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Detection or quantitative analysis of a corrosion inhibitor, the sodium monofluorophosphate, in concrete

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Abstract

In the context of the corrosion of steel in reinforced concrete, one possible solution of protection is the use of corrosion inhibitors. The aim of this paper is to present two methods to analyse quantitatively the inorganic inhibitor sodium monofluorophosphate (MFP, no. CAS[10163-15-2]) in concrete. The first method using ion chromatography leads to very accurate results and permits the determination of the ionic compounds of MFP (PO_4^{3-}, F^- or PO_3F^{2-}). The second method proposes the analysis of fluoride using an ion specific electrode. This low cost method allows the detection of the presence of MFP and quantification of fluoride ions brought by MFP. The choice of method depends on the type of result needed. For both methods, various ways of extraction have been tested. Finally, it is concluded that extraction using a cation exchanger is the most efficient method to extract the MFP ions from concrete.

Keywords: Corrosion inhibitor; Sodium monofluorophosphate; MFP; Fluoride; Ion chromatography; Fluoride specific electrode

1. Introduction

Reinforced concrete is a composite material consisting of concrete and steel. These two components are chemically balanced; the concrete protects the steel rebars from corrosion so that the reinforcement can play a mechanical role in the structure. Due to the aging of constructions, two phenomena can disturb this balance and generate corrosion: the carbonation of concrete and the penetration of chlorides.

Among the methods to avoid corrosion, there are technical design recommendations, electrochemical methods and corrosion inhibitors.

Corrosion inhibitors can be divided into three categories depending on the way they act:

- Anodic inhibitors that reduce steel dissolution;
- Cathodic inhibitors that limit the reaction associated with the dissolution of the metal;
- Mixed inhibitors that are both anodic and cathodic inhibitors.

Only certain corrosion inhibitors can operate in steel reinforced concrete, because of the basic pH of concrete. Our study deals with a specific corrosion inhibitor: sodium monofluorophosphate (MFP) which is an inorganic inhibitor. Even though several studies [1–3] have established that MFP is an actual corrosion inhibitor, none of them have managed to determine the way in which MFP inhibits the corrosion of steel in reinforced concrete (anodic, cathodic or mixed). This corrosion

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inhibitor is used in solution and applied on the surface of reinforced concrete structures. The solution penetrates in depth of concrete so that it protects steel rebars.

MFP can diffuse inside concrete in the form of MFP ions. When it is in contact with concrete, MFP is also able, by partial hydrolysis, to liberate PO_4^{3-} and F^- ions that diffuse separately. In addition, each PO_4^{3-} and F^- ion is able to interact with hardened cement paste to form insoluble phases. In order to follow the penetration of MFP into concrete and characterise its interactions with the hardened cement paste, it is necessary to quantify these various ions.

Methods exist to quantify fluoride by ion chromatography [4], but cannot be used to quantify MFP in concrete, because interactions between MFP and hardened cement paste fix the MFP in the concrete and not allow an easy extraction.

This article presents two methods suitable for quantitative analysis of MFP in concrete.

The first one is an ion chromatographic procedure. After a short presentation of the principle, the feasibility of the analysis is presented. The influence of various extraction solutions and hydrolysis conditions are examined. In particular, it is intented to show the role that a cation exchanger can play in the extraction process, and then present the quantitative evaluation.

The second one is a method based on quantitative analysis of fluoride using a specific electrode. After a study of the hydrolysis phenomenon, two practical methods of extraction are compared.

2. Ion chromatography

2.1. Principle

Ion chromatography is a technique of separation of ion species contained in a solution. It is based on the separation of the species we wish to analyse between a mobile and a stationary phase. The separation and the migration time of species to elute both depend on the difference of affinity between these species for the mobile and the stationary phases. The quality of the separation is usually described using three essential parameters:

- The resolution:

  $$R = \frac{\text{Distance between the top of two peaks}}{\text{Average width at the base of the peaks}}.$$

  Generally, a minimal resolution of 1 is necessary for a good quantitative determination of the components.
- The efficiency is a measure of the dispersion of species through the chromatographic system. High efficiency is characterised by very thin peaks.
- The selectivity, thermodynamic function of the exchange, is defined as the ratio between the retention time of the two components, and is equal to the ratio between the constants of balance. When it is equal to 1, there is no resolution and the two components co-elute.

2.2. Operating conditions

The instruments used in this study comprised a Dionex DX 500 chromatograph with Dionex IonPac AG14A (Guard) 3 × 50 mm, AS14A 3 × 150 mm columns and a conductivity detector [5].

The eluant phase is composed of a mix of Na_2CO_3 8 mmole/L and $NaHCO_3$ 3 mmole/L.

