

A STUDY ON APPLICATION OF VOLATILE CORROSION INHIBITORS FOR EQUIPMENT PROTECTION IN THE PETROLEUM INDUSTRY

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Summary

While usage of volatile corrosion inhibitors (VCI) is one of the effective methods in corrosion protection for rough, complicated and multi sub-component equipment, traditional protecting methods show no obvious efficiency. The results of an applied research at Ca Mau Power Plant and Dung Quat Refinery showed that volatile corrosion inhibitors have an ability to absorb on metal surface to prevent corrosion with high efficiency of above 80% for copper coupons, above 85% for steel coupons in electrical boxes and up to over 90% for steel coupons attached to flanges of air exposed pipeline.

Key words: Corrosion, protection of metal, volatile corrosion inhibitor.

1. Introduction

In the petroleum industry, equipment works under an aggressive environment, especially at seaside locations where a high percentage of Cl⁻ ions and a high humidity are the strong corrosive factors. If there is no appropriate protection, the equipment and machines would be vulnerable to corrosion leading to failure after a short time in operation.

Using metal, organic or composite coating or spreading grease to keep metal surface from exposing to the surroundings are possible and widely used methods.

However, the traditional methods prove ineffective for rough, complicated equipment and multi sub-component machines which make it difficult to reach their small details such as electrical panels of onsite monitoring systems, flanges of pipelines and other apparatus and air exposed parts of distillation towers, separators, and heat exchangers during maintenance duration.

Volatile corrosion inhibitors have, therefore, been studied and applied by many scientists for corrosion protection at these locations [1 - 5].

Volatile corrosion inhibitor is a chemical substance with an ability to vaporise and absorb on every position on a metal surface, protecting it by either creating a molecular sized thin film attached to the metal surface to prevent moisture and other corrosive factors from directly contacting the surface or reacting with the metal surface to have it passive to inhibit corrosion process.

In Vietnam, studies on manufacturing and applying volatile corrosion inhibitors are still limited, most of

them were experimented at laboratories for weapon storage [5].

Study, development and application of volatile corrosion inhibitors would increase the effectiveness of equipment protection. In addition, volatile corrosion inhibitors may be used as a useful tool to ensure asset integrity in oil and gas plants.

This paper showed the preliminary results of applying volatile corrosion inhibitor for electrical panels of onsite monitoring systems and flanges of pipelines and other apparatus at Ca Mau Power Plant and Dung Quat Refinery.

2. Experiments

The volatile corrosion inhibitors used in our research were products of Cortec Corporation – USA in the form of plastic bags or granules.

In this research, VCI impregnated plastic bags were used to wrap flanges while VCI granules were attached directly to an appropriate position in electrical box.

To evaluate corrosion rate, coupons were placed in the vicinity of experimental locations. At each plant, 4 flanges and 4 electrical boxes were chosen for our research.

To evaluate VCI efficiency, 3 shelves of coupons placed in 3 electrical boxes with VCI protection were compared to 1 shelf of coupons placed in 1 electrical box without VCI.

Similarly, 3 shelves of coupons placed in 3 VCI impregnated plastic bags were compared to 01 shelf of coupons placed in normal plastic bag.

Coupons were taken three times: after 3 months, after 6 months and after 9 months of experiment. Surface

analysis and corrosion rate evaluation using weight loss method were carried out after that.

2.1. Analysis of corrosive factors in atmosphere

Tempet 100 (USA) and HS-1050, HN-1050 (France) were used to identify such corrosive factors in the atmosphere as SO₂, H₂S, NO₂, NH₃, CO, and CO₂ with high accuracy (error ≤ ±1%). Detector Tube was used to reaffirm these results.

2.2. Coupon preparation

Copper coupons were made from pure copper with clarity of 99% equivalent to materials for fabricating electrical circuit panel. Steel coupons were made from steel equivalent to materials of pipeline flanges.

Coupons fabricated in the form of flat specimen with dimensions of 10 x 40 x 2 (mm x mm x mm) were ground and polished using silicon carbide grinding paper ranging from coarse (600, 800 grit sizes) to fine (1000, 1200 grit sizes). The coupons were then degreased, cleaned, dried, weighted and kept in anti-humidity container according to ASTM G1-03 - Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. The prepared coupons were attached to shelves with 6 copper coupons and 6 steel coupons for each shelf.

2.3. Surface analysis

The volatile corrosion inhibitor and coupons (copper and steel) after experiment were analysed morphologically and chemically using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX).

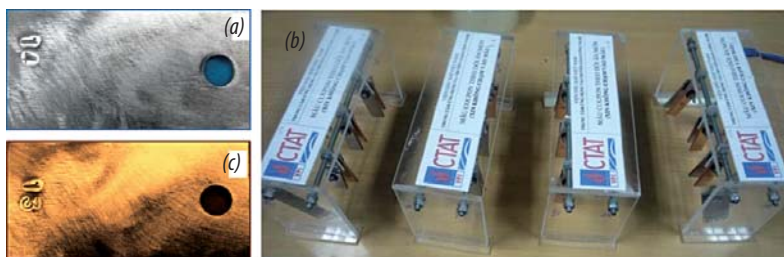


Figure 1. Steel coupons (a), Copper coupons (b) and Shelves of coupons (c)

