

# CaSO<sub>4</sub> Scale Formation on Vibrated Piping System in the Presence Citric Acid

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**Abstract.** Vibration in many industries commonly generated by the operation mechanical equipment such as extruder, mixer, blower, compressor, turbine, generator etc. Vibration propagates into the floor and attacks the pipe around those mechanical equipment. In this paper, the influence of vibration in a pipe on the CaSO<sub>4</sub> scale formation was investigated to understand the effect of vibration on the kinetics, mass of scale, crystal phases and crystal polymorph. To generate vibration force, mechanical equipment was prepared consisted of electrical motor, crankshaft, connecting rod and a vibration table at where test pipe section mounted. Deposition rate increased significantly when the vibration affected to the system i.e. 0.5997 and 1.6705 gr/hr for vibration frequency 4.00 and 8.00 Hz. The addition 10.00 ppm of citric acid declined the deposition rate of 8 Hz experiment from 3.4599 gr/hr to 2.2865 gr/hr.

## 1 Introduction

Vibration in piping system encounters in most industries because of the existing two factors i.e. internal and external factors. Categorized as internal factor is fluctuation of fluid velocity which promotes the vibration mean while vibration produced by the operation of mechanical equipment such as blower, extruder, mixer, turbine, generator, pump, compressor are categorized as external factors [1]. At industrial building, vibration propagates throughout the floor and wall, subsequently vibrates the pipes where are mounted around. Vibration is suspected affects the scaling process take place in the inner pipe.

In industries, pipe transports the fluid from one section to others. The fluid could be the water which comprises some impurities such as Ca, Na, SO<sub>4</sub>, Cl, Mg salts [2]. When the saturation of those salt are exceeded the scale are formed through either homogeneous and heterogeneous crystallization [3].

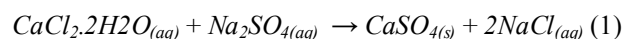
In the current research, the formation CaSO<sub>4</sub> scale be the focus of the experiment by the consideration that CaSO<sub>4</sub> scale take place in almost of all industrial piping system [4]. CaSO<sub>4</sub> scale formation in piping system has been investigated by many researchers such as Muryanto, Hoang, Chunfang, Uchymiak [5, 6, 7, 8]. They reported that the scale forms a layer in the inner surface of the pipe and elevate thermal resistance. The existence of the scale affects the disturbance to industrial processes [9] i.e. decreases overall heat transfer coefficient [10]; prolongs the time of process [11]; waste the energy and increases the production cost [12]. Even CaSO<sub>4</sub> scale formation has been widely investigated but

its formation in vibrate piping system has not been reported yet and supposed will be the novelty of this study. To complete the study, citric acid was added to the solution to inhibit scale growth. Indeed, citric acid has been used as inhibitor widely but its performance to inhibit CaSO<sub>4</sub> scale growth in vibrate piping system is still needed to investigate.

## 2 Methods

### 2.1 Material

CaSO<sub>4</sub> scale formation was carried out experimentally by mixing CaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> powder which was supplied by Merck® according to the reaction such as shown in equation (1).



Concentration of calcium solution was determined as 4.000 ppm, prepared by dissolved 147 gr of CaCl<sub>2</sub>·2H<sub>2</sub>O into 10,000 ml of demineralized water.

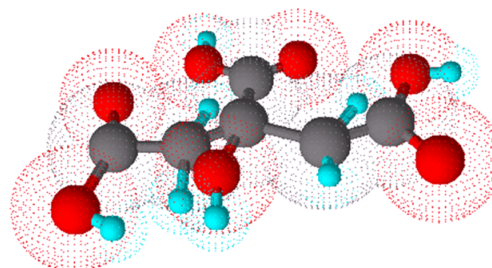


Fig. 1. Citric acid with three carboxylates form

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Based on calculation of  $\text{Ca}^{2+}$  concentration in the solution, sodium solution was also prepared by dissolved 142 gr of  $\text{Na}_2\text{SO}_4$  into the 10,000 ml. The solution was subsequently filtrated two times by 0.22  $\mu\text{m}$  micropore® paper to ensure no unwanted particles remained in the solution. Each solution was then stored in a covered vessel to avoid from dusk and other dirty material.

