# Some Studies on Continuous Carbonation

R. A. McGinnis[1]

A NUMBER OF YEARS AGO a study was initiated by the research department at the Woodland factory of the basic variables of Dorr system continuous first carbonation from a strictly empirical viewpoint. The purpose of these studies was primarily to determine the optimum setting for the best possible quality of thin juice. Some of this material has been published previously (3),[2] and this paper will partake in part of the nature of a review.

In 1939 Professor Dedek published a paper (2) in which he propounded the thesis that any experimental results pertaining to the processing of sugar are valid only for the particular beets concerned, and he supported this thesis with very convincing data; as a result we must specify that the results here reported are essentially valid only for the particular raw materials that were used. Most of the work was carried out with diffusion juice derived from fresh beets. Some of the diffusion juice, however, was obtained from dried cossettes. Much of the work reported has since been checked a number of times, and we can say safely that while the work was carried out with differing raw materials and is strictly valid only for them, nevertheless the general qualitative picture presented seems to hold true for almost any raw materials we have met with in the central California area.

## Apparatus and Methods

After some experience with pilot plant scale apparatus, the conclusion was quickly reached that the work would be most advantageously carried out with bench-scale equipment. Over a considerable period of time an apparatus was developed which, through close imitation of the full-scale equipment, produces a thoroughly characteristic first carbonation juice, even to the settling properties of the mud (figure 1).

A method was developed for studying the settling properties of first carbonation mud, based on the procedure of Coe and Clevenger (1, 3), which has given very satisfactory results.

Second carbonation was carried out in a standardized fashion to individually determined optimum end-points. Reference is made to the publication (3) for complete experimental details.

## Factors Affecting Dorr First Carbonation

The most important factors are, pH or alkalinity, temperature, amount of lime, rate of recirculation, retention time, and rate of gas absorption. These will be discussed individually, presenting our own data when occasion offers and summarizing our own current practice.

[1] Head Research Chemist. Spreckels Sugar Company, Woodland, California.
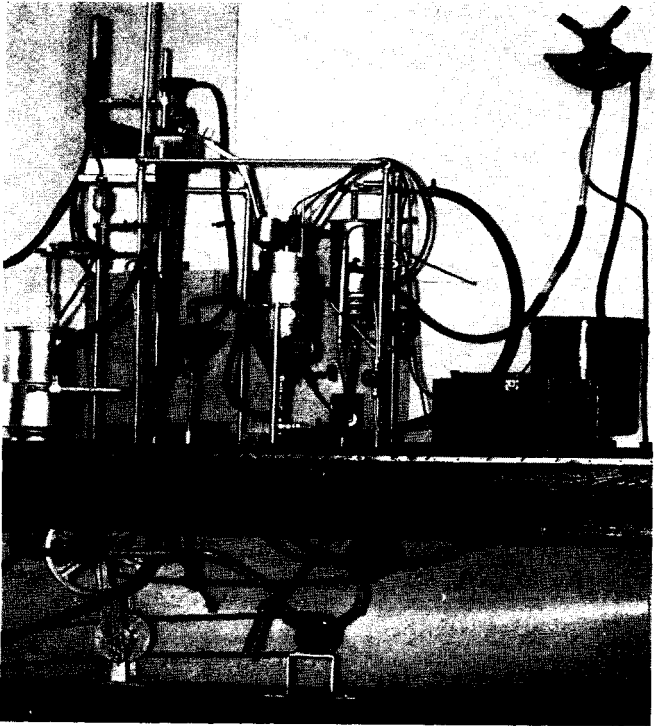[2] The numbers in parentheses refer to literature cited.

Figure 1.—Bench-scale Dorr system first carbonation apparatus, used in obtaining the data reported.

## 1. pH or Alkalinity

The traditional control analysis in first carbonation has been the alkalinity, expressed in grams of CaO per 100 cc. of filtered juice. This analysis has had the disadvantage that it is a titration (see another paper to be presented at this meeting).

The Dorr system almost invariably uses a continuous indicator of the first carbonation end-point, and very frequently automatically controls the end-point. Originally control was by conductivity measurement. This was

generally found unsatisfactory for several reasons. In the first place the electrodes tended to scale very rapidly, resulting in a continued drift in what should have been a constant reading. This drift, however, could be allowed for. More serious is the fact that conductivity measurements are in general far too insensitive for satisfactory control. In addition, the conductivity is frequently affected by variations in concentration of substances other than desired ions.

In the early thirties it was discovered that the antimony electrode could apparently be used successfully in measuring pH in hot liquids, and has very largely replaced the conductivity apparatus. The antimony electrode has, however, been shown to have serious faults as a pH measuring apparatus. Scaling is not serious, as with the conductivity apparatus, but a film does form over the antimony electrode which must be polished off at least every 8 hours. The voltage produced varies with the velocity of the liquid flow past the electrode. Also the electrode is readily poisoned by certain chemicals which are sometimes present in the juices, and at such times gives false measurements.

A few years ago, Dr. A. O. Beckman introduced the hot glass electrode, which is far more sensitive than the antimony electrodes, and is free from the above mentioned faults. Many installations have been made with considerable success.

It was early found at Woodland, however, that while a measurement of pH is quite satisfactory for control, the controlling pH must be set to give the alkalinity desired. As is known,

$$pK_w = pOH + pH$$

| Temp. °C | $pK_w$ |
|---|---|
| 80 | 12.55 |
| 90 | 12.34 |

Since $pK_w$ varies with temperature, the relation between pH and pOH must also vary with temperature.

