Bentonite

Always a clear advantage:

Bentonite for effective clarification and stabilization Origin and applications

Characteristics

Use and advantages



Progress is our future

Origin and composition

The term bentonite (from Fort Benton, Montana, USA, one of the places it was first discovered) is used to describe clay minerals, whose main component is montmorillonite. Highquality bentonite contains 80% or more montmorillonite, with at least 60% being required for the clay mineral to be described as bentonite. Montmorillonite is a microscopic crystalline hydrous aluminium phyllosilicate (Fig. 1). When water is added, water molecules are absorbed between the layers, which enlarge the distances between layers as a result of intercrystalline swelling and produce negative charges. These are compensated for by the adsorption of exchangeable cations, such as sodium, calcium and magnesium. The ability to exchange adsorbed cations for other charged molecules (e.g. proteins) is responsible for bentonite's effect, used in beverages treatment, of adsorbing proteins and other charged substances.

The bentonite deposits available today were created by volcanic activity around 100 million years ago and subsequent weathering of the resulting volcanic rocks (see

Fig. 2). Important European deposits are found in Bavaria (Landshut, Mainburg) and around the Mediterranean, such as on the islands of Milos and Sardinia. Not all bentonite deposits are suitable for use in beverages treatment.

Bentonite's purity can usually be inferred from the colour. As a general rule the paler a bentonite, the greater its purity; darker colouration indicates greater proportions of iron (reddish) or copper (bluish) (see Fig. 3).

The crystal lattice in bentonite predominantly consists of silicon and aluminium oxide as the main chemical components, plus oxides of iron, calcium, magnesium and sodium. Only small proportions of the elements, that are embedded in the lattice are soluble. This explains why the bulk elements aluminium and iron are only released in very small quantities, whilst alkali metals sodium and calcium are found in the medium almost all the time when priming bentonite.

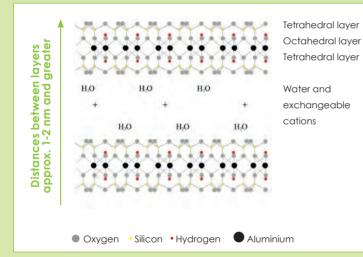


Fig. 1: Structure of montmorillonite's crystal lattice

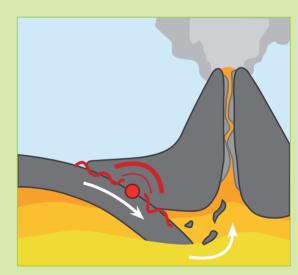


Fig. 2: Creation of bentonite through weathering of volcanic rock



Fig. 3: Crude bentonites from various sources and in different grades of purity

Table 1 shows that inclusion of the ions does not necessarily depend on the size. Whilst iron exhibits similar poor solubility to aluminium, the heavy metals arsenic and lead are much more soluble. The International Organisation of Vine and Wine (OIV) has specified threshold values for the release of metal ions in tartaric acid, which represent the current purity criteria for use in wine.

Element	Content in bentonite (Ø)	Soluble propor- tion (%)	OIV threshold value	Soluble content in Erbslöh bentonites	
Aluminium	100 g/kg	2 %	2.5 g/kg	0.1–0.2 g/kg	
Calcium	11 g/kg	36 %	5 g/kg	1–4g/kg	
Iron	3.8 %	2.4 %	600 mg/kg	30 – 90 mg/kg	
Arsenic	4 mg/kg	22 %	2 mg/kg	0.1–0.8 mg/kg	
Lead	20 mg/kg	16%	5 mg/kg	0.9–1.8 mg/kg	

Table 1: Elements in bentonite, absolute content and soluble proportion in 1% tartaric acid

Use of bentonite for clarification and stabilization

In the beverages sector bentonite is used for clarification, protein adsorption and to prevent subsequent protein precipitation. The clarifying effect is based on coarse flocculation occurring just a few minutes after the bentonite is added to the beverage. This flocculation caused by the bentonite includes fine particles. The particles become heavier, causing them to be deposited. The stabilization effect through protein adsorption is also accompanied by a certain tannin adsorption. Experience has shown, that abrupt clarification using premium bentonites can also lead to an extensive reduction in neutrally charged colloids, e.g. neutral polysaccharides, associated with a particular stability of the beverage. Bentonite can also reduce biogenic amines and insecticide residues.

The need for bentonite can vary greatly in different beverages. The type of fruit is decisive where fruit juice is concerned. In winemaking the need varies from year to year, but also depends on the grape and site.

Years with low precipitation, especially in late summer and autumn, lead to beverages with a greater need for bentonite. Wine grown in vineyards with loose sands or gravels and on shallow soil usually need more bentonite, than wines from vineyards on deep or heavy loess soils. This increases in dry years.

