

## **EFFECT OF THE PRESENCE OF DISSOLVED METALS, Fe AND Al, ON NEUTRALIZATION OF ACIDIC AQUEOUS SOLUTION**

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**Abstract:** The efficacy of neutralization of an acidic aqueous solution is generally dependent on the type of alkaline material used. However, another limiting factor but often overlooked is the presence of dissolved metals. In this study, the effect of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  on the neutralization of acid aqueous solutions was investigated. Potentiometric titrations using 0.01 M NaOH were performed on aqueous acidic solutions, with initial pH pre-adjusted to 3.0, in the absence and presence of 10 mg/L and 100 mg/L  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . The results showed that the presence of  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  resulted in a strong buffering at pH 3.0-3.5 and 4.0-4.5, respectively. Meanwhile, no significant pH buffering was observed for the non-metal acidic aqueous solutions. Consequently, more alkalinity (base) is required to increase the solution pH from pH 3.0 to the prescribed value (pH=7.0), particularly at high metal concentration. At a similar concentration, the presence of  $\text{Al}^{3+}$  resulted in more intense pH buffering and thereby more alkalinity is required for neutralization compared with  $\text{Fe}^{3+}$ .

**Keywords:** Neutralization; dissolved metals; hydrolysis; pH buffering.

### **INTRODUCTION**

Neutralization by the addition of an alkaline material is a standard technique for treatment of acidic water and wastewater. Typical alkaline materials used include caustic soda, quick or hydrated lime, magnesium hydroxide and ammonium hydroxide [14, 18, 20]. The used alkaline generating materials such as limestone, fly ash, olivine, serpentinite, lignite have also been reported [2, 8, 11, 14]. Neutralization raises the pH of the water or wastewater to a desired value (e.g pH ~ 7.0), thereby reducing its' acidity. However, the efficacy of this process depends on several factors including the type of alkaline material used, particle size (if the material is solid in nature), contact time as well as on the characteristics of the water or wastewater [14].

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In general, the acid characteristic of an aqueous solution can be expressed either by its pH value and/or total acidity value. pH is a measure of free acidity ( $H^+$ ) present in solution while total acidity is represented by the combination of free acidity and mineral acidity. This mineral acidity associated with dissolved metals in particular  $Fe^{3+}$  and  $Al^{3+}$ . These metal ions readily undergo hydrolysis at pH 3.5-4.0 and 4.0-4.5, respectively to produce additional  $H^+$  [4, 9]. In many common aqueous systems such as groundwater and surface water where the acid character is dominated by free acidity, neutralization process (i.e. increase in pH) can proceed in the usual manner as expected for a typical acid-base neutralization reaction. However, in acidic metal-rich aqueous systems such as acid mine drainages and industrial wastewater where mineral acidity predominates, *in situ* generation of  $H^+$  attributed to  $Fe^{3+}$  or  $Al^{3+}$  hydrolysis can cause a sluggish increment in pH despite addition in the amount of alkalinity [3, 6, 10]. This pH buffering characteristic inevitably hinders or reduces the neutralization process efficiency. This factor however is often disregarded since the design of neutralization treatment process is usually based on the initial pH of the acid water or wastewater rather than its' total acidity value. In this study the effect of dissolved  $Fe^{3+}$  and  $Al^{3+}$  on acid neutralization efficacy was investigated and compared.

