

Leaching of Cementitious Materials: A Review

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Abstract—Concrete is one of the widely used construction materials in the world. Performance of concrete depends on its mechanical and durability properties. Properties of concrete can be deteriorated for various reasons. Water can be considered as one of the main deterioration factors of concrete. Dissolution and alteration of cementitious materials occur due to long term contact with water. Many concrete structures such as hydraulic structures, water purification plants, radioactive waste containers, underground structures, tunnels etc. are contacted with water. When these structures in contact with water for a long time, there will be a chance of leaching which degrades the performance of structures. The composition and structure of the materials must be known for safety prediction of these structures. A state-of-the-art review of the leaching of cementitious materials is presented in this paper. The review includes the basic concept of leaching, evaluation methods of leaching, improvement of methodology, leaching effects on structures, etc. Based on the scope, the future work on the topic is outlined.

Index Terms—Leaching, Dissolution, Durability, Hydration products, Review.

I. INTRODUCTION

To predict the long-term behavior of concrete structures requires a sound knowledge of the various deterioration mechanisms. One of the most deterioration mechanisms for concrete structure is leaching. Leaching is a diffusion-reaction phenomenon which takes place when cementitious materials are exposed to demineralized or poorly mineralized water [1]. Hardened cement paste or concrete is a porous material which has solid hydrates as well as pore space. Main solid hydrates include portlandite (CH), calcium silicate hydrates (C-S-H), AFm, and AFt. Pore spaces are filled with interstitial solution which is highly charged with alkaline Na^+ , Ca^{2+} , K^+ and OH^- ions [2]. Normally interstitial solution and solid hydrate remain thermodynamically equilibrium in hardened concrete. However, when concrete contacts with demineralized or poorly mineralized water the thermodynamic equilibrium condition does not exist. The contact of hardened concrete with an aqueous solution of low mineral content creates concentration gradients in the interstitial solution between the surface and the core of the concrete. These gradients lead to the diffusion of ions from the highly concentrated interstitial solution. In addition, to maintain local equilibrium between the interstitial solution and solid phase, dissolution or precipitation of the solid phase occurs [2], [3], [4]. Leaching destroys C-S-H and CH as well as AFm and AFt phases. As the concrete surface is approaching to water, the first phase to disappear is CH, followed in sequence by monosulfate, ettringite and C-S-H, though the last became progressively more decalcified [5].

The rate of attack depends on the quality and shape of the concrete, the rate at which the water percolates through or flows over it, the temperature and the concentration of solutes in the water [6]. Attack on cement concrete by water with a low mineral content and approximately neutral pH is one of the worst possible scenarios [2]. Therefore, an attack is most severe with soft or demineralized water.

The consequence of this chemical attack increased the porosity and decreased the mechanical performance [7]. The pore structure of concrete has great influence on strength, toughness, durability and overall performance of the concrete [8]. The pore structure of the concrete is of primary importance for understanding and modelling the transport phenomena that influences the overall performance of concrete. The transport properties of cement pastes are of crucial importance to the durability of much of the civil infrastructure.

II. ANALYSIS METHODS

To evaluate the leaching behavior of cementitious materials there were many works. Many experiments were conducted in different experimental condition such as different water cement ratio sample, different leachant condition, different leaching periods, etc. Cement paste, mortar or concrete was selected as a cementitious materials for most of the studies. Again in few cases cement was partially replaced by some modified agent like fly ash, glass powder, silica fume, etc. As leaching change the pore structure, different analytical method such as mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), thermogravimetry, X-ray diffraction (XRD) etc. were used to detect the pore structure in different studies. Most of the work tends to predict the leaching behavior using mathematical models based on the amount of Ca ions, the leaching depth, the loss of mass and strength, the porosity, the diffusion coefficient, etc. A few studies have considered microstructural variation [9].

A. Mercury intrusion porosimetry (MIP)

The MIP measurement is a good method for pore structure evaluation due to its large range of pore size measurement and easy operation [10] [13]. Therefore, bulk density, pore size distribution of leached sample can be done using the MIP method. But MIP measurement has some problems. It is reported that pore diameters obtained from MIP measurements are smaller than those observed by SEM (Scanning electron microscope). This is thought to depend on a factor known as the inkbottle problem [11]. In addition, as mercury past through the narrowest pores connecting pore network, MIP cannot give a true pore size distribution of pore structure [12].

