THE USE OF SEQUESTERING AGENTS FOR CHEMICAL CLEANING AT UBOMBO SUGAR

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Abstract

The chemical cleaning of certain evaporator types requires the use of an alkali cleaning agent, followed by an acid cleaning agent. The use of acid under these circumstances is expensive, as most of the acid used during the process is consumed in neutralising the residual alkali present in the system following the caustic clean and water rinse. An alternative to the use of acid in the chemical cleaning process is the use of sequestering agents (such as EDTA or sodium gluconate), which are compatible with the alkaline environment present in the system and are thus not rendered less effective by the presence of caustic residues. The use of sequestering agents for chemical cleaning was tested at the Ubombo sugar mill in Swaziland, and the results of these factory trials are discussed. Both EDTA and sodium gluconate were found to be effective at replacing acid during the cleaning procedure. The economic advantages of using sequestering agents for cleaning are outlined.

Introduction

Investigations in the local sugar industry have indicated that evaporator fouling is a major contributor towards poor heat transfer in evaporators (Walthew, 1994). As evaporation is an important unit operation in a raw sugar mill, a broad investigation into fouling was undertaken over the past few years in the southern African sugar industry. The overall aims of this study were to identify methods of reducing or preventing scale formation and to improve the efficiency of cleaning of fouled evaporator surfaces.

The chemical cleaning of evaporators in the southern African sugar industry is discussed by Walthew *et al.* (1997). Most evaporators can be cleaned using an alkali cleaning agent (such as caustic soda) only. However, the presence of significant quantities of certain calcium salts (such as calcium oxalate and calcium carbonate) which are essentially insoluble in caustic soda makes the use of an additional acid cleaning step necessary for the effective cleaning of certain evaporators. Furthermore, the use of acid cleaning in addition to alkali cleaning leads to the breaking up of the evaporator scale into smaller pieces. In the case of narrow gap plate evaporators, the acid is thus beneficial in helping the scale to be flushed from between the plates. However, in these circumstances, a large proportion of the acid used in the cleaning process is actually expended in neutralising the persistent caustic residue in the evaporators, and does not contribute towards the cleaning of the heat transfer surfaces. In order to avoid this wasteful use of acid, other methods of cleaning were investigated, including the use of sequestering agents, which are compatible with the alkaline environment which exists in the evaporators following the caustic soda cleaning process. Chelating agents (or complexing agents) are molecules which form multiple stable attachments with metallic ions. Sequestering agents are a sub-group of chelating agents which combine with metal ions to produce **soluble** complexes in a solution (discussed at a later stage).

The most versatile and widely used sequestering agent is the tetrasodium salt of ethylenediaminetetraacetic acid (this tetrasodium salt is commonly referred to as EDTA – also known as *Versene*). Trials were carried out at the Ubombo sugar mill to determine the technical and economic feasibility of using EDTA to replace the acid cleaning step in the chemical cleaning process. While the relative cost of EDTA compared with phosphoric acid is about three times more (in terms of equivalent quantities of calcium removed), the inefficient use of acid in the normal cleaning procedure means that, in practice, significantly less EDTA would be required to carry out the same degree of cleaning. As EDTA is relatively expensive, the use of a cheaper sequestering agent, sodium gluconate, was also investigated.

Conventional chemical cleaning at the Ubombo sugar mill

As part of an expansion programme and a drive for energy efficiency, Ubombo sugar mill converted its evaporator station from a quadruple effect to a quintuple effect in 1996. The existing evaporator vessels were rearranged, and plate evaporators were incorporated as the second and third effects (De Beer and Moult, 1998). Unfortunately, a very high rate of fouling was experienced in the plate evaporators, and an effective cleaning procedure was required.

Chemical cleaning is essential for the routine cleaning of the plate evaporator packs because physical cleaning would take too long to carry out[1]. Furthermore, the inter-plate gaskets

[1] While the plate evaporators are undergoing cleaning, a caustic soda solution is boiled in the other evaporators in order to soften the scale. The Roberts and climbing film vessels are, however, still cleaned mechanically.

undergo damage each time they are disturbed, and replacement of these gaskets is expensive. Additionally, analysis of the evaporator scale formed at the Ubombo sugar mill has shown the presence of significant quantities of calcium carbonate, which is not effectively removed by caustic soda, but is attacked by acid cleaning.