The plants deposit proteins in their fruits as reserves, i.e. as a source of energy. The greater the stress to which the plant is exposed, the more reserves it stores. This explains the increased need for bentonite in low precipitation years.

The beverage's pH value is linked to bentonite's effectiveness. Bentonite's protein adsorption is more intensive for low pH values than for high. This property can be explained by changes in the charge of the proteins dissolved in the beverage, which is influenced in the event of only slight changes in the pH value.

Bentonite quality has a major impact on its effectiveness in the beverage. Bentonites, that have a low swelling ability (pure calcium bentonite) have a lower protein adsorption, which is especially apparent for pH values above 3.4-3.5. Special bentonites, such as NaCalit® PORE-TEC, with a higher swelling ability, have much better protein adsorption, especially for pH values of 3.4 and higher. From this it is clear that attention to the pH value is particularly important when using bentonite.

NaCalit® PORE-TEC Premium sodium-calcium bentonite granulated using PORE-TEChnology Visibly more uniform Specifically selected granulation mineral Intentional porous, spongy surface structure

- Extremely low in iron

Characteristics of Erbslöh bentonites

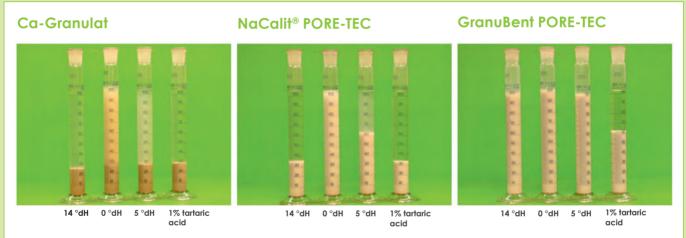
		NaCalit® PORE-TEC	FermoBent® PORE-TEC	Seporit PORE-TEC	GranuBent PORE-TEC	MostRein [®] PORE-TEC	Calcium granulate
Character N		Na-Ca bentonite	Na-Ca bentonite	Ca-Na bentonite	Na bentonite	Ca bentonite Activated charcoal	Ca bentonite
State Colour	tate	PORE-TEC granulate	PORE-TEC granulate	PORE-TEC granulate	PORE-TEC granulate	Granulate	Granulate
	Colour	Light coloured	Light coloured	Light coloured	Light coloured	Grey	Greenish-grey
F	locculation activity	Very high	High	Moderate	Very high	Moderate	Moderate
P	Protein adsorption	High	High	Moderate	Very high	Moderate	Moderate
	ffectiveness with igh pH values	Very good	Very good	Less good	Very good	Good	Less good
	ediment volumes	Moderate	Moderate	Slight	High	Slight	Slight
	uspendability	Very good	Very good	Very good	Moderate	Very good	Good
S	wellability	High	High	Low	High	Low	Low
P	Pre-swelling	3–5 times volume	5 times volume or direct addition possible	3–5 times volume	10–12 times volume	3–5 times volume	3–5 times volume
P	riming in h	4–6, 12 better	4–6	3–6	6–12	3–6	2–5
	Customary dosage g/100 L	50–150 (more if necessary)	100–200 (more if necessary)	100–200 (more if necessary)	20–150 (more if necessary)	150–250 (more if necessary)	100–200 (more if necessary)
F	ield of use	Wine/Fruit juice	For fermenting in must	Must	Wine	Must contaminated with botrytis/rot	Wine/Fruit juice
N	Aoisture (%)	≤8	≤8	≤8	≤8	≤ 12	≤8
p	oH value	8.5–10	8.5–10	8.5–10	10	8.0–9.5	7.0–9.0
S	odium (%)	0.45–0.5	< 0.5	0.2–0.4	1.1–1.3	0.3–0.5	< 0.1
C	Calcium (%)	< 0.4	< 0.4	< 0.4	0.1-0.4	< 0.5	< 0.5
lr	ron (%)	< 0.05	< 0.05	< 0.07	< 0.05	< 0.09	< 0.14

Protein adsorption adsorption

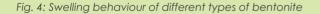
The storage of positively charged ions such as sodium and calcium in montmorillonite's layered crystal lattice causes bentonite to swell when water is added. This effect is all the more marked the more exchangeable cations are available. Monovalent sodium ions cause complete swelling, as they are able to fully penetrate the lattice structure, whilst double-charged calcium ions can only be stored in peripheral areas. A completely primed, or swollen, bentonite is required for optimum adsorption of proteins and other charged substances. The use of hard or acidic water makes the swelling less effective, as it inhibits cation exchange (see Fig. 4).

