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Research on the pH of Discharged Acidic Wastewater and its Mathematical Model of Turbulence

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ABSTRACT

The discharge of acidic wastewater impacts the acidity of the receiving water. The interplay process can directly determine the level of water pollution and the living environment of aquatic organisms. However, in contrast to the weighted combination model commonly applied for the concentration of other pollution factors, consistency diffusion and ion balance are also combined determinants for changes in mixed water acidity. This leads to complexity in accurately calculating the pH. This paper analyses the process of ion balance. Considering the influence of carbonic acid on the pH, the authors constructed a two-dimensional turbulent mathematical model based on the pH of discharged acidic wastewater. The research was carried out through experiments on mixing acidic wastewater and standing water, discharging the water pool through an open channel to examine the simplified calculation method and developing calculation model for the pH. The results show that in the complete mixing experiment, which considers the influence of carbonic acid balance, the estimated result is consistent with the actual measured result with a maximized relative error of 2.9%. In the still water pool experiment, the authors supposed that the pH model of acidic wastewater discharge is influenced by dispersion effects, and diffusion and ion balance can relatively accurately simulate changes in the receiving water pH. The consequence is that the simulated value is in accordance with the actual measured value.

INTRODUCTION

As one of the most common industrial wastewaters, acidic wastewater, with pH below 6, mainly comes from chemical factories, power plants and mines that produce wastewater (Luo et al. 2009). The low pH of acidic wastewater increases the solubility of metal compounds. After being discharged into receiving waters, the low pH and high concentration of metal ions can produce significant adverse impacts on the ecosystem (including physical, chemical, biological and ecological impacts). In a bad situation, the discharge of acidic wastewater can lead to the death of fish, algae, plankton and a large number of aquatic organisms. In a worse situation, even sensitive species inhabiting biological communities will disappear, which will result in the simplification of the food chain and a great reduction in the stability of the ecosystem. When wastewater flows through the surface of the earth, the long-term accumulation of wastes will lead to the acidification of soil, consequently producing harmful effects on crops (Herlihy 1990, Cong 2003, Jia 2009 and Park 2015).

In contrast to the simple weighted mixing method of the pollution concentration factor, the precise calculation of wastewater pH is very complicated because of changes in the mixing water acidity, which is affected by the diffusion of its concentration and the combined effects of OH^-, HCO_3^-, and CO_3^{2-}. Considering the need for fast calculations in practical applications, the completely mixed dilution model (Xia et al. 1989) is commonly applied as a traditional calculation method for wastewater pH. Another condition is that when only the transportation and diffusion effects of materials are considered, the ion balance process will exert a huge influence on the calculation result with relatively greater error. Therefore, simulations of the pH should not only consider the pattern of transportation and diffusion of hydrogen ions, but at the same time should also obey the coupling law of water chemical equilibrium.

Based on relations between natural water and its different components, Qian Hui (1996) and other researchers calculated the mixed water pH under different mixing proportions. The results showed that the pH of mixed water is not a linear function of the mixing proportion, correcting the idea that the mixed water pH and mix proportion has an approximately linear relationship. However, their research focused on the pH calculation of two kinds of completely mixed waters, regardless of pH changes in the process of water transportation. Based on the transportation and diffusion theory of normal pollutants, Xun & Zhang (2001) and fellow researchers determined the distribution of the acid-base pollution zone in a two-dimensional uniform flow. On this basis, the research considered hydrogen ion concentration changes caused by the combination of carbonate ions and hydrogen ions. The research thus determined the pollution zone of hydrogen ions. The limit of the research lies in the lack of simultaneous consideration of transport diffusion and ion balance effects, resulting in relatively large calculation errors for the pollution zone of hydrogen ion. This can further affect the calculation of the concentration of other pollutants in acidic environments.

