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Reinforcing concrete: comparison of filler effects

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ABSTRACT

We have applied six different fillers to a typical polymer cement. Silica fume, furnace slag, fly ash, marble powder, natural sand and boron were used at different percentages mixed in a commercial epoxy. The concentration of the fillers varied from 10 to 50 wt.% at 10% intervals. The composites were subjected to 3-point bending and compression testing. Weight loss of each sample was evaluated in a hydrochloric acid bath. There are differences in densities or weights of the samples that need to be taken into account when considering mechanical parameters. Boron and fly ash powders provide flexural strength determined by 3-point bending higher than the neat epoxy. Some fillers lower the flexural strength of the cement, a result of the filler agglomeration. Fly ash, furnace slag and boron increase the elastic modulus in compression; so does also silica fume but only at 30 wt.% concentration. Marble powder has a small negative effect on the compressive modulus while natural sand has little effect. However, when one takes into account densities or specific weights, only 10% boron enhances the compressive performance per unit weight. Weight losses in hydrochloric acid solutions are the largest for natural sand (13 wt.%), for boron up to 11%, for marble powder up to 8%, for furnace slag also near 8%. Silica fume and fly ash have the changes below 1.8%.

1. Introduction and scope

Worldwide, around 2.6 billion tons of cement is produced annually, much of it used for making concretes. Concretes can be divided into two major categories, mineral and polymer based; the former have a long tradition (Mindess, 1982; Regoud, 1986); the two categories have been compared in a review (Martinez-Barrera et al., 2011a). New ways of improvement of cement and concrete properties are being developed practically continuously. Several approaches are in use, such as steel fibers (Mor, 1992; Clarke and Birjandi, 1993; Song and Hwang, 2011; Campione et al., 2005; Bouazaoui and Li, 2008; Pul, 2010; Gencel et al., 2011) or else polymeric fibers (Martinez-Barrera et al., 2005, 2006; Gencel et al., 2011a, 2013a; Martinez-Barrera et al., 2011).

Various fillers in concrete contain for instance rubber tires (Thomas and Gupta, 2015) – what results in somewhat lower but acceptable compressive strength, while resistance to water absorption and carbonation are improved. Actually, the building industry is the biggest user of polymeric materials, accounting for 25–30% of the total consumption of polymers. Portland cement has insufficient properties in certain applications such as strengthening existing structures against earthquakes, repair after earthquakes, insulation against water and heat, decoration or restoration in general. However, polymer concrete has also a large drawback: all polymeric materials are viscoelastic, which results in creep and insufficient properties at low temperatures. In the present paper we focus on powder fillers as the reinforcement. Within this approach, a large variety of fillers have been applied (Gencel et al., 2010a,b, 2011a,b,c, 2012a,b, 2013b,c,d, 2014; Barrera-Díaz et al., 2011; Hossain and Lachemi, 2007; Topcu and Uygunoğlu, 2008; Uygunoglu et al., 2012; Koksal et al., 2012; Korkut et al., 2013; Contractors Section, 2014; Instructables, 2014; Technical Bulletins, 2014; Sua-lam and Makul, 2015; Bravo et al., 2015; Benta et al., 2015; Rana et al., 2015). However, one usually applies one or two fillers and studies the dependence of mechanical or other properties on the filler concentration. In the present work six different materials were applied and compared: silica fume, furnace slag, fly ash, marble powder, natural sand and boron were used at different

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Table 1
Materials used.

Material	Particle size, μm	Density (specific gravity)
Silica fume	0.15	2.2
Furnace slag	50	2.2
Fly ash	100	1.9
Boron waste	125	2.3
Natural sand	500	2.6
Marble powder	125	2.7

Table 2
Elemental analysis results for fillers.

