

THE USE OF OZONE FOR COLOUR REMOVAL AT THE MALELANE REFINERY

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Abstract

The refinery at Malelane is currently evaluating refining technologies other than the existing carbonatation and sulphitation processes with a view to improving decolourisation. As part of this programme, and following successful laboratory trials at the Sugar Milling Research Institute (SMRI) with ozone decolourisation of refinery melt, a full scale trial was undertaken at Malelane. A Wedeco ozone generator with a nominal capacity of 6 kg/h of ozone and using pure oxygen as a feed was used to treat the raw melt stream. After initial problems with the contacting equipment, the plant has been able to run steadily at a dosage rate of about 90 ppm on brix. Melt colours have decreased by between 10 and 15%, while decreases in the colours of all four sugars boiled have been noted, leading to a reduction in refined sugar colour of about 20%. The pH of the melt has dropped by half a unit, but this does not appear to have had any significant negative effects. All streams have been sampled and analysed for organic acids that may have been produced by oxidation. The ozone appears to break down both colour bodies and colour precursors that can cause further colour formation in the pans, and these breakdown products are better removed than the original compounds in the carbonatation/sulphitation processes.

Introduction

In order to remain competitive in the world sugar market, as in any business, it is necessary to investigate new technologies and techniques in order to produce the best quality product for the lowest cost. Part of the role of the SMRI in the South African sugar industry is to investigate these new techniques and to assist with technology transfer to factories where appropriate. Transvaal Suiker Beperk (TSB) is striving to improve the performance of their refinery at Malelane in terms of both throughput and product quality. To meet these goals, several new and traditional methods of colour removal are being investigated and evaluated.

One of the methods that shows great promise is the use of ozone for decolourisation. Little work has been done on sugar decolourisation with ozone worldwide, although ozone has long been used for potable water decolourisation and sterilisation. Initial investigations performed at the SMRI (Getaz, 1989; Patel and Moodley, 1991) concluded that the process was too expensive for the amount of decolourisation achieved, and no further work was done. Recent advances in

the design of ozone generators have lowered the cost per kilogram of ozone production, while at the same time more efficient contacting arrangements have improved the usage efficiency. Further laboratory trials were carried out on a number of raw house and refinery streams (Davis, 1995a and 1995b) and, by 1996, plans for a large scale trial were proposed (Davis, 1996). TSB took up this challenge, and a three-way partnership was formed between TSB Malelane, the SMRI and Fedgas (Pty) Ltd, the suppliers of both the laboratory ozone generator used in the initial tests and the full scale plant. This paper will provide a brief summary of the early work, but will concentrate on the full scale trials and the results achieved to date.

The chemistry of ozone

Ozone is a pale blue gas with a pungent odour, formed commercially by high voltage electrical discharge through a stream of dry air or oxygen. It consists of three oxygen atoms bound together in a highly unstable molecule that is very reactive and a powerful oxidant. It is so unstable that it cannot be stored in cylinders, and must be generated on site as required. Although it is toxic, its characteristic odour is detectable at concentrations well below dangerous levels, as is the case with sulphur dioxide.

The mechanisms by which ozone destroys colour are direct and varied. Different functional groups are attacked by the strongly oxidising molecule and broken apart. Conjugated double bonds, responsible for much colour in organic compounds, are readily attacked and the compounds are cleaved. Previous work on decolourisation using hydrogen peroxide, a less powerful oxidant (Patel and Moodley, 1991), showed that colour returned on boiling treated syrups, although this was greatly reduced when the peroxide was added before a precipitation step such as carbonatation (Moodley, 1992). This is thought to arise from the incomplete cleavage of the double bond, which could reform on boiling. The greater power of ozone breaks this bond completely and it cannot reform, hence the colour return is less. Ozone also attacks phenolic groups, breaking the benzene ring structure, and many amines, precursors to Maillard-type reactions, are oxidised to nitrates. These mechanisms, shown in Figure 1, are useful in destroying colour bodies present in raw sugar, and an extra benefit is that colour precursors are also destroyed, preventing additional colour formation during pan boiling.

