SELECTION OF ADDITIVES FOR REDUCING THE TOXICITY OF QUARTZ IN CERAMIC COMPOSITIONS

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ABSTRACT

The inhalation of crystalline silica, for example in the form of quartz, produces the well-known pathological reaction called silicosis. Traditional ceramic industries use quartz-containing raw materials such as clays, sands, and separate quartz. Consequently, the occupational environments of this type of company can contain appreciable quantities of this pollutant. However, quartz cannot be replaced in ceramic compositions because of the major role it plays in the ceramic process.

The toxicity of particulate toxic agents, in contrast to that of molecular toxic agents, is not wholly determined by their chemical formula. Instead, their reactivity largely depends on factors such as the chemical, thermal, and mechanical history of the particles.

Numerous studies suggest that the toxicity of quartz is conditioned by the surface

chemistry of the quartz particles and, in particular, by the density and abundance of silanol groups. Blocking these groups so that they do not interact with cellular membranes would theoretically be possible in order to reduce or even to eliminate the toxic effect. This postulate has been repeatedly verified by various researchers who, on treating quartz with different substances, managed to reduce its toxicity. The mechanism by which these substances act consists of the formation of a surface coating on the quartz so that its silanol groups are no longer accessible for interaction in biological media.

The present study examines the incorporation into ceramic compositions of certain additives to coat the surface of the quartz contained in the compositions, thus reducing quartz toxicity. The selected substances were nano-alumina, aluminium lactate, and organosilanes. Organosilanes are a very extensive family of compounds that simultaneously enable quartz toxicity to be reduced and the quartz surface to be functionalised, providing it with various properties.

In this study, the incorporation of these compounds was conceived such that no substantial alteration of the ceramic process would be required. In addition, compounds were selected that would not adversely affect product behaviour during the process.

1. INTRODUCCIÓN

It is generally recognised that prolonged inhalation of crystalline silica particles can lead to the disease known as silicosis. In 1997, the International Agency for Research on Cancer (IARC) classified respirable crystalline silica (RCS) in the form of quartz and cristobalite as carcinogenic to humans (Group 1) [1]. The ceramic industries could be affected by these circumstances, as a great many ceramic products (bricks and roofing tiles, ceramic tiles, sanitary ware, tableware, etc.) are made with raw materials that contain quartz.

Despite having found "sufficient" evidence for the above classification, the IARC recognises that silicosis appears to be a necessary precursor for the increase in the risk of lung cancer. In addition, this increased risk is not detected in every industrial scenario, and it would appear to depend on characteristics inherent to the silica itself and/or on external factors [1].

The fact that the toxicity of RCS is conditioned by "external factors" suggests two possibilities: that RCS is not toxic of itself, but that it needs to be activated by another substance or, which is more likely, that other substances that accompany RCS could inhibit its toxicity [2]. In any event, in practice, this means that one might find two chemical agents with the same nominal composition (SiO_2), but with a radically opposed toxicity.

Schlipköter and Brockhaus [3] postulated that it is precisely the silanol groups (Si-OH) at the surface of the quartz that mediate in the pathological effect of RCS and, even more remarkably, that it should be possible to neutralise these active centres by means of molecules that were strongly adsorbed on them. Polyvinylpyridine-N-oxide (PVPNO) has this characteristic. The O^- group of this compound forms hydrogen bridges with the silanols, thus coating the RCS particles. The treatment of RCS with PVPNO reduces haemolysis, cytotoxicity, and damage to the macrophages [4].

Another substance that is able to inhibit the toxicity of quartz is aluminium lactate [5-7]. Aluminium lactate has a comparable efficiency to that of PVPNO [8]. Its effect is so evident that it has been used to distinguish the specific toxicity of quartz in dust mixtures [9].

The use of organosilanes has also yielded excellent results in this regard [10-12]. Unlike PVPNO, which forms hydrogen bridges with quartz, organosilanes react chemically with the silanol groups at the quartz surface. A coating is thus obtained that can last through the subsequent processing of the treated powder, as well as in the biological fluids. Organosilanes are widely used in treating (functionalising) siliceous surfaces [13].

Finally, certain authors [14] have shown that strong Lewis acids, such as $AlCl_3$ or $FeCl_3$, are also able to modulate the harmful action of RCS. Moreover, these authors verified that the quantity required to produce the maximum inhibition coincided exactly with the quantity required to make quartz iso-electric, thus endorsing the hypothesis of the silanol-based mechanism.

It may be noted that, though this research line was started in 1960, none of these substances appear to have been used for these purposes on an industrial scale. In all likelihood, the low added value of quartz as raw material has been of influence in this regard. However, given the wide range of available compounds and the potential benefit in terms of worker health protection, it was considered convenient to explore this possibility for the traditional ceramic sectors.

In this study, the most economical compounds have been identified that could be readily incorporated into the ceramic process. The possibility was examined of coating the quartz contained in traditional ceramic compositions with selected compounds so that the process would not be significantly altered. It was also verified whether the quartz was appropriately coated by the compound involved.