Inhibitor that been used in the current research was citric acid which set at 10.00 ppm. Citric acid has been known as green inhibitor which was deliberately chosen because this acid had three carboxylates form (COOH) as shown in Fig. 1. The carboxyl the was supposed to vary the ion and destructed the crystal lattice to inhibit its growth [13].

## 2.2 Deposition rate

Deposition rate in flowing and vibrating system must be defined earlier because of the existing new phenomenon in the system. (i). Vibration inserts reciprocal force to the precipitation processes and might affects the stretching and bending of molecule dissociation and association which can promotes more deposition rate. (ii). Vibration has potential to remove the younger crystals which not strong enough adheres in the pipe surface and being transported by fluid flowing, furthermore declines the deposition rate. (iii). Vibration also suspected will be the barrier of the scale to attach in the surface and brought by flowing force which such phenomenon often named as homogenous crystallization.

In fact, too difficult to distinct the crystals between the removal and homogeneous crystallization but both of crystals could be measured by seizure them through smooth strainer and was then named as deposition in the strainer ( $W_{\text{strain}}$ ).

To accommodate such phenomenon, the formula suggested by Sheikholeslami will be used as the basic. As it has published by Sheikholeslami that deposition rate has known as particulate, precipitation and removal [14] which expressed in equation (2)

$$W_{\text{net}} = A. W_{\text{precip}} + B. W_{\text{part}} - W_{\text{rem}} \quad (2)$$

Where  $W_{\text{net}}$  is net deposition rate;  $W_{\text{precip}}$  is deposition rate through precipitation process;  $W_{\text{part}}$  is deposition rate because of the existing particulate;  $W_{\text{rem}}$  is the deposition rate of the removal and A, B are the constant.

Particle scaling is deposition process of particles carried by the fluid which the term particle is general and may refer to particulate matter or corrosion product. In this work, by filtrating the solution with strain paper 0.22  $\mu\text{m}$  two times, all particles in the solution were separated and deposition rate of the particulate could be neglected. Then, equation (1) was modified into equation (3) as follow :

$$W_{\text{net}} = W_{\text{precip}} + W_{\text{strain}} \quad (3)$$

The transpose minus sign of  $-W_{\text{rem}}$  to  $+W_{\text{strain}}$  was considered that all the deposition of the strainer stand as a whole part of reaction that must be calculated and

inserted as the product of reaction, addressed to investigate the real deposition.

## 2.3 Variable

In this experiment, in depend variable was defined as vibration frequency which was chosen in 0.00; 4.00 and 8.00 Hz. The experiment under various vibration frequency was conducted for either blank and antiscalant experiment. Depend variable was defined as deposition rate; induction time; morphology; crystal phase of blank and antiscalant experiment. Otherwise displacement of the vibration; temperature; flow rate and calcium concentration were set as fix variable. All of test was conducted in atmospheric pressure. The summary of experiment variables was given in Table 1.

**Table 1.** Experiment variable

Variable	Test I	Test II	Test III
Frequency (Hz)	0	4.00	8.00
Displacement (mm)	0	4	4
Flow rate (ml/min)	30	30	30
Caconcent. (ppm)	4,000	4,000	4,000
Temperature ( $^{\circ}\text{K}$ )	318	318	318

Experiment of the addition citric acid to the solution in amount of 10 ppm was done in Test II and Test III and namely antiscalant experiment.

