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Resistance of different types of concrete mixtures to sulfuric acid

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ABSTRACT

The resistance of seven different concrete mixtures against a 0.5% sulfuric acid solution was examined. The difference between high sulfate resistant Portland cement and blast furnace cement, as well as the influence of polymer modifications of the concrete and the addition of silica fume were issues of the investigation. All concrete mixtures were submitted to an alternating immersion and drying during 18 weeks in a 0.5% sulfuric acid solution using a testing apparatus for accelerated degradation tests. The corrosion of the concrete was quantified by measuring the change in dimensions of the test specimens with laser sensors. The mixture with addition of silica fume was most vulnerable to corrosion. Depending on the polymer type used, polymer modification of the concrete resulted in an increase and a decrease in the resistance of the concrete respectively. The concrete made with blast furnace cement had the highest resistance of all tested concrete types.

RÉSUMÉ

La résistance de sept bétons différents à l'action corrosive d'une solution contenant 0,5% d'acide sulfurique a constitué le sujet de cette recherche. La différence entre un ciment Portland à haute résistance aux sulfates et un ciment de haut fourneau, ainsi que l'influence de la modification de polymères et de l'ajout de fumée de silice ont été examinées. Tous les bétons ont été soumis, en alternance pendant 18 semaines, à une immersion dans la solution sulfurique et à un séchage, au moyen de l'appareil d'essais de corrosion accélérée. L'action de la corrosion a été mesurée avec des lasers mettant en évidence les changements de dimension des éprouvettes. Le béton contenant de la fumée de silice a présenté la moins bonne résistance par rapport aux autres bétons. La résistance du béton augmente ou diminue suivant le type de polymère utilisé. Parmi tous les bétons, c'est le béton fait de ciment de haut fourneau qui a offert la meilleure résistance.

1. INTRODUCTION

It is well known that concrete is not very resistant to acids. Especially contact between concrete and sulfuric acid, which is a very strong acid, often leads to a severe kind of concrete corrosion [1]. For instance the walls of concrete sewer pipes which are in contact with soils rich in sulphates can be deteriorated by this kind of corrosion. Due to the action of sulphate-reducing bacteria, the sulphates in the soil can be converted to sulphides, which can combine with iron to form pyrites. When oxygen and water are available pyrite is converted in iron sulphate and sulfuric acid is formed. The reaction between the sulfuric acid and the calcium hydroxide (CH) in the concrete leads to the formation of gypsum. This is associated with an increase in volume by a factor of 1.2 to 2.2 [2-5]. The formed gypsum further reacts with the calcium aluminate (C_3A) hydrate in the concrete. The reaction product is the ettringite mineral, which has a volume a few times greater than the volume of the initial compounds. Thus the formation of ettringite creates a large volume expansion, which leads to an increase in internal pressure and subsequent deterioration of the concrete.

In the literature the positive effect of polymer modification on the durability of concrete has been mentioned before [6-8]. The addition of a polymer latex to the fresh concrete mixture results, during the hydration of the cement, in the formation of a more or less continuous film, depending on the film formation capacity of the added polymer and the amount of polymer added.

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The presence of the polymer film leads to changes in the properties of the microstructure of the concrete, which has an influence on durability. Although the changes depend on the type and amount of polymer used, in general positive influences are reported. As the effect on the pore structure gives rise in most cases to a decrease in the volume of the larger pores (radius > 0.2 μm) together with an increase in the smaller pores (radius < 0.075 μm), this results in a refinement of the pore grading and often a decrease in the total porosity [7, 9]. Due to the presence of the polymer film some pores are filled or sealed so that they do no longer participate in the transport of gas, vapour or liquids through the concrete. Most polymers have some water-reducing qualities so that for a given target workability a lower w/c ratio can be used which also results in a higher concrete quality [9, 10]. The above mentioned effects, characteristic for polymer modified concrete, provide a significant decrease in the permeability of the modified concrete.

A lot of investigations have pointed out that the interface aggregates-cement paste is one of the most vulnerable parts of the cement paste also concerning chemical attack [11, 12]. Polymer modification attributes to a better performance of the transition zone [8, 13, 14]. The quality of the transition zone is improved because of the relatively high concentration of polymer particles in this zone and/or because of the bridging effect between the cement paste and the aggregates.

