

FRIT SOLUBILITY IN GLAZE SUSPENSIONS. EFFECT OF CERTAIN OPERATING VARIABLES ON PROCESS KINETICS

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ABSTRACT

In this study a set of kinetic leaching experiments was conducted on frit suspensions with a view to determining the effect of suspension solids content, operating temperature, and additives on the ion quantity extracted from the frit and on suspension pH.

It was shown that for a frit suspension in water at 60% solids content and temperature of 30°C, the most soluble elements were: boron, potassium and calcium, in this order. The leaching process rate at experiment start was observed to be almost instantaneous. More than half of the amount extracted in 24 hours was found to solubilise in the first five minutes. The reaction kinetics giving rise to variations in solution ion concentrations and suspension pH are analysed and discussed.

An increase in suspension solids content was shown to raise the ion concentration extracted from the dissolved frit and suspension pH. Of the three additives employed (kaolin, carboxymethylcellulose, and sodium tripolyphosphate), tripolyphosphate was found to have the greatest effect on frit solubility, by considerably raising the zinc, calcium and magnesium quantities extracted from the frit.

Finally, it was shown that in a suspension containing 0.25% sodium tripolyphosphate, the effect of temperature on frit ion extraction was greater for silicon, boron and zinc than for the other elements

1. INTRODUCTION

The ceramic frits currently employed in glazed floor and wall tile manufacture are intrinsically quite resistant to chemical attack by water, compared to normal glasses. However, all materials of a glassy nature react with water at ambient temperature, albeit only to a minor degree. When small frit particles are found in a concentrated glaze suspension (high surface area/unit water volume) at moderately high temperatures, for instance during milling, reactions between frit and water can develop quickly and extensively. The most important reactions that arise in a frit suspension are^[1-4]:

- i) Extraction or leaching of network-modifying ions, basically alkaline and alkaline-earth ions by water.
- ii) Selective dissolution of network-forming ions.

Studies on these reactions are reported, which may be characterised as follows:

- i) Simple glassy systems were used, mostly of three components.
- ii) Leaching was studied by working with aqueous suspensions of glass particles with a very low solids content, in which the reaction area (total surface area of glass in contact with water) was therefore very low.
- iii) pH was held steady in these experiments.

The results of these studies are not directly applicable to glaze suspensions. As in processing a glaze, it is very important to know the effects of water attack on the frit particle surface, it was decided to investigate the mechanism and kinetics of chemical attack by water in an industrial suspension of frit particles and the effect of certain operating variables on this process.

A set of kinetic experiments on leaching in frit suspensions was carried out in this study to determine the effect of suspension solids concentration, operating temperature and additives on the quantity of ions leached from the frit, and on suspension pH.

2. MATERIALS AND EXPERIMENTAL METHOD

A so-called zirconium white frit was used, having a molar composition in the following range: 59-62% SiO₂, 3% Al₂O₃, 4% B₂O₃, 10-12% CaO, 2-5% MgO, 3% K₂O, 3-5% ZrO₂ and 8-10% ZnO. The frit was dry milled with a jet mill, until a 2 wt% reject was obtained on a 40 µm screen. Frit particle-size distribution, determined by laser diffraction is given in Fig. 1. Mean particle size was 14.7 µm. Specific surface area, determined by nitrogen adsorption (BET method) was 1.2 m²/g.

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- [1]. HERNÁNDEZ, J.A ; OTEO, J.L. *Reacciones de la superficie del vidrio con soluciones acuosas*. Bol. Soc. Esp. Ceram. Vidr., 21(2), 81-97, 1982.
 - [2]. NEWTON, R.G. *The durability of glass - a review*. Glass Technol., 26(1), 21-38, 1985.
 - [3]. MARCO, J.; GIMENO, R.; LUCAS, F., et al. *Rheological behaviour of glaze suspensions. Influence of frit solubility, pH, water hardness and additives*. In: IV World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1996, p. 257-275.
 - [4]. ANDREOLA, F.; BONAMARTININ, A.; MANFREDINI, T., et al. *Concentrated glaze suspensions*. Am. Ceram. Soc. Bull., 73(10), 75-78, 1994.
 - [5]. LACOURSE, W; MASON, W. *The role of water in glaze defects*. Ceram. Eng. Sci. Proc., 18(2), 237-245, 1997.

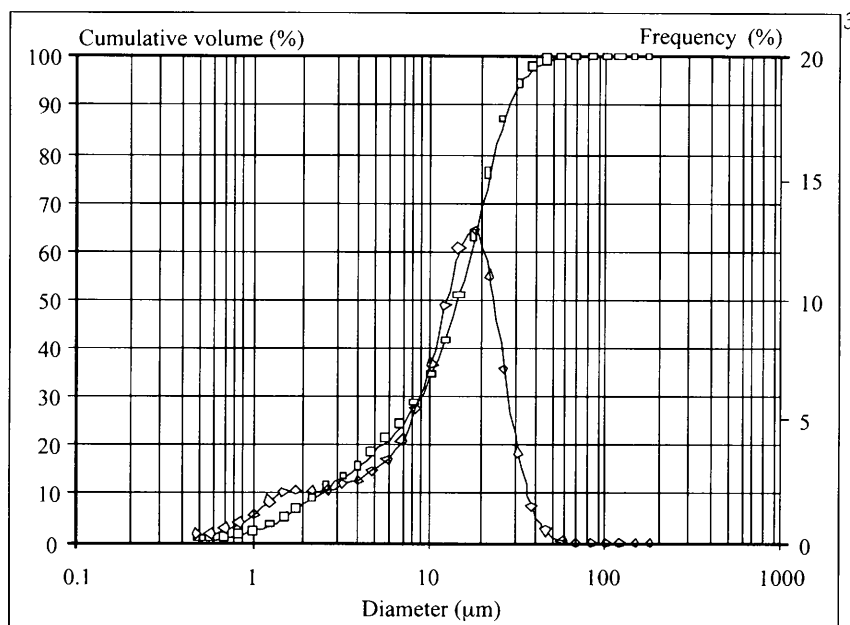


Figure 1. Particle-size analysis of the frit used. Laser diffraction method.

