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Effect of acidic environments on cement concrete degradation

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ABSTRACT

The paper presents assessment of the chemical resistance of five concretes containing different binders, including common normal and high early strength cements CEM I ÷ CEM IV and mix of Portland cement and siliceous fly ash, treated with hydrochloric acid. Concrete compositions fulfilled conformity with standard EN 206-1 for the most stringent chemical exposition class XA3. Due to the lack of the commonly used standard procedures for testing concrete exposed to environment of low pH, tests were performed following the own procedure assuming treatment of different duration and with different concentrations of HCl. Assessment of concrete ability to resist the chemical attack was based on its change of mass, compressive and tensile strength. Specimens exposed to acid aggression showed significant mass loss and mechanical properties decrease. It was statistically confirmed that aggressive environment parameters have a significant effect on the chemical resistance of tested concretes.

Keywords. Acid resistance, chemical resistance, chemical attack, acid resistance test method

INTRODUCTION

Concrete chemical resistance, considered as a measure of its durability, is increasingly being raised as an important issue [1,9,10,11,12].The least recognized is the issue of cement concrete resistance to acids. This is mainly due to the fact that the cement concrete is traditionally considered as not resistant to acids and unsuitable for use in such a conditions. The development of cement and concrete technology caused, however, that it becomes possible to obtain a certain level of cement concrete resistance to acids. The basic obstacle to a clear determination of this level is the lack of standards for testing methods and relevant criteria for assessing the ability of concrete to resist the destructive effects of acids. This creates the need to formulate individual testing procedures, which are sometimes published in literature [1,12]. Such procedures are not always suitable for wider use due to the fact that they have been developed for specific intended use of concrete.

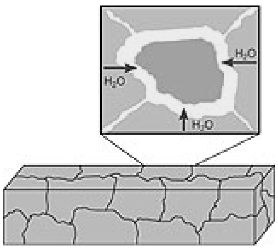
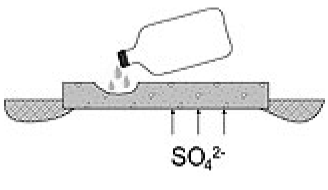
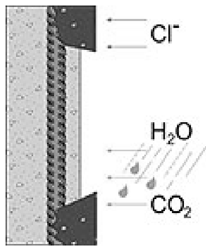
The ability of concrete to resist chemically aggressive environments (including acidic environments) can be improved by impregnation or protecting concrete surfaces with insulating layers [2,4,3]. But even though applies the rule of concrete double protection, including – except applying layers that reduce or completely cut off aggressive agents from concrete surface – also concrete material-structural protection, consisting of proper concrete design and realization, providing the highest possible resistance to corrosion [3]. Therefore, determining the resistance of concrete to action of acids, appears to be necessary.

The paper presents assessment of the resistance to hydrochloric acid of five concretes, containing common normal and high early strength cements of types CEM I ÷ CEM IV and mix of Portland cement and siliceous fly ash. The compositions of tested concretes fulfilled conformity with standard EN 206-1 for the most stringent chemical exposition class XA3. Due to the lack of the commonly used standard procedures for testing concrete exposed to the environment of low pH, the tests were conducted according to the procedure specially developed for this purpose in DBME. The parameters of chemically aggressive environment were hydrochloric acid concentration and duration of exposition concrete to acid. The criteria of evaluation concrete ability to resist the destructive action of hydrochloric acid were chosen as following: change of mass of concrete after treatment with HCl, decrease in compressive and flexural strength of concrete chemically loaded in comparison to properties of unloaded one.

TEST METHODS – LITERATURE STUDY

There are no Polish nor European standards for testing the chemical resistance of cement based concrete. American standards ASTM provide varied concrete tests depending on exposure conditions and mechanisms of destruction of concrete structures (Table 1) [8]. However there is a lack of clear criteria for the evaluation of results obtained in these tests.

