

# CONDITIONING BOILER FEEDWATER FOR THE SUGAR MILL

by G. E. ANGUS

## Introduction

In the opening address of the annual congress of your association last year, Dr. Aston R. Williams quoted Sir Richard Livingstone as having said in 1954:

“In all subjects, not only in technology, there tends to be too much detail put in. If you are going to study a subject you must know the general principles behind it. You must know the way in which to learn all about it.”

Dr. Williams concluded his address with:

“In an age of specialisation it is all the more, not all the less, important to understand basic principles.”

You are sugar technologists and your members comprise people engaged in numerous specialised occupations all linked with the production of sugar.

This paper deals with a specialised activity within your industry, a vital process to you all, because the whole mill, the refinery, the personell engaged, all rely on the boilers providing steam.

The term “water conditioning” is being used more and more now in preference to the term “water treatment”. “Water conditioning” is the application of proved scientific methods to render a water suitable for a specialised industrial usage.

## Water and the Sugar Mill

Water is as much a raw material in the manufacture of sugar as sugar cane itself. Both of these raw materials are of variable compositions and require regular control testing. Mill laboratories are naturally occupied in testing all stages of the manufacture of the final product. Efficient modern practice calls for regular control testing of water quality, particularly the quality of the boiler feedwater and the control of feedwater conditioning.

Water conditioning has developed practical techniques that permit of “Tailor made” water, a feature quite unheard of thirty years ago. What we are required to do is to integrate the new techniques into the industry, to obtain maximum use of the equipment our predecessors have left us. This equipment is still of immense value in practice in the mills processing cane today, no matter what value the accountants have recorded in their balance sheets. Many mills are installing new boilers and the fact that you are holding this symposium is evidence of the importance you are placing on the efficiency of steam generation in your industry.

The extraction of sugar from sugar cane depends on steam being available at the mill. The site chosen for a mill depends on a number of factors. Among the principal of these is the positioning on the sugar estate in relation to transport of cane to the mill and also the availability of a source of water of sufficient quantity, and of suitable quality for the general water requirements of the mill and residential areas adjacent to it.

The class of water utilised is in general classified as “lowland surface water”.

This class of water depends on catchment areas. By the very nature of its origin, and the course of the river or canal, it takes up a number of substances in solution or suspension.

Lowland surface water may contain excessive quantities of mud and silt in suspension, and variable quantities of mineral salts and vegetable matter. The mineral salts are derived from the rocks and soils and farmlands through which the water passes. In lowland areas also, very frequently swampy lands contribute organic contamination, and excess of fertilisers from farmlands sometimes complicates matters.

## Components of water

Completely pure water is non-existent.

The impurities in water may be roughly classified as:

- Dissolved solids.
- Dissolved gases.
- Suspended matter.

### *Dissolved Solids*

The minerals which water picks up from rocks and soil consist chiefly of:

- Calcium carbonate (limestone),  $\text{CaCO}_3$ .
- Magnesium carbonate (magnesite)  $\text{MgCO}_3$ .
- Calcium sulphate (gypsum)  $\text{CaSO}_4$ .
- Magnesium sulphate (Epsom salts)  $\text{MgSO}_4$ .
- Silica (silicates),  $\text{SiO}_2$ .
- Sodium carbonate (soda ash)  $\text{Na}_2\text{CO}_3$ .
- Sodium chloride (common salt)  $\text{NaCl}$ .
- Sodium sulphate (Glauber's salt)  $\text{Na}_2\text{SO}_4$ .

These are soluble in water under various conditions and constitute the inorganic dissolved solids, i.e. the inorganic residue that is left when a filtered water is evaporated to dryness. To the above must be added any dissolved vegetable matter, and also material derived from trade effluents.

### *Dissolved Gases*

All natural water contains dissolved gases. The principal gases are:

Oxygen.  
Carbon dioxide.

Oxygen is soluble at atmospheric pressure and ambient temperature to the extent of approximately 9 parts per million by weight (p.p.m.). Carbon dioxide can be absorbed from the air to the extent of approximately 10 p.p.m.

The solubility of gases in water decreases as the temperature is raised.

Carbon dioxide dissolved in water reacts with chalk or limestone to form soluble bicarbonate of lime, and it is in this form that we find in water supplies.

#### *Suspended Solids*

These are materials in suspension, such as finely divided vegetable matter, and silt.

#### **Units and Terminology**

In view of the fact, that in the past and also in various countries at the present time, a number of different methods are used for describing the quantity of substances found in water, it is only natural that an attempt at standardisation has been made.

We in the Republic of South Africa in common with a number of overseas countries, including the United Kingdom and the United States of America, have adopted as our unit, "parts per million by weight" (p.p.m.) and this unit will be used in this paper.

Each profession has its own technical terminology.

The following terms commonly used in analytical reports and discussions dealing with the quality of water for industry are set out to simplify matters. They will be used in this paper.

The scale forming substances, with the exception of iron, alumina and silica, contribute what is called the total hardness of water or "H" figure. The terms "temporary" and "permanent hardness" that one sees in many of the older textbooks, are being replaced today by the terms, "carbonate" and "non-carbonate hardness".

Total hardness = carbonate hardness + non-carbonate hardness.

Total Hardness is also sub-divided into: calcium hardness and magnesium hardness or CaH and MgH figures.

The terms "hardness" is a relic from early days when it was used in relation to soap consuming power in laundry and domestic usage.

