

Influence of the Chemical Composition of Ceramic Frits on the Kinetics of their Dissolution Process

A. Barba, J.C. Jarque, M. Orduña*, M.F. Gazulla

Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I, Castellón, España.

received July 13, 2015; received in revised form September 2, 2015; accepted October 5, 2015

Abstract

A study about the influence of the chemical composition of frits on the kinetics of their dissolution process has been performed, in order to have obtained a more extensive knowledge about the solubility of different types of frits and to predict their behavior regarding to their dissolution process. The study has been conducted with using four frits of the most used four of the frits most commonly used in the preparation of ceramic glazes: a zirconium white frit, a lead-containing boracic crystalline frit, a crystalline frit containing calcium and zinc and a sodium-containing boracic crystalline frit. The results have been fitted to a kinetic model in which the overall rate of the process is controlled by diffusion except the initial moments of the process, which are controlled by the chemical reaction. The differences in solubility observed can be explained based on the differences in the chemical composition of the frits. The kinetic model reproduces the experimental results using adjusting parameters that have physical meaning for the four studied frits.

Keywords: Frit solubility, glass-ceramics, kinetics, glazes, chemical durability

I. Introduction

In the manufacture of ceramic tiles, ceramic glazes, applied as aqueous suspensions on ceramic substrates, are used to form the fired glazes, which give character to the ceramic tiles, since the glazed surface of the tiles is the part that is visible after their installation.

All the glazes incorporate frits in their composition, in varying proportions depending on the type of product for which they are intended, as well as other additives as suspending agents, binders or deflocculants. The main reason for the use of the frits in glaze preparation is to turn the soluble components of the raw material into an insoluble glass so as to obtain coatings with smoother and shinier surfaces.

The use of the frits in glaze preparation decreases the solubility of the soluble compounds present in the raw materials used (feldspars, zinc oxide, calcium carbonate, dolomite, etc.), since ceramic frits are almost insoluble in water. However, a small proportion is still soluble. This leads to one of the main problems of the glaze suspensions: the instability of their rheological properties, which are generated in the interaction between the cations coming from the frit that are dissolved in water and the additives. It is therefore very important to know the solubility of the frits used in glaze preparation.

In previous publications of the same workgroup, the influence of the temperature of a zirconium white type frit on the dissolution of its components was studied, and a kinetic model proposed to explain the dissolution mecha-

nism of the frit components¹.

A large number of the studies in the literature concern the influence of the chemical composition on the solubility of different type of glasses. The effect of the different oxides in the composition of different glasses, such as Ga₂O₃- and Ag₂O-containing zinc-phosphate-based glasses², calcium fluoroaluminosilicate glasses used as implants in dentistry³ and other bioglasses⁴, has been studied. Another study on the same topic establishes a relationship between the glass compositions and the dissolution kinetics in borosilicate glasses⁵.

Cailleteau *et al.*⁶ studied the effect of the chemical composition in three glasses – borosilicate, aluminosilicate and silicate with lead – in aqueous media, maintaining a fixed pH and controlling the surface/leaching solution ratio. They found a strong increase with the proportion of oxides that are more soluble than silica (such as alkaline or alkaline earth oxides) in the glass composition.

Hernández Povedano *et al.*⁷ also studied the effect of the chemical composition on glass dissolution and found that glasses with a high content of network modifiers exhibit high resistance to the network dissolution processes, whereas glasses with a high content of network formers were more resistant to desalkalinization processes governed by ionic exchange mechanisms between glass ions and the H⁺ of the dissolution.

The effect of different oxides on the glass dissolution process has been widely studied. The addition of alkaline oxides to glass produces a progressive opening of the network that makes the extraction of the modifier ions easy,

* Corresponding author: monica.orduna@itc.uji.es

but when two alkali oxides are present, the mixed-alkali effect can produce a stabilization of the glass network. The incorporation of alkaline earth oxides or other trivalent oxides increases chemical resistance on account of the presence of cations of higher valence, which reinforces the network and makes the diffusion of alkaline ions difficult, but all this depends on the concentration of the cations in the composition. Other oxides such as ZnO, Al₂O₃, PbO, TiO₂ and ZrO₂ considerably increase the chemical resistance of the glass⁸.

Considering the structural similarity of ceramic frits and glasses, the dissolution of frits should occur based on similar mechanisms to that of glasses. However, the process is more complex in the case of frits because of the high number of components that make up the frit composition, since, as stated by Strachan⁹, the number of reactions that takes place in a glass dissolution process is at least equal to the number of glass components, so in the case of the frits, very many reactions take place, which complicates study of their dissolution process.

