

Designer silicates for breakthrough performances in mycotoxin binding

by Dr Elke Schoeters, Kemin AgriFoods Europe, Toekomstlaan 42, 2200 Herentals, Belgium.

Silicate minerals are rock-forming minerals which contain silicon and oxygen. Silicon dioxide in silicate minerals is mainly organised into tetrahedra, interconnected by differing anions like aluminium, manganese, magnesium, iron, zinc and others. The tetrahedra can occur isolated, in rings, chains, sheets or in a three dimensional framework. Silicates are widely used in all kind of industries and in this context a lot of effort has been put into characterisation of these minerals and studying the effect of different treatments on efficacy.

More specifically, clays are used in the battle against animal mycotoxicosis. Big differences exist between clay mineral efficacies towards mycotoxin binding. Understanding the relationship between mycotoxin binding and clay characteristics may result in binder products, designed for maximal efficacy.

Complexity of minerals

Determination of the right silicate mineral treatment to maximise efficacy is not straightforward because of the complexity of the minerals. Exfoliation is very often applied onto different kind of silicates in order to maximise surface area and interfaces. However, these kind of treated silicates

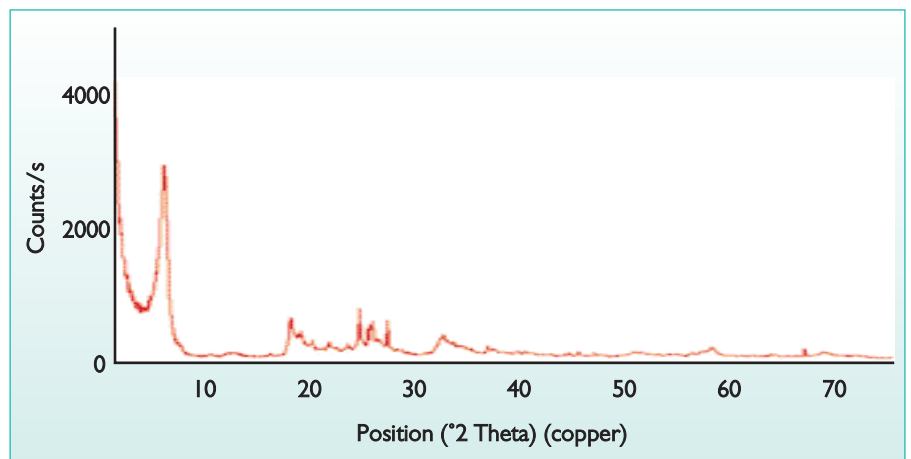


Fig. 2. Specific X-ray diffraction pattern of a silicate mineral.

have not yet gained commercial success. The reason is that the structure and morphology of the untreated and treated silicates is not very often investigated and although they are structurally similar, properties differ considerably.

The structure is more complex than generally assumed and besides individual layers and intercalating stacks, other formations may be present. For instance, face to face interactions between mineral layers might lead to aggregation; edge to face interactions to network formation.

This will change the efficacy tremendously. It is therefore very important to characterise (un)treated silicate minerals by means of different techniques in order to get as much

information as possible on the specific properties of the minerals. This will lead to better prediction of changes in efficacy.

Specific properties

Because of specific properties such as high cation exchange capacity (CEC), adsorption, high surface area, basal spacing and swelling behaviour, several silicate minerals are widely applied in sorption, catalysis, membrane separation, environmental remediation and animal feed. They are, for instance, used to remove toxic contaminants from the environment. For this purpose, silicates with high adsorption and ion exchange capacity and a large surface area can be selected. The silicates can even be exfoliated by use of surfactants to maximise the surface area. Some of the important silicate properties are described below.

