REFEREED PAPER

LABORATORY AND PILOT PLANT TEST WORK TO EVALUATE POWDERED ACTIVATED CARBON AS AN *AD HOC* REFINERY DECOLOURISING ADDITIVE FOR USE DURING PERIODS OF HIGH RAW COLOUR

SIBIYA T AND SINGH I

Tsb Sugar, PO Box 47, Malelane, 1320, South Africa
sibiyat@tsb.co.za *singhi@tsb.co.za*

Abstract

Decolourisation at the Malelane cane sugar refinery is achieved by conventional carbonatation and cationic polyamine flocculant followed by light sulphitation. This technology is adequate to produce EEC2 specification refined sugar. However, occasional high input raw sugar colour increases the blended sugar colour to above the specification limit. Under these conditions the fourth sugar is rejected and only again accepted for blending once the combined sugar colour is within the specification limit. Powdered activated carbon (PAC) is an established decolourising agent for sugar application. However, its once-off use contributes to its high operating cost and therefore limits wider use. The intermittent nature of the out of specification colour problem has prompted interest in PAC as an *ad hoc* additive for use during problem periods. PAC application requires carbon dosage equipment, contacting tanks and dedicated filters. The main purpose of this test work has been to determine whether PAC can be applied as an additive into the existing process without the need for any new equipment. For this reason, dosage directly into carbonated liquor prior to filtration was made the main focus area. After initial laboratory screening tests, a carbonated liquor slip-stream was treated with PAC and filtered in a pilot plant plate and frame filter unit alongside the factory pressure leaf filters. The decolourisation results obtained from laboratory testing and pilot plant performance have shown that PAC activity is not inhibited in the presence of carbonatation sludge and therefore could be used on an *ad hoc* basis to decolourise unfiltered carbonated liquor during periods of high input sugar colour.

Keywords: sugar refining, decolourisation, powdered activated carbon (PAC), carbonatation, filtration

Introduction

The Malelane sugar refinery is a 55 ton/h back-end cane sugar refinery that obtains raw sugar for refining from both the Malelane and Komati mills. Decolourisation is achieved by conventional carbonatation followed by cationic polyamine flocculant and then filtration. The filtered carbonated liquor is lightly sulphited using liquid SO_2 and then filtered. This technology is adequate to produce EEC2 specification refined sugar; however, occasional high input raw sugar colour, as high as 50-60% above the desired 1200 ICUMSA units (ICU), increases the blended sugar colour to above the specification limit. Under these conditions the fourth sugar is rejected to melt and only again accepted for blending once the combined sugar colour is within the specification limit. The intermittent nature of the out of specification colour problem at the Malelane Refinery has prompted interest in powdered activated carbon (PAC) as an *ad hoc* additive for use during problem periods.

Objective

Initial laboratory PAC screening trials focused on dosage rates and different points of application. Following successful laboratory trials, testing progressed to pilot plant filter work to determine whether the results could be replicated. PAC application requires carbon dosage equipment, contacting tanks and dedicated filters to remove the spent powdered carbon. The main purpose of this test work was to determine whether PAC could be applied as an additive into the conventional carbonatation process without the need for any new equipment. For this reason dosage directly into carbonated liquor prior to filtration was made the main focus area. The process flow diagram is shown in Figure 1. The pilot plant trials involved a slip-stream of factory carbonated liquor being treated with PAC and filtered in a mini plate and frame filter unit.

The methodology for laboratory testing and pilot plant testing and the decolourisation results are discussed in this paper.