Only few studies attempting to determine the influence of chemical composition on the solubility of ceramic frits have been found. The determination of the chemical resistance of different fired glazes in different media has been studied¹⁰ as the influence of the crystalline phase composition on durability^{11,12}. Furthermore, the effect of different additives added to the glaze suspensions (kaolins, carboxymethylcellulose and sodium tripolyphosphate) on frit solubility has been studied¹³, as well as the solubility of a synthetic borate in order to assess the viability of its use as ceramic glaze component¹⁴. In another publication, frits of the system SiO₂-PbO-B₂O₃ have been studied¹⁵, showing that the solubility of the ions is defined by the chemical composition of the frit, and the greater presence of alkaline and earth alkaline ions, as well as Pb, Ba, Zn, Zr or Ti, up to certain concentration values, increases the chemical resistance of the frit.

The aim of this work is to obtain more extensive knowledge about the solubility of different types of frits so as to predict their behavior with regard to their dissolution process.

To do this, the dissolution process of four of the frits most commonly used in the preparation of ceramic glazes has been studied: a zirconium white frit type, a boracic crystalline frit type containing lead, a crystalline frit type containing calcium and zinc and a boracic crystalline frit type containing sodium. The concentration of Ca, Mg, Zn, Si and B dissolved has been determined by means of ICP-OES, and the results obtained have been fitted to a kinetic model proposed previously in which the overall rate of the process is controlled by diffusion except at the initial instants of the process, when the chemical reaction controls the overall rate of the process.

II. Materials and Equipment

The frits used were referenced as follows: “FBZr” was the zirconium white frit type, “FCB/Pb” was the lead-containing boracic crystalline frit type, “FCP” was the crystalline frit type containing calcium and zinc and “FCB/Na” was the sodium-containing boracic crystalline frit type.

In order to characterize the frits, the chemical composition and the specific surface area were determined. Furthermore, their density was calculated using the Huggins and Sun method¹⁶.

In the determination of the chemical composition, the boron was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) using a Direct Reading Echelle spectrometer from Leeman Labs Inc. The other elements were analysed by means of wavelength dispersive x-ray fluorescence spectrometry (WD-XRF) using a PANalytical AXIOS spectrometer.

To obtain the samples to conduct the experiments with a similar specific surface area ($1.8 \pm 0.1 \text{ m}^2 \cdot \text{cm}^{-3}$), the frits were milled in a Hosokawa Alpine AFG-100 jet mill.

The specific surface area was determined with the BET method using a Micromeritics TriStar 3000 analyzer, and the density was determined with a Quantachrome ULTRAPYCNOMETER 1000 helium stereopycnometer.

The glycine used as an additive to conduct the experiments was supplied by Merck. Pure water was obtained with an Elgastat ELGASTAT MAXIMA water purification instrument, and the concentration of the elements of interest (Ca, Mg, Zn, Si and B) in water was lower than $0.1 \text{ mg} \cdot \text{L}^{-1}$.

III. Experimental

(1) Experimental procedure

The experiments were performed in a batch reactor, made of stainless steel and closed with a lid, in which a stirrer, a thermometer and a probe sample were hermetically fitted. In the batch reactor, each of the frits was mixed with the water and the additives in the appropriate proportions. The batch reactor was introduced into a Selecta Unitronic 2000 thermostatic bath in order to maintain a constant temperature.

Portions of the reaction mixture were extracted at previously established times (5, 10, 15, 30, 60, 180, 300, 450, 600, 900, 1800, 3600 and 5400 seconds) and the liquid fraction was separated in a vacuum filtration system using cellulose nitrate filters with a pore size of $0.2 \mu\text{m}$.

Calcium, magnesium, zinc, silicon and boron were determined in the liquid phase because they are the cations that further dissolve from the frit, and they represent, with regard to the dissolution process, the behaviour of all types of cations: the glass network formers (Si (IV) and B (III)), the glass network modifiers (Ca (II) and Mg (II)) and intermediate (Zn (II))

To obtain adequate experimental results that enable study of the kinetics of the dissolution process, a set of experiments was performed in a previous work to ascertain the optimum conditions for conducting the experiments¹. The time of the experiments was 90 min, because in a previous work¹⁷ it had been observed that after that time the variation of the concentration is very small and not relevant for the kinetic study of the process.

The concentration of the cations obtained in the liquid phase was too small to perform a kinetic study of the process, so that an additive was added to the frit-water system in order to increase the cation concentrations in solution. Glycine was selected as additive for the purpose of the

study because it was stable at the conditions of agitation and temperature used in the experiments and is a complexing agent of Ca(II), Mg(II) and Zn(II). A test was conducted to select the optimum concentration of glycine, the concentration selected being the minimum concentration that does not produce an appreciable increase in the concentration of cations in solution. The mass fraction that provides adequate results to do the study was 0.015.

The agitation rate was studied in order to eliminate the influence of matter transfer steps through the liquid phase on the overall rate of the process, avoiding the sedimentation of solid particles in the suspension during each experiment. Agitation rates from 3000 to 7000 rpm were tested, with the conclusion that an agitation rate of 5500 rpm was the optimum rate to achieve the proposed premises.

