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Study of interactions between sodium monofluorophosphate and hardened cement paste and their consequences on concrete transfer properties

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Abstract

Surface applied corrosion inhibitors are one of the methods used to protect embedded reinforcing bars from corrosion. This paper presents a study of interactions that can occur between sodium monofluorophosphate (MFP) and concrete during its transport from the applied surface to the steel. Interactions of MFP with portlandite have clearly been observed with X-ray diffraction diagrams. Tests with solutions have been realised, and show that an amorphous gel appears when MFP is in contact with a saturated calcium hydroxide solution. Percolation tests have highlighted the consequences of these reactions on concrete properties. In the last part of this study, quantitative chemical analysis of the percolate is presented: they show that when the concentration of the MFP solution increases, more MFP is found in the percolate even if a large part is kept in the concrete sample.

Keywords: X-ray diffraction; Transport properties; Corrosion; Adsorption; Sodium monofluorophosphate; Percolation

1. Introduction

Corrosion of embedded reinforcing steel is the main cause of degradation of concrete constructions. Its development can lead to damage or even ruin of the construction. That is why standards recommend some precautions during construction to reduce the risks of corrosion.

Also, to protect reinforcing bars from corrosion, various processes have been developed. There are electrochemical methods (cathodic protection, chloride extraction, concrete realkalization),and the use of corrosion inhibitors.

Corrosion inhibitors can be classified in three categories according to the way they act:

- Anodic inhibitors: reduce the steel dissolution.
- Cathodic inhibitors: avoid the associated reaction of steel dissolution.
- Mixed inhibitors: act at the same time as anodic and cathodic inhibitors.

Because concrete is a basic medium, only a few inhibitors can be used to protect embedded reinforcing steel.

This study deals with sodium monofluorophosphate (MFP), an inorganic corrosion inhibitor.

MFP is applied on the surface of concrete structure as an aqueous solution. When the inhibitor migrates from the surface to the steel, MFP is in contact with concrete and can interact with hardened cement paste. Some authors [1] think that reactions that can occur between MFP and calcium hydroxide prevent the inhibitor from reaching the embedded steel. On the other hand, numerous field observations show that MFP is migrating deep into concrete to rebar level in real structures, even in absence of significant carbonation [2,3].

In the first part of this study, we evaluate the interactivity between MFP and hardened cement paste using X-ray diffraction, adsorption isotherms etc . . . Then we present the consequences of these interactions on the concrete transfer properties using percolation tests to determine the propor-

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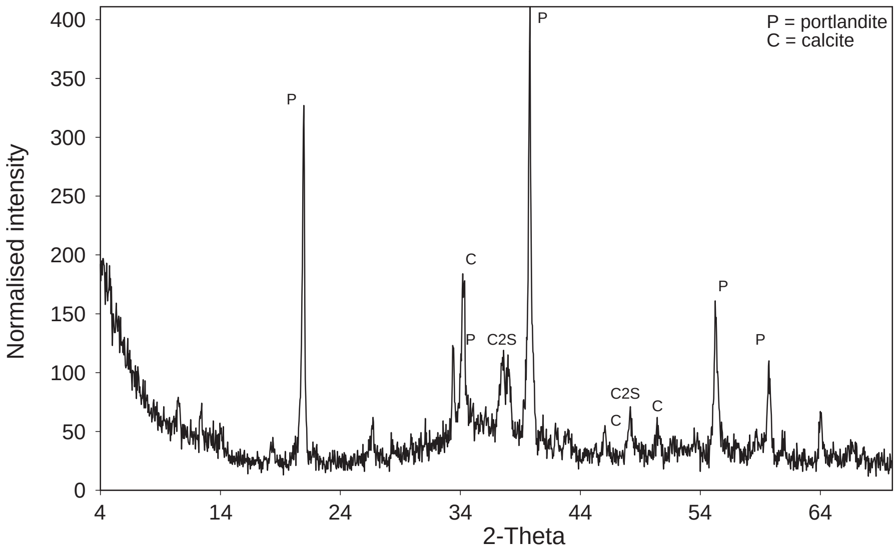

Fig. 1. X-ray diffraction diagram, cement paste, reference sample.

tion of MFP available after moving through concrete sample.

2. Interactions between MFP and hardened cement paste

To understand interactions that occur between MFP and concrete components, we carried out X-ray diffraction analysis on cement paste that had been in contact with MFP solution, studied the precipitate made of MFP and calcium hydroxide and the possibility of MFP adsorption on concrete.

2.1. Study of products from the reaction between MFP and cement paste

A test specimen of cement paste (W/C=0.5) has been prepared using CPA CEM I cement. After 30 days in a controlled atmosphere (temperature: 20 °C, relative humidity: 55%), it has been sawed into 10 mm thick slices. To guarantee the homogeneity of the powder submitted to XRD analysis, we needed to work with samples having a small volume and a large surface exposed to MFP treatment. This slices presented these two characteristics. One slice has been saved as reference sample, and another one received 7 applications of a 20% MFP solution. After 1 week, slices have been ground to powder (80 μm).