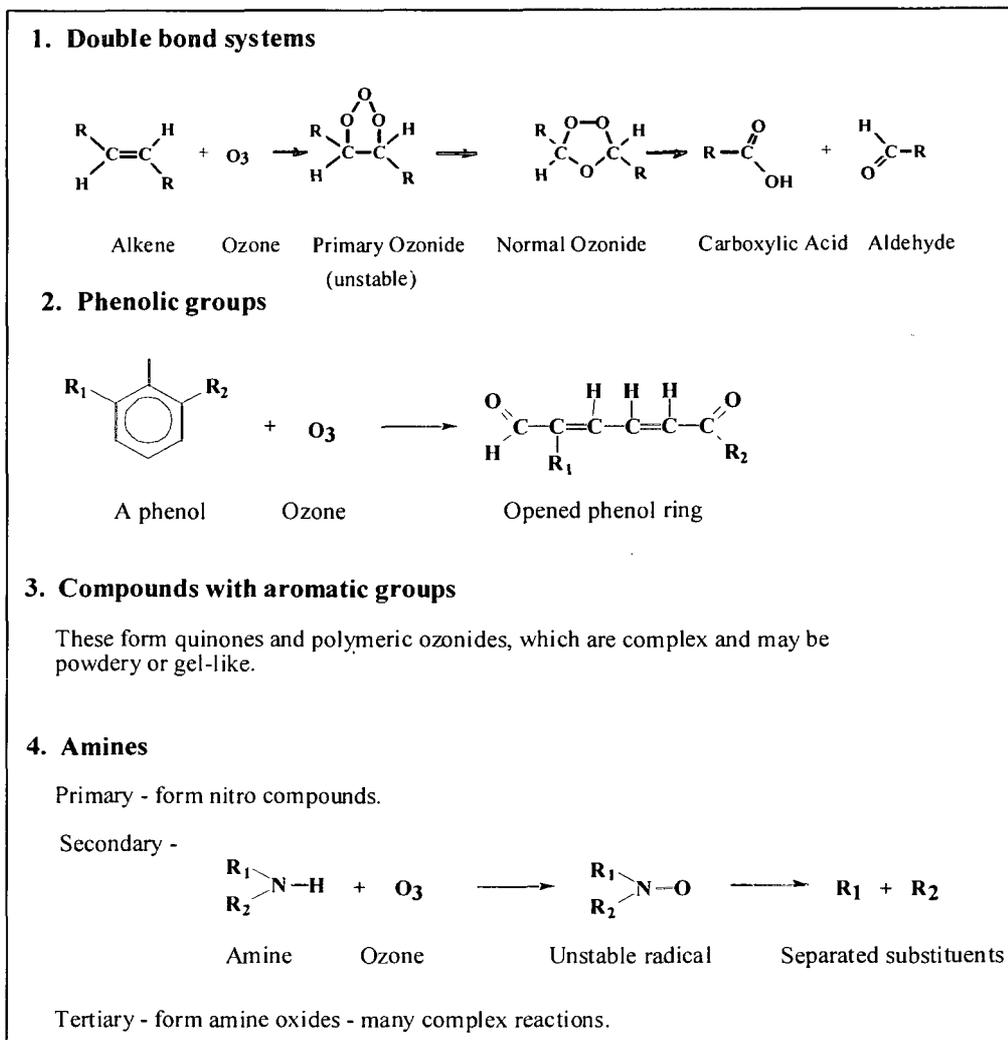


Figure 1. Reactions of ozone with organic compounds.

There was naturally some concern that such a powerful oxidant might also destroy sucrose and the reducing sugars, but work done by Gomez *et al.* (1980) showed that sugars are only appreciably attacked at pH values in excess of 8,5. This potential problem was considered at all stages of the project, and possible sucrose destruction was monitored several times by analysis of sugars present before and after ozonation, and no sugar loss was found.

