

NEW FINDINGS ON CLARIFICATION, STABILIZATION AND FILTRATION OF FRUIT JUICES AND FRUIT JUICE CONCENTRATES

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In order to meet market requirements and ensure economic success, producers of fruit juices and fruit juice concentrates and their suppliers have to get to grips with changing consumer expectations and ever stricter product specifications. Anyone who fails to meet these expectations and specifications will become less competitive.

BENTONITE UNDER DISCUSSION

The name bentonite was derived from the place where it was first found near Fort Benton, Wyoming (USA). Its amazing characteristics are principally determined by the clay mineral Montmorillonite. This name is derived from the Southern French town of Montmorillon, where these clays also occur. The mineral Montmorillonite is characterized by high water-absorbing and swelling capacity. Since it is found in the earth's crust, it naturally also contains other minerals such as quartz, mica, feldspar, pyrite and calcite. Montmorillonite is generated by weathering of volcanic ash. In addition to substitutable ions (Na, Ca), bentonite also contains small quantities of heavy metals. The *International Code for Wine Treatment Agents* specifies maximum limits for soluble ions in bentonites that are used in beverage production. No such code exists for fruit juices.

Bentonite is under discussion in view of the possibility that it may contaminate fruit juices with undesired ions and other substances. Earlier reservations relating to iron content and an associated risk of hazing have been superseded by the issue of potential heavy metal contamination.

The discussion was triggered by an article published in the German *Ökotest* magazine back in 1977, reporting small quantities of uranium in apple juice spritzer. Since then, the industry has sought ways and means to reduce or eliminate such contamination. Later it turned out that the uranium originated mainly from the mineral water and only to a very small degree from the other raw materials used for the spritzer. Despite the fact that the quantities found were significantly lower than the safe load for mineral water of 15 ppb (parts per billion), manufacturers of spritzer raw materials have since been faced

with demands for a maximum limit of 1 ppb. Discounters and research labs are both striving towards halving the limits for a range of undesired substances such as heavy metals, HMF (hydroxymethylfurfural), patulin and pesticides in fruit juices.

The focus is on the following questions:

1. Can the use of bentonite be avoided altogether, and are practical replacement products or processes available that would make its application unnecessary in future?
2. Do different conditions and processes lead to a change in the migration characteristics of heavy metals and other undesired substances from bentonite into the juice?

When applied in high doses and under unfavourable conditions, bentonite can increase the heavy metal content by up to 5 ppb. Although this is still far below the current limit for mineral water, the requirement stipulated by the market of less than 1 ppb is still not met. The following findings can be derived from a range of trials that examined heavy metal migration from bentonite under cold and hot clarification conditions. The maximum quantity of heavy metals migrating into the juice from SIHA Ca-Bentonite and SIHA Active Bentonite was 1 ppb. To verify the suitability of SIHA Ca-Bentonite for hot filtration it is advisable to carry out laboratory tests. SIHA Active Bentonite can be used for hot filtration without restriction.

Heavy metals are not firmly bonded to bentonite and can easily be flushed out with water. By increasing the water quantity during pre-swelling and subsequently decanting of the supernatant liquid, the heavy metal content of the bentonite prepared for application can be reduced significantly. Any heavy metals dissolved in the pre-swelling water are removed by discarding the supernatant liquid.

ALTERNATIVES TO BENTONITE

In the quest for alternatives, the following substances were examined that are used in the beverage sector and the food industry.

Silica gels (amorphous silicon oxide for adsorption of protein substances) are unreliable for the purpose of stabilization and can only be used for complementary residual stabilization.

Acrylic polymers with macroporous structure for protein adsorption can only be used in fully clarified and prefiltered juice. High colour adsorption limits their application in red juice and apple juice spritzer.

China clay and *titanium dioxide*, which are used as food additives E171 and E559, are practically ineffective.

Proteases (enzymes that are able to split proteins or peptides) are currently under close scrutiny. They may present an opportunity for the fruit juice sector, where, in contrast to the wine sector, the application of proteases is permitted.

