



The 3rd International Conference on Sustainable Future for Human Security
SUSTAIN 2012

Development of sucrose and citric acid as the natural based admixture for fly ash based geopolymer

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Abstract

Geopolymer is the state of the art binder in concrete technology. It utilizes alkaline solution to activate alumina and silica precursors from source material and forms aluminosilicate-based binding material. Nevertheless, the presence of high calcium content in the source material can reduce the performance of geopolymer binder, particularly in terms of its workability performance. The available commercial admixture cannot provide significant improvement to the rapid setting time generated by high calcium in geopolymer system. This research studied the effect of sucrose and citric acid as the proposed natural admixture in fly ash based geopolymer binder. Based on Vicat setting time result, these materials behave oppositely in fly ash based geopolymer paste. Sucrose tends to increase the setting time of geopolymer paste, while citric acid has an accelerating effect. An unexpected trend is also shown from the relation between porosity and compressive strength of hardened specimen. It appears that the rapid production of geopolymer gels to fill the water-filled voids was not followed by the quality of gel structure. However, these results have presented an encouraging prospect for natural-based material to be developed as the admixture for geopolymer concrete.

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Selection and/or peer-review under responsibility of SUSTAIN conferences committee and supported by Kyoto University; (OPIR), (GCOE-ES), (GCOE-HSE), (CSEAS), (RISH), (GCOE-ARS) and (GSS) as co-hosts.

Keywords: geopolymer; fly ash; sucrose; citric acid; setting time

1. Introduction

Geopolymer binder was first introduced by Joseph Davidovits in 1972 to identify the reaction product between geological-origin source material and alkaline solutions [1]. Its unique characteristic has

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delivered an engaging perspective to the future of concrete technology since it can replace the function of Portland cement as the main binder in concrete structure. The main structural framework of geopolymer generally consists of aluminosilicate skeleton, which is different from calcium silicate hydrate possessed by Portland cement based binder. The suitability of one source material significantly contributes to the properties of geopolymer binder produced, since Aluminium (Al) and Silicon (Si) precursors are dissolved from the source material particles. Low calcium fly ash is commonly preferred as the main source material to be activated with alkaline solution. The presence of high calcium content can interfere with the geopolymerization process, which results in the reduction of geopolymer binder mechanical strength [2].

The plasticity of fresh geopolymer paste is also prone to the rapid stiffening when high calcium fly ash is used as the source material in geopolymer mortar and geopolymer concrete phase. It has created additional issue to the application of geopolymer mortar and concrete for in-situ casting application. Several researches have been conducted to overcome this issue, yet resulted in less significant improvement to the setting time properties, particularly in the high-calcium-based source material. The incorporation of commercial chemical admixture like high range water reducing admixture has been studied by many researchers without any significant result.

Isozaki et al [3] have stated in their study that formalin condensates of β -naphthalene sodium sulphonate did not exhibit any improvement to the rheological properties of geopolymer paste. Meanwhile Douglas and Brandstetr [4] have specifically revealed up to 1.0% and 5% inclusion of sodium lignosulphonate and sulphonated naphthalene-based superplasticizer respectively contributed to negligible change in paste consistency. Improvement started to occur when 9% sulphonated naphthalene-based superplasticizer was used; yet it significantly decreased the early strength of paste specimen [4]. Other similar findings were presented by Gifford and Gillot [5] in the area of high-range and normal-range water reducing admixture. It was found out that these admixtures were incompatible with Na_2SO_4 and Na_2CO_3 based geopolymer, and a very high impractical dosage was needed to achieve a reasonable workability for $\text{Na}_2\text{O}.\text{SiO}_2$ based system [5].

Therefore further researches are needed to obtain a practical admixture for geopolymer concrete. This paper deliberates the effect of sucrose and citric acid in the polymerization process and their possibility to be used as the principal substances in the alternative admixture for geopolymer binder. Setting time, compressive strength, and porosity test were used as the basic indicator to evaluate the performance of these chemical reagents in the geopolymerization process.