In other words, this paper comprehensively integrates basic theories of environmental chemistry and environmental hydraulics. Concentrating on the calculation of the pH of specific acid wastewater pollutants and coupling ion balance effects and water transport diffusion effects, this paper establishes a mathematical model of turbulence targeting the pH value of the discharged acidic wastewater. Additionally, an experiment is carried out on completely mixed acid wastewater, and a prediction model is developed for wastewater discharge under the influence of transportation and diffusion effects in water flow.

ANALYSIS AND ESTABLISHMENT OF THE MATHEMATICAL MODEL OF TURBULENCE FOR THE pH OF DISCHARGED ACIDIC WASTEWATER

When acidic wastewater is discharged into the receiving water, H^+ undergoes a hydrolysis balance process with OH^-, HCO_3, and CO_3^{2-} during transportation and diffusion in the water. Therefore, the mathematical model of discharged acidic wastewater includes the ion transportation equation and the ion balance equation.

Ion transportation equation: The ion transportation equation for discharged acidic wastewater mainly includes water dynamics equation and the ion transportation equation. A detailed description is as follows:

Continuity equation:

$$\frac{\partial^2(\rho U_i)}{\partial X_i} = 0 \qquad \text{...(1)}$$

Momentum equation:

$$\frac{\partial(\rho U_i U_j)}{\partial X_j} = -\frac{\partial P}{\partial X_i} + \frac{\partial}{\partial X_j}\left[(\mu + \mu_t)\left(\frac{\partial U_i}{\partial X_j} + \frac{\partial U_j}{\partial X_i}\right)\right] \qquad \text{...(2)}$$

In the equation, *p* represents the density of the water. According to practical characteristics of the discharged wastewater, changes in the water density are ignored in the process of acidic wastewater discharge. X_i and X_j represent the direction of *i* and *j*. U_i and U_j represent the value of the directed speed. μ represents the dynamic viscosity. μ_t represents the viscosity of turbulence. The expression is:

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \qquad \text{...(3)}$$

Equation *k*:

$$\frac{\partial(\rho U_i k)}{\partial X_i} = \frac{\partial}{\partial X_i}\left[(\mu + \frac{\mu_t}{\sigma_k})\frac{\partial k}{\partial X_i}\right] + \mu_t\left(\frac{\partial U_i}{\partial X_j} + \frac{\partial U_j}{\partial X_i}\right)\frac{\partial U_i}{\partial X_j} - \rho\varepsilon \qquad \text{...(4)}$$

Equation ε:

$$\frac{\partial(\rho U_i k)}{\partial X_i} = \frac{\partial}{\partial X_i}\left[(\mu + \frac{\mu_t}{\sigma_\varepsilon})\frac{\partial \varepsilon}{\partial X_i}\right] + \mu_t\left(\frac{\partial U_i}{\partial X_j} + \frac{\partial U_j}{\partial X_i}\right)\frac{\partial U_i}{\partial X_j} - \rho\varepsilon \qquad \text{...(5)}$$

In the equation, $C_{\varepsilon 1}$, $C_{\varepsilon 2}$, σ_k, and σ_ε are empirical constants and are separately adopted as 1.44, 1.92,1.0 and 1.3.

Transportation and diffusion equation of the H^+ density:

$$\frac{\partial C_{H^+}}{\partial t} + \frac{\partial(C_{H^+}U_i)}{\partial X_i} = \frac{\partial}{\partial X_i}\left\{(\mu + \frac{\mu_t}{\sigma_t})\frac{\partial C_{H^+}}{\partial X_i}\right\} \qquad \text{...(6)}$$

Transportation and diffusion equation of the OH^- density:

$$\frac{\partial C_{OH^-}}{\partial t} + \frac{\partial(C_{OH^-}U_i)}{\partial X_i} = \frac{\partial}{\partial X_i}\left\{(\mu + \frac{\mu_t}{\sigma_t})\frac{\partial C_{OH^-}}{\partial X_i}\right\} \qquad \text{...(7)}$$

