On magnetite concentrate grains with respect to their use in concrete

J. Borucka-Lipska[1], W. Kiernożycki[2], N. Guskos[3], M. R. Dudek[4], D. Q. Ho[5], W. Wolak[6], M. Marć[7], J. J. Kozioł[8], J. K. Kalaga[9]

[1,2]Faculty of Civil Engineering and Architecture, West Pomeranian University of Technology, Al. Piastów 50, 70-311 Szczecin, Poland
[3]Institute of Physics, West Pomeranian University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland
[3]Department of Solid State Physics, University of Athens, Panepistimiopolis 15 784, Greece
[4,5,6,7,9]Institute of Physics, University of Zielona Góra, ul. Szafrana 4a, 65-069 Zielona Góra, Poland
[5]Vinh University, 182 Le Duan street, Vinh city, Nghe An, Vietnam
[8]Faculty of Biological Sciences, University of Zielona Góra, ul. Szafrana 1, 65-516 Zielona Góra, Poland

Abstract— *Magnetic iron oxide grains and/or micrograins embedded into concrete are suggested for pH-protection of concrete. To this aim a phenomenological formula for the change in pH of the water solution after contacting iron oxides was derived. It has a broader meaning because it refers to all materials for which surface electric potential varies with pH of the contacting solution. It may be used to design a suitable composition of the mortar. In addition, the important property of magnetite concentrate grains that they may increase compressive strength of the mortar is shown. In the study, all the mortar under consideration was made from Portland cement CEM I 42.5 R, natural aggregate - quartz sand fraction 0-2 mm and magnetic material was magnetite concentrate supplied by Magnetite-Grochow Sp. z o. o.*

Keywords— compressive strength, concrete, magnetite concentrate, magnetite grains, pH value.

I. INTRODUCTION

Placement of the magnetic iron oxide grains, micrograins as well as nanograins in mortars causes emergence of a new type of material which is expected to be promising in the construction for use with the following objectives:

1. Materials for electromagnetic shielding, e.g. magnetic materials for absorption and shielding of electromagnetic radiofrequency radiation [1, 2], design of heavyweight concrete containing iron oxides which is suggested for radiation shielding of nuclear reactors [3],
2. design of materials for acoustic shielding [4] and thermal protection (also as pigments in paints),
3. chemical protection against acidic environment [5, 6], protection of concrete against waste water [7]
4. protective barrier against organic pollution (magnetic micrograins and nanograins),
5. Increase of compressive strength of concrete [3].

In this study, two objectives have been chosen for a discussion, the ability of magnetic grains to increase of compressive strength of concrete and their role with respect to chemical protection of mortars. It is well known that stability of mortar made from Portland cement strongly depends on pH and the best for it is the value of around of pH 11 [8]. Long-term exposition to acid rain, salt, carbonation [6] (generation of carbonic acid in the pores of concrete after its reaction with atmospheric CO_2) or contacting low pH wastewater decreases pH and cement degradates - it stops to keep the quartz sand and other possible components of concrete together. At the same time, the iron containing wastes generated by metallic industry is steadily increasing and some forms of the waste could be successfully used in building materials to improve their properties both mechanical and chemical [7]. Recycling of such waste materials is environmentally friendly and inexpensive way to deal with them. In this study, the magnetic material which was used in mortars is magnetite concentrate supplied by Magnetite-Grochow Sp. z o. o. in Poland. Different sources of magnetite could be used equally, also the natural magnetite resources.

II. EXPERIMENTAL AND METHODS

2.1 Magnetite concentrate

Magnetite concentrate was supplied by Magnetite-Grochow Sp. z o. o. located in Poland. Its physical and chemical parameters are represented by 49% - 52% of Fe, in this at least 43% of Fe_2O_3 and 28% of FeO but the concentrate includes also small amounts of SiO_2, Al_2O_3, CoO, Cu, TiO_2 and other chemicals of negligible amounts. In the concentrate, 80% of grains has dimension below 0.063 mm.

