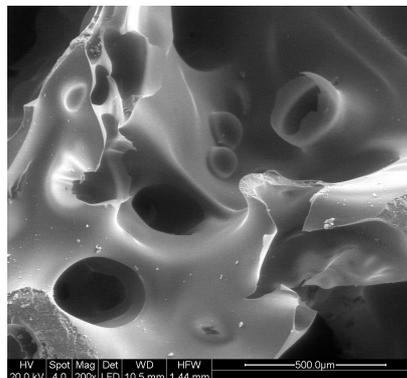




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Adsorption Performances and Application Study of Ceramic Foams

Life Cycle Assessment Case Study

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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.

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 addition, 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*

Resumo

A Bosch-Siemens Home Appliances projectou um novo sistema de secagem para máquinas lavadoras com base num material aplicado pela primeira vez aplicado, que pertence à família das zeólites.

Durante os últimos anos, a sustentabilidade tornou-se um factor chave na indústria de electrodomésticos, necessitando de responder à regulamentação internacional (Ecodesign, 2005), reflectir a sensibilidade crescente da sociedade sobre as questões ambientais, mas também a obtenção de uma melhor imagem da empresa.

A questão chave colocada nesta tese é se pode ter um melhor desempenho e ser menos nocivo no ambiente nomeadamente através da escolha dos materiais utilizados nos produtos. Este trabalho consiste numa primeira parte assim numa avaliação comparativa dos impactes entre o novo sistema com as zeólites e os sistemas usual de secagem.

A metodologia utilizada para comparar os impactes dos dois sistemas é a análise ciclo de vida, sendo que as conclusões do estudo revelam as vantagens ambientais do novo sistema de secagem com zeólites sobre a tecnologia comum.

Numa segundo parte analisa-se ainda a possibilidade de substituir a zeólite por espumas cerâmicas, já que dispõem de propriedades interessantes, nomeadamente uma alta superfície de área para adsorção, uma elevada estabilidade térmica e química e potencial de redução do impacte ambiental.

Esta segunda parte do trabalho assenta em ensaios laboratoriais com um solução de espumas cerâmicas desenvolvida pelo autor, tendo em vista avaliar a sua potencial substituição dos zeólites. Os resultados mostram que esses materiais precisam de ainda de melhorias em termos de eficiência para ser considerados como substitutos efectivos das zeólites neste campo de aplicação.

Palavras chave: *Análise do Ciclo de Vida, Espumas Cerâmicas, Zeólites, Electrodomésticos, Impacte Ambiental.*

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List of Abbreviations

ADP	=	Abiotic Depletion Potential
AP	=	Acidification Potential
BET	=	Brunauer, Emmet, Teller
EIOLCA	=	Environmental Input-Output Life Cycle Assessment
EP	=	Eutrophication Potential
FDIR	=	Final Draft International Standard
FTIR	=	Fourier Transformed Infra-red
GWP	=	Global Warming Potential
IR	=	Infra-red
ISO	=	International Organization for Standardization
LCA	=	Life Cycle Assessment
LCI	=	Life Cycle Inventory
LCIA	=	Life Cycle Impact Assessment
MgO	=	Magnesium Oxide
ODP	=	Ozone Layer Depletion Potential
POCP	=	Photochemical Ozone Creation Potential
PP	=	Poly(propylene)
PPS	=	Poly(phenylene sulfide)
SEM	=	Scanning Electron Microscopy
SiOC	=	Silicone Oxycarbide
TiO ₂	=	Titanium Dioxide
wt	=	In Weight

Introduction

Ceramics foams could be use to several ends as air filters or dehumidifiers (Scheffler and Colombo, 2005). Their performances and special environmental impacts are still under studies and the state-of-the-art research needs further improvements. Improvements in manufacturing and process techniques of ceramic foams (Colombo, 2006, Colombo and Bernardo, 2003) not always go hand in hand with applicative studies, which is the core of this thesis.

The aim of this thesis is:

- To investigate and evaluate the performances of ceramic foams as air filters or dehumidifiers.
- To carry out a Life Cycle Analysis of a household appliance which has a ceramic foam device installed.

The potential applications of such devices consist in:

- Air purification maintenance-free systems, (i.e. auto-regenerated) to be applied in the kitchen, for example in hoods, refrigerators, ovens, to generally improve indoor air quality;
- Air dehumidification systems, to be applied in dishwashers or dryers, to improve energy efficiency while reducing the cycle time (as an alternative to zeolites).

The main features that are pursued from the devices to comply with these applications are:

- High efficiency in technical and economical terms
- Reliability
- Reduced environmental impact in terms of Life Cycle Assessment and hazardous substances

The subject is vast and the particular solution to be developed within the thesis is likely to be found out along the route.

The reason why new materials for this application are studied is that conventional materials used nowadays, even if very good for adsorption of volatile substances and water vapour, present some disadvantageous aspects that can't be solved for specific operating conditions. For example, the most common adsorbent, activated carbon, cannot be used in conditions of high temperature because of its degradability and of pore plug due to polymerisation of some volatile organic compound catalysed by ashes present on activated carbon surfaces. Ceramic foams are a specific class of materials which are used in many fields such as catalyst supports, porous burners and liquid metal filters. Moreover, they are predicted to have good gas adsorption behaviour too due to their specific surface area. They also

have several properties, such as high thermal and chemical stability, that allows them to be used in a wide range of conditions, and that makes this class of materials very interesting.

The work done by the author involves two academic institutions, Instituto Superior Técnico and Università di Padova, and an industrial institution, Electrolux Italia S.p.A. The work consists in obtaining bibliographical information about the main topics of the work, ceramic foams and LCA. A wide focus will be put in this part, in order to understand as much as possible about the field in which the thesis is contained.

This report contains an overview about ceramic foams, with special attention to typical fabrication modes, consequently focusing attention on commonly used materials. After that, a wide section is dedicated to the experimental, with description of the characterization methods involved and explanation of the procedure that will be followed. In the last part an analysis will be conducted over the two main techniques in use for Life Cycle Assessment of single products, the Process-based Life Cycle Assessment and the EIO LCA (Economic Input-Output Life Cycle Assessment), in order to point out advantages and disadvantages of each one as far as the specific case described.

The Life Cycle Assessment case study and the experimental outcomes on materials constitute the second part and the core of the work and a wide section is dedicated to them.

Chapter 1 - Ceramic foams

According to Gibson and Ashby, 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.

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 such 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. Cell size, morphology and degree of interconnection are also important factors that influence potential applications for these materials.

A wide variety of processing routes to manufacture ceramic foams has been developed and patented in many countries around the world. However, they can be crudely divided into two categories with a series of variations on the basic themes.

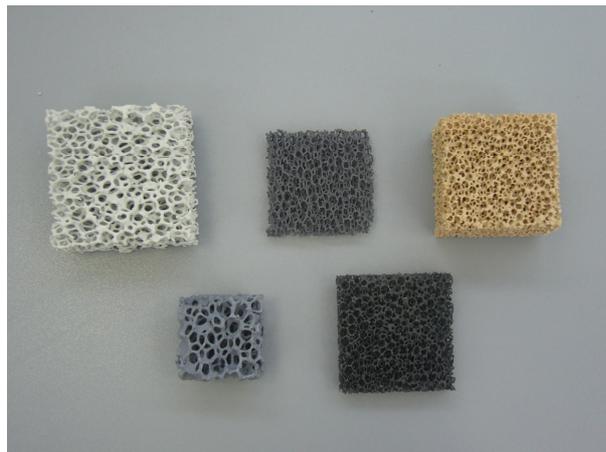


Fig. 1: Some examples of ceramic foams

1.1 Replication Techniques

One of the oldest approaches 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. Despite this, these foams are manufactured in large quantities and used extensively in industry, often as filters for molten metals. Many different polymers can be used for the precursor foam. These include polyurethane, polyvinyl chloride, polystyrene and cellulose. Reproducibility of the properties of the organic foam is extremely important. It must be able to spring back after being squeezed out and have controlled tolerances to ensure consistency in the ceramic product. Finally, the foam must burn out

cleanly and completely during sintering without damaging the ceramic replica. Generally, any fine ceramic powder can be used that can be made into a suitable suspension. The rheological characteristics are similar to those required for other slurry-based production routes for ceramic components. The solid content usually lies in the range 50-70%. Typically the suspension is thixotropic, that is, the viscosity decreases with time at a fixed rate of shear and on removal of the stress the material regains its original structure with a consequent increase in viscosity. Once the polymer foam and ceramic slurry are ready the coating process is carried out. This involves immersing the foam in the slurry and compressing it to remove air. While still in the slurry the foam is allowed to expand again, causing the slurry to be sucked into the open cells of the foam. When the foam has been coated appropriately, it is dried in an oven to solidify the ceramic structure, after which it is exposed to an initial thermal treatment that is designed to burn out the polymer from inside the ceramic struts as well as remove any organic additives from ceramic slurry.

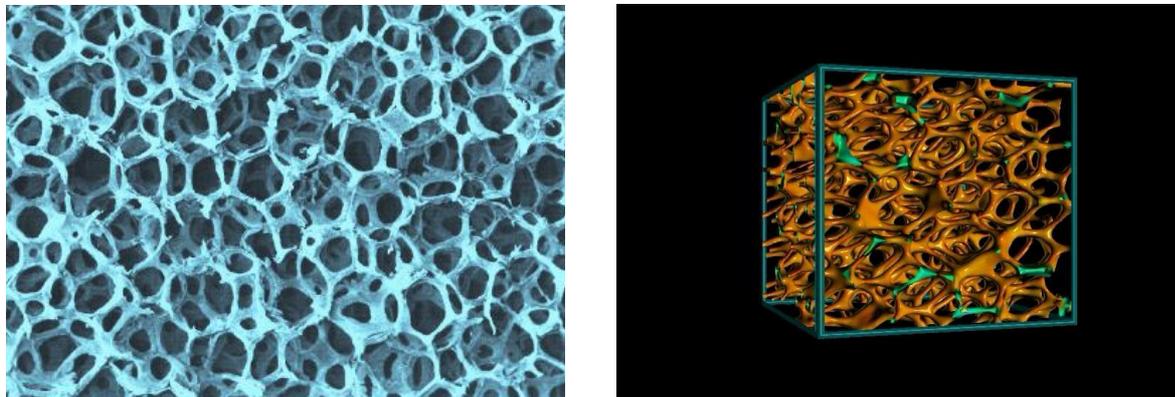


Fig. 2: Reticulated ceramic foams produced by replication of a polymeric foam

1.2 Foaming Techniques

The second basic approach relies on foaming a ceramic slurry by mechanical agitation or in situ evolution of gases. These approaches probably yield the widest range of cellular structures and hence properties, but they are generally less open than the replicated foams. While a very wide range of applications are now being considered it is probably true to say that the most of them are still in the development stage.

During the process, the addition of surfactant is required to reduce the surface tension of the gas-liquid interfaces and thus stabilize the gas bubbles developed within the slurry. Such stabilization only works for a limited period of time, however, since several transformations in the bubble structure may subsequently occur due to thinning of their surrounding lamellae. So other techniques have been developed to ensure the stability of the needed transient structures. Various companies have patented processing routes for the manufacture of foam ceramics by entraining an external gas phase. All of them incorporate a material that orientates itself at the gas-water interface, thereby stabilizing the gas phase and one or more additives that cause the structure to set prior to drying and firing. Some

examples of these production processes are given by Du Pont, Mitsubishi Chemical Industries, BASF, Hi-Por Ceramics and others.

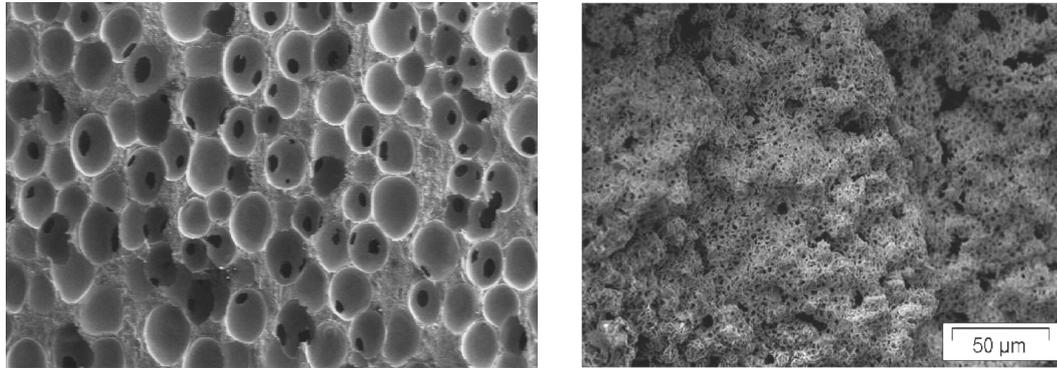


Fig. 3: Structures of foams obtained from direct foaming

Recently, an experimental procedure was carried on by Colombo and Bernardo⁽³⁾ that produced cellular silicon oxycarbide (SiOC) open cell ceramic foams by in situ evolution of preceramic polymers. They mixed a methyl polysiloxane with precursors for polyurethane (polyols and isocyanates) in dichloromethane, together with appropriate surfactants and catalysts. Blowing was started by vigorously stirring the mixture and inserting the sample into an oven at a controlled temperature in the range of 25-40°C. The expansion was caused by a combination of evaporation of the solvent as a result of the exothermic reactions occurring in the solution (physical blowing) and chemical blowing arising from the reaction between the water generated by condensation of the SiOH groups in the silicone resin with the isocyanate to form carbon dioxide gas.

The choice of polyurethane precursors and the type and amount of surfactants influenced the viscosity of the mixture and hence the final foam architecture and characteristics, while the type and amount of catalysts controlled the rising profile of the foam. Due to immiscibility of with the preceramic polymer, during the blowing stage the polyurethane phase separated into small islands, typically measuring 50-300 μm in diameter, embedded within the preceramic polymer matrix. This controlled the resulting green foam morphology and characteristics. Depending whether the precursors were the basis for so-called flexible, semirigid or rigid polyurethane foams, the foams produced ranged from completely open-celled, owing to the presence of windows in the cell walls, to completely closed-celles.

This kind of ceramic foam has also been used in the experiment described in the later section.

Chapter 2 - Materials

Here are presented the materials that are or could be used for applications as air filters.

2.1 Common Adsorbents

The requirement for adequate adsorptive capacity restricts the choice of adsorbents for practical separation processes to microporous adsorbents with pore diameters ranging from a few Angstroms to a few tens of Angstroms. This includes both the traditional microporous adsorbents such as silica gel, activated alumina and activated carbon as well as the more recently developed crystalline aluminosilicates or zeolites. There is however a fundamental difference between these materials. In the traditional adsorbents there is a distribution of micropore size, and both the mean micropore diameter and the width of the distribution about this mean are controlled by the manufacturing process. By contrast, the micropore size of a zeolitic adsorbent is controlled by the crystal structure and there is virtually no distribution of pore size. This leads to significant differences in the adsorptive properties.

2.1.1 Silica gel

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid (Sorbentsystems, 2010). The chemical composition can be expressed as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The water content, which is present mainly in the form of chemically bound hydroxyl groups, amounts typically to about 5 wt.%. The material appears first to have been developed during the First World War for use in gas masks although in this service it proved inferior to activated carbon. A variety of methods for the manufacture of silica gel have been described including the hydrolysis of soluble alkali metal silicates with acid and the direct removal of sodium from sodium silicate solutions by ion exchange. The silicic acid liberated polymerizes and condenses in the aqueous solution to form chains and nets of linked SiO_4 tetrahedra, which aggregate to form approximately spherical particles of 20-200 Angstrom diameter. On drying, the particles agglomerate to form a microporous structure in which the pore size is determined mainly by the size of the original microparticles. Bond formation between adjacent particles occurs with the elimination of water between neighboring hydroxyl groups and the final structure is therefore physically robust. The size of the original microparticles and consequently the size of the micropores in the final dried gel is sensitive to pH and the presence of other cations in the solution during precipitation. By careful control of the synthesis conditions it is therefore possible to control the pore size, which generally shows a unimodal distribution. The presence of hydroxyl groups imparts a degree of polarity to the surface so that molecules such as water, alcohols, phenols, and amines (which can form hydrogen bonds) and unsaturated hydrocarbons (which can form π -complexes) are adsorbed in preference to nonpolar molecules such as saturated hydrocarbons. Because of its selectivity for aromatics silica gel was used as the adsorbent in the Arosorb process for separation of aromatics from paraffins and naphthalenes but by far the most important current application is as desiccant because of its capacity, at least at low temperatures.



