According to European standard EN 934-2, the concrete compositions do not require more than 5% of superplasticizers (referring to the cement weight) for common applications. Concrete is a material currently used in contact with drinking water (for example water towers and pipes). It is therefore essential to assess whether organic molecules are released during the leaching process or trapped by the cement matrix even if low concentrations of organic compounds are involved.

Numerous physical and chemical processes can occur when the cementitious material is in contact with water that give rise to a transfer of compounds from the solid to the liquid phase called ‘leachant’. After dissolution of the charged molecules, the leaching product is called “leachate”. All these processes are generally grouped under the term leaching. Concerning the cementitious matrix, many studies have led to a good understanding of the leaching mechanism.[1-5] The major physico-chemical phenomena have been described as related to the porous structure of cement paste and the local equilibrium existing between the pore solution (saturating the porous network) and the cement paste hydrates. More precisely, after a contact with a leaching solution (e.g. demineralized water), a concentration gradient appears and leads to the diffusion of ions from the pore solution to the leachant. This process ends when the leaching solution has reached the composition of the pore solution. During this process, the ion contents of the pore solution are disturbed. Consequently, to maintain the local equilibrium (and hence its composition), hydrates and possible residues of anhydrous phases dissolve in the pore solution. This process can be related to a combination of diffusive transport processes and reactions of dissolutions. It varies depending on the composition and structure of the hydrates considered and is also associated with precipitation reactions.[6-8] Several test methods have been developed to simulate leaching of hardened cementitious materials. The physico-chemical leaching process presented above remains the same for all techniques. In the case of the leaching of organic admixtures, the most common test method used is called semi-dynamic. This consists in a cement paste monolith placed for a defined time in a container of leachant. The phenomenon of leaching occurs until the leachant and interstitial solution have reached the same composition. The process is repeated by renewing the solution at defined times. This technical procedure is prescribed in the standards NF X 31-211 TANK TEST and ANSI/ANS/16.1.

Concerning superplasticizers, studies were first carried out on Polynaphtalene sulfonates (PNS) and Polymelamine sulfonates (PMS) by analyzing the leachates with a UV-VIS spectrophotometer.[9] As the chemicals constituting the admixtures become much diversified, several co-workers perform Total Organic Carbon measurements in order to detect numerous organic admixtures in leachates.[10] Overall, in case of usual superplasticizer dosages, it was demonstrated that PNS and PMS admixtures are not leached and are well trapped by the cement matrix. Organic admixtures were only detected at loading contents much higher than the one used in practice. Among the different organic admixtures used in concrete, PolyCarboxylate-co-Polyethylene glycol (PCP) superplasticizers are more and more used for economic and environmental reasons. To understand the leaching at a smaller scale, Nuclear Magnetic Resonance (NMR) has been used to analyze leachates obtained after a semi-dynamic leaching of a CEM II/A-LL 32.5 R admixed with PCP superplasticizer.[11] The analytical procedure allows detecting PolyEthylene Glycol (PEG; constituting side chains of the PCP copolymer) up to 20 ppm. In this way under certain

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conditions; it was possible to detect PEG in leachates of CEM II cement pastes admixed with a PCP based superplasticizer. In addition to the leaching technique, NMR measurements pointed out the impact of the analytical sensitivity on the conclusions. Due to the very low concentration of released organic materials in the leachates; only very sensitive analytical tools are suitable. Mass spectrometry measurement has not been applied yet to this type of studies even though this analytical technique allows performing very fine and accurate analysis of many organics compounds. Detection threshold reached are suitable to attempt the analyses of mineral matrix containing traces or ultra-traces of organics admixtures. In case of superplasticizer, mass spectrometry studies remain rare. Some analyses of Sulfonated Naphthalene-Formaldehyde-Condensates (SNFC) and Melamine Sulfonate Condensates (MSFC) are reported in the literature.[12] However mass spectrometry technique has never been applied to the detection of the last generation of superplasticizer. A dedicated protocol based on two techniques has therefore been developed.[13] This has enabled us to detect traces of PCP copolymers by mean of Pyrolysis coupled to Gas Chromatography and Mass Spectrometry (Py-GC-MS). Traces of synthesis residue constituted by non-grafted PEG have been also detected thanks to Matrix Assisted Laser Desorption and Ionization coupled to a Time of Flight Mass Spectrometer (MALDI-TOFMS).

