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A COMPREHENSIVE EXPERIMENT OF CORROSION INHIBITION BY OVERDUE MEDICINES TO CARRY OUT THE ENVIRONMENTAL EDUCATION

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Abstract: The corrosion problems of metallic materials, especially steel materials, almost exist in all aspects of industrial production especially in oil field, resulting in huge economic losses. Common medicines contain amino, carboxyl and phenolic hydroxyl groups, which can coordinate with metal through the empty orbit and adsorbed on the metal surface. Based on the structural characteristics of commonly used medicines, the experiment of using the overdue commonly used medicines as a corrosion inhibitor was designed and the mechanism of corrosion inhibition was discussed. In this experiment, the corrosion inhibition effect of common medicines on steel in hydrochloric acid solution was evaluated by weight loss method. It helps students deepen the understanding of theoretical knowledge of metal corrosion and protection, and get the comprehensive training and analysis ability and innovative ability training of relevant experimental skills. At the same time, the medicine, as daily used resources, can be used as experimental materials, which can cultivate the concept of comprehensive utilization of students.

Key words: Environmental education; medicines; corrosion; corrosion inhibitor; comprehensive experiment; oil field chemistry

Introduction

Environmental education (EE) refers to organized efforts to teach how natural environments function, and particularly, how human beings can manage behavior and ecosystems to live sustainably[1-3]. It is a multi-disciplinary field integrating disciplines such as biology, chemistry, physics, ecology, earth science, atmospheric science, mathematics, and geography.

EE is the teaching of individuals, and communities, in transitioning to a society that is knowledgeable of the environment and its associated problems, aware of the solutions to these problems, and motivated to solve them[4]. The United Nations Educational, Scientific and Cultural Organization (UNESCO) states that EE is vital in imparting an inherent respect for nature amongst society and in enhancing public environmental awareness. UNESCO emphasizes the role of EE is safeguarding future global developments of societal quality of life, through the protection of the environment, eradication of poverty, minimization of inequalities and insurance of sustainable development[5].

The task of engineering higher education is to cultivate engineering, practical and innovative high-quality talents for social needs. In recent years, in order to adapt to the needs of teaching reform in colleges and universities under the new situation, a new experimental mode to cultivate students' scientific research and innovation ability has been one of the trends of experimental teaching reform[6]. The teaching and research section of this lesson combines scientific research results, and establishes a vertically and horizontally closely linked grid structure, applies scientific research results to experimental teaching. In fact, our "University" is a university major in oil field and petroleum. Oil field chemistry is a necessary professional course for petroleum related majors. Oil field chemistry requires students to combine theory with practice and cultivate students' abilities of comprehensive analysis, experimental operation, data processing, document retrieval, problem solving and collaboration [7].

The corrosion problems of metallic materials, especially steel materials, almost exist in all aspects of industrial production and life, resulting in huge economic losses. Especially in the process of oil field mining, it is necessary to inject acid solution in order to increase production and cause economic losses in all aspects (as shown in Figure 1).

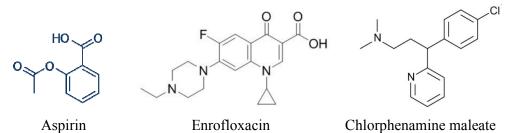


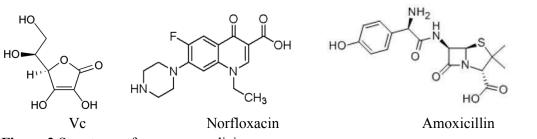


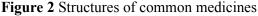
Figure 1 The corrosion in oil field

In order to reduce the corrosion of acid solution to metal pipeline and equipment, control acid rock reaction rate, improve acidizing effect, place bottom pollution and reduce construction cost, corrosion inhibitor must be added. Acidification inhibitor is the main content of the students majoring in chemical direction applied chemistry in oil field. Organic compounds as corrosion inhibitors for mild steel have assumed great significance due to their application in preventing corrosion under various aggressive conditions [8]. Many organic compounds containing suitable atoms, for example P, S, N or O, can be widely used as corrosion inhibitors [9]. However, the cationic organic inhibitors (such as quaternary ammonium salt) in the presence of the chloride ions show synergistic effect in the corrosion inhibition [10,11]. The available data show that most organic inhibitors are physisorption on the metal surface [12], while in the presence of non-bonded and *p*-electrons, the inhibitor molecules may undergo chemisorption [13].

