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Ball Milling of Silica-Based Pyroclastic Scoriae: Measurement of Mechanochemical Reactivity by Radical Scavenging

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ABSTRACT: The present work concerns the mechanochemical reactivity of *Pozzolane Rosse*, a historical constituent of ancient Roman mortars and concretes. Suitably sieved *Pozzolane Rosse* powders were subjected to mechanical activation. Chemical behavior was investigated both during and after the mechanical treatment using an ethanol solution containing a free radical scavenger. Experimental findings indicate that the mechanical processing induces a decrease in scavenger concentration. The scavenger consumption is significantly larger when *Pozzolane Rosse* is exposed to the ethanol solution during the mechanical treatment, due to

fracturing processes resulting in the increase of specific surface area of *Pozzolane Rosse* powder and to frictional processes between particles. The surface density of active sites is indirectly evaluated, and the emerging mechanochemical effects are discussed. Kinetic effects of the mechanical processing on the reaction between *Pozzolane Rosse* and calcium hydroxide in water are also evaluated. The accurate measurements of experimental observables and their interpretation based on a reliable kinetic model allowed a quantitative assessment of the mechanochemical reactivity of the material.
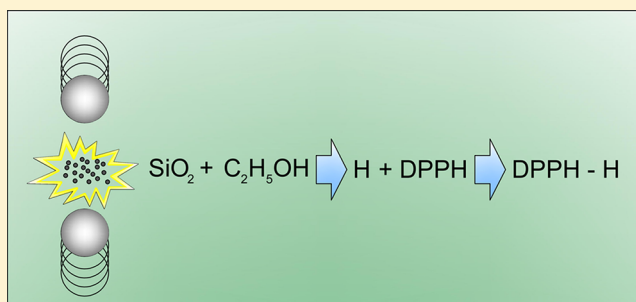
1. INTRODUCTION

Pozzolans constitute a broad class of naturally occurring inorganic materials of volcanic origin.[1] The term derives from the ancient Latin *pulvis puteolanum*, which designates the fine volcanic scoriae forming natural deposits in so-called *Campi Flegrei*, the volcanic area in the neighborhood of Pozzuoli, the Roman *Puteoli*, in the South of Rome.[2,3]

Possessing a chemical composition characteristic of the specific volcanic activity underlying their formation,[4] pozzolanas primarily consist of crystalline and amorphous silica (SiO_2). Typically, pumices and ash have SiO_2 content in the intermediate range between 52 and 66 wt %. Acid pozzolanas with SiO_2 content larger than 66 wt % are also relatively common, whereas basic, or ultrabasic, chemical compositions with SiO_2 content within the range from 52 to 45 wt %, or less, are relatively rare.[4] Generally, pozzolanas contain alumina (Al_2O_3) in significant amount, while Fe oxides, mostly Fe(III) oxides (Fe_2O_3), and Mg oxides (MgO) represent minor components. Ca oxides (CaO) and other alkaline constituents can be also present.[4]

In the presence of water, pozzolanic ash exhibits unique capability of reacting at room temperature and pressure with the forms of Ca hydroxide ($Ca(OH)_2$) obtained from quicklime. The reaction produces inorganic compounds, mostly Ca silicate hydrates and Ca silicate aluminate hydrates,[5−7] with pronounced cementitious properties.

For this reason, pozzolanic materials such as volcanic ashes and ceramic fragments were added to lime since antiquity to form hydraulic mortars and enhance the performance of aerial lime-based mortars. Archaeological findings in Galilee show that pozzolanic materials have been utilized for architectural purposes starting from the Neolithic period, i.e., approximately 7000 BC.[8] More recent evidence has been found in buildings of the Minoan civilization in Crete dating back to about 2700 to 1400 BC[9] and in Greece starting from 1500 BC.[10] However, after the discovery of the Italian deposits of natural pozzolan,

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ancient Romans became the greatest users of this material in their public, private, and marine architectures.

In its classical treatise on architecture *De Architectura Libri Decem* (*On Architecture*, 10 volumes),[11] dating back to the end of the first century BC, Marcus Vitruvius Pollio suggests preparing mortars by mixing one part of limestone with three parts of *harena fossicia*, i.e., excavated sand in scoriae.[12] Starting from the Augustan age, between 27 BC and 14 AD, and up to the third century AC, common practice privileged the use of scoriae belonging to the currently termed mid-Pleistocene *Pozzolane Rosse* pyroclastic flow erupted from nearby Alban Hills volcano during the so-called *Tuscolano−Artemisio* phase.[3,5,12,13] Corresponding to the red constituent of *harena fossicia*, this pyroclastic material exhibits chemical composition rich in K and tephrite, an igneous extrusive rock, which enhances its pozzolanic activity.[3,5,12,13]

Mixed with coarse-grained volcanic tuff and brick fragments, the mortar prepared using *Pozzolane Rosse* formed the so-called *opus caementicium*, a concrete with conglomeratic structure similar to the one of sedimentary rocks consisting of coarse rock fragments embedded into a matrix of fine-grained material.[13] Such concrete was used to build foundations, walls, and vaulted ceilings of the most spectacular examples of Roman Empire monumental architecture.[14,15]

For two millennia, the *opus caementicium* resisted structural failures during earthquakes and chemical degradation associated with atmospheric and environmental agents.[16−18] To a significant extent, the secret of such structural and chemical stability, which translates into exceptional material durability, lies in the pozzolanic activity of *Pozzolane Rosse*, which was enhanced further refining their scoriae by grinding.[19]

The Vitruvian recommendation of preparing mortars using finely grained material has been generically connected with the empirical observation that pozzolanic reactions proceed at higher rate in the presence of finely divided pozzolanas because of the increased specific surface area.[19] However, vast literature demonstrates that extensive grinding can enhance chemical reactivity independent of surface area effects.[19]

