Fouling Resistance of CaCO₃ Scale on Shell and Tube Heat Exchanger in The Presence Formic and Oxalic Acid

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 $CaCO_3$ fouling in Shell and Tube Heat Exchanger has been reported by several researchers that its existance declines heat transfer process until 30 times lower. Therefore, the current research was conducted to investigate the fouling resistant and addressed to minimize of investment cost. The method used in was chategorized as chemical mitigation which antiscalant reagent i.e. formic acid (CH₃O₂) and oxalic acid (C₂H₂O₄) was added to the solution.

Keywords : CaCO₃, Heat Exchanger, formic acid, oxalic acid, crystal, morphology

1. Introduction

CaCO₃ fouling in Shell and Tube Heat Exchanger (STHE) has been known as the disturbance in heat transfer processes¹. Several researchers reported that the existance of CaCO₃ fouling declines heat transfer process until 30 times lower² which the term usually called as fouling resistance³. When the phenomenon taken place, STHE design would not suitable to the system anymore as same as those that the design and capacity too smaller. To answer those fouling resistance problem, STHE designer marks up the capacity approximately one-third or 35% of the initially even though higher cost must be paid⁴. Therefore, the current research was conducted to investigate the fouling resistant and addressed to minimize of investment cost.

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In the current research, chemical method will be used to answer the problem through the addition chemical substances to the solution which often be called as inhibittor⁵. The inhibitor was choosen based on any consideration, i.e : i). The chemical substance must be save material, not toxicity, not harvest the environment, construction and human. ii). It must be has capability to inhibit scale growth in some way for example through thermodynamically or physically. Two chemical substances that match to the criteria are formic acid and oxalic acid which have been known as organic material, save for the human.

The use of chemical substance was assessed through the calculation fouling resistant (\mathbf{R}_f) that promoted by Al-Mutairi⁶ as equation $W = [\pi/4 (D_0^2 - D_f^2) L]\rho_f$ and $R_f = [ln (D_o/D_f)]/2\pi k_f L$. Here, W is mass of scale; \mathbf{D}_f is inner diameter after fouling; \mathbf{D}_o is initial inner diameter; ρ_f is scale density; L is pipe length; \mathbf{k}_f is thermal conductivity of the fouling.

2. Methods

A. Material

CaCO3 scale in STHE module was carried out experimentally by mixing the solution of

CaCl₂ and Na₂CO₃ which made by powder that supplied by Merck[®] to guarantee its purity. Demineralized water which supplied by PT Brataco Indonesia was used as the solvent. The reaction of those two material was supposed that occured according to the reaction such as shown in equation $CaCl_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$. Concentration of calcium was determined as 3.500 and sodium solution was set in its stoichiometry. The solution was subsequently filtrated two times by 0.22 µm micropore[®] paper to waste dirty material.

B. Experimental design

Inhibitor was defined as independ variable either other wise concentration of calcium; solution tmperature and flow rate was functioned as fixed variable. Calcium concentration was set at 3,500 ppm; inhibitor concentration was set at 5,00 and 10.00 ppm; inlet temperature of STHE was set at 60[°]C and flow rate at 30.00 ml/min. Scale deposited was defined as depend variable either of blank and antiscalant experiment. Cold water that was needed to absorb the heat was inserted in the STHE modul at 30[°]C either for lineair flow and cross flow, both at the flow rate 60 ml/min. Temperature of cold and hot water that left the modul was also measured and stand as depend variables.

C. Experimental process

Experimental process was schematically ilustrated in Fig.1. Vessel (1) contained solution of CaCl₂.2H₂O and vessel (2) contained solution of Na₂CO₃. An electrical heater was employed in each vessel (3) to control solution temperature automatically at the value needed and helped by a sensor (4) under computerized program control(7). To provide the solution in homegeneous either in temperature and chemical substance, a stirrer (5) was employed and set at 30 rpm automatically by computer program. Solution in vessel (1) and (2) was pumped by dosing pump CHEM FEED Ca-92683 (6) similarly in flowrate 30.00 mL/min and was met in STHE module (10). Ground water in cool water tank (12) was pumped by pump (13) to the module. Temperature at point (8), (9) and (11) was acquisitioned by computer program.

D. Shell and Tube Heat Exchanger Module

STHE module was employed to conduct the experiment which fouling process was investigated. Design STHE module was depicted in Fig.2. Pipe lenght was determined 250 mm and its inner diameter in 16 mm. The pipe made of copper which comercially sold in the market. Nomenclature of D_0 ; D_f ; k_f ; ρ_f and L are obviously described that needed when substituted the parameter to the equation (1) and (2).

Rubber seal was mounted at the end of pipe to avoid the leakage. Temperature of inlet and outlet either for cold and hot water was measured and recorded in computer program. The direction of cold water flow could be replaced from right to left to provide even cross flow or lineair flow model. Out side cover at two end of pipe could be released which was done when dryer processing; mass collecting and pipe cleaning.