2. Experimental investigations

2.1. Materials

Fly ash was used as the main source material in this research. Fly ash was obtained from Manjung Coal-Fired Power Plant, Malaysia with the dominant content consist of SiO_2 (51.7%), Al_2O_3 (29.1%), and CaO (8.84%). Table 1 shows the properties of fly ash used in this research. A combination of sodium hydroxide and sodium silicate solution was prepared to activate the aluminosilicate precursors in fly ash through the series of dissolution-hydrolysis-polycondensation. Sodium hydroxide pellets with 99% purity was diluted in water to produce 8 Molar (M) sodium hydroxide (NaOH) solution. Sodium silicate (Na_2SiO_3) solution with $M_s = 2.0$ (Na_2O : 14.73%; SiO_2 : 29.75%, and H_2O : 55.52%) was mixed with 8 M NaOH solution 1 hour prior to the mixing process to prevent the excessive heat from the dissolution of NaOH pellets. Analytical reagent grade of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were used as the proposed alternative admixture.

Table 1. Properties of fly ash

| Oxide composition (%) | | | | | | | Particle size characteristic | | | |
|--------------------------------|------------------|-------------------------------|-----------------|------------------|------|--------------------------------|------------------------------|----------------------|----------------------|--------------------------------------|
| Al ₂ O ₃ | SiO ₂ | P ₂ O ₅ | SO ₃ | K ₂ O | CaO | Fe ₂ O ₃ | d ₁₀ (μm) | d ₅₀ (μm) | d ₉₀ (μm) | BET Surface Area (m ² /g) |
| 29.1 | 51.7 | 1.7 | 1.5 | 1.6 | 8.84 | 4.76 | 2.97 | 16.54 | 99.21 | 4.26 |

2.2. Specimen preparations

Geopolymer specimens were prepared in accordance with the designed mixture proportions as listed in Table 2. Fly ash and sand were dry mixed in an automatic mortar mixer for 1.5 minutes. Sodium silicate and sodium hydroxide were then introduced into the dry mix and continuously mixed for another 2.5 minutes. Fresh geopolymer mortar produced was cast into 50 mm steel cube molds for further compressive strength and porosity test purpose. Two curing methods, namely ambient and oven curing method were adopted in this study to observe the effect of the proposed admixture in different curing conditions. In ambient curing, geopolymer specimens were placed in the covered area that was protected from direct rainfall and sunlight until the testing day. Meanwhile, in oven curing, the specimens were placed in an electric oven with temperature setting of 60 °C for 24 hours. The specimens would be demolded after 24 hours and placed in the ambient curing condition until the testing day. To prevent data disruption from the existence of fine aggregate during Vicat setting time analysis, other batches of geopolymer paste were mixed by eliminating sand proportion from the mixture.

Table 2. Detail of mixture proportions

| Code | Fly ash | Na ₂ SiO ₃ | NaOH | Sand | Sucrose | Citric Acid | Curing |
|------|---------|----------------------------------|------|------|---------|-------------|---------|
| | | | | | | | |
| A0 | 350 | 103 | 41 | 650 | - | - | Ambient |
| AS1 | 350 | 103 | 41 | 650 | 5.25 | - | |
| AS2 | 350 | 103 | 41 | 650 | 8.75 | - | |
| AC1 | 350 | 103 | 41 | 650 | - | 5.25 | |
| AC2 | 350 | 103 | 41 | 650 | - | 8.75 | |
| O0 | 350 | 103 | 41 | 650 | - | - | Oven |
| OS1 | 350 | 103 | 41 | 650 | 5.25 | - | |
| OS2 | 350 | 103 | 41 | 650 | 8.75 | - | |
| OC1 | 350 | 103 | 41 | 650 | - | 5.25 | |
| OC2 | 350 | 103 | 41 | 650 | - | 8.75 | |

3. Result and discussion

3.1. Vicat setting time

Observation through Vicat setting time reveals two different characteristics possessed by sucrose and citric acid in geopolymerization. As presented in Figure 1, sucrose has some sort of retarding effect compared to acceleration mechanism hold by citric acid. It is considerably different from the ordinary Portland cement (OPC) based system where both of those chemical reagents have similar retarding effect in the hydration of OPC binder [6-8].

