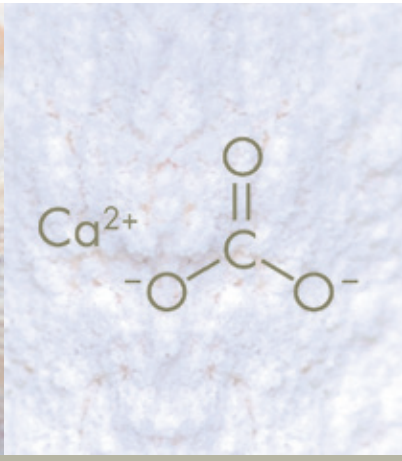
KLUG CONSERVATION

Technical Knowledge folder no. 4

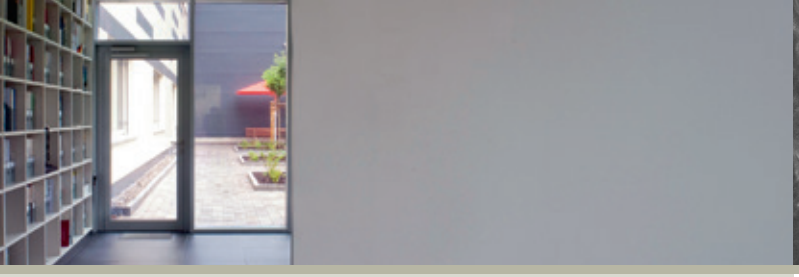


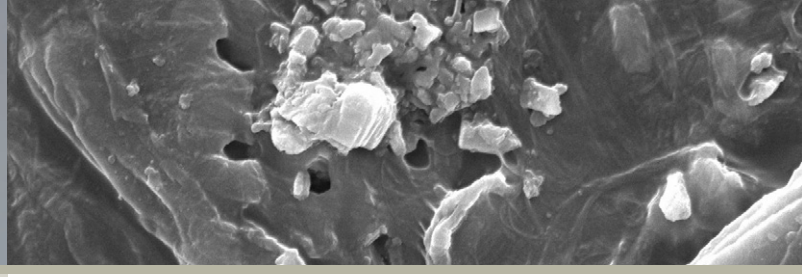
Fillers

Natural, ground or chemically precipitated calcium carbonate

QUALITY FOR THE FUTURE

YOUR PARTNER FOR PRESERVATION MATERIALS





KLUG's expertise

Research and development for preservation solutions

KLUG-CONSERVATION, with over 140 years of experience, has the know-how to produce premium-quality products made from ageing-resistant paper and board, ensuring maximum permanence and durability for long-term preservation of assets in archives, museums and libraries. Close collaboration with our customers and intense cooperation with the paper industry, development and research institutes, universities and academies allows us to continually improve our existing products as well as develop new ones. This is essential for maintaining a consistently high quality standard, as well as keeping up-to-date with latest developments in the field. We would like to share this knowledge with you in the form of our "Technical Knowledge folders". Should you have any further questions, please refer to our website (www.klug-conservation.com), our printed publications or contact us personally.

Michael Kühner

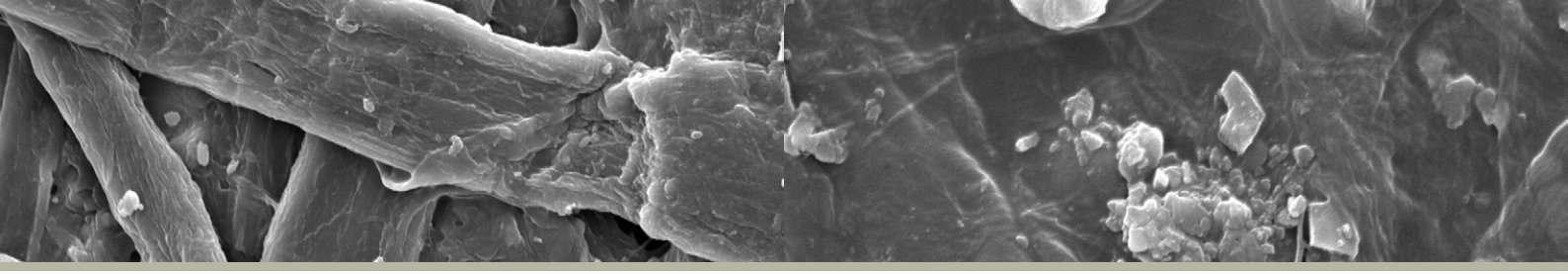
Peter Lang

Calcium carbonate ($CaCO_3$)

Permanent, ageing resistant paper in accordance with ISO 9706 contain a minimum of 2 % calcium carbonate as the equivalent alkaline reserve, to provide adequate protection from acidic attack generated in paper through ageing or due to environmental influence. Today, one basically differentiates between two types of calcium carbonate, one used as a filler and the other used as a coating pigment during paper manufacture:

- (N)GCC: (Natural) Ground calcium carbonate
  Natural, ground calcium carbonate – which is formed after chemical preparation, i.e. after decomposition, purification and grinding of limestone or marble.
- PCC: Precipitated calcium carbonate
  Precipitated calcium carbonate – is produced by treating lime water solution calcium hydroxide $Ca(OH)_2$ (solid content of minimum 20 %) with carbon dioxide gas CO_2, where it precipitates to form $CaCO_3$.