Furthermore, polymer modification should have a positive effect on the structure of the hydration products. A more amorphous structure, with smaller amount of large crystals would be formed. This favours the mechanical strength of the concrete but also the chemical resistance of the hydration product [14, 15].

All those aspects should make polymer modified concrete more suitable than ordinary concrete for use in chemical aggressive environments with regard to acid attack [8]. Different investigations have already confirmed the beneficial effect of polymers on the chemical resistance of concrete [16-20]. The positive effect with regard to organic acid such as lactic and acetic acid has been shown in previous experiments [18, 19]. Kaempfer [16] and Kaempfer and Berndt [17] also found a better performance due to the addition of styrene butadiene polymer and styrene acrylic polymer in tests using sulfuric acid solutions with different pH values.

Most researchers share the same opinion that creating a good quality concrete, by lowering the porosity, improves in most cases the overall durability of the concrete [1, 21-23]. A decrease in the porosity of concrete can be obtained in different ways: use of low w/c ratio, use of superplasticizers, use of mineral admixtures such as fly ash and silica fume. The general advantages regarding the structure of the cement paste due to the use of silica fume are well known. All investigations show a positive influence on the pore size distribution. An increase in small pores and a decrease in large pores results in a refinement of the pore structure [21, 24-26]. Although a decrease in the total porosity is not confirmed in all investigations, in most cases a decrease in the permeability was found [26, 27]. Generally it can be stated that the addition of silica fume results in a concrete with a denser structure [23, 27]. Furthermore the addition of silica fume leads to a decrease or a complete elimination of the free and leachable calcium hydroxide [21, 23-27].

In spite of all those positive aspects the use of silica fume, in case there is a risk of sulfate attack, is an object of controversy. Lots of researchers have found positive results concerning durability of concrete subjected to sulfate attack by adding silica fume to the concrete mix [21, 24, 27-30]. The better performance of those mixes was mostly attributed to the refinement of the pore structure, the decrease in the permeability and the lowering of the calcium hydroxide content. Durning *et al.* [21] reported that calcium silicate hydrate paste formed with silica fume should be more stable in low pH environments, which also contributes to the better concrete performance. In this respect Taylor [23] also mentioned that the use of silica fume leads to the creation of a more uniform structure of the calcium silicate hydrate phase. Other positive effects of silica fume should be the lower C/S ratio in the calcium silicate hydrates which includes the possibility to incorporate a higher amount of aluminium, thus lowering the amount of aluminium available for ettringite formation. On the other hand some investigations show less or no positive effect of silica fume addition with respect to sulfate attack [1, 31, 32]. Neville [1] stated that in case of sulfate attack, the influence of silica fume is ambiguous. Talero [32] 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.

2. MATERIALS AND METHODS

2.1 Materials

Three parameters were tested: the influence of the cement type (high sulfate resistant Portland cement ↔ blast furnace slag cement), the influence of polymer modification and the influence of the addition of silica fume. Therefore eight different concrete mixtures were made: two mixtures without addition of neither polymer nor silica fume (one reference mixture with high sulfate resistant Portland cement and one mixture with blast furnace slag cement), one mixture with addition of silica fume and five mixtures with addition of polymer.

All tested concrete mixtures, except one, were made with 350 kg/m^3 CEM I 42.5 HSR/LA Portland cement (EN 196). River sand (0/4 mm) and coarse aggregates (4/14 mm) were used in the mass proportion sand/coarse aggregates of 0.75. The reference mixture with Portland cement and the mixture with blast furnace cement (350 kg/m^3 CEM IIIB 42.5 LA/HSR, EN 196) were made with a w/c ratio of 0.4. Superplasticizer was added till a slump of class S1 (10 to 45 mm) was obtained.

