

Practical Application of Surfactants for Respirable Silica Dust Control

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ABSTRACT

Respirable crystalline silica poses a significant health risk, with the American Lung Association estimating that 2.3 million workers are exposed to silica in the workplace. This includes mine workers as well as those in many other industries. Reducing dust formation is sometimes not possible so other methods to reduce exposure are critical. These methods include the use of surfactants to reduce airborne dust particles. However, it is the proper selection and application of surfactants that leads to reduced dust exposure. A discussion of how surfactants work, especially for silica dust, leads to guidance for surfactant selection followed by a review of technologies for their application.

INTRODUCTION

Respirable crystalline silica has been studied as a potential carcinogen in dusts from many sources, including those produced in mines. Whether mining specifically for silica or mining other minerals, it is likely that silica is in the mined product as it is an accessory mineral phase in many common commodities as indicated in Table 1 (1). While coal is not on the list, it is certainly well known that coal also contains quartz, with a 1990 US Bureau of Mine work, Sources and Characteristics of Quartz Dust in Coal Mines, initiating some of the research on silica in coal (2).

Researchers have also indicated that quartz cannot be treated as a single mineral phase as there are many variations in contaminants and associated minerals (see, for example, 3, 4, 5). In general, however, it appears that the issue with crystalline silica, most notably α -quartz, is the formation of reactive oxygen species (ROS) on the surface of dust particles, forming “silanols” that interact with lung tissue to cause fibrosis and lung cancer (3, 4, 5). These works and others along with the increase in the occupational respiratory diseases silicosis and coal worker’s pneumoconiosis (6, 7, 8, 9) spawned new research, including recent international papers by Azam et al. (10), LaBranche et al. (11), and Li et al. (12). These and many other papers document research regarding respirable dust and, especially, silica dust. As this paper takes a practical look at surfactants for respirable silica dust, this is not the place to document these many papers, though Arnold and her team have a review paper in progress. Suffice it to say that respirable silica dust and its toxicity is the subject of many current National Institute of Occupational Safety and Health (NIOSH) studies (13).

In addition, it is important to note that the US Mine Safety and Health Administration has put forth new silica dust regulations for comment (14). The use of surfactants to control dust and, especially, silica dust, is a timely topic to review.

QUARTZ SURFACE PROPERTIES

Two surface properties that are important when considering dust suppression are the hydrophobicity/ hydrophilicity of the particle surfaces and the surface charge. Hydrophobicity is a measure of the wettability of a surface and is often measured using contact angle techniques. In the sessile drop technique, a drop of water or surfactant or other chemical solution is placed on the surface of a polished piece of material. If the droplet spreads, it gives a low value for contact angle and indicates the ease of wetting the surface, which is a requirement for the application of dust suppressants. An alternative technique, the captive bubble technique, places the specimen in the liquid and an air bubble is applied to the surface with the angle of contact being measured. Contact angle values for quartz can be found in the literature as shown in Table 2. Compared to values for known hydrophobic materials, like high rank coal, these values are low and would represent surfaces that are hydrophilic or wettable.

Another surface property that is important is the zeta potential or surface charge. This affects the interaction between particles in a slurry, with highly charged particles (either negative or positive) repelling each other and oppositely charged particles being attracted to each other. Another phenomenon that can be investigated using the zeta potential technique is spontaneous flocculation when the surface charge becomes close to zero. This is rapid when the surface charge is 0 to ± 5 mV and can be considered strong even at ± 25 mV. This change in surface charge can occur in the presence of different ions in solution, meaning that it is critical to assess surface charge, as well as hydrophobicity, using water from the site that is being evaluated. Some examples of zeta potential measurements for quartz from the literature are given in Figure 1 (20, 21, 22). The quartz surface charge is generally negative across the entire pH range shown. This will affect the type of chemical that can be used as a surfactant as some of these chemicals also have ions that carry a charge (cationic being positively charged, anionic being negatively charged, etc.).

