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Véronique Rouchon, Oulfa Belhadj. Calcium Hydrogen Carbonate (Bicarbonate) Deacidification. *Journal of Paper Conservation*, 2016, 17 (3-4), pp.125-127. <10.1080/18680860.2016.1287406>. <hal-04160313>

HAL Id: hal-04160313

<https://hal.science/hal-04160313v1>

Submitted on 12 Jul 2023

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To cite this article: Véronique Rouchon & Oulfa Belhadj (2016) Calcium Hydrogen Carbonate (Bicarbonate) Deacidification, *Journal of Paper Conservation*, 17:3-4, 125-127, DOI: [10.1080/18680860.2016.1287406](https://doi.org/10.1080/18680860.2016.1287406)

To link to this article: <https://doi.org/10.1080/18680860.2016.1287406>



Published online: 26 Apr 2017.



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Calcium Hydrogen Carbonate (Bicarbonate) Deacidification

What you always wanted to know but never dared asking

Véronique Rouchon, Oulfa Belhadj

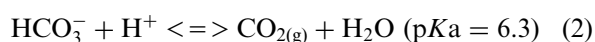
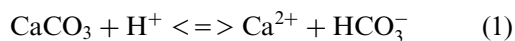
Keywords: Calcium carbonate, deacidification, hydrogen carbonate, bicarbonate

Introduction

Calcium hydrogen carbonate deacidification has been largely experienced in the paper conservation field, but is not always well understood by paper conservators mainly because it uses acidic solutions, a point that appears puzzling in first approach. This article aims at recalling the basic principle of this treatment and gives some highlights on the underlying chemistry.

Why does calcium carbonate act as a buffer?

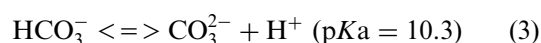
Calcium carbonate (CaCO_3) is commonly found in rocks and soils in the form of different minerals: calcite (trigonal), aragonite (orthorhombic), and vaterite (hexagonal). It was largely used in paper making to whiten the paper. It has in addition a positive impact on paper ageing by acting as a pH buffer. This impact is mainly attributable to the fact that calcium carbonate is capable to consume protons via the following reactions:



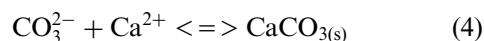
Reactions (1) and (2) show that carbonates (CO_3^{2-}) can be converted to hydrogen carbonate (HCO_3^-) and finally to gaseous carbon dioxide (CO_2) [1]. Calcium carbonate is also considered as an alkaline reserve capable to consume proton and also prevent paper acidification. However, when acting as a buffer, it is itself consumed meaning that its impact is time limited when the paper is continuously exposed to acidic factors (acidic pollutions, oxidation of carbonyl groups leading to carboxylic acids, etc.)

What does calcium hydrogen carbonate (CHC) deacidification mean?

Hydrogen carbonate (HCO_3^-), also called 'bicarbonate' is an amphoteric compound that behaves as a base through reaction (2) or as an acid through reaction (3).



When acidic papers are immersed in CHC solutions, labile protons are removed from the paper through reaction (2). Meanwhile, a small alkaline reserve of calcium carbonate is introduced in the paper taking advantage of reaction (3) that forms carbonates (CO_3^{2-}) which precipitate to calcium carbonate (CaCO_3) through reaction (4).



This precipitate mainly corresponds to calcite because it is, among the different polymorphs of calcium carbonate (calcite, aragonite, and vaterite), the one that is thermodynamically stable in normal conditions.

Taking advantage of chemical equilibria for CHC deacidification

One should keep in mind that reactions (1) to (4) correspond in fact to chemical equilibria that involve both direct (\rightleftharpoons) and reverse (\leftleftharpoons) reactions. These equilibria can be displaced in different directions depending on the amount of chemicals that are initially present. For instance, in low pH solutions, the concentration of protons is high which favours their consumption by calcium carbonate. As a result, the direct reaction (\rightleftharpoons) of equilibrium (1) prevails, explaining the high solubility of calcium carbonate in acidic solutions.

Conversely, when the pH is relatively high, the reverse reaction (\leq) is favoured, because protons are so to say 'missing'. The dissociation of calcium carbonate is no more possible. Instead, if calcium ions (Ca^{2+}) and hydrogen carbonate (HCO_3^-) are simultaneously present, they will rapidly precipitate to calcium carbonate.

The principle of CHC deacidification lies in the fact that reactions (1) to (4) are equilibria that can be displaced in one or another way according to the step of the process to be considered. For the preparation of the deacidification solution, the direct reaction (\Rightarrow) of equilibrium (1) is first considered: CHC solutions are obtained from the dissolution of calcium carbonates in an acidic medium taking advantage to the fact that their solubility is considerably enhanced when protons are present. In order to avoid addition of exogenous chemicals, the acidic medium is prepared by dissolving gaseous carbon dioxide (CO_2) in pure water. The resulting high concentration of dissolved carbon dioxide promotes the reverse reaction (\leq) of equilibrium (2) that leads to formation of protons and hydrogen carbonate.

