Original Paper

Dissolution of $(50-x)Na_2O-xCaO-50P_2O_5$ metaphosphate glasses in different saline solutions: mechanism and kinetic control

Florence Delahaye, Lionel Montagne and Gérard Palavit

Laboratoire de Cristallochimie et Physicochimie du Solide, URA CNRS 452, Ecole Nationale Supérieure de Chimie de Lille, Villeneuve d'Asq (France)

Patrick Baillif and Jean Claude Touray

Equipe de Ressources Environnements et Matériaux, UMR CNRS 6530, Ecole Supérieure de l'Energie et des Matériaux, Orléans (France)

The dissolution of $(50-x)Na_2O-xCaO-50P_2O_5$ metaphosphate glasses has been investigated at pH 3 in solutions containing in Na^+, Ca^{2+}, Cl^-, NO_3^- and $(PO_3^-)_n$ ions. Whatever the conditions, a hydrated layer develops over a surface covered with etch pits. Na^+ and Cl^- have no specific effect on the dissolution kinetics and mechanism. In Ca^{2+}-containing solutions, XPS, electrophoretic mobility and ^{31}P NMR show that Na^+ is exchanged for Ca^{2+} in the hydrated layer, resulting in a decreased dissolution rate. Polyphosphate anions, $(PO_3^-)_n$, act as complexing agent for Ca^{2+}, and counterbalance its inhibiting effect on the dissolution rate.

Auflösung von $(50-x)Na_2O-xCaO-50P_2O_5$ Metaphosphatgläsern in unterschiedlichen Salzlösungen: Mechanismus und kinetische Steuerung

Es ist die Auflösung von Metaphosphatgläsern des Systems $(50-x)Na_2O-xCaO-50P_2O_5$ in Na^+-, Ca^{2+}-, Cl^--, NO_3^-- und $(PO_3^-)_n$-Ionen enthaltenden Lösungen mit dem pH-Wert 3 untersucht worden. Unabhängig von den jeweiligen Bedingungen bildet sich eine hydratisierte Schicht auf der mit Ätzgruben bedeckten Oberfläche. Na^+- und Cl^--Ionen haben keine besondere Wirkung auf Kinetik und Mechanismus der Auflösung. Bei Ca^{2+}-enthaltenden Lösungen zeigen Röntgen-Photoelektronenspektren (XPS), elektrophoretische Beweglichkeit und magnetische Kernresonanzspektren (NMR) von ^{31}P, daß in der hydratisierten Schicht Na^+- gegen Ca^{2+}-Ionen ausgetauscht werden, was zu einer verringerten Auflösungsrate führt. Polyphosphatanionen, $(PO_3^-)_n$, wirken als Komplexbildner für Ca^{2+}-Ionen und heben deren hemmende Wirkung auf die Auflösungsrate auf.

1. Introduction

Phosphate glasses are interesting materials for technological applications like seals [1 and 2], optical devices [3], or biomaterials [4]. But their application is actually limited because they generally have poor chemical durability [5], although lead-iron phosphate glasses have been proposed as matrix for waste materials [6]. However, a poor durability, when controlled, can be interesting for biomaterials or fertilizer glasses [7].

Biomaterials are in contact with biological fluids that are a complex mixture of salts and amino acids [8]. The development of bonds between an implant and the surrounding biological matrix implies ionic exchanges that are controlled by surface reactions between the glass or glass-ceramic and the biological fluids. So there is an interest in investigating the effect of saline solutions on phosphate glass durability.

Some phosphate glasses are used in agriculture for soils deficient in micronutrients like zinc [9] or molybdenum [7]. Controlled release of ions depends upon the glass matrix as much as on the soil conditions.

Astonishingly, compared to the great amount of papers devoted to the structure of phosphate glass [10 and 11], few work has dealt with the mechanism and kinetics of their dissolution [12 and 13]. A set of data on the dissolution of metaphosphate glasses has been published by Bunker and Arnold [14]. They reported that metaphosphate glasses dissolve congruently, with a two-stage mechanism: first surface hydration, then release of metaphosphate chains in solution without chain hydrolysis. Water diffusion is the limiting step of the alteration kinetics in the first stage, and surface reactions are the limiting step in the second stage.