HOW SURFACTANTS WORK

Surfactants are “surface active agents.” They reduce the surface tension of water, allowing it to spread over the surface of a particle more easily, wetting the particle. Finer droplets of water can be produced to increase the likelihood of particle-droplet contact in a spray or foam application. The use of surfactants allows for a residual dust suppression effect as water has no additional effect once it is evaporated (23). Studies estimate a 50 percent reduction in water requirements with the improved efficiency associated with the use

Table 1. Silica as an accessory phase in common commodities (1)

Commodity	Type of Silica
Antimony	Quartz
Bauxite	Quartz
Beryllium	Quartz
Cadmium	Quartz, jasper, opal, chalcedony
Concrete	Quartz
Clay	Quartz
Copper	Quartz
Crushed stone	Quartz
Diatomite	Quartz
Dimension stone	Quartz
Feldspar	Quartz
Fluorite	Quartz
Garnet	Quartz
Germanium	Quartz
Gold	Quartz
Gypsum	Quartz
Industrial sand	Quartz
Iron ore	Chert, quartz
Iron oxide pigment	Chert, quartz, opal
Lithium	Quartz
Magnesite	Quartz
Mercury	Quartz
Mica	Quartz
Perlite	Opal, quartz
Phosphate rock	Quartz, chert
Pumice	Obsidian
Pyrophyllite	Quartz
Sand and gravel	Quartz
Selenium	Quartz
Silicon	Quartz
Silver	Quartz, chert
Talc	Quartz
Tellurium	Quartz
Thallium	Quartz, chert, chalcedony, opal
Titanium	Quartz
Tungsten	Quartz
Vanadium	Quartz, opal
Zinc	Quartz, chert, chalcedony, opal
Zircon	Quartz

Table 2. Contact angle values of quartz from various sources (15, 16, 17, 18)

Contact Angle	Source
27.8–50.3	Deng et al. (15)
35	Szyszk (16)
43 \pm 2	Kowalczyk (17)
26.8	Janczuk and Zdziennicka (18)
26.15	Xie et al. (19)

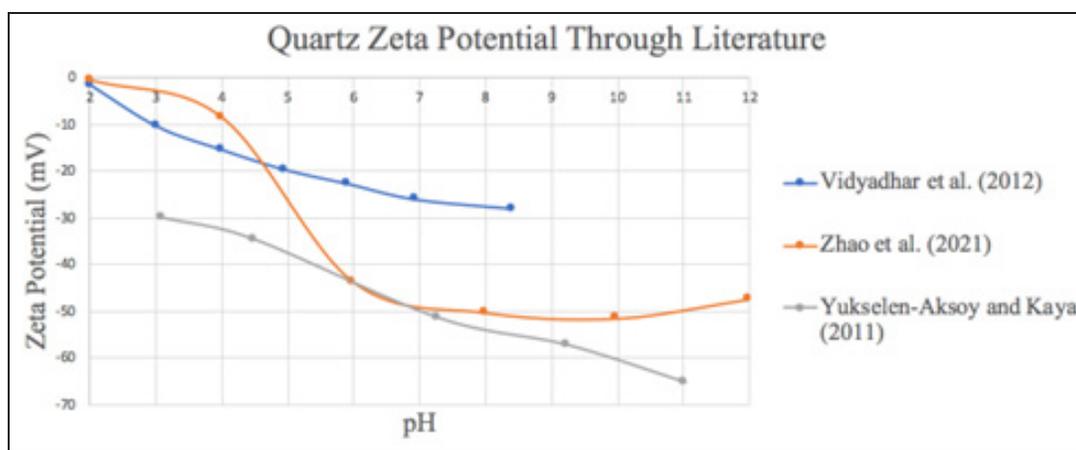


Figure 1. The zeta potential of quartz from various sources (20, 21, 22)

of surfactants (24, 25), resulting in considerable cost savings as well.