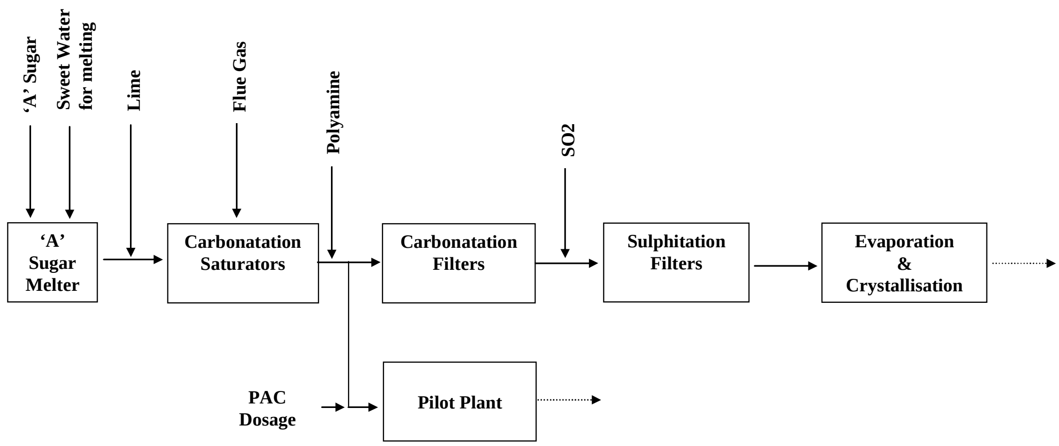

Figure 1. Malelane refinery decolourisation process, showing position of carbonated liquor slip-stream to pilot plant.

Activated carbon

Activated carbon is produced from carbonaceous materials such as nutshell, wood or coal. The carbon may be impregnated with an acid or strong base or a salt before pyrolysis at 600 to 900 °C in the absence of oxygen, and then activation in an oxidising atmosphere (oxygen or steam) at temperatures usually in the range 450 to 1200 °C (www.wikipedia.org Activated carbon, 2011).

Activated carbon is available either as a granular activated carbon (GAC) or as a powdered activated carbon (PAC). Activated carbon can be described simplistically as a carbonaceous skeleton with an extremely large network of pores. Although the starting material and the adsorptive properties are the same, the method of application differs significantly. Commercially available activated carbons are manufactured from a wide variety of starting materials depending on the properties desired in the carbon. Special properties are conferred by physical and/or chemical treatment and, as a consequence, activated carbons can vary significantly in their distribution of pore sizes (Davis, 2001).

Activated carbon can be characterised by its physical and activity properties. Important physical properties are surface area, density, particle size, abrasion resistance and ash content. The smaller the particle, the less far the colourant has to diffuse to reach the core of the particle, hence the rate of uptake of colourant overall is faster and subsequent adsorption is increased. However, smaller particles create more pressure drop across a carbon bed. Ash level is the inorganic residue in carbon and reduces overall activity with potential for leaching into the treated liquid stream. Activity properties include pore size distribution which defines the available pore volume of a carbon over three pore sizes, *viz*. micropore (<10 nm), mesopore (100 nm) and macropore (>100 nm). Taste, odour and colour bodies and organics removal require a carbon with a broad range of pore sizes. The iodine number (mg I_2/g carbon) defines the micropore capacity. Colour bodies are generally large molecules and their removal requires a carbon with large macropore volume, which is represented by the molasses number (Deithorn and Mazzoni, www.tigg.com Activated carbon properties, 2011). However. molasses number is generally a poor and variable test method. The best method for assessing carbons for sugar refining looks at the mesopore range, namely the methylene blue number.

Activated carbon is widely used for the purification of highly coloured liquids in the food, chemical and pharmaceutical industries. Decolourisation is by adsorption of plant pigments derived from the sugarcane (polyphenols) and colours created during processing, such as melanoidins and caramels. Activated carbon also has the capability to remove non-colorant impurities such as amino acids, polysaccharides, etc. along with the colour (www.unionchemicals.com Norit sugar refining, 2011).

In the sugar industry activated carbon is used to decolourise sugar syrups prior to crystallisation of refined white sugar. The activated carbon treatment step typically follows a clarification step such as carbonatation, phosphatation etc. The filtered clarified melt usually has a concentration of 60° to 65° Brix and a colour of 500 to 900 ICU. PAC is used as a powder with particles less than 0.045 mm in size and is usually dosed as slurry in water or syrup into a stirred batch contact tank with a retention time of 30 to 45 minutes. The mixture is maintained at a temperature of 80 to 90 °C. The decolourised liquor colour is typically 100 to 400 ICU (Dominiguez and Hyndshaw, 1977).

The filterability of the PAC can be improved by the use of a pre-coat, which is typically applied at a dose rate of 1 kg/m² of filter area and added as a body feed at a dose rate of 30 to 50% of the carbon weight. The first filtrate contains carbon fines and must be recycled. After filtration, the filter cake is de-sweetened and discarded.

A novel approach to powdered activated carbon use is that of layer filtration. A layer of powdered carbon is deposited on top of a pre-coat layer in a filter and the liquor is then pumped through. The properties of the carbon are carefully controlled to ensure rapid colour removal from the liquor with minimal pressure drop. Only a few millimetres thickness of carbon is claimed to achieve decolourisation (Potwora *et al*., 1998).

