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Adsorption Performances and Application Study of Ceramic Foams

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Abstract

Bosch-Siemens Home Appliances designed a new drying system for dishwashers based on a first-time-applied material, belonging to the family of zeolites. It's a ceramic substance whose property of interest is the high capacity and affinity for adsorbed moisture. This solution is told to drastically reduce the product environmental impact (BSH Corporate Comunications, 2010).

Ceramic foams, a novel class of materials with interesting properties, are potential substitute products for zeolites because of their specific properties, such as high specific surface area for adsorption of gases and high thermal and chemical stability.

During the last years, sustainability has become a key factor within the home appliances industry. This comes from the necessity to obey to the international normative (Eco-design, 2005), which reflects the increasing sensitivity of the society towards environmental issues, but also from strategic matters, namely the purpose to get a better image of the brand. One important field to focus on for being less harmful towards environment lays on the choice of materials used in the products.

This work consists in a comparative evaluation between the newly designed drying system and a common one, taken as reference, in terms of environmental impact. The means of analysis is the Life Cycle Assessment. In addiction, tests of moisture adsorption on ceramic foams have been conducted. The study shows the environmental advantages of the zeolitic drying system over the common technology. Tests on ceramic foams, instead, show that these materials need further performance improvements to be considered as practical substitutes of zeolites in this application field.

Keywords: Life Cycle Assessment, Ceramic foams, Zeolites, Household Appliances, Environmental Impact

1. Introduction

According to Gibson and Ashby (1999), foams represent a class of materials whose peculiar feature is that the relative density of the material, defined as ρ/ρ_s, where ρ_s is the density of the bulk, is less than 0,3.

Over the past few years there has been a significant increase in interest in the production and use of highly porous ceramic materials. This is mainly associated with the properties these materials offer, such as high surface area, high permeability, low density, low specific heat and high thermal insulation. These characteristics are essential for technological applications such as catalyst support and filters for molten metals and for gases, but also as ion exchangers, refractory linings for furnaces, thermal protection systems, heat exchangers and as porous implants in the area of biomaterials (Scheffler and Colombo, 2005).

A wide variety of processing routes to manufacture ceramic foams has been developed and patented in many countries around the world (Colombo, 2006, Colombo and Bernardo, 2003).

The classical approach is based on the replication of polymer foams by applying a ceramic slurry that is dried in place prior to the polymer template's being burnt out and the ceramic sintered. While this leads to a very open, reticulated foams, burning out of the polymer leaves hollow and damaged struts that can reduce the mechanical properties of the final foam significantly.

The second basic approach relies on foaming of ceramic slurry by mechanical agitation or in situ evolution of gases. This way probably yields the widest range of cellular structures and hence properties, which nonetheless are generally less open than the replicated foams.

Ceramic foams could be used as gas and vapour adsorbers. Even though application studies regarding this are a few, their properties make think so. In addiction, similar ceramic media such as activated alumina and zeolites have always been used for this scope (Wilhelm *et al*. 2005), along with materials belonging to different families, such as activated carbon.

Recently, zeolites have been used in the drying system of a dishwasher for the first time. This technological innovation, from the words of the producer (http://www.siemens.com/innovation/en/publications/publications_pof/pof_spring_2010/zeolith.htm), allows to save energy during the drying/rinse phase, because of the different concept that exploits the properties of the adsorbent without making use of electrical energy as normally happens.

Life Cycle Assessment appears to be a good way to evaluate whether the solution with the zeolites actually brings any benefit in terms of environmental impact.

In this paper the Life Cycle Assessment of the drying system under consideration, compared with a reference one, will be carried on. The result is the technological judgement about which one can be considered better. The work is carried out also by means of the software GaBi. Finally, adsorption tests of a particular type of ceramic foams produced in the laboratories of Università di Padova, are carried out. The objective in this case is to define wether ceramic foams can be considered as substitute products of zeolites in the vapour adsorption field.

2. Experimental Procedure

The Life Cycle Assessment of the two products under analysis was first made. A previous study about the different LCA types showed that the most appropriate one for this type of comparison is the widely used process-based LCA. Its methodological framework is described directly in the ISO 14040 normative and in many other correlated guides and articles (Jensen *et al.*, 1997, Jeshwani *et al.*, 2009). The choice of this kind of LCA approach raises from the lack of information about the products. In fact the process-based LCA makes use of databases more complete than for any other method, like for example Environmental Input-Output LCA (Hendrickson *et al.*, 1998), even though it presents some conceptual weaknesses.

