IMPACT OF ORGANIC ACID ADDITION ON THE FORMATION OF PRECIPITATED IRON COMPOUNDS

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Abstract

In this work, acetic and citric acids were used along with ammonium chloride in the removal of iron from reduced Hatinh ilmenite. Iron removal was carried out at 70ºC, 4 liter/min of air flow rate, 7/1 of liquid/solid ratio and 0.5% NH_4Cl as catalyst. After 9 hours, metallic iron was decreased from 30.3% in reduced ilmenite to 0.5% in synthetic rutile. The addition of 0.4% acetic acid into NH_4Cl solution reduces removal time to 5 hours, residual metallic iron (RMI) was also 0.5%. The addition of 0.4% citric acid also reduces removal time to 5 hours, RMI was reduced to 0.33%. The rusting rate of metallic iron increased when acid concentration increased from 0.1 to 1%. The results indicated that acetic and citric acids could be used as additional catalysts along with NH_4Cl in the removal of metallic iron in reduced ilmenite. The acid have the capability to form complexes with iron and also showed impact on the formation of precipitated iron compounds.

Keywords: iron compounds, metallic iron, acid addition, ilmenite

1 Introduction

Aeration is one of the major stages in the Becher process for ilmenite processing. The stage involves rusting and transport of metallic iron away from reduced ilmenite using aerated ammonium chloride solution [1, 2]. The mechanism of iron rusting can be considered as an accelerated electrochemical corrosion in which metallic iron was corroded by dissolved oxygen followed by oxidizing ferrous to ferric. These compounds are subsequent hydrolysis and precipitation as hydrous iron oxides [3-10]. The precipitated iron compounds were separated from the solution yielding synthetic rutile.

Ammonium chloride was used as catalyst for aeration in the Becher process due to its three important properties: ability to buffer the solution, to prevent passive iron oxides film forming on particle surface and its ability to form a complex with the iron (II) ions [5]. This iron complex breaks apart upon entering the bulk solution [11].

Industrial NH_4Cl catalyzed aerations are reported to take up to 20 hours [10]. Shortening aeration time therefore has potential for yielding considerably commercial benefit. One of the effective methods to improve efficiency of aeration is using organic acids as additions along with NH_4Cl.

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In this work, acetic acid (CH_3COOH) and citric acid ($C_6H_8O_7$) were used along with NH_4Cl. Influences of these acids on rusting rate and residual metallic iron in rutile are investigated. The role of additional acid and their impact on precipitated iron compounds were also discussed.

2 Experimental procedure

Ilmenite concentrate was obtained from Ha Tinh Minerals and Trading JSC., Vietnam. The concentrate containing 55% TiO_2 was supplied in powder form with an average particle size of 150 μm. Ammonium chloride, acetic acid and citric acid were commercial grade of 99% purity.

Reduced ilmenite was prepared following the experimental procedure described in previous work [12], the compositions were given in **Tab. 1**.

Table 1 Composition of reduced ilmenite.

Component	**wt. (%)**
TiO_2	60.2
Metallic iron	30.3
Iron in compound	6.0
Other impurities	3.5

In a typical aeration experiment, 40g of reduced ilmenite was suspended in 280 ml of 0.5% NH_4Cl solution. The pulp was placed in an stirred aerator with air bubble through the solution at the rate of 4 liter/min. Aeration temperature was controlled using a thermostats.

Residual metallic iron in rutile was determined by wet chemical analysis involving dissolution of RMI in $CuSO_4$ solution followed by quantitative addition of potassium dichromate to convert Fe^{2+} to Fe^{3+}. The RMI value represent the average of three independent experiments. An XRD (Bruker D8-Advance) was used for phase analysis.

3 Results and discussion

In order to study influence of additional acids on iron removal, experiments were carried out at 70ºC in three different solutions: 0.5% NH_4Cl, 0.5% NH_4Cl + 0.4% CH_3COOH and 0.5% NH4Cl + 0.4% $C_6H_8O_7$. Residual metallic iron as a function of time are shown in **Fig. 1**.

