



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: [www.elsevier.com/locate/corsci](http://www.elsevier.com/locate/corsci)

## Determination of the key parameters involved in the formation process of akaganeite in a laboratory-simulated wet-dry cyclic process

Haigang Xiao<sup>a,b</sup>, Wei Ye<sup>c</sup>, Xiaoping Song<sup>c</sup>, Yanmin Wang<sup>d</sup>, Yuantai Ma<sup>a</sup>, Ying Li<sup>a,\*</sup>

<sup>a</sup> Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Wencui Rd 62, Shenyang, 110016, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100049, China

<sup>c</sup> Analysis and Testing Department (Testing Center), Institute of Metal Research, Chinese Academy of Sciences, Wenhua Rd 72, Shenyang, 110016, China

<sup>d</sup> Tarim Oilfield Company, Petrochina, Korla, Xinjiang, 841000, China

### ARTICLE INFO

#### Keywords:

A. Carbon steel  
C. Rust  
C. Chloride  
B. IR spectroscopy  
B. X-ray diffraction

### ABSTRACT

To determine the key parameters of akaganeite formation during a wet-dry cyclic process, cyclic immersion tests and simulated experiments were employed under laboratory conditions. The constituents of rust were characterized using XRD and FTIR. According to the results, green rust ( $\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_{2-x}(\text{OH})_{12+x}$ ) was a crucial intermediate product during the formation of akaganeite. The evaporation rate of the electrolyte and the amount of  $\text{Cl}^-$  per area played a key role in the formation of the green rust. Additionally, the required amounts of salt for akaganeite formation were determined from simulation experiments in different relative humidity environments.

### 1. Introduction

Rust layers formed on steel by atmospheric corrosion strongly affect the subsequent steel corrosion behaviour. Normally, dense and electrochemically inert rust layers reduce the corrosion rate of the substrate; hence, the corrosion products are protective [1,2]. However, in marine atmospheres that are rich in chloride, the protective rust layer cannot form [3–6]. Akaganeite, which is the characteristic corrosion product formed on steel exposed to coastal environments [7–10], notably accelerates the corrosion rate and reduces the protective ability of rust layers [8,11–15]. Consequently, the corrosion rate under such conditions is pretty high [5,16–18]. Due to the essential influence of akaganeite on marine atmospheric corrosion, investigating its formation process and conditions is significant for interpreting and predicting the corrosion performance of steel in marine environments.

To understand the mechanism of the significant effect of akaganeite on corrosion behaviour, its chemical structure and electrochemical properties reported in previous studies are reviewed in the following discussion. The general chemical formula of akaganeite has been proposed as  $\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$  [19], and its structure is similar to that of hollandite, which is characterized by the presence of tunnels parallel to the c-axis of the tetragonal lattice [20]. These tunnels are partially occupied by chloride anions that give the crystal its structural stability [21,22]. As proposed by Evans [23], corrosion products as oxidants can be reduced and participate in further corrosion action.

Thus, the reduction ability of corrosion products has a great influence on the corrosion behaviour of steel. Lair et al. [24] tested the reduction ability of common atmospheric corrosion products, such as goethite, lepidocrocite and akaganeite, using electrochemical methods and noted that akaganeite has the most active reduction ability among them. Nishimura et al. [14] demonstrated that akaganeite was not only electrochemically active but also easily reduced to amorphous intermediate oxide during a wet cycle; this result suggested that akaganeite could accelerate corrosion as a cathode. Other causes for the destructive effect of akaganeite include its low density compared with other corrosion products, [25] causing its volume to be much higher than other corrosion products. Therefore, the transformation from other phases to akaganeite causes crack formation [26] and even exfoliation [4] in the rust layer.

Due to its important influence on marine atmospheric corrosion, substantial outdoor exposure experiments and accelerated experiments were conducted in the laboratory with a focus on the formation process of akaganeite. The formation process of akaganeite has usually been investigated by conducting accelerated experiments in the laboratory. Refait et al. [27–29] mixed aqueous solutions of  $\text{FeCl}_2$  and  $\text{NaOH}$  and then stirred the solution to generate akaganeite. During this process, green rust with the chemical formula  $[\text{Fe}_3^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_8]^+ [\text{Cl}\cdot n\text{H}_2\text{O}]^-$  formed as an intermediate product. Nishimura et al. [11] wetted the surface of steel using a 3% NaCl solution and aged the steel in a 25 °C and RH = 60% environment for 12 h. During this process, one wet-dry

\* Corresponding author.

