3

THE INFLUENCE OF FERRITE PARTICLE SIZE ON THE QUALITY OF THE MAGNETIC MARKER IN SHALE GAS HYDRAULIC FRACTURING

3.1 INTRODUCTION

Hydraulic fracturing, fracking, is method to induce fracturing of shale. During fracking water, proppant that is sand or other ceramics and some chemicals are pumped in high pressure into the well. As a result of fracturing, large amount of very small cracks, fractures are made in shale. Proppant prevents closing the fractures [16]. If fractures are fully open, natural gas can migrate from shale, through well, into receiver such as gas tank or pipeline.

One of main unknowns during shale gas exploration is to assess the range and efficiency of hydraulic fracturing. It is also essential to assess the distribution of proppant, which keeps the fracture pathways open. Solving these problems may considerably increase the efficiency of the shale gas extraction.

Because of that, the idea of marker, which can be detected when added to fracturing fluid, has been considered for a long time. The range of hydraulic fracturing can be assessed with smart magnetic marker, by measurement of vertical and horizontal changes of magnetic field before and after fracturing. The difference should be caused by magnetic marker particles. The potential magnetic marker could to be soft magnetic material, especially spinel ferrite. Ferrite grain sizes have crucial influence on markers' magnetic properties.

3.2 RELEVANT MAGNETIC PARAMETERS

One of the most important parameter defining the magnetic material properties is a volume magnetic susceptibility, proportionality coefficient in the equation determining the size of magnetization as a function of magnetic field strength [14] (Eq. 3.1):

$$M = \chi_V * H \tag{3.1}$$

where: M is magnetization, that is, magnetic moment of substance unit volume, χ_V is volume magnetic susceptibility and H is magnetic field intensity. Volume magnetic susceptibility is a dimensionless parameter. In addition to the volume magnetic susceptibility, χ_V, mass magnetic susceptibility, χ_m, is also distinguished. It is described in SI units as m^3/kg, while in the cgs units as cm^3/g. In order to convert between mass and volume susceptibilities, the following formula can be used (Eq. 3.2):

$$\chi_V = \chi_m \cdot \rho \quad (3.2)$$

where: χ_V is volume magnetic susceptibility, χ_m is mass magnetic susceptibility and ρ is density. Depending on the substance properties, magnetic susceptibility considerably changes [17] for diamagnetic, paramagnetic and ferromagnetic materials respectively. Another parameter which describes the magnetic properties of magnetic permeability, which is a function of the magnetic field intensity (Eq. 3.3):

$$B = \mu \cdot H, \quad \mu = \mu_0 \cdot \mu_r \quad (3.3)$$

where: B is magnetic induction, H is magnetic field intensity, μ is magnetic permeability, μ_r is magnetic permeability of a free space, μ_0 is magnetic permeability of a specific medium.

Non-linear medium permeability is not a constant but a function. In the case of certain materials is has hysteresis. Magnetic permeability of a specific medium and magnetic susceptibility are linked by the formula (Eq. 3.4):

$$\mu_r = 1 + \chi, \quad (3.4)$$

Hysteresis of magnetic material is shown at Fig 3.1. The most important magnetic hysteresis parameters are [5, 19, 25] are saturation magnetization defined as saturation magnetic flux density of a magnetic material at a given magnetic field strength and coercive force (H_c) defined as magnetizing field strength (H) required to bring the magnetic flux density (B) of a magnetizes material to zero.

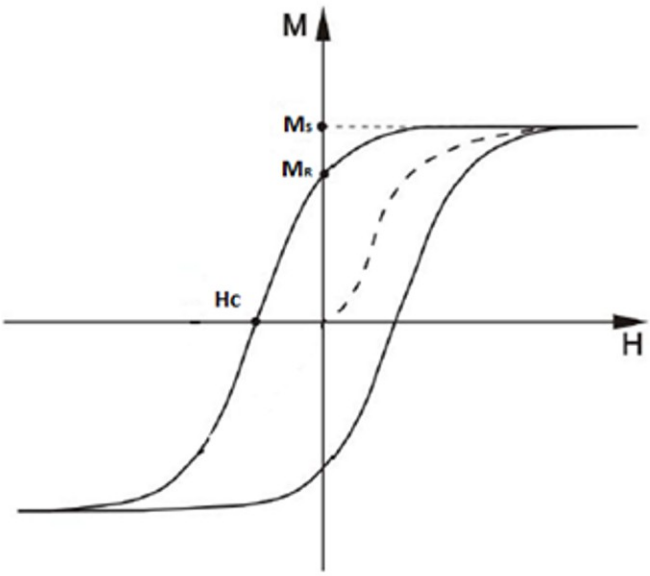

Fig. 3.1 Exemplary hysteresis loop for magnetic material.

