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INFLUENCE OF THE CEMENT TYPE ON THE RESISTANCE OF CONCRETE TO FEED ACIDS

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ABSTRACT

Concrete in animal houses is subject to aggressive substances from feed and manure. Chemical attack by the most important feed acids, lactic and acetic acid and abrasion caused by animals and cleaning, were simulated and studied using accelerated corrosion tests. The resistance of concrete prisms with different cement types and approximately constant water-to-cement ratio, to simulation liquids with different pH-values, was investigated. The decrease of volume in terms of percentage and the mass loss per unit area were measured, as well as the pH-change and calcium content of the liquids. It appeared that the cement type had an important influence on concrete resistance in the highly to very highly aggressive simulation liquids. Four groups with decreasing vulnerability to the attack were distinguished: portland cement without C_3A, ordinary portland cement, cement containing fly ashes, blastfurnace slag cement. The percentage of slag in the slag cement and the cement content of the pozzolanic cement had no significant influence.

Introduction

Concrete in animal houses is subject to aggressive environmental conditions. Chemical components from feed remnants and manure may attack the concrete floor surface. By mechanical impact from animals and high-pressure cleaning this unstable surface material is removed. The increased concrete roughness and enlarged gap between beams of slatted floors can result in animal injuries (1,2). In a further stage the attack may even cause failure of slat beams.

The attack of concrete floors is especially severe near the feed- and water-supply (3). In preliminary investigations, the souring of mixtures of pig meal and water was registered and samples taken on floors in pig houses were analysed. The results showed that acetic and especially lactic acids are formed in meal-water-mixtures, resulting in a pH possibly below

4.5. In samples on the floor also mainly lactic and acetic acids were found. Lactic and acetic acid are very aggressive, because their reaction with free lime ($Ca(OH)_2$) of the concrete produces very soluble calcium salts (4). When those salts are leached, the concrete porosity will increase and the pH in the pores will decrease. Furthermore calcium lactate crystals may cause an internal stress in the concrete, resulting in cracks. The hydrates of the hardened cement paste will start decomposing and the concrete disintegrates. For weak acids such as lactic and acetic acid, the acceptable pH-limits are even higher than for strong acids, because weak acids must be present in a higher (more aggressive) concentration to cause the same pH (5).

The resistance of concrete to chemical attack is mainly determined by its permeability, its alkalinity and the chemical composition of the cement paste. The permeability mainly depends on the geometry of the pores and their distribution. The lower $Ca(OH)_2$ content and the finer pore structure of blast furnace slag concrete and fly ash concrete could therefore contribute to a larger resistance.

The hydration products of portland-slag cements are the same as for portland cement, except that, at higher slag contents, smaller quantities of calcium hydroxide are found. The inclusion of slag affects both the porosity and pore-size distribution of pastes at ambient temperatures. Especially the volume of large pores (> 300 mm diameter) is reduced, which decreases the permeability and increases the strength of the cement paste (6). The increase in time of setting and hardening and the lower early-age compressive strength (7) partly explain why blast furnace slag concrete has not been used for precast concrete slats up to now. Furthermore these concretes should be given more curing to ensure proper strength and durability, because of the slower hydration.

The hydration products of fly ash-cement mixes are also essentially the same as those of portland cement under normal conditions of curing, but the rate of development of hydration products is slower for low calcium fly ash (8). A cement-fly ash paste contains more CSH gel, with a lower Ca/Si ratio and less $Ca(OH)_2$ than portland cement alone, because of the pozzolanic reaction. The capillary porosity of hardened cement paste with fly ashes is very homogeneous, which improves the concrete quality (9). Partial replacement of cement by fly ash, implies relatively larger pores at early age: because of the lower cement content, the actual water-to-cement ratio is increased (10). Therefore proper curing is very important. Because of the pozzolanic reaction however, relatively smaller pores are found after 1 to 3 months (11).

Materials

Test Specimens. Concrete prisms with different cement types were compared. Table 1 shows the classification of cement in accordance with the Belgian standard NBN B12-001, based on the draft of the European EN 197.1.