B. Scanning electron microscopy (SEM)

Scanning electron microscopy can be used for the micromorphology investigation of the leached sample [9]. SEM helps to observe the hydrates in the cross-section. The chemical composition of microstructure can be represented in the images using gray scale. Pore structures also can be distinguished and quantified by image analysis of the 2-D section. However, SEM provides two-dimensional information. Therefore 3-D pore network or connectivity information cannot be directly observed using SEM.

C. Thermogravimetry

Thermal measurement can be carried out by differential thermal analysis and thermogravimetry (DTA/TG). DTA/TG gives the quantitative measurement. The calcium hydroxide and calcite content could be determined by measuring the mass loss in TG-DTA [9], [14].

D. X-ray diffraction

X-ray diffraction (XRD) can be used for quantitative and qualitative analysis of crystalline compounds. This method has an important role for characterizing materials. X-ray diffraction is based on the scattering of x-rays. Every crystalline substance produces a specific diffraction pattern, which depends on the atoms present, their locations, and thermal motion. In cementitious materials, the strength of the diffraction peaks are also dependent on W/C and other leaching condition. The peak strength of the portlandite became smaller as the samples were leached for longer periods. The larger the W/C of the samples, the peak strength of portlandite became smaller rapidly [14]. Therefore, it is very easy to detect the mineral change in leached sample using XRD. [9], [15].

Moreover Mossbauer spectroscopy [16], X-ray absorption fine structure (XAFS) spectroscopy [17], mechanical tests such as compressive strength test and other physical tests [18], [19] were conducted on different leaching samples.

III. EFFECTS OF LEACHING

A. Changes of pH and Ca concentration

Usually cementitious materials are alkaline, which has high pH values and Ca ions. On the other hand demineralized or pure water has a low pH and Ca ions (for pure water; pH is around 7.00 and Ca ion is almost zero) compared to cementitious materials. Therefore, when cementitious materials contacted with water, calcium ion as well as pH increased in the water. Haga et al. [20] observed the pH and Ca concentration changes using different water to cement ratio samples. They noticed that for higher water to cement ratio samples, higher amount of Ca was found in the leachant for the initial leaching period. The pH and Ca concentration of leachant, for the Ordinary Portland cement (OPC) samples with W/C of 0.8 and 1.0 increased as the leaching period was increased. However, after a certain period (56 days) the pH and the concentration of Ca showed a tendency to converge into a constant value, which indicates the equilibrium state of the aqueous and solid phases. On the other

hand, the pH and the Ca concentration of the aqueous phase for the samples with W/C 0.4 and 0.6 continued to increase as the leaching period was increased from 56 days, instead of converge into constant values. Here the aqueous and solid phases of these samples were not in an equilibrium state, which suggests that after 56 days the leaching was continued [20] for low water to cement ratio sample.

The similar behavior that is as the leaching time increased the concentrations of calcium are also increased in leachants were presented in several studies [1], [12], [21]. Here the amount of leached calcium presented as a function of the square root of the leaching period.

Again, as the calcium hydroxide (CH) leached from the solid paste, after a certain leaching period CH content decreased in the solid paste. CH contents remaining in the unleached cement pastes can be determined from thermogravimetric analysis. Jain and Neithalath [22] observed that the CH contents in the specimens are decreasing rapidly in the first 28 days leaching period. As there is a higher concentration gradient between the pore solution and the leachant (pure deionized water initially), high amount of CH content decreased. However, the rate of leaching of Ca ions from CH is seen to slow down after 28 days because of the lower difference in concentration gradients. Therefore, due to leaching, the CH contents in the specimens decrease and those in the leachant increase. It is also noticed that the plain paste suffers the maximum CH loss during the 90 days of leaching. On the other hand, the glass powder and fly ash modified pastes show reduced loss of CH than the plain paste, indicating higher leaching resistance for these modified mixtures. The silica fume modified paste shows the lowest CH content after leaching among the modified pastes, attributable to its lower initial CH content because of the increased secondary hydration of silica fume [22]. Xiang and PeiYu [9] also represent the CH content and the leaching period relationship considering different amount of fly ash content. Haga et al. [14] observed this relationship considering the effect of the different water to cement ratio samples.