The LCA was carried out also by means of the software GaBi (v.4.3) available by Instituto Superior Técnico as educational version. In particular, some secondary Life Cycle Inventory data and the final results of the Life Cycle Impact Assessment were calculated by the software and recorded into the report.

After this phase, adsorption test on ceramic foams were made. They took place at Electrolux plant in Porcia (Italy), specifically at the *CTI – Cross Technology and Innovation* laboratories.

This part of the work consisted in a preliminary characterisation step to know the new materials properties like specific surface area (SSA, [m^2/g] by BET analysis and their morphology by SEM image acquisition. After this, vapour adsorption tests on reference zeolites, similar to the ones used in the zeolitic drying system were made, in order to set a reference performance. Finally tests on given ceramic foams were carried out. The comparison between their performances and the ones of zeolites would allow to say whether the two materials can be considered substitutes.

3. LCA Case Study

3.1 Goal

The goal of the study is to compare two different products fulfilling the same function with the purpose of verifying whether one possesses a not negligible advantage over the other in terms of environmental impact. This LCA was commissioned by Electrolux Italia S.p.A.

3.2 Scope

- Product code: drying system
- Function of the products: drying dishes and cutlery in a dishwasher after a washing cycle.
- Functional unit: drying a fully loaded household dishwasher of standard dimensions within a time of 15 minutes once every two days along 10 years.
- Reference flow: it is assumed that in both cases only one dishwasher, thus only one drying system, is needed to accomplish the scope defined by the functional unit.
- Cut-off criteria: the drying systems aren't made by a single component; instead their whole function is carried out by different parts that can be even detached one from the other inside the dishwasher. Nonetheless, it is misleading to compare the whole household appliance for the scope of the work, since the comparison among the parts not involved in the drying process would make no

difference to the final result. Thus, the main cut-off criterion for an appliance component to be part of the chosen product system is being directly involved in the drying process. To a secondary extent, the contribution in mass of every considered part must be of at least 5% to the overall weight of the system. No cut-off criteria for components are taken founded on estimated impacts since no information is preliminarily available.

3.2.1 *Scenarios Under Comparison*

The solution taken into account will be referred as:

- The reference drying system
- The alternative drying system

The first one is a model of the system utilized in the appliances produced by Electrolux.
It is composed by a heating element and a plastic container (condenser). The working principle consists in heating a certain amount of water after the washing cycle and let it inside the washing chamber. At the same time cold water flows through the condenser placed outside the washing chamber. Cold water keeps the wall at low temperature so that the vapour can condensate on it.
Informations about the components are generally of primary type. Since the model is produced by the company to which this study is addressed, it was of their interest to supply as precise information as possible. Information sources were the model itself, which has been manually disassembled, and the data provided by the real suppliers of the company, like for example IRCA S.p.A. Company for the heating element.
The alternative one is a model of the system implemented by Bosch-Siemens, including the zeolite pellets. The principle of working is briefly described as follows: a fan blows damp air out from the washing chamber, through a pipe, over the zeolite granules. Those adsorb the moisture with an exothermic reaction. Generated heat is used to increase the speed of the drying process and thus its efficiency. After this phase dishes and cutlery are dried and zeolites get regenerated by a thermal treatment at 240°C during the subsequent washing cycle. In this case, precise information about the components of this system is not directly achievable, due to industrial confidentiality issues. Nonetheless, qualitative and quantitative data are gathered from:

- Impressions from disassembling a commercially available dishwasher having the alternative system installed.
- Analysis of the patent of the drying system available (“Dishwasher with a Rinse Container and Drying Arrangement”, Pub. No: US2010/0043845 A1).
- Technical assumptions supported by specialists’ opinion.

In addiction the cut-off criteria described above are applied. So the system is assumed to be formed by the following components:

- A polypropylene inlet pipe
- An electric fan to create the air flow
- A container for the zeolites in stainless steel presenting a outlet opening
- A certain amount of zeolite pellets (1,15 kg)
- A cover for the zeolite container in stainless steel
- A heating element represented by a composed wirewound resistor to regenerate the zeolites.

3.2.2 *Life Cycle Boundaries*

The analysis takes into account the entire life cycles of the products, so it is of the type “cradle-to-grave”.

