Carbonate of Lime: Its Revivification and Use as a Filtering Medium

By G. C. Dymond

The following paper was then read by Mr. G. C. Dymond:—

Clarification of Uba Juice.

Adverting to our juices and their treatment, the first step usually taken in varying degrees of efficiency is the elimination of a portion of the fine particles from the juice by means of screens. The gradual evolution of more effective screening devices is evidence of the recognition of the inadequacy of our clarification process of effecting the same object.

The addition of a filtering medium whereby the whole juice may be filtered at a comparatively low temperature exists only in carbonatation. This process is unfortunately a comparatively expensive one, and is in any case unsuited to the production of Raws for a central refinery.

The following suggestions are modifications of carbonatation based on one dominating factor.

The success of carbonatation lies in the physical condition of its filtering medium, a flocculent form of calcium carbonate formed only under specified conditions.

No amount of grinding calcite will ever produce anything approaching this physical formation.

This condition is a constant up to such time as it is again dissociated by heat into CaO and CO_2.

Thus if carbonatation press-cake, which contains approximately 60% water, 30% $CaCO_3$, and 10% of organic matter, be burnt, an ash can be obtained containing roughly 100% $CaCO_3$ or 100% CaO, according to the temperature employed in the operation.

In practice it will be found that an efficient ash can be obtained at temperatures which at least dissociate from 5—10% of the carbonate into CaO, and this is the lowest quantity of free lime required in one of the following processes.

Suggestions for Use in the Carbonatation Process.

The huge quantity of limestone used in this process might be greatly reduced by the intelligent revivification of the same $CaCO_3$, which is discarded in the press-cake.

It might be asked why this has not been done before in other countries? The answer is, no doubt, that limestone is so common and cheap that it has never been considered.

The re-utilisation of the press-cake for carbonatation may be accomplished in a variety of ways.

For example, the cake may be burnt at a dull red heat in a reverbatory furnace in order to destroy all the organic matter; the resulting ash may then be transferred to a high temperature kiln and dissociated into CaO and CO_2, and the process continued as usual. Or, the cake need not be transferred to a high temperature kiln, but burnt in a reverberatory furnace at a bright red heat, whereby an ash containing 20—70% or more carbonate can be obtained, and this can then be mixed with the fresh slaked lime from limestone. This carbonate, it must be remembered, has still the same physical characteristics of that originally produced by the union of CaO and CO_2 in the juice. It mixes very rapidly with water, forming a remarkably smooth milk, and from a number of experiments can be used over and over apparently indefinitely.

The above suggestions have been carried out without any hitch in the laboratory. Unfortunately, no means of demonstrating their practicability on a larger scale have been available up to the present.

The actual kind of furnace required is unknown, but mention was made in a Sugar Journal some years ago of an excellent cement which was being made in France from the lime obtained from beet carbonatation press-cake.

The Utilisation of Carbonatation Press-Cake in other Factories.

The carbonatation press-cake may be efficiently burnt as stated above so that the resulting ash has a CaO content of about 5—10%, and this can very effectively be used in any factory for the production of either Raws or Whites.

The difficulty may be to make a normal net titre raw sugar, but there will be no complaints from the refineries or from the Home market where the serious position of high SO_2 contents has arisen.

Assuming, for example, that a source of supply is available. The carbonate of lime ash containing 5—10% of free lime is made into a milk containing, say, 33% of dry substance. 7½—15% of this is added to the cold mixed juice.

The amount required fluctuates with the percentage of free CaO in the ash and the quality of the juice. Thus it will be found that an ash containing 5% of free lime requires 15% to be added and an ash containing 10% only 7½%. The latter only contains 50% of carbonate employed in the former, but the same amount of free lime.

This free lime must normally be kept under control, as it has subsequently to be neutralised by SO_2 or phosphoric acid.

The carbonate present is the physical filtering medium.

Juices so treated in the cold will give a mud one quarter to one-fifth of the total volume in two hours. No fermentation occurs, the microorganisms being all enveloped in the filtering medium.

The juice may be pre-heated to 60°C.; but bearing in mind the recent discoveries on gums it is not essential.

The juice is run into ordinary subsiders and decanted.

The muds are diluted and pressed cold and the cake washed to a low sucrose content. This cake may then be collected and burnt and re-utilised in the same way an indefinite number of times, bearing in mind that 5—10% is always lost as CaO in solution with the juice.

The decanted juice and that from the presses is now heated to 70°C. and sulphited or phosphoric acid used alone. The latter is preferable as the resulting almost pure calcium phosphate has a marketable value.

The whole juice is now re-filtered, which it does very easily, yielding a brilliant, absolutely clear filtrate.