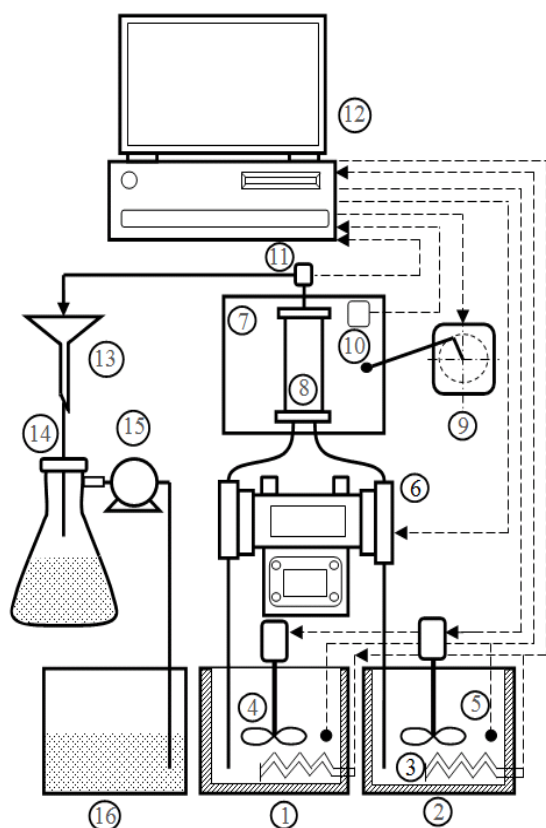
## 2.4 Phreeqc prediction

Scale potential prediction was analyzed by Phreeqc program. To operate this program, firstly, composition of the mineral in the solution was calculated based on the concentration of calcium, i.e. Ca: 2.00 ;Cl: 3.5499; H2: 0.20; O<sub>2</sub> : 1.600; Na : 2.0125 and SO<sub>4</sub> : 4.800 in the unit gr/kg water as the default unit in the program. After insert individual composition to the program, the program was run. The time needed to run the program was reported in 0.33 second only and the prediction of scale potential was ready. Specific conductance was predicted 15,222  $\mu\text{S}/\text{Cm}$ , density 1.0049 gr/cm<sup>3</sup>, saturation index (SI) was predicted 0.24 and 0.54 for  $\text{CaSO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . According to the number of saturation index, production of dehydrate was higher than anhydrate. Crystal polymorph will be predominated by  $\text{CaSO}_4$  dihydrate.

## 2.5 Experimental process and characterization

To investigate the influence of vibration on  $\text{CaSO}_4$  scale formation, an experimental rig was employed. This build in house experimental rig schematically illustrated in Fig. 1. Vessel (1) contained solution of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and vessel (2) contained solution of  $\text{Na}_2\text{SO}_4$ . An electrical heater was employed in each vessel (3) to control solution temperature and agitated by a stirrer (4) which had set at 30 rpm to provide homogeneous

solution. 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 test pipe section (8). In this test pipe section solution of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  was reacted and precipitated as  $\text{CaSO}_4$  scale. Four pair of coupons made from copper with 12.5 mm in inner diameter and 30 mm long was inserted in to the test pipe section where scale was needed to form. The pipe was mounted at the table (7) and vibrated by electrical motor (9) which the frequency was set by computer program (12). Vibration meter Lutron VT-8204(10) sensed the vibration parameter such as displacement peak to peak (m), velocity (m/s) and acceleration(m/s<sup>2</sup>) in RMS.



**Fig. 2.** Build inhouse experimental rig

Conductivity of the solution after left the coupon was measured by TDS meter (11). The data of conductivity and vibration was acquisitioned by computer program (12) to fulfill the accuracy. A strain paper 0.22  $\mu\text{m}$  (13) was used to seizure the scale brought by the flow. A flask tube (14) and a vacuum pump (15) were used to help in sucking the water from the strainer and sent to vessel (16).

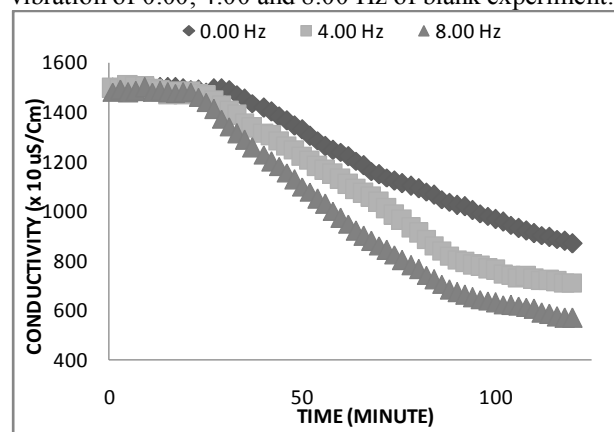
Scale of the coupon was heat in 60<sup>0</sup>C as long as four hours to waste water molecule in the crystal. The weighing scale mass was done include coupon mass after dryer processing. Mass of scale was found by calculate the mass of coupon with scale deminished by the mass of coupon without scale. Furthermore, scale was labeled as the experiment i.e. frequency 0.00; 4.00 Hz and 8.00 Hz and kept in the dry cup.

