

# AN INVESTIGATION INTO THE CAUSES OF VAPOUR PIPE CORROSION AT FX MILL

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## Abstract

Serious corrosion of vapour and condensate lines has occurred at Felixton during the past two seasons. Analysis indicated that vapour two condensates contained excessively high levels of acetic acid. Acetate levels in mixed juice were also found to be significantly higher than at other factories. Preliminary work in both the laboratory and factory indicated that the high acetate levels are a direct result of the liming conditions in the diffuser causing hydrolysis of hemiacetyl groups present in the bagasse. When liming was stopped, acetate concentrations dropped to acceptable levels.

## Introduction

During 1986 the Institute, in collaboration with FX mill, began an intensive study of inversion losses in the evaporator station. At the same time process staff voiced their concern regarding the serious corrosion of vapour and condensate lines, vapour two being especially affected. Corrosion was severe in condensates pipes and in the steam-chests of vacuum pan calandrias. Because of its known aggressiveness in corrosion<sup>1</sup> and due to its volatility, acetic acid was determined in V1, V2 and V3 condensates from FX during the 1986 season.<sup>2</sup> FX results were by far the highest in the Industry with over 80% of the V2 condensate samples containing at least 20 ppm acetic acid. In contrast other mills produced much lower results (PG = 2%, NB = 6%, ME and ML = 0%). FX's results for last season indicated that acetic acid levels in V1 condensate were generally less than 10 ppm, whilst V2 condensate levels ranged between 30 and 40 ppm and V3 condensate levels were within 20 to 30 ppm. Damage to piping has been considerable and replacement costs have been high. In 1987 the mill was forced to neutralise V2 condensate with a mixture of ammonia and cyclohexylamine. This was however only a short term treatment and work was initiated in 1987 to:

- confirm the high acetic acid levels in V2 condensates
- pinpoint where and how acetic acid was being produced
- reduce acetic acid concentrations to acceptable levels.

## Experimental

*Sampling* V1, V2 and V3 condensates (10 ml) from both the A and B evaporator sets were taken, once per shift, and sealed in pre-labelled sachets. Preservative was not added. The samples were rapidly frozen and stored in a deep freeze. The shift samples were composited to daily samples and these were analysed for acetic acid. Mixed juice (MJ) samples were generally the SICB official weekly samples. Samples of DAC and clear juice (CJ) were taken hourly and composited on either a daily or weekly basis.

*Analysis* Gas Chromatography (GC) was used to determine acetic acid in the samples. Condensates were injected directly, and juice samples subjected to a vacuum micro-distillation technique prior to GC.<sup>3,4</sup>

## Results

Condensates Statistical data for V1, V2 and V3 condensates are shown in Table 1.

Table 1  
Acetic Acid (ppm) in FX Condensates July 87

Condensate	V1		V2		V3	
	A	B	A	B	A	B
Evaporator						
No. of samples	25	24	24	25	24	25
Min. ppm	0	1	13	8	3	5
Max. ppm	32	44	129	116	53	62
Mean ppm	10	10	50	44	28	24
SD	7	9	27	26	14	15

Acetic acid levels in V2 condensates for July 1987 are also shown in Figure 1.

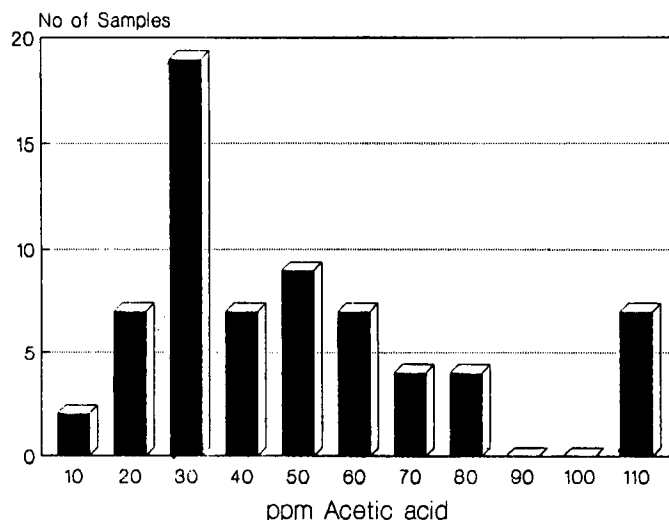


FIGURE 1 Acetic Acid Levels (ppm) in V2 Condensates FX Mill July 1987.

Results from Table 1 and Figure 1 indicate that:

- For V1 condensates both evaporator sets contained similar low concentrations of acetic acid.
- For V2 condensates the levels were much the same for both sets with levels peaking above 100 ppm. Acetic acid concentrations were even higher than those measured in 1986. Average levels were high at almost 50 ppm.
- For V3 condensates both phases were again comparable with amounts intermediate between V1 and V2.