In this way all colloids and gums are removed from the juice immediately after crushing, thereby yielding a juice easily worked, which must result in a marked increase in recovery.

When no Carbonatation Press-Cake is Available.

In this case the process is somewhat more compilcated, but still simple.

The process commences with unslaked burnt lime, of which 200 tons plus 85 tons for making up the first week's supply of 152 tons of carbonate of lime are required for a crop of 200,000 tons of cane—that is, 2 lbs. per ton of cane as against 7—8 lbs. for defecation.

In cases of refractory juices the free lime has to be increased to 4 lbs. per ton of cane, and this can always be done by the addition of ordinary lime as in defecation.

In order to arrive at the amount required normally it is assumed that 8,000 tons of cane are crushed, yielding 1,600,000 gallons of mixed juice. At 2 lbs. per ton cane the amount required will be 8 tons of lime (CaO). Taking the amount of free lime required in the milk of carbonate of lime as 5% there will be 95% of the carbonate required for 152 tons. Therefore 160 tons of CaO and $CaCO_3$ are required for the first week's supply.

One gallon of the milk contains 3.3 lbs. of dry substance, so that 160 tons of dry substance represents 97.800 gallons of milk of carbonate of lime required to be in stock.

This represents .06 gallons per gallon of juice, or 1 gallon of the milk per 16.6 gallons of mixed juice.

Method of Preparing the Initial Milk of Carbonate of Lime.

Eight tons of lime are required, plus 85 for conversion into carbonate.

The amount of CO_2 gas required to convert 85 tons of lime (CaO) into 152 tons of carbonate ($CaCO_3$) is 66 tons or 132,000 lbs. Now one gallon of molasses can yield 3 lbs. of CO_2, so that 44,000 gallons of molasses are required to produce 132,000 lbs. of CO_2.

The molasses is fermented in closed fermentation tanks, a practice universally adopted nowadays in up-to-date distilleries, the gas drawn off and passed into the slaked lime which has been thinned down with water to the required density. The gas is passed until the required percentage of carbonate is obtained, when the milk is ready for use.

With regard to the 44,000 gallons of molasses required to produce 66 tons of CO_2, this quantity represents 220,000 gallons of wash for fermentation.

The Process.

The milk of carbonate of lime is added to the mixed juice, either cold or at 60°C., in the proportion of 1 of milk to 16.6 parts of mixed juice. The limed juice is agitated and run into subsiders, where it settles for the same time as in defecation.

The clarity of this first juice, within certain limits, is of no great importance.

The rate of subsidence, clarity of the juice, filtration rate of the muds, and quantity of defecose subsequently required are all dependent on the quantity of free lime originally present in the milk of carbonate of lime, or subsequently added.

The larger the amount of free lime, within reasonable limits, the better the subsequent clarification ,but the rate of subsidence and filtration of the first muds are greatly retarded.

This may, however, be obviated by passing the juice through a tower with some of the excess gas derived from fermentation, entering at the bottom, whereby the value of a little extra free lime is obtained, and increased subsiding and filtration subsequently obtained by increasing the amount of $CaCO_3$.

The muds from this settlement are treated with cold water and pressed. The cake is collected and burnt. The resulting ash consists of carbonate and a high or low percentage of free CaO, the amount fluctuating with the temperature and the length of time it has been in the furnace.

It is assumed that 25% of the original carbonate is dissociated into lime to ensure complete destruction of all organic matter present in the cake.

The resulting ash is mixed with water and passed again into the carbonating tank, where the percentage of carbonate is brought up to that required.

So, for the second week (and every week thereafter), although 8 tons of free lime and 152 tons of carbonate are required, 75% or 114 tons of carbonate have been recovered from the press-cake in the same form as that originally produced, while 38 tons, or 25%, have been dissociated into 21 tons of CaO. To reconvert this 21 tons of lime into 38 tons of carbonate 17 tons of CO_2 gas are required, which may be obtained by the fermentation of 11,300 gallons of molasses, representing 56,500 gallons of wash—that is, four to five days' work under poor fermenting conditions.

Total CO_2 Required for the Crop.

For the first week 66 tons of CO_2 are required, and thereafter 17 tons per week. Assuming, therefore, a twenty-six week crop, the amount required will be :—

First week	66 tons.
25 weeks (17 x 25)	425 tons.
Total	491 tons.

Gallons of molasses required to produce 491 tons or 982,000 lbs. CO_2 gas = 327,300, representing 1,638,500 gallons of wash.

Acutally 1,000,000 gallons of molasses are available, representing 5,000,000 lbs. of CO_2.

It is likely, however, that the available molasses under the conditions of this process will be reduced.

Press-Cake.