3.2.3 *Impact Categories*

The following potential impacts will be reported, taking into account the characteristics of the products evaluated:

- Abiotic Depletion (ADP)
- Acidification Potential (AP)
- Eutrophication Potential (EP)
- Global Warming Potential (GWP)
- Ozone Layer Depletion Potential (ODP)
- Photochemical Ozone Creation Potential (POCP)

3.2.4 *Data Quality*

The analysis will be conducted by means of the software GaBi Education, version 4.3. It will be used for both the Life Cycle Inventory definition and the subsequent impacts definition. The data are characterized as follows:

- <u>Time related coverage</u>: it will be normally within 8 years
- <u>Geographical coverage</u>: when available, data will be kept from a German source, since they are the most complete by default being the software from that country.

- Technology coverage: the description of the technological quality will be described for each one of the steps within the life cycles. Normally for the power supply in every process it's taken an average mix of energetic sources for the country into consideration (basically Germany). Whenever data are not available by the software, they will be obtained by primary sources, typically suppliers, and other secondary sources such as articles or public documentation.

3.3 *Life Cycle Inventory*

The LCI encompasses the following steps in the life cycle of each drying system studied:

- Raw material extraction, for example nickel and chromium extraction for producing the resistor wire.
- Processing of raw materials to produce the specific components for the systems
- Transportation of the components onto the dishwasher
- Usage of the product
- End-of-Life management

secondary input/output data provided by the used software database were normally used. A small number of secondary data not coming from the database of GaBi have been used, too, specifically coming from scientific articles or other databases (Faberi, 2007, Fawer *et al.*, 1998). When necessary, primary data had to be collected through direct communication with producers. In addiction, as a rule producers' data were not directly usable for the impact assessment, but needed to be rearranged and normalized case by case.

3.3.3 *Cradle-to-gate process schemes and data*

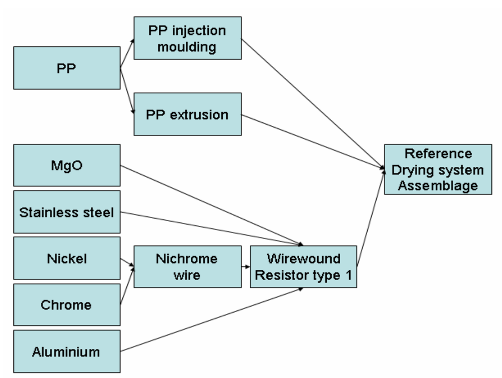


Fig. 1: Cradle-to-Gate life cycle scheme for reference drying system

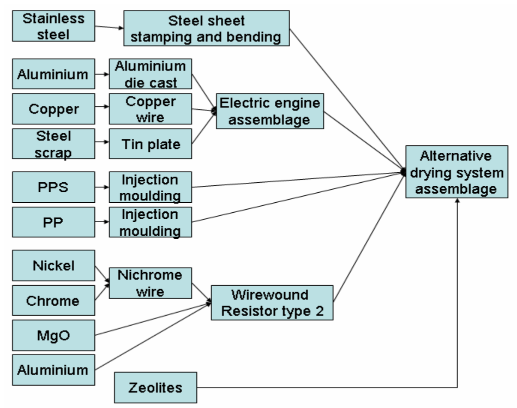


Fig. 2:Cradle-to-Gate life cycle scheme for alternative drying system

Tables and notes about the resulting data for the Life Cycle Inventory can be found in appendices.

3.4 *Life Cycle Impact Assessment*

The LCIA results in this chapter were derived from the LCI emissions using the CML 2001.
It is an impact assessment method collection, which restricts quantitative modelling to relatively early stages in the cause-effect chain to limit uncertainties and group LCI results in midpoint categories, according to themes. These themes are common mechanisms (e.g. climate change) or commonly accepted grouping (e.g. ecotoxicity).to the assembly line
Final assemblage of the components
The data for the impact categories "CML 2001" are according to the information of the Institute of Environmental Sciences, Leiden University in The Netherlands, published in a handbook (Guinée *et al.*, 2001) and based on various different authors. Furthermore a spreadsheet presents characterisation factors for more than 1700 different flows. Besides this, this methodology encompasses the steps of normalization and evaluation.
Final outcomes are shown as follows:

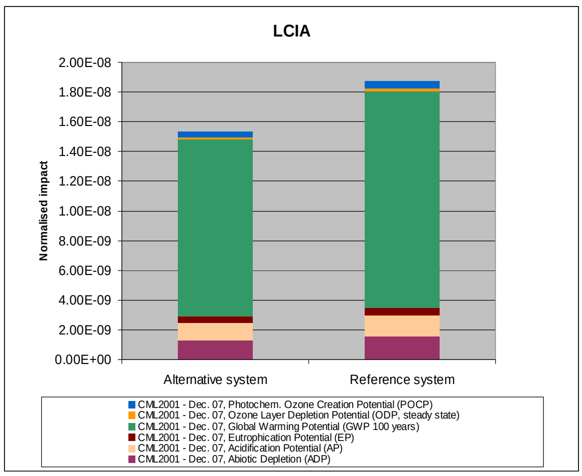


Fig. 3: LCIA data

Table 1: LCIA data

Impact category	*Reference system [normalised]*	*Alternative system [normalised]*	*Variation [|%|]*
Abiotic Depletion (ADP)	1.56E-09	1.27E-09	18.37
Acidification Potential (AP)	1.43E-09	1.19E-09	17.01
Eutrophication Potential (EP)	4.83E-10	4.52E-10	6.44
Global Warming Potential (GWP 100 years)	1.46E-08	1.19E-08	18.44
Ozone Layer Depletion Potential (ODP, steady state)	1.80E-10	1.45E-10	19.09
Photochem. Ozone Creation Potential (POCP)	4.45E-10	3.71E-10	16.62
Overall Impact Value	1.87E-08	1.53E-08	17.97

The previous graph and table show the difference in terms of environmental impact between the two systems. It is noticeable the big normalized impact as far as Global Warming Potential, in both cases. This is due to the generally high energy usage of household appliances. The table shows that absolute impact reduction as far as this point is of 18,44%, using the drying system with zeolites. This is the main affecting component of the overall impact value, that shows a reduction of about 18% from the reference to the alternative system. Another way to evaluate the LCIA is to see the contribution of each life cycle phase for every system under analysis. The results are shown below:

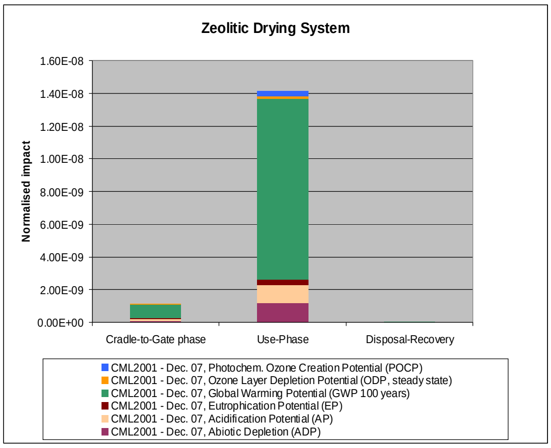


Fig. 4: LCIA data sorted by phase, alternative system

The table referred to this graph shows in detail each category value for each phase of the product life cycle:

Table 2: LCIA data sorted by phase, alternative system

Impact category	*Cradle-to-Gate phase [normalised]*	*Use phase [normalised]*	*EoL [normalised]*
ADP	9.38E-11	1.18E-09	2.96E-13
AP	1.06E-10	1.08E-09	7.09E-13
EP	7.79E-11	3.64E-10	1.04E-11
GWP 100 years	8.29E-10	1.10E-08	3.94E-11
ODP, steady state	9.28E-12	1.36E-10	1.11E-14
POCP	3.46E-11	3.36E-10	1.25E-12
Overall Impact Value	1.15E-09	1.41E-08	5.21E-11