An example will be given. While we do not know the precise values of $k_w$ in first carbonation juice, we may take the values for pure water as a first approximation. Thus, if carbonation is being operated at 10 pH and 80° C,

$$12.55 = pOH + 10.00, \quad pOH = 2.55$$

This means that the concentrations of the two ions are,

$$(H^+) = 0.000\ 000\ 000\ 1$$
$$(OH^-) = 0.003$$

At 90° C, however

$$12.34 = pOH + 10.00, \quad \text{or } pOH = 2.34$$

and while the concentration of $H^+$ is the same, $(OH^-)$ has increased to 0.005.

While the pH measuring equipment is measuring the concentration of hydrogen ions, it is apparent that it is the hydroxide ions which must be affecting the reactions in defecation. If the temperature remained constant a measurement of pH would suffice for a measurement of pOH. If the temperature changes, however, it is clearly no longer sufficient. In figures 2 and 3 are shown the relationship of pH and of pOH with the alkalinity of first carbonation at various temperatures, for a number of data taken from many types of materials, using saccharate milk defecation. Other factors also change the relationship between pH and pOH, such as variations in the nature of non-sugars, variations in the amount of lime used, and variations in the density of the diffusion juice.
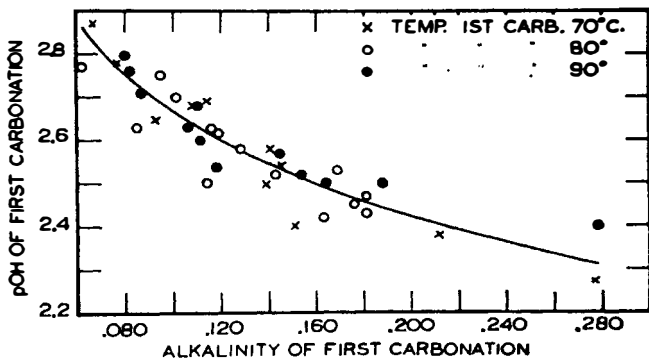


Figure 2.—Relation between pH and alkalinity of various first carbonation juices at indicated temperatures.

There is no practical method, as far as is known, for continuously and directly measuring the hydroxide ion concentration. Alkalinity titrations, however, are very close to being proportional to such measurements. The best proof of this statement is empirical. Apparently the bulk of the alkalinity is free, and the part that is bound is roughly constant.

Thus, until a practical electrode for measuring hydroxide ion directly shall have been found, titrateable alkalinity must be considered the best control measure for first carbonation. At the present time this can best be effected by making frequent alkalinity titrations and resetting the pH control point to give the desired alkalinity.

The second consideration under this heading is what alkalinity to choose for the first carbonation end-point. Our work showed that the

higher the alkalinity, up to a certain point, the better the quality of the thin juice produced, as measured by its lime salts, color and colloids content (figures 4, 5, 6 and 7). The "certain point" is about 0.130 for saccharate milk defecation and between 0.100 and 0.120 for milk of lime defecation. On the other hand, the lower the alkalinity, the more easily the carbonation mud can be filtered and settled out, as will be shown later. As a result, the alkalinity chosen is a compromise, depending upon the capacity and efficiency of the mud separation apparatus.
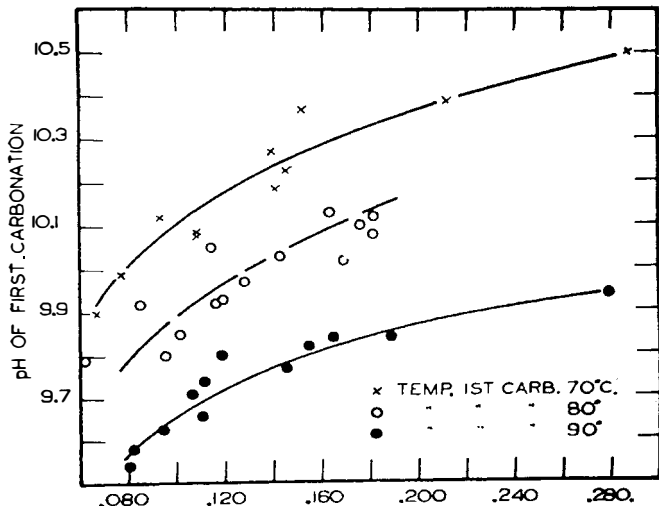


Figure 3. –Relation between pOH and alkalinity of various first carbonation juices at indicated temperatures (same data as figure 2).

### 2. Temperature

The higher the temperature is carried in first carbonation, the easier is the settling and filtration of the mud. As before, however, the worse it is for juice defecation, as shown by the foregoing figures. Once again a compromise must be made.

### 3. Amount of Lime

Studies have been made on the effect of the amount of lime used, both at normal operating alkalinities and at the optimum alkalinities for best juice quality.

Figure 4.—Effect of first carbonation alkalinity and temperature on thin juice lime salts. Saccharate milk defecation.



