

A COMPARATIVE ASSESSMENT OF DECOLOURISING RESIN PERFORMANCE WHEN TREATING LIQUOR FROM HULETT'S AND NOODSBERG REFINERIES

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Abstract

The operating life of decolourising resin used in the Noodsberg refinery (NB) has been found to be about 30% shorter than that of similar resins operating at Hulett Refineries (HR). Both resin plants operate under similar conditions but the clarification process used at HR is carbonatation while that used at NB is phosphatation. The results of pilot plant studies using the same resin to treat liquor from NB and HR, to investigate what influence the nature of the liquor had on resin life, are reported. No substantial differences in resin performance were detected and the shorter resin life at NB is attributed mainly to more stringent decolourising requirements.

Introduction

The refineries of Noodsberg (NB) and Hulett's (HR) both practice resin decolourisation using macroreticular acrylic-based strong base resins. Their operating procedures are very similar, consisting of a cycle lasting roughly 24 hours, with the decolourising step treating 52–54 bed volumes at a flow rate of 2,5 to 3,5 bed volumes per hour. A 10% NaCl, 0,1% NaOH solution is used for regeneration. Partial brine reclamation and re-use is practised, giving a regenerant consumption of around 240 g NaCl and 9 g NaOH per litre of resin. An acid wash, with a 4% HCl solution, is conducted approximately every 20 cycles. Operating temperature of the liquor, regenerant and rinse water is maintained at around 80°C, although NB have reduced their temperatures to about 75°C because of concern for their resin life.

The HR resin decolourising station, commissioned in 1978, originally consisted of a single stage plant with 4 columns operating in parallel, each containing 12,5 m³ of resin. A fifth was added later. In this installation the average decolourisation achieved was 65% with a resin life of roughly 300 cycles. To handle both an increase in refining capacity and to boost the decolourisation to 77%, the plant was expanded in 1987 with the addition of 5 more columns. In the new installation, liquor decolourisation takes place in two stages in primary and secondary columns. New resin is placed initially in a secondary column and, following about 250 cycles, this resin is moved to a primary column and replaced with another batch of new resin. In this way the resin life is increased to about 500 cycles. The initial charge has been increased to 15 m³, mainly to allow for the increased losses of resin due to attrition as a result of the longer resin life.

The NB resin decolourising plant was built as an integral part of the new refinery commissioned in 1982. This plant originally consisted of 3 columns run in parallel, but has also recently been expanded and now has five columns, each with 7,75 m³ of resin. In this single stage plant, colour removal averages around 65% with the resin life averaging about 200 cycles.

The cost of resin replacement, at around R11,00 per litre, forms a substantial portion of the total decolourising costs, and therefore resin life is a very important economic con-

sideration. When comparing the single stage operation, as previously practiced by HR and still used at NB, it can obviously be appreciated that the relatively short resin life at NB (200 versus 300 cycles) gave the mill staff cause for concern. It was speculated that since the major process difference between the two refineries was the method of clarification (carbonatation at HR and phosphatation at NB) this could be implicated in the differences in resin life. In the context of broader studies on resin life it was decided to investigate this matter.

Experimental Procedure

The basic principle behind the experimental work was to run a pilot plant with multiple columns charged with the same resin. This plant would be able to treat clarified liquor from both NB and HR under virtually identical operating conditions. Any detected difference in resin performance between columns would then be attributable to differences in the liquors.

Pilot plant

The only way available at present to study properly the long term aspects of resin performance is to employ the resin for many cycles in a situation as close as possible to that encountered in practice (Williams³). A pilot plant is therefore necessary and, to maximise time use and minimise labour requirements, it should be fully automated.

The Sugar Milling Research Institute (SMRI) pilot plant consists of 4 columns, each having a resin bed volume (BV) of roughly 1 litre, and it is supplied with the necessary product holding tanks. Liquor, regenerant solutions and water are pumped through the columns by means of peristaltic pumps, with a single drive unit and one module for each column. The product lines leading from the pumps to the columns pass through stainless-steel heating coils contained in a thermostatically controlled water bath. To minimise heat loss the columns and the plastic tubes used to convey the products are lagged.