B. Changes of the dissolution front

When concrete or hardened cement paste exposed to water, then concrete is degraded. But the amount of degradation varies from exposed surface to core. Therefore, at the edge surface amount of existing calcium are less or in other words loss of calcium are high compared to core [7], [14]. Carde et al. [18], [19] presents a relationship between distance from the edge of the sample and percentage of calcium where calcium was determined using microprobe automatic analysis. Indirectly we can get the idea of dissolution front from this relation as the amount of calcium in degraded zone is less compared to sound zone. Haga et al. [11] observed that in the early stage of leaching, a linear relationship can be derived by plotting the distance (surface to CH dissolution front) against the square root of the time. This relation suggests that the transport of Ca, the dissolved component of the portlandite, is by diffusion. The test results also showed that the prolonged leaching period resulted in a change of the slope compared to that in the early stage. This happened due to the influence of the change in composition of the leaching water and solid phases associated with the dissolution. However, that slope leached for a longer

period was steeper than that of the early stage, indicating that the Ca transport rate was becoming higher. This suggests the possibility of a strong effect due to the increase in the pore volume generated by the dissolution [11].

Kamali et al. [23] also proposed some models for the leached depth considering material and environmental parameters such as water to binder ratio, silica fume content, pH, temperature and protocol of reference.

C. Changes of the mass, bulk density and strength

Leaching changes the pore structure of cementitious materials. As the dissolution occurs in leaching process, there will be a loss of mass and strength. Carde and Francois [19] showed a relationship between the loss of mass of the sample and the square root of immersion time in the aggressive solution. From that relation it was observed that as the leaching period increased mass loss is also increased. Adenot and Buil [5] also found a linear relationship between the weight loss and the square root of time, where change of weight was evaluated by a hydrostatic weighing system. Xiang and PeiYu [9] showed the cumulative mass loss rates of hardened pastes in different leaching durations. They observed that with the extension of leaching periods, the cumulative mass loss rate of hardened paste increased gradually. It is also noticed that plain cement paste showed a better capacity for anti-leaching and a smaller mass loss than the other (fly ash modified) samples [9]. Rozière et al. [1] presented mass variation of leaching sample under external sulphate attack.

As the loss of mass occurred, density and strength of cementitious materials decreased during the leaching process. The bulk density became smaller with the increasing leaching period, which indicates that the dissolution progressed gradually [11]. Haga et al. [20] observed that the weight reduction due to dissolution was mostly completed in 28 days for the samples with W/C 0.8 and 1.0. On the other hand, the bulk density of the samples with W/C 0.4 and 0.6 continued to change as the leaching period was extended, which suggests that the leaching was continued for those samples after 28 days [20].

Leaching process effect the mechanical and physical properties of cement based materials. Leaching of calcium hydroxide and progressive decalcification of C-S-H leads to a gradient of C/S ratio in the leaching zone. Carde et al. [7], [18], [19] proposed a mechanical model considering the strength and porosity of micro-cylinder samples. The loss of compressive strength could be linked to the increase of porosity due to the dissolution of the calcium hydroxide [7]. They showed the variation of the loss of strength in relation to the degraded ratio. The degradation level was assessed by the ratio of the peripheral area (A_d) over the total area (A_t) of the sample [19]. The results suggested that the decrease of stress $\Delta\sigma_c$ is independent of the size of the sample and is a linear function of the degraded ratio which can be expressed as

$$(\Delta\sigma_c)/\sigma_c = 0.76 A_d/A_t \quad (1)$$

Here σ_c is the average compressive strength.