Different polymer modified concrete mixtures were used to test if polymer modification would have a positive effect on the resistance against sulfuric acid. The influence of the type of polymer was taken into account by using four different polymer types (a styrene-acrylic ester polymer, an acrylic polymer, a styrene butadiene polymer and a vinylcopolymer). For the acrylic polymer two different latexes were tested (acrylic polymer A1 and A2). All five polymer modified mixtures were made with 7.5% D.W. polymer on cement content (= 26.25 kg/m^3 D.W. polymer). It appeared from earlier experiments [33] that this polymer concentration provided an economic optimum for concrete submitted to lactic/acetic acid attack. All those mixtures were made based on a fictitious w/c ratio of 0.4, meaning that the whole amount of latex added, was taken into account to calculate the fictitious w/c ratio. Depending on the workability of the mixture more water was added. The real w/c ratio was calculated taking into account the water content of the added latex. As an example 54.7 kg/m^3 (= 26.25 / 0.48) latex must be added of the styrene butadiene latex with dry weight of 48% to obtain a 7.5% dose polymer dry weight on a cement content of 350 kg/m^3; 85.3 l water must be added to the mixture to obtain a fictitious w/c ratio of 0.4 (140 – 54.7 = 85.3). To obtain concrete with a slump of at least class S1, the amount of water added had to be increased to 90.6 kg/m^3. The total amount of water added was 119 kg/m^3, including the water of the added latex (28.4 kg/m^3 = 0.52 x 54.7). So this mixture had a real w/c ratio of 0.34 (= 119/350).

To investigate the possible improvement due to addition of silica fume one mixture was made with addition of 8.6% silica fume by weight of cement. This mixture was also made with the purpose to create very dense concrete, so that this effect would improve the durability by less penetration of the acid into the concrete. The silica fume mixture was made by adding 30 kg/m^3 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. The mix proportions of all eight mixtures investigated are given in Table 1.

Table 1 – Mix proportions of the different concrete mixtures

Material (kg)	Concrete Mix							
	R	B	SBR	A1	SA	A2	VPV	SF
CEM I 42.5 HSR/LA	350	-	350	350	350	350	350	350
CEM IIIB 42.5 HSR/LA	-	350	-	-	-	-	-	-
Silica fume	-	-	-	-	-	-	-	30
Gravel 4/14	1120	1120	1124	1130	1119	1124	1092	1120
Sand	840	840	843	848	839	843	819	840
Water	140	140	90.6	48	97.3	86.9	104	130
Polymer (as latex) (polymer type)	-		54.7 (SBR)	93.75 (A1)	51.5 (SA)	58.3 (A2)	65.6 (VPV)	-
Superplasticizer	2.5	2.5	-	-	-	-	-	5
w/c ratio (-)	0.40	0.40	0.34	0.33	0.35	0.34	0.41	0.34

CEM I 42.5 HSR/LA: Portland cement
CEM IIIB 42.5 HSR/LA blastfurnace slag cement
SBR: styrene butadiene
SA: styrene-acrylic ester polymer
A: acrylic polymer
VPV: vinylcopolymer

2.2 Mechanical tests

The slump (NBN B15-232, 1982), the flow (NBN B15-233, 1982), the bulk density (NBN B15-213, 1982) and the air content (NBN B15-224, 1970) of the fresh concrete were measured during the production of the different mixtures.

The compressive strength (NBN B15-220, 1990) and the water absorption (NBN B15-215, 1989) at 28 days were determined for each mixture on 3 cubes (158 x 158 x 158 mm).

2.3 Accelerated chemical test method

The resistance of the different concrete compositions to sulfuric acid attack was investigated with a testing apparatus for accelerated degradation tests (TAP). A more detailed description of the used test method is given by De Belie *et al.* [34].

During the chemical test for each mixture three cylinders (Ø 270 mm, h = 70 mm) were subjected to a cyclic procedure of immersion in a 0.5% sulfuric acid solution and drying by air. The cylinders, fixed on horizontal axes, turned with a speed of 1 revolution per hour through separate recipients. Each point of the outer circumference was submersed during 1/3 of the rotation time. After each cycle, which lasted for 12 days, the cylinders were brushed with rotary brushes to remove weakly adhering concrete particles.

The corrosion of the specimens was measured using laser sensors, connected with a computer. Out of those measurements the change of the radius of the different cylinders could be calculated. The measurements were performed before as well as after brushing the cylinders. In that 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. A large expansion of the concrete as result of the immersion period does not always implicate a large loss of material due to brushing and vice versa. So because there was not always a clear relation between the two parameters quantifying both parameters was necessary to observe the whole corrosion process.