The suppressor is the Anion self Regenerating Suppressor ASRS-Ultra.

The volume of injected solution that we analysed is 5 µl.

2.3. Analysis of MFP in a solution containing typical ions

2.3.1. Study of the resolution of the MFP peak

In order to study the feasibility of a simultaneous analysis of the MFP, PO_4^{3-} and F^- ions, we have recorded them in identical conditions. On the one hand the chromatogram of a solution of MFP (10^{-3} mole/L) and on the other hand the chromatogram of a Fluka standard solution (no. 63597) containing the principal typical anions F^-, Cl^-, Br^- (10 ppm) and PO_4^{3-}, NO_3^-, SO_4^{2-} (20 ppm).

The pH of the standard solution is acid: 4.64.

The two chromatograms obtained are superimposed on Fig. 1. The MFP peak is clearly identified among the other peaks, even though we can notice a slight overlapping on the lower part with phosphate and sulphate peaks. For these three anions, the resolution is closed to 1 and we can expect a slightly over-estimated determination when they are simultaneously present.

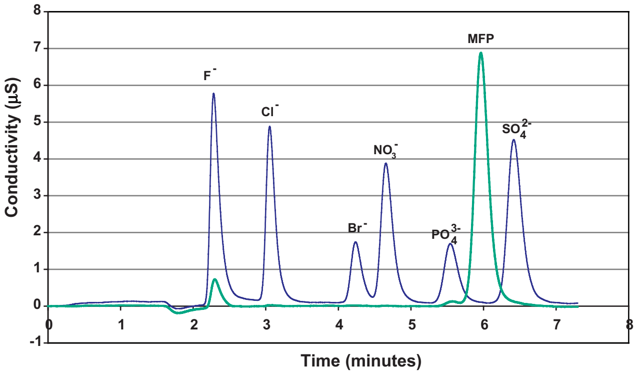

Fig. 1. Superposition of chromatograms of the standard solution and a MFP solution.

The quantitative analysis of MFP in such a mix will depend on the relative proportion of the various components and on the stability of the position of the peaks. But phosphate ions can be found in solution in various forms: PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$. We had to consider whether the position of the peak of the phosphate solution was dependent or not on the form of phosphate.

2.3.2. Study of the stability of the phosphate peak

To study the stability of the phosphate peak in relation to the phosphate species (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$), we have successively recorded the chromatogram of three phosphate species: H_3PO_4, $(NH_4)_2HPO_4$ and Na_3PO_4 in the same conditions.

These chromatograms are presented in Figs. 2–4. They show that the position of the phosphate peak is very stable whatever the phosphate species in solution. The reason is that the volume of solution injected is very small (10 μl) and the nature of the major species is determined by the pH of the eluant and the suppressor. In our operating conditions, this major species is the HPO_4^- anion whatever the form of the phosphate in solution.

Finally, MFP, F^- and HPO_4^- ions can be simultaneously identified on the chromatogram of a solution containing these three components. MFP can be quantitatively analysed but the determination is slightly over-estimated when sulphate and phosphate are simultaneously present in the solution.

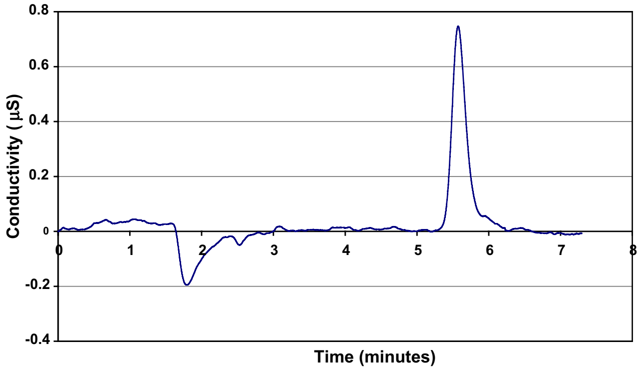

Fig. 2. Acid pH: H_3PO_4, pH = 3.83.

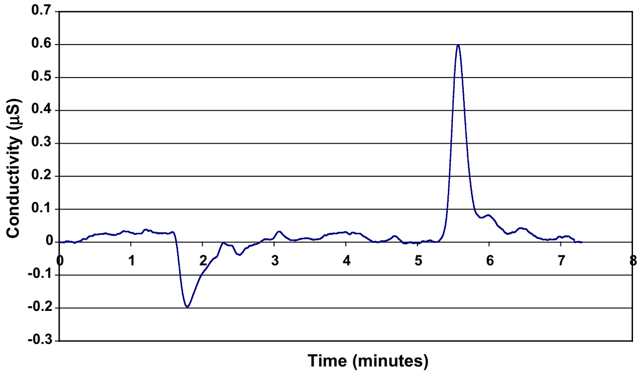

Fig. 3. Neutral pH: $(NH_4)_2HPO_4$, pH = 7.39.