Other commonly used terms and symbols used in industrial water analyses are as follows:

T.D.S.	Total Dissolved Solid matter.
"P"	Alkalinity to Phenolphthalein.
"M"	Methyl orange alkalinity or Total Alkalinity.
P(BaCl <sub>2</sub> ) or "O"	Hydroxides (2 P-M).
"S"	Soda Alkalinity (M-H).
PO <sub>4</sub>	Phosphates.
NaCl	Chlorides.
pH	Hydrogen ion concentration (degree of acidity or alkalinity).

For convenience in calculations, H, CaH, MgH, P, M, O and S are expressed in terms of CaCO<sub>3</sub>.

pH values range from 0 to 14.

Values from 0 to 7 indicate decreasing acidity.

Values from 7 to 14 indicate increasing alkalinity.

pH 7.0 indicates neutrality.

#### **Boilers in Sugar Mills**

Boilers in Sugar mills are what are known as water tube boilers.

In a water tube boiler, the air and fuel (bagasse and/or coal) are burned in a furnace. The hot products of combustion are guided from the combustion zone over the exterior surfaces of the water-tubes. As the gases flow through the boiler they are cooled by transferring their heat to the water contained in the tubes. The tubes are in nests inter-connecting cylindrical pressure vessels called "drums". A mixture of steam and water is formed in the tubes and considerable velocity of flow is attained as the water and steam move to the drum where steam is separated for use. The water which has become concentrated by formation of the steam is diluted by incoming feedwater and returns to the steam generating tubes through special drums. Modern water-tube boilers often are provided with water walls. These are essentially cages of vertical tubes that surround the furnace areas and are supplied by down-comers and headers with water. These discharge their mixtures of steam and water into the steam drums as described above.

It is natural that in the older mills there are numerous boilers which by modern standards are old-fashioned. These have been in use for many years and are still good. They form the back-bone of the power stations. Modern boilers are often added to these power stations but do not necessarily replace the old boilers.

The operating pressures of these older boilers vary in general from 160 to 200 p.s.i.g.

Modern boilers operating at 400 p.s.i.g. are in use at several mills, and being erected at others.

It is noted that at the factory of Triangle Limited in Rhodesia the boilers operate at 475 p.s.i.g.

There is a considerable difference between the conditioning required for the feedwater to the old boilers operating at approximately 200 p.s.i.g. and that required for the boilers operating at 400 p.s.i.g. and higher.

#### **Feedwater**

In a sugar mill the feedwater consists largely of condensate, i.e. distilled water. In a mill in full production more than enough condensate is provided from various sources to provide 100 per cent. of the feedwater and have some over. It is claimed that some mills are near to attaining this in practice. There are inevitable steam losses as we all know. The extra condensate is derived from the cane in the form of water in the cane and in make-up water used in mill tandems for leaching the cane to form the mixed juice. This water is recovered by evaporation and condensation. The magnitude of the percentage

which can be made available to the boiler is determined by the purity of the condensate. The main contaminants are sugar, lubricating oil and cooling water.

Mr. J. Bruijn<sup>2</sup> of the Sugar Milling Research Institute reports: "In the alkalisated feedwater, sugar tends to decompose into sugar acids and other products which lower the pH and in this way increase the rate of corrosion of boiler tubes. In addition the boiler water has a tendency to foam which results in carry-over of salts in the steam".

Mr. Bruijn records a fact that should be appreciated widely, namely that pure sucrose is not readily detected by conductivity readings. The impurities that accompany sugar in early stages of manufacture increase conductivity and thus contamination in the early stages can be detected by this means.

The Sugar Milling Research Institute has reported on the use of conductivity apparatus in detecting contamination from sugar. The general question of conservation of condensate has received much attention.

Modern practice in a mill appears to be keeping various condensates separate and testing each flow. If the quality is satisfactory it is sent direct to the feedwater tanks. If it contains sugar it is not wasted but diverted to where it can best be used.

Every endeavour should continue to be made to develop practical automatic equipment to take care of this matter.

In older mills using steam operated reciprocating drives the condensate from these machines becomes contaminated with lubricating oil. The steam and condensate should receive special attention and never be released into the feedwater unless the oil content is consistently only in small trace quantities.

Leakage of cooling water into turbine condensers can be detected in several ways of which conductivity is probably the best. This can cause a serious increase in costs of internal chemicals if not checked in time.

In the majority of mills it is necessary to use make-up of river water to add to the condensate available, in order to provide the quantity of feedwater required by the power station.

You may well ask if it is water impurities which cause boiler problems, why not remove all the impurities before the water is used? Completely purifying water is costly and providing purer water than is necessary is economically unsound.

Preparing water for boilers requires considerable study and planning. It is not just a case of finding a magic "muti" or magic gadget and using either of these and relaxing.

Careful analyses of raw water supplies must be conducted and these should be done on a number of samples over a reasonable period of years to gain some idea of seasonal variations. The older mills have this information and also much experience. New mills have not as a rule got this information. It is frankly amazing how frequently water conditioning special-

lists are asked to advise on schemes of which only one "grab" sample has been submitted for analysis. Quite frequently an analysis is set before one that gives detailed information as to the suitability of the water for general domestic purposes. In many cases essential details required for calculations for water conditioning are not available.

As the title of this paper indicates, the feedwater and its composition are decisive factors in deciding the conditioning required. Feedwater is the material that provides steam and its composition must be such that its impurities can be concentrated inside the boiler without exceeding the tolerance limits of the particular boiler design.

