Nitrogen Oxides Absorption into Sodium Hydroxide Solution in a Packed Column Column: Effect of NaOH Concentration

by

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Abstract

Experiments have been conducted to evaluate the effect of sodium hydroxide (NaOH) concentration upon the absorption rate of nitrogen oxides (NO_x) and packed column performance. The absorption process was carried out at atmospheric pressure and 298 K, using NaOH concentrations between zero and 19% w/w, NO/NO_2 ratio of 0.5 and NO_x concentrations between 150 and 10000 ppm in an air mixture.

The performance of the column was enhanced by the presence of hydroxyl ions (OH^-) relative to the absorption into water, however, it was found to be independent of NaOH concentration. The absorption rate of NO_x into NaOH solution was similar to that into water, suggesting that there is no direct reaction between NO_x species and OH^- ions, and thus in both cases, the absorption process was controlled by the hydrolysis of the main transporting species.

Column absorption efficiencies of about 92% and 87% were obtained during NO_x absorption into NaOH and water, respectively.

Introduction

During simultaneous absorption of NO and NO_2 mixtures into aqueous solutions, it is believed that at higher NO_x concentration (ie > 2000 ppm) the dissolution and hydrolysis of N_2O_4 are the major controlling mechanisms of absorption process[1-4] and below 2000 ppm the hydrolysis of NO_2[3,4] and gas phase formation and physical absorption of HNO_2[5-9] are the more predominant steps. However, it has been found that each reaction mechanism contributes significantly towards total absorption rate, at all NO_x concentration levels.[6,7]

In the presence of OH^- ions, the hydrolysis products are believed to be rapidly ionised and neutralized, so that any reversibility of the hydrolysis reactions is reduced or eliminated altogether. The decomposition of HNO_2 is, however, believed to be fast enough to compete with the ionisation and neutralisation process.[10] If this happens it could result in NO formation which might diffuse out of the solution.[11,12] Komiyama and Inoue,[4] and Aoki et al[2] reported that OH_- ions prevent the HNO_2 decomposition, thereby increasing the apparent absorption rate relative to similar absorption into water. They also reported that the rate of absorption does not vary with NaOH concentration for pH above 12.

Kameoka and Pigford[13] and Joshi et al, [3] however, reported that although the solubility and diffusivity of N_2O_4 decrease with increasing NaOH concentration, the hydrolysis rate constants of the same increase more strongly with NaOH concentration, so that the absorption rate increases with increasing NaOH concentration. They proposed the following absorption rate equations.

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$$R_{N2O4}=\bar{H}\sqrt{D\ k[H_2O]\ =\ k_1[OH^-]p_{N2O4}} \tag{1}$$

$$R_{N2O3}=\bar{H}_{N2O3}\sqrt{D\ k_2[H_2O]\ +\ k_3[OH^-]p_{N2O3}} \tag{2}$$

In light of this disagreement, the present experiments have been carried out to establish the effect of NaOH concentration upon the NO_x absorption rate and column performance.

Theory

The following equilibria and reactions take place during NO_x absorption into sodium hydroxide solution.[3,6]

$$2NO_g + O_{2g} \rightleftharpoons 2NO_{2g} \tag{3}$$

$$2NO_{2g} \rightleftharpoons N_2O_{4g} \tag{4}$$

$$NO_g + NO_{2g} \rightleftharpoons N_2O_{3g} \tag{5}$$

$$NO_g \rightleftharpoons NO_1 \tag{6}$$

$$NO_{2g} \rightleftharpoons NO_{21} \tag{7}$$

$$N_2O_{4g} \rightleftharpoons N_2O_{41} \tag{8}$$

$$N_2O_{3g} \rightleftharpoons N_2O_{31} \tag{9}$$

$$2NO_{21} \rightleftharpoons N_2O_{41} \tag{10}$$

$$NO_1 + NO_{21} \rightleftharpoons N_2O_{31} \tag{11}$$

$$N_2O_{41} + 2OH^- + (H_2O) \rightarrow NO_2^- + NO_3^- + H_2O \tag{12}$$

$$N_2O_{13} + 2OH^- + (H_2O) \rightarrow 2NO_2^- + H_2O \tag{13}$$

$$2NO_{21} + 2OH^- + (H_2O) \rightarrow NO_2^- + NO_3^- + H_2O \tag{14}$$

Also

$$NO_g + NO_{2g} + H_2O_g \rightleftharpoons 2HNO_{2g} \tag{15}$$

$$HNO_{2g} \rightleftharpoons HNO_{21} \tag{16}$$

$$HNO_{21} + OH^- \rightleftharpoons NO_2^- + H_2O \tag{17}$$

The important NO_x species in the gas phase include NO, NO_2, N_2O_3, N_2O_4 and HNO_2. The partial pressure of the effective nitrogen dioxide and nitric oxide, therefore may be defined as follows.[14]

