

# DEPOSITION RATE OF CHLORIDE DRC AS A CORROSIVE AGENT IN SEVERAL LOCATIONS IN THE KLANG VALLEY, MALAYSIA

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**ABSTRACT:** *The corrosivity of the atmosphere has received a great attention worldwide. Amongst some of the agents used to classify atmospheric corrosivity, the deposition of chloride is one of the most important used. Chloride is a significant natural contaminant in the atmosphere; especially in a marine environment, and it plays an important role in the corrosion process of structural materials. The current study was conducted in different locations in the Klang Valley, from September 2014 to July 2015, with the main aim of determining the concentration of chloride using wet candle (as mentioned in ISO 9223). The findings show that the mean deposition rate of chloride is  $27.44 \pm 11.24$  mg/m<sup>2</sup>.day, with values ranging between 8.83 and 66.20 mg/m<sup>2</sup>.day. Shah Alam had the highest mean, while Puchong had the lowest. The results also show that the classification of chloride in Shah Alam fell between categories S<sub>1</sub> and S<sub>2</sub>, while all other locations were category S<sub>1</sub>.*

**Keywords:** Airborne salinity, ISO 9223, ISO 9225, corrosivity, corrosion product.

## 1. INTRODUCTION

Chloride ion (Cl<sup>-</sup>) (airborne salt) is one of the most significant natural contaminants and anthropogenic source in the atmosphere; particularly in a marine environment. It plays a major role in the corrosion process of structural metallic, such as steel [1–3]. Chlorides are generally deposited in a marine atmosphere either as droplets or as crystals formed by the evaporation of ocean spray carried by the wind [4]. Although the corrosion product may protect metal, these ions can penetrate the corrosion products layer and reach the metal's surface; resulting in a significant speeding-up of corrosion rate. Because chloride ion is very soluble, it can easily be removed from metallic surfaces through wet precipitation. A relation between chloride concentration present in corrosion products and corrosion rate was stated by [5], [6].

Many authors have reported the influence of chloride ion on the atmospheric corrosion of metals. Exposure test results, performed in environments with various amounts of chloride contents, revealed that the chloride ion either disturbs corrosion prevention by rust layers formed on steel surfaces, or speeds up the corrosion of metals. It is reported that the corrosion loss of weathering steel, mild steel, and low carbon steel is clearly correlated to the amount of airborne salt particles present. Protective rust layer cannot be formed in environments with high amounts of chloride, and corrosion loss increases with the amount of airborne salt particles [1], [3], [7], [8]. Allam *et al.*, [2] studied the atmospheric corrosion of steel in the Arabian Gulf, and the authors showed that chloride ions were more aggressive than sulphate ions during the initial atmospheric corrosion stage of steels. The effect of SO<sub>2</sub> on the corrosion behaviour of steel in an atmosphere containing Cl<sup>-</sup> is unclear, and the corrosion of steel in a coastal industrial atmosphere has not yet been systematically studied.

Understanding the role of climate conditions has attracted more attention and has therefore improved. Actually, chloride ion is a natural pollutant that effects corrosion; however, this role may change depending on the climate conditions [1], [9]. For instance, rainwater could change the rapidity of corrosion, due to the chloride ion on metal, Corvo *et al.*, [10] concentrated on the role of rainwater on the acceleration rate

caused by chloride ions, between two stations with remarkable differences in rain regimes. The first station was located in Havana, Cuba and the second station in Medellin, Colombia. Their findings showed that the acceleration rate caused by chloride ion on the atmospheric corrosion of steel and copper was based on the rain regime. However, the corrosion rates of these metals were higher in Havana than in Medellin. These differences were attributed to the rain regime; because the rain amount was over three times greater at Medellin; therefore a high washing and cleaning effect was present at Medellin.

The severity of atmospheric corrosive constituents can be evaluated by determining several factors, such as climate and pollution, or by measuring the corrosion rate of exposed metals [11]. Of these factors, the deposition rate of chloride (airborne salinity), which is one of the most corrosive agents, has an important role in atmospheric corrosion. However, there is a scarcity of deposition rate of chloride (DRC) data in the Klang Valley. Therefore, this study aims to evaluate the value of DRC in several locations within the study area, and hopefully classify this contaminant based on ISO 9223 [12]. The findings will also be used to classify atmospheric corrosivity with other factors, such as sulphur dioxide (SO<sub>2</sub>), time of wetness (TOW) and the corrosion rate of metals.

