Accelerated Degradation Testing Of Concrete In Acidic Environment: Resistance To Lactic And Sulfuric Acid

N De Belie J Monteny L Taerwe
Concrete Research Ghent University Ghent Belgium

Summary: This research was initiated because of durability problems related to building materials in agricultural constructions. Resistance against corrosion caused by lactic and acetic acids is of major importance both for floors in animal houses and silos. Furthermore, concrete manure tanks, walls of manure pits in animal houses and the underside of concrete slats and slabs are exposed to biogenic sulfuric acid corrosion.

To examine the degradation of concrete by aggressive liquids, a testing apparatus for accelerated degradation tests (TAP) was developed. It was conceived to obtain acceleration of the deterioration process through alternate wetting and drying, because this procedure simulates the real-life situations under investigation. This is achieved by an experimental set-up with concrete cylinders that rotate through containers with the test solutions. Cycles of chemical attack are followed by abrasion using rotary brushes. The change in dimension of the concrete specimens and the surface roughness are determined through a non-contact distance measurement with laser sensors.

In a first experiment the durability of concrete exposed to a solution with 30 g/l of both lactic and acetic acid was examined (pH=2.0-2.2). The effect of the aggregate type, the cement type and the influence of polymer modification (polymer (d.m.)/cement ratio = 0.10) were considered. The results showed that concrete with blastfurnace slag cement was more resistant than the reference concrete with ordinary Portland cement. Use of limestone sand (and aggregates) led to a quicker neutralization of the aggressive liquid, but this was insufficient to reduce the average attack depth. The polymer modifications, especially the use of styrene acrylic ester latex, increased the concrete resistance significantly, although SEM-investigation showed that the emulsified polymer had not completely formed a film.

Secondly the resistance to a 0.5% sulfuric acid solution was considered (pH=1.0). Here it was necessary to measure twice per attack cycle: after the alternated wetting and drying stage to determine concrete expansion and after brushing to quantify the decrease in radius due to mechanical action. Compared to the reference concrete with high sulfate resistant Portland cement, durability could be improved by addition of styrene acrylic ester polymer, as well as by using blastfurnace slag cement. Modification with vinylcopolymer had little effect, and addition of silica fume, styrene butadiene or acrylic polymers led in this case to a reduced resistance.

Keywords: concrete degradation, lactic acid, sulfuric acid, polymer, silica fume

1 INTRODUCTION

1.1 Concrete degradation in agricultural constructions

Various concrete building components in agricultural constructions are subject to acid attack, the main aggressive agents being lactic, acetic and sulfuric acid.

Concrete floors in animal houses

Floor types in animal houses can be classified into solid, unperforated floors that are laid directly on the ground and floors that are suspended above ground and may be perforated to assist in the drainage of liquids and passage of fecal material. For solid as well as for suspended floors, those constructed of concrete are the most common. Results from a survey, carried out by De Belie (1997a) on farms with fattening pigs, showed that even for high-quality precast concrete slats, on 15% of the farms surveyed, the coarse aggregates of some slats were exposed within two years of use. After five years, wear was observed on 40% of the farms. Consequences were an increased gap between slat beams and increased surface roughness (resulting in animal injuries), corrosion of the reinforcement and a reduced slat stability. The reason for this degradation are the specific aggressive conditions occurring on floors in animal houses. Chemical components from feed residues and manure may attack the concrete floor surface. Animals and cleaning exert a mechanical impact. Pressures used for high-pressure cleaning can amount to 80-150 bar (Frénay & Zilverberg 1993). Different authors (Hoeksma 1988; Mathiasson *et al.* 1991; Nilsson 1993; De Belie *et al.* 1996a) mention the presence of large amounts of lactic and acetic acid, and aggressive ions such as SO_4^{2-}. The major amount of aggressive ions and acetic acid would come from the manure. Lactic acid originates from acidified meal/water mixtures (De Belie *et al.* 1996a) and is the main source of severe concrete degradation near feed and water supply. Acidified meal/water mixtures can reach acid concentrations of 31.0 mg lactic acid and 3.1 mg acetic acid per ml filtrate. The pH can drop to 3.8, in correspondence with the pK_a of lactic acid (3.86 at 25°C). Some farmers add whey to the drinking water and dairy cows and pigs can be fed with silage, which again contains lactic and acetic acids.

Silage storage structures

Silage storage structures are used to conserve fodder under anaerobic conditions. Depending on the dry matter content of the crop, the silo, and the silo drainage system, more or less silage effluent is produced, with possibly a pH as low as 3.5-4.0, the main acids being again lactic and acetic acid. On many farms, silage is stored in bunker silos with reinforced concrete floors (and walls), which are readily attacked by the corrosive effluent. Furthermore, wear (abrasion and impact) is caused by farm machinery such as block cutters.