SURFACTANT SELECTION

Many different chemical dust suppressants have been used, including salts, asphalt emulsions, vegetable oils, molasses, synthetic polymers, mulches, and lignin products (26). Many of these are certainly non-toxic and will do no harm to the environment or to workers. However, as Piechota et al. (26) describes, it is important to have a full analysis of any material as some may be toxic waste products from other industries. Health issues for workers may arise, and soil could become contaminated. A Safety Data Sheet should be requested for any material considered as a dust suppressant additive/surfactant.

The next consideration is the improvement in wettability of the dust particles with the addition of the surfactants. According to a comprehensive review by Zhao et al. (27), these tests can be classified as static or dynamic tests. Static tests include contact angle measurements, liquid surface tension tests (lower surface tension should correlate to better wetting), capillary rise tests, liquid penetration tests, and the simplest or most common sink test or Walker test (28). Dynamic tests can include wind tunnel or other field tests (27). All these tests measure the potential to wet the surface of a dust particle. Xu et al. (29) provides a good description and review of these and other static tests methods.

In the Walker test as illustrated in Figure 2, an air-dried sample of the dust is placed on top of the liquid in a small beaker or graduated cylinder, and the time to completely wet and settle the dust is measured. Tests can be conducted easily with different surfactants and at different surfactant concentrations. Quicker settling times give better wettability. Note that the water used in these experiments must be

the water used on site as the contained ions will affect the ability for the surfactant to reduce the water's surface tension. This test is thought to simulate the particle capture mechanism (28) and might be used to set initial concentrations for field tests of any surfactant.

Foaming agents need to be evaluated for wettability as well as for their ability to foam in water from the site.

Going forward, wettability might not be the most important criterion for a good surfactant. As research progresses into the surface chemistry of dust and the health effects of ROS and, specifically, silanols on respirable crystalline silica, it will be important to evaluate whether these surfactants might increase the ROS content making the dust more toxic or reduce the ROS content making the dust less toxic. One such project is in progress at Penn State with Arnold as the Principal Investigator (30). Results with several potential surfactants are given in Table 3 for quartz collected from coals representing different coal ranks. The hydroxyl content ($10^{-9} \text{ mol.L}^{-1}$) on the surface of particles pulverized to < 10 microns to represent respirable dust sizes was measured using a spectrofluorometer for the bare surface in distilled water at pH 7 and for nine different reagents at two concentrations each. As indicated, the OH content generally decreased in the presence of the surfactants, with the addition of some of the surfactants causing a very large drop in OH content. It can also be noted, as stated previously, that all the quartz samples did not exhibit the same behavior in the presence of the various surfactants, further indicating that testing must be conducted for each individual sample. Also, note that all surfactants did not reduce the OH content to the same extent. The presence of other contaminants with the quartz may have played a role and the interaction of the chemicals with the surfaces certainly affected the results.

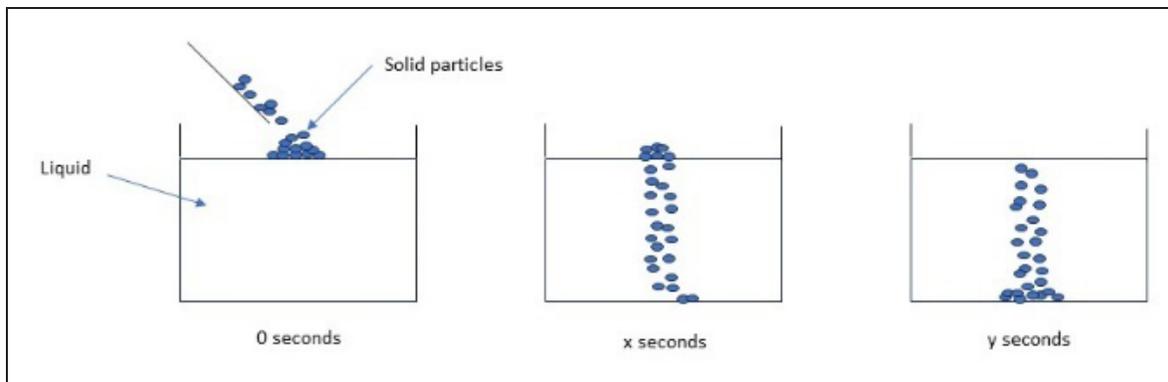


Figure 2. Dust Settling Rate Test (Walker Test)

