

ANALYSES OF BOILER-FEED (MAKE-UP) WATER IN NATAL.

By J. L. DU TOIT.

INTRODUCTION.

In the report⁴ for the year ending April, 1940, the Chemical Control Committee stressed the necessity for strict boiler control—a field which in the past had been rather overlooked. The water used as make-up in Natal is in most factories obtained directly from rivers or dams, and only in a few treated before entering the boilers. Chemical control leaves a lot to be desired, considering the valuable plant involved.

The Committee afterwards decided that a general survey of the inorganic constituents of the water used in our factories may serve a useful purpose. Arrangements were made to send samples of make-up water from all the various factories to the Experiment Station, where the necessary analyses were done.

GENERAL.

The crushing season in Natal coincides with the dry season. This may give rise to stagnant water contaminated with a certain amount of organic acids, as was pointed out by Camden Smith³. The inorganic impurities are also increased. This unfavourable condition was accentuated by the fact that 1941, the year in which this survey was undertaken, was one of the driest on record. It is therefore likely that the waters will be of somewhat better quality in normal years.

The sugar belt is situated mostly on the following geological formations: Ecca, dwyka, Table Mountain sandstone and granite. Table Mountain sandstone and granite are generally found somewhat further inland. The former has the reputation of being a good water-bearing formation and the water is of a high purity. There is therefore a fairly wide variation in the amounts of soluble solids in the waters obtained from different localities and from various formations. Waters from factories Glen. and Nos. 9 and 3 are very pure, and it is interesting to compare the analyses of waters from factories Nos. 9 and 12, both drawing their water from the Nonoti, and factories Glen. and No. 19, getting their supply from the Umvoti.

Even in the same locality, however, variations are found. The following are the analyses of the Marshall and Dumat

dams, both of which are on ecca formation but the Marshall dam draws most of its water from the Umgeni.

	Marshall.	Dumat.	
Specific conductivity $\times 10^{-6}$	180	450	ohms ⁻¹ cm ⁻¹
Total solids	19.8	32.2	parts per 100,000
Suspended solids	5.7	4.3	parts per 100,000
Loss on ignition	3.5	5.1	parts per 100,000
Chlorides (Cl)... ..	2.1	7.1	parts per 100,000
Sulphate (SO ₃)	0.6	2.2	parts per 100,000
Silica (SiO ₂)	5.6	3.8	parts per 100,000
Iron oxide, etc. (Fe ₂ O ₃ etc.)	2.9	2.5	parts per 100,000
Calcium oxide (CaO)	1.3	3.2	parts per 100,000
Magnesium oxide (MgO) ...	1.2	1.5	parts per 100,000
Total hardness	5.6	9.3	parts per 100,000 as CaCO ₃
pH	7.1	7.1	

Waters derived from boreholes or springs may vary even more. The analyses of two borehole waters from much the same locality as these two dams are given. The one water is from a borehole on the Experiment Station and the other from a nearby farm.

	Experiment Station.	Farm.	
Total solids	72.2	282.5	parts per 100,000
Chlorides (Cl)... ..	18.0	103.0	parts per 100,000
Sulphate (SO ₃)	2.2	1.4	parts per 100,000
Silica (SiO ₂)	—	4.0	parts per 100,000
Iron oxides, etc. (Fe ₂ O ₃ etc.)	0.4	0.6	parts per 100,000
Calcium oxide (CaO)	5.8	25.7	parts per 100,000
Magnesium oxide (MgO) ...	5.9	23.8	parts per 100,000

ANALYSES OF WATERS.