Fig. 4: Silica gel in pellets

2.1.2 Activated Alumina

Activated alumina is a porous high area form of aluminium oxide, prepared either directly from bauxite ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) or from the monohydrate by dehydration and recrystallization at elevated temperature. The surface is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal. At room temperature the affinity of activated alumina for water is comparable with that of silica gel but the capacity is lower. At elevated temperatures the capacity of activated alumina is higher than 10 silica gel and it was therefore commonly used as a desiccant for drying warm air or gas streams. However for this application it has been largely replaced by molecular sieve adsorbents which exhibit both a higher capacity and a lower equilibrium vapour pressure under most condition of practical importance.

2.1.3 Activated Carbon

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1100°C). The activation process involves essentially the removal of tarry carbonization products formed during the pyrolysis, thereby opening the pores. The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The pore size distribution is typically trimodal but the actual distribution and the total pore volume associated with each pore size range are sensitive to the conditions of the initial pyrolysis and activation procedures. The surface of carbon is essentially nonpolar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. They are therefore widely used for the adsorption of organics in decolorizing sugar, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and as a general purpose adsorbent in range hoods and other air purification systems. In order to decrease the mass transfer resistance, the activated carbons used for

adsorption from the liquid phase generally have somewhat larger pore diameters than those used for adsorption from the gas phase.



Fig. 5: Activated carbon

2.1.4 Carbon Molecular Sieves.

Activated carbon adsorbents generally show very little selectivity in the adsorption of molecules of different size. However, by special activation procedures it is possible to prepare carbon adsorbents with a very narrow distribution of micropore size and which therefore behave as molecular sieves. The earliest examples of carbon molecular sieves appear to have been prepared by decomposition of polyvinylidene dichloride but more recently a wide variety of starting materials have been used. Most commercial carbon sieves are prepared from anthracite or hard coal by controlled oxidation and subsequent thermal treatment. The pore structure may be modified to some extent by subsequent treatment including controlled cracking of hydrocarbons within the micropore system and partial gasification under carefully regulated conditions.

By these means it is possible to prepare carbon sieves with effective micropores diameters ranging from about 4 to 9 Angstrom. The micropore size distribution of such sieves is much narrower than in a typical activated carbon and the porosity and therefore the adsorptive capacity are generally very much smaller. The ability to modify the effective pore size by adjusting the conditions of the manufacturing process makes it relatively easy to tailor a carbon sieve to achieve a particular separation. However, it is difficult to achieve absolute reproducibility between different batches and the existence of a distribution of pore size, even if narrow, means that the molecular sieving selectivity of a carbon sieve seldom approaches the almost perfect separation achievable under favourable

circumstances with a zeolite sieve. Nevertheless, the kinetic selectivities which may be attained with a well-prepared carbon sieve are remarkably high.

At present the most important large scale application is in air separation (C. R. Reid and K. M. Thomas, 2001, De Q. Vu and William J. Koros, 2002). Surprisingly, deterioration of the sieve due to oxidation appears not to have proved a significant problem. Other potential areas of application include the clean-up of the off-gases from nuclear facilities and the production of pure hydrogen from gas streams containing small amounts of hydrocarbons. However, in the former application considerations of safety make the use of a combustible adsorbent highly undesirable and in the latter application hydrogen purification processes based on zeolite molecular sieves are well established. A wider range of process applications seems likely to emerge as the technology of producing carbon sieves develops further.

2.1.5 Zeolites

Zeolites are porous crystalline aluminosilicates (U.S. Environmental Protection Agency, 1998). The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the micropore structure is determined by the crystal lattice it is precisely uniform with no distribution of pore size. It is this feature which distinguishes the zeolites from the traditional microporous adsorbents.

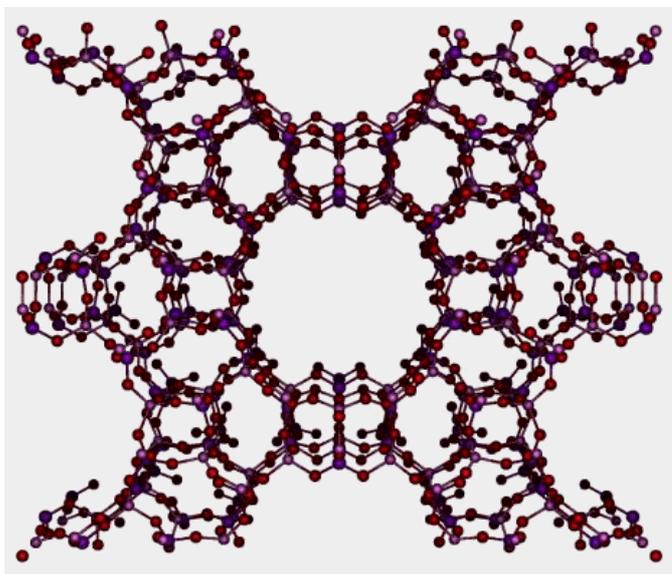


Fig. 6: Example of zeolites atomic structure

Each aluminium atom introduces one negative charge on the framework which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties. The Si/Al ratio in a zeolite is never less than 1.0 but there is no upper limit and pure silica analogs of some of the zeolite structures have been prepared. The

adsorptive properties show a systematic transition from the aluminium rich sieves, which have very high affinities for water and other polar molecules, to the microporous silicas such as silicalite which are essentially hydrophobic and adsorb n-paraffins in preference to water. The transition from hydrophilic to hydrophobic normally occurs at a Si/Al ratio of between 8 and 10. By appropriate choice of framework structure, Si/Al ratio and cationic form, adsorbents with widely different adsorptive properties may be prepared. It is therefore possible. In certain cases, to tailor the adsorptive properties to achieve the selectivity required for a particular separation. The intercrystalline diffusivity and hence the kinetic selectivity and, in extreme cases, the molecular sieve properties are determined mainly by the free diameter of the windows in the intercrystalline channel structure. This dimension is ranged between 2,8-7,4 Angstrom for all types of zeolites (Iza Structure Commission, 2010) but these windows may be penetrated by molecules with critical kinetic diameters which are somewhat greater than the nominal aperture. The effective diameters of the unobstructed windows are actually diminished. The reduction in the free diameter of the windows by blocking cations causes a dramatic reduction in the diffusivity of the guest molecules but also, in certain cases, permits to obtain a molecular sieve separation between species which can both diffuse easily in an unobstructed sieve.

Chapter 3 - Characterization Methods

The methods that are described are connected with all the influencing aspects in play in the experiment, from the structural characteristics of a foam to the chemical composition of a gas. In addition, a brief description of the instrumentation utilized in the work is made.

3.1 Structural Characterization

As far as ceramic foams, it is known that many of their properties depend on their internal architecture. Therefore, two of the most important parameters to evaluate are specific surface area pore characteristics. The classical methods to describe them are respectively BET-nitrogen adsorption and image acquisition. Subsequently they are explained.

3.1.1 BET-nitrogen adsorption

The BET gas adsorption method has become the most widely used standard procedure for the determination of the surface area of finely-divided and porous materials (Commission on Colloid and Surface Chemistry Including Catalysis (1985)), in spite of the oversimplification of the model on which the theory is based. This model was introduced in 1938 by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller⁽¹⁾ and represents a trial to well describe the phenomenon of surface coverage by adsorption at constant temperature. It is customary to apply the BET isotherm equation in the linear form:

$$\frac{p}{n^a(p^0 - p)} = \frac{1}{n_m^a C} + \frac{(C-1)p}{n_m^a C p^0}$$

where n^a is the amount adsorbed at the relative pressure p/p^0 and n_m^a is the monolayer capacity. According to BET theory C is as constant related exponentially to the enthalpy of adsorption in the first adsorbed layer:

$$C = \frac{e^{\frac{-\Delta H_{ads}}{RT}}}{e^{\frac{-\Delta H_{vap}}{RT}}}$$

The BET equation requires a linear relation between $p/n^a(p^0 - p)$ and p/p^0 . The range of linearity is restricted to a limited part of the isotherm – usually not outside the p/p^0 range of 0.05-

0.3. Some adsorption systems give linear or nearly linear BET plots over several ranges of p/p^0 but it is only in the region around $\theta = 1$ that the BET plot can be expected to yield the true value of n_m^a .

After having obtained the value of n_m^a , the second stage is the calculation of the surface area (or BET area) from the monolayer capacity. This requires a knowledge of the average area a_m (molecular cross-section area) occupied by the adsorbate molecule in complete monolayer. Thus:

$$A_s = n_m^a L a_m$$

$$a_s = A_s / m$$

where A_s and a_s are the total and specific surface areas, respectively, of the adsorbent (of mass m) and L is the Avogadro constant.

At present time, nitrogen is generally considered to be the most suitable adsorptive for surface area determination and it is usually assumed that the BET monolayer is close-packed, giving $a_m(N_2) = 0.162 \text{ mm}^2$ at 77 K. With other adsorptives, arbitrary adjustments of the a_m value are generally required to bring the BET area into agreement with the nitrogen value.

It should be appreciated that the BET analysis does not take into account the possibility of micropore filling or penetration into cavities of molecular size. These effects can thus falsify the BET surface areas and in case of doubt their absence should be checked by means of an empirical method of isotherm analysis or by using surface area reference samples.

3.1.2 Image acquisition

Image acquisition is the first step in the important method of image analysis, that as a general rule consists in extract meaningful numerical information starting from an image. As could be guessed, this kind of approach has proved its value in different fields of applications, including geology, medicine and biology. The results from an image analysis for a porous material can include several important pore characteristics like the number of intersections, the perimeter, the pore size distribution, the porosity and the shape factor of the pores.

The conventional approach for image acquisition is microscopy. As the magnification of the image is governed by the pore size of the sample, this can be done by light scanning or scanning electron microscopy (SEM). Careful preparation of the sample is required to obtain sufficient difference in brightness or contrast between the different parts of it. The most common solution is to coat the structure with a thin electrically conductive layer, usually gold or graphite. Another expedient is cutting

thin slices, infiltrating the cellular material with a black resin and finally polishing the plane of interest.

3.2 Infrared Spectrometry

The infrared spectrum of a compound is essentially the superposition of absorption bands of specific functional groups, yet subtle interactions with the surrounding atoms of the molecule impose the stamp of individuality on the spectrum of each compound (H.H. Willard, 1988) . For qualitative analysis, one of the best features of an infrared spectrum is that the absorption or the lack of absorption in specific frequency regions can be correlated with specific stretching and bending motions and, in some cases, with the relationship of these groups to the rest of the molecule. Thus when interpreting the spectrum, it is possible to state that certain functional groups are present in the material and certain others are absent.

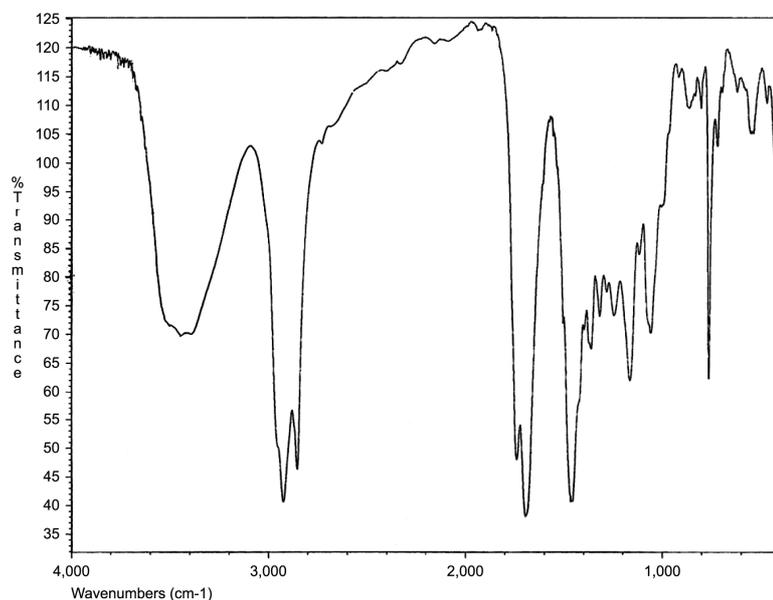


Fig. 7: Resulting FTIR spectrum for acetone

It is useful to recall that the infrared region of the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region. The region includes radiation at wavelengths between 0,7 and 500 μm or, in wave number, between 14000 and 20 cm^{-1} . The spectral range evaluated in the experiment is included in the mid-infrared region and covers frequencies from 4000 to 200 cm^{-1} , in which many useful correlations between signals and functional groups are reported in literature. This part is divided into the “group frequency” region, 4000-1300 cm^{-1} , in which the principal absorption bands are assigned to vibration units consisting in only two atoms, that is not depending on the complete molecular structure, and “fingerprint” region, 1300-650 cm^{-1} , in which the major factors in the spectrum are single-bond stretching frequencies and bending vibrations.

Compound Type	Bond	Wavenumber Range [cm^{-1}]
<i>Aldehydes, Ketones, Esters, Carboxylic acids</i>	C=O	1760-1670, stretch
<i>Alcohols, ethers, carboxylic acids, esters</i>	C-O	1200-1000, stretch
<i>Alkanes</i>	C-H	2960-2850, stretch

Table 1: Some characteristic IR absorption bands in which there are picks of liberated energy (CSUSTAN, 2010)

Infrared radiation has been analyzed by means of a scanning Michelson interferometer. This 988) of a movable mirror, a fixed mirror and a beamsplitter. Radiation from the infrared source is collimated by a mirror, and the resultant beam is divided at the beamsplitter. Half the beam passes to a fixed mirror, half is reflected to a moving mirror. After reflection the two beams recombine at the beamsplitter and, for any particular wavelength, constructively or destructively interfere, depending on the difference in optical paths between the two arms of the interferometer. With a constant velocity, the intensity of the emerging radiation at any particular wavelength modulates in a regular sinusoidal manner. In the case of a broadband source the emerging beam is complex mixture of modulation frequencies that, after passing through the sample compartment, is focused onto the detector. This detector signal is sampled at precise intervals during the mirror scan. Both the sampling rate and the mirror velocity are controlled by a reference signal incident upon a detector, which is produced by modulation of the beam from the helium-neon laser. The resulting signal from detector is known as interferogram and contains all the information required to reconstruct the spectrum via the mathematical process known as Fourier transformation. The transform is carried out by a computer, which is an essential part of the spectrometer, by an appropriate algorithm such as Cooley-Turkey transform algorithm.

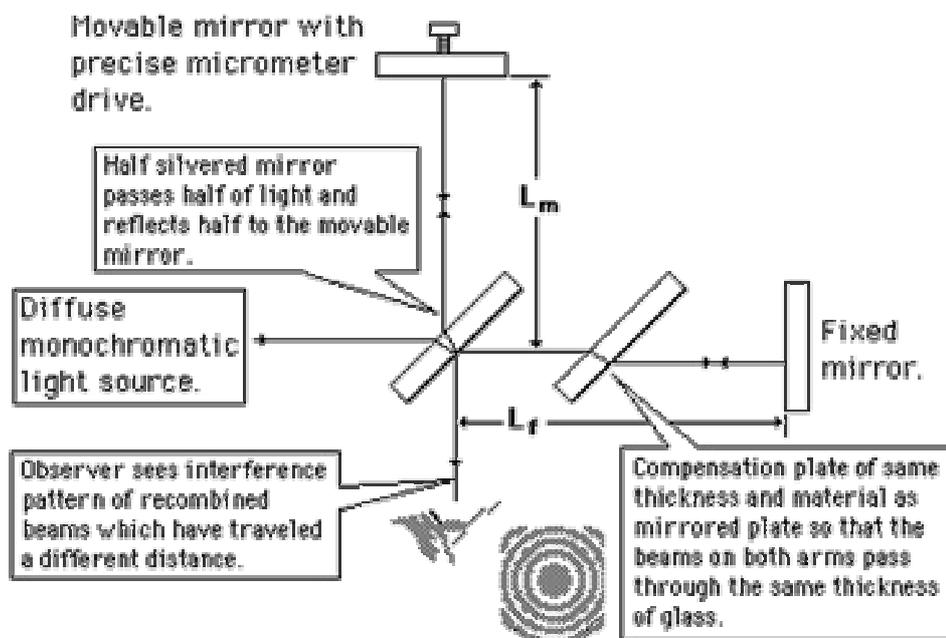


Fig. 8: Optical path diagram of infrared Fourier transform spectrometer

Compound type Bond Wavenumber Range [cm⁻¹] Aldehydes, Ketones, Esters, Carboxylic acids
C=O 1760-1670, stretch Alcohols, ethers, carboxylic acids, esters C-O 1200-1000, stretch Alkanes C-H
2960-2850, stretch

3.3 Analysis of a Batch Adsorber

This method belongs to the category of techniques to characterize the adsorption and diffusion properties of an adsorption system. The feature that distinguishes this from, for example, gas chromatography consists in the simplicity to set up and in the ability to handle practically any complexities of an adsorption system. Since many types of batch systems could be prepared, the scheme that has been developed for the present work is now explained. The sample to test is placed inside a reactor, an hollow cylindrical glass body, connected to a closed loop. Then an amount of adsorbate is injected into the loop by a syringe and it is circulated by means of a pump at an appropriate flow rate. A little part of the flux is constantly deviated in a secondary loop. This fraction is monitored to determine the adsorbate concentration in the gas phase by means of aforesaid FTIR spectrometry and after that it is brought again in the primary loop. The practical result consists in a concentration/time graph that basically illustrates the kinetic of the process. Important aspects to which attention must be paid are the operating conditions, such as: humidity, pressure and temperature. In this work, these physical properties are maintained constant and controlled by sensors and valves.