This work aims exactly at investigating the effects of mechanical grinding on the chemical reactivity of *Pozzolane Rosse* in the presence of water. To this aim, the chemical behavior of *Pozzolane Rosse* not subjected to mechanical grinding is compared with that of *Pozzolane Rosse* during, and immediately after, mechanical activation. Chemical reactivity is evaluated referring to radical activity. Indeed, the formation of radicals at the surface of inorganic phases subjected to mechanical activation provides a measure of the reactivity enhancement caused by the application of impulsive mechanical stresses.[20] Being SiO_2 the majority component of *Pozzolane Rosse*, the results obtained can attract significant interest from one of the most active research areas in the field of mechanochemistry.[21−31]

Experimental findings show that mechanochemical effects emerge during the mechanical activation of *Pozzolane Rosse*, not exclusively connected with the increase of specific surface area due to particle size reduction. In particular, the radical species formed at the surface of *Pozzolane Rosse* particles exhibit unusually high reactivity that can be related, to a first approximation, to the generation of highly metastable states during grinding. Surface reactivity rapidly decays with time once mechanical activation is interrupted. Nevertheless, *Pozzolane Rosse* subjected to mechanical activation maintain a

chemical reactivity significantly higher than pristine material if not exposed for long time to air.

These results have the potential of attracting interest from two quite different areas of investigation in materials science and engineering.

On the one hand, they provide novel information on the chemical behavior of *Pozzolane Rosse*, thus advancing knowledge on one of the most important constituents of mortars and concretes utilized during the first centuries of Roman Empire. Hence, a better comprehension of the chemical processes underlying the formation of ancient Roman mortars that can benefit both restoration activities and modern concrete formulation.

On the other hand, the results obtained throw new light on the mechanochemistry of inorganic phases. In particular, they demonstrate that the mechanical activation determines the generation of short-lived surface states far from thermodynamic equilibrium that contribute to overall chemical reactivity. Therefore, a new piece of information can be added to the lively debate currently involving scientists and scholars interested in mechanochemistry.

The experimental methodologies used to achieve such results are detailed in the following.

2. EXPERIMENTAL METHODS

Experiments have been suitably designed to investigate the reactivity of active sites generated at the surface of *Pozzolane Rosse* powders during their mechanical grinding. Since SiO_2 is the major constituent of pozzolanic ash, mechanical activation of *Pozzolane Rosse* can be expected to result in the generation of radicals at the surface of ground SiO_2 phases.

In view of their relevance for different areas of research, SiO_2 surface radicals have been intensely studied in the past.[21−26] In principle, the fracture of SiO_2 crystalline and amorphous phases, as well as frictional processes at their surfaces, determines the formation of at least two types of surface sites.[27] On the one hand, the homolytic cleavage of ≡Si−O− chemical bonds gives rise to silyl ≡Si• and siloxyl ≡Si−O• radicals. On the other, the heterolytic cleavage of ≡Si−O− chemical bonds allows generating ≡Si⁺ cations and ≡Si−O⁻ anions. More complex species can also form.[28] Radicalic and charged species are in a metastable state that tends to decay by direct recombination to form siloxane ≡Si−O−Si≡ units or by heterogeneous reaction with chemicals in the surroundings.[29]

The reactivity of surface sites and their surface density can be measured exploiting their reaction with suitable chemical compounds. In this regard, precise measurements can be performed using a methodology originally developed for evaluating the kinetics of radical generation during the mechanical processing of quartz.[31] Literature shows that the mechanical activation of quartz dispersed in ethanol (C_2H_5OH) induces the consumption of the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH).[31] More specifically, DPPH reacts with the hydrogen radicals H• generated by the interaction of the SiO_2 surface radicals with the solvent C_2H_5OH.[31]

Based on its simplicity and reliability, the above-mentioned methodology was chosen to evaluate the reactivity of *Pozzolane Rosse*. To such aim, *Pozzolane Rosse* powders were dispersed in absolute C_2H_5OH and subjected to mechanical activation under inert Ar atmosphere in the presence of DPPH. The mechanical processing was performed in a suitably designed mechanochemical reactor that allows controlling collision frequency and energy. The mechanochemical reactivity of the

system was investigated by measuring the specific surface area of *Pozzolane Rosse* and the concentration of DPPH in C_2H_5OH as a function of the number of collisions.

Control experiments involving the mechanical activation of *Pozzolane Rosse* in the presence of water using a commercial ball mill have been also performed.

2.1. Materials. Absolute C_2H_5OH and DPPH were purchased from Aldrich and used as supplied. *Pozzolane Rosse* was excavated in the neighborhood of the ancient Roman caves located near Rome in the Alban Hills outcrops. The powders were sieved to eliminate coarser scoriae. To narrow the particle size distribution further, the sieved material was ground in an agate mortar using an agate pestle. The material refined manually was sieved to select particles with average size between 53 and 44 μm. According to the analysis carried out, the specific surface area of the sieved powders amounts to 0.041 $\pm$ 0.002 m^2 g^{-1}. Experiments were carried out on such powders.

2.2. Mechanical Processing. Mechanical activation of *Pozzolane Rosse* was performed in a mechanochemical reactor consisting of a stainless steel cylindrical reactor fixed on a mechanical arm that undergoes a vertical harmonic oscillation. A schematic description of the reactor is given in Figure 1.
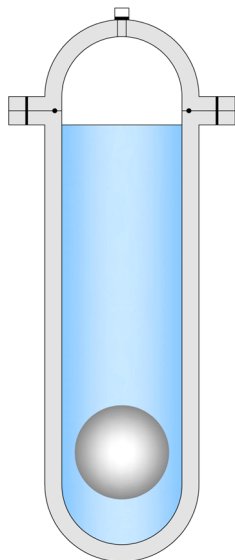

Figure 1. Schematic description of the mechanochemical reactor.