The following are the analyses of the waters used in the factories:—

Factory	1.	2.	3.	4.	5.	6.	8.	9.	10.	11.	12.	14.	15.	16.	17.	18.	19.	20.	21.	Ref.	Pros.	Glen.
Specific conductivity $\times 10^{-6}$	130	250	97	200	110	500	300	100	360	530	210	300	840	1420	430	200	200	180	340	400	740	170
Total solids... ..	10.5	17.1	8.0	13.7	14.9	32.9	21.1	7.4	26.6	35.8	12.9	19.6	58.9	86.0	25.7	13.6	15.7	14.4	20.8	24.9	51.3	14.9
Suspended solids ...	0.6	0.3	0.3	0.7	2.5	0.6	0.9	0.4	5.3	1.3	0.1	0.9	4.3	0.5	0.1	0.4	1.0	0.8	0.3	—	1.2	2.1
Inorganic suspended solids	0.6	0.2	0.3	0.4	2.2	0.6	0.9	0.4	3.5	1.1	0.1	0.8	3.6	0.4	0.1	0.4	0.9	0.8	0.3	—	0.9	2.0
Loss on ignition... ..	1.7	1.2	1.9	2.1	2.1	3.0	1.4	0.6	3.7	6.0	1.7	2.0	9.1	6.6	3.9	1.6	1.9	1.6	2.4	2.0	6.8	2.0
Chlorides (Cl)	1.4	3.6	2.1	2.5	2.1	9.9	5.7	2.1	5.7	10.7	3.6	5.0	19.9	36.2	7.8	4.3	2.1	2.1	7.1	6.0	16.0	2.1
Sulphate (SO ₃)	0.3	1.0	0.2	0.4	0.3	1.1	1.7	0.2	0.9	2.4	0.6	0.4	1.6	4.4	0.2	0.9	0.4	0.4	0.7	2.9	7.1	0.4
Silica (SiO ₂)	3.0	1.8	1.6	2.7	6.1	5.1	2.8	1.8	4.7	3.3	1.5	2.4	5.6	3.6	0.8	2.2	4.0	3.7	2.6	1.6	3.6	4.2
Iron oxides, etc. (Fe ₂ O ₃ etc.)	0.3	0.2	0.3	0.4	1.8	0.7	0.5	0.4	1.5	1.5	0.3	0.4	2.1	0.5	0.2	0.5	0.5	0.6	0.3	0.1	1.2	1.0
Calcium oxide (CaO)... ..	1.0	2.5	0.3	1.6	0.4	1.8	1.3	0.5	2.3	2.2	1.1	1.7	4.9	3.7	3.3	0.7	1.6	1.0	1.6	2.9	2.2	1.4
Magnesium oxide (MgO) 0.8	0.3	0.4	1.1	0.5	2.4	1.5	0.4	2.0	2.7	1.0	1.6	4.2	5.0	2.8	0.8	1.0	0.9	1.7	1.5	3.0	1.0	
Total alkalinity	3.5	8.0	1.0	7.0	1.5	10.0	5.5	1.0	10.5	8.5	4.5	7.5	15.5	17.0	12.5	2.5	6.5	5.0	7.5	7.5	6.5	6.0
pH	7.2	9.4	6.9	7.5	7.2	7.2	7.3	6.9	7.5	7.2	7.3	7.4	7.0	7.1	8.2	7.0	7.4	7.4	7.6	7.2	7.1	7.4

The specific conductivity is expressed as ohms⁻¹ cm⁻¹ and the inorganic constituents as parts per 100,000 with alkalinity as calcium carbonate.

Sodium concentration was found high in waters containing large amounts of chlorides. Thus the sodium as Na₂O parts per 100,000 in the waters from factories 16, 15, Pros., 11 and 6 were 30.1, 12.5, 11.1, 6.7 and 9.1.

It will be seen that a rather close correlation exists between conductivity and total solids as well as chlorides. This is the case in a series of analyses where the soluble solids vary in composition, the usefulness of routine conductivity tests at a factory working with a water containing the electrolytes in an almost constant relative proportion, can therefore be readily realised.

"Loss on ignition" does not necessarily mean organic matter, as some carbon dioxide is probably also given off, especially where magnesium carbonates are present.

From these analyses the hardness can be calculated. This was done and the results compared with that obtained by the potassium palmitate method and the soap solution method for total hardness. The agreement between the results was good. The potassium palmitate method is, however, preferred, as it is far less tedious than the soap method. In certain cases the soap method cannot be relied upon either. The permanent hardness was also calculated from the analyses and by subtracting this figure from the calculated total hardness, the calculated temporary hardness was obtained. This figure was compared with the temporary hardness obtained as alkalinity. The soap method

was also tried here, but the results were so unreliable that the method was discarded. Bond¹ also found that the soap method for total hardness, except in cases of waters containing large amounts of magnesium and chlorides, gave fairly reliable results,

but as a method for determining temporary hardness it was very misleading.

These comparisons are given as parts per 100,000 calcium carbonate in the following table:—

Factory	1.	2.	3.	4.	5.	6.	8.	9.	10.	11.	12.	14.	15.	16.	17.	18.	19.	20.	21.	Ref.	Pros.	Glen.
Total hardness (castile soap)	4.2	5.0	1.5	5.9	1.5	9.9	5.4	1.5	9.6	11.0	5.5	7.1	19.9	20.0	13.9	4.0	5.9	4.0	7.2	8.6	11.3	4.7
Total hardness (potassium palmitate) ...	3.7	5.1	1.6	5.8	1.8	8.8	6.0	1.6	8.8	10.4	4.4	6.4	19.0	19.4	13.0	3.7	5.1	3.7	6.9	8.8	11.3	4.6
Total hardness (calculated)	3.8	5.2	1.5	5.6	1.9	9.2	6.0	1.9	9.1	10.6	4.5	7.0	19.1	19.0	12.8	3.2	5.3	4.0	7.0	8.9	11.3	5.0
Temporary hardness (calculated)	3.4	3.9	1.2	5.1	1.5	7.8	3.9	1.6	8.0	7.6	3.7	6.5	17.1	13.5	12.5	2.1	4.8	3.5	6.1	5.3	2.4	4.5
Temporary hardness (alkalinity)	3.5	—	1.0	7.0	1.5	10.0	5.5	1.0	10.5	8.5	4.5	7.5	15.5	17.0	12.5	2.5	6.5	5.0	7.5	7.5	6.5	6.0