The composition of the first cake is, roughly :—

60% water.
30% $CaCO_3$.
10% organic matter.

One week's press-cake is therefore constituted as follows :—

304 tons of water.
152 tons $CaCO_3$.
51 tons organic matter.

Total = 507 tons or 6.34% on cane. This amount must be burnt every week.

Clarification of the Juice.

The partially clarified juice from the subsiders and press juice is alkaline and contains in solution that amount of free lime calculated originally at 2 lbs. per ton cane.

The juice is now raised to 80°C. and may be first sulphited and then tempered with phosphoric, or the latter only employed. The whole is then filtered very easily and quickly.

The cake consists of water, calcium phosphate, and a little organic matter, this amount varying with the quality of the first clarification. This cake is valuable either as a fertiliser or may be reconverted into phosphoric acid by means of sulphuric.

A point worthy of note is that the amount of fermented wash required to produce 491 tons of CO_2 is capable of yielding 130,920 gallons of motor fuel containing alcohol and ether.

The cost of production of such fuel would be much lower than normal, owing to the fact that it becomes now a secondary product.

The foregoing methods were developed three years ago, primarily for the production of white sugar. As carbonatation is too good a process to waste on the production of raw sugar, so these processes involving the use of phosphoric acid and double filtration would render a central refinery redundant.

The only chemical used in Hawaii is lime, where only 1.75 lbs. are used per ton of cane. The resulting juice has a pH frequently above 8. Were such a simple procedure attempted in this country, you can all imagine what would happen.

If, however, sufficient properly prepared carbonate of lime be added as well, there comes a point at which the whole juice may be readily filtered in ordinary presses. The resulting juice is then equal to the Hawaiian juice, and there appears no reason why a raw sugar equal to theirs should not be produced without the use of either sulphurous or phosphorous acid ; thereby not only solving the SO_2 in raw sugar problem, but also decreasing the cost of production.

No work other than laboratory experiments has so far been attempted on the foregoing processes. It is to the interest of the Industry to prove whether these processes or modifications thereof are practical propositions under factory conditions.

One other use for carbonate of lime should not be overlooked, and that is its use in the treatment of effluents. Its revivification and neutralisation are here again simple and practical.

Chairman: These papers to my mind illustrate very well the remarkable powers of observation and originality of the writer. We took the liberty of dividing them into two separate papers because it seemed to us that the subjects treated were fundamentally different, one part dealing with the effect of mealy bug and the other with the possible utilisation of calcium carbonate. Both of them are of very great interest and importance.

To refer to the mealy bugs, although they have been recognised as a minor pest for a good many years, I don't think any of us realised what an effect they might possibly be having on the clarification of juice, and it is a very good thing to have this pointed out. In other countries, particularly in Louisiana. I don't think they can possibly have had the same results or effects on the clarification. The occurrence of the mealy bug was studied with considerable detail in that country some years ago and it was noticed that certain districts were very much infested while others were almost free, and I think it would have been noticed had there been any marked difference in the clarification of the juice between the two. However, not only are conditions different, but it was a different species of insect. Although they are both classed as mealy bug, the one in Louisiana is known as Pseudococcus calceolaria and mainly inhabits the lower portions of the cane, whereas under our conditions our species (P. sacchari) is always found near the growing point.

Both these papers are very interesting and suggest many new ideas for your consideration. The revivification of carbonate of lime is also a very fascinating possibility. It occurs to one, perhaps, that there must necessarily be a rapid accumulation of inorganic insoluble impurity in any material used as a settling medium which would eventually render its revivification impracticable, but no doubt it could be done for several times at all events.

Mr. Dymond: The increase in inorganic matter is considered especially as regards sand and so on. Certain minute portions of sand in a very fine state, even clay, were added to it but I think it can be obviated by simple washing. I used the same portion over and over again—about sixteen times—and at the end of that after re-burning it did not seem to give quite such good results as the original, but all I did was to burn it again, mix it with water and decanted it off the top and it seemed quite all right. I used it over and over again indefinitely.

Mr. Moberly: In connection with the mealy bug, is this gum precipitated by alcohol? I asked that because in Louisiana we used to get something in certain of the juices which caused an extraordinarily high apparent purity, and we found that by treating it with alcohol we got precipitation of a dextro-rotatory gum and thereby a normal purity.

Mr. Dymond: From experiments I carried out I found these gums are not precipitated except in very small amounts of alcohol.

Mr. Booth: You realise that this sweeps the Fahey Agreement off the board inasmuch as all this bonus business must be reconsidered?

Mr. Dymond: I don't think so. You know the Fahey Agreement was based on certain figures which were based on old methods and present methods in determining bagasse.