FIRST CARBONATION ALKALINITY
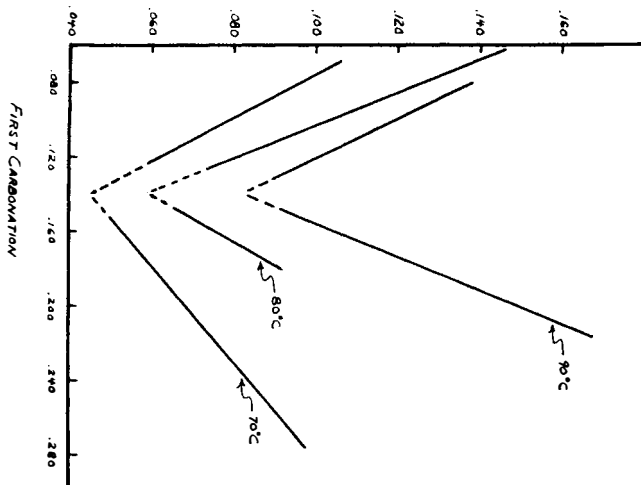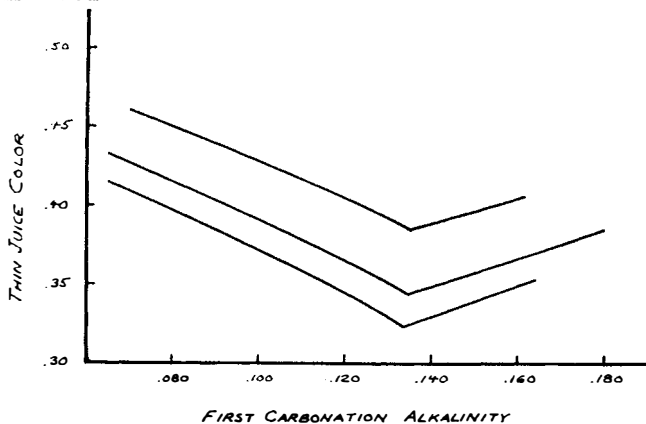
Figure 5.—Effect of first carbonation alkalinity and temperature on thin juice color. Saccharate milk defecation.
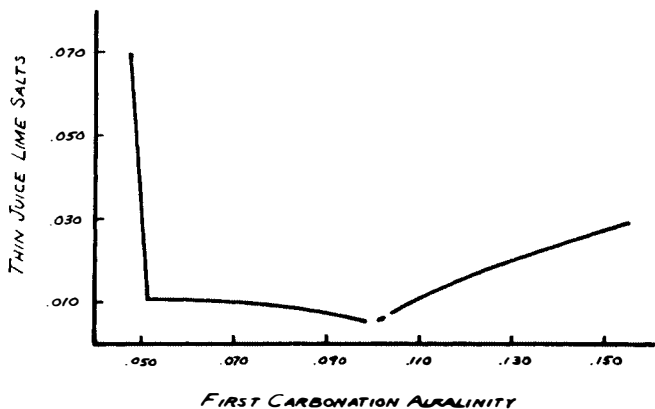
Figure 6.—Effect of first carbonation alkalinity on thin juice lime salts. Milk of lime defecation at 80°C.
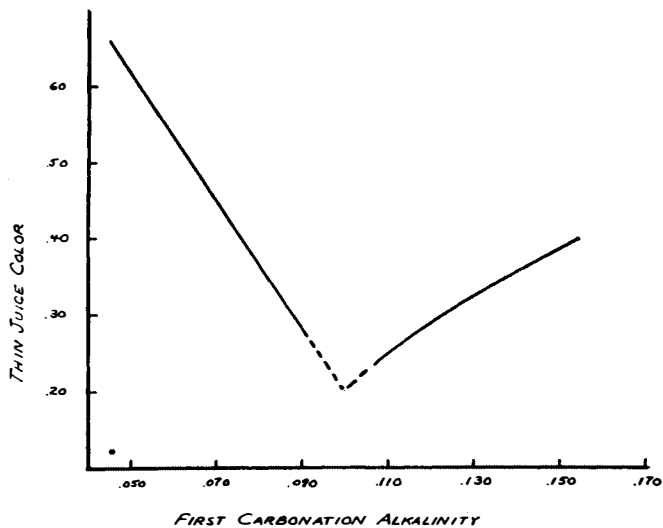


Figure 7.—Effect of first carbonation alkalinity on thin juice lime salts. Milk of lime defecation at 80°C.

Figures 8, 9, 10, and 11, show that at normal alkalinities, the greater the amount of lime used, the better is the thin juice quality, up to at least 5.5—6.0 percent CaO on beets, which was the limit of the tests. An exception is found at very high lime addition with prediscard saccharate milk, where the lime salts content increases. There appears to be no confirmation of the belief sometimes voiced that only very small amounts of lime are required for adequate defecation, the major portion of the lime being useful only as a source of filter aid.

The defecation efficiency decreases with large lime additions, in most cases. Definite decreases may be said to become appreciable above the following approximate percentages of lime on beets.

Table 1.— Defecation efficiencies with increasing lime additions.

| Type defecation | Alkalinity | —with respect to— | |
| | | Color | Lime Salts |
|---|---|---|---|
| Saccharate milk | .080 | over 6 percent | over 3.5 percent |
| | .130 | over 2 percent | over 3.5 percent |
| Milk of lime | .080 | over 3.6 percent | over 3.0 percent |
| | .100 | over 2.3 percent | over 2.3 percent |

At the optimum alkalinity for thin juice quality, the effect is the same, excepting that the defecation efficiency is much greater.

Table 2.—Defecation efficiencies with increasing lime additions at optimal alkalinities.

| Type defecation | Percent of normal lime addition at .080 alkalinity necessary to obtain equivalent value at optimal alkalinity | |
| | Color | Lime Salts |
|---|---|---|
| Saccharate milk | 35.5 percent | 63 percent |
| Milk of lime | 59 percent | 74 percent |

At the optimum alkalinity with both types of defecation there is indication that a lime salts value of about 0.016 represents probably the lowest value that we can hope to attain with central California beets.

The point at which the juice quality improvement does not justify the cost of additional lime, must, of course, be individually determined for each factory.

The actual amounts of lime required to obtain adequate defecation vary with many factors, chiefly the amount and nature of the non-sugars. There are localities in which the beets are of such high purity that relatively little lime is required. For example, excellent defecation has been secured with lime additions as low as 1.1 percent CaO on beets, with comparatively high purity diffusion juice. On the other hand, in another section, 2.5 percent CaO on beets is required with a comparatively low purity raw juice.