The water supply to sugar mills is normally clarified (coagulated), filtered and chlorinated. These processes which are part of what is termed external treatment, render the water suitable for domestic purposes. The result is a water, crystal clear, but containing dissolved salts and the gases, oxygen and carbon dioxide.

It is the presence of these substances that give rise to the major problems of water conditioning for boilers. Admixture with good quality condensate merely dilutes these impurities. If the condensate carries impurities such as oil or sugar these have to be taken into consideration also. The first step to be taken then is to calculate the composition of the feedwater without any special conditioning having modified its composition. This is the starting point for developing a conditioning scheme.

In order to be able to appreciate the necessity for the various steps in a conditioning programme let us examine what might occur if we did nothing but mix average domestic water with condensate and proceeded to generate steam.

Table I gives the solubility of various chemical compounds that are common in waters:

**Table I**  
**Solubility of Chemical Compounds**

	ppm. as CaCO <sub>3</sub>	
	32° F	212° F
<i>Calcium</i>		
Bicarbonate	1,620	decomposes
Carbonate	15	13
Sulphate	1,290	1,250
<i>Magnesium</i>		
Bicarbonate	37,100	decomposes
Carbonate	101	75
Sulphate	170,000	356,000
<i>Sodium</i>		
Bicarbonate	38,700	decomposes
Carbonate	61,400	290,000
Chloride	225,000	243,000
Hydroxide	370,000	970,000
Sulphate	33,600	210,000

### Scale Formation in the Boiler

Calcium and Magnesium compounds in the water are precipitated by the heat and pressure and form scale and sludge.

Magnesium sulphate is very soluble, as will be seen, but it usually reacts in boiler water to form less soluble magnesium salts such as the hydroxide. Calcium sulphate tends to remain in solution in the colder areas of the boiler but becomes a deposit, crystal by crystal, inside steam bubbles that are forming in the hotter parts of the boiler, where scale can cause the most damage. The presence of dissolved silica, iron and alumina complicate matters and these deposit with the calcium and magnesium scales.

The scales derived from the carbonates or bicarbonates of calcium and magnesium usually form suspended solids in the boiler water, and if permitted to concentrate too much, settle out and become "baked on" to heat-transfer surfaces to form scale. Oil if present in condensate, adsorbs on to sludge (or suspended matter), and if this becomes baked on forms a very dense insulating scale.

The danger of scale formation in tubes deserves a short discussion in order to examine the principles involved.

"As water circulates through boiler tubes it absorbs heat and cools the metal. Scale forms a barrier between the circulating water and the tube, decreasing the efficiency of heat transfer. As the result, the metal of a scaled tube has to be hotter to transfer the same amount of heat as a clean tube. When boiler-tube steel is heated to about 900° F it starts to weaken." When it is appreciated that furnace temperatures are normally in excess of 2000° F it can be realised how important it is to maintain relatively scale-free conditions at points of high heat transfer.

### Foaming in the Boiler

It will be noted that sodium salts are very soluble and this solubility increases as water is heated. Sodium salts do not normally cause boiler deposits but contribute to causing foaming which will be discussed later. Soluble organic matter such as sugar often assists in giving the foam "body" or strength. Some forms of suspended material have the same effect. The result of course is entrainment of boiler water in the steam which is very undesirable.

### Corrosion of Steel in the Boiler

There are two main agents concerned with corrosion of boiler steel; oxygen and salinity.

*Oxygen:* At atmospheric pressure and ambient temperature about 9 parts per million of oxygen can be dissolved in water. Water, as delivered to the mill after only external conditioning for domestic purposes, is saturated. As water is heated the oxygen becomes less soluble and some escapes. As feed-water enters a boiler the oxygen remaining either begins corroding (oxidising steel) or goes off into the steam lines.

*Salinity:* Sodium chloride particularly, and sodium sulphate to a lesser extent, assist oxygen to penetrate through deposits to steel surfaces, and the result is corrosion unless inhibitors are present.

### Damage to Superheaters

Superheaters consist of tubes carrying steam that are exposed to hot products of combustion with the result that the steam is heated well above the temperature for saturated steam at the pressure of generation. Maintaining the steel of the tube within safe temperatures depends on the cooling effect of the flowing steam which is being heated. Foaming or "carry over" of boiler saline in water causes re-boiling in the superheaters and formation of deposits. These deposits interfere with heat transfer and also if excessive, cause restrictions and diminution of flow of steam. This can cause either softening followed by bursting of the superheater tube (or element as it is commonly called) or corrosion by direct action of hot steam on hot steel forming oxide of iron and hydrogen gas.

### Damage to Turbines

Sodium salts carried over with the steam can form incrustations on turbines. These if detected in time can be removed by washing with water.

In boilers operating above 400 p.s.i.g. selective silica carryover has to be considered. Scientific study by G. C. Kennedy and other<sup>3 4 7</sup> has shown that:

- (a) Steam is a solvent for silica.
- (b) The ratio of silica in the steam to silica in the boiler water increases rapidly as boiler pressures increase.
- (c) At 400 p.s.i.g. silica in the boiler water should not be permitted to rise above 100 p.p.m. (as SiO<sub>2</sub>) in order to keep silica in the steam at or below 0.02 p.p.m.
- (d) With silica in steam at or below 0.02 p.p.m. (as SiO<sub>2</sub>) appreciable turbine deposits would not normally occur.

### Corrosion of Non-Ferrous materials in the boiler

If concentration of alkaline water is carried too far and very high pH values result, bronze fittings can be attacked and fail.