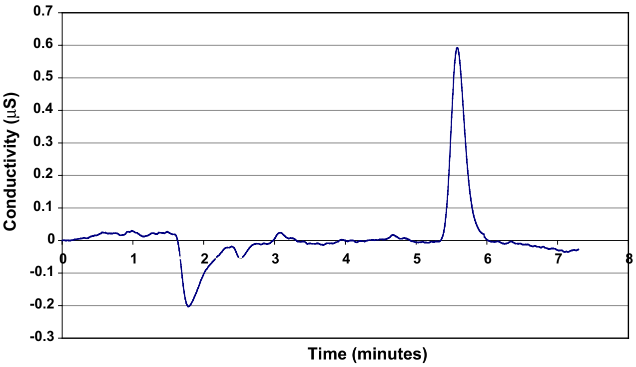

Fig. 4. Basic pH: Na_3PO_4, pH = 9.48.

2.4. Quantitative analysis of the MFP, F^- and PO_4^{3-} ions extracted from concrete samples, using a solution

To analyse the MFP, F^- and HPO_4^{2-} ions contained in the concrete, they first need to be extracted. We know that the MFP ion can suffer partial hydrolysis when it is in contact with hardened cement paste and release F^- and PO_4^{3-} ions. Those two ions are able to combine with the calcium of the concrete to form sparingly soluble compounds such as calcium phosphate and calcium fluoride.

Therefore, the method of extraction will have to facilitate the prior dissolution of these neo-formed compounds.

We have examined the effect of three extraction solutions with acid or neutral pH. For each trial, the material we have used composed of 2 g of concrete powder that has previously been impregnated with a defined quantity of MFP. The extraction is realised by agitation of the mix in presence of 13 ml of water, 13 ml of a buffer solution, acetic acid/sodium acetate or 0.5 ml of nitric acid. The chromatogram is then recorded after filtering the mix on a filter paper able to stop the particles bigger than 0.45 μm.

2.4.1. Extraction using water

The chromatogram recorded after extraction of ions using water is presented in Fig. 5. On this diagram, there are neither the MFP nor the phosphate peaks. Only low fluoride and sulphate peaks are noticeable on the chromatogram.

Using water, it does not seem to be possible to extract MFP ions that have been adsorbed on the hardened cement paste or those that have reacted with it. This result has already been obtained by other authors [6].

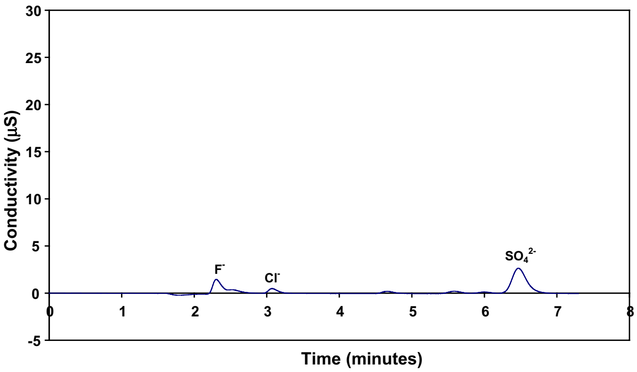

Fig. 5. Extraction using water.

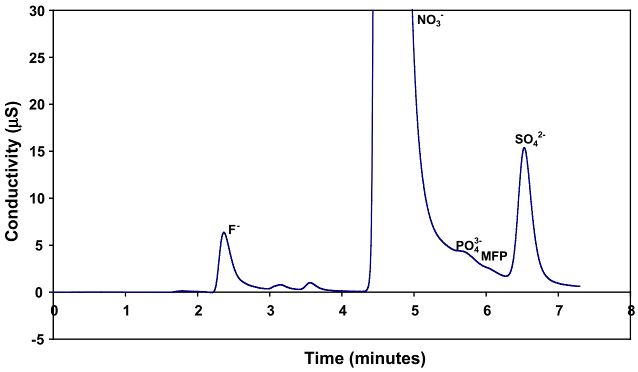

Fig. 7. Extraction using nitric acid.

2.4.2. Extraction using a buffer solution: acetic acid/sodium acetate

The chromatogram recorded is presented in Fig. 6. This time, there is a weak MFP peak and a sulphate peak slightly higher than the one obtained using water. Nevertheless, we remark that the acetate anion brought by this solution of extraction gives an intense and massive peak that overlaps the fluoride peak and conceals the peaks of the other components of the solution.

