https://doi.org/10.24840/978-989-54863-4-2_0285-0290

STUDY OF THE OXIDISING CAPACITY OF DIFFERENT MATERIALS IN RELATION WITH SILICA CONTENT

Hector Garcia-Gonzalez[1], Mª Teresa Lopez-Pola[2] , Daniel Antuña-Jiménez[3], María Begoña González García[4], Pablo Fanjul Bolado[5]
[1] Instituto Nacional de Silicosis; hectorg@ins.es; ORCID 0000-0002-7285-2347
[2] Instituto Nacional de Silicosis; teresal@ins.es; ORCID 0000-0003-2226-1327
[3] Metrohm DropSens S.L.; daniel.antuna@metrohm.com; ORCID 0000-0001-5808-8154
[4] Metrohm DropSens S.L.; begona.gonzalez@metrohm.com; ORCID 0000-0002-1402-6506
[5] Metrohm DropSens S.L.; pablo.fanjul@metrohm.com; ORCID 0000-0002-9224-1666

Abstract

Background: Silica dust is a significant concern in the industry; it is clear that freshly fractured silica is more dangerous than aged fractured silica. However, it is not well studied if the oxidation-reduction potential (ORP) can be the key to the dangerousness of silica. **Objective**: Evaluate the oxidising capacity of four materials with different content in silica (SiO_2) (marble, granite, Silestone, quartz). **Method**: The materials were ground and tested using a portable handheld kit for ORP measurements at different ages. **Results**: The ORP values of the materials are increasingly oxidising until reaching 2-3 hours, where they get a stable ORP value. As the % of silicon increases, the oxidising power of the material also increases, except for the Silestone. **Conclusion**: There is a relation between the % of silica and the ORP, but some mixtures can reduce the ORP from materials with a high % of silica. **Application**: A well know ORP from the materials could establish different occupational limits for fresh or aged silica, but more research is required.

Keywords: ROS, Silica, Silicosis, ORP, Lung Diseases

Introduction

Lung diseases like silicosis or lung cancer are well-known occupational diseases concerning mining activities, like the extraction and processing of natural or artificial rocks; nowadays, it is clear that the risk of raw material in terms of generating silicosis will depend fundamentally (although not only) on its free crystalline silica content, and the fraction of free crystalline silica that can be breathed and reached the alveoli, the called "respirable crystalline silica" (Carballo Menéndez et al., 2022) (Madera Garcia et al., 2015).

It is clear that the surface of the nanoparticles is primarily responsible for the negative consequences. An important toxicity factor is the total surface area of the dust retained in the lungs (Respirable Crystalline Silica - Phase 1, 2002). In comparison to the same substance in bulk, nanoparticles have a higher surface area to volume ratio, making them a more accurate measure of risk than the common (and officially) used mass-based approach. (van Broekhuizen et al., 2012), (García & Pola, 2022).

Freshly fractured quartz is associated with a more severe and widespread cellular influx than aged quartz. A higher level of lipid peroxidation and a more extensive formation of reactive oxygen species (ROS) by phagocytes (35% greater than with aged quartz or control) indicated that freshly fractured quartz caused more oxidative stress in the lung than aged quartz (*Respirable Crystalline Silica - Phase 1*, 2002).

Because crystalline silica is piezoelectric, it generates opposing electric charges on opposing sides of the physical structure when force is applied. The oxygen free radicals created on the split surfaces of silica molecules are partly formed due to this piezoelectricity. Freshly cracked silica, such as that produced by abrasive blasting, has a higher redox potential on the fresh surface, which is more likely to continue creating free radicals because it is highly reactive with hydrogen, oxygen, carbon, and nitric oxide (Barnes et al., 2019).

