Minimizing the creation of spent pickling liquors in a pickling process with high-concentration hydrochloric acid solutions: Mechanism and evaluation method

Bing Tang[*], Wen Su, Jing Wang, Fenglian Fu, Guojun Yu, Jianyin Zhang

Faculty of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

ABSTRACT

The purpose of this investigation is to propose a strategy for minimizing the creation of spent pickling liquors through the synergistic corrosion inhibition of OP-10 and potassium iodide, thus facilitating a cleaner production process for acid pickling of metals with a high-concentration solution (6.0 mol/l) of hydrochloric acid. Results obtained with the methods of weight loss and electrochemical polarization showed that adding KI and OP-10 could enhance the energy barrier of the corrosion reaction and improved the corrosion inhibition for mild steel in high concentration of HCl solutions. A synergistic effect was identified when KI and OP-10 were present in suitable proportions. The results of the electrochemical experiments and scanning electron microscope (SEM) observations showed that the complex inhibitor was a mixed-type inhibitor and it formed a compact film on the metal surface, thus providing an effective protection for the metal in the aggressive solutions, which significantly minimized the creation of spent pickling liquors. A simple and convenient method was also proposed for the quantificational evaluation of the inhibition degree in the creation of spent pickling liquors.
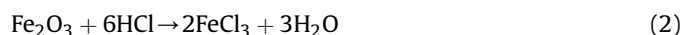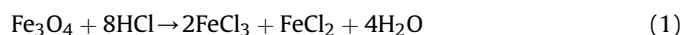
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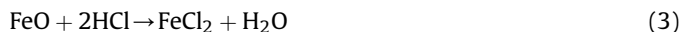
1. Introduction

Steel and iron often become rusty during the processes of transportation, rolling, and storage. Therefore, acid pickling is a necessary pre-treatment step prior to surface treatment to remove the rust and produce a clean surface. In industrial acid pickling, solutions of strong acids, such as sulfuric, nitric, hydrochloric, and phosphoric acids, are often used for derusting. Although strong corrosive acid solutions efficiently remove rust from metal surfaces, they also result in undesirable dissolution of the base metal, which consumes additional acid solution and wastes some of the metal. As a result, excessive spent pickling liquors are produced inevitably. Because of the corrosive nature and presence of residual acid as well as high metal content, spent pickling liquors are considered as hazardous wastes and designated as K062 in the Environmental Protection Agency (EPA) hazardous waste list of the USA. In the past decade, some processes on the regeneration of spent pickling liquors including acid and metal recovery have been reported (Agrawal and Sahu, 2009; Regel-Rosocka, 2010). These processes significantly reduced the volume

of wastes to be discharged to the environment and generated several useful products. However, implementing a recovery process near a surface treatment workplace or for centralized treatment not only means huge investment or environment risk during transportation, it needs skillful operators as well, and sometimes, the generated products such as iron salts and iron oxides may be subjected to market restrictions (Tang et al., 2009). Hence, minimizing the creation of spent pickling liquors in an acid pickling process should be the utmost priority both for environmental and economic concerns.

Hydrochloric acid (HCl) is a commonly used acid in the surface treatment of metal products. Compared with sulfuric acid, use of HCl allows faster cleaning rate at normal temperatures and with lower dosages. Compared with nitric acid and phosphoric acid, it is environmentally safer since it does not release effluents containing N and P. In recent years, sulfuric acid has been replaced by HCl in pickling liquors. However, HCl pickling has drawbacks such as the irritant acid fog and strong corrosion of the base metals. In an industrial pickling process with HCl solutions, the chemical reactions on the metal surface can be expressed by the following equations:

$$Fe_3O_4 + 8HCl \rightarrow 2FeCl_3 + FeCl_2 + 4H_2O \quad (1)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (2)$$

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O \tag{3}$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \uparrow \tag{4}$$

The reactions expressed by Eqs. (1)–(3) are useful in cleaning up rust, while Eq. (4) illustrates the phenomenon of over corrosion, which is the main reason for wastage of metal materials and acid media, likewise, it is the cause of excessive production of spent pickling liquors. Among the methods available for controlling over corrosion, the addition of a corrosion inhibitor in the acidic media is the cheapest and most convenient. A number of investigations on acid corrosion inhibitors have been reported (Chambers et al., 2005; Emranuzzaman et al., 2004; Kanojia and Singh, 2005; Oguzie, 2006; Solmaz et al., 2008), and some of the results have shown potential for practical application in the fields of acid pickling (Jabeera et al., 2006; Li et al., 2006) and oil well acidizing (Jeyaprabha et al., 2005). Undoubtedly, corrosion inhibitors not only reduce the wasteful consumption of acid solution, but also decrease the creation of spent pickling liquors, thus delivering pronounced economic and environmental benefits. According to the literature (Feng et al., 1999), organic compounds contained S, N, P, and O elements in their molecular structures were effective inhibitors. As a traditionally heavy polluting process, the pre-treatment step with acid pickling has been contending with an increasing number of strict environmental limitations. Therefore, considerable interest has been focused on environmentally friendly corrosion inhibitors that can operate with higher efficiency.

