Torres-Carrasco, M., Reinosa, J.J., De la Rubia, M.A., Reyes, E., Alonso Peralta, F., Fernández, J.F. (2019). Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage. *Construction and Building Materials*, v. 223, 360-367.

DOI: https://doi.org/10.1016/j.conbuildmat.2019.07.023

Dear author,

Please note that changes made in the online proofing system will be added to the article before publication but are not reflected in this PDF.

We also ask that this file not be used for submitting corrections.

JCBM 16297
5 July 2019
ARTICLE IN PRESS
No. of Pages 8, Model 5G

Construction and Building Materials xxx (xxxx) xxx

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage

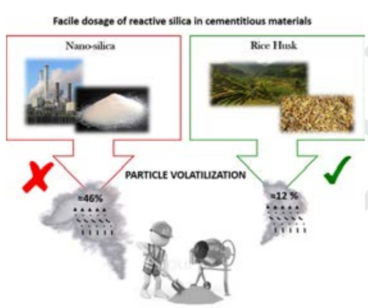
M. Torres-Carrasco [a,c,*], J.J. Reinosa [a], M.A. de la Rubia [b], E. Reyes [b], F. Alonso Peralta [d], J.F. Fernández [a]

[a] Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, Madrid 28049, Spain
[b] Dept. Ingeniería Civil-Construcción, Civil Engineering School, Universidad Politécnica Madrid, Madrid 28040, Spain
[c] Materials Science and Engineering Department, IAAB, Universidad Carlos III de Madrid, Avda. Universidad 30, 28911 Leganés, Madrid, Spain
[d] Dept. Ingeniería Forestal, E.T.S.I. Agronómica, Alimentaria y Biosistemas, Universidad Politécnica de Madrid, Madrid 28040, Spain

HIGHLIGHTS

- Rice husk ash is an environmental alternative in the cementitious materials production.
- The use of nano-silica entails a significant economic cost.
- The handling of rice husk ash is healthier than the use of nano-silica.
- Nano-silica addition improves mechanical and durability behaviour.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 February 2019
Received in revised form 17 June 2019
Accepted 4 July 2019
Available online xxxx

Keywords:
Rice husk ash
Nano-silica
Cement
Mortar
Health

ABSTRACT

Nano-silica addition improves mechanical and durability behavior in mortars. However, nanomaterial handling requires use of occupational risk prevention measures as Individual Protection Equipment for the workers. Moreover, the high agglomeration of nanomaterials produces uncertainty in the expected mortar performance. Rice husk ash as a source of reactive silica in cement compositions is compared with nano-silica. The use of rice husk ash provides similar physical-chemical cementitious materials than other commercial nano-silica providing relevant differences during the composition. Near 50% wt of volatility is found for the silica nanoparticles during the handling dosage. Thus, the rice husk ash presents a reduced volatility, ~12% wt and it allows ensuring high content with adequate workability. Mortars with addition of rice husk ash reach higher compressive strength and resistivity in correlation with lower porosity. For that, the use of rice husk ash is viable as safer alternative material than nano-silica in the cementitious compositions. In addition, as the rice husk ash comes from agricultural waste resources their use as secondary raw material will contributes to circularity in the economy by reducing engineered nanomaterials consumption.

1. Introduction

Currently, nano-modification of Portland cement is used to improve mechanical and durable properties of mortars and concrete [1]. The addition of micro or nano-silica allows cementitious materials to reach high resistance values (above 40%) with low amounts of addition to the cement. In addition, durable properties

* Corresponding author at: Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, Madrid 28049, Spain.
E-mail address: mtorres@icv.csic.es (M. Torres-Carrasco).

https://doi.org/10.1016/j.conbuildmat.2019.07.023

also benefit from the incorporation of this silicon source, such as the low permeability to chloride ions and the high resistivity of concrete against corrosion. However, the use of nanomaterials in cementitious composition requires high water demand combined with superplasticizer additives to promote its workability. In spite of this, the use of silica nanoparticles is limited in percentage due to the volatilization problems during their dosing that imply labor risk problems. Moreover, the cost of nanomaterials makes the cement products which are improved with nanotechnology excessively expensive. For this reason, their use is limited for selected applications.

The rice husk has led to different studies in recent years since, after a calcination process, the rice husk ash is rich in silica, SiO_2 [2]. In the countries where rice production occurs, the husk of the same is a problematic waste. Therefore, studies have been undertaken to be able to give these resources a later usefulness. Hence, through incorporating rice husk waste into the cementitious compositions, a reduction in the consumption of raw materials can be achieved, in addition to contribute to the circular economy. Moreover, the use of rice husk ash has become an alternative option for environmentally friendly energy production when it replaces different raw materials in Portland cement, minimizing CO_2 emissions during the clinker production process [3].

There are numerous publications in which rice husk ash has been incorporated as Supplementary material to Portland cement in the preparation of mortars and concretes [4–10], and also, when rice husk ash is combined with other nanoparticles to replace ordinary Portland cement [3]. The rice husk ash possesses relevant pozzolanic capacity and high silica content, typically >95%, which is usually non-crystalline or amorphous.

The use of nano-chemistry in cementitious materials allows the engineering of these materials to evolve in relation to hydration mechanisms at short ages, improving mechanical and durability properties [11]. Nano-silica [1,12–15], nano-alumina [16], nano-titania [17], nano-iron oxide [18] and nano-clay particles [19] have been used over the last years as supplementary cementitious materials in the preparation of cements with additions. Nano-SiO_2 particles significantly affect the mechanical and durable properties of cement-based composites, mainly due to their high purity and high surface area. However, it must take into account that achieving an improvement in the materials performance through the use of nanotechnology can endanger health of live bodies and environment. Therefore, a safe, integrated and responsible use of nanotechnology must be considered.