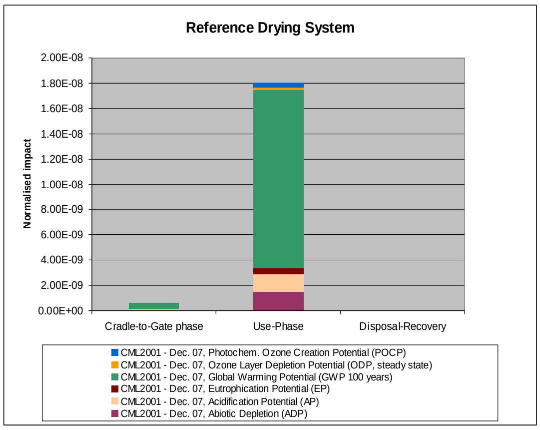


Fig. 5: LCIA data sorted by phase, reference system

Table 3: LCIA data sorted by phase, reference system

Impact category	*Cradle-to-Gate phase [normalised]*	*Use phase [normalised]*	*EoL [normalised]*
ADP	5.22E-11	1.50E-09	1.28E-13
AP	4.90E-11	1.39E-09	2.30E-13
EP	1.75E-11	4.65E-10	6.43E-13
GWP 100 years	4.75E-10	1.41E-08	1.12E-11
ODP, steady state	5.69E-12	1.74E-10	9.03E-15
POCP	1.63E-11	4.29E-10	1.64E-13
Overall Impact Value	6.15E-10	1.81E-08	1.24E-11

The reference system shows less impact for the Cradle-to-Gate and EoL phases, due to the more complex nature of the alternative system, formed by more components to be produced and managed in the end of life. Nonetheless, the savings in the use phase are much higher. Specifically, these are in the order of 22% for the alternative system.

It is also interesting to look at other categories linked to the environment, even if not taken into consideration in the CML methodology. The following graph shows the savings of the alternative system in terms of primary energy usage and water usage:

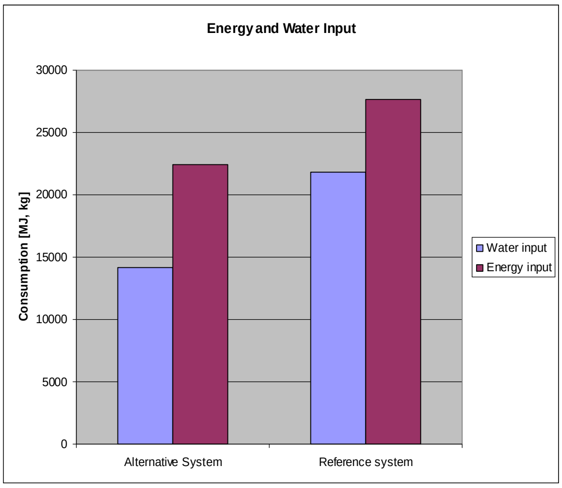


Fig. 6: Energy and water consumption

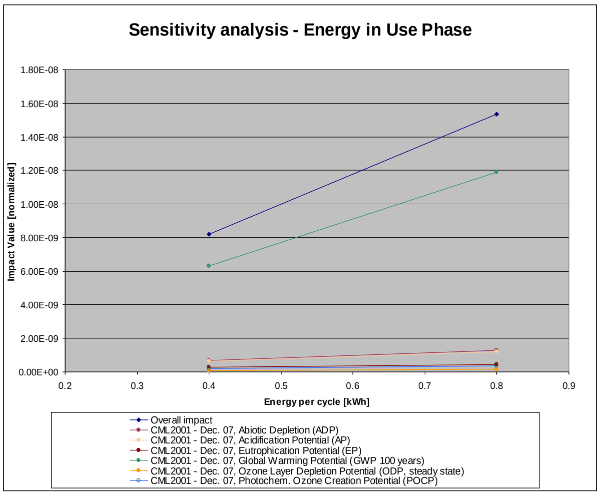
Again the alternative system presents better performances. The fact that no water is utilised during the usage for the alternative system surely helps in these terms. The weight of use phase is again the highest, with values above 90% for each system.

3.5 Sensitivity Analysis

It is useful, also in terms of the experimental study, to evaluate the more significant what-if scenarios. From the dishwasher working analysis it is shown that the energy consumption takes place only in the first part of the washing cycle. Thermal energy is transferred both to the inlet water and to the zeolites, in order to regenerated. It is demonstrated that about half of the energy is used for each purpose. Thus, it's assumed that around 0,4 kWh are to regenerate the adsorbent. Zeolites have the property of forming a strong bond with the water molecules and this has also bad implications, namely a very high temperature of desorbing. Data from the manufacturers talk about 280°C of minimum regeneration temperature. Hence the need of such relatively high energy input requirement in desorption and the consequent value of environmental impact. Table and graph below show the trend of impact corresponding to a decrease of energy employed in desorption.