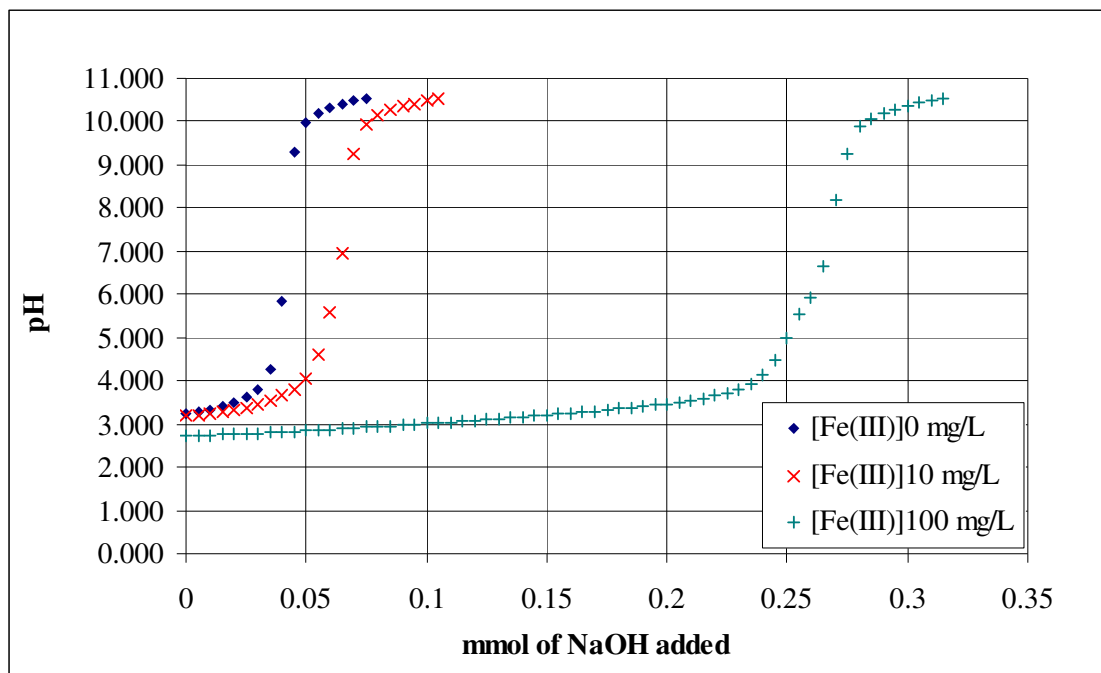
## MATERIALS AND METHODS

Aqueous stock solutions (1000 mg/L) of  $Fe^{3+}$  and  $Al^{3+}$  were prepared from  $FeCl_3 \cdot 6H_2O$  and  $Al_2(SO_4)_3 \cdot 16H_2O$ , respectively. Subsequently, metal solutions with initial concentrations of 10 mg/L and 100 mg/L were prepared and their initial pH adjusted to 3.0 with 1M  $H_2SO_4$ . Additionally, an aqueous solution with initial pH  $\approx$  3.0 was also prepared. All aqueous samples (50 mL) were titrated potentiometrically with 0.01 M NaOH to pH > 7.0 [6, 22].

## RESULTS AND DISCUSSION

### *Effect of $Fe^{3+}$ on neutralization*

In the absence of  $Fe^{3+}$ , the titration graph is typical for a strong acid-strong base reaction (**Fig. 1**), whereby a sharp increase in pH was observed at equivalent point. In the presence of 10 mg/L  $Fe^{3+}$ , a similar trend in the increase of pH was also observed but slightly higher amount of alkalinity was required to raise the solution pH to 7.0. By contrast, in the presence of 100 mg/L  $Fe^{3+}$  a strong *pH buffering* was evident at pH 3.0-3.5. The pH value showed a very small increase from pH~ 3.0 despite the increasing amount of base (alkalinity) added. After a specific lag time, the pH eventually increased to the desired value.