Automatic control of the plant is accomplished by means of various solenoid valves operated by a controller. The controller was constructed using a BASIC programmable single board computer, to which were added two eight bit optically isolated triac output cards and an eight bit isolated input card. The liquid level in the columns is sensed by Omron three probe level sensors which are connected to the inputs of the computer. Various programmes have been written to control the plant through different sequences of operation, and they may be selected by a switch on the front panel. This computer system was chosen instead of a PLC because its function can easily be extended to include measurement and data logging with standard cards, a useful feature in a research project.

Experimental programme

In the course of the programme 107 cycles were completed. Two different resins were used in the pilot plant. The

first was new Duolite A-173 and was part of the same batch put in NB's No. 1 vessel at the beginning of the season. The second was Rohm & Haas IRA-958 which had already completed 89 cycles in NB's No. 3 vessel. By using these two resins of different ages, the test programme could effectively span a range of cycles from 0 to 195, instead of only the actual 107 cycles conducted. Furthermore pilot plant performance could be compared with actual factory operation. At the beginning of the tests the pilot plant was set up as illustrated in Table 1.

The test programme required that substantial quantities of liquor be transported between the factories and the SMRI. In practice this meant delays were unavoidable and it was therefore necessary to take steps to prevent microbiological deterioration, by adding formalin to the liquors. Despite these precautions some deterioration of the liquors, as evidenced by a drop in pH averaging about 0,6 units, did occur. It is known that at higher pH's increased ionisation of colorants leads to better decolourisation by resin, and therefore a pH drop will result in poorer resin performance (Williams³). This observed pH drop will therefore have affected the resin performance. However, since the tests were conducted on a comparative basis and both liquors suffered pH drops of the same order of magnitude, it is considered that the conclusions obtained are still valid.

Liquor samples were generally taken from each column, every cycle. These samples were analysed for pH, refractometer brix and ICUMSA 420 colour. The volume of liquor treated during each cycle was also recorded. Every 20 cycles, following an acid wash, samples of resin (50 ml) were taken and analysed by standard Duolite methods (Anon¹). Since the volume of resin in each column is small, the taking of these samples resulted in significant reductions in the bed volumes. In order to compensate for this the liquor flow rate should have been reduced. However when this was done it was found that the pumping rate became unacceptably erratic. The effect of this gradual increase in effective flow rate

(to values far above the factory norms) has therefore to be taken into account when interpreting the results.

Table 2 gives some details of the conditions under which the pilot plant ran and under which the tests were conducted.

Results and Methods

Several comparisons between the resin treating HR liquor and the resin treating NB liquor have been made from the test results. In Table 3 the average values of both the quantities of colour (in terms of colour load) in the feed liquors and that actually absorbed by the resins are compared.

As illustrated in Table 1, columns 1 and 2 were normally fed with HR liquor while columns 3 and 4 were normally fed with NB liquor. For a truly equitable comparison of the decolourising performance of the two sets of the resins (viz. that treating HR liquor and that treating NB liquor) it was necessary to conduct a few runs using the same liquor to feed all 4 columns. This was done for one cycle towards the middle of the tests and for three cycles at the end of the tests. The results of these runs are supplied in Table 4.

It was mentioned earlier that the resins used in the pilot plant were of the same batches as those in NB's No. 1 and No. 3 vessels. The last cycles run on the pilot plant were conducted in order to compare the decolourising performance of these resins, which had been used under factory conditions, with those used in the pilot plant. In a run of three cycles all the columns were filled with Duolite A-173 resin as follows: column No. 1 contained the resin that had been used to treat HR liquors, column No. 3 contained the resin that had been used to treat NB liquors and columns 2 and 4 contained samples of the resin that had been used in NB's No. 1 vessel. In a further run of three cycles all the columns were filled with Rohm & Haas IRA-958 resin as follows: column No. 2 contained the resin that had been used to treat HR liquors, column No. 4 contained the resin that had been used to treat NB liquors and columns 1 and

Table 1
Configuration of pilot plant columns at the beginning of the tests

Column Number	Treats Liquor from	Resin Details		
		Type	Age	BV
1	HR	Duolite A-173	New	900 ml
2	HR	Rohm & Haas IRA-958	89 cycles	900 ml
3	NB	Duolite A-173	New	900 ml
4	NB	Rohm & Haas IRA-958	89 cycles	900 ml

