STUDY OF FRIT LEACHING IN AQUEOUS MEDIA

O. Ruiz[1], Laura Brugada[1], F. Sanmiguel[1], A. Tamayo[2], J. Rubio[2], F. Rubio[2].

[1]. GRUPO TORRECID. Spain

[2]. INSTITUTO DE CERÁMICA Y VIDRIO - CSIC. Spain

1. INTRODUCTION

The study of chemical interactions between glazes and water constitutes a very wide field of research, given the multitude of industrial applications in which they occur, such as formulations for glazing ceramic tiles, tableware, and metallic surfaces, among others[1]. In this sense, several chemical mechanisms are considered to be involved in glass degradation or attack when glasses are found in aqueous media, such as hydration, ion exchange, and hydrolysis, followed by possible reconfiguration of the glass network. Hydration is a process that affects the bonds between the cations in the frit and oxygens associated with polyhedron formation, giving rise to hydrated cations that can be released into the solution. Hydrolysis is characterised by a reaction between water and the bridging oxygens between two polyhedron network formers, which leads to breakage of the glass network. On the other hand, ion exchange is a process by which cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}, in a glass structure, are replaced with hydronium protons or ions (H^+, H_3O^+), liberating these into the aqueous medium. These different reactions can be coupled and contribute to glaze leachability. Investigations have shown that the degree of influence of each of these depends on a multitude of factors, such as frit composition and operating conditions (pH, temperature, particle size, time, etc.)[2,3].

This study assesses the ability of three frits used in formulating glossy, opaque, and matt ceramic glazes, respectively, to release cations on being subjected to attack by water. To do so, the water resulting from frit leaching was analysed by ICP-OES spectrometry. In addition, with a view to better understanding the relationship between glass reactivity in water and glass structure, the frits were analysed by DTA, to calculate the activation energy (Ea), as well as by Raman spectroscopy.

2. EXPERIMENTAL and RESULTS

2.1. DETERMINATION OF THE LEACHING TIME

With a view to evaluating how long the frit released cations into an aqueous medium, three frits were selected that provided a glossy, matt, and opaque effect, respectively. In the three cases, particle size, expressed as D90, was 1 micrometre. Each frit was placed in a precipitate glass with a known amount of osmosised water and stirred for different times: 1, 5, 48, 72, and 120 hours. After each of these times, the water was extracted and the solubilised cations in the water were analysed by the ICP-OES technique. The cation concentration in the osmosised water without frit addition (blank) was also analysed.

Figures 1, 2, and 3 show how leaching evolved with time for each frit, expressed as the relationship between leached cation ppm (in the form of an oxide) and grams of frit subjected to leaching, after subtracting the cation concentration in the osmosised water (blank).