## 2. METHODOLOGY

### 2.1 Study Area

The Klang Valley is a basin located in the south-western part of the Malaysian Peninsular that is surrounded by highlands to the east and by the Straits of Malacca to the west [13], [14]. It consists of Kuala Lumpur, Putrajaya, and adjoining cities and towns in the State of Selangor, such as Petaling Jaya, Shah Alam, Klang, Gombak, Hulu Langat and Sepang, which had a population of around 3.98 million in the year of 2000 [15], and over four million in 2004 [16]. Due to its location, and because it is one of the most developed areas following rapid urbanization, population growth and industrial activities, it is constantly exposed to the problem of air quality [17], [18]. Five locations, Shah Alam, Cheras, UPM, Kajang, and Puchong, were selected as sampling points (as shown in Fig. 1).

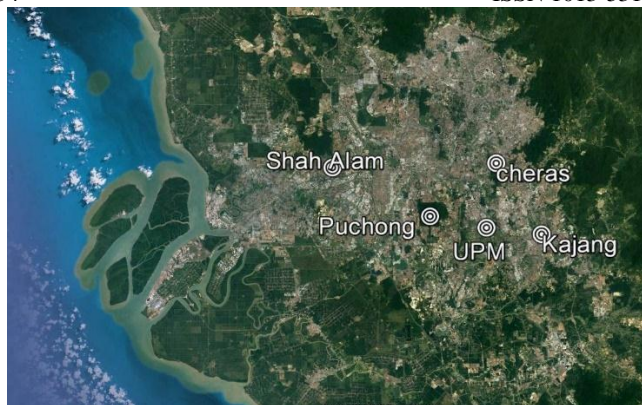


Fig. (1) the study area of the Klang Valley

**2.2 The Apparatus & Procedure**

DRC can be determined using several techniques. Wet candle is one of the most commonly used techniques that can be used in the study of the corrosivity of the atmosphere. According to ISO 9225-1992, “a rain protected wet textile surface, with a known area, is exposed during a specific time. The amount of chloride deposited is determined by chemical analysis. From the results of this analysis, the DRC is calculated and expressed as milligrams per square metre day [mg/(m<sup>2</sup>.d)].” The samples will be collected monthly from Sept 2014 to July 2015. The amount of chloride in the sample is determined by mercurimetric titration (as mentioned in ISO 9225 [19]).

**2.3 The classification of DRC**

The results obtained will be used to classify the severity of the atmosphere in accordance with ISO 9223 [20] (as shown in Table 1).

Table 1 Classification of deposition rate of chloride according to ISO 9223

DRC [mg/m <sup>2</sup> day]	Category
$S \leq 3$	$S_0$
$3 < S \leq 60$	$S_1$
$60 < S \leq 300$	$S_2$
$300 < S \leq 1500$	$S_3$

**3. RESULTS**

**3.1 DRC VALUES**

This experiment was conducted between September 2014 and July 2015. The results show that the mean DRC was  $27.44 \pm 11.24$  mg/m<sup>2</sup>.day, with minimum and maximum of 8.83 and 66.20 mg/m<sup>2</sup>.day, respectively. Fig. 2 shows a scheme of the mean monthly of DRC during the study period. It shows that the values of DRC are higher during the dry season and lower during the wet season.

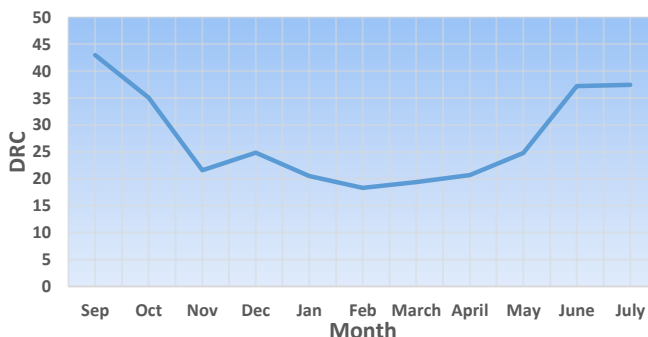


Figure 2. The mean monthly of DRC in the study area

Fig. 3 shows the frequency of the deposition rate of chloride (DRC). As shown, the histogram is slightly skewed to the left (or negatively skewed), and most frequencies are distributed between 20 and 40 mg/m<sup>2</sup>.day. Several values of DRC are atypical; which are greater than 60 mg/m<sup>2</sup>.day - and without these values, the histogram would be reasonably symmetrical. In addition, the analysis of variance (ANOVA) exhibits there are significant differences between mean of locations (sig. 0.000), in particular between Shah Alam and other locations.