In a previous paper [15], the authors focused on the comparison of the dissolution of metaphosphate glasses in neutral and acid solutions. It was observed that the dissolution was congruent in both media, and SEM, EDS, XPS and NMR analyses clearly showed the presence of an hydrated layer on the surface of the corroded glass samples. The dissolution kinetics obeys a linear law in neutral medium, whereas in acid solution (pH 3), after a linear stage, a slowing down of the dissolution rate is observed. SEM, EDS, XPS and NMR analyses showed that this decrease of the dissolution rate

Table 1. $(50-x)Na_2O-xCaO-50P_2O_5$ glass compositions in mol% (analytical values)

glass no.	P_2O_5 (± 1.5)	CaO (± 1)	Na_2O (± 0.6)
1	50.0	11.3	38.7
2	50.0	15.9	34.1
3	50.0	19.1	30.9
4	50.0	31.3	18.7
5	50.0	40.0	10.0
6	50.0	50.0	–

Table 2. Ionic concentrations in leaching solutions ($\pm 10\%$) versus dissolution time in HCl at pH 3 of $34Na_2O \cdot 16CaO \cdot 50P_2O_5$ glass

dissolution time in h	$[Na^+]$ in mol/l	$[Ca^{2+}]$ in mol/l	$[PO_3]$ in mol/l
0.5	$2 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$
1	$3.8 \cdot 10^{-3}$	$8.5 \cdot 10^{-4}$	$5.2 \cdot 10^{-3}$
1.5	$8 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$
2	$1 \cdot 10^{-2}$	$1.8 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
5	$1.3 \cdot 10^{-2}$	$2.9 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$

is not due to a modification of the morphology, composition, or structure of the hydrated layer. However, as this hydrated layer can be considered as a polyphosphate colloid, the increase in ionic strength of the leaching solution increases the electrostatic interactions between the polyphosphate chains, which leads to the observed decrease in dissolution rate.

Owing to the effect of the ionic strength on the dissolution in acid medium, it is interesting to investigate the effect of different electrolytes on the mechanism of metaphosphate glass alteration. This paper compares the dissolution of $(50-x)Na_2O-xCaO-50P_2O_5$ metaphosphate glasses in synthetic solutions containing ions that are released by the congruent dissolution of these glasses in water at pH 3: Na^+, Ca^{2+} and $(PO_3^-)_n$. The effect of each ion will thus be characterized separately.

2. Experimental procedure

2.1 Glass preparation

$(50-x)Na_2O-xCaO-50P_2O_5$ glasses are prepared from NaH_2PO_4 and $Ca(H_2PO_4)_2$, H_2O, washed in acetone to eliminate the H_3PO_4 impurity. The mixture is melted at 1000 °C for 6 h in platinum crucibles, quenched in a graphite mold and annealed. The analyzed compositions, obtained from solution analyses, are listed in table 1.

2.2 Durability test

Glass slabs ($(2 \times 1 \times 1)$ cm^3) are polished to 5 μm grade. Samples are suspended in a plastic flask containing the

leaching solution at (40 ± 0.5) °C. The volume of the solutions was adjusted according to the sample surface, in order to keep the ratio of sample surface to solution volume constant ($A/V = 0.035$ cm^{-1}). Hence for a $(2 \times 1 \times 1)$ cm^3 sample, the solution volume is 286 cm^{-3}. The pH value is kept constant at 3 by addition of a drop of concentrated HCl when necessary. After the durability test, the sample is removed, rinsed and dried until constant weight. As the sample surface may be altered by drying, a new sample is used for each measurement. The dissolution results are expressed as weight loss divided by initial surface area (mg cm^{-2}) versus immersion time, or as the dissolution rate, i.e., normalized weight loss during one hour of dissolution (mg cm^{-2} h^{-1}).

2.3 Synthetic leaching solutions

In order to evaluate the effect of ions on the dissolution mechanism, the durability tests are conducted in solutions containing known amounts of NaCl, CaCl$_2$ or $(NaPO_3)_n$. They are designated in the following text as synthetic solutions. The pH of synthetic solutions is also kept constant at pH 3 with HCl. The pH value was adjusted with a concentrated HCl solution to avoid the use of buffer solution that could introduce other effects, like complexation. The alteration of metaphosphate glasses in synthetic solution will be compared to the alteration in water at pH 3, reported in [15]. The concentrations of Na^+, Ca^{2+} and $(PO_3^-)_n$ ions have been measured after dissolution experiments in water at pH 3, they are reported in table 2. The concentrations of Na^+, Ca^{2+} and $(PO_3^-)_n$ ions in the synthetic solutions are adjusted in order to obtain the same concentration as in table 2. Owing to the effect of the ionic strength on the dissolution rate that the authors reported in the previous paper [15], such procedure enables one to compare the dissolution rate in water and in synthetic solutions.

