ACETIC ACID AND SODIUM ACETATE MIXTURE AS AN AERATION CATALYST IN THE REMOVAL OF METALLIC IRON IN REDUCED ILMENITE

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Abstract

Acetic acid and sodium acetate mixture (AASAM) was used as an aeration catalyst in the removal of metallic iron in reduced ilmenite. The efficiency of the catalyst was then compared to the standard ammonium chloride catalyst used in industry. Obtained results show that faster rate of iron removal could be achieved with AASAM while the molar concentrations of both AASAM and ammonium chloride were 0.1M. The highest rate of iron removal was achieved at the mixture proportion of 0.025M CH_3COONa and 0.075M CH_3COOH, aeration parameters of 70 °C, solid/liquid ratio of 1/7 and air flow rate of 4.0 lit/min. At those experimental conditions, the aeration time was shortened from 9 hours when NH_4Cl was used to 6 hours when AASAM was used. In both cases, the obtained rutile contains approx. 82% TiO_2 and less than 0.5% metallic iron. The results indicated that AASAM could be used as a replacement for the NH_4Cl catalyst in the aeration of reduced ilmenite.

Keywords: Acid acetic, sodium acetate, aeration catalyst, metallic iron, ilmenite

1 Introduction

The Becher process developed by the Western Australia Government Chemical Laboratory in 1961 is a two step procedure for the production of synthetic rutile [1, 2]. The process requires two stages; a selective reduction stage in which iron oxides present within the ilmenite were reduced to metallic iron by a reducing agent, and an aeration stages in which metallic iron are removed from the reduced ilmenite grain by the use of aerated ammonium chloride solution [2].

Ammonium chloride is an established and widely used catalyst in the removal of metallic iron from reduced ilmenite. It has the ability to buffer solution, to prevent passive iron oxides film forming on particle surface and its ability to form a complex with the iron (II) ions [3-6].

Throughout the years, there have been studies on the possibility of accelerating the aeration process. The studies are focus on the addition of other chemicals into NH_4Cl solution or substitute NH_4Cl using other catalyst [7-9].

In this work, acetic acid and sodium acetate have been investigated as alternative catalysts. The possibility of combining acetic acid and sodium acetate as a catalyst also investigated. The choices of acetic acid were based on its potential to assists iron rusting [10]. Meanwhile, sodium acetates provides addition acetate ion to the aeration solution. Addition of acetic acid into the aeration solution provides proton, which helps neutralized the hydroxyl ion formed in the

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cathode reaction. Therefore, prevents the precipitation of iron II hydroxide on the particle surface. On the other hand, the acetate ion can form a complex with iron [11-13]:

$$[Fe(H_2O)_6]^{2+} + nCH_3COO^- \Leftrightarrow [Fe(CH_3COO)_n(H_2O)_{6-n}]^{2-n} + nH_2O \quad (n \leq 3)$$

The formation of iron acetate complex prevents iron form precipitates on the grain surface. This complex then diffuses into solution, where it hydrolysis and oxidized to form FeO(OH) and Fe_3O_4 [14]. The acetate ion works as an transporter in the transportation of ferrous ion into aeration solution.

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 sodium acetate were commercial grade of 99% purity.

Reduced ilmenite was prepared following the experimental procedure described in previous work [10, 15], the compositions were given in **Table 1**.

Table 1 Composition of reduced ilmenite

Component	wt. (%)
TiO_2	60.2
Metallic iron	30.3
Other	Balance

In a typical aeration experiment, 40g of reduced ilmenite were added to 280 ml of the reaction solution. Aeration temperature was controlled using a thermostats. Air was bubble through the solution.

Residual metallic iron (RMI) 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

3.1 Effects of catalyst on aeration

Previous experimental works using ammonium chloride as a catalyst had found a concentration of 0.1 M to be the optimum required to leach a reduced ilmenite slurry [15]. In this series of experiments, acetic acid and sodium acetate were used independently and together as a replacement for the ammonium chloride catalyst. Other aeration parameters were 70°C of aeration temperature, 4 l/min of air flow rate and 7 hours of aeration time. The concentration of acetic acid was raised from 0.0 M to 0.1 M and the concentration of sodium acetate were decreased from 0.1 M to 0.0 M in order to maintains a total catalyst concentration of 0.1M. The results of these experiments are shown in **Fig. 1**.