To perform the solubility tests, frit particle suspensions were prepared in distilled water with different solids contents. In some suspensions kaolin, sodium tripolyphosphate (TPP) and carboxymethylcellulose (CMC-30) were added in proportions similar to those used in industry for preparing glaze suspensions.

The experimental set-up used consisted of a stainless steel container, with a 6-l capacity, fitted with a lid, equipped with a stirrer, a thermometer, and a sampler. In certain experiments the reactor lid was modified to allow fitting a suspension electrode, so as to continuously monitor pH evolution during the whole leaching run. The system was kept in a thermostatted water bath throughout testing. Fig. 2 schematically illustrates the experimental assembly employed.

The experiments were conducted by first filling the reactor with water and waiting for it to reach the set temperature (30, 50, and 70°C). The corresponding amount of frit was subsequently added, in terms of the solids content (10, 30, 60% by weight) and additives (kaolin, TPP, CMC). This was taken as experiment zero time. Extractions were then run on the suspension for different times.

In each extraction of about 100 ml, a part was separated to determine pH and solids content, the latter being a parameter that allowed controlling whether frit particles had settled during the experiment. The remainder of the sample was filtered. Filtration was performed in a vacuum system, making the sample pass through two filters. The first filter was made of fibreglass with a pore size of 2 μm. The sample was then put through a cellulose nitrate filter with an 0.2 μm pore size.

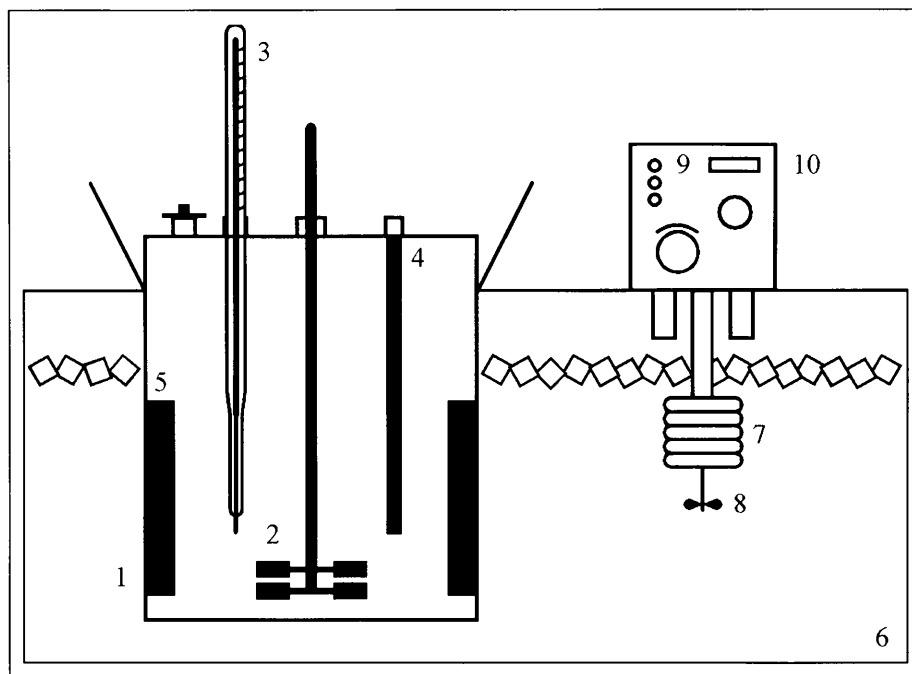
Chemical analysis was subsequently run on the filtrate. Silicon, calcium, magnesium, zinc and potassium were determined by atomic absorption; boron was determined by UV-visible spectrophotometry. The following standards were used to ensure the accuracy of the measurements performed:

-SRM 3107 (5000 ±30 mg B/l)

-SRM 3179-I (100 ± 0.5 mg K/l) -SRM 3179-I (100 ± 0.5 mg Mg/l)

-SRM 3179-II (100 ± 0.5 mg Ca/l)

-SRM 3168a (10000 ± 30 mg Zn/l)



- | | |
|----------------|------------------------------------|
| 1. Reactor | 6. Thermostatted bath |
| 2. Stirrer | 7. Heating system |
| 3. Thermometer | 8. Stirrer |
| 4. Sampler | 9. Bath temperature visual display |
| 5. Deflectors | 10. Bath control system |

Figure 2. Schematic of the experimental assembly.

3. RESULTS AND DISCUSSION

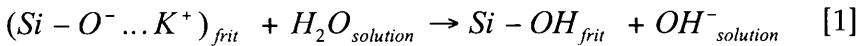
3.1. LEACHING OF FRIT PARTICLES WITH DISTILLED WATER

Fig. 3 depicts the plots of the ion concentrations in the filtrate and solution pH versus leaching time. Fig. 4 is an amplification of Fig. 3 for reaction times of less than an hour. Experiment operating conditions were as follows: 60% suspension solids content and temperature of 30 °C.

An examination of these plots shows:

i) Extraction of glassy network modifying ions. Ions K^+ and alkaline-earth ions, Ca^{+2} and Mg^{+2} , were in this order, the most easily extracted glassy network modifying ions from the frit by water. The amount of extracted zinc was virtually negligible (less than 2 p.p.m). These values are very low when compared with those obtained on

treating soda-lime glasses to a similar attack procedure^[6]. The presence of dissolved alkaline and alkaline-earth cations was due to the break up by water of weak bonds between oxygen and the glassy network modifying cations, in accordance with the reaction schemes:



and



where, $R^{+2} = Ca^{+2}, Mg^{+2}, Zn^{+2}$, etc.