2.4 Sample characterization

Magic angle spinning ^{31}P spectra were obtained using an ASX 100 Brucker spectrometer. Spectra were acquired at a magnetic field strength of 2.4 T with spinning speed of 7 kHz. 1.4 μs pulses with 60 s delay time were used. ^{31}P chemical shifts are expressed in ppm relative to an 85% H_3PO_4 solution.

The X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out using a spectrometer AEI ES 200B fitted with a magnesium anode. All binding energies have been referenced to the C(1s) binding energy of the adventitious carbon (284.6 eV). For XPS measurements, an uncorroded glass surface was used as reference.

For electrophoretic mobility measurements, a Zetameter II apparatus was used. A suspension is prepared with 0.5 g of $19Na_2O \cdot 31CaO \cdot 50P_2O_5$ glass powder in 100 ml solution containing an electrolyte of known concentration (KNO$_3$ at 10^{-3} and 10^{-2} mol l^{-1} and CaCl$_2$

at $3 \cdot 10^{-3}$ mol l^{-1}). The average particle diameter is 2 μm. The applied electric field is 6.4 V cm^{-1}. Particle displacement rate is measured with a microscope, over 50 μm. Electrophoretic mobility is expressed as the velocity (μm s^{-1}) divided by the electric field (V cm^{-1}).

3. Results and discussion

The effect of each ion will be discussed separately. Firstly, it was checked whether the chloride ions, introduced to maintain a constant pH value, may influence the dissolution process. Then, the effect of the ions produced by the congruent glass dissolution [15], Na$^+$, Ca^{2+}, and $(PO_3^-)_n$, will be presented and discussed.

3.1 Effect of Cl$^-$ ions

The dissolution experiments were reproduced at constant pH value using HNO$_3$ as acid addition instead of HCl. As shown in figure 1, whatever the anion is, the results of weight loss measurements versus time are similar. So it was concluded that Cl$^-$ and NO$_3^-$ have the same effect on the dissolution of the metaphosphate glass. In the other experiments that will be described below, chloride ions were always used to prepare the synthetic solutions.

3.2 Effect of Na$^+$ ions

Figure 2 shows the dissolution rates measured in water at pH 3 after several dissolution times and in synthetic solutions. Note that for each leaching time the dissolution rate in water can be compared to that in synthetic solutions because both solutions have the same concentration. Increased dissolution time in figure 2 corresponds to increased NaCl concentration in the synthetic solutions. Dissolution rates in NaCl solution are constant whatever the sodium concentration is, thus it can be concluded that Na$^+$ ions do not affect the dissolution rate.

3.3 Effect of Ca^{2+} ions

In synthetic solution containing CaCl$_2$, the dissolution rate decreases strongly when the calcium concentration increases (figure 2). Furthermore, synthetic solutions were prepared with both NaCl and CaCl$_2$ with the same calcium concentration as measured after leaching experiment in water at pH 3 (table 2). In these synthetic solutions, a decrease in dissolution rate is also observed compared to the dissolution in water at pH 3. Thus it is assumed that calcium ions affect the dissolution of metaphosphate glasses. They may be at the origin of the decrease in dissolution rate observed in water at pH 3,
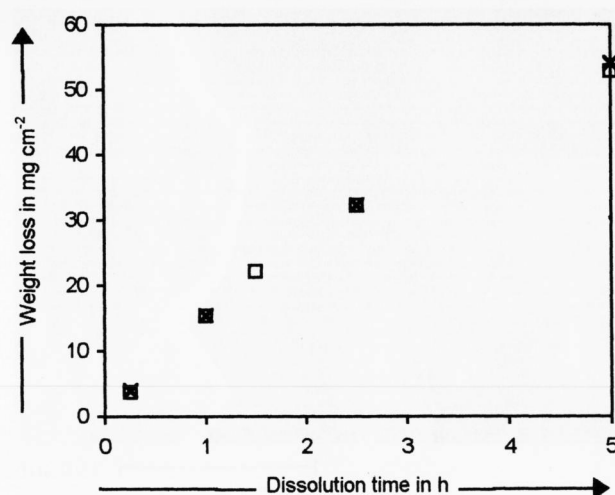