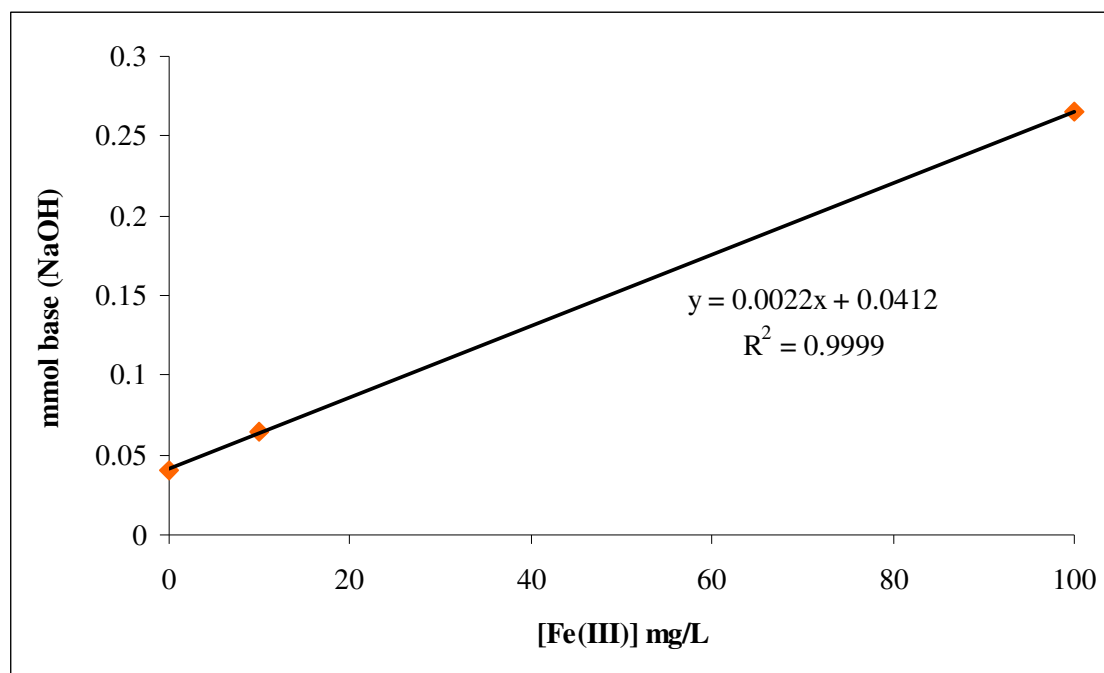


**Fig. 1** Titration curves in the absence and presence of  $\text{Fe}^{3+}$  in acidic aqueous solution

During the titration, the added  $\text{OH}^-$  react rapidly with the  $\text{H}^+$  in solution, resulting in an increase in pH from  $\text{pH} \sim 3.0$  (Eq.1) [10]. In the presence of  $\text{Fe}^{3+}$ , however, the increase in pH triggers the hydrolysis of  $\text{Fe}^{3+}$  (Eq. 2). This hydrolysis produces acidity which temporarily suppresses the increase in pH.



The amount of mineral acidity generated can also be greater at higher  $\text{Fe}^{3+}$  concentration. Consequently, the pH buffering effect at 3.0-3.5 is more pronounced at highest concentration of  $\text{Fe}^{3+}$ . The pH only increases above 3.5 when all the  $\text{Fe}^{3+}$  ions have undergone hydrolysis or its' mineral acidity is depleted. Comparatively, the amount of alkalinity required to increase the pH to 7.0 is about 4 times higher for 100 mg/L  $\text{Fe}^{3+}$  compared to 10 mg/L  $\text{Fe}^{3+}$  (**Fig.2**).

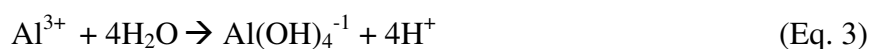


**Fig. 2** Effect of  $\text{Fe}^{3+}$  concentration, on the amount of base required for neutralization (pH 7.0) of acidic aqueous solution

#### *Effect of $\text{Al}^{3+}$ in neutralization*

In the presence of 10 mg/L of  $\text{Al}^{3+}$ , the increment in the solution pH (>3.0) at initial stage also displayed a similar trend to a strong acid-strong base titration curve (**Fig. 3**). However, as soon as pH approached 4.0, the graph displayed a small plateau before it starts to increase sharply to pH 7.0. Also, the amount of alkalinity required for the increment is relatively higher than acidic aqueous solution without the presence of  $\text{Al}^{3+}$ . However, at the highest concentration of  $\text{Al}^{3+}$  (i.e. 100 mg/L), a very conspicuous pH plateau was observed at pH 4.0-4.5. Only a small increment in pH was observed despite the amount of base added was increased.

The increased in pH to pH~4.0 following the addition of base prompted the hydrolysis reaction of  $\text{Al}^{3+}$  [9, 10, 22].

