



A novel hydrogen peroxide stabilizer in descaling process of metal surface

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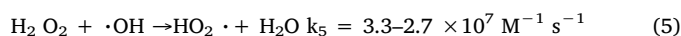
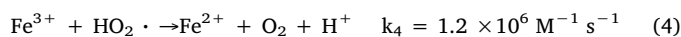
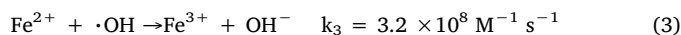
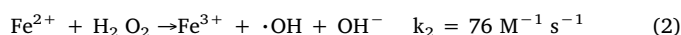
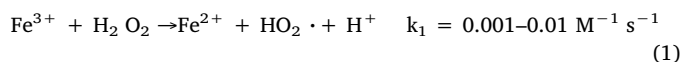
ABSTRACT

A recently developed descaling process for metal surface, which utilizes sulphuric, hydrofluoric acid and hydrogen peroxide (H₂O₂), has attracted great attention in consideration of eco-friendly sustainable process development. However, the intrinsic presence of metal ions, especially Fe(III), dramatically accelerates H₂O₂ decomposition, resulting in undesirable economic losses and even paralysis of operation. In this study, the stability of H₂O₂ in aqueous descaling acid was assessed by varying the ferric content from 0 to 30 g/L and the temperature from 32 to 45 °C. The results showed that any minor fluctuation in either factors causes a big attenuation in the life span of H₂O₂, necessitating the addition of a stabilizer. Thereby, a comprehensive screening test for potential stabilizers was carried out for an attempt to decelerate the H₂O₂ decomposition. Among all prospects, 2-anilinoethanol (AE, 100 mg/L) showed the most prominent stabilizing potential by successfully extending the half-life of peroxide by a factor of 2.66 compared to a controlled condition. The feasibility of AE as a stabilizer was further explored by elucidating its fate with GC-MS and IC analyses. A series of aromatics and short-chain organic acids was identified as the reaction intermediates. Aniline, with great H₂O₂ stabilizing capacity, was a predominant byproduct, which could help explain the superb positive effect of AE.

1. Introduction

Certain high-temperature processes in the steel manufacturing industry, including hot-rolling and annealing, can result in the formation of thinner or thicker metal depleted layers on the surface of products. Considering of the clean, uniform, and corrosion-resistant material surface, a technique named pickling which utilizes an inorganic acid mixture, is performed to achieve the polished and glossy finish [1]. In particular, nitric (HNO₃)-hydrofluoric (HF) mixed acid is most widely used in the traditional industrial descaling lines [2,3]. However, the emission of toxic nitrous fumes and nitrate effluents has caused extremely severe environmental problems, marking this method as one of the most hazardous processes to the environment [4,5]. Hence, a nitrate-free descaling procedure based on a combination of sulphuric acid (H₂SO₄) – hydrofluoric acid (HF) - hydrogen peroxide (H₂O₂) has been developed as sustainable technology development viewpoint [4,6,7]. The ability of H₂O₂ to exothermally decompose into water and oxygen (H₂O₂ → H₂O + 1/2O₂) has labeled itself as an appealing clean oxidant. The newly designed procedure using H₂O₂ serves as an important step forward in environmental-friendly technology, and its expansive application potential is anticipated to attract further attention.

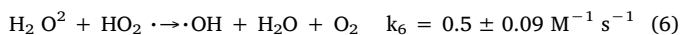
H₂O₂ is fed into an acidic bath to maintain the active oxides staying in the dissolved state by controlling its redox potential. Such effect is not only desirable but also necessary for efficient descaling [7]. However, its stability can be negatively influenced by a number of variables including temperature, pH, light, and the existence of chemical impurities [8–10]. The decomposition proceeds slowly in the absence of a catalyst, but any impurities, especially multivalent metal ions, will accelerate the reaction rapidly. Metallic iron is one of the most active catalysts dissociating H₂O₂ via the Fenton reaction (Fe²⁺/H₂O₂) or the Fenton-like reaction (Fe³⁺/H₂O₂). According to Haber and Weiss [11], ·OH and HO₂· are involved in the iron-mediated chain reactions [12–14]:



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Judging from above equations, both Fe(II) and Fe(III) iron species and radical intermediates are highly responsible for H_2O_2 consumption.

The fact that Fe(III) is ubiquitous in descaling acid bath has caused great concerns regarding H_2O_2 stability, threatening the universal acceptance of the related application. Accordingly, it is necessary to guarantee the existence of adequate amount of H_2O_2 by offsetting the unavoidable decay. Recent studies have demonstrated that certain metal-iron sequestrates, owing to their ability to remove or inactivate catalysts, can be effectively used for H_2O_2 stabilization strategy [15,16]. For instance, a stabilizing effect by certain ligands would occur if the rates of some or all of involved reactions (1), (2), and (4) are slowed down significantly. Phosphates, porphyrins, fluorides, and various other substances are categorized in this group [17]. Aside from ferric ions, the rapid yield of specifically reactive oxygen species also leads to great H_2O_2 loss. On this note, an effective radical scavenger is required to capture those troublesome intermediates and convert them into relatively unreactive species; this would help preventing the occurrence of reactions (5) and (6) [15]. Owing to the radical's inherently non-selective properties, plentiful organic molecules have been reported to undergo radical-induced transformation [18,19]. For the molecules possessing faster reaction rates, their stabilizing potential can be anticipated.