Figure 1. Weight loss versus time of $34Na_2O-16CaO-50P_2O_5$ glass at pH 3. The pH is adjusted with HCl or HNO$_3$.
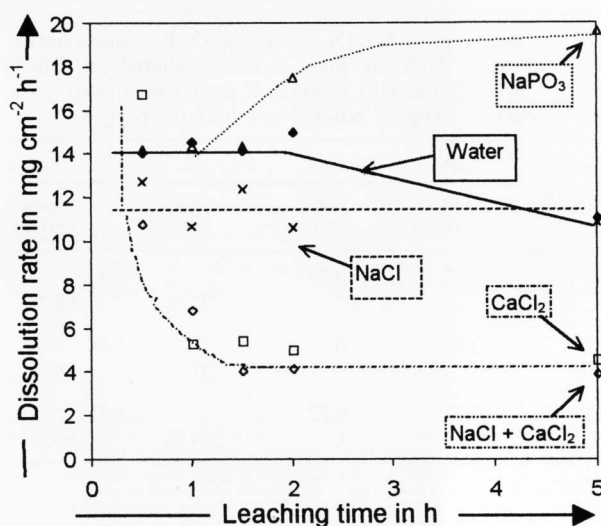

Figure 2. Dissolution rates of $34Na_2O \cdot 16CaO \cdot 50P_2O_5$ glass, measured in water for increased leaching time and in synthetic solutions NaCl, CaCl$_2$, NaCl + CaCl$_2$ or NaPO$_3$, at pH 3.

although the decrease in dissolution rate is less important in water at pH 3 than in the synthetic solutions containing the calcium ions.

The corroded glass surface leached for one hour in CaCl$_2$ solution $(3 \cdot 10^{-3}$ mol $l^{-1})$ is shown on SEM micrograph of figure 3. A layer, partly removed before observation for a better contrast, is observed. Below this layer, etch pits are visible on the glass surface. The same surface morphology was observed after leaching in water at pH 3 [15].

When a dissolution experiment is conducted in synthetic solutions containing CaCl$_2$, XPS analysis (table 3) shows an enrichment in calcium and a total depletion of sodium in the corrosion layer, compared to a pristine
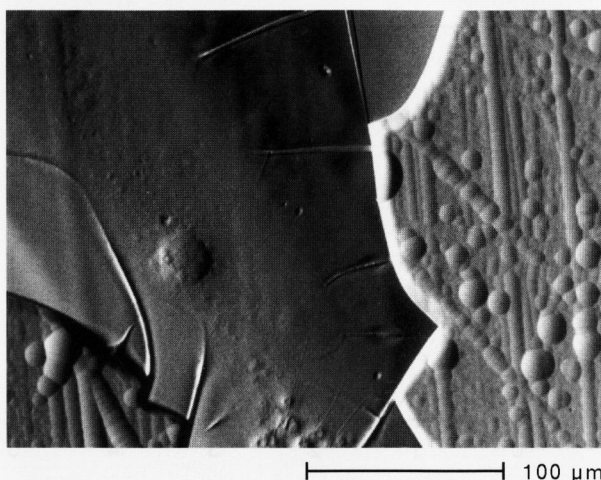
Figure 3. SEM micrograph (backscattered electrons) of the glass surface after 1 h corrosion in $CaCl_2$ solution ($3 \cdot 10^{-3} \, mol \, l^{-1}$). The surface layer has been removed on the right part. Magnification is $\times 350$.

Figure 4. Electrophoretic mobility of $19Na_2O \cdot 31CaO \cdot 50P_2O_5$ glass powder versus pH, in KNO_3 solution at $10^{-3} \, mol \, l^{-1}$ (◆) and $10^{-2} \, mol \, l^{-1}$ (□), and in $CaCl_2$ solution at $3 \cdot 10^{-3} \, mol \, l^{-1}$ (▲).