In recent years, the exposure to nanoparticles significantly increases in both industrial and domestic areas. Despite the growing number of exposed workers to the nanotechnology, there are still not conclusive studies addressing toxicological aspects, health surveillance and industrial hygiene in the nanotechnology sector [20]. Although the use of nanotechnology is not very widespread in the construction sector (it is due to the high price involved in the use of large quantities of nanometric materials), silica plays an essential role in the cement sector, so other compounds with different chemical composition could not replace it [20]. In particular, the inhalation of silica produces its deposition on lungs, which may cause illnesses as silicosis or lung cancer [21]. The fact of being as nanosize makes it acts as fine airborne dust and therefore the risk of illness increases because of its ability to be breathed. In order to decrease this main negative effect, the industry has developed dispersions of fume silica for construction applications. Another factor is the fact of machining nano-products in construction sector (for example by drilling, sanding or cleaning activities) whose effects can only be partially supplemented by personal protective equipment [22].

The objective of this work is to address the challenge of using alternative materials or processes for the use of nanomaterials in cement mortars with the comparative analysis of addition between nano-silica and rice husk ash. The study evaluates their effect on mechanical and durable behavior. In addition, a study of workability/volatility of silicon particles during their handling in the preparation of dosages is attempted due to it is the most critical step in relation to workers health.

2. Materials and methods

2.1. Materials

2.1.1. Sample preparation and trials conducted

In this study, three different materials were used, whose chemical analysis in equivalent oxides obtained by FRX (Philips PW-1004 X-ray spectrometer) is shown in Table 1. The ordinary Portland cement (CEM I 52.5R) possesses an average particle size (d_{50}) of 6.28 μm and a specific surface (BET) of 1.45 m^2/g. The different silica sources as rice husk ash and nano-silica have compositions rich in SiO_2, differing mainly in their physical properties (see Table 2). The rice husk ash (RHA) was obtained after a process of calcination for 1 h at 800 °C from rice husk residues in delta Del Ebro region, Spain. Particle size was measured by dynamic light scattering (DLS). The particles in suspension diffract the light and the diffraction angle is inversely proportional to the particle size. Specific surface BET is measured by absorption of inert gas (N_2) at low temperature.

Three different mortar mixtures were prepared by water/binder (L/S) of 0.5 and sand/binder ratio of 3:1, according to the UNE-EN-196-1. The different dosage of the prepared samples is shown in Table 3. In addition, a reference mortar (CEM I) and mortars with different percentages of cement substitution were prepared by rice husk ash (CEM I + 10%RHA) and nano-silica (CEM I + 2% NS). In this work, commercial nano-silica powder or rice husk ash were manual mixed with cement 52.5 type I previously to the following processing steps such as mixing with water and sand. This manual mixing process followed to achieving homogeneous cement-based materials implies an increase in exposure time to nanoparti-

Table 2
Physical properties of the precursors materials used.

wt%	Particle size d_{50} (μm)	BET (g/m^2)
OPC	6.3	1.45
Rice husk ash	25.5	117.6
Nano-silica	0.025	200

Table 1
Chemical analysis in equivalent oxides of precursors materials used as determined by FRX (%).

Wt%	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	MnO	SO_3	*LoI
OPC	61.7	20.0	5.0	2.07	3.46	0.16	1.07	–	3.73	1.5
Rice husk Ash	–	95.8	–	0.35	–	<0.1	0.32	–	–	2.0
Nano-silica	–	99.8	–	–	–	–	–	–	–	–

*LOI = loss on ignition.

Please cite this article as: M. Torres-Carrasco, J. J. Reinosa, M. A. de la Rubia et al., Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage, Construction and Building Materials, https://doi.org/10.1016/j.conbuildmat.2019.07.023

Table 3
Composition of mortar mixtures prepared in this study.

Mortar	L/S	Cement (g)	Sand (g)	Water (g)	SP (g)	Silica (g)
CEM I	0.5	450	1350	225	–	–
CEM I + 10%RHA	0.5	405	1350	225	1.8	45
CEM I + 2%NS	0.5	441	1350	225	1.8	9

RHA = Rice Husk Ash; NS = Nano-silica; SP = superplasticizer.

cles and therefore an increase in health risks. It is worth to note that in some of the mortars containing different percentages of silica (B and C) it was necessary to use additives (superplasticizer SIKA Viscocrete 5720) to achieve a L/S ratio of 0.5 (comparable to the reference mortar, A). The superplasticizer addition or superplasticizers content is based in a previous work of the authors studying the hydration behavior of blended cement pastes mixtures with micro and nano silica particles with a wide range of specific surfaces and particle sizes [23]. Also, different percentages of silica were incorporated depending on the type of silica used, based mainly on the workability of the system [23,24]. The mortars were cured in a chamber with a 99% relative humidity and at temperature of 22 ± 2 °C for 7 and 28 days.

The differential thermal analysis and thermogravimetry (DTA-TG) of the cement pastes was performed by using LABSYS evo equipment provided by SETARAM Instrumentation, in the range of 25 °C to 1100 °C with a heating rate of 10°/min in N_2 atmosphere in alumina crucibles. For the mechanical strength tests (7 and 28 days), the standard UNE-EN 12390–3 was used. The samples were conducted in an IBERTEST press, with a maximum capacity of 1500 kN. Mercury intrusion porosimetry (MIP) tests were carried out on Micromeritics Autopore IV 9500 according to ASTM D 4404-84. Relationship between applied pressure and pores size is defined by Washburn equation assuming pores with cylindrical geometry [25]:

$$P = -4\gamma \cos\theta / D$$

P = needed pressure for mercury to enter in a pore with a D size.
γ = mercury surface tension (485 N/mm)
θ = Contact angle between mercury and the pore surface
D = Pore diameter (nm)

and total porosity (tP) is calculated means of the following rate:

$$tP = (Vp/Vm) \cdot 100$$

where:

tP = total porosity (%)
Vp = Pores volume (mm^3)
Vm = Sample volume (mm^3)

The electrical resistivity test was carried out in accordance with the standard UNE 83988-1, 2008 on the determination of electrical resistivity. It is a non-destructive test that can be done on saturated and partially saturated samples. This test indirectly measures the parameters of connectivity and tortuosity of the porosity in the material, which have a significant influence on the resistance against the penetration of chlorides. The age of the mortars testes was 7 and 28 days after a curing process at room temperature (20 ± 2 °C) and 95% of relative humidity in order to analyze the evolution over time. The equipment used was a Concrete Resistivity Meter (RCON^{tm}) from GIATEC SCIENTIFIC.

