

## Influence of turbulence on Naphthenic Acid Corrosion of A335-P5

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**Abstract.** Fluent6.2 was used to analog the turbulence and flow rate around the specimens installed in the pipeline and results indicated that the specimens varied the fluid flow direction and increased flow rate of fluid from  $20\text{ m s}^{-1}$  to  $50\text{ m s}^{-1}$ , strong turbulence was formed around the specimens and the max turbulence in work areas could reach 10%. Naphthenic acid corrosion experiments showed that the max influence of turbulence on average corrosion rate was limited to 46.3%, obviously lower than the max influence of temperature. But in high turbulence areas the local corrosion depth was 2-3 times of the corrosion depth in the low turbulence areas, then we could deduce the max corrosion depth from average corrosion depth and estimate the residual lifetime of oil refining equipments.

### Introduction

Naphthenic Acid Corrosion (NAC) of refinery distillation units keeps being a reliability issue in oil refineries for a long time. NAC occurs via chemical reaction between iron and organic acids existed in high acid crude oil. Existing researches indicated that the main factors that could influence NAC were temperature<sup>[1,2]</sup>, total acid number (TAN)<sup>[3-5]</sup>, type of naphthenic acid<sup>[6]</sup>, content of active sulfide<sup>[7-9]</sup>, local flow conditions of crude oil<sup>[10-12]</sup>.

Temperature is an important parameter that could significantly influence the rate of NAC, NAC mainly occurs in the temperature range of 220°C-400°C. Total acid number (TAN) is also an important factor to evaluate NAC. Obvious NAC only occurred above critical TAN of  $0.5\text{ mg KOH/g}^{[2]}$ . Type of naphthenic acid determined the corrosivity of naphthenic acid, the corrosivity of various naphthenic acid differs obviously even under the same TAN. Researches by Omar indicated that the corrosivity of carboxylic acids depended on the solubleness of iron naphthenate in the oil and the ring structure in iron naphthenate<sup>[6]</sup>. Existence of active sulfide might limit NAC through formation of sulfide film on the substrate. But the formation of sulfide film needed appropriate content of active sulfide. Insufficient content of active sulfur would lead to incomplete protection film formed on the substrate and could not play enough protection role. Excess content of active sulfur could lead to serious sulfide attack. Severe corrosion often occurred on the spots that remarkable turbulence existed indicated that local flow conditions of crude oil could also influence the corrosion rate<sup>[11,13,14]</sup>. The activation energy of corrosion reaction above boiling point was lower than the activation energy below boiling point, so NAC was more serious at the dew-point temperature than the vapour condensed to liquid on the surface of metal<sup>[15,16]</sup>.

Since the influence of temperature, TAN, content of active sulfide on the corrosion rate had been investigated by some researchers and got some research progress. In this paper the main target was focused on the influence of turbulence on NAC and uncover how and to what extent could it influence NAC.

## Experimental procedures

**Experiment conditions and devices.** Because NAC would not occur below 220C and naphthenic acids cracked above 400C, the temperature selected in the experiments were 240, 280, 320 and 360C, the corrosion time was controlled at 8h. In order to investigate the influence of turbulence on NAC, two flushing angles (0° and 90°) at pipe flow mode were selected to create turbulence in the experiments. The sketch of high temperature, high flow rate naphthenic acid corrosion simulation device was shown in Fig.1, the max flow rate in the device could reach 100m s<sup>-1</sup> and the flow rate selected in the experiments was 20m s<sup>-1</sup> at pipe flow mode. the specimens were installed in the pipeline (shown in Fig.2) .