M_R – remanance (saturation remanance) M_S – saturation magnetization
H_c – coercivity, dotted line – initial curve

Source: own elaboration

The notion of a magnetic material is commonly used in relation to the ferromagnetic materials. Magnetic marker has to be soft, which means it is relatively easily magnetized or demagnetized have low coercivity, low hysterisis loss, high initial permeability and large magnetic induction.

3.3 FERRITES

One of the most commonly magnetic materials that can be used as smart markers, are ferrites, belonging to group minerals called spinels. Spinels are compounds of the general formula AB_2O_4. Among them are three groups can be indicated: $A^2 + B^3 + 2O_4$, $A^4 + B^2 + 2\ O_4$ and $A^6 + B + 2\ O_4$. Most common spinel type is $A^2 + B^3 + 2\ O_4$, where: A is metal of the second group of the Periodic Table or a transition metal in the second oxidation state, B is metal of the second group of the Periodic Table or a transition metal in the third oxidation state.

When in position B is Fe atom, spinel is called ferrite. When also the A position is occupied by Fe, magnetite is created. The soft ferrites, are compounds of a typical chemical composition $M_O\ \cdot\ 6\ Fe_2O_3$ where M is Mg, Mn, Ni and Zn [15, 17, 24]. Ferrites with best electromagnetic properties are ZnMn and Ni ones, and because of that they are the most commonly industrially used. These ferrites are commonly used in electromagnetic and electronic systems, such as the coils' cores etc. [24]. In this paper, the most important ferrites forms are described: traditional sintered ferrites and ferrite nanomaterials.

3.4 TECHNOLOGICAL ISSUES

Production of ferrite is a series of consecutive process actions that are namely: weighting and blending, calcining, milling, granulation or spray drying, pressing, and sintering. Blending may be done by different methods, wet or dry and with or without grinding. Most commonly used method is wet ball milling.

The typical ferrite production includes selecting suitable reagents and conducting the reaction in the aqueous phase. As a result of reaction precipitated iron with the desired non-ferrous admixtures compounds are in the formed. The precipitated material is then dried and calcined. Calcining involves heating the blended material to 900-1100°C. Temperature should be 100-300°C lower than the final firing temperature. Calcining is to start ferrite lattice forming process. This process transfers oxides into a chemically and crystal graphically uniform structure. Calcining allows better control of the final dimension control, in cases where this is necessary. It also helps to homogenize the material, which obviously is advantageous. It is done in rotary calciners, with controlled rotation speed, angle of incline, heat input, temperature, and depth of fill. Calcinated material has to be then milled, usually in ball mills. Milling determines the particle size distribution. The optimum particle size depends on further applications. After milling, the slurry must be converted to powder. Many additives may be added during this step: binders, plasticizers or lubricants. As a result of granulation particles are denser, spray drying seems to be better option, according to better flow characteristics of obtained powders. Sintering is used in order to achieve even higher magnetic permeability; the temperature is raised up to 1400°C.

3.5 GRAIN SIZE INFLUENCE ON FERRITE MAGNETIC PROPERTIES

The grain size is crucial for the magnetic properties of ferrite. The relationship between the magnetic permeability and the particle size is not linear. The magnetic permeability is affected by i.e. grain size homogeneity and the presence of defects, pores and impurities. The largest size of the magnetic permeability is usually observed for particles with a diameter of 5-20 microns. The increase in permeability for grain size bigger than 5 microns associated with a change in the rotation of the magnetic domains with the wall of ferrite grains. In contrast, decreasing the permeability for particles of diameter greater than 20 microns, was bonded to the effect of the porosity of the grain. Similar properties were observed for the ferrite ZnMn or ZnNi. If the particles are reduced to size comparable with dimensions of magnetic domains, magnetic susceptibility will increase by a few orders of magnitude [8]. It is then possible, to use lower amount of magnetic marker, to obtain the same effect.