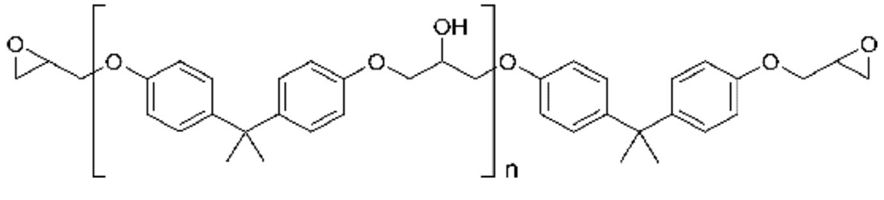
Component, %	Slag	Fly ash	Silica fume	Boron waste	Marble powder
CaO	39.8	6.66	1.48	17.7	51.8
SiO_2	32.8	47.4	74.7	15.5	4.67
Al_2O_3	11.8	19.8	0.46	1.38	–
Fe_2O_3	1.45	11.8	0.84	0.22	0.03
B_2O_3	–	–	–	12.09	–
MgO	4.15	4.76	3.64	13.79	0.4
Na_2O	0.51	0.57	0.85	3.34	–
K_2O	0.91	2.62	5.05	0.5	–
SO_3	2.06	1.86	2.48	–	–
Cr_2O_3	0.02	0.13	2.83	–	–
TiO_2	0.63	0.88	0.63	–	–
LOI	2.2	2.76	5.97	34.4	41.0
Specific weight	2.20	1.99	2.20	2.30	2.70
Fineness (Specific surface)	$5.0 \cdot 10^3$	$3.1 \cdot 10^3$	$1.4 \cdot 10^4$	$1.7 \cdot 10^3$	$6.14 \cdot 10^2$

percentages mixed in a commercial epoxy. Each filler was added to an epoxy at 10–50 wt.% concentration at 10% intervals. These samples plus a pure epoxy provided a total of 31 sample compositions to be investigated. On each sample we have performed 3-point bending, compression testing, and we also determined weight loss in hydrochloric acid baths.

2. Materials and methods

2.1. Materials used

Epoxies are known to have a wide range of applications (Bilyeu et al., 2001). The epoxy used has been obtained from System Three Co. and is called by them a General Purpose Epoxy Resin. Its chemical formula is



System Three Co. offers three different hardeners for this epoxy. The hardener we have used is # 2 Medium Hardener. The company specifications say: minimum application temperature: 55 °F; gel time under 77 °F (25 °C): 30 min; tack free time under 77 °F: 2–4 h. We have applied the volumetric proportion of the epoxy to the hardener 2:1.

Important properties of the fillers used are listed in Table 1. Their true densities have been determined using a Micromeritics AccuPyc 1330 gas pycnometer with helium gas (purity 99.999% He).

Silica fume is a byproduct of silicon-containing metals and alloys, including a byproduct obtained in the production of ferrosilicon. One of the main uses of silica fume is in concrete due to its chemical and physical properties. The raw materials used to make silica fume are quartz, coal, and woodchips. The smoke is then collected from burning these materials and sold as silica fume. Silicon dioxide is the main component of silica fume. The fume has a high surface area and is amorphous; the glassy structure imparts resistance to penetration by chloride ions.

Natural sand can have a wide array of compositions, but it mainly consists of quartz and calcium carbonate. The particle size of natural sand is much larger than that of silica fume powder.

Marble mostly refers to metamorphosed (recrystallized) and un-metamorphosed minerals. The material being tested is composed mainly of silicon dioxide and aluminum oxide. Aluminum oxide is a porous, granular substance that is used as a substrate for catalysts and as an adsorbent for removing water from gases and liquids.

Furnace slag is mostly composed of calcium oxide and silicon dioxide. Calcium oxide is usually obtained by decomposition of calcium carbonate and causes a strong exothermic reaction when added to water.

Fly ashes compositions mainly consist of silicon dioxide, aluminum oxide, and iron oxide.

Boron is obtained from minerals such as tincalconite ($Na_2O \cdot 2B_2O_3 \cdot 5H_2O$), ulexite ($Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$) and colemanite ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$). About 400,000 tons of different types of boron wastes are formed and rejected in tailing dams per year (Uygunoglu et al., 2015).

Characterization of fillers used in terms of elemental analysis is displayed in Table 2. The Table contains also loss on ignition = LOI determined by strongly heating a sample at 1000 °C, allowing volatile substances to escape, until the sample mass ceases to change and recording the weight loss. We also list the specific weight in g cm^{-3} and fineness, that is specific surface in cm^2 g^{-1}, determined using Blaine's permeability apparatus in which the resistance to flow of air through a porous bed of a powder (a filler in our case) is determined. The specific weight of neat epoxy cement without fillers is 1.05 g cm^{-3}.