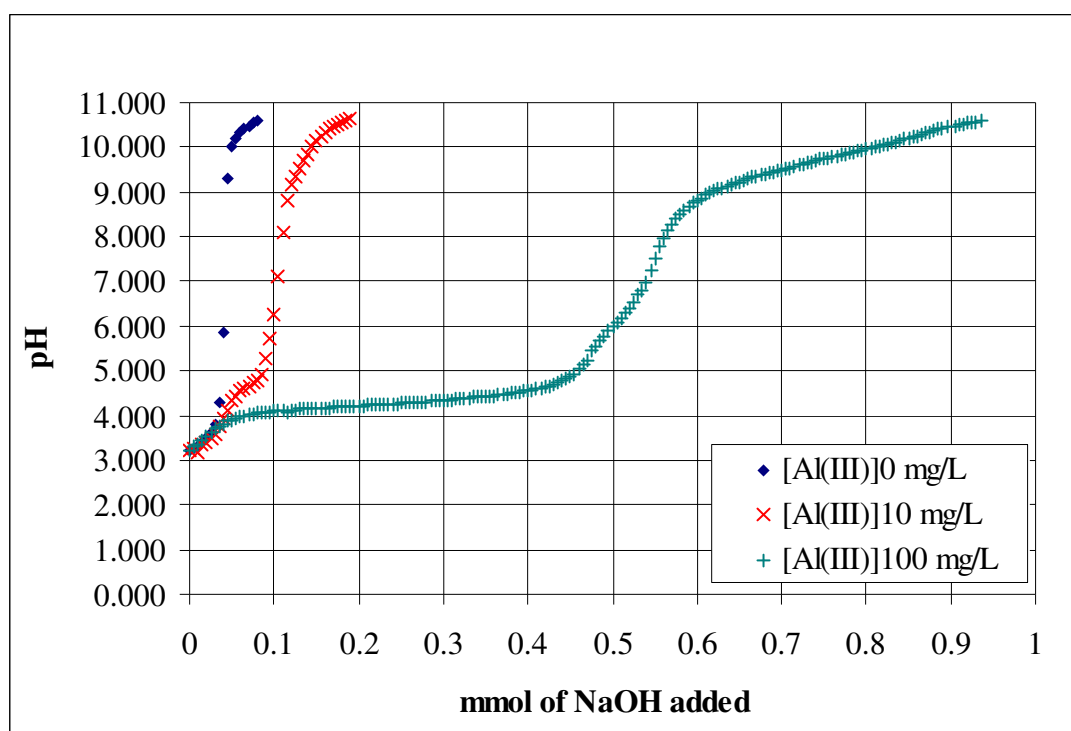


The rapid release of  $\text{H}^+$  inevitably causes a lagtime because every liberated mole of  $\text{H}^+$  during hydrolysis is quickly counteracted with a mole of the added base. Hence, the pH value of solution remained fairly constant as indicated by the pH plateau in the titration graph.

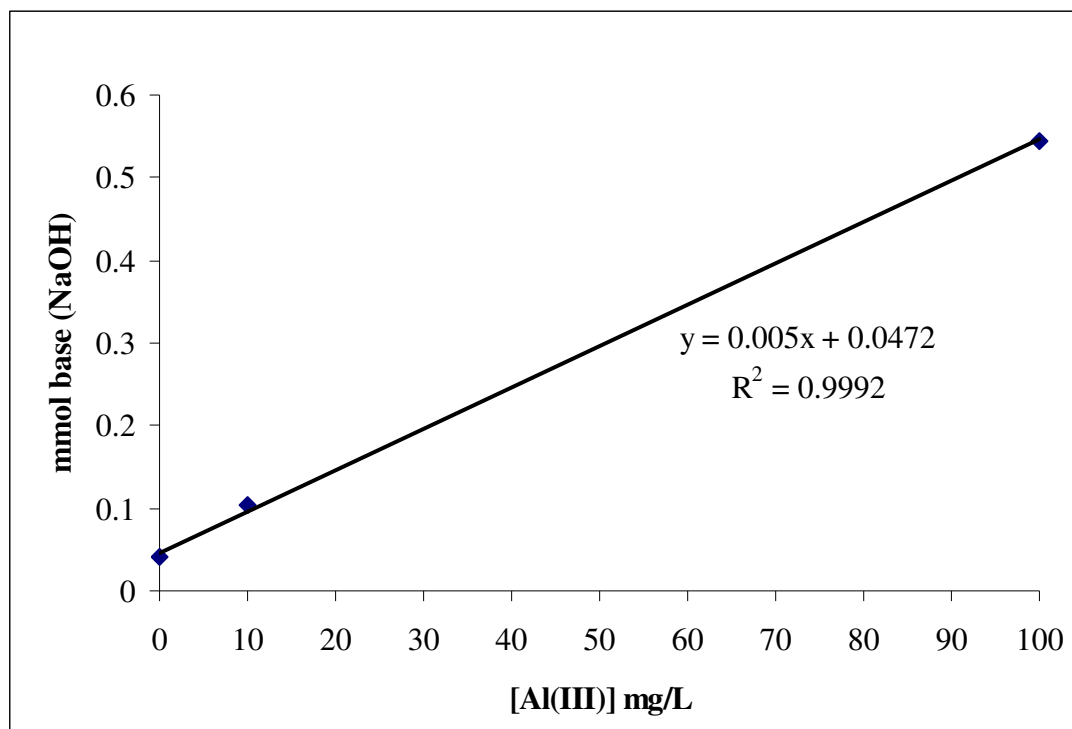
This buffering reaction continued until the mineral acidity has been depleted. Subsequent addition resulted in sharp increment in pH. Comparatively, the presence of 100 mg/L of  $\text{Al}^{3+}$  in acidic aqueous solution required 5.2 times more alkalinity than 10 mg/L to increase the