On this basis, combined with the characteristics of the undergraduate students of oilfield chemistry, the common medicines in life can be selected as corrosion inhibitors. Common medicines, such as Vc, aspirin, amoxicillin, norfloxacin, enrofloxacin, chlorphenamine maleate, paracetamol (as shown in Figure 2), contain amino, carboxyl and phenolic hydroxyl groups, which can coordinate with metal through the empty orbit and adsorbed on the metal surface. The absorbed molecules on the metal can inhibit the corrosion in a corrosive environment, as the hydrophobic groups of the compounds formed in the metal surface protective film thus. This experiment combined with life closely, which makes students to understand the application and practicality of chemical knowledge from the updated perspective. The students have gained a lot from the participation of the experiment, the arrangement of the data, the objective analysis, and the divergence of the thinking and so on [14].







It is well known that organic inhibitors establish inhibition by adsorption onto the metal surface, and the adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption, that are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte.

The presence of N, O, S atoms and conjugated double bonds in the organic structures makes the formation of p–d bonds resulting from overlap of *p*-electrons to the 3d vacant orbital of iron atoms, which enhances the adsorption of the inhibitors on the metal surface. Generally, organic inhibitors may be absorbed on the metal surface in one or more of the following ways^[10-12]:

- (a) electrostatic interaction between the charged molecules and the charged metal;
- (b) interaction of unshared electron pairs in the molecules with the metal;
- (c) interaction of p-electrons with the metal;
- (d) a combination of the above types.

But owing to the complex nature of adsorption and inhibition of a given inhibitor, it is impossible for single adsorption mode between inhibitor and metal surface. The steady conformation of enrofloxacin was shown in **Figure 3** (left), which were simulated by a minimize energy of MM2 in Chem 3D, and the *p*-electrons of the hydroxyl groups and ether groups were colored in pink. The possible reaction centers are unshared electron pair of heteroatoms and/or *p*-electrons of aromatic ring. The schematic illustration of different modes of adsorption on metal was shown in **Figure 3** (right).

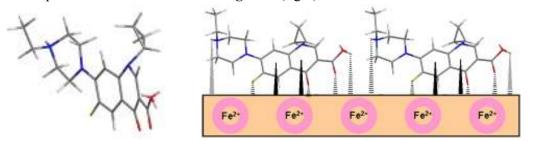


Figure 3 The absorption of enrofloxacin on the steel surface by coordination

Design of the experiment

Purpose

(1) Master a method of measuring the corrosion rate of steel sheet (static steel weight loss method).

(2) Understand the corrosion inhibition mechanism of corrosion inhibitors.

(3) Understand the effective components of the commonly used detergents.

(4) Learn the evaluation of the inhibition of different inhibitors and analysis the reasons for the change of related parameters through the data processing, analysis and calculation of

related parameters.

Principle

The corrosion of steel sheet in acid medium is electrochemical corrosion. In the case of hydrochloric acid, the corrosion reaction of steel sheets is:

Anodic reaction: Fe \rightarrow Fe²⁺ + 2e

Cathodic reaction: $2HCl + 2e \rightarrow H_2 \uparrow + 2Cl^-$

Cell reaction: Fe + 2HCl \rightarrow FeCl₂ + H₂ \uparrow

In order to reduce the corrosion of the acid medium to the metal, the commonly used method is to add corrosion inhibitor in the acid medium. According to the mechanism of action, the acid medium corrosion inhibitor can be divided into two types: adsorption membrane type (such as formaldehyde) and "intermediate phase" type (such as butylynol). Commonly used medicines contain amino groups, carboxyl groups, phenolic hydroxyl and other functional groups, which can be adsorbed on the metal surface through coordination action to form protective films, and play a protective role in the corrosive environment. The most commonly used method of determining the corrosion rate is weight loss. It can quantitatively evaluate the inhibition effect of corrosion inhibitors, and calculate the corrosion rate by determining the mass loss of steel sheets in the medium without or adding inhibitors.