Transportation and diffusion equation of the H_2CO_3 density:

$$\frac{\partial C_{H_2CO_3}}{\partial t} + \frac{\partial(C_{H_2CO_3}U_i)}{\partial X_i} = \frac{\partial}{\partial X_i}\left\{(\mu + \frac{\mu_t}{\sigma_t})\frac{\partial C_{H_2CO_3}}{\partial X_i}\right\} \qquad \text{...(8)}$$

Transportation and diffusion equation of the HCO_3^- density:

$$\frac{\partial C_{HCO_3^-}}{\partial t} + \frac{\partial(C_{HCO_3^-}U_i)}{\partial X_i} = \frac{\partial}{\partial X_i}\left\{(\mu + \frac{\mu_t}{\sigma_t})\frac{\partial C_{HCO_3^-}}{\partial X_i}\right\} \qquad \text{...(9)}$$

Transportation and diffusion equation of the CO_3^{2-} density:

$$\frac{\partial C_{CO_3^{2-}}}{\partial t} + \frac{\partial(C_{CO_3^{2-}}U_i)}{\partial X_i} = \frac{\partial}{\partial X_i}\left\{(\mu + \frac{\mu_t}{\sigma_t})\frac{\partial C_{CO_3^{2-}}}{\partial X_i}\right\} \qquad \text{...(10)}$$

Ion balance equation: Considering that the speed of reac-

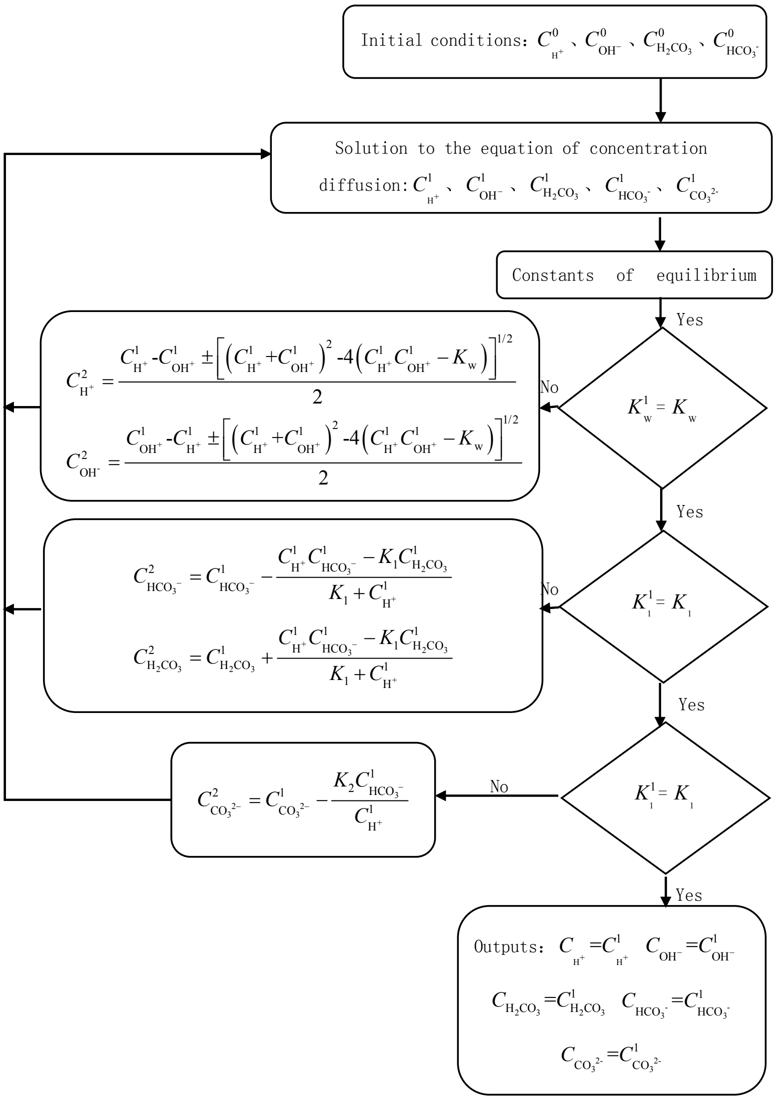

Fig. 1: Coupling process of ion transportation and ion balance (including the ions H^+, OH^-, HCO_3^-, and CO_3^{2-}).