Subsequent studies will determine the reduction in toxicity associated with the use of these coatings.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. SELECTION OF COMPOSITIONS AND PROCESS STAGES IN WHICH TO INCORPORATE THE COATING

This study focuses on traditional ceramic products made by the wet method. There were various reasons for restricting the field of application of the coating technology. The following may be noted:

- The ceramic products made by the dry method (mainly bricks and roofing tiles) usually have a much lower added value per unit mass, which adversely affects the economic feasibility of the coating process.

- Aqueous suspensions are the appropriate media for dispersing the additives and for the chemical reactions and/or colloidal processes producing the coating to take place.

- Certain products made by the wet method incorporate enriched quartz in their compositions. Separate quartz is biologically more active than quartz that is integrated, for example, in clays [9].

The following ceramic sectors were considered: ceramic tiles, sanitary ware, and porcelain tableware. Four compositions were selected to represent the different stages involved in these processes:

- Red-firing porous wall tile body
- Porcelain tableware body formed by isostatic pressing
- Vitreous china sanitary ware body
- Raw glaze for porcelain tableware

The first composition contained no separate quartz. This was integrated in the clays, whereas in the other three compositions the quartz was a differentiated constituent.

As regards the process stage in which the additives were to be incorporated, the preparation of aqueous suspensions was deemed particularly appropriate for the technical and economic reasons indicated previously. The porous wall tile body and the glaze compositions for tableware were subjected to a wet milling process in ball mills, whereas the other two suspensions were prepared by dispersion.

2.2. PRELIMINARY SELECTION OF ADDITIVES AND SAMPLE PREPARATION

As noted, a wide range of additives are available that could be used to reduce the toxicity of the quartz contained in ceramic compositions. With a view to establishing a first selection of these additives, the following criteria were used:

- That the additive should be available in industrial quantities. PVPNO, for example, is only supplied on a laboratory scale.
- That its current price for large quantities should not exceed 5 €/kg, so that the proportioning of reasonable quantities of the compound would not entail excessive costs.
- That it should not have foreseeable adverse effects on the process. For example, the flocculating effect of $AlCl_3$ is well known.

Based on these criteria, aluminium lactate and several organosilanes with various functional groups were chosen from the compounds noted previously.

Although no studies are available in the literature, nano-alumina was also deemed a possible additive for reducing quartz toxicity. As a result of the presence of silanol groups at the quartz surface, quartz exhibits an extremely low iso-electric point (pH at which the zeta (ζ) potential is 0), the quartz iso-electric point being about 2. The iso-electric point of alumina, in contrast, is about 9 [15]. This means that, in a relatively wide range of pH, the quartz and the nano-alumina will have opposite surface charges, thus producing the coating by electrostatic mechanisms.

The test quartz used in the sanitary ware composition was selected to define the coating procedure and to verify that it did indeed take place. However, spot trials with other quartzes were also performed to verify the representativeness of the results.

Quartz treatment, in general, consisted of the following steps:

1. Certain organosilanes required preliminary hydrolysis in which their alkoxy groups dissociated, giving rise to silanol groups. As hydrolysis took place more quickly in acid medium, this preliminary step was performed in the relevant cases, adding a certain quantity of HCl 0.01 M to the additive and stirring until a homogeneous liquid was obtained.
2. Dispersion of the additive in water. The additive was incorporated into the quantity of water required in the formula. In the case of the nano-alumina, this was stirred for 30 minutes to encourage appropriate dispersion.
3. Addition of the quartz. The resulting suspension was stirred for the corresponding reaction time.
4. Filtering the suspension and washing with ethanol. Once the reaction time had ended, the suspension was filtered with a Büchner flask and the resulting powder was repeatedly washed with ethanol to remove any surplus additive.

2.3. EFFECTIVENESS OF THE COATINGS

In order to verify the efficiency of coating formation on the quartz particles, various instrumental techniques were used. Their greater or lesser appropriateness in each case depended on the nature of the coating.

The samples were observed by scanning electron microscopy (SEM). The nano-alumina particles coating the quartz could be directly observed with this technique. In contrast, the organic coatings formed a thin layer that could hardly be detected by SEM. In these cases, SEM enabled verification that the samples contained no unreacted additive aggregates.

Thermogravimetry (TG) has been used in the literature to characterise organosilane coatings on silica nanoparticles [16]. This technique allows the stability of the coating with temperature to be evaluated and the amount present in the sample to be quantified.

The ζ potential of quartz in an aqueous suspension is a measure of its surface electric charge. Thus, a coating by additives with a positive charge should increase the ζ potential of the quartz (which is negative at $pH > 2$). This effect has been observed in treatments with $AlCl_3$ [14], as well as with silanes with amino groups [17]. Nano-alumina should have a similar effect, as noted previously. For certain compounds, it was thus possible to evaluate the coating by determining the ζ potential.