The measurements with the laser sensors were also used to calculate the surface roughness of the concrete after brushing the cylinders. The surface roughness was expressed by means of the R_a-value, which is based on

Table 2 – Properties of the different fresh concrete mixtures				
Concrete Mixture	Slump (mm/class)	Flow (-/class)	Density (kg/m^3)	Air content (%)
R (Reference mixture)	20/S1	1.69/F2	2430	3.0
B (Mixture with blast furnace cement)	15/S1	1.26/F1	2400	3.8
SBR (Mixture with styrene butadiene polymer)	40/S1	1.62/F2	2410	4.4
A1 (Mixture with acrylic polymer A1)	165/S4	2.25/F4	2025	17
SA (Mixture with styrene-acrylic ester polymer)	40/S1	1.47/F1	2370	4.0
A2 (Mixture with acrylic polymer A2)	105/S3	20.4/F3	2190	9.7
VPV (Mixture with vinylcopolymer)	75/S2	1.71/F2	2370	5.2
SF (Mixture with silica fume)	105/S3	1.71/F2	2420	3.6

the British standard BS1134. This value was calculated by determining the line, which represents the average of the measured profile, and counting all surfaces between that line and the measured profile. The division of this sum by the length of the specific line (a reference length of 50 mm was used) gives the R_a-value.

3. RESULTS AND DISCUSSION

3.1 Properties of the fresh concrete mixtures

The results of the measurements on the fresh concrete mixtures are given in Table 2. The addition of the different polymers caused an increased incorporation of air in the fresh mixtures. This resulted in a lower density of those mixtures compared with the reference mixture without polymer. The mixtures with the styrene butadiene polymer (SBR), the styrene-acrylic ester polymer (SA) and the vinylcopolymer (VPV) had an air content which was only 1 to 2% higher than the air content of the reference mixture. However the mixtures with the acrylic polymer had an air content of 10% (acrylic polymer A2) and 17% (acrylic polymer A1).

The air content and the density of the mixture with silica fume and the mixture with blast furnace cement were of the same order of magnitude as the reference mixture. In spite of the low w/c ratio (0.34) of the mixture with silica fume, a very good workable concrete was obtained with a slump of class S3, due to the addition of a high amount of superplasticizer.

Only for the mixture with addition of the acrylic polymer the amount of water calculated on basis of a fictitious w/c ratio of 0.4 was enough to create a workable concrete. The workability of this mixture was not only directly influenced by the addition of the polymer but also indirectly by the increase in the air content through polymer modification. For the other mixtures more water must be added. For the mixture with the styrene butadiene polymer (SBR) and the styrene-acrylic ester polymer (SA) a fictitious w/c ratio of 0.42 and 0.43 respectively had to be used to obtain a slump of class S1. An increase in the fictitious w/c ratio to 0.48 was needed for the mixture with the vinylcopolymer (VPV). For this mixture water was added till a slump class S2 was obtained because even with a slump of class S1 the concrete was not workable because of the stickiness of the mixture.

3.2 Compressive strength and water absorption of the different mixtures

The values of the compressive strength and the water absorption of the different concrete mixtures determined on 28 days are shown in Table 3. The polymer modification of the concrete resulted in a decrease in compressive strength compared to the reference mixture. The lowest value was measured for the mixtures with the acrylic polymers. Decreases in strength of 60 and 35% were measured for the mixture with the polymers A1 and A2 respectively. The mixture with addition of silica fume had an average compressive strength of 84.6 N/mm^2 which was significantly higher that of the reference mixture.

Table 3 – Compressive strength and water absorption the different concrete mixtures		
Concrete Mixture	Compressive strength (N/mm^2)	Water absorption (% of dry weight)
R (Reference mixture)	68.3	2.58
B (Mixture with blast furnace cement)	62.5	2.28
SBR (Mixture with styrene butadiene polymer)	58.2	1.56
A1 (Mixture with acrylic polymer A1)	28.7	3.82
SA (Mixture with styrene-acrylic ester polymer)	61.3	1.84
A2 (Mixture with acrylic polymer A2)	43.8	2.28
VPV (Mixture with vinylcopolymer)	50.6	2.71
SF (Mixture with silica fume)	84.6	1.78

