Influence of various acids on the physico–mechanical properties of pozzolanic cement mortars

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Abstract. Acidic attack represents a topic of increasing significance, owing to the spread of damages of concrete structures in both urban and industrial areas. Cement type is an important factor affecting performance of cement based materials in an aggressive environment. The goal of this study was to compare the acid resistance of a pozzolanic cement (CEM IV-A/32·5) with Portland cement (CEM I 32·5) that was made from the same clinker. For this purpose, 50 mm mortar cubes were prepared with two different kinds of cement according to TS EN 196-1. After 28 days of hardening, the samples were immersed into four different concentrations of hydrochloric, nitric and sulfuric acid solutions for a period of 120 days. The changes in weight loss and compressive strength values for each acid solution within the test period were recorded. The acid resistance of mortars made from Portland cement was better than the pozzolanic cement incorporated samples after 120 days of acid attack.

Keywords. Pozzolanic cement; hydrochloric acid; nitric acid; sulfuric acid; loss of weight; compressive strength.

1. Introduction

Durability is an important engineering property of concrete, which determines the service life of concrete structures significantly. Due to the interactions of concrete with external influences, the mechanical and physical properties of concrete may be threatened and lost. Among the threatening factors like freezing and thawing, abrasion, corrosion of steel, chemical attack may also deteriorate concrete within time.

ACI Committee Report 201 (2001) has classified chemical attacks into several types that include; acidic attack, alkali attack, carbonation, chloride attack, leaching and sulfate attack. It can be accepted as a general rule that acids are deleterious to concrete.

The spectrum of aggressive acidic media is wide. Acidic attack usually originates from industrial processes, but it can even be due to urban activity. Even natural exposure conditions may cause acid attacks. Free acids in natural waters are rare. Exceptions are carbonic waters and sulfurous and sulfuric acids in peat waters. Soils may contain huminous acids. Several organic and inorganic acids may occur in shallow regions of sea-water as a consequence

of bacteriological activity. Significant quantities of free acids in plants and factories may be found. In these cases, the concentration of acid, which comes in contact with concrete structures, may reach to high values (Ecob & King 1990; Baradan *et al* 2002).

The degree of aggressivity of an acid is dependent on the chemical character of anions present. The strength of acid, its dissociation degree in solutions and, mainly, the solubility of the calcium salts formed are dependent on the chemical character of anion. The acidic attack is affected by the processes of decomposition and leaching of the constituent of cement matrix (Gutt & Harrison 1997; Mehta 1986). An acidic media may achieve values under 7, predominantly 6 and lower. However, pH values give no correct information about the real quantity of the acid in the solution, because the pH value is dependent on the dissociation degree of acid. Besides, for the aggressivity of acidic solutions, the real concentration of acid is more significant than pH value (Živica & Bajza 2001; Živica & Bajza 2002).

Aggregate type also affects the performance of mortars against acid attack. Limestone aggregate is more vulnerable to acid attacks. However, aggregates like river gravel and similar silicious materials are more resistant (Živica & Bajza 2001; Rostam 1997; Neville 1997).

The type of cement is another factor affecting the performance of concrete in an aggressive environment. It is known that acids are always hazardous on any type of cement (Parrot 1991; Alegre 1978). The integrity of hardened Portland cement binders is highly dependent on maintaining the high levels of alkalinity which normally stabilize the gel compound responsible for cementitious properties. Acids react with alkaline components of the binder (calcium hydroxide, calcium silicate hydrates and calcium aluminate hydrates) lowering the degree of alkalinity. In extreme cases, acids may completely neutralize the alkalinity. These chemical changes are disastrous and disintegration of the matrix is the inevitable result. Portland cements are the most vulnerable cement type to acidic attack, since they contain a high proportion of calcium hydroxide released during hydration of the calcium silicates (Hewlet 1997). According to Zivica and Bajza (2002) blended Portland cements with pozzolans and slags are considered to be more resistant to the acidic attack than Portland cements. It should also be considered that, the efficiency of blending for acid resistance may be affected by other factors e.g. the type of cement used for blending, the amount and fineness of pozzolan used and especially curing conditions (Hewlet 1997; Mehta 1985; Calleja 1980). Nevertheless, the blended Portland cements with pozzolans, such as blast furnace slags, fly ashes and others, have slow strength gain and hence slow reduction in permeability properties at early ages. Additionally, these cements are more curing sensitive than Portland cement (Živica & Bajza 2001).