The series of experiments with determining pH of magnetic powder of micron size in a water solution was done. In this case, the magnetite concentrate was placed in a ball mill where it was grinded for a period of two hours. The distribution of the grain size used in experiment has been presented in Fig. 1. It was measured with the help of Malvern Zetasizer Nano-ZS using dynamic light scattering (DLS) technique.

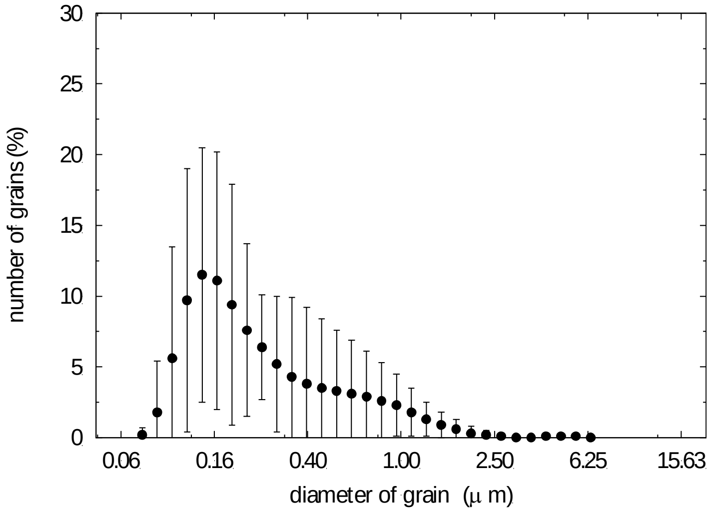

FIGURE 1: DISTRIBUTION OF GRAIN DIMENSIONS USED IN pH MEASUREMENTS.

2.2 Measuring pH of magnetite concentrate

Experimental part concerning measurement of pH of the water suspension of magnetite concentrate powder was consisting of the following steps. Two grams of magnetite grains were taken from the grinded magnetite concentrate. Grinding was taken place in a ball mill for a period of two hours. Next, the obtained magnetic powder was dispersed in 100 ml of distilled water, followed by stirring the solution for 5 minutes. After immobilizing the grains with the help of external magnet the supernatant was removed and the grains were subjected to subsequent washing and stirring in 50 ml of 0.25 M HCl for 5 minutes. Next the grains were washed with distilled water ten times.

The prepared magnetite powder was used to determine two values of pH, pH = pH_{susp} which was measured directly in the water suspension and pH = pH_{bulk} which was measured in an area far beyond the suspension, in the bulk of solution. This enabled the measurement of pH change caused by grains of magnetite, i.e.,

$$\Delta pH = pH_{susp} - pH_{bulk} \quad (1)$$

The measurements of pH value were carried out with the help of a microelectrode type MI-4154 Micro-Combination MICROELECTRODES.

2.3 Mortar preparation

All mortars were made from Portland cement CEM I 42.5 R, natural aggregate - quartz sand fraction 0-2 mm. Their composition was determined by the recipe ZP I based on standardized proportions of cement mortar in accordance with the norm EN 196-1:2005 [9]. The detailed composition of the mortar denoted as ZP I has been presented in Table 1.

TABLE 1
COMPOSITION OF STANDARD MORTAR ACCORDING TO RECIPE ZP I.

RECIPE ZP I						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	450	225	-	0.5
ρ	g/cm3	2.65	3.10	1	-	0.5
V	cm3	509.43	145.16	225	-	0.5

TABLE 2
COMPOSITION OF MODIFIED MORTAR ACCORDING TO RECIPE ZP II, ZP III and ZP IV WITH CONSTANT RATIO W/C.