Fig.1 naphthenic acid corrosion simulation device

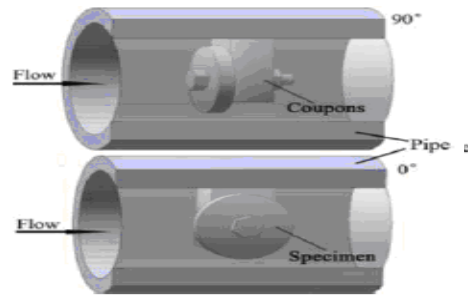


Fig.2 installation of specimens at pipe flow mode

**Experiment materials.** A335-P5 was full quenched, the compositions were listed in Table.1. The specimens were cut from sheets and machined to ring structure with external diameter of 18mm, internal diameter of 3mm. The specimens were ground to 1000# by abrasive papers and polished by 1μm polishing paste, then the specimens were degreased and rinsed by de-ionized water. The weights of the specimens were recorded after drying for 12h. The medium selected in experiments was high temperature heat conductive oil (high-purity Dibenzyl toluene) mixed with refined naphthenic acids, the TAN was 4.6mg KOH g<sup>-1</sup>. Finally the weight loss of each specimen was measured by an analytical balance. According to Eq. (1), the average corrosion rate could be calculated by weight loss and exposed area.

$$\text{Average Corrosion rate}(\text{mm} \cdot \text{a}^{-1}) = \frac{3650 \times (\text{Weight loss} / \text{g})}{\text{Density of metal}(\text{g} \cdot \text{cm}^{-3}) \times \text{Area}(\text{cm}^2) \times \text{time}(\text{day})} \quad (1)$$

Table.1 Chemical composition of test specimens (mass%)

Alloy	C	Si	Mn	P	S	Cr	Cu	Mo	Ni
A335-P5	0.07	0.20	0.39	0.009	0.001	4.37	0.07	0.49	0.06

**Analysis of turbulence and topography.** The software of Fluent6.2 was used to analyze the turbulence on the specimen. Three-dimensional digital microscope KH-7700 was used to scan the corrosion topography of specimens.

## Experiment results and discussion

**Analysis of flow rate and turbulence around the specimens.** The flow rate of medium in the pipeline was controlled at 20m s<sup>-1</sup> at pipe flow mode and Fluent6.2 was used to analyze the turbulence and flow rate around the specimens, the results were shown in Fig.3. Fig.3 indicated that the max flow rate at flushing angle of 90° could reach 50m s<sup>-1</sup> around the specimen (Fig.3-a), and the max flow rate at flushing angle of 0° could reach 45 m s<sup>-1</sup> (Fig.3-b). so the specimens installed in the pipeline varied the direction of fluid flow, highly increased the flow rate around and formed strong

turbulence.

The results indicated that the highest turbulence existed in the middle part on the specimen under flushing angle of 90°(Fig.4-a),while the highest turbulence existed in the area facing the fluid direction under flushing angle of 0°(Fig.4-b). Strong turbulence existed under both two flushing angles and the highest turbulence intensity both exceeded 8%.

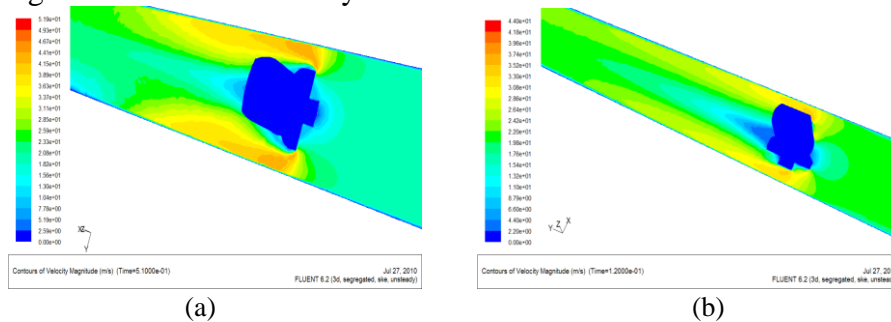


Fig.3 flow rate distribution around the specimens(a-flow rate distribution at 90°, b-flow rate distribution at 0°)