As a result of a series of chemical cleaning trials over an extended period, the following cleaning procedure was developed for the effective cleaning of the plate evaporators:

- Evaporator stops are scheduled fortnightly.
- When the flow of juice to the evaporators stops, the vessels are desweetened by displacing the residual juice with water.
- After displacing the juice, water is introduced into the vessels and boiled under normal operating conditions for one hour. The water is introduced into the second effect and discarded after the third effect.
- The water boiling is followed by boiling a 12,5% caustic soda solution under normal operating conditions for five hours. To this solution is added 0,25 to 0,5% (by volume) of wetting agent, which significantly increases the cleaning effectiveness of the caustic. The caustic is circulated from the second effect to the third effect and then back again. The condensate from the vessels is returned to the caustic solutions so as to maintain a constant caustic concentration during the cleaning process.
- The caustic solution is then drained from the evaporators and replaced with water, which is boiled under normal operating conditions for one hour. The water is introduced into the second effect and discarded after the third effect.
- Following the water boiling, the steam supply is isolated (and mechanical cleaning of the tubular evaporators takes place).
- Flushing of the vessels with water is maintained until the pH of the discharged water drops to below 8. This typically takes three to four hours.
- Phosphoric acid, of strength 10 to 15% and containing 1 to 2% inhibitor, is then circulated through the plate packs for a period of about four hours. As the steam supply is unavailable, the acid cannot be heated during circulation, and the temperature typically does not exceed 40°C. This is not ideal, as the acid should be circulated at 70 to 95°C.
- Following the acid clean, the evaporators are rinsed and returned to service.

The major disadvantage of the current cleaning procedure is the acid cleaning step. The removal of the residual caustic soda in the system is extremely difficult and requires large quantities of water. Large quantities of acid are wasted in neutralising the persistent caustic residue, rather than contributing towards the cleaning of the evaporator surfaces.

Sequestering agents

Sequestering agents are molecules which form stable, soluble complexes with heavy metal or alkaline earth ions (for example, calcium and magnesium ions). The complexes so formed are so effective that the metals remain in solution even in the presence of anions which would normally result in their precipitation from solution. This property can be exploited in the cleaning of fouled evaporators, as calcium and magnesium salts are generally a major component of evaporator scale in the sugar industry. In the presence of a sequestering agent, these salts readily dissolve, the calcium and magnesium forming soluble complexes.

The most widely used and versatile sequestering agent is the tetrasodium salt of ethylenediaminetetraacetic acid, also known as EDTA or *Versene*. The normal complexing reaction which this compound undergoes with the calcium ion is shown in Figure 1 (Bersworth Chemical Co., 1953), where one molecule of EDTA reacts with one calcium ion.

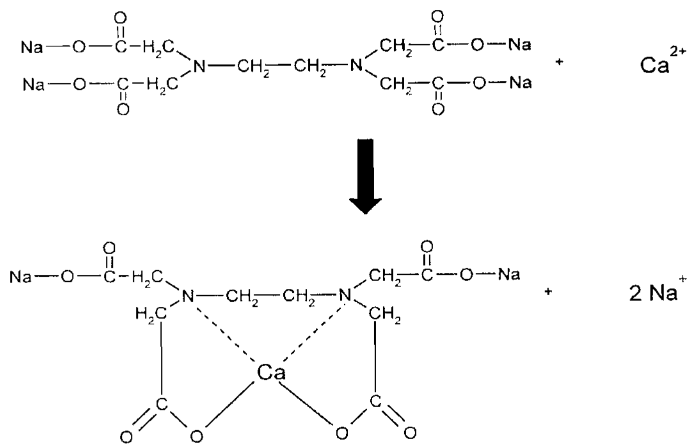

Figure 1. The general complexing reaction of EDTA with the calcium ion.