Manure storage structures

In 1945, it was found (Parker 1945), that the formation of sulfuric acid in sewers was not due to purely chemical transformations in the sewer atmosphere but to the action of aerobic sulfur oxidizing bacteria, mainly of the *Thiobacillus* species. Anaerobic sulfate reducing bacteria, such as *Desulfovibrio* species, living in manure or in the mud at the bottom of sewer pipes and in the slime at the sides, reduce sulfates and other oxidized sulfur compounds to hydrogen sulfide (H_2S). This hydrogen sulfide is released in the air above the liquid level and dissolves in moisture on the walls and on the underside of the slatted floors. There, H_2S can be oxidized to sulfur, a reaction that is catalytically accelerated by the high alkalinity of the concrete surface. The *Thiobacillus* bacteria oxidize the sulfur to sulfuric acid, using the energy released for their cell mass production. Very low pH values (1-2) may occur locally (Mori *et al.* 1991).

1.2 Reaction mechanisms

Lactic and acetic acid are very aggressive, because their reaction with free lime [$Ca(OH)_2$] of the concrete produces very soluble calcium salts (Kleinlogel 1960). When those salts are leached, the hydrates of the cement matrix start decomposing and the concrete disintegrates. Sulfuric acid first reacts with the calcium hydroxide in the concrete to form gypsum. Although the formation of gypsum is associated with an increase in volume by a factor of 1.2 to 2.2 (Attiogbe & Rizkalla 1988; De Ceukelaire 1989; Wafa 1994), the reaction between gypsum and calcium aluminate (C_3A) with the formation of ettringite is much more detrimental. Some authors mention an increase of volume with a factor two (Attiogbe & Rizkalla 1988; Wafa 1994), while others mention even a factor 7 (De Ceukelaire 1989). Thus the formation of ettringite is mainly responsible for the large volume expansion, which leads to increase of internal pressure and deterioration of the concrete matrix.

2 MATERIALS AND METHODS

2.1 Aggressive Liquid

For the first experiment the simulation liquid consisted of lactic and acetic acid in water both in concentrations of 30 g/*l*, the highest concentrations registered on floors in animal houses during the preliminary investigations (De Belie *et al*., 1996a). This liquid had a pH of 2.0-2.2, which is extremely aggressive to concrete. The lower pH compared with the pH measured for instance in soured meal-water mixtures with the same acid concentrations, is due to the absence of buffering feed ingredients, and will in reality only occur under specific circumstances. In previous experiments also highly to moderately aggressive liquids were used, with pH-values of 3.8 and 4.5, but it appeared that the three liquids resulted in a very similar classification of the concrete types (De Belie et al. 1996b; 1997a). For the second experiment a 0.5% sulfuric acid solution (pH of around 1.0) was used.

2.2 Apparatus for accelerated degradation tests

At the Magnel Laboratory for Concrete Research of Ghent University, an apparatus for accelerated degradation testing (TAP) was developed (Fig.1). A more detailed description of the used test method is given by De Belie (1997c).

Fig. 1 Apparatus for accelerated degradation testing (TAP)

It was designed to achieve acceleration of the deterioration process through alternate wetting and drying, because this procedure simulates the real-life situations under investigation. Three cylinders (∅ 270 mm, h = 70 mm) of each concrete mixture were subjected to a cyclic procedure of immersion in an acidic solution and drying by air. The cylinders, fixed on horizontal axes, turned with a speed of 1 revolution per hour trough separate recipients. Each point of the outer circumference was submersed during 1/3 of the rotation time. After each cycle, which lasted for 6 days for the lactic/acetic acid attack and for 12 days for the sulfuric acid attack, the cylinders were dried in air and brushed with rotary brushes to remove weakly adhering concrete particles. In Table 1 the different steps in the test procedure are related to different stages occurring during the degradation in practice.

Table 1. Relation between different steps in the TAP test procedure and real-life situations

TAP	*Lactic/acetic acid attack* *(a) concrete floors in animal houses* *(b) silage storage structures*	*Sulfuric acid attack* *(a) sewers* *(b) manure storage structures*
Cyclic immersion and chemical attack	(a) wetting by feed+water residues and manure, drying in between (b) wetting during effluent release from silage	(a & b) wetting/drying by fluctuation of the wastewater/manure level
Drying in air	(a&b) drying during periods the compartment or silo is not in use	(a) dry weather situation with low wastewater level (b) emptying of manure storage facility
Abrasion by brushing	(a) abrasion by animals, cleaning with brushes or high-pressure hose (b) abrasion by animals (in self-feeding silo), cleaning and farm machinery (block cutters)	(a) high flow rates because of high loading or rain; abrasion by flowing water, turbulence (b) abrasion by cleaning (less common)

The corrosion of the specimens was measured using laser sensors, connected with a computer. The sensor amplifiers supply a Volt signal, which is linearly related to the distance between the concrete surface and the sensor. Five measurements per mm are taken along the concrete surface. A software trigger is programmed to start the measurement of a cylinder profile when the raised edge of a stainless angle steel, fixed on the concrete cylinder, passes by the laser beam. The first 50 measurements of a contour line are performed on the horizontal part of the angle steel, which acts as reference plate. The three sensor heads are mounted on a mechanical device which can always be placed in the same position on the frame of the TAP. This device allows to adjust the position of the sensor heads in a direction parallel to the cylinder axes in steps of 0.5 mm with an accuracy of 0.01 mm. In this way it is possible to scan the circumference of a cylinder every time at the same position along the cylinder height. By moving the system a few times, for every cylinder several parallel profiles can be measured, equally distributed along the cylinder height. For the experiments discussed here, 5 (sulfuric acid attack) to 7 profiles (lactic/acetic acid attack) per cylinder were measured. The laser measurements were also used to calculate the surface roughness of the concrete, expressed by means of the R_a-value (BS1134 1972).