How can we obtain a CHC solution?

The preparation of deacidification solutions consists in dissolving approximately 1 g of solid calcium carbonate in 1 L of carbon dioxide (CO_2) saturated water. In laboratory conditions, solutions enriched in CO_2 can be obtained by CO_2 bubbling, but this way of preparation is laborious and not easy to handle. In the context of a conservation workshop, a convenient alternative can be found with sparkling water that already contains dissolved CO_2 . Sparkling water bottles from the market may be sufficient when small quantities are requested. In this case, one should choose the trademark that contains the highest quantities of hydrogen carbonate and the lowest quantities of other chemicals. Another option consists in using a home sparkling water dispenser. This enables the preparation of larger volumes and a better control of the chemical composition of the solution when it is combined with a water purification system.

In order to limit release of gaseous CO_2 during opening, the bottles should be kept in cold storage and should not be shaken before use. The addition of calcium carbonate provokes effervescent bubbles of carbon dioxide. To limit this release, the bottles should be firmly closed immediately after calcium carbonate addition and left overnight. Afterward, most of the calcium carbonate powder is dissolved.

The dissolution of calcium carbonate depends on the initial concentration of dissolved carbon dioxide and thus on the system used for preparing the solutions. It is often not complete and some powder often remains in the bottom of the bottles. This point is often puzzling for the paper conservator because it directly questions the quality of the deacidification solution. If calcium carbonate is not completely dissolved, does it mean that the water initially used already contained some calcium? Or that there was not enough dissolved carbon dioxide? To evaluate the reliability of the preparation protocol, it is advised to check that the concentration of dissolved calcium carbonate in the supernatant is above 0.8 g L^{-1} (or 800 ppm). This can be easily done with a colorimetric test kit (Belhadj & Rouchon, 2017).

When hermetically closed, the bottles can be stored for a long period before use. The deacidification solution corresponds to the supernatant that can be obtained by gently tilting the bottles. It should be used immediately after collection and has a pH value between 5.5 and 6.

How can an acidic solution deacidify?

The deacidification process consists in immersing the paper to be treated (typical pH between 3 and 4) in the CHC solution for approximately 10–20 minutes. Immediately after its removal from the bath, the paper still has an acidic pH. It is only after drying that the pH rises up to more alkaline values (pH 6–8 depending on the paper).

This rise of pH during drying is due to the fact that carbon dioxide is released in the atmosphere and thus lost. The concentration of dissolved carbon dioxide also decreases which favours the direct reaction (\Rightarrow) of equilibrium (2), and thus proton consumption by hydrogen carbonates. As protons are consumed, the reverse reaction (\leq) of equilibrium (1) is enhanced, provoking calcium carbonate precipitation. As a result, some part of the hydrogen carbonate is converted to carbon dioxide while the other part is precipitated as calcium carbonate. These two reactions can occur simultaneously because hydrogen carbonate ions are initially brought by carbon dioxide and calcium carbonate and also available in great excess with respect to calcium ions.

Conclusion

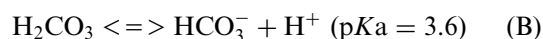
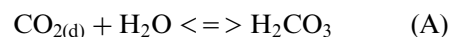
The above considerations help understanding why the calcium hydrogen carbonate treatment is efficient

despite the fact that the treating solutions are acidic. It is moreover the softest of all available deacidification treatments in that the pH of the paper gradually rises from acidic values to mild alkaline ones. Indeed, during the treatment, the paper is never exposed to a highly alkaline medium. This point substantially differs from deacidification treatments based on highly alkaline solutions (pH > 9). It is particularly important to consider when the paper supports drawings or writings made of pH-sensitive media. For instance, some of the synthetic dyes used for stamps may change colour at different pH values. Another example can be found with iron gall inks. It is well known that the risk of ink fading is much higher when a manuscript is immersed in a strong alkaline solution than in a close to neutral one. We do not intend here to particularly advocate for deacidification treatments on iron gall ink manuscripts (mainly because water-based treatment induce several side effects). However, if, for whatever reason, a water-based deacidification treatment is foreseen on an iron gall ink manuscript, the use of a CHC solution should be clearly preferred to that of highly alkaline hydroxide solutions.

Note

- [1] In fact dissolved carbon dioxide (CO₂) is solvated by water through reaction A, forming carboxylic acid (H₂CO₃), a highly unstable molecule that releases a proton through reactions B. The reaction (2) can also be seen as the sum of two

reactions A and B, both involving carboxylic acid (H₂CO₃).



As the solvation constant of reaction (A) is very weak, very few carbonic acid forms in CO₂ saturated solutions. H₂CO₃ should be considered as an intermediate and unstable molecule that very easily dissociates to dissolved carbon dioxide (CO₂) and water. Therefore the writing of reaction (2) is usually preferred to that of reactions (A) and (B).

Reference

- Belhadj, O. & Rouchon, V. 2017. Deacidification Solution of Calcium Hydrogen Carbonate: Controlling Calcium Concentration with a Colorimetric Test. *Journal of Paper Conservation*, 17(3–4):130.

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