2.2. Testing methods

3-point bending: we have used a machine from MTS Systems Corp., Eden Prairie, Minnesota. The samples were prepared by mixing the components, then poured into a silicon mold for three point bend testing. Sample sizes as defined by the ASTM D-7264 standard were 3.2 mm × 12.7 mm × 125 mm. The samples were left for 24 h to fully cure and then tested.

Compression testing: the same MTS machine was used. The molds dimensions were 12.7 mm × 12.7 mm × 25.4 mm, again according to the appropriate ASTM D-695 standard. All materials were allotted a total of 7 days to fully cure due to the slow hydration process or slow strength development dependent on the hardener. Photos of specimens before compression testing are shown in Fig. 1.

Weight loss in an acidic solution: a 100% epoxy sample was placed in 2 different baths. Each bath had a different molarity; 2 and 4.

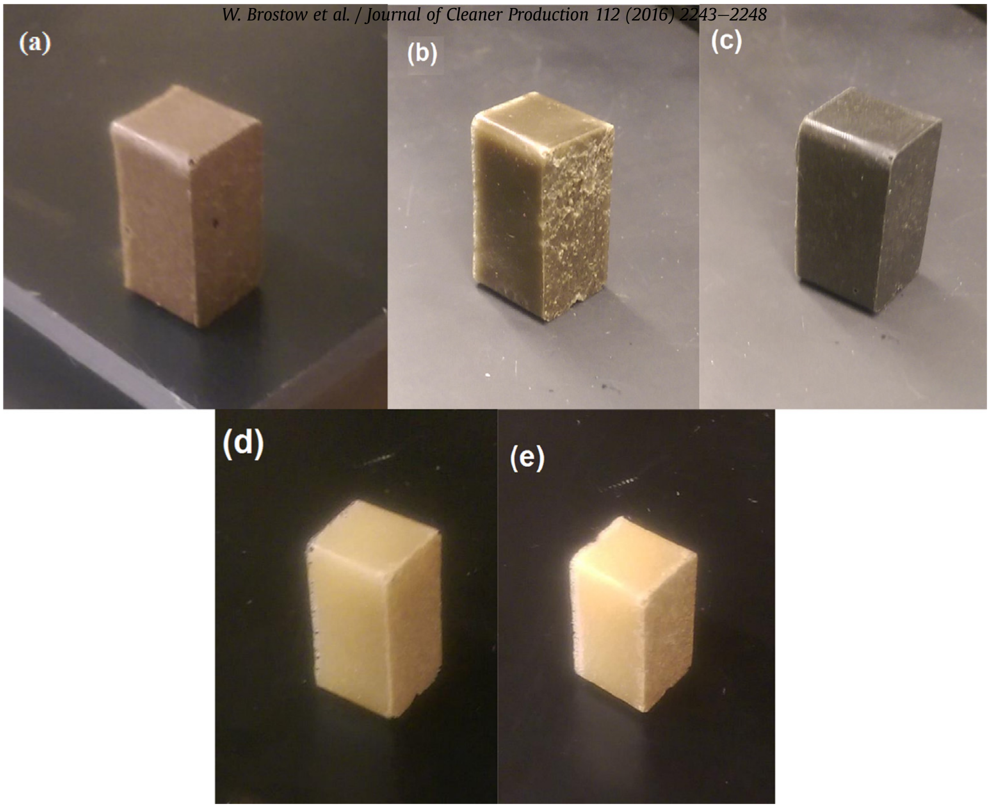


Fig. 1. A view of epoxy based composites with different type of fillers (a: fly ash; b: furnace slag; c: silica fume; d: boron waste; e: natural sand).