E-mail address: [liyong@imr.ac.cn](mailto:liyong@imr.ac.cn) (Y. Li).

<http://dx.doi.org/10.1016/j.corsci.2017.09.010>

Received 12 December 2016; Received in revised form 8 September 2017; Accepted 9 September 2017  
0010-938X/© 2017 Elsevier Ltd. All rights reserved.

cycle involved wetting the sample surface and drying the surface at the end. In situ X-ray diffraction was used to investigate the continuous changes in the rust components during one wet-dry cycle. Nishimura et al. found that the akaganeite in the rust was consumed after wetting the surface, and after the solution evaporated, green rust with the chemical formula  $\text{Fe}(\text{OH}, \text{Cl})_{2.55}$  (JCPDS 400127) formed. Then, the green rust disappeared, and akaganeite formed again. Nishimura et al. suggested that green rust  $\text{Fe}(\text{OH}, \text{Cl})_{2.55}$  was the intermediate phase of the akaganeite formation process. Notably, green rusts are unstable Fe (II)-Fe(III) hydroxy-salts that are oxidized in the presence of oxygen [30], and the composition of green rust differs as the Fe(II)/Fe(III) ratio is varied under different conditions [27,31]. Although there appears to be unanimous agreement that green rust is the intermediate product during the akaganeite formation process, the specific chemical formula of green rust in this process is still open to discussion. Additionally, investigations on the formation conditions and important parameters of this intermediate product during wet-dry cycles are scarce; hence, such studies may provide essential information for the mechanism of akaganeite formation.

In addition to green rust, other corrosion products, such as lepidocrocite and magnetite, have also been mentioned in the formation process of akaganeite. Ohtsuka [32] monitored the change in the rust composition on weathering steel with NaCl deposits exposed to the atmosphere under cyclic 4 h and 10% RH – 4 h and 90% RH conditions using in situ Raman spectroscopy. The evolution of the rust composition from lepidocrocite and magnetite to akaganeite was observed under wet (RH = 90%) conditions after several wet-dry cycles. However, the roles of the initial corrosion products, lepidocrocite and magnetite, play during the formation process of akaganeite has not been elucidated.

The formation conditions of akaganeite have also been investigated by many researchers. Refait et al. [27] mixed aqueous solutions of  $\text{FeCl}_2$  and NaOH and then stirred the solution to simulate the formation process of akaganeite. Refait et al. found that when  $R' (R' = [\text{Cl}^-]/[\text{OH}^-]) \geq 8.0$  in the solution, the end product was akaganeite alone. Remazeilles et al. [33] mixed  $\text{FeSO}_4$ , NaCl and NaOH solutions to generate akaganeite and determined the conditions favouring the formation of akaganeite. The results indicated that large amounts of dissolved Fe(II) species and high chloride concentrations were both necessary for akaganeite formation. Ma et al. [12] studied the rust composition of low carbon steel exposed to a marine atmospheric environment with different amount of  $\text{Cl}^-$  deposition and found that high amounts of  $\text{Cl}^-$  deposition above the critical concentration were instrumental for the formation of akaganeite. Morcillo et al. [34] performed a study in a pure marine atmosphere with different annual average chloride deposition rates and summarized the published results of marine atmospheric corrosion field studies related to akaganeite. Finally, Morcillo et al. reported that the environmental conditions necessary for akaganeite formation are an annual average RH of approximately 80% or higher and, simultaneously, an annual average chloride deposition rate of approximately  $60 \text{ mg/m}^2/\text{d}$  or higher. These studies made great progress towards understanding the conditions akaganeite formation. However, atmospheric corrosion occurs in a thin layer of electrolyte that alternately grows and decreases [35]. In the previous study, the formation process and conditions were not combined with the wet-dry cycle, which is a key feature of atmospheric corrosion. In addition, the results in the outdoor exposure tests were cooperatively affected by a variety of parameters during the field exposure tests. Thus, it is complicated to describe the exact effect of a single parameter on the formation of akaganeite. The mechanisms of the influence of salt deposition and relative humidity on akaganeite formation have not been clarified yet.