Once at work, the reactor allows the single ball placed in the internal chamber to establish an impulsive regime. Accordingly, the ball collides with the reactor base, thus trapping and loading part of the powder charge. Within a certain range, the amplitude and frequency of reactor oscillation can be adjusted to select the desired frequency and energy of collisions. This latter corresponds to the mechanical energy dissipated by the ball during each collision and therefore transferred to powder. Experiments on *Pozzolane Rosse* were performed using a 20 g stainless steel ball. Collisions took place every 3 s, the collision energy being equal to about 0.07 J. Mechanical activation was carried out on a powder charge, m_p, of about 2 g.

The reactor chamber was filled with Ar gas, and 30 mL of C_2H_5OH was introduced subsequently. The liquid phase was periodically sampled to study the chemical transformations induced by mechanical activation. To this end, the reactor top basis was equipped with a gas-tight septum connector.

2.3. X-ray Diffraction (XRD). XRD analyses were carried out on a Rigaku Miniflex II diffractometer equipped with a Cu Kα radiation tube. XRD patterns were analyzed using the Rietveld method, which provided information on the relative amounts of phases and on their microstructure.[32]

2.4. Specific Area of *Pozzolane Rosse*. The mechanical processing was interrupted after selected numbers of collisions. Then, powder was separated by the ethanol solution by centrifuging the dispersion for 15 min at 2 × 10^4 rpm. Afterward, the powders, up to 30 g, were kept for 2 h at 393 K to dry, degassed at 300 K, and exposed to nitrogen at about 77 K in a Fisons Sorptomatic 1900 apparatus. The specific surface area was estimated by physical adsorption of nitrogen according to the so-called BET method.

2.5. Scanning Electron Microscopy (SEM). SEM observation was used to monitor the size reduction of quartz powders and measure their size distribution. A Zeiss EVO LS15 microscope was utilized.

2.6. Measurement of DPPH Concentration in Ethanol. The free radical DPPH is a reactive scavenger. Therefore, it provides clear indication about the radicalic nature of a chemical reaction.[33] DPPH exhibits a strong absorption band approximately centered around 520 nm, which gives rise to an intense violet color in solution. The violet solution turns into pale yellow, or even colorless, when DPPH is neutralized by H$^\bullet$ radical species.[33]

The color change allows monitoring accurately the variation of DPPH concentration as its reaction with radicals proceeds using UV−vis spectrophotometry. To such aim, a Varian Cary 50 Scan apparatus was utilized. Measurements of DPPH concentration were performed on samples of ethanol solution separated by centrifugation from the *Pozzolane Rosse* powders. The sample was placed in a suitable PMMA cuvette with optical path 1 cm long. The absorption spectrum was recorded in the wavelength range between 300 and 900 nm. DPPH concentration values were obtained from absorption curves using an optical absorption coefficient of 11 300 L mol^{-1} cm^{-1}.[34] The initial concentration of DPPH in ethanol was equal to 0.1 M.

2.7. Mechanical Activation of *Pozzolane Rosse* in the Presence of Water. Experiments aimed at investigating the reactivity of *Pozzolane Rosse* in the presence of water were performed using the commercial ball mill SPEX Mixer/Mill 8000. A powder mass of 10 g was sealed under Ar atmosphere in a stainless steel cylindrical reactor with 4 stainless steel ball of 8 g and about 2.7 mL of water. The reactor was fixed on the arm imparting movement, and the mill operated at about 14.6 Hz. Mechanical activation was interrupted after selected milling times. Every time, the reactor was emptied and refilled with new powder and water. A fraction of the processed powder was used to prepare disk-shaped powder samples for XRD.

3. RESULTS

Starting material exhibits a chemical and mineralogical composition in line with expectations based on available literature.[13] The XRD patterns of *Pozzolane Rosse* powder obtained by manual crushing and subsequent sieving are shown in Figure 2.

The cross comparison of peak positions with values tabulated in inorganic substances databases reveals that convoluted reflections can be attributed to different mineralogical phases, namely leucite, clynopyroxene, diopside, muscovite, analcime, and hydrotalcite. Other contributions to the scattered intensity
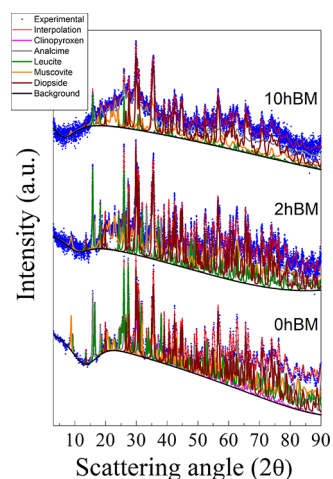
Figure 2. XRD patterns of *Pozzolane Rosse* powder obtained by manual crushing and subsequent sieving and by mechanical processing under Ar atmosphere. The processing time is indicated.

are present but well below any reasonable detectability and identification. The quantitative Rietveld analysis results in the mineralogical composition summarized in Table 1. Accordingly, *Pozzolane Rosse* mainly consist of leucite, clynopyroxene, diopside, and muscovite.

Table 1. Mineralogical Composition of *Pozzolane Rosse* As Obtained from Quantitative Analysis of XRD Patterns by the Rietveld Method

phases	wt %	phases	wt %
leucite	42.8	analcime	3.8
clinopyroxene	22.1	hydrotalcite	2.6
diopside	14.3	unknown	1.4
muscovite	13.0		

The mechanical processing of *Pozzolane Rosse* under Ar atmosphere induces a microstructural evolution that can be appreciated from XRD patterns shown in Figure 2 even in the absence of rigorous analysis. In particular, crystalline reflections undergo a generalized reduction in intensity and a significant broadening.

