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## Dynamic identification of water permeability of silica hydrogel

### Introduction

Permeability is a physical quantity showing the material's ability to transport fluids inside the structure of the body under a pressure difference, and can be termed in different ways depending on e.g. type of fluid (gas or liquid) [Galvan *et al.*, 2014]. Permeability has a unit of area [m<sup>2</sup>].

The issue of predicting liquid permeability based on gas permeability has been under investigation since the 1940s, by the application of gas slippage theory. Gas flow through porous media regime has also been a subject of considerable attention in soil mechanics, shale extraction, and in environmental protection and restoration projects. Generally, in these porous media and nanostructures, the mean free path of gas molecules is in the order of the pore size and for such microscale pores the gaseous flow through these structures may be affected by the slip effect [Añez *et al.*, 2014; Lee, Quesnel, 1998].

The literature on the liquid and vapor permeability of different types of building materials like concrete, wood, plaster etc. (in most cases non-shrinking during drying) is very extensive [Ma, 2014; Li *et al.*, 2016]. Less publications are available on permeability of gels, which can be found in medical, horticultural, food and other products also used in dry state for thermal or acoustic insulation [Claisse *et al.*, 2009; Kameche *et al.*, 2014]. The water transport property of materials is determined by their structural characteristics. The most important issue is how the micro structural aspects of the gel network and deformability of the network by an applied force affect water exudation rate from the material [Urbonaite *et al.*, 2015].

Silica gels from year to year gain in popularity and have many potential applications like host matrices for chemical species or nuclear waste storage. These materials are also used as structural model to understand and improve efficiency of e.g. sequestration of CO<sub>2</sub>, more, silica gels are interesting for both technological applications and theoretical research. The permeability of the porous structures is a key parameter for mentioned applications. However, permeability has only been measured in silica hydrogels by a small number of research teams [Añez, 2014].

Water and/or vapor transport is a key process in many industrial processes such as drying calcination etc. The permeability of a porous solid is a macroscopic property which depends on other microscopic properties of material such as tortuosity, pore size distribution and uniformity [Szymkiewicz, 2013]. In most cases when water transport mechanisms in gels are studied, components like network stiffness and time- or force-dependent changes of the gel-morphology are usually neglected [Chemkhi and Zagrouba, 2008].

In the work of Hermansson [2008] one can find described three different components of water transport inside the gel structure: hydrodynamic flow, capillary flow and molecular diffusion. Hydrodynamic and capillary flows are apparent on macro- to micro scales. Hydrodynamic flow is dominant in large, open structures, and is driven by external forces like gravity. Capillary flow also depends on surface tension of the liquid, where the external pressure must be higher than the capillary pressure – a result of surface tension in order to displace water. Molecular diffusion is dominant on nanometer scale and is of importance for the mass transport of molecules of bound moisture [Kocher and Foegeding, 1993].

Permeability is either measured by commercially available dedicated permeameters or self-made devices constructed by researchers [Galvan *et al.*, 2014]. The direct way of measuring liquid permeabil-

ity is to apply *Darcy* law to data of liquid flux at given pressure drop. There are also several methods which are indirect.

The main aim of this work is to propose a method of determining the current water permeability coefficient for saturated bodies such as silica hydrogel, undergoing a process of convective drying. The developed method and obtained results can be useful for researchers who design structures of different materials for fluid transport and need to know their permeability in the design process.

The advantages of the method used in this work include:

- dynamic, direct measurements of driving force (pressure gradient), more reliable than results from the other methods presented in literature.
- cheap and easy experiment, which can be used in drying chambers in order to avoid cracking of dried material.
- it can be used for both shrinking and non-shrinking materials, provided that data of the constant-drying-rate period are used.

### Materials and methods

#### Apparatus

Drying tunnel used in the experiments shown in Fig. 1 is described in details in the work of Adamski *et al.* [2014a] where the procedure of determining drying shrinkage of a sample, based on camera images, is also explained. In this work the evolution of tunnel air temperature and RH as well as the sample mass, temperature and picture were recorded. The internal pressure, which is the *Darcy* driving force is also recorded.