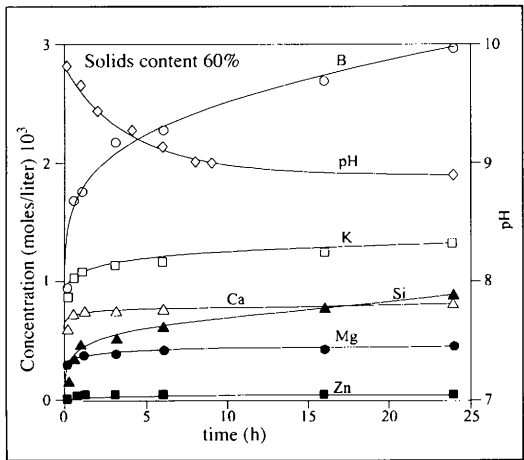


Figure 3. Variation of solution ion concentration and pH with time.

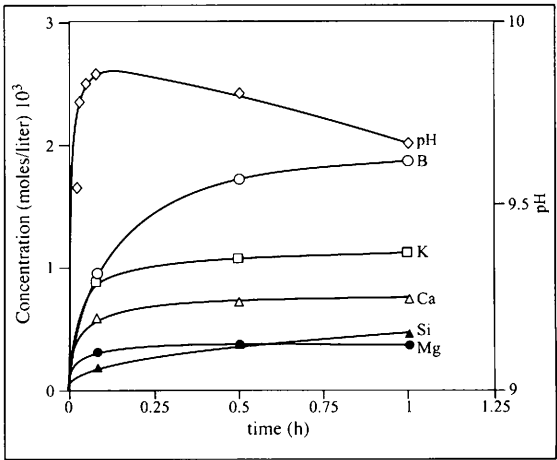


Figure 4. Amplification of Fig. 3.

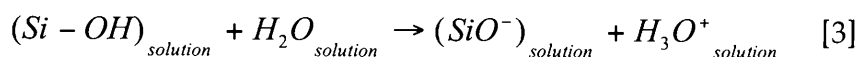
The reaction free energy values, in this case of hydration (ΔG_{hyd}) corresponding to reactions [1] and [2], for the alkalines and alkaline earths were sufficiently negative for both to develop even at high pH values ($pH > 9$) and appreciable concentrations of dissolved free cations^[7]. Now the values of ΔG_{hydr} , or in other words, the thermodynamic tendency at which these reactions arise, depend among other factors on the nature of the modifying cation. It deserves highlighting, in this sense, that for the alkalis and alkaline earths, the higher the cation field strength (charge/ratio), the stabler is the glassy network, which means fewer mobile cations, so that they are therefore less attackable by water, as Fig. 3 shows. Thus, Mg^{+2} , which has greater field strength, is less soluble than Ca^{+2} , which has less field strength, which is in turn less soluble than K^+ , which is larger and has a lower charge.

With regard to the kinetics of these reactions, Figs. 3 and 4 show that for all the elements, after 5 minutes' leaching over 50% of the total quantity leached from the frit

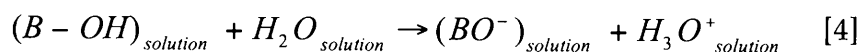
[6]. YOON, C.H.; LACOURSE, W.C.; MASON, W. *Water/frit interactions as a source of glazing problems*. Ceram. Eng. Sci. Proc., 18(2), 435-454, 1997.
 [7]. JANTZE, G.M. *Prediction of glass durability as a function of glass composition and test conditions*. In: Advances in the fusion of glass. Edited by D.F. Bickford. Westerville: American Ceramic Society, 1988, p. 24.1-24.17.

in 24 hours had already been extracted. These data indicate that such reactions initially take place at the frit particle surface, so that they are very fast and practically instantaneous. However, a few minutes after leaching start, the leaching rate progressively decreased. This was due to the accumulation in the solution of reaction products and to the fact that the process was controlled by diffusion of the species through the leached frit layer^[1]. Thus, for ion extraction from the frit to continue, the cation needed to diffuse through an already leached frit surface layer of growing thickness, into the solution, while the water must also diffuse in the opposite direction.

ii) Selective dissolution of network-forming ions. Boron was the frit element that most readily solubilised. Silicon, the major glassy network former, dissolved to a much lesser extent and the extracted aluminium content was virtually negligible (less than 5 p.p.m). Both silicon and boron practically started dissolving from the very start of the experiment. Owing to the high rate at which reactions [1] and [2] developed, solution pH also rose very quickly, exceeding pH 9 in less than a minute, which is the threshold value for soluble species of boron and silicon to start forming^[8]. Thus for pH>9 the hydrated forms of boron and silica ionised, contributing protons to the solution, in accordance with the following simplified schemes:



and



Although these reactions did not appear to be controlled by diffusion of chemical species through the leached frit layer^[1], the rate at which the reactions developed also decreased as the dissolution process advanced. This was likely to be due to the drop in solution pH and accumulation of reaction products in the solution with reaction time.

iii) Variation of solution pH. The curve of solution pH variation versus leaching time peaked at pH=9.9, 5 minutes after experiment start (Fig. 4), subsequently gradually decreasing to a pH value around 9 at 24 hour leaching (Fig. 3). These data were consistent with the variation exhibited by dissolved ion concentrations, owing to the advance of reactions [1] and [2], which tended to lower pH. Thus, for short-time reaction runs below 5 min, the hydroxyl generation rate as a result of the advancing extraction reactions of potassium, reaction [1], and of calcium and magnesium, reaction [2], must be greater than the rate of hydronium ion contribution (or hydroxyl consumption) by means of boron and silicon dissolution, so that pH increased. However, for longer reaction times, the situation was inverted since the boron and silicon dissolution rates (slopes of the corresponding curves in Fig. 4) were greater than the calcium, potassium and magnesium extraction rates, so that pH dropped.