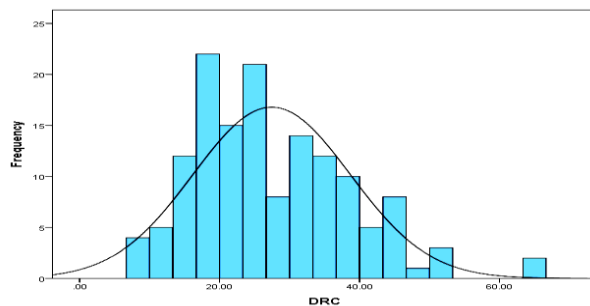


Figure 3. Frequency distribution of DRC in the Klang Valley, during the test period

The highest DRC was observed in Shah Alam with a mean of  $38.11 \pm 11.48$  mg/m<sup>2</sup>.day and the lowest value was 25.04 mg/m<sup>2</sup>.day. Meanwhile, the maximum value was 66.20 mg/m<sup>2</sup>.day. As this area is located adjacent to the marine area (about 20 km), it receives remarkable amounts of chloride which are derived from sea water; particularly during the dry season (as shown in Fig. 4). Fig. 5 reveals the scheme of mean monthly of DRC in Cheras, which is located in KL, had a lower value than Shah Alam, with a mean DRC of  $27.05 \pm 9.91$  mg/m<sup>2</sup>.day, a minimum of 14.10 mg/m<sup>2</sup>.day and a maximum of 44.58 mg/m<sup>2</sup>.day.

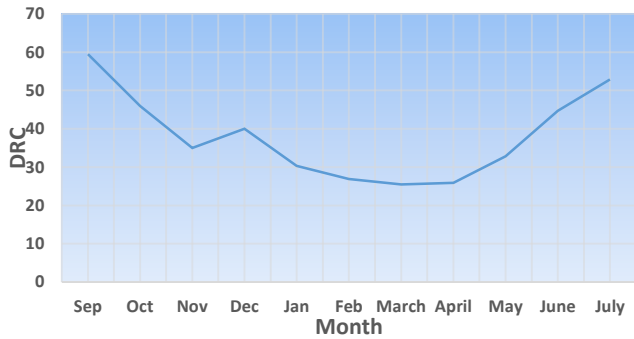


Figure 4. Mean monthly of DRC of Shah Alam

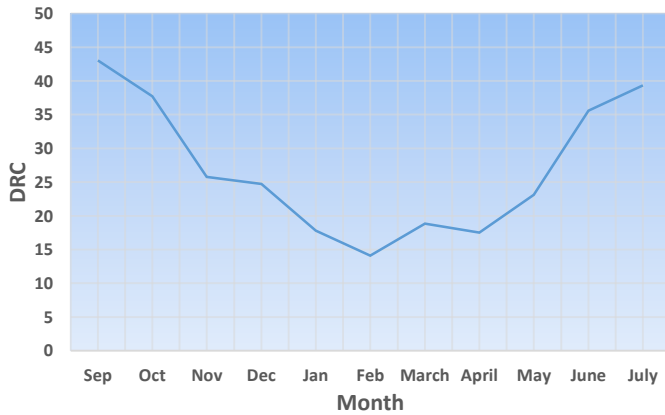


Figure 5. Mean monthly of DRC of Cheras

All other locations had similar shaped curves, but all values of chloride were lower than Shah Alam and Cheras; except Puchong, which showed a fluctuated curve, possibly due to its forest area location. The mean concentration reached  $24.14 \pm 7.08$  mg/m<sup>2</sup>.day (14.13-37.16 mg/m<sup>2</sup>.day) in Kajang (see Fig. 6). In UPM, the mean of DRC reached  $23.16 \pm 9.54$  mg/m<sup>2</sup>.day (8.83- 41.36 mg/m<sup>2</sup>.day) (see Fig. 7). The obtained findings demonstrate that Puchong had the lowest mean of  $18.49 \pm 6.78$  mg/m<sup>2</sup>.day, with minimum and maximum depositions of 9.39 and 30.02 mg/m<sup>2</sup>.day, respectively (as shown in Fig. 8).

