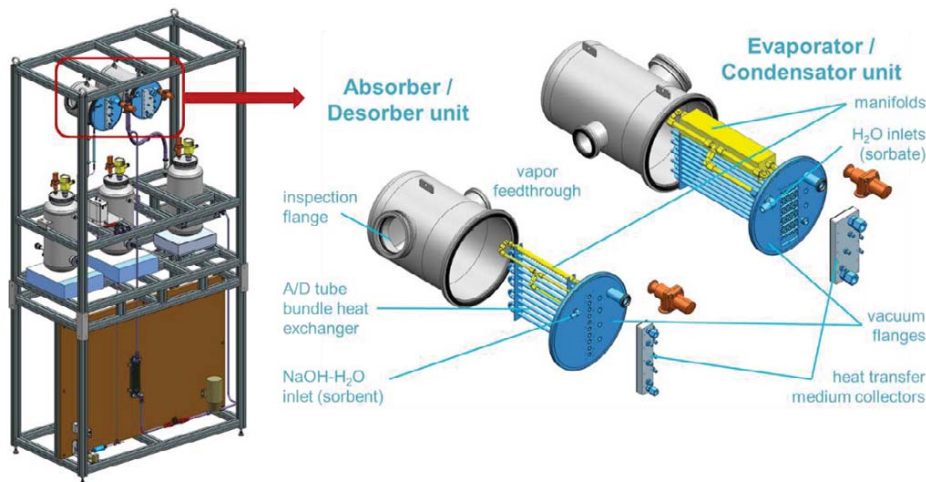

Fig. 1: Experimental 1kW thermochemical storage using sodium hydroxide - experimental facility (left) and construction details of the heat and mass exchangers: absorber/desorber unit (A/D) and evaporator/condenser unit(E/C), right

During the discharging process, the ground heat is used as a heat source to evaporate the stored water under reduced (sub-atmospheric) pressure in the evaporator. In the other chamber, the sorbent, concentrated NaOH solution (50 wt.%) is flowing as a falling film over the tube bundle of the A/D unit. Heat is gained from the water vapor absorption. Dissolution of the sodium hydroxide in water is a highly exothermic process (heat of solution at infinite dilution of NaOH is -44.51 kJ/mol at 25°C) (Parker, 1965). The heat is transferred to a working fluid (floor heating). Sodium hydroxide has a high water affinity; nevertheless, the fluid wetting on the tube bundle influences the efficiency when a fixed transfer area is involved.

3. Theoretical methods to improve the wetting

Wetting (Fig. 2) can be improved by modifying the liquid's properties (e.g. surface tension) or by changing the solid surface structure and chemistry.
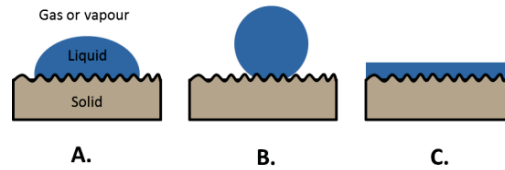
Fig. 2: Surface wetting : A - partial wetting, B - complete non-wetting, C - complete wetting

Surface tension of liquids at constant temperature and pressure and in equilibrium is physically equivalent to the specific surface free energy. The surface tension for liquids is depending on the London dispersion forces and hydrogen or metallic bonds, if they are present. According to Zisman (Tadros, 2006), total wetting is dictated by a single parameter called the critical surface tension, which is independent of the liquid. This model applies when only dispersion forces are considered. In other cases, the value obtained is not equal to the free energy of the surface, but it is a good practical measure of its liquid repellency. Stainless steel AISI 316L, the typical material used for tube bundle construction when NaOH is involved, has the critical surface tension between 20 to 33 mN/m. The value depends on the surface treatment: mechanically, electropolished or plasma treatment (Trigwell and Selvaduray, 2006). The surface tension is decreasing with temperature increasing, thus the highest value is expected to be at the minimum temperature from the system (room temperature in the 1kW system). In addition, the surface tension is decreasing for lower concentration, thus the worst case is for the concentrated solutions at low temperatures.