4. *Rate of Recirculation*

What few studies we have made of this variable tend to confirm the recommendations of the Dorr Company. The rate is ideally 7:1, but apparently can vary within 5:1 and 9:1 without undue disadvantage.
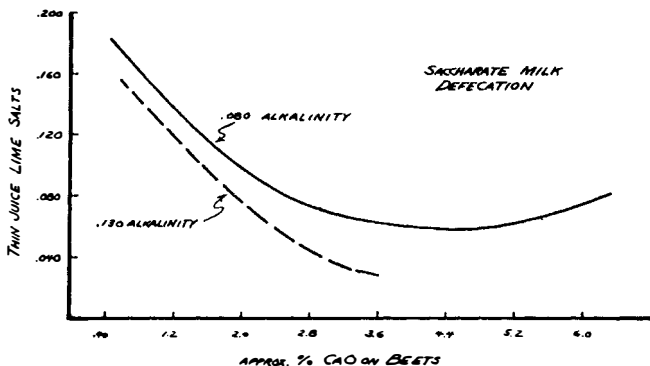
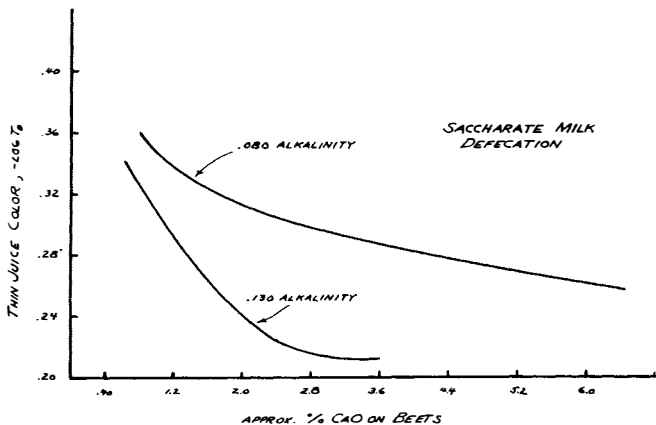Figure 8.—Effect of amount of saccharate milk on thin juice lime salts. Standard conditions.



Figure 9.—Effect of amount of saccharate milk on thin juice color.

## 5. Density of Diffusion Juice

Data which will not be presented in detail at this time have shown that as the concentration of dry substance in the diffusion juice is increased, the proper end-point alkalinity for operation also increases. Thus, a thin juice of very irregular quality will result if care is not taken to keep the

raw juice density constant. However if the optimum alkalinity is maintained in spite of change, the defecation is somewhat more efficient at higher densities, at least with respect to lime salts. Considering both this fact, and the cost of evaporating water, it is apparent that it is advantageous to carry as high a diffusion juice density as possible without increasing battery losses.
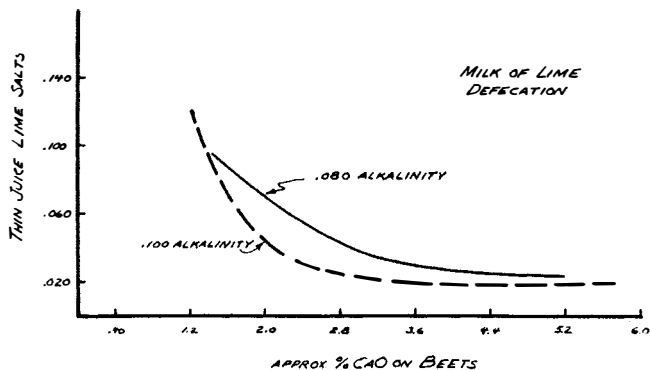


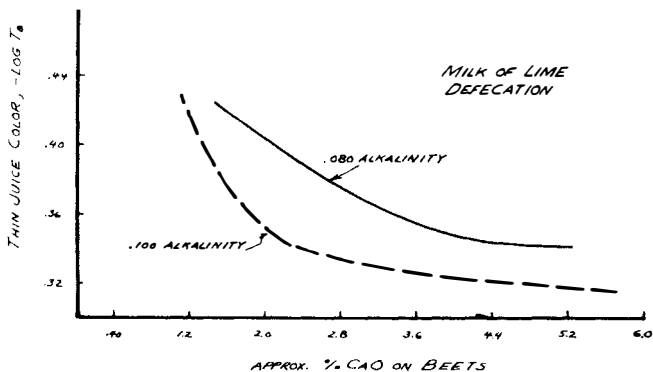Figure 10.—Effect of amount of milk of lime on thn juice lime salts. Standard conditions.



Figure 11.—Effect of amount of milk of lime on thin juice color.

*6. and 7.  Rate of Gas Absorption and Retention Time*

As our studies have not yet adequately covered these subjects, we will merely mention them.

## Importance of Smooth Operation

As was stated, the best setting for the operating variables in first carbonation is a compromise between good thin juice quality and ease of mud separation. The best operating alkalinity is as high a one as possible, without interfering with settling or filtration.

Due to irregularities in various factors, it is never possible to maintain an absolutely constant alkalinity. The magnitude of the irregularities determines how high the alkalinity can be carried. For example, if in a given factory the Dorr overflow becomes seriously cloudy at 0.100 alkalinity, and the magnitude of the irregularity is of the order of 0.020 units, then 0.080 is the highest alkalinity that can be safely carried. If the irregularity is reduced to 0.010, then 0.090 alkalinity can be aimed for, with a much better quality thin juice produced.

Thus, if first carbonation is to be operated at its maximum efficiency, all the variables must be smoothed out as far as possible to reduce the magnitude of the irregularities. Among these variables are raw juices density, temperature and rate of flow, carbon dioxide gas pressure and $CO_2$ content, saccharate or milk of lime density and flow rate, and quality of burned lime.