In the lactic/acetic acid test procedure the radius of the cylinders was determined at the beginning of the experiment and after each cycle of alternated immersion, drying and brushing. In the sulfuric acid test procedure the measurements were performed twice per cycle, before as well as after brushing. In this way it was possible to determine the average change of the radius of the cylinders due to chemical reaction of the concrete with the sulfuric acid solution during the immersion as well as the change of the radius due to mechanical action of brushing the cylinders. The change in radius during the immersion stage corresponded mostly to an expansion of the concrete due to the formation of voluminous reaction products. However, a decrease of the radius could also occur during the period of immersion because of loss of adhesion of the expanded parts.

2.3 Test Specimens

The composition of the concrete mixes tested in experiment 1 with lactic/acetic acid is shown in table 2. The composition of the concrete mixes tested in experiment 2 with sulfuric acid is shown in table 3. From each concrete mix three cylinders and six cubes with sides 158 mm were made. The test specimens for experiment 1 were stored for 28 days at 20 ± 2 °C and a relative humidity of 90-95%. The test specimens for experiment 2 were moist cured for 1 day (>90% humidity, 20°C), followed by 3 days of dry curing conditions (60% humidity, 20°C) and subsequent air curing. At 28 days three cubes were measured for compressive strength as prescribed by the standard NBN B15-220 (1990) and the three others were submitted to a water absorption test, which gives an indication of the porosity, as prescribed by the standard NBN B15-215 (1989). The three cylinders of each type were mounted together on one side of an axle of the TAP for the degradation tests.

Experiment 1: lactic/acetic acid attack

Table 2. Composition and characteristics of the fresh and hardened (28 days old) concrete used in experiment 1

	Concrete mix							
	Ref I	*III/A*	*LS-G*	*LS-L*	*SBR1*	*SBR2*	*A*	*SAE*
CEM I 42.5R (kg)	375	-	375	375	375	375	375	375
CEM III/A 42.5 (kg)	-	375	-	-	-	-	-	-
Sand (kg)	700	700	350	350	700	700	700	700
Lime sand (kg)	-	-	350	350				
Gravel (kg)	1170	1170	1170	-	1170	1170	1170	1170
Limestone (kg)	-	-	-	1170	-	-	-	-
Latex* (kg)	-	-	-	-	81.6	75	75	75
d.m. in latex (%)					46	47	47	51
Polymer(d.m.)/cement (%)					10.0	9.4	9.4	10.2
Water** (kg)	146	146	146	155	128.5	110.7	150.7	107.7
W/C** (-)	0.39	0.39	0.39	0.41	0.34	0.30	0.40	0.29
Slump (mm)	5	8	0	3	130	105	-	25
Flow (-)	1.32	1.18	1.08	1.02	1.93	1.89	-	1.32
Fresh density (kg/m^3)	2400	2385	2395	2420	2271	2286	2310	2375
Compressive strength (N/mm^2)	52.0	51.9	51.7	54.1	34.7	37.2	28.6	51.2
Water absorption (%)	3.95	3.70	4.30	4.40	2.90	2.33	3.89	1.73

* The latexes used are styrene butadiene, acrylic and styrene acrylic ester latex for SBR, A and SAE, respectively

** Includes the water present in the latex

Manufacturers of precast concrete slats normally use a properly compacted high-quality concrete with the ordinary Portland cement CEM I 42.5 R (nomenclature according to the Belgian standard NBN B12-001 1993, based on the European ENV 197-1). The concrete composition of one of those manufacturers was chosen for the reference concrete *Ref I*. Furthermore concrete with blastfurnace slag cement CEM III/A 42.5 (36-65% slag), which showed a superior performance in previous experiments (De Belie *et al.*, 1996) was tested. For the concrete mixes *LS-G* and *LS-L*, half of the natural sand was substituted with limestone sand in order to neutralize the aggressive environment more quickly and reduce concrete attack afterwards. For *LS-L* also limestone aggregates were used instead of gravel. The Belgian Ministry of Agriculture advised in the past to use only rounded gravel aggregates for slatted floors in animal houses, which would reduce claw injuries compared to the sharp-edged limestone aggregates. Buist (1987) and Bayoux *et al*. (1990), however, claim that the limestone aggregates make an important buffer and that their use would therefore reduce acid attack. Furthermore the sharp edges would be rounded by the attack.

Table 2 shows that flow and slump of the concretes with limestone sand were very low, which aggravated compaction. This can be attributed to the shape of the sand and to the larger amount of particles smaller than 80 μm, compared to natural sand.

