

The role of chemical activities in leaching models and experiments

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Abstract

Acetic acid leachant exhibits leaching that varies with the square root of the concentration. The dependence was thought to arise from the free hydrogen ions resulting from the dissociation of precursor acetic acid. This paper shows that better agreement can be obtained between the experimental and theoretical values by considering hydrogen ion activity rather than concentration. Activities take into account the effects due to other ions that do not participate directly in the chemical reactions and therefore provide a more realistic picture.

1. Introduction

Recently, Cheng and Bishop presented their excellent penetration leaching mode [1]. They observed that the acetic acid leachant did not exhibit leaching in proportion to its concentration. It was found that the extent of leaching varied as the square root of the concentration. This dependency was explained in terms of the free hydrogen ions arising from the dissociation of the precursor acetic acid.

In their experiments, the authors used 15 meq g⁻¹ and 5 meq g⁻¹ acetic acid solutions. The former solution leached approximately 1.65 times as much hardness as the latter. By simple calculation, it was shown that the 15 meq g⁻¹ leachant contains 1.73 times more free hydrogen ions than the leachant of 5 meq g⁻¹ concentration which agreed reasonably well with the experimental value of 1.65.

It is commonly agreed that free hydrogen ions play a dominant or active role

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in leaching. In this communication we show that the ratio of concentration of hydrogen ions (calculated in the same manner as Cheng and Bishop is actually 1.76 and not 1.73, leading to somewhat poorer agreement with the experimental value of 1.65. However, we also show that the agreement between theory and the experiments is far better than has been realized earlier. A better agreement between theory and experiment is obtained by considering the activities and not the concentrations of the hydrogen ions. We emphasize that the activities should be considered (instead of concentration) for at least two reasons; (1) activities represent the concentration of a species which is really effective in causing a chemical change; (2) for a fixed concentration of an acid, the activity of hydrogen ions can change because of the presence of other ions which otherwise do not participate directly in the chemical reactions. Therefore, for testing and simulation of complex systems, such as expected leaching of the waste in landfills, etc., activities take into account the effects of non-participating material and thus are more realistic.

2. The ratio of concentration of hydrogen ions in 15 meq g⁻¹ and 5 meq g⁻¹ acetic acid (AA) solutions

The characteristics of the two acetic acid solutions are given in Table 1.

The value of dissociation constant, K_a for AA is $1.75 \cdot 10^{-5} \text{ mol}^2 \text{ l}^{-2}$ at 25°C or $\text{p}K_a = -\log K_a = 4.76$. A simple mathematical treatment of the dissociation equilibrium (also done by Cheng and Bishop [1] in the same manner) leads to the concentration of hydrogen ions in a give solution of:

$$[\text{H}^+] = (K_a \cdot C_a)^{1/2} \quad (1)$$

where C_a is the initial molar concentration of AA. Substituting the values of the analytical concentration of each AA solution and taking the ratio of the concentrations of H^+ ions gives:

$$[\text{H}^+]_{15 \text{ meq g}^{-1}} / [\text{H}^+]_{5 \text{ meq g}^{-1}} = (15.953/5.180)^{1/2} = 1.76$$

and not 1.73.

TABLE 1

Characteristics of the acetic acid (AA) solutions using densities [2].

Solution (meq g ⁻¹)	%AA (g g ⁻¹)	Density (g ml ⁻¹)	Concentration (mol l ⁻¹)
15	90	1.0663	15.953
5	30	1.0388	5.180

3. Ionic processes in solutions

The chemical reactions in which ions participate naturally depend on the number or concentrations of the ions. However, a fact often neglected is that ions carry electrical charges and the presence of other ions can influence the electrostatic interactions between ions. These ions can arise from the same substance (acetic acid in the present case) or from other substance. The ions of the latter influence the properties of the former. If the second substance has an ion common with the former, the solubility and other properties are influenced through the common ion effect.

Even when there is no common ion, the ions from the second substance influence the electrostatic environment and the abilities of the ions to participate in a chemical reaction. The ions in solution do not exist as bare single species. Each ion is found in an ionic atmosphere of oppositely charged ions, which reduces its mobility and ability to interact with other ions, i.e. the ions participating in chemical reactions are shielded from each other, decreasing their effective concentration. Thus, in summary, in ionic reactions two factors must be considered: (a) concentration, (b) electrostatic interactions. The electrostatic interactions can be measured by ionic strength, I , defined as:

$$I = \frac{1}{2} \sum (C_i \cdot Z_i^2) \quad (2)$$

where C_i is the concentration of an i th ion of charge Z_i . The ionic strength of an electrolyte which forms ions of unit charge is equal to the concentration of the ions. For example, a 0.1 M solution of NaCl completely dissociates to form sodium and chloride ions in concentrations of 0.1 M each. The ionic strength of such a solution is:

$$\begin{aligned} I &= \frac{1}{2} (C_{\text{Na}^+}) \times Z_{\text{Na}^+}^2 + C_{\text{Cl}^-} \times Z_{\text{Cl}^-}^2)^{1/2} \\ &= \frac{1}{2} (0.1 \times (1)^2 + 0.1 \times (-1)^2) = 0.1 \text{ M} \end{aligned}$$

For two solutions identical in concentration but containing ions of different charges, the ionic strength can vary drastically. For example, for solutions of NaCl and MgSO_4 identical in concentration, the ionic strength of the latter solution is four times that of the former. The ionic atmosphere generated from ions of higher charges is much stronger than one created by lower charges. Solutions containing even small amounts of higher charged ions will have much higher ionic strength. The presence of diverse salts (having no common ions) can influence the dissociation of weak electrolytes or the solubility of the precipitate. Activity coefficient (f) and activity (a) explain such chemical reactions more accurately. Activity and concentrations are related as follows:

$$a = f \cdot c \quad (3)$$

The "effective concentration" of ions or other substance is called activity. Activity can change mathematically whenever the numerical value of f changes.

But why should the value of f change? The value of f and, thus, a depends on the concentrations and nature of the various ions present in the solution. Activities and the activities coefficient of an i th ion in the solution can be measured or calculated mathematically from the following simple Debye-Hückel equation:

$$\log(f_i) = -0.509Z_i(I)^{1/2} \quad (4)$$

Using eq. (1), the concentrations of hydrogen ions in two AA solutions are found to be $1.671 \cdot 10^{-2}$ and $9.52 \cdot 10^{-3} M$ and, as shown above for NaCl, the ionic strength of these solutions are identical to the concentrations of H^+ in each solution. Using these values of I , the activity coefficient for H^+ in $15.953 M$ AA solution is 0.86 and the activity is $1.439 \cdot 10^{-2} M$, while in $5.180 M$ solution the activity coefficient is 0.892 and the activity is $8.501 \cdot 10^{-3} M$ and the ratio of activities of hydrogen ions is 1.692, which is in excellent agreement with experimental observations. The difference between 1.76 and 1.65 is about 6% but the difference is only 2.4% between 1.69 and 1.65. The observed value of 1.65 for penetration leaching is better explained when activities rather than concentrations are used. However, it is even more important to consider the activities of the leaching solution.

The calcium ions leached from the cement are expected to have pronounced effect as mentioned earlier. The role of the calcium ions has not been considered here because no data for its concentration were available. If the role of calcium ions had been considered in our discussion, the agreement would have been even better. The role of higher valent ions is important in radioactive or mixed wastes where trivalent and trivalent ions are encountered. These ions may enhance leaching. Work is in progress to estimate the effects of higher valent ions in leaching radioactive or mixed wastes.

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References

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