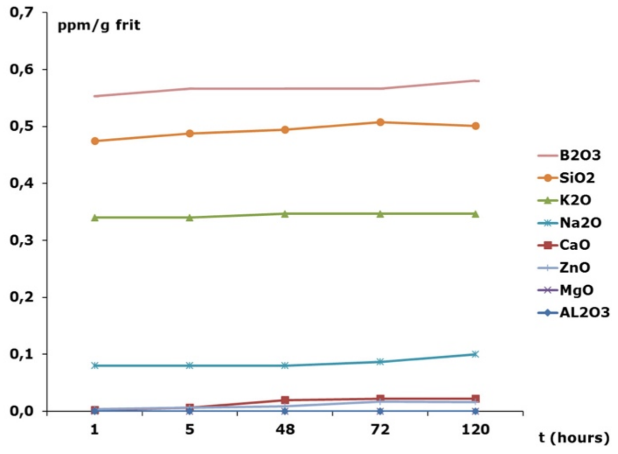

Figure 1. *Evolution of cation leaching with time. Gloss frit.*

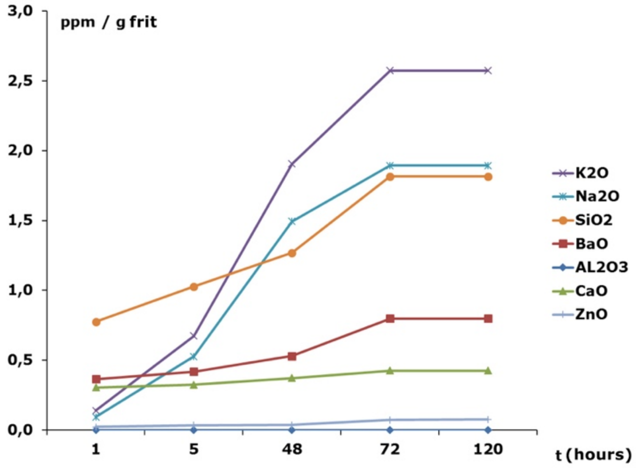

Figure 2. *Evolution of cation leaching with time. Matt frit.*

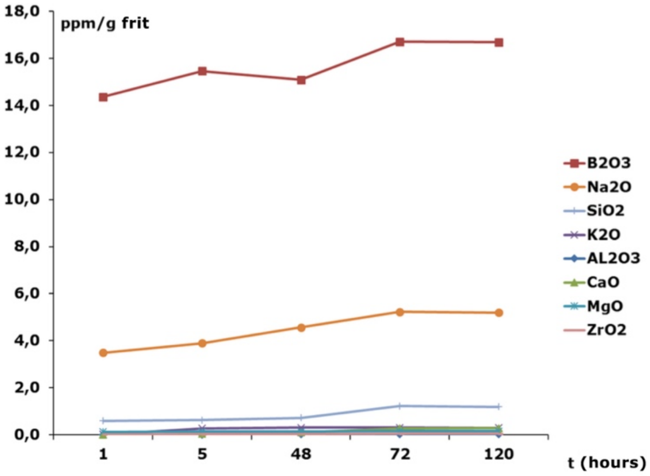

Figure 3. *Evolution of cation leaching with time. Opaque frit.*

The results obtained enabled the following conclusions to be drawn:

- The oxides that exhibited the greatest leaching in the three types of frits were SiO_2, B_2O_3, Na_2O, and K_2O.
- B_2O_3 exhibited the highest leaching rate, in the case of the opaque frit almost reaching 17 ppm B_2O_3/g frit. This stems from the fact that borate or B-containing glasses are more reactive in aqueous media than glasses only containing Si in their structure[4].
- In every case, it was observed that maximum leaching occurred after 72 hours.
- The gloss frit exhibited the least leaching, whereas the opaque frit leached most.

2.2. STUDY OF THE INFLUENCE OF FRIT PARTICLE SIZE ON LEACHING

Once the cations with the greatest leaching ability had been identified, the influence of particle size was studied. The experimental procedure consisted of milling each frit in osmosised water to the desired particle size (D90): 1 micrometre, 500 nanometres, and 250 nanometres. The water and milled frit were then stirred for 72 hours. After this time, the Si^{4+}, B^{3+}, Na^{+}, and K^{+} cation concentrations in the water were analysed by ICP-OES. The results for each particle size, in the three types of frit, are detailed below.

	1 μm (ppm/g frit)	500 nm (ppm/g frit)	250 nm (ppm/g frit)
SiO_2	0.5	0.6	0.8
B_2O_3	0.6	1.2	1.4
Na_2O	0.1	0.2	0.4
K_2O	0.3	0.6	0.8
Total	**1.5**	**2.6**	**3.4**

***Table 1**. Gloss frit.*

	1 μm (ppm/g frit)	500 nm (ppm/g frit)	250 nm (ppm/g frit)
SiO_2	1.8	1.9	2.4
B_2O_3	n.p.	n.p.	n.p.
Na_2O	1.9	2.3	2.5
K_2O	2.6	4.6	6.2
Total	**6.3**	**8.8**	**11.1**

***Table 2**. Matt frit.*

	1 μm (ppm/g frit)	500 nm (ppm/g frit)	250 nm (ppm/g frit)
SiO_2	1.2	1.8	2.4
B_2O_3	16.7	25.2	59.5
Na2O	5.2	6.6	12.5
K_2O	0.3	0.4	0.6
Total	**23.4**	**34.0**	**75.0**

Table 3. *Opaque frit.*

It may be observed in every case that, as frit particle size decreased, leaching increased, B_2O_3 again leaching most. It may also be noted that the greatest leaching at 250 nm was observed in the opaque frit, while the lowest occurred in the gloss frit.