Four PCCs were tested with different polymer latexes: two styrene-butadienes *SBR1* and *SBR2*, an acrylic latex *A* and a styrene acrylic acid ester *SAE*. A polymer (d.m.)/cement proportion of about 0.1 was chosen. The polymers were added to the mixing water as latex. Normally polymers when added to concrete, exhibit water reducing qualities, because of the dispersing agents in the polymer latexes and the spherical shape of the polymer drops (Bijen 1991). The characteristics of hardened PCC are the result of the lower water-to-cement ratio and the formation of a three-dimensional polymer structure through the hardened cement paste. The nature of microstructural modification and void filling and bridging of cracks that occurs when polymer formulations are incorporated in cement systems, is such that polymers will substantially change, in a favorable manner, the pore structure. The porosity is decreased in the pore radius range of 240 nm or more, whereas it increases greatly in the smaller pore radius range of 140 nm or less. The net result of such changes would be to improve the resistance of PCC to liquids (Swamy 1995). However, the addition of polymers increases the concrete cost and would cause an increase in price of concrete slats with about 20-40%. Table 2 shows that slump and flow of *SBR1* and *SBR2* were quite high, which implies that the water content could be reduced further. In spite of the higher amount of water added to *A*, its workability was bad and slump and flow could not be measured. It is also clear that the presence of the polymer films inhibits water absorption. The *SAE*-concrete showed the smallest water absorption, but also for the *SBR1*- and *SBR2*-concretes the water absorption was remarkably lower than for the reference concrete. The *A*-concrete contained many air voids due to its bad workability, which explains for its higher water absorption.

Experiment 2: sulfuric acid attack

Table 3. Composition and characteristics of the fresh and hardened (28 days old) concrete used in experiment 2

	Concrete Mix						
	Ref II	*III/B*	*SBR*	*SAE*	*A*	*VPV*	*SF*
CEM I 42.5 HSR/LA (kg)	350	-	350	350	350	350	350
CEM III/B 42.5 HSR/LA (kg)	-	350	-	-	-	-	-
Silica fume (kg)	-	-	-	-	-	-	30
Sand (kg)	840	840	843	839	843	819	840
Gravel (kg)	1120	1120	1124	1119	1124	1092	1120
Latex* (kg)	-	-	54.7	51.5	58.3	65.6	-
Superplasticizer (kg)	2.5	2.5	-	-	-	-	5
Water** (kg)	140.0	140	90.6	97.3	86.9	104	130
W/C** (-)	0.40	0.40	0.34	0.35	0.34	0.41	0.34
Slump (mm/class)	20/S1	15/S1	40/S1	40/S1	105/S3	75/S2	105/S3
Flow (-/class)	1.69/F2	1.26/F1	1.62/F2	1.47/F1	2.04/F3	1.71/F2	1.71/F2
Fresh density (kg/m^3)	2430	2400	2410	2370	2190	2370	2420
Air content (%)	3.0	3.8	4.4	4.0	9.7	5.2	3.6
Compressive strength (N/mm^2)	68.3	62.5	58.2	61.3	43.8	50.6	84.6
Water absorption (%)	2.58	2.28	1.56	1.84	2.28	2.71	1.78

* The latexes used are styrene butadiene, styrene acrylic ester, acrylic and vinylcopolymer latex for SBR, SAE, A and VPV, respectively

** Includes the water present in the latex

All concrete mixtures tested were made with 350 kg/m³ high sulfate resistant Portland cement (CEM I 42.5 HSR/LA), except for one mixture that was made with blast furnace slag cement CEM III/B 42.5 HSR/LA (66-80% slag). Four different polymer types were used: a styrene-acrylic ester polymer, an acrylic polymer, a styrene butadiene polymer and a vinylcopolymer. The polymer cement concrete mixtures were made with a polymer/cement ratio of 7.5% (polymer d.m./cement). The reference mixture without polymer was made with a W/C ratio of 0.4. For the mixtures with polymer, the water content was adjusted till a slump of class S1 (10 to 45 mm) was obtained (Belgian standard NBN B15-232 1982). Although the mixture with the acrylic polymer had a low W/C ratio (0.34), due to a high air entrainment of the fresh concrete, a slump of class S3 (100 to 150 mm) was obtained. Because the mixture with the vinylcopolymer was too sticky, it was not possible to work with an S1 class and more water had to be added to create a workable concrete mixture. The final W/C of the different mixtures was calculated taking into account the water content of the added latexes. All polymer modified concrete mixtures had a lower density than

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the reference mixture without polymer. This was mainly due to the higher air entrainment of the concrete with addition of polymer. The addition of the styrene butadiene polymer, the styrene-acrylic ester polymer and the vinylcopolymer caused an increase in air content of the fresh mixture by 1 to 2% compared to the reference mixture (*Ref II*). The addition of the acrylic polymer resulted in an increased air content of almost 10%. The silica fume mixture was made by adding 30 kg/m³ silica fume to the reference mixture. The low w/c ratio (0.34) of this mixture combined with the addition of a high amount of superplasticizer created very dense and still good workable concrete.