[1]. HERNÁNDEZ, J.A ; OTEO, J.L. *Reacciones de la superficie del vidrio con soluciones acuosas*. Bol. Soc. Esp. Ceram. Vidr., 21(2), 81-97, 1982.

[8]. YOUSSEFI, A. *Resistence chimique de quelques verres du système Na₂O-CaO-SiO₂*. Verres Refract., 32, 663-668, 1976.

3.1.1. EFFECT OF SUSPENSION SOLIDS CONTENT

To study the effect of this variable on frit particle leaching, three suspensions were prepared with solids contents of 10, 30 and 60%. All the experiments were run at 30 °C.

It was shown that on raising frit suspension solids contents (C.S), the frit particle surface area/volume aqueous solution ratio SA/V, Table I grew even further, which meant an increase in the concentration of dissolved ions extracted from the frit.

C.S. (kg solid/100 kg suspension)	SA/V (m ² /m ³)
10	0.132x10 ⁶
30	0.514x10 ⁶
60	1.800x10 ⁶

Table I. Relationship between suspension solids content (C.S%) and particle surface area/volume aqueous solution ratio (SA/V).

Fig. 5 depicts the plots of the leached ion concentrations after 24 hours versus frit particle surface area/volume aqueous solution ratio. It was generally observed that for every element, the dissolved ion concentration rose as frit attack surface grew (SA/V). However, the quantitative effect of this variable on solubility depended on the nature of the cation. Thus, the rise in solubility with solids content was larger for boron and silicon (especially on going from 30 to 60%), than for the remaining elements, potassium, calcium, etc., which were network modifiers.

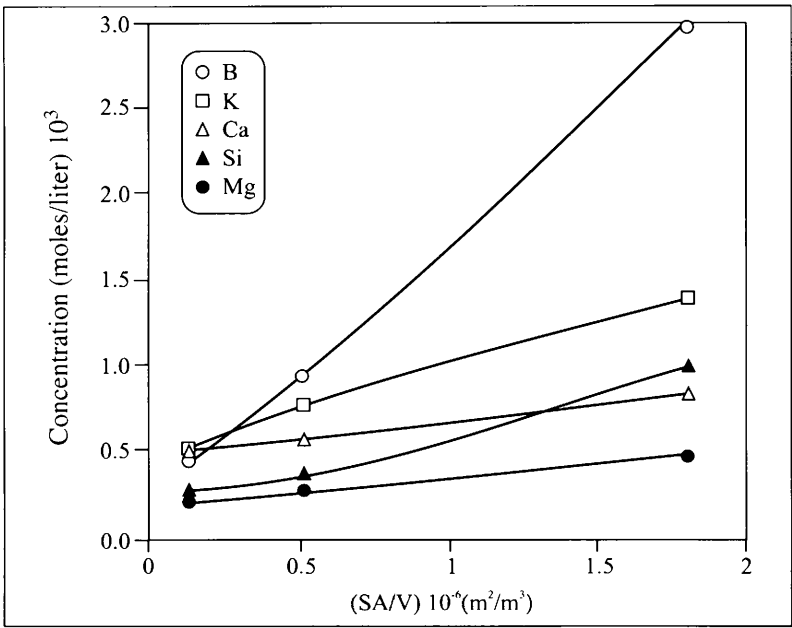


Figure 5. Variation of extracted ion concentration after 24 hours with particle surface area/liquid volume ratio.

The results found for shorter leaching times followed the same trend. Thus, as an example, Figs. 6 and 7 plot the variation obtained for calcium and boron ion concentration versus leaching time for the three tested solids contents. It can be observed that at each leaching time, the effect of suspension solids content on solubility was always greater for boron than for calcium.

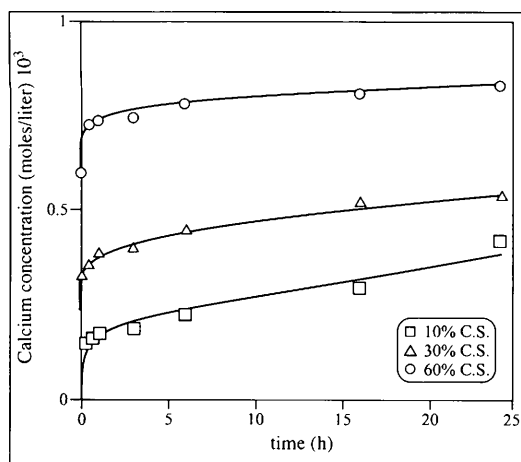


Figure 6. Effect of suspension solids content on calcium extraction

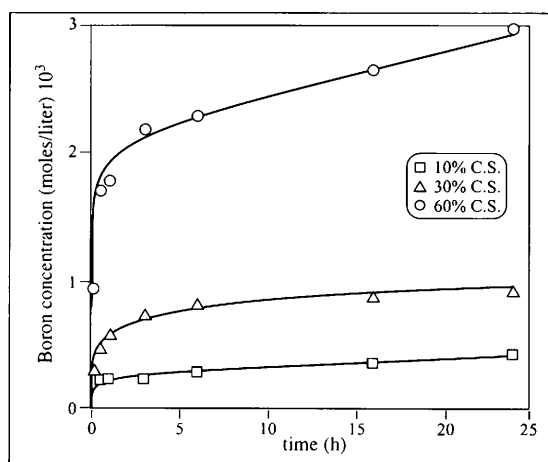


Figure 7. Effect of suspension solids content on boron extraction

Fig. 8 plots the variation of solution pH versus frit leaching time. It can be observed that on raising suspension solids content, solution pH rose for each leaching time. This was because with the rise in the frit surface area/volume aqueous solution ratio, the number of dissolved ions increased and thus so did the hydroxyl concentration, i.e. the pH.