Relatively low values for the water absorption were determined for all mixtures, with exception of the mixture with the acrylic polymer A1. Although polymer modification of concrete is known to decrease the water absorption in fact the addition of polymer induces two opposite phenomena concerning the water absorption. On the one hand the polymer forms a barrier for water absorption but at the other hand the addition of polymer is often associated with an increase in air content of the fresh concrete. This implies a higher porosity, which often leads to higher water absorption. Depending on the amount of air included in the concrete combined with several other factors (such as degree of hydration of the cement, degree of film formation of the polymer) poly-

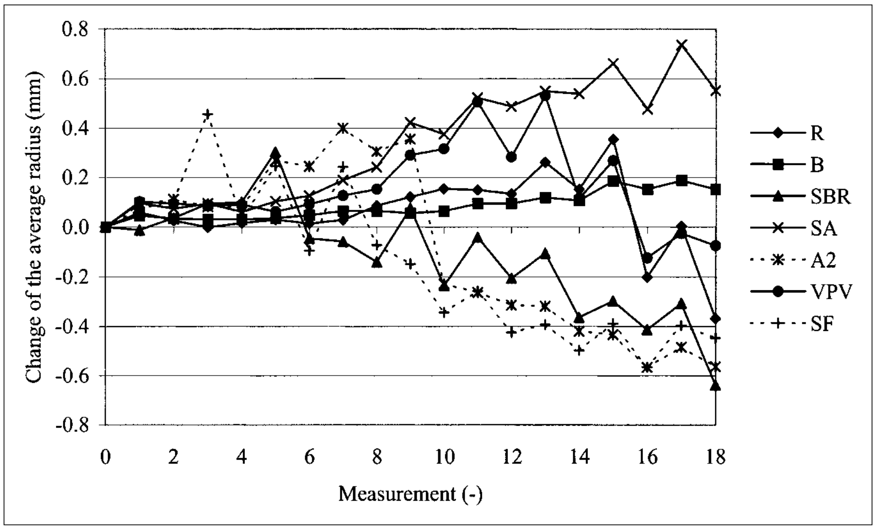

Fig. 1 – Average change of the radius of the cylinders of the different concrete mixtures versus the number of measurements.

mer modification can still lead to lower water absorption. In case of the acrylic polymer A1 the high water absorption of this concrete mixture was probably due to the exceptionally high air content of the fresh concrete. Such a high air content must create a high porosity which was reflected in the high water absorption. The same phenomenon, but in smaller proportions, was seen for the mixture with the acrylic polymer A2 (air content of 9.7%, water absorption of 2.28%) and the mixture with vinylcopolymer (air content of 5.2%, water absorption of 2.71%). The mixtures with the styrene-acrylic ester polymer and the styrene butadiene polymer had lower water absorption than the reference mixture.

The mixture with addition of silica fume created indeed very dense concrete, which had average water absorption of only 1.78%.

3.3 Chemical test with sulfuric acid

As the mixture with the acrylic polymer A1 showed inferior results concerning air content, compressive strength and water absorption it was not considered in the chemical test.

In Fig. 1 the average change of the radius of the cylinders is shown versus the number of measurements 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 in the radius corresponds to alternating expansion of the concrete due to immersion and formation of reaction products and subsequent material loss due to brushing. Eventually the decrease in the radius could also occur during the period of immersion of the cylinders due to loss of adhesion of the expanded parts.

A statistical analysis was performed on the results after brushing, (even measurements in Fig. 1) using a student-Newman-Keuls test with level of significance 0.05. In the first four cycles few significant differences were detected. From the fifth cycle on the different mixtures could be classified in at least two groups. One group included the reference mixture, the mixture with blast furnace cement and the mixtures with the styrene-acrylic ester polymer and the vinylcopolymer. The other group included the mixtures with the acrylic polymer and the styrene-butadiene polymer and the mixture with the silica fume. The mixtures of the second group were most vulnerable to degradation. Already after three and five cycles a resulting decrease of the radius was noticed for the mixtures with silica fume and the styrene-butadiene polymer and the mixture with the acrylic polymer respectively. The reference mixture and the mixture with vinylcopolymer showed only after eight cycles a negative value (decrease in the radius compared with the initial radius). On the other hand the mixtures with the blast furnace cement and the styrene-acrylic ester polymer showed after nine cycles still a positive value meaning that the cylinders were still larger in dimension than the initial cylinders. For the mixture with the blast furnace cement the difference with the initial radius was only 0.1 mm. For the mixture with the styrene-acrylic ester polymer an expansion of the concrete specimen of 1.2 mm (increase in the radius with 0.6 mm) was measured. After nine cycles there was a significant difference between the mixture with the styrene-acrylic ester polymer, the mixture with blast furnace cement and the mixture with the vinylcopolymer. All those mixtures showed a significant difference in change of the average radius. On the other hand the reference mixture was added to the second group. Hence, no significant difference could be noticed between the reference mixture, the mixture with silica fume, the mixture with the acrylic polymer and the mixture with the styrene-butadiene polymer.