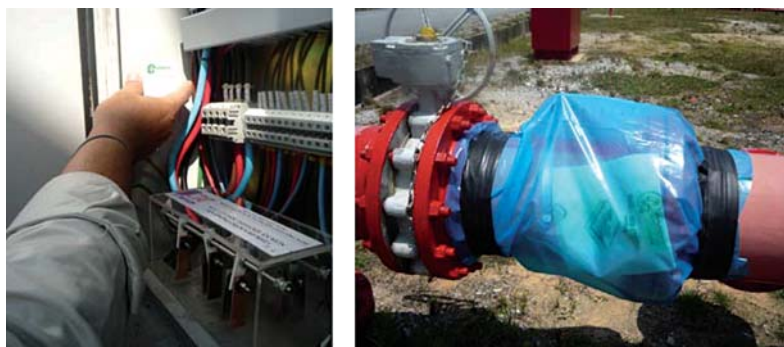


Figure 2. Coupons are experimented at field (a) Coupons placed in electrical box (b) Coupons placed at flange

2.4. Corrosion rate calculation

The resistance method and the weight-loss method were used to identify the corrosion rate and the protection efficiency of inhibitors. The resistance method allows measuring corrosion rate by inserting of an electrical resistance probe into any corrosive environment to be studied. Because of corrosion, any changes in dimensions would result in changes in probes' resistances.

After experiment, probes were connected to CK – 3 Portable Corrosometer to calculate corrosion rates.

Protection efficiency was calculated using the following formula:

$$\eta = 100\% \frac{V_{kuc} - V_{uc}}{V_{kuc}} \quad (1)$$

Where: V_{kuc}: Corrosion rate in case of not using corrosion inhibitor (mm/year)

V_{uc}: Corrosion rate in case of using corrosion inhibitor (mm/year)

The weight-loss method is one of the common practices. In the method, weighed coupons were exposed for a fixed duration and then retrieved and reweighed; corrosion rate (CR) can be determined by the following Eq.:

$$CR = (8.76 \times 10^4 \cdot W) / (A \cdot T \cdot D) \quad [mm/y]$$

Where: K = 8.76 x 10⁴

T is time of exposure in hours;

A is area in cm²;

W is weight loss in gram;

D is density in g/cm³

3. Results and discussion

3.1. Analysis results in atmosphere at Dung Quat Refinery and Ca Mau Power Plant

Analysis results of corrosive factors in the atmosphere at Dung Quat Refinery and Ca Mau Power Plant were shown in Tables 1 and 2.

Both Dung Quat Refinery and Ca Mau

Table 1. Concentration of corrosive factors in atmosphere at Dung Quat Refinery

Sampling date	SO ₂ (ppm)	NO ₂ (ppm)	CO (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	NH ₃ (ppm)	Salinity (mg/m ³)
Before experiment (16/10/2011)	1.5	<1	<1	380	<1	<1	69
15/1/2012	1.5	<1	<1	379	<1	<1	71
21/4/2012	1.5	<1	<1	379	<1	<1	68
22/7/2012	1.5	<1	<1	378	<1	<1	69

Table 2. Concentration of corrosive factors in atmosphere at Ca Mau Power Plant

Sampling date	SO ₂ (ppm)	NO ₂ (ppm)	CO (ppm)	CO ₂ (ppm)	H ₂ S (ppm)	NH ₃ (ppm)	Salinity (mg/m ³)
Before experiment (23/10/2011)	2	<1	<1	382	<1	<1	79
22/1/2012	2	<1	<1	382	<1	<1	76
28/4/2012	2	<1	<1	381	<1	<1	78
29/7/2012	2	<1	<1	382	<1	<1	78

Table 3. Steel coupons in electrical boxes at Ca Mau Power Plant













Steel coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Fe-TĐ-CM 1 (Without VCI)			
Fe-TĐ-CM 2 (With VCI)			
Fe-TĐ-CM 3 (With VCI)			
Fe-TĐ-CM 4 (With VCI)			

Table 4. Steel coupons at flanges at Ca Mau Power Plant













Steel coupons at flanges	After 3 months	After 6 months	After 9 months
Fe-MB-CM 1 (Without VCI)			
Fe-MB-CM 2 (With VCI)			
Fe-MB-CM 3 (With VCI)			
Fe-MB-CM 4 (With VCI)			

Table 5. Steel coupons in electrical boxes at Dung Quat Refinery













Steel coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Fe-TĐ-DQ 1 (Without VCI)			
Fe-TĐ-DQ 2 (With VCI)			
Fe-TĐ-DQ 3 (With VCI)			
Fe-TĐ-DQ 4 (With VCI)			

Table 6. Steel coupons at flanges at Dung Quat Refinery













Steel coupons at flanges	After 3 months	After 6 months	After 9 months
Fe-MB-DQ 1 (Without VCI)			
Fe-MB-DQ 2 (With VCI)			
Fe-MB-DQ 3 (With VCI)			
Fe-MB-DQ 4 (With VCI)			

Table 7. Copper coupons in electrical boxes at Ca Mau Power Plant











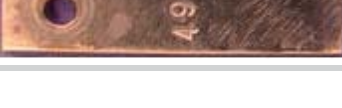













Copper coupons in electrical boxes	After 3 months	After 6 months	After 9 months
Cu-TĐ-CM 1 (Without VCI)			
Cu-TĐ-CM 2 (With VCI)			
Cu-TĐ-CM 3 (With VCI)			
Cu-TĐ-CM 4 (With VCI)			