There has not been a legitimate candidate for H_2O_2 stabilizers since the stabilizing effect seems to be dependent on the solution nature including solution pH, temperature, presence of a catalyst, etc. Jung et al. [20] pointed out that the stabilizing effect of phthalic acid was quite substantial when $\text{pH} < \text{pK}_{a1}$, while it was negligible at pH above pK_{a2} . To gratify the demand for an ideal stabilizer that is suitable for practical use in industries, this study aims to explore H_2O_2 decomposition behavior and develop a reliable H_2O_2 stabilizer for the environmental-friendly descaling process. There were several stabilizers have been used to be applied in related process, such as quinones, diols, pyrophosphates, various aromatic compounds and amino carboxylic acid salts. However, many of suggested compounds have problems and challenges such as environmental issue and poor performance. [34–36] Previously suggested 49 chemicals were screened to evaluate their stabilizing or catalysing capacities regarding the H_2O_2 dissociation. Comparing to other previously reported stabilizers the 2-anilinoethanol was found to show the best performance in stabilization of H_2O_2 in acidic solutions, and its mechanism was completely studied in this study. The broad practicability of AE as a novel H_2O_2 stabilizer was further investigated by examining the temperature and Fe(III) concentration influences. Moreover, the intermediates from AE oxidation were identified by mass spectrometry and ion chromatography to suggest its proper oxidation pathway and stabilizing mechanism.

2. Experimental

2.1. Experimental setup

Experimental setup was shown in Fig. 1. Screening tests were performed in 250 mL amber colored glass bottles in an isothermal bath. The commercially available 35% H_2O_2 solution was added to the bottle with 200 mL descaling acid ($[\text{H}_2\text{SO}_4] = 120 \text{ g/L}$; $[\text{HF}] = 30 \text{ g/L}$; $[\text{Fe}^{3+}] = 30 \text{ g/L}$) to initiate reactions at its initial concentration of 10 g/L. The bottle was immediately capped with a rubber plunger to prevent gas leakage. By connecting reaction vessel to a cylinder tank filled with water, any emitted gas was allowed to vent and trapped inside the cylinder, while water was pushed out. Using a computer, real-time water level was monitored and recorded in increments of one minute. Under each experimental condition, H_2O_2 loss was proportional to the volume of oxygen gas liberated. H_2O_2 loss was relative amount, which is calculated as the ratio between the consumed amount and the monitored level. The ratio was obtained using the following equation

(Eq. (1))

$$R = \frac{H - H_f}{H_i - H_f} \times 100 \quad (1)$$

where R was relative value of H_2O_2 in the reactor, H_i is the initial water level, H_f is water level when the reaction finished, and H is the present water level monitored on the display.

2.2. Screening for potential H_2O_2 stabilizer

In the present study, 49 chemicals including ferric-chelators and radical scavengers were tested, and furthermore their influence on H_2O_2 stability in the environmentally-benign descaling acid solution was examined. The selected chemicals were added in the acid solution to achieve the same initial concentration of 100 mg/L before adding H_2O_2 . The rates of H_2O_2 decomposition were then compared to that in the parallel system without any additives. The effectiveness of the most prominent stabilizer, AE, was further analyzed at different temperature (28–45 °C) and ferric content (0–30 g/L).

2.3. Analytical methods

To determine dynamic change of AE, 1 ml aliquot was withdrawn at selected time intervals and added into 1 ml methanol to quench Fenton-like reaction instantly, followed by chromatographic analysis using a HPLC (Agilent 1100) equipped with a Luna C-18(2) column (150 × 4.6 mm, 5 μm, Phenomenex) and a diode-array detector (210 nm). Mobile phase composition consisted of methanol and water (6:4 v/v). The more exact H_2O_2 content was measured using a modified peroxytitanic acid colorimetric procedure by UV-visible spectrophotometer at 400 nm [21] to figure out the pathway of AE oxidation.

To identify the oxidation products of AE, aqueous samples were extracted twice with equal volume of ethyl acetate, followed by dehydrating with anhydrous sodium sulfate. The extract was then analyzed by gas chromatography mass spectrometry by a trace GC 2000 system coupled with Polaris Q Iontrap Mass Spectrometer (Thermo Quest, Jan Jose, CA) equipped with DB-5 column (30 m length × 0.25 mm, 0.5 μm film thickness, Agilent, USA). The initial oven temperature of 50 °C was maintained for 2 min, before being ramping up to 200 °C at a rate of 5 °C/min, which was held for 2 min, and subsequently to 250 °C at 25 °C/min. The injector was operated in a splitless mode. The injection port, transfer line, and ion source temperature were set at 250, 250, and 200 °C, respectively. The detector was operated in electron ionization mode (70 eV) using segment scan with a mass range of m/z 50–250. About 1 μL sample was injected at each time.

The possible intermediate ions of AE were quantified using an ion chromatograph (IC, Dionex DX-120) equipped with Dionex IonPac AS-14 column and a conductivity detector. The eluent composition was 3.5 mM Na_2CO_3 + 1 mM NaHCO_3 at a flow rate of 1.2 mL/min.

3. Results and discussion

3.1. Screening test for potential H_2O_2 stabilizer

The relative activity of all the selected chemicals towards H_2O_2 decomposition in descaling acid solution was summarized in Table 1. Note that $\cdot\text{OH}$ has often been cited as the main functional species in Fenton chemistry, and it is quite reactive and capable to react readily with many substances [18]. However, not all compounds which can be attacked are good H_2O_2 stabilizers. In this study, a fairly small number of tested reagents were found to prolong the life span of H_2O_2 , while 18 tested reagents exhibited minimal or no influence on the reaction.

It is worthwhile to discuss the major behavior of $\cdot\text{OH}$ which has been a popular research topic during the recent years. The $\cdot\text{OH}$ -induced transformation primarily proceeds through three types of reactions: (i)

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