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Rheology of pure and mineral admixture modified cement pastes and their degradation due to calcium leaching

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Abstract. This paper is to deal with the modeling of compressive strength of leached pastes subjected to aggressive lechant. Firstly, rheology testing was performed on fresh pastes by using Con-Tec Viscometer. The slump flows in relation to rheological parameters were obtained. Then uniaxial compressive test was carried out on both well-preserved and corrosive pastes. The loss of compressive strength has a significant linear correlation with leached ratio for all pastes specimens. Finally, a prediction model forecasting reduction in strength was proposed.

1. Introduction
Cementitious materials have been widely used in nuclear industry, underground buildings or hydraulic structures constantly exposed to aggressive solution such as pure water or soft water. The durability of these constructions is influenced by several factors including both objective factors such as chemical environments and mechanical degradation velocity of the structures themselves. Leaching is one of the important factors affecting the durability of cementitious based materials [1-2].

The flowability of fresh pastes is mainly characterized by traditional experiential testing methods like slump, J ring slump flow, T500, L-type flow instrument, sieve stability and so on. These measurements are usually very susceptible to manipulation, because minor changes in performance could produce different outcomes. For this reason, different test devices have been developed. For example, ConTec used in this study, measure the rheological parameters of fresh cementitious materials, including yield stress and plastic viscosity.

The mechanical behavior of leached cementitious based materials has been proposed in many literatures [3-4]. The compressive strength obviously declined in leaching [5-8]. During chemical degradation, some models have been constructed in order to formulate the chemo-mechanical mechanics and thermodynamic equilibrium [9-11].

During leaching process, mechanical properties degraded a lot and the relationships have been proposed by many investigators, but the functions for predicting the long-term performance of pure cement pastes or mineral admixture modified pastes were published very rarely. This article predicted not only the evolution of rheology of fresh mixtures but also the relationship between reduction in strength of leached pastes with different mix proportions, namely in fly ash contents and water to cement (W/C) ratios.
2. Methods and Materials

2.1. Leaching Solution Selection

The common methods accelerating the calcium leaching procedure are as follows: using relatively high temperature or replacing pure water with accelerated solvent such as nitric acids, hydrochloric acid or some other organic acids. In this study, ammonium chloride (NH₄Cl) solution is prepared and used.

2.2. Materials and Samples

The chemical analysis was performed on cement as well as fly ash and Table 1 proposed the results. Different mineral additions were used as blinder materials. The mineral materials were characterized in the same way as cement and the chemical compositions of them are presented in Table 1. The mixture content was calculated by mass.

| Table 1. Chemical composition of cement and mineral admixtures |
|---------------------------------------------------------------|
| Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | K₂O | TiO₂ | MnO | LOSS |
|---------------|-------|-------|-------|-----|-----|------|-----|------|-----|-------|
| Cement        | 21.70 | 5.09  | 4.32  | 64.64 | 0.92 | 0.21 | 0.53 | 0.14 | -   | 5.38  |
| Fly ash       | 46.45 | 30.35 | 3.98  | 3.18 | -   | -   | -   | -    | -   | -     |
| Slag          | 31.92 | 9.83  | 4.46  | 42.07 | 8.55 | -    | -    | 0.79 | 0.26 | -     |
| Limestone powder | 1.10 | 0.38  | 0.24  | 53.82 | 0.49 | 0.00 | 0.01 | -    | -   | -     |
| Silica fume   | 92.08 | 0.38  | 0.81  | 0.29 | 0.13 | 0.12 | 0.35 | -    | -   | 4.02  |

Cylindrical paste samples with a diameter = 100mm and a height = 200mm were made. They were divided into two groups: test group and contrast group. The former ones were immersed in a 6.0N NH₄Cl solution after curing and the latter ones always cured in saturated limewater. The rheological parameters of fresh concrete were tested by ConTec Viscometer. Then the leaching parameters, for example, the depth of CH dissolution front and compressive strength of both groups were tested during leaching.