Even though major progress has been made in understanding the formation mechanism of akaganeite, currently, unsolved problems still exist that scientists must solve. Regarding the wet-dry cycle, the formation and consumption stages for akaganeite have not been clarified, and its formation process cannot be stated clearly. The roles that

lepidocrocite and magnetite play in the formation process are unknown. Few studies have been performed regarding the formation conditions and influencing parameters of green rust during wet-dry cycles, and the conditions for akaganeite formation are still open to discussion.

Electrolytes can form on or arrive at steel surfaces by two modes: direct deposition and sorption [36]. Hence, these modes can affect the wet-dry cycle process. In the present work, we concentrate on the direct deposition mode and try to describe the formation process of akaganeite during one wet-dry cycle. To investigate the specific formation stage that occurs during the complete immersion (the thickness of the electrolyte layer  $\delta > 1 \text{ mm}$ ) or drying stage ( $\delta < 1 \text{ mm}$ ), cyclic immersion tests (including the complete immersion and drying stages) were performed to simulate the wet-dry cycles induced by direct deposition. Furthermore, simulated experiments were carried out to investigate the akaganeite formation process and determine the influential parameters for akaganeite formation. XRD and FTIR were employed to characterize the evolution of the constituents of the rust layer formed during this process. Finally, the formation conditions of akaganeite were proposed.

## 2. Experimental methods

### 2.1. Material

For this investigation, plain carbon steel specimens (Q235; Table 1) were cut into coupons with dimensions of  $10 \text{ mm} \times 15 \text{ mm} \times 5 \text{ mm}$ . The coupons were wet-polished down to 1000 grade emery paper, cleaned ultrasonically in acetone, rinsed with distilled water, dried and stored in a moisture-free desiccator prior to use. The NaCl solution was prepared using analytically pure sodium chloride and distilled water.

### 2.2. Characterization of the iron rust phases

XRD is the preferred method for characterising crystalline samples; however, weaknesses existed when identifying the iron rust phases using this technology. First, it is difficult for XRD to differentiate between closely related phases with similar crystal structures, such as  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  [37]. In addition, the top three diffraction peaks of the common atmospheric corrosion products that were used to identify the phases overlapped, as shown in Table 2. Amorphous products do not yield defined peaks but broad bands that are difficult to assign. Fourier transform infrared spectroscopy is by far the best identification technique for detecting solids and noncrystalline phases. The characteristic FTIR peaks of common atmospheric corrosion products are summarized in Table 3 [38,39]. However, other corrosion products have not been investigated and reported in detail. Hence, in this work, both XRD and FTIR were employed to identify the constituents of rust comprehensively.

For the FTIR tests, the rust powder was scraped off from the metallic substrate using a razor blade. Approximately 3 mg of rust was mixed with approximately 100 mg of pure anhydrous KBr and ground to a fine size in a mortar with a pestle. The mixture was pressed into a transparent circular flake that was approximately 1 mm thick. A Nicolet Corporation Model Magan-IR560 infrared spectrophotometer was used to determine the IR spectra of the rust powder in the ranges from  $400$  to  $4000 \text{ cm}^{-1}$ . The spectra were recorded with Omnic software at a resolution of  $4 \text{ cm}^{-1}$ , with 64 scans and a gain of 1. The XRD analysis was performed directly on the rusted steel plate. XRD measurements were

**Table 1**  
Chemical compositions of the carbon steel studied (wt.%).

Steel	C	S	P	Mn	Si	Cu
Q235	0.176	0.023	0.019	0.57	0.233	0.033

Download English Version:

<https://daneshyari.com/en/article/7894262>

Download Persian Version:

<https://daneshyari.com/article/7894262>

[Daneshyari.com](https://daneshyari.com)