**HPLC** Due to the corrosiveness of acetic acid, the very high levels measured were of obvious concern and the possibility of a co-eluting interferant inflating the results could not be overlooked. HPLC using both cation exchange and reverse phase columns and ultra-violet detection were therefore used to cross-check the GC method. HPLC yielded results that were virtually identical to the GC results.<sup>5,6</sup>

**Diffusion** Theoretical calculations suggested that invert decomposition in the evaporator could not be the primary cause of the high acetic acid levels. Recently workers in Australia<sup>7</sup> compared non-sucrose data from mills and diffusers as they were concerned that diffusion may extract more undesirable impurities for a given sucrose extraction resulting in higher losses in molasses. The addition of lime to diffusers was evaluated. The authors pointed out that the hemicellulose fraction of bagasse although mainly xylan-based usually carries with it a small amount of acetate esters and in the presence of lime these can hydrolyse to form calcium acetate. Acetate levels dropped dramatically when the diffusers were not limed. As a direct result of this information FX stopped liming for three weeks. Acetic acid levels in V2 condensates are given in Table 2.

Table 2

Effect of Diffuser Liming on Acetic Acid Levels (ppm) in V2 condensates, FX - 1987

Liming	Mean Acetic	SD	No. of samples
ON	50	27	24
OFF	8	5	17
ON	20	10	8

Liming appeared to have a definite effect on the acetic acid level in V2. There was a significant drop when liming was stopped. An increase was again observed when liming was restarted.

**Evaporator juices** Acetic acid can be measured directly in condensates. To determine this acid in juices a vacuum micro distillation procedure was used to isolate the acid from juice prior to GC.<sup>3</sup> A limited number of evaporator juices was analysed for acetic acid to determine the effect of diffuser liming on acetate levels. The results are summarised in Table 3.

Table 3

Acetic Acid Levels in Evaporator Juices (ppm on Bx) Effect of diffuser liming

Treatment	CJ	1st effect	2nd effect	No. of samples
Lime	1 610	1 770	1 650	8
No Lime	420	430	450	6

The levels of acetic acid in evaporator juices showed similar trends to the condensate samples, i.e. diffuser liming appeared to release acetic acid and raised the levels in evaporator juices. There was also no significant change in acetic acid from CJ to juice exiting and second effect, confirming the theoretical calculation that high concentrations of acetic acid were not connected to monosaccharide breakdown. Approximately 90% of the acetic acid in evaporator juices is present as calcium acetate and is naturally not volatile. Therefore the amount in the vapour is small compared with the amount in juice.

**Factory Trials of Lime Versus No Lime** The diffusers at FX were run for a period of 19 days without lime addition. MJ acetate levels averaged 260 ppm with a scatter of  $\pm 70$  ppm. When liming commenced again the average acetate levels in MJ jumped to 640 ppm with a scatter of  $\pm 150$  ppm. Again liming appeared to have increased acetate levels. In a further attempt to determine the effect of high temperature liming on acetate production, process staff at FX ran the A-diffuser for 1 week at 85°C using their normal liming procedure. The B-diffuser was not limed and it was run at 75°C. The conditions in the 2 diffusers were then reversed for the following week. Results are included in Table 4.

Table 4

Effect of Lime and Temperature on Acetate and Lactate Production in mixed juice at FX, 1987 Season (ppm on Bx)

w/e	Diffuser	Lime	Temp.	Acetic	Lactic
5/12	A	Yes	85°C	960	600
5/12	B	No	75°C	310	610
12/12	A	No	75°C	270	720
12/12	B	Yes	85°C	960	825

The following comments regarding Table 4 are appropriate:

- High concentrations of acetate were obtained when either of the diffusers was limed at 85°C.
- When liming ceased levels dropped to those found in DAC samples (see table 6).
- Temperature and liming appeared to have no effect on lactic acid production. This was expected as even thermophilic bacteria are not active at temperatures greater than 70°C.<sup>8</sup>

**Inter-factory comparison of acetate levels in MJ** Weekly MJ samples from 2 mills, 3 cane diffuser and a bagasse diffuser were analysed for acetic acid and the results are shown in Table 5.