The occupational exposure limit value (OELV) for silica dust is based on a mass approach, and the legal limit in most European countries is 0,05 mg/m^3. However, it is not considered if the silica is freshly fractured (for example, in a countertop factory) or aged quartz (for instance, on a beach). Some studies show that silica can cause lung damage from ROS from inhaled particles (Fubini & Hubbard, 2003), and the carcinogenicity of respirable quartz is considered to be driven by ROS (Berlo et al., 2010). Some studies suggest that ROS are a promising metric linking aerosol compositions to toxicity and adverse health effects (Zhang et al., 2021), and some publications are about measuring the oxidative potential in particulate matter (Frezzini et al., 2022). However, some limitations remain (Carlino et al., 2023). The oxidative potential was assessed as the ability of particles to generate ROS (Borlaza et al., 2021). It may be a more health-relevant metric than other physicochemical properties of particles (Khurshid et al., 2019). Some studies evaluate different oxidative potential measurement techniques (Shahpoury et al., 2022). However, for the moment, there is no standardised method and consensus to measure the oxidative potential.

The study evaluates the oxidation-reduction potential (ORP) evolution of some leading construction materials with different silica contents, such as granite (pink Porriño), marble, and northern white Silestone. For comparison, it was also added pure quartz. It was evaluated as freshly fractured from minute two after milling and the evolution during the first 15 days.

Material and Methods

The primary materials are an excentric mill (Figure 1), the rocks (granite, marble, Silestone and quartz) and a portable kit for ORP (oxidation-reduction potential) measurements (Metrohm DropSens) (Figure 2) with electrodes DRP-ORPSEN.

It was selected samples of different materials, granite, marble, Silestone and quartz, with different content in silica, as shown in Table 1. Each material was ground in an excentric mill for 3 minutes, previously cleaned to avoid contamination. It is a simulation of what happens when someone works with these materials. It is known that cutting these materials produces different PSD (particle size distribution).

Figure 1. *Preparation for grinding granite (2022).*

The following protocol was used to carry out the tests. Firstly the electrodes (DRP-ORPSEN) were opened, washed with Milli-Q water, and dried before measurement. Secondly, 1 mg of material has been weighed on an Eppendorf in analytical balance with a resolution of 0.0001 g, and 1 mL of Milli-Q water has been measured to have a 1 mg/mL suspension. Thirdly the materials were measured as soon as they had been ground, so the first data was obtained after 2 minutes, given the time it takes to measure the DRP-ORPSTAT. Subsequently, each material was suspended and measured around 15-30 minutes after the first measurement. Finally, they have suspended again, and a second measurement was carried out between 2 and 3 hours after the first measurement. Lastly, the materials were left to rest for 15 days in open containers to see if they evolved in the air, simulating the conditions in a countertop factory. These materials have been measured as before, 15 days after being ground. Each material has been measured with two different electrodes to achieve a duplicate at the initial time. These electrodes have been used again to measure at 15-30 min and 2-3 hours, taking advantage of their reusable use. The electrodes used at 15 days were new, and those used on the day of the initial measurements were not used. All the tests were conducted in laboratory conditions, with all the materials at the same temperature.

Figure 2. *Portable kit for ORP measurements and electrodes (DRP-ORPSEN).*

Results and Discussion

Table 1 and Figure 3 show the potential in mV from the four materials at different ages (2 minutes, 15 minutes, 160 minutes, and 15 days), mean (μ), standard deviation (σ) and relative standard deviation (RSD). When measuring pulverulent samples, results are not as precise as the ones obtained when liquid solutions are tested. Using DRP-ORPSEN with Zobell solution, a typical ORP standard, a value of 240 mV, is obtained with an RSD less than 5 % (n=3).