X-ray diffraction diagrams that have been obtained from these powders are presented on Figs. 1 and 2. On the X-ray diffraction diagram of the reference sample (Fig. 1), main peaks correspond to portlandite, calcite and C_2S. On the diagram of the sample treated with MFP (Fig. 2), there are no new phases clearly crystallised. In addition, portlandite peaks have decreased. This is a sign of the reactivity of MFP

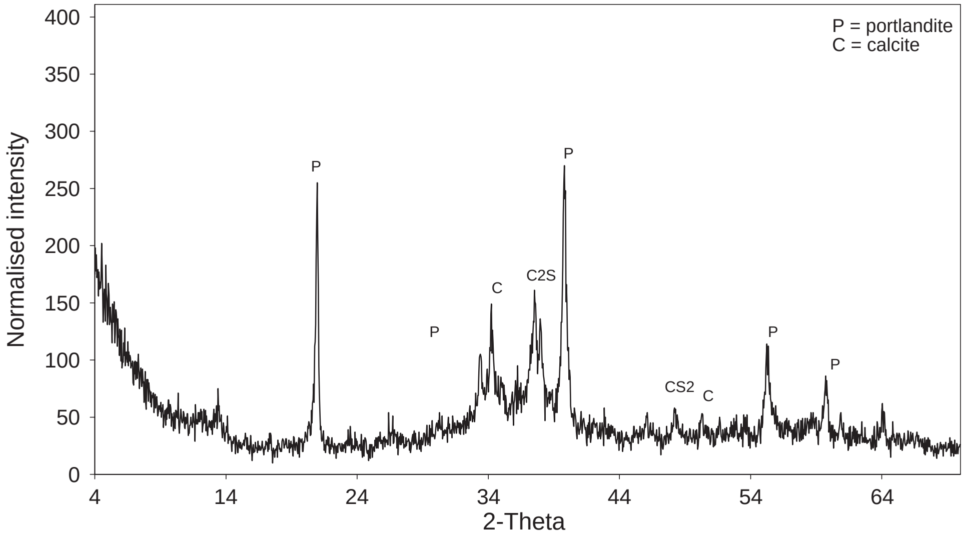

Fig. 2. X-ray diffraction diagram, cement paste treated with MFP.

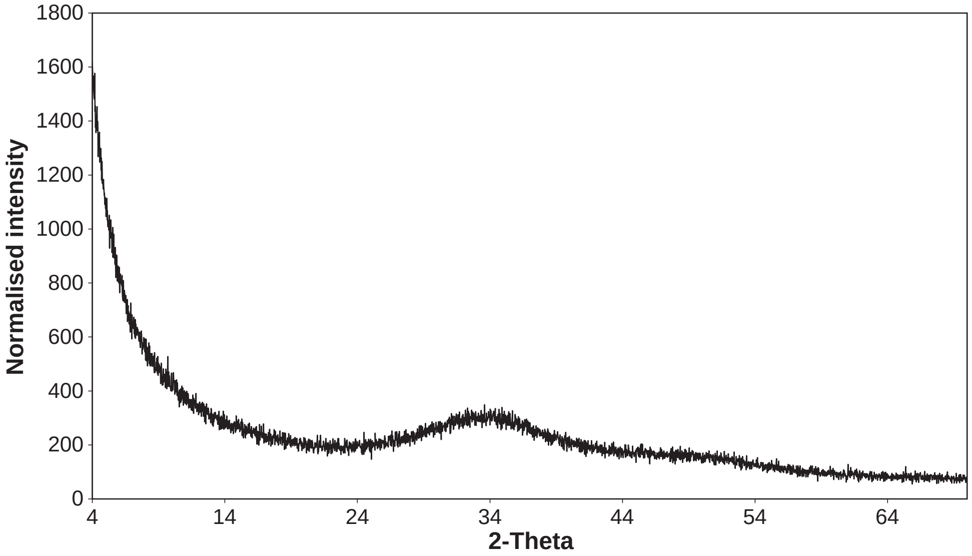

Fig. 3. X-ray diffraction diagram: precipitate directly after filtration.

in the presence of calcium hydroxide and the likely formation of amorphous products.

2.2. Study of the precipitate formed by MFP in presence of calcium hydroxide

To examine in detail the nature of products formed by the reaction between calcium hydroxide and MFP, we mixed a saturated solution of calcium hydroxide with a 20% MFP solution. A precipitate appeared in few minutes, it was collected by filtration and analysed by X-ray diffraction after three different treatments

- ✓ Analysis of the precipitate directly after filtration (Fig. 3)
- ✓ Analysis of the precipitate filtered and freeze dried (Fig. 4)
- ✓ Analysis of the precipitate filtered and dried at 50 °C for 12 h (Fig. 5)

The aim of the dehydration by freeze drying is to fix phases present in the precipitate and avoid possible formation of new minerals that might have crystallised during the 50 °C drying.

On the diagram of the hydrated precipitate (Fig. 3), we notice a halo centred in the vicinity of a theta value of 34°, which is the characteristic of an amorphous precipitate. On the two other diagrams (Figs. 4 and 5), MFP peaks are superimposed on the halo of the amorphous precipitate observed on Fig. 3.

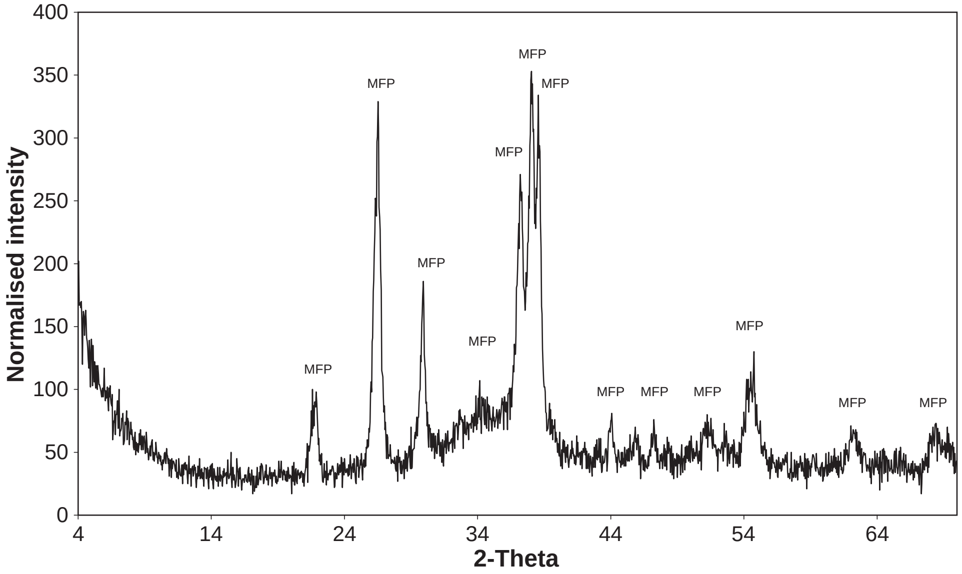

Fig. 4. X-ray diffraction diagram: precipitate filtered and freeze dried.