### Corrosion (Erosion) of gauge glasses

Slight leaks even on boilers operating as low as 160° F causing concentration of alkali at the point of leakage can cause solution of glass and failure. In high pressure boilers gauge glasses are protected by mica sheet from direct alkaline attack.

### External Conditioning

By this term we mean conditioning that is completed external to the boiler itself such as:

- (a) Clarification, (Coagulation), Filtration.
- (b) Precipitation Softening.
- (c) Ion Exchange techniques.
- (d) Evaporation.
- (e) De-aeration.

### Clarification (Coagulation), Filtration

These are normally arranged for the main water supply to the mill and for domestic purposes.

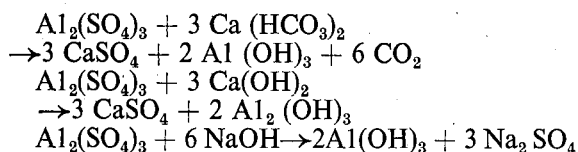
Only a small proportion of this supply is used as make-up to the boilers.

It is important nevertheless, that the fact that it is used for boiler feed should be realised. Sometimes large quantities of aluminium sulphate are used for coagulation. To render the water alkaline with this large quantity a correspondingly large quantity of lime is required. The result is a considerable increase in calcium sulphate content and this has to be removed by special external conditioning or dealt with in the boiler itself. A thing like this literally causes a chain reaction and can cause costs of conditioning to soar. Sometimes, particularly with water coloured with organic material it is necessary to coagulate with aluminium sulphate at pH values nearer 5.0.

This type of water needs the addition of alkali—usually lime, after filtration, to minimise corrosion of steel piping, tanks, etc.

For boiler water conditioning the use of caustic soda as the alkali would be preferable, but this is normally impossible to justify for the whole supply from the cost aspect. This also applies often to the use of soda ash which is the second choice.

Normal chemical reactions in this type of conditioning, with the primary coagulant alum, are:



The use of very small dosages (up to 4 p.p.m.) of an organic coagulant-aid can, in many cases, enable satisfactory coagulation to be achieved with a minimum amount of primary coagulant. This has considerable merit from all points of view including that of conditioning of the boiler make-up water. Organic coagulant aids add virtually no dissolved solids to the water.

### Precipitation Softening

The principle of operation may be summarised as follows:

A predetermined quantity of selected chemicals is added to a quantity of water and rapid mixing ensures the dispersion of the chemicals. The treated water is subjected to a slow mixing to enable chemical reactions to proceed, crystal growth to occur, and separation of the precipitates to commence. This period, known as the flocculation period, is followed by a period of sedimentation either in a quiescent state or under continuous flow conditions, but sufficiently slow to permit of the separation of the precipitates to the bottom of the tank or basin from which point they can be removed as a sludge.

The chemicals used are lime, soda ash and sodium aluminate. These are normally mixed into a thin

slurry with water and fed by proportionating dosage equipment. Such equipment must be regularly cleaned of all deposits liable to affect accurate dosing.

This type of softening has not found favour with sugar mills because of control difficulties associated with seasonal quality variation of lowland surface supplies. Without adequate chemical control this type of softener can cause considerable difficulty in the power station.

### Ion Exchange techniques

We now meet the terms ion exchange materials and cations and anions. The origin and exact meaning are matters for physical chemists, but let us regard them as terms for use in our processes.

Let us take common salt, sodium chloride. This is written as NaCl. In aqueous solution, it splits up into the Sodium cation  $\text{Na}^+$  and the chloride anion  $\text{Cl}^-$ . Similarly calcium sulphate,  $\text{CaSO}_4$ , splits up into cation  $\text{Ca}^{++}$  and anion  $\text{SO}_4^{--}$ . The + and - signs indicate the nature of the electrical charges carried by the ions.

The common feature with all ion exchange processes is the use of ion exchange resins (complex synthetic organic materials) in granular or bead form.

These materials, which are insoluble, are rather like storage batteries. When exhausted, they can be regenerated and are thus rendered ready for a further cycle of operation. The normal usage of these resins is to allow the water to be treated to flow through a bed of the material not less than 30 inches deep. The ion-exchange reaction is, under these conditions, very rapid.

### Cation Exchange—Sodium cycle

Water is passed through a bed of ion exchange material. During its passage through the bed, hardness cations, calcium and magnesium, are taken up by the exchange material and are replaced in the water by sodium. In this reaction the ion exchange material eventually becomes saturated with calcium and magnesium and further exchange action ceases. To restore this capacity a solution of common salt (sodium chloride) is passed slowly through the exchanger. The effect of an excess of this is to drive out the calcium and magnesium and to replenish the sodium in the material, which is then available for a further cycle of softening.

The reactions in this process merely change the bases. Calcium and magnesium ions go into the ion-exchange material and are replaced in the water by sodium ions. This process does not alter the quantity of dissolved solids in water appreciably, nor does it alter the anions (bicarbonate, sulphate, chloride). This process does not remove silica from solution.

Most of the modern base exchange plants offered utilise polystyrene synthetic resins in bead form. These resins are available from a number of manufacturers. They have a high exchange capacity and high resistance to deterioration under service conditions. The exchange capacity of an ion exchange material is usually expressed in terms of the grains of hardness (expressed as  $\text{CaCO}_3$ ) removed by a cubic

foot of the material. Water, having a total hardness of 100 p.p.m. (as  $\text{CaCO}_3$ ) has a hardness of 7 grains per Imperial gallon. A gramme (metric) is equivalent to 15.43 grains.