The composition of the reference concrete mix was based on the mix used by a manufacturer of precast concrete slats: a stiff mix with a quite high cement content and a low water-to-cement ratio. CEM I is currently the only cement used for slatted floors in Belgium and it is also the cement most frequently used for solid floors. The composition of all experimental mixes is shown in Table 2. The cement name is usually followed by the strength class: 32.5, 42.5 or 52.5, pointing to the minimum strength in N/mm^2 at 28 days. A letter R is added for cement with a high strength at early age. For CEM II two different cement contents were applied. The higher cement content compensates for the lower percentage of clinker in the

TABLE 1
Cement Types in Accordance with the Standard NBN B12-001 (Mass Percentages Referring to the Main Part of the Cement, excl. Calcium Sulphate and Additives)

Type	Name	Abbreviation	Main components				
			Clinker	Slag	Fly ash	Lime-stone	Additional components
I	Portland cement	CEM I	95-100	-	-	-	0-5
II	Pozzolanic cement	CEM II/A-M	80-94	← 6-20 →			
		CEM II/B-M	65-79	← 21-35 →			
III	Blastfurnace slag cement 36/65	CEM III/A	35-64	36-65	-	-	0-5
	Blastfurnace slag cement 66/80	CEM III/B	20-34	66-80	-	-	0-5
	Blastfurnace slag cement 81/95	CEM III/C	5-19	81-95	-	-	0-5
V	Composite cement	CEM V/A	40-64	18-30	18-30	-	0-5

pozzolanic cement. The fly ash used in CEM II is a low calcium fly ash. Beside the common cement types a CEM I without C_3A was tested. Because C_3A is the cement component most vulnerable to sulphate attack, cements with low C_3A-content are usually recommended for concrete having to resist solutions with high sulphate content. The Belgian standard NBN B12-108 specifies that a C_3A-content below 3% is required for a portland cement to be referred to as a HSR (high sulphate resistant) cement. The flow of the concrete mixes in accordance with the standard NBN B15-233 is shown in Table 2, which proves that the mixes are quite stiff. The slump in accordance with the standard NBN B15-232 was too small to be significant (5 to 10 mm).

Tiles with dimensions 400 × 400 × 40 mm were cast, as well as cubes with 158 mm side. The concrete was compacted using a vibrating plate. The test specimens were stored at 20 ± 2°C and a relative humidity above 90%. At 28 days two or three cubes were measured for compressive strength as described in the standard NBN B15-220. The results are shown in Table 2. Out of the tiles, prisms with dimensions 40 × 40 × 80 mm were cut for the corrosion tests, which began when the concrete was about 2 months old. Three half tiles of each concrete mix were submitted to a water absorption test as prescribed by the standard NBN B15-215. The results are also shown in Table 2.

Aggressive Liquids. To simulate the actual conditions floors in pig houses are subject to, four simulation liquids were prepared with a lactic acid concentration of 30 g/l and an acetic acid concentration of 30 g/l, the highest concentrations registered during the preliminary investigations. A first simulation liquid (SL1), containing only lactic and acetic acid in water, had a pH of 2.0 - 2.2, which is extremely aggressive to concrete. To obtain buffers with different levels of aggressiveness, a certain amount of NaOH was added, based on the acid dissociation constants of the acids (12): for lactic acid $K_a = 1.38 \cdot 10^{-4}$ at 25°C ($pK_a = 3.86$); for acetic acid $K_a = 1.8 \cdot 10^{-5}$ at 25°C ($pK_a = 4.74$). This allowed us to obtain three more

TABLE 2
Concrete Composition, Flow, Density, Compressive Strength and Water Absorption