It was envisaged that in sucrose-based admixture, the diluted alkalis have converted HO-C-C=O groups from sucrose particle into acid complexes. These acid complexes adsorbed by fly ash particles, mostly by Ca⁺ ions and poisoned the calcium complex nucleating sites. Sucrose also combined with Ca, Al, and Fe in the mixture to form insoluble metal organic complexes that covered the fly ash particles and delay the geopolymerization process [8, 9]. Meanwhile, the fate of citrate in geopolymer system is not fully understood since the theory of retardation from OPC based system has presented a different outcome.

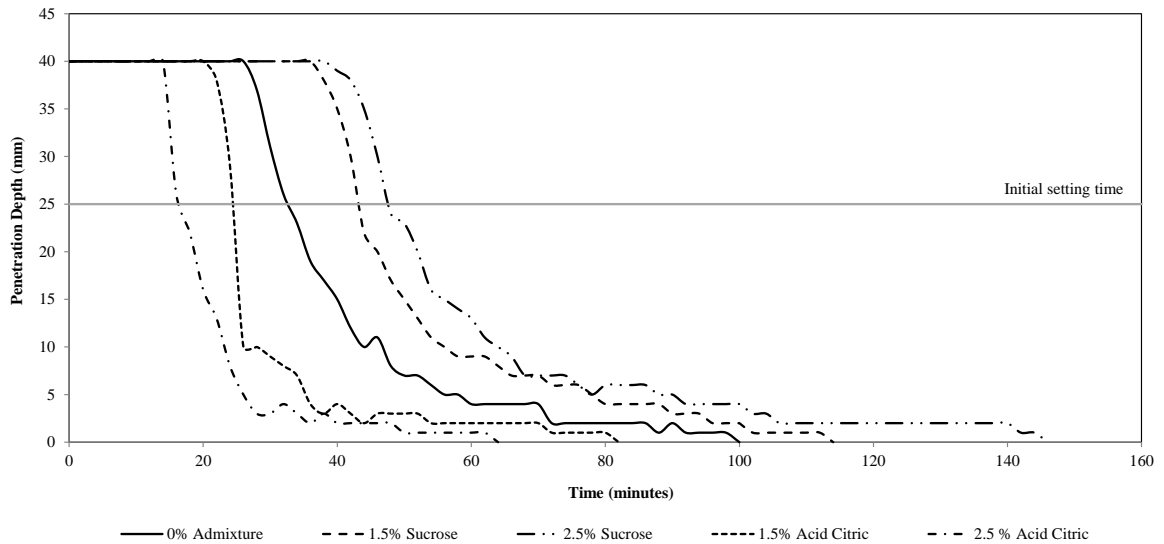


Figure 1. Vicat setting time of geopolymer paste with admixtures

Geopolymer structure that consists of aluminosilicate framework is distinctly different from the calcium hydroxide structure of gypsum-containing OPC. Nakui *et al* [10] have studied the importance of electric charge on coal ash particle surfaces to the dispersion of coal ash particle in the presence of citric acid particularly in a high pH environment. It is estimated that for fly ash with the composition of SiO₂ = 62% and Al₂O₃ = 21%, coal ash particle will show an electronegative charge at pH 5 or 10 [10]. Meanwhile, based on the values of dissociation constant (*K_a*) hold by citric acid, it will dissociate to anions more than pH 2.9 and will be negatively charged at pH 5 and 10 [10, 11]. Due to this repelling mechanism, only a small amount of citric acid adsorbed on fly ash. Nevertheless, this preferential adsorption may promote the formation of hexagonal phases from the hydration of C₃A [8] hence results in the acceleration of geopolymer stiffening process during early stage.

As observed in Figure 1, normal geopolymer mixture has the initial setting time of 33 minutes and reaches the final setting time after 100 minutes. The addition of sucrose as the admixture has delayed the initial setting time by 10 minutes and 15 minutes for 1.5% and 2.5% sucrose addition respectively. Meanwhile the addition of citric acid has accelerated the initial setting time by 9 minutes and 16 minutes for 1.5% and 2.5% citric acid addition respectively. Similar trend is also observed in the final setting time result where 1.5% sucrose, 2.5% sucrose, 1.5% citric acid, and 2.5% citric acid have the final setting time of 115, 145, 80, and 65 minutes respectively.