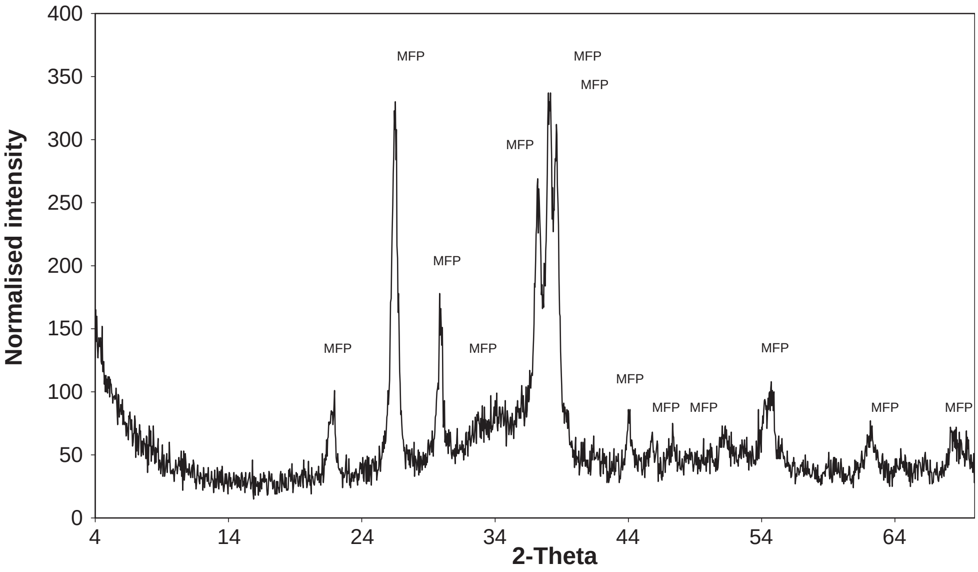

Fig. 5. X-ray diffraction diagram: precipitate filtered and dried at 50 °C for 12 h.

These results show that in the test conditions of our study, the reaction that occurs between MFP and calcium hydroxide produces mainly and rapidly a gel. It is not excluded that crystallisation can happen over a long period of time. Some authors have found the formation of apatite under specific test conditions [4] whereas other authors do not identify any crystallised new phase [3]. In another context than MFP studies, some authors have observed that interactions between calcium hydroxide and a phosphorous compound can produce an amorphous gel [5]. Finally, it seems that the nature of the product formed can be different according to the relative proportion of the two components: calcium hydroxide and phosphorus.

Interactions between calcium hydroxide and MFP that have been highlighted are probably not the only one to occur in concrete. MFP can be bound by physic adsorption on the C–S–H. To evaluate the importance of the adsorption phenomenon of the MFP on the hardened cement paste, adsorption isotherm tests have been carried out.

2.3. Study of MFP adsorption on concrete components

These tests have been realised at a constant temperature (20 °C). 5 g of a concrete powder (80 μm) was mixed with a known volume and concentration of MFP solution. The

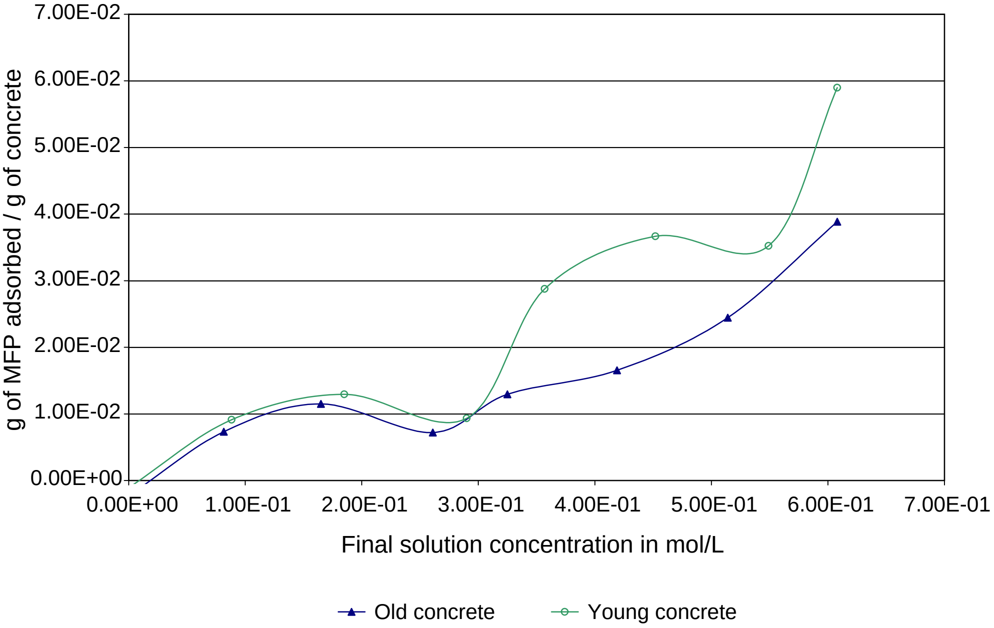

Fig. 6. Adsorption isotherms on young and old concrete powder.