2.3. MODIFICATION OF THE FRIT COMPOSITIONS

In view of the above results, changes were made to the opaque frit composition, as this frit exhibited the greatest leaching, and to the gloss frit, which exhibited the lowest leaching. It was thus sought to verify the influence of the B^{3+} (network former) and Na^+ (alkali network modifier) cations in frit reactivity in aqueous media. In all cases, each frit was milled in osmosised water to a particle size (D90) of 250 nanometres , then stirring the water and frit for 72 hours. After this time, the relevant cation concentration in the water was analysed by ICP-OES.

Decrease in B_2O_3 in the opaque frit composition

The composition of the starting opaque frit (OP, 12.5% B_2O_3) was modified, reducing the B_2O_3 contents (10%, 8%, 6.5%, and 3%). The following graph shows the evolution of the ppm B_2O_3 in the water per mol B_2O_3 as a function of the moles of this cation in the frit. It may be observed that, as frit B_2O_3 concentration decreased, leaching diminished, confirming the leaching character of this cation.

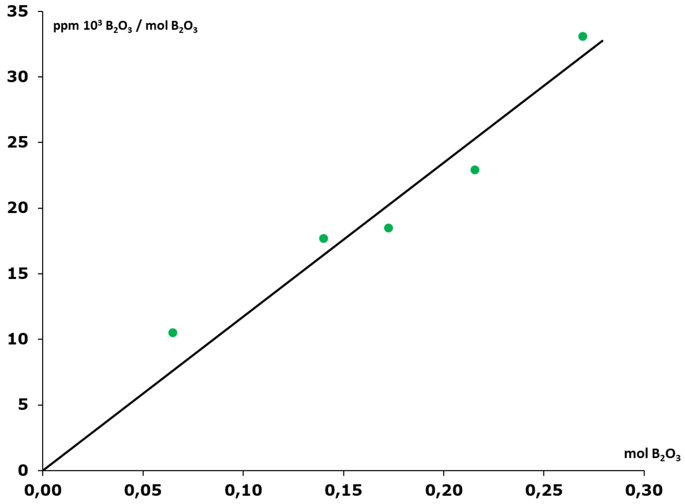

Figure 4. *Evolution of B_2O_3 leaching in the opaque frit.*

Decrease in Na_2O in the opaque frit composition

As in the previous case, the starting opaque frit (OP, 4.5% Na_2O) was used to prepare four frits with decreasing contents of Na_2O (3%, 2%, 1%, and 0.5%). In this case, leaching per mol Na_2O also diminished on lowering the concentration of this cation in the opaque frit.

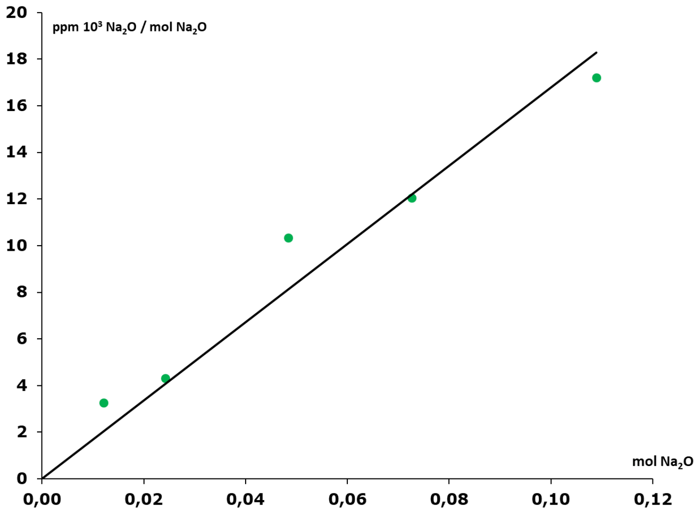

Figure 5. *Evolution of Na_2O leaching in the opaque frit.*

Increase in B_2O_3 in the gloss frit composition

In the gloss frit (Br, 1% B_2O_3), an opposite approach was used. As it behaved as a low-leaching frit, gloss frit composition was modified by increasing the B_2O_3 content (2%, 3%, 4%, and 5%), the effect of water attack then being examined. The following figure shows that raising the B_2O_3 content in the gloss frit composition led to greater water leaching.