The desired properties of PAC for sugar decolourisation as set out by Potwora *et al*. (1998) are summarised in Table 1.

Table 1. Desired properties of powdered activated carbon (PAC).

Parameter	**Properties**
Colour loading	The adsorptive properties and pore structure of a chemically activated carbon are generally suited to decolourise feed colour levels of 500 to 900 ICU.
pH	A neutral carbon is mandatory! Acid carbons lead to hydrolysis of sucrose (sugar loss). Alkaline carbons lead to formation of melanoidins.
Filtration	Good filtration characteristics are beneficial and can result in higher throughputs and lower pressure drops.
Concentration	There is a proportional relationship between the concentration of PAC in the fluid and the amount of impurities removed at a given temperature. With fine particles adsorption is much more rapid.
Retention Time	Adequate retention time is needed to allow the PAC to adsorb as much of the impurities as possible. The amount of impurities adsorbed increases with increased retention time until equilibrium is reached.
Agitation	Shaking or aerating gives better surface area for adsorption than stirring.

The benefits of using activated carbon in a sugar refinery are summarised below.

- Sugar purity: Improvement in sugar liquor purity results in a higher quality refined sugar crystal.
- Yields: Increased pan yield due to improved quality of mother liquor and therefore lower return of high colour syrups to the recovery house.
- Rejects: Quicker start-up due to lower reject rate.
- Centrifugals: Less crystal washing in the centrifugals resulting in reduced recycling with concomitant increase in production and reduction in energy usage.

Mechanism of decolourisation by PAC

Davis (2001) states that appreciation of the types of colour present is important when choosing and operating refinery processes, as different processes may remove different types of colour. There are generally four recognised types of colour associated with sugar crystals, *viz*. plant pigments, melanoidins, caramels and alkaline degradation products of fructose. The last three are factory produced colour pigments. Other factors that can influence the degree of colour are solution pH and the polarity of the colour molecules. Activated carbon actually removes the impurity, unlike bleaching operations in which the coloured impurity is only changed to a colourless product.

The most important factor determining the decolourisation efficacy of carbon is the non-polar nature of the surface. The surface forces (van der Waal's forces) create a stronger attraction between the carbon surface and the colour molecules than between the colour molecules and the sugar liquor (Truemper, 1968). The enormous surface area due to its porous structure (500 to 2000 m^2/g) means that large quantities of colour may be absorbed before the carbon is exhausted. This is physical adsorption, and is responsible for most of the colour removal from the sugar liquors. However, carbon also has some oxygenated functional groups that cause chemisorption, which allows some polar molecules to be adsorbed. As a result, carbon is not specific for any type of colour, but gives high overall colour removal (typically up to 80%). An important factor to be noted in colour removal by carbon is the size of the colourant molecules relative to the pore sizes. Clearly, before a colourant can be adsorbed onto the carbon, it must diffuse into the carbon pores and orientate itself correctly. The diffusion process determines the rate at which colour can be removed and therefore the smaller particle size of PAC allows more rapid adsorption of colour than in the case with larger GAC particles, although the total colour removed per unit mass is similar (Davis, 2001).

PAC is an established decolourising agent for sugar application. Its once-off use contributes to its high operating cost and therefore limits wider use. Rein (2007) points out that colour removal is dependent on the quantity of carbon being dosed and decolourisation can be as high as 90%, and lists the advantages and disadvantages of powdered carbon as:

- Low investment cost as no regeneration is required.
- Very high operating cost (0.1 to 0.5% on sugar) due to discarding carbon after use.
- Very high decolourising effectiveness due to large surface area, mainly physical adsorption and little chemisorption.
- Highly flexible and ash does not affect crystallisation.
- Minor environmental hazard.
- Best suited to low throughput and/or batch operations.

Jones (1984) conducted PAC decolourisation trials at the Malelane refinery on 'A' melt, i.e. before carbonatation. His findings were that no significant colour reduction was observed at a dosage rate of 0.05% PAC on Brix; however, at 0.1% PAC on Brix an additional 6% decolourisation was observed in fine liquor. To assess the effect of PAC on high input colour, he conducted laboratory trials and concluded that at 3000 ICU raw sugar colour, a

PAC dosage rate of 0.4 to 0.5% was required to produce fine liquor of acceptable colour. He concluded that at these dosage rates, PAC was not economically viable at that stage.