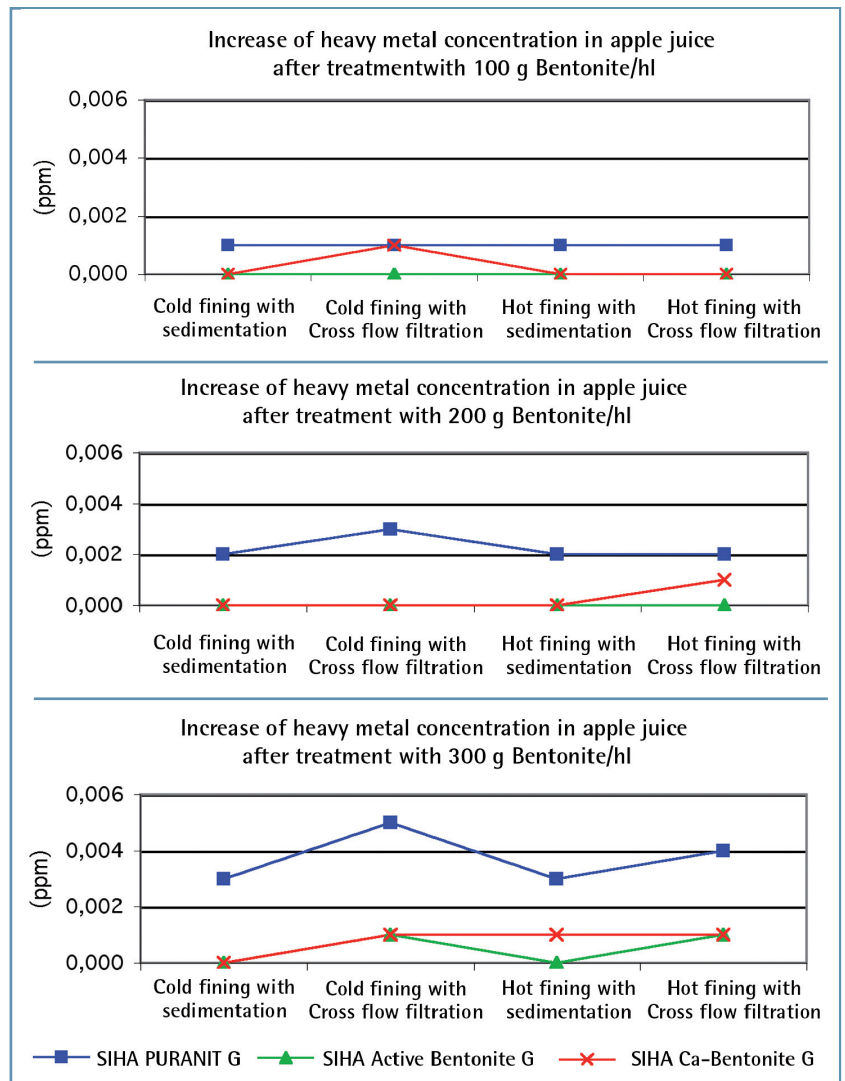
Filter additives with negative zeta potential proved effective, but have not yet achieved the high stabilization performance of bentonites. This product line offers significant development potential.

In summary, it is currently not possible to avoid the use of bentonite for stabilization. Undesired contamination of products can be reduced significantly by using an appropriate, top-quality and cleaned bentonite, and by selecting suitable process parameters such as the volume of pre-swelling water, stirring and maceration times and process temperatures.

VISION OF FULL CONCENTRATE STABILIZATION

In 2009 the price of AJC reached a historic low, while at the same time heating oil prices reached record highs. This fact illustrates the significance of continuous process optimization for reaching or maintaining competitiveness.

The production of highly stable, ready-to-fill concentrates requires these products to be re-diluted to 20 °Brix and then highly concentrated to 70 °Brix, following stabilization. If this process step could be avoided, it would not only reduce process times but also cut the energy costs associated with re-concentration significantly.



Figs. 1 - 3: Heavy metal content in apple juice (mg/l) after treatment with 100, 200 and 300 g of bentonite/hl

FIG. 4: OVERVIEW OF ALTERNATIVES TO BENTONITE

Product	Clarification flocculation	Stabilization			Adsorption of anthocyanins
		Bentotest	H/K test	Gushing	
Bentonite	+++	+++	+++	+++	+
Silica gel	±	±-++	±-++	±-+	+
Protein absorber	-	+++	+++	+++	+++
Filter additive	±	+++	++	+	+
White clay	+	+	+	+	+
Titanium dioxide	-	-	-	-	-