3.2. Compressive Strength

Regardless of contrary setting time results shown by sucrose-added and citric-acid-added specimens, the compressive strength result presents a similar strength development for both chemical reagents mixtures. Control specimen (without admixture) constantly has the highest compressive strength after 56 days for both ambient and oven curing. Nevertheless, 1.5% addition of sucrose in the fly ash based geopolymer has presented an encouraging result, particularly with the ambient curing condition. Statistically analyzed, at 95% confidence level, there is no significant difference between: A1 and AS1; O1 and OS1 in terms of compressive strength performance after 56 days of curing. It is believed during the adsorption of sugar acid on to fly ash cations, it also increased the concentration of several geopolymer precursors (Ca, Si, and Al) through some sort of precipitation process [8]. However, these additional geopolymer precursors cannot actively prevent the disruption in the dissolution and polycondensation of fly ash due to the formation of insoluble metal organic complexes. It clarifies the significant reduction of specimen strength when higher concentration of sucrose is added.

Meanwhile, acceleration in the stiffening process by citric acid has resulted in the reduction of geopolymer strength, even in the presence of elevated temperature during the curing process. Rapid formation of hardened structure in geopolymer gel has prevented further dissolution and polycondensation of the remaining fly ash particles, hence reduced the quality of aluminosilicate gel produced. In ambient curing, 1.5% and 2.5% sucrose additions reduce the geopolymer mortar strength by 5.56% and 22.24% respectively, while 1.5% and 2.5% citric acid significantly reduce the geopolymer mortar strength up to 18.47% and 25.33% respectively. Similar depreciation trend also occurs in oven-cured specimens where 1.5% and 2.5% sucrose contribute to the 9.31% and 27.27% strength reduction respectively and 1.5% and 2.5% citric acid have the strength up to 15.02% and 21.60% lower than control specimen respectively.

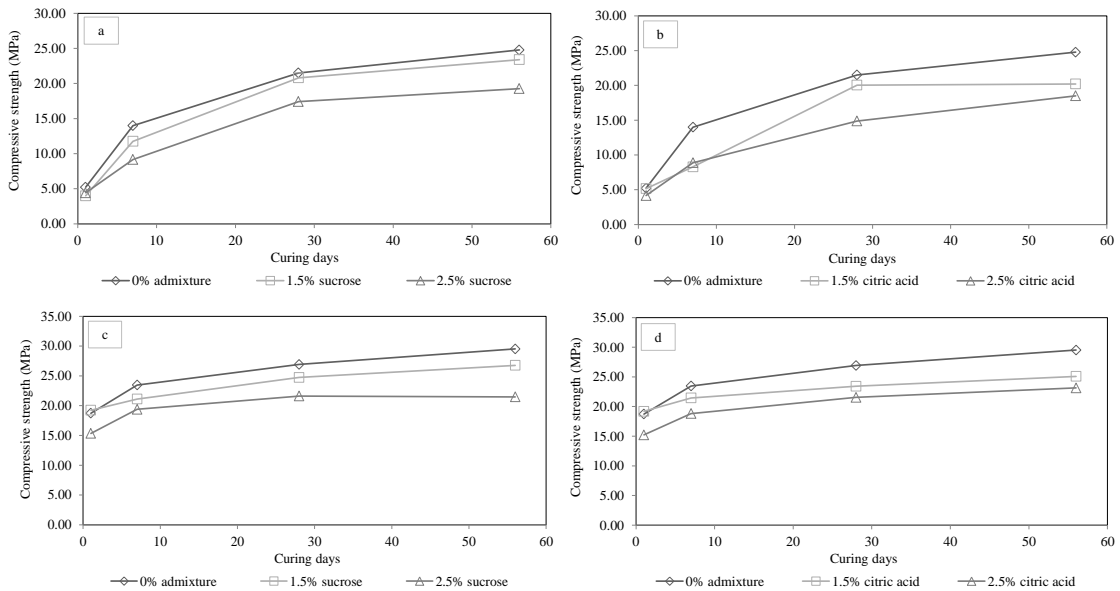


Figure 2. Compressive strength development of geopolymer specimen with: (a) sucrose addition in ambient curing, (b) citric acid addition in ambient curing, (c) sucrose addition in oven curing, (d) citric acid addition in oven curing.