3 RESULTS

3.1 Experiment 1: lactic/acetic acid attack

Average attack depth

An analysis of variance was carried out with the average attack depth of the cylinder profiles as the dependent variable and the concrete composition (eight classes), the cylinder (three classes) and the profile (seven classes) as independent variables. Only interactions of second order were taken into account. The average attack depth of the profiles closest to the troweling surface was often smaller than for the other profiles. Some segregation could have taken place during compaction, which resulted in less aggregates in the upper concrete layer, coming loose by chemical attack and brushing. When these profiles were left aside, the concrete composition remained the only significant factor. Fig. 2 shows the accumulated average attack depth of the different concrete types versus the number of attack cycles.

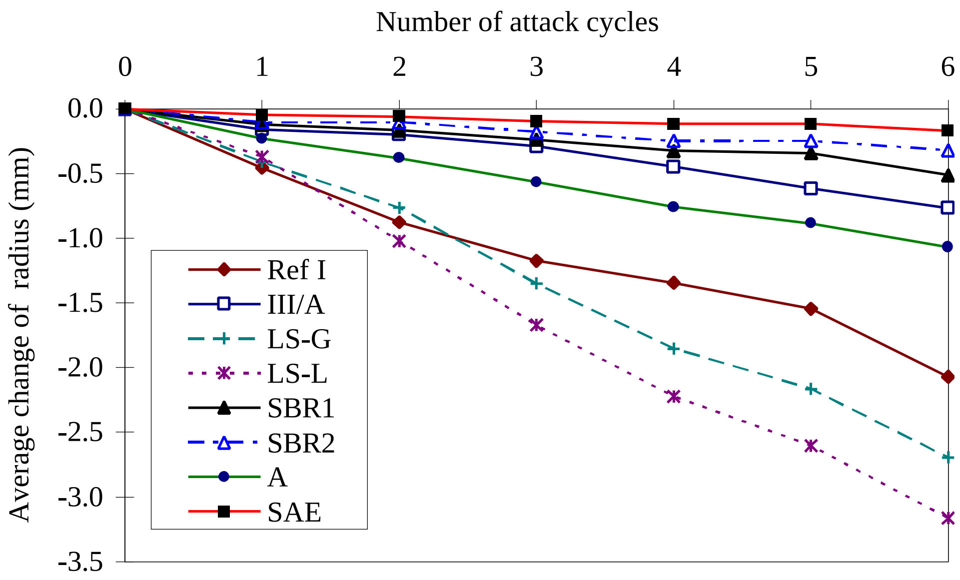

Figure 2. Average attack depth of the different concrete types of experiment 1 (lactic/acetic acid) vs. number of attack cycles

Already after the first attack cycle, the PCCs and the concrete with blastfurnace slag cement appeared to be significantly more resistant than the reference concrete and the concretes with limestone sand (Student-Newman-Keuls test with level of significance = 0.05). This difference increased after every cycle. Also the polymer cement concrete *A* appeared to perform significantly worse than the other PCCs. This could be expected from the difficulties encountered during compaction of *A* and the inferior physical characteristics. From cycle three onwards the average attack depth of the concretes with limestone sand surpassed the average attack depth of the reference concrete. Furthermore the concrete with limestone sand and limestone aggregates was more degraded than the one with limestone sand and gravel. The neutralizing effect of limestone sand and limestone aggregates was insufficient to limit the total attack. After six attack cycles the average attack depths for the different concrete compositions were all significantly different and varied between 0.17 mm for *SAE* and 3.16 mm for *LS-L*. The vulnerability to attack by lactic and acetic acid increased in the following order: PCC with the styrene acrylic acid ester *SAE*; PCC with the styrene butadiene latex *SBR2*; PCC with the styrene butadiene latex *SBR1*; concrete with blastfurnace slag cement III/A; PCC with the acrylic latex *A*; reference concrete with ordinary Portland cement *Ref I*; concrete with lime sand and gravel aggregates *LS-G*; concrete with lime sand and limestone aggregates *LS-L*. Modification of the concrete with styrene acrylic ester therefore seemed to be the best solution, even though investigation with the scanning electron microscope showed that the emulsified polymer had not completely formed a film. This would be due to the relatively high minimum film forming temperature of this polymer (32°C). Comparison with an on-farm trial (De Belie 1997b) revealed that the degradation of the reference concrete after two attack cycles of the TAP was similar to the attack of concrete slats in houses for fattening pigs after 9 months in front of the wetfeeders.