RECIPE ZP II						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	450	225	22.5	0.5
ρ	g/cm^3	2.65	3.10	1	4.21	0.5
V	cm^3	509.43	145.16	225	5.34	0.5

RECIPE ZP III						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	450	225	45	0.5
ρ	g/cm^3	2.65	3.10	1	4.21	0.5
V	cm^3	509.43	145.16	225	10.69	0.5

RECIPE ZP IV						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	450	225	90	0.5
ρ	g/cm^3	2.65	3.10	1	4.21	0.5
V	cm^3	509.43	145.16	225	21.38	0.5

TABLE 3
COMPOSITION OF MODIFIED MORTAR ACCORDING TO RECIPE ZP V, ZP VI and ZP VII WITH THE VARIABLE RATIO w/c.

RECIPE ZP V						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	427.5	225	22.5	0.53
ρ	g/cm^3	2.65	3.10	1	4.21	0.53
V	cm^3	509.43	137.90	225	5.34	0.53

RECIPE ZP VI						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	405	225	45	0.56
ρ	g/cm^3	2.65	3.10	1	4.21	0.56
V	cm^3	509.43	130.64	225	10.69	0.56

RECIPE ZP VII						
symbol	units	standard sand	cement	water	magnetite	w/c
m	g	1350	360	225	90	0.63
ρ	g/cm^3	2.65	3.10	1	4.21	0.63
V	cm^3	509.43	116.13	225	21.38	0.63

Other mortars, the ones modified by magnetite concentrate, were divided into two groups. The first group consisted of mortars based on the standard mortar recipe with a constant water to cement ratio and with the addition of magnetite in amounts of 5%, 10% and 20% by weight of cement, respectively. The detailed composition of the mortars denoted by ZP II, ZP III and ZP IV, respectively, has been presented in Table 2.

The second type of mortar was modified by reducing the amount of cement and replacing it with magnetite by 5%, 10% and 20% by weight of cement, respectively. The composition of the mortar changed respectively to the reduction of cement. The detailed composition of the prepared mortars denoted by ZP V, ZP VI and ZP VII, respectively, has been presented in Table 3.

III. DISCUSSION AND RESULTS

Recently, it has been shown in [5] that when some amount of acid or base is added to a water solution containing magnetic grains then the solution close to the grains becomes, respectively, less acidic and less alkaline than it is expected. This property of iron oxides holds independently of their dimension, i.e. the same takes place for magnetic nanograins, micrograins and grains. In paper [5], a theoretical explanation of this special kind of pH-buffering was based on electric double layer description of the surface charge acquired by magnetic nanoparticles after contacting water solution. The corresponding surface charge potential $\Psi_s(\mathrm{pH})$ was approximated by the Nernst potential $\Psi_s(\mathrm{pH})$ [10, 11]:

$$\Psi_S(\mathrm{pH}) = 2.3026\frac{\mathrm{RT}}{\mathrm{F}}(\mathrm{PZC} - \mathrm{pH}) \tag{2}$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and 2.3026 is the approximate value of $1/\log_{10}(e)$. $\Psi_s(\mathrm{pH})$ is positive for pH < PZC, where PZC denotes the point of zero charge, and it is negative otherwise. PZC is such a value of pH that the sum of all positive and negative surface charges acquired by magnetic grains is equal to zero. The value of PZC of iron oxides strongly depends on the way they are prepared. It ranges from 6.3 to 7.2 in Ref [12], it takes the value of around of 7.9 in Ref. [13], and 7.72 in Ref. [5]. The pH-buffering property of iron oxide which was discussed in Ref. [5] means that the larger the value of pH of the solution differs from PZC of iron oxides, the greater the effect of buffering. In the case of strongly acidic or alkaline solution it can reach the values of around of ΔpH = ±0.5, respectively. This property is promising for using iron oxides against the long-term impact of aggressive surrounding both acidic and alkaline. In particular, magnetic grains contacting acidic water in pores of concrete will decrease the degradation speed of cement. In the case of carbonation process resulting in the appearance of carbonic acid in the pores of concrete it typically takes a year or two to degradate concrete to a depth of 1 mm [8].

