Strength Assessment in Portland Cement and Geopolymer Composites with Abrams’ Law as Basis

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Received 14 April 2020, accepted 29 May 2020 doi:10.3151/jact.18.320

Abstract
In the recent past, there is growing interest to study the two modes of cementing of materials - i.e., conventional cement concrete and geopolymers in the same investigation to bring about their merits and demerits. As a complement to such studies, in this investigation, the analysis and assessment of strength development within the basic framework of Abrams’ Law are examined. It is interesting to note that the generalized Abrams’ Law holds valid both in the case of chemically bonded OPC and thermally bonded geopolymers in the analysis and assessment of strength development for the data generated by independent researchers. The pattern of strength development in conventional concrete and geopolymers is the same. This is useful in re-proportioning cementitious composites irrespective of the binder.

1. Introduction
Despite Portland cement concrete being a brittle material with very low tensile strength, it is the most widely used construction material across the globe. Quest for alternative construction materials is ongoing and directed towards sustainable development. Geopolymer is found to be a viable alternative to conventional cement composites. The primary constituent of geopolymer is the fly ash, a discard of thermal power plant (Palomo et al. 2005; Fernandez-Jimenez et al. 2006; Zhang and Sun 2006; Rangan et al. 2006). Close to 1100 million tons of fly ash is estimated to be generated by India and China alone annually by 2025 (Hardjito et al. 2004).

Geopolymers, which can be produced with simple processing technology, possess high compressive strength and durability (Weil et al. 2005). Materials rich in silica and alumina such as ground granulated blast furnace slag, metakaolin, red mud etc. (Palomo et al. 2005) can be incorporated to make the production of geopolymers less energy intensive thus encouraging the utilization of locally available materials. Many new technological developments and recent innovations in the construction sector are directed towards geopolymers. The market value is expected to reach US$ 16.2 billion by 2024 (IMARC 2019).

According to Hardjito et al. (2004), structural behavior and the elastic properties of hardened geopolymer composites are similar to that of Portland cement concrete. In addition, drying shrinkage and creep are low in the case of geopolymers compared to OPC composites. According to Fernandez-Jimenez et al. (2006), geopolymer possess good bond strength with steel reinforcement. The workability of geopolymer mortars and concrete is very good even at a low fluid/binder ratio of 0.3 even without the use of superplasticizers. On the other hand, the compressive strength may be as high as 60 MPa. These attributes make the geopolymers a suitable structural material.

There are reports of proportioning the geopolymer mix for a given compressive strength. Many researchers believe that the compressive strength of geopolymers mainly depends on the molarity of an alkaline solution, fly ash to fluid ratio, ratio of sodium salts and age (Radhakrishna et al. 2014; Parthiban and Saravana Raja Mohan 2014; Dao and Trinh 2019; Mallikarjuna Rao and Gunneswara Rao 2018; Montes et al. 2013; Nagajothi and Elavenil 2018; Manjunatha et al. 2014). According to Fan et al. (2018), the parameters like water to fly ash ratio, type of curing and cooling methods have a major effect on the compressive strength and other properties of the geopolymer. Lokuge et al. (2018) have developed a mix design method using a multivariate adaptive regression spline model, whereas Mehta et al. (2017) have developed mathematical models using multiple regression analysis for strength and absorption and confirmed with independent experimental test results. On the other hand, the Taguchi method was used to optimize fly ash in geopolymer mixtures and study the mechanical and durability properties of concrete (Olivia and Nikraz 2012). The same method was used by Hadi et al. (2017) to proportion geopolymer concrete to obtain a strength of 60.4 MPa at a fluid to binder ratio of 0.35. Pavithra et al. (2016) have established a correlation between the alkaline solution to binder ratios (0.4 to 0.8) and compressive strength to propose a conceptual mix design.

Phoo-ngernkham et al. (2018) have successfully developed a mix design procedure using different parameters including alkaline solution to fly ash (AAS/FA) ratio. The model developed by Ren et al. (2020) predicts

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that, under the strong influence of phosphoric acid, geopolymer pastes could exhibit better resistance against phosphoric acid compared to ordinary Portland cement-based composites. An equation with a high correlation coefficient is proposed by Yeddula and Karthiyaini (2020) to predict the residual compressive strength of ferrosialate geopolymer mortars prepared using red mud and fly ash. Luhar et al. (2020) have optimized different parameters to produce geopolymer concrete having a compressive strength of 25 MPa.

Though several researchers have developed different procedures to proportion geopolymer concrete, the effect of fluid to binder ratio alone is not explored when all other parameters are same. In this paper, an attempt is made to study this.