While the cement types differ in their degree of resistance to acids, these differences are small and none of the concretes made with such materials is truly and continuously resistant to inorganic acids. Currently emphasis is towards producing dense and compact high-performance concrete to achieve durability and better performance of concrete in aggressive environments.

There exist a number of factors that control hardened cement pastes deterioration in acid solutions. These include the type, the concentration and pH of the acidic solution, the mobility of the solution, the water/cement ratio, the type of cement and mineral admixtures (Pavlik & Uncik 1997).

The signs of acidic attack are loss of alkalinity (also disturbing of electrochemical passive conditions for the embedded steel reinforcement), loss of mass, loss of strength and rigidity. These degradation effects are gradual (Regourd 1981).

Despite the fact that various physical and chemical tests on the resistance of concrete to acids have been developed, there are no standard procedures available (Hewlet 1997). It is essential that tests performed under realistic conditions because, when a concentrated acid

Table 1. Chemical analysis, physical and mechanical properties of cements.

Chemical composition	Cement type	
(%)	CEM I-32·5	CEM IV-A/32·5
SiO_2	19·96	29·89
Al_2O_3	4·33	7·33
Fe_2O_3	4·43	4·20
CaO	64·52	46·09
MgO	1·92	2·02
Na_2O	0·27	1·34
K_2O	0·57	1·97
SO_3	2·30	1·77
Cl	0·0011	0·00
Loss on ignition	1·18	3·84
Lime (CaO), free	1·27	-
$Na_2O + 0.658K_2O$	0·65	2·64
C_3A	3·98	3·98
7-day (MPa)	27·8	22·9
28-day (MPa)	38·4	35·2
Specific surface (Blaine m^2/kg)	340·9	398·9
Specific gravity	3·13	2·94
Pozzolanic additive	-	28 % trass, 6 % C-type fly ash

is used, all cement components attacked and assessment to their relative resistance is not possible. Also aggressive solutions with low acidic concentrations do not harm the specimens. For this reason the magnitude of low or high concentration can not be generalized. Besides, exposure period is another important factor determining the relative acid resistance of various cement based materials. In summary, care is required in interpreting the results of accelerated tests (Alegre 1978). In the interest of the reliability of the study and testing of factors of acidic attack of cement based materials and of the comparability of the results obtained, some experimental principles are recommended by Živica (2004).

In this study, the effect of different concentration of hydrochloric, nitric and sulfuric acids on the loss of weight and compressive strength of mortars incorporating pozzolanic and portland cements has been investigated.

2. Experimental study

2.1 *Materials*

2.1a *Cement:* Portland cement CEM I 32·5 and a pozzolanic cement (CEM IV-A/32·5) were used in the experimental program. Cements, in accordance with Turkish Standards (TS EN 197-1), were manufactured by Denizli Cement Plant. The cements were produced by using the same clinker. The chemical analysis and physical properties of cements are presented in table 1. The pozzolanic cement was a blended cement incorporating 28 % of trass + 6 % fly ash (C type).

2.1b *Aggregate:* Natural river sand in accordance with TS EN 12620 was used as fine aggregates. Maximum aggregate size and specific gravity were 4 mm and 2·550 respectively.

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Table 2. The pH values of the aggressive solutions.

Acid type	Concentrations and pH values of inorganic acids			
	0·05(M)	0·075(M)	0·100(M)	0·125(M)
Hydrochloric	1·3	1·2	1	0·9
Nitric	1·2	1·1	0·9	0·8
Sulfuric	1·2	1·0	0·9	0·8

2.1c *Water:* The type of mixing water that was used in the experiments was ordinary drinkable tap water with pH value of $6·2 \pm 0·1$.