N°	I	I*	II	II*	III/A	III/B	III/C	V
Cement type	CEM I 42.5 R	CEM I 42.5 R 0% C_3A	CEM II/B-M 42.5	CEM II/B-M 42.5	CEM III/A 42.5	CEM III/B 42.5	CEM III/C 32.5	CEM V 32.5
Cement content (kg)	375			420	375			
Sand° 0/2 (kg) 0/5 (kg)	280 420			270 400	280 420			
Gravel° 4/7 (kg) 4/14 (kg)	120 1050			114 1030	120 1050			
Water (kg) W/C	146 0.39			155 0.37	146 0.39			
Flow (-)	1.25	1.31	1.16	1.15	1.28	1.15	1.21	1.21
Mean density (kg/m³)	2405	2410	2405	2395	2415	2435	2400	2410
Mean compressive strength at 28 days (N/mm²)	63.7	64.0	63.7	57.8	66.5	66.4	45.6	53.7
Mean water absorption (%)	3.85	3.90	4.20	4.50	4.15	4.15	4.95	4.60

° sand : a mixture of 40% sand 0/2 and 60% sand 0/5
gravel : a mixture of 10% gravel 4/7 and 90% gravel 4/14
sand/gravel ≈ 0.6

simulation liquids: SL2: 8.22 g NaOH/l, pH = 3.8; SL3: 18.06 g NaOH/l, pH = 4.5; SL4: 29.97 g NaOH/l, pH = 5.5. The pH-value of 3.8 was the lowest pH measured in acidified meal-water-mixtures. The pH = 4.5 is the limit between the classes 'very highly' and 'highly' aggressive, and 5.5 between 'highly' and 'moderately' aggressive (Dutch standard NEN 5996). As a reference tap water was used (SL0).

Experimental Procedure. For each concrete mix 15 prisms of 40 × 40 × 80 mm were subject to four cycles of 8 days in a simulation liquid. The cyclical exposure procedure with alternate wetting and drying accelerates the attack (13). Before each cycle and at the end of the test the prisms were kept in water until they reached a constant mass. Then the volume was determined by hydrostatic weighing. The samples were dried at 60 ± 5% humidity for one day and afterwards the samples were put in threes in containers with 800 ml of the liquids. After four days of a cycle the pH of the liquids was adjusted to the original pH for SL2, SL3 and SL4 and to a pH = 3 for SL1, by adding concentrated lactic and acetic acid. At the end of a cycle, before determination of the volume, the dry prisms were brushed to detach the unstable concrete. For brushing a stationary drilling-machine was used, on which a circular brush was fixed. Each face of the prisms was brushed at a constant pressure during 40 seconds at 350 rpm. The detached material was dried at 105°C and weighed. The simulation liquids were filtered to determine the mass loss by mere chemical attack. A sample of the liquids was taken to measure the calcium content by flame photometry.

To judge the concrete deterioration several characteristics were measured or calculated after each cycle:

-the decrease of volume in terms of percentage
-the decrease of the saturated mass per unit area
-the mass loss by mere chemical attack and the mass of the material detached by brushing
-the pH-change of the simulation liquid
-the calcium content of the simulation liquid

The first two characteristics were used to search for significant differences between concrete compositions with the Student-Newman-Keuls test of the statistical package SPSS. These two measures may result in a different classification. A decrease of volume can be caused by desintegration of the hardened cement paste or by aggregates falling out of the matrix. Cement paste and aggregates have a different density and the density of the cement paste may also differ from place to place. Furthermore the mass loss includes the leaching of components under the concrete surface. For these reasons a measured change of volume can correspond to different mass losses. When considering slim elements, subject all around to an aggressive solution, the decrease of volume may be most important; when working with flat elements, subject to attack at the surface, the mass loss should be taken into account.

Results and Discussion

Decrease of Volume and Mass Loss Per Unit Area. In Fig. 1 and Fig. 2 the decrease of volume in terms of percentage and the mass loss per unit area after 4 cycles are shown, except for SL0 (tap water), in which the changes were very small.