$$p_{eNO2} = p_{NO2} + 2P_{N2O4} + p_{N2O3} + \frac{1}{2}p_{HNO2} \tag{18}$$

and

$$p_{eNO} = p_{NO} + p_{N2O3} + \frac{1}{2}p_{HNO2} \tag{19}$$

The concentration of different species can be calculated by assuming the above equilibria to be fully established, thus;

$$p_{N24O} = K_1 p_{NO2}^2 \tag{20}$$

$$p_{N2O3} = K_2 p_{NO} p_{NO2} \tag{21}$$

$$p_{HNO2} = \sqrt{K_3 p_{NO} p_{NO2} p_{H2O}} \tag{22}$$

The absorption into NaOH at all NO_x concentrations was assumed to be controlled by pseudo first order hydrolysis of N_2O_4, pseudo second order hydrolysis of NO_2, gas phase formation and physical absorption of HNO_2 and physical absorption of NO and NO_2. Also partial oxidation of NO was assumed to be present.[6]

The mass balance across a differential volume of the column yields

$$G(C_{6in} - C_{6out}) = a\ A\ R_6 \Delta h \tag{23}$$

$$\underset{\Delta h \to 0}{limit} \frac{(C_{6in} - C_{6out})}{\Delta h} = \frac{dC_6}{dh} = \frac{aA}{G} R_6 \tag{24}$$

$$\int_{C_{6in}}^{C_{6out}} \frac{dC_6}{R_6} = \frac{a\ A}{G} \int_{h=O}^{h=H} dh \tag{25}$$

Where

$$R_6 = R_{eNO2} + R_{eNO} \tag{26}$$

$$R_{eNO2} = R_2 + 2R_4 + R_3 + \frac{1}{2}R_5 + R_2' - R_1' \tag{27}$$

$$R_{eNO} = R_3 + \frac{1}{2}R_5 + R_1 \tag{28}$$

From the two film absorption theory, the general equation for a pseudo nth order reaction is given by the following equation.[15] Therefore,

$$R_4 = \widehat{H}_4 \sqrt{(k\ D)_4 p_3} \tag{30}$$

$$R_x = \sqrt{\frac{2}{n+1} D_x k_x (\bar{H}_x p_x)^{\frac{n+1}{2}}} \tag{29}$$

$$R_3 = \bar{H}_3 \sqrt{(k\ D)_3 p_3} \tag{31}$$

$$R_2 = \sqrt{\frac{2}{3}\ k_2 D_2 (\bar{H}_2 p_2)^{1.5}} \tag{32}$$

And

$$R_2' = k_1 . \bar{H}_2 . p_2 \tag{33}$$

$$R_{HNO2} = k_g \sqrt{K_5\ p_1\ p_2\ p_{H2O}} \tag{34}$$

$$R_1 = k_1 \bar{H}_1 p_1 \tag{35}$$

$$R_1' = k_1 . p_1^2 . p_{o2} \tag{36}$$

Table 1 shows the parameters used to make model predictions for various absorption conditions present.[6]

Table i: Model Parameters

Parameter	Value	Units	Ref. Number
$(\bar{\underline{H}}\surd(kD))_{N204}$	0.116	m/s	6
$(H\surd(kD))_{N203}$	2.721	m/s	6
k_g	2.10E-2	m/s	7
k_1	3.75E-5	m/s	7
K_4	6.86	atm^{-1}	16
K_3	0.535	atm^{-1}	16
K_5	1.01	atm^{-1}	16
$\underline{k}_1$	2.62E-11	$ppm^{-2}s^{-1}$	17
$\underline{H}_2$	1.2E-2	$kmol/m^3atm$	16
$\bar{H}_1$	1.93E-3	$kmol/m^3atm$	16
a	157	1/m	7
k_2	2.16E7	$m^3/kmol.s$	16
D_2	1.5E-9	m^2/s	16
p_{o2}	2.1E5	ppm	(% 0_2 in air)
p_{H20}	2.0E4	ppm	(thermodynamic tables)