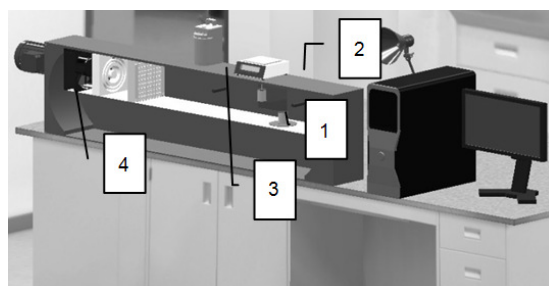


Fig. 1 Diagram of drying tunnel, 1 – sample, 2 – balance, 3 – humidifier, 4 – fan

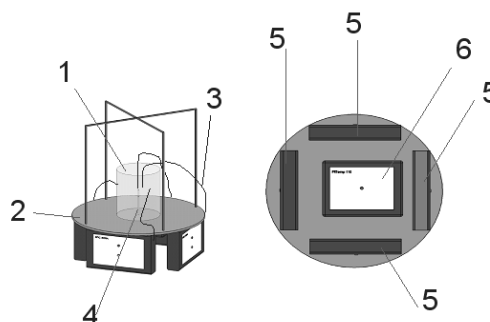


Fig. 2 The measuring tray with sensors and sample; a) 1-sample, 2-tray, 3-thermocouple, 4- needle of pressure sensor, 5-temperature loggers, 6 – pressure logger

The dynamic values of internal pressure in the sample during drying were measured by a pressure transducer equipped with a thin

syringe needle inserted axially in the sample and its readings recorded by the data logger. Two cylindrical samples were used in each experiment having 32 mm in diameter and 22 mm high, prepared as explained in the next section. One, with a needle inserted, was placed on the balance tray which also carried the data transducer and transmitter. The tray slowly rotated around its vertical axis in order to equalize surface conditions. This sample allowed for simultaneous measurement of drying kinetics and pressure evolution. The other one was stationary and had two thin J-type thermocouples inserted: one axially in the center and the other near the surface. Both upper and lower cylinder bases were insulated with Plexiglas disks against axial mass transfer and, to some extent, heat transfer.

The experiments were performed at two temperatures of 30°C and 40°C with varying RH of air flowing at velocity of 1m/s. Upon completion of the experiment the sample was dried in 105°C to constant weight in order to determine the residual moisture content of the material and its dry mass.

### Sample synthesis

Silica gels used in experiments were synthesized by a three stage sol-gel method. The silica precursor was commercial sodium metasilicate solution in water (*water glass* DRAGON R-145) containing 35% to 45% pure SO<sub>2</sub>. Details of the synthesis are available elsewhere [Adamski *et al.*, 2014b].

Samples were cast in the form of gel cylinders of diameter 32 mm and height 22 mm. The resulting hydrogels have initial water content of 20 kg/kg dry basis, which corresponds to dry density of 50 kg/m<sup>3</sup>.

## Results and discussion

The *Darcy* permeability coefficient is the physical quantity especially important in modeling of the internal moisture transport in the solid during drying. It has a significant role in the first stage of drying when the body is fully saturated therefore the results presented are interpreted only in the time when the body remains in that period. The following assumptions apply:

- only one-dimensional mass and heat transfer in radial direction is assumed;
- the solvent that is removed during the drying is incompressible and the solid skeleton of samples is shrinking during drying;
- the initial temperature and moisture distribution in solid is uniform;
- in the experiments no mechanical external load or forces exist (gravity force is neglected);
- since the skeleton shrinks during evaporation it is assumed that the mass transport takes place only in the liquid phase and is described by the *Darcy* law.

Permeability was calculated from the steady state mass balance equation in cylindrical coordinates:

$$\frac{k_L \rho_L}{\mu_L} \left( \frac{dp}{dr} + r \frac{d^2 p}{dr^2} \right) = 0 \quad (1)$$

The equation was solved with the following boundary conditions:

$$\begin{aligned} \text{for } r = r_{ax} & \quad p = p_{ax} \\ \text{for } r = R & \quad p = p_{atm} \end{aligned}$$

and the solution has the form:

$$k_L = \frac{j_i \cdot \mu_L \cdot (r - r_{ax})}{\rho_L \cdot \Delta p} \ln \left( \frac{r}{r_{ax}} \right) \quad (2)$$

where:

- $j_i$  – evaporation flux at surface, [kg/(m<sup>2</sup>s)]
- $k_L$  – liquid permeability, [m<sup>2</sup>]
- $r$  – radius of the cylinder, [m]
- $r_{ax}$  – internal radius of the needle (0.035) [m]

- $\Delta p$  – pressure difference between pressure inside the sample  $p_{ax}$  and ambient pressure  $p_{atm}$  [Pa]
- $\mu_L$  – viscosity of liquid water, [Pa·s]
- $\rho_L$  – density of liquid water, [kg/m<sup>3</sup>]

The current porosity of the sample was calculated from the equation:

$$\varepsilon = \frac{\rho_s - \rho_m}{\rho_s} \quad (3)$$

where:

- $\rho_s$  – density of dry sample skeleton obtained from gas pycnometer, [kg/m<sup>3</sup>]
- $\rho_m$  – apparent density of material (dry mass/current volume of sample), [kg/m<sup>3</sup>]

The current volume and shrinkage of sample was obtained from sample images (Fig. 3) based on the method described in the work of Adamski *et al.* [2014a].

