

From Alkali Aggregate Reaction to Alkali Activated Cementing Materials: the Reaction Conditions Mechanism and Products

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Abstract: The authors have summarized their works from alkali-silica reaction (ASR) to alkali-activated cementing materials (AAC) since 80's last century and proposed some basic regulation and principle. The property of alkali-silica sol (solution) which is either formed in concrete reaction or added as alkaline material is underlying the most important factor. It not only determines the initiating condition of reaction, i.e. pH value, but also provides the resource of various configurations of dissolving SiO_4 as the important reactants. Differently polymerizing state of SiO_4 possesses different physical or chemical properties, as a result, bring in different behavior and different products.

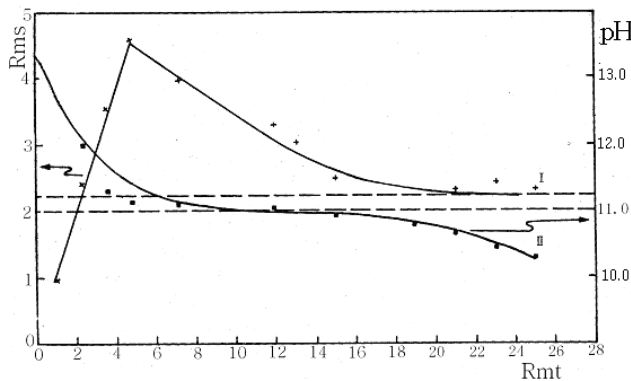
1. FOREWORD

Since several decades, the reactions of the system of $\text{Na}_2(\text{K}_2)\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}-\text{CO}_2$ has attracted strongly attentions. Firstly, alkali-aggregate reaction of concrete has aroused many studies for longtime, which possibly leads to extend consumedly the serve life of concrete. Secondly, the naissance of new type materials of alkali activated aluminosilicate minerals ignited the desire to replace classical Portland cement. These both researches seem to be quite deferent. One is for preventing or restraining the structural excessive expansion owing to the formation of expansive products. Another is to manufacture several new materials which possess cementing function sometime even better than traditional cement. These two researches have gone forward individually for longtime. Ones would wonder that alkali seems here to be a "magician" who brandishes a kopsis, in one hand, to destroy the word, in another hand, to build a new word. It is so interesting that what are the underlying oneness and common regulation between these two types of reactions.

2. THE BASIC REGULATION OF ASR

Through a lot of research, the authors proposed in a series of papers [1-5] since 1989 a new academic point that ASR should be a kind of sol-gel reaction dissolving through solution. No matter what kind of siliceous aggregate begins the reaction in alkali solution with dissolving of SiO_4 , the start-up pH value

being at least over 12.20. The dissolved SiO_4 may be in different polymerizing state (showed as different colloid particle size) depending on the pH value of the final solution. Through an experiment of testing sol osmotic pressure [5] the authors has found that the osmotic pressure of ASR sol, when it sealed by calcified alkali-silica gel, was well related with its chemical composition and existed an explicit Pessimun Point regulation. They has thereby proposed a new Osmotic Theory[4,5] that the expansion pressure of ASR should produce by the osmotic pressure of ASR colloidal product when it was sealed by $\text{CaO-Na}_2\text{O-SiO}_2$ gel and formed many dependent osmotic cells, but not from the swell of the gel product when imbibed water[5].The dissolving SiO_2 at "Pessimun" point is a polymer in low polymeric degree (≈ 10) and in high concentration, the pH value being about 11.1, the concentration of SiO_2 about 1.50mol/l, $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio about 4.50.This "Pessimun" sol could result in maximum osmotic pressure. Fig.1 establishes t he relation between initial $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of the ASR system, R_{mt} , and the final $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio, R_{ms} . It also shows t he theoretical area in which ASR could happen ($R_{mt}=2.2\sim 4.5$) [1], as well as demonstrats obviously the concept of "Pessimun" point in which the sol possesses maximum number of sol particles therefore could generate the highest osmotic pressure.



Practically, there exists everywhere osmotic membrane in hardening cement



Fig.2 Show of Sol-Gel Expansion

Fig.1 Relation of R_{mt} and R_{ms} and evolution of pH

Su surveymeter

paste (hcp). The most possible osmotic membrane for alkali-silica sol is hcp itself within its micropores filled with calcified alkali-silica gel. Such hcp would enwrap and seal alkali-silica sol in it to form an osmotic cell. Numerous such osmotic cells together produce superposition osmotic pressure which may destroy the structure of concrete [3,5].