Table 2
Summary of pilot plant operating conditions

Operating Condition	Average	Range
Cycle Length (hours)	18	-
Flow Rate (Bed volumes/hr)	4,4	2,5-6,0
Operating temperature (°C)	80	-
Resin Age (No. of cycles)	-	1-195
HR Liquor:		
Feed Colour (ICUMSA units)	746	1074-536
Product Colour (ICUMSA units)	320	545-115
Brix %	64,8	67,3-57,7
pH	7,5	8,4-6,8
NB Liquor:		
Feed Colour (ICUMSA units)	865	1176-651
Product Colour (ICUMSA units)	376	723-150
Brix %	61,7	65,7-57,1
pH	6,6	7,6-5,4

3 contained samples of the resin that had been used in NB's No. 3 vessel. The average results of these tests are given in Table 5.

From all these results it seems clear that no major difference in the decolourising performance of the resins exists between either those which had been used to treat HR and NB liquors or between those used on the pilot plant and industrially.

The decolourising performance results from the tests were also subjected to multi-linear regression analysis. This type of analysis of pilot plant data has already been conducted by Williams³ who looked at the effects of the feed and decolourised liquor colours, as well as the liquor flow rate, pH, brix and ash content and the effect of acid washes on resin performance. All these parameters, except ash content, were also investigated for their effects on the present results. The results for the resin treating HR liquor are:

Decolourised liquor colour

Table 3
Comparison of average colour loads

Colour load* (per BV per cycle)	Resin used to treat		Difference
	HR liquor	NB liquor	
In feed liquor	38463	42129	9,5%
Absorbed by resin**	21376	23400	9,5%
Colour Load Removal	55,6%	55,5%	-

* Colour loading = BV * Brix%/100 * ICUMSA colour.

** Calculated by subtracting decolourised liquor colour load from feed liquor colour load.

Table 4
Comparison of the decolourising performance of the resins at the middle and end of the trial (when using the same feed liquor)

Column Number	Normal use (i.e. treats liquor from)	Cycles	Liquor Flow (BV/h)	Liquor Colour		Per Cent Decolor.
				Feed	Product	
1 3	HR NB	41	3,8	727	179 160	75,3 77,9
2 4	HR NB	130	3,8	727	346 253	52,4 65,2
1 3	HR NB	101-103	6,0	803	353 360	56,0 55,2
2 4	HR NB	190-192	6,0	803	487 497	39,4 38,1

Table 5
Comparison of the decolourising performance of the NB factory and SMRI pilot plant resins at the end of the trial (when using the same feed liquor)

Column Number	Normal use (i.e. treats liquor from)	Cycles	Liquor Flow (BV/h)	Liquor Colour		Per Cent Decol.
				Feed	Product	
1 2 3 4	HR (P. Plant) NB-Vessel 1 NB (P. Plant) NB-Vessel 1	104-107 140-143 104-107 140-143	6,0	858	432 435 408 438	49,6 49,3 52,4 49,0
1 2 3 4	NB-Vessel 3 HR (P. Plant) NB-Vessel 3 NB (P. Plant)	189-191 193-195 189-191 193-195	6,0	815	515 490 470 500	36,8 39,8 42,3 38,7

$$= 1,52 X_1 + 0,515 X_2 + 15,0 X_3 + 6,26 X_4 - 689,6$$

(n = 193, r = 0,91) (1)

The results for the resin treating NB liquor are:

Decolourised liquor colour

$$= 1,42 X_1 + 0,413 X_2 + 20,4 X_3 + 10,1 X_4 - 841,0$$

(n = 190, r = 0,89) (2)

where:

- X₁ = Cycle number
- X₂ = Feed liquor colour
- X₃ = Liquor flow rate (bed volumes per hour)
- X₄ = Brix % liquor

Graphical illustrations of the decolourised liquor colour values calculated from these regression equations together with the actual colours of feed and decolourised liquors (on a 5-cycle average) are given in Figures 1 and 2.