Table 1. *Electrical potential from different materials at different ages*

			Potential / mV				
Material	**Time**	**Elec. 1**	**Elec. 2**	**Elec. 3**	**μ**	**σ**	**RSD**
Quartz (SiO_2 >95 %)	2 min	110	138	74	107	32	30
	15 min	188	192	165	182	15	8
	160 min	282	263	228	258	27	11
	15 days	286	300	239	275	32	12
Pink granite (Porriño) (SiO_2 =42%)	2 min	245	230	176	217	36	17
	20 min	170	225	189	195	28	14
	140 min	195	215	210	207	10	5
	15 days	227	209	198	211	15	7
Silestone (White North) (SiO_2 >90%) (Quartz = 80.8%) (Cristobalite =16,5%)	2 min	111	110	175	132	37	28
	30 min	202	182	150	178	26	15
	190 min	119	107	106	111	7	7
	15 days	183	168	196	182	14	8
White marble (SiO_2<5%)	2 min	133	144	121	133	12	9
	15 min	164	167	182	171	10	6
	120 min	174	178	192	181	9	5
	15 days	169	191	212	191	22	11

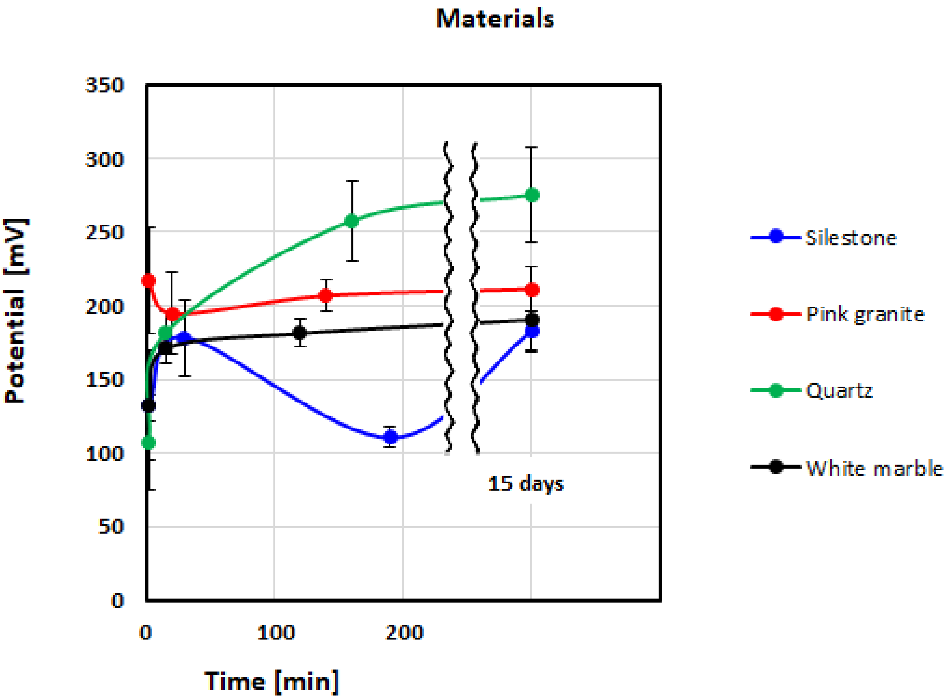

Figure 3. *Electrical potential from different material evolution*

As time passes, the materials evolve, reaching most of them a stable ORP value at 2-3 hours after being ground. This is inferred from the curves where it is seen how their ORP values do not change after 2-3 hours or even after 15 days have passed. This fact contrasts with the initial idea in which it was thought that the materials started from a more oxidising ORP as soon as they were ground. However, it makes sense because a regular shift in the countertop factory is at least 8 hours long, and the worker could be breathing the dust the rest of the shift. The most oxidising ORP values with this methodology are obtained after 2-3 hours, and this ORP value remains practically stable for up to 15 days.