2.4.3. Extraction using nitric acid

For this extraction we made use of a concentrated nitric acid solution. The chromatogram obtained is presented in Fig. 7. The fluoride and sulphate peaks are clearly identifiable. Nevertheless, the nitrate peak widely dominates the diagram and conceals the peaks of the other components in the solution, i.e. the MFP and the phosphate.

2.5. Quantitative analysis of MFP after an extraction using a cation exchanger

On one hand, even though the acid solutions used are able to extract partially the MFP, they bring to the solution a significant proportion of anions that conceal all the other peaks and prevent the calculation from being accurate. On the other hand, demineralised water extracts with difficulty the MFP from its combination with the hardened cement paste.

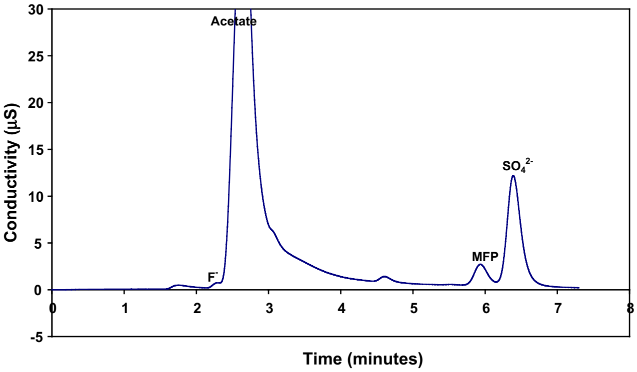

Fig. 6. Extraction using a buffer solution: acetic acid/sodium acetate.

That is why another method to extract the MFP has to be sought.

A new method proposed by Lutz [7] consists of extracting the MFP using a cation exchanger (amberlite IR-120, no. CAS[9002-23-7]). The acidity required for the extraction is brought in by the cation exchanger in a process during which H^+ ions of the exchanger take the place of the Na^+ ions of the solution. The SO_4^{2-} ions fixed on the cation exchanger are released in small quantities and do not affect the sensitivity of the analysis. We used such a cation exchanger to extract and analyse the MFP present in samples of concrete powder.

The procedure used by LUTZ [7] is based on the principle of extraction using the solid cation exchanger called amberlite IR 120, as described in the method presented in the following paragraph.

2.5.1. Description of the analysis procedure

The quality of quantitative analysis by chromatography depends closely on the preparation of the solutions. Here is the preparation we used:

- 100 mg of concrete powder,
- 1 ml of cation exchanger (solid phase + residual water),
- 1.5 ml of demineralized water,
- 10–20 min of agitation,
- Filtration through a 0.45 µm filter,
- Quantitative analysis.

Three major aspects of this method have been considered: the feasibility of analysis after extraction using a cation exchanger, the proportion of MFP hydrolysed by the cation exchanger and finally a quantitative evaluation was carried out at the end of the process.

2.5.2. Feasibility of analysis after extraction using a cation exchanger

As in the previous trials, the material used is a concrete powder mixed with a defined quantity of MFP. The fineness of the powder (<80 μm) is required to facilitate the interactions of the MFP with hardened cement paste. After 30 min of contact between MFP and the concrete powder, the extraction was carried out using the solid cation exchanger mentioned previously: amberlite IR120. The solution obtained is analysed by ion chromatography. The chromatograph recorded is given in Fig. 8.

Unlike the extractions previously realised with the demineralized water and the acid solutions, the MFP peak can be clearly identified. A low phosphate peak and a very low fluoride peak can be noticed. The sulphate peak stays the same. This peak is likely to be higher due to more sulphates present in concrete than those which could be brought in by the cation exchanger.

This test shows that the MFP present in concrete can easily and efficiently be extracted using a solid cation exchanger.

The presence of phosphate ions on the chromatogram could be an indication of a partial hydrolyse of the MFP. This hydrolyse could be due to the acidity of the cation exchanger, but in this case a fluoride peak would have also been present on the chromatogram in a more significant way. This phosphate should then be brought in by the concrete.

To study the possibility of an hydrolyse of MFP generated by the acidity of the cation exchanger, we have recorded the chromatogram of a solution of MFP after having been in contact with the cation exchanger.

2.5.3. Study of the proportion of MFP hydrolysed by the cation exchanger amberlite IR 120

The profiles of F^-, PO_4^{3-} and MFP ions are required to evaluate the effectiveness of a treatment on a structure with MFP.

To be sure of the interpretation of the profiles, it is necessary to evaluate the proportion of MFP that can be hydrolysed by the cation exchanger IR 120.

For this purpose, 5 ml of solution of MFP (1000 ppm) and 2 ml of cation exchanger were mixed. After being in contact for 2 h, the MFP was quantitatively analysed.