Laboratory trials

The laboratory trials were performed on several factory products, namely clear juice, raw syrup, sweetwater, raw melt, brown liquor, fine liquor and fourth jet. With a high enough dosage of ozone, all of these products could be decolourised by at least 70%, but the quantities needed for the raw house products were of the order of thousands of parts per million (ppm) and would not be economical. The fourth jets responded relatively poorly, with maximum colour removal of about 25%, and the emphasis was placed on brown and fine liquors, which responded well. Tests were also done to determine the optimum temperature and pH for

ozonation, and the conclusion was reached that a temperature above 70°C and a pH₇₀ between 6,0 and 7,0 produced the best results.

Some of the breakdown products formed are organic acids, and this had the effect of lowering the pH of the liquor upon ozonation. It was therefore found to be necessary to add a neutralising agent such as lime or caustic soda to maintain a neutral pH to prevent sucrose inversion. The pH drop was generally small, about 0,5 unit for 250 ppm of ozone added, and little neutralising was needed.

Combination tests using ozonation and carbonation or sulphitation in series did not show great improvements over ozonation alone, but laboratory carbonation trials do not simulate factory conditions well, and better results could be expected in the factory. The original strategy was to use ozone as a tertiary or polishing colour removal step, following the idea that the cheapest colour removal method should be used first to take out the bulk of the colour, and the more advanced processes used last to mop up the remainder of the difficult colour. In order to determine how permanent the colour removal by ozone was, in the light of the colour return

upon boiling when hydrogen peroxide was used, a series of pilot pan boilings on treated liquors was done using untreated liquors for comparison. TSB Malelane provided samples of fine liquor, brown liquor and raw melt to determine how the Malelane refinery streams would respond.

These tests showed (Table 1) that ozonation of sulphited and fine liquors did not improve the crystal colours significantly, although the liquor samples provided were already of a low colour. However, ozonation of raw melt followed by carbonation showed a considerable reduction in sugar colour, from 35 ICUMSA units to 22 units using 250 ppm of ozone. In addition, the run-off colour was reduced from 1 810 to 870 units, and the colour increase from boiling was within the normal range for refinery products. It was concluded from these tests that the maximum benefit from ozonation can be gained by following it with a precipitation step such as carbonation, as was the case with hydrogen peroxide, as the ozone is thought to make the colour bodies and precursors more susceptible to adsorption on, and removal by, the calcium carbonate precipitate. Hence, not only does the ozone cause a bleaching effect, but it also appears to enhance the effectiveness of the carbonation.

Table 1. Results of pilot pan boilings of refinery liquors.

Liquor boiled	Ozone dose (ppm)	Feed colour	Masseccuite colour	Run-off colour	Affinated sugar colour
Fine liquor, ozonated	0	480	565	1 250	17
	250	320	435	1 005	19
Sulphited liquor, ozonated	0	370	450	910	15
	250	240	340	900	15
Raw melt, ozonated and carbonated	0	640	740	1 810	35
	250	290	370	870	20

An extra benefit was found to be that ozone caused a substantial decrease in colour values measured at pH 9, an indication that plant pigments such as flavonoids and other phenolic compounds are strongly attacked. As most colour in raw sugar is reported to originate from plant pigments (Kennedy and Smith, 1976; Clarke *et al.*, 1985) and pH sensitive colour has a greater transfer rate to crystal than pH insensitive colour formed in the factory, ozonation should yield a considerable reduction in crystal colour.

Full scale trials

After the laboratory trials had demonstrated the effectiveness of ozonation of raw melt followed by carbonation, the bold decision was taken to run a factory trial at the Malelane refinery. The low run-off colours produced from the pilot pan boilings indicated that reduced crystal colours might be obtained from all boilings, not just the first, but only a factory trial could prove this. In addition, laboratory carbonation tests are rarely as efficient as continuous carbonation, and it was felt that even better results might be obtained in the factory.