*1.  Raw juice density.* In order to achieve even density smooth battery operation is essential. Due to the fact that the juice density unavoidably changes within each draw of juice, there should be enough capacity in the raw juice tanks to even the density out. Those fortunate factories possessing continuous batteries do not have any worries on this score.

*2.  Raw juice temperature.* It is possible by careful operation of the raw juice heaters to keep the temperature fairly uniform.

*3.  Raw juice rate of flow.* This factor is a very important one, and its control is much easier if the raw juice receiving tanks are of adequate size. Some satisfactory type of flow meter should be used such as a Root-Connersville meter or an orifice meter to measure the flow to the primary tank. If the rate of flow does vary, the saccharate or milk of lime flow rate should vary with it.

*4.  Kiln gas pressure.* This pressure should be constant to at least 1 percent of the nominal gauge pressure for really smooth control. Since variation of the gas pump speed will frequently interfere with lime kiln operation, some form of pressure controller independent of the gas pump, close to the carbonators, is indicated.

*5.  Carbon dioxide content of kiln gas.* This is a factor that is frequently ignored, but it is just as important as the gas pressure. Large varia-

tions in the percentage of $CO_2$ are ordinarily due to leaks in the kiln. A common cause is the kiln door failing to close entirely after a charge of rock. A continuously recording carbon dioxide analyzer is a great help to both kiln and carbonation operators.

6. *Saccharate or milk of lime density.* Unless the density of the milk is constant, carbonation operation will be very irregular. This station frequently does not receive the attention it deserves, considering the importance of the uniformity of its output. The installation at Woodland has an automatic control in the form of a Foxboro density controller.

7. *Saccharate or milk of lime flow rate.* Although in many factories the lime milk flow is merely controlled by a valve, scaling in such installations is so rapid that a constant flow rate cannot be maintained. Much better results are obtained with feeders of the bucket wheel type.

8. *Quality of burned lime.* If the burned lime rock is not constant in its CaO content, constancy of milk density will obviously not suffice.

### The Clarifier

Normally, retention times in the clarifier of from $1\frac{1}{2}$ to 3 hours are found. The dilute juice cannot be held at appreciable alkalinities and at advanced temperatures for such lengths of time without undergoing some form of degradation. This degradation has been determined for a number of different juices, and the average magnitude from many determinations is shown in figures 12 and 13. Thus, at normal alkalinities, and at 80 degrees centigrade, increases of about 7 percent in color and 0.010 in lime salts per hour were found for juice defecated with saccharate milk. The degradations are decreased as the alkalinity becomes higher. With milk of lime defecation, the degradation is also much less.

In addition to its normal mechanical adjustments, the clarifier is affected by the following variables: temperature, alkalinity of first carbonation juice, amount of lime used, density of first carbonation juice, form in which lime is used, and percentage recirculation in first carbonation.

1. *Temperature,* has an important effect on the rate of sedimentation of the mud through its effect on the viscosity of the liquid phase. This factor is quite an appreciable one, and is thoroughly understood.

2. *Variation* of the alkalinity of the first carbonation juice has a very important effect, which requires preliminary explanation. It is apparent that in the clarifier, mixtures of mud and juice may be found of any composition between the rather dilute mixture entering as feed to the rather concentrated mixture leaving as underflow. Examination of the settling properties of these materials, by the modified Coe-Clevenger method previously mentioned shows that the overall settling rate is fixed by the slowest settling rate found in any of these possible mixtures (figures 14). Thus, in

one instance the slowest rate of settling might be found in the most dilute mixture of mud and juice, corresponding to the composition of the feed material; in another instance the slowest rate might be found in the most concentrated mixtures, corresponding to the composition of the underflow; and in a third instance the slowest rate might be found in an intermediate mixture. For convenience in reference, we have termed these three types A, C, and B, respectively. As far as operation is concerned, it is apparent that increasing the stroke of the mud pumps and consequently lowering the density of the underflow will not increase the clarity of the materials in cases of type A materials, but that a very positive advantage will be obtained in type C materials.

The alkalinity of first carbonation is one of the most important factors in determining the type (figures 15 and 16). At low alkalinities with normal juice densities the materials are almost invariably of type A. As the alkalinity is raised the curves go through the intermediate type B, reaching type C in the vicinity of 0.085 to 0.100 alkalinity. As a rule type C materials settle more slowly than type A materials, so that the overall settling rate, and the size of the clarifier required increase almost steadily with increase in alkalinity.

However, if there is ample mud filter capacity, and difficulty is being experienced with turbid overflow, it may frequently be advantageous to raise the alkalinity to the point at which a type C curve is obtained, so that the turbidity may be decreased by drawing out the underflow more rapidly.

3. The *amount of lime used* affects the settling in two ways. In the first place, if the amount of beets sliced remains the same, the amount of mud is increased. In the second place, the curve type is changed, there being a tendency to shift toward the A type of settling curve with increasing amounts of lime. In general, the sum of these effects is to retard the overall settling rate somewhat with increasing amounts of lime (figures 17, 18, 19 and 20).

4. The *density* of the first carbonation juice has an effect on the settling type of the material. The alkalinities required to give the same type of material are higher if the density of the juice is raised. A second effect is the increase of the viscosity of the juice obtained with increase in density. If the volume of diffusion juice flow is kept constant as its density is increased, larger settling capacity is required. However, if the weight of dry substance entering carbonation in unit time is unchanged, settling is somewhat more rapid with increase in juice density.