solution pH to 7.0 (**Fig.4**). By comparison with acidic aqueous solution without the presence of  $\text{Al}^{3+}$ , this value became more significant where it requires 13.6 times more alkalinity to attain pH 7.0.

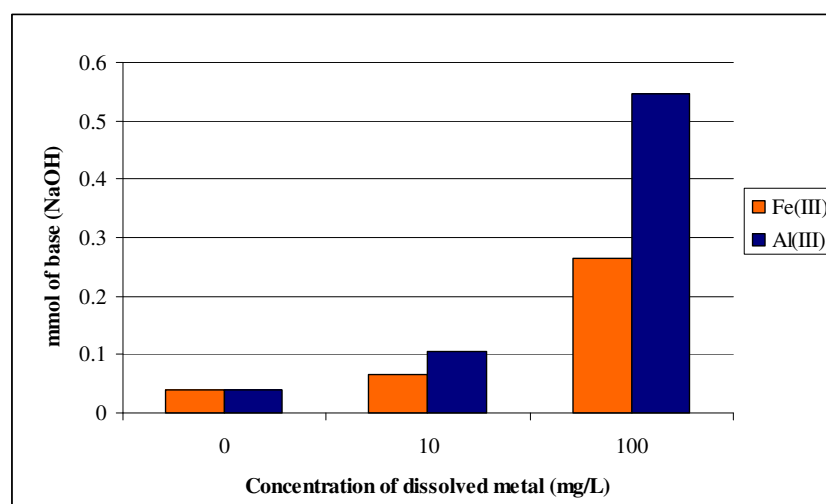
Comparatively, the magnitude of pH buffering in the presence of  $\text{Al}^{3+}$  was significantly higher and more prominent than in the presence of  $\text{Fe}^{3+}$ . At similar concentrations 10 mg/L and 100 mg/L, acidic aqueous solution in the presence of  $\text{Al}^{3+}$  would require 1.6 and 2.1 times more alkalinity, respectively to attain a similar pH at 7.0 (see **Fig. 5**). This can be attributed to a higher ionic potential (i.e. charge/size ratio) in  $\text{Al}^{3+}$  compared to  $\text{Fe}^{3+}$ . Higher ionic potential gives a greater inductive effect during hydrolysis to attract electron density from oxygen atom in water molecule [7]. This substantially weakens the O-H bond of an attached water molecule making the release of a proton,  $\text{H}^+$  relatively easier and faster. Ultimately, high intensity of hydrolysis reaction is expected for acidic aqueous solution containing significant presence of  $\text{Al}^{3+}$  rather than  $\text{Fe}^{3+}$ . As a result, neutralization process (i.e. increment in pH) becomes sluggish and inefficient.



**Fig. 3** Titration curves in the absence of  $\text{Al}^{3+}$  and presence of different concentrations of  $\text{Al}^{3+}$



**Fig. 4** Effect of concentration of  $\text{Al}^{3+}$  on the amount of base required for neutralization of acidic aqueous solution to pH 7.0



**Fig. 5** Effect of  $\text{Fe}^{3+}$  vs.  $\text{Al}^{3+}$  concentration on the amount of base required for neutralization of acidic aqueous solution to pH 7.0

## CONCLUSION

The presence of  $\text{Fe}^{3+}$  and/or  $\text{Al}^{3+}$  in an acidic aqueous solution can inhibit the increase in pH thereby reducing the efficacy of neutralization process. This effect is more apparent at high

concentration in particular for  $\text{Al}^{3+}$ . It is therefore crucial that neutralizing of an aqueous acidic solution needs to take into consideration the presence of dissolved metals (i.e. mineral acidity) instead of solely on the apparent pH value.

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