Sodium hydroxide has a surface tension of 116.72 mN/m for a 50 wt.% aqueous solution at 20°C (Feldkamp, 1969). To decrease it, surface active agents (or surfactants) in very low concentration can be used. The surfactant ability to reduce the surface tension is due to both hydrophilic and hydrophobic components (Tracton, 2006). The surfactant efficiency depends on the chemical structure and concentration, pH-value, temperature, and solid surface properties (e.g. composition, pore structure, surface roughness). Surfactants have a point of critical concentration called CMC – critical micelle concentration (Fig. 3). For higher solution concentrations than CMC, the surface tension does not decrease any more (reaches a rather constant value at constant temperature).
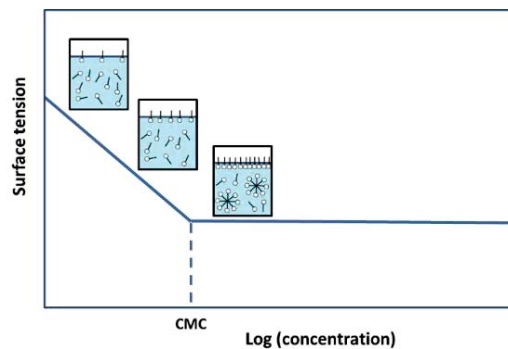

Fig. 3: Evolution of the surface tension depending on the critical micelle concentration

Based on their stability in hot alkaline solutions, two surface active agents (surfactants) were chosen for our study: 1,4-bis(1,3-dimethylbutyl) sulphonatosuccinate sodium salt (S1) and Triton™ QS-15 (S2). Sulfosuccinate surfactants are used in a wide range of industries from paints, adhesives, agrochemicals, plastics to cosmetics. Previous studies were performed on the wetting properties and stability of di-alkyl sulfosuccinate salts under alkaline solutions at different temperatures. It was shown that these anionic surfactants are stable in solutions with high pH and high temperature up to 80°C (Majmudar, 2014), which is at the desorption temperature level in a sodium hydroxide sorption heat storage. Triton™ QS-15 is also an anionic surfactant based on polyether sulfate (C12–14-tert-alkyl-ethoxylated sodium sulfate). It is soluble and stable in hot alkaline solutions, biodegradable and it will not persist in the environment. It is used for highly alkaline metal cleaners, bottle washing, zinc plating brightener, gas well cleaning, steam cleaners, etc.

The second category of methods for wetting improving is related to solid surfaces modifications. There are

three mechanisms: mechanical, physical and chemical. Better wetting is promoted when a large surface area is in contact with the liquid. Higher surface area is obtained by varying the surface roughness and mechanical texturing. According to Wenzel's equation, increased roughness will decrease the contact angle on hydrophilic surfaces, but it will increase the contact angle on hydrophobic surfaces. Thus, roughness amplifies both hydrophilicity and hydrophobicity, but not necessarily linearly (Brutin, 2015). In order to modify the surface chemistry, more techniques can be applied, e.g. changing the surface functional groups (Trigwell and Selvaduray, 2006). Studies have shown that a heat treatment is increasing the chromium oxide content in the surface (Williams, 2011). This would promote a better wetting due to the formation of physical bonding with the polar groups from the aqueous sodium hydroxide solution. It is favorable to have chromium and nickel oxide on the surface due to corrosion issues. However, different surface treatments have different effects. For example, the Cr concentration decreases, while the Fe concentration increases in the case of mechanically polishing process. In addition, the surface nickel content is reduced to about 3%. After mechanically polishing, Cr is mainly bounded in the oxide form (Cr_2O_3). The oxygen bonding in the oxide form is reduced by electropolishing, simultaneous to a considerably increase in oxygen bonding as hydroxide. This is because the process is done in an aqueous environment. An enrichment of chromium on the surface oxide layer normally occurs when stainless steel is electropolished. After plasma treatment, the proportion of Cr as Cr_2O_3 and Fe as Fe_2O_3 is increasing, to the detriment of metallic Cr and Fe and their hydroxides. In addition, the divalent Fe is oxidized. A chromium depleting effect takes place in the case of plasma treatment (Trigwell and Selvaduray, 2006).