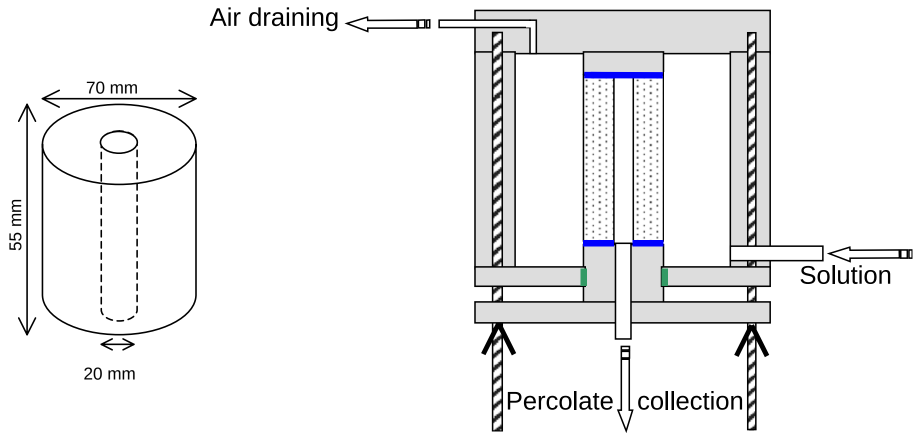

Fig. 7. Percolation cell.

powder fineness is required to facilitate the easy interactions and permit to obtain equilibrium after 3 h. After this period, the solution was filtered and the residual content of MFP measured. For this purpose, total fluoride was quantitatively analysed after a total hydrolysis. This total hydrolysis is obtained by agitating 10 ml of filtrate during 3 h at 50 °C, in presence of 1 ml of nitric acid.

In this study, the test was realised using 7 different initial concentrations of the MFP solution (1 10^{-1}, 2 10^{-1}, 3 10^{-1}, 4 10^{-1}, 5 10^{-1}, 6 10^{-1} and 7 10^{-1} mol/L) and two concrete formulations using CPA CEMI cement. One of this concrete was 2 years old (young concrete) and the other 16 (old concrete). The old concrete powder has been made from a superficial concrete sample that is naturally carbonated.

On Fig. 6, the adsorption isotherm presents the mass of MFP adsorbed by concrete unit mass according to the MFP concentration at the equilibrium.

The two curves are superimposed in the first part of the diagram, when concentrations are low, whereas important differences can be observed in high concentrations, the young concrete adsorbing more MFP than the old one. This experiment has been realised five times and the difference between young and old concrete has been observed every time. The composition of the concretes used in this study are very close, the sole difference is the age, the oldest being 16 years old. The concrete powder was extracted from its 3 cm depth carbonated zone. The content of calcium hydroxide in this zone is low, so in these conditions, there is less reaction between concrete and MFP.

To realise a link between laboratory tests and real MFP applications, we have evaluated the potential depth of penetration of MFP under the conditions as above if we apply 1 L of a 10% (0.7 mol/L) MFP solution on a 0.5 m^2 surface. On Fig. 6 we can read that for the young concrete, and with a 0.7 mol/L concentrated solution, each gram of concrete powder can adsorb 6 10^{-2} g of MFP (4.16 10^{-4} mol). To consume these 0.7 mol present in 1 L of a 10% MFP solution, 1.6 Kg of concrete is needed. If we consider 2300 Kg/m^3 as the volumetric mass of concrete, on the 0.5 m^2 surface, all the MFP would be adsorbed within a depth of 1.4 mm. Under these conditions, the MFP would not reach the embedded steel.

However, these calculations are based on the adsorption isotherms realised on concrete powder. The important surface area of the powder (80 μm) and the creation of new fresh calcium hydroxide surfaces through grinding vastly increase the reactivity of the MFP compared to normal concrete. In the real MFP applications [6], it is likely that fewer interactions will occur and the MFP quantity that is adsorbed should be lower than the one observed in the adsorption isotherm. Moreover, amorphous phases formed by MFP in contact with hardened cement paste might obstruct concrete pores and modify its characteristics. That is why it seems interesting to study interactions in concrete samples by examining the evolution of transfer properties and the composition of percolate.

3. Effect of interactions on concrete transfer properties

To study the effect of interactions on concrete transfer properties, percolation tests have been realised. The objective was to evaluate the proportion of MFP that was still remaining in a solution after it has moved through a 25 mm thick concrete.

It was not expected that the results of this specific experimentation would permit to conclude on the ability of MFP to penetrate concrete deeply by a capillary process, in field conditions. The questions to be answered were: Is there still some MFP in a solution after it has moved through a concrete sample? And, if yes, what is the quantity left?

During these tests a MFP solution was injected under a 0.6 MPa pressure through sample. The cell we used is represented diagrammatically on Fig. 7.

Table 1
Initial radial permeability

Sample name	A	B	C
Permeability ($10^{-16}m^2$)	4.14	4.20	5.00

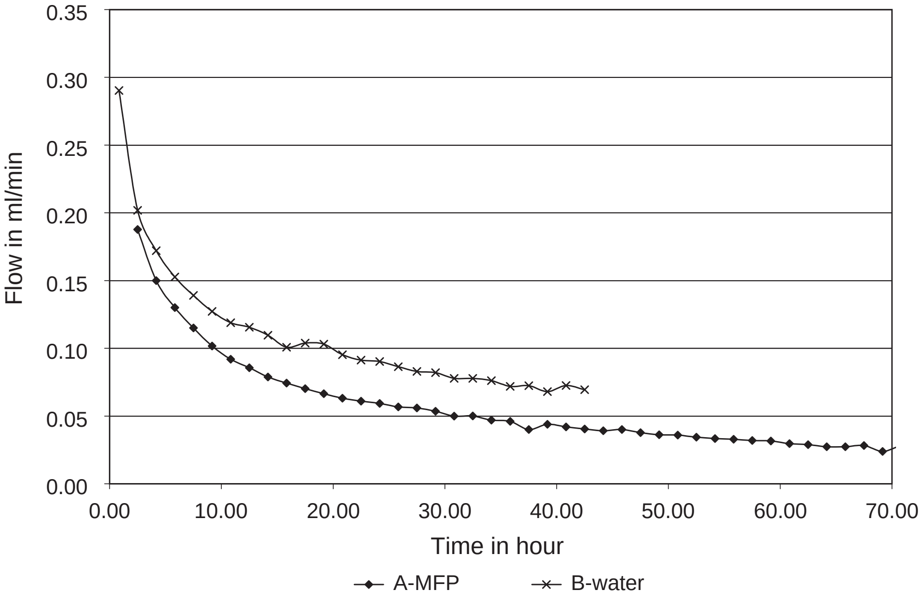

Fig. 8. Percolation flow for two samples with identical initial permeability.