The volatility test of the different materials used was carried out in a laboratory extractor hood, where an assembly was carried out as shown in Fig. 1. In a container, a certain amount of the raw material was introduced and it is dropped from a height of 50 cm. At the base of the assembly a collecting tray was placed with an analytical balance. To facilitate the visualization of the volatilized nanoparticles, the extractor hood was covered with black cloth and white light were provided.

3. Results and discussion

3.1. Effect of nano-silica and rice husk ash contents on mortars properties: Mechanical and porosity properties

Table 4 shows the results obtained in relation to the physical properties of the different mortars evaluated at the ages of 7 and 28 days. In all cases, the mortars have been prepared using constant L/S = 0.5. At the early hydration age (7d) CEM I and CEM I + 10% RHA show identical strength values (54 MPa) slightly higher than the value for the mixture with nanosilica (51 MPa). The addition of rice husk (CEM I + 10% RHA) produces a slight increase in the mechanical properties for 28 days hydration age (63.5 MPa) in comparison with the rest of mixtures, showing both of them compression strengths values around 60 MPa (see Table 4 and Supplementary info, Fig. S1).

This improvement of the mechanical strength correlates with the decrease of the total porosity value. Hence, in samples with silica at the age of 28 days of curing, total porosity is reduced by 10% compared to the reference system CEM I. According to the results, the mortars with rice husk ash showed the lowest total porosity in both ages 7 and 28 days. One key factor that could affect the reduction of porosity is related to the effective distribution of the different nano and micro silica during mixing with the presence of agglomerates. The high agglomeration state of nano-silica causes lack of homogeneous distribution. Moreover, the low apparent density impedes that the mixing forces distribute effectively the material during the mortar preparation. Several white spot are present in the cast mortar in spite of the low percentage of addition. By the contrary, the rice husk ash presents a more homogeneous distribution due their micrometric size that resulted most efficient in terms of mixing homogeneity for the mortars. The reduction of the porosity value is an evidence of the better homogeneity for the rice husk ash in the mortar. The presence of agglomerates could difficult the hydration reaction and therefore reducing the content of the main reaction product, the C-S-H gel, making the system more porous.

CEM I shows critical diameter and threshold diameter that are the double that cements with RHA or NS for both hydration ages. Both diameters are identical for both hydration ages except for sample with RHA that shows a slow decrease in the critical diameter between 7 and 28 days (Table 5).

Regarding the classification of the pore size, all the mortars showed a higher percentage in the ranges of medium capillaries, 10 < Ø < 50 nm, and large capillaries, 50 nm < Ø < 10 µm, as it could be expected (see Supplementary info, Table S1). It is important to highlight the pore size distribution values in the rice husk ash silica mortar presents the lowest percentage of pores in the range of large capillaries and the highest percentage of pores in the range of medium capillaries from 7 days. In this sense, the addition of silica from rice husk ash represents an advantage

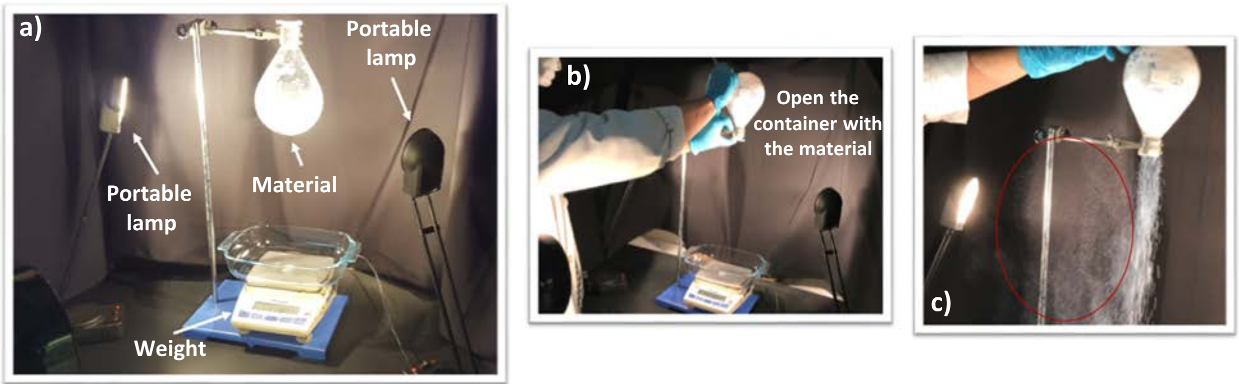


Fig. 1. a) image of the experimental assembly for the volatility test of the different materials used in this study; b) image before the opening of the container that contains the material; c) image of nanoparticles flowing during the volatility test.

Table 4
Mechanical strengths and total porosity at 7–28 days of the different mortars evaluated with the incorporation of nano-silica and rice husk ash.

Mortar	L/S	Mechanical strengths			
		Flexural (MPa)		Compressive (MPa)	
		7d	28d	7d	28d
CEM I	0.5	7.3 ± 0.5	8.1 ± 0.4	54.0 ± 1.4	60.0 ± 2.0
CEM I + 10%RHA	0.5	7.2 ± 0.4	7.8 ± 0.4	53.5 ± 1.2	63.5 ± 1.8
CEM I + 2%NS	0.5	7.4 ± 0.3	7.9 ± 0.2	51.0 ± 1.1	59.0 ± 2.1

Table 5
Critical and threshold diameters and total porosity at 7–28 days of the different mortars evaluated with the incorporation of nano-silica and rice husk ash.