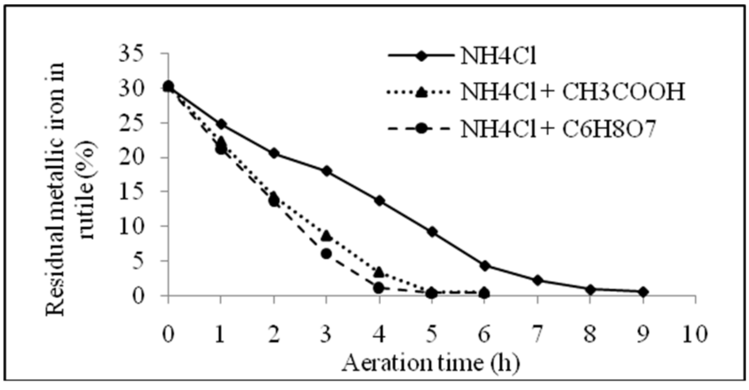

Fig. 1 Effects of acids addition on residual metallic iron in rutile

After 9 hours of aeration with NH_4Cl catalyst, RMI in rutile was 0.5%. Passivation was observed after 6 hours of rusting where RMI was 4.29%. In the case of acetic acid addition, after 5 hours of rusting RMI in rutile was already decreased to 0.5%. Passivation was observed after 5 hours and RMI in rutile was still 0.5% after 6 hours. In the case of citric acid addition, passivation was observed after only 4 hours and RMI in rutile was 1.11%, after 6 hours of rusting RMI decreased to 0.33%.

The results indicated that rusting rate increased when acetic and citric acids were used along with NH_4Cl. Generally, organic acid could aid rusting in several ways. Firstly, acid leaching of metallic iron can occur when acid is added into bulk solution. The reaction between acid and metallic iron promoted the removal of metallic iron in reduced ilmenite. Secondly, the acids have several similar properties to NH_4Cl in aeration which facilitated iron rusting. The acids provide addition H^+ to the bulk solution. The additional protons not only reduce pH of bulk solution which facilitate iron rusting but also buffer the solution, similar to NH_4^+ when NH_4Cl is used. The organic anions from the acids also have the capability to form complexes with iron.

Reactions between iron and acetate, citrate anions have been excessively studied [13-15]. According to Palmer [13], iron acetate complexes are formed following equation below:

$$Fe^{2+} + nCH_3COO^- \Leftrightarrow Fe(CH_3COO)_n^{2-n} \text{ with } (n \leq 3) \tag{1.}$$

In another study, Hamm *et al.* [15] described the formation of iron citrate (Cit) complex. Firstly, the citric acid electrolyzed in solution provides H_2Cit-, $HCit^{2-}$ and Cit^{3-}:

$$H_3Cit \Leftrightarrow H^+ + H_2Cit^- \tag{2.}$$

$$H_2Cit^- \Leftrightarrow H^+ + HCit^{2-} \tag{3.}$$

$$HCit^{2-} \Leftrightarrow H^+ + Cit^{3-} \tag{4.}$$

These anions then react with iron to form different complexes.

$$Fe^{2+} + HCit^{2-} \Leftrightarrow FeHCit \tag{5.}$$

$$Fe^{2+} + Cit^{3-} \Leftrightarrow FeCit^- \tag{6.}$$

$$Fe^{3+} + HCit^{2-} \Leftrightarrow FeHCit^+ \tag{7.}$$

$$Fe^{3+} + Cit^{3-} \Leftrightarrow FeCit \tag{8.}$$

In the aeration of reduced ilmenite, the formation of these complexes (reaction 1,5-8) limited the precipitation of a passive layer on the ilmenite particle surface, the complexes break apart upon entering bulk solution and iron precipitates out as iron oxyhydroxyl [5-6,16]. The acetate and citrate anions acted as a transporter in the movement of corroded iron from reduced ilmenite into bulk solution.