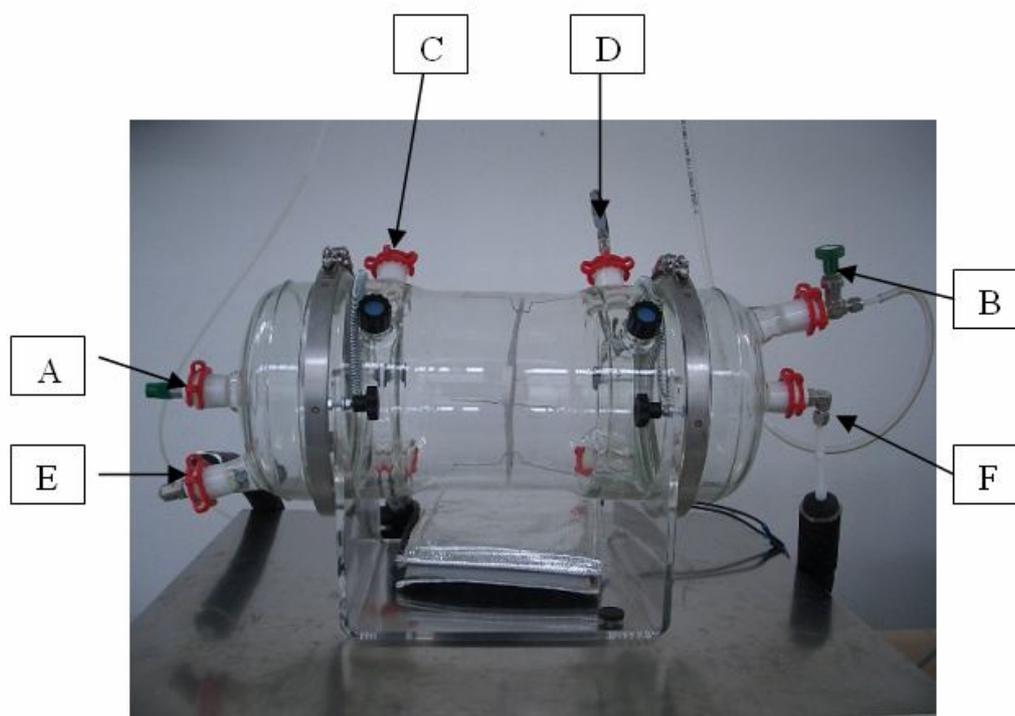


Fig. 9: Reactor: safety valve (A), escaping valve (B), humidity sensor (C), temperature sensor (D), inlet line (E)

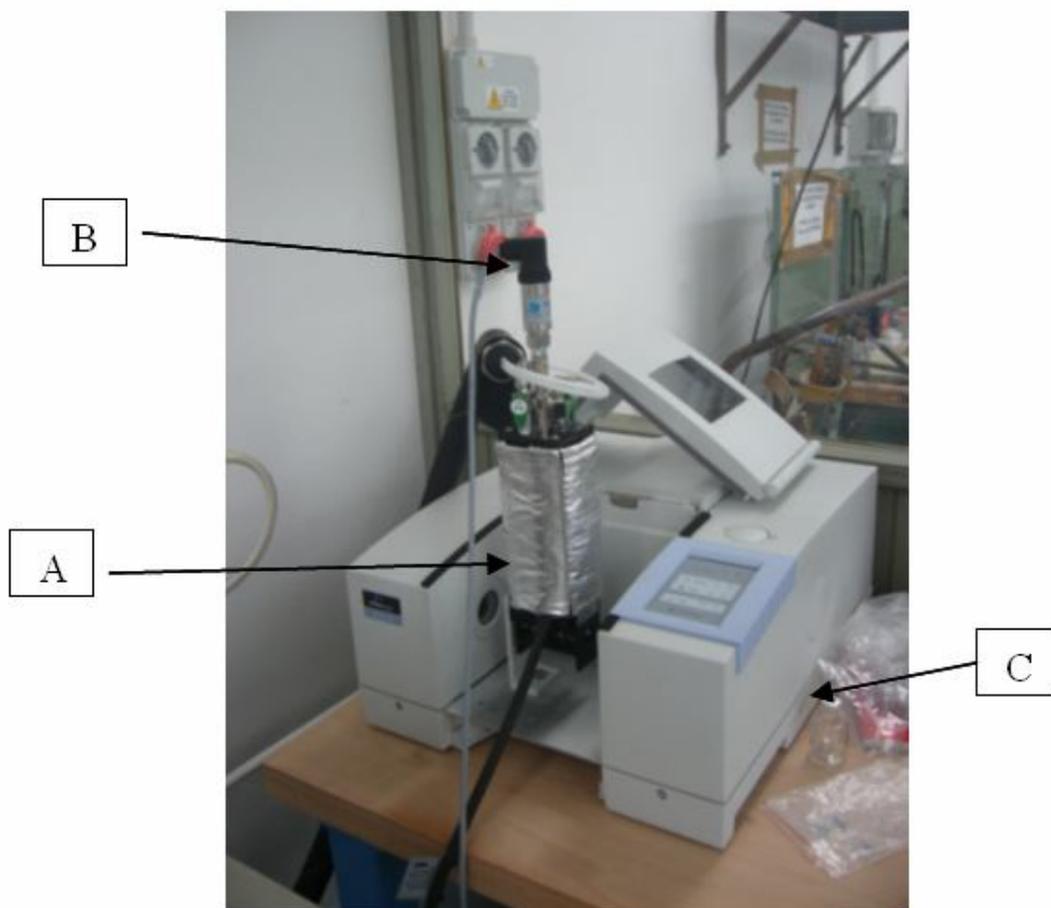


Fig. 10: IR spectrometer: cell in which enters the gas phase to be analyzed (A), pressure sensor (B) and analytical equipment (C)

Chapter 4 - Notes on Life Cycle Assessment

The second part of the study will consist in a Life Cycle Assessment (LCA) of a product which is supposed to have the ceramic foam filter installed. More precisely, a comparison will be carried on between this type of product and a similar product that doesn't have the device installed. The goal is to point out whether this solution brings any benefit in terms of environmental impact, for example as far as indoor air quality or usage effectiveness, reducing cycle time. In the next section a general overview about Life Cycle Assessment is made, with references to the normative ISO 14000 that rules this field. A description of the two most used approaches in LCA, the Process-based LCA and the Environmental Input-Output LCA, will be made in order to clarify these options to later choose the most appropriate one for the kind of product on study.

4.1 Definition by ISO/FDIS

The ISO/FDIS standard in Life Cycle Assessment (1997a) gives the following definition:

"LCA is a technique for assessing the environmental aspects and potential impacts associated with a product, by:

- *compiling an inventory of relevant inputs and outputs of a system;*
- *evaluating the potential environmental impacts associated with those inputs and outputs;*
- *interpreting the results of the inventory and impact phases in relation to the objectives of the study"*

LCA studies the environmental aspects and potential impacts throughout a product's life from raw material acquisition through production, use and disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences.

4.2 Methodological Framework

According to the ISO 14040 and 14044 standards, a Life Cycle Assessment is carried out in four distinct phases.

4.2.1 Goal and scope

In the first phase, the LCA-practitioner formulates and specifies the goal and scope of study in relation to the intended application. The aim of an LCA study goal-definition is to state the intended application, including the reasons for carrying out the study, the intended audience and the expected use of the results. The definition of the scope of the life cycle assessment sets the borders of the assessment - what is included in the system and what detailed assessment methods are to be used. The object of study is described in terms of a so-called *functional unit*. Apart from describing the functional unit, the goal and scope should address the overall approach used to establish the system

boundaries. Finally the goal and scope phase includes a description of the method applied for assessing potential environmental impacts and which impact categories that are included.

4.2.2 Life cycle inventory

This second phase 'Inventory' involves the following main points:

- data collection
- refining system
- boundaries calculation
- validation of data relating data to the specific system
- allocation

Data encompassed are those related to environmental (e.g., CO₂) and technical (e.g., intermediate chemicals) quantities for all relevant unit processes within the study boundaries that compose the product system. Data must be related to the functional unit defined in the goal and scope definition, they can be presented in tables and some interpretations can be made already at this stage. Examples of inputs and outputs quantities include inputs of materials, energy, chemicals and 'other' – and outputs of air emissions, water emissions or solid waste. Other types of exchanges or interventions such as radiation or land use can also be included. Usually Life Cycle Assessments inventories and modeling are carried out using dedicated software packages. Nowadays, the most used LCA softwares are Gabi and Simapro. Compilation of a proper process diagram is also a fundamental issue to do along the data collection in order to get a better LCA study, for example to be sure to include all relevant processes etc. The process diagram has also a function of improving the clearness of the study. The results of the inventory is an LCI which provides information about all inputs and outputs in the form of elementary flow to and from the environment from all the unit processes involved in the study.

4.2.3 Life cycle impact assessment

The third phase 'Life Cycle Impact Assessment' is aimed at the following main issues:

- category definition
- classification
- characterization
- valuation/weighting

This phase corresponds to the main result of a LCA, which explains its crucial importance. According to ISO normative:

“The life cycle impact assessment framework and its procedure should be transparent and provide the flexibility and practicality for this wide range of application. A large range in the levels of effort and

intensity of the analysis are possible with life cycle assessment for different applications. In addition, impact assessment should be effective in terms of cost and resources used.”

A brief explanation of each issue in impact assessment is following:

- **Category definition:** a certain number of environmental aspects affected by the product on study must be chosen and analyzed starting from the LCI. Numerous environmental categories have been proposed for life cycle impact assessment, nonetheless the selection of categories should be consistent with the goal and scope of the study.
- **Characterization:** here, impact potentials are calculated based on the LCI results.
- **Normalization and Weighting** (eventhough these are both voluntary according the ISO standard): normalization provides a basis for comparing different types of environmental impact categories (all impacts get the same unit). Weighting implies assigning a weighting factor to each impact category depending on the relative importance. The weighting step is not always necessary to create a so called “single indicator”. See for instance the prevention based model of the Eco-costs.

4.2.4 Interpretation

The phase stage 'interpretation' is the least developed part of the ISO 14000 standard. It consists in a systematic procedure to identify, qualify, check, and evaluate information from the conclusions of the inventory analysis and impact assessment of a system, and present them in order to meet the requirements of the application as described in the goal and scope of the study. Typical contents of a LCA interpretation are an analysis of the major environmental issues and a sensitivity/uncertainty analysis in order to give consistency and a deeper significance to the work. Interpretation stage leads to the conclusion whether the requirements of the application as described in the goal and scope of the study are met, and also it clarifies what can be learned from the LCA. All conclusions are drafted during this phase. Sometimes an independent critical review is necessary, especially when comparisons are made that are used in the public domain.

4.3 Models and methods to perform Life-Cycle Assessment

4.3.1 Process-Based LCA

A common approach to completing a life cycle assessment is a process-based LCA method. Many variants exist as far as this approach to LCA. They differ in the starting and finishing point of their cycle. So a complete process-based LCA is known as cradle-to-grave, while an assessment of a partial product life cycle from manufacture to the factory gate (i.e., before it is transported to the consumer, omitting usage and recycling processes) is called cradle-to-gate. When, finally, the end-of-life disposal step for the product is a recycling process, the LCA is defined cradle-to-cradle. In any

case, in a process-based LCA, one itemizes the inputs (materials and energy resources) and the outputs (emissions and wastes to the environment) for all the given steps in producing a product. So, for a simple product, such as a disposable paper drinking cup, one might list the paper and glue for the materials, as well as electricity or natural gas for operating the machinery to form the cup for the inputs, and one might list scrap paper material, waste glue, and low quality cups that become waste for the outputs.

4.3.2 Problems with process-based LCA

Some issues arise with process-based LCA methods. One is defining the boundary of the analysis. An initial step of a process-based LCA is defining what will be included in the analysis, and what will be excluded and ignored. In order to keep the analysis tractable, most LCAs limit the scope of analysis only to the major inputs at each stage, leading to problems of subjective boundary definition and comparability across studies. For the paper cup example, one might choose to exclude the impacts for making the steel and then manufacturing the processing equipment that makes the cups. While necessary to create a manageable LCA project, defining the boundary for the analysis automatically limits the results and creates an underestimate of the true life cycle impacts. Moreover, data on input requirements and emissions for even such truncated LCAs have to be collected from a large number of different suppliers leading to high cost, time, and issues of data confidentiality and verifiability. Finally, another main issue with process-based LCA methods is circularity effects. In modern world, it takes a lot of the same "stuff" to make other "stuff." So, to make the paper cup requires steel machinery. But to make the steel machinery requires other machinery and tools made out of steel. And to make the steel requires machinery, yes, made out of steel. Effectively, one must have completed a life cycle assessment of all materials and processes before one can complete a life cycle assessment of any material or process.

4.3.3 The EIO-LCA

The fact that process-based LCA has been taken as the leading method to implement an environmental study about products doesn't mean it is absolutely the best method. The main alternative way to conduct a LCA is the Environmental Input-Output Life Cycle Assessment (EIO-LCA). Economic input-output life-cycle assessment takes a top-down approach and treats the whole economy as the boundary of analysis. Another strength of EIO-LCA approach is that economy-wide interdependencies in inputs are modelled as a set of linear simultaneous equations, as for the economical studies that imply the use of an Input-Output matrix. In the first study done with this approach, the authors used the 498*498 commodity sector direct requirements matrix published by the U.S. Department of Commerce as a part of the 1987 U.S. input-output tables (U.S. Commerce 1994), but beyond this representation of input interdependencies as systems of equations can be found quite easily in the LCA literature.

4.3.4 Mathematical Structure of EIO-LCA approach

Input-output analysis is a well-established tool in economic analysis, where the interdependencies across different sectors of the economy are represented by a set of linear equations. The core of the model is the inter-sectoral direct requirements (or technical coefficients) matrix denoted as a . An element a_{ij} of matrix a represents the dollar value of input required from sector i to produce one dollar worth output of sector j ($i = 1 \dots n$, and $j = 1 \dots n$). Let x represent the vector of total outputs of the sectors. The exogenous change in final demand for the output of these sectors is represented by a vector f . Because the total output of a sector is the sum of final demand f and intermediate demand ax , (i.e. demand as input requirement for producing the output of other sectors), the input-output system can be written:

$$x - ax = f$$

The vector of sectoral outputs to meet a given exogenous demand f is obtained by premultiplying the equation by $[I - a]^{-1}$:

$$x = (I - a)^{-1} * f$$

The input-output technique can be extended for environmental analysis.¹ Suppose r is a $k \times n$ matrix of environmental burden coefficients, where r_{kj} is environmental burden k (e.g. carbon monoxide emissions) per dollar output of sector j , and e is the vector of total environmental burdens, then the economy-wide total (direct and indirect) environmental burden associated with an exogenous demand vector f becomes

$$e = rx = r * (I - a)^{-1} * f$$

The environmental burden matrix r can include coefficient vectors for any environmental impact of interest such as energy use, non-renewable resource use, greenhouse gas emissions, etc. The contribution of individual industry sectors to the total environmental burden can be found by replacing each of the environmental burden coefficient vectors in r , by its diagonal matrix. In theory, one can develop very large technical coefficient and environmental burden matrices representing all possible products as separate commodity sectors, and then use the equation above to estimate economy-wide burdens to meet an incremental demand for any product. However, this approach is not practical in view of the immense data requirements. The largest available technical coefficient matrix, published by the U.S. Department of Commerce, has 498 commodity sectors (U.S. Commerce 1994).