Crystal polymorph was analyzed through scanning electron microscopy (SEM) to study the different shape as the presence of vibration. Crystal component was investigated through SEM EDX to show the alteration of crystal structure as the presence of vibration. Crystal phase was also investigated through X-Ray Diffractometer and then was confirmed to Powder Diffraction File to identify the crystal phase. Ion-molecule interaction was characterized through FTIR analysis.

### 3 Results and discussion

#### 3.1 Induction time

Conductivity of the solution after left the coupon was measured by TDS meter and recorded by computer program every one minute during process of crystallization. Measurable change of conductivity showed that a number of ions in solution has been reacted and precipitated as the scale, so the amount of ions decrease and either conductivity of the solution. The time of first measurable change of conductivity called as an induction time [15] and shows the initial time of the nucleation as the start of crystallization. The induction time found were 31 ; 27; and 23 minute for frequency vibration of 0.00; 4.00 and 8.00 Hz of blank experiment.



**Fig. 3.** Conductivity of the solution over the time

According to the data found, conductivity of solution at first measuring is 14,821  $\mu\text{S}/\text{Cm}$  and after 31 minute TDS meter showed the change to be 14,076  $\mu\text{S}/\text{Cm}$  for experiment without vibration. Thus, induction time was recorded at 31<sup>st</sup> minute as shown in plot of conductivity over time in Fig. 2 which shows the graph of induction time of the experiment when reaction process was affected by the vibration of 0.00; 4.00 and 8.00 Hz. The data prove that vibration affects  $\text{CaSO}_4$  scale formation i.e. decrease nucleation time and shows that crystallization process was done more faster.

Unfortunately, no references found to explain the mechanism of vibration in affecting the nucleation time but it might be caused by the increase ionic collision which vibration of 8.00 Hz in this system would insert external force 57,600 times per hour or as much as

8,592kJ during four hours, for such experimental that has been done.

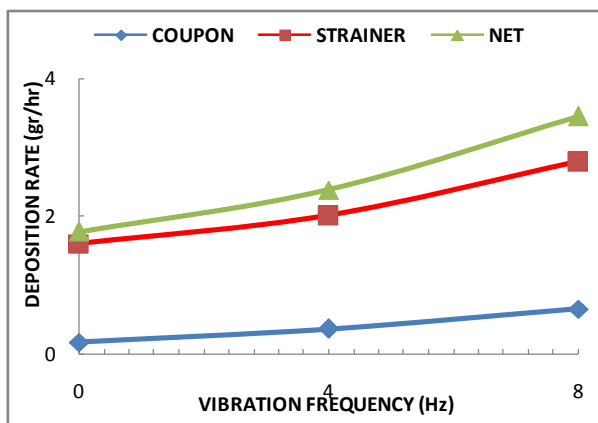
### 3.2 Deposition rate

The concept of deposition rate has been discussed in section two that scale formed was classified into deposition rate of precipitation ( $W_{precip}$ ), deposition rate in the strainer ( $W_{strain}$ ) and net deposition rate ( $W_{net}$ ) as the influence of vibration.