Table 8. Copper coupons in electrical boxes at Dung Quat Refinery

Copper coupons at flanges	After 3 months	After 6 months	After 9 months
Cu-TĐ-DQ 1 (Without VCI)			
Cu-TĐ-DQ 2 (With VCI)			
Cu-TĐ-DQ 3 (With VCI)			
Cu-TĐ-DQ 4 (With VCI)			

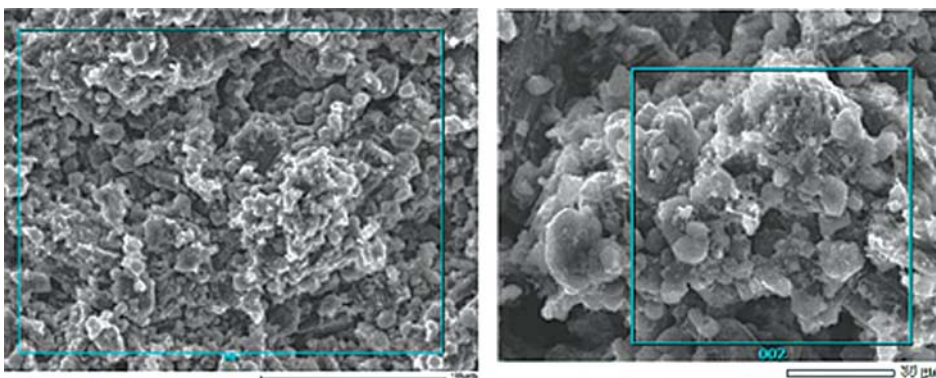


Figure 3. SEM images of VCI

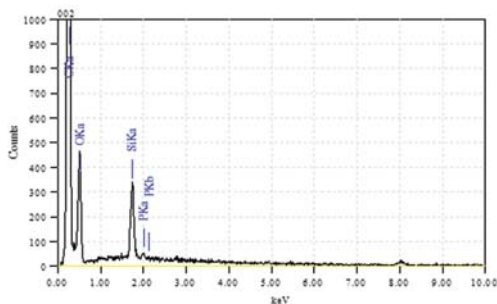


Figure 4. EDX pattern of VCI

Elements	(keV)	Mass, %	Atom, %
C K	0.277	60.14	67.77
O K	0.525	35.81	30.29
Si K	1.739	3.81	1.84
P K*	2.013	0.24	0.10

Power Plant are located at the seaside. Due to the effects of a tropical monsoon climate with relatively high average temperature of 25 - 28°C (according to data from the National Centre for Hydro-Meteorological Forecasting), high concentration of Cl⁻ ion and high temperature are the main factors promoting corrosion. Besides, oxygen and CO₂ in the atmosphere are additional factors accelerating corrosion. Salt content and CO₂ concentration are stable in all samples.

3.2. Surface analysis of coupons before and after on-site experiments

3.2.1. Images of coupons after on-site experiments

In general, when volatile corrosion inhibitors were not used, some traces of rust occurred with the increase of exposing time (after 9 months > after 6 months > after 3 months). As compared to coupons placed in closed

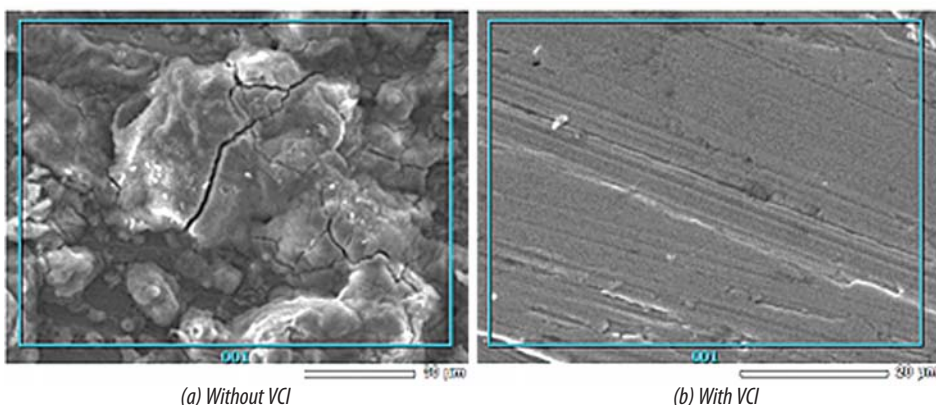
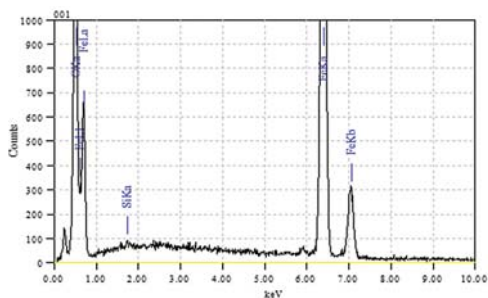
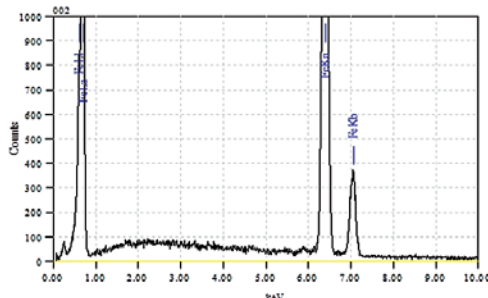