Average Surface Roughness

The most important factor influencing the R_a-value, was again the concrete composition. Fig. 3 shows the R_a-value of the different concrete types versus the number of attack cycles. Initially *SAE* showed a significantly larger surface roughness (R_a = 0.10 mm) than the other concretes, except *LS-L* (Student-Newman-Keuls test with level of significance = 0.05). The subsequent increase in roughness was however extremely small (R_a = 0.18 mm after six cycles). The increase in surface roughness of the two PCCs with styrene-butadiene latex, *SBR1* and *SBR2*, was also limited. The R_a-value of *A* surpassed the others till cycle four; then *LS-G* began to show the largest surface roughness. The surface of the *LS-L* concrete remained much smoother, due to the equal erosion of limestone aggregates and cement paste. After the six attack cycles the surface roughness increased as follows: PCC with the styrene acrylic acid ester *SAE*; PCC with the styrene-butadiene latexes *SBR2* or *SBR1*; concrete with limestone sand and limestone aggregates *LS-L*; concrete with blastfurnace slag cement *III/A*; PCC with the acrylic latex *A*; reference concrete with ordinary Portland cement *Ref I*; concrete with limestone sand and gravel aggregates *LS-G*.

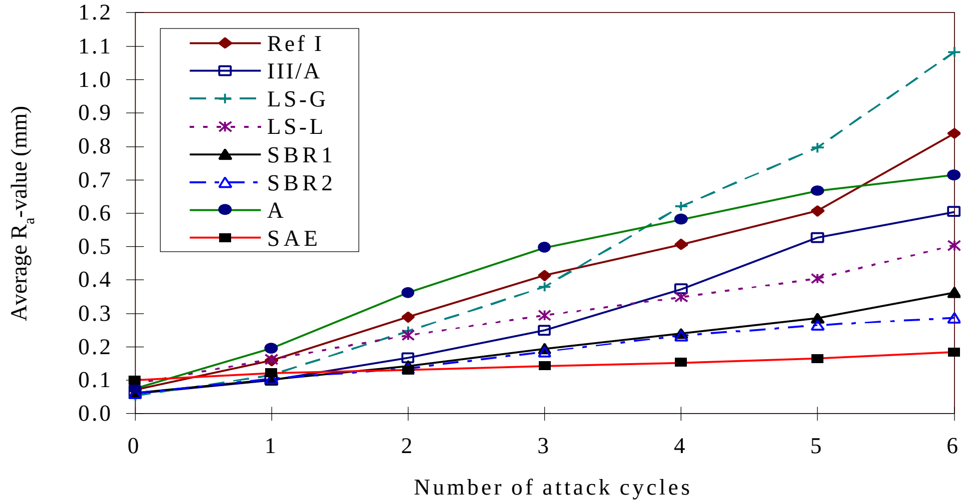

Figure 3. Average surface roughness of the different concrete types of experiment 1 (lactic/acetic acid) vs. number of attack cycles

3.2 Experiment 2: sulfuric acid attack

Average change in radius

In Fig. 4 the average change of the radius of the cylinders is shown versus the number of attack cycles for the different concrete mixtures. For every cycle two measurements were performed: one before and one after brushing the cylinders. A positive value represents an expansion of the cylinders compared to the initial size, while a negative value means that due to loss of material, the radius of the cylinder decreased compared to the initial dimensions. The alternating increase and decrease of the radius corresponds to alternating expansion of the concrete due to immersion and formation of reaction products and subsequent material loss due to brushing.

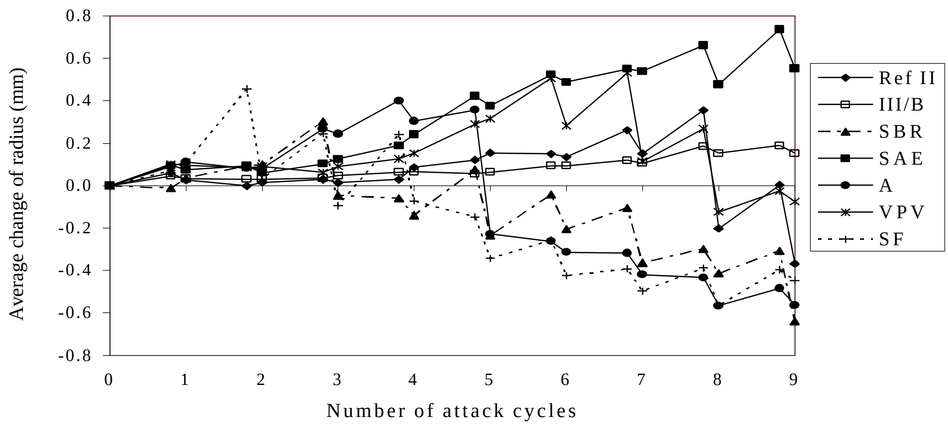

Figure 4. Average change of radius of the different concrete types of experiment 2 (sulfuric acid) vs. number of attack cycles

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From the fifth cycle on the different mixtures could be classified in at least two groups (student-Newman-Keuls test with level of significance 0.05). One group included the reference mixture, the mixture with blast furnace slag cement and the mixtures with the styrene acrylic ester polymer and the vinylcopolymer. The other group, which appeared to be more vulnerable to degradation, included the mixtures with acrylic polymer, styrene butadiene polymer and silica fume. The reference mixture and the mixture with vinylcopolymer showed only after eight cycles a decrease of the radius relative to the initial radius. The mixtures with the blast furnace cement and the styrene acrylic ester polymer still showed a resulting expansion after nine cycles. For the mixture with the styrene acrylic ester polymer the increase of the radius was significantly larger (0.6) mm than for the mixture with blast furnace slag cement (0.2 mm). After nine cycles the reference mixture joined up with the second group, including also the mixture with silica fume, the mixture with the acrylic polymer and the mixture with the styrene-butadiene polymer.

