

THE USE OF SODIUM HEXA METAPHOSPHATE FOR PREVENTING THE FORMATION OF CALCIUM OXALATE SCALE IN EVAPORATORS DURING THE MANUFACTURE OF SOLID WATTLE BARK EXTRACT

By D. M. RICE.

Presented by D. R. SCHLEISS

Summary.

It is of course appreciated that the scale in sugar evaporators is of a different chemical composition from that found in tannin evaporators, but the physical principles of its formation are undoubtedly similar, and it is possible therefore that its prevention may be accomplished on similar lines.

When the liquor obtained from the extraction of wattle bark is concentrated in multiple-effect evaporators, a hard scale consisting mainly of calcium oxalate is formed. The quantity of this scale produced appears to be directly proportional to the concentration of calcium ions in excess of a critical value, which is assumed to be a function of the solubility of calcium oxalate under the prevailing conditions.

The scale can be reduced in quantity, although not entirely eliminated, by preventing the introduction into the system of any foreign calcium salts. The addition of sodium hexa metaphosphate, equivalent as a sequestering agent to the amount of calcium in excess of the above assumed solubility value of calcium oxalate, has, however, been found to prevent the scale altogether, and an excess of metaphosphate to have a softening and removing action on old deposits of scale.

Introduction.

Solid wattle bark extract, which is one of the world's foremost tanning materials, is prepared by extracting the chipped bark with water and concentrating the resultant solution in copper evaporators. This solution, known as "thin liquor," contains about 15 per cent. solid material and it passes continuously through multiple-effect evaporators, where it is concentrated to "thick liquor" containing about 50 per cent. solids. Thereafter, single-effect evaporators known as "finishers" concentrate this liquor in batches to the finished product with a residual moisture content of about 17 per cent.

During the initial evaporation in the multiple-effect evaporators, a very troublesome hard scale, consisting mainly of calcium oxalate, normally forms, and frequent regular removal of this deposit by chipping and scraping has in the past been necessary. Such drastic mechanical methods of cleaning are usually very undesirable, and this is especially so in

the case where the plant is constructed of relatively soft non-ferrous metal. Furthermore, the labour required for manual cleaning, and the fact that this can be carried out only while the plant is not operating, are also factors to be considered.

The Character of the Scale.

Where triple-effect evaporators are employed using parallel current operation, the most troublesome scale has always formed in the second and third effects. This scale, of whitish colour, has been hard and rather crystalline. The relative and the total quantities found in these effects have varied considerably from time to time, but the reasons for this have been rather obscure.

Compared with that in the third effect, the scale in the second has been of a finer particle structure and has given the impression of forming as a result of evaporation rather than by cooling. In the third effects, the scale has consisted of much larger crystalline particles, and deposition of such material has continued on all surfaces in contact with the liquid where cooling could occur. Thus, in addition to the scale forming in the evaporator tubes where it had its most adverse effect on the efficiency of the plant, it was also to be found in all the outlet pipes and pumps removing the concentrated liquor.

A deposit has also appeared in the first effects which are usually operated at about atmospheric pressure, but this has differed somewhat from that forming in the later stages. It has been blackish in colour and of a powdery nature, and, although small amounts of the white scale have been detected at times in the upper portions of the first effects, the deposit has generally never been of a serious nature. Samples analysed have shown it to consist of about 83 per cent. organic material and the remainder copper, iron, aluminium and calcium.

Preliminary Experimental Work.

Attention has been largely concentrated on the scale formed in the second and third effects which had been found to consist essentially of calcium oxalate, although small amounts of other metals were also present.

No success at all was achieved when attempts were made to produce this type of scale in a copper

evaporator in the laboratory, even though in some cases the concentrations of the component scale forming ions were deliberately increased.

Investigation of the problem has consequently not been simplified by being able to reproduce factory conditions on a laboratory scale.

Several possible methods of preventing the scale have been considered, but owing to this very limiting restriction, little in the way of testing has been attempted. It was possible to test the effect of electrolytic action on the scale formation and several preliminary experiments were carried out, but the results were far from encouraging.