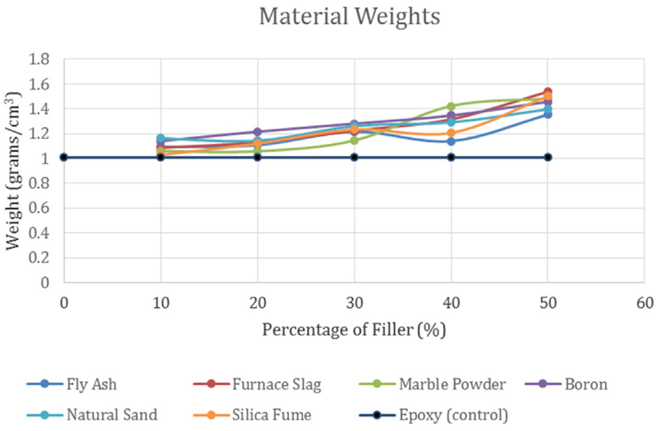


Fig. 2. Weights of samples as a function of the filler concentration, starting with 4.0 g of the epoxy without powder fillers.

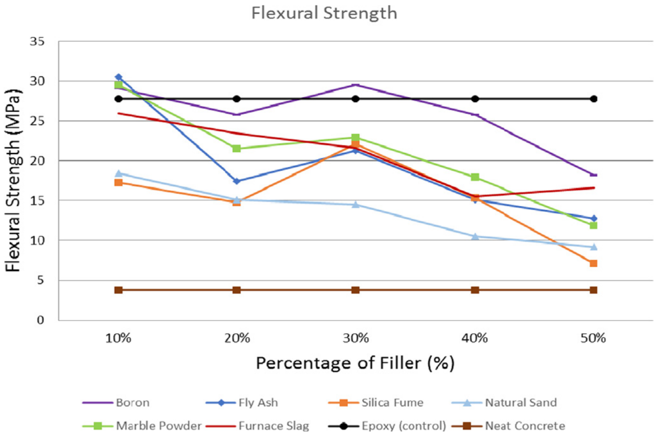


Fig. 3. Flexural strength in 3-point bending tests as a function of filler concentration.

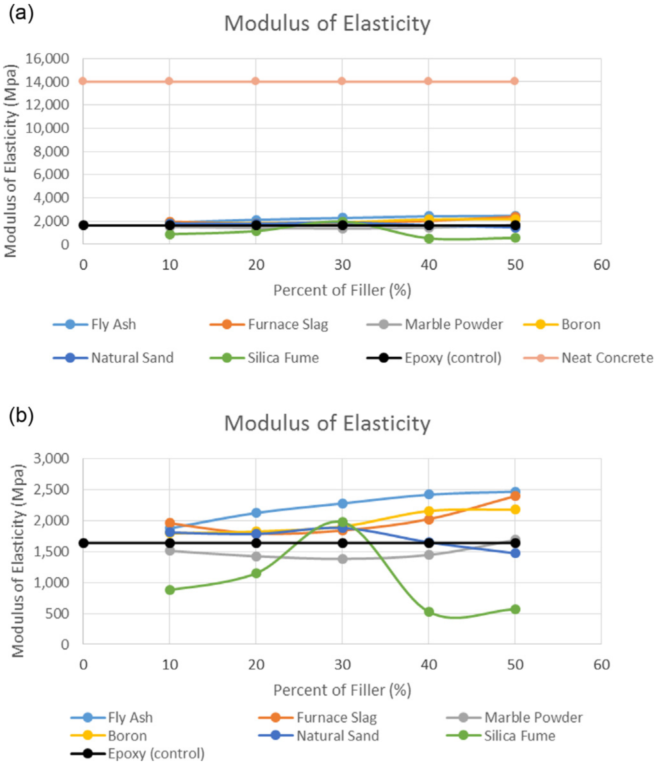


Fig. 4. Elastic modulus in compression as a function of filler concentration; top (a): neat concrete included; bottom (b): enlarged view for different fillers and for neat epoxy.