Laboratory trials

Initial laboratory screening trials focused on different dosage rates of PAC and at different points of application in the refining process. An initial screening decolourisation trial was performed on raw melt to determine the degree of the decolourisation. Only a single commercially available PAC (product ‘A’) was available for testing at this stage of the trials. High colour and low colour melt samples were dosed with PAC ‘A’ at dosage rates of 0.025, 0.05 and 0.1% on Brix. The samples were vigorously stirred for 20 min and left to stand for 30 min. Samples were kept in a constant temperature water bath at 70 °C. The samples were filtered through a 0.45 micron filter prior to colour measurements. Results are shown in Figure 2.

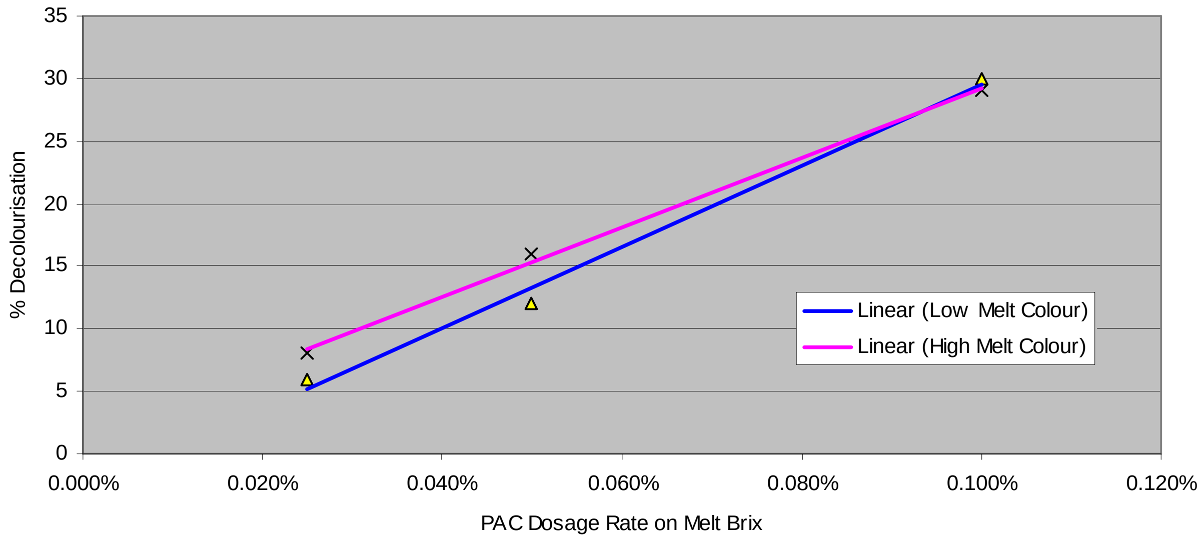

Figure 2. Melt decolourisation with powdered activated carbon (PAC) – laboratory trial.

Both the high and low colour treated melt samples show progressive decolourisation proportional to the dosage rate.

With a view of using the existing refinery carbonated liquor and sulphited liquor filters to filter out the spent carbon, a second set of laboratory decolourisation trials was conducted on unfiltered carbonated and unfiltered sulphited liquor. Results are shown in Table 2. At 0.1% PAC on Brix the colour removal achieved (±30%) was similar to results for melt decolourisation. With the possibility of progressing to plant trials, it was decided that further test work should be concentrated on unfiltered carbonated liquor. The rationale for this was that there would be two sets of factory filters (carbonatation and sulphitation) to mitigate against the risk of carbon particle breakthrough into refined sugar.

Table 2. Decolourisation of unfiltered carbonated and sulphited liquor by powdered activated carbon (PAC).

Liquor	Untreated		Dosed 0.1% PAC 'A'	
	°Brix	Colour ICU	Colour ICU	% Decol.
Carbonated	60.2	670	480	28
Sulphited	61.9	647	437	33

In anticipation that retention times would be reduced if PAC was dosed into the existing factory unfiltered carbonated liquor tank, a third set of tests was undertaken to examine the impact of retention times. Results are shown in Figure 3. Predictably, decolourisation dropped off with reduced retention time. It was decided that for further test work the supplier recommendation of 30-40 minutes contact time would be maintained.

