

## Simulation on the distribution of metal-picolinate complexes in the model waste solution

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### Abstract

The distribution of vanadium and iron ionic species in the presence of picolinate ligand has been simulated and evaluated at different pH values and various compositions of the model waste solution. A computer program was useful for the calculation of the speciation of metal picolinate complexes. In spite of the variations of metal concentration, there are little differences in the shape of distribution diagrams under the high-picolinate LOMI condition if the molar ratio of picolinate to metal is fixed at a constant value. Also, for a model solution under low-picolinate LOMI condition, it is hard to find out some significant changes in shape of distribution diagrams regardless of the variations of metal concentration in solution. However, the reduced amount of picolinate from 6 times to 3 times on the basis of vanadium concentration affects shape of distribution diagrams. For vanadium(III)-picolinate complexes, a peak corresponding to the vanadium tris picolinate,  $V(\text{Pic})_3$  is reduced greatly. In case of iron(II)-picolinate complexes, shape of the distribution diagram was changed significantly. In a model solution of low-picolinate LOMI condition, the fraction of iron(II) complex species is maintained at a constant ratio in the region over pH 4. Especially, the speciation of iron(II)-picolinate complexes is dependent upon the concentration of iron in a model solution under the low-picolinate LOMI condition. This phenomenon is attributed to the shortage of picolinate ligand in solution, and originated from the difference of stability constants between vanadium(III) and iron(II) species with picolinate.

### I. Introduction

The adjustment of the solution pH value can sometimes be advantageously employed in the treatment of wastes containing metal ion complexes in order to form an undissociated acid or base. By pH decrease or increase, the undissociated acid or base species is formed and the complex is broken, thus providing opportunities for further treatment procedures. Complex formation gives a significant problem in waste treatment. There are two ways of solving the problem (apart from avoiding the use of complexing agents): one is to isolate the stream for special treatment, for example with techniques to recover the complexing agent for reuse; the other is chemical destruction of the complexing agent which generally involves oxidative or reductive agents.

The variation of the pH value can be used to modify the ionic species present in the waste stream. This may affect the choice of precipitates and the operating conditions used in the treatment process. It is easy to obtain the relative amount of each species in solution, which can be calculated from the well-known equilibrium constants of the acids and complexes involved, and from the pH of the solution. However, in recent computer modelling is being increasingly used to predict the ionic speciation in solution and the effect of constituents of the waste stream on the solubility of other components. Knowledge of the adsorption behavior of metal-ligand complexes in model systems may enable better predictions of their behavior in practical systems. The speciation of chelate, therefore, has a strong influence on metal ion uptake on the ion exchange material systems [1, 2].

In this study, for the purpose of investigating the ion exchange characteristics of metallic cations in the spent LOMI (low oxidative-state metal ion) decontamination solution, the complex equilibrium distributions of vanadium and iron ionic species in the presence of picolinate ligand have been simulated and evaluated at different pH values and various compositions of the model LOMI formulation. A computer program was used for the calculation of the speciation of metal picolinate complexes.

## II. Calculation of complex equilibria for the vanadium-iron-picolinate system

The equilibrium concentrations of all species in multi-metal, multi-ligand systems can be calculated by solving a series of simultaneous equations, comprising of mass balance equations and equilibrium constant equations, from given pH value of the solution, the total concentration of each metal and each ligand, and the relevant equilibrium constants. Electronic computer has been applied successfully in this [3, 4].