Both features become more evident with the time of mechanical processing, i.e., with the number of collisions occurred. The variation of peak aspect ratios can be ascribed to microstructural evolution. In this respect, the Rietveld analysis suggests that the mechanical processing determines a size reduction of crystalline grains down to the nanometer scale and a simultaneous increase of lattice disorder. This is widely expected based on the nature of the mechanical processing by ball milling.[19,35]

Simultaneous with microstructural evolution, fracturing processes take place consequent to the high-strain-rate mechanical loading that occurs during individual collisions. The result is the gradual refinement of powder particles and the corresponding increase of specific surface area, S. Evaluated by BET measurements, S values are shown in Figure 3 as a function of the number of collisions, n. The specific surface area undergoes a monotonic increase, finally reaching an asymptotic value of about 3.3 m^2 g^{-1}. The plot in Figure 3 indicates that S variation becomes negligible after 7000 collisions.
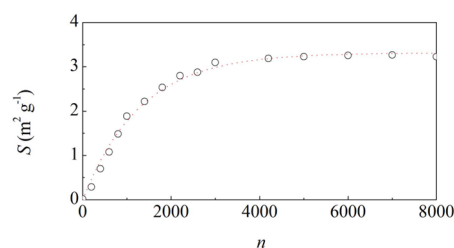

Figure 3. Specific surface area, S, as a function of the number of collisions, n.

The fracture of powder particles, and the consequent generation of fresh surfaces, involves the rupture of chemical bonds. Therefore, the increase of specific surface area can be expected to involve significant surface rearrangement processes, with formation of highly reactive surface sites. Overall, radicals can be regarded as the product of the fracturing process.

The interaction of powder with the ethanol solution of DPPH provides a reliable method to evaluate the surface reactivity of *Pozzolane Rosse*. In this regard, initial material does not show any significant level of reactivity. As shown in Figure 4a, the absorbance curve of DPPH in C$_2$H$_5$OH does not
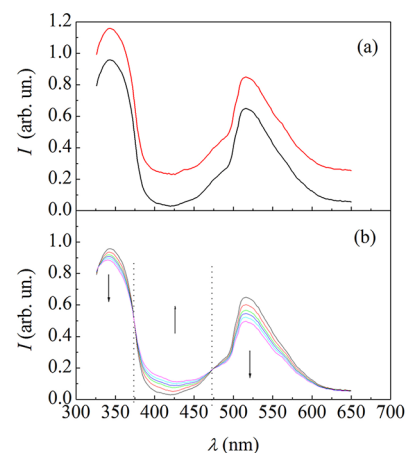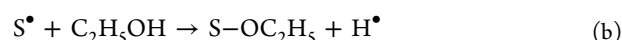

Figure 4. (a) Absorbance curve of DPPH in C$_2$H$_5$OH after 0 and 5 h long contact with pristine *Pozzolane Rosse* powder and (b) and after contact with *Pozzolane Rosse* subjected to an increasing number of collisions. In panel a, the absorbance curve obtained after 5 h exposure has been shifted upward for facilitating comparison. In panel b, vertical dotted lines indicate the isosbestic points. Arrows indicate the intensity variation of absorbance induced by the mechanical processing.

change after 5 h long contact with *Pozzolane Rosse* powder. Experiments were performed using 20 g of *Pozzolane Rosse* to enhance detectability. The relative intensity of the two absorption peaks at wavelengths λ equal to about 343 and 516 nm does not vary. Accordingly, the solution maintains the initial violet color with no detectable variation in intensity.

In contrast, definite color change is observed when the DPPH ethanol solution is exposed to *Pozzolane Rosse* subjected to mechanical activation under Ar atmosphere. Also in this case, a total mass of 20 g of processed *Pozzolane Rosse* was used for enhancing measurement capability. The optical absorption curves shown in Figure 4b display a progressive decrease in the intensity of absorption peaks at wavelengths λ equal to about 343 and 516 nm, whereas an increase in intensity is observed in the spectral region roughly between 400 and 450 nm. Two isosbestic points lie approximately at 370 and 470 nm.

The UV−vis spectrophotometric data shown in Figure 4b indicate a decrease of DPPH concentration in C_2H_5OH. The observed DPPH consumption can be ascribed to the interaction of DPPH with the $H^\bullet$ radicals formed in solution by reaction of C_2H_5OH molecules with surface active sites, $S^\bullet$, according to the following scheme:

$$S-S \rightarrow S^\bullet + S^\bullet \qquad (a)$$

$$S^\bullet + C_2H_5OH \rightarrow S-OC_2H_5 + H^\bullet \qquad (b)$$

$$DPPH + H^\bullet \rightarrow DPPH-H \qquad (c)$$

Stage (a) accounts for the mechanical activation of the powder, which determines the formation of active sites and surface radicals, $S^\bullet$. In stage (b), surface radicals react with C_2H_5OH molecules to form hydrogen radicals, $H^\bullet$. Final stage (c) involves the recombination of hydrogen radicals with DPPH molecules to form neutralized DPPH−H.

Experiments indicate that the consumption of DPPH in C_2H_5OH solution varies with the number of collisions undergone by *Pozzolane Rosse* powder. As shown in Figure 5a, the number of DPPH moles in ethanol solution, N_{DPPH}, decreases monotonically until a final asymptotic value is reached.