Figure 5. SEM images of steel coupons in electrical boxes in Ca Mau Power Plant



Elements	(keV)	Mass, %	Atom, %
O K	0.525	30.97	60.85
Na K*	1.041	0.27	0.38
Si K*	1.739	0.11	0.12
Fe K	6.398	68.65	38.65

(a) Without VCI



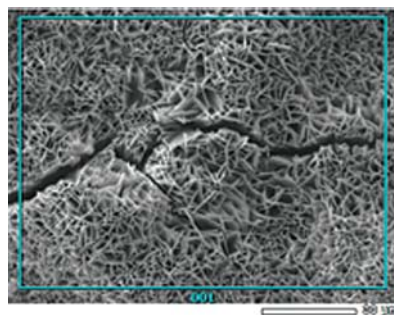
Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.09	0.18
Fe K	6.398	99.91	99.82

(b) With VCI

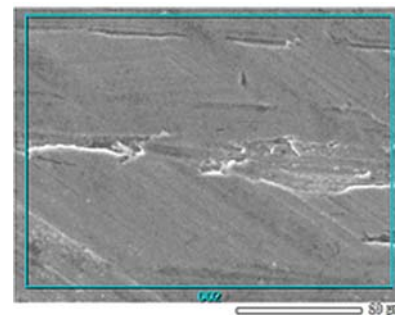
Figure 6. EDX pattern of steel coupons in electrical boxes in Ca Mau Power Plant

boxes which lacked contact with the atmosphere, coupons placed at flanges had more rust spots of deeper and wider size demonstrating more extreme corrosion. In the same conditions, the coupons with volatile corrosion inhibitors had negligible spots (Tables 3 - 6).

As compared to the steel specimens, the copper specimens were more stable to the atmosphere, thus the copper coupons had less rust in spite of some visible rust spots and stains on the surfaces of coupons without VCI. When the copper coupons were placed in electrical boxes with VCI, there was almost no sign of corrosion after 9 month experiment (Tables 7 and 8).

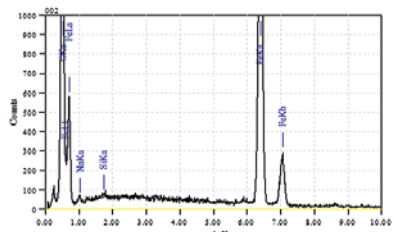


(a) Without VCI



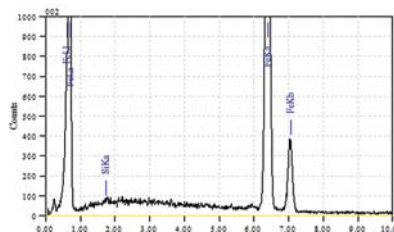
(b) With VCI

Figure 7. SEM images of steel coupons at flanges in Ca Mau Power Plant



(a) Without VCI

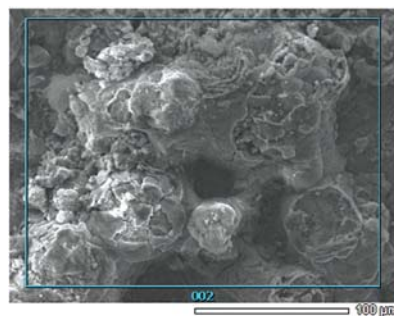
Elements	(keV)	Mass, %	Atom, %
O K	0.525	30.97	60.85
Na K*	1.041	0.27	0.38
Si K*	1.739	0.11	0.12
Fe K	6.398	68.65	38.65



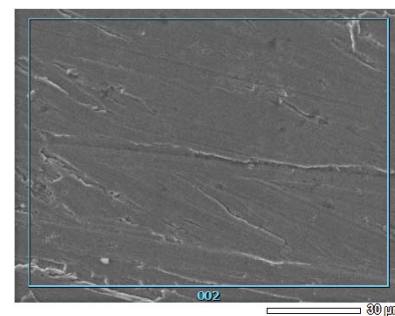
(b) With VCI

Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.08	0.17
Fe K	6.398	99.92	99.83

Figure 8. EDX patterns of steel coupons at flanges in Ca Mau Power Plant



(a) Without VCI



(b) With VCI

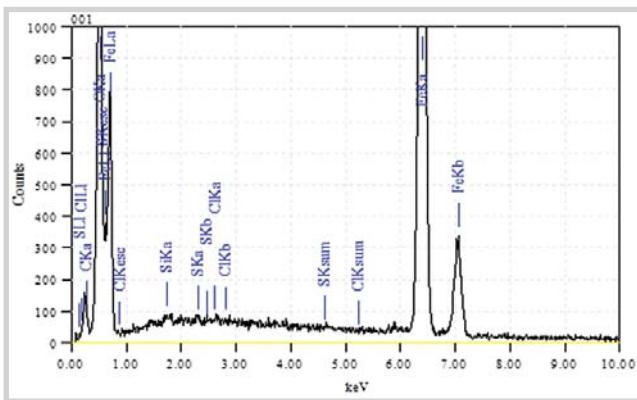
Figure 9. SEM images of steel coupons in electrical boxes in Dung Quat Refinery

3.2.2. Morphological characteristic and chemical components of VCI, coupon surfaces and corrosion products

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) was used to identify morphological characteristic and chemical components of VCI, coupon surfaces and corrosion products.