2.1d *Acid solutions:* Solutions of hydrochloric, nitric and sulfuric acid with the concentrations of 0·05, 0·075, 0·100, 0·125 mol/L (M) were used in experiments. The pH values of the solutions are presented in table 2. The pH values of acid solutions had been reached the neutral value (pH $\cong 7 \pm 2$) in 12 days and 14 days initial approximate pH values of 1, for pozzolanic and Portland cement mortars respectively. For this reason, the solutions were renewed at every two weeks. The temperature of the solutions was $20 \pm 2°C$ during a period of 120 days.

2.2 *Preparation of specimens and test procedure*

The mortar mixes have been prepared with the same river sand for two different types of cement. The cement:sand and water:cement ratios were 1:3 and 1:2 respectively for all specimens. The mixing and preparation procedures were made in accordance with TS EN 196-1. Specimens prepared with CEM I 32·5 and CEM IV-A/32·5 were labelled as M1 and M2 respectively. The fluidities of mortars have been determined by flow table test according to ASTM C124 and flow values were between 105 and 116 %. In order to determine the deterioration effect in early periods small test specimens were chosen. A total of 156 mortar specimens were cast into 50 mm cube molds including control mixes. The mortar samples were cured 24 hours at $20 \pm 2°C$ and relative humidity above 80 %. The specimens were cured in lime-saturated water after demolding.

After 28 days of curing, the specimens were dried in an oven at $105°C$ and the initial weights were measured. Then the specimens were stored into solutions of hydrochloric, nitric and sulfuric acids with four different concentrations. For each acid and concentration, six specimens were subjected to each solution. After exposure to acids, the specimens were washed in order to remove the porous layer of the corrosion products such as soft and crystallized acidic materials or calcium salts. Then specimens were dried in an oven at $105°C$. Loss in weight of the specimens was measured weekly during the testing period of 120 days. Compressive strength of the control (non-exposed) specimens after 28 days of their hardening in water and the test specimens subjected to solutions of acids for 120 days were determined. The compressive strength values of specimens were calculated by using the original cross-sectional area of the original cubes.

3. Results and discussions

Average loss of weight of mortars in various acidic solutions within 120 days of testing period is presented in table 3. The loss of compressive strength compared to control specimens after

Table 3. Loss of weight of cement mortars after 120 days in various inorganic acid solutions.

Acid type	Exposure Time (days)	Average loss of weight of mortars (%) Concentrations (M)							
		0·05		0·075		0·100		0·125	
		M1	M2	M1	M2	M1	M2	M1	M2
HNO$_3$	30	0·75	0·70	0·60	0·63	0·62	0·89	1·21	1·29
	60	1·70	2·35	2·08	2·67	1·68	2·42	2·59	3·90
	90	2·75	3·40	3·25	3·47	3·20	3·78	4·69	5·24
	120	3·40	4·15	3·98	4·43	4·72	5·48	6·24	7·25
HCl	30	0·68	0·65	1·50	2·23	1·04	1·33	1·67	1·27
	60	1·56	1·88	2·71	3·64	2·34	2·69	2·94	4·54
	90	2·57	3·25	3·52	4·91	4·64	5·20	4·25	6·75
	120	3·28	3·94	4·91	6·23	5·47	6·60	6·45	7·80
H$_2$SO$_4$	30	0·30	0·53	0·32	0·44	0·36	0·40	0·53	0·66
	60	0·89	1·11	0·83	1·22	1·37	1·66	1·12	1·70
	90	1·42	1·89	1·48	2·07	2·18	3·44	2·52	2·93
	120	2·04	2·98	3·16	3·58	3·55	4·83	4·22	4·94

28 days of hardening in water are presented in figure 1. The test results represent the average value of six specimens.
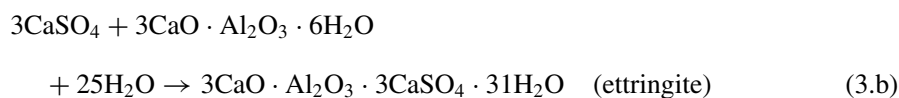
3.1 *The effect of acid type and concentration*