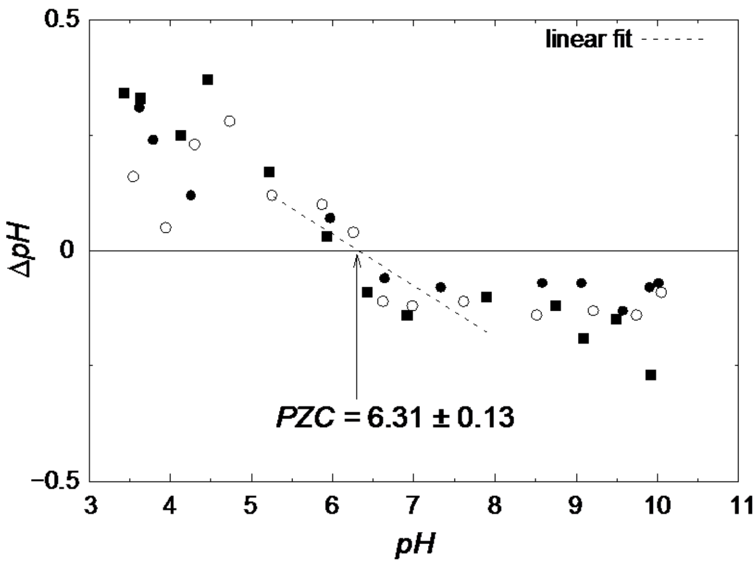

FIGURE 2: CHANGE IN pH BY THE VALUE OF ΔpH AFTER PLACEMENT OF MAGNETITE GRAINS (GRINDED MAGNETITE CONCENTRATE WASHED IN HCL BY 5 MIN) IN A WATER SOLUTION WITH A GIVEN pH. RESULTS OF THREE EXPERIMENTS DENOTED BY DIFFERENT SYMBOLS ARE SHOWN. THE DASHED LINE SHOWS THE LINEAR TREND OF ΔpH WITH RESPECT TO pH CLOSE TO PZC = 6.30 ± 0.13. THE SLOPE OF THE TREND γ = - 0.11 ± 0.02.

In order to measure PZC of the magnetite concentrate used in this study the concentrate was first grinded for two hours and next it was washed by HCl for 5 minutes to remove majority of chemicals which are different from magnetite. The resulting material which was used in pH measurement was consisting of grains of micron size. The distribution of grain's dimension has been shown in Fig. 1. In Fig. 2, the change ΔpH of the water solution with a given value of pH has been presented after addition of the magnetic grains. It can be observed that the approximate value of PZC of the grinded magnetite concentrate is equal to 6.3. This is very low value of pH but the replacement of the inexpensive magnetic concentrate with magnetite of better quality can shift the value of PZC even to pH ≈ 7.9 [13]. The change, ΔpH, of the water solution in the area close to the magnetic grain surface was described with the help of Eq. (19) in Ref. [5]:

$$\Delta \mathrm{pH} = -\frac{1}{2}\log\left(\frac{\varphi^{+}(\mathrm{pH})}{\varphi^{-}(\mathrm{pH})}\right) - \gamma \mathrm{pH} \tag{3}$$

where

$$\gamma = -\frac{1}{2\mathrm{PZC}}\log\left(\frac{\varphi^{+}_{\mathrm{PZC}}}{\varphi^{-}_{\mathrm{PZC}}}\right) \tag{4}$$

is the slope of the linear trend of ΔpH close to pH = PZC, $\varphi^{+}(\mathrm{pH})$ and $\varphi^{-}(\mathrm{pH})$ denote the fractions of H_3O^+ and OH^- ions in the nearest neighbourhood of the magnetic grain surface, respectively, $\varphi^{+}_{\mathrm{PZC}} = \varphi^{+}(\mathrm{pH} = \mathrm{PZC})$ and $\varphi^{-}_{\mathrm{PZC}} = \varphi^{-}(\mathrm{pH} = \mathrm{PZC})$. In the following, we consider Eq. (3) on the phenomenological level by assuming that $\varphi^{+}(\mathrm{pH})$ and $\varphi^{-}(\mathrm{pH})$ represent equilibrium values of the fraction of H_3O^+ and OH^- ions in the solution contacting the magnetic grains. After linearization of the right hand side expression of Eq. (3) around $\varphi^{+}_{\mathrm{PZC}}$ and $\varphi^{-}_{\mathrm{PZC}}$ we obtain the following equation substituting for Eq. (3):