3. Results and Discussion

3.1. Workability in fresh statement

The density, air content, T₅₀₀ and slump flow of different mixtures was provided. It can be seen that fly ash and slag could obviously reduce the air content of fresh concrete, leading to the increment of T₅₀₀. The air content of concrete containing limestone powder changed little comparing to the control group, and T₅₀₀ declined slightly only when the dosage was large. The addition of silica fume increased air content of concrete in general, regardless of the addition content. The results are shown in Table 2.

| Table 2. Workability of fresh cementitious materials containing different mixtures |
|-----------------------------------------------|
| Mix No | Mix ID | W/B (-) | Cement (%) | Fly Ash (%) | Slag (%) | Limestone Powder (%) | Silica fume (%) | Density (kg/m³) | Air content (%) | T₅₀₀ (s) | Slump flow (mm) |
|-------|--------|---------|-------------|-------------|----------|---------------------|----------------|----------------|---------------|----------|----------------|
| 1     | P      | 0.34    | 100         | -           | -        | -                   | -              | 2.346          | 5.5           | 5         | 440            |
| 2     | F50    | 0.34    | 50          | 50          | -        | -                   | -              | 2.299          | 4.0           | 6         | 660            |
| 3     | F80    | 0.34    | 20          | 80          | -        | -                   | -              | 2.286          | 2.5           | 8         | 600            |
| 4     | K50    | 0.34    | 50          | -           | 50       | -                   | -              | 2.459          | 4.0           | 6         | 460            |
| 5     | K80    | 0.34    | 20          | -           | 80       | -                   | -              | 2.374          | 2.8           | 7         | 630            |
| 6     | L20    | 0.34    | 80          | -           | -        | 20                  | -              | 2.313          | 5.0           | 6         | 570            |
| 7     | L50    | 0.34    | 50          | -           | -        | 50                  | -              | 2.349          | 5.5           | 4         | 670            |
| 8     | L80    | 0.34    | 20          | -           | -        | 80                  | -              | 2.353          | 5.0           | 3         | 670            |
| 9     | S5     | 0.34    | 95          | -           | -        | -                   | 5              | 2.328          | 6.0           | 5         | 640            |
| 10    | S10    | 0.34    | 90          | -           | -        | -                   | 10             | 2.325          | 6.0           | 7         | 530            |

It could also be concluded from Table 2 that fly ash and limestone powder improved the rheological properties greatly. For instance, the slump flow of control group is 440mm, while the slump flows of F50 and L80 are 660mm and 670mm, increasing 50% and 52% comparing to the
control group, respectively. There is a strong relationship between the slag dosage and the slump flow. The change in slump flow is 5% when slag content is 50% while increases to 43% when slag content equals to 80%. Silica fume will result in a better workability, about 40% higher than the control group.

3.2. Depth of CH dissolution front
For each specimen, a CH dissolution front move from outside to inside, and it was found to have a good linear relationship with the square root of leached time. Fig.1 shows the linear dependence as well as the values of correlation coefficient $k$. The linear tendency could be described as:

$$d_{\text{leach}} = k \cdot \sqrt{t}$$  \hspace{1cm} (1)

One could see that the leaching depth increases with leached time, resulting in that the correlation coefficient $k$ increases with W/C ratio.

![Fig.1. Leached depth versus the square root of erosion time for (a) PC and (b) FA pastes and their fitting curves.](image-url)

3.3. Effect of different admixtures on rheological parameters
The rheological parameters, namely yield stress and plastic viscosity, as well as their changes in percent were measured. It can be clearly seen that different mineral admixtures have different effects on the rheology of fresh concrete as the following.

For fly ash modified samples, it can be seen that the influence of fly ash on the plastic viscosity is not obvious when the content of FA is 50%; but the yield stress declines 86%, reflecting an improved rheological characterization. However, when fly ash content increases to 80%, the change in plastic viscosity highly increases to 226%, while the change in yield stress is 91% at the most. It is indicated that more dosage of fly ash, especially exceeding 50%, will result in a high plastic viscosity and hence causes a worse flowability.

For slag modified samples, with the increase of slag addition from 50% to 80%, the yield stress $\tau_0$ declines gradually. The change in yield stress is 63% and 91%. The plastic viscosity $\mu$ increases 68% and 85% respectively corresponding to 50% and 80% slag content.

For limestone powder modified samples, both the yield stress $\tau_0$ and the plastic viscosity $\mu$ decline with limestone powder content. But the yield stress declines more quickly at lower limestone powder content while the plastic viscosity $\mu$ declines more quickly at higher limestone powder content.