Table 1 shows the experimental conditions established in a previous work ¹.

Table 1: Experimental conditions.

Reactives	Mass fraction	Agitation rate (rpm)	Temperature (K)
Water	0.685	5500	313
GLY	0.015		
Frit	0.300		

(2) Kinetic model proposed for the frit dissolution process in aqueous media

The overall reaction scheme proposed in the previous work ¹ was:



where the partial dissolution of the cations (M^{n+}) of the vitreous network occurs at the solid-liquid interface.

The kinetic model proposed works on the premise that almost the whole dissolution process is controlled by diffusion (Fig. 1, Situation b), except at the initial instants of the process, in which the chemical reaction between water and the cations of the species A_j (any cation M^{n+}) located at the surface of the particles (probably in the edges and corners of the particles) controls the rate of the whole process (Fig. 1, Situation a). Both situations of releasing of the A_j ions were established (Fig. 1).

An extensive discussion of the proposed kinetic model can be found in the previous paper ¹. In this work, only the most representative equations are shown.

Fick's law governs mass transfer diffusion in the non-stationary state from the inside of the frit particle to its surface through an area. So, taking into account a flat layer geometry:

$$\frac{\delta}{\delta x} \left[D \cdot \frac{\delta c_{j,v}}{\delta x} \right] = \frac{\delta c_{j,v}}{\delta t} \quad (2)$$

where D is the diffusion coefficient in m^2/s , x is the distance to the surface reaction in m , $c_{j,v}$ is the concentration of A_j inside a frit particle in $kmol A_j/m^3$ and t is the time in s .

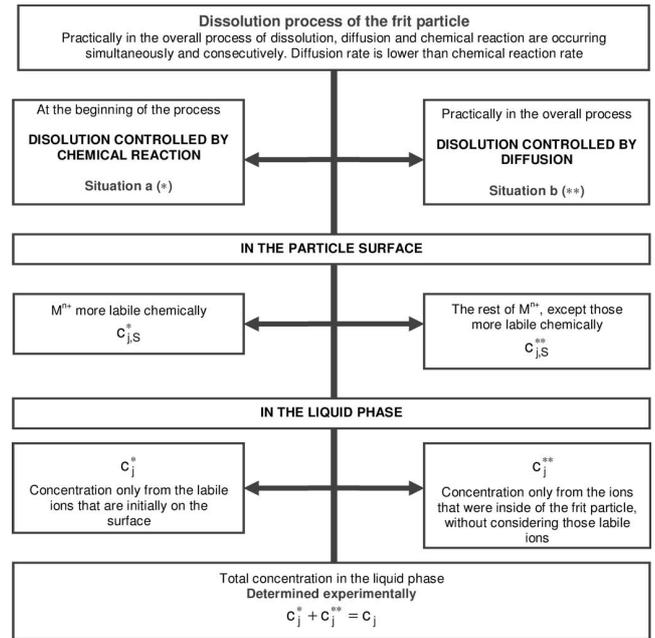


Fig. 1: Scheme of the kinetic model proposed for the dissolution process of a frit.

Considering that the diffusion coefficient depends on the position in the diffusion area ^{18, 19}, the relationship between D and x is:

$$D = D_S - (D_S - D_V) \cdot \text{th} \left[\frac{x}{\lambda} \right] \quad (3)$$

where D_S is the diffusion coefficient on the particle surface, in m^2/s , D_V is the diffusion coefficient at a point far away from the particle surface, in m^2/s , and λ is a factor in m , that makes the ratio (x/λ) dimensionless. The inverse of λ represents the change rate of D with the position x in the diffusion area between D_S and D_V limiting values.

Considering a system of frit particles and a constant volume over the dissolution process, the concentration of A_j in the liquid phase at any time, but only of those ions that were inside of the particle frit from all over the system of frit particles (c^{**}), can be expressed as:

$$c_j^{**} = \left[\frac{\rho_{H_2O}}{M_{H_2O}} \right] \cdot \left[S_e \cdot \frac{M}{\rho} \right] \cdot \int_{x=0}^{x=\infty} (c_{j0,P} - c_{j,v}) \cdot dx \quad (4)$$

where c_j^{**} is the concentration of A_j from all over the system of frit particles, in the liquid phase at a t time, but only of those ions that were inside the particle frit in $kmol A_j/m^3$; M_{H_2O} is the total mass of water introduced in the batch reactor, in kg ; ρ_{H_2O} is the water density, in kg/m^3 ; S_e is the specific surface of the frit, in m^2/m^3 ; M is the total mass of the frit, in kg ; ρ is the frit density, in kg/m^3 ; and $c_{j0,P}$ is the initial concentration of A_j inside a frit particle, in $kmol A_j/m^3$. Calculating the concentration c_j^{**} at different times, the curve $c_j^{**} = f(t)$ can be plotted, but this concentration is impossible to determine experimentally.