Three peaks of F^-, PO_4^{3-} and MFP are clearly identified in Fig. 9. Calculations have shown that more than 90% of the MFP introduced had been found and only 10% had been hydrolysed.

The use of a cation exchanger in the process of analysing MFP in concrete powder permits us to know the form under which the MFP is present in the concrete. This information is important in the evaluation of the quality of a treatment with MFP.

2.5.4. Quantitative evaluation

To evaluate quantitatively the rate of MFP that it is possible to extract using a cation exchanger, two series of trials were carried out with concrete powder mixed with a defined quantity of MFP solution. The way the MFP is introduced is the sole difference between those two series.

In the first one, the sample was composed of 2 g of concrete powder and 0.04 g of MFP powder. The extraction was carried out by adding 10 ml of cation exchanger in defined conditions. After 30 min of interaction, the mix was filtrated and diluted in a 50 ml volumetric flask before analysis. The concentration expected was 5.56 mole/L. At the same time, a reference sample consisting of 2 g of concrete powder without MFP was prepared. The results showed the presence of a significant quantity of phosphate (8×10^{-5} mol/L), even in the absence of MFP. The analysis of phosphate was corrected to take into account the initial amount of these ions in the concrete powder. In the case of a real MFP treatment, it is necessary to take reference samples either before treatment or in an untreated part of the construction because the cement may contain significant initial quantities of phosphorous and fluoride (depending on its manufacturing process).

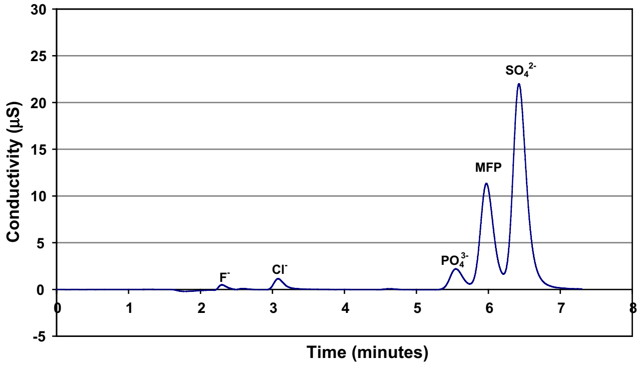

Fig. 8. Extraction using a cation exchanger.

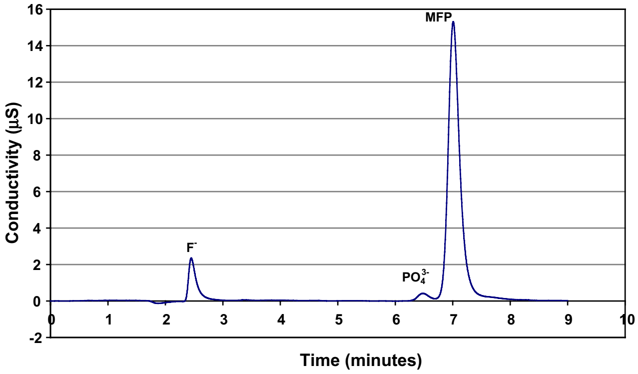

Fig. 9. Hydrolyse due to cation exchanger.

Table 1
Quantitative analysis of MFP powder after extraction from concrete powder

	Phosphate		MFP		Sum PO_4^{3-} corrected + MFP	
	Ct[a] (mole/L)	Cc[b] (mole/L)	C[c] (mole/L)	% found	Cc[d] (mole/L)	% found
Average over 10 samples	1.10×10^{-3}	1.02×10^{-3}	4.50×10^{-3}	**80**	5.52×10^{-3}	**99**

[a] Total phosphate concentration.
[b] Corrected phosphate concentration = total concentration − initial concentration in concrete.
[c] MFP concentration.
[d] Corrected phosphate concentration + MFP concentration.

Table 2
Quantitative analysis of MFP in solution after extraction from concrete powder

	Phosphate		MFP		Sum PO_4^{3-} corrected + MFP	
	Ct[a] (mole/L)	Cc[b] (mole/L)	C[c] (mole/L)	% found	Cc[d] (mole/L)	% found
Average over 10 samples	1.02×10^{-3}	9.41×10^{-4}	9.87×10^{-4}	**35**	1.93×10^{-3}	**70**

[a] Total phosphate concentration.
[b] Corrected phosphate concentration.
[c] MFP concentration.
[d] Corrected phosphate concentration + MFP concentration.

From the mix containing 2 g of concrete powder and 0.04 g of MFP powder, 10 samples were extracted. Thanks to a series of quantitative analysis of the same solution containing MFP, the uncertainty was evaluated to be 6%. The results are presented in Table 1. The corrected phosphate and the MFP amounts are indicated. The last column presents the sum of hydrolysed and non-hydrolysed MFP.