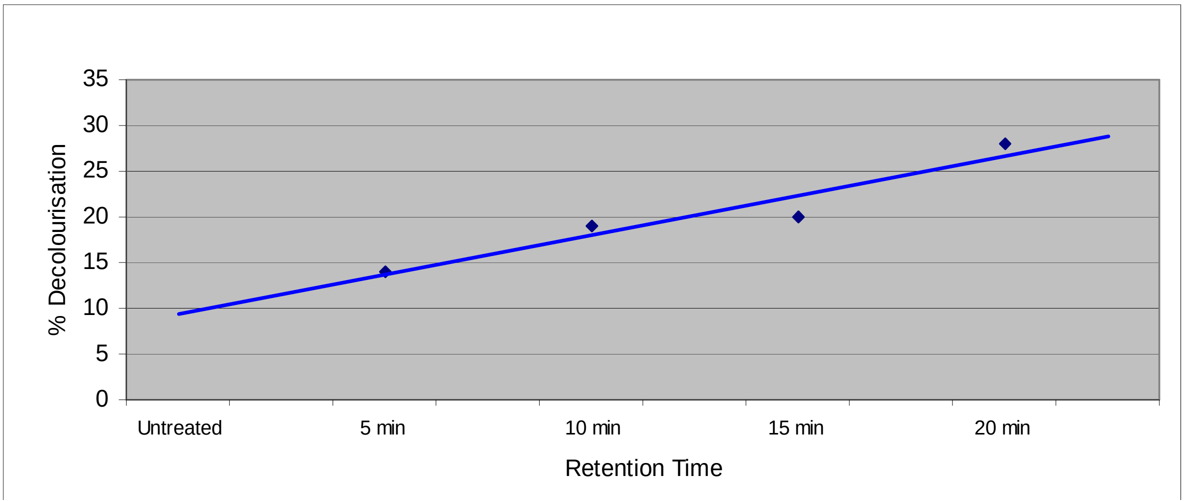

Figure 3. Impact of retention time on decolourisation of carbonated liquor dosed with 0.1% powdered activated carbon (PAC) on brix.

The conclusions drawn from the laboratory trials confirmed:

- The suitability of PAC for decolourising refinery streams specifically the polyamine + carbonatation + sulphitation decolourisation process applied at the Malelane refinery.
- The laboratory tests indicate that the decolourising capacity does not appear to be inhibited by the presence of carbonatation and sulphitation sludge.
- The above laboratory tests only considered decolourisation and suitability of PAC dosage and not the mechanism of PAC adsorption.

Pilot plant trials

The laboratory screening trials identified the opportunity to dose PAC directly into unfiltered carbonated liquor. The purpose of the next phase of testing was to determine if the laboratory results could be replicated under factory conditions. The pilot plant test work concentrated on decolourising an unfiltered carbonated slip stream using PAC and filtering on a pilot filter unit. Figure 4 shows the process flow arrangement.

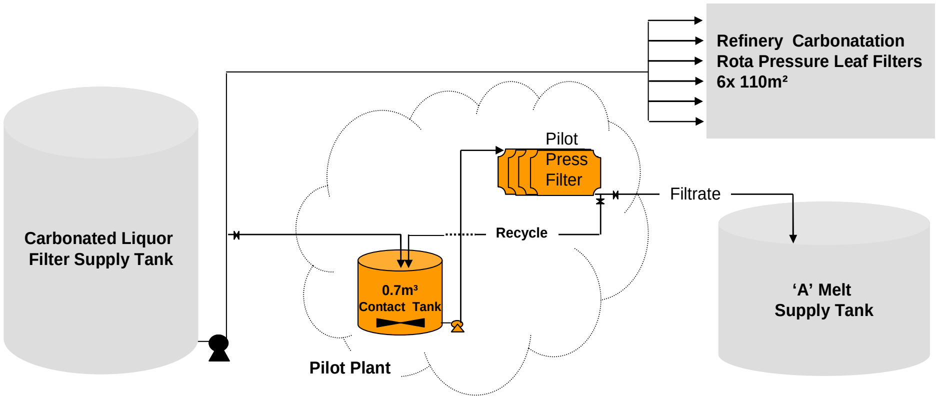

Figure 4. Pilot plant process flow diagramme.

Methodology

A slip-stream of factory unfiltered carbonated liquor (already pre-treated with polyelectrolyte and filter body aid) was accumulated in a 700 litre stirred tank and dosed with PAC. Commercial grades of PAC from three different suppliers were tested. The activated carbon was introduced as a water based slurry into the mixing tank and the average contact time was 45 min. The treated liquor was filtered on a 12 frame pilot press filter shown in Figure 5.