Concrete samples were 70 mm cylinders in the centre of which a 20 mm core has been extracted to obtain a 25 mm percolation thickness. The injected solution went through the sample from the outside to the heart of the core, and drips from the central part of the core to a programmable fraction collector.

Before each test, gaz radial permeability was measured in the same cell under a 0.4 MPa helium pressure. This measure permits to characterise the initial state of the sample. This method is non-destructive and helium doesn't react with concrete hydrates. The permeability constant (k) was calculated using Eq. (1). In Table 1, permeability constants for the three studied samples are presented. These three cores have been sampled in the same concrete block.

$$k = \frac{Q_2.P_2.\mu}{\pi.L.\left(P_1^2 - P_2^2\right)} \cdot \ln\left(\frac{R}{r}\right) \qquad (1)$$

with:

- Q_2: measured flow rate in m^3/s
- P_1: pressure at the entry of the cell in Pa

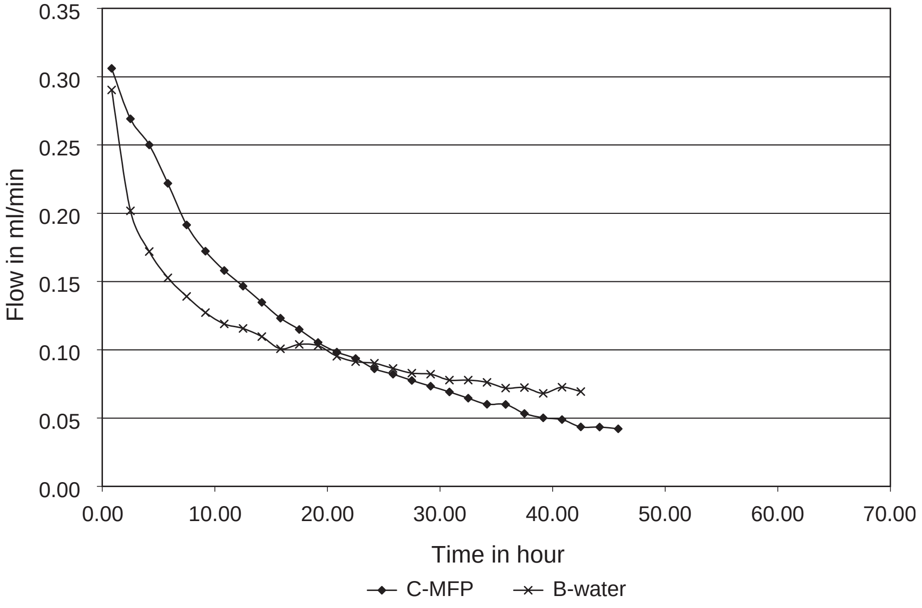

Fig. 9. Percolation flow for two samples with different initial permeability.

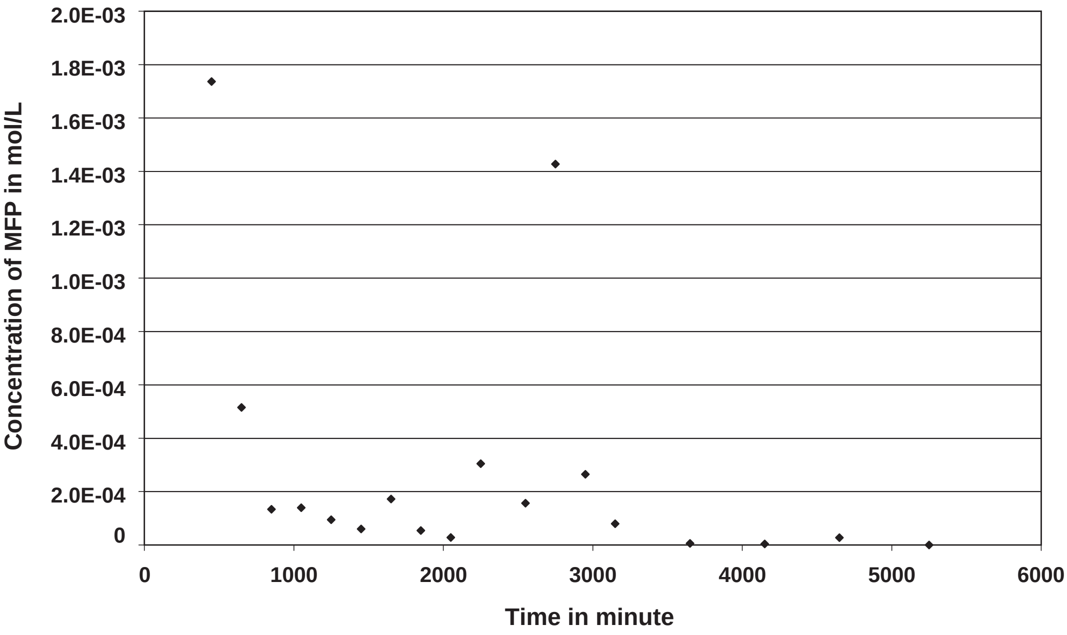

Fig. 10. MFP concentration in percolate during 5% MFP solution percolation.

- P_2: pressure at the exit of the cell in Pa
- L: height of the sample in meters
- R: external diameter of the sample in meters
- r: internal diameter of the sample in meters

To highlight the effect of MFP on concrete transfer properties, measures of flow rate during MFP percolation using a 10^{-2} mole MFP solution, have been compared to those obtained during de-mineralised water percolation.