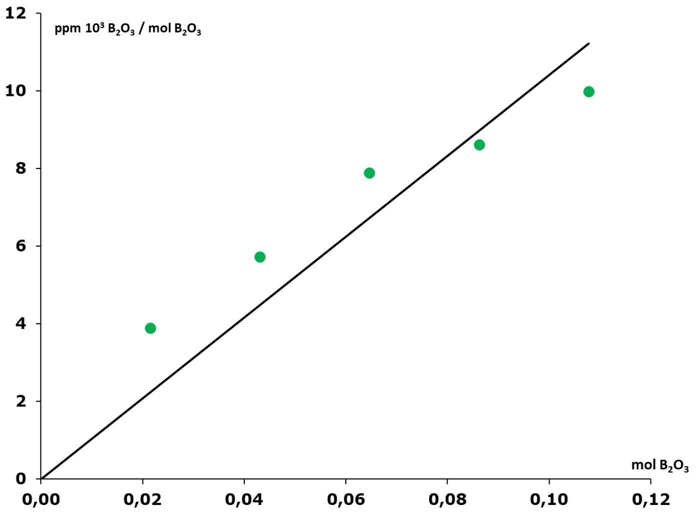

Figure 6. *Evolution of B2O3 leaching in the gloss frit.*

Increase in Na_2O in the gloss frit composition

The increase in Na_2O content (0.5%, 1%, 2%, and 3%) in the starting gloss frit (Br, 0.1% Na_2O) again showed that Na^+ was a leaching cation, as a rise in Na_2O content in the frit led to greater leaching, as may be observed in the following graph.

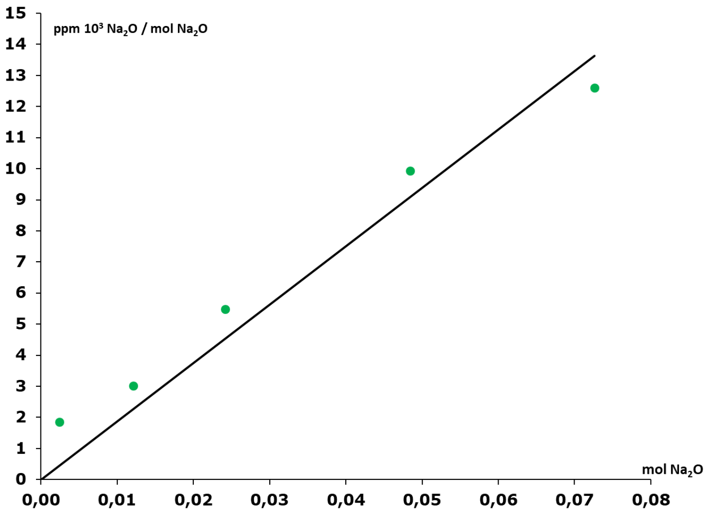

Figure 7. *Evolution of Na2O leaching in the gloss frit.*

2.4. STRUCTURAL STUDY OF THE FRITS

With a view to better understanding the relationship between glass reactivity in water and glass structure, the structural relaxation of the frits was studied by calculating the activation energy (Ea) and by Raman spectroscopy, in order to determine the glass network polymerisation degree. Specifically, the opaque frit (OP) and the gloss frit (Br), as well as the corresponding modifications in the B2O3 and Na2O contents noted above, were selected.

2.4.1. STRUCTURAL RELAXATION

The structural relaxation or thermodynamic fragility of a glass allows its greater or lesser structural resistance to water attack to be evaluated. This parameter was obtained by calculating the activation energy (Ea), such that a higher value of Ea corresponded to a less breakable glass structure and, hence, to a decreased proneness to leaching. Experimentally the methodology consisted of performing a DTA of the frit to calculate the glass transition temperature (Tg) at a certain heating rate[5,6]. Taking different values of this heating rate and the corresponding Tg, and applying the Kissinger equation, the activation energy was calculated. In this study, Ea was determined from the unmilled test frits, in each case making four DTA measurements corresponding to heating rates of 5, 10, 15, and 20 ºC/min.