The authors also found that the alkali-silica sol formed by AAR could corrode cement hydrates in certain speed depending on its $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio. If the corroded target was Ca(OH)_2 , there existed a breaking area (the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio=1.6~2.0) in which Ca(OH)_2 crystal was attacked much strongly and sostenuto and the product was similar to C-S-H in shape and chemical

composition.[3,4], see Fig. 2. Outside this area, i.e, higher or lower than 1.6~2.0, much poorer corrosion was occurred on $\text{Ca}(\text{OH})_2$ and some compact layer even formed on the surface to prevent from further corrosion. The same but much slower reaction was once seen on milled calcite crystal. The attack to C-S-H seemed, however, to be harmful for lowering its Ca/Si ratio and leading it to be more amorphous and gelatinous so hcp would shrink and crack, which

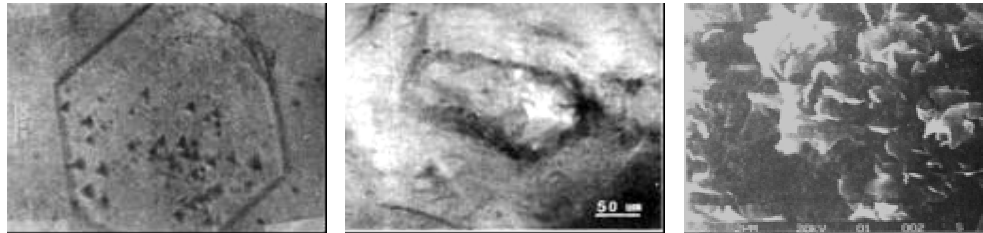


Fig.3 Corroded $\text{Ca}(\text{OH})_2$ Crystal by Alkali-silica Sol and the Product

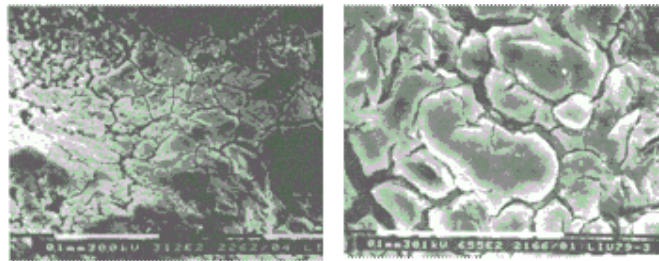


Fig.4 Corroded Cement Paste by Alkali-silica Sol

was showed in Fig.4. Therefore, alkali continually attacking would in general bring on the hydrates and their structure to be degenerated..

Based on the above studying, the authors invented a methodologically new method for testing aggregates alkali reactivity, named “sol-gel expansion” method [6, 7]. The main points are as following: to carry out in ambient temperature the reaction between milled aggregate sample and the alkali (NaOH) solution in proper concentration, to dry in vacuum the final mixture and then, to test, using a special instrument seen in Fig. 2, the free expansion and expansion pressure of the dried mixture when it absorbs $\text{Ca}(\text{OH})_2$ saturated solution through an osmotic membrane so as to evaluate the aggregate alkali reactivity. The program of the method is showed in Fig. 5,

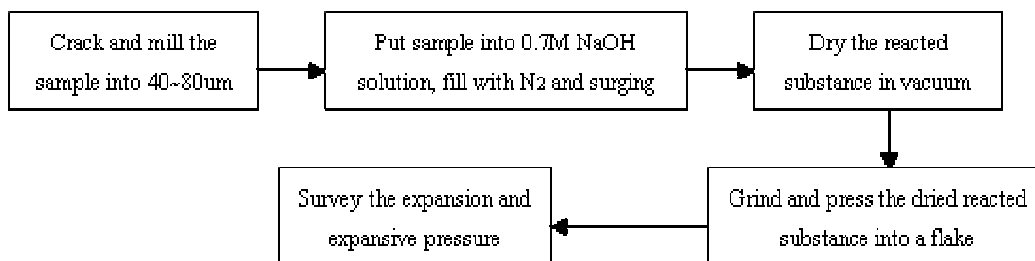
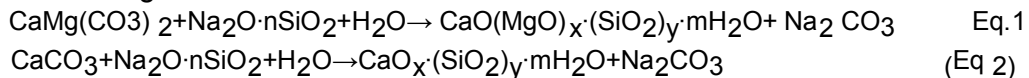