D. Changes of the porosity and diffusion coefficients

The porosity of cementitious materials depends on water to cement ratio, degree of hydration, presence of cement replacement materials, and their activity [22]. The porosity becomes larger with longer leaching periods. Jain and Neithalath [22] presented the changes in the pore volume with increasing leaching period for plain and modified pastes. It was observed that the increase in porosity resulting from leaching is seen to be the highest for the plain paste, which could be due to its higher initial CH content. On the other hand, the glass powder modified paste showed the least change in porosity with leaching. This indicates that calcium ions are being leached at a lower rate from the glass powder modified pastes as compared to the other pastes. One reason for this observation could be the higher Na₂O content of glass powder, which results in the production of NaOH in the pore solution, thereby reducing the dissolution of CH due to the common ion effect [22]. The addition of alkali hydroxides to a solvent is reported to significantly reduce the solubility of CH, and the reduction depends on the alkali hydroxide concentration [24]. The silica fume modified paste shows the lowest porosity in an unleached state because of the higher degree of secondary hydration and denser pore structure. However, with increased leaching duration, the porosity of silica fume modified paste increases at a faster rate than for fly ash and glass powder modified pastes.

In contrary, Xiang and Y. PeiYu [9] observed that the incorporation of fly ash contributes to the increase of the porosity of pastes. The higher the fly ash content in binders, the higher the porosity of paste. Here when fly ash content was 50%, the pores made by leaching cannot be filled completely by the pozzolanic reaction products. Therefore, the porosity of paste FA50 increased sharply while leaching duration prolonged. Mainguy et al. [12] proposed a model to calculate the porosity as a function of the calcium concentration by assuming a rapid dissolution of portlandite, followed by a progressive dissolution of ettringite and monosulphoaluminate.

Haga et al. [20] noticed that after 56 days, the porosity increase rate becomes moderate. It was also observed that the increase of pore volume became larger with a larger decrease in the quantity of Ca(OH)₂. Pore volume consists of different size pores. The distribution of pore sizes was carried out by many studies using mercury intrusion porosimetry (MIP) [11], [13], [20], [25].

Haga et al. [11] suggests that pores of 0.2 μm or smaller were attributed mainly to the C-S-H gel, while those larger than 0.2 μm were attributable mainly to the portlandite. Gaitero et al. [25] presents the pore volume and pore diameter distribution of different types of sample where silica nanoparticles used as a calcium reducing additives. From pore size distribution analysis and NMR results, they suggested that any reduction of calcium hydroxide during the degradation process is just a consequence of the degradation and not of the reaction with the silica nanoparticles [25]. Carde and Francois [19] suggest that the increase in porosity is due to the total removal of the calcium hydroxide and then the decrease of the C/S ratio of the C-S-H has a very small effect on the measurement of the porosity.

Mainguy et al. [12] observed that the effective diffusion coefficient exponentially increases with increase in porosity. A

similar relationship was found by Jain and Neithalath [22]. Mainguy et al. [12] also provide a relation between effective diffusion coefficient and calcium concentration in pore solution or in solid phase. Here as the calcium concentration decreased in pore solution or solid phase, the effective diffusion coefficient was increased.

Moreover, micromorphological observation [1], [9], [11], [26]; mineral characterization [9], [11], [26] and element distribution [11] were studied by using scanning electron microscope (SEM), X-ray diffraction (XRD) and electron probe microanalyser (EPMA) analysis. However, for future works, more advanced method can be used where the detectable order for measurement will be more precise.

IV. CONCLUSION

A state-of-the art review of the leaching of cementitious materials is presented in this paper. The review does not include all the research work conducted in this field. However, most widely used methodology and the effect of leaching has been added in this review study. Based on the above discussed work, some following conclusions can be drawn:

- a) The leaching of cementitious materials by demineralized or poorly mineralized water created a calcium concentration gradient in the interstitial solution, which induced the dissolution of portlandite. As the leaching period increased, portlandite dissolution is also increased.
- b) Portlandite dissolution changed the bulk density and pore volume. The changes in the pore volume were not only for portlandite dissolution, but also for the precipitation and dissolution of C-S-H and ettringite.
- c) The degraded zone can be separated from the sound zone by the dissolution boundary of portlandite. The boundary between the two zones is known as portlandite dissolution front. As the leaching period increased, portlandite dissolution front shifted towards the inner part of the specimen.
- d) Leaching of the calcium hydroxide creates a macroporosity which has greater effect on the loss of strength.
- e) Calcium leaching can be reduced using the addition of cement replacement material such as silica nanoparticles.

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