3.3. Porosity

In geopolymer system, proper polycondensation and improper precipitation, both are resulting in a hardened geopolymer structure, yet the quality of gel produced should be carefully taken into consideration [11]. Precipitation of dissolved species produces a more porous structure than polycondensation process. Figure 3 shows the interesting features of relationship between porosity and compressive strength in the presence of sucrose and citric acid. In sucrose-added system, the increasing compressive strength is followed by the increasing porosity of geopolymer mortar. It appears that particle morphology of fly ash also contributes to some portion in the porosity measurement. There are three types of fly ash based on its particle morphology, solid spheres, plerospheres, and cenospheres [12]. Cenosphere is a particle type of fly ash where the cavities inside are filled with gas only, while plerosphere has small mineral particles, foam or other porous framework [13]. During the dissolution of alumina and silica precursors from fly ash surface, the cenosphere type of fly ash tended to leave a hollow space structure that contributed to the analysis of pore characteristic since this hollow structure permitted fluid penetration.

Meanwhile, in citric-acid-added specimen, the increasing compressive strength is followed by the decreasing porosity of geopolymer mortar. It supports the indication of false setting time promoted by the hydration of calcium compounds. The formation of aluminosilicate gels is able to fill some voids in geopolymer mortar. However due to the acceleration in stiffening process, further dissolution was not possible to have higher compressive strength than control specimen.

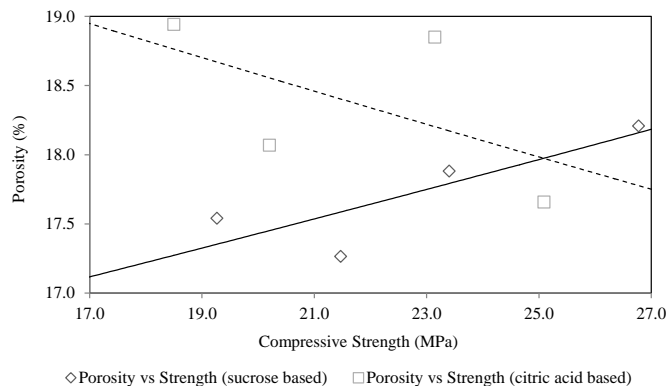


Figure 3. Relationship between porosity and compressive strength of geopolymer mortar

In general, sucrose-added specimens have compressive strength higher than citric-acid-added specimens. Geopolymer gel produced from the precipitated species has partially contributed to the strength enhancement of geopolymer mortar, yet their porous nature has presented an unconventional trend to its relationship with the compressive strength. Nevertheless, in terms of compressive strength properties, they have presented a comparable performance as the control specimen.

4. Conclusion

The addition of sucrose and citric acid as the alternative admixture in fly ash based geopolymer has portrayed an encouraging result, particularly in the modification of rheological properties of geopolymer paste. Sucrose tends to provide a retardation effect to the plastic geopolymer paste, while citric acid can

be used to accelerate the stiffening process. Even though improvement on the compressive strength was not optimized, yet sucrose-added specimens have a comparable compressive strength to the control specimen. The additional precipitation of dissolved species in the presence of sucrose has also affected the evaluation of porosity characteristic. Contrasting to citric acid, sucrose-added specimen has an unconventional relationship between porosity and compressive strength, where smaller porosity is correlating with lower compressive strength. Nevertheless, these chemical reagents have presented a prospective future as the alternative admixture basis in geopolymer binder.

Acknowledgements

The authors gratefully acknowledge the financial support from Universiti Malaysia Pahang under research grant RDU120365.

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