Table 1. ASTM test methods used for the assessment of concrete destruction (based on [8])

	Alkali-Aggregate Reaction	Chemical resistance	Corrosion of reinforcement
Durability Aspect/Exposure			
Mechanism	Alkali-Silica Reaction Alkali-Carbonate Reaction	Sulphates Seawater **ACIDS**	Corrosion Carbonation
Test method	ASTM C227-10 ASTM C289-07 ASTM C1260-07 ASTM C1105-08a ASTM C1293-08b	ASTM C1012 **ASTM C267** *Test Method for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes*	ASTM C1202-10 ASTM C1556-11 ASTM C1152 / C1152M-04 ASTM C1218 / C1218M

Requirements for chemical resistance of monolithic floors are formulated in ASTM C722-04 and EN 1504-2 but as they involve requirements for coating materials, they cannot be directly applied as a general requirements for concrete.

Concrete and concrete-like composites resistance to acids tests were conducted also according to individual procedures that differed in i.a. aggressive agents types, size and shape of the specimens. Diagnostic criteria included loss of mass and volume, decrease of mechanical strength [11,5], state of structure evaluated visually, including microscope observation, change in the pH of the aggressive solution [10,5], depth of corrosion [10]. In most cases these methods did not include clear criteria for the evaluation of obtained results – the values were used for comparison purpose. Developing of evaluation criteria of acid resistance would require multi-staged experimental program carried out in order to establish the influence of the type and concentration of individual acids, the duration of exposition to acid, acid temperature and other factors on the properties of concrete characterized by different qualitative and quantitative compositions. This paper presents the results which are part of a preliminary study of larger research program aimed at developing a research method and a set of clear criteria for assessing the concrete ability to resist the acid corrosion.

EXPERIMENTAL PROGRAM

This study investigated the ability of various concretes to resist the destructive action of hydrochloric acid, thus acid resistance. Five types of mineral binders were applied into concretes: four pure cements (CEM I ÷ CEM IV) of strength class 32.5 and the mix of Portland cement (CEM I 32.5 R) and siliceous fly ash (FA) in equal proportions. For all materials the basic morphology (particle size distribution, specific surface area and density in the Le Chatelier flask) was determined. Siliceous fly ash was used as it is one of the most common additives applied to concrete that improve properties of concrete mix (e.g. workability) as well as properties of hardened concrete, i.a. tightness, freezing resistance [7]. Tests of high volume fly ash concrete (HVFAC) were proceeded also due to the fact that during setting of such composite proceeds the reaction between fly ash and calcium hydroxide, the result of which is a reduction of $Ca(OH)_2$, i.e. compound which later reacts with the hydrochloric acid [7].

Concretes were exposed to aqueous hydrochloric acid solution of concentration 7.5%. In case of concrete containing only the Portland cement various acid concentrations (2.5%, 5% and 7.5%) as well as different duration of exposition was applied. After chemical loading and proper preparation of specimens (washing, drying) change of mass was determined and mechanical tests (compressive and flexural strength) were carried out. A detailed description of the applied test procedure was included in the later part of the paper.

MATERIALS AND COMPOSITIONS OF TESTED COMPOSITES

Cements. Cements applied into concretes (all of nominal strength of 32.5 MPa) were as following: high early strength Portland cement CEM I 32.5 R, high early strength Portland-composite cement containing siliceous fly ash and lime stone CEM II/B-M (V-LL) 32.5 R, normal early strength blast furnace cement of low hydration heat, high resistance against sulphates and limited alkali content CEM III/A 32.5 N LH/HSR/NA and high early strength pozzolanic cement containing siliceous fly ash CEM IV/B (V) 32.5 R. The cement density (Table 2) was tested according to Polish standard PN-B-06714-02. The granulation, presented in the form of granulometric curve (Fig. 1) and surface specific area (Table 2) were tested using the laser granulometer Horiba L300.

Fly ash. The fly ash (characteristic: Table 2, Fig. 1) applied into one of the tested concretes was a siliceous fly ash, fulfilling the expectation of class V according to the standard EN-450-1 and class F according to standard ASTM C 618-08a.

