

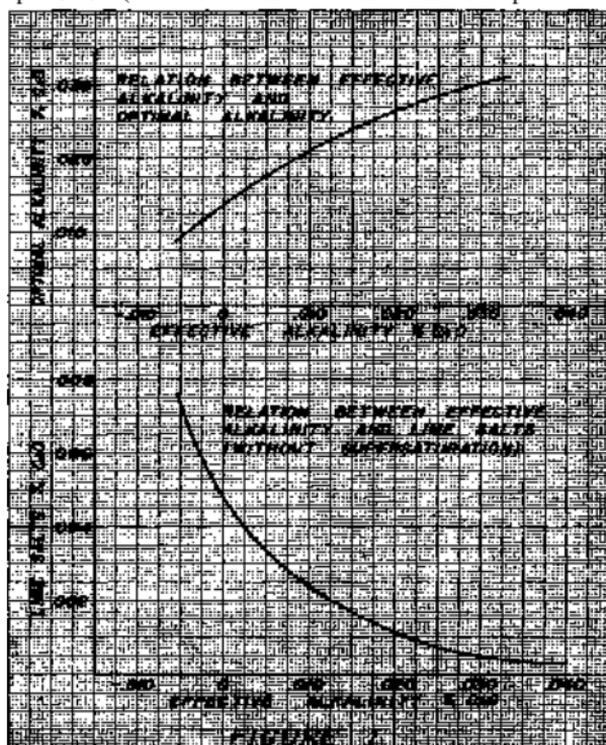
Second Carbonation Studies Based on Commercial Application of the "Effective Alkalinity" Concept

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In October, 1947, H. Brunicke-Olsen of the Danish Sugar Company explained the "Effective Alkalinity" concept in the article, "The Physical Chemistry of Second Carbonation," published in the magazine "Sugar." Mr. Olsen and A. Brieghel-Muller elucidated further on the subject in the April, 1949, issue of "Sugar."

Effective alkalinity is measured on first carbonation juice and is that alkalinity which is active in binding carbon dioxide and deliming the juice. It is measured by taking the difference between alkalinity at titration to *pH 9.25 (established as the most insoluble point for the calcium ion in a

pure calcium carbonate water solution) and the lime content as measured by soap titration. Knowing this value, Mr. Olsen was able to predict the minimal lime content of the juice at saturation with carbon dioxide and the optimal alkalinity, that is, the alkalinity which should be maintained at second carbonation to produce the minimal lime content. The above relationships were expressed as curves which were found to lend themselves nicely to the control of second carbonation. These curves are shown in Figure 1. The principle of the *Effective Alkalinity Concept* may be compared to that of



¹ The Amalgamated Sugar Co.

any solubility curve (that is, with a known constant temperature it is necessary to carbonate to an alkalinity at which the lime salts will be least soluble. This alkalinity, known as optimal alkalinity, is established only by first measuring the effective alkalinity). Table 1 describes the calculation of effective alkalinity.

Table 1. Calculation of Effective Alkalinity.

EXAMPLE		
Original pH 10.40 Titration to pH 9.25		
ML N/28 H ₂ SO ₄		27.40
ML Soap Solution		17.40
	Difference	+ 10.00
Effective Alkalinity =	+ .010% CaO	

The first efforts of the Amalgamated Sugar Company to apply this concept in the control of lime salts provided such promising results that a systematic examination of the commercial possibilities of this method of control was undertaken.

These studies extended through two campaigns. During the first campaign the work was limited to studies on a small experimental carbonator. The results in some cases showed that it was possible to obtain a very nearly complete elimination of lime salts. The principles of the pilot unit were then incorporated with a flocculator for the design of a new full scale carbonator which was installed at the Nampa, Idaho, mill.

During the following campaign examinations were conducted under normal operating conditions of the mill, and where special conditions were imposed they were established in the mill and not synthetically in the laboratory. The following is a discussion of the subjects examined and the results obtained:

(1) Effective Alkalinity and Optimal Alkalinity.

The new commercial carbonator with its three carbonating compartments offered an excellent opportunity to study the relationship between effective alkalinity and the optimal alkalinity in producing minimal lime salts. In the first carbonating compartment the juice was purposely undercarbonated, allowing an alkalinity slightly higher than the optimal point to exist. In the second compartment the juice was carbonated to the exact optimal alkalinity corresponding to the effective alkalinity. The juice was then further carbonated in the third compartment reducing the alkalinity to a point slightly below the optimal alkalinity. The lime salts were then determined on the effluent of each carbonating compartment and compared. In every case the lowest lime salts were obtained from the second compartment where the optimal alkalinity was held. Furthermore, these results showed that only a slight deviation from the optimal point resulted in a severe rise in lime salts.

(2) Control of Second Carbonation and Soda Ash Addition by the "Effective Alkalinity" Method.