4.3.5 Problems with Environmental Input-Output LCA

As for process-based LCA methods, EIO-LCA is still subject to several well-recognized limitations, even though different from the previous ones. First, it is controversial how to define the product of interest. An experimented way is to think the product approximated by its commodity sector in the national input-output tables with respect to input requirements and environmental coefficients. But the

commodity sectors in the national input/output tables are broad aggregates that include a large number of products and this causes a lack in representativeness. Other ways to define the product more in details are on study. Second, EIO-LCA captures the upstream environmental burdens associated with raw materials acquisition and manufacturing stages, but not those associated with product use and end-of-life option. A comprehensive LCA study would not be possible unless adopting strong assumptions about the use and end-of-life phases.

Chapter 5 - Goal and Scope Definition

5.1 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 Home Appliances S.p.A.

5.2 Scope

5.2.1 Product Description

- 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.

5.2.2 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 addition 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.

5.2.3 Life Cycle Boundaries.

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

5.2.4 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)

Other important categories like Biotic Depletion or human health related categories haven't been considered, because they don't belong to the CML method utilized in this case study.

5.2.5 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:

- Time related coverage. It will be normally within 8 years
- Geographical coverage. 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.

Chapter 6 - Life Cycle Inventory

6.1 LCI Methodology

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 to the assembly line
- Final assemblage of the components onto the dishwasher
- Usage of the product
- End-of-Life management

A number of decisions and assumptions were made along the life cycle inventory phase, as far as single inputs, single outputs and process data. They will be explained case by case. As mentioned before, 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. When necessary, primary data had to be collected through direct communication with producers. In addition, as a rule producers' data were not directly usable for the impact assessment, but needed to be rearranged and normalized case by case.

6.2 Cradle-to-gate process schemes

The general schemes of the phases of raw materials extraction, materials processing and components assembly are described for both the systems studied.

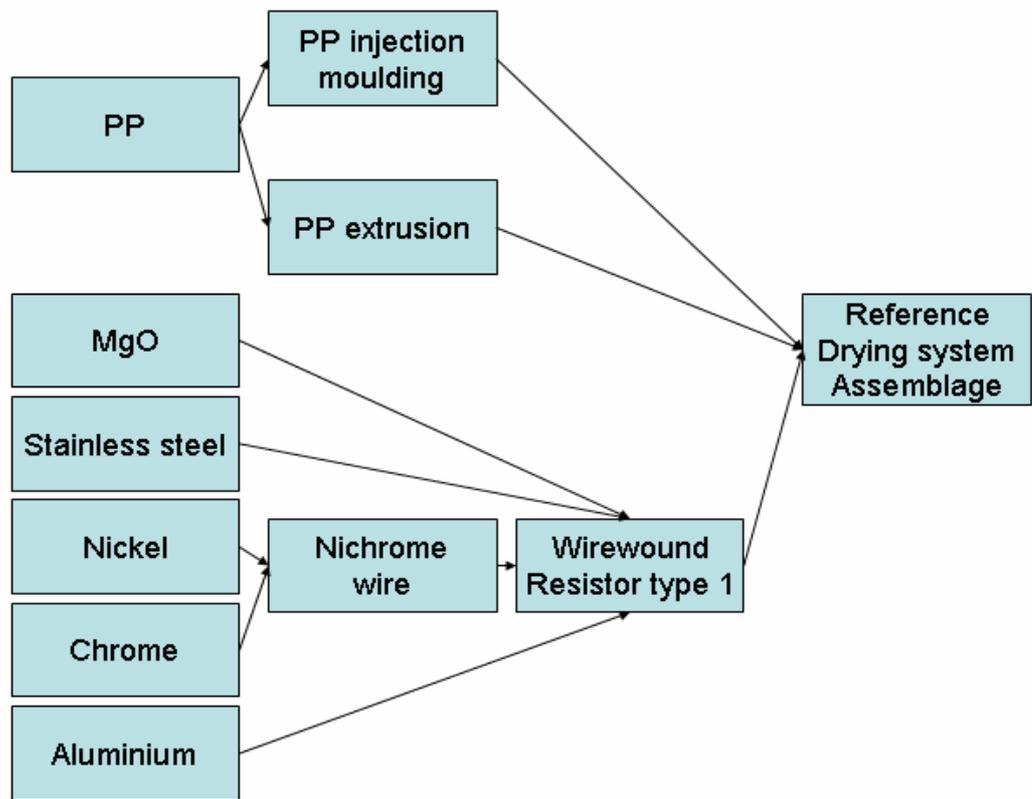


Fig. 11: Cradle-to-Gate life cycle scheme for reference drying system

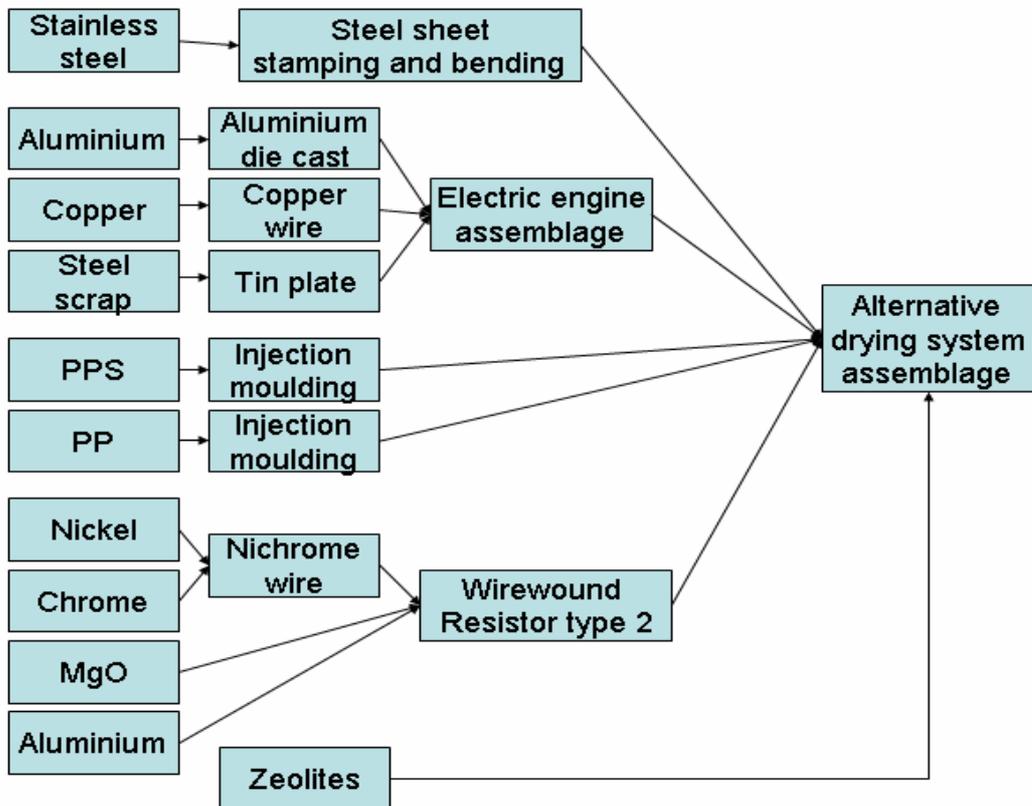


Fig. 12: Cradle-to-Gate life cycle scheme for alternative drying system

6.3 Inventory Notes

Few clarifications about data for the phases' processes are needed. In this section assumption and measurement methodologies will be explained for all the relevant point of the life cycle. Alternative and reference products will be analysed separately.

6.3.1 Alternative System

- Raw materials production: data for stainless steel, aluminium, copper and polypropylene production were found in the GaBi database. For Chrome, MgO and PPS production, available data for similar materials were assumed to be valid for them, too. In particular, chrome Production data are assumed to be the similar to the ones for ferro-chrome production; lime production data are taken as reference for MgO production and for PPS production the reference is the production of a Polyamide, that can even be considered as a substitute product. For nickel production data are gathered from the "ETH-ESU 96 system processes" database, while zeolite Production data are taken from literature (Fawer, M. *et al.* 1998).

Quantitative data are dependent on the final components dimensions.

- Materials processing: All the processes belonging to this family are chosen among the ones existing in the given database, apart from Copper casting and drawing to wire. This process has been built from the free CPM LCA database (<http://www.cpm.chalmers.se/CPMDatabase>). Quantitative data are provided by indirect measurements of the single components.
- Components assemblage: due to the specificity of the processes, primary data must be gathered by suppliers. As for resistance assembly the reference supplier was I.R.C.A. S.p.A., while for the general assembly of the drying system data are collected from the production department of Electrolux S.p.A. Resistance assembly inputs are the raw materials coming from the extraction phase, while the specific energy consumption for each piece is supplied by I.R.C.A., as it is already been calculated.

The general assembling of the drying system is assumed to be equal in terms of resource utilization for both the systems. To get the required data, average values for a dishwasher of reference dimensions (12 places) are collected. Then the contribution in weight of the drying system over the whole household appliance is calculated. The assumption is that the part of the total assembling energy required to assembly the drying system to the machine is proportional to its percentage in weight in the whole appliance. This strong assumption is chosen because the upper limit of the drying system assembling energy requirement can't be above the total assembling energy requirement for the dishwasher. Then, this value is very low, compared to the value of consumption during the use phase, thus variations under said limit would not affect significantly the final outcome. Finally, negligible emissions and wastes come out from this type of process, so that the overall impact for the other categories is not influenced either.

- Transportation of the components to the final assemblage line: for the sake of simplicity only the transportation of the sub-assembled components has been modelled. The parameter of the distance has been modified taking into account the concentration of the respective components

producers. It is assumed that an average distance for the wirewound resistor transportation is 150 km, while for the electrical engine it is of 20 km.

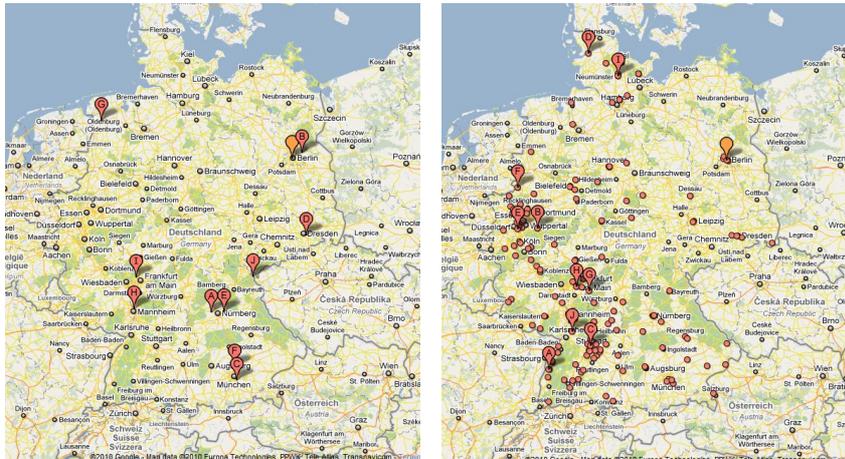


Fig. 13: Wirewound resistors and electrical engines manufacturers in Germany

- Usage of the product: the fundamental information is about the energy required in the use phase of the product. First of all, taking into account the functional unit chosen, it is assumed that the product is used 220 times per year for 10 years of useful life (Faberi, S., 2007). Thus, to understand the overall consumption, only the value of inputs for one cycle is needed. This comes from a test made by the (...), in which the energetic consumption was calculated in 0,81 KWh/cycle (2,916MJ/cycle). The consumption is basically due to the regeneration of the zeolites by using the resistance. It turns out simple to calculate the overall energy consumption in the use phase:

$$E_{tot} = 220 * 10 * 0,81 = 1782KWh = 6415,2MJ$$

No water or other resources consumption is included in this phase, due to the specific working of the drying system.

- End of life of the product: the scenario for this phase prefigures a high percentage of recovery of materials. This approach comes from the European Directive in force since February 2003 regarding wastes coming from this type of products. EU legislation restricts the use of hazardous substances in electrical and electronic equipments (Directive 2002/95/EC) and promotes the collection and recycling of such equipment (Directive 2002/96/EC). The legislation provides for the creation of collection schemes where consumers return their used e-waste free of charge. The objective of these schemes is to increase the recycling and/or re-use of such products. In details, as for household appliances, at least the 75% of the total amount of materials has to be recycled and a smaller percentage of materials can be addressed to other treatments, like incineration, still with recovery purposes, in this case of energy. Focusing on the product that is studied in this work, it is assumed that outputs from the use phase consist in steel scrap and zeolites. No further separations are made, for example between steel and plastic components, since steel is the

material that is mostly represented in terms of contribution in weight. Moreover, such an assumption appears to reflect the real life management of this product phase. Thus a big amount of produced metal waste is placed on top of the product life cycle, closing in this way the loop, while a less relevant portion is supposed to be treated as municipal waste.

6.3.2 Reference System

- Raw Materials production: data for stainless steel, aluminium, copper and polypropylene production were found in the GaBi database. For Chrome and MgO production, available data for similar materials were assumed to be valid for them, too. In particular, chrome Production data are assumed to be the similar to the ones for ferro-chrome production. Lime production data are taken as reference for MgO production. For nickel production data are gathered from the “ETH-ESU 96 system processes” database.
- Materials Processing: data are provided by the direct measurements of the single components and by experts opinions about the production methods. For example, poly-propylene parts evidently come from two distinct processes, extrusion and blow moulding, both modelled in GaBi. In this case allocation rule for the PP resource takes into account the respective weight of the parts coming for each process.
- Components Assemblage: the same methodology for the processes in the alternative model is used. Namely, the wirewound resistor assemblage data are gathered from IRCA S.p.A. company, while for the general reference system assemblage, the energetic consumption is assumed to be proportional to the overall consumption of a single dishwasher, taking into account the weight contribution of the drying system to the overall weight. The value of energetic consumption for the reference system is lower than the one for the alternative system due to the lower weight of the reference system. For the justification of such approach, see the correspondent section in the data notes for the alternative system.
- Transportation: only the transportation of the sub-assemblies is taken into account. The wirewound resistor transportation distance is set at 100 km, considering the real distance of the IRCA S.p.A. plant from the final assemblage plant.
- Usage phase: the same source for the alternative system is used, as far as duration of use phase and rate of utilisation of the dishwasher. That is, the household appliance is used 220 times a year for 10 years. The single consumption for a cycle is obtained from (...). Its value is of 1,0356 KWh/cycle (3,726 MJ/cycle). The total energy amount is:

$$E_{tot} = 220 * 10 * 1,0356 = 2278,32 KWh = 8201,952 MJ$$

This value is due to the double step consumption of the wirewound resistor in the washing and hot-rinse. In addition to the energy consumption, it has to be considered the water consumption in the drying phase. This comes from the reference system working principle. It has been calculated that two liters of water per cycle are used only for the hot-rinse, which makes an overall consumption in the use phase of:

$$W_{tot} = 2 * 10 * 220 = 4400 \text{liters}$$

As easily noticeable, no water consumption is seen in the alternative system usage, due to the particular properties of the zeolites. This difference will most probably have a certain influence on the LCIA results.

End of Life: in this case a separation between plastics and metals is assumed to happen, since the plastic components are more relevant in this product. All the plastic is assumed to undergo an incineration process, while for the metallic waste, it is modelled as steel scrap and aluminium scrap, being recycled as much as possible (100% for the aluminium scrap, 30,95 for steel scrap).

6.4 LCI Data

Data of interest obtained by the chosen methods are summarized below. Data are divided by product and subdivided by macrophases Production, Use Phase and End of Life.