Figure 5. Photograph of pilot plant press filter.

The pilot filter comprises 12 frames in parallel with a total area of 4.88 m². The pilot plant filtration rate of 0.12 $m^3/(m^2.h)$ was selected to match the factory carbonated liquor filter rates. The temperature of the feed liquor was recorded for each batch trial as well as the filter pressure. The first runnings from the filter (cloudy liquor) were recycled back to the contact tank. Once the liquor became clear the valves were switched and the filtered liquor was diverted to the refinery melt tank.

Samples taken were analysed for colour, pH and Brix. As a qualitative check, the laboratory filter disk (after filtering under vacuum) was inspected for evidence any carbon break-through during filtration. The ICUMSA method was used for colour and turbidity measurement. Decolourisation % was determined by referencing the pilot plant filtrate colour to the colour exiting the factory carbonated liquor filters.

The duration for each cycle (start filling to tank empty) was approximately 55 minutes. At five minute intervals during the cycle the pressure in the filter and volume of the filtrate were recorded. This information was then used to calculate the filtration rate. The pilot plant conditions are summarised in Table 3. Commercial grades of PAC obtained from three different suppliers (labelled product A, B, C) were tested. The specification of the carbons tested is given in Appendix 1. It was decided that initial testing would be done with dosage rates based on work done by Jones (1984). Each PAC was evaluated at three dosage rates, *viz*. high (0.1% on Bx), medium (0.05% on Bx) and low (0.025% on Bx).

Table 3. Pilot plant operating conditions.

Total Flow rate (m^3/h)	0.7
Area (m²)	4.88
Average filtering time per run (min)	55
Filtration rate ($m^3/(m^2.h)$)	0.12
Press filter operating pressure (kPa)	60 to 160
Inlet temperature (°C)	80
Inlet Brix (°)	62 to 63
Inlet pH	8.2 to 8.3
Inlet colour (ICU)	857 to 1830
PAC dosage on Brix	0.025 %, 0.05% and 0.1%
Carbon used per run @ 0.1% (kg)	0.52
Sampling	Catch every 5 minutes

Pilot plant results and discussion

The typical pressure, pH and filtration rate profiles during the filtration cycle for the PAC dosage rate of 0.1% on Bx are shown in Table 4. All filtration tests on the pilot plant filter were done without pre-coat to be consistent with factory carbonatation practice. No significant pH drop was evident between pilot plant filtrate and factory filtered liquor (clear liquor). The increase in pressure across the pilot filter for all PAC runs was fairly similar, starting at 60 kPa and increasing gradually up to 160 kPa over 55 minutes. The measured filtration rates for all runs were in the range 0.11 to 0.12 $m^3/(m^2.h)$. This rate was similar to factory conditions. At the end of the cycle the cake was de-sweetened using hot water and the mud volumes estimated once the filter frames were opened up.

Table 4. Typical pH, temperature, pressure and filtration rate profile during pilot plant filter cycle.

Time (min)	Refinery Carb Unfiltered Liquor			Refinery Carb Filtered Liquor				Filtered liquor ex Pilot Plant PAC 0.1% on Bx				
	pH	Temp °C	°Bx	pH	Temp °C	°Bx	Filtration Rate $m^3/(m^2.hr)$	pH	Temp °C	°Bx	Filtration Rate $m^3/(m^2.hr)$	Pressure kPa
5	8.16	83	62	8.25	79	62	0.12	8.17	78	62	0.11	120
10	-		-	8.26				8.29			0.11	120
15	-		-	8.09				8.15			0.12	150
20	-		-	8.00				8.20			0.12	150
25	-		-	8.13				8.24			0.12	150
30	-		-	8.19				8.19			0.12	150
35	-		-	8.23				8.16			0.11	150
40	-		-	8.24				8.15			0.12	150
45	-		-	8.26				8.16			0.12	160
50	-		-	8.17				8.14			0.12	160
55	-		-	8.19				8.13	73		0.12	160
Ave.	8.16	83	62	8.18	79	62	0.12	8.18	78		0.12	147

Figure 6 shows the laboratory discs after vacuum filtration. The pilot plant disc shows no evidence of carbon breakthrough even though no pre-coat had been used.