This paper presents the results of the application of a dynamic leaching test chosen for accelerating the degradation of the cement matrix and improving the release of the chemical admixture. Beside, sensitive analyses based on mass spectrometry technique were performed to analyze the leachates. Tests carried out on cement pastes admixed with PCP superplasticizer show the efficiency of the leaching and analytical techniques protocols developed. It has been even possible to extend the work carried out on cement pastes to concrete formulations used for contact with water involving superplasticizer dosages closer to the one used in reality.

RESEARCH SIGNIFICANCE

It is increasingly required to prove that materials do not modify their environment and that, for example, they don't release much organic molecules by leaching process. Previous studies were conducted with conventional detection techniques. They have shown that the organic admixtures are completely immobilized by the cement matrix during a semi-dynamic leaching test. We present in this work results obtained with an accelerated leaching process that simulates a cementitious material exposed to severe and exaggerated environmental conditions. In addition, we demonstrate the high efficiency of mass spectrometry measurements to detect traces of organic compounds in leaching products. Thereby, it has for example been possible to clearly distinguish the leaching behavior of PCP copolymer from one of its non-grafted PEG synthesis residue.

EXPERIMENTAL INVESTIGATION

Two series of leaching tests were performed in order to assess the leaching of PCP superplasticizer. First series concerns cement pastes admixed with superplasticizer added in the mixing water. The purpose of these tests is to validate first the overall protocol (dynamic leaching/mass spectrometry detection) by testing cement pastes with high excessive admixture contents. Subsequently, we have been able to assess the susceptibility of each organic compound to be leached for standard dosages by decreasing admixtures quantities. The

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Table 1—Concrete formulas used for specimens CC1 and CC2

Water pipe concrete CC1		Water tank concrete CC2	
Materials	kg/m^3	Materials	kg/m^3
Lime stone aggregate	594	Lime stone aggregate	1030
Sand	1308	Sand	883
Cement CEM I 52.5R	300	Cement CEM III/A 42.5 N	300
Water	157	Water	185
Superplasticizer	3.6	Superplasticizer	3.6
The slump of a cone of fresh CC1 concrete is zero (measured according to the test EN 12350-2)		The slump of a cone of fresh CC2 concrete is from 160 to 210 mm (measured according to the test EN 12350-2)	

second series enables the extension of investigations to more representative materials. Two concrete formulations with usual admixture content have been made. They respectively correspond to an extruded concrete used for water pipe fabrication and water storage (water tank or wastewater treatment plant).

Materials

Studied superplasticizer is mainly constituted by 21% of PCP copolymer whose average molecular weight is around 30,000 g.mol^{-1}. This copolymer was obtained by partial grafting of PEG on PolyMethAcrylic Acid (PMAA) through an esterification process. Such synthesis route involves the presence of non-grafted PEG residue quantified at 1% referring to the liquid superplasticizer weight. Furthermore, the grafting degree of the PCP carboxylic functions is equal to 40%. This admixture was supplied by Syndicat National des Fabricant d'Adjuvants pour Mortiers et Bétons (SYNAD, Paris). Cement pastes are manufactured with an OPC (CEM I 52,5 N), a water/cement ratio of 0.4 and the PCP based superplasticizer. Specimen OPC-1 has been made with 10% of liquid superplasticizer. This high excessive dosage is used to validate the leaching and detection protocol. Specimen OPC-2 contains 5% of superplasticizer. This is the highest dosage following the standard EN 934-2: 1997 for an admixture. Above this percentage, the admixture is considered as an addition. Finally, OPC-3 has been admixed with 1.2% of superplasticizer that corresponds to an average standard industrial dosage.