The prevention of the scale by the addition of metaphosphate was one of the possibilities considered, although, owing to the lack of knowledge of the whole problem, no special importance could at first be attached to any one particular method. However, when laboratory tests indicated that calcium can be prevented from being precipitated as the oxalate in extract liquor by the presence of metaphosphate, it was realised that this was a likely practical solution to the problem. Owing to the failure to produce scale in the laboratory evaporator, small scale tests of any real value were not possible, and arrangements were made to conduct large scale factory trials. It was decided to start the experiments using a larger quantity of metaphosphate than would be economically possible in practice, and then if successful, to reduce the amount progressively until the minimum quantity possible had been found.

The evaporators could only be opened for inspection at week-ends and accordingly each test lasted a week. For the first two weeks amounts of metaphosphate considerably in excess of that later found to be necessary were used. In these cases there was no sign of scale on the hotter parts of the evaporators such as in the tubes, but on the cooler parts and in the thick liquor pumps quite a heavy deposit had formed, which was of an entirely new type compared with any previously encountered. It was fairly easily removed and contained a fair amount of phosphate as shown by its analysis:

Organic matter	62.2 per cent.
Calcium (CaO)	31.6 per cent.
Phosphate (P ₂ O ₅)	6.20 per cent.

This deposit which did not, however, appear when the amount of metaphosphate was reduced, was apparently caused by too large an excess being used, and this is not likely to occur in normal practice.

It was also shown in the early experiments when large quantities of metaphosphate were used, that after passing through an evaporator, the metaphosphate in the liquor had apparently lost its beneficial character owing probably to instability of the complex under the effect of prolonged heating. In a case where two evaporators were used in series, a heavy

dosage of metaphosphate in the first caused a considerable quantity of black powdery material to be deposited in the first and hottest effect of the second evaporator, the analysis of which is as follows:

Organic matter	81.5 per cent.
Calcium	14.8 per cent.
Phosphate	2.6 per cent.
Copper, iron, etc.	1.1 per cent.

In view of this, the single effect evaporators, which concentrate the thick liquor after it leaves the multiple effect evaporators, were kept under careful observation. Nothing more than about the usual amount of deposit was found in these evaporators, although the material now contained phosphate as shown by its analysis:

Organic matter	80.2 per cent.
Calcium (CaO)	18.0 per cent.
Phosphate (P ₂ O ₅)	1.8 per cent.

A strict watch was also kept for any possible detrimental effect of the metaphosphate on the extract, but even when a large excess was being added, no significant difference could be detected. In fact, it was firmly believed by factory personnel that the greater quantities of metaphosphate had a beneficial effect on the colour of extract. This can be explained by a possible inhibiting action of the metaphosphate on the multivalent metal catalysts present, although no conclusive evidence in this direction could be obtained.

A quantity of metaphosphate as large as 1 lb. for every ton of extract manufactured increases the mineral ash content, expressed as a percentage of dry extract by only about 0.05, which is seen to be insignificant when it is realised that the normal mineral ash can vary naturally between about 1.3 per cent. to 1.9 per cent. Moreover, the constituents of metaphosphate, sodium and phosphorus, occur naturally in wattle extract in varying amounts.

Development of the Use of Metaphosphate and Theoretical Considerations.

Owing to the initial success obtained with metaphosphate, it was decided to continue the trials on a much larger scale and its use was introduced at all factories of The Natal Tanning Extract Co. Ltd.

The quantity of metaphosphate required at the different factories for keeping the evaporators free from scale ranged between about 0.5 lb. and 1 lb. per ton of extract manufactured, and in view of the high cost of metaphosphate, this difference was of special interest. One difference between the methods of operation at the various factories, which appeared to bear some relation to the metaphosphate required, was the amount of raw water used for extraction purposes. Where this was greater, a greater amount of metaphosphate appeared to be necessary, and

this suggested that possibly the extra calcium entering the system from that source was the cause. This hypothesis was supported by the fact that on a previous occasion when for a short period raw water was used which contained a slightly increased calcium content owing to the clarification treatment employed, considerably more scale than usual was found. Furthermore, it was an established fact that the quantity of scale increased when a greater proportion of "dry" bark was processed in the place of fresh "green" bark, the former being the material which has been allowed to dry to a moisture content at which storage without deterioration is possible. There is consequently considerably more water required for the extraction of dry bark than for green, and this has therefore led to the introduction of increased quantities of raw calcium-containing water as greater proportions of dry bark have been used. This is illustrated by the following data on the water used in the process.