Generally, ferrous ions in solution are oxidized to ferric. As a consequence, the ferric compound precipitates out as lepidocrocide (FeOOH). The introduction of citrate ions into solution create relatively stable Fe(II)-ligand complexes. Such complexes decrease the rate constant of Fe(II) oxidation and thus, influent the form of precipitated iron compounds [17].

Fig. 2 shows XRD patterns of precipitated iron compounds after aeration with a) NH_4Cl, b) NH4Cl + CH_3COOH and c) NH4Cl + $C_6H_8O_7$.

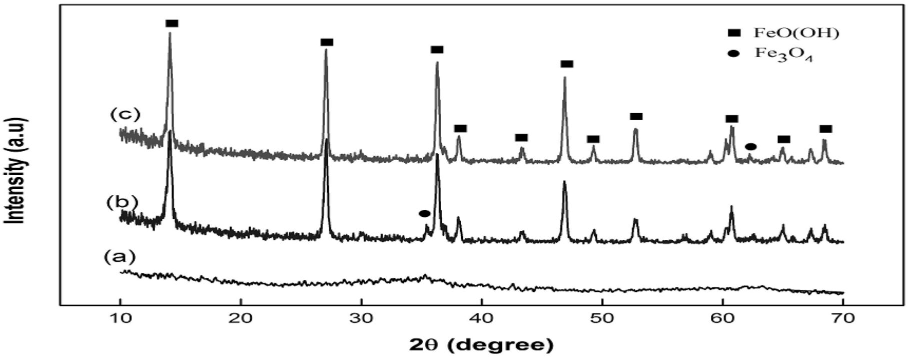

Fig. 2 XRD patterns of precipitated iron compounds: a) citric acid + ammonium chloride, b) ammonium chloride and c) acetic acid + ammonium chloride

In case of NH_4Cl catalyst, the iron compounds were identified as FeO(OH) and Fe_3O_4 (**Fig. 2b**). The addition of acetic acid shows no effect on the form of precipitated iron compound (**Fig. 2c**). Meanwhile, poorly-crystalline iron compound was precipitated when citric acid is used (**Fig. 2a**). The results are in agreement with Krishnamurti and Huang study [17] who concluded that poorly-crystalline iron oxides are formed when a minor amount of citrate was introduced into solution.

Acetic and citric acids could be used as additional catalysts for the aeration of reduced ilmenite. For further understanding on the role of the acids in aeration, effect of temperature on aeration with acids addition was also studied. RMI as a function of aeration temperature are shown in **Fig. 3**. The experiments were carried out at 50, 60, 70 and 80ºC for 5 hours in three different solution: NH_4Cl, NH_4Cl + 0.4% CH_3COOH and NH_4Cl + 0.4% $C_6H_8O_7$.

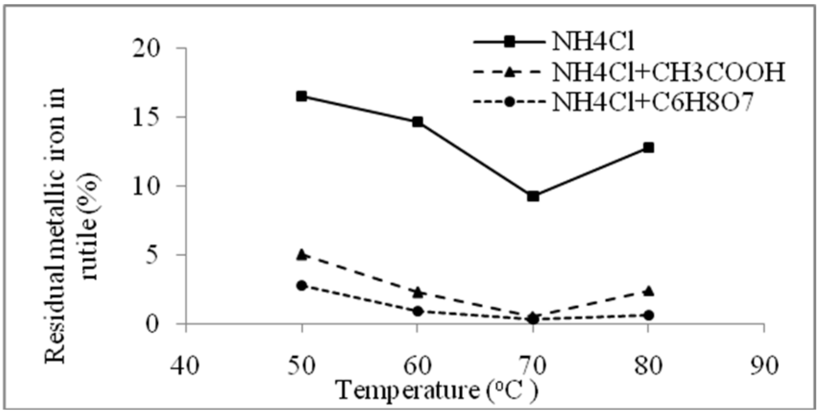

Fig. 3 Effects of temperature on residual metallic iron in rutile

As depicted in **Fig. 3**, at 70ºC maximum rusting was achieved with all three solution, NH_4Cl, NH_4Cl + CH_3COOH and NH_4Cl + $C_6H_8O_7$, RMIs were 9.22% and 0.5% and 0.33%, respectively. The addition of acids significantly influents RMI in rutile, at the same conditions, RMI was gradually dropped from 9.22% when NH_4Cl was used, to 0.5% when NH_4Cl + CH_3COOH was used, and to 0.33% when NH_4Cl + $C_6H_8O_7$ was used.