X-ray photoelectron spectroscopy (XPS) enabled a surface layer (of about 10 nm) of the samples to be analysed. This technique was used to quantify the presence of identifying elements in the quartz surface coatings.

2.4. PROCESS BEHAVIOUR

The study of the ability of the selected additives to coat the quartz allowed the most effective additives, as well as the most appropriate proportioned quantities and reaction times, to be identified. For the aluminium lactate, it was not necessary to perform this preliminary study because this compound had been used in toxicological tests to differentiate the specific toxicity of quartz [9] and it was thus possible to establish the minimum dose required to produce inhibition.

The compositions for the study of process behaviour were prepared in the most similar possible way to the procedure used in the study of additive effectiveness:

- In the compositions of the sanitary ware and porcelain tableware bodies, the quartz was treated in the way described (except for the filtration of the powder) and the remaining constituents were then added in the usual way.

- In the case of the wall tile composition, as it had no separate quartz, the treatment was performed on the composition as a whole.

- Tableware glaze is typically subjected to vigorous milling (70 h) that, on the one hand, might degrade the additive and, on the other, is hardly reproducible in the laboratory. In this case, it was therefore decided to add the additive to a glaze suspension that had been industrially prepared.

Different controls were performed on the treated compositions, depending on the product manufactured.

The suspensions of the selected ceramic tile and tableware body compositions were dried by spray drying. The viscosity and thixotropy that these suspensions exhibited after the treatment were controlled with a torsion wire viscometer of the Gallenkamp type. The suspensions were atomised in a semi-industrial spray dryer. The resulting spray-dried granules were used to obtain compaction diagrams, and the dry mechanical strength of the formed pieces was determined. For the ceramic tile composition, its tendency to black core formation was also determined. The procedures followed are described elsewhere [18].

The suspensions of the sanitary ware composition were subjected to a slip casting process. For this composition, the influence of the additives on the rheological behaviour of the treated suspensions was studied using a rotational viscometer. In addition, the slip casting rate was determined by means of a procedure in which the slip casting time of increasing suspension volumes was recorded.

The effect of the addition of the additives to the glaze suspension for tableware was also studied with a rotational viscometer.

3. RESULTS

3.1. COATING EFFECTIVENESS

Although a wide range of compounds were studied, for the sake of brevity only the results obtained with the additives that exhibited the most promising behaviour are presented. These were as follows:

- Propyltrimethoxysilane (PTMO). This is a relatively simple organosilane, which has three methoxy groups and a functional propyl group.

- SIVO160. This is a commercial aminosilane polymer used for coating siliceous as well as metallic surfaces.

- Nano-alumina. For economic reasons, dispersability, and risk prevention, it was decided to use nanoparticles of alumina stabilised in an aqueous suspension.

The PTMO was hydrolysed with HCl 0.01 M in a ratio by mass of 2.5:1 PTMO:HCl. The SIVO160 required no preliminary hydrolysis and it contained an unknown quantity of water. The solids content of the nano-alumina suspension used was 30% by weight. All the proportioned quantities indicated hereafter refer to the mass of the diluted compound (either in HCl or in the water that they contained) with respect to the mass of quartz.

The results obtained in the TG of samples treated with different proportioned quantities of PTMO, in all cases keeping a reaction time of 3 h, are shown in Figure 1. The samples exhibited a characteristic peak at a temperature of about 570ºC, which was absent in the starting quartz. This peak was thus assignable to coating decomposition. Apart from a larger peak being obtained on proportioning 0.1%, than on proportioning 0.5%, it was noted that a greater quantity of coating tended to develop as the proportioned quantity of PTMO increased.