5. Whether the lime is added to first carbonation juice in the form of milk of lime or saccharate milk makes quite a difference in mud settling rates. Milk of lime, in general, yields a more difficultly settling mud.
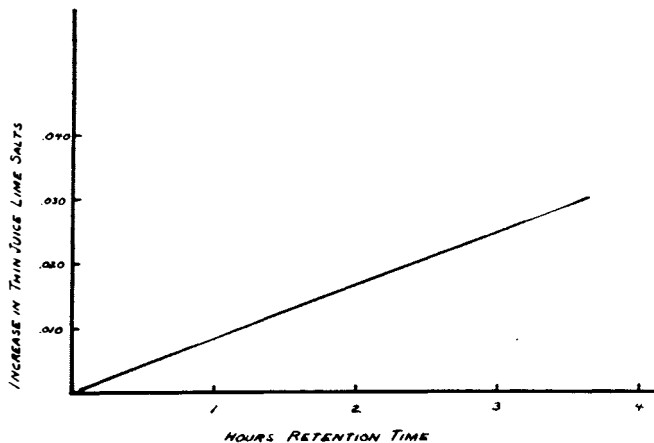
Figure 12.—Effect of time in clarifier on thin juice lime salts. Saccharate milk defecation.
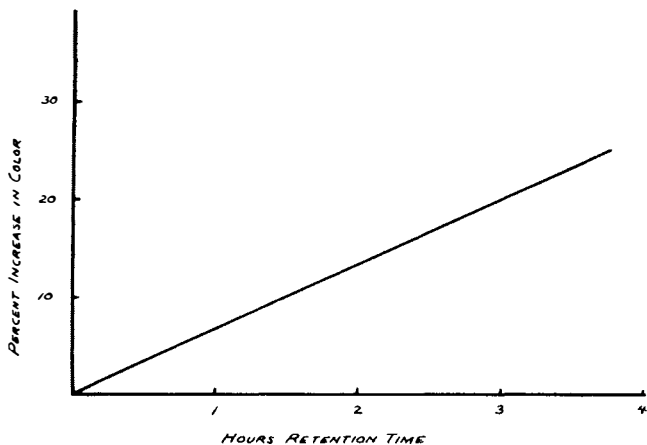


Figure 13.—Effect of time in clarifier on thin juice color, Saccharate milk defecation.

6. The *percentage recirculation* in first carbonation has a very great effect. Without recirculation or its equivalent it is not possible to clarify by settling. This is due to the fact that clumps of granules are said to be built up by recirculation (figures 21 and 22).
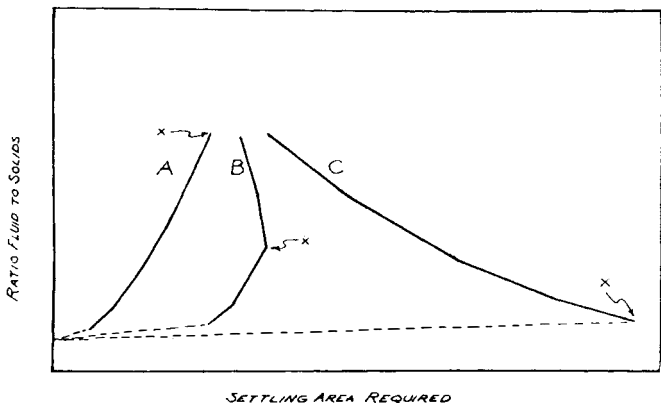


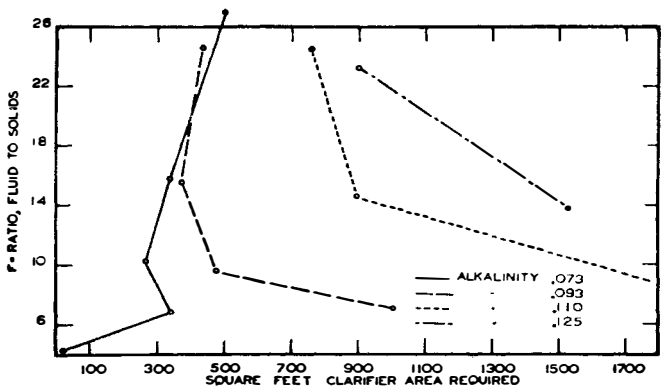Figure 14.—Three types of first carbonation mud settling curves.



Figure 15.—Effect of first carbonation alkalinity on mud settling curves. Saccharate milk defecation.
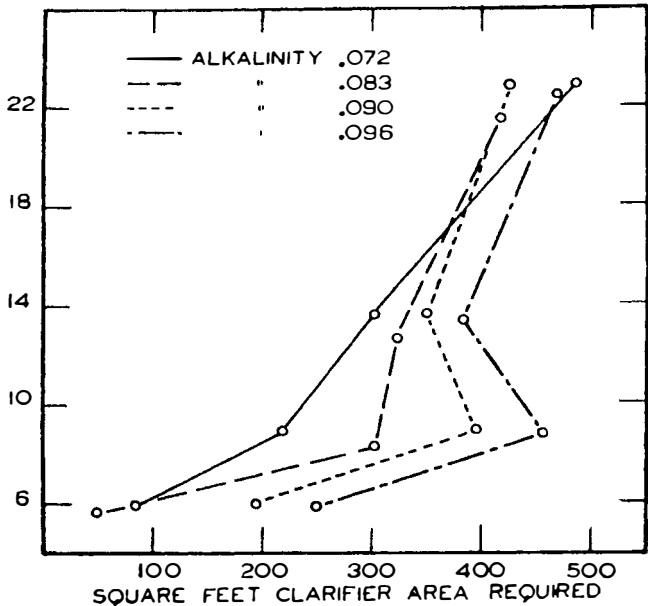
Figure 16.—Effect of first carbonation alkalinity on mud settling curves. Milk of lime defecation.