6.4.1 Alternative System Data

PRODUCTION	
Raw materials	Quantity (g)
Stainless steel	2000
Nickel	16
Chrome	4
MgO	40
Tin plate	600
Copper	300
Aluminium	250
PP	667
PPS	83
Zeolite	1150
Materials processing	Quantity (g)
Zeolite production	1150
Steel stamping and bending (5% loss)	2000
Copper casting and drawing to 0,6mm wire	300
Tin plate secondary (without detinning)	600
Plastic injection moulding part (unspecific)	750
Components production and Assemblage	Energy consumption (MJ)
Electrical engine	50
Wirewound resistor	213,63
Drying system	95,436

USE PHASE	
Energy consumption	
Energy consumption over one cycle (MJ)	2,916
Number of cycles per year	220
Product life (years)	10
Total energy consumption (MJ)	6415,2
Other resources' consumption	
Water (m ³)	0

END OF LIFE (%) (Assumptions based on the normative in force)	
Dismantling – Re-use of parts	39,74
Recycling	35,92
Energy recovery	9,6
Landfilling (non hazardous waste)	14,74
Total	100

6.4.2 Reference System Data

PRODUCTION	
Raw materials	Quantity (g)
Stainless steel	56,324
Nickel	16
Chrome	4
MgO	40
Steel, zinc plated	104,32
Aluminium	150
PP	344,28
Materials processing	Quantity (g)
Plastic extrusion	67,32
Polypropylene injection moulding part (unspec.)	276,96
Components production and Assemblage	Energy consumption (MJ)
Wirewound resistor	213,63
Drying system	50

USE PHASE	
Energy consumption	
Energy consumption over one cycle (MJ)	3,728
Number of cycles per year	220
Product life (years)	10
Total energy consumption (MJ)	8202
Other resources' consumption	
Water (m ³)	4,4

END OF LIFE (%) (Assumptions based on the normative in force)	
Recycling	30,53
Energy recovery	48,01
Landfilling (non hazardous waste)	21,46
Total	100

Chapter 7 - Life Cycle Impact Assessment

This chapter presents the results of the Life Cycle Impact Assessment (LCIA) of the drying systems LCA. In the LCIA phase the inventory of the emissions from the LCI is first classified into categories in which the emission may contribute to impacts in human health or environment. Within each impact category the emissions are then characterized to a common reporting basis, using characterization factors that express the impact of each substance relative to a reference substance.

After these two mandatory steps for every LCIA, a normalization step and an evaluation step will be made, too, even if not strictly necessary especially for a comparative study. Various LCIA methodologies have been developed and can be used to conduct LCIA analyses. ISO 14044 does not require the use of one specific methodology or support underlying value-choice that may be used to group the impact categories. The LCIA results in this chapter were derived from the LCI emissions using the CML 2001.

7.1 CML Methodology

The different methodologies for the LCIA are founded on different impact category systems that can be used. This differentiation shall not be confused with the choice of impact categories phase, which is a necessary step in building every LCA. There are two types of impact categories: midpoints and endpoints. A mid-point category does not refer to actual damages caused to human health, ecosystems or resources, but only groups a certain number of influence flows under a single voice from a more environmental point of view. For example, the widely used mid-point "Acidification" takes into account the potential of acidify rain by an emission, for example, more than the effects that acid rains would have on monuments, human health or other valuable objects. Other methods like Ecoinvent 99 make use of damage-oriented categories, the so-called endpoints. The advantage of midpoints is that factors to group flows under that category system are internationally available and scientifically accepted, while damage-oriented methods are conceptually interesting because directly connected to the consequences of a product life cycle. Modelling endpoint categories presents issues of a certain scientific relevance because the choice of the damage amount deriving from an environmental aspect is not immediate. Hence careful evaluation is necessary.

The CML 2001 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).

The data for the impact categories "CML 2001" are according to the information of the Institute of Environmental Sciences, Leiden University, The Netherlands, published in a handbook 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, thus the resulting assessment turns out to be very complete and consistent.

7.2 Classification and Characterization

As stated in the scope phase, the following potential impacts will be used in the environmental impact assessment using CML 2001 characterization factors as published in GaBi 4.3 software:

- Abiotic Depletion (ADP) [kg Sb-Equiv]
- Acidification Potential (AP) [kg SO₂-Equiv.]
- Eutrophication Potential (EP) [kg Phosphate-Equiv.]
- Global Warming Potential (GWP 100 years) [kg CO₂-Equiv.]
- Ozone Layer Depletion Potential (ODP, steady state) [kg CFC-11-Equiv.]
- Photochemical Ozone Creation Potential (POCP) [kg Ethilene-Equiv.]

Follows a brief description of the categories and the characterization methodology.

7.2.1 Abiotic Depletion

“Abiotic resources” are natural resources (including energy resources) such as iron ore, crude oil or wind energy, which are regarded as non-living. Abiotic resource depletion is defined as the decrease of availability of the total reserve of potential functions of resources. This category is one of the most frequently discussed impact categories and there is consequently a wide variety of methods available to characterize contributions to this midpoint. To a large extent, these different methodologies reflect differences in problem definitions. Depending on the definition, this impact category includes only natural resources, or natural resources, human health and the natural environment, among its areas of protection. The debate on the characterization of depletion-related categories is not settled.

The CML methodology uses the approach developed by Guinée, 1995, with modifications for crude oil, hard coal and soft coal. The Overall indicator is formulated as follows:

$$abiotic_depletion = \sum_i ADP_i * m_i$$

The results are expressed in kg of the reference resource antimony. equivalent. ADP_i is the Abiotic Depletion Potential for resource i , while m_i is the quantity (in kg except for natural gas and fossil energies) of resource i used.

7.2.2 Acidification Potential

Natural rain is slightly acidic due to the presence of various acids in the air that are washed out by rain. However, a number of man-made emissions are either acid or they are converted to acid by processes in the air. Examples of such emissions are sulphur dioxide (which becomes sulphuric acid) and nitrogen oxide (which becomes nitric acid).

As a result, the acidity of rain can be substantially increased. In a number of areas the soil and water have a limited capacity to neutralize these added acids. If water becomes too acid, an increasing

number of aquatic species are harmed. If the soil becomes too acid, the ability of plants to grow and thrive is harmed.

An acidification indicator is derived by assuming that 100% of an emission is converted to acid and falls into a sensitive area. The acidity of each emission is converted into equivalent amounts of sulphur dioxide. All emissions are then added into an overall acidification indicator score that represents the total emission of substances that may form acids.

To interpret the acidification indicator, it is important to realize that the site where an emission takes place relative to a sensitive area is important. Also, acid falling into the sea is easily neutralized. Newer acidification indicators are being developed to include these variables as well as the buffering or neutralizing capacity of soils. Additional investigation to better understand the environmental meaning of the indicator is suggested.

The indicator used in the CML method is expressed as follows:

$$AP = \sum_i AP_i * m_i$$

The indicator result is expressed in kg SO₂ emitted in Switzerland. Equivalent. AP_{*i*} is the Acidification Potential for substance *i* emitted to the air, while *m_i* is the quantity of substance *i* emitted. Data are based on various different authors

7.2.3 Global Warming Potential

The earth's climate is driven by the balance of energy or heat added by the sun and lost by the earth. The primary energy is lost through heat radiation. Gases in the atmosphere, called greenhouse gases, can reflect some of this heat back to the earth. This effectively warms the earth and may alter the climate over time as these gases increase in concentration.

A greenhouse gas indicator is derived from two basic properties of each gas. The first is its ability to reflect heat. The second is how long the gas remains in the atmosphere, that is, how long it may act to reflect heat. These properties are then compared to the properties of carbon dioxide and converted into carbon dioxide equivalents. Then the individual equivalents are added together, for the overall greenhouse gas indicator score that represents the total quantity of greenhouse gases released. Most of the methods used in Life Cycle Impact Assessment (LCIA) are based on the International Panel on Climate Change (IPCC).

To interpret the greenhouse gas indicator, an important variable is the time horizon used (e.g., 50 or 500 years). Short horizons tend to emphasize gases with short residence times in the atmosphere, like methane. In addition, the indicator does not consider the effects of clouds and aerosols in reflecting the sun's heat and reducing the warming.

In the CML methodology the overall contribution to the GWP for each substance is given as:

$$GWP = \sum_i GWP_{100,i} * m_i$$

where $GWP_{100,i}$ is the global warming potential for substance i integrated over 100 years, that is in a middle-long-range, while m_i is the quantity of substance i emitted. The reference quantity is the kg CO₂ equivalent. The source for the coefficients of GWP is the IPCC.

Greenhouse Gas	Chemical Formula	Global Warming Potential		
		SAR ^a	TAR ^b	AR4 ^c
Carbon Dioxide	CO ₂	1	1	1
Methane	CH ₄	21	23	25
Nitrous Oxide	N ₂ O	310	296	298
Hydrofluorocarbons				
HFC-23 (Trifluoromethane)	CHF ₃	11,700	12,000	14,800
HFC-32 (Difluoromethane)	CH ₂ F ₂	650	550	675
HFC-41 (Monofluoromethane)	CH ₃ F	150	97	92
HFC-125 (Pentafluoroethane)	CHF ₂ CF ₃	2,800	3,400	3,500
HFC-134 (1,1,2,2-Tetrafluoroethane)	CHF ₂ CHF ₂	1,000	1,100	1,100
HFC-134a (1,1,1,2-Tetrafluoroethane)	CH ₂ FCF ₃	1,300	1,300	1,430
HFC-143 (1,1,2-Trifluoroethane)	CHF ₂ CH ₂ F	300	330	353
HFC-143a (1,1,1-Trifluoroethane)	CF ₃ CH ₃	3,800	4,300	4,470
HFC-152 (1,2-Difluoroethane)	CH ₂ FCH ₂ F	—	43	53
HFC-152a (1,1-Difluoroethane)	CH ₃ CHF ₂	140	120	124
HFC-161 (Ethyl Fluoride)	CH ₃ CH ₂ F	—	12	12
HFC-227ea (Heptafluoropropane)	CF ₃ CHFCF ₃	2,900	3,500	3,220
HFC-236cb (1,1,1,2,2,3-Hexafluoropropane)	CH ₂ FCF ₂ CF ₃	—	1,300	1,340
HFC-236ea (1,1,1,2,3,3-Hexafluoropropane)	CHF ₂ CHFCF ₃	—	1,200	1,370
HFC-236fa (1,1,1,3,3,3-Hexafluoropropane)	CF ₃ CH ₂ CF ₃	6,300	9,400	9,810
HFC-245ca (1,1,2,2,3-Pentafluoropropane)	CH ₂ FCF ₂ CHF ₂	560	640	693
HFC-245fa (1,1,1,3,3-Pentafluoropropane)	CHF ₂ CH ₂ CF ₃	—	950	1,030
HFC-365mfc (Pentafluorobutane)	CF ₃ CH ₂ CF ₂ CH ₃	—	890	794
HFC-43-10mee (Decafluoropentane)	CF ₃ CHFCF ₂ CF ₃	1,300	1,500	1,640
Perfluorocarbons				
Perfluoromethane	CF ₄	6,500	5,700	7,390
Perfluoroethane	C ₂ F ₆	9,200	11,900	12,200
Perfluoropropane	C ₃ F ₈	7,000	8,600	8,830
Perfluorobutane (FC 3-1-10)	C ₄ F ₁₀	7,000	8,600	8,860
Perfluorocyclobutane	c-C ₄ F ₈	8,700	10,000	10,300
Perfluoropentane	C ₅ F ₁₂	7,500	8,900	9,160
Perfluorohexane (FC 5-1-14)	C ₆ F ₁₄	7,400	9,000	9,300
Sulfur Hexafluoride	SF ₆	23,900	22,200	22,800
Nitrogen Trifluoride	NF ₃	—	10,800	17,200

Sources: ^aIntergovernmental Panel on Climate Change, *Climate Change 1995: The Science of Climate Change* (Cambridge, UK: Cambridge University Press, 1996). This document was part of the Second Assessment Report (SAR) by the Intergovernmental Panel on Climate Change. ^bIntergovernmental Panel on Climate Change, *Climate Change 2001: The Scientific Basis* (Cambridge, UK: Cambridge University Press, 2001), web site www.ipcc.ch/ipccreports/tar/wg1/index.htm. This document was part of the Third Assessment Report (TAR) by the Intergovernmental Panel on Climate Change. ^cIntergovernmental Panel on Climate Change, *Climate Change 2007: The Physical Science Basis: Errata* (Cambridge, UK: Cambridge University Press, 2008), web site http://ipcc-wg1.ucar.edu/wg1/Report/AR4WG1_Errata_2008-12-01.pdf. This document describes errata in parts of the Fourth Assessment Report (AR4) by the Intergovernmental Panel on Climate Change.

Fig. 14: Example of GWP conversion factors

7.2.4 Eutrophication Potential

Aquatic plants and algae gradually fill in freshwater lakes and estuaries over time in a natural process called eutrophication. This process is controlled by low concentrations of certain nutrients (like phosphate and nitrogen) that the plants and algae require to grow. Usually, phosphorus is the limiting nutrient in freshwater and nitrogen in estuaries and salt water. However, when humans release nutrients like phosphate (agriculture ~50%, human metabolism ~20%, industry ~10%, detergents ~10% and natural erosion ~10%), the process of eutrophication is

accelerated. In a worst-case scenario, the excess growth of plants and algae can smother other organisms when they die and begin to decay.

A eutrophication indicator is derived by converting the different chemical forms of phosphorus and nitrogen into a common or equivalent form. Then, the proportion normally found in aquatic algae is used to weight the phosphorus and nitrogen. These values are added into an overall indicator. To interpret the eutrophication indicator, it is important to realize that the background concentration of the nutrient is the baseline. A similar quantity of added phosphorus at one site may trigger a substantial increase in the level of nutrient, while remaining small at another site. Thus, the actual impact cannot be precisely predicted.

Again the indicator in the case of CML is built from a sum:

$$EP = \sum_i EP_i * m_i$$

The results are expressed in kg PO₄⁻³ equivalent. EP_{*i*} is the Eutrophication Potential for substance *i* emitted to the air, water or soil, while m_{*i*} is the quantity of substance *i* emitted. Data are based on various different authors

7.2.5 Ozone Depletion Potential

High in the earth's stratosphere, chemical processes maintain a balanced concentration of ozone. This protects the earth by absorbing much of the harmful ultraviolet radiation from the sun.

If a gas can stay in the atmosphere long enough to reach the stratosphere, and if the gas carries bromine or chlorine atoms, the ozone balance may be threatened as free bromine and chlorine can accelerate the breakdown of ozone. This is especially true when bromine and chlorine are on the surface of tiny ice crystals and sunlight catalyses the reaction.

The ice crystals may form at the Arctic and Antarctic poles during their winters, when sunlight does not reach them. When sunlight first reaches them in the spring, ozone holes may be created for about a month before the crystals melt and the ozone is regenerated.

An ozone depletion indicator is derived through several properties of a gas. These include its stability to reach the stratosphere and the amount of bromine or chlorine the gas carries. These properties are then compared to CFC-11, a once common refrigerant*. The properties of each gas are then compared to the properties of CFC-11 and converted into CFC-11 equivalents. Then the individual equivalents are added together for the overall ozone depletion indicator score, which represents the total quantity of ozone depleting gases released.

Although CFC-11 is now banned by the Montreal Protocol in industrialized nations, it is still manufactured in many developing economies.

This indicator is made as follows:

$$ozone_depletion = \sum_i ODP_{oi} * m_i$$

The measure unit is kg of the reference substance, CFC-11. $ODP_{\infty i}$ is the steady state ozone depletion potential for substance i , while m_i is the quantity of substance i emitted.

7.2.6 Photochemical Ozone Creation Potential (POCP)

It is the name given to the category of formation of photo-oxidant species in the air. Ozone is the most common of them. These reactive chemicals are formed by the action of the sunlight on certain primary air pollutants. These reactive compounds may be injurious to human health and ecosystems and may also damage crops. The relevant areas of protection are human health, the man-made environment, the natural environment and the natural resources. Photo-oxidants may be formed in the troposphere under the influence of ultraviolet light, through photochemical oxidation of Volatile Organic Compounds (VOCs) and carbon monoxide (CO) in the presence of nitrogen oxides (NO_x). Ozone is considered the most important of these oxidizing compounds, along with polyacetylnitrate (PAN). Photo-oxidant formation, also known as summer smog, Los Angeles smog or secondary pollution, contrasts with winter smog, or London smog, which is characterized by high levels of inorganic compounds, mainly particles, carbon monoxide and sulphur compounds. This latter type of smog causes bronchial irritation, coughing etc. Winter smog is considered as part of Human toxicity category.

The photo-oxidant potential overall contribution s_i given by:

$$oxidant_formation = \sum_i POCP_i * m_i$$

The indicator result is expressed in kg of the reference substance, ethylene. $POCP_i$ is the photochemical ozone creation potential for substance i , while m_i is the quantity of substance i emitted. It is of specific importance to distinguish NO_x emissions in terms of NO and NO_2 since the POCP values of these two chemical species are extremely different.

3.3 Normalisation

According to ISO 14042, normalisation is defined as “calculation of the magnitude of indicator results relative to reference information”. The reference information may relate to the features of a specific geographic area, person, or other system, over a given period of time. Other reference information may be adopted, still, such as the future target addressed by the political forces. For the sake of simplicity, it can be said that a normalisation operation answer to the question “how much does the impact for a given category is relevant, compared to the reference overall impact for that category”. The main aim of normalizing the category indicator results is to better understand the relative importance and magnitude of these results for each product system under study. Normalization can

also be used to check for inconsistencies, to provide and communicate information on the relative significance of the category indicator results and to prepare for additional procedures such as

weighting and interpretation. Although not being mandatory, Normalisation is a strongly recommended step for any LCA.