Figure 5 shows the cumulative changes of the average radius of the different mixtures due to brushing of the cylinders. These values represent the sum of all differences between the radius measured after brushing and the radius measured before brushing during the same cycle. This figure, excluding the effect of expansion during immersion in the sulfuric acid solution, makes more clear that especially the concrete types with blastfurnace slag cement or styrene acrylic ester polymer are quite resistant to abrasion. The compositions with silica fume or styrene butadiene showed the most severe loss of material. Especially the results of the silica fume mixture were below expectations. In general silica fume addition induces an increased resistance of concrete to chemical aggression, due to a refinement of the pore structure, a reduced permeability, a reduction of the calcium hydroxide content and an increase of the content of calcium silicate hydrates. Many researchers have found positive results in the specific case of concrete subjected to sulfate attack by adding silica fume to the concrete mix. The results of compressive and water absorption tests (Table 3) indicate that also in our case the silica fume concrete was of high quality. Nevertheless there are some other investigations which show little or no positive effect of silica fume addition with respect to sulfate attack. Neville (1981) stated that in case of sulfate attack, the influence of silica fume is ambiguous. Talero (1996) found that ettringite formation associated with the reaction of puzzolans occurred much faster than with the ordinary hydration products. This resulted in an increased corrosion rate. Another reason might be that the pore refinement leads to a lack of expansion space for the voluminous reaction products gypsum or ettringite. Scherer & Fidjestöl (1995) use the same theory to explain why a greater water-cement ratio (>0.5) can result in a decrease in degradation by sulfates.

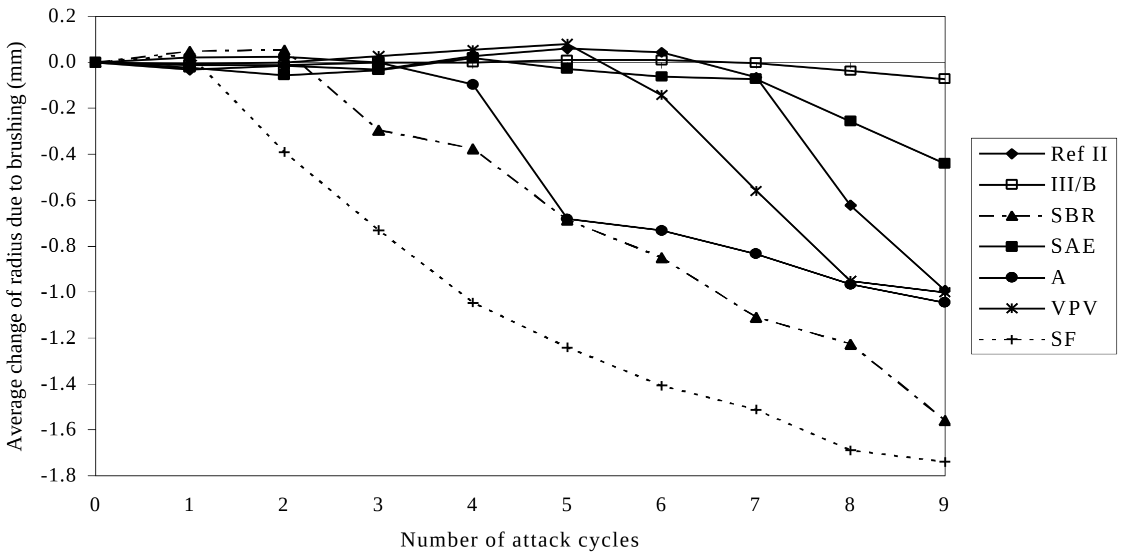

Figure 5. Cumulative change of the average radius of the concrete types of experiment 2 (sulfuric acid) due to brushing

The average R_a-value of the cylinders versus the number of cycles is shown in figure 6. The specimens with blast furnace slag cement showed a limited change in roughness. For all other mixtures, with exception of the mixture with the acrylic polymer, a gradual increase was measured during the subsequent cycles. The mixture with the acrylic polymer showed a peak after cycle 4 followed by a decrease of the roughness after cycle 5 and 6. This peak corresponds with a large expansion of the cement paste, followed by a significant amount of matrix material being detached. By this detachment the difference in level between the cement paste and the aggregates was again reduced.