Based on the above-mentioned kinetic considerations, the number of DPPH moles provides an estimate of the number of surface radicals formed during the mechanical processing. It can
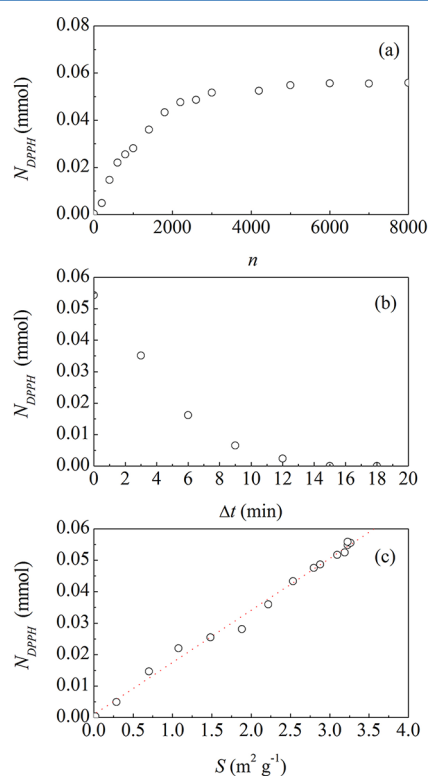
be expected that such number also varies with the time interval separating the interruption of mechanical activation and the contact with DPPH ethanol solution. Indeed, the longer the time interval, the higher the probability that surface radicals are quenched, somehow, by surface rearrangement or chemical interaction with surroundings. However, suitably designed experiments demonstrate that the difference ΔN_{DPPH} in the number of DPPH moles in ethanol solutions exposed to *Pozzolane Rosse* 15 min after the interruption of mechanical processing, and after 10 and 24 h is 5% or less, which is comparable with experimental uncertainties. Therefore, it can be reasonably assumed that the number of surface radicals for *Pozzolane Rosse* subjected to mechanical processing under Ar atmosphere and never exposed to air does not vary. In contrast, the exposure of mechanically activated *Pozzolane Rosse* to air induces a rapid quenching of surface radicals. As shown in Figure 5b, after 15 min of exposure to air, *Pozzolane Rosse* powder is unable to induce a detectable variation in the concentration of DPPH in ethanol solution. It follows that all radical species have been quenched by interaction of surface sites with air molecules.

The capability of *Pozzolane Rosse* subjected to mechanical processing under Ar atmosphere of inducing a consumption of DPPH can be related to the formation of radicals distributed all over the free surface accessible to ethanol solution. The relationship is clearly highlighted by data shown in Figure 5c, where the amount of DPPH consumed by the reaction of surface radicals with C_2H_5OH molecules is plotted as a function of the specific surface area. The linear plot obtained indicates that the consumption of DPPH is proportional to the surface area available to the reaction. This suggests that the mechanical activation finally results in the formation of surface radicals that make the *Pozzolane Rosse* subjected to a static exposure regime exhibit remarkably high reactivity compared with pristine, untreated powder.

Interestingly, experimental measurements performed during mechanical activation, i.e., under a dynamic exposure regime, indicate that surface reactivity is even higher under working conditions. The number N_{DPPH} of DPPH moles in ethanol solution consumed by *Pozzolane Rosse* during their mechanical activation is shown in Figure 6 as a function of the number of collisions, n. It can be seen that N_{DPPH} undergoes a monotonic increase. After about 5000 collisions, the increase becomes approximately linear.

Compared with data shown in Figure 5, the N_{DPPH} decrease under mechanical activation conditions exhibits two different features. First, the number of collisions being the same, the number of DPPH moles that react during mechanical activation is definitely higher than the one observed after mechanical
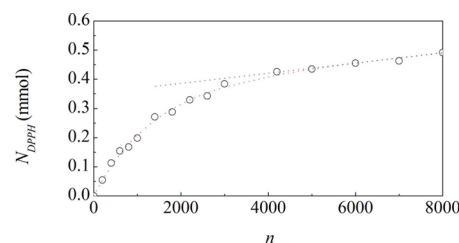
Figure 5. (a) The number of DPPH moles in C_2H_5OH, N_{DPPH}, consumed by *Pozzolane Rosse* under static exposure regime conditions as a function of the number of collisions, n. (b) The number of DPPH moles in C_2H_5OH, N_{DPPH}, consumed by *Pozzolane Rosse* under static exposure regime conditions as a function of the time interval, Δt, of exposure to air. (c) The number of DPPH moles in C_2H_5OH, N_{DPPH}, consumed by *Pozzolane Rosse* under static exposure regime conditions as a function of the specific surface area, S. Best-fitted line is also shown.

Figure 6. Number of DPPH moles in C_2H_5OH, N_{DPPH}, consumed by *Pozzolane Rosse* under dynamic exposure regime conditions as a function of the number of collisions, n. Best-fitted curve is shown. The dotted line best fits the final portion of data.

activation. Second, the consumption of DPPH molecules proceeds steadily even after the specific surface area no longer increases.

Regarding the latter observation, it is worth noting that collisions have no effect on the concentration of DPPH in ethanol solution in the absence of *Pozzolane Rosse* powder. Experiments performed under such conditions, i.e., with the ethanol solution 0.1 M in DPPH and without *Pozzolane Rosse*, indicate that the number N_{DPPH} of DPPH moles decreases, approximately, by only 0.01 mmol after 8000 collisions have taken place. Already observed in previous work,[20] the small reduction of DPPH concentration can be tentatively related to the formation of reactive sites at the surface of reactor walls and ball. Whatever the causes of such N_{DPPH} decrease, it is negligible compared with the N_{DPPH} decrease induced by collisions in the presence of *Pozzolane Rosse*.

4. DISCUSSION

The experimental findings described heretofore clearly demonstrate the existence of marked differences in the rate of DPPH consumption under static and dynamic exposure regimes. In the former case, the number of DPPH moles consumed by surface radicals, and therefore the number of surface radicals itself, is proportional to the surface area of *Pozzolane Rosse* available to chemical reaction with the surrounding ethanol solution. In the latter, the consumption of DPPH is significantly larger and no longer proportional to the available surface area. Nevertheless, it seems still reasonable to relate the observed DPPH consumption to the surface area available to the reaction.