Additionally, it was found that reducing grain size to nanometres; materials possess clearly superior magnetic properties, as compared to the same structure but having a larger particle size. Therefore, the use of magnetic nanomaterials, for example zinc-manganese ferrites, guarantees excellent magnetic properties. Research on properties of new nanomaterials dominated in modern materials engineering reports, but nanomaterials, especially magnetic nanomaterials are not yet produced on a mass scale. This makes the nanomaterials production unit cost several orders of magnitude greater than cost of the same material, but with the larger particle size. Therefore, the use of magnetic nanomaterials, for example zinc-manganese ferrites, could guarantee excellent properties of magnetic proppants. Magnetic nanomaterials are particles that stay in a single domain state for all magnetic fields. Recently, research on properties of new nanomaterials dominated in modern materials engineering reports, but nanomaterials, especially magnetic ones are not yet produced on a mass scale. The magnetic nanomaterials production cost is usually several orders of magnitude greater than cost of the same material, but with the larger particle size. Changes in properties of ferrites with the grain size and method of production are shown in Fig. 3.2 – 3.4.

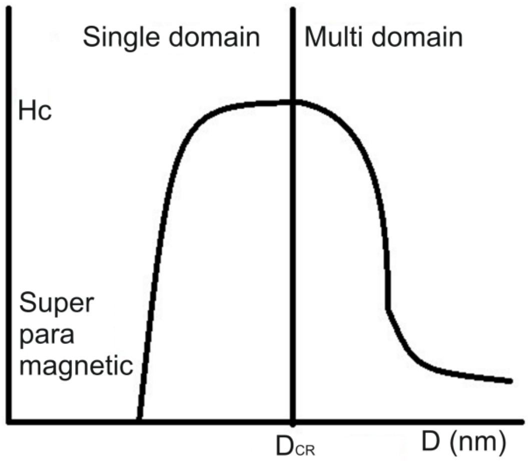

Fig. 3.2 Grain size influence on the value of coercivity

Source: [22]

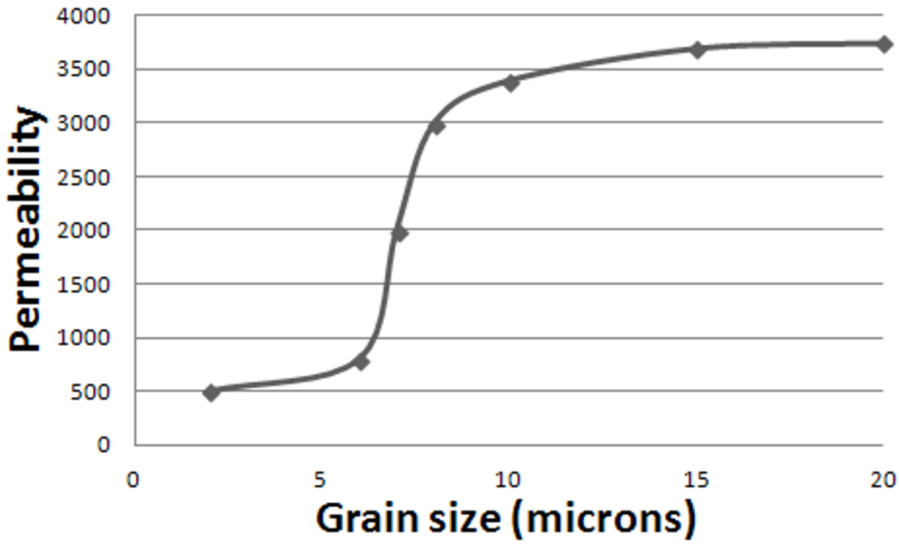

Fig. 3.3 The example of grain size influence on the value magnetic permeability for ZnMn ferrite

Source: own elaboration based on: [12, 13]