The following table details the Ea data obtained on both frits and on the changes made to them. It may be observed that, as the B_2O_3 and Na_2O content increased, Ea decreased, indicating that the glass structure was weaker and, therefore, prone to greater leaching. This result corroborates the leaching data from water analysis by ICP-OES. In this sense, the study of the activation energy may be considered a method for predicting, in a type or family of frits, how resistant a given composition is to attack in aqueous medium and, therefore, for optimising a frit composition to minimise the effect of such an attack.

	Ea (kJ/mol)
OP (12.5%B_2O_3) (4.5%Na_2O)	462
OPB1 (10%B_2O_3)	477
OPB2 (8%B_2O_3)	492
OPB3 (6.5%B_2O_3)	502
OPB4 (3.0%B_2O_3)	543
OPNa1 (3%Na_2O)	490
OPNa2 (2%Na_2O)	519
OPNa3 (1%Na_2O)	564
OPNa4 (0.5%Na_2O)	575

	Ea (kJ/mol)
Br (1%B_2O_3) (0.1%Na_2O)	752
BrB1 (2%B_2O_3)	708
BrB2 (3%B_2O_3)	657
BrB3 (4%B_2O_3)	644
BrB4 (5%B_2O_3)	626

	Ea (kJ/mol)
BrNa1 (0.5%Na_2O)	741
BrNa2 (1%Na_2O)	683
BrNa3 (2%Na_2O)	637
BrNa4 (3%Na_2O)	554

Table 4. *Ea data.*

2.4.2. RAMAN SPECTROSCOPY

As mentioned above, Raman spectroscopy analysis was also performed on the unmilled frits to correlate the presence of certain structural groups and frit behaviour relative to water leaching. To do so, a Renishaw model inVia instrument was used, irradiating the sample with an Ar laser at a wavelength of 514 nm and excitation energy of 2.54 on an area of 1 μm2. A Leica optical microscope with 50 magnification lens was used to view the samples. Spectra acquisition was performed for 10 seconds and with a total of 50 scans per test, in a spectral range of 100 cm-1 to 1500cm-1. The Raman spectrum obtained was analysed by deconvolution to generate a Gaussian band distribution. Finally, assignment was performed of the bands corresponding to the Qn structural groups of SiO2 and the area was calculated.

Decrease in B2O3 in the opaque frit composition

The evolution of the Raman bands area assigned to the SiO2 structural groups in the opaque frit (OP) and its compositional modifications, based on the reduction in B3+ content, is plotted below. The figure shows that, as B2O3 content in the frit diminished, structural groups Q4 (1136 cm-1), Q3 (1075 cm-1), and Q2 (1005 cm-1) increased, while groups Q1 (939 cm-1) and Q0 (877 cm-1) decreased. This all indicates that the decrease in B3+ in the frit gave rise to more polymerised and, hence, structurally less fragile glasses, which would explain their greater resistance to leaching.

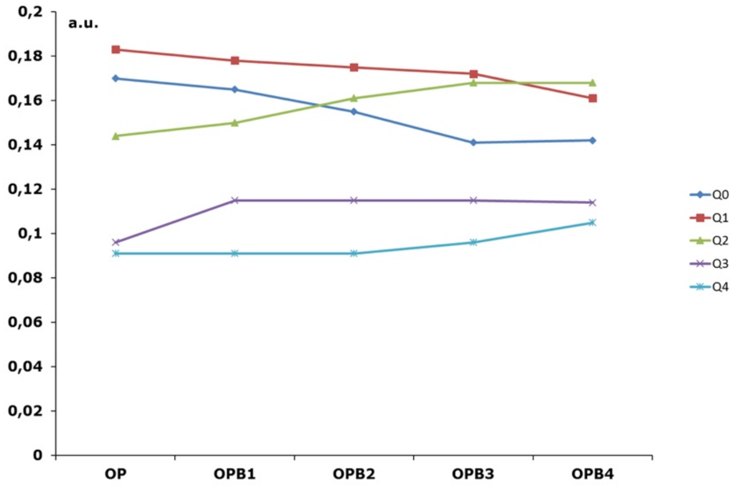

Figure 8. *Evolution of the Q-bands area with decrease in B_2O_3.*

Decrease in Na_2O in the opaque frit composition

In this case as well, the evolution of the area of the bands assigned to the SiO_2 structural groups (Q^0 at 877 cm^{-1}, Q^1 at 939 cm^{-1}, Q^2 at 1005 cm^{-1}, Q^3 at 1075 cm^{-1}, and Q^4 at 1136 cm^{-1}) was studied. The graph shows that the decrease in Na^+ in the frit composition corresponded to an increase in Q^4 and Q^3 units and, therefore, to a greater number of SiO_4 tetrahedra with 3 or 4 bridging oxygens. Concurrently, the Q^1 and Q^0 groups were observed to decrease. This all explains why the frits that reduced their Na^+ content exhibited greater resistance to water attack.