EDTA in its acid form (ethylenediaminetetraacetic acid) contains four ionisable hydrogen atoms, and therefore the following equilibria exist:

$\Leftrightarrow$

$$H_4Y \Leftrightarrow H^+ + H_3Y^-$$
$$H_3Y^- \Leftrightarrow H^+ + H2Y^{2-}$$
$$H_2Y^{2-} \Leftrightarrow H^+ + HY^{3-}$$
$$HY^{3-} \quad H^+ + Y^{4-}$$

where Y^{4-} is shown in Figure 2.

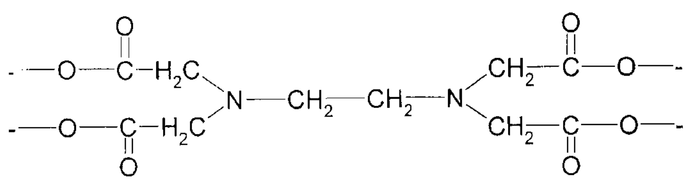

Figure 2. The fully ionised EDTA molecule (Y^{4-}).

In an acidic solution, H_4Y is the dominant species present. As the pH is increased, hydrogen ions are removed, with Y^{4-} eventually becoming the predominant species (typically above a pH of 11 or 12). The ions which form complexes with the calcium ion are Y^{4-} and HY^{3-} (Holland *et al*, 1954). Thus, in alkaline conditions, calcium will form complexes:

$$Ca^{2+} + Y^{4-} \Leftrightarrow CaY^{2-}$$
$$Ca^{2+} + HY^{3-} \Leftrightarrow CaHY^{-}$$

Under acidic conditions, however, where the Y^{4-} and HY^{3-} ions are present in small concentrations, calcium is not complexed. It is thus essential to maintain alkaline conditions for the effective use of sequestering agents for chemical cleaning[2]. These reversible equilibria associated with EDTA mean that an EDTA cleaning solution can be regenerated by acidification with sulphuric acid. The acidification results in the precipitation of calcium sulphate (gypsum), which can be filtered off. Addition of caustic soda then returns the EDTA to the tetrasodium salt form, which can be re-used for chemical cleaning (Holland *et al.*, 1954; Bennett *et al.*, 1955).

Another effective sequestering agent is sodium gluconate. The structure of this molecule is shown in Figure 3.

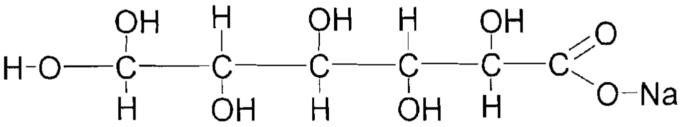

Figure 3. The structure of the sodium gluconate molecule.

Sodium gluconate, being the sodium salt of gluconic acid, behaves in a similar fashion to EDTA with regard to the ionisation of its hydrogen ion under alkaline conditions. The complexing power of this sequestering agent is thus also very dependent on maintaining an alkaline environment during its use (typically a pH of above 8 is required), as shown in Figure 4.

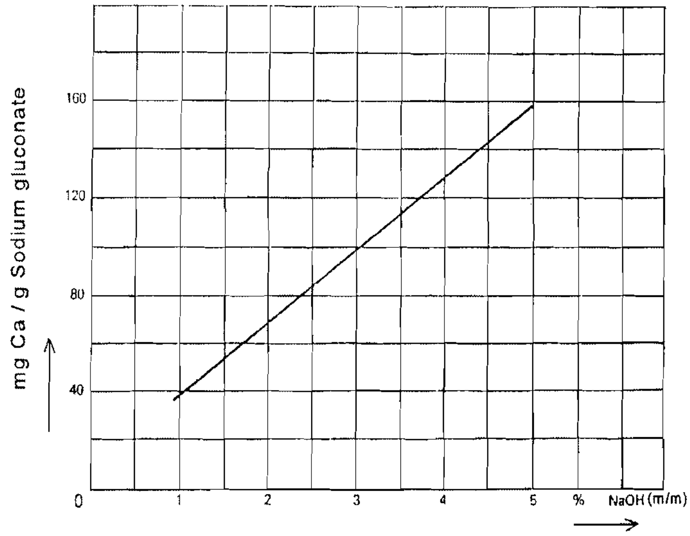

Figure 4. The sequestering power of sodium gluconate as a function of caustic soda concentration.