FIG. 5 Procedure of Sol-Gel Expansion Method

3. THE FOUNDATION AND REGULATION OF ALKALI-CARBONATITE CEMENTING MATERIAL (ACCM)

Alkali carbonate reaction of concrete (ACR) has been known, in which the reaction products are CaCO_3 , $\text{Mg}(\text{OH})_2$ and Na_2CO_3 . This reaction when it takes place in some rock structure would be of topochemical category and would produce topical stress and destroy structure of concrete. However, the authors have otherwise realized, from ASR studying, that certain alkali-silica sols are capable of reacting with calcareous materials and generating C-S-H type materials. the mechanism of which is similar to ACR but it is contrarily useful, so, have begun to study the Alkali-Carbonatite Cementing Material (ACCM) [9,10] .The basic raw materials were natural carbonatites rocks milled into ultrafine powder; its content of MgO was from 6% to 20%, and industrial water glass (alkali silica solution) which was ameliorated into a proper $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio. By the reaction of the both materials in ambient temperature, hydrated calcium-magnesium silicates would partly generate .The major new products were serpentine-type hydrated magnesium silicate and gyrolite-type hydrated calcium silicate, but remaining some solid silica gel. The reaction formula are as following, the microscopic figures of the products are seen in Fig.6~7.



A Chinese Patent [8] has been acquired . At present, this material is mainly used to solidify sand-clay soft stratum and make its proof infiltration. The compressive strength of the sand-fixation body after grouting is about 2~4MPa, the permeability is in the order of 10^{-8} . The authors have also made a lot of groping research [10] on the system of $\text{Na}_2\text{O}-\text{Ca}-\text{MgO}(\text{CO}_3)_2-\text{SiO}_2-\text{H}_2\text{O}$ and systematically probed into the thermodynamics, influence factors, reaction products and processing techniques of the reaction. It has demonstrated that, for the carbonatites chemically between calcspar and pure dolomite, the

Fig.6 SEM of ACCM paste of 60d

Fig.7 SEM of ACCM mortar of 60d

formation of gyrolite and serpentite was more favorable with the increase of MgO content; and the particle size of the powder greatly influenced its activity, seeming to exist a threshold value for the reactive kinetics. The reaction is certainly a sostenuto progress although it sometime went slowly. The authors have already made study on the composite materials based on alkali-carbonatite in which ggbs, fly ash and metakaolin have been introduced. and has improved greatly the performances such as strength and proof infiltration [11]. It was detected that there is certainly some cooperation effect in these composite materials systems.

4. THE MECHANISM AND REGULATION OF ALKALI-ACTIVATED METAKAOLIN (GEOPOLYMERIC) REACTION

Using cross experiment method, the authors have systematically studied Alkali-activated Metakaolin (Geopolymeric) Reaction in the influences of the reaction processing parameters, i.e. the module, concentration of alkali-silica solution, the weight ratio of liquid/solid in the mix, the calcined temperature and heat reservation time of kaolin, upon the compressive strength, workability and setting time of goepolymers and have found some important regulations: [12,13] as following: (1) All the parameters particularly imposed on the

compressive strength of 3d; as seen in Fig.7-9. All the parameters except the module had particularly influence on the compressive strength of 7d. But only the liquid/solid weight ratio possessed particular force on the 28d strength[15], as showed in Fig.8. (2) The concentration of the solution and the liquid/solid ratio exerted particularly obvious influence on the workability (extending scope) of the fresh paste [13], see Fig.10. (3) All the parameters had no particular influence on the setting time of the paste [13] ..

It is easy to understand that the liquid/solid weight ratio was consecutively the most important factor because of the formed structure matter. But, it appears to be some strange that the module exerted only influence on 3d strength but not on all ages, as seen in Fig.7 and 8. It should mean that the pH value of the solution is significance to the reaction initiation and must be enough high to destroy the structure of metakaolin, but lose its effect afterward because the content of the reactants in solution is just important to advance the reaction, therefore, the concentration and the ratio of liquid/solid behaves as the major factors. Until 7d, the calcined temperature and heat reservation time have still important influence on strength but not afterward, that seems to say that the structure of metakaolin imposes on the reaction speed only before 7d, but after that, well destroyed structure lose its force to reaction kinetics. .