Along this line, the first necessary step consists of the mathematical description of the variation of specific surface area, S, with the number of collisions, n. In this regard, the expression

$$S = S_{in} \exp(-kn) + S_{fin}[1 - \exp(-kn)] \qquad (1)$$

represents a satisfactory solution. Here, S_{in} and S_{fin} are respectively the initial and final S values, whereas k is the apparent rate constant for surface area increase. As explained elsewhere,[20] to a first approximation eq 1 can be regarded as the weighted average of the surface areas S_{in} and S_{fin} exhibited by the fractions of *Pozzolane Rosse* powder equal to $\exp(-kn)$ and $1 - \exp(-kn)$, respectively. The fraction $\exp(-k\,n)$ accounts for the amount of *Pozzolane Rosse* that still have the initial specific surface area, S_{in}, after n collisions, whereas the fraction $1 - \exp(-kn)$ measures the amount of *Pozzolane Rosse* that have attained the final specific surface area, S_{fin}.

Equation 1 can be used to best fit the data set shown in Figure 3. It can be seen that the curve is able to interpolate the experimental points to a satisfactory extent. Based on the statistical nature of the mechanical processing by ball milling,[36] the fact that the summation of the fractions equals 1, the observed best-fitting ability suggests that a fraction k of *Pozzolane Rosse* powder changes discontinuously its average specific surface area from S_{in}, approximately equal to 0.02 m² g⁻¹, to S_{fin}, about 3.3 m² g⁻¹, during any given collision. It follows that the apparent rate constant k of surface area increase corresponds to the amount of *Pozzolane Rosse* that undergoes particle refinement due to the mechanical stresses at work during individual collisions. The surface area increase can be ascribed to a discontinuous change of the size of quartz particles from the initial value, ranging from 53 and 44 μm, to a final one around 0.3 μm. This value is comparable with the

average particle size of powder, equal to about 0.32 μm, measured by SEM at the end of the mechanical treatment. A representative SEM micrograph is shown in Figure 7.
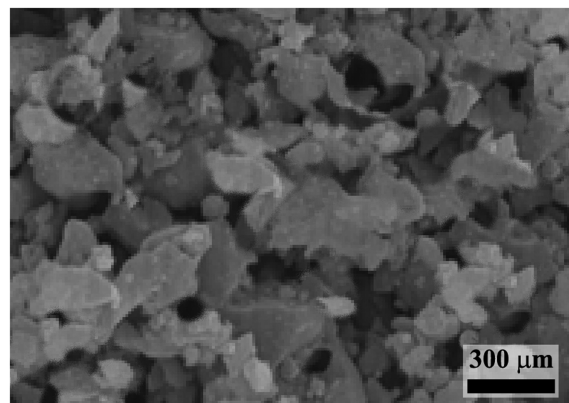

Figure 7. A representative SEM micrograph of quartz powder at the end of the mechanical processing in the presence of the DPPH–ethanol solution.

The best-fitted k value is approximately equal to $7.7 \times 10^{-4} \pm 0.3 \times 10^{-4}$. Therefore, the mass of *Pozzolane Rosse* effectively crushed during individual collisions, which can be calculated by the product between k and the mass of powder inside the reactor, m_p, is equal to about 1.5 mg. The derivative of eq 1 allows expressing the increase of specific surface area per collision as

$$dS = k(S_{fin} - S_{in}) \exp(-kn)\, dn \qquad (2)$$

At the beginning of the mechanical processing, i.e., when n is very small and the fraction of *Pozzolane Rosse* with initial specific surface area is close to 1, the surface area increases by about 5.0×10^{-3} m² per collision.

Under static exposure regimes, the consumption of DPPH in the ethanol solution in contact with mechanically activated *Pozzolane Rosse* is proportional to the specific surface area. Therefore, the number of DPPH moles reacted can be expressed as

$$N_{DPPH} = K_s m_p S \qquad (3)$$

where K_s represents the density of radical species, or sites, still active on the surface of *Pozzolane Rosse* after the mechanical processing. Based on experimental results, K_s is approximately equal to 8.5×10^{-7} mol m⁻².

Kinetic analysis becomes more complex in the case of dynamic exposure regimes, i.e. when *Pozzolane Rosse* powder is exposed to DPPH in ethanol solution during the mechanical activation. In this case, eq 3 is not sufficient to explain experimental findings. Here, the key feature seems to be the linear consumption of DPPH that takes place once collisions are no longer able to induce further change in the specific surface area. In this regard, two considerations can be made. On the one hand, there is no reason to rule out for dynamic exposure regimes a contribution of surface area similar to the one observed under static exposure regimes. Therefore, the consumption of DPPH can be still expected to depend somehow on specific surface area. On the other hand, a second contribution can be expected to superpose to the above-mentioned one, thus determining the linear decrease of DPPH concentration in ethanol solution.

Following previous work,[20] this second contribution can be related to the generation of radical species no longer related to the fracture of powder particles, and the consequent formation of fresh surfaces, but to the intense friction of powder particles against each other caused by collisions. In particular, once the specific surface area has reached its final value, the occurrence of intense frictional processes within the volume of trapped powder can be expected to generate approximately the same amount of surface active sites during any given collision. Hence, the linear decrease of DPPH concentration in the liquid phase.