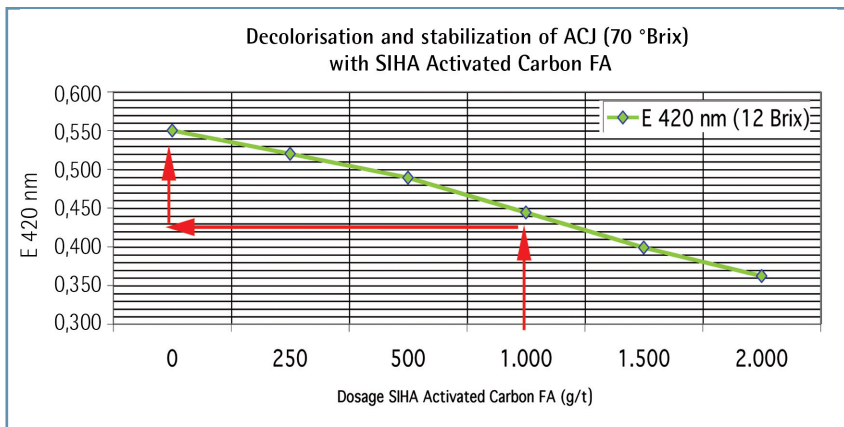


Fig. 5: Decolourization and stabilization of AJC (70 °Brix) with SIHA Activated Carbon FA

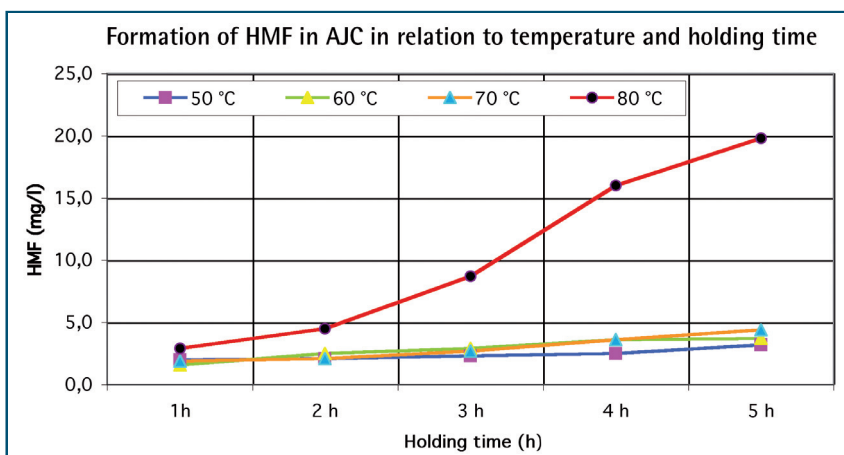


Fig. 7: HMF formation in AJC (70 °Brix, 32 g acid/kg as citric acid) as a function of temperature and holding time

FIG. 6: STABILIZATION OF APPLE JUICE FULL CONCENTRATE WITH ACTIVATED CARBON AND BENTONITE

SIHA Activated Carbon FA Dosage (g/t)	1000	1000	1000	1000	1000
SIHA PURANIT Dosage (g/t)	0	250	500	750	1000
NTU increase during heat/cold test	+ 4,1	+ 2,2	+ 0,9	+ 0,2	+ 0,4
Gushing test; Time (min:sec) until foam collapses totally	> 10:00	3:35	0:30	0:40	0:20

Viscosity is exponential to the temperature and concentration. Full concentrates are therefore highly viscous. This can be counteracted by increasing the temperature and associated exponential reduction in viscosity. The following questions are therefore of interest:

1. Is there a temperature range for full concentrates that allows economic filtration while avoiding the negative consequences associated with temperature increases?
2. Are treatment media such as bentonite and activated carbon effective at high viscosity, and is the concentrate still able to enter the pores of macroporous adsorbents such as silica gel or adsorbents?
3. What is the situation regarding the formation of HMF, if the temperature is increased in order to reduce viscosity?

The test results shown in Figs. 5 and 6 indicate that full concentrates can be stabilized with activated carbon and bentonite. In a field test the colour reduction achieved with SIHA Activated Carbon FA was 0.188 absorbance units at a dosage of 1 kg activated carbon per tonne of AJC. In semi-concentrate the value was 0.239. The effect in full concentrate was reduced by 21 %. Stabilization with silica gel was not possible. Compared with the stabilization of semi-concentrate (20 – 24 °Brix), the tested polyphenol and protein adsorbents exhibited only 2 – 4 % of the usual performance (1 – 2 bed volumes compared with 50 bed volumes or more).