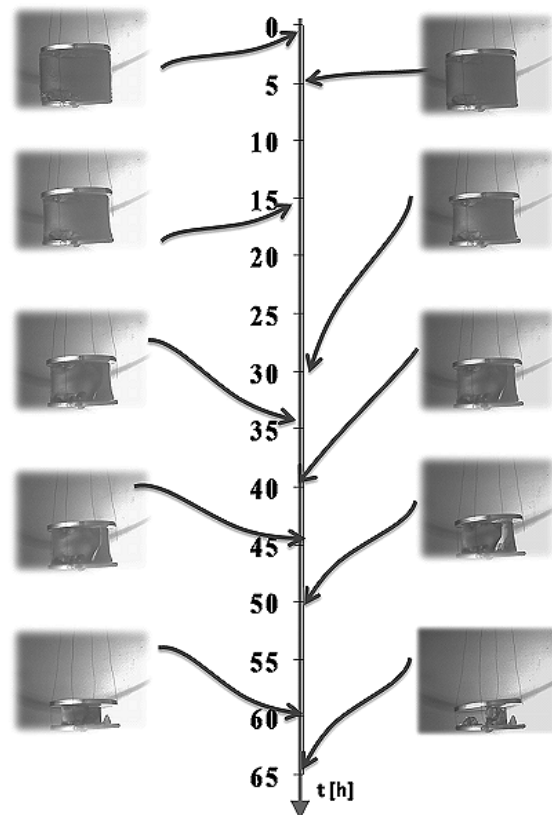


Fig. 3. The progress of sample shrinkage during drying at 30°C

Summary of the obtained results from drying tunnel experiments in the form of drying kinetics curves, temperature curves and pressure curves are shown in Fig.4 and 5. In graphs, because of the amount of data presented, applied the same axis of ordinate for temperature and moisture content. Measurements were repeated 10 times for each temperature, the graphs show results of the selected measurement series.

In the first stage of drying the gel heats up and *Darcy* flow of the liquid towards the surface begins. Simultaneously the porosity of gel starts to decrease (Fig.6 and Fig.7) slowly. The liquid permeability coefficient is decreasing gradually at this time (Fig.8 and Fig.9). In the second stage, after 5 hours of drying, the liquid inside thermally expands and simultaneously the evaporation on the surface makes the soft gel shrink, the porosity of gel decreases rapidly, the water is forced from pores and the value of permeability stabilizes. The value of permeability stabilized after 14 hours of processing in 40°C and after 20 hours of processing in 30°C, the shrinkage stopped.

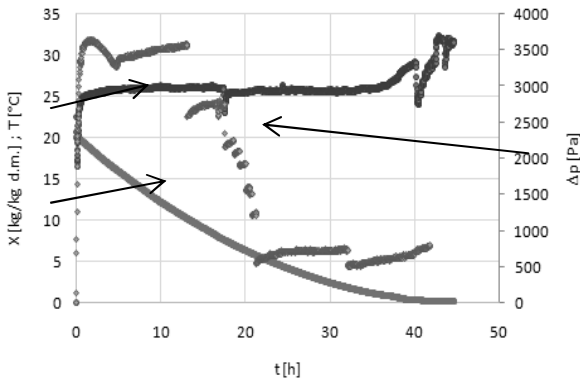


Fig. 4. Results for 30°C, average air humidity = 0.014 kgH<sub>2</sub>O/kg dry air