Therefore, to a first approximation, a mathematical description for the kinetics of DPPH consumption under dynamic exposure regimes can be developed considering two terms. One term estimates the number of active sites formed at the surface of *Pozzolane Rosse* consequent to the occurrence of fracturing events. Such number can be expected to be proportional to the increase of surface area that takes place during each collision. Therefore, it is related to the variation of specific surface area expressed by eq 2. The second term, in contrast, accounts for the number of active sites generated by frictional processes involving the amount of *Pozzolane Rosse* effectively worked during a collision. This term, then, is expected to be proportional to the surface area susceptible of friction.

Considerations above can be summarized in the expression

$$-dN_{DPPH} = K_{d,a} m_p \, dS + k m_p K_{d,f} S \tag{4}$$

which describes the variation of the number of DPPH moles in the ethanol solution with the number of collisions, n. The two terms on the right-hand side of the equation account for the number of surface sites formed respectively by fracture and by friction. $K_{d,a}$ is the proportionality constant that relates the increase of specific surface area to the active sites, thus representing the surface density of active sites formed by fracture. Similarly, $K_{d,f}$ represents a measure of the surface density of active sites formed by friction. The product $k m_p$ corresponds to the amount of powder effectively processed during individual collisions. The entire expression refers to individual collisions.

Substituting eqs 1 and 2 into eq 4, the differential expression can be readily integrated into

$$N_{DPPH} = m_p K_{d,a} \{ S_{in} \exp(-kn) + S_{fin}[1 - \exp(-kn)] \}$$
$$+ k m_p K_{d,f} \{ S_{fin} n + (S_{fin} - S_{in})[1 - \exp(-kn)] k^{-1} \} \tag{5}$$

Equation 5 can be used to best fit the experimental data shown in Figure 6. Overall, interpolation is quite satisfactory, which allows obtaining reliable estimates for the quantities $K_{d,a}$ and $K_{d,f}$ in light of the k, S_{in}, and S_{fin} values already known from BET measurements and subsequent data analysis. Specifically, the surface density of active sites formed by fracture under dynamic exposure regimes, $K_{d,a}$, is approximately equal to $5.1 \times 10^{-5} \pm 0.3 \times 10^{-5}$ mol m^{-2}, whereas the analogous estimate for active sites formed by friction, $K_{d,f}$ is equal to $3.3 \times 10^{-6} \pm 0.2 \times 10^{-6}$ mol m^{-2}.

A first point is worth of note. Both $K_{d,a}$ and $K_{d,f}$ are significantly larger than K_s. Accordingly, the number of active sites available to reaction at the surface of *Pozzolane Rosse* during mechanical activation is larger than the number of active sites surviving to relaxation processes after mechanical processing under an Ar atmosphere. In this respect, striking evidence comes from the comparison of the above-mentioned

estimates with the number of dangling bonds, γ, that can be formed when fracturing processes generate new surfaces. To a first approximation, γ corresponds to the maximum possible surface density of active sites. Although a reliable γ value for *Pozzolane Rosse* is not available, the corresponding γ estimate for pure quartz can be used. In this latter case, γ represents the maximum possible number of dangling Si−O chemical bonds. Taking into account that lower energy pertains to (001), (011), (101), and (112) surfaces,[37] an approximate calculation indicates for the surface density of dangling bonds, γ, a value of about 2.1×10^{-5} mol m^{-2}.

Experimental findings suggest that the surface density of active sites under static exposure regimes, K_s, only amounts to about the 4% of the maximum possible value given by γ. The surface density of active sites associated with frictional processes, $K_{d,f}$, taking place in *Pozzolane Rosse* during the mechanical activation once the specific surface area has already reached the final value, is significantly larger, amounting to about the 16% of γ. Therefore, it is approximately 4 times larger than K_s. Quite surprisingly, the surface density of active sites generated by fracture, $K_{d,a}$, during the mechanical activation is about 2.5 times larger than the maximum possible surface density of dangling bonds, γ. Hence, it is also almost 90 times larger than the surface density of active sites estimated under static regime conditions, K_s.

The observed behavior supports previous findings on pure quartz and can be tentatively interpreted invoking the same scenario. In particular, the apparently unreasonable evidence that the number of active sites at the surface of *Pozzolane Rosse* is 2.5 times larger than the maximum possible value can be explained in light of the extremely high reactivity of surfaces formed by fracture. In this respect, it is worth remembering that fracturing events generate surfaces rich in local energy that is dissipated subsequently through relaxation and rearrangement processes.[38−42] Although such processes take place in relatively short time,[37−41] surfaces can be expected to give rise to energetic, transient species capable of interacting repeatedly with the DPPH ethanol solution. Consequently, an unexpectedly large number of H$^\bullet$ radicals could be formed, finally resulting in estimates of surface density of active sites larger than the maximum possible value.

The observed reactivity of *Pozzolane Rosse* surfaces under dynamic exposure regimes can be regarded as the result of mechanochemical effects. Both contributions to overall reactivity arising from fracturing and frictional events originate from the chemical response of unrelaxed surfaces under the influence of mechanical stresses or immediately after their removal. Under such conditions, surfaces and bulk are driven far from thermodynamic equilibrium, thus displaying unusual chemical behavior mostly dictated by the attempt of redistributing local excess energy. It follows that the enhanced reactivity of *Pozzolane Rosse* powder can be ascribed to both extensive and intensive factors. Accordingly, reactivity is determined not only by the surface density of active sites available to reaction but also by the intrinsic instability of surface species formed immediately after the fracture or the frictional event.

The enhanced reactivity of *Pozzolane Rosse* subjected to mechanical activation has important consequences on their pozzolanic behavior in the presence of water and Ca(OH)$_2$. To throw some light on this aspect, a few independent experiments have been performed using a commercial ball mill. A reactant mixture was prepared inside a stainless steel cylindrical reactor

using 8 g of powder and water in Vitruvian proportion. Once placed a single milling ball inside the reactor, this was sealed and fixed on the mechanical arm of a SPEX Mixer/Mill 8000. Reactants were subjected to mechanical processing for selected time intervals. Once activated for the desired time interval, the mixture was removed from the reactor and immediately subjected to a measurement of viscosity. To this aim, a Viskomat NT rotational viscosimeter, Schleibinger Testing Systems, was used. An impeller with lateral blades was immersed in the testing material contained in the cylindrical sample chamber. A torque was applied to the impeller to make it rotate at the constant rotational speed of 20 rpm. The applied torque was recorded as a function of time.