Concrete formulation CC1—suitable for extruded materials such as water pipe—has been designed with the OPC, limestone coarse aggregates and sand. In case of water storage concrete formula CC2, cement with blast furnace slag additions (CEM III/A 42.5 N) has been combined with limestone coarse aggregates and sand. For the two concrete formulations mix designs, the granular squeleton has been optimized in order to obtain the suitable flow properties by keeping the amount of liquid superplasticizer constant and equal to a standard dosage of 1.2% (referring to cement weight). This is done by measuring the slump characterizing the fresh concrete collapse and estimating the material workability. The test is described in the standard EN 12350-2, and results are reported in Table 1.

Both cements are provided by the Association Technique de l'Industrie des Liants Hydraulique (ATILH, Paris La Défense), the phases composition are given in Table 2. Concrete mix designs are detailed in Table 1. Water used for the specimens manufac-

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Table 2—Phases composition of the cements

Phases, %	CEM I 52.5 R	CEM III/A 42.5 N
C_3S	65.4	30.8
C_2S	9.2	10.9
C_3A cubic	6.2	2.0
C_4AF	14.6	2.9
$CaSO_4$, $2H_2O$	2.3	2.6
$CaSO_4$, $0.5H_2O$	2.4	0.5
$CaCO_3$	—	2.3
Glass phase	—	47.8

Note: — = not measured items.

turing and for filling the leaching device is ultrapure demineralized water prepared with a Simplicity Personal Ultrapure Water System (Millipore, Molsheim, France).

Specimens

Hardened cementitious cylindrical specimens used for leaching tests have a diameter of 3.54 in. (90 mm) and are 3.93 in. (100 mm) long. To manufacture the admixed cement pastes, 1500 g of cement is placed first in a bowl mixer type Hobard (1551-1093-1985, Tonindustrie Pruftecnik, Berlin). The required amount of admixture is then introduced in 600 ml of demineralized water. The additional water brought by admixture is taken into account in the total mixing water balance. After mixing cement and admixed water, the fresh cement paste is poured into one liter high density polyethylene bottles. After 24 hours, 0.394 in. (10 mm) of water is added on the top of the specimen to ensure the best hydration. One day later, the specimens are removed from the bottles, rinsed with demineralized water and sawn to obtain a cylinder of 3.93 in. (100 mm) long, with a diameter of 3.54 in. (90 mm) and a weight of 1200g. The specimens are then stored in a curing room at 20°C and 60% relative humidity during 28 days. This treatment ensures a high degree of hydration but also the development of a carbonation layer (dry room) on the specimen's surfaces. This curing condition is chosen to simulate realistic conditions encountered in the field of concrete based materials production.

In case of concrete formulation, cube-shaped molds of 7.87 in. (200 mm) edge were used. After 48 hours, cylinders of 3.54 in (90 mm) diameter are drilled in the cubes. The cylinders are after rectified to obtain the dimensions of cement paste one. The curing conditions are identical to cement paste case.

ITEMS OF INVESTIGATION

At the age of 28 days, the leaching tests are started with the help of five dynamic leaching devices "CTG-LEACHCRETE" (Fig. 1). This setup was initially developed for the heavy metals leaching assessment.[14] It is based on the Soxhlet extractor principle and is made with Borosilicate glass. It is mainly constituted by a cylinder reactor containing the sample and a boiler which concentrates the leachates and produces water vapor. The leaching reactor has a cylindrical shape (∅ = 4.72 in. (120 mm), h = 6.89 in. (175 mm)) and contains the leachant (demineralized water) in which the specimen is immersed. This sample is placed on a triangular glass support that enables a bar magnet wrapped with