Fig. 2 shows the cumulative changes of the average radius of the different mixtures due to alternated immersion in the sulfuric acid solution. These values represent the sum of all differences between the values of the radius measured after brushing and the values of the radius measured before brushing of the subsequent cycle. Hence, the effect of brushing is excluded. Less significant differences between the different mixtures were found. The mixture with the silica fume showed the largest cumulative expansion and this was mainly due to the expansion after cycles 2, 3 and 4. On the other hand the mixture with the blast furnace cement showed a relatively small expansion. After nine cycles a cumulative increase in the radius of only 0.2 mm was measured. All polymer modified mixtures, with exception of the mix-

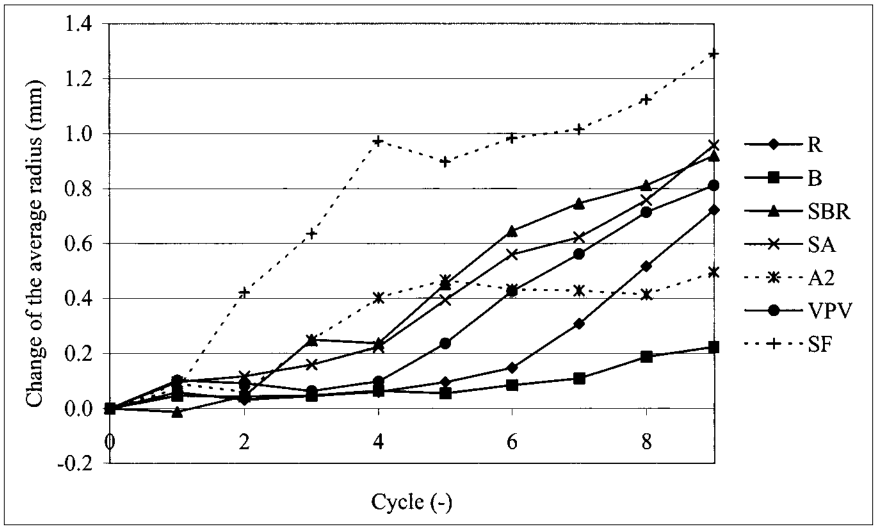

Fig. 2 – Average change of the radius of the cylinders of the different concrete mixtures only due to alternated immersion in the sulfuric acid solution.

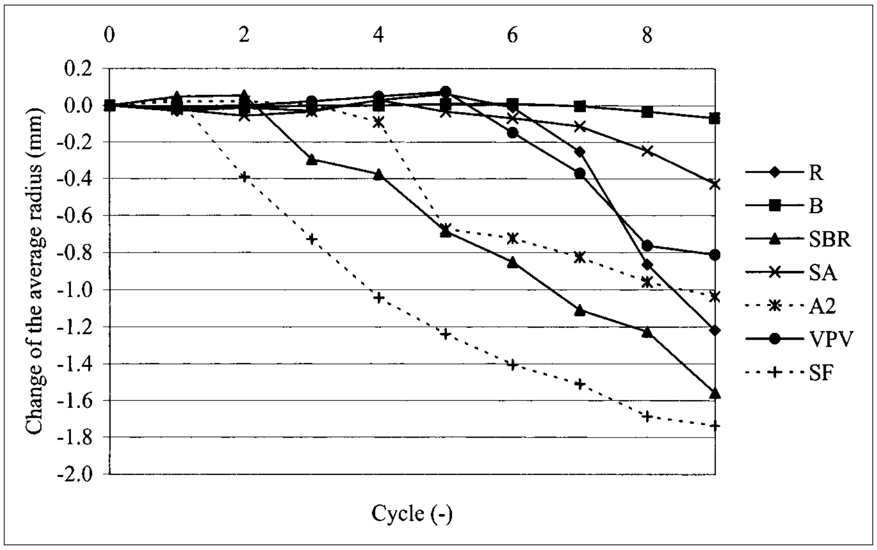

Fig. 3 – Average change of the radius of the cylinders of the different concrete mixtures only due to brushing of the cylinders.