The exchange capacity varies with the salt usage and a general average for a polystyrene resin would be the following:

Salt lb/ft <sup>3</sup>	Exchange capacity, grains/ft <sup>3</sup> as $\text{CaCO}_3$
6	20 000
10	25 000
15	30 000

A 30 inch depth of bed is recommended as a minimum. The operation of a base exchange softener consists of:

- Backwashing to clean the resin and loosen it up.
- Brining to regenerate the resin (i.e. the use of a salt solution).
- Rinsing to wash all excess salt away.
- Softening.

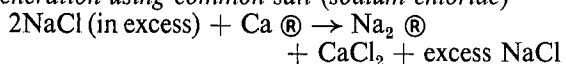
Reactions concerned in this type of softening can be expressed in a simplified form as follows:

#### Softening cycle

$\text{Ca}(\text{HCO}_3)_2 + \text{Na}_2 \textcircled{\text{R}} \rightarrow 2\text{NaHCO}_3 + \text{Ca} \textcircled{\text{R}}$   
 Calcium carbonate + Base exchange material in sodium form  $\rightarrow$  Sodium bicarbonate + Base exchange material in calcium form.

$\text{MgSO}_4 + \text{Na}_2 \textcircled{\text{R}} \rightarrow \text{Na}_2\text{SO}_4 + \text{Mg} \textcircled{\text{R}}$   
 Magnesium sulphate + Base exchange material in sodium form  $\rightarrow$  Sodium bicarbonate + Base exchange material in magnesium form.

#### Regeneration using common salt (sodium chloride)



Sodium chloride + Base exchange in calcium form  $\rightarrow$  Base exchange in sodium form + Calcium chloride.

In the above  $\textcircled{\text{R}}$  is the Resin material

The plant required consists essentially of a cylinder containing the active ion exchange material supported on gravel beds, beneath which is a specially designed collecting system, and a salt saturator, suitable piping arrangement and valves. Salt solution is injected into the system at a 10 per cent strength by use of a hydraulic ejector diluting a 30 per cent brine solution (saturated), three times. This brine solution requires to be removed thoroughly by rinsing and then the softener is ready for operation on the softening cycle.

When the softening action is exhausted, backwashing is done to cleanse and loosen the ion exchange resin bed and regeneration using salt is done as described above.

The above process can be arranged for manual operation using standard valves.

By eliminating the standard valves and using in their place a single control valve whereby all operations are carried out either by the turning of one handle or by the moving of a lever to fixed settings, the sequence

of operations is simplified. Backwash and rinse flows should be controlled by butterfly valves operating against orifice plates to enable correct rates of flow from each operation to be attained.

With softeners using a multiport valve with a rotating motion it is a relatively straightforward matter to render the complete operation fully automatic.

The multiport valve is motorised and is connected to a make and break contactor head which rotates the valve to the correct positions for softening, backwashing, brining and rinsing. The period between regenerations for all types should be altered to suit seasonal variations in the hardness of the raw water supply. This is a vital control procedure.

#### Cation exchange—Weakly Acidic

This unit is similar to the base exchange unit described above, except that the cylinder and piping are rubber lined, the ion exchange material is a special weakly acidic cation exchange material and the regenerant is dilute sulphuric acid.

Weakly acidic cation exchange material only reacts with cations combined with the bicarbonate anion. The cations are absorbed and replaced by the hydrogen ion. The result is the formation of carbonic acid ( $\text{H}_2\text{CO}_3$ ). Sulphates and all other salts pass through the plant unchanged. Carbon dioxide is removed from the water by a scrubbing tower in which the carbonic acid is broken up by an up-flow air stream. The water which has been treated in this way is then passed through a standard base exchange softener to remove the non-carbonate hardness. The water is now of low alkalinity, of zero hardness and with sodium chloride and sodium sulphate. The pH of the water after degassing is 6.5. Caustic Soda solution is added to raise the pH to 8.2 to prevent corrosion of the base exchange unit, the pipelines and the pre-boiler system.

This type of treatment plant enables control of alkalinity to be achieved, and if carefully supervised, zero hardness can be assured.

It has to be appreciated that this process does not remove silica.

As is well known fully demineralised water is obtainable with special ion-exchange plant. With boilers operating under 500 p.s.i.g. the expense of obtaining this is seldom justified.

At sugar mills as yet, as far as known, none have been installed.

A feature of the ion exchange processes described is the fact that the operation is not complicated, control is relatively simple and the reactions are automatic.

#### Deaerating equipment

In low pressure equipment with cast iron economisers it is not vital to provide deaerating plant for the feedwater, to protect the boiler from corrosion.

In the case of boilers operating at 400 p.s.i.g. and above, with steel tube economisers, it is necessary to deaerate efficiently.

The method most commonly used is to provide a pressure type deaerator heater. In this type of equipment the feedwater is broken up into a fine spray and scrubbed with low pressure steam. Part of the steam is vented carrying with it the bulk of the dissolved oxygen from the water. This type of deaerator heater reduces the dissolved oxygen content of the feedwater to 0.007 parts per million. Final oxygen scavenging is done chemically as described later.

### Hot well arrangements

The hot well or surge tanks should be protected from ingress of air, if possible utilising steam blanketing. Hot wells should be painted with special protective paints to prevent corrosion and they require regular maintenance. Feedwater in hot wells should be maintained at a pH value in excess of 8.2.

