Ion Balance and Chemistry of Juice Evaporation, Upasiri Samaraweera; Jeffrey L. Carlson and Ken A. Kubat MINN-DAK FARMERS COOPERATIVE, 7525 red River road, Wahpeton ND 58075.
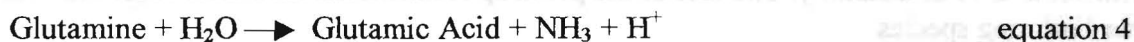
ABSTRACT

The Minn-Dak lab has been investigating the cause of pH changes during juice evaporation. This current work is an analysis of four compounds (glutamine, ammonia, inorganic carbon and sulfur dioxide) responsible for pH change in the evaporators. This study identifies the contribution to H^+ and OH^- from these compounds based on the work by van der Poel et.al

1. Decomposition of carbonates and bicarbonates results in the formation of OH^- (equations 1 and 2).
2. Evaporation of ammonia contributes H^+, the quantity of which is determined by the equilibrium constant at a given pH (equation 3).
3. Decomposition of glutamine forms glutamic acid and ammonia. If the ammonia evaporates glutamic acid contributes H^+ (equation 4).
4. Evaporation of SO_2 contributes OH^- (equation 5).

$$HCO_3^- \rightarrow CO_2 + OH^- \qquad \text{equation 1}$$

$$H_2O + CO_3^{2-} \rightarrow CO_2 + 2OH^- \qquad \text{equation 2}$$

$$NH_4^+ \rightarrow NH_3 + H^+ \qquad \text{equation 3}$$

$$Glutamine + H_2O \longrightarrow Glutamic\ Acid + NH_3 + H^+ \qquad \text{equation 4}$$

$$SO_3^{2-} + H_2O \rightarrow SO_2 + 2OH^- \qquad \text{equation 5}$$

To establish the contribution to H^+ and OH^- from the carbonate and ammonia, this study used the following equilibrium constants (1.35%)for CO_3^{2-}/ HCO_3 and (0.007 %) for NH_3/NH_4^+ at pH 8.7.

One analysis of thin and thick juice gave 64 ppm and 157 ppm for SO_2, 37 ppm and 8 ppm for ammonia, 21 ppm and 4 ppm inorganic carbon, 99 ppm and 130 ppm for glutamine 17 and 63 for refractive dry substance. When concentration factor of 3.7 was considered, the number of meq/L lost in evaporation was calculated to be 2.46, 7.52, 6.04 and 1.60 for sulfur dioxide, ammonia, inorganic carbon and glutamine respectively. The contribution from ammonia and carbonate were adjusted to reflect their equilibrium values at pH 8.7. The contribution to H^+ from ammonia in the form of ammonium and glutamine was 4.8 meq/L while contribution from inorganic carbon and sulfur dioxide to OH^- was calculated to be 8.58 meq/L. These results show an excess alkalinity of 3.8 meq/L. In theory one would expect a pH rise but instead a pH drop from 8.7 to 8.3 was observed.

Analyses of several thin juice and thick juice samples through the year and found that at times the inorganic carbon values went up as high as 80 ppm (a measure of natural alkalinity),

resulting an excess alkalinity of 20 meq/L. The data always showed excess alkalinity in varying amounts even with pH drops. The possible reasons for the excess positive alkalinity may be due not fully accounting for all the H^+ ions. This can be due to the following reasons.

a) The NH_3/NH_4^+ equilibrium values may be in error.
b) Other amino acids like aspargine were not considered in this experiment
c) Contribution from invert breakdown was not determined as inverts may be forming and breaking down at the same time during evaporation.
d) Factory composite samples analyzed were assumed to be the same juice. However, the samples were collected eight minutes apart -the estimated time the juice spends in the evaporator train. Therefore it is possible that the thin and thick juice samples may be slightly different.

Methods to adjust alkalinity
Typically when the pH drops across the evaporators (low alkalinity juice) alkali can be added before the 2nd carbonation. As a result one can reduce the lime salts and also increase the alkalinity of the juice (the portion alkali that contributes to alkalinity is determined by the concentration of the lime salts). If the intention is to only increase alkalinity, then the alkali could be added after the 2nd carbonation.

If the alkalinity reserve is high, there are three ways to reduce a pH rise. First, after the 2nd carbonation a mild pH rise can be gassed down with SO_2. But with a high pH rise, experience at Minn-Dak has shown gassing the pH down with SO_2 inadequate. While ammonia and glutamine (and other amino acids) remain somewhat constant in any juice, the concentration of CO_3^{2-} / HCO_3^- is high. At the second carbonation of pH 9.2 the ratio of carbonate to bicarbonate is 0.019. Because 98.1 % is in the bicarbonate form any SO_2 addition has the potential to react with only with about 2 % of alkalinity. The rest of the pH drop results from reversible reactions with the other buffering species

A juice with a high alkalinity reserve has high amount of potassium and sodium hydroxide (KOH and NaOH) after the 1st carbonation, which is converted to carbonates and bicarbonates after the 2nd carbonation. This excess alkali can be reduced quantitatively in two ways. First, adding a desired amount of an acid like HCl (equation 6). Second, adding a salt like $CaCl_2$, in or before second carbonation. Carbonation will remove the alkalinity and calcium leaving only sodium chloride (equation 7). In both situations the excess sodium ions are balanced by chloride ions.

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad \text{equation 6}$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2\,NaCl \qquad \text{equation 7}$$