Table 4: What-if analysis 1 data

Impact category	*Impact at 0,4 kWh/cycle [normalised]*	*Variation from the alternative system [%]*
ADP	6.75E-10	-46.87
AP	6.42E-10	-46.07
EP	2.68E-10	-40.73
GWP 100 years	6.32E-09	-46.92
ODP, steady state	7.64E-11	-47.38
POCP	2.02E-10	-45.72
Overall Impact Value	8.18E-09	-46.65



It **Fig. 7: What if analysis 1**

It is shown that using a material with the same zeolites capacity but with less desorption temperature would allow to decrease the single and overall impacts up to around 46%.

Not such savings would be obtained by varying other features of the system. For example, the scenario of the same zeolitic system without the zeolite steel container has been modelled. It would correspond to the utilisation of materials not requiring this device, such as massive ceramic filters inserted directly in the air loop. The what if analysis is described below:

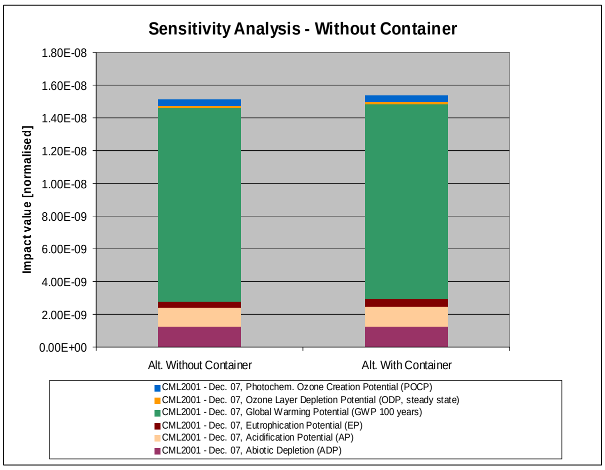


Fig. 8: What if analysis 2

4 Moisture Adsorption Tests

4.1 Description of the Materials

The ceramic foams tested were produced in the laboratories of the University of Padua and University of Sassari. Three main materials have been tested and they are named as MaNW, SS-TiO_2 and BAF.

MaNW: it is formed by a commercially available ceramic foam substrate in silicium carbide, produced via replica technique. Its surface is activated by growing nanowires via thermal treatment in an oven at about 1200ªC and using appropriate catalytic substances. The resulting chemical and morphological properties should be favourable for gas adsorption, thanks to an increased value of specific surface area.

SS-TiO2: this material is formed, again, of a SiC porous substrate. In this case the surface treatment consists in a wash-coating in a sol-gel substance in which nanoparticles of Titanium oxide are dispersed. After this, the samples are thermally treated at 350ªC in order to solidify the surfacial layer. The obtained structure should consist in an omogeneous TiO_2 layer with a periodical porous structure and a specific surface area between 100 and 200 m^2/g, thus good for gas adsorption purposes

BAF: this foam is obtained by direct foaming technique. It is obtained by mixing 3 types of powders, namely a poly-dimethylsiloxane, a poly-borodiphenylsiloxane and azodicarbonic acid diamide. The first two substances belong to the category of preceramic polymers, that is substances that present an irreversible polymer-to-ceramic transition at a fixed temperature (around 800ªC). The latter substance has the function of blowing agent, to create the required porosity. Among the three types of materials, BAF is supposed to offer the poorest results, since it has not undergone any surfacial treatment to increase its adsorption capacity.

4.2 Description of Experimental Instrumentation

Samples were tested in an appliance named Moisture Chamber. It is a chamber where set levels of humidity and temperature can be reached. Its function as far as these experiments is to simulate the inner environment of an household appliance that has to be dried up.
Moisture chamber working is briefly explained as follows: desalinated water is let flow through a pipeline. This is connected to the external net and to two tanks placed on the bottom of the instrument. One tank has to keep the moisture bulb at a controlled temperature in order for it to allow calculating the humidity level in the chamber. The other tank provides water to the chamber, which is heated up by a resistor to generate the moisture.
Experiments were conducted in the following way. The chamber was set at the desired values of humidity and temperature. Standard values were 100% humidity and 40°C. Then, after the necessary time to let the machine reach the set values and stabilize, samples of determined dimensions were placed inside the chamber. Then, at fixed times, samples were weighted outside the chamber by means of a microbalance. The test was conducted for a variable time, depending on the time needed by the specific material to reach the adsorption equilibrium. Data obtained in this way were fitted with an appropriate curve, in order to evaluate both the kinetics and the total capacity of the material.