For SL2 and SL3 four groups can be clearly distinguished: the CEM III concretes show the best resistance, followed by the CEM II and CEM V concretes; the usually used CEM I concrete is more attacked and the concrete with CEM I with 0% C_3A is even more vulner-

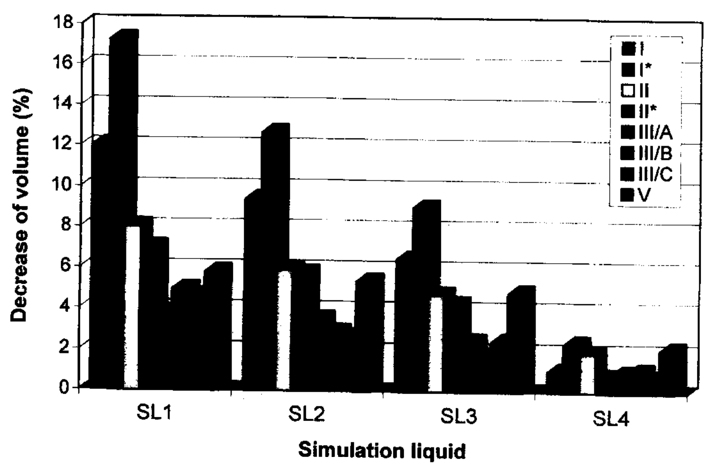

FIG. 1.
Decrease of volume of concrete prisms with different cement types in simulation liquids with lactic and acetic acid after 4 attack cycles.

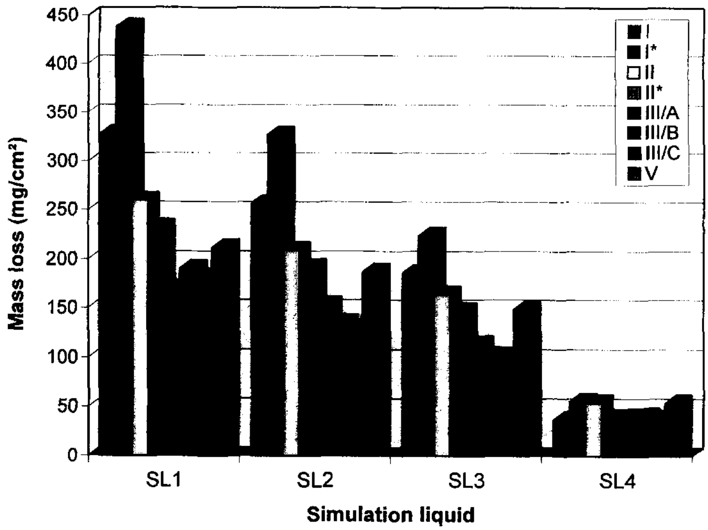

FIG. 2.
Mass loss per unit area of concrete prisms with different cement types in simulation liquids with lactic and acetic acid after 4 attack cycles.

able. For SL3 the differences in the decrease of volume between these four groups are significant, for SL2 the difference between the first two groups is not significant. When considering the mass loss per unit area, less significant differences can be found, but the difference between the CEM III concretes and the CEM I concretes remains significant.

In an extremely aggressive environment (SL1) it appears that CEM V concrete is slightly better than CEM II concrete. Only the differences between the concretes with CEM I without C_3A, ordinary CEM I and the other concretes are significant however.

In moderately aggressive conditions (SL4) the deterioration of the prisms is much reduced and the differences are less pronounced. Nevertheless there is a small (significant) difference between the concretes with CEM I with 0% C_3A, CEM V and CEM II with a cement content of 375 kg/m^3 concrete at the one hand, and the concretes with ordinary CEM I, CEM III and CEM II with a cement content of 420 kg/m^3 concrete, which are less attacked, at the other hand.

There are only slight and insignificant differences between the different CEM III types. The amount of slag, when exceeding 35% seems therefore of little importance. For CEM II the concrete with a higher cement content has a slightly better performance in all simulation liquids. The fact that the influence of the cement content is rather small is in agreement with previous results (14).

In Fig. 3 the evolution of the mass loss per unit area is represented.