Table 3. Effect of Surfactants on Surface OH Content for Various Quartz Samples Collected from Coal of Various Ranks at pH 7 (30)

Coal Quartz → Surfactant	OH (10^{-9} mol.L $^{-1}$) at pH 7			
	Anthracite Quartz	LVb Quartz	MVb Quartz	HVAb Quartz
Bare Surface	65	75	97	89
1 Dosage 1	63	14	7	9
Dosage 2	59	12	6	7
2 Dosage 1	24	60	14	12
Dosage 2	15	55	13	11
3 Dosage 1	11	21	8	12
Dosage 2	9	15	7	11
4 Dosage 1	10	20	8	8
Dosage 2	9	14	7	8
5 Dosage 1	8	31	8	10
Dosage 2	6	15	8	9
6 Dosage 1	8	10	9	8
Dosage 2	8	9	7	8
7 Dosage 1	13	14	8	7
Dosage 2	10	13	7	6
8 Dosage 1	12	17	42	47
Dosage 2	12	16	41	44
9 Dosage 1	6	7	7	10
Dosage 2	6	6	7	7

LVb is low volatile bituminous, MVb is medium volatile bituminous, and HVAb is high volatile A bituminous coal ranks

It should be noted that Walker tests for the quartz samples were conducted without the addition of surfactants (30). As shown in Table 4 and expectedly, the longest settling times were in deionized water (the absence of ions) giving the full LVb is low volatile bituminous, MVb is medium volatile bituminous, and HVAb is high volatile A bituminous coal ranks effect of the surface charge of the particles. In process water and simulated lung fluid, the settling times decreased for the bare surfaces as the surface

Table 4. Walker Tests for Bare Quartz with Different Water Quality (30)

Sample	Time (s)		
	Deionized Water	Process Water	Sim. Lung Fluid
Anthracite Quartz	126	64	35
LVb Quartz	226	84	55
MVb Quartz	219	92	64
HVAb Quartz	229	96	83

charges would have been decreased in the presence of the ions in these fluids. Water quality obviously plays a role in surfactant effectiveness, showing the importance of any surfactant testing with site water.

TECHNOLOGIES FOR SURFACTANT APPLICATION

Water spray systems designed for dust control use two modes of dust suppression: 1) water sprays wet the material to prevent dust particles from becoming airborne during the mining or mineral beneficiation process or 2) water sprays are used to knockdown dust particles after they have become airborne. (31). These systems use water as the medium for dust control and may include the use of surfactants added to enhance dust control efficiency.

Surfactants are added to water at a low dosage and are then applied to the bulk material surface to prevent airborne dust generation or to the area above the bulk material to knockdown airborne particles by particle agglomeration to return the dust particles back to the material bed. The application devices are typically sprays, though the application of foam or fog has been successful as well (32). As mentioned previously, the addition of surfactants to water can reduce the water requirement by ~50%, while the use of a foam system with surfactants can reduce water consumption to less than 1/20th of that of water alone (32). Dry fog systems use considerably less water.

Spray velocity, nozzle orifice size, and spray location are all considered when setting up a spray system. For dust particle knockdown, droplet-particle collision efficiency is key, so reducing droplet size, increasing droplet frequency and velocity, and decreasing droplet surface tension are all key parameters for system set up (32, 33). Water sprays are used in many locations to mitigate the production of respirable and fugitive dust. For example, Caterpillar has developed a new spray water truck that uses a unique water spray design with a water delivery system specially designed to deliver appropriate water flow onto the haul road based upon truck speed (34).

Foam applications are directly applied to material or sources in order to prevent the generation of airborne dust particles because foam is generally not effective once dust particles are airborne (35), create even finer droplets to maximize the probability of droplet-particle collisions/attachment (32, 33).