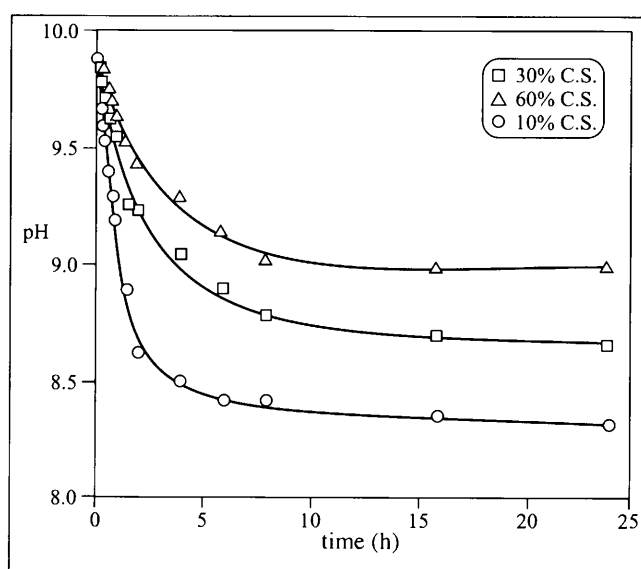


Figure 8. Variation of solution pH with reaction time.

The marked effect of suspension solids content on solution pH may one of the reasons why the variation of silicon and boron solubility with this variable was greater than that of the other elements, which were network modifiers. Thus, the dissolution of network-forming elements, as indicated above, required values of $\text{pH} > 9$ and was encouraged when pH increased. Therefore, for boron and silicon, when suspension solids content was raised, the frit attack surface and pH increased, both of which were factors favouring dissolution of these elements. However, the solubility of the network modifying elements (potassium, calcium, magnesium and zinc), in accordance with reaction schemes [1] and [2], was encouraged with lower pH. Hence for these elements, the solution's rise in pH with increased solids content impaired their solubility.

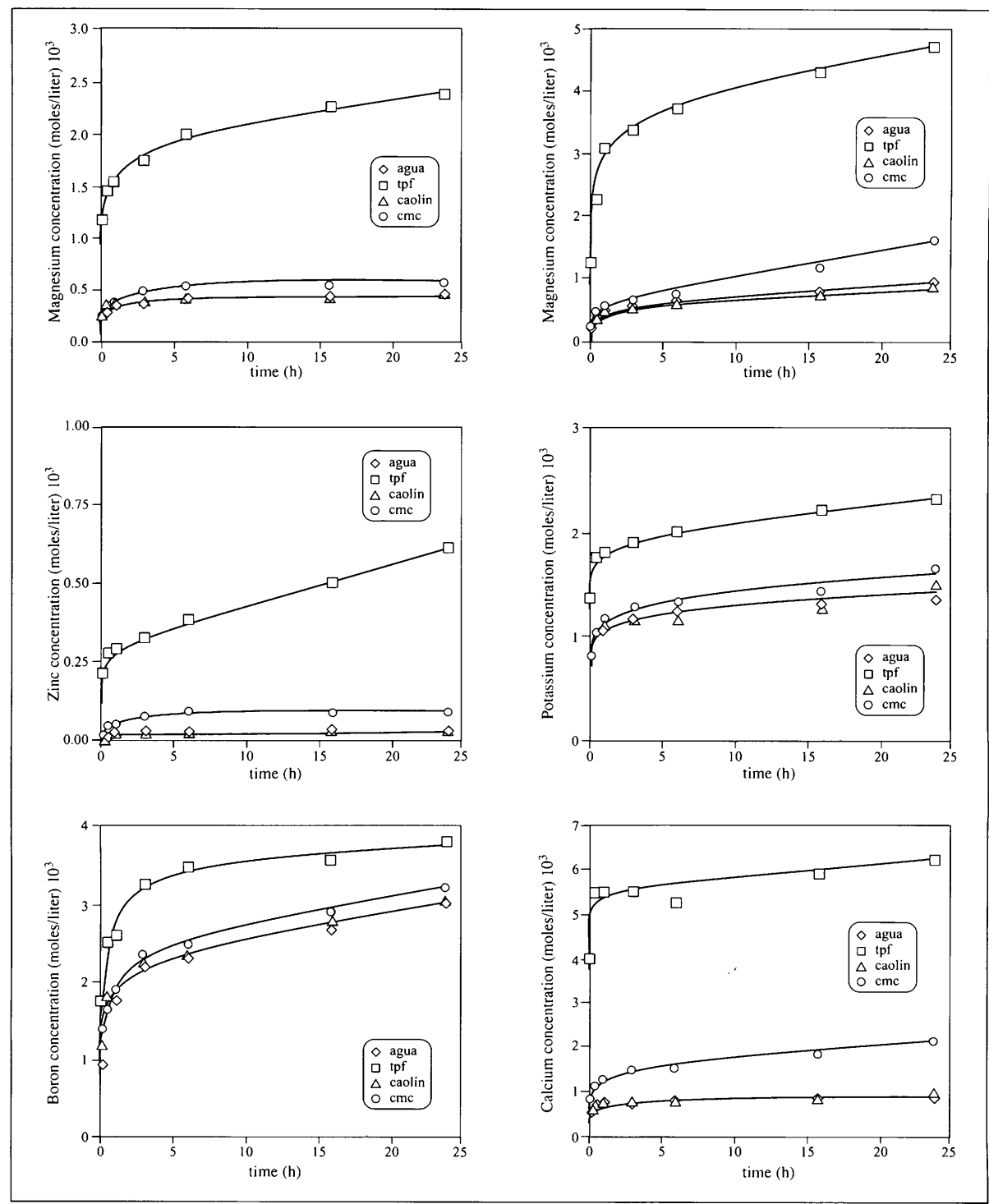


Figure 9. Effect of the studied additives on frit leaching.