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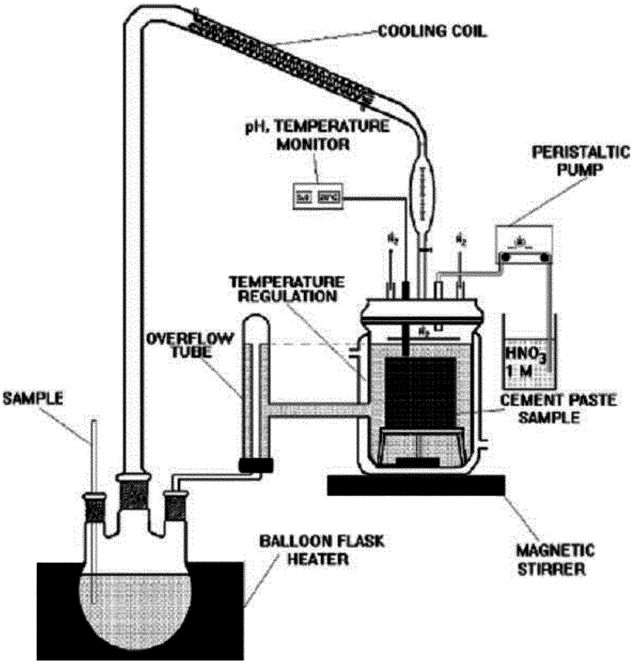

Fig. 1—CTG-Leachcrete device principle (reproduced from Reference 14 with permission).

Teflon and placed below to homogenize the solution. Leachant pH is regulated at 7 ± 0.5, using progressive additions of a 0.7 M HNO_3 solution (Merck, Suprapur Nitric Acid 65%) with a peristaltic pump (COLE PALMER, Masterflex 7518-10 model). Tests were carried out in a thermostatic room maintained at 20°C. The process is called "dynamic" through the continuously renewed leachant. This is done by boiling the water in the flask; vapor is then condensed by the cooling coil and refills continuously the reactor. The constant volume of the reactor is maintained thanks to an overflow tube placed at the bottom of the reactor. In this way, excess liquid loaded with leached materials refills the flask where these materials were accumulated. This process occurs with a flow rate of about 6 ml/min. All the liquid contained in the device flow over the specimen in about six hours. 300 hours total test duration corresponds therefore approximately to 50 renewal of total solution. Leached organic elements accumulated in the balloon flask are collected for mass spectrometry analysis at different times: 24, 72, 200, and 300 hours. In a preliminary experiment the PCP and PEG stability was demonstrated by circulating the superplasticizer diluted in water and by controlling the stability of chemicals thanks to infrared spectroscopy.[15]

ANALYTICAL INVESTIGATION

The PCP content of the leachate was assessed by performing Pyrolysis coupled with a Gas Chromatograph and a Mass Spectrometer (Py-GC-MS). More precisely, an in-situ pyrolytic hydrolysis and methylation (trans-esterification) of the PCP molecules is done in

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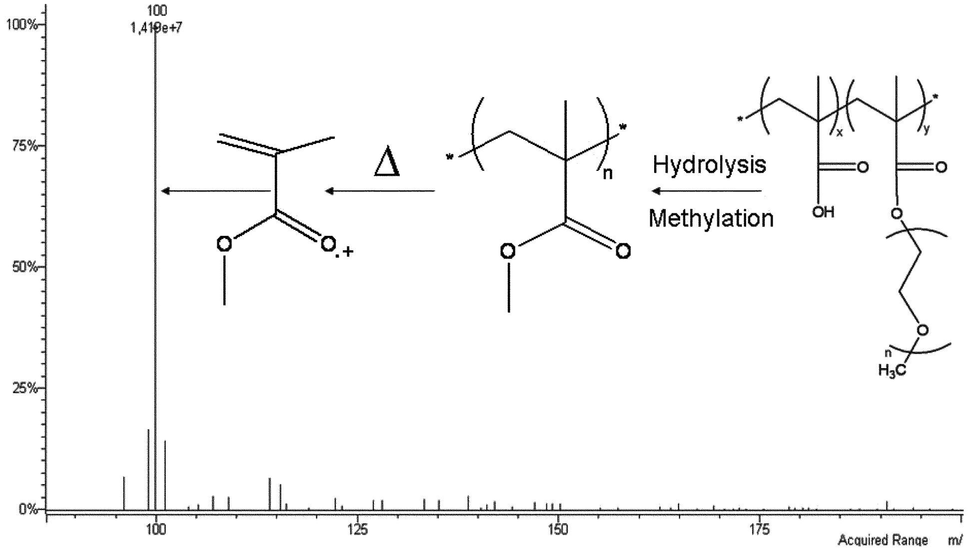