Table 3. Atomic ratio X/P (X = Ca, Na, O; P = phosphorus) measured with XPS of glass surfaces altered in $CaCl_2$ ($3 \cdot 10^{-3} \, mol \, l^{-1}$) and HCl at pH 3. R is an uncorroded glass. (BO = bridging oxygens, NBO = non-bridging oxygens)

| | X/P | | | |
	Ca (±0.02)	Na (±0.08)	$O_{(BO)}$ (±0.33)	$O_{(NBO)}$ (±0.33)
R	0.22	0.75	3.3 32 %	68 %
$CaCl_2$ pH 3	0.62	0	3.44 31 %	69 %
HCl pH 3	0.22	0.72	3.35 34 %	66 %

glass. Previous XPS analyses [15] have shown that the composition of the layer is the same as that of the bulk glass when dissolution is conducted in water at pH 3.

The effect of calcium ions on the glass surface was monitored with electrophoretic mobility measurement. Figure 4 represents the electrophoretic mobility versus pH in KNO_3 reference solutions (10^{-2} and $10^{-3} \, mol \, l^{-1}$). In $CaCl_2$ synthetic solution ($3 \cdot 10^{-3} \, mol \, l^{-1}$), electrophoretic mobility is lower than in KNO_3 reference solution. This result reflects that positive calcium ions interact strongly with the negative glass surface, and emphasizes the inhibiting role of calcium ions on the dissolution process of the metaphosphate glasses.

Structural information on the corrosion layer was obtained with NMR: ^{31}P MAS-NMR spectra (figure 5) of the layer formed in $CaCl_2$ synthetic solution ($3 \cdot 10^{-3} \, mol \, l^{-1}$) and of an uncorroded glass show one resonance at -22 ppm, attributed to middle chain groups Q^2 [16]. A very weak one due to end-chain
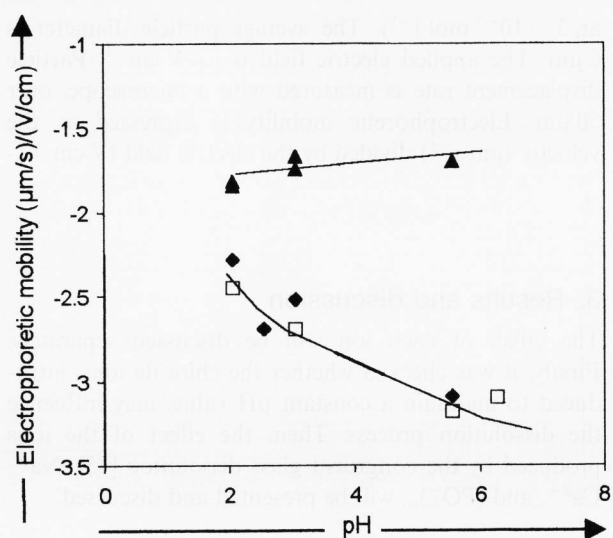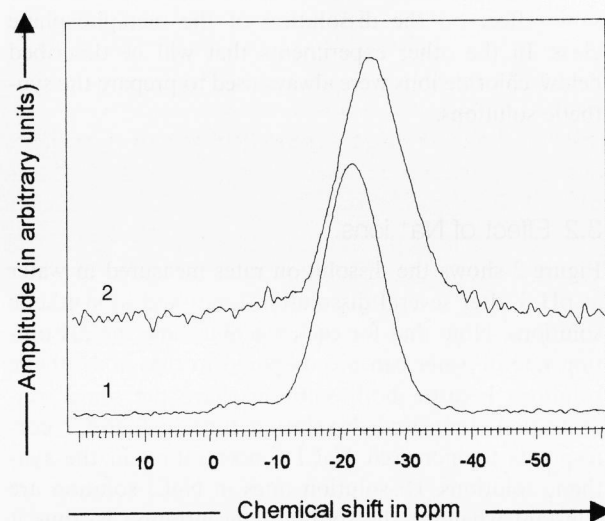

Figure 5. ^{31}P MAS-NMR spectra of a pristine $34Na_2O \cdot 16CaO \cdot 50P_2O_5$ glass (curve 1) and of the layer developed in $CaCl_2$ synthetic solution at $3 \cdot 10^{-3} \, mol \, l^{-1}$ (curve 2).