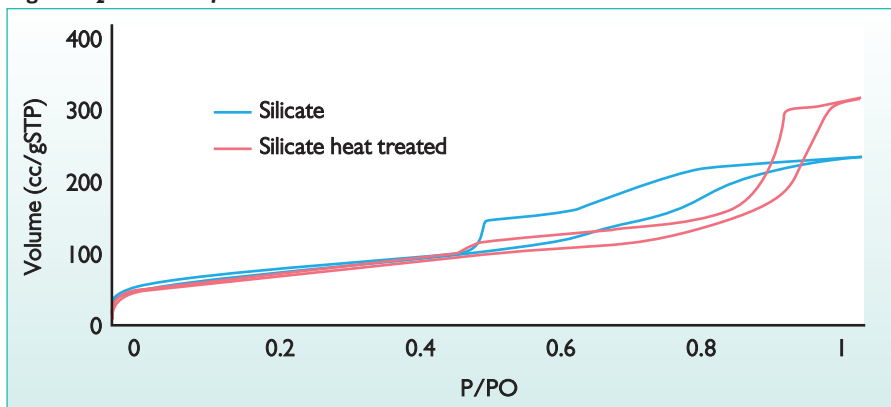
Basal spacing is defined as the distance from a certain plane in one layer to the corresponding plane in another parallel layer. It thus includes features of the geometry of stacking of layers, as well as any material present between the layers.

Cation exchange capacity is defined as the capacity to exchange the cations 'trapped' inside the silicon dioxide layers.

In the layers of silicate minerals, silicon is partly replaced by cations like Al^{3+} or Mg^{2+} resulting in negatively charged minerals

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Fig. 1. N_2 isotherm for a non-treated and heat-treated silicate mineral.



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(Si_2O_4 versus SiAlO_4). This attracts positively charged ions like Na^+ or Ca^{2+} . These ions can again be exchanged by cationic surfactants. Pore volume is defined as the ratio of a porous material's void volume (for example filled with air or water) to a porous material's total volume. Specific surface area is the surface area of the silicate mineral onto which adsorption can take place.

Silicate treatments

Several treatments can be applied onto silicate minerals in order to manipulate them to achieve the highest possible efficacy.

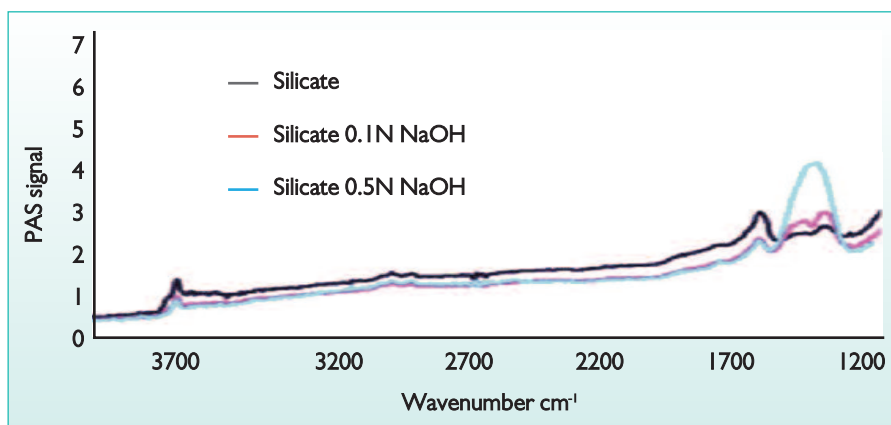


Fig. 3. IR-PAS spectra for a silicate mineral with and without base treatment.

Depending on the application of the silicate, the desired treatment might be different. A first possible treatment is the production of organic derivatives.

The organic modifiers used for this purpose are generally cationic quaternary amine compounds which are commonly known as surfactants. Sodium dodecylsulphate (an anionic surfactant) modified montmorillonite shows a much more negative zeta potential and exhibits higher affinity for Cu and Zn as compared to the naturally available montmorillonite.

The sorption of Cd, Pb and Zn by hexadecyltrimethylammonium and benzyltrimethylammonium modified bentonite is non-linear and the adsorption of metals decreases with the increase in surfactant loadings in the organoclays from 25 to 100% of the CEC of the bentonite.