To accentuate interaction phenomena, and better see the effect produced by MFP solution on percolation flow rate, these tests have been realised on young concrete samples (2 years old).

Fig. 8 presents the evolution of flow rate for two samples with nearly identical initial radial permeability ($4.14\ 10^{-16}$ m^2 for sample A and $4.20\ 10^{-16}$ m^2 for sample B). In both cases, a rapid decrease of the flow rate can be observed at the beginning of the test, and a progressive stabilisation until the end of the test. This

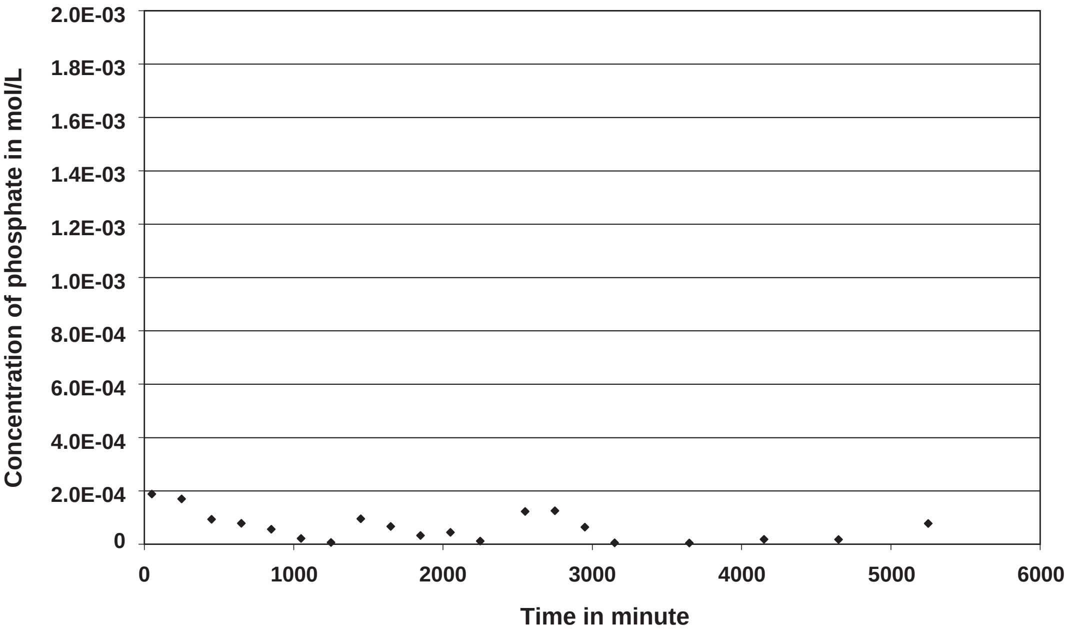

Fig. 11. Phosphate concentration in percolate during 5% MFP solution percolation.

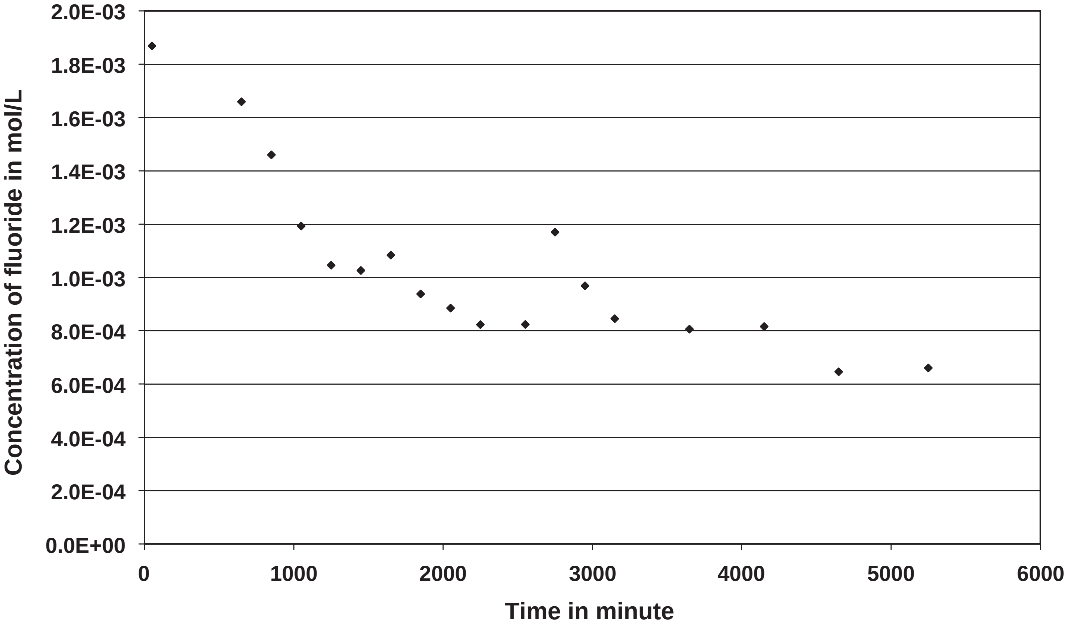

Fig. 12. Fluoride concentration in percolate during 5% MFP solution percolation.

decrease reveals a partial closing of interconnected pores. A complementary hydration of the anhydrous cement and the probable formation of new amorphous phases presented in previous paragraph can explain it. We can notice that the flow rate measured during MFP percolation is lower that the one measured during water percolation. Because this difference appears for each measure, we can think that MFP solution must have a special behaviour in concrete. The amorphous gel formed by the reaction of MFP with calcium hydroxide could explain the difference between water and MFP percolation.