Fig. 1 indicates a decreasing trend in the amount of residual metallic iron present as the concentration of acetic acid increases to a value of 0.075 M. At concentrations of higher than 0.075 M it was found, within experimental error, that the same level of iron removal had occurred in the same amount of time as for the lower concentration of 0.075 M. This indicates that the use of concentrations in excess of 0.075 M achieved no further advantages in the leaching rate of metallic iron.

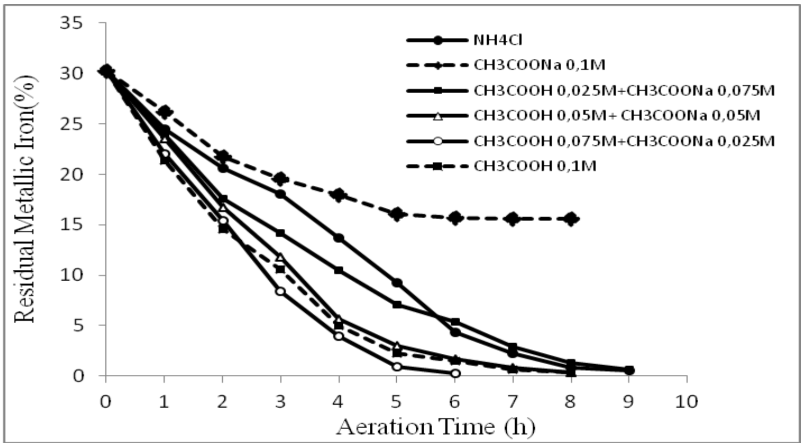

Fig. 1 Residual metallic iron versus aeration time with different catalysts

In the case of independently CH_3COONa use, slow aeration was observed and passivation was reached after 5 hours, whistle metallic iron in the sample is still over 15%. In the case of independently CH_3COOH use, higher rate of iron rusting was achieved compare to the rate when CH_3COONa was used. Passivation was also observed after 5 hours whilst metallic iron already reduced to 1.63%.

During aeration, the hydroxyl ions produced from the reaction could reacts with Fe^{2+}, the reaction product precipitates on the particle surface. Overtime, the thickness of the precipitated iron hydroxyl layer increases and this layer prevents the diffusion of ions and thus, hindered the rusting reaction. For further experiments, the mixture of CH_3COOH 0.075M and CH_3COONa 0.025M was used as aeration catalyst.

3.2 Effect of aeration temperature

Temperature of the ammonium chloride slurry had a significant effect on the rate of iron leaching [15] so the effect of temperature changes on aeration with the AASA mixture catalyst was investigated. The slurries used for this series of experiments consisted of 40 g of reduced ilmenite, 280 ml of AASAM solution contain 0.075M CH_3COOH and 0.025 M CH_3COONa. An air flow of 4.0 l per minute was maintained through the slurries. The temperature ranges used for this study were 50, 60, 70 and 80 °C. The results of these experiments are shown in **Fig. 2**.

Fig. 2 demonstrates the effect of variations in temperature on the aeration rate. The lowest residual metallic iron value in the shortest amount of time was achieved at 70ºC, giving a residual level of less than 1% after 6 h of aeration. On the other hand, after 6 h of leaching at 50ºC, residual metallic iron was still above 5.0 %. A similar spread in results across the temperature ranges was found for aerations based on ammonium chloride [10] Reaction rates appear to be the only major difference between the 2 catalysts, the AASAM slurry required only 6.0 h of aeration to reach the same stage of completion as ammonium chloride in 9.0 h

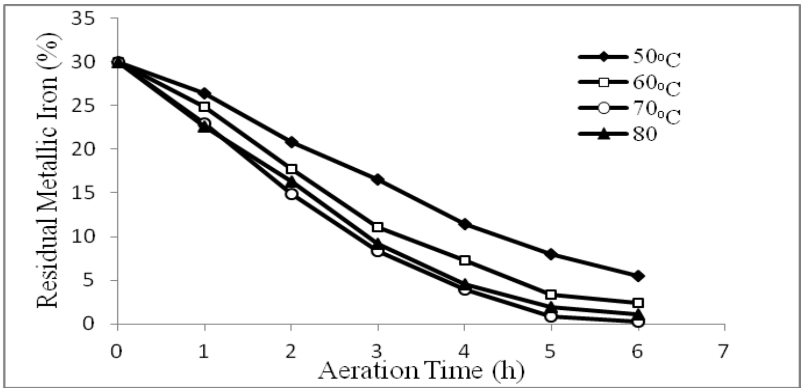

Fig. 2 Residual metallic iron versus aeration time at different aeration temperatures

3.3 Effects of Air Flow Rates

In order to oxidize the metallic iron in the reduced ilmenite grain, some form of oxidant is required. In this case, oxygen in the form of air was supplied. This series of experiments was aimed to find the optimum air flow rate for the AASAM slurries.