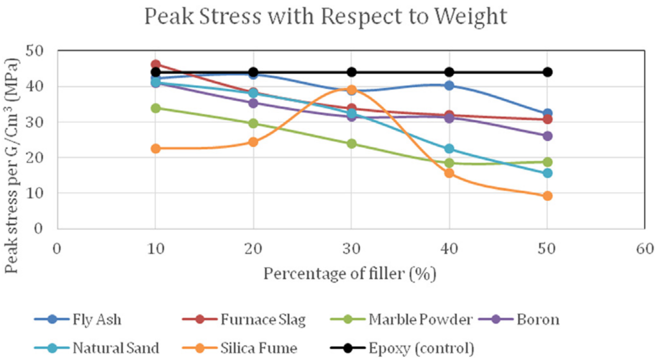


Fig. 5. Peak stress in compression testing per 1.0 g as a function of the filler composition.

Afterwards, 10–50 wt. % of each filler was added to an epoxy. After the curing of the concrete plus epoxy composite, the new specimens were placed in 3 different baths for every filler concentration and each molarity (example: 10% silica fume in 2 and 4 M baths). The specimens were first dried for a full 24 h and then weighed every 1, 4, 9, 16, and 25 days. To speed up the drying process, a desiccant was placed in the oven. After the weighing of the samples, they were placed back into the bath until the next date for the following measurement.

3. Results and discussion

Tables 1 and 2 show us differences in densities or specific weights. This translates into differences in materials weights as a function of filler concentration shown in Fig. 2. The reference line is for the epoxy without filler. The weight changes are a factor to be taken into account in choosing a material composition for a given application.

We now consider the 3-point bending results. By the nature of the test, peak stress is obtained at the mid-point of the specimen, with lower values of the stress elsewhere, and peak loads determined. 4-point bending is also available, but we find the symmetry of the 3-point bending with respect to the center of the specimen an advantage. We present the results in Fig. 3 in the form of flexural strength as a function of concentration of the filler for all six fillers used. Flexural strength is a measure of the specimen resistance to