The effect of temperature on rusting is quite complicated because of several temperature-dependent parameters are involved. The increasing of temperature facilitates rusting reaction but also reduces dissolved oxygen in solution, the lack of dissolved oxygen could retard rusting. Temperature has a less effect on aeration with acids addition. When NH_4Cl was used, difference between RMIs at 50 and 70 ºC was 7.28%. The addition of acetic and citric acids has reduced this difference to 4.48% and 2.49%, respectively.

In order to study the influence of acid concentrations on aeration, a series of aerations were conducted with acid concentrations raised from 0.0% to 1.0%. Residual metallic iron in rutile as a function of aeration time with different acetic and citric acids concentrations are shown in **Fig. 4** and **5**, respectively.

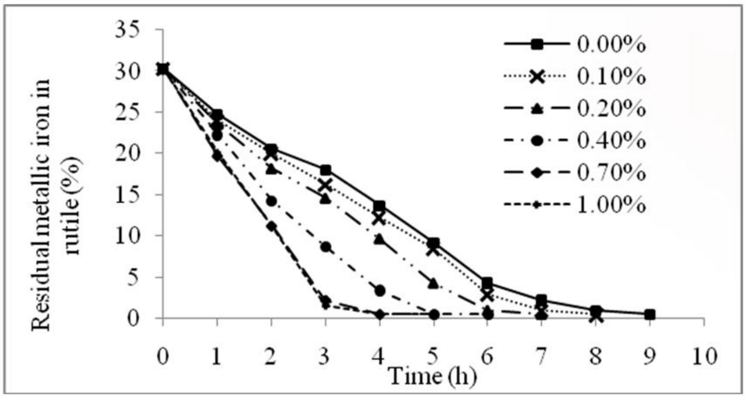

Fig. 4 Effects of acetic acid concentration on residual metallic iron in rutile.

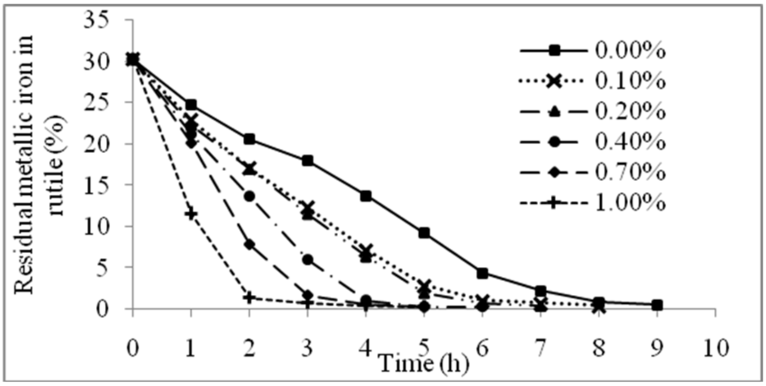

Fig. 5 Effects of citric acid concentration on residual metallic iron in rutile

In the case of acetic acid, the increasing of acid concentration from 0.0% to 0.7% resulted in much faster rusting, RMI was downed to 1.64% after just 2 hours. At 0.7% CH_3COOH and above, aeration was difficult due to foaming. At 1% CH_3COOH, rusting rate and RMIs were almost identical to those at 0.7% CH_3COOH. In the case of citric acid, rusting rate was continued to increase at above 0.7% $C_6H_8O_7$. At 1% $C_6H_8O_7$, passivation was observed after only 2 hours and RMI in rutile was already decreased to 1.34%. Aeration was ended after 5 hours and RMI was downed to 0.33%. In both cases, increasing of acid concentration increased rusting rate. Citric acid showed somewhat better catalyzed ability than acetic acid. At the same acid concentrations, rusting rate was faster when citric acid was used. Better catalyst ability of citric acid compare to acetic acid could be attributed to its molecular structure. The acetate ion has only one possible active site (COO^-) compare to three of the citrate ion. Because those active site may complex the ionic iron during aeration, ion with more active site could be more efficiency in transporting iron into bulk solution.