Table 2. Density (determined in Le Chatelier flask) and surface specific area of cements and siliceous fly ash (FA) applied into tested concretes

No	Binder type	Density		Surface specific area [cm^2/cm^3]
		Average [kg/m^3]	CV [%]	
1	CEM I 32.5 R	3102	0,14	18174
2	CEM II/B-M (V-LL) 32.5 R	2760	0,41	11229
3	CEM III/A 32.5 N LH/HSR/NA	2910	0,27	10707
4	CEM IV/B (V) 32.5 R	2503	0,08	9969
5	FA	2027	0,55	10749

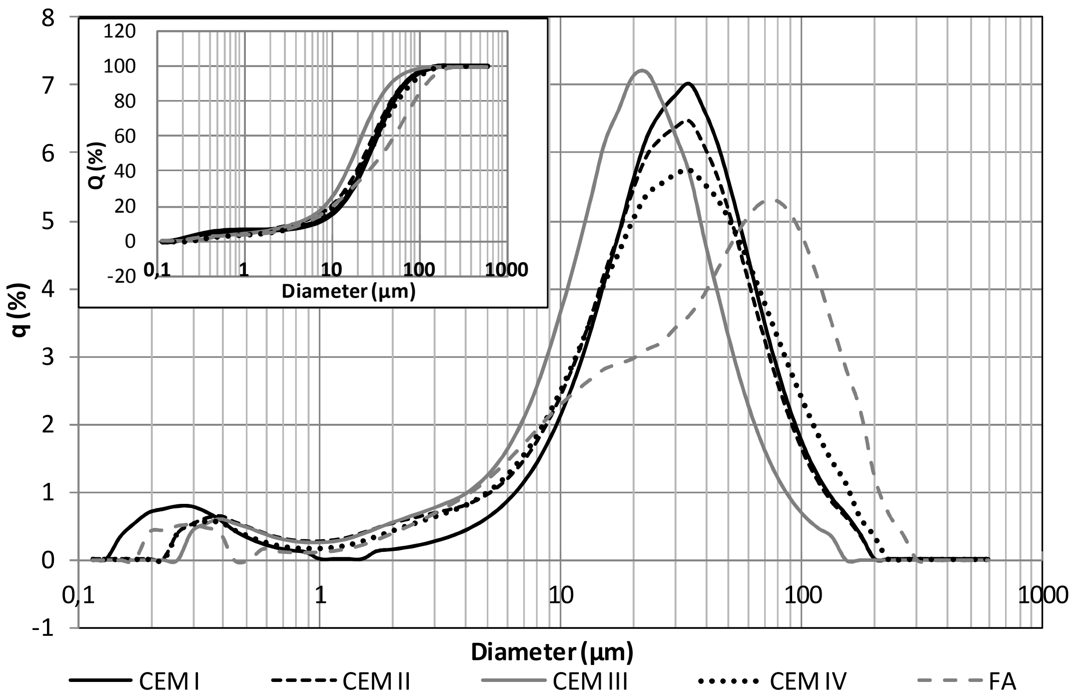


Figure 1. Grain size distribution curves of cements (CEM I ÷ CEM IV) and siliceous fly ash (FA) - relative and cumulative content

Cements granulation was very similar (although pozzolanic cement contained less grains of diameters 20 ÷ 50 µm), while fly ash contained more thicker grains (diameters up to 300 µm). Specific surface area of cements and fly ash were comparable. The exception was the Portland cement which was characterized by almost twice as large specific surface area.

Aggregate. The concretes aggregate was described by a continuous aggregate grading curve. The fine aggregate consisted of standard sand (according to European standard EN

196-1) and natural river gravel of fraction 2/4 mm while the coarse aggregate was natural river gravel of fraction 4/8 mm. The aggregates were applied (by mass): in the proportion $A_{0/2} : A_{2/4} : A_{4/8} = 5 : 1 : 4$, fulfilling the requirements of German standard DIN 1045 for aggregate mix of grading 0 ÷ 8 mm.

Admixture. Each concrete mix was modified by the plasticizing admixture (of various contents – see Table 3) to obtain the consistency class at level S-1 (according to slump test).

Compositions of tested concretes are presented in the Table 3.