The action of HCl and HNO$_3$ on cement hydration products, in particular Ca(OH)$_2$ and the resulting products are presented in the following chemical equations:

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \tag{1}$$

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O \tag{2}$$
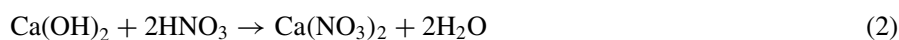
From equations (1) and (2) it can be seen that, consumption of Ca(OH)$_2$ results with formation of salts of CaCl$_2$ and Ca(NO$_3$)$_2$. By the help of water, these soluble salts may easily be transported to the outer parts of mortars. In this situation, continuous reactions increase the porosity of cement paste and increased pore volume speed up the rate of reaction.

In case of H$_2$SO$_4$ attack, the evaluation of deleterious reactions can be divided into two parts (Equations 3·a and 3·b). At the first stage, deterioration of Ca(OH)$_2$ resulted with expansive gypsum formation. The gypsum then reacts with C$_3$A in aqeuous environment and forms a more expansive product called 'ettringite'. In this study, due to the low C$_3$A content of cements, mortars were less susceptible to the attack of H$_2$SO$_4$. Test results of compressive strength loss (figure 1) confirmed this theoretical assumption.

$$Ca(OH)_2 + 2H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \quad \text{(gypsum)} \tag{3.a}$$

$$3CaSO_4 + 3CaO \cdot Al_2O_3 \cdot 6H_2O$$
$$+ 25H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \quad \text{(ettringite)} \tag{3.b}$$
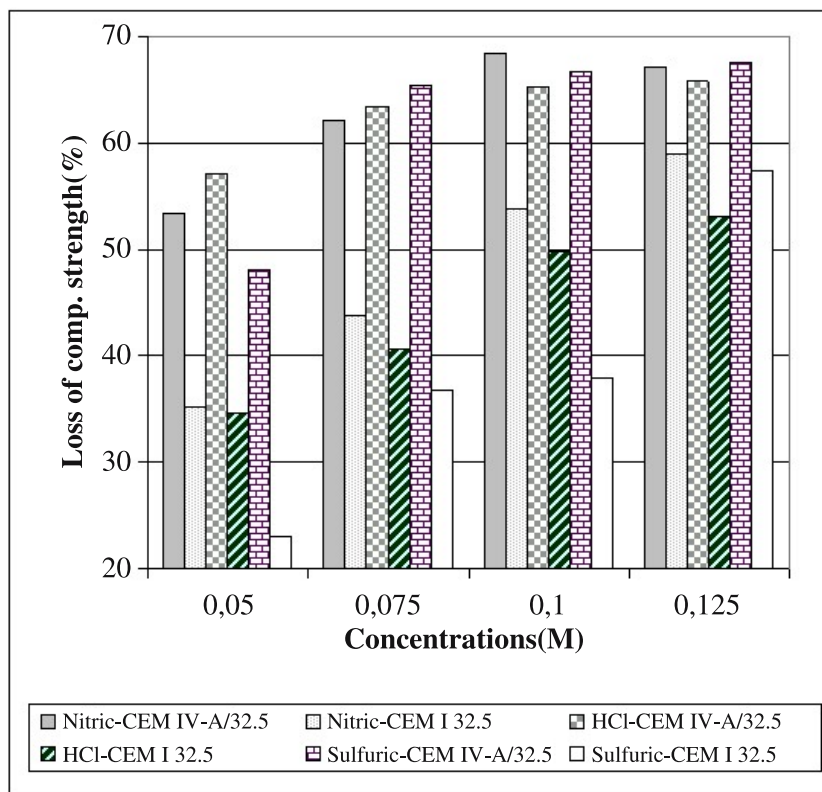
Figure 1. The loss of compressive strength of cement mortars after 120 days of attack by different inorganic acids of various concentrations compared to control specimens after 28 days of curing in water.