Apparently in SL1 and SL2 and for some compositions also in SL3 and SL4, the rate of attack is larger during the first cycle than during the second and third cycle and often increases again during the last cycle. After attack on the vulnerable $Ca(OH)_2$ at the concrete surface and removal of the unstable concrete, the acids will penetrate deeper until larger entities of the cement paste are detached. In SL1 and SL2 also some of the coarse aggregates are removed during the fourth cycle. CEM I without C_3A seems to be a little more resistant than

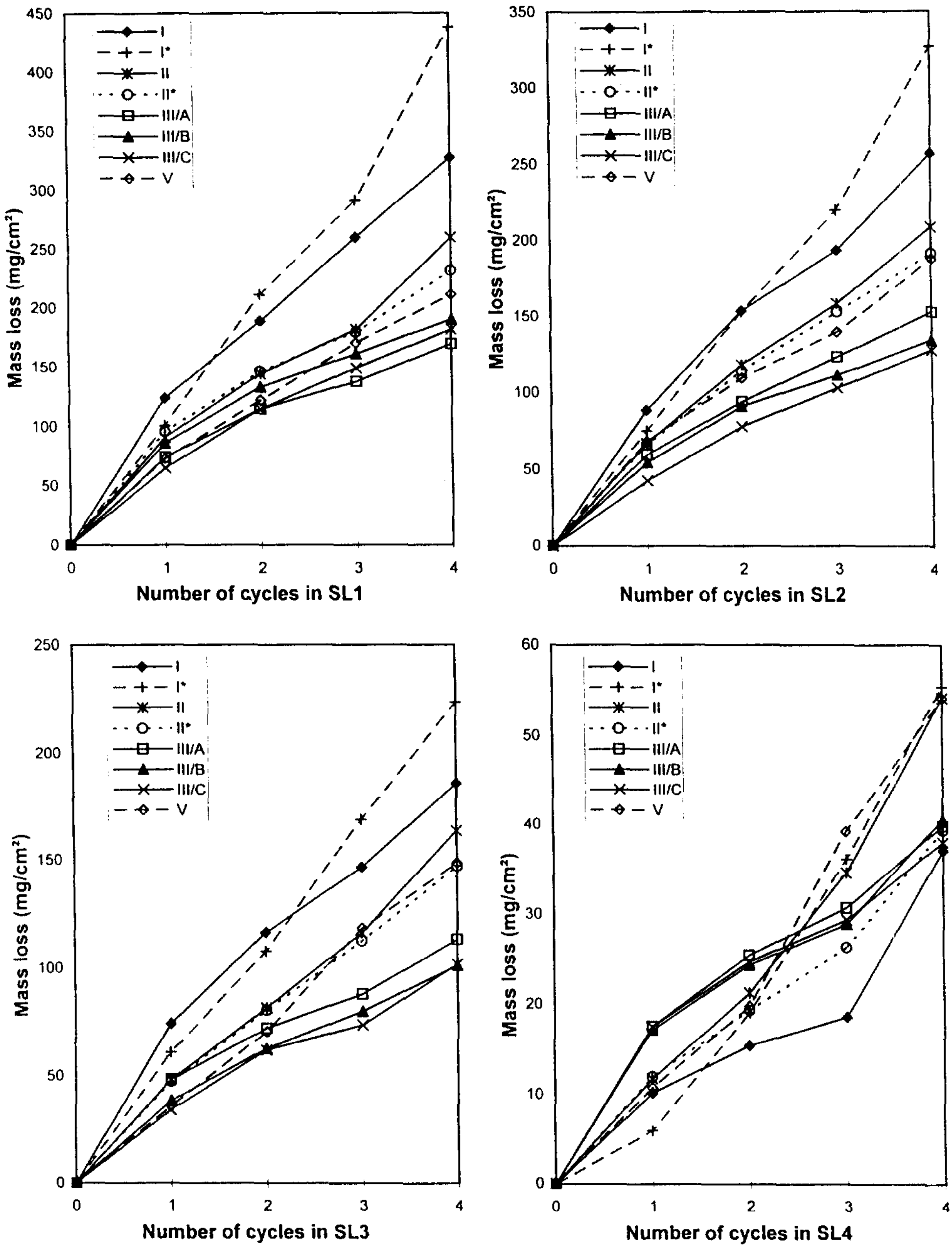

FIG. 3.
Evolution of the mass loss per unit area of concrete prisms with different cement types in simulation liquids with lactic and acetic acid.

ordinary CEM I during the first cycle. This alters during the 2nd or 3rd cycle and the difference becomes more pronounced during the 4th cycle. Also the difference between CEM I, CEM II and CEM III becomes more clear when the deterioration process proceeds. In SL4 the two groups mentioned above can only be distinguished from the third cycle onwards.