Discussions between the three parties led to the conclusion that only a full scale trial would be feasible, as a pilot scale unit would not allow the effect of ozonation on four boilings to be determined. It was also necessary that the installation of the trial unit be designed so as to cause minimum disruption of normal refinery operation at a time when it was running at full capacity, and that the refinery could operate as normal when the trial unit was not in operation.

After some delays due to a number of factors, the trial unit was installed in August 1997. The core of the unit is a Wedeco ozone generator capable of producing 6 kg/h of ozone at a concentration of 12% in oxygen. The ozone is introduced into a circulating loop pumped from the raw melt tank via a venturi eductor as shown in Figure 2. A static mixer blends the melt and the gas before the mixture passes into a baffled reactor vessel, necessary to give the ozone time to react before the melt pH is raised by liming. The retention time required was estimated to be of the order of five minutes, based on laboratory tests. The reacted mixture then passes into a flash tank, from where the inert oxygen is flashed to atmosphere, and the ozonated melt returns to the melt tank. The original design was for a once through system, with the flash tank discharging into the liming tank, but pressure limitations on the venturi system precluded this. However, by using the existing melt pump next to the discharge point of the flash tank, relatively little recirculation of ozonated liquor can be achieved.

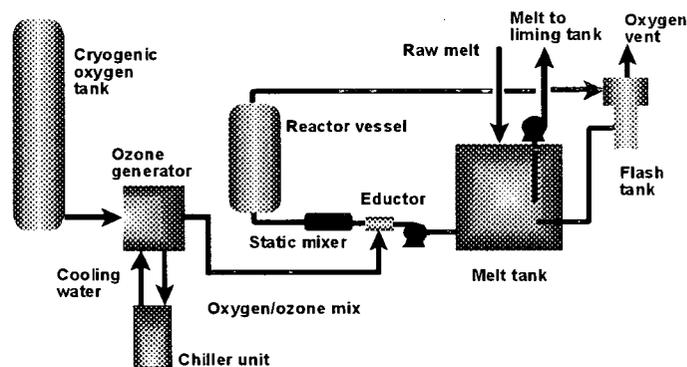


Figure 2. Installation of ozone trial unit at the Malelane Refinery.

The ozone generator is fully instrumented and run by a programmable logic controller (PLC) and includes many safety features. The product gas is continuously analysed on-line and the system is interlocked to the recirculating melt pump. Thus, in the event of cooling water failure or overheating, gas pressure failure, or melt pump failure or trip, the ozone generator automatically shuts down after purging the gas line with oxygen so that no ozone remains in the pipes. A fail-safe solenoid valve is also installed just before the ozone line enters the venturi, so that in the event of a power failure, melt will not flow into the ozone lines. Thus, once the generator is started and the required ozone concentration has been set, the plant can be left to run unattended.

After commissioning on 1 October, problems were encountered with the contacting equipment, and poor mixing was experienced. The venturi throat was found to be too small,

and the flow rate of melt was limited to 46 m³/h, instead of the design rate of 65 m³/h. The gas to liquid ratio was therefore too high for efficient mixing, and some ozone was passing out of the flash tank unreacted. The throat was subsequently opened out and the flow rate increased to the design figure. This improved the situation for a while, but occasional problems arose when pieces of rubber or metal found their way into the melt tank and partially blocked the venturi or the static mixer.

Finally, the mixer was opened and it was found that two of the four elements had collapsed, and the pieces of metal were choking the line. It appeared that a combination of mechanical damage and fatigue failure had caused the elements to disintegrate. Pieces of metal striking the elements at high speed after leaving the venturi throat were thought to have initiated the failure, but this must have happened in the initial stages of the trial, as, after the first blockages were encountered, the returns to the melt tank were screened to eliminate all foreign objects from the melt. The fatigue failure resulted from vibration caused by extreme turbulence downstream of the venturi throat, where the pressure dropped from 8 bar to 1 bar and 40 m³/h of oxygen combined with 65 m³/h of melt. The elements have subsequently been replaced with eight elements of more robust construction, and the contacting has improved.