**Table 2.** Deposition rate in various vibration frequency

No	Vib (Hz)	$W_{precip}$ (gr/hr)	$W_{Strain}$ (gr/hr)	$W_{net}$ (gr/hr)
1	0	0,1774	1,612	1,7894
2	4	0,3745	2,0146	2,3891
3	8	0,6657	2,7942	3,4599
4	4	0,2084	1,6379	1,8963
5	8	0,3306	1,9559	2,2865

Deposition rate of precipitation was measured in the coupon in respect to the time (hour) and named as grow rate of precipitation. Deposition rate in the strainer was measured in the strainer for every running. Net deposition rate ( $W_{net}$ ) as the presence of vibration was calculated as equation (3) for all vibration frequency. The result was listed in Table 2 and graphically depicted in Fig. 4. Number 4 and 5 of Table 2 shows the deposition of experiment with the presence citric acid in 10 ppm.



**Fig. 4.** Deposition rate of precipitation and strainer

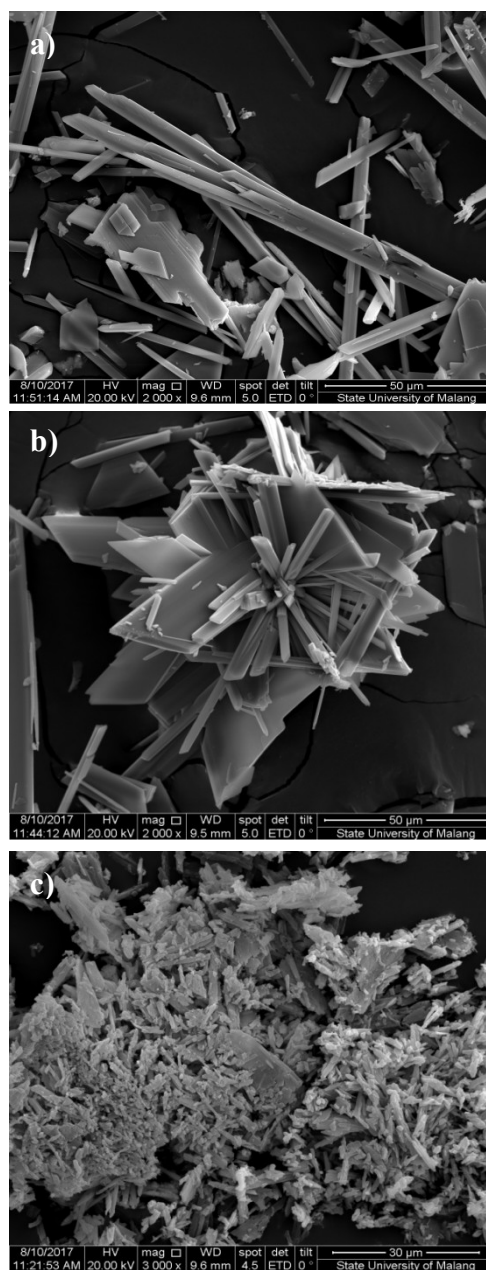
Deposition rate increased significantly when the vibration affected to the system i.e. 0.5997 and 1.6705 gr/hr for vibration frequency 4.00 and 8.00 Hz. The addition 10.00 ppm of citric acid declined the deposition rate of 8 Hz experiment from 3.4599 gr/hr to 2.2865 gr/hr.

### 3.3 Crystal morphology

The phases of  $CaSO_4$  crystal are anhydrate ( $CaSO_4$ ), hemihydrate ( $CaSO_4 \cdot 0.5H_2O$ ) and dihydrate ( $CaSO_4 \cdot 2H_2O$ ) [16]. All polymorph has no differences in

shape so it phases could not be identified through the SEM. Even though, SEM could gives the information about the amount of needle and crystal size [17] as the influence of research parameter.

Crystal polymorph was investigated after it was characterized by Scanning Electron Microscopy FEI Inspect S50 to the scale found in the coupon of unvibrated-blank sample (Fig. 4a); 8.00 Hz vibrated-blank sample (Fig. 4b) and 8.00 Hz vibrated-antiscalant sample (Fig. 4 c) where all of them were in needle shape or orthorhombic [18]. The difference between those three crystals mainly emphasize at the size of needle which in experiment of frequency 8.00 Hz had larger needle compared to the other. This phenomenon could be caused by nucleation process of the experiment in which performed faster as the data found by induction time investigation.