4.3 Results

Reference tests: two types of zeolites have been tested first. They are both predicted to have good moisture adsorption performances, as stated by the manufacturer. So the scope of these measurements is to set reference values for the subsequent tests. The zeolites are commercialized by Zeochem AG and are indicated by their commercial names, ZEOCHEM® Z4-01 and ZEOX® O_{II}. Both types are in form of spherical pellets. Comparative properties of the two types are shown in the following table:

Table 5: Reference materials data

Data type	Z4-01	ZEOX O_{II}
Type of structure	A	X
Si/Al ratio	1,0	1,18
Pore opening [Å]	4	9
Tapped bulk density [kg/m³]	720	650
Bead size nominal	2,5-5	0,4-0,8
Residual water content, as shipped [%]	1,5 max	0,5

The amount of material tested is the same for both the types and it's of 11 g. The moisture adsorption behaviour is shown in the graphs below:

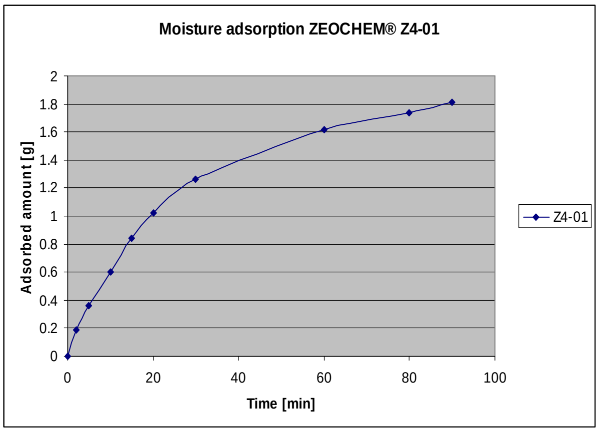


Fig. 9: Material 1 performance

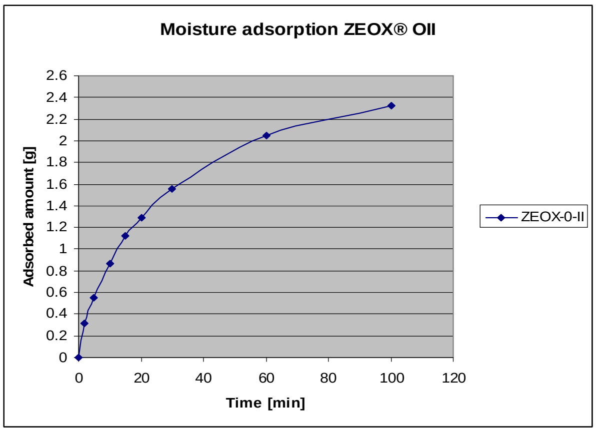


Fig. 10: Material 2 performance

Both the materials present excellent adsorption performances. This is justified by the small value of Si/Al ratio. In fact the presence of Al is proportional to the amount of sites that present a negative charge and these sites are where the water molecules are adsorbed. ZEOX® O_{II} tends to a slightly higher equilibrium value, which means higher capacity in the test conditions. This could depend on the higher value of pore opening and smaller value of bead size. More open pore structure consents an easier diffusion of the adsorbed species within the structure. Furthermore, data are in qualitative accordance with the specifics for the drying system that makes use of zeolites. In fact, it is indicated in the patent that the amount of zeolites employed, 1,15 kg, adsorb up to 200 g of moisture in a cycle. Assuming that adsorption capacity is proportional to the amount of adsorbent, all other operating conditions being equal, data are at least of the same magnitude with the ones obtained in the test.

Tests on BAF, MaNW and SS-TiO_2 samples: samples of the same weight of the reference materials were placed in the moisture chamber, in the same conditions of humidity and temperature. Results are shown in the following graphs:

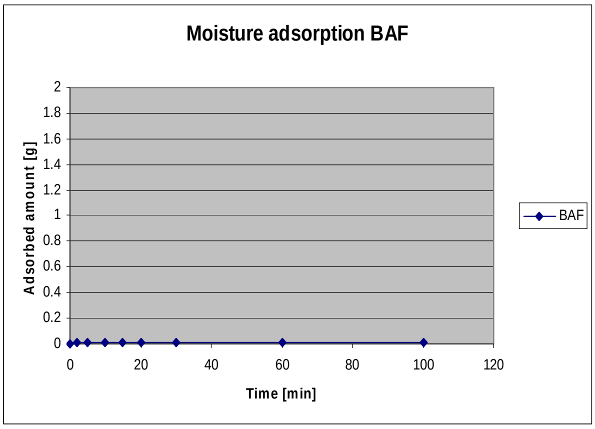


Fig. 11: BAF performance

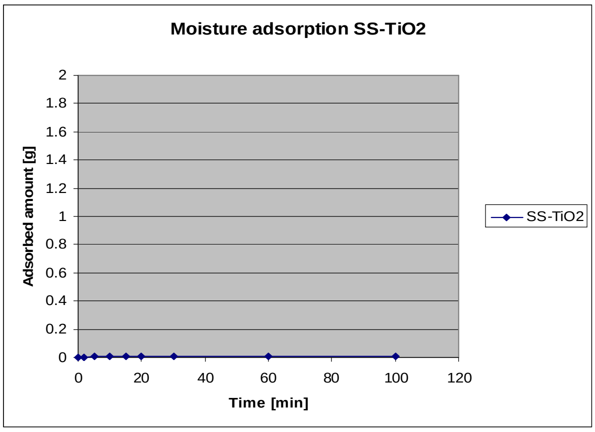


Fig. 12: SS_TiO_2 performance

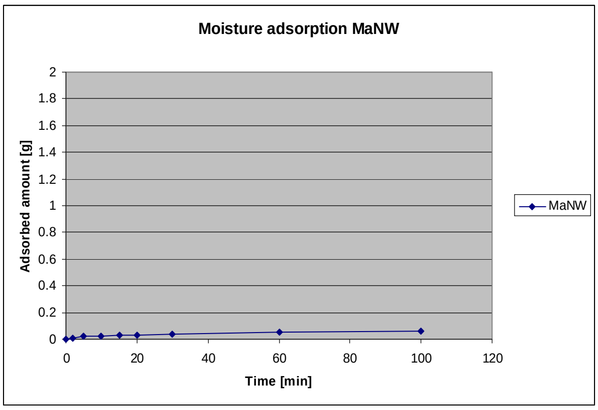


Fig. 13: MaNW performance

5 Conclusions

Results of the conducted LCA showed the environmental advantages derived from the use of a desiccant material (zeolites) in the drying phase of a dishwasher cycle. An overall saving of about 18% was observed. Specifically, the most relevant outcome was the reduction of Global Warming Potential in the use-phase of the household application, which is of about 22%. A sensitivity analysis proved that a further increase in desiccant performances would allow saving up to almost 47% of the overall impact. Hence the appropriateness of studying substitute products for zeolites. The used desiccant has been successfully tested as far as moisture adsorption in order to evaluate the general behaviour that a substitute product ought to possess to at least equal its already exceptional performances. After this, a series of three different material prototypes has undergone the same moisture adsorption tests. The materials were produced following procedures never tried before, nonetheless exploiting the technological background of the personnel at the University of Padua and University of Sassari. The prototypes showed very low performances. As a result, for BAF and SS-TiO_2 no adsorption is observed in any of the samples tested. Specifically, neither microporous mechanism nor condensation phenomena, typical of mesoporous media, are noted. Since the humidity value is of 100% it is assumed that the same behaviour would be observed at lower values. The reasons of such negative results are different for the two types of materials. As for BAF samples, low values of SSA are the main cause. In addiction, the chemical nature of the surface doesn't show any affinity with polar water molecules. In the case of zeolites, the electrically charged sites play a fundamental role in adsorbing them, while in the materials tested the surface do not have that kind of property. As for SS-TiO_2, the layer is predicted to possess higher values of SSA, so the explanation must be different. In this case the absence of adsorption must depend on the quantity of active material with which the substrates are coated. In fact, it was not possible to evaluate with precision the thickness of the layer grown on the surface. Moreover, data from EDX characterization showed the presence of TiO_2 only in traces. Thus, for SS-TiO_2 samples, the evaluation on the moisture adsorption performances should be postponed to further investigations. MaNW samples present a weak adsorption activity, most likely due to the condensation of water on the surface of the nanowires. Nonetheless, the low values of adsorbed amount are dependent on the limited SSA of the material, which is just a little higher.

A future development possibility is shown here, which is developing new materials able to adsorb water and to be regenerated by a thermal treatment. These tests and the connected literature show that ceramic foams can be the right path to follow, because of their natural resistance at high temperatures and aggressive environments. Although, room of improvement is still very high.

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