Results from factory trials

The performance of the unit has been monitored in two ways: by sampling and analysis at several points in the front end of the refinery, and by the routine refinery analyses. Catch samples were taken from the raw melt, the melt after ozonation, the limed melt, clear liquor and fine liquor, and taken for various analyses at the SMRI. The reduction in melt colour during ozonation can clearly be seen in Figure 3, apart from the second set of samples, which was taken during the period of poor contacting when low ozone usage efficiencies were experienced. Consequently, the small reductions in colour that might have resulted from the low ozone dosages were masked by the normal variation in liquor colours, and no significant differences were noted.

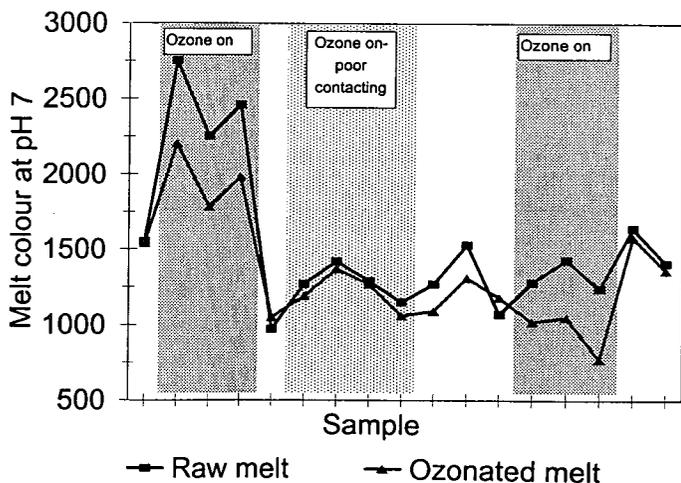


Figure 3. Colours of raw and treated melt samples taken during ozonation trials.

However, once the static mixer had been replaced, significant differences were observed in the sugar colours as monitored by regular analyses, and the operation of the ozone generator consistently corresponded with a drop in refined sugar colours, as can be seen in Figure 4. During these periods, the average ozone dosage was 90 ppm on brix, somewhat lower than was originally planned, but the positive effect of the ozone was nevertheless clear. It must be remembered that there is some delay between the addition of ozone and the drop in refined sugar colour due to the large hold-up in the refinery. Nevertheless, the melt colours respond rapidly, followed by the sugar colours 12 to 24 hours later.

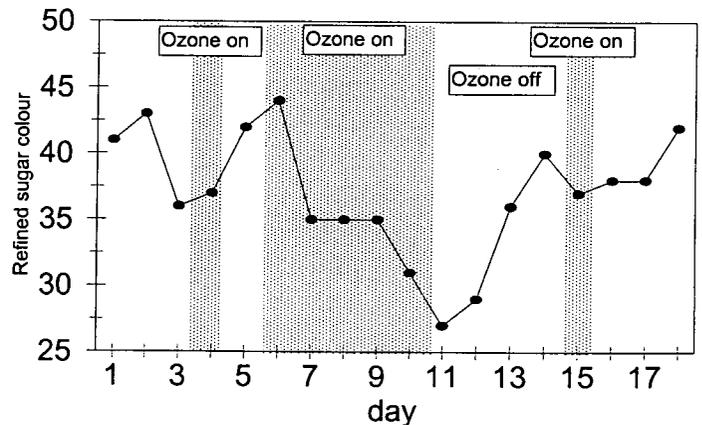


Figure 4. Refined sugar colours over a three week period.