Experimental Apparatus and Procedure

A schematic diagram of the experimental equipment is shown in Figure 1. It consisted of a 7.75 cm i.d. glass column, packed with 1.25 cm (diameter x length) stainless steel lessing rings to a height of 87.75 cm. The column was fitted with wall wiper rings to reduce wall effects so that plug flow was approached closely.[19] The absorption of NO_x gas ($NO/NO_2 = 0.5$) was performed at atmospheric pressure, 298 K and constant liquid and gas flow rates, of 0.8 and 40 l/min,

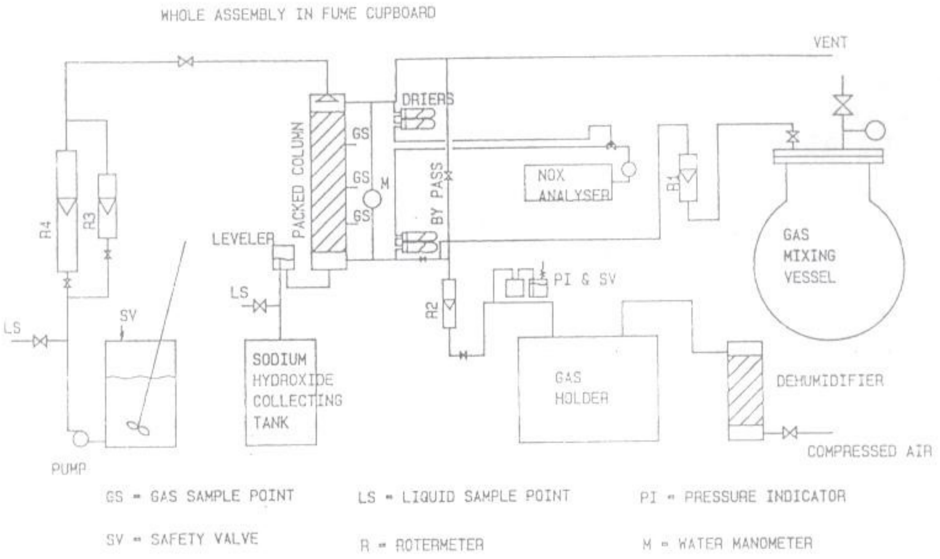

FIGURE 1 GENERAL PURPOSE ABSORPTION RIG

respectively. The NaOH concentration was varied from zero to 19% w/w. The liquid and gas streams were manually controlled with the aid of floatmeters to the top and bottom of the column, respectively. The feed and effluent gaseous NO_x concentrations were measured by a chemilunimescent gas NO_x/NO analyser (Grubb Parson Chemitox). The NaOH concentration was monitored by a standard titrimetric method.

Results and Discussion

The application of the model to predict the NO_x absorption rate and column absorption efficiency is reported in a separate paper.[6]

Figure 2 shows the plot of the relative column absorption efficiency using water and NaOH solution (5.88% w/w). The column absorption efficiency is defined as follows.

$$\eta = \frac{[NO_x]_{absorbed}}{[NO_x]_{in}} \tag{37}$$

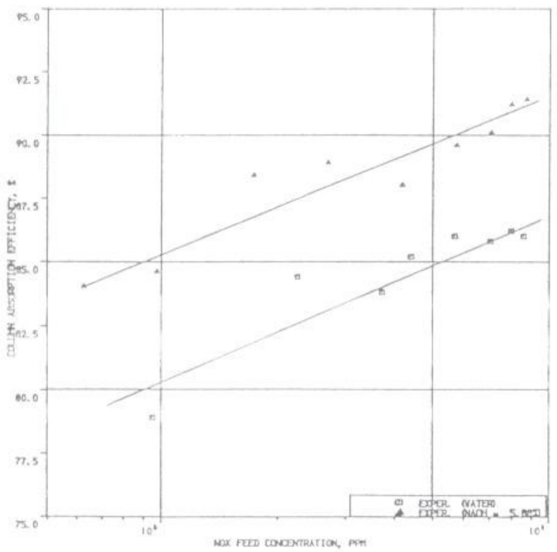

FIGURE 2 RELATIVE COLUMN ABSORPTION EFFICIENCY OF NOX INTO WATER & NAOH SOLUTION (NO/NO2 = 0.5)