Table 3. Compositions of tested concretes (water/binder ratio 0.35)

No	Binder (B)					Water (W)	Aggregate (A)			Admix-ture
	CEM I	CEM II	CEM III	CEM IV	Fly ash (FA)		0/2 mm	2/4 mm	4/8 mm	
1	390	-	-	-	-	137	977	195	782	9.70
2	-	390	-	-	-					7.57
3	-	-	390	-	-					9.34
4	-	-	-	390	-					9.95
5	195	-	-	-	195					6.36

TEST METHODS

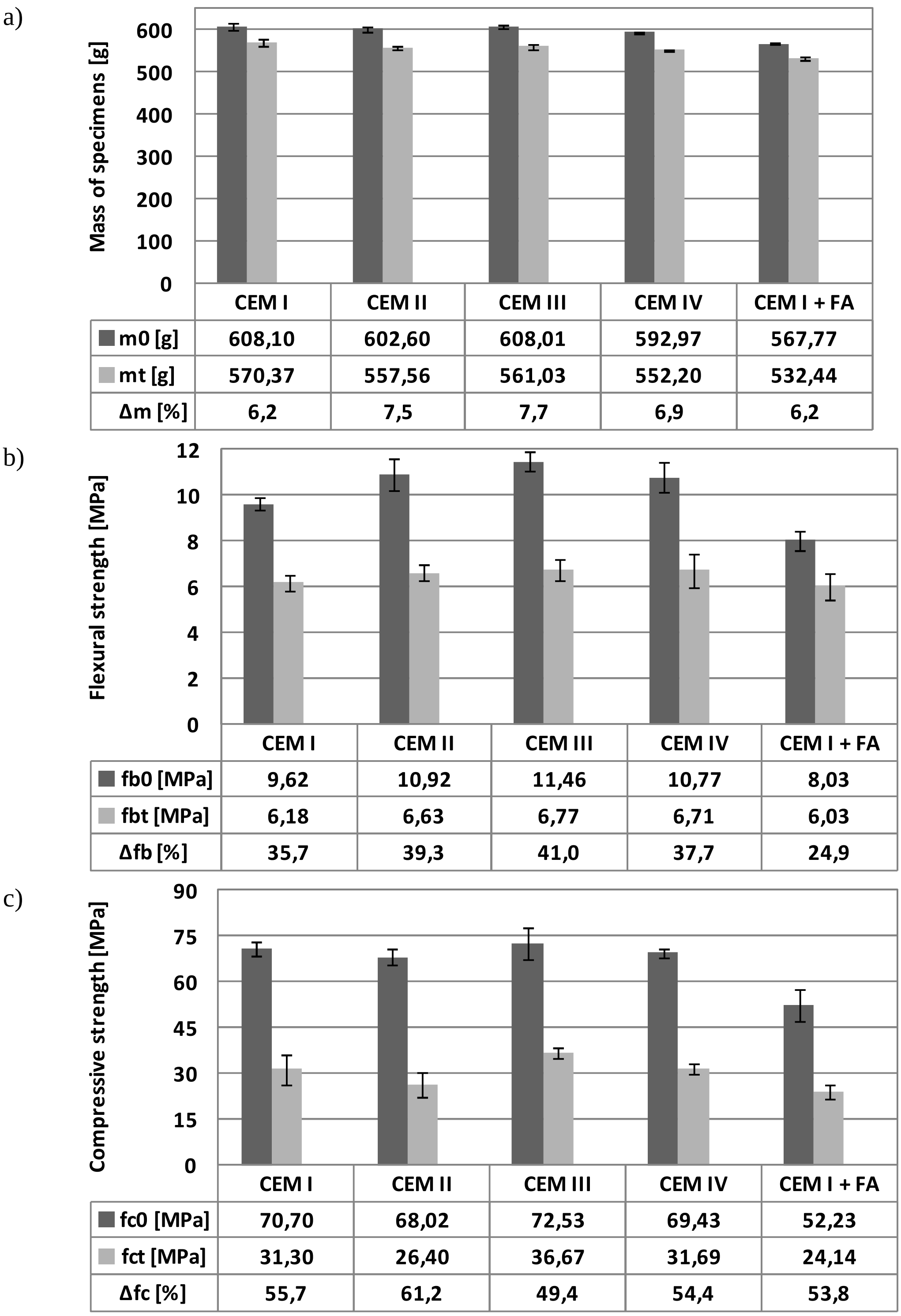
Concretes acid resistance was tested according to the method developed in DMBE. The procedure was as follows: concrete specimens with dimensions 40×40×160 mm were cured in water for 28 days, then dried at room temperature (20 ± 5)°C to state of constant mass, (when the bulk density of concrete can be determined). In the next step the specimens were placed in oven at temperature of (60 ± 5)°C, dried to the state of constant mass and immersed for 1 h, 6 h, 24 h and/or 48 h in distilled water and in aggressive solutions at temperature of (20 ± 2)°C. In the study as the chemically aggressive agents the water solutions of hydrochloric acid of concentrations 2.5%, 5% and 7.5% were used. After immersing, the specimens were washed with distilled water, then placed in the oven and conditioned at a constant temperature of (60 ± 5)°C for 72 h and weighed. The result of the test was the percentage of weight loss. In the next stage, testing of concretes compressive strength and flexural strength was performed to specify the change in the strength (in MPa and %) compared to strength of control specimens not loaded by chemical attack. The mechanical properties – compressive strength and flexural strength were tested according to methods formulated in European standards (EN 196-1:2006), in three point bending test and later in compressive strength test.