Mortar	Critical diameter (μm)		Thershold diameter (μm)		Total Porosity (%)	
	7d	28d	7d	28d	7d	28d
CEM I	0.062	0.062	0.151	0.121	15.6	14.0
CEM I + 10%RHA	0.032	0.026	0.077	0.077	13.2	12.6
CEM I + 2%NS	0.032	0.032	0.077	0.077	13.9	13.4

against the nano-silica additive in terms of porosity and pore distribution. A higher percentage of medium capillary pores has an important role in terms of mechanical properties and durability, since the presence of a larger number of pores with small diameter entails a reduction of pore connectivity and an increase in tortuosity.

Regarding the critical pore radius, as in the previous analysis of porosity and distribution, the mortars containing rice husk ash present similar values than the ones having nano-silica at the age of 7 days (~32 nm). Nevertheless, at 28 days, the samples with rice husk ash reduce its value to 26 nm meanwhile samples with nano-silica maintain 32 nm. This fact is in agreement with the higher reactivity of the nano-silica for short ages that implies a lack of further porosity evolution from 7 to 28 days (see Table 5).

3.2. DTA-TG analysis

By using the DTA-TG, information related to the weight loss of the samples at different temperature ranges that corresponds to different hydrated compounds is attained. Fig. 2 provides the data from the DTA-TG analysis at 7 and 28 days (Fig. 2a and b, respectively). At ~100 °C the free water is lost and the physisorbed water is removed in the temperature range of 120–140 °C. In this way, the first TG interval up to 140 °C is assigned to water removal. Subsequently, at approximately 430 °C the mass loss is associated to water combined in C-S-H gel (interval 140–430 °C). The content of portlandite is related to the weight loss of water of crystallization that takes place in the temperature range between 430 and 515 °C. Finally, due to the possible carbonation of the portlandite, it is necessary to adjust the amount of portlandite and include the part corresponding to the weight loss in the temperature range where the carbonate loss occurs (515–1000 °C). According to different studies [24,26], the calcium carbonate ($CaCO_3$) resulting from the carbonation of the C-S-H dissociates in a lower temperature range than the $CaCO_3$ resulting from the carbonation or portlandite, which makes it possible to thermally differentiate both carbonation processes.

The results of the TG for the evaluated pastes are shown in Fig. 2, where it is possible to see graphically the water percentages of the C-S-H gel (140–430 °C) for 7 and 28 days of curing. At the age of 7 days of curing, the water content in the gel structure (140–430 °C) is higher for the mortar with nano-silica (CEM I + 2% NS), but this mortar presents the least increase up to 28 days (see Fig. 2c and d). At the age of 28 days of curing, the mortar with micro-silica from the rice husk ash (CEM I + 10%RHA) presents a higher percentage of combined water in the form of gel, also presenting a greater increase of 7–28 days in this range. Fig. 2e shows the percentage of total combined water (140–1000 °C) for both ages of curing. In all cases both the water corresponding to the C-S-H gels and the total combined water increase with the curing time. These results show that the hydration of the cementitious material forms a greater amount of C-S-H gels, and therefore, mortars are more densified. This fact is the main factor that directly influences the resistance to compression.

Please cite this article as: M. Torres-Carrasco, J. J. Reinosa, M. A. de la Rubia et al., Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage, Construction and Building Materials, https://doi.org/10.1016/j.conbuildmat.2019.07.023