These results show that this process permits to extract almost all the MFP introduced. The MFP is found either under the native form (80%) or under the hydrolysed products phosphate and fluoride (20%).

In the second series of trials, 2 ml of a MFP solution (10,000 ppm) was introduced to 2 g of concrete powder. After 30 min of interaction, 10 ml of cation exchanger IR 120 was added to the mix and left for a further 30 min, to extract the MFP. The mix was then filtered and diluted in a 50 ml volumetric flask. The expected concentration was 2.78×10^{-3} mole/L. The results are presented in Table 2.

It was noticed that when there was a very strong interactivity between MFP and concrete powder (when MFP was added in solution), about 70% of the MFP introduced were found either under the MFP form or the phosphate form. This is due to the fineness of the concrete powder and its long period of interaction with MFP solution.

In the case of the simultaneous addition of MFP powder, cement concrete powder and cation exchanger, interactions could not occur, and 100% of MFP was found.

In practice, in the case of real application of MFP, even if the duration of interaction is very long, the surface of interaction is much smaller than with powder, and most of the MFP is extracted from samples.

2.6. Comments on ion chromatography

The use of water or acid solutions does not give satisfactory results as water extracts the MFP with difficulties and the acid solution brings to the solution a significant proportion of anions that conceal all the other peaks.

Extraction of MFP using a cation exchanger is an efficient method even though it does not allow the extraction of the whole of the MFP.

These results also show that the interactions between MFP and concrete generate the formation of insoluble phases that cannot be totally extracted with a cation exchanger.

We also remark that when MFP was introduced in the form of solution only 35% of the MFP were not hydrolysed whereas 80% were not hydrolysed when the MFP was introduced in the form of powder. The hydrolyse of a MFP solution in contact with concrete is an important phenomenon to consider when MFP is applied on structure.

As a conclusion, the MFP can be extracted from concrete using a cation exchanger and then analysed by ion chromatography.

3. Quantitative analysis of fluoride using a specific electrode

The second method presented in this article attempts to determine the quantity of MFP in concrete by measuring the total fluoride obtained following a procedure of extraction and hydrolysis.

This method does not distinguish the fluoride formed by hydrolysis during the contact of the MFP with the concrete or the fluoride initially present in the concrete, from the fluoride hydrolysed during the analysis. Therefore, the method could not give accurate information on the form the MFP stands in the concrete.

However, as fluoride is not a common element in concrete, this method of determination using specific electrode, is an alternative and easier way to quantify approximately the MFP penetration in concrete.

In this study we will compare two methods of extraction:

(A) Extraction with nitric acid,
(B) Extraction with cation exchanger amberlite IR120.

3.1. Procedure, material and instruments

The tools used for these analyses are described in the following list:

- Ionometre: consort C733,
- Fluoride electrode: ELIT 8221 fluoride,
- Reference electrode: ELIT 001n AgCl,
- Concentrated nitric acid,
- Buffer solution of acetic acid/sodium acetate (0.1 mole/L) (pH = 4.2 by adding nitric acid).

The various stages are bulleted below:

- 2 g of concrete powder,
- *Extraction*:
  (A) 20 ml of demineralized water + 0.5 ml concentrated HNO_3, waiting 30 min,
  (B) 13 ml of cation exchanger IR120, waiting 2 h,
- Filtration and rinsing,
- *Hydrolyse*:
  (A) 0.5 ml of concentrated HNO_3,
  (B) 1 ml of concentrated HNO_3,

and 3 h of agitation in a 50 °C thermostat controlled bath,

- Dilution,
- *Quantitative analysis*:
  (A) 5 ml of the solution to analyse,
  (B) 1 ml of the solution to analyse,

in 25 ml buffer solution of acetic acid/sodium acetate,

- *Ionic meter calibration*:
  (A) 5 ml of NaF solution from 10^{-1} to 10^{-6} mole/L,
  (B) 1 ml of NaF solution from 10^{-1} to 10^{-6} mole/L,

in 25 ml buffer solution of acetic acid/sodium acetate.

3.2. pH fluoride window

The measure of the concentration of fluoride by direct potentiometry is a sensitive measure that permits the analysis of very low concentration, down to 10^{-6} mole/L. This measure is sensitive to the pH of the solution containing the fluoride. As shown in Fig. 10, analysis in an acid medium underestimates the real amount of fluoride. Indeed, in this condition, the fluoride ions react with the protons to form hydrofluoric acid feebly dissociated. Nevertheless, in a basic medium, the fluoro lanthane crystal of the electrode reacts with the OH^- ions and frees fluoride ions. In these conditions the amount of fluoride is overestimated. To realise a measure of the fluoride concentration as accurate as possible the pH of the solution to be analysed must be in a certain range.