Synergistic inhibition is a special phenomenon that increases inhibition efficiency when two or more inhibitors are used together. Several compounds have been reported to have exhibited some extent of synergistic effect in an acidic medium (Eddy et al., 2009; Li et al., 2008; Wu et al., 2009). Such results indicate that the synergistic effect not only increases inhibition efficiency at less cost, but also provides more opportunities for choosing appropriate and environmentally safer inhibitors. Halide ions with surfactants have recently been shown as capable of obvious synergistic effect on the corrosion of metals in different acidic solutions (Amin et al., 2009; Bouklah et al., 2006; Eddy et al., 2009; Merah et al., 2008; Umoren and Ebenso, 2007; Wu et al., 2009). The important role of halide ions in maintaining the stability of surfactants on the metal surface has been confirmed and their inhibiting effects in acidic solutions have been shown to decrease in the order of $I^- > Br^- > Cl^-$ (Umoren et al., 2010).

Researchers have reported synergistic inhibition in HCl solutions at a low concentration (approximately 1.0 mol/l) (Mu et al., 2004; Obot et al., 2009). However, there is minimal information available on synergistic inhibition at high concentrations of HCl. Relevant information is important because in the practical process of industrial acid pickling, the concentration of HCl solutions is generally within 18–22 (wt.) % (Fresner et al., 2007), corresponding to approximately 6.0 mol/l in molar concentration.

To our knowledge, available reports related to the pollution abatement of spent pickling liquors mainly adopted a recovery approach. The present investigation focused on a strategy to minimize the creation of spent pickling liquors in a pickling process with high-concentration HCl solutions by the synergistic inhibition effect of OP-10 and potassium iodide (KI), so, two main aspects were considered: 1) investigation of the synergistic effects of OP-10 with KI in the inhibition of over-corrosion for mild steel in 6.0 mol/l HCl solutions using physical–chemical calculations, electrochemical measurements, and scanning electron microscopy (SEM) observations; and 2) proposal of a simple and convenient method to evaluate the degree of minimizing the creation of spent pickling liquors.

2. Materials and methods

2.1. Materials and reagents

The mild steel samples were purchased from Wuxi Xineng Metal Products Co. Ltd. (China), with the following compositions (wt. %): C (0.14–0.22%), Mn (0.3–0.65%), Si ($\leq$0.3%), S ($\leq$0.05%), and P ($\leq$0.045%), with the remainder corresponding to Fe. The corrosive solutions were dilutions of A.R. grade HCl from Guangzhou Dong-hong Chemical Reagent Factory (China) with distilled water. In order to replicate the concentration of industrial pickling liquors (18–22 (wt.) % HCl), the concentration of the acidic solutions were all set at 6.0 mol/l. A. R. grade KI was purchased from Shanghai Runjie Chemical Reagent Co. Ltd., (China). All other reagents were of C.P. grade.

2.2. Apparatus

An electronic analytical balance (FA2004B), purchased from Shanghai Precision & Scientific Instrument Co. Ltd. (China), was used to weigh the samples. All the electrochemical measurements were performed using a CHI601B instrument (Shanghai Operation Instrument Co. Ltd., China). A SEM (S-2400, Hitachi, Japan) was used to observe the surface of the samples after immersion in the HCl solutions in the absence and presence of inhibitors.

2.3. Gravimetric measurements

Prior to each run of experiments, samples of mild steel with dimensions of 40 mm × 13 mm × 2 mm were abraded with a series of emery papers from #200 to #1200 and subsequently washed three times with distilled water, degreased with acetone, and dried with a stream of air. After accurate weighing, the samples were immersed in 250 mL beakers containing 200 mL HCl solutions with and without inhibitors at different temperatures (20–50 ± 0.5 °C). After 2 h, the samples were taken out immediately, washed with distilled water and acetone, dried, and accurately weighed again. Each experiment was repeated three times with the same procedure, and the average value was regarded as the experimental datum. The corrosion rate was calculated using the following equation:

$$v = \frac{(m_1 - m_2)}{(S \cdot t)} \tag{5}$$

where m_1 and m_2 are the masses of the sample before and after immersion in the corrosive solutions, respectively; S is the total area of the sample; t is the immersion time; and v is the corrosion rate.

With the calculated corrosion rate, the inhibition efficiency was derived using the following equation:

$$IE(\%) = 100 \times \frac{(v_0 - v)}{v_0} \tag{6}$$

where v_0 and v are the corrosion rates of the sample in corrosion solutions in the absence and presence of inhibitors, respectively.

2.4. Polarization measurements

Electrochemical measurements were conducted in a conventional three-electrode cell assembly. The sample, embedded in a PVC holder with an epoxy resin seal and with an exposed area of 1 cm^2 (0.155 in^2), operated as the working electrode. The auxiliary electrode was a platinum foil, and a saturated calomel electrode (SCE) was designated as a reference electrode with a Luggin capillary, the tip of which was located between the working electrode and the auxiliary electrode.