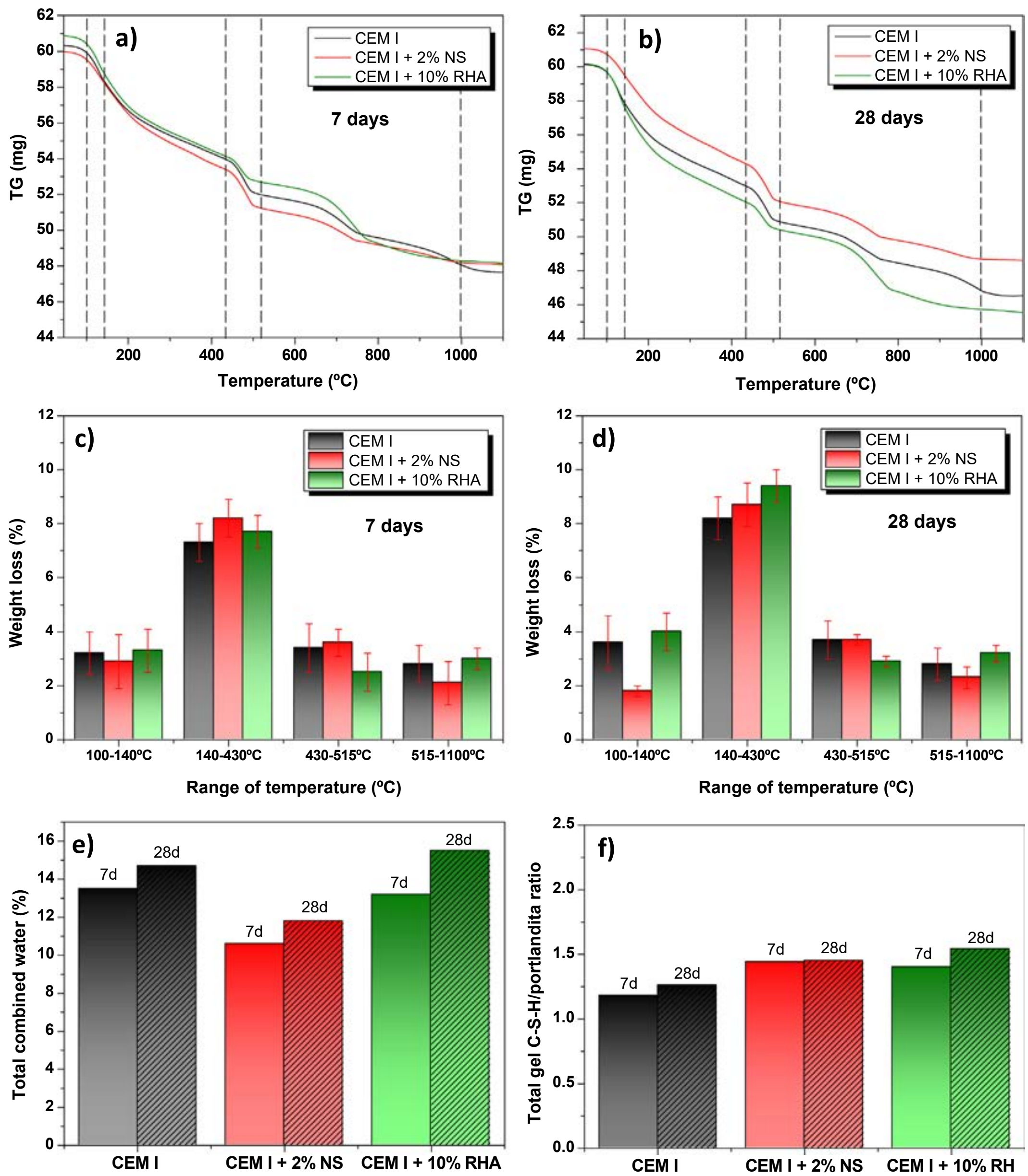


Fig. 2. a) TG analysis of different materials used at 7 days; b) TG analysis of different materials used at 28 days; c) percentage of C-S-H gel water at the age of 7 days; d) percentage of C-S-H gel water at the age of 28 days; e) percentage of total water combined at 7 and 28 days; f) C-S-H/portlandite gel ratio at 7 and 28 days.

Something similar happens with the total content of combined water, as can be seen in Fig. 2e. The highest percentage of total combined water at 7 days is obtained for the mixture with nano-silica (CEM I + 2%NS), although it is subsequently the system that presented a smaller increase up to 28 days. The mixture with micro-silica from the rice husk ash presents the highest percentage of total combined water at 28 days of age, being the one that presented a greater increase with age.

Fig. 2f shows the gel relationship C-S-H/total portlandite for the two ages studied. The lowest total C-S-H/portlandite gel ratio occurs for the reference cement (CEM I), being higher for the samples with addition of the different types of silica. This is a consequence of the high reactivity of mortar systems containing high specific surface area silica particles.

3.3. Addition effect of nano-silica and rice husk ash in mortars. Expected durability properties (impediment to diffusion-migration of chloride ions), resistivity to chloride ions

An effective parameter to evaluate the risk of corrosion in this type of materials is the electrical resistivity [27]. The electrical resistivity is dependent on the mortars or concrete quality and on the exposure conditions, such as the humidity conditions, temperature, sample composition, etc. [28–30]. In this work the main difference between mortars is the silica reactivity.

Table 6 shows the results of the resistivity test for mortars cured at 7 and 28 days. At the age of 7 days of curing, the lowest value of resistivity corresponds to the mixture containing micro-silica from the rice husk ash (CEM I + 10%RHA) due to its

Table 6
Resistivity at 7 and 28 days for the different systems evaluated.

System	L/S	Resistivity (Ω*m)	
		7d	28d
CEM I	0.5	30.0	43.0
CEM I + 10%RHA	0.5	26.4	64.0
CEM I + 2%NS	0.5	42.4	54.8

slow reaction kinetics. The slow reaction kinetic does not significantly refine the porosity at early ages although it does lead to a considerable reduction of the total porosity; but at 28 days reaches the highest resistivity value. Thus, the resistivity values correlate with the pore distribution in which a greater reduction of total porosity having large contribution from small capillary pore results in resistivity increasing of ~50% for mortars with 10 wt% of rice husk ash in comparison with standard OPC mortar.

In this way, the electrical resistivity is a very important parameter that could indicate us what level of corrosion is expected to reach fundamental parameter in the determination of the intensity of the corrosion process in concrete, particularly when corrosion is induced by an attack by chlorides [27,30,31]. A material that has a high electrical resistivity will have a very slow corrosion compared to a material whose electrical resistivity is lower, where the current can penetrate better (less impediment) from the anode to the cathode. Therefore, in view of the obtained results, it can be concluded that the mortar prepared with CEM I + 10% RHA at the age of 28 days of curing behaves as a material with a high resistivity due to a denser C-S-H gel. In addition, the mortar having rice husk ash allows the reactive silica to distribute more homogeneously throughout the mortar in comparison with the mortar incorporating nano-silica particles (NS).

To sum up, in view of the physical-chemical results obtained, it can be concluded that it would be viable the use of silica from calcination of rice husk ash for partial substitution of cement in mortars [32]. The so modified mortar presents higher percentage of gel phase and reduced porosity. Thus, functional properties of mortar are favored in terms of mechanical strength and resistivity for mortar having reactive silica substituting cement particles. The use of silica from rice husk ash allows the contribution of a higher percentage of active silica in conditions of workability of the mortars, thus contributing to a remarkable improvement of the properties that cannot be achieved through the use of highly reactive silica. Beyond the interest of using a product that comes from an agricultural waste, the technical properties of developed mortars are superior. This example also allows considering aspects related to the manipulation of silica nanoparticles that present potential problems of nanotoxicity.

3.4. Critical aspects in the handling of reactive silica: Particle volatility test

Fig. 3 shows the results obtained in the volatilization test of each of the materials used. In all cases, an amount of the materials (cement, nano-silica and rice husk ash) drops from a 50 cm height towards the weighing tray. The result provides information in terms of particles volatilization. In the case of CEM I (reference material), there is a slight volatilization of the particles, ca. 0.2 wt%. However, highly reactive silica particles combined a high surface as result of the low particle size that produces an enhancement of the electrostatic repulsion forces [33]. As consequence, nanoparticles volatilize easily, which produce an environmental contamination that can be detrimental for life and in particular for human health.