Surface modifications by texturing or annealing and fluid properties tuning by using surfactants were experimentally investigated.

4. Experimental part for surface wetting improvement

Different tubes with a flat surface or structured (with horizontal, perpendicular or cross grooves) made from stainless steel AISI 316L were used. Moreover, a heat treatment in air at 300°C was applied for the optimum surface textured tube and for a plane tube.

Prior to the surface wetting experiments the samples were first washed with demineralized water and then with ethanol. To avoid carbonization of the sodium hydroxide with CO_2 from the air, experiments were performed into a glove bag (ca. 94x94x64 cm) filled with N_2. The N_2 4.5 (purity ≥99.995%) functions as the inert gas.

The following chemicals were used for performing the wetting experiments: sorbent to be used in the heat and mass exchanger - sodium hydroxide, 50 wt.% in H_2O (Sigma Aldrich), wetting agents: 1,4-bis(1,3-dimethylbutyl) sulphonatosuccinate sodium salt (S1, Sigma Aldrich) and Triton™ QS-1 (S2, DOW), demineralized water and ethanol (technical).

A computer-controlled multipurpose tension-meter (Sigma 700, Biolin Scientific, with OneAttension v. 1.6) from Transilvania University of Brasov was used to determine the surface tension of the sodium hydroxide solution with surfactant.

In order to avoid the influence of gravity, small volumes (100 μL) were used for the wetting experiments. When the radius of the droplet is much smaller than the capillary length, the effects due to gravity are negligible and the drop deposited on the solid substrate maintains a spherical shape.

5. The influence of surfactants and mechanical texturing on the surface wetting

5.1 The surfactant influence on the surface tension of the aqueous sodium hydroxide solution

Wetting and spreading of sodium hydroxide is mainly depending on the following physical properties of fluid: the dynamic viscosity of the liquid and the surface tension (Fig. 4 and Fig. 5, Feldkamp, 1969; Olsson et al., 1997). The values corresponding to aqueous sodium hydroxide solution are considerably higher compared with water, which is the low cost fluid for the classical sensible storage method. In order to have a good heat and mass exchange, the fluid properties must be tailored together with the surface properties of the

solid surface.

Thus, the influence of surfactants (e.g. S1) on the surface tension of concentrated sodium hydroxide solution was assessed. Previous research studies recommend the use of di-alkyl sulfosuccinate salts under alkaline solutions in concentration from 0.1 to 0.5 wt.%, under the critical micelle concentration (Majmudar, 2014).

The surface tension of different surfactant solutions (0.1 wt.%, 0.3 wt.%, 0.5 wt.%) was determined (at room temperature) and compared with the one corresponding to aqueous NaOH solutions and to NaOH-surfactant system (Fig. 6). The addition of small amounts of surfactant solution reduces the surface tension of the sodium hydroxide with approx. 39% in the case of concentrated sodium hydroxide (30 wt.%). Therefore, the wetting of the NaOH-H$_2$O over the tube bundle surface from the absorption unit can be improved. Further tests are under development for assessing the stability of the sodium hydroxide solution with surfactant in different system configuration.
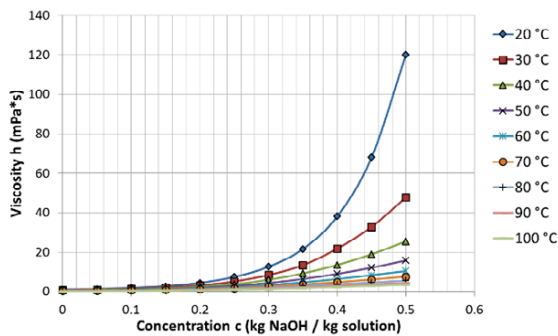