At the beginning of the process, only the chemical reaction controls the overall rate of the process. So the concentration of A_j in the liquid phase, at a t time, but only from the ions that were initially on the surface (more labiles lo-

cated in the edges and corners of the particles) of all the particles (c_j^*) can be expressed as:

$$c_j^* = \left[\frac{\rho_{H_2O}}{M_{H_2O}} \right] \cdot \left[S_e \cdot \frac{M}{\rho} \right] \cdot c_{j0,S} \{1 - \exp[-k \cdot t]\} \quad (5)$$

Obviously, c_j^* and c_j^{**} are useful concentrations for calculation purposes, but it is impossible to determine them experimentally.

At any time, situations “a” and “b” (see Fig. 1) take place simultaneously. Each of them has a different influence on the total concentration of A_j in the liquid phase, depending on the elapsed process time. The concentration can be calculated using the expression:

$$c_j = c_j^* + c_j^{**} \quad (6)$$

and can be determined experimentally.

IV. Results and Discussion

(1) Frit solubility

The results obtained in the determination of the chemical composition of the frits used in the study are detailed in Table 2.

Table 2: Chemical composition of the frits

Oxides (% by weight)	FBZr	FCB/Pb	FCP	FCB/Na
SiO ₂	56.5	57.2	60.0	63.1
Al ₂ O ₃	4.5	7.5	6.5	8.8
B ₂ O ₃	3.60	4.41	1.74	11.4
Fe ₂ O ₃	0.04	0.10	0.03	0.05
CaO	9.8	9.1	14.1	5.69
MgO	2.45	0.50	1.75	0.06
Na ₂ O	0.19	2.07	0.34	6.5
K ₂ O	3.71	3.53	4.37	2.40
ZrO ₂	6.5	0.14	0.06	1.70
BaO	0.07	1.51	0.09	0.02
PbO	0.05	4.66	0.01	0.01
ZnO	12.0	9.0	10.6	0.05

The results obtained in the determination of the specific surface area, as well as the density of the frits, are detailed in Table 3.

Table 3: Specific surface area and density of the frits

FRIT	Specific surface area (m ² ·cm ⁻³)	Density (g·cm ⁻³)
FBZr	1.880	2.685
FCB/Pb	1.882	2.650
FCP	1.884	2.654
FCB/Na	1.815	2.269

Experimental results obtained in the tests conducted for each frit are shown in Fig. 2. Three replicates were conducted for each frit. The results shown are the average of the three replicates.

The ratio between the dissolved concentration of each cation and the total concentration of each cation present in the frits was calculated in order to compare the results obtained⁶.

In the case of frit FCB/Na, since the concentration of Mg and Zn in its composition is very low, only Ca, Si and B were analysed.

The results obtained show that the frit which presents a higher solubility of the components studied in the experimental conditions is frit FCP. Studies regarding glass solubility⁷ point out that a calcium concentration of around 15 % in the glass greatly increases the extraction of all the elements in the glass. This could be the reason why frit FCP, which has 14.1 % CaO in its composition, is the one with greater dissolution of its components.

If the results for each element are compared, it can be observed that the Ca concentration is higher in the case of frit FCP. This effect could be explained based on the initial concentration of Ca in the frit and the presence of elements such as Zr and Zn in the frit composition. These elements can generate a stabilization of the glass network, decreasing the solubility of the other components. Frit FCB/Na presents the lower solubility of Ca, probably owing to the low content of calcium in the frit, and because the elements that increase the chemical resistance of the frits (such as Zn, Zr or Pb) are either not present or only in a low concentration¹⁵.

In the case of Mg, FBZr and FCP frits present very similar solubility. The solubility of frit FCB/Pb is slightly lower, possibly owing to the low concentration of Mg in the frit, and besides the presence of elements such as Ba, Pb and Zn, which increase the chemical resistance of the frit.

The solubility of Zn is very similar in all the frits studied. Although frit FBZr presents the highest concentration of Zn in its composition, this frit exhibits the lowest solubility, probably owing to the presence of a high concentration of Zr, which increases the chemical resistance of the frit⁸, so the solubility of the frit components decreases. With regard to frit FCB/Pb, despite having a lower concentration of Zn in its composition, the Zn solubility is higher than that of FBZr, possibly because of the absence in its composition of other cations that stabilize the glass network.

In the case of Si, FCP presents the highest solubility and FCB/Na the lowest. Although frit FCB/Na presents a higher concentration of Si, this effect could be explained based on the concentration of CaO and Al₂O₃, which makes the network dissolution process less favourable⁷.

The frit with a higher solubility of boron is FCP, although it is very similar for all studied frits. FBZr frit exhibits lower boron solubility, although it contains 3.60 % B₂O₃; the low solubility of this frit could be due to the high concentrations of ZrO₂ and ZnO in the frit composition as these increase the chemical resistance of the frit. Moreover, frit FCB/Pb also has a lower solubility of boron than FCP and FCB/Na, probably because of the presence of ZnO and PbO as these increase the resistance of the frit⁸.