Silica nanoparticles (NS) are the material with largest volatilization, > 42 wt%. This fact is of special relevance due to the high breathable amount of nanomaterial that is released to the air in an open dosage, as occurs in a manual dosage. As a result, uncertainty is generated in the correct dosage and hence a doubt about the pursued final properties of the mortars. In laboratory conditions, this problem is corrected by a direct weighing of the dosed material. However, the translation to a real process of use would require either closed dosing systems or the use of an incorporation vector, as is the case of a liquid. The use of closed dosing systems is restricted to materials with adequate fluidity, which does not occur in silica nanoparticles. Therefore, the only alternative up to date is to use liquid dosages in aqueous phases that imply an extra cost in the use of nanomaterials.

In the case of reactive silica from rice husk ash, the volatilization test records ca. 12 wt%. This is a 75% reduction of volatilized material for a product that maintains a high specific surface area. However, the great difference between both reactive silicas lies in the particle size. While the nano silica has an average size of 25 nm, the rice husk ash has an average size of 25 μm, that is, 3 orders of magnitude greater. In this way, the fluidity of rice husk particles is suitable for a closed system, such as pneumatic transport of pulverulent material or simply dosing by gravity. An additional data recorded during the volatilization test consists of the percentage of material that is deposited outside the weighing tray, but in the work area of the volatilization test. In the case of nano silica, a 12 wt% is recorded, while for rice husk ash the value is 2 wt%. Therefore, the proportion that is incorporated into the atmosphere in the case of nano-silica is much higher, 42–12 wt%, than in the shell of the rice husk, 12–2 wt%. This aspect is an indicator of the proper fluidity of the rice husk ash.

With these results, it could be considered if the use of nanoparticles (nano-silica) in cements is worthwhile to achieve high mechanical and durable results, or if, on the contrary, it is preferred to opt for worse mechanical and durable results, but with a lower risk to health.

How can these volatilized nanoparticles affect human health? There is very little information on the short and long-term effects on human health and the environment, although it has been observed that engineered nanoparticles can cause different damage from those produced by natural substances. This is because the properties of the substances in their natural state (many already know) are different when the matter is presented on this very small scale, behaving differently in the body. The small size of nanoparticles facilitate its respiratory absorption and through the skin, circulating through the blood flow and allowing its penetration into organs and tissues "closed" for those same substances in other sizes.

The possible effects on health may be related to the number of particle and the exposure surface, but other characteristics such as shape, charge, chemical components, catalytic properties, association with other pollutants, degree of agglomeration and solubility in biological fluids, they could decisively influence the biological response. In this sense, the degree of solubility in biological fluids seems to be an important factor, and depending on their chemical compositions, some NPs can dissolve more quickly than others in biological fluids and acquire toxic properties of a systematic nature, in addition to their possible local effects. However, despite the growing number of industries and populations exposed, there is still a great lack of knowledge about toxicological aspects related to NPs, as well as the most effective health surveillance systems and industrial hygiene problems within the nanotechnology sector.

Very few studies address the possible relationship between occupational exposure of nanoparticles and the appearance of damage to health. At the inhalation level, the toxic effects of nanoparticles at the respiratory level have been the most studied

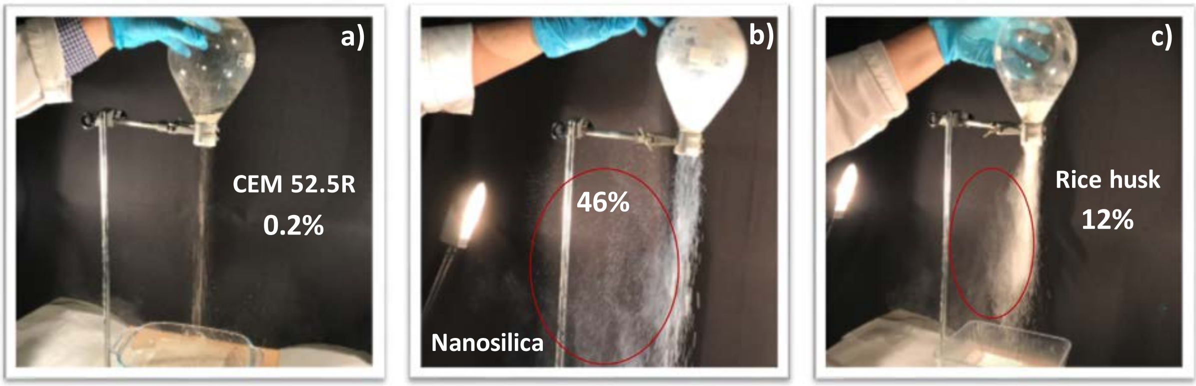


Fig. 3. Images of the particle volatilization test at the laboratory level. a) CEM I; b) nano-silica (NS) and c) rice husk ash (RHA).

so far. Once the nanoparticles are inhaled, 50% of the nanoparticles smaller than 15–20 nm are deposited at the alveolar level; while those <10 nm are deposited mainly in the extra thoracic region. In the case of silica, there are differences between crystalline and amorphous silica regarding the human risks, being highly toxic and the exposure risk increases for the crystalline one. In this sense, the use of rice husk is an advantage because it ensures the absence of crystalline silica by calcination temperatures reached in the obtaining process. In a concrete way, silica particles may get trapped in the nose and throat and they are likely to find their way into the lungs [34]. There, silica forms silanol groups (—SiOH) in the presence of water. Hence, it reacts with lung cells, leading to lipid peroxidation that damages the cell membrane. By stimulating alveolar macrophages, silica dust leads to the production of reactive oxygen species (ROS), leading to reduced antioxidant defenses, and thereby resulting in lipid peroxidation and damage to the lungs [35].

Because the respiratory system is a unique target for the toxicity of nanoparticles and that in addition to being the gateway for inhaled particles, receives the full cardiac output, there is a possibility that exposure of the lung to the nanoparticles that enter in the body through breathing or any other way, may end up in a systemic distribution of them [36]. Therefore, special attention should be given to the use of respiratory protection, especially when the particles are applied in the form of an aerosol (spray), which is confirmed in some way by the results of Phillips et al. [37].