RESULTS AND DISCUSSION

The results of measurements of tested concretes mass are presented on Fig. 2a and on Fig. 3, while the results of mechanical tests are presented on Fig. 2b (flexural strength) and Fig. 2c (compressive strength). Each time the properties of specimens exposed to chemical attack were compared to the properties of control specimens (stored in the laboratory conditions).

Loss of mass of concretes with various binders noted after 48 h-long exposure specimens to hydrochloric acid of concentration 7.5% adopted values in the range 6.2 ÷ 7.7%. The most sensitive to the HCl effect was concrete with blast furnace cement CEM III/A 32.5 N LH/HSR/NA. This cement meant to be highly resistant against sulphates and of limited alkali content, moreover it contained only 35 ÷ 64% of Portland clinker (while the content of blast furnace was ≥ 55%), which qualifies this binder as more resistant to acidic aggression. It is also recommended for acid resistant applications in Polish national appendix to standard PN-EN 206-1. However this was also cement of low hydration heat. Taking into consideration that the speed of heat generation during the setting and hardening translates into a speed of increasing strength, it can be assumed that the tested concrete with cement CEM III/A 32.5 N LH/HSR/NA had not obtained its final properties after the 28 days of curing and that the microstructure of concrete was not tight enough to resist the penetrative action of acid. Similar conclusions can be formulated when referring to concrete with Portland-composite cement containing fly ash and limestone CEM II/B-M (V-LL) 32.5 R. The development of compressive strength of this two particular cements in time longer than 28 days was demonstrated by Giergiczny [6] – he showed that CEM III/A 32.5 N LH/HSR/NA after 90 days obtained 20% higher compressive strength than after 28 days, while cement CEM II/B-M (V-LL) 32.5 R after 90 days obtained even 25% higher compressive strength than after 28 days. That leads to the conclusion that next tests of acid resistance of concretes with cements CEM II or CEM III should be performed after at least 90 days of curing. Such prolonged hardening time would ensure the full use of pozzolanic activity of mineral additives for densifying concrete matrix microstructure. Other important factor, that negatively influenced the intensity of mass loss of concrete with cement CEM II/B-M (V-LL) 32.5 R was the content of limestone, that reacted with acid producing easily soluble compounds which were later leached from the concrete. Slightly less sensitive to HCl aggression was concrete with pozzolanic cement containing siliceous fly ash CEM IV/B (V) 32.5 R (mass loss of 6.9%). Concretes with Portland cement CEM I 32.5 R and mix of Portland cement with fly ash were characterized by the lowest mass loss (6.2%). The positive effect of fly ash on tightness of concrete by densifying its structure is well known [7]. Moreover, as mentioned above, fly ash reacts with calcium hydroxide, reducing its content. Lower content of $Ca(OH)_2$ (the main potential reagent in acid corrosion reactions) results in reduced content of compounds that might later leach from concrete.