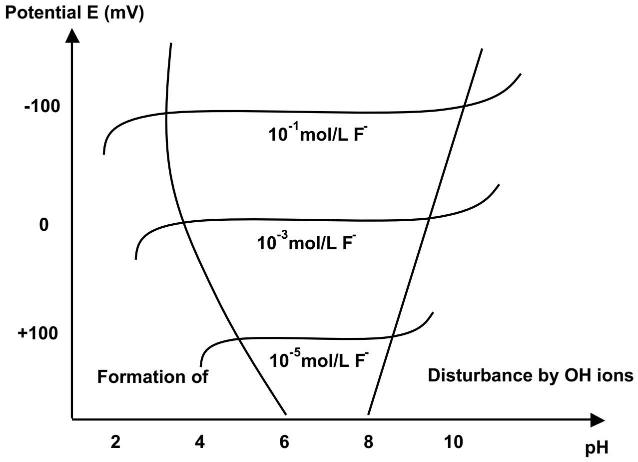

Fig. 10. pH fluoride window.

According to the procedure described in Section 3.1, at the end of the hydrolyse phase the solutions contain 1 ml of nitric acid. Therefore their pH is very acidic when they are ready to be analysed. To avoid the need to adjust the pH to a value in accordance with Fig. 10, we introduced a defined quantity of the solution to be analysed in 25 ml of a buffer solution (acetic acid/ sodium acetate).

Moreover by using the same process when preparing the standard solutions and the solutions to be analysed, the difference between the ionic forces is very small, and so the quality of the analysis is better. But as this quality also depends on the quality of the hydrolyse, this stage needs to be examined.

3.3. Hydrolyse

The procedure developed (in LMDC) for analysing MFP is based on fluoride analysis. To have the greatest amount of fluoride available in the solution, it is necessary to hydrolyse the greatest quantity of MFP. Hydrolyse is an essential stage of the process.

In an article describing the fluoride analysis in toothpaste, it is recommended to do the hydrolyse with hydrochloric acid at 80 °C for 30 min [8]. The introduction of Cl^- through the use of acid would prevent the analysis of chloride in the same sample. That is why another strong acid is being used: nitric acid.

The repeatability of the process has been checked with 10 samples prepared as described below: 1 ml of concentrated nitric acid was added to 5 ml of a MFP solution (0.4 mole/L). The mix was put in a thermostatic bath for 3 h at 50 °C. After dilution in 200 ml, fluoride was analysed as described in Section 3.1.

The average over 10 samples was 9.97×10^{-3}mol/L (standard deviation: 1.20×10^{-4}), when the expected concentration was 1×10^{-2} mole/L. 99.7% of the MFP was detected with an uncertainty of 3.61%. Based on these results, it was decided to apply this method to concrete extracted solution.

3.4. Comparing two methods of extraction

A calibration curve and a validated hydrolyse method are available to analyse the fluoride reliably. In the case of analysing the MFP present in concrete, the major problem is the extraction. The following compares two methods of extraction: using nitric acid and using a cation exchanger: amberlite IR 120.

3.4.1. Extraction using nitric acid

The first method of extraction proposed makes use of nitric acid to dissolve fluoride calcic salts. But in a media too acidic, the formation of hydrofluoric acid leads to a loss of fluoride. The best compromise between an acidity sufficient to extract the MFP, and an acidity that does not lead to an excessive loss of fluoride by formation of fluoridric acid, is the addition of 0.5 ml of nitric acid for 2 g of concrete powder. The extraction is then carried out in a pH 4 media.

To assess the repeatability of extraction of MFP from concrete powder using nitric acid we made a series of 17 samples prepared as described below:

- 2 g of concrete powder (maximum diameter <80 μm),
- 5 ml of MFP solution (0,4 mole/L),
- 20 ml of demineralized water,
- Waiting time of 60 min to let MFP interacts with concrete powder,
- Application of the procedure described in Section 3.1.

The results are presented in Table 3.

Table 3

Expected concentration	Fluoride concentration (average over 17 samples)	MFP detected	Uncertainty
1×10^{-2}	4.85×10^{-3} mol/L	48%	27%

Table 4

Expected concentration	Fluoride concentration (average over 10 samples)	MFP detected	Uncertainty
1×10^{-2}	9.12×10^{-3} mol/L	91%	3.5%

The average of the 17 samples is 4.85×10^{-3} mole/L. 48.5% of the MFP introduced was detected with an uncertainty of 27%. It is worth noting that a significant part of the MFP has not been detected. The study of the hydrolyse phase presented above shows that this stage does not induce massive losses, so the extraction is the cause of most of the lack of precision.