Acid washing and liquor pH, which are known to influence resin performance significantly, did not produce statistically valid effects in these tests. Loker² has reported marked im-

provements in HR resin performance after acid washes. In the present tests however this effect will be masked by the fact that resin sampling took place immediately after an acid wash thereby reducing the bed volumes and effectively increasing the flow rates. Williams³ provided for the acid wash effect in an ingenious way by including a parameter in the regression, which he named CSA (cycles since last acid wash), to account for the gradual drop in resin performance between washes. However, using this parameter with the present results did not give statistically significant answers. This must be attributed to this effect being swamped by the magnitude of the influence of other parameters. This explanation is also given for not detecting any effect large enough to be statistically valid for the liquor pH parameter. While the HR liquor pH fell within a relatively narrow range of values (95% of all values were within the range 7,5 ± 0,37) the NB liquor had a broader range (95% of values within 6,6 ± 0,66) and it is therefore a little surprising that a pH effect was not detected.

When comparing the two regression equations it is apparent that when using the same values for cycle number,

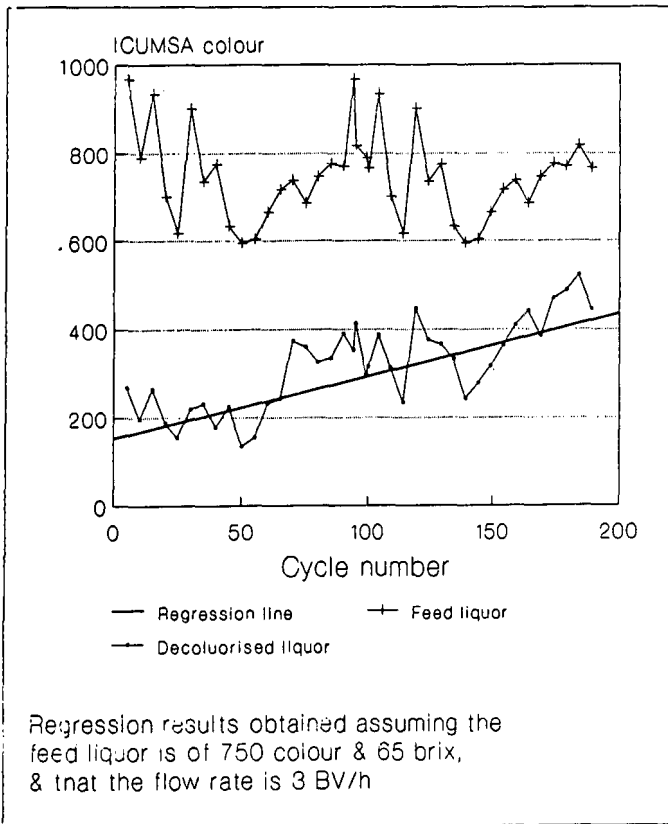


FIGURE 1 HR Feed & Decolourised Liquor Colour.

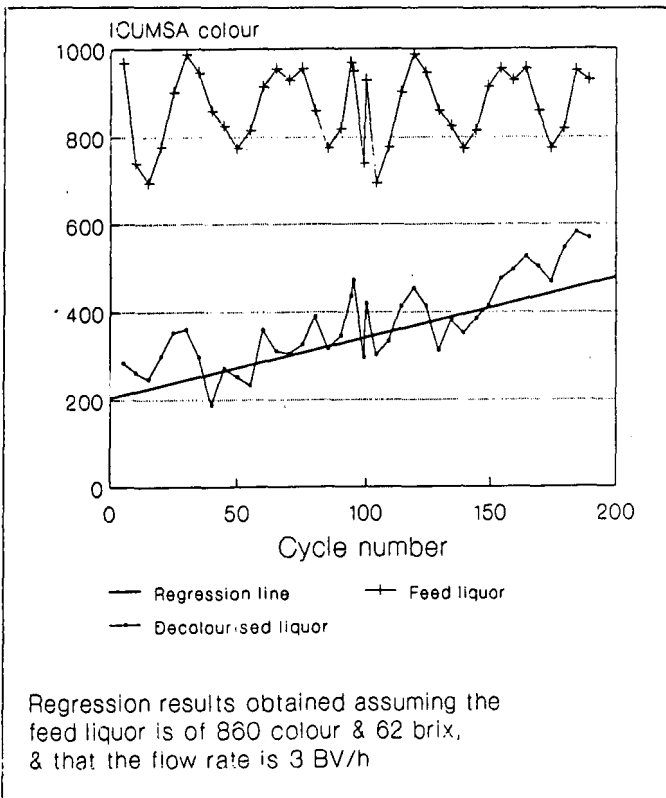


FIGURE 2 NB Feed & Decolourised Liquor Colour.