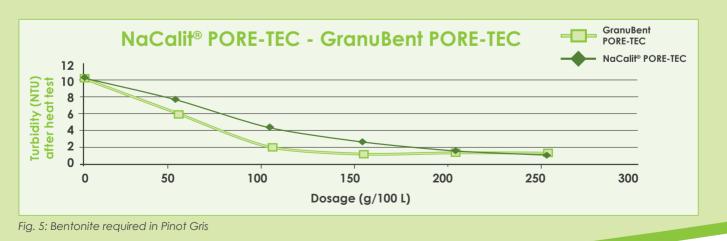
Pure sodium bentonites' greater adsorption compared with calcium and sodium-calcium bentonite mixes is only apparent in use after priming, as only a fully swollen crystal lattice can ensure bentonite's maximum adsorption power. In unprimed bentonite, for example, the protein adsorption of GranuBent is only slightly greater than that of calcium granulate, whilst it is almost double in primed bentonite. Methods for measuring protein adsorption are based on model solutions. This allows bentonites to be classified and compared for their adsorption ability, but it is only possible to draw a limited direct conclusion with regard to use in wine.

In practical application, differences emerge regarding the quantity of bentonite required to stabilize proteins, especially for grape varieties with a greater bentonite requirement and more complex wine protein composition. Taking a Pinot Gris as an example, it can be seen that although there are differences in the use of sodium bentonites compared to a mixed sodium-calcium bentonite, these are mostly limited to an increase in the dosage by 50-100 g/100 L (see Fig. 5).



The differing ways various types of bentonite swell is most clearly shown when used with hard water. In this case only pure sodium bentonite swells completely. To swell completely, NaCalit® PORE-TEC needs soft water, whilst even in optimum conditions the calcium granulate exhibits only a limited ability to swell. In the acidic medium of a 1% tartaric acid solution (as "model wine"), the swellability is generally reduced.





Process to determine bentonite requirement ement

Fining bench tests with increasing quantities of bentonite (gradations of 50 or 100 g/100 L) are customarily used to determine the bentonite required in wine and then the treated wines are tested for protein stability. Processes used in practice are the bentotest and the heat test. For the bentotest the proteins are precipitated using a chemical reagent (Dr. Jakob's process); for the heat test a denaturing process is caused by exposure to heat and subsequent cooling of the wine. In both cases the protein stability is determined by measuring the turbidity. In the case of the bentotest, turbidity below 5 NTU is seen as still stable; this also includes a purely visual assessment of the turbidity. In the case of the heat test, only turbidity below 2 NTU is rated as stable; measurement with a turbidimeter is required in this case. In practice a version at 80 °C for 2–3 hours, with subsequent cooling in an ice bath, has proved to be successful. Heat tests with temperatures below 60 °C are not meaningful. In most cases the bentotest establishes slightly higher bentonite requirements than the heat test. The bentotest can be used for a rough estimate of the bentonite required; the heat test is recommended for a nuanced determination of the volume of bentonite required.

The following points should be considered during use:

- Always conduct the bentotest at room temperature (18-25 °C)
- Always adhere exactly to the temperature, heating and cooling time for the heat test
- Measure with a turbidimeter, as the eye can be deceived by colour and light
- The same bentonite should be used for preliminary tests and in the cellar

Some other test methods are offered as ready-made test kits, but mostly apply the chemical precipitation principle. Attempts to develop more selective tests based on immunological methods have so far failed due to lack of the requisite user friendliness.

Vinification of must using bentonite

Must treatment with bentonite, which has been the standard treatment for several decades, has produced massive improvements in quality during vinification. The result are purer wines with more pronounced flavours.

Undesirable noble rot components and pesticide residues are eliminated at an early stage, especially when MostRein® PORE-TEC, a bentonite-activated charcoal granulate is used. Depending on operational processes, must quality and the bentonite used, either separation takes place before fermentation (Seporit PORE-TEC, MostRein® PORE-TEC), or the particularly pure, special bentonite FermoBent® PORE-TEC is included in the fermentation process.