The use of sequestering agents for chemical cleaning at the Ubombo sugar mill

Cleaning with EDTA

The first step in the use of a sequestering agent for chemical cleaning is to determine the quantity of the chemical required to carry out the cleaning process. For the trials under consideration here, samples of phosphoric acid were taken at the Ubombo sugar mill before and after an acid clean of the plate evaporators, and analysed at the SMRI for calcium content. From these analyses, it was found that 24 kg of calcium had been removed from the evaporators by the 16 m^3 of acid used during the cleaning process. The total surface area cleaned was 2762 m^2. Given that one molecule of EDTA is required to complex one calcium ion, it was calculated that approximately 250 kg of EDTA would be required to complex the equivalent amount of calcium. This is roughly equivalent to a requirement of 10 kg of EDTA per 100 m^2 of surface area. By comparison, in the beet sugar industry the EDTA requirement is approximately 65 kg per 100 m^2. However, the scale to be cleaned is rich in calcium oxalate and calcium carbonate, and the cleaning is only carried out once per season.

During the next cleaning cycle at the Ubombo sugar mill, EDTA was substituted for the phosphoric acid. The major advantage of using EDTA for chemical cleaning was that the time consuming water boiling and flushing steps could be omitted, allowing the second stage of cleaning to take place whilst heating steam was still available. After the caustic boiling, most of the caustic was drained out, and the sequestering agent was added before the steam was isolated. The chemical could be boiled, and it remained hot during the recirculation period of four to five hours, even after isolation of the steam supply.

A further reduction in cleaning time could be obtained if the EDTA could be added at an earlier stage, with the boiling caustic soda. However, this would require that the scale solids be removed from the caustic before the EDTA is added, in order to prevent the expensive sequestering agent from preferentially dissolving the scale which has already broken away from the heat transfer surface.

Cleaning with sodium gluconate

During the following fortnightly clean, the use of sodium gluconate as a substitute for acid cleaning was tested. The sodium gluconate was simply added to the caustic cleaning agent in the evaporators following four hours of caustic boiling. A dosage rate of 6 kg of sodium gluconate per 100 m^2 of evaporator surface area was used. A comparison between the procedures used for the sequestering agent cleaning processes and that used for the conventional acid cleaning process is shown in Figure 5.

[2] The EDTA sold for chemical cleaning is usually sold as the tetrasodium salt (i.e. Na_4Y), which is essentially ethylenediaminetetraacetic acid neutralised with caustic soda.

Conventional cleaning

Time	Function	Flow Configuration
In service		
	Water flush	Once through
1 hour	Water boil	Once through
5 hours	Caustic boil	Recirculate with condensate return
1 hour	Water boil	Once through
3 to 4 hours	Water flush	Once through
4 hours	Acid clean	Recirculate
	Water flush	Once through
In service		

EDTA cleaning

Time	Function	Flow Configuration
In service		
	Water flush	Once through
1 hour	Water boil	Once through
5 hours	Caustic boil	Recirculate with condensate return
4 to 5 hours	EDTA boil / circulate hot	Recirculate with condensate return
	Water flush	Once through
In service		

Sodium gluconate cleaning

Time	Function	Flow Configuration
In service		
	Water flush	Once through
1 hour	Water boil	Once through
4 hours	Caustic boil	Recirculate with condensate return
4 to 5 hours	Sodium gluconate boil / circulate hot	Recirculate with condensate return
	Water flush	Once through
In service		

Steam
Available
Isolated

Figure 5. Comparison between acid and sequestering agent cleaning procedures.