The plant operated for much of the remainder of the year, with the season's refined sugar colours showing noticeable dips when the ozone generator was in operation (Figure 5). The decision was made to continue running the trial during the period of off-crop refining in February and March 1998. During off-crop refining, the mill burns coal to generate steam and power, and insufficient carbon dioxide is available from the boilers for the full carbonation process. Thus the quantities of lime and carbon dioxide added to the melt are reduced and lower colour removal results. It was felt that the extra decolourising power of the ozone would assist the refinery in maintaining the low refined sugar target colour during off-crop refining, and this has proved to be correct.

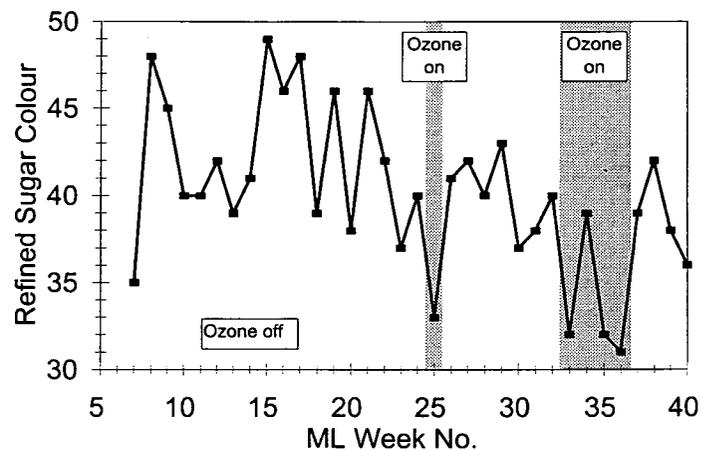


Figure 5. Weekly refined sugar colours at Malelane for the 1997 season.

The refinery ran at a mean throughput of 850 tons of refined sugar per day, with a peak production of 980 tons per day, and the lime addition was reduced from 9 000 to 7 000 ppm of CaO on melt. Although the melt colour was reduced by between 10 and 15% on ozonation, the destruction and removal of colour precursors also led to smaller colour increases across the boiling house than usual. Thus, despite the increased throughput and reduced liming, it was possible to bag five sugars and produce a refined sugar colour of 35 ICUMSA units on average over this period, compared with a refined sugar colour of between 40 and 45 units produced during previous off-crop refining campaigns.

Another benefit of ozonation was that the average bacteria count in refined sugar was reduced by 50% during the period when ozone was being added. This was to be expected, as

ozone is well-known to be a powerful bactericide. Ozonation was thought to have the possible disadvantage of increasing the organic acid levels in the refinery, and this was checked by analysis of the liquor samples by solid phase extraction followed by ion exclusion chromatography, as used by Walford and Walthew (1996).

The average results for raw and ozonated melts, for both the in-crop and off-crop refining periods, are shown in Table 2, from which it can be seen that no significant increase in organic acid levels occurred. Large differences were found between the liquors during in-crop refining and those during off-crop refining, particularly with regard to citric, glycolic and malic acids but, as these differences were present in the raw melt, they must have originated from the different raw sugars used during the two periods.

Table 2. Organic acid contents of raw and ozonated melt (ppm on brix).

Sample	Ozone (kg/h)	Oxalic	Citric	Aconitic	Glycolic	Lactic	Acetic	Malic
Average raw melt, in-crop	0	11	46	345	382	11	69	0
Average ozonated melt, in-crop	3,5	13	43	312	258	18	73	0
Average raw melt, off-crop	0	13	0	131	0	0	28	20
Average ozonated melt, off-crop	3,0	26	0	136	0	0	42	20

There also does not appear to be significant destruction of sugars at these levels of ozonation, as seen from Table 3. It was felt that a small (<0,1%) loss of sugars could be sacrificed if necessary in view of the great improvement in colour and the effective capacity increase associated with ozonation. Nevertheless, possible sugar destruction must still be monitored carefully.

Table 3. Reducing sugar analyses and purities of raw and ozonated melt.