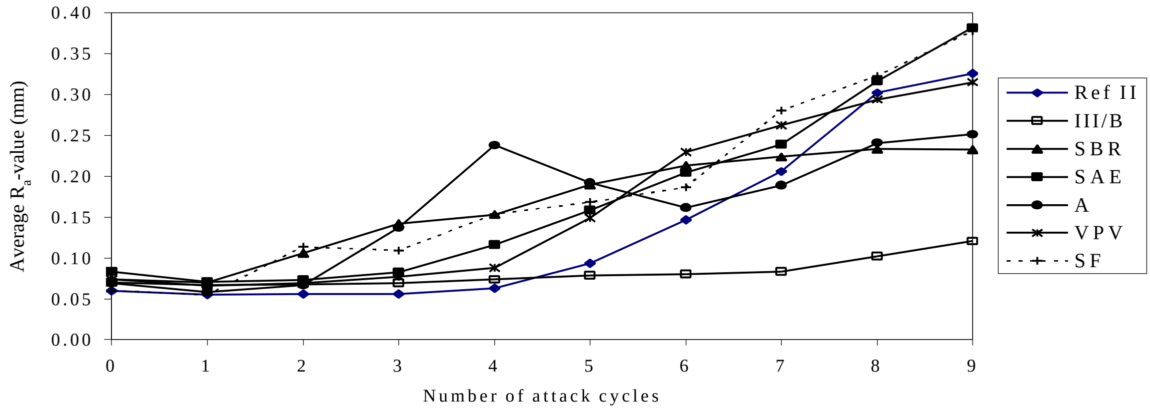

Figure 6. Average surface roughness of the different concrete types of experiment 2 (sulfuric acid) vs. number of attack cycles

3.3 Comparison of lactic/acetic and sulfuric acid attack

De degradation mechanism is completely different for the two liquids. The reaction between concrete and the organic acids involves an acid-base reaction with formation of soluble salts which are leached. Because of the continuing removal of free lime and the associated pH-drop the calcium silicate hydrates become unstable. The concrete surface is weakened and surface material is easily detached by brushing. On the contrary, the sulfuric acid attack is mainly described as the formation of expansive reaction products such as gypsum and ettringite. The latter is formed by reaction between calcium sulfate and the tricalcium aluminate of the cement and contains 32 water molecules in its structure. The increase in internal pressure results in development of cracks. Although some authors mention that also calcium lactates can cause an internal pressures (Kleinlogel 1960), no expansion was noticed during our experiments. In addition no cracks were found during the microscopic examinations on thin sections and with scanning electron microscopy (De Belie *et al*. 1997b). Figure 4 shows that the expansion linked to sulfuric acid attack was relatively large: up to 1.3 mm cumulative expansion over the 9 cycles for the silica fume concrete and about 0.7 mm for the reference concrete with Portland cement, even though high sulfate resistant cements were used in all compositions.

The organic acids used are much weaker than sulfuric acid, and the associated pH amounted to 2 compared to a pH of 1 for the sulfuric acid solution. Also the attack cycles involved a 6 day immersion for the organic acid attack and a 12 day immersion for the sulfuric acid attack. Nevertheless, the degradation caused by these organic acids was more severe. The reference concrete with Portland cement showed a decrease in radius of about 2 mm after 6 attack cycles of 6 days in the lactic/acetic acid solution (Fig. 2) and only 1 mm after 9 cycles of 12 days in the sulfuric acid solution (Fig. 5: cumulative decrease in radius without taking the expansion into account). Also the surface roughness at the end of the experiment was larger for the reference concrete subjected to lactic/acetic acid (about 0.8 mm compared to about 0.3 mm for the sulfuric acid solution). Apart from the different reaction mechanism, also the difference in acid concentration may be a reason for this effect (60 g lactic + acetic acid per liter simulation liquid compared to 5 g sulfuric acid). Bayoux *et al*. (1990) also mention that for weak acids such as lactic and acetic acid the acceptable pH limits are higher than for strong acids, because weak acids must be present in a higher concentration to cause the same pH. However, it must be noted that the concentrations used were realistic concentrations occurring on floors in animal houses and in sewer systems, respectively.

4 CONCLUSIONS

De resistance of different concrete compositions to aggressive solutions, firstly with lactic and acetic acid, and secondly with sulfuric acid, was tested with an apparatus for accelerated degradation tests (TAP). The aim was to simulate degradation in agricultural environments: on floors in animal houses and silage storage structures, and in manure storage facilities, respectively. It appeared that the degradation by the organic acids proceeded much faster, although the associated pH was higher. The degradation mechanism was also completely different, and involved mainly a leaching action for the lactic/acetic acid attack and the formation of expansive compounds for the sulfuric acid attack.

In both cases the use of blastfurnace slag cement instead of Portland cement was beneficial, even though high sulfate resistant Portland cement was used in the case of sulfuric acid attack. The effect of polymer modification depended highly on the type of polymer used. Addition of a styrene acrylic acid ester was the optimal solution in the case of lactic/acetic acid attack, whereas it resulted in a high expansion and increase in surface roughness in the case of sulfuric acid attack. Nevertheless, this expansive reaction was not associated with a loss of structural integrity and the detachment of material by abrasion was very limited. Modification with styrene butadiene polymer gave the second best results in the case of lactic/acetic acid attack, where it had rather a negative effect in the case of sulfuric acid attack. Acrylic polymer addition did help in neither case. Modification with vinylcopolymer was only tried in the case of sulfuric acid attack, but did not lead to a clear improvement, and silica fume addition caused a decrease in resistance.

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