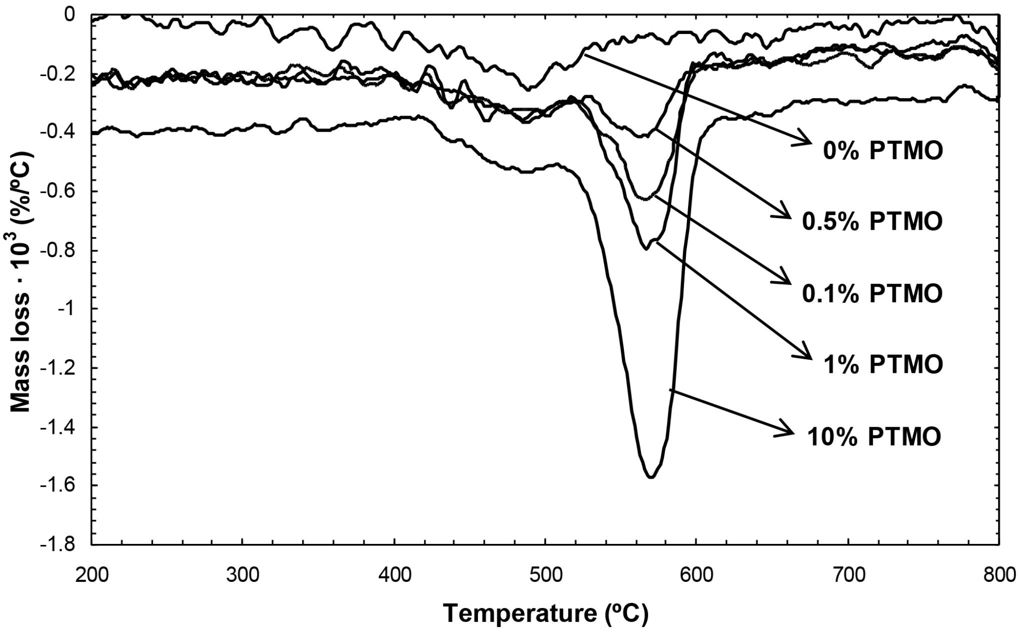

Figure 1. Influence of the proportioned quantity of PTMO on the mass losses of the treated quartz. A reaction time of 3 h was used in every case.

The influence of the PTMO reaction time with quartz was also studied. The results obtained by TG for the samples treated at various reaction times are shown in Figure 2. The trend again suggests that, when reaction time increased, a greater quantity of PTMO reacted

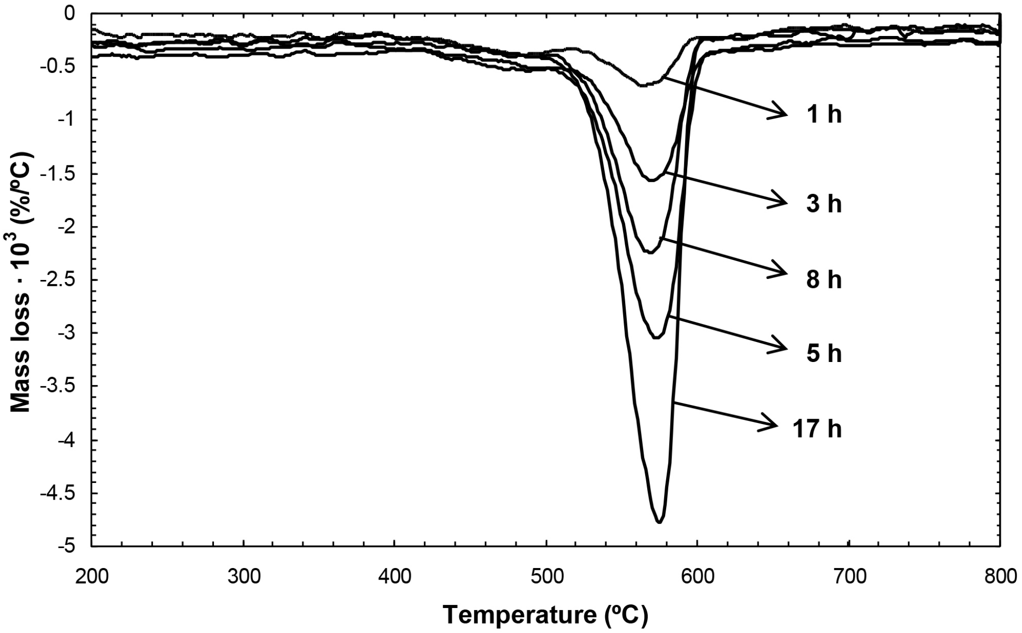

Figure 2. Influence of reaction time on the mass losses of quartz treated with PTMO. The proportioned quantity of PTMO was 10% in every case.

In contrast, the quartz samples treated with SIVO160 displayed no characteristic peak in TG (Figure 3). However, this compound has amino groups and, when coating quartz, it should provide the quartz with a positive surface charge. Indeed, it was verified that, by treatment with increasing quantities of SIVO160, the quartz ζ potential was modified until it was made net positive (Figure 4). Similar results were obtained with other aminosilanes, such as aminopropyltrimethoxysilane. A possible explanation might be that these compounds tend to form a thin coating that is not detected by TG.

