Effect of acid on the strength of solidified sewage sludge

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Abstract. The solidification technology can meet the requirements of landfill by enhancing the sewage sludge strength. The solidified sludge strength would be decreased by landfill leachate action because the acid could dissolve the hydrated materials. Chemical kinetics equation was obtained by reaction order α, β and rate constant k, which reflected the acid effect on hydrated materials by Ca²⁺ and were got based on the laboratory experiments. The research results showed that the strength loss could be neglected in engineering because pH value of leachate possessed less impaction on solidified sludge strength. Moreover, after adding clay minerals, the strength loss is smaller and the buffering capacity is stronger.

1. Introduction
It was one of the commonly used disposal technologies at home and abroad to backfill sludge in domestic waste landfills or used as cover soil for resource utilization[1-2]. Due to the high moisture content and low strength of sludge, direct landfill disposal without treatment is likely to cause landfill engineering accidents. To improve the physical and mechanical properties of sludge, the most commonly used method at present is adding cement, lime and corresponding auxiliary solidification materials to the sludge. Current researches mainly focus on the selection of solidified materials, the strength of solidified sludge and the evaluation of secondary pollution[3-5]. However, the long-term service performance of solidified sludge under complex biochemical conditions of landfill needs to be considered when it is buried in the landfill or used as cover soil. In addition to the influence of soaking and softening on the strength of solidified sludge[6], the acidic landfill leachate with pH value in the range of 1.5 to 9.5 also has a certain effect on the strength of solidified sludge[7]. The generation of strength and change of mechanical properties after sludge solidification mainly depend on the hydration products produced by cement hydration. The hydration products can generally exist stably under alkaline conditions but inevitably decompose once under acidic conditions[8], which affects the stability of the solidified body.

Aiming at the effect of acid on the long-term strength of solidified sludge, a quantitative relationship among the decomposition amount of hydration products, the pH value of acid and the reaction time is established using chemical kinetic method, and the relationship between the decomposition amount and strength loss of hydration products is simulated by laboratory tests. The strength loss rate of solidified sludge with acid with different pH values and action time is obtained from the relationship.
2. Experimental materials

The sludge used in the test was dehydrated sludge taken from a sewage treatment plant. In order to increase the proportion of inorganic particles in the sludge, waste dredged silt was selected as the auxiliary solidification material to improve the solidification effect and reduce the cost of solidification treatment[9]. The 325 ordinary portland cement is adopted. The basic indicators of sludge and silt are shown in table 1.

Five preparation ratios namely 5: 0.5: 2, 5: 1: 2, 5: 2: 0, 5: 2: 1, 5: 2: 2 (mass ratio of sludge, cement and silt) were selected to prepare solidified sludge. Mix them evenly and put them in a curing box of constant temperature and humidity for 28 days.

Table 1. Basic properties of sludge and silt.

| Sample  | Moisture content (%) | Specific Gravity | Void Ration (%) | Liquid Limits (%) | Plastic limits (%) | Organic Matter (%) |
|---------|----------------------|------------------|----------------|-------------------|-------------------|-------------------|
| Sludge  | 664                  | 1.61             | 11.6           | 380               | 160               | 56.29             |
| Silt    | 120                  | 2.74             | 3.3            | 73                | 29                | 1.39              |

3. Chemical kinetics equation

3.1. Chemical kinetics equation of acid and hydration products

Under certain temperature and pressure environments, the reaction rate $\gamma$ of reaction equation: $A + B + C + \ldots \rightarrow P$ can be expressed by the following equation:

$$\gamma = k[A]^x[B]^y[C]^z$$

where $[A]$, $[B]$, $[C]$ represents the concentration of reactant, $x$, $y$, $z$ is the reaction order, $k$ is the reaction rate constant, independent of reactant concentration but related to the temperature and pressure of chemical reaction[10].

Assuming that the reaction between hydration product and acid is an n-order reaction, the chemical equation can be expressed as:

$$C-M+H^+\rightarrow Ca^{2+}+M+H_2O$$

where $M$ represents the groups in different hydration products. The chemical kinetic equation of the reaction between hydration product and acid at temperature $T$ can be expressed as follows:

$$\gamma = \frac{d[Ca^{2+}]}{dt} = k[C-M]^a[H^+]^b$$

where $\gamma$ is the reaction rate, $[Ca^{2+}]$, $[C-M]$ and $[H^+]$ represent the concentration of $Ca^{2+}$, hydration products and acids in the reaction system respectively, $a$ and $b$ are the reaction order of hydration products and acids, $k$ is the rate constant and $t$ is the reaction time. The parameter $\gamma$ can be determined by experiment, and the required parameters are $k$, $a$ and $b$. According to the calculation method provided in [11], it can be obtained by reasonably arranged experiments, as shown in table 2.