Table 5

Comparison of Acetate levels in MJ Samples (ppm on BX)

W/E	PG	FX	AK	MS-D	MS-M	ME
19/9	290	280*	210	260	310	270
26/9	310	N/S	210	270	230	180
10/10	310	900	270	350	310	290
17/10	395	1 100	280	300	250	260
MEAN	330	—	240	295	275	250

\* Diffuser not limed

N/S no samples (floods)

PG - Bagasse Diffuser - uses lime

FX - Cane Diffuser - lime added at eight points

AK - Cane Diffuser - lime added at two points

MS-D - Cane Diffuser - lime added at one point

MS-M - Milling tandem

ME - Milling tandem

From Table 5 the following points can be noted:

- Levels of acetate were not significantly different in diffuser and mill juice at MS.
- AK also has a cane diffuser like FX. Even so AK has much lower MJ acetate levels than FX, implying that liming procedures could be the reason for the significant differences between the two.

- (c) The bagasse diffuser at PG has acetate levels only marginally higher than other factories.
- (d) FX produced the highest acetate levels (900–1 110 ppm on brix) for the period when the factory was liming. This was about 4 to 5 times higher than the other factories. During the week ending 19/9 when no lime was added, acetate levels in MJ from FX were similar to the other factories. The evidence to date suggests that the high levels of acetate in MJ at FX may be due to differences in the liming procedure.

*DAC samples* Acetic acid can also be produced by bacteria at temperatures lower than those normally used in diffusers.<sup>9</sup> In order to acquire more information on background levels of acetic acid prior to bagasse hydrolysis, DAC samples were tested for both acetic and lactic acids over a 5 day period. Results are presented in Table 6.

Table 6

Organic Acids in DAC Samples, FX w/e 29/11/87 (ppm on Bx)

Date	Bx	Acetic	Lactic
25/11	5,19	230	390
26/11	5,13	210	430
27/11	4,95	260	360
28/11	4,80	310	310
29/11	4,68	280	830
Mean	4,95	260	460
SD		± 40	± 210

Comparison of results from table 6 with the MJ data from FX and the other mills indicate that:

- (a) Background levels of acetic acid in MJ should lie between 200 and 300 ppm.
- (b) Due to the diffuser temperature at FX any increase in acetic acid over the background level is probably an indication of acetyl hydrolysis rather than microbiological breakdown of sucrose.
- (c) Lactic acid levels, a sensitive indicator of bacterial loss of sucrose<sup>9</sup> were always higher and more variable than acetic acid concentrations.

#### *Effect of Temperature and pH on Acetate Production*

A laboratory experiment was carried out in order to obtain a preliminary idea of the effect of temperature and pH on acetyl hydrolysis. Fresh cane was finely prepared in a Jeffco cutter-grinder and was then heated in laboratory diffusers<sup>10</sup> for 115 minutes at 68° and 82°C. pH ranged from 6,3 to 7,0 for the 4 runs. Calcium hydroxide was used to adjust pH. The juice from each experiment was analysed for brix and acetic acid. Temperature was read every 15 minutes and averaged. pH values were obtained by averaging initial and final pH data. From these tentative results it appears that under the laboratory conditions we can expect:

- (a) acetate levels to rise by 200–300 ppm for a 10°C increase in temperature. (Note higher temperatures would also increase the volatility of acetic acid leading to more acid condensing on the colder parts of the diffuser and

hence higher corrosion rates). Australian workers found that 75°C is adequate to avoid bacterial losses of sugar.

- (b) acetate levels in juice to climb by 220 ppm for a half unit increase in pH. A compromise pH together with good control is essential if acetate levels are to be kept at acceptable levels whilst avoiding inversion losses and corrosion in the diffuser.

*Observations and Future Work* Lime is normally added to diffusers to reduce inversion and corrosion. Bagasse retention in the FX diffusers is approximately 120 minutes. This coupled to the high temperature (85°C) (used to prevent bacterial losses and to ensure maximum extraction) could result in significant inversion if juice pH dropped below 5,5. The SMRI intends carrying out laboratory work to determine the effect of time, temperature and pH on the rate of acetate production from bagasse. At the same time FX staff plan on examining their liming procedure and hope to compare their procedure with those used in other diffusers. Collaborative work between the SMRI and FX should result in a drastic reduction in vapour pipe corrosion whilst at the same time maintain low losses of sucrose and insignificant corrosion in the diffuser. Besides the evaporator corrosion aspect, liberation of acetate wastes lime and raises ash levels, contributing to lower sucrose recoveries. Liming could perhaps be avoided provided temperatures were held below 80°C and cane supplies yielded juices with pH's above 5,5. If this is not possible then liming techniques will need closer attention.

#### Conclusions

FX Mill has been plagued by serious vapour and condensate pipe corrosion. The problem is a result of high acetic acid levels in the vapours, particularly vapour two. It appears that the high levels of acetic acid are a direct result of the liming procedure used in the Felixton diffusers. When liming was stopped acetate concentrations dropped to acceptable levels. In future work attempts will be made to reduce acetate production by modifying the liming procedure.

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