The flow rates obtained with samples that have a slightly different permeability are presented on Fig. 9 (4.20 10^{-16} m^2 for sample B and 5 10^{-16} m^2 for sample C). The sample B has been percolated by water while the sample C has been percolated by a 10^{-2} mol/L MFP solution. As expected, the sample C with a high initial permeability presents the higher initial percolation flow rate. On the other hand, after 20 h, the percolation flow rate of the test specimen percolated by

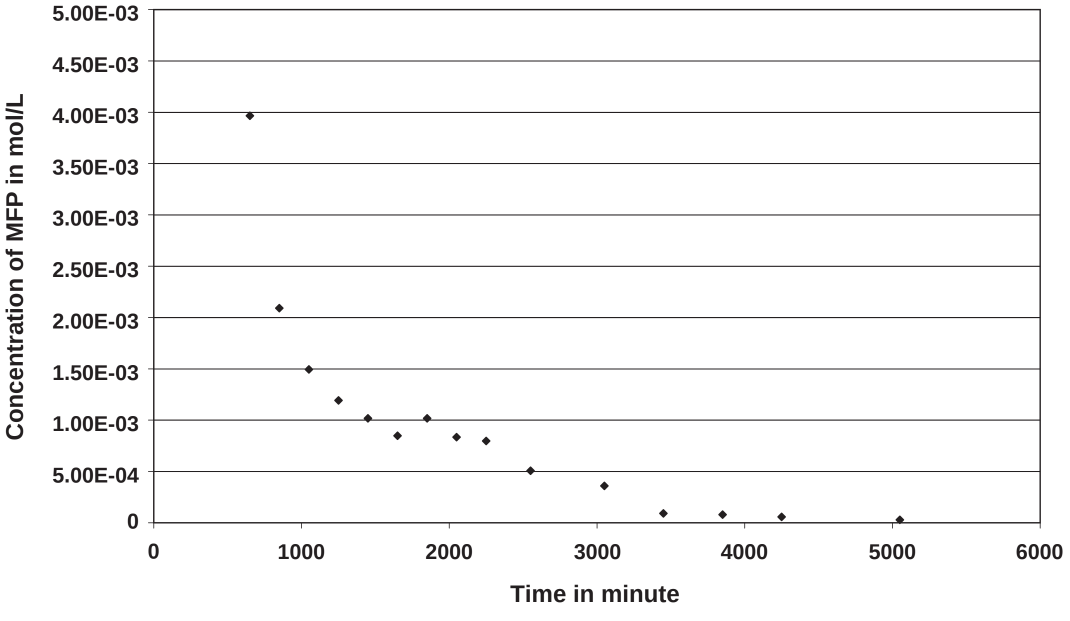

Fig. 13. MFP concentration in percolate during 10% MFP solution percolation.

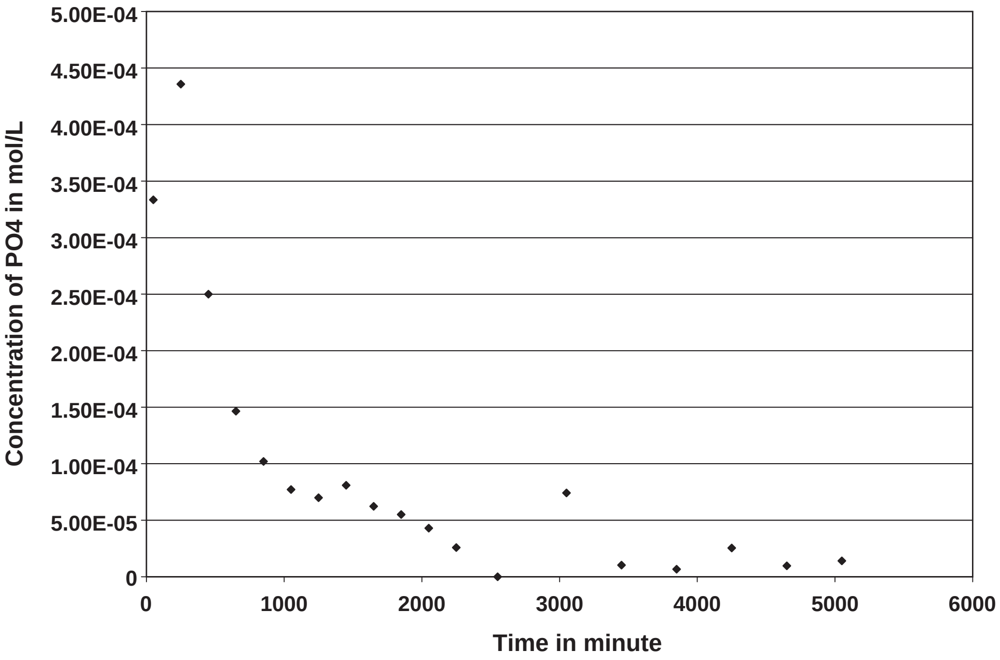

Fig. 14. Phosphate concentration in percolate during 10% MFP solution percolation.

MFP solution decreases more quickly than the one percolated by water despite a higher initial permeability.

So it can be thought that specific reactions occur when MFP is in concrete and the clogging of interconnected pores is more pronounced.

4. Effect of interactions on the residual amount of MFP in the percolate

Phosphate, fluoride and fluorophosphate amounts in the portions of the percolate collected during the percolation test have been determined by an external laboratory, Analytic-Lutz Laboratory, by ion chromatagraphy [7]. To better approximate the real field conditions, experiments have been carried out with 2 different MFP solutions (5% and 10%) and using old concrete samples.