According to equation (3) and table 2:

$$\gamma_1 = \frac{d[Ca^{2+}]}{dt_1} = k[C-M]^a[H^+]^b$$

$$\gamma_2 = \frac{d[Ca^{2+}]}{dt_2} = k[C-M]^a[H^+]^b = k[C-M]^a[H^+]_2^b$$

$$\gamma_3 = \frac{d[Ca^{2+}]}{dt_3} = k[C-M]^a[H^+]^b = k[C-M]^a[H^+]_3^b$$

Table 2. Test plan for solidified sludge and acid reaction.

| Number | [C-M] (mol/l) | [H+] (mol/l) | $T$ (h) | [Ca$^{2+}$] (mol/l) |
|--------|----------------|---------------|---------|---------------------|
| 1      | $[C-M]_1$     | $[H^+]_1$    | $t_1$   | $[Ca^{2+}]_1$      |
| 2      | $[C-M]_2$     | $[H^+]_2$    | $t_2$   | $[Ca^{2+}]_2$      |
| 3      | $[C-M]_3$     | $[H^+]_3$    | $t_3$   | $[Ca^{2+}]_3$      |
From equations (4), (5) and (6), the parameters of the chemical kinetic equation for the reaction between hydration product and acid can be obtained:

\[
\alpha = \frac{\lg \gamma_1 - \lg \gamma_2}{\lg [C-M]_1 - \lg [C-M]_2}, \quad (7)
\]

\[
\beta = \frac{\lg \gamma_1 - \lg \gamma_2}{\lg [H^+]_1 - \lg [H^+]_2}, \quad (8)
\]

\[
k = \frac{\gamma_1}{[C-M]_0 [H^+]_0^\beta}, \quad (9)
\]

3.2. Reaction test of acid with hydration products

According to the above test method and kinetic equation, the chemical kinetic parameters of the reaction between solidified sludge and acid are calculated as shown in table 3.

It can be seen that the kinetic parameter \( \alpha \) of the reaction between solidified sludge and acid can be approximately 0.5 and \( \beta \) is approximately 1.5. The value of \( k \) decreases gradually, which means that the reaction rate with acid is slower in the case of high consolidation degree and low reaction temperature.

3.3. Calculation of decomposition amount of hydration products

Assuming that the initial concentration of hydration product and acid are \( A \) and \( B \), the decomposition amount of hydration product after time \( t \) is \( x \), that is, the amount of \( \text{Ca}^{2+} \) generated is \( x \), then \( 2x \) of the amount of acid is consumed. According to equation (3) and obtained \( \alpha \) and \( \beta \) values:

\[
\frac{dx}{dt} = k(A - x)^{0.5} B^{1.5} \quad (10)
\]

By integrating equation (10), we can get:

\[
\int_0^x \frac{1}{\sqrt{A-x}} \, dx = \int_0^t k B^{1.5} \, dt \quad (11)
\]

The \( \text{Ca}^{2+} \) concentration generated after time \( t \) can be obtained, that is, the amount of reacted hydrated product is:

\[
b = A - \left(\sqrt{A - a} - \frac{ktB^{1.5}}{2}\right)^2 \quad (12)
\]

Table 3. Chemical kinetic parameters of solidified sludge and acid reaction.

| Parameters | Samples | \( T \) (°C) | 20      | 30      | 40      |
|-----------|---------|-------------|---------|---------|---------|
| \( \alpha \) | 5:2:0   | 0.52        | 0.52    | 0.42    |
|           | 5:2:1   | 0.48        | 0.38    | 0.52    |
|           | 5:2:2   | 0.56        | 0.41    | 0.49    |
|           | 5:0.5:2 | 0.47        | 0.53    | 0.49    |
|           | 5:1:2   | 0.46        | 0.46    | 0.51    |
| \( \beta \) | 5:2:0   | 1.43        | 1.42    | 1.41    |
|           | 5:2:1   | 1.48        | 1.55    | 1.43    |
|           | 5:2:2   | 1.48        | 1.42    | 1.42    |
|           | 5:0.5:2 | 1.41        | 1.46    | 1.39    |
|           | 5:1:2   | 1.40        | 1.39    | 1.45    |
| \( k \)   | 5:2:0   | 5.232E-02   | 6.580E-02| 9.262E-02|
|           | 5:2:1   | 6.599E-04   | 7.372E-03| 3.538E-02|
|           | 5:2:2   | 6.144E-05   | 2.150E-03| 1.255E-02|
|           | 5:0.5:2 | 1.364E-02   | 4.394E-02| 4.973E-02|
|           | 5:1:2   | 1.513E-03   | 2.396E-03| 3.158E-02|
4. Strength of solidified sludge under the action of acid

4.1. Relationship between decomposition amount and strength of hydration product

In order to obtain the relationship between the reduction of hydration products and the loss of strength caused by acid action of solidified sludge within laboratory time scale, measures such as increasing the acid concentration and vacuum saturation were adopted to shorten the time scale. The specific experimental scheme is as follows:

(1) Curing the solidified sludge for 28 days with different ratio. The solid-liquid ratio is 1:10 and the leachate is deionized water. The total amount of soluble Ca\(^{2+}\) is determined;

(2) Unconfined compressive strength test was conducted after the sample was vacuumed and saturated in hydrochloric acid of different concentrations for 24h. The vacuumed container was transformed from a plastic bucket;

(3) Determining the total amount of Ca\(^{2+}\) dissolved in hydrochloric acid in step (2);

(4) After the damaged sample was air-dried and crushed, the total amount of Ca\(^{2+}\) is determined according to the solid-liquid ratio of 1:10, the leaching liquid is deionized water;

(5) Adding the amounts of Ca\(^{2+}\) obtained from (3) and (4) and subtracting the amount of Ca\(^{2+}\) obtained from (1) is the amount of hydrated products decomposed under the action of acid.

The relationship between the amount of hydration product decomposition (ie, loss amount of Ca\(^{2+}\)) and strength loss of solidified sludge with different ratios under the action of acid was obtained using the above experimental scheme.

Table 4 compares the Ca\(^{2+}\) ion loss difference between the calculated value and the measured value. It can be seen that the average relative error between hydration product decomposition rate (Ca\(^{2+}\) ion loss amount) calculated using formula (12) and experimentally measured is about 15.9%, which is satisfactory for the accuracy of engineering calculations.

| Samples | Time(h) | Acid Concentration(mol/l) | Hydration Product Decomposition Rate |
|---------|---------|---------------------------|-------------------------------------|
|         |         |                           | Test Value | Calculated Value |
| 5:0.5:2 | 48      | 0.2                       | 2.23       | 2.78             |
|         |         | 0.3                       | 4.14       | 5.07             |
|         |         | 0.4                       | 6.84       | 7.76             |
|         | 264     | 0.2                       | 1.21       | 1.43             |
|         |         | 0.4                       | 3.08       | 4.00             |
|         |         | 0.6                       | 5.89       | 7.29             |
| 5:2:0   | 48      | 1.0                       | 0.54       | 0.56             |
|         |         | 2.0                       | 1.09       | 1.58             |
|         |         | 3.0                       | 2.24       | 2.89             |
|         | 264     | 0.1                       | 2.08       | 2.42             |
|         |         | 0.3                       | 11.32      | 12.24            |
|         |         | 0.5                       | 21.12      | 25.34            |
| 5:2:1   | 264     | 0.4                       | 1.18       | 1.42             |
|         |         | 0.6                       | 2.31       | 2.60             |
|         |         | 0.8                       | 3.75       | 3.99             |

4.2. Long-term strength of solidified sludge under the action of acid

In this paper, the strength loss rates of solidified sludge with different proportions from 10 years to 90 years under two conditions of pH=4 and pH=5 are calculated, as shown in table 5. It can be seen from table 5 that the pH value of leachate has little effect on the strength of the solidified sludge, which is basically negligible.

5. Conclusion

(1) Ca\(^{2+}\) is used as the landmark ion to characterize the stability of hydration products. The loss of Ca\(^{2+}\) under the action of different concentrations of acids can be quantitatively obtained by the kinetic
equation of the reaction between hydration products and acids.

(2) Under the action of landfill leachate, the strength loss of solidified sludge is basically negligible and will not affect the stability of landfill.

(3) Vacuum saturation and other means were adopted to enhance the acid's ability to dissolve the sample, and the actual permeability of solidified sludge is very low. How to connect the data obtained from the laboratory with the field needs further research.

Table 5. Solidified sludge strength loss ratio under different pH value and time.

| Time | pH=4 | | | | | pH=5 | | | |
|------|------|---|---|---|---|---|---|---|---|
|      | 5:0:5:2 | 5:1:2 | 5:2:2 | 5:2:0 | 5:2:1 | 5:0:5:2 | 5:1:2 | 5:2:2 | 5:2:0 | 5:2:1 |
| 10   | 0.12  | 0.01  | 0.00  | 0.38  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |
| 30   | 0.37  | 0.02  | 0.00  | 1.14  | 0.01  | 0.01  | 0.00  | 0.00  | 0.04  | 0.00  |
| 50   | 0.61  | 0.03  | 0.00  | 1.90  | 0.02  | 0.02  | 0.00  | 0.00  | 0.06  | 0.00  |
| 70   | 0.86  | 0.05  | 0.00  | 2.66  | 0.03  | 0.03  | 0.00  | 0.00  | 0.08  | 0.00  |
| 90   | 1.10  | 0.06  | 0.00  | 3.41  | 0.03  | 0.03  | 0.00  | 0.00  | 0.11  | 0.00  |

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