Based on the results of mechanical tests one can draw different conclusions. When referring to flexural strength (Fig. 2b) it should be highlighted that after 48 h-long exposure specimens to 7.5% hydrochloric all concretes characterized by almost the same flexural strength (6.03 ÷ 6.77 MPa), while concretes not treated with HCl characterised with different values. The highest flexural strength (11.46 MPa) and consequently the highest difference between strength of chemically loaded and unloaded specimens (41.0%) were noted in case of concrete with blast furnace cement CEM III/A 32.5 N LH/HSR/NA. Lower changes were obtained in case of concretes with Portland-composite cement CEM II/B-M (V-LL) 32.5 R (39.3%), pozzolanic cement CEM IV/B (V) 32.5 R (37.7%) and Portland cement CEM I 32.5 R (35.7%). The lightest effect of HCl action on concrete flexural strength was noted in case of concrete with Portland cement and fly ash – decrease was lower than 25%. When referring to compressive strength (Fig. 2c) we can confirm the finding about the highest strength of concrete with cement CEM III/A 32.5 N LH/HSR/NA – 72.53 MPa and the lowest strength of concrete with Portland cement and fly ash – 52.23 MPa (other concretes characterized by similar strength: 68.02 ÷ 70.70 MPa), however the negative effect of HCl action on compressive strength was different than it was in case of flexural strength. The highest influence was noted in case of concrete with cement CEM II/B-M (V-LL) 32.5 R (decrease of 67.2%), similar effect was noted in case of applying pure Portland cement, mix of Portland cement and siliceous fly ash and pozzolanic cement containing siliceous fly ash (an average decrease of 54,63%). The lightest effect of HCl action on concrete compressive strength was noted in case of concrete with blast furnace cement CEM III/A 32.5 N LH/HSR/NA – decrease was lower than 50%.



a)

	CEM I	CEM II	CEM III	CEM IV	CEM I + FA
m0 [g]	608,10	602,60	608,01	592,97	567,77
mt [g]	570,37	557,56	561,03	552,20	532,44
Δm [%]	6,2	7,5	7,7	6,9	6,2

b)

	CEM I	CEM II	CEM III	CEM IV	CEM I + FA
fb0 [MPa]	9,62	10,92	11,46	10,77	8,03
fbt [MPa]	6,18	6,63	6,77	6,71	6,03
Δfb [%]	35,7	39,3	41,0	37,7	24,9

c)

	CEM I	CEM II	CEM III	CEM IV	CEM I + FA
fc0 [MPa]	70,70	68,02	72,53	69,43	52,23
fct [MPa]	31,30	26,40	36,67	31,69	24,14
Δfc [%]	55,7	61,2	49,4	54,4	53,8

Figure 2. Properties of concretes with various binders (cements CEM I ÷ CEM IV and fly ash FA): a) mass of specimens before (m_0) and after (m_t) 48 h long treatment with 7.5% HCl, b) flexural strength, c) compressive strength of specimens unloaded (f_{b0}, f_{c0}) and loaded (f_{bt}, f_{ct}) with the chemical attack of 7.5% HCl acid for t = 48 h

The second stage of research concerned the influence hydrochloric acid concentration and duration of exposition specimens to acid action on the character of corrosion process and the intensification of concrete destruction expressed by concrete mass loss. The tests were performed on specimens of concrete with Portland cement CEM I 32.5 R (composition No 1 according to Table 3). The concentration of applied acids were: 2.5%, 5.0% and 7.5%. The duration of concrete exposition to acidic environment were: 1 h, 6 h, 24 h and 48 h. The results were compared to strength of control specimens not loaded by chemical attack. The results (Fig. 3) confirmed that increase of HCl concentration is followed by intensification of concrete destruction process. Moreover this tendency was observed regardless of the time of immersion the specimens in acid solutions. It must be highlighted that the deterioration was the most intense during the first 6 hours of the test, then the destructive process slowed down. Relation between the value of acid concentration and concrete mass loss (Fig. 3) was described by square functions providing very good correlation between experimental data and model (correlation coefficient $R \geq 0.985$, determination coefficient $R^2 \geq 0.970$). Though, high correlation and determination coefficients are obtained also when using linear models.

Analysing the research results authors came to the conclusion that when testing concrete resistance to hydrochloric acid, test must be performed using solutions of higher concentrations than 2.5%. Acid concentration of 2.5% seemed to be too low, as similar mass loss was noted in case of different duration of exposition concrete specimens to such acid.