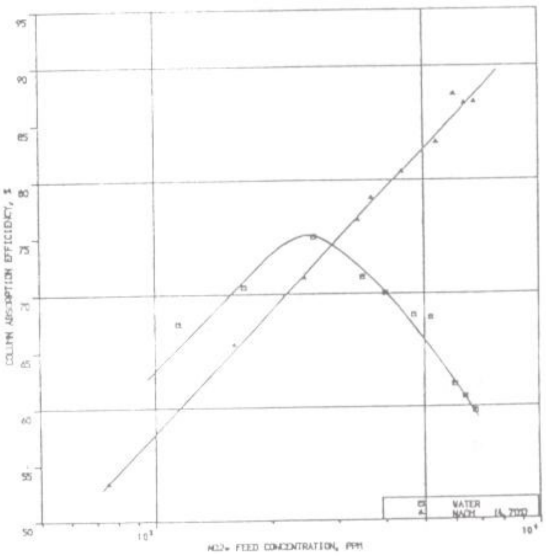

FIGURE 3 RELATIVE COLUMN ABSORPTION EFFICIENCY OF NO2* ABSORPTION INTO WATER AND NAOH SOLUTION

It can be seen that there is about 5% increase in absorption efficiency in favour of absorption into NaOH solution. This increase can be attributed to the substitution of HNO_2 decomposition, which tends to increase the NO_x concentration in the outlet stream, by neutralisation. This explanation is supported by the results shown in Figure 3, which depicts the relative absorption efficiency of NO_2^* ($NO_2^* = NO_2 + 2N_2O_4$) into water and NaOH solution in the same column. During NO_2^* absorption into water the absorption efficiency increases with increasing NO_2^* concentrations up to 2500 ppm, then it start falling with a further increase in NO_2^* concentration.

During NO_2^* absorption the hydrolysis products are both HNO_2 and HNO_3, whereas HNO_2 is the predominant product during NO_x absorption. The HNO_2 can decompose in the liquid phase according to the following reaction mechanism.

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \tag{38}$$

This means, when absorbing NO_x, the neutralisation of the hydrolysis products, or the diffusion and decomposition of HNO_2 with associated formation and desorption of NO, accelerate the formation and dissolution of more N_2O_3 and HNO_2 so that the column absorption efficiency increase with increasing NO_x concentration for both NaOH and water absorbants. But the decomposition of HNO_2 and subsequent accumulation of free HNO_3, locally reduces the rate of hydrolysis of N_2O_3 and the column absorption efficiency when water is used as absorbant. Since the NO in the outlet stream was always smaller than that in the inlet stream, it was not possible to tell whether the NO in the outlet was "unreacted portion" of the inlet NO or was formed within the column as a result of HNO_2 decompositon. The absorption of NO_2^* into water, however, revieled that at least part of NO was formed within the column (since the NO was present in the outlet stream and its concentration increased with NO_2^* concentration) suggesting the presence of HNO_2 decomposition in the absence of OH^- radicals.

The formation of HNO_3, locally reduces the rate of hydrolysis of N_2O_4 so that the building up of free HNO_3 decreases the rate of uptake of NO_2^* (according to Le Chatelier's principle). At low NO_2^* concentrations (< 2500 ppm) the NHO_2 formed is far below its pseudo

steady state equilibrium concentration, at which it decomposes steadily, thus the NO_2^* flux and column absorption efficiency will appear to increase with increasing mass transfer driving force (ie NO_2^* concentration). It is worth mentioning that in the absence of HNO_2 decomposition the column absorption efficiency is higher when water is used as absorbant. this is probably due to the fact that the solubility and diffussivity of NO_2^* species are lower in concentrated NaOH than in water, see Table ii.