3.2. FRIT PARTICLE LEACHING IN AQUEOUS SOLUTIONS

3.2.1. EFFECT OF ADDITIVES

To determine the effect of additive type on frit solubility, a suspension, with a 60% solids content was used, to which the following additives were separately added: kaolin, sodium tripolyphosphate (TPP) and carboxymethylcellulose (CMC), thus obtaining three types of suspensions. The kaolin addition was 6%; the tripolyphosphate proportion was

0.25% and that of carboxymethylcellulose 0.2%, relative to the solid. Leaching experiments were run at a temperature of 30°C. Fig. 9 plots the leached dissolved ion concentrations versus reaction time for each element and each type of suspension. Fig. 10 plots solution pH values versus leaching time for each type of suspension. The graphs include the data obtained for the suspension just prepared with distilled water, in order to compare the effect of the additives.

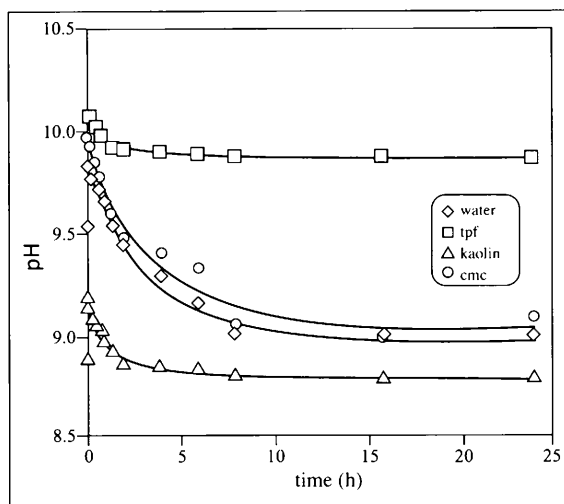
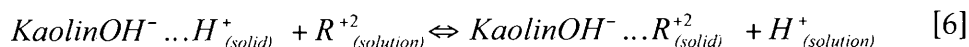
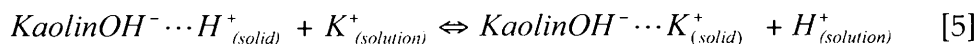


Figure 10. Effect of the studied additives on suspension pH.

An examination of these plots allow highlighting the following:

i) Kaolin.

The introduction of 6% kaolin into the frit suspension hardly modified the different dissolved ion concentrations. This was probably because kaolin formed no type of stable compound (soluble or insoluble) with the elements making up the frit, so that it hardly affected frit leaching kinetics. On the other hand, the pH of this suspension at every leaching time was considerably lower than that of the other suspensions (Fig. 10). It can moreover be observed that after 2 hour leaching, suspension pH hardly varied. These last data can be interpreted on the basis of the ion exchange process arising at the kaolin surface. Thus, for pH values exceeding 6, the kaolin isoelectric point in water, alkaline and alkaline-earth cations were adsorbed onto the kaolinite particle surfaces, preferentially at crystal edges, freeing protons in accordance with the schemes:



where $R^{+2} = Ca^{+2}, Mg^{+2}$.

It should be pointed out that although chemiadsorption of the alkaline and alkaline-earth ions on the kaolin surface can to some extent favour the extraction of these cations from the frit, on remaining held in the solid phase (on kaolin particles), no change was observed in filtrate concentration.

ii) Sodium tripolyphosphate.

Adding 0.25% tripolyphosphate to the frit suspension was found to considerably raise ion concentration in the filtrate and solution pH. However, the effect of this additive was much greater on the leaching of zinc, the alkaline earths, calcium and magnesium, than on the other elements. In fact, at a leaching age of 24 hours, the zinc concentration in the filtrate with tripolyphosphate was 20 times higher than for the suspension without this additive. For calcium, the tripolyphosphate addition raised the leached ion concentration by 8, and for magnesium by about 6. This was because of the chelating effect of the tripolyphosphate anion, which formed soluble, very stable complexes with Zn^{+2} and with the alkaline-earth cations Ca^{+2} y Mg^{+2} [9]. The formation of these highly stable chelates, capturing the cations present in the solution, favoured reaction [2] thermodynamically and kinetically, hence considerably raising the extraction of these frit elements. The fact that zinc solubility grew so strikingly was probably because the chelate that this cation formed is around 100 times more stable than those formed with calcium and magnesium.

It should furthermore be highlighted that although the tripolyphosphate anion did not form chelates with potassium, boron or silicon, the solubility of these cations was considerably heightened. This could be due to the following factors:

a) On raising the zinc, calcium and magnesium proportions extracted from the leached frit particles, diffusion was favoured of the remaining species.

b) Raising the quantity of leached network-forming and network-modifying ions must increase frit particle surface area and encourage leaching.

Fig. 10 shows that for any leaching age, suspension pH values with tripolyphosphate were higher than the corresponding values of the other suspensions. This was because the tripolyphosphate addition directly raised solution pH (the pH of these solutions was 9.9)^[10], and increased frit solubility. It can also be observed that after an hour's leaching, the pH value changed very little, which could be due to partial transformation of tripolyphosphate in orthophosphate and pyrophosphate^[10].

iii) Sodium carboxymethylcellulose.

The dissolved ion concentration in the suspension prepared with sodium carboxymethylcellulose (CMC) was generally observed to be a little larger than in the suspension made up without any additives; only zinc tripled its concentration. These data clearly underscore the capacity of this anionic linear polymer to react in an aqueous medium with the cations present.