Many sets of normalisation factors are provided with the GaBi software within the CML methodology, mainly for the baseline impact category indicators. They are in general of annual extent and they are divided by geographical region of interest rather than person. For the purposes of this work, the normalisation factors chosen are for Germany, since in the scope phase it is stated that the geographical coverage of the data is mainly limited that nation. Nonetheless, the choice of the normalisation reference is subjective and wouldn't affect the comparative performances between the two drying systems studied. The normalisation step is implemented as follows:

$$indicator_result_{cat,ref} = \sum_i m_{i,ref} * characterization_factor_{i,cat}$$

$$normalised_indicator_result_{cat} = \frac{indicator_result_{cat}}{indicator_result_{cat,ref}}$$

where:

$indicator_result_{cat,ref}$	indicator result for impact category <i>cat</i> and reference system <i>ref</i> (i.c. kg*yr ⁻¹). The reciprocal indicator $result_{cat,ref}$ is here referred to as the normalisation factor for impact category <i>cat</i> and reference system <i>ref</i> .
m_i	magnitude of intervention <i>i</i> (emission, resource extraction, land use..) associated with the reference system <i>ref</i> (i.c. kg*yr ⁻¹).
$characterization_factor_{i,cat}$	characterization factor for intervention <i>i</i> and impact category <i>cat</i> (i.c. kg*kg ⁻¹).
$normalised_indicator_result_{cat}$	normalised indicator result for category <i>cat</i> (yr)
$indicator_result_{cat}$	indicator result for category <i>cat</i> (i.c. kg)

Chapter 8 - Interpretation

The fourth phase of the study consists in the interpretation of the results of the life cycle analysis. This section contains the overall outcome of the GaBi software analysis about the two product systems. After this the results are analysed by life cycle phase in order to better describe the situation. Other outcomes are later mentioned, even though not considered in the impact categories chosen. Consistency check and sensitivity analysis are subsequently carried out to validate the case study and propose further perspectives as far as the application field. In the end, a subsection is dedicated to the results of the tests on moisture adsorption of the prototypes of ceramic foams. This is something that goes beyond the purpose of a normal life cycle assessment case study, but it seemed appropriate to include this experiment in the work due to analysis completeness.

The tests on materials represent the core of the thesis that has been made for the Master course in Materials engineering at the University of Padua (2010), within the TIME exchange project programme. Only the results will be mentioned in the present work. For further information about this topic, please defer to the referenced work.

8.1 LCIA Results

The Life Cycle Impact Assessment gives the results shown in the table and in the graph below. The measurement unity for each category is the one indicated in the previous table, divided by a normalisation factor depending on the geographical area considered for the case study.

<i>Impact category</i>	<i>Reference system [normalised]</i>	<i>Alternative system [normalised]</i>	<i>Variation [%]</i>
<i>Abiotic Depletion (ADP)</i>	1.56E-09	1.27E-09	18
<i>Acidification Potential (AP)</i>	1.43E-09	1.19E-09	17
<i>Eutrophication Potential (EP)</i>	4.83E-10	4.52E-10	6
<i>Global Warming Potential (GWP 100 years)</i>	1.46E-08	1.19E-08	18
<i>Ozone Layer Depletion Potential (ODP, steady state)</i>	1.80E-10	1.45E-10	19
<i>Photochem. Ozone Creation Potential (POCP)</i>	4.45E-10	3.71E-10	17
<i>Overall Impact Value</i>	1.87E-08	1.53E-08	18

Table 2: LCIA data

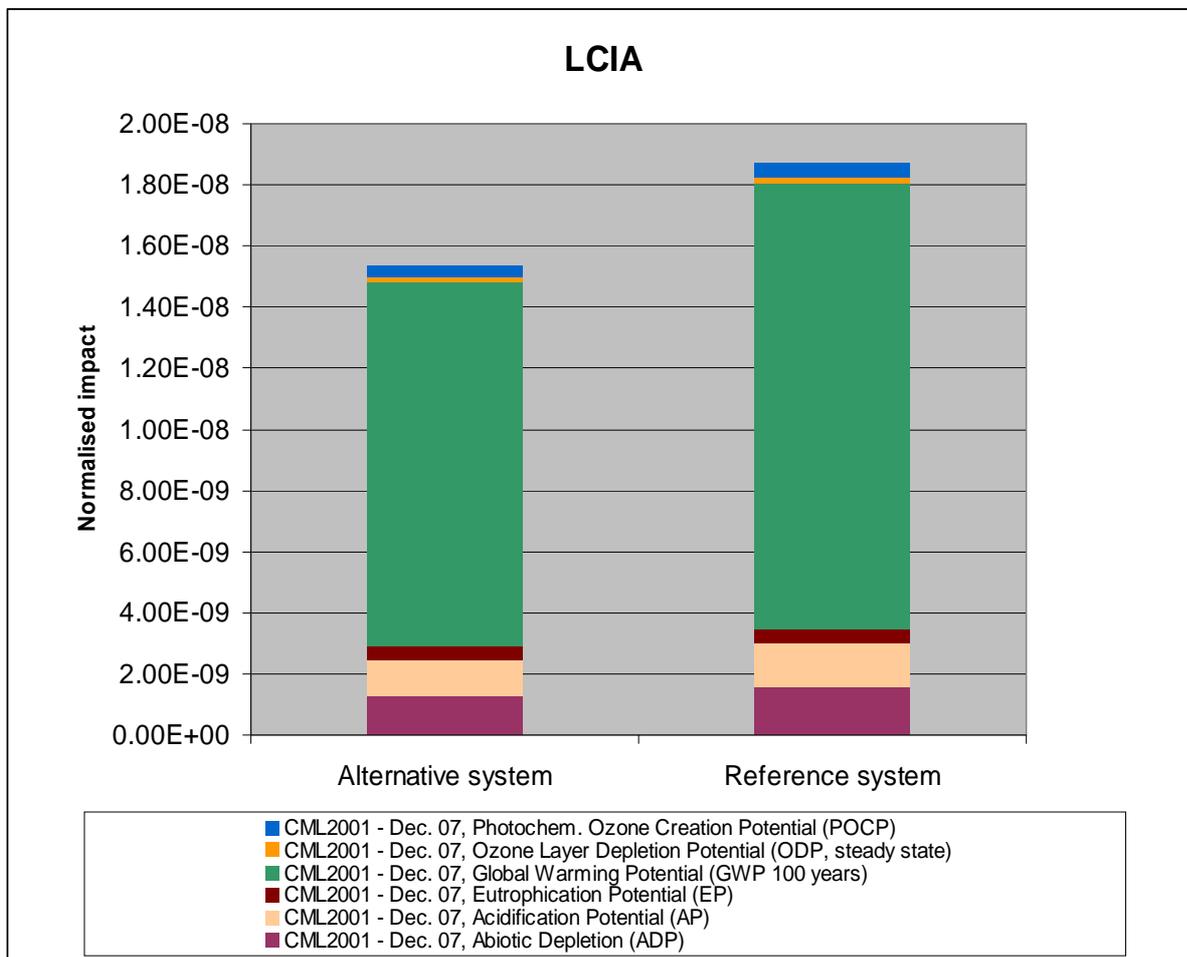


Fig. 15: LCIA data

The biggest impact is in terms of global warming in both cases, with an overall contribution of around 78%. The savings in terms of environmental impact are highlighted for every impact category considered. Variations are in the range of 16-20%, apart from Eutrophication potential, which is however a less significant category in this case study.

8.2 Phases contribution

Data can be analyzed considering each significant phase of the life cycle. In this case raw materials extraction, components production, components assemblage and transportation are grouped together due to their low weight on the overall result. They are consecutive phases and the group is indicated as “Cradle-to-Gate phase”.

<i>Impact category</i>	<i>Cradle-to-Gate phase [normalised]</i>	<i>Use phase [normalised]</i>	<i>EoL [normalised]</i>
<i>Abiotic Depletion (ADP)</i>	9.38E-11	1.18E-09	2.96E-13
<i>Acidification Potential (AP)</i>	1.06E-10	1.08E-09	7.09E-13
<i>Eutrophication Potential (EP)</i>	7.79E-11	3.64E-10	1.04E-11
<i>Global Warming Potential (GWP 100 years)</i>	8.29E-10	1.10E-08	3.94E-11
<i>Ozone Layer Depletion Potential (ODP, steady state)</i>	9.28E-12	1.36E-10	1.11E-14
<i>Photochem. Ozone Creation Potential (POCP)</i>	3.46E-11	3.36E-10	1.25E-12
<i>Overall Impact Value</i>	1.15E-09	1.41E-08	5.21E-11

Table 3: LCIA data sorted by phase, alternative system

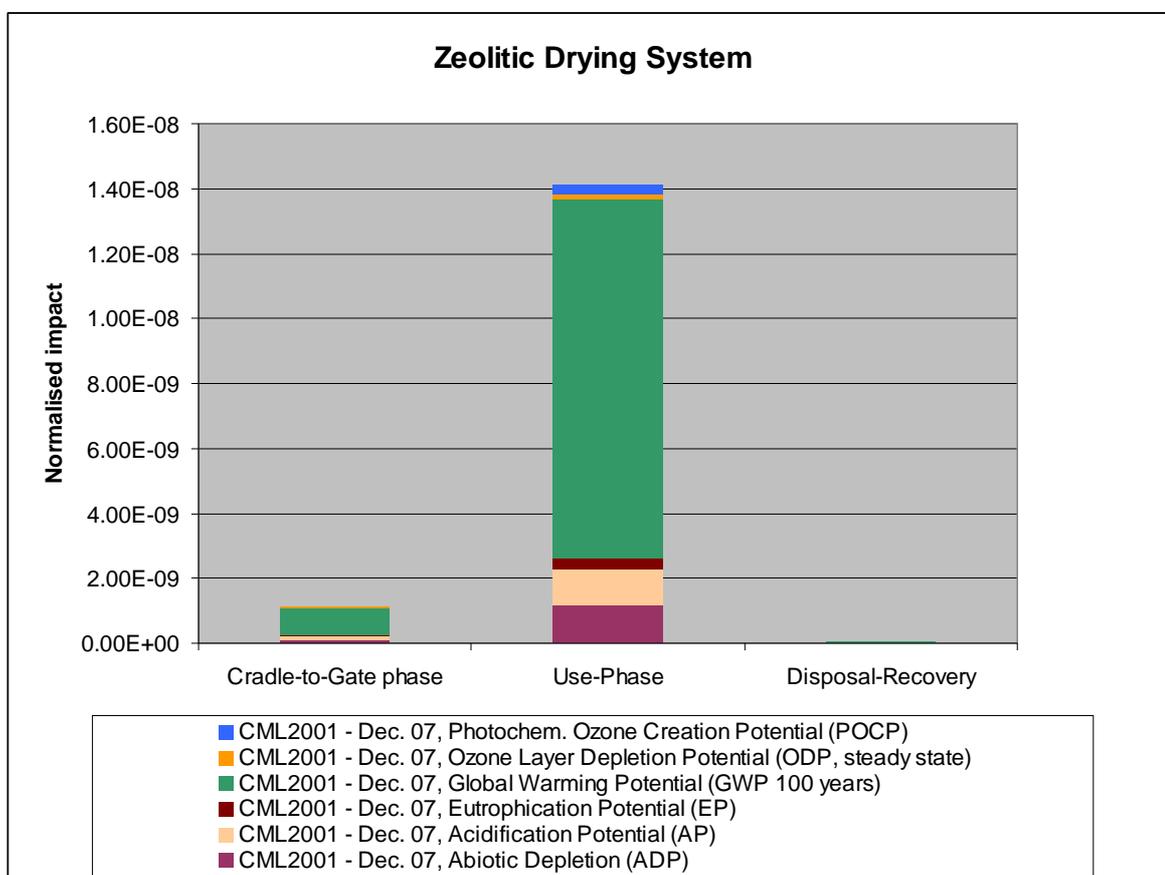


Fig. 16: LCIA data sorted by phase, alternative system

<i>Impact category</i>	<i>Cradle-to-Gate phase [normalised]</i>	<i>Use phase [normalised]</i>	<i>EoL [normalised]</i>
<i>Abiotic Depletion (ADP)</i>	5.22E-11	1.50E-09	1.28E-13
<i>Acidification Potential (AP)</i>	4.90E-11	1.39E-09	2.30E-13
<i>Eutrophication Potential (EP)</i>	1.75E-11	4.65E-10	6.43E-13
<i>Global Warming Potential (GWP 100 years)</i>	4.75E-10	1.41E-08	1.12E-11
<i>Ozone Layer Depletion Potential (ODP, steady state)</i>	5.69E-12	1.74E-10	9.03E-15
<i>Photochem. Ozone Creation Potential (POCP)</i>	1.63E-11	4.29E-10	1.64E-13
<i>Overall Impact Value</i>	6.15E-10	1.81E-08	1.24E-11

Table 4: LCIA data sorted by phase, reference system

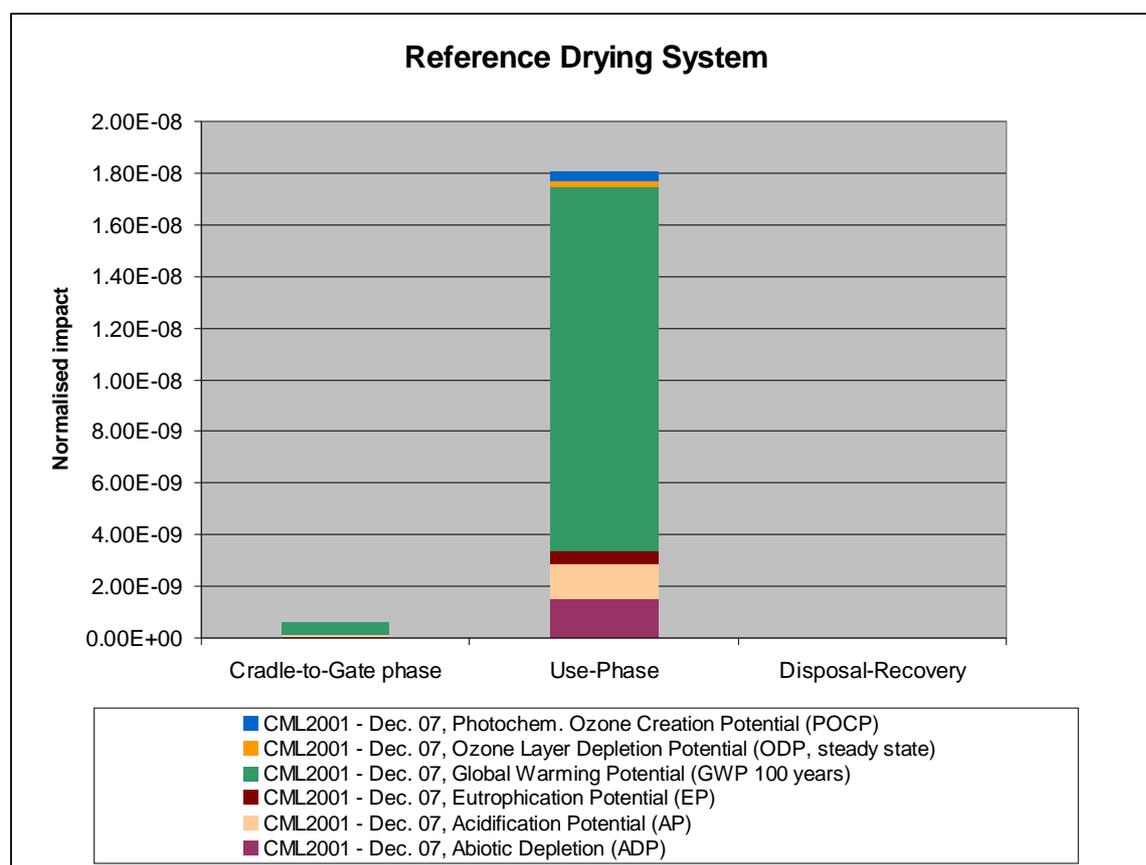


Fig. 17: LCIA data sorted by phase, reference system

Use phase is in both cases the more influent within the entire life cycle. This is due to the long time and high rate of utilisation of the product. Use phase contribution to the overall impact is of 92,15% for the alternative system and of 96,64% for the reference system. Performances in this point are far and away the most relevant for the final result. The difference between the systems is shown in the following table:

<i>Impact category</i>	<i>Cradle-to-Gate phase variation [%]</i>	<i>Use phase variation [%]</i>	<i>EoL variation [%]</i>
<i>Abiotic Depletion (ADP)</i>	79	-22	131
<i>Acidification Potential (AP)</i>	117	-22	208
<i>Eutrophication Potential (EP)</i>	346	-22	1513
<i>Global Warming Potential (GWP 100 years)</i>	75	-22	251
<i>Ozone Layer Depletion Potential (ODP, steady state)</i>	63	-22	23
<i>Photochem. Ozone Creation Potential (POCP)</i>	112	-22	665
<i>Overall Impact Value</i>	87	-22	320

Table 5: Comparison between systems grouped by phase

The reference system shows less impact for the Cradle-to-Gate and EoL phase, 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, as stated above, the savings in the use phase make of the alternative system a more environment-friendly product.