Must vinification using Seporit PORE-TEC and MostRein $^{\odot}$ PORE-TEC

Specifically selected mineral

- Clearer fermentation
- Early reduction of sediments
- Early removal of oxidases; less need for SO₂
- Removal of biogenic amines, such as histamine
- Adsorption of insecticide residues and other impurities, which cause fermentation problems can be avoided
- More effective, the lower the pH
- Bentonite prevents foaming
- Wine is protected by early treatment
- Compact sediment deposit
- Eliminates need for additional processing stages Protects product

Bentonite incorporated in the fermentation process

Inclusion in the fermentation process exhibits some advan-tages over traditional treatment with bentonite during preliminary must clarification or fining of young wine:

- Saves time during the busy autumn season (especially effective when combined with flotation)
- Bentonite is extremely effective as a result of long contact time
- Gentle treatment, which avoids additional separation and filtration stages, as the bentonite deposits are drawn off with the lees

A bentonite's suitability for inclusion in fermentation is determined by the following requirements:

- Good dispersion and distribution in the must
- Highly effective at adsorbing proteins
- Formation of a stable deposit after fermentation
- Optimum purity, above all extremely low release of iron

If these requirements are met, generally there is no need for further treatment of the wine to achieve protein stability, if the bentonite is appropriately used in the correct volumes.



Fig. 6: Fermentation process and temperature variation during fermentation, LWG Veitshöchheim trials, with and without bentonite

How does the use of FermoBent® PORE-TEC influence fermentation and/or the availability of nitrogen that can be converted by yeast?

According to LWG Veitshöchheim trials, it was not possible to establish variations either during fermentation (Fig. 6) or in the case of nitrogen, that can be converted by yeast (NOPA). It neither delays nor accelerates fermentation.

Is direct use (without priming) suitable to save time? Will it still be fully effective?

When FermoBent® PORE-TEC was developed, we emphasized very good suspendability. It is not possible, however, to fully compensate for the disadvantage of incomplete swelling. It is possible to compensate for this effect by adapting the quantity used and achieve a protein-stable wine after fermentation in the event of direct use (Fig. 7). Priming is essential, however, if the aim is to work using the optimum quantity of bentonite (Fig. 8).

Does fermentation using FermoBent® PORE-TEC lead to a need for less bentonite overall? Under what conditions?

Following more than two years of trials, it can be said, that under no circumstances has a greater need for bentonite been established after fermentation using FermoBent® PORE-TEC than for treatment in must and racking off before fermentation. In most cases, there was no further need for bentonite after fermentation with FermoBent® PORE-TEC in the wine. In the control specimens that were not treated in must, the requirement in wine was mostly on a similar scale to that used in fermentation.

If fermentation including bentonite does not as a rule reduce the bentonite required, when used in appropriate quantities it can, however, save subsequent laborious and taxing wine treatments.

To what extent does the content of iron and other heavy metals rise when bentonite is included in fermentation?

Iron is one of the components of bentonite that dissolves less well. During low contact-time treatments of a few hours up to one day, only very small quantities dissolve in the treated product (must, wine). The situation is different for contact times of up to several weeks during fermentation. When alcohol and CO₂ develop simultaneously, the transfer of iron increases by up to ten times the value for a standard treatment. When using a bentonite with customary iron content, this can lead to an increase in the wine's iron content of up to 2-3mg/L. This is why the iron content in the bentonite used for fermentation including bentonite becomes very important. Only bentonites that release < 0.05% iron in tartaric acid extract can be used in fermentation without the wine's iron content rising above 5 mg/L when greater quantities are used, thus running the risk of iron turbidity (Figs 9 and 10).

Trial results using FermoBent® PORE-TEC



Fig. 7: Use of FermoBent® PORE-TEC with and without priming (trial by Vier Jahreszeiten Winegrowers' Cooperative, Palatinate region, Germany)

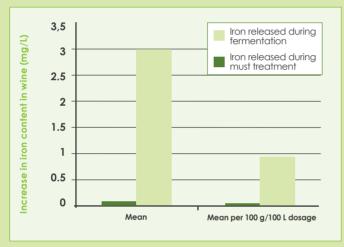


Fig. 9: Iron released compared between must treatment and fermentation



Fig. 8: Use of FermoBent® PORE-TEC with and without priming (trial by Oppenheim Rural Service Centre, Rheinhessen, Germany)



Fig. 10: Increase in iron content after fermentation using FermoBent® PORE-TEC (Iron released < 0.05%) compared to an alternative bentonite (iron released 0.15%)

Blancobent UF and UltraBent PORE-TEC UF: Premium bentonites for crossflow filtration

Crossflow filtration plants are frequently used to clarify juice bases and young wines. As it is not enough to merely remove particles in order to stabilise beverages, a specially prepared bentonite is used within the filter circuit. Blancobent UF and UltraBent UF contain no abrasive larger particles (>100 μ m) and do not damage membranes or other parts of the system, even in the event of long-

term use. At the same time formation of an overlay on the filter membranes (fouling effect) is significantly reduced, greatly extending the filtration cycle. The clarifying and stabilizing effect of crossflow filtration and Blancobent UF or UltraBent PORE-TEC UF perfectly complement each other. The bentonite dosages required as standard are therefore lower than for traditional fining