Results

Unfortunately, it was impossible to measure the heat transfer coefficient during the sequestering agent cleaning processes, as the condensate flow meters installed at the Ubombo sugar mill for this purpose were inoperative. Thus, the only assessment of the cleanings which could be made was visual. Following the EDTA cleaning, it appeared that a lot of scale flakes had been dislodged, and partially blocked some of the plate evaporator passages. It is possible that these flakes were scale which had not been effectively removed during the previous acid cleaning cycles during the season. There was an obvious difference in the scale residue appearance when using sodium gluconate for cleaning. While acid cleaning resulted in the scale flakes being black in colour, the scale which was removed by the sodium gluconate cleaning process was found to be light brown. This scale residue also appeared to break up much more easily.

Scale residue samples were collected from the Ubombo sugar mill following the acid and sodium gluconate cleaning trials and analysed by x-ray fluorescence (Walthew and Turner, 1995) and organic acid analysis. These samples of scale consisted of pieces which had broken free of the evaporator plates during cleaning and had fallen to the bottom of the plate evaporators, where they were collected following the cleaning process. The estimated scale compositions based on these results are shown in Tables 1 and 2, which indicate that the phosphate and silica components of the scale appear to have been more readily attacked by the sodium gluconate than they were by the phosphoric acid. As calcium silicate is one of the most difficult scale components to

Table 1. Scale compositions (in %) based on x-ray fluorescence and organic acid analyses.

	SiO_2	CaO	MgO	P_2O_5	Ca oxalate	Aconitate	Loss on ignition
Acid clean scale residue	28,4	17,9	3,5	10,6	1,3	0,5	35
Sodium gluconate clean scale residue	14,1	18,5	0,3	0,9	10,4	0,0	66

Table 2. Scale compositions (in %) based on x-ray fluorescence and organic acid analyses.

Compound	Amorphous calcium phosphate	MgO . H_2O	$SiO_2 . H_2O$	Mixed oxalate	Ca. Mg aconitate	Lime hydrate	Amorphous organic
Acid residue	28,6	5,1	36,9	1,3	0,5	6,4	21,1
Sodium gluconate residue	2,4	0,5	18,4	10,4	0,0	18,5	49,8

remove during the evaporator cleaning process, it is encouraging that this component is readily attacked by sodium gluconate.

Following the cleaning cycles, heat transfer measurements made during normal operation suggest that the sequestering agent cleaning processes were as effective as the acid cleaning process. The Ubombo sugar mill plans, in the 1999/2000 season, to alternate between using phosphoric acid and sodium gluconate for chemical cleaning of their plate evaporators.

Cost implications

The chemical costs for the three cleaning processes evaluated in this study are shown in Table 3. It can be seen that the use of sodium gluconate for evaporator cleaning results in a significant saving in cleaning cost. Over a 40 week season (comprising of 20 cleaning cycles), the projected savings resulting from the use of sodium gluconate instead of phosphoric acid amount to R 80 000.

Conclusions

The use of sequestering agents for the chemical cleaning of evaporators was tested at the Ubombo sugar mill in Swaziland. Both EDTA and sodium gluconate were found to be effective when used to replace the acid cleaning step in the Ubombo cleaning procedure. The use of sequestering agents for evaporator cleaning holds an economic advantage, and the Ubombo sugar mill plans to alternate the use of

Table 3. Chemical costs for evaporator cleaning at the Ubombo sugar mill.

Chemical cleaning agents used	Cost of chemicals	Savings
1. Caustic soda + wetting agent 2. Phosphoric acid + inhibitor	R 10 018	-
1. Caustic soda + wetting agent 2. EDTA	R 8 037	20 %
1. Caustic soda + wetting agent 2. Sodium gluconate	R 6 000	40 %

phosphoric acid and sodium gluconate during the 1999/2000 season.

Further work needs to be carried out on the use of sequestering agents for chemical cleaning, particularly with regard to:

- the development of a reliable analytical technique for the measurement of the concentration of sequestering agent in solution, so that this may be monitored during the cleaning procedure
- the effectiveness of sequestering agents for cleaning the scale in a factory experiencing high silica concentrations
- the rate at which calcium-containing scale components are attacked by sequestering agents, so that the length of time required for optimally effective cleaning can be determined.

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