### Internal Conditioning

Since even minute amounts of impurities can cause trouble, and these can escape from external conditioning, a follow-up treatment is needed, regardless of how the make-up water is prepared. In a sugar mill the make-up water is only a small percentage of the feedwater, and hence the feedwater contains only minute quantities of impurities per 1,000 gallons. Nevertheless these impurities cannot be ignored, and it is general practice to use a form of internal treatment as a final conditioning.

A complete final conditioning for sugar mill boilers includes:

- (a) Softening chemicals to react with feedwater hardness.
- (b) Sludge conditioners to disperse sludge and keep it from sticking to metal surfaces.
- (c) Oxygen scavengers and alkali to prevent corrosion.
- (d) Chemical antifoams to prevent carryover.

### Softening Chemicals

Softening chemicals used are sodium phosphates and caustic soda. The type of phosphate selected depends on boiler conditions and the method of feeding used.

Sodium phosphates used are:

Disodium phosphate  $\text{Na}_2\text{HPO}_4$ , Trisodium phosphate  $\text{Na}_3\text{PO}_4$  and sodium polyphosphates such as hexameta-phosphate  $\text{Na}_6\text{P}_6\text{O}_{18}$  and septaphosphate  $\text{Na}_7\text{P}_7\text{O}_{22}$  and similar complex phosphates.

Where a number of boilers are fed from one ring main and there is no provision for phosphate addition to individual boilers, formulae containing selected organic matter and sodium polyphosphates are used. These do not react and form precipitates in the mains, and economisers. It is necessary with these to ensure that there is alkali (caustic soda) in excess. This ensures that when the polyphosphates reach the boiler they form trisodium ortho phosphate. This trisodium phosphate reacts with the small amounts of calcium hardness and forms hydroxy apatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . In this form it is non-adherent, and is removed via the blowdown cock.

Under these conditions also magnesium hardness is precipitated as either magnesium silicate or magnesium hydroxide.

All of these are non-adherent particularly if *dispersing* type organic materials are used in the treatment. If insufficient caustic soda (or sodium carbonate) is used to satisfy the requirements to form trisodium ortho phosphate then adherent calcium compounds can be formed, and calcium may combine with silica to form very hard scale.

It is, for the above reasons, vital to ensure that sufficient residual trisodium phosphate and caustic soda are carried in the boiler water. Caustic soda excess assists in maintaining silica in solution as sodium silicate.

It must be appreciated that internal conditioning for control of scale formation is done in the boiler itself despite the fact that the chemicals are usually added to the feedwater at the feed pump suction. It is when the feedwater meets the boiler water under full pressure, and consequent temperature, that softening reactions proceed speedily to completion. The softening chemicals brought in with the feedwater merely replenish the reserve of softening chemicals in circulation in the boiler itself.

### Sludge conditioning chemicals

Specially processed temperature stable organics are used. Under conditions in sugar mills where feedwater is very soft due to a high percentage of condensate return and the volume of sludge formed from each 1,000 gallons of feedwater is relatively low, it is considered that the sludge conditioning preferred is more a dispersion than a coagulation. It is for this reason that specially processed lignin derivatives combined with starch type organics are being utilised. Tannins are particularly effective in conditioning calcium carbonate and magnesium hydroxide precipitates where the total sludge content is high. The action of tannins is more coagulation than dispersion.

The starch type organics are particularly effective in waters having high silica content, preventing adherence of silica scale. When moderate oil contamination is present the use of starch type organics is beneficial. The action here appears to be keeping the calcium phosphate sludge bulky and in a condition suitable for maximum adsorption of oil into the sludge.

In this form oil is removed with the blowdown, and does not adhere to metal surfaces. Boilers with a fair quantity of precipitated sludge are more tolerant of oil than boilers which have little or no sludge.

### Oxygen scavengers and alkali

Even with the best deaerating equipment some oxygen gets through. Chemical oxygen scavengers complete the work in the case of boilers in the 300 p.s.i.g. (and higher) class. Sodium sulphite is normally used with these boilers, and this is preferably catalysed with a special chemical to provide very speedy reactions. Hydrazine is used normally in boilers operating at higher pressures where the fact that it does not contribute to boiler water dissolved solids is important.

Oxygen scavenging chemicals are dosed to the feed-water after it has passed through the deaerator, if one has been installed.

As explained earlier in many of the older installations operating at 200 p.s.i.g. or lower, deaeration as such is not practised. In these the use of the lignin based organic, and alkali in sufficient quantity, protect boiler metal by protective film formation, and retardation of corrosion by relatively high pH values.

#### Chemical antifoams to prevent carry-over

The causes of foaming or "carry-over" are quite complex but in general this distressing phenomenon is related to the concentration of dissolved solids in the boiler water. High alkalinities generally assist in the formation of foam, and organic matter such as sugar can give it strength. Most modern antifoams utilise complex synthetic materials to combat this. These specially developed chemicals have two basic properties; they are insoluble in water, and are surface active. When properly dispersed in boiler water exceedingly small quantities affect the skin of the steam bubble and weaken it. There are distinct advantages in combining antifoams with sludge conditioners which act as carriers of the antifoam to where it is needed.

#### Internal Conditioning—Summary

Internal conditioning for sugar mills with a large percentage of condensate in the feedwater requires:

- Phosphates.
- Alkali.
- Dispersing organic material preferably lignins and processed starches.
- Antifoam chemicals.
- Oxygen scavenging materials.