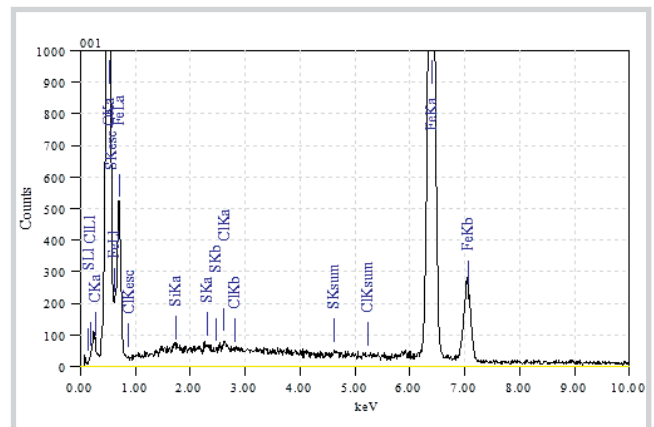
- Volatile corrosion inhibitor

As can be seen from Figures.3 and 4, the structure of VCI is relatively porous with about 60% (w/w) C and above 35% (w/w) O. There could be a small amount of Silicon (3.8%) and Hydrogen (out of detectable range of EDX). These results demonstrate that VCI is a silicon compound.



Elements	(keV)	Mass, %	Atom, %
C K*	0.277	2.97	8.38
O K	0.525	21.42	45.47
Si K*	1.739	0.04	0.05
S K*	2.307	0.23	0.24
Cl K*	2.621	0.13	0.13
Fe K	6.398	75.21	45.73

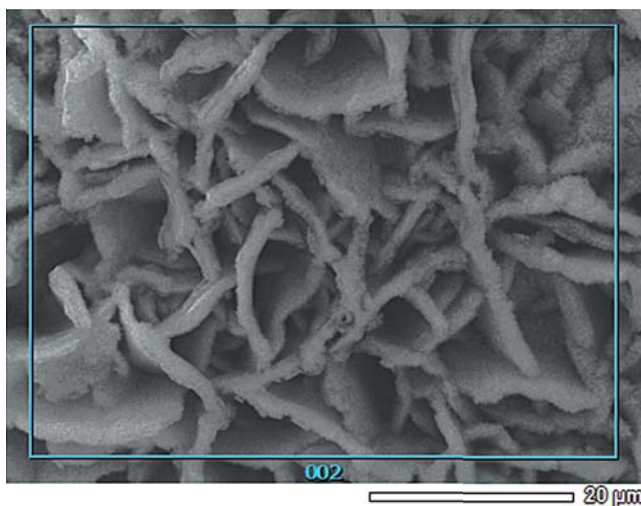
(a) Without VCI



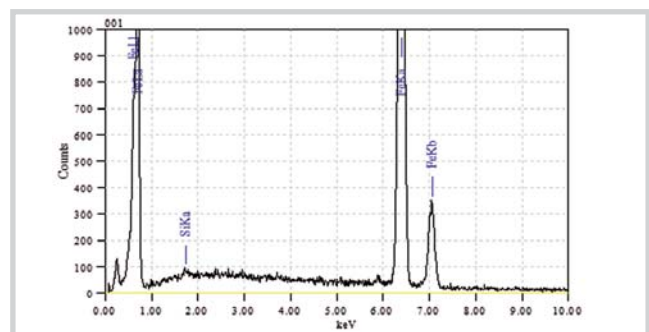
Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.23	0.46
Fe K	6.398	99.77	99.54

(b) With VCI

Figure 10. EDX patterns of steel coupons in electrical boxes in Dung Quat Refinery



(a) Without VCI

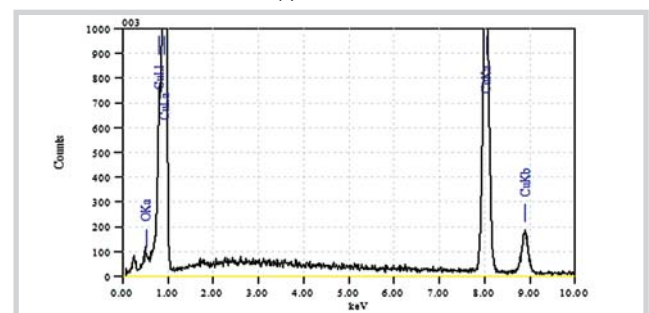


Elements	(keV)	Mass, %	Atom, %
C K*	0.277	2.13	5.42
O K	0.525	29.69	56.93
Si K*	1.739	0.13	0.15
S K*	2.307	0.18	0.17
Cl K*	2.621	0.19	0.17
Fe K	6.398	67.68	37.16