Thus, according to various authors^{[11], [12]}, CMC reacts with zinc, calcium, and magnesium cations to form compounds that can precipitate at high concentrations. Carboxymethylcellulose reacts similarly with alkaline ions to form soluble salts.

[9]. MCCRARY, A.L; HOWARD, W.L.. *Chelating agents*. EN: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. New York: Wiley, 1979, vol. 5, p. 339-368.

[10]. *Stability constants of metal-ion complexes*. 2nd ed. London: Chemical Society, 1964, p. 179-203.

[11]. STELZER, G.I. ; KLUG, E.D. *Carboxymethylcellulose*. *Handbook of water-soluble gums and resins*. New York: McGraw-Hill, 1980, cap. 4.

[12]. GREMINGER, G.K. *Cellulose derivatives, ethers*. EN: Kirk-Othmer encyclopedia of chemical technology. 3rd ed. New York: Wiley, 1979, vol. 5, p. 143-163.

The limited increase in solubility of silicon and boron on adding CMC was probably due to a slight increase of the effective coefficients of diffusion of these species and frit particle surface area, as mentioned previously.

With regard to pH, the values corresponding to the CMC bearing suspension were a little higher than those found for the frit suspension in water. This was likely due to a rise in the number of solubilised ions.

3.2.2. EFFECT OF TEMPERATURE

Three series of experiments were conducted at 30, 50 and 70°C to determine the effect of temperature on frit leaching. In each case, suspension solids content was 60% and sodium tripolyphosphate was 0.25%, relative to the solid. This suspension was chosen because this additive finds widespread use in glaze preparation and because it was the additive that most affected frit solubility.

Fig. 11 summarises the results obtained, plotting the ion concentrations in the filtrate, extracted from the frit after 24-hour treatment, versus experiment temperature.

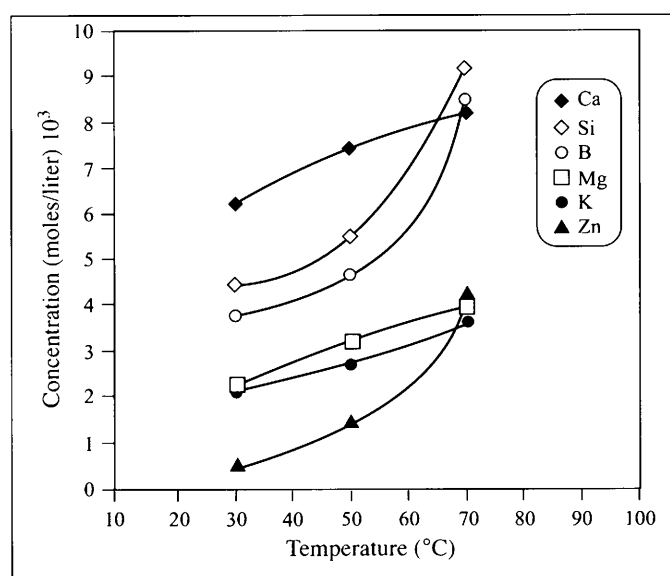


Figure 11. Effect of temperature on extracted ion concentration after 24 hours.

It was found that for all the species present in the solution, a rise in leaching temperature led to an increase in the ion quantity extracted from the frit. However, the effect of temperature on the solubility of the different elements depended on their nature. Thus for zinc, a rise in reaction temperature of 30 to 70 °C yielded an increase of up to seven times the amount extracted from the frit with 24 hour leaching. However, for silicon and boron this rise in temperature only entailed roughly doubling the extracted amount. For potassium, calcium and magnesium this change in operating temperature involved an even lower extract increase than the foregoing, especially for calcium.

The data obtained for shorter leaching times followed the same trend, except for zinc, as Figs. 12, 13 and 14 show. These figures depict the plots obtained for boron, magnesium and zinc concentration in the filtrate versus leaching time for the three tested

temperatures. The results for silicon resembled those of boron, while those of potassium and calcium were similar to those found for magnesium, which is why they have not been included.

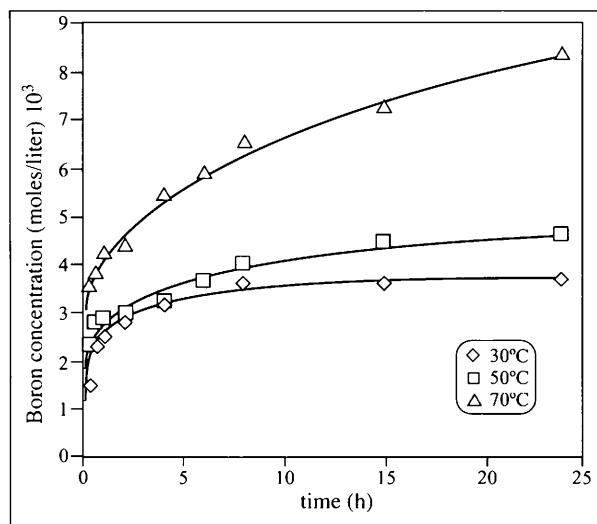


Figure 12. Effect of temperature on boron extraction from the frit.

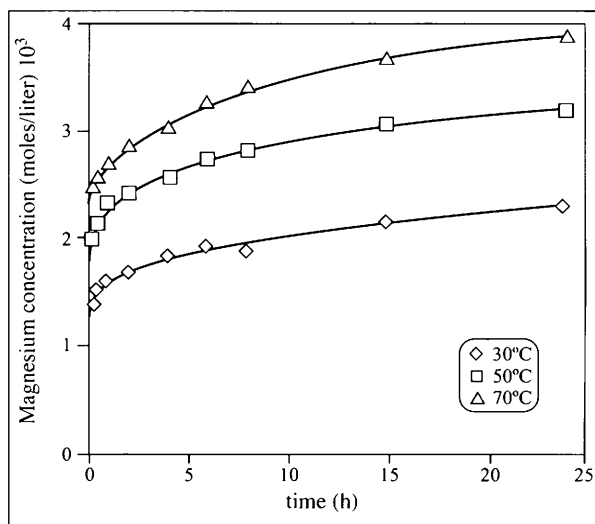


Figure 13. Effect of temperature on magnesium extraction from the frit.