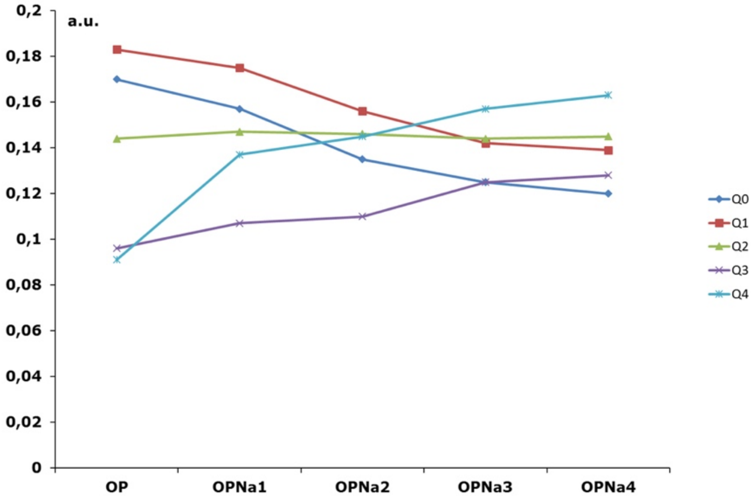

Figure 9. *Evolution of the Q bands area with decrease in Na_2O.*

Increase of B_2O_3 in the gloss frit composition

The calculation of the area of the bands associated with SiO_2 in the Raman spectra of the gloss frits yielded the following evolution (Figure 10) of the structural groups Q^0 (885 cm^{-1}), Q^1 (948 cm^{-1}), Q^2 (1013 cm^{-1}), Q^3 (1074 cm^{-1}), and Q^4 (1137 cm^{-1}). The graph shows that the gloss frits that contained more B^{3+} exhibited greater leaching owing to the greater weakness of the glass structure, as the Q^0 and Q^1 groups increased while the Q^4 and Q^3 groups decreased.

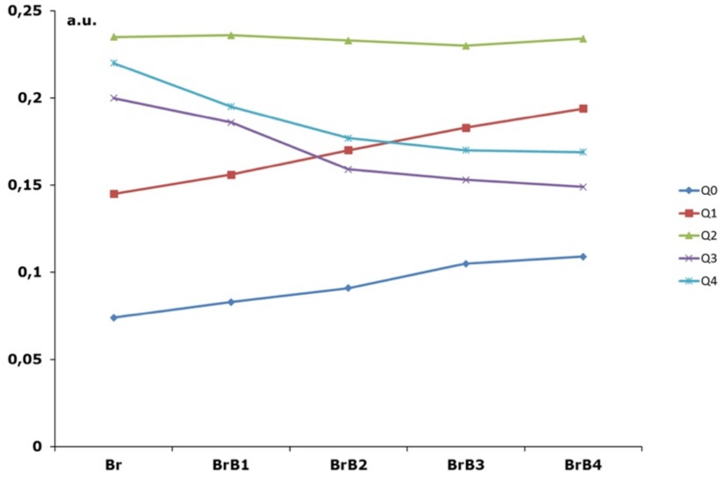

Figure 10. *Evolution of the Q bands area with increase in B_2O_3.*

Increase in Na_2O in the gloss frit composition

The following graph shows the evolution of the Q bands area of SiO_2 in the gloss frit when the Na^+ content was gradually increased (Q^0 at 885 cm^{-1}, Q^1 at 948 cm^{-1}, Q^2 at 1013 cm^{-1}, Q^3 at 1074 cm^{-1}, and Q^4 at 1137 cm^{-1}). In this sense, it may be noted that the bands associated with greater polymerisation (Q^4 and Q^3) decreased, indicating a greater fragility of the glass structure and, hence, a greater predisposition to leaching. This proneness was corroborated by the behaviour of the Q^0 and Q^1 groups, which increased with Na^+ content in the frit structure. In short, the data confirmed that greater Na^+ concentration in the glass structure gave rise to less stable structures, which were consequently more sensitive to leaching.