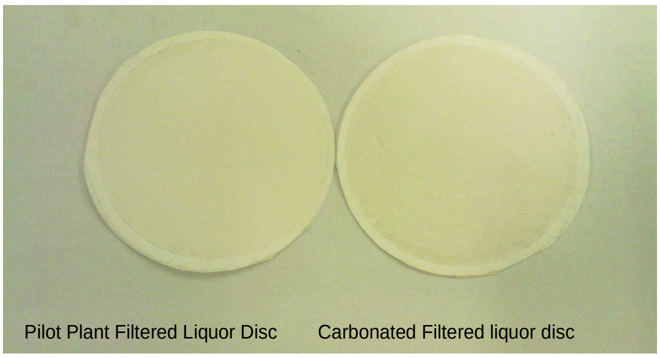

Figure 6. Comparison of laboratory filter discs after vacuum filtration – no carbon breakthrough evident on pilot plant disc.

Figure 7 shows the decolourisation results at 0.025, 0.05 and 0.1% PAC on Brix for PAC from different suppliers. Significant decolourisation variation is evident between suppliers. The highest decolourisation results were obtained using PAC product 'A' for high, medium and low dosage rates.

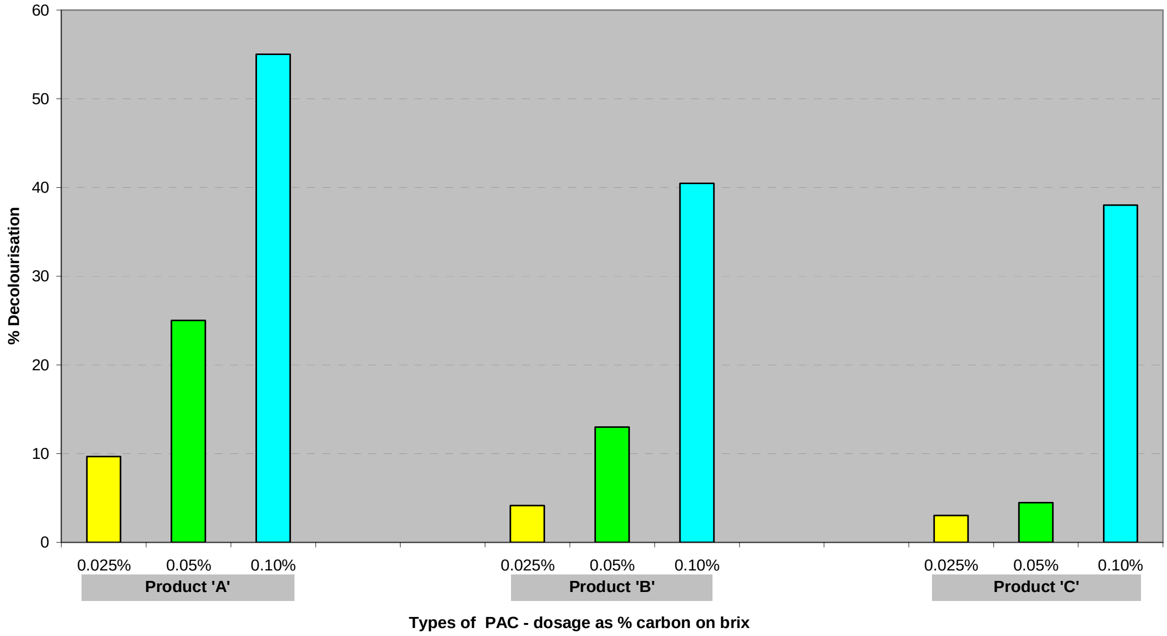

Figure 7. Decolourisation with different powdered activated carbon (PAC).

When the factory was processing high colour raws (1830 ICU) the opportunity to determine the decolourising efficacy of PAC at higher input sugar colour arose. Due to time constraints, only the PAC from supplier 'A' was evaluated. Results are shown in Figure 8. A similar level of decolourisation (55%) was achieved and no significant pH drop was evident. Decolourisation was fairly linear at the dosage rates tested. Filtration rates were similar to other tests.