tion between H^+ in the acidic wastewater and HCO_3^- in the water is relatively rapid and the transformation of CO_2 into gas and liquid water is slow (Tang et al. 1989), this paper consequently ignores CO_2 transformation between gas and mixed water as well as the influence of CO_2 in the air on the carbonic acid balance. This paper mainly focuses on the balance between H^+ and OH^-, H^+ and HCO_3^-, and H^+ and CO_3^{2-}. The balance equations are as follows:

Equilibrium equation for the H^+ and OH^- concentration:

$$H_2O \rightleftharpoons H^+ + OH^- \quad ...(11)$$

$$C_{H^+} = \frac{K_w}{C_{OH^-}} \quad ...(12)$$

Equilibrium equation for the H^+ and HCO_3^- concentration:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad ...(13)$$

$$C_{H^+} = \frac{K_1 C_{H_2CO_3}}{C_{HCO_3^-}} \quad ...(14)$$

Equilibrium equation for the H^+ and CO_3^{2-} concentration:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad ...(15)$$

$$C_{H^+} = \frac{K_2 C_{HCO_3^-}}{C_{CO_3^{2-}}} \quad ...(16)$$

In the equations, K_1, K_2 and K_w are the first and second

Table 1: The conditions for mixing acidic water (pH=1.0) and tap water (pH=8.0).

Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Proportion	1:1	1:2	1:3	1:4	1:9	1:19	1:23	1:25	1:29	1:31	1:33	1:35	1:37	1:39

Table 2: The conditions for mixing acidic water (pH=2.0) and tap water (pH=8.0).

Number	1	2	3	4	5	6
Proportion	1:1	1:2	1:3	1:4	1:9	1:19

Table 3: Boundary conditions of the experiment.

Fracture surface	Flow speed (m/s)	pH	$C_{H_2CO_3}$ (mg/L)	$C_{HCO_3^-}$ (mg/L)
Flow from water tank	0.145	7.3	18.6	140.3
Flow of acidic wastewater	0.85	1.5	161.2	0

dissociation constants of H_2CO_3 and the dissociation constant of water. At normal temperature, their values are $10^{-6.5}$, $10^{-10.3}$ and 10^{-14}.

Coupled solution to ion transportation and ion balance: The density transportation equations of ions were identified by adopting the finite volume method. Assuming that the hydration and hydrolysis of ions occur within a very short time and, at the end of each time step, H^+, OH^-, HCO_3^-, and CO_3^{2-} can reach reaction equilibrium within every grid, the user-defined functions can be amended. The initial value of ion density is calculated by the diffusion equation. Based on the equilibrium equation of ions, hydration and hydrolysis processes are analysed and calculated. The ion density is also guaranteed to obtain the ion balance state. The coupling process of H^+ and the OH^-, HCO_3^-, and CO_3^{2-} density is shown in Fig. 1.

VERIFICATION OF THE CALCULATED pH OF FULLY MIXED WATER

Considering the influence of the carbonate equilibrium on the pH simulation method, this research first carried out a fully mixed water experiment and verified that the pH value is influenced by the ion balance process without ion transportation.

The initial experiment mixed acidic water, with pH values of 1.0 and 2.0, with tap water, with a pH value of 8.0, at different proportions. The different conditions are listed in Table 1 and 2. The pH is measured after the water was mixed, adopting a glass-electrode method (GB/T5750.6-20064.2).