Fig. 4: Viscosity in function of temperature and concentration for aqueous solutions of sodium hydroxide
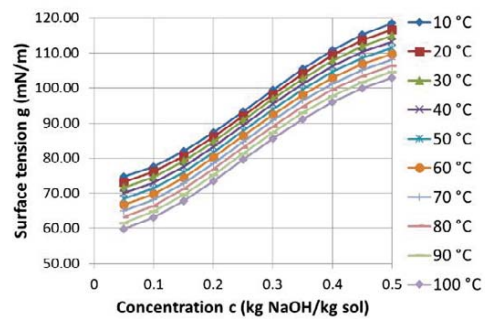

Fig. 5: Surface tension in function of temperature and concentration for aqueous solutions of sodium hydroxide
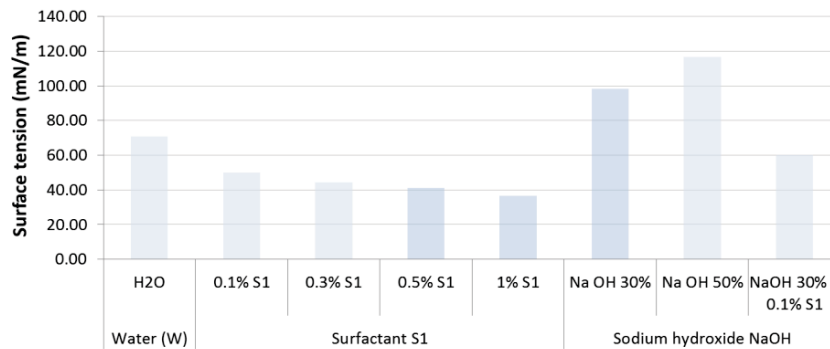

Fig. 6: Influence of the surfactant 1,4-bis(1,3-dimethylbutyl) sulphonatosuccinate sodium salt (S1) on the surface tension values

5.2 Surfactant impact on wetting stainless steel plane tubes

The influence of the two selected surfactants and concentration NaOH solutions on wetting the as received plane tubes was performed. The reference was a solution of NaOH 45 wt.%. The surfactants had the same concentration (1000 ppm). In order to quantify the wetting of the fluid over the tube, wetting time was used (Stache, 1995). This is defined as the shortest time until the drop (100 μL) wets and falls over the tube. Both surfactants lead to good wetting, compared to only sodium lye case (Fig. 7). In the reference case, the droplet was stable for minutes.
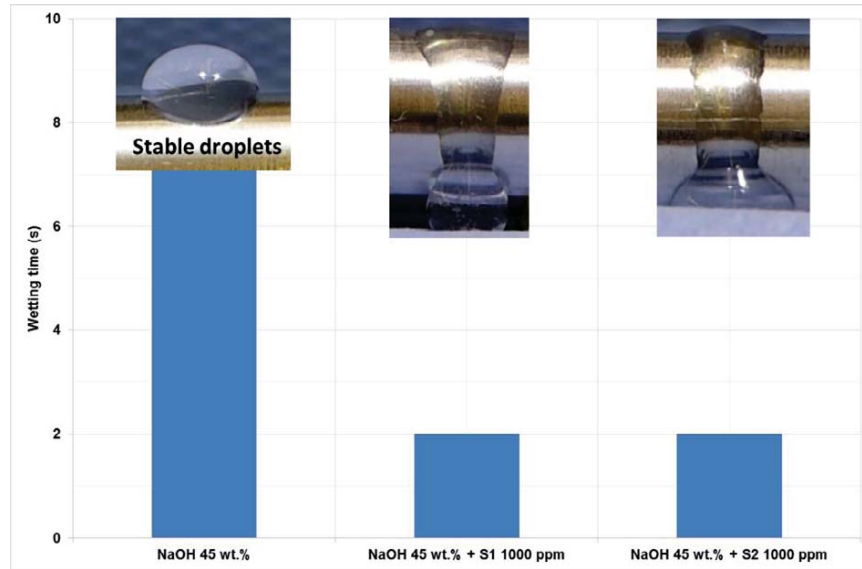
Fig. 7: Influence of the surfactants: 1,4-bis(1,3-dimethylbutyl) sulphonatosuccinate sodium salt (S1, 1000 ppm) and Triton™ QS-15 (S2, 1000 ppm) (S2, 1000 ppm) on the wetting time