With the methods of SEM observation and ^{29}Si and ^{27}Al NMR analysis and testing the individual components concentration in reaction solution, the authors have found some important regulations of geopolymeric reaction and proposed mechanism of the reaction progress as following [13,15] The reaction between alkali-silica solution and metakaolin begins with dissolving of metakaolin consistently both in layers of SiO_4 and in layers of AlO_6 . But the situation is not the same afterward. With decrease of pH value, SiO_4 dissolution gradually reduced but AlO_6 dissolution (it changes to AlO_4 in solution) maintained continually, therefore, dissolved AlO_4 gradually increased. When pH value descended to a certain point, dissolved AlO_4 and SiO_4 began to polymerize to form some gelatinous structure and the setting occurred. It is showed that the initial product was Si-O-Al polymer in low connection and the Al-O is in AlO_4 tetrahedron state, .but not as sad in some literatures[17], that a product formed with the only dissolving AlO_6 embedding into the structure of metakaolin. The initial formed product has substantially some unsaturated SiO_4 bond carry ing positive charge. The destroyed metakaolin had become many fine particles with negative charge in the site of dissolved AlO_6 . So, the initial gelatinous product made easily connection with the metakaolin relics to form an agglomerating and hardening structure. After that, both dissolving and polymerizing progresses continued and circulated, and the final situation structure and strength depended on the balance of these two evolutions. If the alkaline of the system were strong enough, geopolymerization would carry out drastically. Therefore, the final product would be either completely in Si-O-Al polymeric structure or remained some micro metakaolin particles relics. The

Fig.11 shows the geopolymer conformation and its structure in different ages[13].

Based on the above study, the authors have compared pure alkali-metakaolin system with pure alkali- ggbs system and alkali-metakaolin- ggbs composite system [13] . Through adding ggbs, the setting time and the early ages (1-3d) strength improved greatly, but the late ages strength (either compressive or adhering strength) did not change obviously. The reaction products were quite

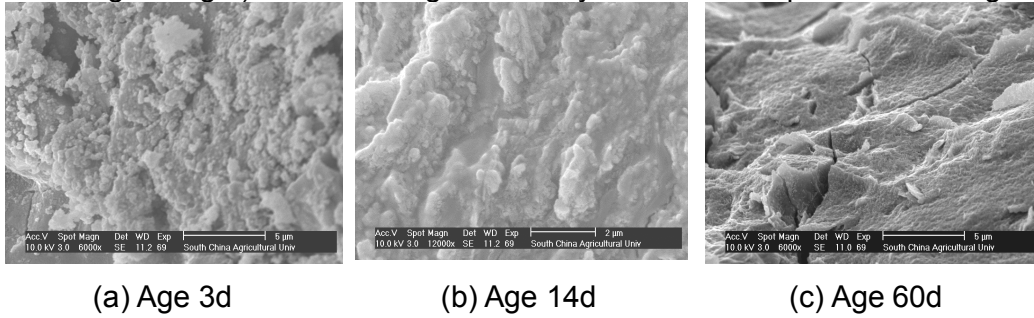


Fig.11 SEM Photos of Geopolymer at Different Ages

different. Geopolymer was completely gelatinous except for the remaining metakaolin relic fragments, but the alkali-ggbs product was a coarse gel with abundant round or isometric grains in micro- or submicrometer size, see Fig.12. These two products were quite different also in their chemical bound water content and the characteristics of IR spectrum and MAS-NMR Spectra of ²⁹Si. Their composite material possesses obviously the characters of the both. When the content of ggbs in the composite was closed to 50%, the character of geopolymer seemed to disappear, and some performance of hardened body would be close to pure alkali- ggbs material. Therefore, it is demonstrated that