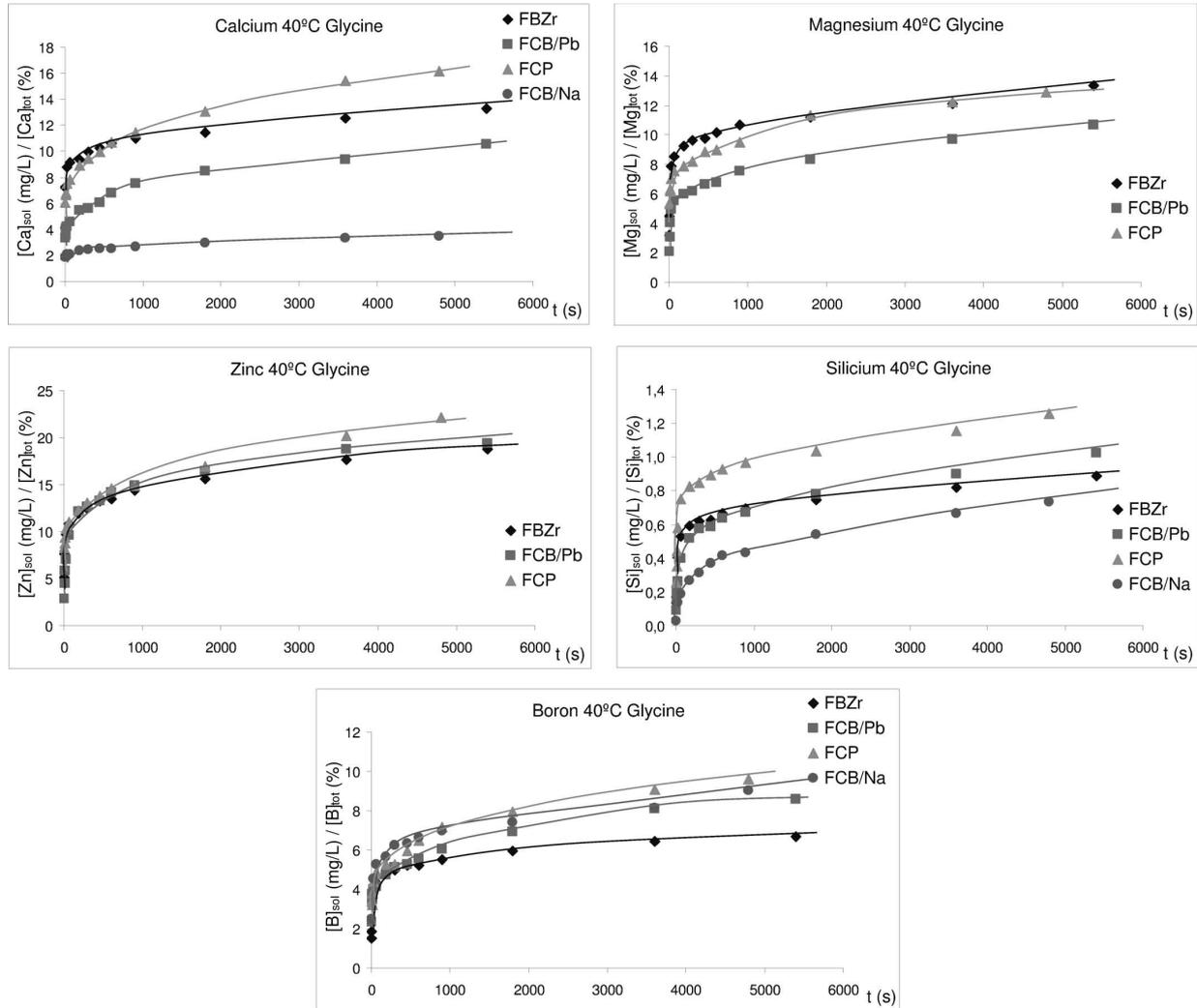


Fig. 2: Experimental results obtained in the tests conducted for each frit. Ratio between the dissolved concentration of each cation and total concentration of each cation.

Table 4: Theoretical values of the parameters used to obtain the curves considering the kinetic model

Frit	Total C_{Ca} (% by weight)	D_V ($m^2 \cdot s^{-1}$)	D_s ($m^2 \cdot s^{-1}$)	λ (m)	k (s^{-1})	$C_{Ca,0,S}$ ($mg \cdot L^{-1}$)
FBZr	9.8	$0.47 \cdot 10^{-16}$	$3.32 \cdot 10^{-16}$	$3 \cdot 10^{-7}$	0.133	83
FCB/Pb	9.1	$0.42 \cdot 10^{-16}$	$2.80 \cdot 10^{-16}$	$3 \cdot 10^{-7}$	0.130	34
FCP	14.1	$1.80 \cdot 10^{-16}$	$4.50 \cdot 10^{-16}$	$3 \cdot 10^{-7}$	0.200	95
FCB/Na	5.69	$0.14 \cdot 10^{-16}$	$1.6 \cdot 10^{-16}$	$3 \cdot 10^{-7}$	0.5	10

In general, frit FCP presents the highest solubility of all the studied frits, for all the analysed elements.