The Quantity of Water Involved in the Manufacture of Wattle Bark Extract.

The following figures are based on some average practical results and can be taken as fairly representative. For convenience and simplicity, a figure of one ton of extract (at 17 per cent. moisture) is taken as a basis, and the quantities of material shown are associated with the manufacture of this quantity of extract.

Analysis of bark considered—

Type	I <i>Green</i>	II <i>Green</i>	III <i>Dry</i>
Extractives	26.9%	28.5%	47.3%
Fibre	23.1%	24.5%	39.7%
Moisture	50.0%	47.0%	13.0%

Water at different stages of process—

	Bark	I	II	III
Moisture	50%	47%	47%	13%
(1) Water in original bark	1.67 tons	1.48 tons	1.48 tons	0.23 tons
(2) Water in spent bark (about 70 per cent. moisture)	1.83 tons	1.83 tons	1.83 tons	1.83 tons
(3) Water in thin liquor (15 per cent. concentration)	4.97 tons	4.97 tons	4.97 tons	4.97 tons
(4) Water in thick liquor (50 per cent. concentration)	1.12 tons	1.12 tons	1.12 tons	1.12 tons
(5) Water in extract (17 per cent. moisture)	0.17 tons	0.17 tons	0.17 tons	0.17 tons

Water balance—

	Bark <i>tons.</i>	I <i>tons.</i>	II <i>tons.</i>	III <i>tons.</i>
Total water required for process (2+3)	6.80	6.80	6.80	6.80
Water present in bark	1.67	1.48	1.48	0.23
Total water to be added	5.13	5.32	5.32	6.57
Water available as condensate from multiple-effect evaporators (3-4)	3.85	3.85	3.85	3.85
Remainder required	1.28	1.47	1.47	2.72
Water available as condensate from "Finishers" (4-5)	0.95	0.95	0.95	0.95
Make-up water required	0.33	0.52	0.52	1.77

Subsequent calculations, as shown below, indicated that the amount of metaphosphate, if presumed to

behave as a sequestering agent, required to react with the extra calcium introduced into the thin liquor, when a fair amount of raw water was being used, was of the order of $\frac{1}{2}$ lb. for each ton of extract. This was additional evidence in favour of the above assumption, and steps were immediately taken to reduce the amount of raw water used for extraction purposes to a minimum by substituting as much evaporator condensate as possible in its place.

It was found that the amount of metaphosphate necessary was then reduced to about $\frac{1}{2}$ lb. from about 1 lb. which, in this case, had previously been required for each ton of extract. Apart from its economic and practical value, this discovery is of considerable theoretical interest. It shows that only about 2 per cent. of the naturally occurring calcium in the thin liquor is liable to form scale in the multiple effect evaporators. This indicates that the remainder of the calcium, in whatever form it is present, remains normally in solution under the existing conditions. It also suggests that, under the circumstances, the concentration of oxalate ions exceeds the equivalent of the calcium present, and any increase in this calcium produces an increase in the calcium oxalate deposited out of solution.

Theoretical Amounts of Metaphosphate Required.

When metaphosphate is used generally for the prevention of calcium scale, it reacts as either a sequestering agent, in which case it persists in its original form, and takes calcium into its complex molecule, thereby causing the calcium to lose its usual properties, or as a normal phosphate, when the calcium is precipitated as the non-scale forming phosphate compound.

As a sequestering agent metaphosphate, $\text{Na}_2(\text{Na}_4\text{P}_6\text{O}_{18})$, forms the compound $\text{Na}_2(\text{Ca}_2\text{P}_6\text{O}_{18})$ when it reacts with calcium and therefore—

7.65 parts metaphosphate are required for 1 part calcium; or

3.06 parts metaphosphate are required for 1 part calcium carbonate.

Metaphosphate required for raw water used (as above when 1 lb. metaphosphate/ton extract was required):

(Again 1 ton extract as basis).

Raw make-up water used for extraction (very approximate)	10,000 lbs.
Calcium (as carbonate) in raw make-up water	0.175 lbs.
Metaphosphate required to react with the calcium in the raw make-up water	0.540 lbs.