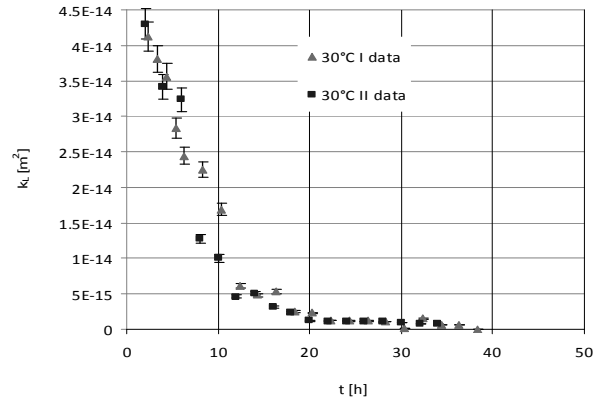


Fig. 8. The liquid permeability kinetics for samples drying at 30°C

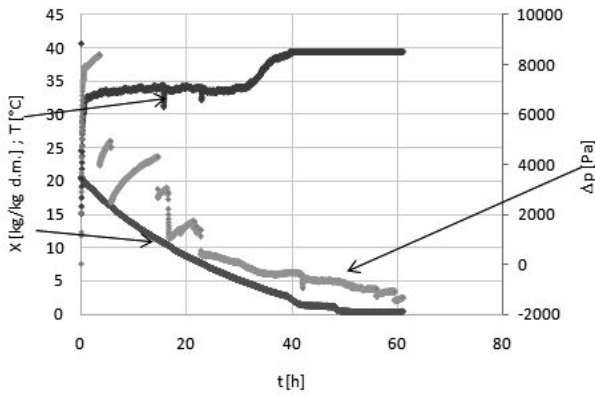


Fig. 5. Results for 40°C, average air humidity = 0.027 kgH<sub>2</sub>O/kg dry air

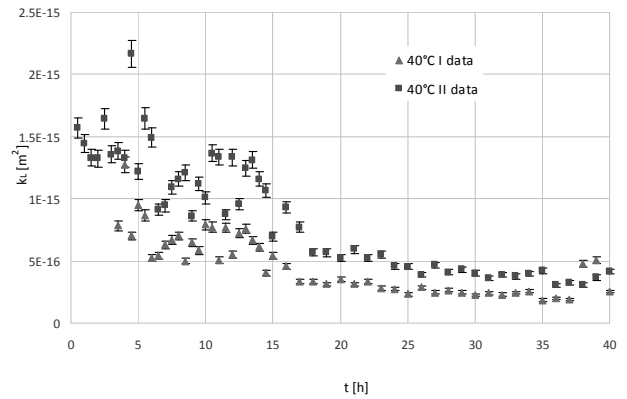


Fig. 9. The liquid permeability kinetics for samples drying at 40°C

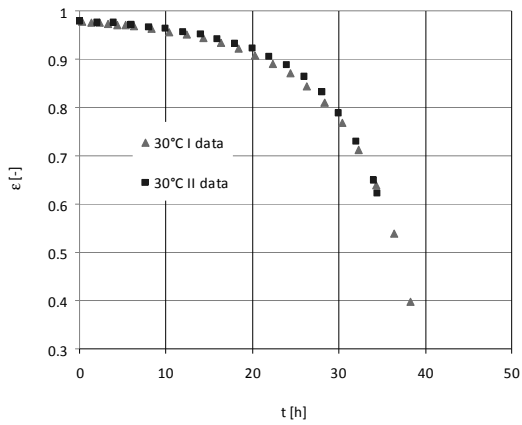


Fig. 6. The kinetics of porosity changes for samples drying at 30°C

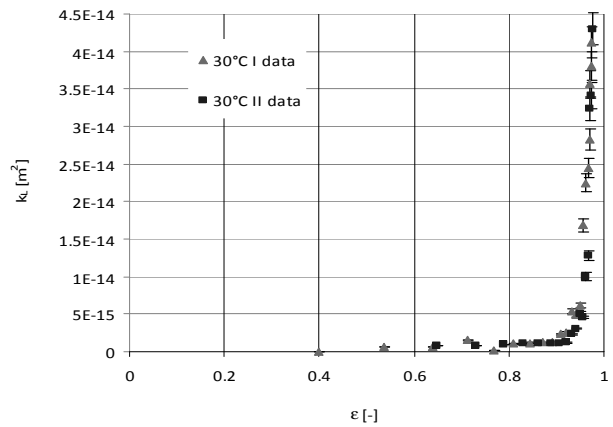


Fig. 10. The liquid permeability coefficient vs. porosity for samples drying at 30°C