*Effect of Clarification on the Juice*

To be successful, the overflow from the clarifier must be reasonably clear. If it cannot be made so, it must be subjected to an auxiliary pressure filtration, and much of the savings made possible by the use of the clarifier are lost. Actually, appreciable amounts of mud can be tolerated in the overflow without causing appreciable degradation of the thin juice. The process was designed to yield an overflow containing not more than 0.0025 percent dry mud on the weight of juice. Experiments have shown us that at least 10 times that amount of mud can be tolerated without producing any measurable degradation. A better juice will in general result from operating with a very slight degree of turbidity and a high alkalinity, rather than with a lower alkalinity and a perfectly clear overflow.
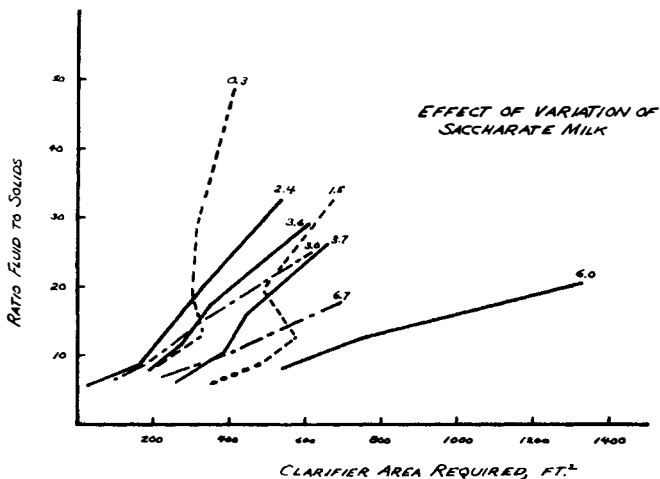
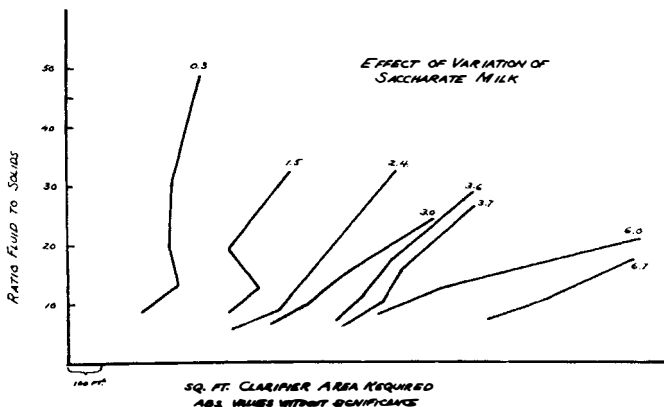Figure 17.—Effect of varying amount of saccharate milk on first carbonation mud settling curves.



Figure 18.—The curves of figure 17 displaced along the X axis to show the change of curve shape with amount of saccharate milk.
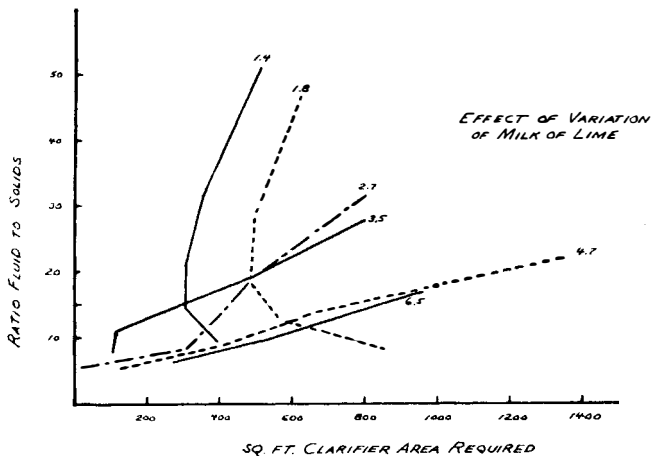
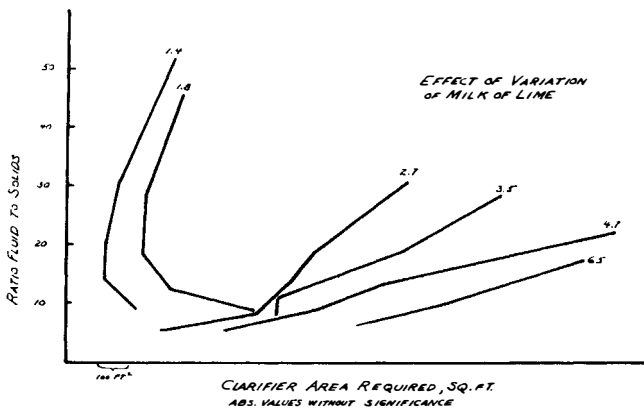Figure 19.—Effect of varying amount of milk of lime on first carbonation mud settling curves.



Figure 20.—The curves of figure 19 displaced along the X axis to show the change of curve shape with amount of saccharate milk.

*Comparison of Continuous with Batch Carbonation*

We have seen that many compromises must be made in adjusting the various variables of continuous first carbonation to their optimum operating positions. The whole system seems to us to be, in itself, a great compromise, in which there is some sacrifice in juice quality to make available the great savings in labor and materials over the batch system.
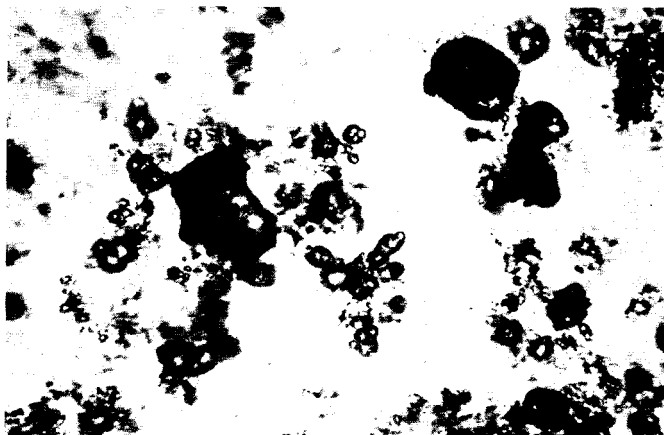


Figure 21.—Microphotograph of Dorr system first carbonation mud. Note clumps of calcium carbonate particles. x 1000.