Although the solubility of the frits studied can be explained by the differences in the frit composition, it would be necessary to modify the composition of one type of the frits and to analyse the changes in the solubility, in order to complete the study.

(2) Adjusting the experimental results with the kinetic model

The concentration profiles obtained were fitted using the kinetic model proposed in previous works¹, in order to

determine if the model reproduced the results obtained for different types of frits. Figs. 3 to 6 show the calcium curves obtained for the frits studied. The data represent the average of three replicates. The uncertainty was calculated and is represented by the corresponding error bars.

In the same way, the curves obtained for the other elements were obtained for the four frits studied and they fit very well with the experimental results.

Table 4 shows the theoretical values for D_v , D_s , λ , k , and $c_{j,0,S}$ used to solve equations Eq. (2), Eq. (3), Eq. (4), Eq. (5) and Eq. (6) and to obtain the curves shown in Figs. 3 to 6.

Table 5: Ionic radius of the cations

Element	Ca ²⁺	Mg ²⁺	Zn ²⁺	Si ⁴⁺	B ³⁺
Ionic radius (m)	1.00·10 ⁻¹⁰	0.72·10 ⁻¹⁰	0.83·10 ⁻¹⁰	0.26·10 ⁻¹⁰	0.12·10 ⁻¹⁰

Table 6: Particle size of the frits

Frit	FBZr	FCP	FCB/Pb	FCB/Na
d ₅₀ ·10 ⁶ (m)	20.4	9.25	8.52	9.46

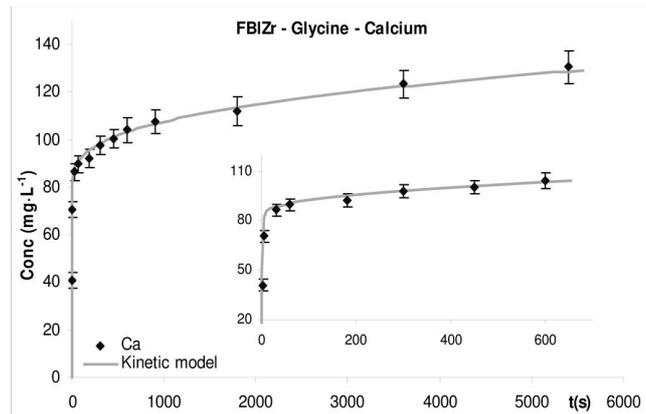
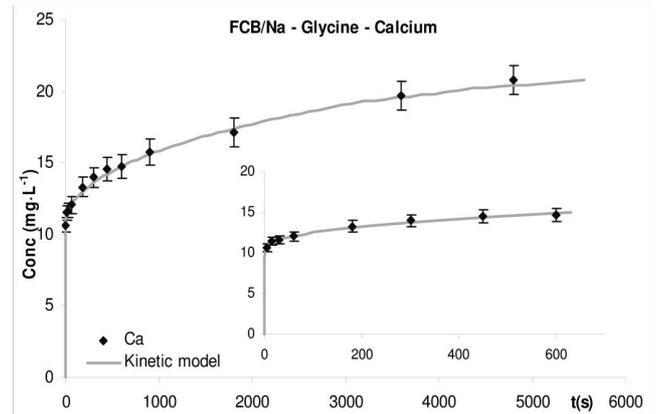
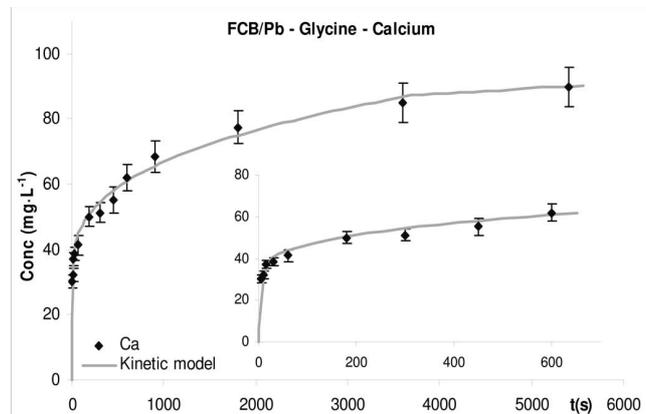
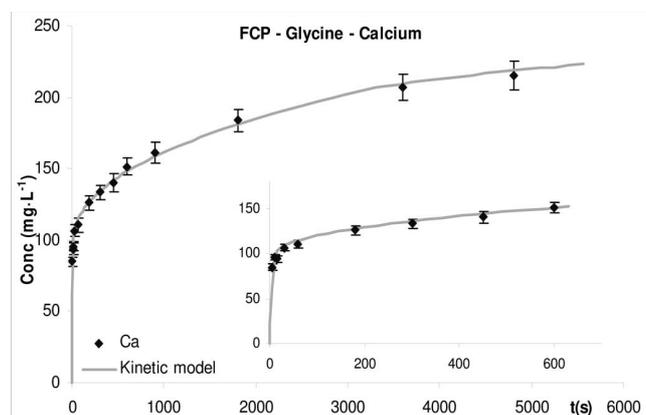
**Fig. 3:** Calculated (—) and experimental (◆) concentration of calcium in the liquid phase of the zirconium white frit type FBZr.**Fig. 6:** Calculated (—) and experimental (◆) concentration of calcium in the liquid phase of the sodium-containing boracic crystalline frit type FCB/Na.**Fig. 4:** Calculated (—) and experimental (◆) concentration of calcium in the liquid phase of the lead-containing boracic crystalline frit type FCB/Pb.**Fig. 5:** Calculated (—) and experimental (◆) concentration of calcium in the liquid phase of the crystalline frit containing calcium and zinc type FCP.