5.3 Surface texturing and surfactant influence on the tubes wetting with concentrated sodium hydroxide solutions

The influence of different surface texturing on the wetting with concentrated sodium hydroxide, without/or with surfactant addition (S1 100 ppm) was assessed. Compared to the reference case (T0), where the aqueous concentrated sodium hydroxide solution forms stable droplets, all the textured tubes present better wetting. The surfactant addition leads to a better wetting, decreasing the wetting time. The best results were obtained in the case of sample T4. This pattern is also used in sodium heat pipes to improve the wetting (Bacanu, 1991). It was proven to have good stability in time in highly corrosion environments. Sample T1, with very small fines in the axial direction is a promising solution that can have good residence time. Sample T3 has lower wetting compared to the others due to the hill like structures. In the case of T5 and T6, good wetting can be achieved, but the vertical fins limit the fluid spreading.
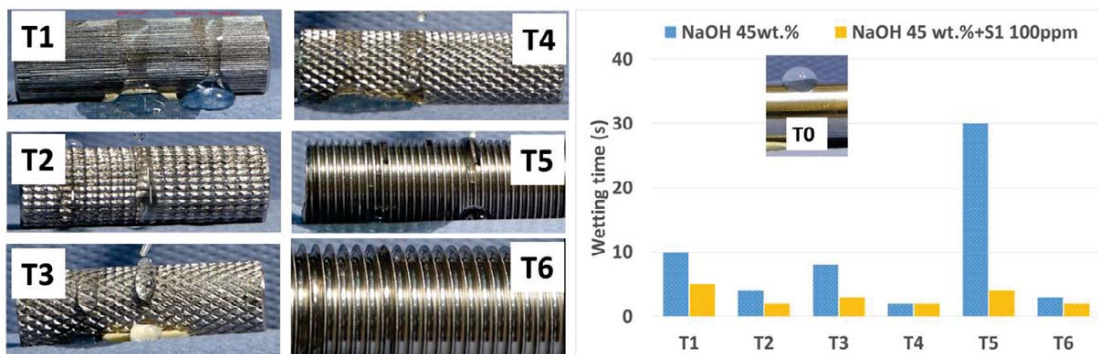

Fig. 8: Influence of surface texturing and surfactant addition (S1 100 ppm) on the surface wetting

5.4 The influence of thermal treatment on the wetting time

Annealing in air increases the surface metal oxide content. A plane tube (as received) and the optimum textured tube were thermally treated in air for 1h, 2h and 3h at 300°C. Wetting experiments were performed by placing a 100μL droplet of concentrated sodium hydroxide solution (45 wt.%), without surfactant or with the addition of Triton™ QS-15 (S2, 1000 ppm). A better wetting was obtained for all the annealed samples (see Fig. 9). The good wetting time values can be explained by physical bonding formation between active