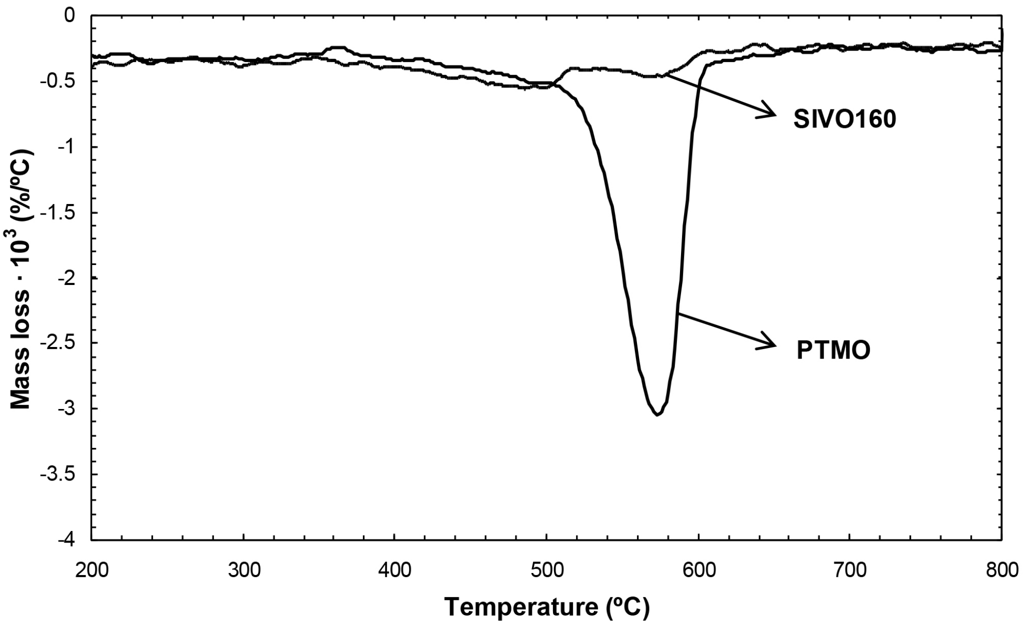

Figure 3. Comparison of the mass losses of quartz treated with PTMO and SIVO160. In both cases, the proportioned quantity was 10% by weight and the reaction time was 5 h.

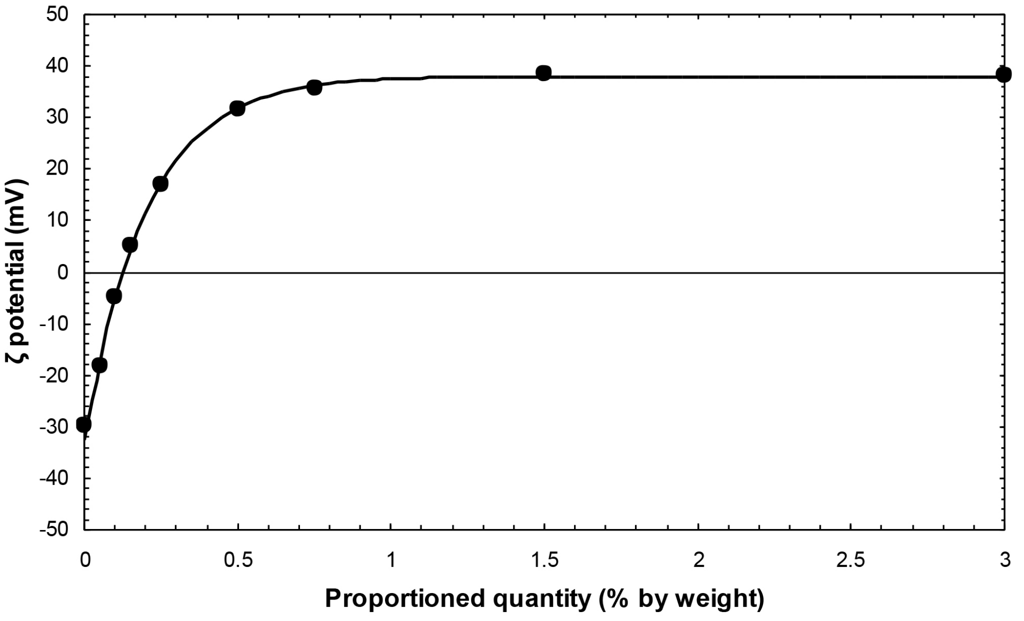

Figure 4. Variation of the ζ potential of a quartz suspension treated with different proportioned quantities of SIVO160.

The coating of quartz with nano-alumina could also be evaluated by determining the ζ potential, as indicated above. Figure 5 shows the variation of the ζ potential of the quartz treated with different nano-alumina additions. It may be observed that, in this case, it was also possible to modify the quartz surface charge, albeit much less effectively than with SIVO160.