An examination of these graphs reveals that for any leaching time, the effect of temperature on the quantity of extracted element was greater for boron (and silicon) than for magnesium (potassium and calcium). These findings matched the outcomes reported by different authors^[13] on studying soda-lime glass attack by aqueous solutions. In these studies, it was shown that the effect of temperature on the dissolution reaction rate of the silica network was greater than on the diffusion rate of the network modifying cations through the glass layer. These findings were attributed to the considerable increase in solubility of the silica and boron hydrated species with temperature, which was much higher than that of the coefficient of effective diffusion of the network modifying ions with temperature.

Zinc behaviour was quite different from that of the other cations (Fig. 14). Although for short leaching times of less than an hour, the effect of temperature on zinc extraction was comparable to the effect of temperature on the extraction of the other elements, for long leaching times the effect of temperature on leaching was much greater. Moreover, the form of the curves obtained in Fig. 14 at temperatures of 50 and 70 °C indicate that unlike what happened with the other elements, the zinc extraction rate (slope of these curves) rose considerably after an initial period of time, which became shorter as temperature rose. These data suggest that after a given leaching time, 8 hours for a temperature of 50 °C and 2 hours for 70 °C, an important change was produced in the microstructure of the leached frit layer, which gave rise to a considerable increase in the coefficient of effective diffusion of the zinc cation, raising its extraction rate. The same inference was drawn on studying lead and potassium extraction by aqueous solutions in simple glasses. In these studies the lead extraction rate was also found to be relatively higher than that of potassium after a certain initial reaction time. This relative lead extraction rate increase was attributed to modification of the microstructure of the attacked glass layer^[14].

[13]. HENCH, L. *Physical chemistry of glass surfaces*. J. Non-Cryst. Solids, 28, 1978, 83-105.

[14]. PAUL, A.; YOUSSEFI, A. *Influence of complexing agents and nature of buffer solution on the chemical durability of glass. Part 2: effect of EDTA, ethyl alcohol, and sugar in the leach solution*. Glass Technol., 19(6), 166-170, 1978.

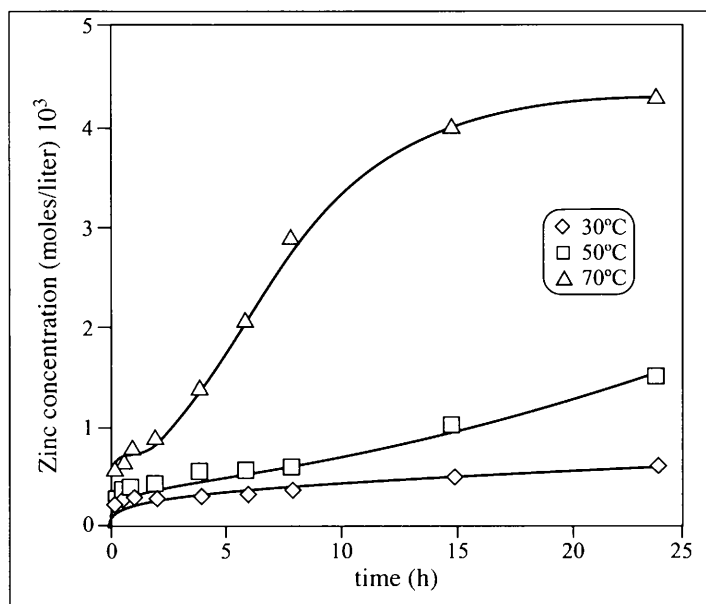


Figure 14. Effect of temperature on zinc extraction from the frit.

4. CONCLUSIONS

The following conclusions may be drawn from the findings obtained in this study:

- i) The solubility of the studied industrial frit in a suspension with distilled water at a 60% solids content and temperature of 30°C was very small. Under these conditions the elements extracted most readily from the frit in the greatest proportions were boron, potassium and calcium, in this order. The rate at which the leaching process developed was at experiment start very high, and practically instantaneous. Of the total extracted amount for each element after 24 hours, more than half had already been extracted within the first five minutes of the experiment. Suspension pH rose with reaction time, peaking at pH=9.8, five minutes after experiment start, subsequently gradually dropping to pH=9 after 24 hour leaching.
- ii) On raising the suspension's solids content, the particle surface area/liquid volume ratio was raised even further, which produced a considerable rise in the dissolved ion concentration extracted from the frit and suspension pH. The effect of solids content was greater for network formers silicon and boron than for the other elements.
- iii) The addition of tripolyphosphate to a frit suspension in distilled water considerably raised the amount of zinc, calcium and magnesium extracted from the frit, as these cations formed very stable complexes with the tripolyphosphate anion. The solubility of the remaining ions also rose, although they did not form complexes with these additives. The addition of kaolin to a frit suspension in distilled water noticeably lowered suspension pH, hardly modifying frit solubility. Adding carboxymethylcellulose to the suspension

[14]. PAUL, A. ; YOUSSEFI, A. *Influence of complexing agents and nature of buffer solution on the chemical durability of glass. Part 2: effect of EDTA, ethyl alcohol, and sugar in the leach solution.* Glass Technol., 19(6), 166-170, 1978.

increased frit solubility slightly, owing to CMC reaction with some glassy network modifier cations.

- iv) On raising the temperature of the suspension containing 0.25% sodium tripolyphosphate, the ion quantity extracted from the frit increased considerably for all the elements. However, this effect was much greater for boron, silicon and zinc than for the other elements.