8.3 Other data

Interesting data are obtained as far as overall energy and water consumption through the entire life cycle. As for water consumption, it has to be kept into consideration that data are not only those of its direct utilisation by the product, but also for all the processes within the boundaries of the life cycle considered. This explains the value different from zero of the zeolitic system, which doesn't make use of water during its working.

	<i>Reference system</i>	<i>Alternative system</i>
<i>Energy , Gross Calorific Value [MJ]</i>	27618	22441
<i>Energy – Use Phase [%]</i>	96	93
<i>Water Input [kg]</i>	21855	14194
<i>Water input - Use Phase [%]</i>	97	93

Table 6: Data for energy and water consumption

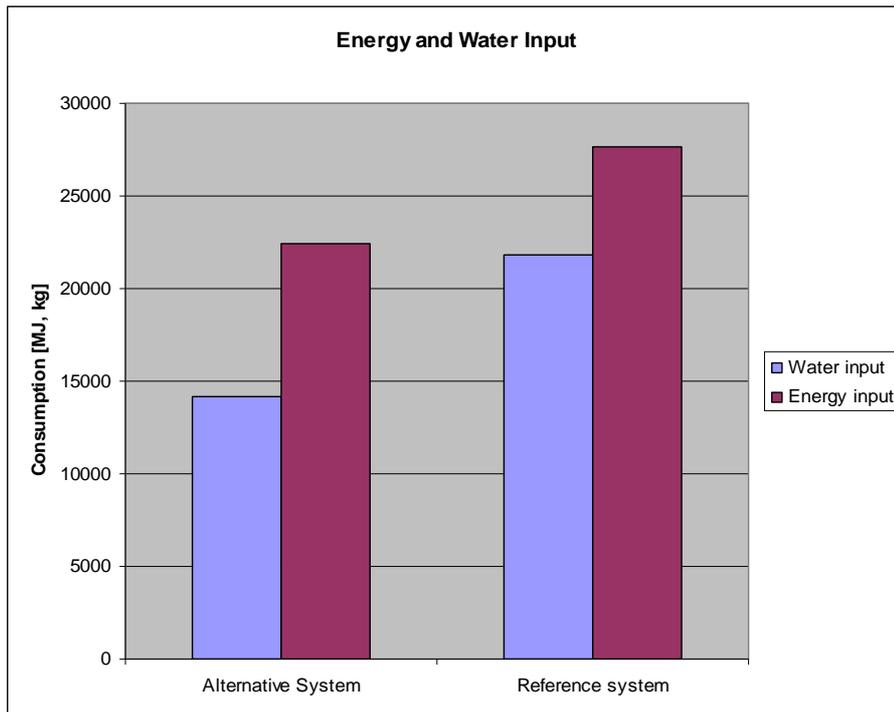


Fig. 18: Energy and water consumption

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.

8.4 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 regenerate. 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.

<i>Impact category</i>	<i>Impact at 0,4 kWh/cycle [normalised]</i>	<i>Variation from the alternative system [%]</i>
<i>Abiotic Depletion (ADP)</i>	6.75E-10	-46
<i>Acidification Potential (AP)</i>	6.42E-10	-46
<i>Eutrophication Potential (EP)</i>	2.68E-10	-40
<i>Global Warming Potential (GWP 100 years)</i>	6.32E-09	-46
<i>Ozone Layer Depletion Potential (ODP, steady state)</i>	7.64E-11	-47
<i>Photochem. Ozone Creation Potential (POCP)</i>	2.02E-10	-45
<i>Overall Impact Value</i>	8.18E-09	-46

Table 7: What-if analysis 1 data

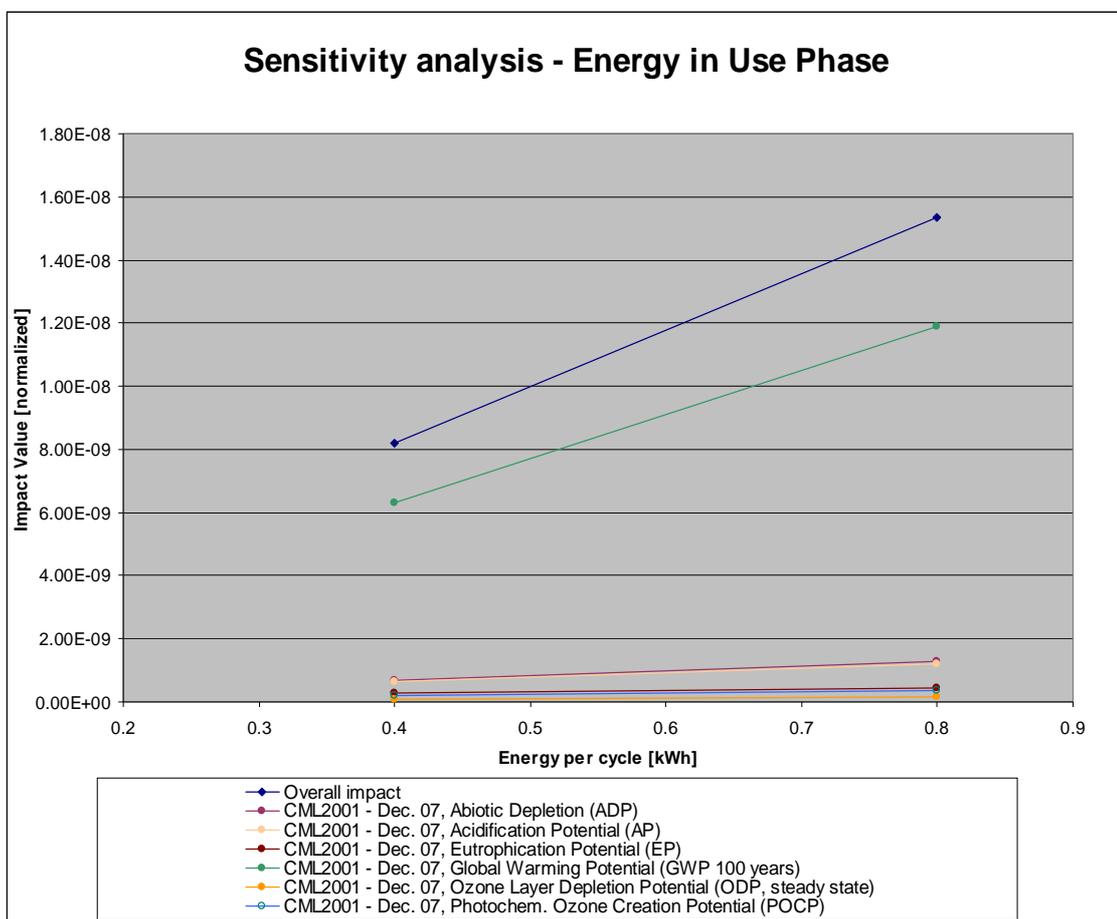


Fig. 19: What if analysis 1

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:

Impact category	Impact of the system without container [normalised]	Variation from alternative system [%]
Abiotic Depletion (ADP)	1.51E-08	-1
Acidification Potential (AP)	1.26E-09	-2
Eutrophication Potential (EP)	1.16E-09	-13
Global Warming Potential (GWP 100 years)	3.95E-10	-1
Ozone Layer Depletion Potential (ODP, steady state)	1.18E-08	-1
Photochem. Ozone Creation Potential (POCP)	1.44E-10	-3
Overall Impact Value	3.61E-10	-2

Table 8: What-if analysis 2 data

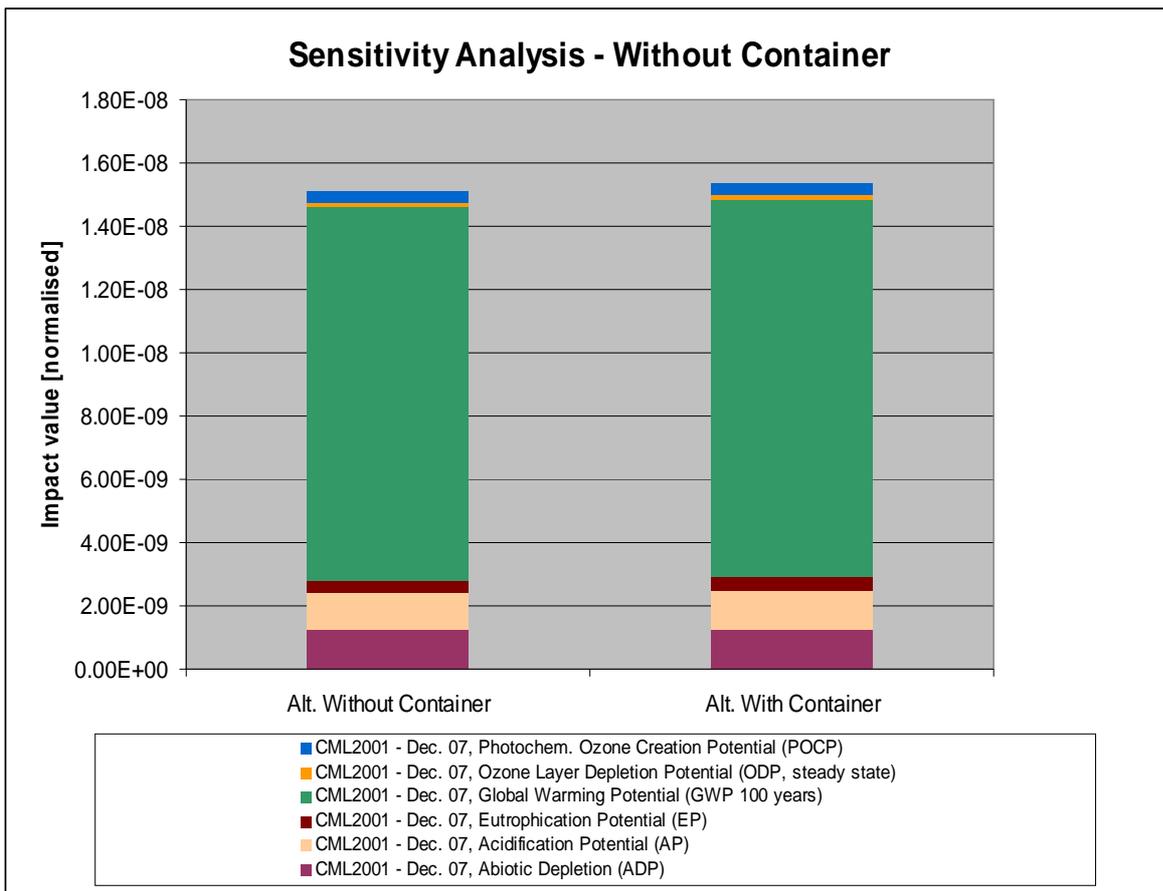


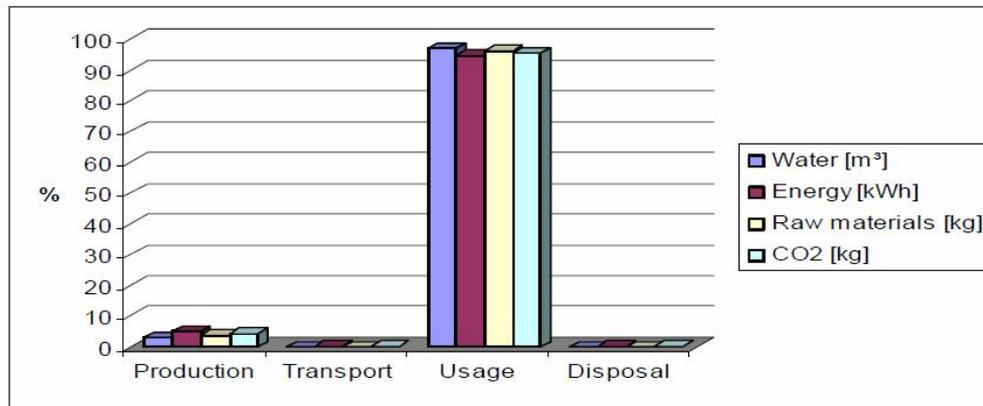
Fig. 20: What if analysis 2

8.5 Consistency Check – Limitations to the case study

This comparative study presented some critical points especially as far as LCI data sources. Dimensions especially connected to assemblage processes were very difficult to obtain, due to the specificity and complexity of the product. In addition, not being able to visit the production plants caused the non-availability of primary data in many processes. However, as for the other scope categories, this LCA presents good level of consistency. Accuracy level of the cycle analysis was the same for both systems, as shown by the cradle-to-gate schemes and the LCI outcomes that have been put in tables. Technical and temporal representation are also mostly the same for the products into consideration, since the GaBi software database was the principal source through all the study. Geographical consistency was not always kept under the scoping purposes, which means LCI data didn't always come from Germany. Again, this was impossible due to the difficulties in obtaining specific data and thus needing to make assumptions. LCIA boundaries and assumptions are at 100% consistent since all the instruments of evaluation were supplied by the software used. In the end, it has to be said that normalisation step, in which data for Germany were used, brings along problems of applicability of the study in other countries, where normalisation conditions change. The issue could have been overcome by utilising normalisation parameters for the whole world, but also this solution presents problems in accuracy. The solution to this issue goes beyond the purposes of the present work.

Even though the few inconsistency issues, data obtained in the LCIA phase are in good accordance with literature estimations and information in this field, namely the work of Kemna *et al.* (2005) and other web sources (Siemens, 2010). Specifically, in the first work it is said that in average the consumption of materials and energy and the CO₂ emissions are for more than 90% in the use-phase. In the present work values are of the same order of magnitude. They are of some percent points higher but this is because the work of Kemna takes into consideration the whole washing machine, thus the impact in the production and transportation phases has more overall weight.

Product lifecycle assessment dishwasher (2004)



More than 90 % of the environmental impacts during the usage phase



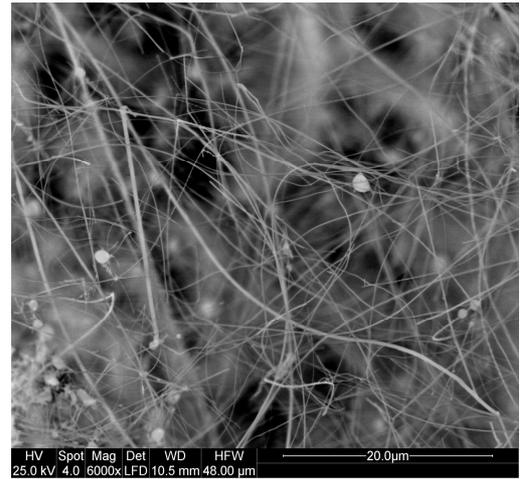
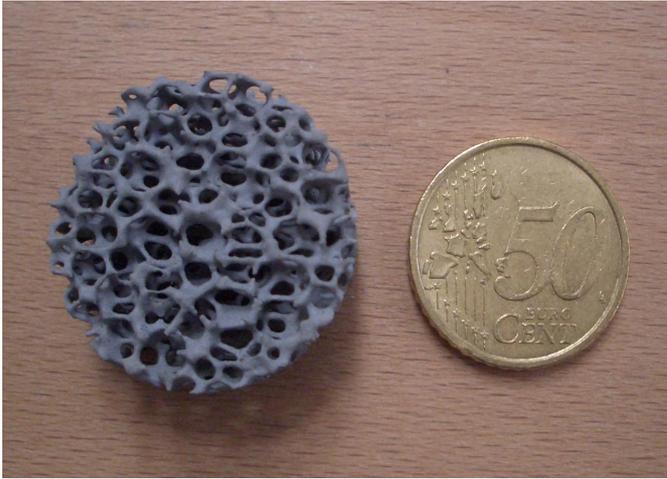
Fig. 21: Life cycle consumption of dishwashers (Kemna et al., 2005)

Besides this work, on the BSH website it is said that savings in environmental impact of the overall zeolitic dishwasher are in the order of 20%, which is again in accordance with the obtained value (17,97%). Eventhough the authoritativeness of this commercial source is not high, it can be still taken as another confirmation of the goodness of the work.