For silica fume modified samples, the rheographs conclude that the yield stress $\tau_0$ remain unchanged with silica fume varies from 0 to 5%, however, when silica fume content increases to 10%, the yield stress increases very rapidly. Besides, the plastic viscosity $\mu$ declines at the beginning and gradually increases, achieving the plastic viscosity of pure pastes. These relationships are true regardless of water reducer content is 1.1% or 1.3%.

3.4. Compressive Strength
The results of the compression testings are shown in Fig 2. The uniaxial compressive strength of partially corroded pastes reduced along with the increment of dissolution time because the pastes specimens become porous gradually. The compressive strength of the contrast group increased with leaching duration due to continuous curing. For a given test date, the loss of compressive strength (in percentage), denoted as $\Delta\sigma(\%)$, can be calculated by
\[
\Delta \sigma(\%) = \frac{\sigma_{\text{con}} - \sigma_{\text{lea}}}{\sigma_{\text{con}}}
\]  
(2)

where \(\sigma_{\text{con}}\): the compressive strength of control group, \(\sigma_{\text{lea}}\): the compressive strength of test group. The reduction in strength of the pastes test samples as a function of leached or curing time (days) is shown in Figure.3.

**Fig. 2.** Compressive strength of each group versus dissolution time for (a) leached PC pastes, (b) leached FA pastes, (c) cured PC pastes and (d) cured FA pastes.

**Fig. 3.** Relationship between \(\Delta \sigma(\%)\) and leaching duration for (a) PC pastes and (b) FA pastes.

It can be seen that no matter the leached time and W/C ratio increase, the value of compressive strength reduction (in percentage) increases with them. At the initial of leaching durations, the slopes of the curves are larger. A small increment in corrosion time could result in a significant increment in compressive strength deterioration. The curve gradually flattened out, that is, the slopes of the curves decrease. The influence of leaching duration on reduction in strength becomes weaker.

The function of compressive strength loss and leaching rate is proposed in Fig. 4 and Table 3. From Fig. 4 and Table 3, it can be observed that the experimental data are well correlated with the fitting curve.

**Table 3.** Slope of regression equation of the reduction in strength for specimens.

| Series | W/C=0.30 | W/C=0.40 | W/C=0.50 | W/C=0.60 |
|--------|----------|----------|----------|----------|
| PC     | 0.8812   | 0.8494   | 0.7778   | 0.6754   |
| FA     | 0.5194   | 0.4894   | 0.4930   | 0.4609   |

3.5. Model Simplification

A hypothesis should first be applied as shown in Fig. 5 that the stress should be borne by both the intact part and the dissolution part. Then the bearing capacity of the partially deteriorated sample could
be calculated by:

\[
F = (1 - \lambda) \cdot \sigma_{\text{con}} \cdot A_{\text{Alea}} + \sigma_{\text{con}} \cdot (A_{\text{tot}} - A_{\text{Alea}})
\]  

(3)

hence the loss of compressive strength is:

\[
\Delta \sigma(\%) = 1 - \frac{\sigma_{\text{Alea}}}{\sigma_{\text{con}}} = 1 - \frac{(1-\lambda) \cdot \sigma_{\text{con}} \cdot A_{\text{Alea}}}{\sigma_{\text{con}} \cdot A_{\text{tot}}} = \frac{\lambda \cdot A_{\text{Alea}}}{A_{\text{tot}}}
\]  

(4)

The calculated results are the same as the regression equation of the measured ones shown above, suggesting the predicting model of compressive strength is feasible.

4. Conclusion

This investigation has studied the fresh behavior as well as the leaching resistance of cement pastes including pure cement pastes series and fly ash modified series. The conclusions are listed as below:

Each constituent has a significantly different influence on the flow behavior of fresh cementitious materials. Among the mineral admixtures considered, the best performance has been obtained for fly ash and limestone powder series. In general, the admixtures improved the slump flow and declined the air content (except silica fume) of fresh concrete.

The effect of mineral admixtures on the rheological parameters is different based on the measurements of the yield stress as well as the plastic viscosity. The two parameters can be both declined (limestone powder), yield stress increased while plastic viscosity declined (silica fume) or inversion (fly ash and slag), comparing to the control group.

Slump flow has a strong correlation with the rheological properties. The slump flow increases with the decrease of plastic viscosity when the plastic viscosity is lower while the slump flow declines with the increase of yield stress when the plastic viscosity is higher.

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