Apart from the inhalation route, another very frequent exposure in workers is contact through the skin [38,39]; so the second most important way of entry of NPs in the body is the cutaneous route, either by the presence of NPs in the workplace that can become deposited on the skin, or by the use of cosmetics and sunscreens [40].

Therefore, by way of summary, it can be concluded that, with the limited information available, while more works are being developed to study in depth possible causes and effects between pathologies and exposures to different NPs and can be determined with greater precision if there is or not risk to health associated with exposure to these agents should be: 1) maintain caution when the possibility of exposure to NPs is suspected and 2) recommend the establishment of prevention measures as one of the most effective ways to currently, it can be counted in order to avoid the risk of developing occupational diseases possibly related to exposure to NPs.

4. Conclusions

The data presented herein will be valuable in the design and development of durable mortars with the addition of micro-nano silicas of different origin. The fact of incorporating this type of materials supposes an improvement in the physical-chemical properties of the mortars besides providing an energetic saving, since part of the Portland cement is replaced. From the point of view of the durability of these materials, we obtain mortars with low porosities that allow reducing the corrosion risks.

From the comparative point of view of the reactive silica studied, the use of rice husk ash as a secondary raw material from an agricultural waste presents favorable properties from the point of view of dosage, handling and mortar functionalization. The use of engineered nano silica entails a significant economic cost, high dosage problems and limited improving of functional properties in mortars.

Regarding the handling of these materials, it is necessary to take into account their particle size. A small particle size promotes high volatilization with material loss, which potentially causes health problems due to inhalation, contact with the skin, etc. As consequence, it is relevant to adopt measures of individual protection of workers during dosage of mortar incorporating nanoparticles. By the contrary, the use of reactive silica from the rice husk ash, having a larger particle size, allows to obtain a microstructure that gives rise to good mechanical and resistive properties. The use of larger silica particle size translates into a very promising durable behavior and, the most important, also reduces considerably the volatilization, which makes its use as a safer material from the health point of view.

Declaration of Competing Interest

None.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness through the Project MAT-2017-86450-C4-1-R, Spanish National Research Council under Project NANOMIND 201560E068 and H2020 project FISSAC grant 642154. Dr. M. Torres-Carrasco is also indebted to MINECO for a postdoctoral fellowship "Juan de la Cierva-Formación" (ref: FJCI-2016-28488).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2019.07.023.

Please cite this article as: M. Torres-Carrasco, J. J. Reinosa, M. A. de la Rubia et al., Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage, Construction and Building Materials, https://doi.org/10.1016/j.conbuildmat.2019.07.023