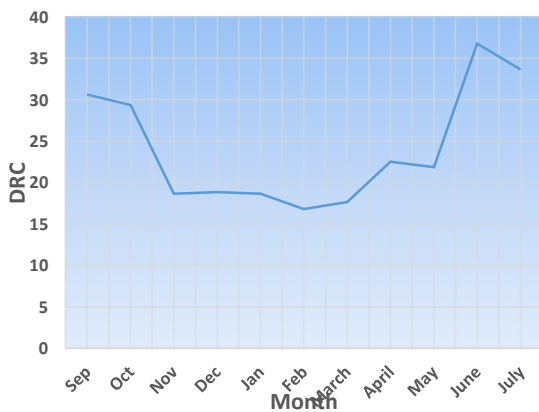


Figure 6. Mean monthly of DRC of Kajang



Figure 7. Mean monthly of DRC of UPM



Figure 8. Mean monthly of DRC of Puchong

### 3.2. CORROSIVITY OF DRC

From the obtained results, it is now possible to classify the corrosivity of the atmosphere in the study area. Table 2 illustrates the mean monthly of DRC in the study area. It can be observed that (based on ISO 9223) the mean monthly of chloride is grouped in the category S<sub>1</sub>. However, when looking at the minimum and maximum values, Shah Alam had the highest category, ranging between S<sub>1</sub> and S<sub>2</sub>, because it is located adjacent to the marine areas, approximately 20 km away, while all other locations fall in the category S<sub>1</sub> (see Table 3).

Table 2: Mean monthly of DRC (mg/m<sup>2</sup>.day) in the study area

Month	Location				
	Shah Alam	Cheras	Kajang	UPM	Puchong
Sep.	59.5	43.04	30.65	38.83	-
Oct.	45.93	37.72	29.37	32.27	20.25
Nov.	34.95	25.77	18.66	9.94	12.77
Dec.	40.02	24.72	18.84	14.13	30.02
Jan.	30.32	17.82	18.67	16.91	15.7
Feb.	26.92	14.12	16.82	14.81	20.18
Match	25.46	18.82	17.66	18.72	10.45
April	25.85	17.53	22.54	20.58	9.39

May	32.83	23.1	21.88	24.32	16.41
June	44.68	35.57	36.77	35.61	25.66
July	52.85	39.33	33.64	28.82	24.08

**Table 3. Classification based on the minimum and maximum values (mg/m<sup>2</sup>.day) of DRC**

Location	Min. – Max.	Category
Shah Alam	25.04-66.20	S <sub>1</sub> -S <sub>2</sub>
Cheras	14.10-44.58	S <sub>1</sub>
Kajang	14.13-37.16	S <sub>1</sub>
UPM	8.83-41.36	S <sub>1</sub>
Puchong	9.39-30.02	S <sub>1</sub>

#### 4. DISCUSSION

It can be observed that all curves were high in September and October but dropped in November, which is the beginning of the wet season, until April. After that, the curve rose again during the dry season. This circumstance occurred at all locations; except Puchong, which may have received amounts of chloride from other sources. The primary source of atmospheric chloride is from the ocean. The wind-induces whitecaps, which burst at the air-sea interface, thus injecting the seawater droplets into the atmosphere, forming sea salt aerosols [21]. Approximately 10% of the total chloride in sea salt aerosols moves inland, and the majority of these aerosols are deposited within 100 km of the coastal area [22], [23]. Consequently, the amounts and concentrations of chloride in deposition do not vary much in inland areas; whereas coastal areas show a great deal of variation [24]. Tiwari *et al.*, [25] reported that the main source of chloride is sea spray, which could be transported over long distances during monsoons. Besides, the obtained results prove that location is a significant factor that effects the concentration of chloride in the atmosphere. Shah Alam had the highest values compared with the other locations that were located further away from the coast. Regarding Puchong, it is located in a forest area, covered by many trees (see Fig. 1 & 8). It could be suggested that there are other sources of chloride emissions, such as coal-burning and municipal incinerators. Most coals have a chloride content between 0.09 and 0.15%. In high chlorine coals, values of 0.7% are found, and when burnt, most of the chlorine is emitted as a gas HCl [4]. In addition, anthropogenic sources may add a remarkable amount of chloride into the atmosphere in some extreme situations where serious air pollution occurs [26]. Thus, these results also demonstrated that the DRC depends on the wind pattern at each location; as cited in Syed, [27].