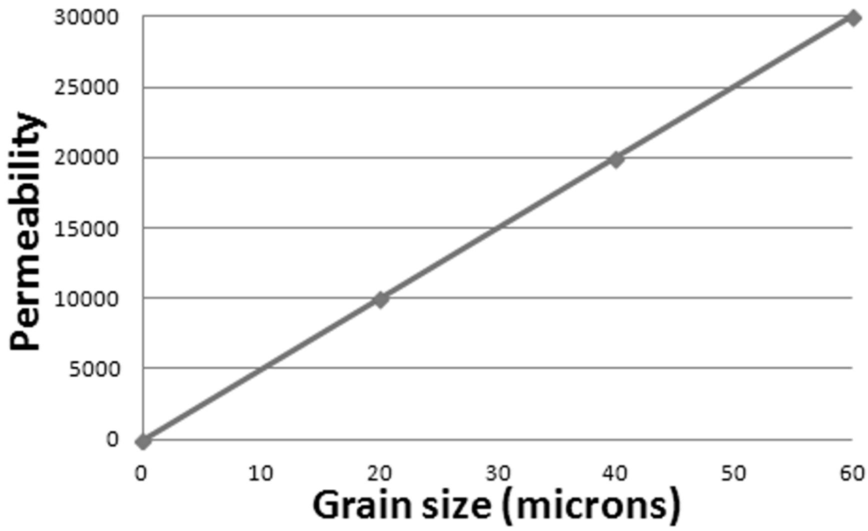

Fig. 3.4 Permeability of MnZn ferrites as a function of grain size

Source: own elaboration based on: [12, 13]

3.6 HYDRAULIC FRACTURING ISSUES

Two kinds of attempts are being made for smart magnetic marker introduction into the fracturing fluid. The first possibility is the markers' electromagnetic activity throughout the whole volume of the fracturing fluid, namely the whole fracturing fluid could be filled up with the marker. Among these hydraulic fracturing solutions, ferrofluid can be considered the second possibility is marker that is one of many components of the fracturing fluid. The main difficulty associated with the later possibility is uniform mixing of electromagnetic marker with the fracturing fluid.

Markers' particles in ferrofluid have to be nano-sized. The use of nanoparticles is related to some risk [11]. Due to the small size of the nanoparticles, they are much more reactive, than the same material with a larger particle size. It is because of much larger specific surface area, for same mass, in comparison with the particle with the bigger grain size diameter. To slow down or prevent overlap of chemical reactions degrading the electromagnetic properties of the markers, its surface could be modified. Two basic ways of protection are proposed. First one is particles surface passivation, which includes covering with a tight layer of non-reactive coating or attachment of non-reactive surface functional groups [22]. The second possibility is placing an electromagnetic marker in a protective capsule, completely insulating it from external conditions [1, 7, 9, 21, 23]. Ferrite nanoparticles can react with many chemical compounds. An example can be hydrogen sulfide (H_2S) present in the fracture, which decreases markers' magnetic properties. As mentioned above, magnetic marker should not react with H_2S and other sulphur containing compounds. It is important to mention here that Mn and Zn iron oxides, that as it was mentioned-above have relatively low reactivity to H_2S, but they are both rather paramagnetic. To prevent chemical degradation on magnetic marker during fracturing, magnetic particles can be also associated with polymers like polyethylenimine (PEI), polyuretane, polyesters, polyacrylates or their co-polymers [20]. Cost may include: fabrication, recycling, cleanup and composition [3]. Research on the possibility of combining commercially available proppants with magnetic markers nanoparticles has been done. The example can include studies on the proppant Carbo HSP, Due to the presence of iron oxide nanoparticles, nanomagnetite, proppant Carbo HSP was characterized by an initial magnetic susceptibility 25,7-214,6 10^{-5}SI [18] and total fracturing costs 1 – 3 billions USD per well.

As nanomaterials use is too expensive, it is better to use cheaper materials with bigger grain size. Because of that it is better to use magnetic materials during fracturing as a part of modified proppants. Adding magnetic material to proppant, it would give the proppant magnetic properties, and because of that it would be possible to use modified proppant as marker active in electromagnetic field [6]. In this case particle size could be bigger, and because of that production cost will be much lower. The research therefore focuses on modification of proppants. Due to proppant primary function of pores closing prevention and gas flow stimulation [4], formed as a result of hydraulic fracturing in shale, proppants has to be able to withstand the pressure and stress. Because of these requirements proppants are ceramic materials. Magnetic markers have no sufficient mechanical strength to be the proppant. It is therefore necessary to combine magnetic marker with proppant (if ferrofluid is not in use). As a result magnetic composite is made. Electromagnetic marker particles may have a broad range of different grain sizes. From the size of maximum proppant diameter, that is, about 2 mm, when the same marker could serve as a proppant, to the size of a few nm, that is typical nanoparticles diameter [9]. If the particle size is low, the marker may be added at the production stage to proper proppant [2]. Particle of marker could be round, but other shapes are also considered [10].