References

[1] F. Sanchez, K. Sobolev, Nanotechnology in concrete – a review, Constr. Build. Mater. 24 (2010) 2060–2071.
[2] J. Prasara-A, S.H. Gheewala, Sustainable utilization of rice husk ash from power plants: a review, J. Clean. Prod. 167 (2018) 1020–1028.
[3] N. Kumar, K. Kupwade-Patil, R. Higuchi, D.P. Ferrell, V.A. Luttrull, J.G. Lynam, Use of biomass ash for development of engineered cementitious binders, ACS Sustain. Chem. Eng. 6 (2018) 13122–13130.
[4] M. Balapour, A.A. Ramezanianpour, E. Hajibandeh, An investigation on mechanical and durability properties of mortars containing nano and micro RHA, Constr. Build. Mater. 132 (2017) 470–477.
[5] H. Chao-Lung, B. Le Anh-Tuan, C. Chun-Tsun, Effect of rice husk ash on the strength and durability characteristics of concrete, Constr. Build. Mater. 25 (2011) 3768–3772.
[6] J. Alex, J. Dhanalakshmi, B. Ambedkar, Experimental investigation on rice husk ash as cement replacement on concrete production, Constr. Build. Mater. 127 (2016) 353–362.
[7] S.N. Raman, T. Ngo, P. Mendis, H.B. Mahmud, High-strength rice husk ash concrete incorporating quarry dust as a partial substitute for sand, Constr. Build. Mater. 25 (2011) 3123–3130.
[8] M. Jamil, M.N.N. Khan, M.R. Karim, A.B.M.A. Kaish, M.F.M. Zain, Physical and chemical contributions of Rice Husk Ash on the properties of mortar, Constr. Build. Mater. 128 (2016) 185–198.
[9] M.F.M. Zain, M.N. Islam, F. Mahmud, M. Jamil, Production of rice husk ash for use in concrete as a supplementary cementitious material, Constr. Build. Mater. 25 (2011) 798–805.
[10] S.K. Antiohos, V.G. Papadakis, S. Tsimas, Rice husk ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness, Cem. Concr. Res. 61–62 (2014) 20–27.
[11] A.F. Jamsheer, K. Kupwade-Patil, O. Büyüköztürk, A. Bumajdad, Analysis of engineered cement paste using silica nanoparticles and metakaolin using29Si NMR, water adsorption and synchrotron X-ray Diffraction, Constr. Build. Mater. 180 (2018) 698–709.
[12] P. Hou, X. Cheng, J. Qian, S.P. Shah, Effects and mechanisms of surface treatment of hardened cement-based materials with colloidal nanoSiO2and its precursor, Constr. Build. Mater. 53 (2014) 66–73.
[13] Y. Qing, Z. Zenan, K. Deyu, C. Rongshen, Influence of nano-SiO2addition on properties of hardened cement paste as compared with silica fume, Constr. Build. Mater. 21 (2007) 539–545.
[14] K. Sobolev, Z. Lin, I. Flores-Vivian, R. Pradoto, Nano-engineered cements with enhanced mechanical performance, J. Am. Ceram. Soc. 99 (2016) 564–572.
[15] T. Ji, Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO_2, Cem. Concr. Res. 35 (2005) 1943–1947.
[16] Z. Li, H. Wang, S. He, Y. Lu, M. Wang, Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite, Mater. Lett. 60 (2006) 356–359.
[17] A.R. Jayapalan, B.Y. Lee, K.E. Kurtis, Can nanotechnology be "green"? Comparing efficacy of nano and microparticles in cementitious materials, Cem. Concr. Compos. 36 (2013) 16–24.
[18] L. Soto-Pérez, V. López, S.S. Hwang, Response Surface Methodology to optimize the cement paste mix design: time-dependent contribution of fly ash and nano-iron oxide as admixtures, Mater. Des. 86 (2015) 22–29.
[19] T.-P. Chang, J.-Y. Shih, K.-M. Yang, T.-C. Hsiao, Material properties of portland cement paste with nano-montmorillonite, J. Mater. Sci. 42 (2007) 7478–7487.
[20] Y. Reches, Nanoparticles as concrete additives: review and perspectives, Constr. Build. Mater. 175 (2018) 483–495.
[21] H. Mohammadi, S. Farhang Dehghan, A. Tahamtan, F. Golbabaei, Evaluation of potential biomarkers of exposure to crystalline silica: a case study in an insulator manufacturer, Toxicol. Ind. Health. 34 (2018) 491–498.
[22] E.F. of building and Woodworkers, Nano-products in the European Construction Industry, (2009).
[23] M.A. de la Rubia, E. de Lucas-Gil, E. Reyes, F. Rubio-Marcos, M. Torres-Carrasco, J.F. Fernández, A. Moragues, Viability study of a safe method for health to prepare cement pastes with simultaneous nanometric functional additions, Adv. Mater. Sci. Eng. 2018 (2018) 1–13.
[24] D. Alonso-Domínguez, I. Álvarez-Serrano, E. Reyes, A. Moragues, New mortars fabricated by electrostatic dry deposition of nano and microsilica additions: enhanced properties, Constr. Build. Mater. 135 (2017) 186–193.
[25] E. Berodier, J. Bizzozero, A.C.A. Muller, Mercury intrusion porosimetry, A Pract. Guid. to Microstruct. Anal. Cem. Mater., 2016, pp. 419–444.
[26] G. Villain, M. Thiery, G. Platret, Measurement methods of carbonation profiles in concrete: thermogravimetry, chemical analysis and gammadensimetry, Cem. Concr. Res. 37 (2007) 1182–1192.
[27] W. Morris, A. Vico, M. Vazquez, S.R. De Sanchez, Corrosion of reinforcing steel evaluated by means of concrete resistivity measurements, Corros. Sci. 44 (2002) 81–99.
[28] S.E. Hussain, M. Rasheeduzzafar, A. Al-Mussallan, A.S. Al-Gahtani, Factors affecting threshold chloride for reinforcement corrosion in concrete, Cem. Concr. Res. 25 (1995) 1543–1555.
[29] B.B. Hope, A.K. Ip, D.G. Manning, Corrosion and electrical impedance in concrete, Cem. Concr. Res. 15 (1985) 525–534.
[30] M. Torres-Carrasco, M. Tognonvi, A. Tagnit-Hamou, F. Puertas, Durability of Alkali-Activated Slag Concretes Prepared using waste glass as Alternative activator, ACI 112 (2015) 791–800.
[31] E. Douglas, A. Bilodeau, V. Malhotra, Properties and durability of alkali-activated slag concrete, ACI Mater. J. 89 (1992) 509–516.
[32] C. Fapohunda, B. Akinbile, A. Shittu, Structure and properties of mortar and concrete with rice husk ash as partial replacement of ordinary Portland cement – a review, Int. J. Sustain. Built Environ. 6 (2017) 675–692.
[33] I. Lorite, A. Del Campo, J.J. Romero, J.F. Fernández, Isolated nanoparticle Raman spectroscopy, J. Raman Spectrosc. 43 (2012) 889–894.
[34] R.B. Hetland, F.R. Cassee, M. Refsnes, P.E. Schwarze, M. Låg, A.J.F. Boere, E. Dybing, Release of inflammatory cytokines, cell toxicity and apoptosis in epithelial lung cells after exposure to ambient air particles of different size fractions, Toxicol. Vitr. 18 (2004) 203–212.
[35] V. Castranova, V. Vallyathan, Silicosis and coal workers' pneumoconiosis, Environ. Health Perspect. 108 (2000) 675–684.
[36] G. Oberdörster, Z. Sharp, V. Atudorei, A. Elder, R. Gelein, A. Lunts, W. Kreyling, C. Cox, Extrapulmonary translocation of ultrafine carbon particles following whole-body inhalation exposure of rats, J. Toxicol. Environ. Heal. – Part A. 65 (2002) 1531–1543.
[37] J.I. Phillips, F.Y. Green, J.C.A. Davies, J. Murray, Pulmonary and systemic toxicity following exposure to nickel nanoparticles, Am. J. Ind. Med. 53 (2010) 763–767.
[38] T. Forbe, M. García, E. Gonzalez, Potencial risks of nanoparticles, Food Sci. Technol. 31 (2011) 835–842.
[39] M. Crosera, M. Bovenzi, G. Maina, G. Adami, C. Zanette, C. Florio, F. Filon Larese, Nanoparticle dermal absorption and toxicity: a review of the literature, Occup. Environ. Heal. 82 (2009) 1043–1055.
[40] J.J. Reinosa, C.M.Á. Docio, V.Z. Ramírez, J.F.F. Lozano, Hierarchical nano ZnO-micro TiO_2 composites: high UV protection yield lowering photodegradation in sunscreens, Ceram. Int. 44 (2018) 2827–2834.

Please cite this article as: M. Torres-Carrasco, J. J. Reinosa, M. A. de la Rubia et al., Critical aspects in the handling of reactive silica in cementitious materials: Effectiveness of rice husk ash vs nano-silica in mortar dosage, Construction and Building Materials, https://doi.org/10.1016/j.conbuildmat.2019.07.023