To control second carbonation by this method it is only necessary to measure the effective alkalinity of the first carbonation juice and then carbonate to the corresponding optimal alkalinity as taken from the curve. In many cases, however, it was found that the effective alkalinities ran off the limits of the curve on the negative

side. When such is the case, it is possible to increase the effective alkalinity to any desired value by the addition of soda ash. It was decided to arbitrarily set the value of + .010% CaO as the effective alkalinity to which the lower values would be corrected.

It would then be possible to control second carbonation with optimal alkalinity corresponding to + .010% CaO effective alkalinity. Charts were established indicating for every value of effective alkalinity below this point the proper amount of soda ash to add to the process to produce the desired value. Thus there was established a logical, rational control of soda addition as well as second carbonation. The above principles were adhered to closely for the entire campaign in order that the results would be evaluated properly. Comparing these results with the previous campaign at the Nampa mill the following conclusions are drawn:

- (a) *Lime salts in filtered second carbonation juice were reduced*
 - (b) *Tons of beets processed for each evaporator body boil out were increased 46%.*
 - (c) *The amount of lime salts remaining in second carbonation was practically constant from hour to hour and day to day for the entire campaign. This was a contrast to previous campaigns when variations of lime salts as much as .100% CaO were not unusual from hour to hour.*
- (3) Effect of Temperature on Lime Salts in Second Carbonation Juice.

In the past there has been an open question as to the effect of higher temperatures in second carbonation on resulting lime salts. The argument for additional heat at second carbonation is based on the assumption that the residual lime salts exist wholly as bicarbonates which could be decomposed by the higher temperatures. Mr. Olsen's work shows also the presence of saccharate in residual lime salts and has indicated the possibility that saccharates may increase slightly faster at the higher temperatures than the bicarbonates decompose. Extensive tests ranging from 84° C, which was the average temperature at which juice is delivered to second carbonation without additional heat, to 94° C. showed no decrease whatsoever in lime salts at the higher temperatures. We have thus been able to effect greater heat economy by eliminating the second carbonation heater.

- (4) Efficacy of the New Carbonator.

Realizing that a substantial decrease in residual lime salts had been effected, an attempt was made to determine whether or not any particular feature of the new design or the carbonator as a whole was responsible for this decline. Comparative examinations were made on lime salts existing in the individual compartments, under various gassing combinations, with the agitator in use and not in use and, finally, with the older conventional type carbonator in use. In all cases the residual lime salts varied but slightly or not at all. It was our conclusion that our new design was not superior to the conventional type in respect to the elimination of lime salts. It does, however, offer other advantages such as ease of control,

ability to retain sediment, provision of longer operating periods without the necessity of cleaning and ease of inspection. These features naturally make it the preferred carbonator at Nampa.

(5) **Supersaturation of Residual Lime Salts.**

These tests indicated, as did Mr. Olsens', that, even in adhering closely to the principles of effective alkalinity method of control, it was impossible to reach the minimal lime content calculated. The principal reason for this was proved to be the fact that the residual lime salts exist in a state of supersaturation. Only by completely breaking this supersaturation can the minimal lime content be obtained. This was accomplished easily in the laboratory by digestion of juice with crystalline calcium carbonate (about one percent) for a period of fifteen minutes at 85° C. The filtered juice lime content had been reduced almost to the minimal calculated value. In comparing the lime content in the last compartment of the carbonator with that in the filtered juice a substantial decrease was noted. It is believed that this is due to the partial breaking of the supersaturation as the juice encounters the calcium carbonate sludge in the filters. This phenomena was further exemplified when the entrance to a sample line in the carbonator became submerged in the lime sludge. The sample effluent became crystal clear, having been filtered through the precipitate, and its measured lime content approached the minimal calculated value. It had been hoped that incorporating the flocculating feature in the new carbonator would break the supersaturated condition of the residual lime salts by creating more effective contact with the precipitate. As previously mentioned, this agitation did not reduce the lime content. Additional milk of lime was added to the carbonator in hopes that a greater amount of precipitate would induce the desired result. Again the results were disappointing. So, while all evidence demonstrates the existence of this condition of supersaturation, no effective practical method has been found to break this supersaturation.

Summary

To summarize briefly, the results of the studies in second carbonation have led to the conclusion that the effective alkalinity concept provides a true and accurate control for second carbonation; that adhering closely to the principles of this concept was responsible for a 34 percent reduction in residual lime salts which allowed an increase of 46 percent in the tons of beets processed for each evaporator body boil-out at the Nampa mill; that this control can be applied to the conventional type carbonator with equal success; that temperatures higher than 84° C. do not create a reduction in lime salts at second carbonation, and, therefore, greater heat economy can be effected by the elimination of the second carbonation heater; that the residual lime content cannot be reduced to the calculated minimum until a method of eliminating the supersaturated condition of the lime salts after second carbonation can be devised.

The Amalgamated Sugar Company has now adopted the *Effective Alkalinity Concept* as the standard method of control of second carbonation. Reports continue to bear out the validity of these findings.