Magnetic marker can be detected with any electromagnetic sensor that can be placed both on the surface and in the wellbore, as shown in Fig. 3.5.

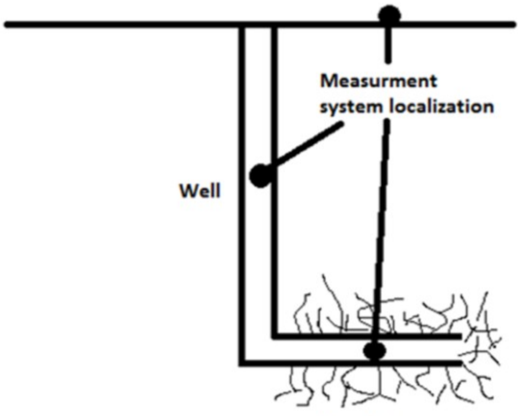

Fig. 3.5 Exemplary electromagnetic sensor localization in the wellbore

Source: own elaboration

CONCLUSIONS

Ferrite particle size influences greatly the cost of production as well as the quality of the magnetic marker in shale gas hydraulic fracturing. The developing of magnetic markers for hydraulic fracturing is not a trivial task. Apart from magnetic properties of intelligent markers the vital problems are posed by fracturing conditions. The use of ferrite nanoparticles is, at the present, not sufficiently explored and requires unrealistic financial funds.

Traditional, relatively cheap ZnMn ferrite powder, with grain size at the micrometer level, could be also considered as an chiper and realistic alternative because it is characterized by good soft magnetic properties. However, further studies, in particular experimental ones simulating real conditions in the fractures during shale gas exploration, are still needed.

ACKNOWLEDGEMENTS

This work was supported by the Polish National Research and Development Center (NCBiR) under grant: EMPROP, "Electromagnetic method to estimate penetration of proppant in the fracturing process".

REFERENCES

1 M. Ashtiani, S.H. Hashemabadi, A. Ghaffari. „A review on the magnetorheological fluid preparation and stabilization." J*ournal of Magnetism and Magnetic Materials,* vol. 374, 2015, p. 716–730.

2 A.R. Barron, R.D. Skala, C.E. Coker, D.K. Chatterjee, Y. Xie. „Method of manufacture and the use of a functional proppant for determination of subterranean fracture geometries". Patent US 2009/0288820 A1.

3 A. Barron, J. Tour, A. Busnaina, Y. Jung, S. Somu, M. Kajn, D. Potter, D. Resanco, J. Ullo. „Big things in small packages". *Oilfield review,* vol. 22 (3), 2010, p. 38-49.

4 D.E. Betzold. „Proppant coating bondable particles and removable particles." Patent no. 6114410, 2000.

5 D. Bhalla, S.K. Aggarwal, G.P. Govil, I. Kakkar. „Manufacturing of Manganese-Zinc Soft Ferrite by Powder Metallurgy." *The Open Materials Science Journal*. Vol. 4, 2010, p. 26-31.

6 J. Bicerano. „Proppants coated with piezoelectric or magnetostrictive materials or by mixtures or combinations thereof, to enable their tracking in a downhole environment." Patent US 2010/0038083 A1.

7 H. Bourne, P. Read. „Well treatment." Patent no: 5964291, 1999.

8 J.D. Byerlee, M.J.S. Johnston. „A magnetic method for determining the geometry of hydraulic fractures." *Pageoph.* Vol. 114, 1976, p. 425 – 433.

9 S. Chen. „Precision making of subsurface locations." Patent no US 2012/0234533 A1.

10 M.D. Clark, P.L. Walker, K.L. Schreiner, P.D. Nguyen. „Methods of preventing well fracture proppant flow-back." Patent no 6116342, 2000.

11 M. Cocuzza, C. Pirri, V. Rocca, F. Verga. „Current and Future Nanotech Applications in the Oil Industry." *American Journal of Applied Sciences,* Vol. 9(6), 2012, p. 784-793.

12 A. Goldman. *Handbook of modern ferromagnetic materials*. Springer, 1999.

13 A. Goldman. *Modern ferrite technology.* Springer, 2006.

14 C.P. Hunt, B.M. Moskowitz, S.K. Banerje. „Magnetic Properties of Rocks and Minerals, Rock Physics and Phase Relations." *A Handbook of Physical Constants*, AGU Reference Shelf 3, American Geophysical Union, 1995, p. 189 – 204.