Table 4 shows that D_V is always lower than D_S for all the frits studied. This fact is logical because the cation diffusion inside the particle frit is slower than in the area near the surface of the particle owing to the gaps from the dissolved cations. Moreover, the values of the diffusion coefficients are in the same order of magnitude than those found in the literature for ion diffusion in glasses^{20–22}.

The thickness of the particle in which the change in the diffusion coefficients is produced from D_V to D_S is represented by λ . So, this parameter is characteristic of each element and should not vary with chemical composition, and in Table 4 it can be observed that the λ value remains constant for all the frits studied. In addition, this value is expected to be between the particle size (around 10^{-5} m) and the ionic radius. Table 5 shows the ionic radius of the studied cations and Table 6 shows the medium particle size of the frits used to perform the experiments, and it is obvious that λ values are always higher than the ionic radius and lower than particle size of the frits. So, the λ values obtained are consistent.

The rate constant k depends on the temperature and follows an Arrhenius type law for the studied frits.

The parameter $c_{j,0,S}$ represents the initial concentration of A_j on the surface of a frit particle which can chemically react. This concentration depends on the temperature¹ and on the particle size. This value must depend on the initial concentration of the element on the frit, as observed in the results obtained, although it is characteristic of each element because it depends on the way that the elements are bonded to other elements in the network. As the frits are vitreous materials and the samples have been obtained

by a milling process in which the milling mechanism is the impact between the particles, the atoms in the surface of the particles may have very different environments and bond configurations, and only the atoms with weak bonds react rapidly with water.

Although only the calcium has been explored in this paper, the same variation in all the parameters was obtained for the other elements studied (Mg, Zn, Si and B).

In summary, the experimental results fitted very well with the kinetic model, both for short and long periods of time. So, the kinetic model developed for the white zirconium frit ¹ is able to reproduce experimental data for any type of frit studied, indicating that it is robust and useful for different types of frits.

V. Conclusions

The following conclusions can be drawn from the study:

- 1) The kinetic model is able to reproduce experimental results for frits with different chemical composition, thus, the solubility behavior of different frits used industrially can be predicted with this kinetic model.
- 2) The parameters used in the reproduction of the curves (D_v , D_s , λ , k and $c_{j0,S}$) have physical meaning and are consistent with those parameters found in the literature.
- 3) The solubility differences observed between the four frits studied can be explained by the differences in the chemical composition, and therefore in their structure. The presence of elements such as Zr, Ba, Pb or Zn generates a stabilization of the network and increases the chemical resistance of the frits.
- 4) Crystalline frit types containing calcium and zinc (FCP) present lower resistance to the dissolution process than the other frits, in general, since unlike the others, no high concentrations of elements that stabilize the network (such as Zn,Pb, Zr or Ba) are present.

To obtain an in-depth knowledge of the effect of the frit composition on the dissolution process of frits, it would be interesting to conduct a study modifying the chemical composition of a specific type of frit.

References

- 1 Barba, A., Jarque, J.C., Orduña, M., Gazulla M.F.: Kinetic model of the dissolution process of a zirconium white frit. influence of the temperature, *J. Eur. Ceram. Soc.*, **35**, 751–764, (2014).
- 2 Massera, J., Bourkhis, K., Petit, L., Couzi, M., Hupa, L., Hupa, H., Videau, J.J., Cardinal, T.: Effect of the glass composition on the chemical durability of zinc-phosphate-based glasses in aqueous solutions, *J. Phys. Chem. Solids*, **74**, 121–127, (2013).
- 3 Nourmohammadi, J., Salarian, R., Solati-Hashjin, M., Mozta-zadeh, F.: Dissolution behaviour and fluoride release from new glass composition used in glass ionomer cements, *Ceram. Int.*, **33**, 557–561, (2007).
- 4 Varila, L., Fagerlund, S., Lehtonen, T., Tuominen, J., Hupa, L.: Surface reactions of bioactive glasses in buffered solutions, *J. Eur. Ceram. Soc.*, **32**, 2757–2763, (2012).