Regarding materials, pink Porriño granite practically does not change its ORP value over time. Quartz is the material that evolves the most over time, and marble and Silestone do not seem to grow as much. The most oxidising material after 2-3 hours and 15 days is quartz, granite, marble, and Silestone. There appears to be a trend between the % silica and the ORP value of the materials. As the % of silica increases, the oxidising power of the material also increases. This only happens 2-3 hours after being ground, and this trend is maintained until 15 days after being ground. Only Silestone seems to be the discordant material. Due to the composite nature of Silestone (it is a mixture between quartz, cristobalite and other plastic materials), its ORP value does not agree with what is expected when comparing the % of silica against the ORP value since it should be more oxidising after 2- 3 hours (because of the results) due to its high percentage of silica. However, its ORP value is even lower than that obtained for marble, so other materials presented in its composition may reduce the ORP value of silica, even below the marble that contains less than 5% of silica. The observed results are interesting, but they disagree with the initial hypothesis in which one would expect to observe more oxidising ORP values as soon as they are milled with a subsequent downward evolution. The opposite effect is observed, an initial low ORP value that increases with time.

Limitations

The ground samples represent a granulometric fraction that can exceed the respirable fraction (4 microns), and different particle sizes may have other behaviours. To ensure the behaviour of the particles within the lung, it should be recommended that particles are in the respirable fraction.

Conclusions

The ORP values of the different materials are increasingly oxidising until reaching 2-3 hours, where they get a stable ORP value.

The most oxidising ORP values within this study are obtained after 2-3 hours, and this ORP value remains practically stable for up to 15 days.

Pink Porriño granite nearly maintains its ORP capability over time. Marble and Silestone don't seem to evolve as much as quartz with time, which changes the most.

After 2-3 hours and 15 days, quartz is the most oxidising substance, followed by granite, marble, and Silestone.

The materials' ORP value and silica content trend in the same direction.

The material's oxidisation ability becomes more potent as silicon content rises, except for Silestone, which requires more research to clarify its low ORP.

In this research, disposable screen-printed electrodes capable of measuring the ORP of suspended pulverulent samples were employed in a combination of a handheld potentiostat to provide a fast method to evaluate the oxidative capacity of four materials with different silica content. This electrochemical platform is suitable for studying these kinds of samples' oxidative capacity as ORP measurements are increasingly used to characterise particulate matter's toxic effects. Preliminary results show promising trends when studying the ORP response, as sensors are capable of monitoring the aged of the materials tested on the field with minimal sample preparation in a fast and reliable way. However, more research needs to be done to establish an occupational limit value for fresh or aged silica. Also, it is necessary to have a standardised method for carrying out the measurements.

Acknowledgements

This study would not have been possible without the exceptional support from the Instituto Nacional de Silicosis and Metrohm DropSens.

References

Barnes, H., Goh, N. S. L., Leong, T. L., & Hoy, R. (2019). Silica-associated lung disease: An old-world exposure in modern industries. *Respirology*, *24*(12), 1165–1175. https://doi.org/10.1111/resp.13695

Berlo, D., Wessels, A., Boots, A., Wilhelmi, V., Scherbart, A., Gerloff, K., Van Schooten, F., Albrecht, C., & Schins, R. (2010). Neutrophil-derived ROS contribute to oxidative DNA damage induction by quartz particles. *Free Radical Biology & Medicine*, *49*, 1685–1693. https://doi.org/10.1016/j.freeradbiomed.2010.08.031

Borlaza, L. J. S., Weber, S., Jaffrezo, J.-L., Houdier, S., Slama, R., Rieux, C., Albinet, A., Micallef, S., Trébluchon, C., & Uzu, G. (2021). Disparities in particulate matter (PM_{10}) origins and oxidative potential at a city scale (Grenoble, France) – Part 2: Sources of PM_{10} oxidative potential using multiple linear regression analysis and the predictive applicability of multilayer perceptron neural network analysis. *Atmospheric Chemistry and Physics*, *21*(12), 9719–9739. https://doi.org/10.5194/acp-21-9719-2021

Carballo Menéndez, M., Fernández Vilas, E. M., Freijo Pasarín, J., & Menéndez Cabo, P. (2022). *Guía Técnica para la prevención del riesgo por exposición a la Sílice Cristalina Respirable (SCR) en el ámbito laboral*. https://energia.gob.es/mineria/Seguridad/Guias/Gu%C3%ADas/Guia-control-riesgo-exposicion-s%C3%ADlice-cristalina-respirable-Empresas-sujetas-RGNBSM.pdf