In this type of experiments, a standard slurry mixture consisting of 40 g of reduced ilmenite, 280 ml of AASAM solution was held at 70ºC for aeration. Air flow rates were varies from 3.0 to 5.0 l/min. Obtained results are shown in **Fig. 3**.

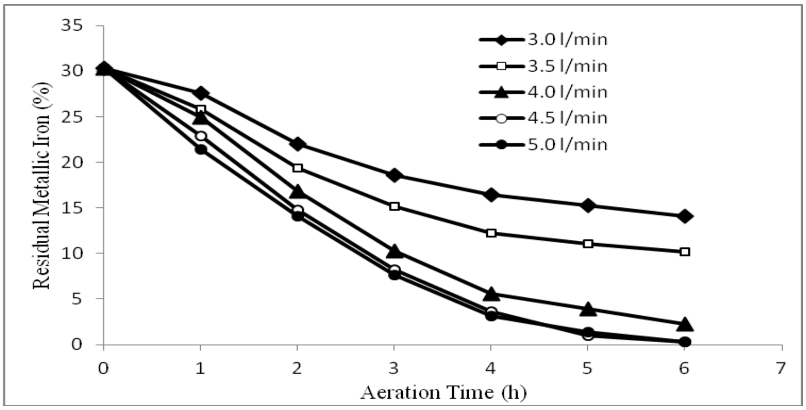

Fig. 3 Residual metallic iron versus aeration time with different air flow rates

When increased air flow rate from 3.0 l/min to 4.0 l/min, the rate of iron rusting was significantly increase. However, further increasing of air flow rate shows little impact as the rate of iron removal at 4.5 l/min and 5.0 l/min were similar to the rate at 4.0 l/min. The 4.0 l/min value was chosen as the optimum air flow rate, for the present study.

3.4 Liquid/Solid (L/S) Weight Ratio.

Experiments were carried out with L/S ratio varied from 5 to 8. The experiments were carried out at 4 l/min of air flow rate, 70°C for 8 hours in AASAM solution contain 0.075M CH_3COOH and 0.025 M CH_3COONa. The obtained results are shown in **Fig. 4**.

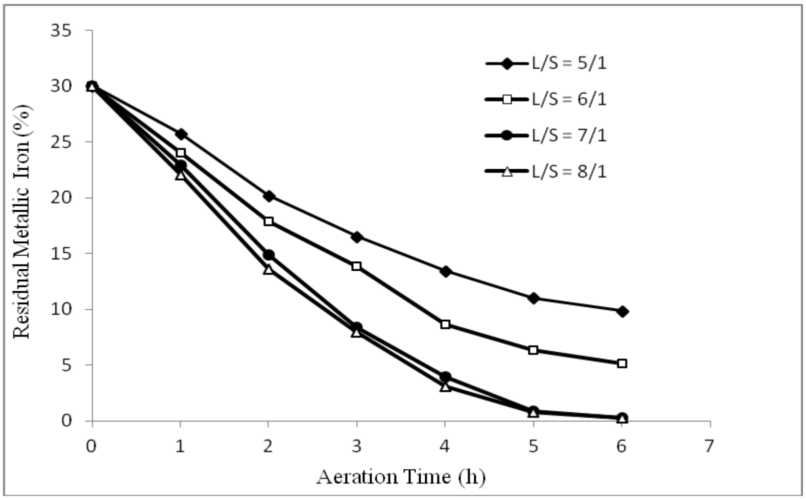

Fig. 4 Residual metallic iron versus aeration time at different L/S ratios

As depicted in **Fig. 4**, the higher L/S ratio, the better rusting archived. At L/S ratio equal to 7, most of metallic iron (98%) has been successfully rusted. Generally, low L/S ratio is used in industrial aeration for saving ammonium chloride and also reduced equipment capacity [10]. In that case, aeration time was extended to ensure the removal of metallic iron. In this work, L/S =7 has been chosen as the optimized L/S ratio for further experiments.