Fig. 6 indicates that the bentonite SIHA PURANIT eliminates turbidity-forming proteins and is highly effective in preventing gushing in full concentrate. This means that it is required in many cases. Both treatment media, activated carbon and bentonite, can be used in combination and have to be separated again through filtration with kieselguhr. Separation of SIHA Activated Carbon via kieselguhr filtration was straightforward, while bentonite blocked the filtration at dosages of more than 250 g per tonne.

HMF formation in full concentrate depends on the temperature and holding time. Treatment media should be applied in the temperature range of 50 – 70 °C, since HMF formation is limited in this range. Short-term temperature increases to 80 °C for separation of treatment media through kieselguhr are acceptable.

USEFUL INDICES FOR STERILE FILTRATION (ACB, TAB) OF FULL CONCENTRATE

In the past, viscosity tables were an essential basis for the configuration of filter systems for ACB filtration. Compared with standard sheets, the

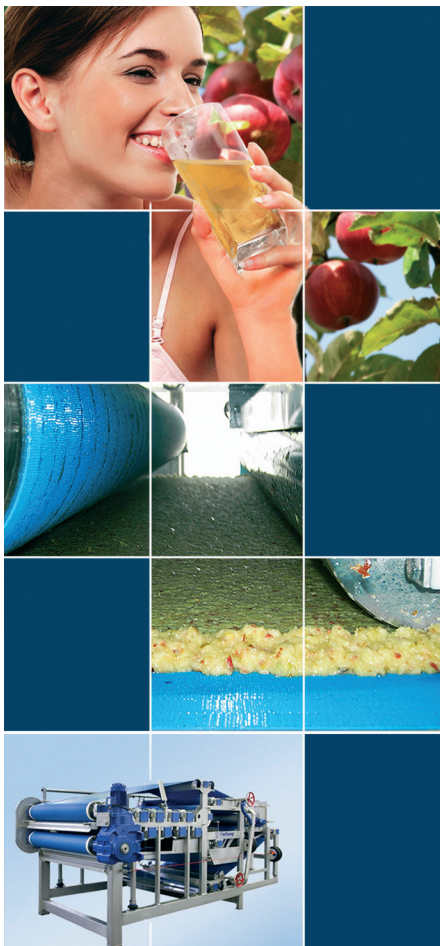
newly developed BECOPAD depth filter medium indicated promising improvements in terms of flow rate, maceration time and germ retention, so that further trials were carried out. They showed the significant potential that can be explored with BECOPAD. Standard sheets do not offer such technical opportunities.

The tests were carried out with a 72 °Brix apple juice concentrate that was subjected to sterile pre-filtration in order to avoid blockages during the test series. BECOPAD 550 and 580 was used for prefiltration. BECOPAD 350 and 270 was used for sterile filtration. Tests were carried out in a temperature range between 15 – 80 °C. The pre-filtration can be carried out at a temperature of 30 °C, both with standard filter sheets or with the BECOPAD depth filter medium. Prefiltration with BECOPAD 580 is possible from 15 °C. Sterile filtration with BECOPAD 270 and 350 is possible from 45 °C, whereas standard filter sheets require a minimum temperature of 60 °C. If the differential pressure is increased from 1.5 to 3.0 bar, sterile filtration of full concentrate could even be realised at 30 °C, if BECOPAD 580 is used in combination with BECOPAD 270.

NEW LABELLING FOR KIESELGUHR

EU directive no. 1272/2008 for the classification, labelling and packaging of substances and mixtures (CLP ordinance) came into effect on 20 January 2009. It integrates the classification criteria of the United Nations Global Harmonized System (GHS) in EU law. The CLP ordinance will gradually replace the directives on hazardous substances (directive 67/548/EEC) and on hazardous preparations (directive 1999/45/EC).

According to the CLP ordinance, manufacturers of substances and mixtures are required to classify, label and pack their products based on the new ordinance from 1 December 2010 and 1 June 2015 respectively. The safety data sheets also have to be adapted. According to the CLP ordinance there are transitional regulations for products that were classified, packed and distributed with the 'old' labelling before 1 December 2010, allowing such products to be sold until 30 November 2012 within the EU.