Fig. 2—Py-GC-MS mass spectrum of a 1% superplasticizer solution in water, detection of the PCP copolymer.

the pyrolysis chamber due to Tetramethylammonium hydroxide addition. Samples were prepared by soaking fused quartz wool with 4 µL of the leachate. The pyrolyse is carried out on a CDS pyroprobe 1000 (Oxford, PA, USA) coupled by a CDS 1500 Valved interface (Oxford, PA) to a gas chromatograph Varian CP3800 (Palo Alto, CA). An inert silica column was used to bring organic compounds up to a Varian (Palo Alto, CA) series 1200 triple quadrupole mass spectrometer. All the parameters of the analytical setup are available in a previous published work.[13] After the trans-esterification process and thermal degradation of the derived polymer, mass spectrum displays an intense single mass peak for $m/z = 100$ (Fig. 2) (m and z represent respectively the molecular mass and the charge on the ion, in this case $z = 1$). The ionic species related to this signal is a methyl-methacrylate ion corresponding to the methylated monomer of PMAA (backbone of the PCP copolymer). In this way, the PCP detection in the leachates can be distinguished from the non-grafted PEG residue. The detection threshold of the PCP in leachate attains with this technique is 10 ppm. Finally, for each leachate sample, three analyses were done to determine the PCP content.

In case of PEG determination, analyses by matrix-assisted laser desorption ionization coupled to a time of flight mass spectrometer has been carried out (MALDI-TOFMS). This soft ionization method has the particularity to allow the detection of ion species resulting from intact PEG oligomers ionization. Like this, the PEG identification is done by measuring the mass gap between two oligomers peaks (44 Da, which is the molecular weight of the PEG monomer) as presented in the Fig. 3 the signals displayed are characteristic of the free PEG (non-grafted PEG) in the leachates. The matrix solution was prepared by dissolving 300 mg of 2,5- dihydroxy-benzoic acid in 1ml with a mixture of acetonitrile/0.1% of trifluoroacetic acid in water (50:50, v/v). MALDI-TOF Mass Spectrometry

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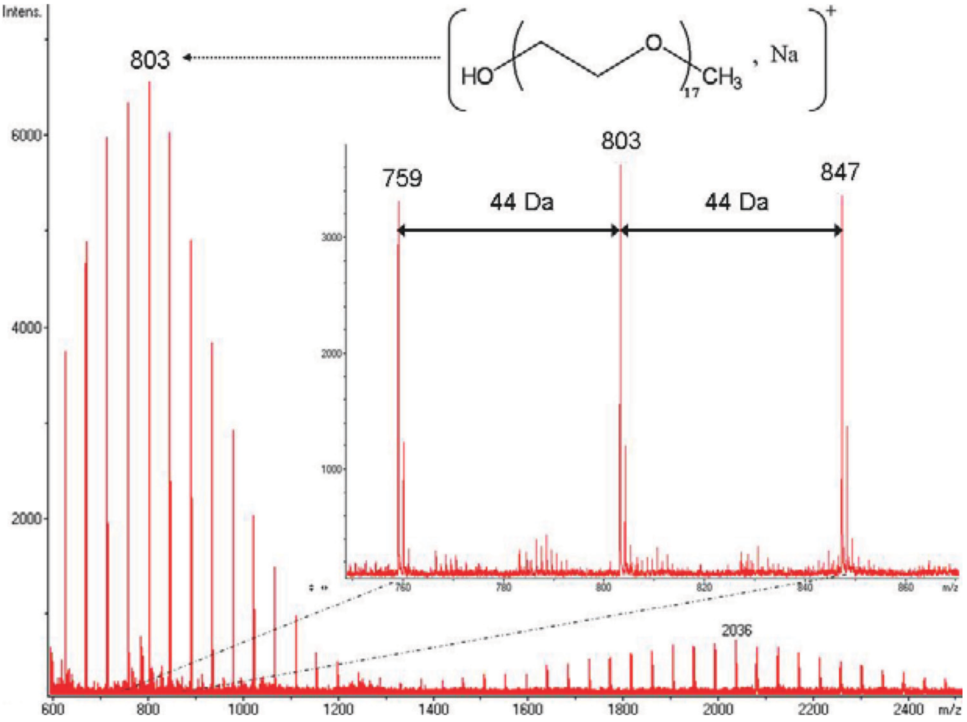