As discussed above, the buffering ability of the catalysts are very important. Without this action, the hydroxyl ion would react with oxidized iron (II) ion to form a solid layer that would block further oxidation of metallic iron. The variation of pH during aeration therefore becomes a major factor that influents iron rusting.

Fig. 6 shows the pH profiles of three different solutions used in aeration: 0.5% NH_4Cl, 0.5% NH_4Cl + 0.4 CH_3COOH and 0.5% NH_4Cl + 0.4% $C_6H_8O_7$.

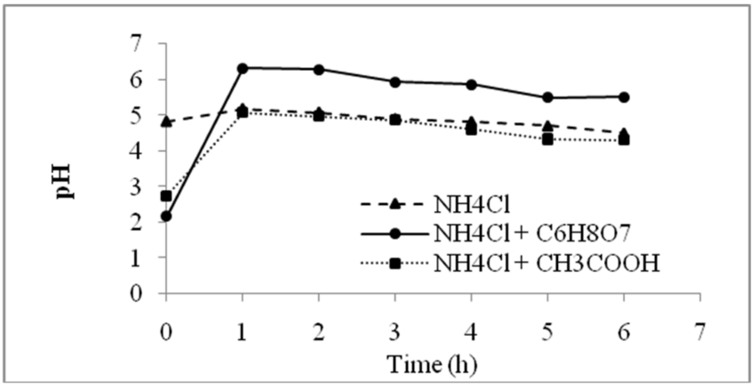

Fig. 6 pH profiles of three solutions used in aeration

In the case of NH_4Cl, the initial pH value measured was 4.8 and minor variation in pH was observed during 6 hours of aeration. In the case of CH_3COOH addition, initial pH dropped to 2.8 then raised to 5.1 after only 1 hour of aeration. From this point onward, pH profile of the NH_4Cl + CH_3COOH solution was almost identical to those of the NH_4Cl solution. In the case of $C_6H_8O_7$ addition, initial pH dropped to 2.2 but increased sharply to 6.3 after 1 hour. pH then decreased slightly during aeration and reached the value of 5.5 after 6 hours.

The variations of pH suggests that when acids were added into solution, acid leaching might occurred in the first hour of aeration. The leaching reactions rapidly consume H^+ and bring up pH. pH values of all three solutions remain under seven throughout aeration. This promotes the transportation of the iron (II) ions out of the ilmenite grain and thus, facilitates iron rusting.

4 Conclutions

The addition of acetic and citric acids into NH_4Cl solution significantly increased rusting rate and thus, reduced the time required for aeration. After 5 hours of aeration with NH_4Cl, NH_4Cl + 0.4% $C_6H_8O_7$ and NH_4Cl + 0.4% CH_3COOH catalysts, RMIs were 9.22%, 0.33% and 0.5%, respectively. The addition of 0.4% acid shortens the aeration time from 9 to 5h.

The catalyzed mechanisms of the acids could be attributed to its similar properties to NH_4Cl in aeration. Similar to NH_4^+, the H^+ in acids can also buffer the solution and the acetate and citrate anions have the capability to form complexes with iron. The addition of acids also influenced the formation of iron compounds, in case of citric acid, poorly-crystalline iron was precipitated after aeration.

The initial pH values were significantly reduced when acids were added. The pH raised rapidly in the first hour of aeration and then remained stable at approximately 5.9 and 4.5 for citric and acetic acids solution, respectively.

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