GCC and PCC are available in average grain sizes 10 – 0.2 microns (µm) with a brightness of approx. 85 – 95 %. Both GCC and PCC are available either in dry or suspension form.



The abrasive effect of calcium carbonate on the headbox (wiring), felts and other machine parts of the paper machine depends upon the morphological stiffness and grain size of its particles. PCC has the advantage of greater volume and higher stiffness; the reason why many papermakers prefer to use PCC as a filler. On the other hand, GCC is preferred for coating because it possesses far better rheological properties. However, both products are equally suitable for either application methods.

Water solubility and pH

The solubility of calcium carbonate in pure water is between 13–16 mg/L, very marginal; even smaller than quartz, but increases significantly under atmospheric conditions[1] – in the presence of carbon dioxide (CO_2) released in the atmosphere – by a factor of 10 while decomposing to $CaCO_3$. The pH of saturated calcium carbonate solution in pure water, with absolutely no carbon dioxide content, is 10.07. In the presence of atmospheric decomposed carbon dioxide CO_2 the level sinks to 8.3[1].

[1] A.W. Smith: Aqueous deacidification of paper. In: G. Banik, I. Brückle Paper and Water, Oxford: Elsevier – Butterworth – Heinemann, 2011, pp. 351–359.

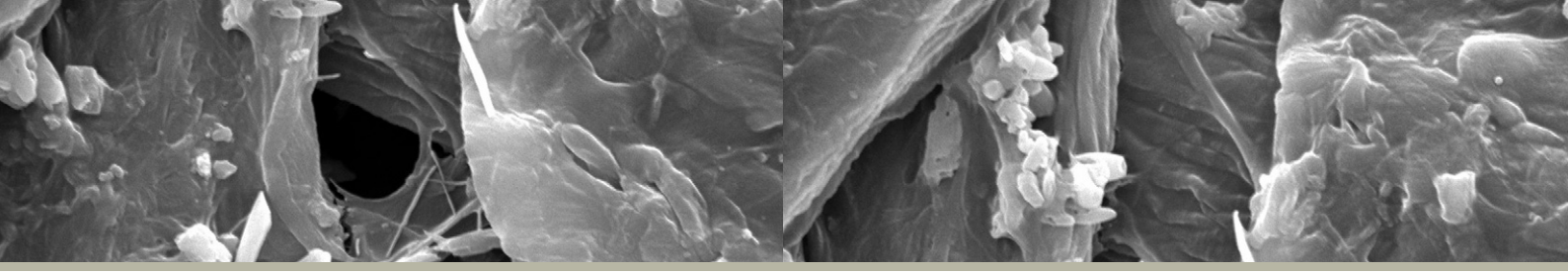
[2] K. Ahn, G. Banik, U. Henniges, A. Potthast: Nachhaltigkeit in der Massenentsäuerung von Bibliotheksgut. In: Eine Zukunft für saures Papier, ZfBB Sonderband 106, Frankfurt: Vittorio Klostermann, 2011, pp. 58 ff.

GCC versus PCC

In accordance with ISO 6588 standard the pH in an aqueous extract of paper filled with GCC is approx. ≤ 8.3. In the case of hard-sized board material, a correct pH can only be achieved if the test material is shredded, because its low water absorbency prevents sufficient $CaCO_3$ extraction from the board.

The extraction pH of PCC filled papers is significantly higher. Values may reach up to 9.5 and < 10. This is most probably due to the incomplete carbonisation of calcium hydroxide $Ca(OH)_2$ during PCC production. The residual calcium hydroxide is more soluble in water and much more alkaline than $CaCO_3$; the pH of a saturated $Ca(OH)_2$ solution is 12.4.

Conservators and scientists are currently discussing whether an alkaline pH of paper exceeding the "moderate" pH range of 7.5 – 9.0 represents a potential risk for so-called **β**-elimination of cellulose. Initial case studies of a research group at the University of Lifesciences Vienna (BOKU) have proven that in the case of already aged and oxidized paper, the probability of this cellulose degradation induced by an alkaline environment can be regarded as low[2].



Protection against acidic degradation of paper

Already in the thirties of the last century it was re-cognized that calcium carbonate increases paper stability on the long-term. An example is the case study published by Hansen[3] in 1939 which set the basic principle of the ISO 9706 standard, sti-pu-lating the requirement of an alkaline reserve of atleast 2 % calcium carbonate in "ageing resistant paper" or related board materials.

Until research proves the application of PCC as a safe alkaline filler in paper and its related products, KLUG-CONSERVATION will exclusively use ground calcium carbonate (GCC) as the alkaline filler, in order to eliminate any risk for alkaline degradation that may be caused due to high the pH of PCC. $CaCO_3$ embedded in the fibrous matrix of paper and board neutralizes acid compounds that are formed during paper ageing or that get absorbed as acid pollutants from the environment. Through neutralization $CaCO_3$ is converted to its corresponding salts and thus consumed. The maximum protective effect is achieved with a small grain size and high concentration of $CaCO_3$ distributed as homogeneously as possible within the paper matrix.

[3] F.S. Hansen: Resistance of paper to natural ageing. Paper Industry and the Paper World 20 (1939): 1157–1163.

The protection is only guaranteed as long as unconverted calcium carbonate is prevelent as an alkaline reserve in the paper. The concentration of calcium carbonate in the paper or board material may therefore be well over 2 % by weight, but is limited because, fundamentally, higher filler concentration generally has a negative influence on the mechanical properties of paper.

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