Nevertheless, it can be seen from Figure 2 that the column absorption efficiency is a strongly dependent upon the NO_x inlet concentration. The absorption efficiencies of up to 92% and 87% were obtained during 10000 ppm NO_x absorption into NaOH and water, respectively.

Figure 4 shows that the column absorption efficiency is always higher into NaOH than into water as long as there is enough OH^- ion present to neutralise the hydrolysis products. The absorption efficiency does not vary with varying NaOH concentration when this concentration is between 3.7 and 11.2% w/w. Above 11.2% w/w the absorption efficiency decreases slightly with increasing NaOH concentration. This can be attributed to the increasing viscosity and decreasing activity coefficient of NaOH solution and a decrease in the solubility and diffusivity of NO_x species with increasing NaOH concentration. It is also worth mentioning that the water vapour pressure decreases with increasing NaOH concentration, which might reduced the contribution due to gas phase formation and absorption of HNO_2 and hence the column performance.

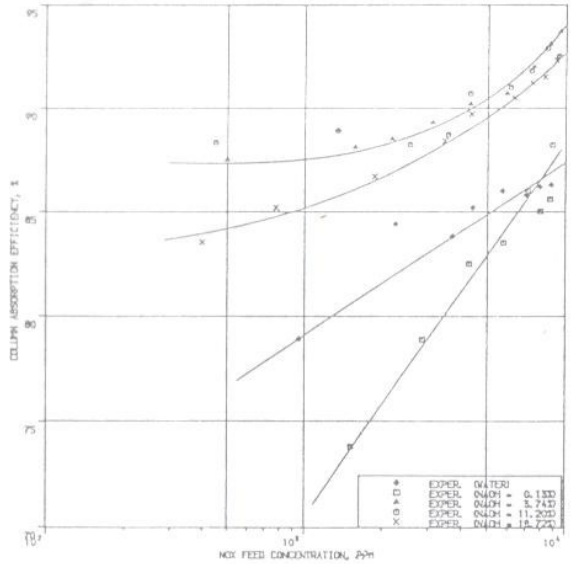

FIGURE 4 EFFECT OF NAOH CONCENTRATION ON COLUMN ABSORPTION EFICIENCY (NO/NO2 = 0.5)

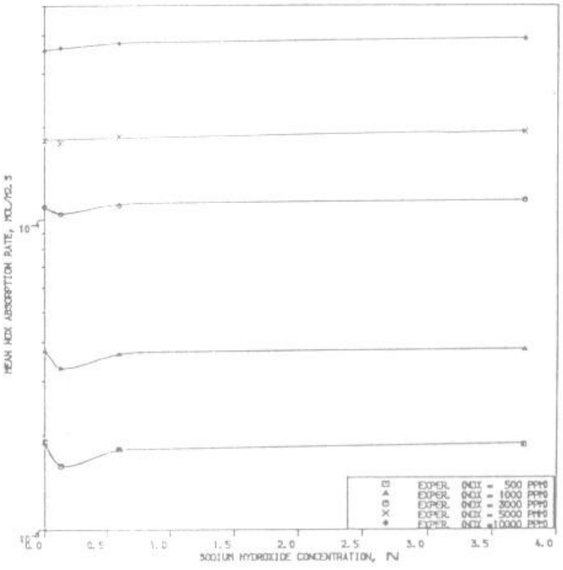

FIGURE 5 EFFECT OF NAOH CONCENTRATION ON NOX ABSORPTION RATE (AT LOW NAOH CONCENTRATION, NO/NO2=0.5)

The column absorption efficiency and NO_x absorption rate for the lower range of NO_x concentrations (below 5000 ppm) into water are higher than into a 0.13% NaOH solution, as shown in Figures 4 and 5, respectively. this can be attributed to the slow transportation of OH^- ions due to the reduced driving force[3] and a slight decrease of the activity coefficient of NaOH solution, the diffusivity and solubility of NO_x species and to a slight increase in the viscosity of the solution, see Table ii. The absorption rate into water and 0.13% NaOH is, however, almost the same when absorbing from 10000 ppm NO_x. This can be explained by the fact that the decomposition of HNO_2 is probably occurring very close to the liquid surface and at the same rate in both water and dilute NaOH.

Table ii: Comparison of physical properties of the absorbants of the absorbants and NO_x species into water and NaOH solution.