The initial concentration of ions in the fully mixed water with different pH values is calculated based on the weighted average method. For example, the weighted computation formula of H^+ ions is as follows:

$$C^*_{H^+} = \frac{C^1_{H^+}V_1 + C^2_{H^+}V_2}{V_1 + V_2} \quad ...(17)$$

In the equation, C_{H+}^* represents the initial concentration of H^+ in the mixed water. C_{H+}^1 and C_{H+}^2 respectively, represent the concentration of H^+ before mixing. V_1 and V_2 are identified as the volume of the solution before mixing. The initial OH^- concentration (C_{OH-}) is calculated based on the equation (17).

The concentration of ions is considered as the initial concentration value. Based on the method recommended in Fig. 1, the ion balance effect is measured. A comparison of the calculated pH and the actual measured pH is shown in Figs. 2 and 3.

The relationship between the calculated pH and the measured pH was determined, as shown in Fig. 2 and Fig. 3. It was identified that the maximum relative calculation error is 2.7% when acidic water with pH 1.0 was mixed with tap water with pH 8.0. When the pH of the acidic water was altered to 2.0, the maximum relative calculation error appeared to be 2.9%. The results show that the carbonate balance impacts the pH of the mixed water, which validates the hypothesis of this paper.

VERIFICATION OF THE pH OF DISCHARGED ACIDIC WASTEWATER AND ITS MATHEMATICAL MODEL OF TURBULENCE

An acidic wastewater discharge experiment in a still water pool further verified the reliability of the turbulence math-

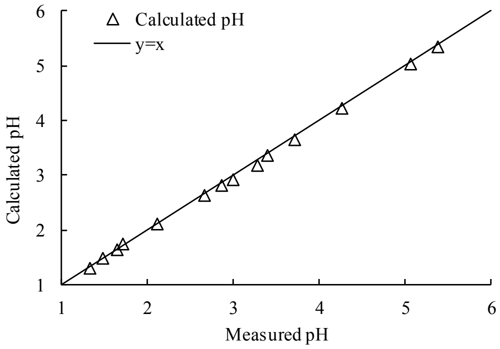

Fig. 2: Comparison between the calculated pH and the measured pH (the acidic water pH is 1.0, and the tap water pH is 8.0, with different proportions of the two).

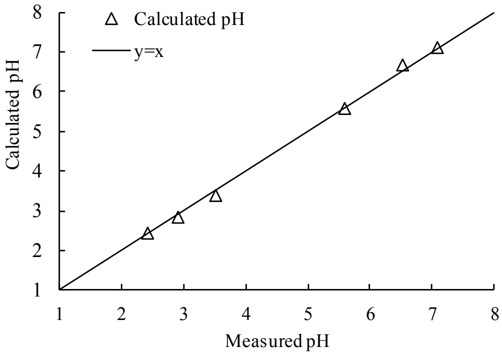

Fig. 3: Comparison between the calculated pH and the measured pH (the acidic water pH is 2.0, and the tap water pH is 8.0, with different proportions of the two).

ematical model, which is mutually affected by water transportation and ion balance.

The experimental setup consists of a still water pool, a supply tank for the acidic wastewater, a wastewater overflow box and so on. Acidic wastewater is discharged in a constant and continuous manner. During the process, acidic wastewater with a specific pH is supplied by the supply tank and flows to the overflow box. The water level inside is controlled through the overflow tube above the box. By doing so, a constant wastewater flow rate is guaranteed. The setup for discharging acidic wastewater and the sampling point are shown in Fig. 4.

In the stable discharging process of the water used in the experiment and wastewater, the water samples on fracture surfaces with values of X=0.80 m and X=1.75 m were collected to measure the pH. The pH measurement adopted the glass-electrode method (GB/T5750.6-20064.2).

In the experiment of discharging acidic wastewater in an open channel, the pH and flow speed were the examined conditions and are shown in Table 3.