Following are the results of four tests, in which direct comparisons were made between continuous and batch carbonation. In each of these tests factory raw juice was used as well as factory saccharate milk. Each sample of raw juice was divided into two parts, and one part then processed by the continuous method and the other by the traditional batch method. The same amount of lime was used in each, the same terminal alkalinities (about 0.080), the same temperatures (80° C.) and the same retention times (27 minutes). Second carbonation was identical for both.

In table 3 is given the percentage of lime salts, color and colloids in the thin juice resulting from continuous carbonation.

Thus on the average, the continuous system of carbonation produced 43 percent more lime salts, 67 percent more color, and 21 percent more colloids than the batch method.
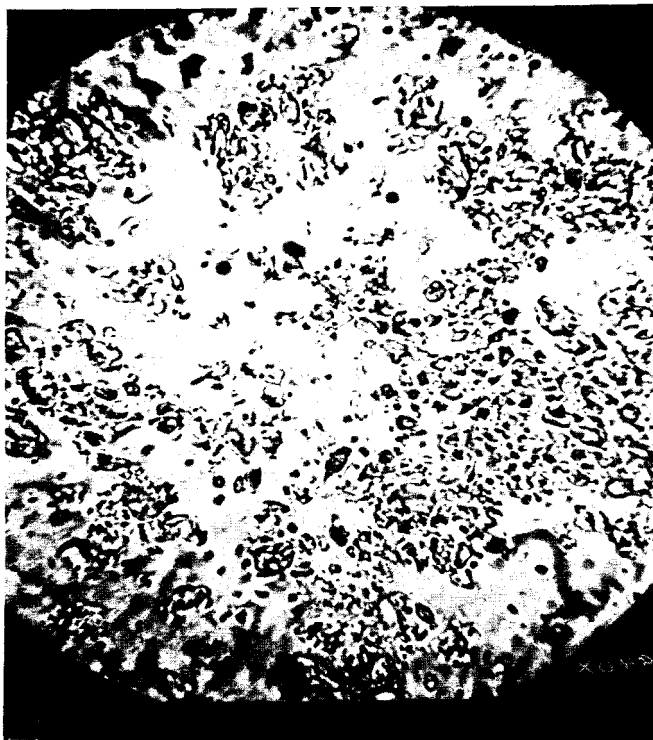
Figure 22.—Microphotograph of first carbonation mud produced by standard batch system defecation. x 1000.

As a further matter of interest, the final second carbonation juices from each of the parts of test 4 were sulfured with 0.007 percent $SO_2$ on 10 RDS juice, and were then concentrated for 1 hour under vacuum to 1/3 the original volumes. The samples were then diluted back to 10 RDS and their transmittancies redetermined (table 4).

These results indicate that within the limits of error the color of batch carbonation juice does not increase more rapidly in the evaporators than that from continuous carbonation.

**Table 3.**—Percentage lime salts, color and colloids in thin juice from continuous carbonation calculated on the results obtained from batch carbonation.

| Test No. | 1 | 2 | 3 | 4 | Average |
|---|---|---|---|---|---|
| Lime salts | 138 | 168 | 138 | 126 | 143 |
| Color | 155 | 143 | 200 | 168 | 167 |
| Colloids | 121 | 97 | 97 | 168 | 121 |

**Table 4.**—Comparison of colors of thin and thick juices originating in batch and continuous carbonation.

| | Continuous | Batch | Difference |
|---|---|---|---|
| Color, thin juice | .342 | .204 | .138 |
| Color, after adding $SO_2$ | .317 | .189 | .128 |
| Color, thick juice | .348 | .214 | .134 |

*Centrifugal Separation of First Carbonation Mud*

In an effort to move the balance point of this compromise further toward the side of better juice quality, an adaptation of the process was contemplated which, if it had been successful, would have eliminated the clarifier retention time and enabled operation of first carbonation to be carried out at the optimum alkalinity for juice quality.

A pilot plant was set up and arrangements made for experiments to be conducted in cooperation with the Merco Centrifugal Company, in which the attempt was made to separate the first carbonation mud by the use of the solid bowl continuous centrifugal.

It was found that the centrifugal would indeed separate the mud, and it made no difference in its separation whether the alkalinity of first carbonation was 0.060 or 0.130, or even whether or not there was recirculation in first carbonation.

Apparently the centrifugal exerted a powerful shearing force on the mud, which was not found in the batch type solid bowl centrifugal, and which broke up the agglomerates of calcium carbonate crystals. There was no difficulty in obtaining a high density underflow from the centrifugal, but it could not be filtered on rotary vacuum filters because the agglomerates had been broken up and the small pieces sealed the filter cloth. The centrifugals were relatively expensive, and the project was abandoned.

## Conclusion

In conclusion we wish to restate that the purpose of this paper was to review work done to determine the optimum settings for the various variables in Dorr system continuous first carbonation. While other systems of carbonation may be superior in certain respects, we have never found one which, as a whole, would be more economically advantageous for us.

## Literature Cited

(1) COE, H. S. AND CLEVENGER, G. H.
        1916. Trans. Am. Inst. Mining Met. Engrs., 55, 356.

(2) DEDEK, J.
        1939. J. Fabr. Sucre, 80, 63.

(3) SKAAR, K. S. AND McGINNIS, R. A.
        1944. Ind. and Eng. Chem., 36, 574.