Assuming that at the final stage of the LOMI decontamination application all bivalent vanadium ions in the solution were oxidized to trivalent state by the reductive dissolution reaction of iron oxide, the total amounts of vanadium, iron and picolinate can be written as the summation of all kinds of respective species contained in the decontamination solution by the mass balance.

$$[V_{\text{total}}] = [V^{3+}] + [V(\text{Pic})_3^{2+}] + [V(\text{Pic})_2^+] + [V(\text{Pic})_3] + [V(\text{Pic})_2(\text{OH})] \quad (1)$$

$$[\text{Fe}_{\text{total}}] = [\text{Fe}^{2+}] + [\text{Fe}(\text{Pic})_3^+] + [\text{Fe}(\text{Pic})_2] + [\text{Fe}(\text{Pic})_3^-] \quad (2)$$

$$[\text{Pic}_{\text{total}}] = [\text{Pic}^-] + [\text{HPic}] + [V(\text{Pic})_3^{2+}] + [2V(\text{Pic})_2^+] + [3V(\text{Pic})_3] + [2V(\text{Pic})_2(\text{OH})] \\ + [\text{Fe}(\text{Pic})_3^+] + [2\text{Fe}(\text{Pic})_2] + [3\text{Fe}(\text{Pic})_3^-] \quad (3)$$

The solution equilibrium data for various species including V(III)- and Fe(II)-Picolinate complexes in the LOMI decontamination solution can be obtained from the literatures [5-8]. In Table 1, the equilibrium reactions and the stability constants are shown. From these equilibrium constants and material balance equations (1), (2) and (3), an equation for picolinate concentration which is the seventh polynomials could be derived. The fractions of ionic, metal-picolinate complex species and the concentration of free picolinate ( $\text{Pic}^-$ ) in the decontamination solution can be

theoretically calculated by using a computer program and input data concerning the initial values of total concentrations such as  $V_{\text{total}}$ ,  $Fe_{\text{total}}$ ,  $Pic_{\text{total}}$  and solution pH value. A computer program to calculate the distribution of the species contained in the decontamination solution in the presence of picolinic acid was used [9].

### III. Results and discussion

For the effective separation of the cations from the spent LOMI decontamination solution, it is required to get informations about the complex equilibria of ions in the solution. At an equilibrium state, the distribution of complexes can be calculated by the total concentrations of metal ions and ligands, and the pH of solutions. The calculations are fairly complicated, but the application of the computer programs developed by Perrin and Sayce [3] and by Ingri et al. [10] are particularly useful. The decontamination solution having a constant composition which consists of the fixed concentrations of vanadium(III), iron(II) and picolinic acid has a variety of ionic species, and it shows different fractions of ionic species due to some changes of solution conditions such as pH. Using the computer program for complex equilibria, the speciation of ionic species according to the variations of solution pH value and its composition could be calculated conveniently. Therefore, the distribution diagrams which simulate the relations of ionic concentration ratio with pH value could be obtained using the theoretical calculation results upon the vanadium(III) and iron(II) picolinate complex equilibria.

#### 1. Distribution diagrams for the high-picolinate LOMI condition

##### 1.1. Model solution of V: Fe: Pic= 1: 0.8: 6

Distribution diagrams were obtained for model solution that the amount of dissolved iron is estimated more than 50% of vanadium, and the ratio of picolinate to vanadium is 6:1 which is the typical formulation of high-picolinate LOMI condition [11].

Figure 1(a) is a distribution diagram, which was plotted the speciation of vanadium(III)-picolinate complexes as a function of pH based on the calculation results for 6mM of vanadium solution by using a computer program (listed in Appendix) applied to the complex equilibria. Figure 1(b) is a distribution diagram for iron(II)-picolinate complexes as a function of pH in case of 4.8mM iron concentration.

Distribution diagram of vanadium(III)-picolinate complexes for 3mM of vanadium concentration, and that of iron(II)-picolinate for 2.4mM iron concentration were obtained. Also, in case of the solution which has an increased concentrations of 10mM and 8mM for vanadium and iron, respectively, distribution diagrams were plotted.

From these distribution diagrams for the variations of metal concentration, it is found that there are little differences in the shape of distribution diagrams if the molar ratio of picolinate to metal is fixed at a constant value.