It can be assumed, however, that a portion of this calcium becomes associated with the spent bark which is discharged at a moisture content of about 70 per cent., and a smaller amount of metaphosphate is consequently required.

If the calcium from the raw water becomes evenly distributed in the water throughout the system, the quantity removed by the spent bark will, therefore, be—

$$\frac{0.175 \times 1.83}{6.80} \times \frac{\text{(water associated with spent bark)}}{\text{total water in process}} = 0.047 \text{ lb.}$$

leaving 0.128 lb. in the liquor which requires 0.4 lb. metaphosphate.

In practice this is most probably not entirely the case, and this amount of metaphosphate necessary will lie somewhere between 0.4 lb. and 0.54 lb.

The indications were, therefore, that by using water free from calcium for extraction purposes, the amount of metaphosphate required would be reduced by about 0.5 lb.

As mentioned previously, this was approximately the case, and this is illustrated in the experimental

results set out below. It can also be seen that presumably about 0.5 lb. metaphosphate is required for every ton of extract to react with naturally occurring calcium. That this is only a small fraction of the total calcium, is shown by the following—

Total calcium in 1 ton extract (CaCO₃) 8.32 lbs.
Metaphosphate required to react with this calcium... .. 25.46 lbs.

Variations in the bark due to seasonal effects and also type and origin of the bark, most probably influence this quantity of metaphosphate required to prevent scale, but this factor has not come within the scope of these experiments.

Experimental Results.

The details of the experiments carried out at one factory are set out below, and all values here are again expressed with reference to one ton of finished extract.

I.	II.	III.	IV.	V.	
Test No.	Metaphosphate added (lb.)	Raw water used (tons).	Metaphosphate (lb.) required for raw water for raw water (lb.) in liquor.	Residual Metaphosphate	General condition of Evaporators.
1	2.720	5.25	0.542	2.178	Tubes very clean. Fair amount of scale on upper portions and in pumps.
2	1.913	5.16	0.533	1.380	Similar to previous week with slight decrease in quantity of scale.
3	0.942	5.14	0.531	0.411	Fair amount of scale in third effect tubes. Slight soft scale in pumps.
4	0.487	5.08	0.525	0.038	Third effect tubes fairly badly scaled. Pumps slightly scaled.
5	1.053	4.14	0.427	0.626	Fair amount of scale present.
6	1.040	4.16	0.430	0.610	Improving. Scale being removed. Pumps clean.
7	1.104	4.20	0.434	0.670	Very slight deposit left in third effect tubes. Pumps clean.
8	1.230	4.12	0.425	0.805	Evaporators very clean. Pumps slightly scaled.
9	1.007	4.14	0.427	0.580	Very slight scale in third effect tubes.
10	1.145	4.14	0.427	0.718	Everything very clean.
11	1.045	4.04	0.417	0.628	Slight scale in third effect tubes.
12	1.014	4.00	0.413	0.601	Very clean.
13	0.923	4.06	0.419	0.504	Slight deposit.
14	0.955	4.04	0.417	0.538	Slight deposit.
15	0.986	4.06	0.419	0.567	Clean.
16	1.012	4.13	0.426	0.596	Clean.
17	0.905	4.35	0.449	0.456	Slight scale and coarse deposit in third effect tubes.
18	0.943	4.25	0.439	0.504	Slight coarse deposit as in previous test.
During the following test the change over to the use of a very much reduced quantity of raw water was made.					
19	0.813	2.52	0.260	0.553	Everything fairly clean.
20	0.534	0.32	0.033	0.462	Very slight amount of coarse deposit in tubes of third effects.
21	0.485	0.25	0.026	0.459	A little more deposit than in previous test.
22	0.489	0.44	0.045	0.444	Further slight increase in amount of deposit.
23	0.508	0.45	0.047	0.461	Similar to previous test.
24	0.498	0.40	0.041	0.457	Fair amount of deposit present.
25	0.559	0.30	0.031	0.528	Improvement, showing excess present by removal of old deposit.
26	0.584	0.34	0.035	0.549	Fairly bad. Large unknown quantity of raw water inadvertently used.
27	0.790	0.28	0.029	0.761	Considerable improvement, although not yet clean.
28	0.792	0.30	0.031	0.761	Improvement continuing. Scale still being removed.