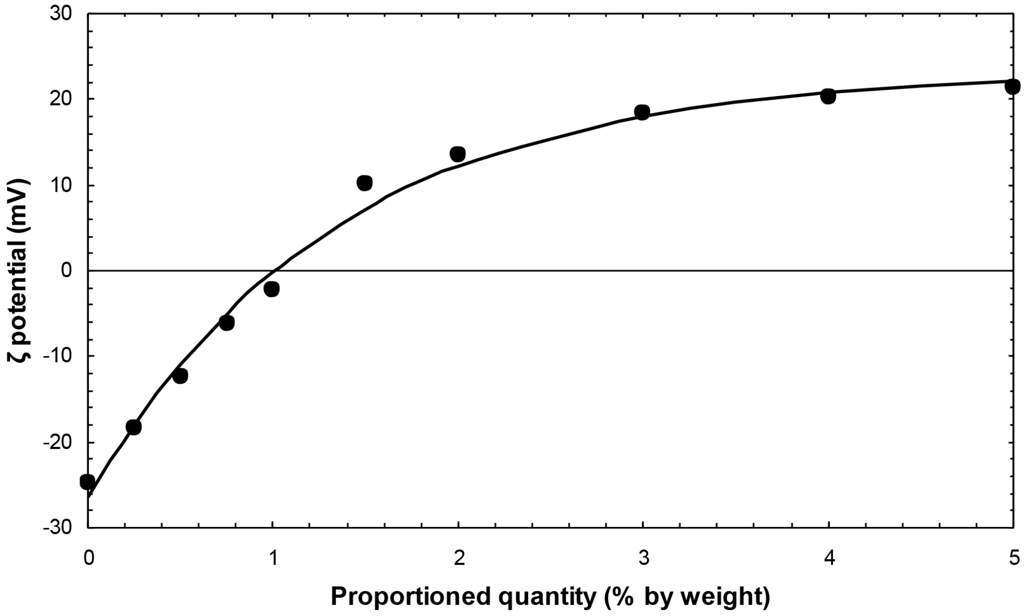

Figure 5. Variation of the ζ potential of a quartz suspension treated with different proportioned quantities of nano-alumina.

Unlike the organosilanes, the nano-alumina coating of quartz could be observed by SEM. The appearance of the quartz surface before and after treatment with nano-alumina is compared in Figure 6. The surface of the treated particles displays a relatively uniform distribution of small adhered particles, which microanalysis showed involved alumina.

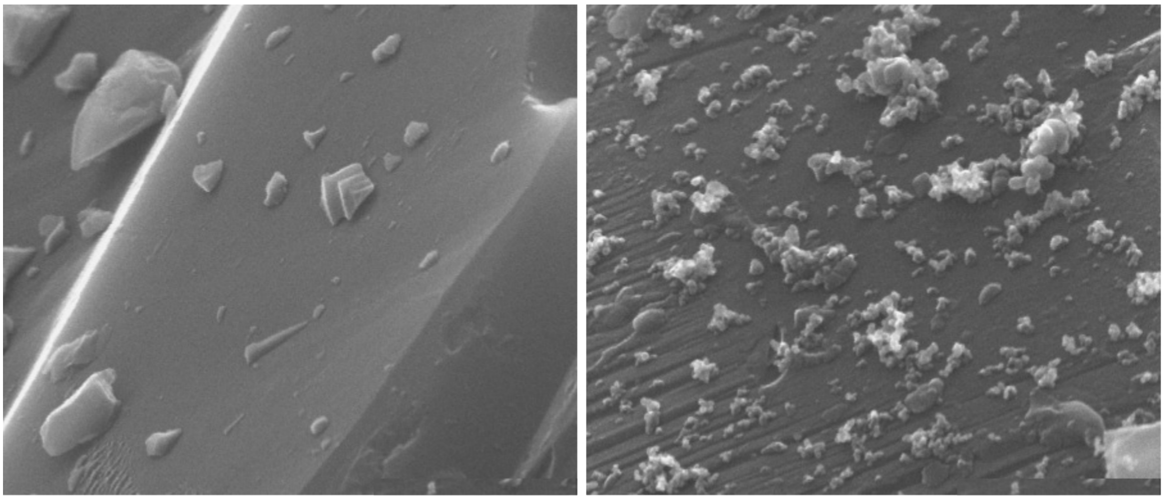

Figure 6. Morphology of the quartz particle surface before (left) and after (right) treatment with 1.5% nano-alumina by weight.

The results obtained were used to define certain proportioned quantities and reaction times, in which a balance was sought between coating quality and the cost and ease of implementation in the industry. Quartz samples treated under these conditions were prepared, the toxicity of which will be determined in subsequent studies. In addition, the surface composition of these samples was studied by XPS.

The selected treatments and the results of the XPS analysis are detailed in Table 1. In the case of the sample treated with nano-alumina, a clear enrichment in Al with relation to the starting sample was observed. On the other hand, the greater carbon content in the samples treated with organosilanes could indicate the presence of organosilanes at the quartz surface, though the existence of carbonaceous matter adsorbed on the starting sample distorted this result to a certain extent.

Additive	Reaction time (h)	Proportioned quantity (% by weight)	Surface composition (atomic %)			
			Si	O	C	Al
Without additive	3(1)(2)	0.0	32.0	59.5	8.1	0.4
PTMO	3	0.1	32.0	60.0	7.4	0.6
		0.5	32.6	57.7	9.0	0.7
		1.4	33.1	57.0	9.3	0.6
SIVO160	2	0.2	32.4	57.6	9.6	0.3
		0.4	31.6	57.6	10.0	0.8
		1.0	31.7	57.5	10.2	0.6
Nano-alumina	1(2)	1.5	24.5	58.3	8.0	9.2

Table 1. Elemental composition of the surface of the quartz treated under the selected conditions.

(1) Sample subjected to an analogous preparation without the incorporation of any additive.