Control experiments were also performed on a mixture prepared using $Ca(OH)_2$, water, and *Pozzolane Rosse* subjected to prolonged mechanical processing and, then, exposed to air. Thus, *Pozzolane Rosse* used in control experiments have a specific surface area equal to the one developed by the *Pozzolane Rosse* mechanically activated in the presence of $Ca(OH)_2$ and water.

All of the experiments were performed using 400 mL samples. The impeller utilized was 6.0 cm in diameter, and the distance between impeller blades and chamber wall was 1.3 cm.

Typical results for mixtures mechanically activated for different times are shown in Figure 8, where the torque, τ, is plotted as a function of time, t.
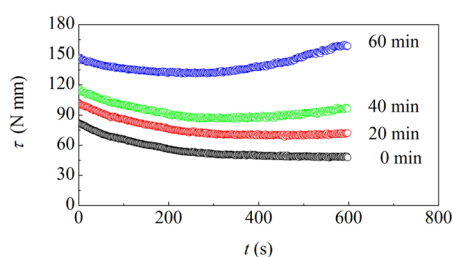

Figure 8. Torque, τ, required to maintain the rotational speed of the spindle constant at 20 rpm as a function of time, t. Data refer to mixtures of *Pozzolane Rosse*, $Ca(OH)_2$, and water mechanically activated for the time intervals (20, 40, and 60 min) indicated besides each curve. A curve describing the rheological behavior of a mixture obtained mixing $Ca(OH)_2$, water, and *Pozzolane Rosse* subjected to mechanical treatment and then exposed to air is also shown for comparison (0 min).

It can be seen that the mechanical activation of *Pozzolane Rosse*, water, and $Ca(OH)_2$ exhibits a rheological behavior completely different from the one of the mixture utilized in the control experiment. In this latter case, the torque undergoes a monotonic decrease that reproduces the usual rheological response of fresh mortars and other dispersions. In the former, data demonstrate the significant effect of mechanical processing on mixture rheology. It clearly appears that mechanical processing enhances the pozzolanic activity. A marked acceleration of chemical processes inside the mixture is observed, which finally determines a rapid hardening of the mixture. Whereas the mixtures utilized in control experiments require weeks to harden, the mechanically activated ones harden within minutes, i.e., on time intervals orders of magnitude shorter. The torque initially shows the usual, expected behavior, with the spindle rotation that induces, somehow, a plasticization of the mixture, thus resulting in a decrease of the applied torque. Subsequently, ongoing chemical

processes become definitely predominant, the mixture hardens, and the torque increases. The duration of mechanical treatment deeply affects the rheological behavior. Indeed, hardening is much faster for the mixtures processed for longer times.

Overall, the above-mentioned evidence indicate for mechanical activation the capability of influencing the rheological behavior of mixtures formed by *Pozzolane Rosse*, water, and $Ca(OH)_2$. Previous studies already pointed out that the rate at which pozzolanic reactions occur is proportional to the surface area of amorphous and glassy silica, the major component of pozzolan.[43] Furthermore, it has been shown that grinding glass powder in ball mills significantly enhances the pozzolanic activity consequent to the increase in surface area available for the pozzolanic reactions to occur.[44] It follows that the results obtained in the present work should not be intended as a first demonstration of the effects of the mechanical activation on silica-based materials. Rather, they definitely suggest the role of surface defects in governing the surface reactivity of such materials and demonstrate that mechanical processing provides a tool for accelerating hardening and preparing mortars with superior rheological properties.

5. CONCLUSIONS

Pozzolane Rosse powders excavated in the neighborhood of ancient Roman caves in the Alban Hills outcrops were suitably crushed and sieved to obtain powder with particle size in the micrometer range. The powder was exposed to an ethanol solution containing the free radical DPPH under static and dynamic regime conditions, i.e., respectively after and during the mechanical processing in a ball drop reactor. Experimental findings indicate a decrease of the DPPH concentration, which is significantly more pronounced under dynamic regime conditions. This suggests the formation of radical species at the surface of *Pozzolane Rosse* due to the occurrence of fracturing and frictional events.

The analysis of reaction kinetics can be based on the simplified reaction scheme according to which active sites at the surface of *Pozzolane Rosse* powder interact with ethanol molecules, thus generating hydrogen radicals able to neutralize the free radical DPPH. Whereas the consumption of DPPH under static regime conditions exhibits a neat relationship with the surface area available to reaction, DPPH neutralization under dynamic regime conditions involves two contributions. These can be related to fracturing and frictional events. The latter, in particular, give rise to a linear dependence of the number of DPPH moles consumed on the number of collisions once mechanical processing is no longer able to increase specific surface area further.

Mechanochemical effects emerge in connection with dynamic regime conditions. Specifically, the kinetic model developed for interpreting empirical evidence suggests that the active sites generated by fracture at the surface of *Pozzolane Rosse* have greatly enhanced reactivity, allowing a consumption of DPPH molecules even higher than the one allowed hypothesizing that the whole surface consists of dangling bonds.

The generation of surface radicals by mechanical processing also affects the kinetics of the reaction between *Pozzolane Rosse* and calcium hydroxide in water. In particular, consolidation kinetics becomes approximately 3−4 orders of magnitude faster.

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Notes

The authors declare no competing financial interest.

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