Regarding the corrosivity of DRC, from these results, it can be seen that Shah Alam had a higher corrosivity than the other locations. In this case, many metals and alloys that will be exposed to this atmosphere will be corroded significantly; especially in the presence of other factors, such as SO<sub>2</sub> and high values of TOW. The results conducted by Suzuki *et al.*, [28] on the island of Oahu, revealed that the mean of DCR was 38.92±56.37 mg/m<sup>2</sup>.day, with minimum and maximum values of 0 and 347.54 mg/m<sup>2</sup>.day, respectively. The corrosivity in this area differed greatly from S<sub>0</sub> to S<sub>3</sub>, because most of its locations received significant amounts of sea

particles from the Pacific Ocean. On the Korean peninsula, Kim *et al.*, [29] evaluated that the DRC values between 0.2 and 40 mg/m<sup>2</sup>.day, and it can be grouped between S<sub>0</sub> to S<sub>1</sub>. Syed, [27] found the DRC in Saudi Arabia ranged from 63 to 740 mg/m<sup>2</sup>.day (S<sub>2</sub>-S<sub>3</sub>). In Portugal, DRC categorized from S<sub>1</sub> to S<sub>2</sub> [30], in Havana, Cuba and Medellin, Columbia, S<sub>1</sub> – S<sub>2</sub> and S<sub>0</sub> - S<sub>1</sub>, respectively. [10] and the DRC grouped between S<sub>2</sub> and >S<sub>3</sub> in Camariñas, Spain [31].

Barton [32] stated that the mechanism that governs the effects of chloride ions in atmospheric corrosion had not been totally explained; and in marine atmospheres, the higher corrosion rate of metals, such as steel, could also be attributed to other causes. Firstly, the chloride species could act as a hygroscopic, and then promote the electrochemical corrosion reaction, preferring the creation of electrolytes at reasonably low relative humidity values. Secondly, the solubility of the corrosion products formed also plays an important role. Consequently, in the case of iron, which does not form stable basic chlorides, the action of chlorides is more obvious than with other metals whose basic salts are only slightly soluble. Since then, there has been great progress in the scientific knowledge of atmospheric corrosion in marine environments. Furthermore, the DRC may influence the pH at the corrosion sites, Kamimura *et al.*, [3] pointed out that pH was affected by chloride ion and pH values decreased to 1.5 at the anodic site and then accelerated the corrosion process. Furthermore, *akaganeite* (as a corrosion product) was formed by the hydrolysis of Fe<sup>3+</sup>-species under concentrated chloride solutions.

In a coastal atmosphere, chloride ion can penetrate the rust layer and directly attack the steel surface, which is the main anodic process; the cathodic corrosion process includes the reductions of dissolved oxygen and FeOOH (corrosion product) [33], [34]. In addition, the contribution of sea salt ions to precipitation can be determined by assuming that all Cl (or Na) and the proportionate amount of other major ions are derived from sea salts [35]–[37]. Corrosion products, which are varied from atmosphere to another, are commonly found in the atmospheric exposure of steel, namely *lepidocrocite* (γ-FeOOH) and *goethite* (α-FeOOH). However, in marine atmospheres, the formation of *akaganeite* (β-FeOOH) and *magnetite* (Fe<sub>3</sub>O<sub>4</sub>) is most significant [31]. Ma *et al.*, [1] proved that the effect of chloride ion on the atmospheric corrosion rate of carbon steel, as well as the morphology and composition of the rust layer. In sites with high levels of DRC, *akaganeite* is formed. Meanwhile, *goethite* and *lepidocrocite* are formed at sites with a low DRC. At the same time, Hara *et al.*, [8] mentioned that the protective rust layer cannot be formed in higher chloride environments, and the corrosion loss increases with an increase in the amount of airborne salt particles. In such environments, *akaganeite* is often detected in the rust layer that has formed on the steels' surface. The mass fraction of *akaganeite* in this layer correlates to the corrosion loss.

#### 5. CONCLUSION

To sum up, the study concentrated on the deposition rate of chloride (DCR) as one of the most important corrosive agents. Although the source of chloride may involve either

natural or anthropogenic sources, the ocean is a significant source. The five locations selected for study were Shah Alam, Cheras, UPM, Kajang and Puchong. The chloride deposition rate was determined using a wet candle method (in accordance with ISO 9223) by mercurimetric titration. As a consequence, the findings showed that the deposition rate of chloride had high values (the mean was  $27.44 \pm 11.24$  mg/m<sup>2</sup>.day); particularly in locations slightly adjacent to coastal areas, such as Shah Alam; and corrosivity categories between S<sub>1</sub> and S<sub>2</sub>. Meanwhile, the locations that were located far from the coastal areas revealed the lowest values of DRC, with corrosivity grouped in the S<sub>1</sub> category. Thus, all of the infrastructure metals that were exposed outside and without protection in Shah Alam corroded significantly more than in the other locations.

### ACKNOWLEDGEMENTS

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