(a) Without VCI



(b) With VCI



Elements	(keV)	Mass, %	Atom, %
Si K*	1.739	0.15	0.30
Fe K	6.398	99.85	99.70

(b) With VCI

Figure 11. SEM images of steel coupons at flanges in Dung Quat Refinery

Figure 12. EDX patterns of steel coupons at flanges in Dung Quat Refinery

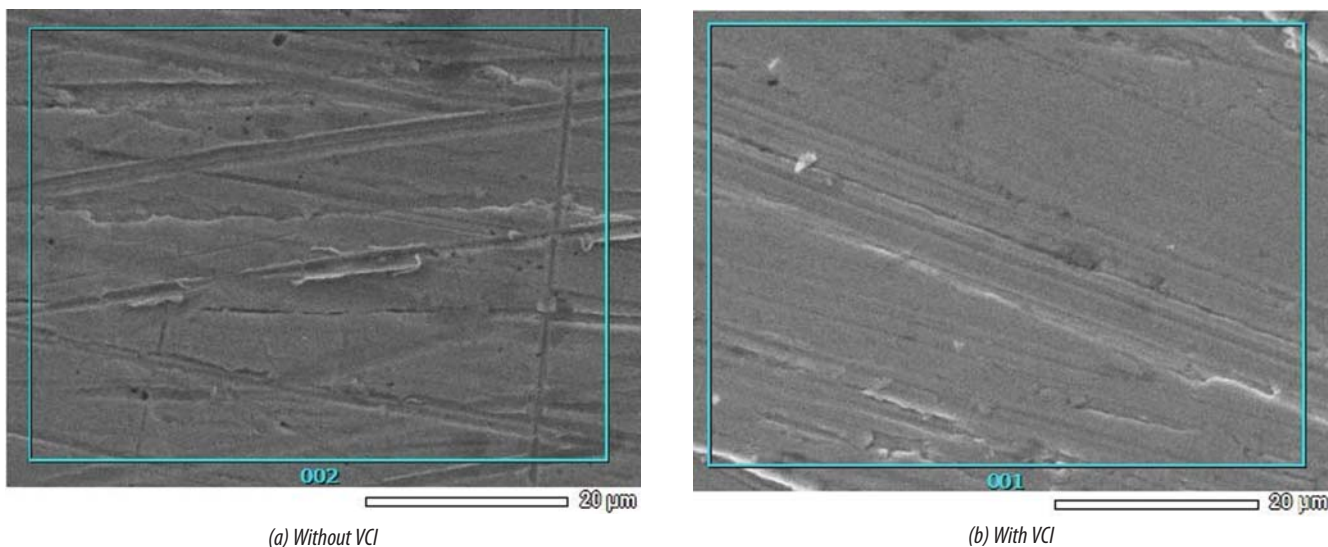


Figure 13. SEM images of copper coupons in electrical boxes in Ca Mau Power Plant

- Steel coupons

Images of corrosion products on steel surface placed in electrical boxes and flanges at Ca Mau Power Plant and Dung Quat Refinery were shown in Figures 5 and 8.

For steel coupons placed in electrical boxes without VCI, the layers of corrosion products were thick and porous. In addition to the main component of Fe, oxygen content accounts for 20%. It indicates that corrosion products were in the form of ferrous oxides (Figures 5 and 6). Similarly, for steel coupons placed at flanges without VCI, corrosion products created a thick and cracked layer of rust with oxygen accounting for up to 30% and a small amount of sodium due to accumulation of salt from the atmosphere (Figures 7 and 8). When using the VCI, there is no sign of corrosion (flat surface and absence of corrosion products) on the coupons' surface in both locations (electrical boxes and flanges). A higher percentage of silicon (as compared to coupons without VCI) combining with the main component of Fe demonstrates that there was an absorption of silicon contained VCI into metal surface to prevent corrosion.

Steel coupons placed at Dung Quat Refinery with and without VCI showed the same tendency as those placed at Ca Mau Power Plant. In case of not using VCI, there was an appearance of Cl⁻ ion which is the corrosive factor in the atmosphere accumulating in corrosion products.

- Copper coupons

Different from steel coupons, copper coupons were stable to marine environment. After 9 months of

experiment, corrosion products did not visibly appear in both two experimental cases with and without VCI (Figures 13 and 14).

3.3. Determination of VCI protection efficiency

3.3.1. Determination of VCI protection efficiency by resistance method

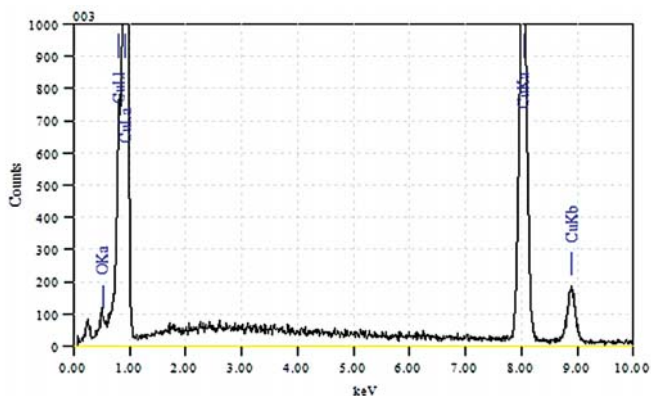
Protection efficiencies of volatile corrosion inhibitor were calculated from results of resistance method by formula (1) and shown in Figure 11.

In case of using VCI, at both plants, because the electrical boxes were closed, limiting contact between the metal surface and the surroundings, the corrosion rates measured in the electrical boxes were lower than the ones measured at flanges. With VCI, the corrosion rates decreased significantly and the protection efficiency reached 85 - 90% for the coupons in the electrical boxes and about 90% for the coupons at flanges. In general, the corrosion rates measured at Ca Mau Power Plant were higher than at Dung Quat Refinery.