Sample	Ozone (kg/h)	Fructose (ppm on brix)	Glucose (ppm on brix)	Purity (Pol/brix)
Average raw melt, in-crop	0	858	859	99,09
Average ozonated melt, in-crop	3,5	1 075	1 061	99,09
Average raw melt, off-crop	0	1 019	868	99,00
Average ozonated melt, off-crop	3,0	1 004	978	99,20

The future of ozone

This trial has proved the effectiveness of ozone in decolourising sugar solutions on a factory scale, and the reduction in sugar colours from all boilings has had an enormous benefit in the production of very low colour refined sugar. As with any new project, once the technical feasibility has been proved, the economic benefits must then be determined. One aspect that must still receive attention is the contacting pro-

cess. The combination of an eductor venturi and static mixer has not proved to be effective when dealing with the gas to liquid ratios required to achieve the desired ozone dosage, and alternative arrangements are being considered.

One of the more promising methods is the use of a gas dispersing impeller in a mixing tank prior to the reactor. Ozone is very reactive and rapidly consumed by the numerous organic compounds present in raw melt. However, the reaction rate is limited by mass transfer of the ozone into the melt, particularly through the gas phase. As oxygen is virtually insoluble in water and melt at 70 to 80°C, bubble size is critical in ensuring high efficiencies. It is therefore essential to produce bubbles of as small a size as possible to ensure the maximum surface area for transfer of ozone to the melt. This can be readily achieved by high shear mixers, the use of which is common in bioreactors for oxygenation.

Another piece of equipment that is commonly used in the process industry for gas-liquid contacting is a packed column or tray absorber. This is also being considered as an option, but these towers are possibly better suited for more soluble gases and are prone to blockages if solids are present in the liquid stream. In addition, the gas to liquid ratio required in this instance is outside the normal range for such towers (Treybal, 1982), and careful design would be necessary to ensure adequate operation.

Overall, the use of ozone for decolourisation holds many advantages over other methods. These derive mainly from the 'clean' nature of ozone, in that the breakdown products are oxygen and water, no effluent is produced and no regeneration is required, as in the case of ion exchange or activated

carbon use. Although the ozone has to be generated on site, modern plants are automatic and safe, as previously described, and the use of pure oxygen as feed has simplified the process and increased the ozone concentrations achievable, leading to smaller required gas volumes and hence better contacting.

The bottom line is always an economic one, though, and all the technical advantages in the world are of no use if the process is too expensive. However, it is believed that ozone will be very competitive with other processes when associated costs, such as effluent disposal, are considered.

Conclusions

Ozone has been shown to be a powerful chemical for the destruction of colour bodies and colour precursors in sugar solutions, and it has a great potential for use in refineries. The ease of application gives it an advantage over more conventional decolourisation methods, and the continued colour reduction effect throughout the refinery boiling house is a major benefit. The possible disadvantage that it was thought to hold of destroying sugars appears not to be valid, given proper control of pH, which is usual in refineries in any case.

The trial at the Malelane refinery has, despite some teething problems that are to be expected with a new process, been a resounding success. It has enabled TSB to continue to produce high quality low colour refined sugar despite very high throughputs in a season that has been marked by frequently high raw sugar colours. It is believed that ozone will prove to be a serious competitor in the drive for improved refined sugar quality.

Acknowledgements

This project has taken many weeks of hard work to reach this stage, and the staff of all three of the partner organisations, TSB Malelane, Messer Fedgas (Pty) Ltd, and the SMRI, have contributed greatly. The authors particularly wish to thank the technical staff of these organisations, notably the fitters, instrument technicians and analysts, without whom the project

would not have succeeded, and Moses Modibela of Messer Fedgas for his significant contribution to the success of this project. Finally, the management staff of these organisations and Messer Germany must be thanked for their strong commitment, both financially and in terms of manpower, to a project that was still an exploratory laboratory project three years ago.

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