This research adopted a two-dimensional numerical model of pH turbulence. Consequently, the distribution of the pollutant zone was simulated, as shown in Fig. 5. Comparisons between the simulation result of the open channel experiment and the actual measured result are given in Figs. 6 and 7.

As seen in Fig. 6, on the fracture surface with X=0.8 m, the calculation error in the simulated pH and measured pH shows a tendency to first increase and then decrease, with an absolute error range of 0.0 to 0.4 and a relative error range of 0.00% to 13.0%. As seen in Fig. 7, on the fracture surface with X=1.75 m, the calculation error in the simulated pH and measured pH shows a tendency to fluctuate, with an absolute error range of 0.0 to 0.1 and a relative error range of only 0% to 4.82%. The simulated pH and measured pH are similar. The results show that the dis-

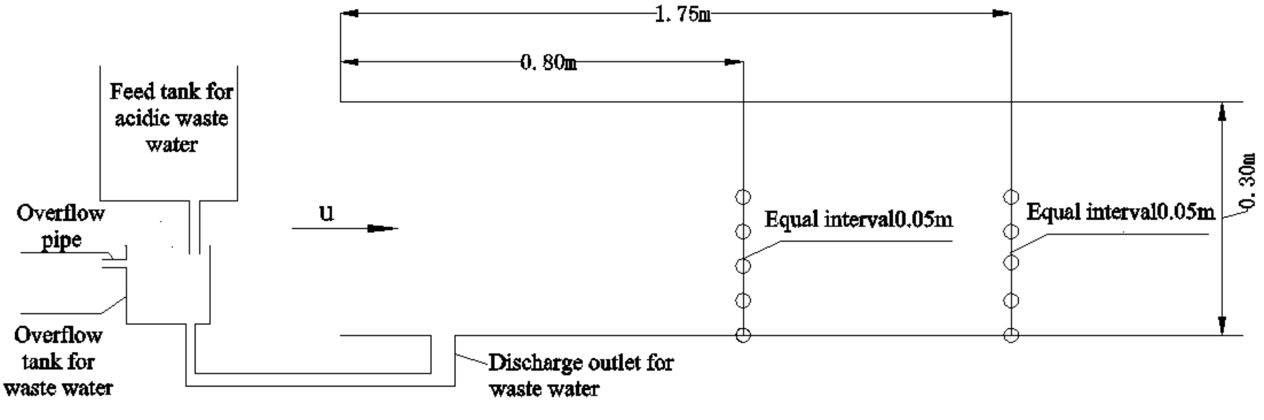

Fig. 4: Setup for the discharge of acidic wastewater and sampling point diagram.

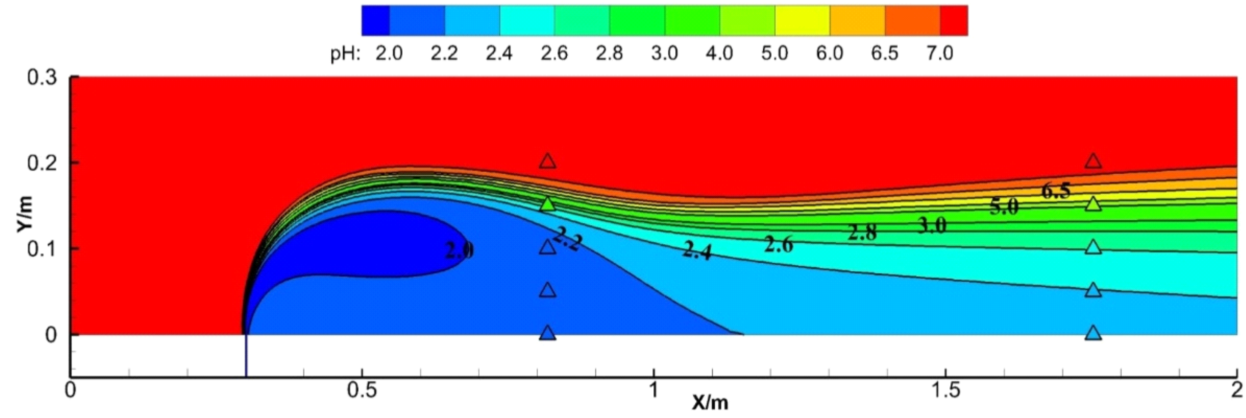

Fig. 5: A two-dimensional pH turbulence numerical simulation of the pollution zone distribution.