(2) In this case, the reaction time refers to the stirring time.

3.2. PROCESS BEHAVIOUR OF THE TREATED COMPOSITIONS

Once the effectiveness of the coatings had been verified, the feasibility of the integration of these treatments in the selected ceramic processes was examined. In those cases in which several proportioned quantities had been proposed, the intermediate quantity was selected. The tested treatments are set out in Table 2. As noted previously, it was not necessary to conduct a preliminary study for aluminium lactate, as previous toxicological tests had determined the quantity required to inhibit toxicity.

Additive	Reaction time (h)	Proportioned quantity (% by weight)
PTMO	3	0.5
SIVO160	2	0.4
Nano-alumina	1	1.5
Aluminium lactate	1	0.75(1)

Table 2. Selected treatment conditions for the study of process behaviour.

(1) Proportioned quantity of the solution used, containing 30% by weight of the salt at issue.

The process behaviour of the treated compositions was compared in every case with that of the corresponding untreated industrial composition. In this section, the generic term "STD" is used hereafter to refer to this reference composition, independently of the sector considered in each case. The compositions were prepared on the basis of the industrial formula with regard both to the main raw materials and to the additives (deflocculants, binders, and plasticisers) used.

The aluminium lactate flocculated the suspensions to the point that the corresponding determinations could not be made in the industrial preparation conditions of these suspensions, probably owing to the contribution of trivalent aluminium ions. For this reason, a complete study was not performed for this additive.

Tables 3 and 4 detail the results obtained for the porous wall tile body and the porcelain tableware compositions, which were processed by spray drying. The data include the apparent viscosity of the treated suspensions, the pressing pressure identified from the compaction diagram, the bulk density associated with this pressing pressure, and the dry mechanical strength of the test pieces pressed at the pressing pressure.

Additive	Proportioned quantity (% by weight)	Apparent viscosity (cP)	Pressing pressure (kg/cm^2)	Bulk density (g/cm^3)	Mechanical strength (kg/cm^2)
STD	0.0	1120	280	1.775	20
PTMO	0.5	1520	270	1.767	19
SIVO160	0.4	1240	270	1.769	19
Nano-alumina	1.5	1280	280	1.771	20

Table 3. Studied process variables for the porcelain tableware body composition.

Additive	Proportioned quantity (% by weight)	Apparent viscosity (cP)	Pressing pressure (kg/cm^2)	Bulk density (g/cm^3)	Mechanical strength (kg/cm^2)
STD	0.0	345	250	1.986	42
PTMO	0.5	260	220	1.985	37
SIVO160	0.4	360	230	1.982	41
Nano-alumina	1.5	300	240	1.982	41

Table 4. Studied process variables for the porous wall tile composition.

For these compositions, the incorporation of the quartz treatments with PTMO, SIVO160, and nano-alumina had a moderate effect, and the resulting suspensions were processable. Of these treatments, the treatment with PTMO produced some results that could be considered negative, with a substantial increase in suspension viscosity of the tableware composition and a slight reduction of the dry mechanical strength of the porous wall tiles. Nevertheless, these effects were deemed tolerable. It was also verified that these compounds did not significantly increase the tendency of the wall tile composition to black core formation.

The flow curves obtained with the suspensions of the sanitary ware composition are shown in Figure 8. The addition of nano-alumina slightly raised suspension viscosity. In contrast, the PTMO and the SIVO160 reduced suspension viscosity. The same trend was reflected in the slip casting kinetics of these suspensions (Figure 9), in which it may be observed that, in the most viscous (most "flocculated") suspensions, the wall formed more rapidly. The treatment with PTMO also reduced suspension thixotropy and the yield stress. In any event, the addition of these additives did not appear to interfere too greatly in the processing and might even decrease the required quantity of deflocculant.

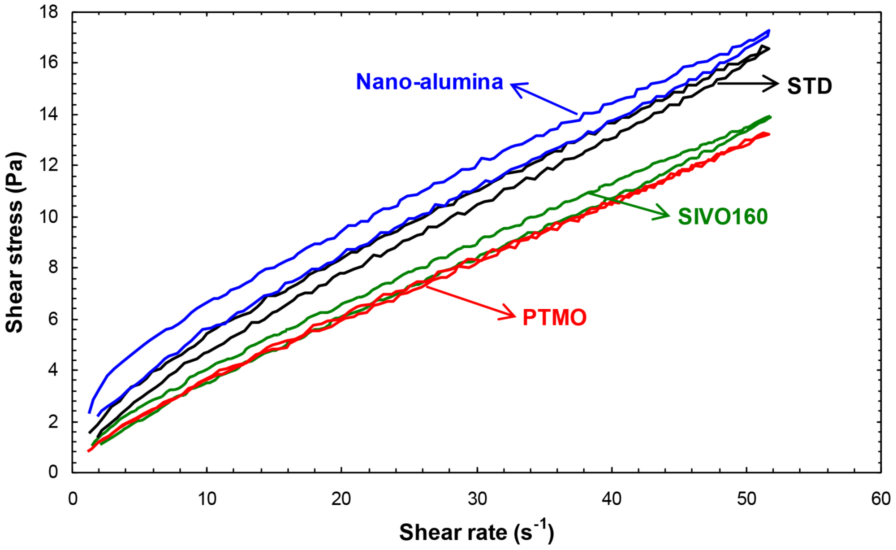

Figure 7. Flow curves of the vitreous china sanitary ware suspension incorporating quartz treatment with different additives.