Materials

The overdue medicines (corrosion inhibitors), such as aspirin, amoxicillin, norfloxacin, enrofloxacin and paracetamol, were purchased from the market and used without further purification. The tested material is A_3 steel plates with the chemical composition of (wt pct) containing 0.02 C, 0.0017 Si, 0.237 Mn, 0.015 P, 0.0016 S, 0.008 Cu, 0.014 Cr, 0.013 Ni, 0.001 Mo, 0.01 Al and Fe balance. The corrosive medium for the study was hydrochloric acid solution of concentrations of 5%. It was prepared from analytical grade 38% HCl and double-distilled water. In each experiment, 250 mL acid solution was used and all corrosion experiments were performed under normal atmospheric pressure.

Methods

Gravimetric measurements are carried out in a glass bottle. Each test was done with two specimens at the same time to guarantee the reliability of the results.

(1) Prior to all measurements, the exposed area of the steel discs was mechanically ground with different grades of silicon carbide abrasive papers (grade 360-600-1200) to get bright mirror finish followed by rinsed with a large amount of water.

(2) Then the plates transferred to petroleum ether and immersed with absolute ethyl alcohol to degrease. And then they were dried by hair drier before their immersion in experimental solution.

(3) Inhibitor efficiency was determined by hanging 2 pieces of the steel coupons into 250 mL 5% HCl with and without the addition of different concentrations (from 100 to 2000 ppm) of the synthesized inhibitors.

(4) After 2 h of immersion, the coupons were removed, scrubbed with bristle brush under running water in order to remove the corrosion product, washed with acetone, degreased by ethanol, dried and reweighed.

(5) Then the tests were repeated with different concentrations of inhibitors at varying

temperatures ($30\sim60^{\circ}$ C). From the initial and final weights of the specimens, the loss of weights was calculated, and the corrosion rate of N80 steel was determined using the relation:

$$V_i = (10^6 \Delta m) / (A_i \bullet \Delta t) \tag{1}$$

Where V_i is the corrosion rate of a single specimen, Δt is reaction time, Δm is the mass loss of specimens corrosion and A_i is specimen surface area.

The percentage inhibition efficiency (IE (%)) was calculated using the relationship below:

$$IE(\%) = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}}\right) \times 100$$
(2)

Where W_{corr} and $W_{corr(inh)}$ are the corrosion rates of mild steel in the absence and presence of inhibitors, respectively.

Attention

The concentrated hydrochloric acid used in the experiment is strong corrosiveness, and the laboratory should be equipped with emergency treatment agents and flushing nozzles. Before the experiment, the safety problems should be emphasized for the students. When suing hydrochloric, we should take protective measures compulsorily. We should monitor any accidents at any time during the operation. After experiment, the waste liquid should be poured into the designated waste liquid barrel, and a special person should be treated harmlessly, and no water should be poured into the sink and the sewer.

Questions and exercises

(1) What are the main causes of corrosion in daily life, and what are the reasons for them? What are the common means of corrosion inhibition and what is the mechanism of the action?

(2) Compare the inhibition effect of several kinds of medicines as corrosion inhibitors, and try to explain the reasons.

(3) Discuss the effective corrosion inhibition components in different medicines and the mechanism of corrosion inhibition.

(4) What are the cautions for using hydrochloric acid? How should the accident be dealt with? How to treat the waste liquid for innocuity after the experiment?

Conclusions

The design of this experiment applies the knowledge of organic chemistry and oil field chemistry to evaluate the corrosion inhibition effect of the medicine in the acid solution. In the experiment, using common medicines as organic corrosion inhibitor can practice the corrosion rate of steel sheet measuring static coupon weight loss method, let the students grasp the basic operation of the corrosion experiment, especially the practice the using of vernier caliper, the subsequent processing of experimental data. This experiment can improve the ability of the students' experiment operation ability, and improve the students' awareness of environmental protection. This experiment is carried out in groups, which is helpful to improve the students' cooperation ability and team spirit.

Compliance with Ethical Standards

This article does not contain any studies with human participants or animals performed by

any of the authors.

Ethical Approval All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee.

Informed Consent Informed consent was obtained from all individual participants included in the study.

Conflict of Interest The authors declare that they have no conflict of interest.

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