Fig. 3—MALDI-TOFMS mass spectrum of a 5% superplasticizer solution in water.

measurements were carried out on a Bruker Reflex IV time-of flight mass spectrometer (Bruker-Daltonic, Bremen, Germany) equipped with the SCOUT 384 probe ion source, using a nitrogen pulsed laser (model VSD-337ND, Laser Science Inc., Boston, MA). All the spectra presented here are the results of the cumulated signal of 1000 mass spectra, obtained on several locations of the sample. All deposits were realized by the dry-droplet method from 1 mL of matrix solution mixed with leachates. The detection threshold of the PEG in leachate attains with this technique is 1 ppm, and for each leachate sample, three analyses were done to determine the PEG content.

EXPERIMENTAL RESULTS AND DISCUSSION

The leachability of a PCP-based superplasticizer from pure hardened cement pastes

Superplasticizer compounds leachability (PCP and PEG) is assessed by performing leaching tests on cements paste prepared with liquid admixture concentrations ranging from 1.2 to 10% (all dosages refer to cement weight). Leaching tests are conducted at 20°C. The leachant pH solution is maintained at a value of 7 with a regulation system. The results of mass spectrometry analyses of the leachates (after 300 hours of leaching) are presented in Table 3.

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Table 3—Superplasticizer content in the cement pastes and results of leachates analyses

	OPC-1	OPC-2	OPC-3
Superplasticizer cement content, %	10	5	1.2
PCP cement content, ppm	20,000	10,000	2520
PEG cement content, ppm	1000	500	120
PCP detection in leachates (Py-GC-MS), ppm	Approximately 10	<10	<10
PEG detection in leachates (MALDI-TOFMS), ppm	8 to 10	1.5	<1

The leaching of OPC-1 specimen containing the excessive dosage of 10% of superplasticizer (2% of PCP and 0.1% of PEG) has been tested for the only purpose of protocol validation. This dosage is not representative of usual superplasticizer applications that are limited to 5% in the standards NF EN 934-2. Furthermore, the too high fluidization effect may involve segregation of the cement matrix. Analyses carried out by mass spectrometry techniques enable the detection of PCP and PEG in leachates. The PCP and PEG content of the leachates are respectively close to the analytical detection limit of 10 ppm and from 8 to 10 ppm.

OPC-2 specimen admixed with 5% liquid superplasticizer (1% of PCP and 500 ppm of PEG) corresponds to extreme dosage used for ultra-high-performance concrete (UHPC) applications. Leachates analyses point out that, after 300 hours of dynamic leaching, the PCP content is below the analytical threshold of the Py-GC-MS technique (10 ppm). MALDI-TOFMS analyses show also that PEG is detected after 300 hours. The leachate PEG content is estimated to be 1.5 ppm.

Concerning OPC-3, 1.2% of liquid superplasticizer—an average value for usual applications—has been introduced (2520 ppm of PCP and 120 ppm of PEG). The leachates analysis demonstrated that the polymers content remain below the analytical detection limit for both superplasticizer components (10 ppm for PCP and 1 ppm for PEG).

The PEG determinations performed in leachates at several sampling times are summarized in Fig. 4. Several conclusions can be drawn. In a first stage, PEG leaching depends on its initial concentration and increases with it. In a second stage, the leachates concentrations remain constant as a function of time. As the dynamic leaching device involves an accumulation of the leached compounds, the majority of the PEG leaching happens during the first 24 hours of the test. We can assume therefore that the leaching process of this polymer is mostly due to a surface washing process.

The results show that PCP and PEG have a different leaching behavior. This may be explained by the molecules ability to interact or not with cement particles and corresponding hydrates. The PCP trapping efficiency highlighted in this work could be related to its methacrylic backbone. It has been demonstrated that the PCP non-grafted carboxylic groups are responsible for the adsorptive capacity of the copolymer.[16-19] The PCP is chemically adsorbed on cement and well trapped in the hydrates structure (e.g. by mean of an intercalation mechanism).[20,21] Contrarily, in case of non-grafted PEG (without adsorptive capacity) little quantities (< 1%) can pass through the hydrates trapping and transfer to the liquid phase such as interstitial solution or directly to the leachant.