feed colour, flow rate and brix, the equation representing resin treating HR liquor gives lower decolourised liquor colours than does the equation representing resin treating NB liquors. This could lead to the conclusion, believed erroneous, that the resin treating HR liquor performed better. The differences are rather ascribed to the fact that the data sets from which the equations were generated are very dif-

ferent in terms of average colour, brix and pH of the feed liquor and merely reflect the degree of imprecision inherent in the equations. Having said this it is interesting to speculate on the possibility that the pH difference between the HR (7,5 average) and NB (6,6 average) liquors could be a contributing factor to the difference in the equations. This is an area that could bear further investigation.

Resin analysis

It is well known that the functional groups of strong base ion exchange resins are relatively unstable, particularly in the presence of OH⁻ ions. It is also well known that the chemical stability of these functional groups is linked with their operating temperatures, and that the 80°C values used in sugar liquor decolourisation are close to the tolerable upper limits. In general, decolourising resins are exposed to harsh operating conditions with high organic loadings, high pressure drops, severe osmotic shock etc. It is generally accepted that resin decolourisation takes place by both ion exchange and absorption and that consequently all aspects of a resin's structure are important for good decolourising performance. It is therefore quite surprising that very little published information exists with regard to relating resin decolourising performance with standard resin analyses which give an idea of the condition of that resin. In one of the few such reports, Loker², in studies at HR, has reported that "due to the good correlation of moisture holding capacity and strong base ion exchange capacity with plant performance, these both appear suitable for monitoring resin condition".

The samples of resin collected after every acid wash were analysed for total anion exchange capacity (TAEC), strong base exchange capacity (SBEC), dry matter and reversible swelling. For ion exchange resins, exchange capacity is defined as the equivalent number of exchange groups present in any given mass or volume of resin. Obviously then the SBEC is a measure of the number of equivalent strong base groups while TAEC is a measure of the equivalent number of the total exchange groups, (i.e. both strong and weak base