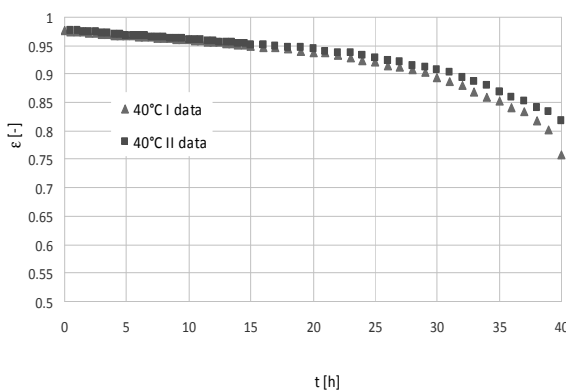


Fig. 7. The kinetics of porosity changes for samples drying at 40°C

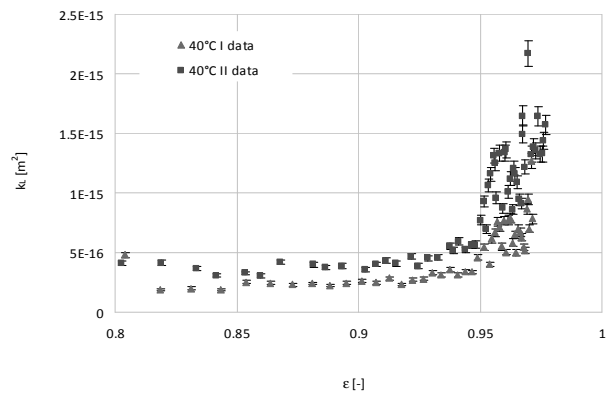


Fig. 11. The liquid permeability coefficient vs. porosity for samples drying at 40°C

Experimental sorption isotherm for prepared hydrogel is presented in the paper [Adamski *et al.*, 2014b]. It provided the value of critical moisture content of 0.35 kgH<sub>2</sub>O/kg d.m. This value is reached after the time of about 35 hours for 30°C and 30 hours for 40°C. At this point material temperature begins to increase to reach the temperature of the drying agent. At this point the solid is no further saturated so water is transported partly in gas phase. The liquid permeability coefficient remains constant when porosity reached average value 0.83 and in this point gas permeability coefficient should be calculated. Cracking of gel at this point is very often observed. The presented method is applicable only to the period of complete saturation i.e. above the critical moisture content where all pores are filled with water.

Calculation of the liquid permeability coefficient was performed until the sample cracked, in order to avoid errors resulting from losing connection between the sample and needle of the pressure sensor. Similar values of liquid permeability coefficient, in the range of  $2.5 \cdot 10^{-16}$  -  $4.5 \cdot 10^{-14}$  m<sup>2</sup> (Fig.10 and Fig.11), were obtained by Lee and Quesnel [1998] for water in TMOS silica gels based on traditional method of measurement by the hydraulic method. In that work, experiments were performed under constant temperature 45°C and the gel remained fully saturated and didn't shrink due to water evaporation.

## Conclusions

The liquid permeability of prepared silica hydrogels was measured by the new method based on direct measurement of the internal pressure in the sample using a modified pressure sensor.

Below the saturation point, liquid permeability coefficient remains constant.

Most of the earlier studies focus on permeability of bodies of constant internal structure represented by one value of permeability coefficient. The present method allows for easy and fast identification of the liquid permeability coefficient in saturated porous solids of varying internal structure (voidage) owing to the variable shrinkage during drying. However, this method is applicable only to the period of complete saturation of the material with solvent. The pressure gradient is seldom the only driving force in drying process in real situations. During drying different types of materials, mass transfer takes place by two-phase flow in which the vapor component is dominant. The calculations presented in this work do not cover such cases and more elaborated model is necessary to identify permeability in such experiments.