##### 1.2. Model solution of V: Fe: Pic= 1: x: 6

For a solution having reduced concentration of dissolved iron less than 50% of vanadium

concentration the effect of composition change on shape of distribution diagram was examined. Figure 2(a) is a distribution diagram for vanadium(III)-picolinate in 5mM vanadium solution, and that for iron(II)-picolinate in 1.2mM iron solution is shown in Fig. 2(b). In this case of low concentration of dissolved iron we can see only a small variations in shape of distribution diagrams.

## 2. Distribution diagrams for the low-picolinate LOMI condition

### 2.1. Model solution of V: Fe: Pic= 1: 0.8: 3

Model solution having low picolinate concentration in which the ratio of picolinate to vanadium is 3:1 was selected for the simulation in the speciation of vanadium and iron picolinate complexes [6-82]. In this model solution the amount of picolinic acid is reduced up to approximately 50% than that of the typical high-picolinate LOMI condition, and the dissolved iron concentration was estimated more than 50% of vanadium.

In Fig. 3(a), a distribution diagram of vanadium(III)-picolinate complexes is shown for vanadium concentration of 5mM, and that of iron(II)-picolinate in Fig. 3(b) for 4.8mM iron concentration (80% of vanadium).

A distribution diagram of vanadium(III)-picolinate complexes for 3mM of vanadium concentration, and that of iron(II)-picolinate for 2.4mM iron concentration were obtained. Also, for the solution having an increased concentrations of 10mM and 8mM for vanadium and iron, respectively, distribution diagrams were plotted.

From the above distribution diagrams, model solution under low-picolinate LOMI condition also shows similar tendency for shape of distribution diagrams in each other. Regardless of the variations of metal concentration in solution, it is hard to find out some significant changes in shape of distribution diagrams. However, the reduced amount of picolinate from 5 times to 3 times on the basis of vanadium concentration affects shape of distribution diagrams. For vanadium(III)-picolinate complexes, a peak corresponding to vanadium tris picolinate,  $V(\text{Pic})_3$  is reduced greatly. In case of iron(II)-picolinate complexes, the shape of distribution diagram was changed significantly. In model solution of low-picolinate LOMI condition, the fraction of iron(II) complex species is maintained at a constant ratio in the region over pH 4.

### 2.2. Model solution of V: Fe: Pic= 1: x: 3

Considering model solution having reduced concentration of dissolved iron less than 50% of vanadium concentration, Fig. 4(a) is a distribution diagram for vanadium(III)-picolinate in 5mM vanadium solution, and that for iron(II)-picolinate in 3mM iron solution is shown in Fig. 4(b). Additionally, another distribution diagrams are shown in Fig. 5. In Fig. 5(b), iron concentration is further reduced to 1.2mM. By comparing Fig. 3(b), Fig. 4(b), and Fig. 5(b), we can find different distribution diagrams in their shapes each other. However, distribution diagrams for vanadium species keep similar shapes. Therefore, it is concluded that speciation of iron(II)-picolinate complexes is dependent upon the concentration of iron in model solution under low-picolinate LOMI condition. This phenomenon is attributed to the shortage of picolinate in the solution and

originated from the difference of stability constants between vanadium(III) and iron(II) species.

#### IV. Conclusions

The distribution of vanadium and iron ionic species in the presence of picolinate ligand has been simulated and evaluated at different pH values and various compositions of the model waste solution. A computer program was useful for the calculation of the speciation of metal picolinate complexes.

In spite of the variations of metal concentration, there are little differences in the shape of distribution diagrams under the high-picolinate LOMI condition if the molar ratio of picolinate to metal is fixed at a constant value. Also, for a model solution under low-picolinate LOMI condition, it is hard to find out some significant changes in shape of distribution diagrams regardless of the variations of metal concentration in solution.