3.3.2. Determination of VCI protection efficiency by weight loss method

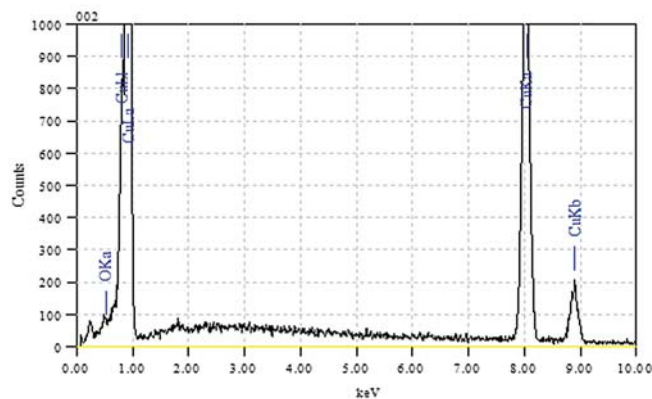
After the on-site experiment period, the coupons were cleaned and dried to constant weight to calculate corrosion rates by formula (2). Protection efficiencies were identified from the corrosion rates. Protection efficiencies of steel and copper coupons from Ca Mau Power Plant and Dung Quat Refinery were shown in Figure 12.

Weight-loss method showed similar results to resistance method. At Ca Mau Power Plant, the VCI



Elements	(keV)	Mass, %	Atom, %
O K	0.525	0.81	3.16
Cu K	8.040	99.19	96.84

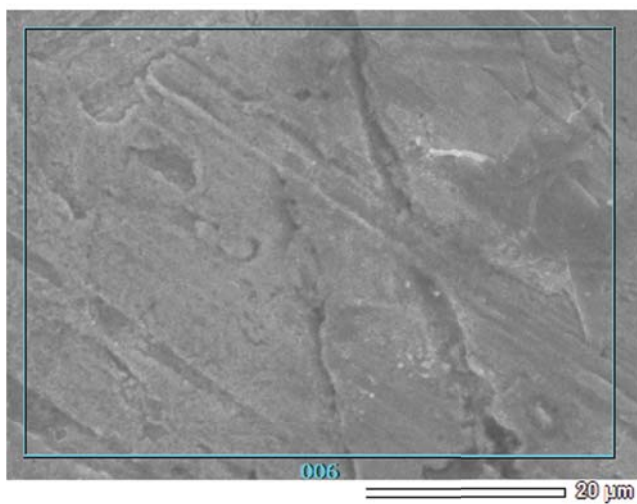
(a) Without VCI



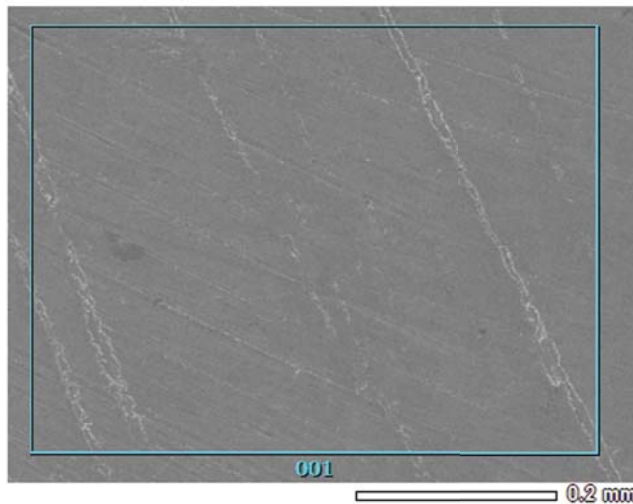
Elements	(keV)	Mass, %	Atom, %
O K	0.525	0.06	0.25
Cu K	8.040	99.94	99.75

(b) With VCI

Figure 14. EDX patterns of copper coupons in electrical boxes in Ca Mau Power Plant

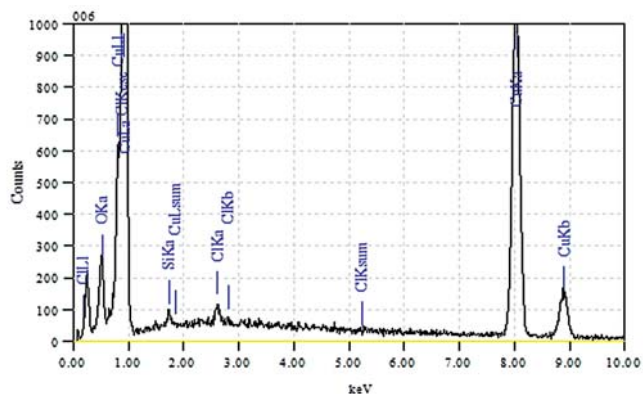


(a) Without VCI



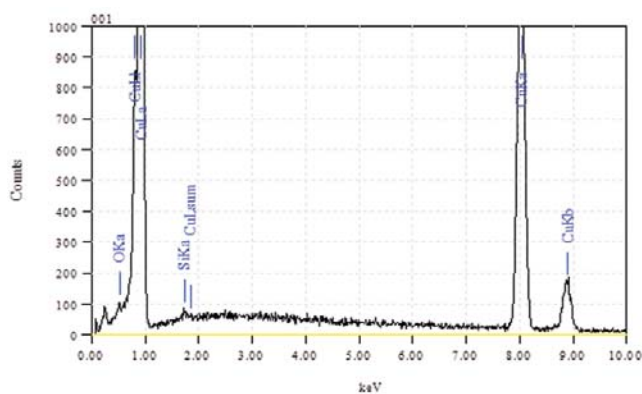
(b) With VCI

Figure 15. SEM images of copper coupons at flanges in Dung Quat Refinery



Elements	(keV)	Mass, %	Atom, %
O K*	0.525	4.71	16.21
Si K*	1.739	0.65	1.27
Cl K	2.621	0.69	1.08
Cu K	8.040	93.95	81.44