3.5 The variation of pH

Fig. 5 shows the pH profiles of two different solutions used in aeration: NH_4Cl 0.1M and CH_3COOH 0.075M + CH_3COONa 0.025M

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 AASAM, initial pH was 4.1 then raised to 5.5 after only 1 hour of aeration. From this point onward, pH profile of the AASAM solution was similar to those of the NH_4Cl solution. pH then decreased slightly during aeration and reached the value of 5.0 after 6 hours.

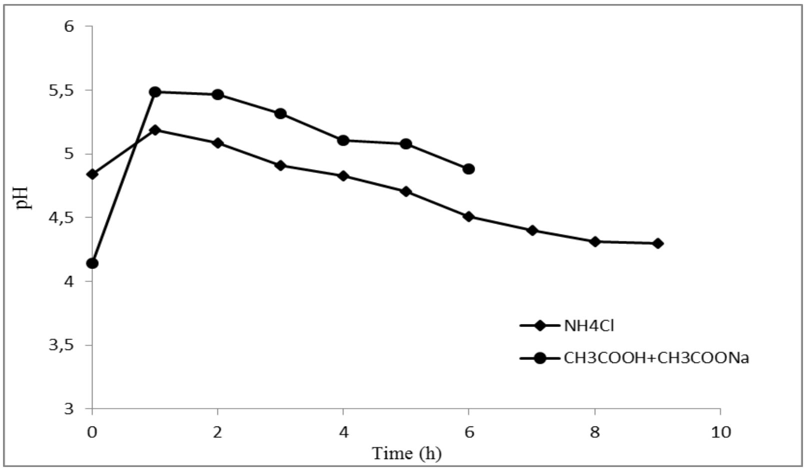

Fig. 5 The pH of bulk solution NH_4Cl and CH_3COOH 0.075M + CH_3COONa 0.025M

The variations of pH suggests that when AASAM was used, acid leaching might occurred in the first hour of aeration. The leaching reaction rapidly consumes H+ and brings up pH of the solution.

3.6 Phase investigation

Fig. 6 shows XRD patterns of reduced ilmenite and synthetic rutile obtained with NH_4Cl and AASAM solutions. The patterns indicated that most of metallic iron has been successfully removed from reduced ilmenite (the iron intensity was vastly decreased). The rutiles obtained contains mostly TiO_2 and $Fe_3Ti_3O_{10}$. Chemical analysis shows that the synthetic rutile contains approx. 80% TiO_2.

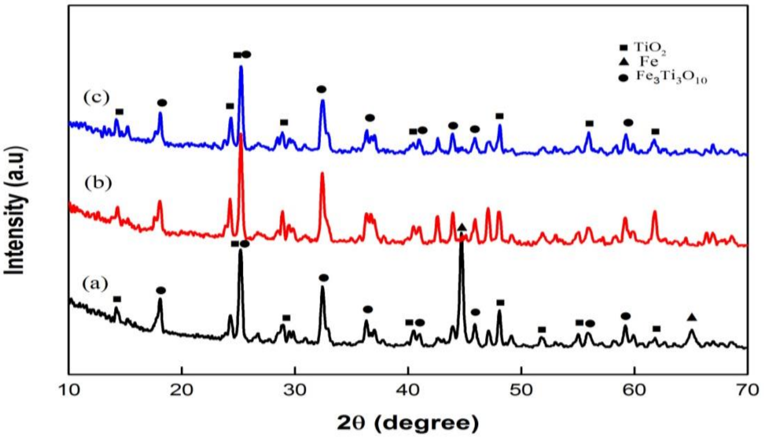

Fig. 6 XRD patterns of a) reduced ilmenite, b) aerated rutile in ammonium chloride and c) aerated rutile in acetic acid + sodium acetate mixture

4 Conclutions

AASAM was chosen because of it similarity to ammonium chloride such as the ability of complexation and passivation resistance.

The comparison between the ammonium chloride and AASAM showed that at an optimum concentration of 0.1 M (CH_3COOH 0.075M + CH_3COONa 0.025M), the AASAM takes 6.0 h to complete a standard aeration compared to 9.0 h for ammonium chloride. This suggests a potential advantages in the use of AASAM in place of ammonium chloride.

The effect of temperature and air flow rate on both the ammonium chloride and the AASAM catalysed aerations was very similar. The maximum rate for AASAM was found at the aeration temperature of 70ºC and the air flow rate of 4.0 l/min, similar to whereas ammonium chloride was used.

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