Minerals with different CEC are treated with several surfactants in multiple concentrations and changes in specific mineral properties are as follows:

- The basal spacing increases with surfactant loading but reaches a maximum.
- The maximum basal spacing increases with the alkyl chain length of the surfactant.
- For a given surfactant, the CEC of the mineral has little influence on the maximum basal spacing of the organomineral.
- For minerals with a given CEC, the maximum basal spacing was reached at lower surfactant concentrations.
- The level of surfactant loading onto the mineral strongly depends on the CEC of the mineral.

Although organic modification of silicates using quaternary ammonium salts can enhance the silicate's mycotoxin binding capacity *in vitro*, the use of these silicates in animal feed nutrition is prohibited in most regions of the world due to the toxicity of these salts. Secondly, the silicate minerals can be physically changed, for example by milling/grinding. The main effect of grinding silicate sheets (montmorillonite) is disruption and loss of the stacking of the layers. This is mainly due to breakdown of Si-O-Al bonds, disrupting the sheets.

Also a decrease in total pore volume and specific surface area of the silicates is observed with increasing grinding time.

Thirdly silicates can be chemically treated. Novakovic et al. (2008) reports the most important changes occurring in smectite that was acid-activated as being:

- Increase in specific surface area and average pore volume, depending on the acid strength, time and temperature of the treatment.
- Large increase in pore volume and broadening of the pore size distribution which indicates that acids cause structural changes and partial decomposition of the silicate mineral.

Finally silicates can be thermally treated. At temperatures between 500 and 800°C a clear weight loss of pyrophyllite is detected, assumed to be due to loss of structural water (dehydroxylation). This might occur at different temperatures for different silicates, depending on the bond energy of the hydroxyl groups in the structure.

At temperatures higher than 1200°C, structural decomposition was detected and X-ray diffraction (XRD) analyses confirmed the formation of other minerals, for example mullite and cristobalite.

All these results again confirm the complexity of the silicates and clearly demonstrate the need for specific and well defined modification of the silicates in order to achieve the specific efficacy that is desired.

Characterisation techniques

● N₂ adsorption isotherms

In order to characterise textural properties of porous solids (like silicate minerals), adsorption/ desorption of probe molecules like Ar, N₂, CO₂, etc. is common. Among these, N₂ adsorption at low temperature (-196°C) is the most widely used. The most important information obtained from these analyses is the specific surface area and pore volume of the porous material. Fig. 1 shows the effect of heat-treatment of a silicate on the N₂ isotherm.

● X-ray diffraction

A silicate mineral consists of different planes. When these planes are lighted with an X-ray beam, the electrons of the atoms of the different planes will scatter the X-rays, resulting in a specific diffraction pattern.

From these X-ray scatterings we can obtain *d*, the distance between lattice planes (basal spacing), resulting from the diffraction angle and the wavelength of the X-ray radiation. For each silicate mineral, a specific X-ray diffraction pattern can be obtained. This way it is easy to define structural decomposition after mineral treatment.

A specific X-ray diffraction pattern of a silicate mineral is presented in Fig. 2.

● Fourier transform infrared photoacoustic spectroscopy (FT-IR-PAS)

This is another spectral technique that can be used for the identification of constituents in complex systems. FTIR-PAS is based on the absorption of electromagnetic radiation

by the sample and non-radiative relaxation that leads to local warming of the sample.

Pressure fluctuations are then generated by thermal expansion, which can be detected by a very sensitive microphone. FT-IR-PAS technique allows the measurement to take place under absolute dry conditions (He gas) and can be successfully applied for the study of hydroxyl groups of a siliceous material.

Treatment of a silicate mineral with 0.1N and 0.5N sodium hydroxide results in manganese leaching from the silicate. This is reflected by an increased bending vibration -OH peak in IR-PAS.

Fig. 3 clearly shows this increased peak at the 1442cm⁻¹ position.

Conclusion

The application of various treatments on different silicate materials and then characterisation of the treated materials using XRD, N₂ adsorption, element analyses and infrared spectroscopy, can provide us with valuable information on basal spacing, total pore volume, specific surface area, diffraction pattern, ionic constitution and structure.

The different treatments can induce changes in the silicate minerals that can be exploited to investigate the change in efficacy of the silicates towards binding of heavy metals, vitamins, minerals and also toxins. ■