groups, Q^1 [16], can be seen at ca. -5 ppm on both NMR spectra. Hence the polymeric structure of the metaphosphate glass is conserved in the layer. It can be concluded that neither hydrolysis, nor the precipitation of insoluble short calcium phosphate chains is involved in the formation of the layer. However, compared to an uncorroded glass, the chemical shift of Q^2 groups in the layer is shifted toward high field (figures 5 to 6). This is in accordance with the enrichment in calcium in the layer, due to an exchange of calcium ions with sodium
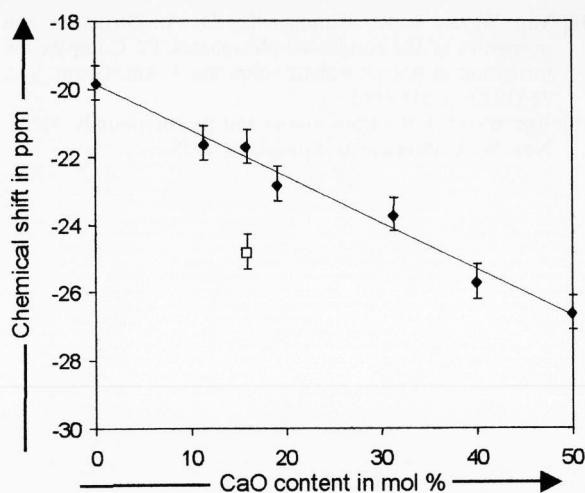
Figure 6. ^{31}P chemical shift of middle-chain groups Q^2 in metaphosphate glasses, versus calcium content, x, for $(50 - x)Na_2O-xCaO-50P_2O_5$ glasses. The open symbol is the chemical shift measured for a $34Na_2O \cdot 16CaO \cdot 50P_2O_5$ ground glass corroded for 1 h in $CaCl_2$ synthetic solution $(3 \cdot 10^{-3} \, mol \, l^{-1})$.

ions along the metaphosphate chains. Figure 6 indeed shows that Q^2 are more shielded when calcium content increases in $(50 - x)Na_2O-xCaO-50P_2O_5$ metaphosphate glasses. This increase in the shielding effect reflects the higher cation potential (charge/ionic radius) $(z/r = 1.75 \cdot 10^{-10} \, m^{-1})$ of calcium ions than sodium ions $(z/r = 0.85 \cdot 10^{-10} \, m^{-1})$, as was reported for $MO-P_2O_5$ metaphosphate glasses [17].

3.4 Effect of $(PO_3^-)_n$ ions

Figure 2 shows that polyphosphate ions, $(PO_3^-)_n$ increase the dissolution rate when the P/Ca ratio in leaching solution is larger than 7. Polyphosphate ions are indeed sequestering agents for Ca^{2+} [18], thus preventing Ca^{2+} incorporation in the hydrated layer. Notice that the dissolution rate increases in polyphosphate synthetic solutions, compared to the dissolution in water. This is due to the complexing effect of polyphosphates which extract calcium ions from the hydrated layer, as EDTA does [19].

4. Summary and conclusions

The dissolution mechanism of $(50 - x)Na_2O-xCaO--50P_2O_5$ metaphosphate glasses at pH 3 in synthetic solutions containing sodium, calcium or polyphosphate ions is similar as in water at pH 3: a hydrated layer develops over a surface covered with etch pits where hydration reaction occurs. This last reaction is the limiting step of the dissolution kinetics. Chloride and sodium ions have no effect on the dissolution process. In $CaCl_2$ synthetic solutions, an exchange $Na^+_{(layer)}/Ca^{2+}_{(solution)}$ occurs, resulting in the formation of a calcium-enriched layer. That decreases the glass solubility and the disso-

lution rate. Electrophoretic mobility measurements have shown that strong interactions develop between glass surface and calcium ions, and ^{31}P MAS-NMR confirms that ion exchange occurs along the metaphosphate chains in the hydrated layer.

The comparison of the effect of each individual ions on the dissolution has led to the conclusion that no ionic exchange could be observed in water at pH 3 because calcium ions released by the congruent glass dissolution are sequestered by polyphosphate chains. This is in accordance with the previous conclusion concerning the mechanism of dissolution of metaphosphate glasses in acid medium. The decrease in dissolution rate is due to an increase in the electrostatic interactions in the hydrated layer, caused by the increase in ionic strength in the leaching solution, and not due to a modification in the structure or morphology of this layer.

5. References

[1] Brow, R. K.; Tallant, D. R.: Structural design of sealing glasses. J. Non-Cryst. Solids **222** (1997) p. 396−406.