Phenolphthalein alkalinity was found in water from factory No. 2 to the extent of 2.0 parts per 100,000 as calcium carbonate. Water from this factory as well as from Ref. and factory No. 17 was treated before analysis.

DISCUSSION.

Scale Formation.—Matthews² points out that scale and sludge may consist of any salt present in the water, and mentions that cases are on record of where sodium sulphate formed the major part of the scale. This, however, is the exception. In practice boiler deposits consist mainly of calcium and magnesium sulphates, carbonates and silicates. Of these the sulphates and silicates form very hard scales and are the more objectionable. Magnesium scales are not generally found as often as calcium scales, but with our boiler waters which contain a relatively high proportion of magnesium salts, magnesium is often present in the scales.

Two scales from a certain sugar factory were sent in and analysed at the Experiment Station. The analyses on a dry weight basis were as follows:—

	Scale 1 per cent.	Scale 2 per cent.
Moisture	3.23	1.70
Loss on ignition	14.14	7.77
Ash	85.86	92.23
Silica (SiO ₂)	6.81	2.35
Calcium oxide (CaO)	25.71	31.41
Magnesium oxide (MgO)	14.10	10.74
Phosphoric oxide (P ₂ O ₅)	0.07	0.08
Sulphate (SO ₃)	31.54	42.32
Iron oxide, etc. (Fe ₂ O ₃ etc.)	3.39	5.21

It can be seen that in both cases the scale consisted mostly of calcium and to a lesser extent magnesium sulphate.

Waters from the two dams were also analysed, with the following results:—

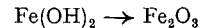
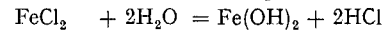
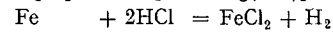
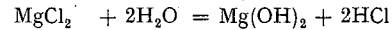
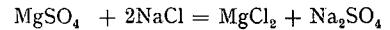
	Dam 1.	Dam 2.
Total solids	31.0	40.8 parts per 100,000
Suspended solids	0.6	1.1 parts per 100,000
Inorganic suspended solids ...	0.6	1.1 parts per 100,000
Loss on ignition	4.2	5.9 parts per 100,000
Chlorides (Cl)	9.9	12.8 parts per 100,000
Sulphate (SO ₃)	0.8	1.7 parts per 100,000
Silica (SiO ₂)	4.1	3.9 parts per 100,000
Iron oxide, etc. (Fe ₂ O ₃ etc.) ...	1.4	1.4 parts per 100,000
Calcium oxide (CaO)	1.4	2.7 parts per 100,000
Magnesium oxide (MgO)	2.1	3.1 parts per 100,000
Total hardness (as CaCO ₃) ...	7.8	12.9 parts per 100,000
Alkalinity (as CaCO ₃)	6.0	9.0 parts per 100,000
pH	7.2	7.5

Although the calcium salt is the predominating constituent of the scale, the water analyses show that magnesium is actually present in greater concentration.

Corrosion.²—Of the numerous causes of corrosion, only those that are caused or influenced by the constituents of the waters given in the tables will be briefly discussed.

The most obvious danger is the comparatively high concentration of magnesium and chlorides.

Magnesium chloride is, of course, very objectionable, as on hydrolysis hydrochloric acid is formed, which reacts with the iron (corrodes it) to form ferrous chloride, which in turn reacts with water, forming hydrochloric acid again, and the process of corrosion is continued. Magnesium nitrate reacts in the same way, forming nitric acid as the corrosive agent. The fact that some of our magnesium may be present in the form of sulphate is no consolation, as this is generally associated with a large amount of sodium chloride and the magnesium chloride is formed in the boiler if not already present in the original water.



Calcium salts may give rise to similar reactions.

Sludge formed in the boilers may be preferable to scale, especially hard scale; nevertheless, it may assist corrosion by helping on differential aeration and trapping hydrochloric acid liberated, carbon dioxide and organic acids.

Soft waters may still be dangerous on account of small amounts of free acid or acid-forming salts. Corrosion under these conditions may proceed almost unchecked because of the relatively small amounts of carbonates present.