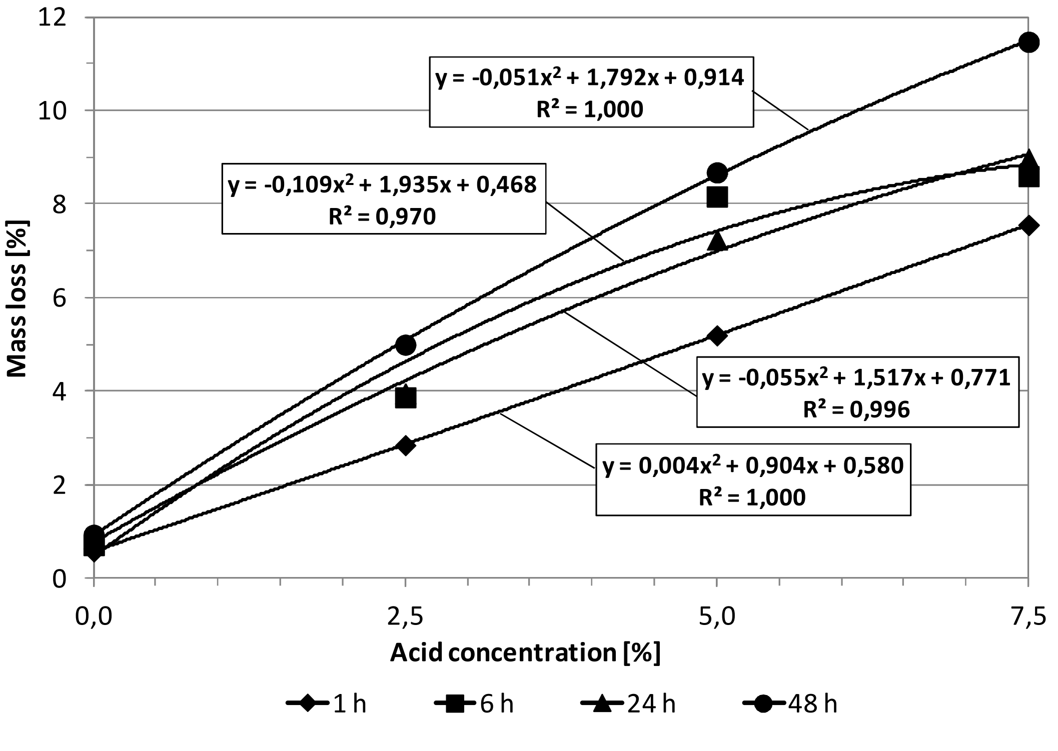


Figure 3. Mass loss [%] of concrete with CEM I 32.5 R (No 1) after immersing specimens for 1 h, 6 h, 24 h and 48 h in HCl acid of various concentration

Except determining the relation between the value of acid concentration and concrete mass loss, additional tests of compressive strength were performed. It was observed that despite the acid concentration the compressive strength decreased with prolongation of exposure time. However the results obtained after treatment concrete with acid of 2.5% concentration indicated that such environment is not aggressive enough for proper testing of hydrochloric acid resistance confirming the conclusion formulated after analyzing the concrete mass loss. Moreover, significant differences in strength loss were noted after 48 h of immersing specimens in hydrochloric acids – after treating concretes with various acids for shorter time the differences were not very clear.

CONCLUSIONS

The obtained results enable to specify the conditions necessary for advanced evaluation of concrete ability to resist destructive influence of hydrochloric acid. The shortest recommended time of exposure cement concrete to hydrochloric acid should be at least 48 hours, while hydrochloric acid concentration should not be lower than 5%.

Taking into consideration results obtained for concretes of the same quantitative composition but different mineral binders it was not possible to clearly indicate the composition of concrete that characterized with the best ability to resist the acidic environment. Depending on analyzed property the most resistant were different concretes. Concrete containing siliceous fly ash as the half substitute of Portland cement CEM I 32.5 R characterized with the lowest sensitivity of flexural strength to destructive activity of HCl. Concrete with blast furnace cement CEM III/A 32.5 N LH/HSR/NA characterized with the lowest sensitivity of compressive strength (though the highest sensitivity of flexural strength) to destructive activity of HCl. The strongest negative impact of HCl acid activity was noted in case of Portland-composite cement CEM II/B-M (V-LL) 32.5 R. It is expected that concretes with cements CEM II or CEM III would be more acid resistant after longer curing which would ensure the full use of pozzolanic activity of mineral additives and densified microstructure which will be further tested by authors.

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