groups from the testing fluid and from the metal surface. In the case of sample A1, very small droplets were added. This has led to a rather stable droplet, with higher wetting time.
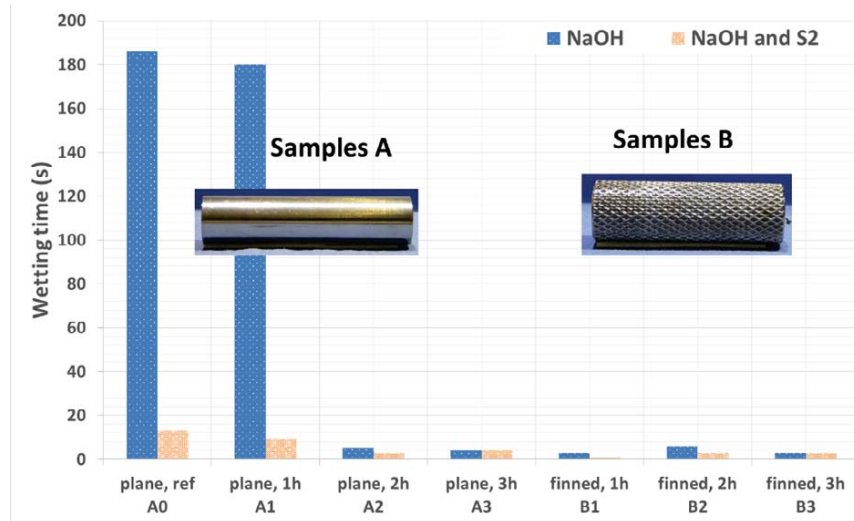

Fig. 9: Influence of thermal treatment on the wetting time for two types of surfaces and for sodium hydroxide with and without the surfactant S2 (Triton™ QS-15)

Moreover, in the heat and mass exchanger from the 1kW prototype, a manifold nozzle will be used. This was simulated by placing three large droplets (1000 µl of testing fluid, see inset image from Fig. 10) compared to the standard experiments where small droplets were used (100 µL). The pipet diameter was similar with the nozzle diameter from the prototype system (Fig. 1). A better spreading was observed in the case of the textured tube compared to the plane tube (see Fig. 10, bottom).
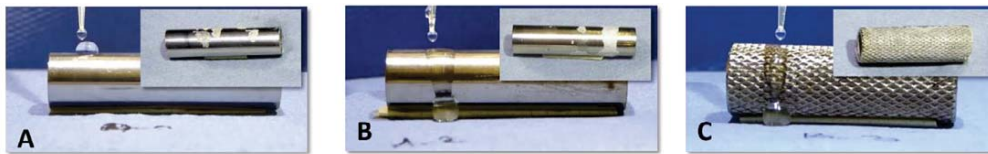

Fig. 10: Comparison between wetting of sodium hydroxide 45 wt.% and different tube surfaces – plane tube as received (A), plane tube, thermally treated for 2 hours at 300°C (B) and optimized textured tube, thermally treated for 3 hours at 300°C (C). The photos are taken 5s after adding 100 µL of sodium lye, while in the inset, a higher volume was used (3x1000 µL) and the photos were taken after the tubes were completely dried.

6.   Conclusions

Water absorption/desorption in a high volumetric energy density fluid, as aqueous sodium hydroxide solution, is an efficient method to develop compact seasonal thermal energy storage. Previous experiments made in the EU funded COMTES project have indicated a lower power during the absorption (storage discharging) phase. This can be explained by the poor wetting of the concentrated sodium hydroxide over the tube bundle from the absorber/desorber unit.

The focus of our work is to develop a 1 kW absorption/desorption demonstrator unit using the falling film working principle with improved wetting of the $NaOH-H_2O$ as sorbent-sorbate pair. One of the first steps is to optimize the heat and mass transfer at the tube bundle surface from the absorption process. This can be done by tailoring the surface wetting.

Different experimental methods were investigated for increasing the surface wetting of stainless steel tubes: surface modifications (structuring, annealing) and fluid properties tuning (use of surfactants). Higher surface area was obtained by mechanical texturing. The development of the structured surfaces not only enhances the heat transfer, but it also reduces the size of absorber unit. Annealing in air increases the surface metal oxide

content. A better wetting in terms of low wetting times was obtained for all the annealed samples. This can be explained by physical bonding between polar groups from the testing fluid and the surface metal oxide. The influence of different surface texturing on the wetting with concentrated sodium hydroxide, without/or with surfactant addition was assessed. Compared to the reference case, the surfactant addition leads to a better wetting, decreasing the wetting time.