Results obtained during the percolation of the 5% MFP solution are presented on Figs. 10–12. It can be seen that fluorophosphate and phosphate concentrations are very low (10^{-4} mol/L), particularly phosphate, and that no clear variation profile is noticeable (Figs. 10 and 11). It looks like the MFP solution stayed in the concrete sample long enough to permit the adsorption and the partial hydrolysis of the

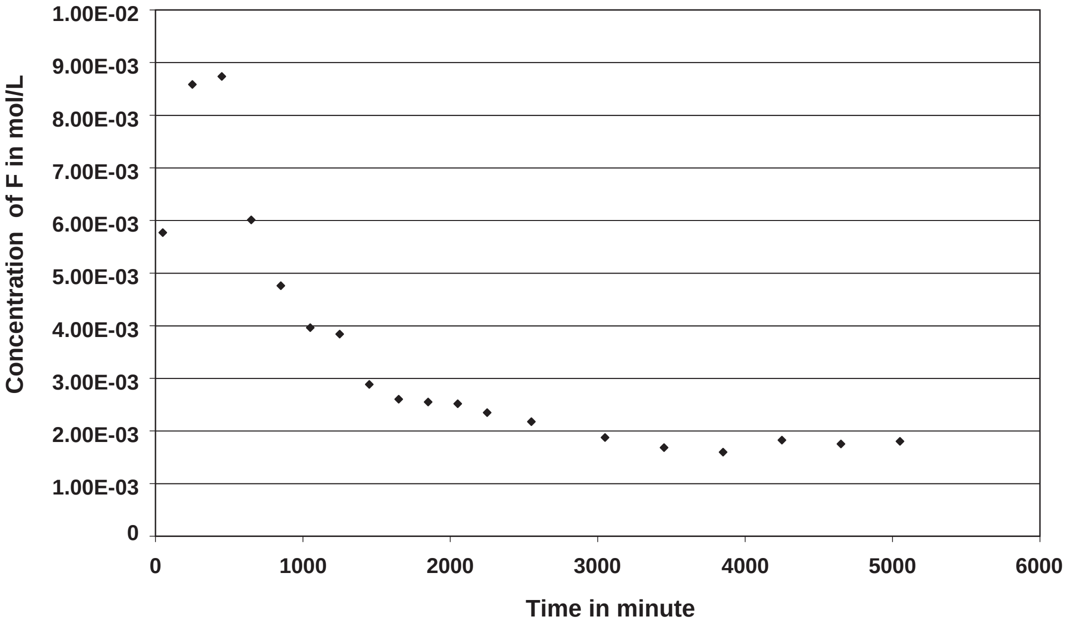

Fig. 15. Fluoride concentration in percolate during 10% MFP solution percolation.

Table 2
Quantitative evaluation of MFP in percolate

	MFP in mol/L	Phosphate in mol/L	Fluor in mol/L	Sum in mol/L MFP+PO_4^{3-}	Sum in mol/L MFP+F^-
5% (3.5 10^{-1} mol/L)	3 10^{-4}	6 10^{-5}	1.8 10^{-3}	3.6 10^{-4}	2.1 10^{-3}
10% (7 10^{-1} mol/L)	3 10^{-3}	3 10^{-4}	8 10^{-3}	3.4 10^{-3}	1.1 10^{-2}

percolated fluorophosphate. The fluoride profile (Fig. 12) indicates a higher initial amount in the percolate but it decreases progressively. The kinetics of the reaction of the fluoride could be slower than the phosphate one.

If we observe Figs. 13–15, presenting the percolation of the 10% MFP solution, we can see that the fluorophosphate, phosphate and fluoride concentrations are ten times higher than in the test with the 5% solution. In addition, the profiles are more clearly defined and show a progressive decrease. These high fluorophosphate concentrations show that MFP has not been totally adsorbed in the concrete sample. Moreover, the decrease of fluorophosphate, phosphate and fluoride amounts during the test must be linked with the decrease of percolation flow. Indeed, low flows provide a long time of contact between solution of percolation and hardened cement paste. Reactions become more important and the percolated amounts of ions from MFP decrease progressively.

In Table 2, a quantitative evaluation is presented: the sum of residual fluorophosphate and fluoride, and the sum of residual fluorophosphate and phosphate in the percolate are calculated. Calculations are made with the maximum values that can be read on Figs. 10–15.

In both cases, whatever the amount of the initial concentration of the MFP solution, most of MFP has been held in concrete sample. So, with the 5% initial MFP concentration, 160 times less inhibitor is found in the percolate whatever the way the amount has been calculated (FPO_3^{2-}+F^- or FPO_3^{2-}+PO_4^{3-}). In the same way, with the 10% initial MFP concentration, 60 times less MFP are found in the percolate.

It can be noticed that there is an important difference between the quantity of FPO_3^{2-} found in the percolate after the 5% or the 10% MFP solution percolation. When the initial MFP concentration is doubled (from 5% to 10%), in the percolate, the FPO_3^{2-}+PO_4^{3-} amount is multiplied by 10, and the amount of FPO_3^{2-}+F^- is multiplied by 5.

These results seem to show a lower reactivity of fluoride with hardened cement paste than the phosphate. Indeed the amount of fluoride in the percolate is much higher than the phosphate one. The pressure that is applied during the test might be partially responsible for this behaviour: phosphates form low mobility hydrates whereas the free fluoride will remain more mobile under pressure.

We could think that the increase of the MFP concentration in the solution could lead to an increase of the formation of gel from fluorophosphate/calcium hydroxide reaction (§2.2), and, as a consequence, find less fluorophosphate in the percolate of the 10% MFP solution than in the 5%. The experiment doesn't confirm this thought: indeed, when the concentration of the MFP solution increases, the concentration of fluorophosphate in the percolate increases as well.

5. Conclusion

This study highlights the complex interactions between MFP and hardened cement paste components, especially calcium hydroxide. The decrease of portlandite peaks that can be observed on the X-ray diffraction diagrams of treated cement paste and the formation of amorphous gel when MFP is mixed with a calcium hydroxide solution, are the consequences of these interactions.

Adsorption and percolation tests have shown that interactions between MFP and hardened cement paste lead to the retention of the major part of the MFP into the concrete and that transport properties of the concrete are modified.

Percolation tests with old concrete samples have shown that even with these interactions, depth of MFP penetration can be increased by increasing the MFP concentration of the percolation solution.

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