(a) Without VCI



Elements	(keV)	Mass, %	Atom, %
O K*	0.525	0.32	1.27
Si K*	1.739	0.26	0.58
Cu K	8.040	99.42	98.15

(b) With VCI

Figure 16. EDX patterns of copper coupons at flanges in Dung Quat Refinery

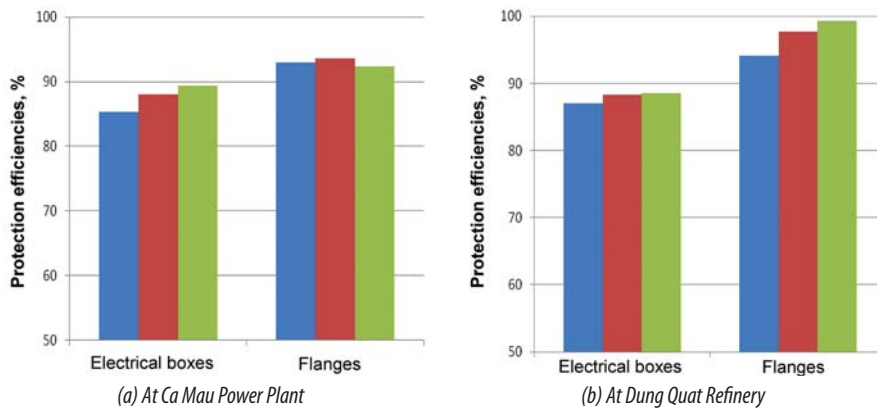


Figure 17. Protection efficiencies of VCI by resistance method

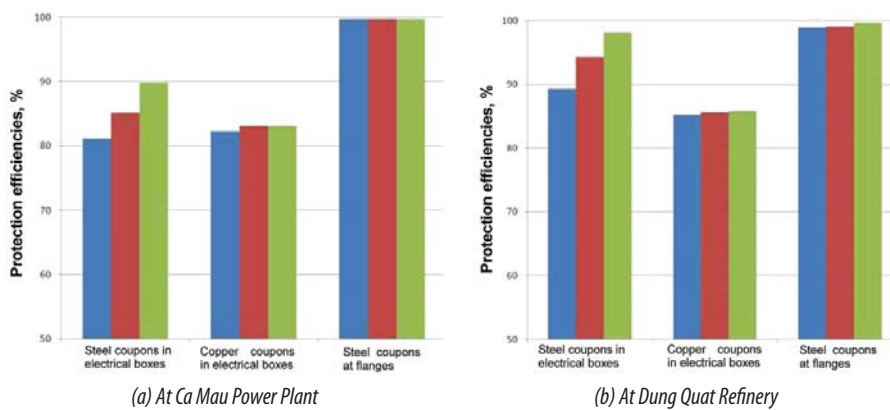


Figure 18. Protection efficiencies of VCI

exhibited an effective protection of 83% for copper specimens and up to 85 - 99% for steel specimens placed in electrical boxes and at flanges. At Dung Quat Refinery, the efficiencies reached 85% for copper coupons, 94% for steel coupons in electrical boxes and 99% for steel coupons at flanges.

4. Conclusions

From the results of applying volatile corrosion inhibitors to electrical panels and flanges of pipeline and apparatuses on field at Ca Mau Power Plant and Dung Quat Refinery, it can be concluded

that volatile corrosion inhibitor have high protection efficiency. At Ca Mau Power Plant, the VCI exhibited an effective protection of 83% for copper specimens and up to 85 - 99% for steel specimens placed in electrical boxes and at flanges. At Dung Quat Refinery, the efficiencies reached 85% for copper coupons, 94% for steel coupons in electrical boxes and 99% for steel coupons at flanges. Because of its ease of use without any disturbance to normal operation, the method of protection was acknowledged and appreciated by leaders from Ca Mau Power Plant and Dung Quat Refinery.

References

1. D.M.Bastidas, E.Cano, E.M.Mora. *Volatile corrosion inhibitors: a review*. *Anti-Corrosion Methods and Materials*. 2005; 52(2): p. 71 - 77.
2. Michael E.Tarvin, Boris A.Miksic. *Volatile corrosion inhibitors for protection of electronics*. NACE, National Association of Corrosion Engineers. 1989.
3. Sakae Amamiya. *Volatile corrosion inhibitor*. Three Bond Technical News. 1987.
4. Eduardo Lozano, John Anthony Shipley. *Vapor Phase Corrosion Inhibitors*. US Patent 6033599. 2000.
5. Trinh Cuong. *Study on synthesis, investigation of structure and structure - activity relationship of several b-aminoxeton volatile corrosion inhibitor*. Doctoral Thesis, University of Science, Hanoi National University. 2007.
6. ASTM G1-03. *Standard practice for preparing, cleaning, and evaluating corrosion test specimens*.