#### Chemical feeding

The chemicals described in this paper and most offered today are in briquette or pulverised form, and require to be dissolved in water and fed as a solution. The major companies specialising in this field of chemistry have spent a great deal of time and money on research and scientific experimentation. This accounts for the fact that often the exact composition of the chemical formulations is not fully revealed to the customer. Nevertheless, the general principles are usually revealed, and analytical control methods used follow accepted chemical techniques.

It is best to feed the alkalis and sludge conditioning chemicals at the feed pump suction in the hot well. If a deaerator is used sodium sulphite should be fed into the feedline just after it.

As explained earlier, it is preferable to feed the sodium phosphate direct to the boiler drum, but where this is not possible sodium polyphosphate is fed with the sludge conditioning chemicals at the hot well.

The use of positive dosing equipment operated by electric power or coupled to the reciprocating steam supply at the feed pumps merits serious consideration.

**Table II**  
**Boiler Water Analytical Control Limits (p.p.m.)**  
**Applicable to Water Tube Boilers in the Sugar Industry**  
**PHOSPHATE RESIDUAL CONDITIONING**

<i>Working Pressure</i>	<i>Up to 200 p.s.i.g.</i>	<i>200 to 350 p.s.i.g.</i>	<i>350 to 450 p.s.i.g.</i>
Total Dissolved Solids	3,000 max.	2,500 max.	2,000 max.
Suspended Solids	800 max.	300 max.	150 max.
Hydroxide Alkalinity (as CaCO <sub>3</sub> )	min. 100 preferable 10% of Dissolved solids max. 400	min. 100 preferable 10% of Dissolved solids max. 350	min. 100 preferable 10% of Dissolved solids max. 300
Soluble Silica (as SiO <sub>2</sub> )	150 max.	100 max.	90 max.
Phosphate (as PO <sub>4</sub> )	40 to 80	30 to 60	20 to 40
Sulphite (as Na <sub>2</sub> SO <sub>3</sub> )	—	30 to 100	20 to 70
Hardness (as CaCO <sub>3</sub> )	zero	zero	zero
Oil	7 max.	5 max.	zero

It will be seen that residuals of alkalinity, phosphate and sulphite are set out. Individual water treatment companies often add to these limits by requiring additional analytical data to suit their particular formulae.

Control of the dissolved solids figure is by blowing down. As the blowdown water is replaced with lower solids feedwater the boiler water is essentially being diluted. Other things being equal more economical usage of chemicals is obtained by endeavouring to operate near the limit of dissolved solids set down.

The pH of the boiler water should always be above 10.0. If the above limits are used the pH always will be above this figure. Sugar can depress this and remedial action by addition of alkali should immediately follow detection.

It will be noted that there is a considerable difference between the analytical control limits applicable to water in boilers operating up to 200 p.s.i.g. and those applicable to water in boilers operating at 400 p.s.i.g. and above.

Table II gives the control limits for "phosphate residual" internal conditioning, which system has been in use for many years. Relatively recent refinements in this technique have been the development of special temperature stable organic materials as sludge conditioners, and antifoams, capable of use in boilers operating up to 2000 p.s.i.g.

#### A New Technique—Chelating

A relatively new technique which differs considerably from the above is now being tried out in South Africa as internal conditioning, after intensive research and practical tests overseas. It is called "Chelating". Specialised synthetic organic materials are used. These have the ability to combine with, or "chelate" calcium and magnesium ions, which are present in boiler waters as carbonates, sulphates, etc. A soluble complex compound is formed. The chelated calcium and magnesium cannot be precipitated by carbonates, phosphate or hydroxide or heat and remain in solution.

At this stage of our experience with this new technique, considerable care must be taken to ensure that the conditions under which it is used are correct.

If boilers are being kept satisfactorily clean with a conventional organic phosphate technique, the use of "chelating" agents will be of little or no additional benefit. This technique requires much more accurate control than the organic phosphate technique.

There are potential corrosion hazards that must be taken into consideration. A very high degree of deaeration of feedwater is essential at all times. "Chelating" has a very marked cleaning effect on calcium and magnesium scale. It is considered that with old boilers of riveted construction it would be exceedingly unwise to try this technique. Leakage could become a serious problem and cleaning out seams could create conditions favourable to caustic embrittlement of steel.

With new boilers of all-welded construction, up-to-date pretreatment of make-up, excellent quality condensate, and precision equipment for feeding chemicals coupled with close analytical control, this new technique is worthy of examination.

The only difference to be noted in the control limits set out in Table II if a "chelating" agent is used, are:

Phosphate and hardness are no longer determined.

Residual chelating agent is required to be present at all times, and special practical analytical techniques have been developed to enable this residual to be controlled. This residual should not normally exceed 100 p.p.m. of chelating agent in the boiler, otherwise corrosion may be encountered.

Dissolved solids, alkalinity and sulphite limits remain unchanged.

We will be hearing a lot more about this technique in the future, as experience is gained in its use.

### Caustic Cracking

(Embrittlement of Boiler Steel)

It would not be right to ignore this matter in a paper dealing with feedwater conditioning. It does not occur very often, but when it does it is a serious matter. The cracking which develops is continuous, predominantly intergranular, and originates at the surface of the metal.

To get embrittlement of boiler steel, there are four conditions which must be present *at the same time*.

1. The metal must be under stress near its yield point.
2. The boiler water must contain caustic soda. (The presence of some silica along with caustic soda accelerates attack).
3. Inhibiting chemicals must be either absent or in too low a quantity to stifle attack.
4. There must be some mechanism (a crevice, seam, leak, etc.) permitting the boiler water solids to concentrate on the stressed metal.