[2] Wilder, J. A.: Glasses and glass ceramics for sealing to aluminium alloys. J. Non-Cryst. Solids **38−39** (1980) p. 879−884.

[3] Proulx, P. P.; Cormier, G.; Capobianco, J. A. et al.: Spectroscopie raman et raman à basses fréquences dans des verres de métaphosphate de plomb, de zinc et de barium dopés avec l'ion Eu^{3+}. J. Phys.: Condens. Matter. **6** (1994) p. 275−283.

[4] Vogel, W.; Höland, W.: The development of bioglass ceramics for medical applications. Angew. Chem. Int. Ed. Engl. **26** (1987) p. 527−544.

[5] Minami, T.; Mackenzie, J. D.: Thermal expansion and chemical durability of phosphate glasses. J. Am. Ceram. Soc. **60** (1977) no. 5−6, p. 232−235.

[6] Sales, B. C.; Boatner, L. A.: Physical and chemical characteristics of lead-iron phosphate nuclear waste glasses. J. Non-Cryst. Solids **79** (1986) p. 86−116.

[7] Pyare, R.; Lal, L. J.; Joshi, V. C. et al.: Leachability of molybdenum from ternary phosphate glasses. J. Am. Ceram. Soc. **79** (1996) no. 5, p. 1329−1334.

[8] Scholze, H.; Conradt, R.: An in vitro study of the chemical durability of siliceous fibres. Ann. Occup. Hyg. **31** (1987) no. 4B, p. 683−692.

[9] Kundu, D.; Roy, S. K.: Release of zinc and phosphate ions from $ZnO-P_2O_5$ glass systems and its characterization. Trans. Indian Ceram. Soc. **47** (1988) no. 4, p. 115−119.

[10] Brow, R. K.: An XPS study of oxygen bonding in zinc phosphate and zinc borophosphate glasses. J. Non-Cryst. Solids **194** (1996) p. 267−273.

[11] Hoppe, U.: Short-range order of phosphate glasses studied by a difference approach using X-ray diffraction results. J. Non-Cryst. Solids **183** (1995) p. 85−91.

[12] Roshchina, Y. V.; Tsekhomskaya, T. S.; Roskova, G. P. et al.: Rate of chemical decomposition of sodium zinc phosphate glass with hydrochloric acid: effect of the ratio of the solution volume to the glass surface area. Glass Phys. Chem. **21** (1995) no. 5, p. 371−376.

[13] Bae, B.-S.; Weinberg, M. C.: Chemical durability of copper phosphate glasses. Glass Technol. **35** (1994) no. 2, p. 83−88.

[14] Bunker, B. C.; Arnold, G. W.; Wilder, J. A.: Phosphate glass dissolution in aqueous solutions. J. Non-Cryst. Solids. **64** (1984) p. 291−316.

[15] Delahaye, F.; Montagne, L.; Palavit, G. et al.: Dissolution in acid solutions of metaphosphate glasses of the system $(50 - x)Na_2O-xCaO-50P_2O_5$. J. Non-Cryst. Solids. (Accepted for publication).

[16] Hartman, P.; Vogel, J.; Schnabel, B.: NMR study of phosphate glasses and glass ceramic structures. J. Non-Cryst. Solids **176** (1994) p. 157−163.

[17] Kirkpatrick, R. J.; Brow, R. K.: Nuclear magnetic resonance investigation of the structures of phosphate and phosphate containing glasses: a review. Solid State Nucl. Magn. Resonance **5** (1995) p. 9−21.

[18] Van Wazer, J. R.; Campanella, D. A.: Structure and properties of the condensed phosphates. IV. Complex ion formation in polyphosphate solutions. J. Am. Chem. Soc. **72** (1950) p. 655−663.

[19] Van Wazer, J. R.: Phosphorus and its compounds. Vol. I. New York: Interscience Publishers, 1958.

0599P004

Addresses of the authors:

F. Delahaye, L. Montagne, G. Palavit
Laboratoire de Cristallochemie et
Physicochemie du Solide, URA CNRS 452
Ecole Nationale Supérieure de Chimie de Lille
F-59655 Villeneuve d'Ascq

P. Baillif, J. C. Touray
Equipe de Ressources Environnements et
Matériaux, UMR CNRS 6530
Ecole Supérieure de l'Energie et des Matériaux
F-45072 Orléans