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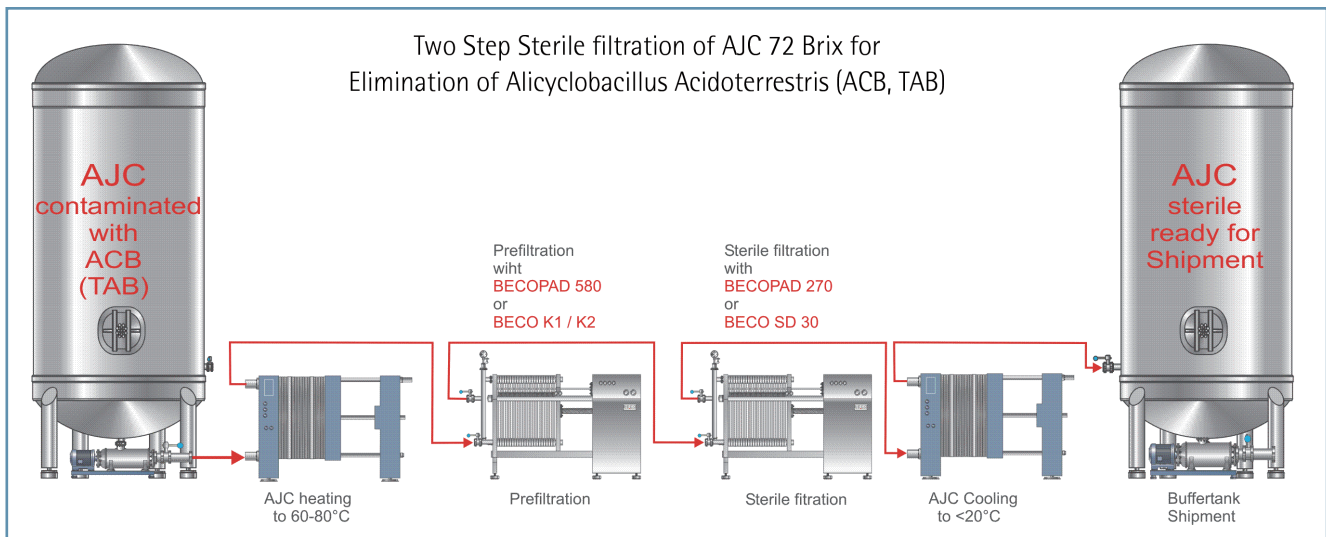
for the production of high quality fruit and vegetable juices

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WHAT DOES THIS MEAN FOR KIESELGUHR?

Many years ago, kieselguhr producers voluntarily decided to label crystalline silicic acid as 'Xn Harmful' in conjunction with R-phrases R 20 (Harmful by inhalation) and R 48 (Danger of serious damage to health by prolonged exposure). No grading/classification according to directive 67/548/EEC was undertaken. Studies relating to risk assessment and potential health effects of respirable, crystalline silicic acid were carried out within the framework of the CLP ordinance and REACH directive (EC) no. 1907/2006 for the Registration, Evaluation, Authorisation of Chemical Substances.

Based on the results of these studies, respirable, crystalline silicic acid (respirable quartz and cristobalite, subsequently referred to as RCS) was classified as:

- STOT RE 1, if the RCS concentration is 10 % or higher,
 - STOT RE 2, if the RCS concentration is between 1 and 10 %.
- (STOT = specific target organ toxicity; RE = repeated exposure)

Risk classification is **not** required if the RCS ratio in a product is less than 1 %.

The RCS ratio in products depends on the ratio of crystalline silicic acid and its grain size distribution. Fine particles are far more likely to penetrate deep into the lungs than coarse particles, thereby posing a health risk. BECOGUR kieselguhrs were examined using the relevant scientific techniques, with a view to reclassify the products. Despite the fact that some products contain crystalline silicic acid, these particles are relatively large, so that the respirable ratio is low. The measurements showed that all BECOGUR types had less than 1 % RCS. For this reason they no longer require risk classification or warning labels. Nevertheless, we still regard it as important to alert users to the fact that the inhalation of

dust from plant-based substances and minerals should be avoided.

SUMMARY

It is currently not possible to substitute bentonite with other stabilizers. Undesired bentonite contamination of juice can be reduced through skilful handling. Increased energy costs and intensified competition necessitate continuous process optimization. Full concentrate stabilization and filtration can reduce energy costs significantly. Through application of treatment media within the right temperature range, temperature-related HMF formation remains within acceptable limits. The new BECOPAD depth filter medium opens up new opportunities for quality-preserving and cost-cutting sterile filtration of full concentrates. Kieselguhr no longer has to be labelled as a hazardous substance in future.



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