Carlino, A., Romano, M. P., Lionetto, M. G., Contini, D., & Guascito, M. R. (2023). An Overview of the Automated and On-Line Systems to Assess the Oxidative Potential of Particulate Matter. *Atmosphere*, *14*(2), Article 2. https://doi.org/10.3390/atmos14020256

Frezzini, M. A., Di Iulio, G., Tiraboschi, C., Canepari, S., & Massimi, L. (2022). A New Method for the Assessment of the Oxidative Potential of Both Water-Soluble and Insoluble PM. *Atmosphere*, *13*(2), Article 2. https://doi.org/10.3390/atmos13020349

Fubini, B., & Hubbard, A. (2003). Reactive oxygen species (ROS) and reactive nitrogen species (RNS) generation by silica in inflammation and fibrosis. *Free Radical Biology & Medicine*, *34*(12), 1507–1516. https://doi.org/10.1016/s0891-5849(03)00149-7

García, H., & Pola, T. L. (2022). Health and safety in 3D printing: Article. *International Journal of Occupational and Environmental Safety*, *6*(1), Article 1. https://doi.org/10.24840/2184-0954_006.001_0003

Khurshid, S. S., Emmerich, S., & Persily, A. (2019). Oxidative Potential of Particles at a Research House: Influencing Factors and Comparison with Outdoor Particles. *Building and Environment*, *163*, 10.1016/j.buildenv.2019.106275. https://doi.org/10.1016/j.buildenv.2019.106275

Madera Garcia, J., Menéndez Cabo, P., Carballo Menéndez, M., Freijo Pasarín, J., & Fernández Vilas, E. M. (2015). *Guía para el control del riesgo por exposción a Sílice Cristalina Respirable*. https://ins.astursalud.es/documents/102310/161072/Gu%C3%ADa+para+el+control+del+riesgo+por+exposici%C3%B3n+a+S%C3%ADlice+Cristalina+Respirable.pdf/3cf5731f-f7ac-8100-a1e3-b9de6321017a?version=1.0

Respirable crystalline silica - phase 1: Variability in fibrogenic potency and exposure-response relationships for silicosis. (2002). HSE Books.

Shahpoury, P., Zhang, Z. W., Filippi, A., Hildmann, S., Lelieveld, S., Mashtakov, B., Patel, B. R., Traub, A., Umbrio, D., Wietzoreck, M., Wilson, J., Berkemeier, T., Celo, V., Dabek-Zlotorzynska, E., Evans, G., Harner, T., Kerman, K., Lammel, G., Noroozifar, M., … Tong, H. (2022). Inter-comparison of oxidative potential metrics for airborne particles identifies differences between acellular chemical assays. *Atmospheric Pollution Research*, *13*(12), 101596. https://doi.org/10.1016/j.apr.2022.101596

van Broekhuizen, P., van Veelen, W., Streekstra, W.-H., Schulte, P., & Reijnders, L. (2012). Exposure limits for nanoparticles: Report of an international workshop on nano reference values. *The Annals of Occupational Hygiene*, *56*(5), 515–524. https://doi.org/10.1093/annhyg/mes043

Zhang, Z.-H., Hartner, E., Utinger, B., Gfeller, B., Paul, A., Sklorz, M., Czech, H., Yang, B. X., Su, X. Y., Jakobi, G., Orasche, J., Schnelle-Kreis, J., Jeong, S., Gröger, T., Pardo, M., Hohaus, T., Adam, T., Kiendler-Scharr, A., Rudich, Y., … Kalberer, M. (2021). *Are reactive oxygen species (ROS) a suitable metric to predict toxicity of carbonaceous aerosol particles?* [Preprint]. Aerosols/Laboratory Studies/Troposphere/Chemistry (chemical composition and reactions). https://doi.org/10.5194/acp-2021-666