Fog applications can be used without surfactants but use droplet atomization to produce droplets of sizes that can match the ultrafine respirable dust size of even 5 microns to improve collision efficiency. These units often

use special ultrasonic nozzles (32). A benefit of the fogging system is the creation of a widely dispersed mist. However, one drawback is that the fine mist can be dispersed by air or wind movement (36).

GUIDANCE FOR DEVELOPING A SILICA DUST SUPPRESSION PLAN INCLUDING APPLICATION OF SURFACTANTS

Combining guidance for the use of surfactants from several resources (37, 38, 39, 40), the following steps should be considered when developing a respirable silica dust suppression plan or any dust suppression plan for that matter.

1. Determine the location(s) and timing for dust suppression applications through a site survey—during mining, processing, and stockpiling, on paved/unpaved roadways, at transfer points, during transportation, etc.
2. Anticipate potential changes in equipment and the need to relocate any dust suppression system.
3. Address any material handling system issues; repair any dust handling enclosures like curtains and skirting.
4. Evaluate mechanical dust collectors as part of the overall dust control strategy, reviewing costs.
5. Address continued housekeeping and equipment maintenance, including work force load.
6. Work with multiple surfactant suppliers to test your material with your water. Note that dust samples should always be collected and sealed to prevent any changes in surface properties prior to testing.
7. Test multiple additives in the lab before any field testing
8. Conduct field tests to ensure the surfactant works under operating conditions. Consider the location of sprays or fog and, perhaps test different application points—directly on the dust source or bulk material or in the air above the source, for example.
9. Select a supplier, evaluating whether they will also provide the dust suppressant application equipment in addition to the surfactant and if they will service the equipment. Evaluate the costs.
10. Install and commission the dust suppression system using reputable companies or site personnel if available.
11. Inspect and maintain the dust suppression system.

The most important part of this guidance is the need for housekeeping and maintenance.

SUMMARY

Of course, eliminating or reducing the production of dust must be considered as the most effective way to reduce this hazard according to the hierarchy of controls illustrated in Figure 3. The use of dust suppression, especially with added surfactants, will also work to eliminate the hazard. The most effective surfactants will allow water to quickly wet the dust particles to cause them to aggregate with the water droplets and return to the bulk material. In the future, however, we must also consider the toxicity of the particulate surfaces as we have better understanding of the presence of ROS on dust particle surfaces, including in respirable dust/water droplet aggregates that can still be airborne, entering workers' lungs. Additives are being investigated to reduce the ROS hazard (30).

Site housekeeping and maintenance, whether underground or on the surface, are critical parts of any dust suppression system whether it is for silica, coal, or other minerals and materials. This cannot be stressed enough.

An overall plan for dust suppression should be developed by:

- Removing the hazard (through reduced dust production, but through dust suppression and the application of surfactants)
- Isolating people using engineering controls, changing the way people work (through automation and removing people from the dust laden areas), and
- Using effective personal protective equipment.

Comprehensive dust suppression plans will reduce worker exposure and reduce the incidence of silicosis and other debilitating lung diseases.

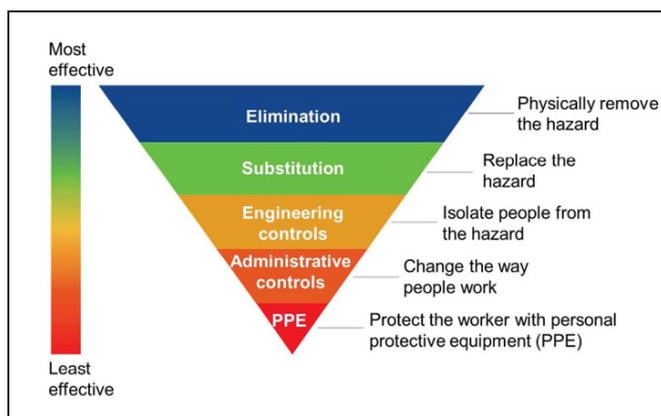


Figure 3. Hierarchy of Controls for Reducing Workplace Hazards (41)

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