8.6 Moisture Adsorption Tests on Ceramic Foams

8.6.1 Description of the materials

The ceramic foams tested were produced in the laboratories of the University of Padua and University of Sassary. Three main materials have been tested and they are named as MaNW, SS-TiO₂ 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 1200^aC 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 350^aC in order to solidify the surfacial layer. The obtained structure should consist in an omogeneous TiO₂ layer with a periodical porous structure and a specific surface area between 100 and 200 m²/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 800^aC). 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.



8.6.2 Description of the 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.



Fig. 22: Moisture chamber

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.

8.6.3 Moisture Adsorption 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 9: 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/m ³]	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:

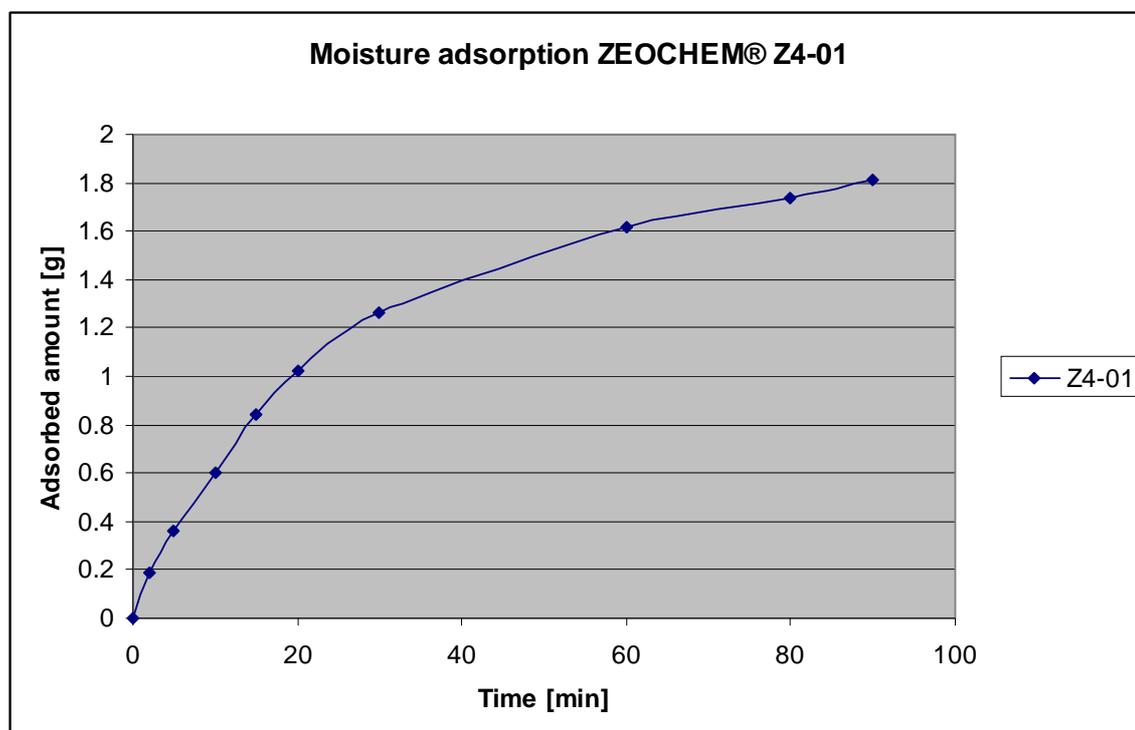


Fig. 23: Material 1 performance

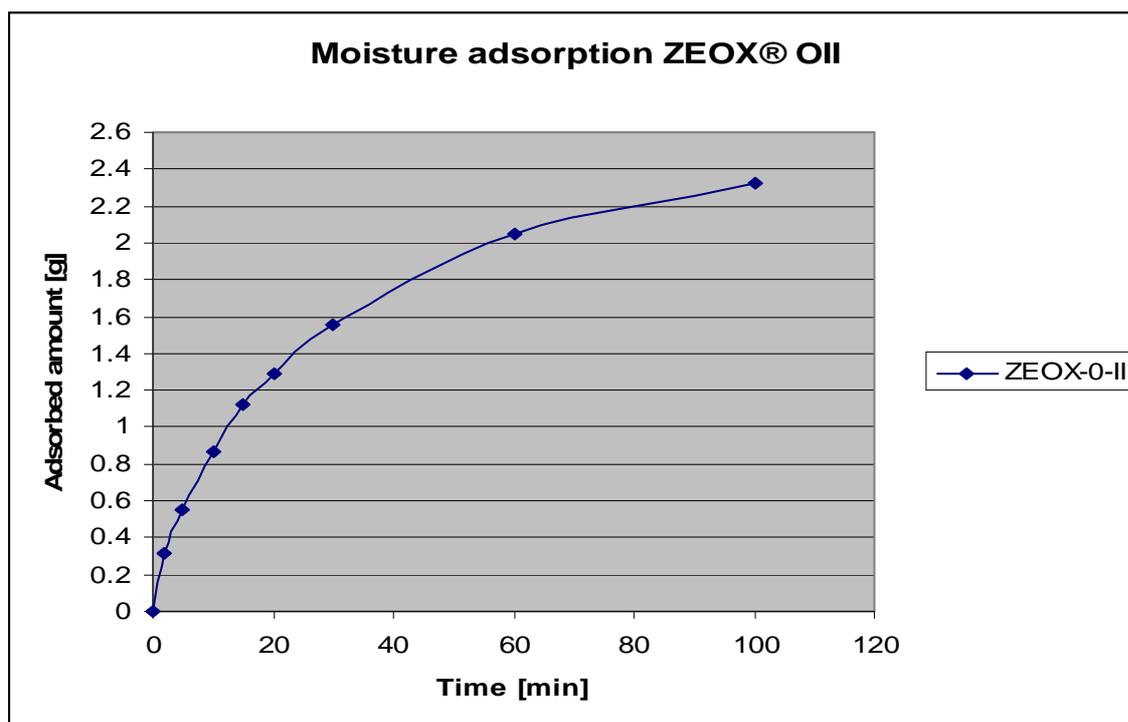


Fig. 24: Material 2 performance

Both of 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-TiO₂ 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:

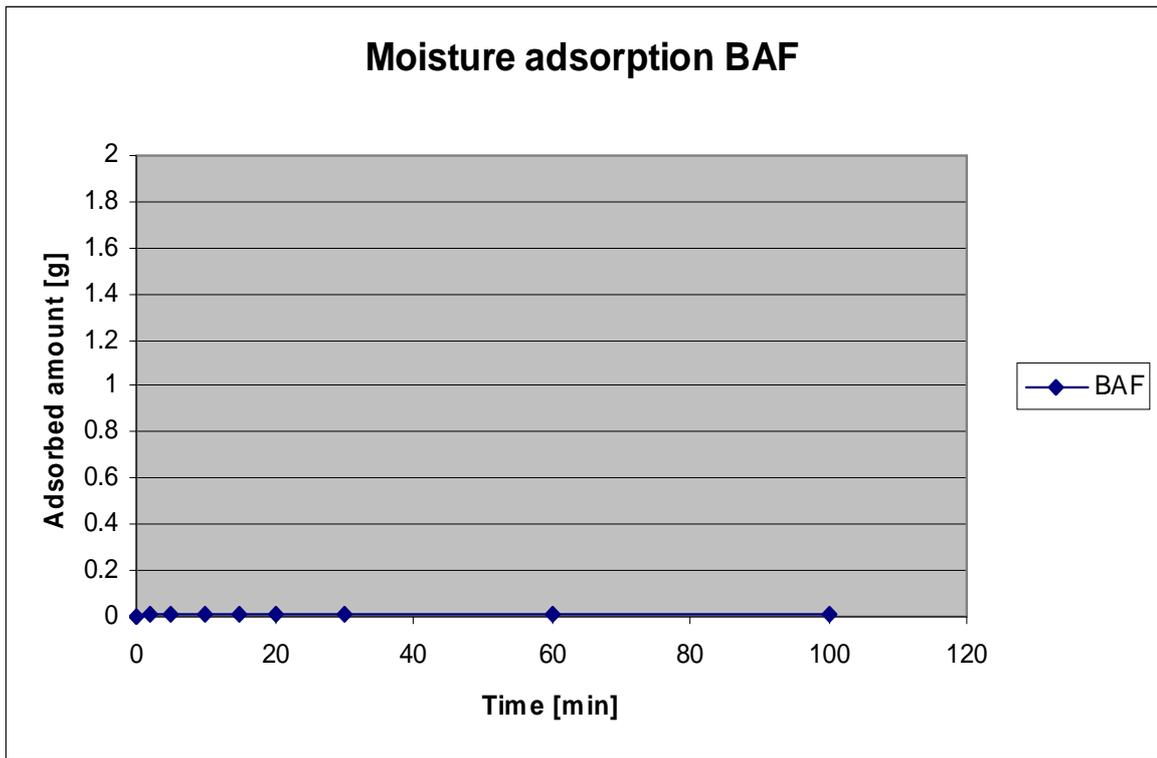


Fig. 25: BAF performance

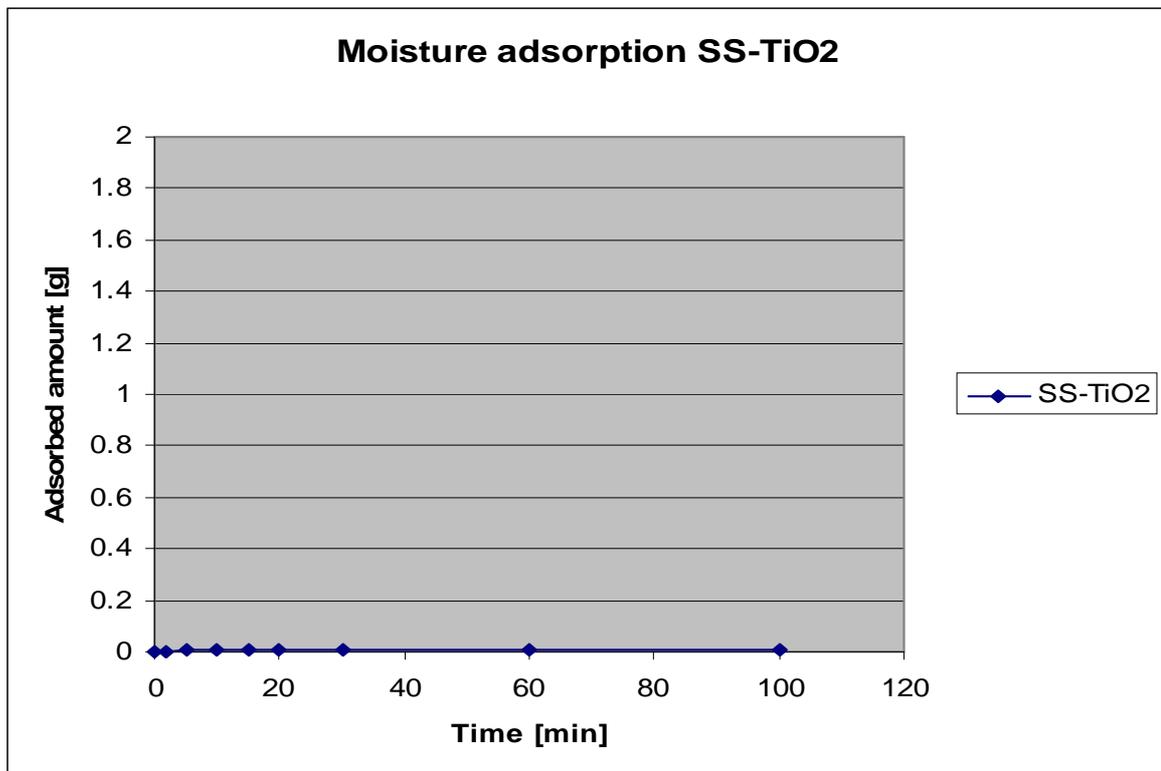


Fig. 26: SS-TiO2 performance

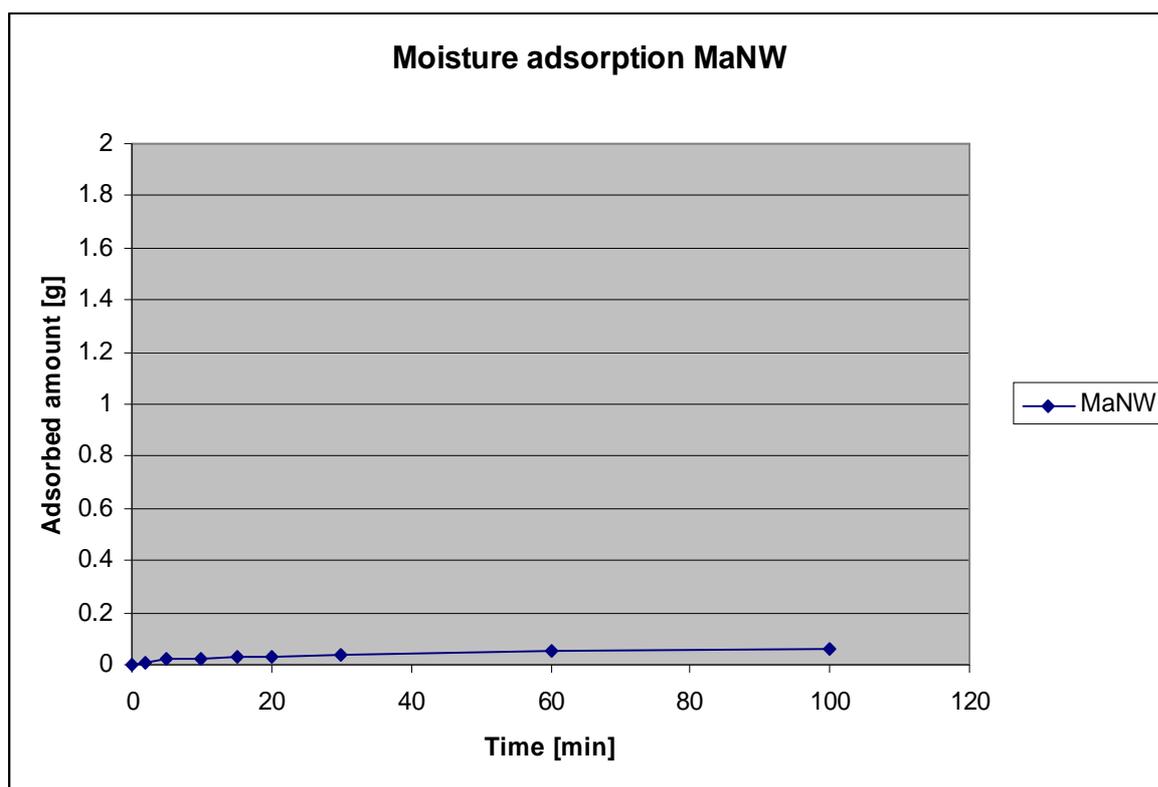


Fig. 27: *MaNW performance*

As a result, for BAF and SS-TiO₂ 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 addition, 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-TiO₂, 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 TiO₂ only in traces. Thus, for SS-TiO₂ 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 than the one of BAF material.

Conclusions

The objectives of the work were testing new materials as air filters and carry out a comparative Life Cycle Assessment about dishwashers. Eventhough the initial methodological scheme underwent a certain number of modifications, the double-task objective was achieved.

A previous study was carried out about the material class of ceramic foams, about the principal common adsorbents and desiccant materials and about characterisation methods in the field of vapour adsorption. Subsequently, a comparative study between two Life Cycle Assessment methods was made, showing pro's and con's of Process-Based LCA and Environmental Input-Output LCA. Unlike the initial idea, a process-based LCA was chosen to be developed in the present case study. The change of plan was due to the higher feasibility of that kind of LCA in the context of a master thesis work. Problems in data availability, already very high with the more used process-based type, turned out not solvable for environmental input-output type, at least in the amount of time provided for the thesis. Nonetheless, this constitutes an interesting future development in case this field would raise further interest.

Results of the conducted LCA indubitably 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. This is probably due to their low values of specific surface area, which is the most important property for an adsorbent device. Another 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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