There was no means of checking the quantity of raw water used and an estimate of this figure for each test was made according to the above table of water requirements, and the calcium content of the raw water was taken as constant at the value mentioned above. Column IV represents the theoretical amount of metaphosphate required for the calcium in the raw water left in the liquor after the removal of an assumed quantity of about half the possible maximum in the spent bark. Column V shows the difference between Column IV and the amount of metaphosphate actually added and this should bear some relation to the condition of the evaporators, which can be seen to be the case. Some of this

metaphosphate must have been used up in some instances in removing scale remaining from previous tests, and there was also the ever-present possibility that the instability of metaphosphate could also affect the results. In addition, it was at times very difficult to assess the condition of the plant accurately. However, if due allowance is made for the discrepancies and approximations, it can be seen that the results do fit in fairly well together.

Acknowledgment.

I am indebted to the Natal Tanning Extract Ltd. for making these results available for publication.

The President said the presentation of this paper was very welcome; it came from a sister industry in Natal and showed that it had some of the difficulties which confronted sugar technologists.

Mr. Schleiss asked Dr. Douwes Dekker whether he had any information on the difference of silicate or calcium silicate, whether any attempt had been made to differentiate between the two and, if so, what the results were.

Dr. Douwes Dekker said that silicic acid scales were assumed to consist mainly of silicic acid usually combined with sesquioxides. Calcium silicate should also be present. He would like to know the pH of the liquid entering the evaporator and the amount of P_2O_5 giving the best results.

Mr. Schleiss said that the pH was fairly low. He thought Dr. Haynes could give an accurate figure. The amount of P_2O_5 worked out at about forty parts per million.

Mr. Rault said the use of river water for imbibition of bagasse, with its amount of hardness, instead of evaporator condensed water might also be a contributor to incrustation, apart from its ash-sugar combining effect in molasses formation. He had determined for a number of years the average ash content of the raw and clarified juice as well as final molasses and also the complete per cent. composition of the ash of these three products.

Occasional tests on evaporator scale had indicated lime sulphite and sulphate, rather than carbonates or phosphates and magnesia, as being the main constituents of the scale. The determination of oxalic acid was not so easy in the presence of organic and SO_2 components.

The lbs. of water evaporated per sq. ft. per hour, should also be of interest, as all factories were not balanced in evaporator capacity and higher syrup concentration threw more solids out of solution.

The determination of hardness by the soap test, as an indication of the lime content of clarified juice, was a useful indication of every-day control in his factory—although it did not always follow that intensity of incrustation was proportional to total lime salts, a good part of which could keep their

solubility right to the molasses stage. Work on this subject should be undertaken and every factory should use the soap test on clarified juice. This test would also include magnesia as well as lime, but if only lime determination was required, oxalate precipitation titrated by permanganate could occasionally be used.

Mr. Dymond said that Mr. Rault had complicated the subject by bringing the quality of water supplies into the question of scale formation. These varied greatly and as the salts in solution contributed through imbibition to the salts present in cane juices and to those added by the chemical methods of clarification, water supplies might have a certain bearing on types of scales found throughout the sugar belt. The only sure way of eliminating scale formation was by the ion exchange process, which seemed to have gone underground recently. The process was said to be too expensive, but to his knowledge a true balance sheet had never been drawn up. Further research should be done on this revolutionary process, for if it could be proved economically sound, refinery conditions would exist on their doorsteps.

Dr. Douwes Dekker considered the result of the soap test as such, and expressed the view that it was a useful type of information, since attempts to reduce the lime salts content of clarified juice could be guided by this simple analytical method. In Mauritius the soap test had recently been introduced as routine analysis and he would like to see this happen in Natal as well. Part of the magnesium salts was always included in the result of the soap test, but this was not a serious shortcoming if it was kept in mind.

Mr. Dymond said that as everyone was unanimous that the soap test should be carried out, he would see to it that this matter was discussed by Council and eventually brought in as a routine test at the mills.

Mr. Schleiss said there was a test which enabled one to distinguish clearly and easily, by volumetric analysis, between magnesium and calcium in solutions. Tests on this new method would be undertaken by African Explosives & Chemical Industries at the Umbogintwini factory in the near future.