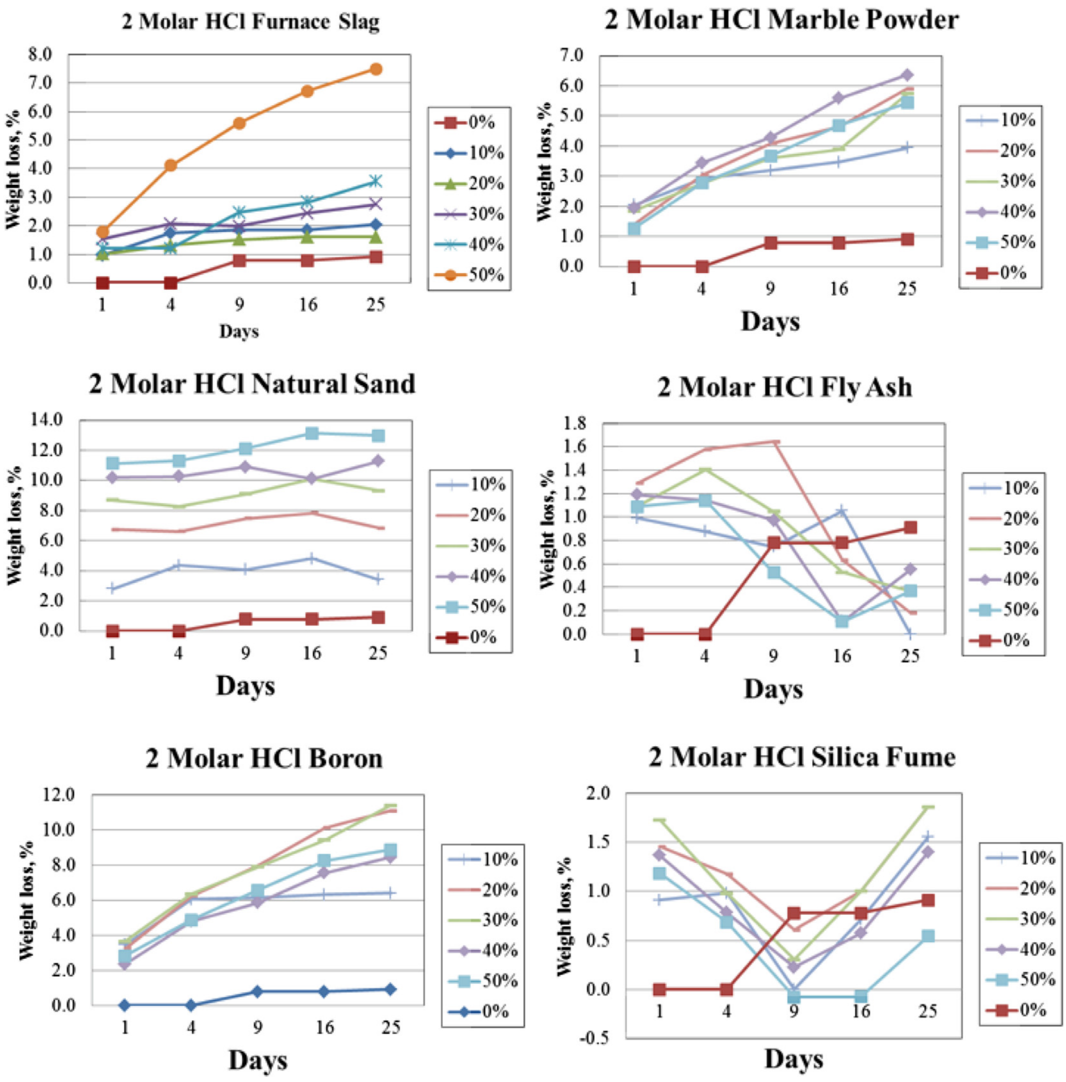


Fig. 6. Weight changes in acidic solutions containing 2 M of hydrochloric acid.

failure in bending; sometimes the term *modulus of rupture* is used for this quantity.

The horizontal line for the epoxy without fillers is provided for improved perspicuity. We see in Fig. 3 that the highest value of the flexural strength is for 30 wt.% of the boron filler. However, the value for 10% only of fly ash is not much lower, while providing a way to use fly ash instead of it becoming waste. Several fillers impart a *decrease* in the flexural strength along with their increasing concentrations. These cases can be explained by agglomeration of the filler.

We now consider the compression testing results. We display in Fig. 4 the compression modulus as a function of concentration of the fillers.

First of all, analysis of Figs. 3 and 4 supports the conventional wisdom: the elastic compression modulus amounts to some 10–20% of the flexural modulus (Aboutconcrete, 2015). Further, the compression modulus increases upon addition of fly ash, furnace slag and boron. Marble powder lowers somewhat the compression modulus. Silica fume provides an interesting behavior, the curve has a maximum at 30 wt.% of the filler. Apparently at low concentrations silica fume lowers the internal cohesion of the cement + epoxy matrix, then it acts as a reinforcement, and finally undergoes agglomeration—thus lowering the compression modulus.

We now recall Fig. 1: there are pertinent differences in weights or densities of the samples. Accordingly, we present peak stresses in compression testing with respect to weight for fillers with varying concentration in Fig. 5.

Fig. 5 takes into account differences in specific weight or density. We find that the peak stresses per gram of nearly all composites are lower than the value for the neat epoxy. The only exception is the composite containing 10 wt. % of furnace slag. Fly ash at 10 or 20% shows peak stresses only slightly lower than the epoxy. As in Fig. 4, the curve for silica fume shows a maximum at 30% of the filler. The explanation for this is analogous to that for the compressive modulus in Fig. 4.

Finally, we consider weight loss in acidic solutions with different molarities. The results are summarized in Figs. 6 and 7. For brevity we display only results for 2 M and 4 M solutions.

For 2 M and 4 M solutions of HCl we see for furnace slag relatively small changes, except for 50 wt.% of the filler. By contrast, for marble powder we see large changes, reaching 8% weight loss after 25 days. For natural sand in 2 M HCl solution we see the largest effects of all, 13% weight loss. For sand in 6 M acidic solution the effects are somewhat smaller but amount to nearly 12%. For fly ash the weight losses are at most 1.6%, a desired result. For boron we see ≈11% weight loss in 2 M acidic solution and up to 7% in 4 M solution. For silica fumes the weight losses are all below 1.8%.