Mr. McRae: In that connection you might find Mr. Moberly having to add to his staff a number of bug-hunters!—(Laughter). I think Mr. Dymond ought to be heartily congratulated on this paper, opening up as it does a new subject. Mr. Dymond mentions polarization; that I take it to be what we call apparent sucrose. Don't you think it would take rather a large proportion of mealy bug on a stick of cane to have any effect on the sucrose content? Perhaps you could give us some idea of the average per cent. of mealy bug on cane.

Mr. Dymond: That varies considerably, from nothing at all to four grammes per stick. I have not collected and weighed many but have sent two or three Indian boys out and they come back in a couple of hours with sufficient weight to do the polarization.

Mr. McRae: At the Experiment Station when we received Mr. Dymond's paper we went bug-hunting, and it took us a long time to get enough to do any experiments with. There are two other points in connection with Mr. Dymond's experiments. Mr. Dymond talks about drying bagasse and extracting with ether. He probably carried out experiments to ascertain whether there was any inversion on drying bagasse. I think it seems quite likely that in drying bagasse you would get inversion taking place. The second point is with regard to extracting mixed juice with ether to see what effect the ether might have on the polarization. A while ago we made up a sugar solution at the Experiment Station and we extracted that with ether, and to our surprise we found that it dropped two degrees in polarization. No doubt Mr. Dymond completely removed the ether before re-polarizing. However, this subject which Mr. Dymond has introduced opens up a big avenue for research work in this connection and I think it is to be hoped that in the coming year more people will carry out experiments in this direction.

Mr. Dymond: My object in this paper was purely to open up new ideas. Regarding the point Mr. McRae has mentioned, we were afraid of inversion but there are two points to consider in determining the drop in sucrose in the bagasse. First of all the bagasse was neutralised and then dried. We did a lot of work without drying it and extracting it with ether but I fear that the water could be taken away by the decanted ether to a certain extent. You cannot separate the two efficiently on decantation to start with. I quite appreciate the point and we were afraid the possibility of an error might creep in by the heating of bagasse which has to be done to remove the final traces of ether. The same difficulty arose in extracting the mixed juice. I don't know if any of you have ever shaken up mixed juice with ether; you will be astonished if you do. The inter-surface becomes exactly like a jelly; it is quite impossible to separate the two entirely, there is always a certain amount of water mingled with the ether layer and it is very difficult to remove all the ether from the lower layer of water. Only by evaporation and drying off the ether in that way were we able to get rid of it all.

Mr. Bechard: In Mr. Dymond's paper on carbonate of lime he gives us some useful information. I was wondering if he has considered the possibility of utilising the CO_2 from the furnace.

Mr. de Froberville: When I read Mr. Dymond's paper I asked "why do you go to the commercial form of CO_2," why not get the gases from the chimney, you can use it for the carbonatation of your lime and afterwards." I don't know whether he has considered that proposition.

Chairman: I think our appreciation is due to the person or persons who collected normal weights of mealy bug for Mr. Dymond (laughter). As Mr. McRae has told you we had a shot at collecting them at the Experiment Station, and we found it quite a tedious business. However, that brings us to another point. Evidently mealy bug is much more prevalent in the cane at Empangeni than in that surrounding the Experiment Station and since this question is of greater importance than it has been supposed, it shows the desirability of a proper entomological study of this insect pest under our conditions, such as we have not yet had. As far as I know the only attempt at control even has been the liberation of specimens of the Australian Ladybird beetles, Cupressus montrozouri, which apparently did not establish themselves in our fields. At all events no specimens could be found after liberation, and observations by Mr. Van der Merwe when he was stationed here as Entomologist were to the effect that Uba with its closely clinging leaves formed a barrier which protected the mealy bug from this insect parasite What is the chief natural control of the mealy bug is difficult to say, but probably the Aspergillus which Mr. Dymond mentions is a principal one.

Mr. Dymond: In your search for mealy bugs you may not be successful in finding them because at certain periods of the year they are not very prolific, but the deposits are almost as important as the mealy bug. If you don't find any actual living insect you will find their deposits, but I think you will find them under almost every leaf of cane except such as are free trashing canes. If you take those deposits you will get almost the same results, and I ascribe a lot of our trouble after rains to that fact. We had about three or four days rain about the beginning of the year and I went out to the fields, but was not able to secure any living insects However, I found under the leaves lumps of jelly which had swollen up with the rain, and there were green and pink Aspergillus feeding greedily on them. That deposit underneath the leaf is the mealy bug deposit and if you boil that up you will get almost the same result as boiling up the insects.

Mr. Dymond was accorded a very hearty vote of thanks for his excellent work.