**Fig.5.** Crystal morphology of: a). Unvibrated blank sample; b). Vibrated blank sample; c). Vibrated antiscalant sample

Fig. 5c) shows crystal polymorph of deposition of the addition citric acid in 10.00 ppm and vibrated at 8.00 Hz. The shape identified in irregular shape and fewer dimension as the evident that citric acid successfully destructed crystal lattice as promoted by Ersen [13].

### 3.4 Crystal structure

Composition of the crystal was characterized by SEM EDX FEI Inspect S50 to the specific area had been chosen and the result shown in Fig. 6 which the composition is given in % weight i.e. 50.91; 20.37 and 25.54 for O, S and Ca respectively. The peak shown in Fig. 6 prove that  $\text{CaSO}_4$  crystal was pure. Its indicate that downstream process of this research such as washing, filtrating, drying and powder storing was done very well [6]. This spectrum was then compared by the one had been published by Helalizadeh that the composition found not any differences [19].

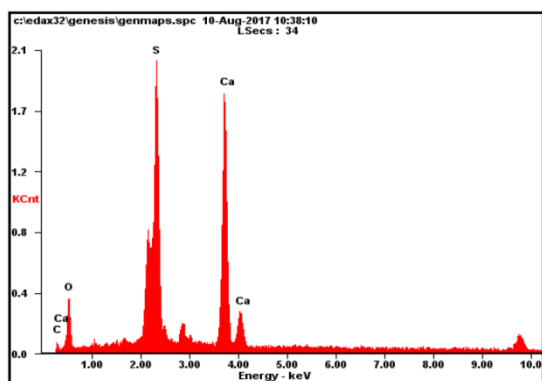


Fig. 6. Composition of  $\text{CaSO}_4$  anhydrate crystal running in four hours and frequency 8.00 Hz

The differences between theoretical and actual value in % weight of crystal composition are 3.91; 2.63 and 3.6 for O, S and Ca respectively. The composition shows that the crystal was  $\text{CaSO}_4$  dihydrate. This phenomenon similar to the prediction by phreeqc program which has been predicted before that polymorph  $\text{CaSO}_4$  dihydrate predominated the scale formed with number saturation index 0.54 even  $\text{CaSO}_4$  anhydrate was predicted only 0.24.

### 3.5 Crystal Phase

Crystal phase was analyzed through X-Ray Diffractometer which was operated in 40 kV, 30 mA and incident beam  $100 < 2\theta < 800$ , step size 0.02 degree ( $2\theta$ ). Start position at 10.0100 even end position at 79.9900, scan type continuous with goniometer radius 240 mm and measurement temperature at 25°C.

The data found was then analyzed through Rietveld quantification method which operated under FullProf program to investigate crystal phase distribution. Three crystal of the experiment i.e. blank; vibrated in 8 Hz and citric acid addition-vibrated in 8 Hz experiment were characterized. AMCS0001807 was used as basic standard to analysis  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  crystal phase. All of

peaks identified as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or recognized in popular name as gypsum.

The spectrum of XRD analysis is completed by miller indices of every peak to show the alteration each plane of every experiment (Fig. 7). Plane of (020); (121); (-141); (051); (042); (-233); (-204) and (-264) in Fig. 5 increases when the experiment was influenced by the vibration. The data shows not contrary to the data of deposition rate which vibrated experiment produced more scale and shows the agreement to the previous research which  $\text{CaCO}_3$  was also increase when affected by vibration [20].