- 5 Gin, S., Beaudoux, X., Angeli, F., Jégou, C., Godon, N.: Effect of composition on the short-term and long-term dissolution rates of ten borosilicate glasses of increasing complexity from 3 to 30 oxides, *J. Non-Cryst. Solids*, **358**, 2559–2570, (2012).
- 6 Cailleteau, C., Weige, I.C., Ledieu, A., Barboux, P., Devreux, F.: On the effect of glass composition in the dissolution of glasses by water, *J. Non-Cryst. Solids*, **354**, [2–9], 117–123, (2008).
- 7 Hernández Povedano, J.A., Oteo Mazo, J.L.: Reactions of glass surfaces with aqueous solutions, (in Spanish), *Bol. Soc. Esp. Ceram. Vidr.*, **21**, [2], 81–97, (1982).
- 8 Fernández Navarro, J.M.: El vidrio: constitución, fabricación y propiedades; 2nd edition. CSIC, Madrid, 1991
- 9 Strachan, D.M.: Glass dissolution: testing and modelling for long-term behaviour, *J. Nucl. Mater.*, **298**, 69–77, (2001).
- 10 Shinkareva, E.V., Bychko, G.V.: Chemical resistance of low-melting enamels for decorating glass products, *Glass Ceram+*, **62**, 9–10, (2005).
- 11 Fröberg, L., Kronberg, T., Törnblom, S., Hupa, L.: Chemical durability of glazed surfaces, *J. Eur. Ceram. Soc.*, **27**, [2–3], 1811–1816, (2007).
- 12 Hupa, L., Bergman, R., Fröberg, L., Vane-Tempest, S., Hupa, M., Kronberg, T., Pesonen-Leinonen, E., Sjöberg A.M.: Chemical resistance and cleanability of glazed surfaces, *Surf. Sci.*, **584**, 113–118, (2005).
- 13 Sanmiguel, F., Ferrando, V., Amorós, J.L., Orts, M.J., Gazulla, M.F., Gómez M.P.: Solubilidad de fritas en suspensiones de esmaltes. Influencia de algunas variables de operación sobre la cinética del proceso, *Técnica Cerámica*, **275**, 689–700, (1999).
- 14 Gómez-Tena, M.P., Bou, E., Moreno, A., Cook, S., Galindo, M.: Nueva materia prima borácica como componente de esmaltes cerámicos. Estudio de su solubilidad en suspensiones acuosas concentradas, *Bol. Soc. Esp. Ceram. Vidr.*, **48**, [1], 45–52, (2009).
- 15 Larena, M.T.: Solubilidad en medio acuoso de fritas cerámicas del sistema SiO₂-PbO-B₂O₃. influencia de la composición química de la frita sobre su solubilidad a pH 7, *Cerámica Información*, **192**, 10–19, (1993).
- 16 Huggins, M.L., Sun, K.H.: Calculation of density and optical constants of a glass from its composition in weight percentage, *J. Am. Ceram. Soc.*, **26**, [1], 4–11, (1943).
- 17 Gazulla, M.F., Barba, A., Orduña, M., Bautista, Y.: Stability of ceramic glaze compositions. Correlation between partial dissolution and rheological properties. Part I, *Glass Technol.-Part A*, **53**, [3], 101–108, (2012).
- 18 Wen, C.Y.: Noncatalytic heterogeneous solid-fluid reaction models, *Ind. Eng. Chem.*, **60**, [9], 34–54, (1968).
- 19 Cable, M., Frade, J.R.: Diffusion controlled mass transfer to or from spheres with concentration-dependent diffusivity, *Chem. Eng. Sci.*, **42**, [11], 2525–2530, (1987).
- 20 Leturcq, G., Berger, G., Advocat, T., Fillet, C., Halgand, O., Vernaz, E.: Chemical durability of aluminosilicate glasses containing low solubility chemical elements, *Mat. Res. Soc. Symp. Proc.*, **506**, 199–206, (1998).
- 21 Dunken, H., Doremus, R.H.: Short time reactions of a Na₂O-CaO-SiO₂ glass with water and salt solutions, *J. Non-Cryst. Solids*, **92**, 61–72, (1987).
- 22 Perera, G., Doremus, R.H.: Dissolution rates of silicate glasses in water at pH 7, *J. Am. Ceram. Soc.*, **74**, [6], 1269–1274, (1991).