The rate of acid attack has been mainly related with the concentration of the solution. As can be expected, loss of weight increased with concentration of acids used (table 3). These results are in conformity with the results (Živica & Bajza 2001) and (Pavlik 1994). The pH values of the acidic solutions were slightly reduced by increasing the acid concentration of solution (table 2). As a result, the pH values of diluted solutions of strong acids approximately corresponds the concentration — therefore aggressive effects of strong acids usually can be related to pH.

Extent of deterioration of majority of samples exposed to hydrochloric and nitric acids during testing period was almost the same. The loss in weight of the samples that were exposed to sulfuric acid was the smallest because calcium sulfate (gypsum) is less soluble in water than calcium chloride or calcium nitrate. These results can be attributed to the formation of soluble calcium salts due to the reaction of acids with cements. Solubility of calcium sulfate, calcium chloride and calcium nitrate were 0·20 %, 46·08 % and 56·00 % (by weight) respectively (Živica & Bajza 2001). Due to this fact, the amount of weight loss of samples that were kept in sulfuric acid solution was the lowest. However, it should be noted that, if the W/C ratio was changed different behaviour might be observed.

The loss of strength values for all types of acids is also dependent on the concentration of the solutions (figure 1). At high concentrations this effect is more significant. For example,

independent of the cement and acid type, the loss of strength was higher than 50 %, at a concentration of 0·125 M. It should be noted that, these values would be smaller if the control specimens were tested in 120 days. All acid types had similar hazardous effects on test specimens for various testing periods.

3.2 *The effect of cement type*

There are controversial results about the acid resistance of pozzolanic cements in technical literature. Živica & Bajza (2002) claim that pozzolanic cements have better durability characteristics against acid attacks, while others (Mehta 1985; Calleja 1980; Fattuhi & Huges 1983) claim vice versa. The results of our research have revealed that the samples prepared with pozzolanic cement have lost more weight compared to the ones prepared with Portland cement (table 3).

The main ingredient of both cements was the same Portland clinker. The above mentioned results indicate that incorporation of pozzolanic mineral additives (fly ash + trass) may not always positively affect the durability properties of cement against acid attacks.

The fineness of cement is also related with the rate of chemical reactions due to the exposed specific surfaces. During the hydration process, cement particles are converted into a mass of cement hydration products. Therefore, specific surface of the hydration products is relevant to the rate of chemical reaction. In this study, also the finer cement (pozzolanic) has lost more weight and compressive strength. The W/C ratio of mortars was kept constant. The flow values of mortars prepared with pozzolanic cements were lower than mortars made from portland cement. As a result, the compactibility of pozzolanic cement incorporated mortars for a constant compaction energy decreased. The low compactibilty of mortars resulted in a more porous surface structure. Besides, samples prepared with pozzolanic cement have larger paste volumes compared to portland cement due to lower specific gravity values (2·94–3·13 respectively). It is known that, cement pastes are more vulnerable to acid attacks than cement mortars, which incorporates fine aggregate. This result is also in conformity with the result of Pavlik and Uncik (1997).

The chemical and mineralogical properties of cement also affect the changes in pH values of the acidic solutions within time (Ceukelaire 1992). The equivalent alkali contents ($Na_2O +$ $0·658K_2O$) of pozzolanic and Portland cements were 2·64 % and 0·65 %, respectively. These values may explain the shorter neutralization period of acidic solutions for pozzolanic cements compared to Portland cements. It should be noted that, these values represent the total alkalis present in pozzolan and clinker for blended cement.

From figure 1, it can be seen that CEM I 32·5 cement (M1) is more resistant against strength loss. This behaviour is significant in all types and concentrations of acids. The higher rate of strength loss of mortars prepared with pozzolan blended cement may be attributed to the lower compactibility of mortars resulted with a more porous microstructure.