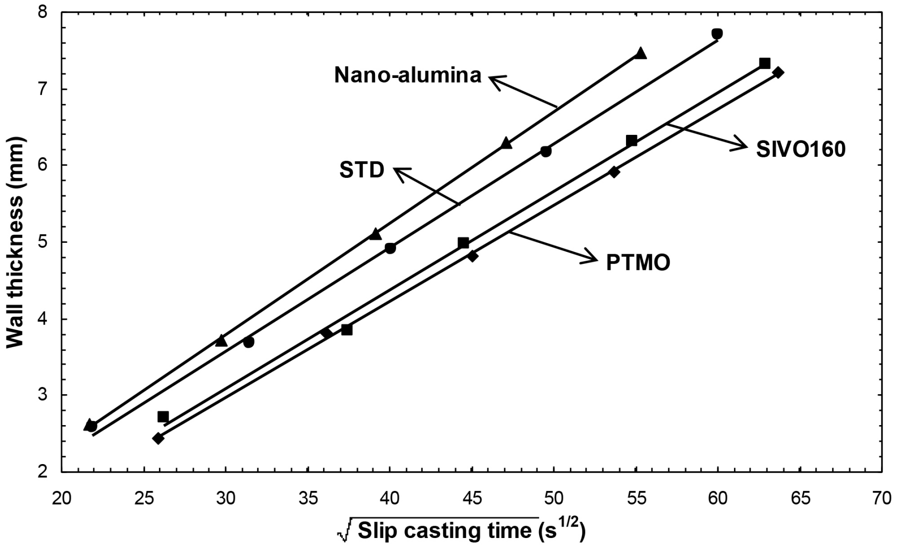

Figure 8. Slip casting kinetics of the sanitary ware composition after treatment with the additives indicated.

The flow curves obtained with the suspensions of the tableware glaze composition are shown in Figure 9. The incorporation of the additives had a similar influence to that obtained for the sanitary ware composition, even though in this case, SIVO160 increased the viscosity of the suspension with relation to that of the STD suspension.

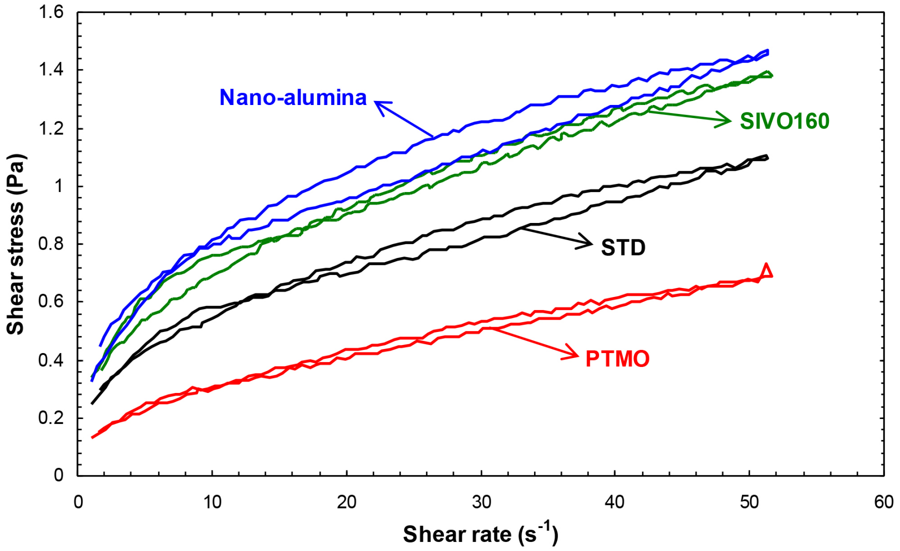

Figura 9. Curvas de flujo de la suspensión de esmalte para vajilla incorporando el tratamiento del cuarzo con diferentes aditivos.

4. CONCLUSIONS

This study shows that the incorporation of additives into ceramic compositions to reduce the toxicity of quartz appears to be technically feasible, at least with regard to the process variables most liable to be affected. Subsequent phases of the study will verify whether the finished product properties (colour, mechanical strength, etc.) are impaired.

The instrumental determinations carried out suggest that the use of these additives produced the necessary quartz coating to reduce quartz toxicity. It is intended to perform the corresponding validation by conducting toxicological tests. Those results will enable the economic feasibility of the treatment to be determined.

5. ACKNOWLEDGEMENTS

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