3.4.2. Extraction using a cation exchanger: amberlite IR 120

The cation exchanger amberlite IR 120 is the second extraction method studied in this article. A series of 10 samples composed of 2 g of concrete powder (80 μm) and 5 ml of MFP solution (0.4 mole/L) were prepared, and the procedure described in Section 3.1 was applied. The results are presented in Table 4.

The average calculated from 10 samples is 9.12×10^{-3} mole/L when the expected concentration was 1×10^{-2} mole/L. The extraction using the cation exchanger IR120 leads to a high rate of MFP detected: 91% of the fluoride introduced under MFP form was found with an uncertainty of 3.5%.

3.5. Comments on method using the specific electrode

It is not easy to prepare a solution to be analysed with exactly the same ionic forces as the standard solution used to build the calibration curve. For this reason, in our case, results are slightly over-evaluated. Because it is not convenient to build a calibration curve for each concrete sample and for each type of cement, we have minimised the influence of the ionic forces by testing the minimum quantity of solution and using a buffer solution of acetic acid and sodium acetate. The best results were obtained by introducing 1 ml of extracted solution in 25 ml of buffer solution. The calibration curve was built in the same conditions by introducing 1 ml of NaF (from 10^{-1} to 10^{-6} mole/L) solution in 25 ml of buffer solution.

4. Conclusion

In the first part of this article a method that allows the quantitative analysis of monofluorophosphate anion (MFP) in the presence of the ions usually found in concrete has been presented. This method consists of extracting the MFP from concrete using a cation exchanger and then analysing it with an ion chromatograph in an eluant phase made of Na_2CO_3 and $NaHCO_3$.

- In this process, the MFP peak is clearly identifiable and can be easily distinguished from the peaks of F^- and HPO_4^{2-}, which can be due to the hydrolyse of the MFP.
- From a practical point of view, this method permits observation of the evolution of MFP in the cement matrix and its possible hydrolyse. This method also allows the identification of the ingredient actually active in the inhibition of corrosion.

In the second part of this article an alternative method to analyse the MFP using a specific electrode has been proposed. The MFP is hydrolysed with nitric acid and quantified by fluoride analysis. It is a global method that does not permit the evaluation of the real quantity of MFP not yet hydrolysed in the hardened cement paste. However as fluoride is rarely present in concrete, this simple process of global analysis will usually be sufficient to establish the depth of penetration of MFP in concrete after a treatment of a structure.

As presented above, the results depend on the technique used to extract the MFP from concrete.

- When the MFP is extracted using a nitric acid solution, 50% of the fluoride introduced under MFP form is detected with a significant uncertainty of 25% because of the loss during extraction.
- The cation exchanger, amberlite IR 120, allows the detection of 91% of the initial fluoride with a low uncertainty of 3.5%.

The determination of total fluoride using a specific electrode is a low cost method to analyse the MFP in concrete even though it does not allow determination of the quantity of MFP not yet hydrolysed.

In summary, ion chromatography and specific electrode are two complementary tools that can be used to evaluate the MFP present in concrete after anticorrosive treatment. If accurate information on the MFP forms at different depths are needed, then ion chromatography will be used. In case of a need to assess the presence of MFP in concrete without requiring more particular information, then the specific electrode method will give the answer.

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References

[1] Duprat M, Bonnel A, Dabosi F, Durand J, Cot L. Les monofluorophosphates de zinc et de potassium en tant qu'inhibiteur de corrosion d'un acier au carbone en solution de NaCl à 3%. J Appl Electrochem 1983;13:317–23.

[2] Duprat M, Lafont M-C, Moran F, Rocher S. Une méthode nouvelle d'inhibition de la corrosion due aux eaux industrielles. L'eau, l'industrie les nuisances, no. 89, Janvier–Février 1985.

[3] Andrade C, Alonso C, Acha M, Malric B. Preliminary testing of Na_2PO_3F as a curative corrosion inhibitor for steel reinforcements in concrete. Cem Concr Res 1992;22:869–81.

[4] Biemer TA, Asral N, Sippy A. Ion chromatographic procedures for analysis of total fluoride content in dentifrices. J Chromatogr A 1997;772:355–9.

[5] Dionex AS14A Manual Doc. no. 031678-01.

[6] Page MM, Page CL, Ngala VT, Anstice DJ. Ion chromatographic of corrosion inhibitors in concrete. Construct Build Mater 2002;16:73–81.

[7] Lutz Th. Anion extraction from concrete and other mineral complexes. In: International ion chromatography symposium, 2000 à Nice.

[8] ISE Application note no. I-1, Fluoride content of toothpaste, Metrhom.