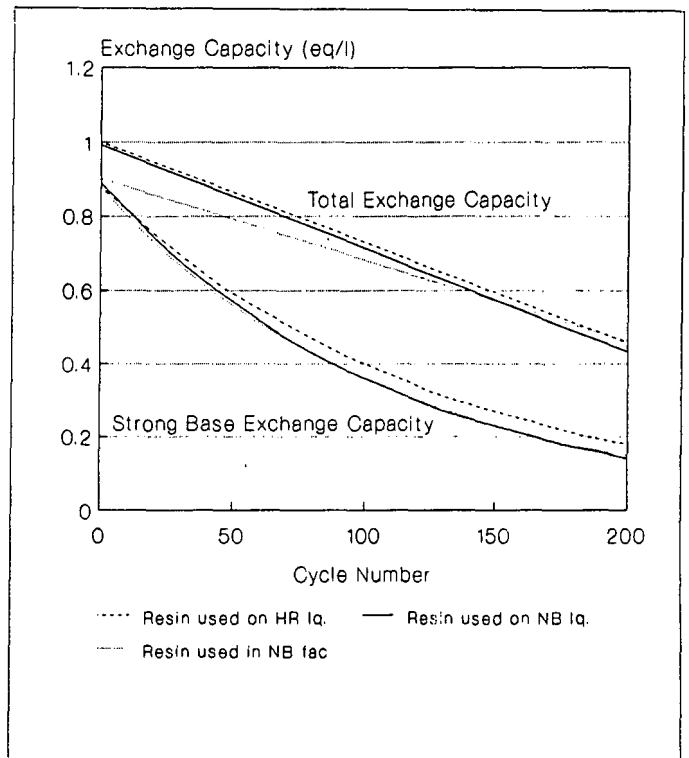


FIGURE 3 A comparison of trends in resin exchange capacities

Table 6
Results of resin analyses

Cycles Completed	Resin Type	Total Exchange Capacity (eq/l in Cl form)			Strong Base Exchange Capacity (eq/l - Cl form)			Dry Matter (g/l in Cl form)			Reversible Swelling (Cl form to OH form)		
		Pilot Plant Duty		Factory	Pilot Plant Duty		Factory	Pilot Plant Duty		Factory	Pilot Plant Duty		Factory
		HR Liq.	NB Liq.	NB Liq.	HR Liq.	NB Liq.	NB Liq.	HR Liq.	NB Liq.	NB Liq.	HR Liq.	NB Liq.	NB Liq.
New	Doulite A 173	0,85	0,85	0,85	0,79	0,79	0,79	217	217	217	15,1%	15,1%	15,1%
24		1,01	1,05	0,82	0,71	0,73	0,70	215	219	226	12,2%	12,9%	14,1%
41		0,96	0,93	0,91	0,67	0,62	0,67	211	218	226	13,3%	15,4%	12,9%
60		1,04	0,98	0,88	0,62	0,55	0,57	209	223	233	14,1%	12,0%	9,0%
80		0,89	0,90	0,84	0,63	0,60	0,52	209	226	235	11,3%	8,0%	5,8%
100		0,82	0,75	0,76	0,58	0,42	0,28	213	244	248	9,6%	4,2%	0,0%
89	Rohm & Haas IRA 958	0,42	0,42	0,42	0,32	0,32	0,32	181	181	181	7,1%	7,1%	7,1%
113		0,60	0,64	0,61	0,29	0,31	0,33	179	191	189	6,0%	12,2%	4,9%
130		0,62	0,57	0,57	0,26	0,24	0,31	168	173	179	4,0%	5,2%	5,6%
149		0,65	0,63	0,61	0,23	0,19	0,29	169	158	181	5,0%	4,3%	4,0%
169		0,52	0,50	0,54	0,23	0,18	0,18	161	158	187	4,3%	3,4%	-4,6%
189		0,52	0,50	0,50	0,23	0,19	0,15	178	148	198	5,8%	4,3%	-10,0%
Correlation with cycles completed (r)		0,74	0,78	0,76	0,91	0,95	0,95	0,84	0,79	0,58	0,89	0,85	0,92

groups). Dry matter is akin to the more familiar moisture holding capacity. Changes in its value could indicate a decrease in resin crosslinkage, a loss of exchange sites or irreversible fouling of the resin. Reversible swelling is a measure of the volume changes that occur when a resin changes from one form to another. Strong base groups cause resins to swell when going from the Cl- to OH- forms, while weak base groups cause resins to swell when they are transformed from the OH- to Cl- forms. A drop in reversible swelling therefore means strong base groups are being degraded to weak base groups. In trying to interpret what changes in these parameters mean, the fact that there are strong links between all the factors represented by the analyses must always be considered. For example, while a drop in dry matter might appear to indicate resin pore blockage due to fouling, it is probable that a large proportion of the change has merely resulted from a lower resin swelling caused by a loss of SBEC.

A complete set of the results of the resin analyses discussed is shown in Table 6, which includes a coefficient representing the correlation of each parameter with the number of cycles completed by the resin. Figure 3 gives a graphical representation of the regression equations generated from the TAEC and SBEC analyses for the three sets of samples. As can be seen SBEC is plotted as an exponential function, which gave a slightly better correlation than a straight line one and fits the known trend in SBEC more closely. In studying the data given in Table 6 and illustrated by Figure 3, it is apparent that the resin analyses give a clear, albeit small, indication that the conditions of the resins can be ranked from best to worst in the order HR pilot plant, NB pilot plant and NB factory. It has already been seen that the decolourising performance of all the resins was substantially the same. It would therefore seem reasonable to conclude that the resin analyses are either more sensitive to a resin's condition or an important factor, such as the degree of fouling, is not accounted for by the analyses conducted. The latter is considered more likely, but the results do indicate that the potential does exist for obtaining useful information from resin analyses and that more work in this area is warranted.

Conclusions

The decolourising performance of resins treating liquor from either HR or NB is substantially the same. Resin analyses give an indication that the resin treating NB liquor deteriorates slightly faster than resin treating HR liquor. It is nevertheless believed that the major reason for the shorter resin life at NB comes from the greater decolourising requirements arising from higher feed liquor colours.

Further work on the influence of pH on resin performance, particularly with regard to NB liquor, is warranted. Resin analyses provide the potential to supply useful information about the condition of decolourising resins. The scope of these analyses does however need to be broadened in order to give more knowledge of the relationship between resin analyses and decolourising performance.

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