However, the reduced amount of picolinate from 6 times to 3 times on the basis of vanadium concentration affects shape of distribution diagrams. For vanadium(III)-picolinate complexes, a peak corresponding to the vanadium tris picolinate,  $V(\text{Pic})_3$  is reduced greatly. In case of iron(II)-picolinate complexes, shape of the distribution diagram was changed significantly. In a model solution of low-picolinate LOMI condition, the fraction of iron(II) complex species is maintained at a constant ratio in the region over pH 4. Especially, the speciation of iron(II)-picolinate complexes is dependent upon the concentration of iron in a model solution under the low-picolinate LOMI condition. This phenomenon is attributed to the shortage of picolinate ligand in solution, and originated from the difference of stability constants between vanadium(III) and iron(II) species with picolinate

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Table 1 The Dissociation Equilibria and pKa Values (5~7)

Dissociation Reactions	pKa
$\text{HPic} \rightleftharpoons \text{H}^+ + \text{Pic}^-$	5.21
$\text{V(III)(Pic)}_3^{2+} \rightleftharpoons \text{V}^{3+} + \text{Pic}^-$	5.72
$\text{V(III)(Pic)}_2^+ \rightleftharpoons \text{V(III)(Pic)}_3^{2+} + \text{Pic}^-$	6.56
$\text{V(III)(Pic)}_3 \rightleftharpoons \text{V(III)(Pic)}_2^+ + \text{Pic}^-$	4.07
$\text{V(III)(OH)(Pic)}_3 + \text{H}^+ \rightleftharpoons \text{V(III)(Pic)}_2^+ + \text{Pic}^-$	2.66
$\text{Fe(II)(Pic)}_3^+ \rightleftharpoons \text{Fe}^{2+} + \text{Pic}^-$	4.90
$\text{Fe(II)(Pic)}_2 \rightleftharpoons \text{Fe(II)(Pic)}_3^+ + \text{Pic}^-$	4.10
$\text{Fe(II)(Pic)}_3^- \rightleftharpoons \text{Fe(II)(Pic)}_2 + \text{Pic}^-$	3.30

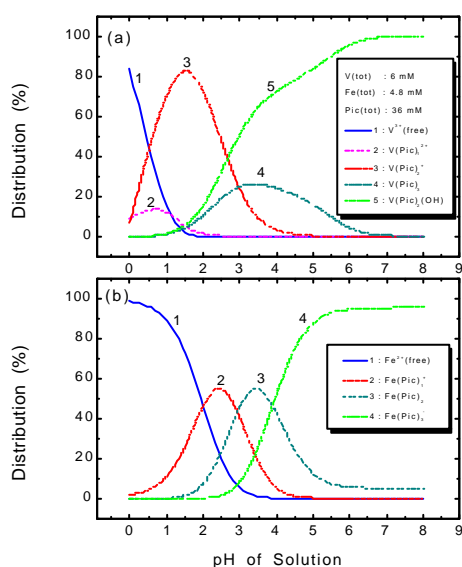


Fig. 1 Distribution diagram of vanadic-picolinate (a), and ferrous-picolinate complexes (b) in the simulated decontamination solution,  $\text{V}^{3+}=6\text{mM}$ ,  $\text{Fe}^{2+}=4.8\text{mM}$ ,  $\text{Pic}^- = 36\text{mM}$

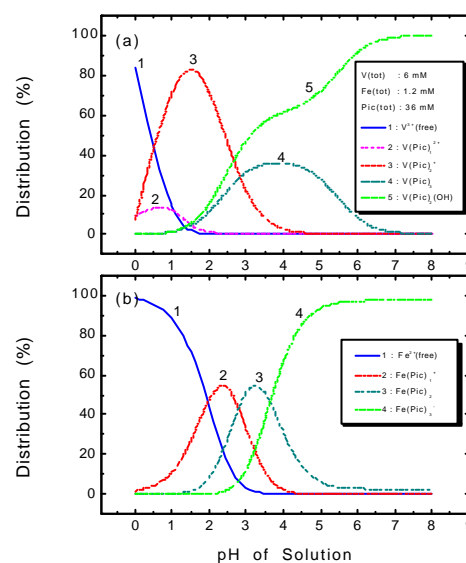


Fig. 2 Distribution diagram of vanadic-picolinate (a), and ferrous-picolinate complexes (b) in the simulated decontamination solution,  $\text{V}^{3+}=6\text{mM}$ ,  $\text{Fe}^{2+}=1.2\text{mM}$ ,  $\text{Pic}^- = 36\text{mM}$