## REFERENCES

- Adamski R., Pakowski Z., Kamińska A., (2014a). The mechanism of moisture transport in a gel cylinder. *Drying Technol.*, 32(11), 1266-1268. DOI: 10.1080/07373937.2014.917320
- Adamski R., Pakowski Z., Kamińska A., (2014b). *Experimental investigation of sorption isotherm and surface area of silica gel* [in:] Andrieu J., Peczkalski R., Vessot S., (Eds). Proc. of 19<sup>th</sup> Int. Drying Symp., 24-27.08.2014, Lyon, France, EDP Sciences (ISBN: 978-2-7598-1631-6)
- Añez L., Calas-Etienne S., Primera J., Woignier T., (2014). Gas and liquid permeability in nano composites gels: Comparison of Knudsen and Klinkenberg correction factors. *Microporous and Mesoporous Materials* 200, 79-85. DOI: 10.1016/j.micromeso.2014.07.049
- Chemkhi S., Zagrouba F., (2008). Development of a Darcy-flow model applied to simulate the drying of shrinking media. *Brazilian J. Chem. Eng.*, 25(3), 503-514. DOI: 10.1590/S0104-66322008000300008
- Claissé P.A., Elsayad H.I., Ganjian E., (2009). Water vapour and liquid permeability measurements in cementitious samples. *Adv. Cement Res.*, 21(2), 83-89. DOI: 10.1680/adcr.8.00046
- Galvan S., Pla C., Cueto N., Martínez-Martínez J., García-del-Cura M.A., Benavente D., (2014). A comparison of experimental methods for measuring water permeability of porous building rocks. *Mater. Constr.* 64 (315). DOI: 10.3989/mc.2014.06213
- Hermansson, A. M. (2008) *Structuring water by gelation* [in:] Aguilera J.M., Lilford P.J. (Eds). Food Material Science. Springer, New York, 13, 255-280.
- Kameche Z.A., Ghomari F., Choinska M., Khelidj A., (2014). Assessment of liquid water and gas permeabilities of partially saturated ordinary concrete. *Constr. Building Mat.*, 65, 551-565. DOI: 10.1016/j.conbuildmat.2014.04.137
- Kocher P.N., Foegeding, E.A., 1993. Microcentrifuge-based method for measuring water-holding of protein gels. *J. Food Sci.*, 58(5), 1040-1046. DOI: 10.1111/j.1365-2621.1993.tb06107.x
- Lee B.I., Quesnel E., (1998). Low density silica gels and solvent permeability. *J. Eur. Ceramic Soc.*, 18, 123-129
- Li K., Stroevev P., Sluys L.J. (2016). Investigation of liquid water and gas permeability of partially saturated cement paste by DEM approach, *Cement Concr. Res.*, 83, 104-113, DOI: 10.1016/j.cemconres.2016.02.002
- Ma D., Miao X.X., Jiang G.H. et al. (2014). *Transp Porous Med.*, 105, 571-595. DOI:10.1007/s11242-014-0385-5
- Szymkiewicz A., (2013). *Modelling water flow in unsaturated porous media. Accounting for Nonlinear Permeability and Material Heterogeneity* Springer-Verlag, Berlin Heidelberg. DOI: 10.1007/978-3-642-23559-7
- Urbonaite V., Jongh H.H.J., Linden E., Pouvreau L., (2015). Permeability of gels is set by the impulse applied on the gel. *Food Hydrocolloids* 50, 7-15. DOI: 10.1016/j.foodhyd.2015.03.024
- Navaee-Ardeh, S.; Bertrand, F.; Stuart, P.R., 2006. Emerging biodrying technology for the drying of pulp and paper mixed sludge. *Drying Technol.*, 24(7), 863-878. DOI:10.1080/07373930600734026
- Niedziółka I., Zuchniarz A., 2006. Analiza energetyczna wybranych rodzajów biomasy pochodzenia roślinnego. *Motrol.*, 8A, 232-237
- PN-73/G-04513, (1973). *Paliwa stałe. Oznaczanie zawartości węgla i wodoru metodą Sheffield*
- PN-75/C-04616/01, (1975). *Woda i ścieki - Badania specjalne osadów. Oznaczanie zawartości wody, suchej masy, substancji organicznych i substancji mineralnych w osadach ściekowych*
- PN ISO 13878:2002. *Jakość gleby - Oznaczanie zawartości azotu całkowitego po suchym spalaniu ("analiza elementarna")*
- PN-ISO 1928:2002. *Paliwa stałe - Oznaczanie ciepła spalania metodą spalania w bombie kalorymetrycznej i obliczanie wartości opałowej*
- Rozporządzenie Ministra Środowiska, (2015) z dnia 9 grudnia 2015 r. w sprawie katalogu odpadów. Dz.U. Nr 112, poz. 1206
- Rutkowska B., 2009. Możliwości rolniczego wykorzystania zużytych podłoży po produkcji pieczarek. Odpady w kształtowaniu i inżynierii środowiska. *Zesz. Probl. Post. Nauk Roln.*, 535: 349-354
- Sugni M., Calcaterra E., Adani F., 2005. Biostabilization-biodrying of municipal solid waste by inverting air-flow. *Biores. Technol.*, 96(12), 1331-1337. DOI: 10.1016/j.biortech.2004.11.016
- Zawadzka A., Krzystek L., Stolarek P., Ledakowicz S., 2010. Biodrying of organic fraction of municipal solid wastes. *Drying Technol.* 28, 1220-1226. DOI: 10.1080/07373937.2010.483034