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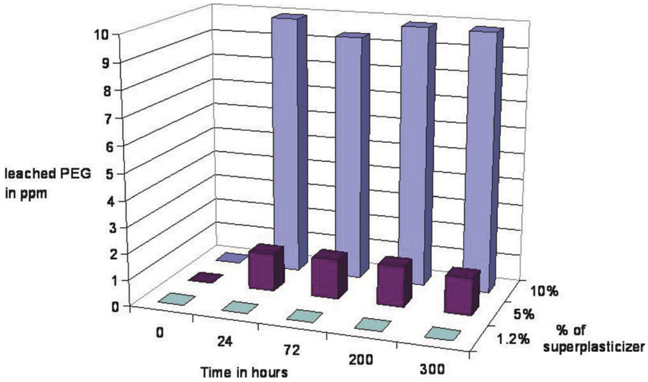

Fig. 4—Concentration of non-grafted PEG detected in leachates collected at different times of dynamic leaching for OPC 1 to 3.

Table 4 – Superplasticizer content in the concrete specimens and results of leachates analyses

Concrete formulation	CC1	CC2
Superplasticizer cement content, %	1.2	1.2
PCP concrete content, ppm	315	315
PEG concrete content, ppm	15	15
PCP detection in leachates (Py-GC-MS), ppm	< 10	< 10
PEG detection in leachates (MALDI-TOFMS), ppm	< 1	< 1

The leachability of a PCP-based superplasticizer from concrete

The same leaching process than the one applied on cement pastes has been used for the concrete specimens CC1 and CC2. The results of mass spectrometry analyses of the leachates after test duration of 300 hours are presented in Table 4. For both CC1 and CC2, the analytical results point out that—even after 300 hours of dynamic leaching at pH = 7—the PCP and PEG content of the leachates is below the analytical threshold. The PCP and PEG concentrations introduced in the concrete specimens are very low. They are below the concentration used for the pure OPC-3 cement paste. The results obtained with the leaching test on concrete are in agreement with those found for the cement pastes. They demonstrate that, even with accelerated leaching conditions and very sensitive analytical method, the small PCP and PEG quantities are well trapped by the concrete matrix.

FURTHER RESEARCH

Our work has shown the efficiency of cement based material to trap the main constituents of a PCP based superplasticizer. First it would be interesting to extend this study to other PCP superplasticizers, obtained by a different synthetic route (radical polymerization), or with different adsorption properties (different degree of grafting and various polymer chain lengths). Secondly, it would be therefore interesting to understand further the trapping mechanism(s). This could be achieved by studying the process of adsorption/intercalation

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of organic molecules in the hydrated material. The leaching kinetics could be understood with the help of the results and the test methods developed and presented here.

CONCLUSIONS

The goal of this study was to measure the leaching of one PCP based superplasticizer like Polycarboxylate-Co-Polyethylene glycol (PCP) and non-grafted PolyEthylene Glycol (PEG) during a dynamic leaching process. The mass spectrometry analyses of the leachates show that the quantities leached are always below the detection limit (10 ppm for PCP and 1 ppm for PEG) for usual superplasticizer dosages in cement pastes or in concrete design for water contact applications. For high dosages such as those encountered for UHPC, the leached quantities remain undetectable for PCP and very low for PEG (less than 2 ppm). Test conducted with high excessive superplasticizer contents (10%) show that, even with these dosages, the PCP leached quantities remain to trace levels near the analytical limit. Furthermore, recording the PEG quantities in the leachant as function of the time, demonstrates that the leaching process of this polymer is mainly governed by surface washing phenomena.

The accelerated leaching process and the high sensitive analytical measurements applied in this work highlight that, given the excellent ability of the studied PCP to be trapped in the hardened material and the small amount of non-grafted PEG in the superplasticizer, the PCP based superplasticizer tested here is a product weakly sensitive to leaching.

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