15 L. Jaswal, J. Singh. „Ferrite materials: A chronological review." *Journal of Integrated Science & Technology,* Vol. 2(2), 2014, p. 69-71.

16 F. Liang, M. Sayed, G.A. Al-Muntasheri, F.F. Chang, L. Li. "A comprehensive review on proppant technologies". *Petroleum,* Vol. XXX, 2015, p. 1-14.

17 D.S. Mathew, R.-S. Juang. „An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in microemulsions." *Chemical Engineering Journal,* Vol. 129, 2007, p. 51–65.

18 L. Morrow, D.K. Potter, A.R. Barron. „Detection of magnetic nanoparticles against proppant and shale reservoir rocks." *Journal of Experimental Nanoscience*, 2014.

19 Ü. Özgür, Y. Alivov, H. Morkoç. „Microwave Ferrites, Part 1: Fundamental properties." *Journal of Materials Science: Materials in Electronics*, 2009, p. 1 -169.

20 D.K. Potter, A.R. Barron, S.J. Maguire-Boyle, A.W. Orbaek, A. Ali, L. Harrison, „Magnetic particles for determining reservoir parameters." Patent WO2011153339.

21 R. Rediger, M.J. Aron, J. Wright. „Reducing flow-back in well treating materials." Patent 7754659 B2, 2010.

22 I. Sharifi, H.H. Shokrollahi, S. Amiri. „Ferrite-based magnetic nano fluids used in hyperthermia applications." *Journal of Magnetism and Magnetic Materials*, Vol. 324, 2012, p. 903–915.

23 A.R. Sinclair, R.L. Johnson II. „Composite and reinforced coatings on proppants and particles". Patent no. 5422183, 1995.

24 R. Valenzuela. „Novel Applications of Ferrites." *Physics Research International*, 2012.

25 „Soft ferrites a user guide." *Magnetic Materials Producers Association,* 1988.

THE INFLUENCE OF FERRITE PARTICLE SIZE ON THE QUALITY OF THE MAGNETIC MARKER IN SHALE GAS HYDRAULIC FRACTURING

Abstract: *The study analyzes the influence of particle size of magnetic ferrite on the possibility of using it, as a marker in magnetic prop pant during hydraulic fracturing. Based on a broad and accurate literature review, it was found, that the ferrite grain size can be one of the critical parameter conditioning the quality of the magnetic marker in shale gas hydraulic fracturing. Hence, the ferrite grain size determines greatly both the costs and efficiency of hydraulic fracturing.*

Key words: *magnetic material, magnetic marker, ferrite, grain size, hydraulic fracturing, shale gas*

WPŁYW WIELKOŚCI ZIARNA FERRYTU NA JAKOŚĆ MARKERA MAGNETYCZNEGO DO SZCZELINOWANIA HYDRAULICZNEGO PODCZAS WYDOBYCIA GAZU ŁUPKOWEGO

Streszczenie: *W pracy przeanalizowano wpływ wielkości ziarna ferrytu na możliwość zastosowania go, jako markera magnetycznego podczas szczelinowania hydraulicznego. Na podstawie szerokiego przeglądu dostępnej literatury, określono, że wielkość ziarna ferrytu może być kluczowym parametrem warunkującym jakość i właściwości markera magnetycznego stosowanego podczas szczelinowania hydraulicznego gazu łupkowego. Zatem, wielkość ziarna ferrytu wpływa zarówno na koszty jak i na efektywność szczelinowania hydraulicznego.*

Słowa kluczowe: *magnetic material, magnetic marker, ferrite, grain size, hydraulic fracturing, shale gas*

Jan BOGACKI, Ph.D.
Warsaw University of Technology
Faculty of Building Services, Hydro
and Environmental Engineering
ul. Nowowiejska 20, 00-653 Warszawa
e-mail: Jan.Bogacki@is.pw.edu.pl

Prof. Jarosław ZAWADZKI, Ph.D. Eng.
Warsaw University of Technology
Faculty of Building Services, Hydro
and Environmental Engineering
ul. Nowowiejska 20, 00-653 Warszawa
e-mail: Jaroslaw.Zawadzki@is.pw.edu.pl

Date of submission of the article to the Editor: 04/15/2016
Date of acceptance of the article by the Editor: 05/08/2016