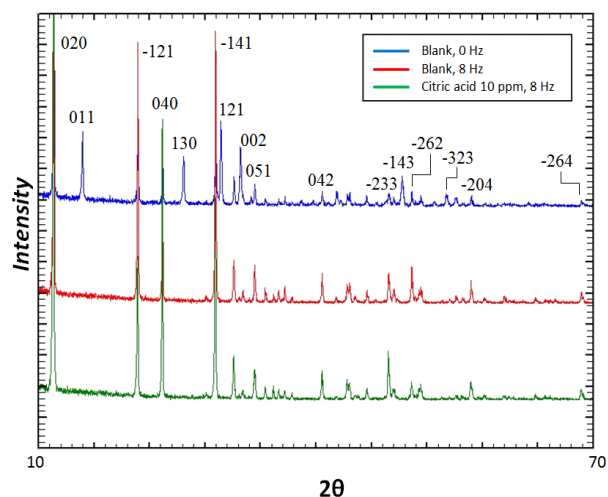


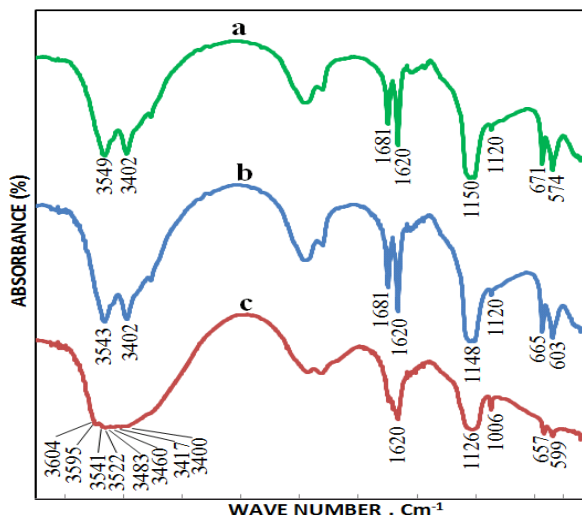
Fig. 7. XRD analysis of blank; vibrated and citric acid – vibrated experiment.

Planes of (011); (130); (002); (121) and (-323) did not arise anymore when the experiment was added by 10 ppm of citric acid and vibrated at 8 Hz mechanically. The loses planes shows the agreement to the deposition rates of the experiment which scale deposition of the addition citric acid decreased in significant value.

### 3.6 FTIR analysis

Fourier Transform Infra Red (FTIR) analysis (Fig. 6) was used to investigate ion interaction and scale formation among the reaction of unvibrated (a); vibrated reaction (b) and antiscalant reaction (c). Bands of 3,549  $\text{Cm}^{-1}$  and 3,402  $\text{Cm}^{-1}$  are assigned as O-H stretching [21]. Band of 1,681  $\text{Cm}^{-1}$  and 1,620  $\text{Cm}^{-1}$  assigned as stretching of water molecule in the crystal. Band of 671 and 574 are assigned as symmetric bending of sulfate ion [22]. The band 3,549  $\text{Cm}^{-1}$ ; 1,150  $\text{Cm}^{-1}$  and 671  $\text{Cm}^{-1}$  of blank experiment changed as the experiment was influenced by the vibration to be 3,543  $\text{Cm}^{-1}$ ; 1,148  $\text{Cm}^{-1}$  and 665  $\text{Cm}^{-1}$  respectively.

These alteration was also accompanied by the increase of scale deposition which unvibrated experiment produced larger scale than unvibrated. The phenomenon shows the agreement to Badge Rule that the lower band indicates the reaction takes place in easier [23].



**Fig. 8.** FTIR analysis of  $\text{CaSO}_4$  crystal. a). Blank-unvibrated experiment. b). Blank-vibrated experiment and c). Citric acid 10 ppm and vibrated experiment.

In the experiment with additive citric acid, more bands in the region  $3,400 \text{ Cm}^{-1}$  to  $3,604 \text{ Cm}^{-1}$  arised that assigned as O-H stretching. The arising peak indicated O-H stretching as the addition citric acid [23] which would be the reason of scale declination.

## 4 Conclusion

The influence of vibration on  $\text{CaSO}_4$  scale formation especially in kinetical, morphology, microanalysis and deposition rate has been investigated systematically. Vibration has positive correlation to the kinetic and deposition rate of scale formation. Increasing vibration frequency would increase speed of reaction and increase mass of scale. Morphology crystal was needle shape or orthorhombic and crystal polymorph predominated by  $\text{CaSO}_4$  dihydrate. The addition citric acid in 10.00 ppm to the solution declined scale deposition and affected crystal polymorph in irregular shape.

## 5 Acknowledgement

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