3.3 *The relationship of loss of weight and compressive strength*

The results revealed that there is a meaningful relationship between the loss of weight and loss of compressive strength for the mortar specimens produced by both cements. The coefficients of correlation has been determined as 0·76, 0·82 and 0·87, respectively for three types of acid (hydrochloric, nitric and sulfuric) attacks during 120 days of testing periods as seen in figure 2.
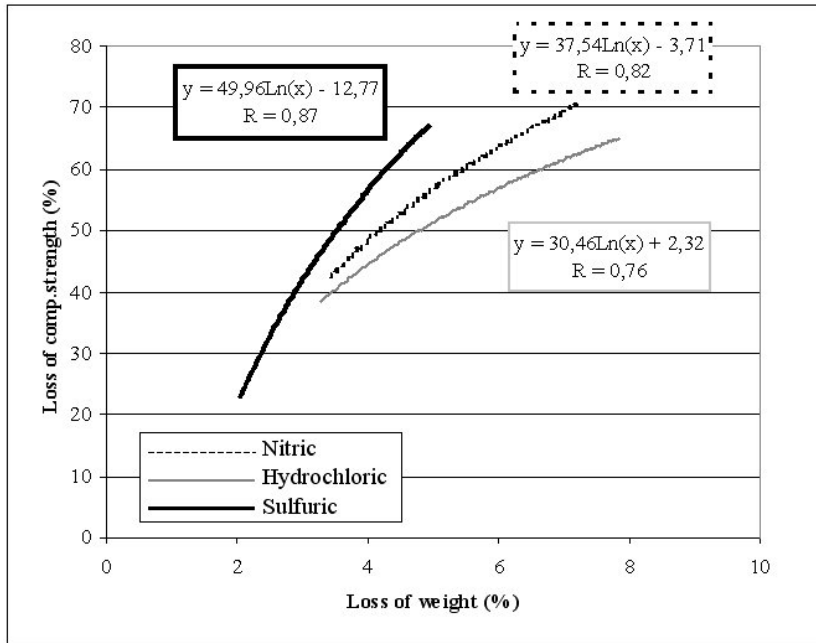
Figure 2. Loss in compressive strength of cement mortars made from both cements in relation to loss in weight after 120 days of exposure to solution.

4. Conclusions

Based on the experimental results reported in this paper, the following conclusions can be drawn:

(i) The loss of weight of cement mortars increases with the increasing values of acid concentration. For example, in case of HNO_3, when the acid concentration increased from 0·05 M to 0·125 M, the increase in weight loss per cent of cement mortars were 84 % for ordinary Portland cement (CEM I 32·5) and 75 % for pozzolanic cement (CEM IV-A/32·5) at 120 days of immersion in acid solution. Similar behaviour was observed in case of other acid types.

(ii) In case of low concentrations, hydrochloric acid and nitric acid caused higher deterioration compared to sulfuric acid during the testing period. It should be noted that; sulfuric acid that produced the least soluble calcium salt had caused the least damage on test specimens especially in terms of both strength and weight loss. The better performance of mortars against sulfuric acid attack can also be attributed to the low C_3A content of employed cements.

(iii) At high concentrations (0·125 M), independent of the cement and acid type, the loss of strength was more than 50 %. Employment of solutions of excessive concentrations is not logical to compare the performance of mortars against different acid types.

(iv) The samples prepared with pozzolanic cement have lost more weight and higher compressive strength loss was observed compared to the ones prepared with ordinary Portland cement. It can be said that, incorporation of pozzolanic mineral additives (fly ash+trass) may not always positively affect the durability characteristic of cement against acid

attack. This unexpected situation comes from consistency difference of mortars prepared with ordinary Portland cement and pozzolanic cement: By keeping the water/cement ratio constant, the consistency of mortar mixtures prepared with finer pozzolanic cement was not enough to maintain good compaction, thus more porous micro-structure was obtained compared to the ones prepared with ordinary Portland cement. It may be noted that, there is a general consensus among scientists and engineers that the performance of pozzolanic cement is better than the ordinary Portland cement against acid exposure. This study has revealed that, it is not enough to use pozzolanic cements, compactability is also important for a mortar to resist against acid attack. In this connection, attention is drawn to the fact that specifications lay emphasis on producing dense and compacted high performance cement mortar or concrete which normally includes pozzolanic materials such as fly ash for durable concrete under aggressive environments.

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