Calcium Content and Dissolved Material. The mass loss can be split up as follows:

mass loss = mass loss caused by mere chemical attack
+ mass of the material detached by brushing
+ mass of the dissolved material
+ other losses

The term 'other losses' comprises the material detached by transportation, water immersion, weighing, ... Accepting this term to be small, the mass of the dissolved material can be calculated. The mass loss by dissolution per unit area has a high correlation with the calcium content of the simulation liquid (correlation coefficient $r = 0.96$). This is shown for the total of the 4 cycles in SL1 in Fig. 4. The correlation of the calcium content with the total mass loss per unit area is somewhat smaller ($r = 0.87$). Obviously there is also some correlation of the pH-rise with the calcium content of the simulation liquid, e.g. with regard to SL1 and the total of the 4 cycles, $r = 0.88$.

Compressive Strength. When the corrosion tests were finished, the compressive strength was determined on two prisms kept in SL0 and two prisms kept in SL1. To adjust the figures for these prisms, that had different dimensions from the cubes measured before the corrosion tests, the standard NBN B15-220 (1970) was consulted. It appeared that allmost all test specimens gained strength in SL0 (tap water), due to the proceeding hydration process. The decrease in strength of the prisms in SL1 was large (17 to 46 N/mm^3) and the remaining strength ranged from 15 to 34 N/mm^3. This shows that the attack process is not so superficial as might be thought. No correlation between the strength loss and the decrease of volume or mass loss per unit area could be found.

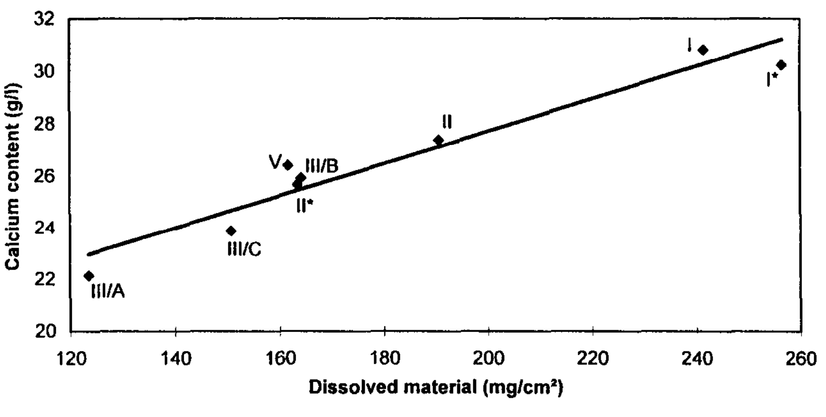

FIG. 4.
Correlation of the dissolved material per unit area with the calcium content of the simulation liquid (total of the 4 attack cycles).

Conclusion

The cement type appears to have an important influence on the corrosion of concrete by feed acids. In very highly to highly aggressive simulation liquids containing lactic and acetic acid (pH-values 2.0-2.2; 3.8; 4.5) four groups with decreasing change of volume in terms of percentage and mass loss per unit area could be distinguished:

1) portlandcement without C_3A,
2) ordinary portland cement,
3) cement containing fly ash,
4) blastfurnace slag cement.

The percentage of slag in the slag cement and the cement content of the pozzolanic cement had no significant influence. In the moderately aggressive simulation liquid (pH = 5.5) there were only small differences between the tested concrete types. The compressive strength of all prisms attacked by the most aggressive liquid was sharply reduced but no correlation between the strength loss and the decrease of volume or mass loss per unit area could be found.

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