Further work is related to the investigation of the fluid residence time in the water vapor. This can be improved by the number of tubes on each other or by a concept of inclined surface (from the vertical) over which the fluid is flowing. In addition, the use of ceramic foams is currently investigated. The improved tube bundles will be tested by integrating them in the 1 kW prototype.

7.   Acknowledgments

8. References

Bacanu, G., 1991. The optimum design of heat pipe heat recovery exchanger. Transilvania University of Brasov, Brasov, Romania.

Brutin, D., 2015. Droplet Wetting and Evaporation: From Pure to Complex Fluids. Academic Press, Marseille, France.

Cabeza, L.F., 2015. Advances in Thermal Energy Storage Systems, Woodhead Publishing Series in Energy. Woodhead Publishing.

Daguenet-Frick, X., Gantenbein, P., Frank, E., Fumey, B., Weber, R., 2015a. Development of a numerical model for the reaction zone design of an aqueous sodium hydroxide seasonal thermal energy storage. Sol. Energy 121, 17–30. doi:10.1016/j.solener.2015.06.009

Daguenet-Frick, X., Gantenbein, P., Frank, E., Fumey, B., Weber, R., Goonesekera, K., 2015b. Seasonal thermal energy storage with aqueous sodium hydroxide - experimental assessments of the heat and mass exchanger unit. Presented at the International Conference on Solar Heating and Cooling for Buildings and Industry, Istanbul, Turkey.

Daguenet-Frick, X., Gantenbein, P., Frank, E., Fumey, B., Weber, R., Williamson, T., 2014. Seasonal Thermal Energy Storage with Aqueous Sodium Hydroxide – Reaction Zone Development, Manufacturing and First Experimental Assessments, in: EuroSun 2014. Aix-les-bains, France.

Feldkamp, K., 1969. Die Oberflächenspannung wäßriger NaOH- und KOH-Lösungen. Chem. Ing. Tech. 41, 1181–1183. doi:10.1002/cite.330412107

Fumey, B., Weber, R., Gantenbein, P., Daguenet-Frick, X., Williamson, T., Dorer, V., 2014. Development of a Closed Sorption Heat Storage Prototype. Energy Procedia, 8th International Renewable Energy Storage Conference and Exhibition (IRES 2013) 46, 134–141. doi:10.1016/j.egypro.2014.01.166

Majmudar, S., 2014. Investigation into the effects of pH, temperature & salinity on the stability and wetting performance of sulfosuccinate surfactants (Technical report, Cytec Industries).

Navarro, L., de Gracia, A., Colclough, S., Browne, M., McCormack, S.J., Griffiths, P., Cabeza, L.F., 2016. Thermal energy storage in building integrated thermal systems: A review. Part 1. active storage systems. Renew. Energy 88, 526–547. doi:10.1016/j.renene.2015.11.040

Olsson, J., Jernqvist, Å., Aly, G., 1997. Thermophysical properties of aqueous $NaOH-H_2O$ solutions at high concentrations. Int. J. Thermophys. 18, 779–793. doi:10.1007/BF02575133

Parker, V.B., 1965. Thermal Properties of Uni-Univalent Electrolytes. Natl Stand Ref Data Ser. 2.

Stache, H.W., 1995. Anionic Surfactants: Organic Chemistry. CRC Press, Marl, Germany.

Tadros, T.F., 2006. Applied Surfactants: Principles and Applications. John Wiley & Sons.

Tracton, A.A., 2006. Coatings Materials and Surface Coatings. CRC Press.

Trigwell, S., Selvaduray, G., 2006. Effect of surface treatment on the surface characteristics of AISI 316L stainless steel. Med. Device Mater. III Venugopalan R Wu M Eds ASM Int. Mater. Park OH 208–213.

Williams, M.C., 2011. Fuel Cell Seminar 2010. The Electrochemical Society.