$$\Delta pH = \gamma\left(PZC - pH\right) + \frac{1}{4.6052}\left(\frac{\varphi^{-}(pH)}{\varphi^{-}_{PZC}} - \frac{\varphi^{+}(pH)}{\varphi^{+}_{PZC}}\right) \tag{5}$$

where $2\log_e(10) \approx 4.6052$. In general, it would be difficult to measure $\varphi^{+}(\mathrm{pH})$ and $\varphi^{-}(\mathrm{pH})$ experimentally. However, even the less accurate estimation of ΔpH by the first part of the expression in the right hand side of Eq. (5), i.e.,

$$\Delta pH = \gamma\left(PZC - pH\right) \tag{6}$$

can appear to be sufficient for approximate assessing the impact of magnetic grains on the local acidity/alkalinity of liquid solutions in concrete pores where the values of γ and PZC can be measured experimentally. The phenomenological formula in Eq. (6) also applies to other Nerstian materials, not only to iron oxides, which could be included in mortar. Therefore it may be promising theoretical approach to design a suitable composition of the mortar with respect to PZC of its different components. Different kind of problems were recently published in paper [14] which are important for low-pH concretes placed in clayey environment. In this case, the role of the low concentration of magnesium in the clayey rocks was under consideration.

The additional use of magnetic grains is their role to the compressive strength of mortar. The compressive strength test was performed on beams which represent building or civil engineering structural elements. The beams had dimensions 40x40x160 mm according to Ref. [9]. The prepared beams were disassembled after 24 hours and stored at 20°C and humidity of 98%. After 28 days of maturation the samples were tested in a destructive testing machine and a compressive strength was determined. The results have been shown in Table 4.

TABLE 4
COMPRESSIVE STRENGTH OF MORTARS ZP I, ZP II - ZP IV, ZP V - ZP VII.

compressive strength f_c [MPa]							
Recipe/Sample	**1**	**2**	**3**	**4**	**5**	**6**	**average**
ZP I	55.78	53.75	51.88	59.38	51.88	48.13	53.46
ZP II	59.38	51.25	56.88	59.38	53.75	57.50	56.35
ZP III	55,63	57.50	56.25	58.13	60.00	59.38	57.81
ZP IV	55,63	58.13	60.63	58.75	57.50	58.13	58.13
ZP V	54.38	54.38	53.75	54.38	53.13	55.00	54.17
ZP VI	51,25	50.63	50.00	48.75	50.00	48.75	49.90
ZP VII	37,50	39.38	40.63	36.88	35.63	43.13	38.85

It is evident from Table 4, that the mortars from the first group ZP II, ZP III and ZP IV, have increased compressive strength comparing to model sample ZP I. With increasing content of the magnetite there is an increase of compressive strength of those samples. This is not the case in the second group of mortars ZP V, ZP VI and ZP VII. In the latter case, there is a visible decrease in compressive strength, which is caused by replacing part of the cement with magnetite dust, thus increasing the w/c ratio of those mortars. It is interesting to compare these results with the results of paper [3] where the chosen magnetic material was hematite and heavyweight concrete was used. In this case, it was observed that hematite increases the compressive strength of plain concrete for 10% hematite but only slightly for 20% hematite.

IV. CONCLUSION

It has been shown that inexpensive magnetite concentrate if added to mortar can increase its compressive strength as well as it can be considered as a material protecting the porous concrete from the long-term impact of acidic/alkalinite environment. The phenomenological formula which determines the change in pH value of water solutions in the pores of concrete by magnetite applies to all Nerstian materials, not only to the magnetite concentrate under consideration. Therefore it has great importance for the design of mortar composition also with respect to the discussion on new cements for 21st century [15].

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