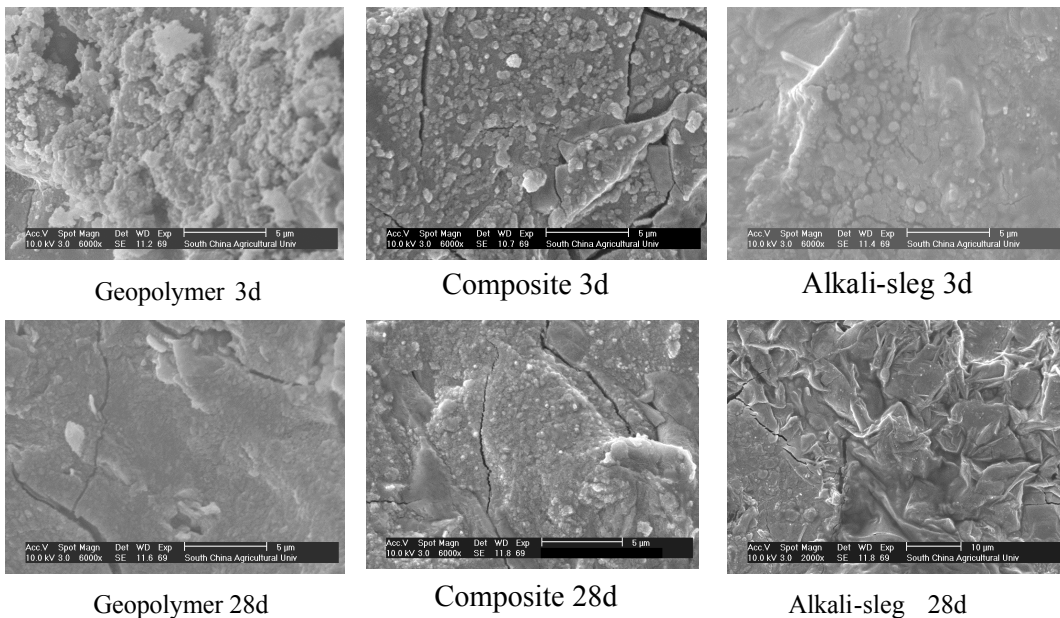


Fig. 12 SEM Photos of Geopolymer, Alkali-sleg and their Composite

there is a boundary in product category and performances between geopolymer and alkali-slag material.

5. CONCLUSIONS

5.1 There are two different processes in the ASR of concrete: the first is the attack of alkali solution to siliceous aggregate to form locally alkali-silica sol. If the diffusion of calcium is slow, a calcified gel membrane could just form to surround alkali-silica sol and lead to bring osmotic pressure and expansion stress, the magnitude of which completely depends on the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of the sol, obviously existing the "Pessimum Point" effect. If the diffusion of calcium is fast and the sol is completely calcified, the osmotic pressure would greatly descend. The second process of ASR is the attack of alkali-silica sol to cement hydrates, substantially, alkali-silica sol robbing Ca-O in hydrates, the speed of which depends also on the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of the sol existing the "Pessimum Point" too, the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of which is between 1.6-2.0. The attack to C-S-H would lead to the deterioration of hardening structure, but the attack of $\text{Ca}(\text{OH})_2$ would form a new calcium silicate hydrate.

5.2 If the attack of proper alkali-silica sol happens to carbonatites, i.e. CaCO_3 or $\text{CaMg}(\text{CO}_3)_2$ especially the latter, some cementing materials, e.g. calcium-magnesium silicates hydrates would generate.. The basic conditions of reaction include: the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of alkali-silica sol is between 1.60~2.00, with pH value about 12.06 12.40 and concentration over 30wt.%; the MgO content of carbonatites should be among 6%-20% and enough fineness should be guaranteed. The major products are gyrolite-type calcium silicate and serpentite-type magnesium silicate. The composite based on alkali-carbonatite materials already show excellent performances and good applying future.

5.3 If the attack of proper alkali-silica solution happens to metakaolin, in which the start-up pH value should exceed 13.20, the so-called geopolymeric reaction would occur. The course of the reaction includes three process : firstly, attacking and simultaneously dissolving of AlO_6 and SiO_4 , secondly, polymerization of SiO_4 and AlO_6 into Si -O- Al amorphous gel and the formation of agglomeration between metakaolin residues and Si -O-Al amorphous gel resulting in setting and hardening, and thirdly, the circulative advancing of the above two process. The effecting factors of the reaction comprise the module and concentration of the sol, the weight ratio of liquid/solid, and the calcined temperature and heat reservation time of kaolin. When compounded with ggbs, the high activity of calcium and magnesium in ggbs greatly accelerates the reaction. But, with increasing of

the amount of ggbfs, the products would translate gradually to hydrated calcium(magnesium) silicates and the polymeric degree of SiO_4 or and AlO_4 would decrease. That means to deviate from the path of geopolymerization.

5.4 In summary, the property of alkali-silica sol (especially $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio and pH value, concentration etc.) is consecutively the most important factor for ASR as well as AAC. It not only determines the start-up condition of reaction, but also provides the resource of various configurations of dissolving SiO_4 as the important reactants. Different polymerization degree of SiO_4 possesses different physical or chemical properties, as a result, brings in different behavior and different products.

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