Sewage sludge has been used as an alternative fuel in Portland cement clinker production (Puig et al., 2013). Shortly before submission of this paper, an article by Baeza-Brotons et al. (2014) came to our attention. Along lines similar to us, the Alicante authors have

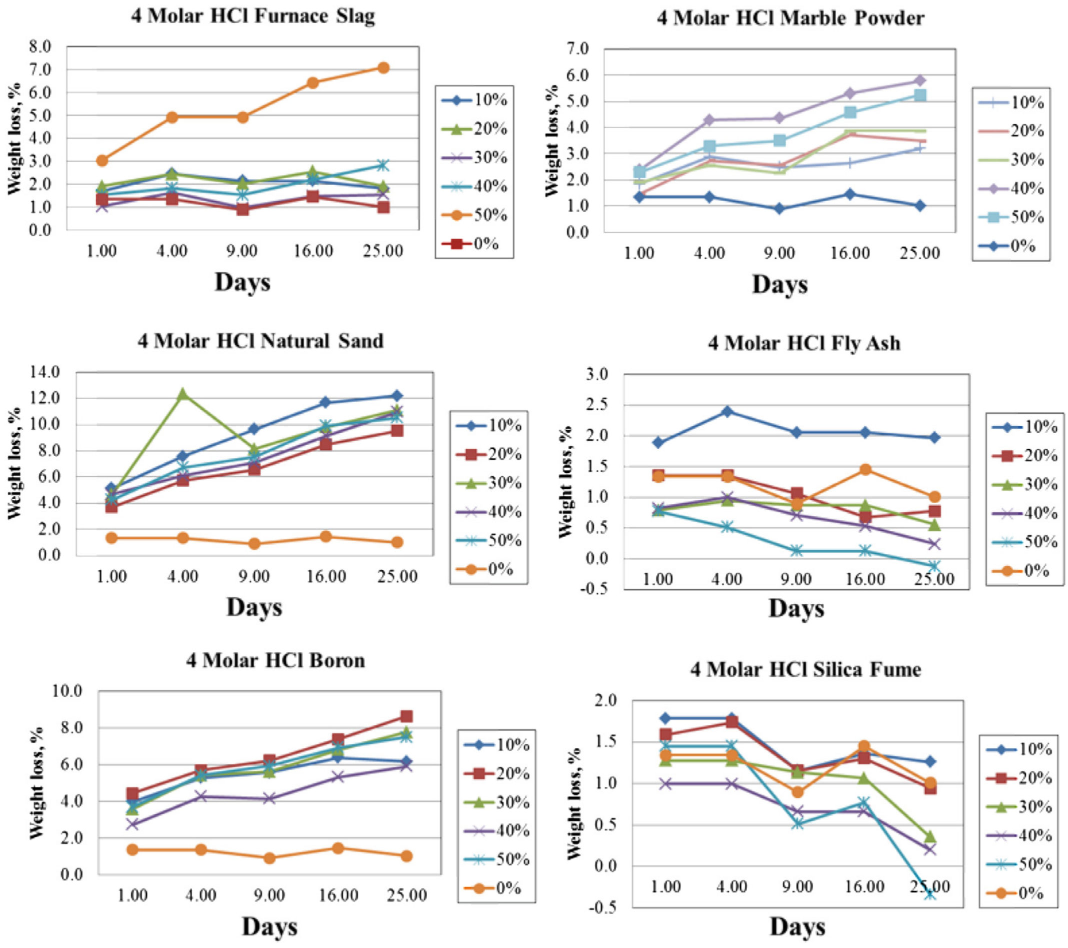


Fig. 7. Weight changes in acidic solutions containing either 4 M of hydrochloric acid.

used sewage sludge ashes up to 20% to reinforce Portland cement—with good results.

4. Conclusions

Specific applications of the compositions we have created and studied depend partially on local circumstances. Thus, given fly ash locally available, incorporating it into concretes providing improvement of flexural strength and of compressive modulus as well as low weight losses in aq. HCl solutions is attractive. Polymers with fillers are used more and more in construction and in other industries. Epoxy glues are used as highly performing adhesives in concrete prefabricated applications. However, they are relatively expensive; those costs can be lowered by using epoxies with fillers.

Our agenda now includes determination of tribological properties of such concretes, dynamic friction in particular.

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