3. Results and Discussion

A. Deposition

Deposition of scale mass either of blank and antiscalant sample are listed in Table 1 after dryer processing was done in 60° C for six hour duration. In the current research the data shows that the deposition of STHE in lineair flow less than the deposition of cross flow model. It could be caused by the heat absorbsion in the first shell by cold water of lineair model of STHE was better than cross flow model.

The table also shows that scale deposition of blank experiment has higher magnitude and the experiment in the presence of formic acid 10.00 ppm is fewer. This would be the evident that formic acid has better performance to inhibit CaCO₃ fouling than oxalic acid.

B. X- Ray Diffraction analysis and Cristal phase distribution

Crystal distribution was quantificated through Rietveld refinery method, supported by FullProf program version 2.0 and confirmed by ICDD-PDF number 00-005-0586; 00-041-1475; 01-072-0506 for calcite, aragonite and vaterite. The results of the quantification was listed in Table 2 and was used to calculate average crystal density (ρ_f) and average thermal conductivity (k_f) of all experiment. Calculation average fouling density and thermal conductivity was done through equation $\rho_f = \rho_{vat}$. % *Vat.* + ρ_{ar} . % *Ar.* + ρ_{cal} . % *Cal and equation* $k_f = k_{vat}$. % *Vat* + k_{ar} . % *Ar* + k_{cal} . % *Cal.* Here, ρ_{vat} ; ρ_{ar} ; ρ_{cal} is the density of vaterite; aragonite and calcite respectively other wise k_{vat} ; k_{ar} ; k_{cal} is thermal conductivity of vaterite; aragonite and calcite respectively. % Vat ; % Ar and % Cal is the percentage of crystal phases that had been quantificated through Rietveld method. The results are listed in Table 3. Abbreviation LF in the table represent the experiment was operated as Lineair Flow otherwise CF was Cross Flow model.

C. Fouling resistance

Fouling resistance was calculated through equation that has been promotted by Mutairi to define diameter of inner pipe after fouling (D_f) and the result substitute to next equation to complete the calculation. The results are graphed in horizontal bar such shown in Fig.3. Fouling resistance of STHE operated in lineair flow (LF) produces fewer scale than operated as cross flow (CF). It might affected by the temperature of each shell which tends lower than the other as the first shell at where hot fluid inserted to the STHE modul was feeded by fresh water. The addition formic acid in 10.00 ppm produced fewer fouling resistance, i.e. $611 \times 10^{-6} \text{ m}^{2.0}\text{K/W}$ than the addition oxalic acid in 10.00 ppm, i.e. $654 \times 10^{-6} \text{ m}^{2.0}\text{K/W}$.

4. Conclusion

Fouling resistance in the pipe of STHE operated as lineair and cross flow model has been investigated. STHE operated as lineair flow produced fewer fouling resistance than cross flow. The use formic acid as inhibitor succesfully declined fouling resistance than oxalic acid.

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Figure Caption :

- Fig. 1. Build inhouse experimental rig
- Fig. 2. Shell and Tube Heat Exchanger module
- **Fig. 3.** Fouling resistance of all experiment $(x10^{-6} \text{ m}^{2.0}\text{K/W})$



Fig.3. W.Mangestiyono

Table Caption :

 Table 1. Deposition of every experiment

Table 2. Crystals phases quantification of all experiment

Table 3. Average fouling density and thermal conductivity of all experiment

Table 1. W.Mangestiyono, etal					
No	Experiment	Deposition (gr)			
1	Blank sample, LF	0.9243			
2	Blank sample, CF	0.9646			
3	Formic acid 5.00 ppm, LF	0.7245			
4	Formic acid 10.00 ppm, LF	0,6486			
5	Oxalic acid 5.00 ppm, LF	0.8164			
6	Oxalic acid 10.00 ppm, LF	0.7672			

Table 2. W. Mangestiyono, etal							
No	Experiment	Phases percentage (%)					
		Vat	Ar	Cal			
1	Blank sample, LF	32	31	37			
2	Blank sample, CF	34	32	34			
3	Formic acid 5 ppm, LF	45	32	23			
4	Formic acid 10 ppm, LF	50	35	15			
5	Oxalic acid 5 ppm, LF	N 34	28	38			
6	Oxalic acid 10 ppm, LF	37	23	40			

Table 3. W.Mangestiyono, etal

No	Experiment	$\frac{\rho_{\rm f}}{({\rm Kg/m}^3)}$	$\frac{k_{\rm f}}{(W\!/\!m^o\!K)}$
1	Blank sample,LF	2,757	2.706
2	Blank sample, CF	2,758	2.672
3	Formic acid 5ppm,LF	2,751	2.540
4	Formic acid 10 ppm, LF	2,754	2.450
5	Oxalic acid 5 ppm, LF	2,749	2.712
6	Oxalic acid 10 ppm, LF	2,736	2.726