The advent of the all welded boiler appears to have caused a slackening of research on this matter. The modern method of ensuring that a water is non-embrittling relies on either tannins or lignins by themselves or sodium nitrate either by itself or with the tannins or lignins. Caustic alkalinities should be kept within the limits laid down and preferably should not exceed 250 p.p.m. If caustic alkalinities are higher than this, consideration should be given to definite control measures, particularly where riveted boilers are in use. It is worthy of note that the water in steam accumulators of riveted construction should conform to anti-embrittling standards. There is no simple test to determine if a boiler water will contribute to embrittlement.

### Oil Contamination of Boiler Feedwater

Detecting and eliminating oil contamination is an important part of a feedwater treatment programme in a sugar mill using steam driven reciprocating drives. Many of these are still in use in the older mills.

Lubricating oil is injected into the steam used in these driving engines, and when the steam has done its work and been condensed, it contains oil.

This, if it gains access to the boilers in more than trace quantities, causes trouble in a number of ways such as increasing insulating power of scale, causing sludge to become sticky and "baked on", and aggravating foaming.

Oil contamination becomes more critical as boiler pressures and heat transfer rates increase.

Removing oil contamination from steam is done by using baffle separators or by centrifugal separators.

Removing oil contamination from condensate is done by filters often using chemical coagulation prior to filtration.

In the case of boilers operating on condensate slightly contaminated with oil, it would be a safe precaution to boil out during the off season with a special chemical formula combining detergent ability and oil emulsifying action, to ensure oil free metal surfaces.

### Conclusion

Adequate water conditioning arrangements and control are vital to the successful generation and usage of steam in the sugar mill. It is now a highly developed and specialised branch of chemistry and engineering.

The exact mechanism and chemistry of many of the reactions described in this paper are beyond the author's comprehension. It is with the authority of the research chemists, and with records of successful practical experience that they are put forward. Sugar technologists can rest assured that what has been stated can be substantiated, and the conditioning methods described are practical and scientific. The time for guess work and magic in water quality work is past.

Mr. Oliver Lyle in the introduction to his excellent book "The Efficient Use of Steam" states:

“Some of the explanations may not be scientifically correct, but the author believes that it is more important to be nearly right and understandable, than to be academically accurate and incomprehensible. (The author is insufficiently equipped to be academically accurate)”.

The author of this paper is in full agreement with this, including the portion in parentheses.

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#### Summary

This paper surveys modern water conditioning practice in respect of feedwater for boilers in sugar mills in Southern Africa. The water conditioning techniques described are applicable to water tube boilers operating with condensate return being a high percentage of total evaporation. Emphasis in this paper is on basic principles and practical application.

#### References

- <sup>1</sup> Angus, G. E. (1959): Water Conditioning with special reference to generation of steam, heat exchangers and cooling systems. *J. Instn. Cert. Engrs. S.A.* 32, 133.
- <sup>2</sup> Bruijn, J. (1962): Automatic Sugar Detection in Boiler Feedwater. *Proc. S.A. Sugar Tech. Assoc.*
- <sup>3</sup> Jacklin, C. and Brower, S. R.: Correlation of Silica carry-over and solubility studies. *A.S.M.E. Paper No. 51-A-91.*
- <sup>4</sup> Kennedy, G. C. (1950): A Portion of the system Silica-Water, *Economic Geology* 45, 629.
- <sup>5</sup> Low, W. A., Davies, W. L. P., Angus, G. E. (1965): The selection and operation of water conditioning plant for steam

boiler installations. *J. Instn. Cert. Mech. & Elect. Engrs. S.A.* 38, 253.

<sup>6</sup> Lyle, O. (1947): *The Efficient use of Steam.* His Majesty's Stationery Office, London.

<sup>7</sup> Nalco Chemical Company, Power Industry Dept. (1961 to 1965): *Technifax Bulletins.*

<sup>8</sup> Straub, F. G. and Grabowski, H. A. (1945): *Silica Deposition in Steam Turbines.* *Trans. A.S.M.E.* 67, 309.

**Mr. Cargill:** What p.p.m. of sucrose is acceptable in boiler feed water?

**Mr. Angus:** At a guess I think 100 to 150 p.p.m. in the boiler itself on the basis of organic content would be the upper limit.

**Mr. Robinson:** In Table II the figure is given of 3,000 p.p.m. for total dissolved solids. Is this for treated or untreated water?

**Mr. Angus:** You can run on 10,000 p.p.m. in some cases but the figure of 3,000 was set by the American Boiler and Affiliated Industries Standards Committee (1956) who laid down the figures for manufacturers to consider in respect of dissolved and suspended solids. It is certainly possible to operate at very much higher figures, particularly with shell type boilers but it is advisable to stick to the limits set out in the paper.

**Mr. Phipson:** We used to rely on magnesia to remove silica in the water by forming magnesium silicate. Mr. Angus talks of removing magnesia but in that case what happens to the silica?

**Mr. Angus:** Magnesia can be added to the water, and magnesium silicate will settle in flocculant form and be removable by blow-down. Some raw waters have sufficient magnesia but softened waters have none. In the absence of sufficient magnesia enough caustic soda must be present to maintain the silica in the form of sodium silicate and the amount required at 200 p.s.i. would be 1.5 times the silica content. Up to 400 p.s.i. it would be 2.5 times. Above 400 p.s.i., particularly where turbines are concerned, other factors must be taken into account.

The maximum use of condensate is required, as the more condensate you have, the less silica will go into the boilers.