Mention may be made here of a rather interesting case where a gauge glass was virtually eaten up. At one of the factories it was found that the gauge glass had worn very quickly and an incrustation formed round a leak. The dry deposit was found to have the following percentage composition:—

Loss on ignition	6.83
Chlorides (Cl)	47.93
Sulphates (SO ₃)	4.13
Phosphoric acid (P ₂ O ₅)	0.06
Silica (SiO ₂)	1.38
Iron oxide, etc. (Fe ₂ O ₃ etc.)	1.06
Calcium oxide (CaO)	2.46
Magnesium oxide (MgO)	0.43
Sodium oxide (Na ₂ O)	44.21
Potassium oxide (K ₂ O)	0.66

Water from the drip of the gauge glass had the following extraordinary analysis:—

Total solids	448.1	parts per 100,000
Suspended solids	3.2	parts per 100,000
Loss on ignition	62.6	parts per 100,000
Chlorides (Cl)	186.4	parts per 100,000
Sulphates (SO ₃)	12.3	parts per 100,000
Silica (SiO ₂)	2.2	parts per 100,000

Iron oxide, etc. (Fe_2O_3 , etc.)	0.7	parts per 100,000
Calcium oxide (CaO)	17.0	parts per 100,000
Magnesium oxide (MgO)	0.2	parts per 100,000
Sodium oxide (Na_2O)	197.5	parts per 100,000
Total hardness	32.4	parts per 100,000 as CaCO_3
Total alkalinity	40.3	parts per 100,000
pH	8.55	

Foaming and Priming.²—Without going into the theory of foaming and priming, it may be stated that the chemical causes are mainly oil and suspended solids. Oils, especially those containing saponifiable matter, are very dangerous when found in an alkaline water. The effect of suspended matter increases rapidly with increase of soluble solids; or, in other words, as the soluble solids increase a progressively smaller amount of suspended matter can be allowed.

SUMMARY.

Analyses of water used as boiler-feed (make-up) are given. They vary considerably in composition. Waters from factories further inland were found to be far more pure than those nearer the coast. In many cases the concentrations of calcium, magnesium, sodium and chloride are rather high.

The effect which the inorganic constituents can have on scale formation, corrosion, priming and foaming is briefly discussed, and some further analyses of scales and waters are given.

The so-called rapid methods, conductivity test and total hardness test were found to give very regular results considering the varying nature of the water constituents. They will be of even more use in the factory where the same water is dealt with all the time. This does not mean, however, that complete water analyses are not necessary. On the contrary, the nature of our boiler-feed waters makes it absolutely essential that the strictest control should exist at each factory.

References.

¹ Bond, G. W. (1936): A Comparison of Routine Methods of Determining Hardness of Water. Jour. S.A. Chem. Inst., xix. No. 2, 50.

² Matthews, F. J. (1939): Boiler Feed Water Treatment. Second edn. Hutchinson's Sc. & Tech. Pub.

³ Smith, E. Camden (1938): Some notes on Machinery Maintenance in a Cane Sugar Factory. Proc. S.A. Sug. Tech. Assoc., 12, 114.

⁴ (1940): Committee for Standardization of Chemical Control. Report for the year ending April, 1940. Proc. S.A. Sug. Tech. Assoc., 14, 100.

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Mr. RAULT welcomed the paper, as so little had been done on the subject and we had no standards to go by in classifying a boiler-feed water.

Mr. BUCHANAN expressed the opinion that water with a total hardness more than two should be treated with lime or soda ash. It was, of course, also necessary to analyse blow-down water, especially for hardness and total solids. Waters intended for sugar factories should have a higher alkalinity than was usual for boilers in other industries, in order to neutralise acids developed in sugar boiling.

Mr. BOOTH said that they found the water at Doornkop very pure. He always made a point of bringing the water up to pH8, however. All the water used at Doornkop, except the actual effluent, went back to the river, and he wanted to know whether this had added appreciable impurities to the water and had affected Darnall factory water adversely.

Mr. DU TOIT, replying to some questions, said that the analyses would help in discriminating between good and bad waters along the coast and eventually in drawing up standard specifications. He agreed that the alkalinity of our natural waters should be brought up a good deal to safeguard the boilers against acid formation from the high content of chlorides present. There was a considerable increase in total solids, hardness and chlorides in the water used at Darnall as compared with Doornkop, but he would not necessarily put that down to contamination of the water supply at Doornkop. There were other natural explanations. Not only was Darnall much nearer the sea, but before reaching it, the river left the Table Mountain sandstone formation and ran along the Ecca-Dwyka border.

Mr. RAULT said that in analysing the waters of various estate dams it was also found that the sodium chloride content of the water showed an increase on approaching the sea. He said the paper provided a good example of the co-operative work that could be and was being done at the Experiment Station.