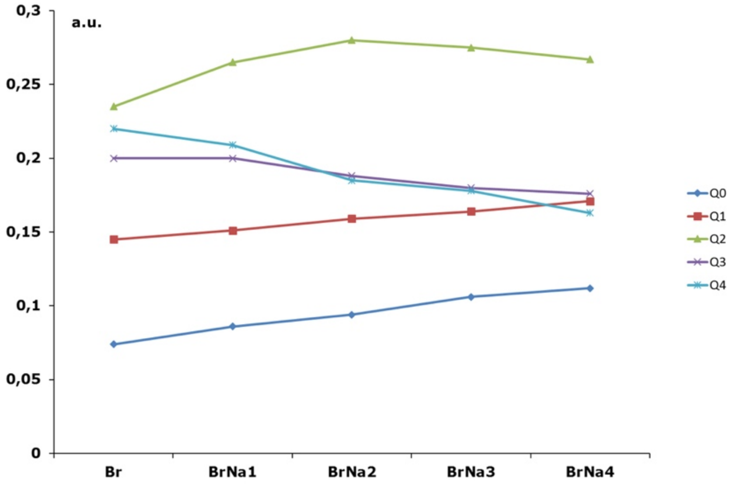

Figure 11. *Evolution of the Q bands area with increase in* Na_2O.

3. CONCLUSIONS

The study results enable the following conclusions to be drawn:

- A method of studying the ability of cations in matt, gloss, and opaque frits to leach has been developed.
- It was determined that maximum leaching in aqueous medium occurred after 72 hours.
- The SiO_2, B_2O_3, Na_2O, and K_2O oxides exhibited the greatest leaching.
- The chemical composition and structure of a frit influences its resistance to attack in aqueous media. Thus, the opaque test frit exhibited higher leaching than the gloss frit.
- As particle size decreased, leaching increased, it being particularly significant at 250 nanometres.
- The decrease in B^{3+} and Na^+ content in an opaque frit with high leaching ability reduced the concentration of both cations released into the aqueous medium. In contrast, the increase in B^{3+} and Na^+ concentration in a low-leaching gloss frit raised the content of both cations in the water.
- An inverse relationship was found between frit activation energy (Ea) and frit predisposition to leach in aqueous media.
- Raman spectroscopy showed that as frit leaching increased, structural units Q^4 and Q^3 decreased while Q^1 and Q^0 increased, indicating a more depolymerised and, therefore, weaker and more reactive glass structure to attack by aqueous solutions.
- A method was established for evaluating and modifying the frit composition to optimise frit stability in aqueous media by studying cation leaching using ICP-OES, determining activation energies by DTA and Q^n structural groups relating to SiO_2 by Raman spectroscopy.

4. REFERENCES

[1] Water solubility in calcium aluminosilicate glasses investigated by first principles techniques. Journal of Solid State Chemistry. F. Bouyer et al. 183 (2010) 2786-2796.

[2] Reacciones de la superficie del vidrio con soluciones acuosas. J. A. Hernández et al. Boletín de Sociedad Española de Cerámica y Vidrio. Vol. 21, nº 2.

[3] Mechanism of calcium lixiviation in soda-lime glasses with a strong biocide activity. J. S. Moya et al. Materials Letters, 70 (2012), 113-115.

[4] Dissolution behaviour of ternary alkali-alkaline earth-borate glasses in water. Kathryn L. et al. Journal of Non-Crystalline Solids, 487 (2018)12-18.

[5] Lithium rich phosphate glass: Crystallization kinetics, structural and conduction characteristics. Prashant D. et al. Journal of Non-Crystalline Solids, 358 (2012) 252-260.

[6] A comparative study of crystallization kinetics between conventionally melt quenched and mechanochemically synthesized $AgI-Ag_2O-CrO_3$ superionic system. Anshuman D. et al. Materials Science & Engineering, B103 (2003) 162-169.