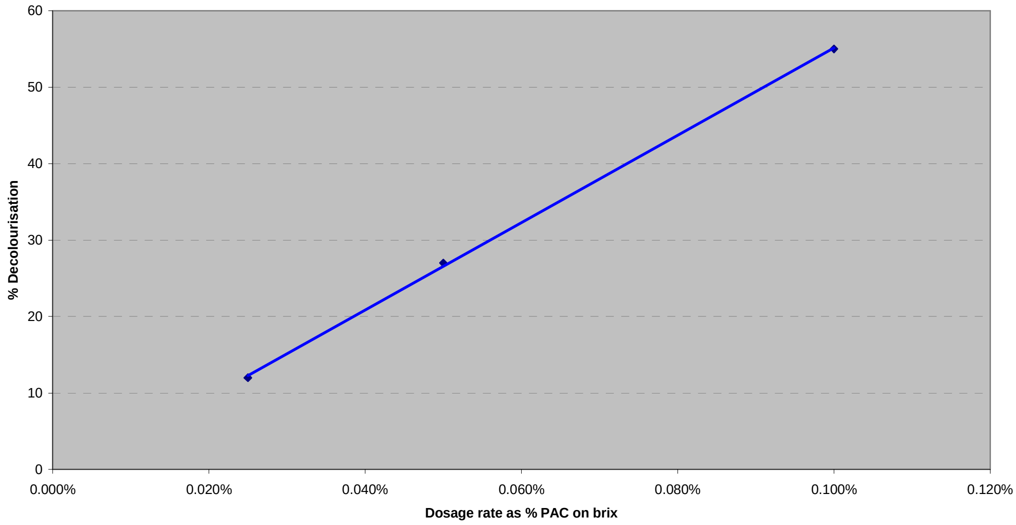

Figure 8. Powdered activated carbon (PAC) decolourisation test on high input colour using PAC product 'A'.

PAC cost

Table 5 gives an indicative cost of using PAC to supplement carbonatation decolourisation. The unit price of the best performing PAC tested was used to establish the cost per ton of sugar melted. The cost of using liquid SO_2 for polish decolourisation after carbonatation has been included as a benchmark. At the 10% supplemental decolourisation level, the cost of using PAC per ton of sugar is more than double that of liquid SO_2. At this level, continuous dosage of PAC will be difficult to justify; however, a case can be made for *ad hoc* dosage to treat problem raws.

Table 5. Indicative powdered activated carbon (PAC) decolourisation cost benchmarked with SO_2 decolourisation cost.

	Decolourisation with PAC			Polish decolourisation with Liquid SO_2
Dosage rate % on raw sugar	0.10%	0.05%	0.025%	0.01%
% decolourisation	50%	25%	10%	10%
Dosage rate on raw sugar (kg/ton)	1	0.5	0.25	0.10
Average cost per kg (Rand)	22	22	22	20
Cost per ton raw sugar (Rand)	22	11	5.5	2

Conclusions

Laboratory and pilot plant decolourisation trials dosing PAC into unfiltered carbonated liquor have been undertaken at the Malelane Refinery with the aim of determining the degree of decolourisation and the subsequent impact on filtration.

The pilot plant decolourisation results for product 'A' show greater colour reduction than the laboratory decolourisation results. At the dosage rates tested, PAC activity does not appear to be inhibited in the presence of carbonatation sludge.

The three carbons initially tested showed significant decolourisation performance difference. At the time of writing, alternative carbons offered by the suppliers had not been tested. The highest percentage decolourisation was obtained using PAC from supplier 'A'. For dosage rates of 0.1, 0.05 and 0.025% on Brix, decolourisation results were 57, 27 and 10%, respectively.

No drop-off in filtration rate was observed during the pilot plant filter cycle, indicating that at rates up to 0.1% PAC dosage the cake resistance is not a capacity limiting factor.

The pH of filtrate from the pilot plant was similar to that of factory filtered liquor, confirming the neutrality of the PACs tested.

Continuous dosage of PAC will be difficult to justify at current costs of PAC; however, a case can be made for *ad hoc* dosage to treat high colour input raws in carbonatation refineries having limited decolourisation capacity and constrained capital availability.
This test work has highlighted the suitability of using a mini filter plant for evaluation of decolourising agents and filter aids on a pilot scale to take out any 'guesswork' before proceeding to full scale factory trials.

These results support progressing to full scale factory testing of PAC at the Malelane sugar refinery.

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APPENDIX 1:
Specification of the different powdered activated carbons (PACs) tested.

PAC Specification	Product A	Product B	Product C
Molasses number	180	200	280
Methylene blue adsorption (g/100 g)	29	26	27
Total surface area (m^2/g)	1400	1200	1000
Ash content (mass %)	2	3	4
Moisture (mass %)	11	10	10
pH	2	5	3
Apparent density (kg/m^3)	370	320	300