ture with the acrylic polymer, showed higher expansions than the reference mixture. For the mixture with the acrylic polymer after the alternated immersion of cycles 6, 7 and 8 no expansion was measured. Probably expansion of the concrete had taken place but the expanded material had not enough cohesion and fell off already during the immersion stage. Due to this phenomenon the expansion shown in Fig. 2 is not the maximum expansion which took place but an underestimation.

Fig. 3 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 values of the radius measured before brushing and the values of the radius measured after brushing during the same cycle. Hence, only the effect of brushing is taking into account. The largest cumulative loss of material was measured for the mixture with silica fume. From cycles 2 to 6 a decrease in the average radius with 0.2 to 0.3 mm per cycle was measured. For the following cycles a more moderate decrease was seen. From cycle 2 on the mixture with the styrene-butadiene polymer had also less resistance against the mechanical action of brushing. Due to an exceptionally high decrease in radius after cycle 5, the mixture with the acrylic polymer A2 had, in spite of the rather moderate decreases in all other cycles, a cumulative decrease of 1.1 mm after nine cycles. No significant loss of material due to brushing could be seen for the mixture with the blast furnace cement.

In most cases large expansion of the concrete during the immersion stage was associated with large loss of material due to brushing. The largest expansion and the largest material loss for the mixture with the silica fume were both measured during cycles 2, 3 and 4. While for the mixture with blast furnace cement less expansion was measured in combination with almost no material loss. An exception on this phenomenon is found for the mixture with the styrene-acrylic ester polymer. This mixture showed a relatively large expansion (1.0 mm) but the material loss was restricted to 0.4 mm. Probably this polymer modified concrete has the enhanced capability to withstand the internal pressures accompanied with the formation of the expansive reaction products. This property can be attributed to the higher capability of plastic deformation due to the incorporation of the polymer.

In spite of the fact that all measured mechanical properties of the mixture with silica fume pointed in the direction of a very dense concrete (low w/c ratio, low water absorption, high strength, high density), inferior chemical test results were obtained for that mixture. In spite of the general statement that concrete durability is augmented with decreased permeability, this aspect could have a negative effect in case of extreme low permeability as for the mixture with silica fume. The authors think of two negative aspects resulting from the refinement of the pore structure. On the one hand the fine pores create probably an increased capillary suction resulting in solution which enters deeper into the concrete. Although the total amount of solution taken up by the concrete is rather small, the solution, which enters the concrete, is very aggressive and dissociates easily into sulfate ions and protons. So even in low concentrations enough aggressive

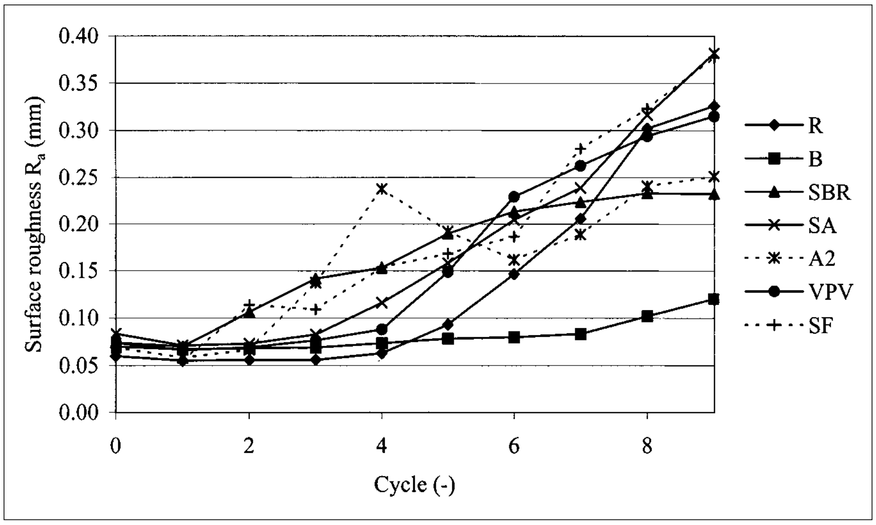

Fig. 4 – Average change of the R_a-value of the different concrete mixtures versus the number of cycles.