	Species	Water	NaOH Solution (0.13%)	Units	Increase or Decrease
Viscosity	–	1.0E-3	1.005E-3	Ns/m^3	+0.51
Activity	–	1.00	0.792	–	-20.8
Solubility	N_2O_4	1.5	1.493	$kmol/m^3atm$	-0.41
	N_2O_3	0.7	0.690	$kmol/m^3atm$	-0.41
	NO_2	1.7E-2	1.47E-2	$kmol/m^3atm$	-13.50
	NO	1.9E-3	1.67E-3	$kmol/m^3atm$	-13.70
Diffusivity	All	–	–	m^2/s	-0.51[6]

Figure 6 shows the variation of mean surface absorption rate with NaOH concentration. Obviously, there is no apparent dependence of the NO_x absorption rate upon the NaOH concentration. This confirms the fact that there is no direct reaction between OH^- ions and NO_x species. The observed increase in absorption efficiency is, therefore, due to neutralisation of the hydrolysis products. The solid line represents the model predictions which are in good agreement with experimental data, and thus the model can be used to predict the absorption rate for various NaOH concentrations without modifying the value of the absorption coefficients $(\overline{H}/(\underline{k}\ D))$.

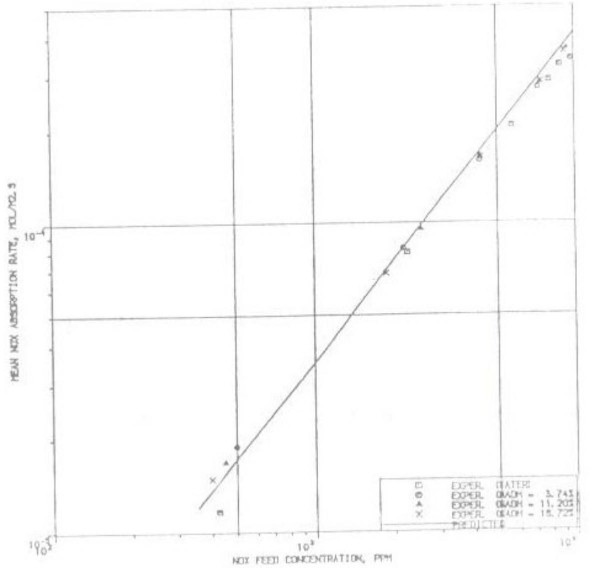

FIGURE 6 EFFECT OF NAOH CONCENTRATION ON NOX ABSORPTION RATE (NO/NO2 = 0.5)

Conclusion

The experimental investigation shows no evidence of direct reaction between OH^- ions and NO_x species. The increase in the column absorption efficiency into NaOH solution relative to that into water can be attributed to the neutralization of the hydrolysis products. This phenomenon eliminates secondary formation of NO, which otherwise would increase the amount of NO_x in the outlet stream, and also enhances the hydrolysis of more NO_2O_3 by removing HNO_2. The reduction in mean absorption into dilute NaOH solution is most probably due to the slower transportation of OH^- ions from the liquid bulk to the interface as a result of the reduced driving force now available.

Good agreement between the model predictions and experimental data confirms that the primary NO_x absorption mechanisms are absorption in the presence of fast pseudo-first order hydrolysis of N_2O_3 and N_2O_4, slow pseudo-second order hydrolysis of NO_2 and gas phase resistance controlled dissolution and reaction of HNO_2 vapour formed by a homogeneous gas phase reaction.

Nomenclature

a = gas liquid interfacial area, m^2/m^3
C_i = species concentration, mol/m^3
D_i = diffusion coefficient for species i, m^2/s
eNO_2 = effective nitrogen dioxide
eNO = effective nitric oxide
G = gas flow rate, m^3/s
$\bar{H}$ = solubility constant, $kmol/m^3atm$
k_g = gas side mass transfer coefficient, m/s
k_l = liquid side mass transfer coefficient, m/s
K = equilibrium constant for reaction, atm^{-1}
k = reaction rate constant, $m^3/kmol.s$
R = absorption rate, mol/m^2s
= amount of NO_x absorbed divided by the total area

Subscripts

1 = NO
2 = NO_2
3 = N_2O_3
4 = N_2O_4
5 = HNO_2
6 = NO_x

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