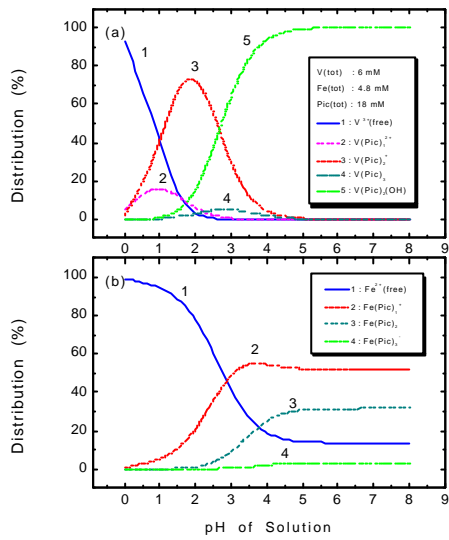


Fig. 3 Distribution diagram of vanadic-picolinate (a), and ferrous-picolinate complexes (b) in the simulated decontamination solution,  $V^{2+}=6mM$ ,  $Fe^{2+}=4.8mM$ , Picolinate= $18mM$

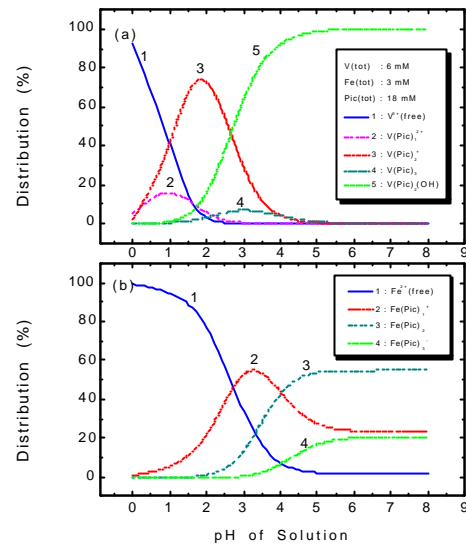


Fig. 4 Distribution diagram of vanadic-picolinate (a), and ferrous-picolinate complexes (b) in the simulated decontamination solution,  $V^{2+}=6mM$ ,  $Fe^{2+}=3mM$ , Picolinate= $18mM$

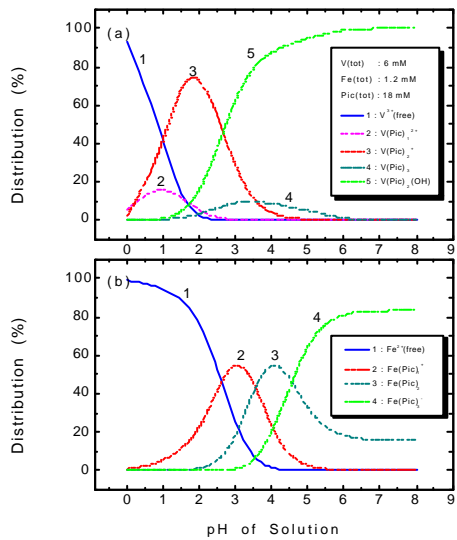


Fig. 5 Distribution diagram of vanadic-picolinate (a), and ferrous-picolinate complexes (b) in the simulated decontamination solution,  $V^{2+}=6mM$ ,  $Fe^{2+}=1.2mM$ , Picolinate= $18mM$