compounds are present to produce expansive reaction products. Due to the refinement of the pore structure the solution comes in contact with a larger concrete surface than when a same amount of solution is taken up by concrete with larger pores. The more concrete surface is in contact with the solution, the more reaction products can be formed. On the other hand smaller pores create less space for the expansive reaction products formed during the immersion stage. This could lead to higher internal pressures resulting in more cracks. So in the case of the mixture with silica fume the extreme refinement of the pore structure had rather a negative effect on the durability than a positive effect.

The average R_a-value of the different concrete mixtures versus the number of cycles is shown in Fig. 4. The initial roughness, measured before the chemical test started, is mentioned at cycle zero. All mixtures had an initial surface roughness in the same order of magnitude (0.05 to 0.10 mm). The mixture with blast furnace cement showed a very moderate change of the roughness during all cycles. 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 in the roughness after cycles 5 and 6. This peak corresponds with the large expansion of the concrete. Only the cement paste is subjected to a large expansion; the aggregates are not attacked by the sulfuric acid and did not show any expansion. This discrepancy probably leads to the large surface roughness measured after cycle 4. As could be seen in Fig. 1 after cycle 5 a significant decrease in the radius of this mixture was measured meaning that the expanded material was removed. So the difference between the cement paste and the aggregates was reduced in that way, which is also expressed in a decrease in the surface roughness after cycles 5 and 6.

4. CONCLUSIONS

Although the method used was phenomenological in nature, the test was a very useful tool to compare the resistance and the behaviour of different concrete mixtures in contact with sulfuric acid.

The addition of the selected polymers to the concrete caused an increase in air incorporation of the fresh concrete. This resulted on the one hand in higher values for slump and flow of the fresh concrete but on the other hand also in lower densities. The addition of 7.5% of the acrylic polymers by weight of cement created concrete with unacceptably high air contents. For this type of polymer maybe lower concentrations must be used to overcome this problem. Due to the addition of a high amount of superplasticizer the mixture with silica fume had in spite of the low w/c ratio (0.34) a high workability (slump S3, flow F2).

All tested polymer modified concrete mixtures had lower compressive strengths than the reference mixture without polymer addition. Depending on the type of polymer, decreases in 10 to 60% were measured compared with the reference mixture. The influence of the polymer addition on the water absorption of the concrete depended on the type of polymer used. The mixture with silica fume had a higher compressive strength and a lower water absorption than the reference mixture.

Concerning the resistance of the different mixtures to the 0.5% sulfuric acid solution, the mixtures could be classified in order of increasing resistance as follows:
– mixture with silica fume
– mixture with styrene-butadiene polymer, mixture with acrylic polymer (A2)
– reference mixture
– mixture with vinylcopolymer
– mixture with styrene-acrylic ester polymer
– mixture with blast furnace cement.

If the different mixtures were compared with the reference mixture with Portland cement, it must be taken into account that this mixture had a relatively high quality (low w/c ratio, relatively high strength, high density, low value of water absorption). Furthermore, it was a cement with low C_3A content, providing a high resistance against sulfuric acid aggression.

The addition of the different polymers caused an increase in expansion of the concrete cylinders during the immersion stage of the chemical test. For some of the polymers (styrene-butadiene polymer and the acrylic polymer), compared with the reference mixture, this increase in expansion was associated with an increased loss of material due to brushing. The combination of those two phenomena resulted in concrete with a lower resistance against sulfuric acid. On the contrary, for some other polymers (vinylcopolymer and the styrene-acrylic ester polymer) the expansion was not associated with an increased loss of material due to brushing. In this case better results were obtained concerning the change of the radius of these specimens compared with the reference mixture.

The low air content, the low water absorption and the high density of the mixture with silica fume were an indication that this mixture must have a low permeability. In spite of this property this mixture seemed to have a quite low resistance against the aggressive action of the sulfuric acid solution. A high expansion of the cylinders was measured during the immersion in combination with large loss of material due to brushing.

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