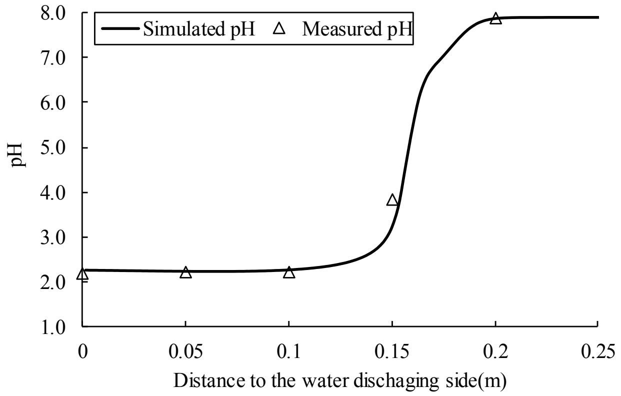

Fig. 6: Comparison between the simulated pH on the fracture surface (X=0.80 m) and the measured pH.

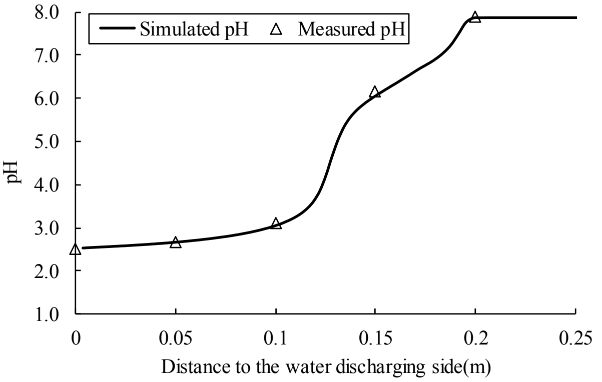

Fig. 7: Comparison between the simulated pH on the fracture surface (X=1.75 m) and the measured pH.

charged acidic wastewater pH and its mathematical model of turbulence, established based on the coupling effect of ion transportation and ion balance, can produce reliable results.

CONCLUSION AND FURTHER STUDIES

This research considered the influence of carbonate balance and carried out a still water hybrid experiment and acidic wastewater experiment in an open channel with different proportions of media. The results showed that for the calculation of the pH of fully mixed water, a smaller difference between the calculated result and the measured results is obtained when the carbonate balance is considered, with a maximum relative error of 2.9%. When the accuracy of the experiment is guaranteed, the pH of mixed water can be predicted using this method. The simulated results of acidic wastewater discharged into an open channel are in good agreement with the experimental results, with a maximum relative error of 13.0%. This model can predict changes in the pH when wastewater is discharged into water, directly or accidentally.

This research established a pH value simulation model that can relatively accurately simulate the distribution of the pH. This work can instruct practical situations, such as determining the volume of chemicals to add to wastewater, improving the processing efficiency and reducing the cost of water treatment. The model is also of both theoretical and practical value for the treatment and risk prediction of wastewater.

The experiments were conducted in an open carbonate balance system, ignoring the influence of CO_2 on the carbonate balance. The still water hybrid experiment concerned the mixing of acidic water (pH=1.0, pH=2.0) with another water (pH=8.0). The experiment concerning acidic wastewater discharge in an open channel considered the condition of pH=1.5. Whether the given model can adapt to other circumstances requires further research in this field.

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