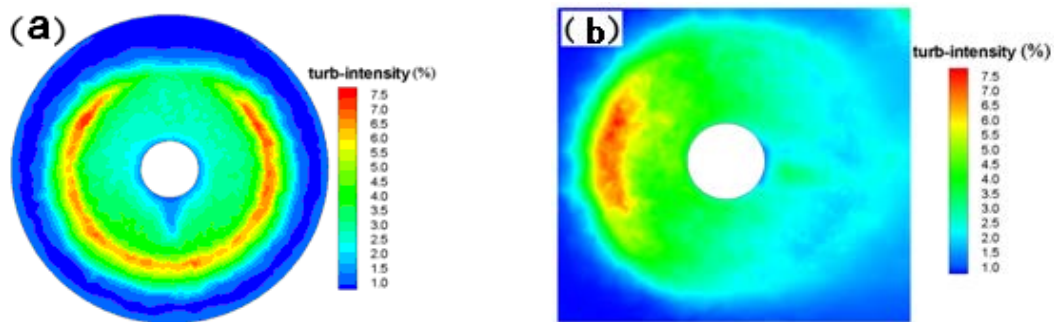


Fig.4 turbulence distribution on the area of specimens(a-turbulence at 90°,b-turbulence at 0°)

**Correlation between turbulence and corrosion rate.**Flow rate and turbulence were important factors that could influence corrosion rate of NAC, and severe corrosion frequently occurred on the spots where high flow rate and turbulence existed in the pipelines of crude oil refineries, but to what extent could turbulence influence the corrosion rate was still unknown. Experiments were carried out and the influence of turbulence on average corrosion rate, corrosion depth and local corrosion morphology were analyzed.

Average corrosion rates of A335-P5 at different temperatures and flushing angles were shown in Table.2. The average corrosion rate at 0° was 1.74mm a<sup>-1</sup> and 2.08mm a<sup>-1</sup> at 90°, the difference of corrosion rate was about 19.5%. When temperature reached 280C, the corrosion rate was 2.28mm a<sup>-1</sup> at 0° and 2.52mm a<sup>-1</sup> at 90°,indicating that the corrosion rates increased with temperature and the corrosion rate difference was about 10.5%. Corrosion rate kept increasing when temperature was reached 320C, the corrosion rate was 2.59mm a<sup>-1</sup> at 0° and 3.79mm a<sup>-1</sup> at 90°, and the difference about 46.3%. When temperature reached 360C, the corrosion rates rapidly decreased to 0.89mm a<sup>-1</sup> at 0° and 0.91mm a<sup>-1</sup> at 90°, the corrosion rate difference was about 2.2%.

Table.2 corrosion rate(mpy) of A335-P5 at different temperature and flushing angle

Temperature(K) Materials	513.15	533.15	553.15	573.15	593.15	613.15	633.15
90°	81.9	87	99.2	117.3	150	70.9	35.8
A335-P5 0°	68.5	76	89.8	96.5	102	65.7	35
difference	19.6%	14.5%	11.2%	21.6%	47.1%	7.91%	2.38%

It is worthy of note that corrosion rate decreased obviously when temperature increased from 320 to 360C. Ref. [2] pointed out that maximum corrosion rate occurred among 270C~320C when no active sulfide existed. The decompound of naphthenic acid could explain the decrease of

corrosion rate. After experiments of 360C the TAN was re-measured and results showed that the TAN was decreased to  $3.5\text{mgKOH g}^{-1}$ , but at experiments of 320C, the TAN kept stable relatively and there was no obvious decrease. So the decrease of corrosion rate at 360C was mainly attributed to the reduction of TAN.

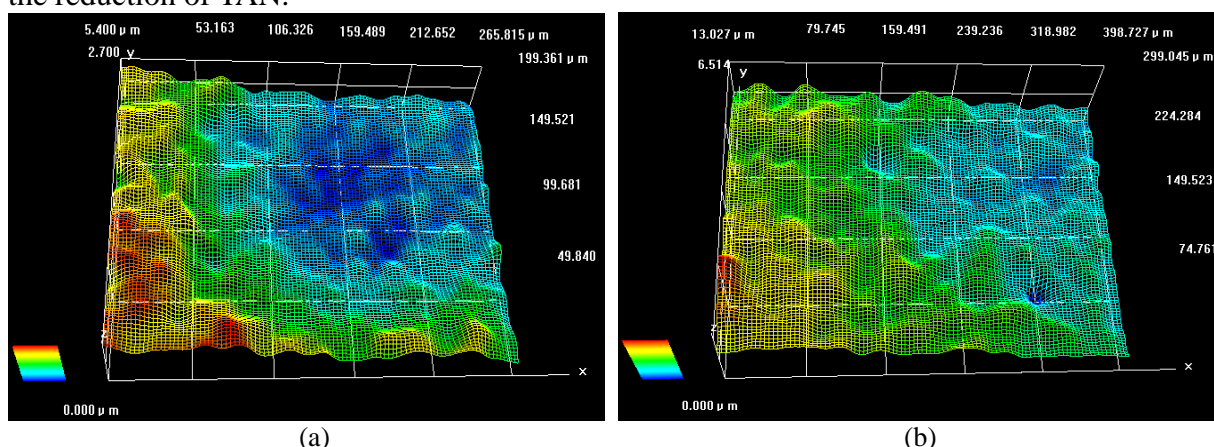


Fig.5 local corrosion depth and wireframe morphology of A335-P5 in low turbulence area turbulence(a-turbulence intensity at about 2% ,b-turbulence intensity at about 8% )

It could be seen from Table.2 that the average corrosion rate of A335-P5 at 320C was about 1.5~2 times of the corrosion rate at 240C, but the max corrosion rate difference under two flushing angle was 46.3%. Analysis of local corrosion morphology of specimens(under temperature of 320C and flushing angle of  $90^\circ$ ) showed that the corrosion depth differed obviously. In the low turbulence area the max corrosion depth was about  $5.4\mu\text{m}$  (shown in Fig.5-a) and the average corrosion depth was  $3.5\mu\text{m}$  calculated by the average corrosion rate ( $3.79\text{mm a}^{-1}$ ), so the corrosion depth in low turbulence area were almost consistent with the average corrosion rate; In the strong turbulence area the max corrosion depth could reach  $13\mu\text{m}$  and even higher(shown in Fig.5-b). The max corrosion depth in strong turbulence area was about 2.4 times of the corrosion depth in low turbulence area and the influence of strong turbulence in local spots was even higher than the influence of temperature. So the influence of turbulence could not be ignored. Under other conditions similar conclusions could be obtained.

From the analysis above,it could confirm that turbulence could significantly enhance the local corrosion depth and the max corrosion depth was directly related with the turbulence intensity on the work areas. Since the corrosion depth in low turbulence areas was almost consistent with the average corrosion depth and the max corrosion depth in high turbulence areas was 2-3 times of the corrosion depth in low turbulence areas. The max corrosion depth was about 2-3 times of average corrosion depth could be deduced. From this the residual lifetime of oil refining equipments could be estimated.

## Conclusion

(1) Analog results indicated that specimens installed in the pipeline varied the fluid flow direction and highly increased the flow rate around and formed strong turbulence. The max turbulence in work areas could reach 10%.

(2) Experimental results showed that turbulence could influence average corrosion rate of NAC, but the influence was obviously lower than the influence of temperature; but in local high turbulence areas the influence of turbulence on corrosion depth was very significant and the extent was almost equal to the max influence of temperature.

(3) The local corrosion depth in high turbulence areas was about 2-3 times of the corrosion depth in the low turbulence areas and average corrosion depth. The max corrosion depth from average corrosion depth could be deduced and the residual lifetime of oil refining equipments could be estimated.

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