2. Research significance

Cement based composites are considered as a chemically bonded system at ambient temperature. This refers to bonding by chemical reactions resulting due to Van der Waals force of attraction. On the other hand, in geopolymer composites, bonding is initiated by thermal energy/geopolymerisation.

A logical method to arrive at the right combination of ingredients to realize a specific strength development at a given age is desirable due to the following.

1. The strength at any age varies depending on application. To optimize the use of materials, simple procedures are required.
2. As the number of ingredients increases, it is challenging to arrive at the required combination with a set of minimum number of trials.
3. The characteristics of the materials may vary, which needs good control to re-check the mix proportions with minimum test data and computations.

It emphasizes a basic framework and develops the confidence to apply this method in the field.

3. Scope of the research

It is a fact that in cement based composites, free water to cement ratio predominantly controls strength development with respect to age. This strength development is very sensitive to water to cement ratio. In cement based materials, where the interacting material, cement, is a variable but the mixing fluid is the same in all cases, the mix follows Abrams’ Law (Abrams 1918) and Bolomey’s Law (Bolomey 1927). In geopolymers, interacting material is the same whereas mixing fluid is different, reflected by its molarity. The detailed study on microstructure of geopolymer mortars by SEM by Fernandez-Jimenez et al. (2006) illustrates that the main reaction product from the alkaline reaction is progressive precipitation of sodium alumino-silicate gel combined with the formation of more gel with involvement of other fly ash particles leading to the formation of a cementing matrix. Pore size distribution studies by mercury intrusion porosimetry by Park and Kang (2006) lend additional support that porosity of geopolymers reduces with age resulting in increased strength with age similar to cement bonded materials.

Both of these cementing systems are constant volume solidification processes with strength development dependent on residual porosity. With these similarities of cement based and geopolymer composites, from an engineering point of view of processing these materials, the following aspects merit examination.

It is to be verified whether the strength development in geopolymer composites are of the same pattern as that of Portland cement concrete as per Abrams’ and Bolomey’s Laws. The possibility of developing a phenomenological model to assess strength is to be verified. If so, the same model can be used to assess the strength of both cement and geopolymer composites. The cardinal aim of this study is to address these issues.

4. Background information

Mix proportioning in concrete depends mainly on the water to cement ratio. Abrams’ Law states that, for a given set of materials, the strength development is solely dependent on free water to cement ratio when other conditions remain the same. The compressive strength development may not the same even if the ingredients and proportions of materials are maintained the same. This may require many trials to proportion the mix. It can be based on purely empirical considerations or any others.

If the result obtained for the trial mix does not satisfy the needs, variation in water to cement ratio must be made. For various mix proportions, it is not possible to arrive at logical relations wholly based on theoretical contemplations alone.

Therefore, developing a phenomenological model merits examination. In phenomenological approach, the combination of parameters would be varied within the basic framework of a scientific law. To apply this model, an input of experimental data of a single trial is required. It may be a strength at a given water to cement ratio. Thus synergy between the ingredients of a given set of materials is taken care of. If the combination of materials is changed, a new experimental data is to be generated again to use the phenomenological model to obtain the corresponding water to cement ratio. This is to arrive at the right mix proportions to meet the specific strength. This method is known as the ‘Re-proportioning Method’.

This method certainly avoids repeated laboratory trials, but can be done with single experimental data making simple arithmetic calculations. This is an easy exercise and has further scope to determine the parameter that would provide a wide spectrum of mixes of concrete.

In cement based composites, data generated for the British method of mix design (Techenne et al. 1988) has
been further analyzed to develop the phenomenological model for Portland cement composites. By considering the strength ($S_{0.5}$) at water to cement ratio of 0.5, as the reference state to reflect the synergy between different ingredients of concrete, the relation between the compressive strength ($S$) and free water to cement ratio has been generalized (see Fig. 1).

The resulting relationships are expressed by the following equation (Nagaraj and Banu 1996):

$$\frac{S}{S_{0.5}} = a + b \left( \frac{c}{w} \right)$$

(1)

where

- $a = -0.2, b = 0.6$ for $S \geq 30$ MPa
- $a = -0.73, b = 0.865$ for $S \leq 30$ MPa

5. Materials and methods

Class F fly ash has been procured from Raichur Thermal Power Station, Raichur, Karnataka State, India. The specific gravity of fly ash was 2.4 and the lime reactivity (BIS 1967) was found to be 7.4 MPa. The ash conforms to the requirements of the Indian Standard Specification for fly ash (BIS 1981).

Commercially available sodium hydroxide flakes (minimum purity 96.0%) and sodium silicates were used to prepare the alkaline activator solution. Locally available fine aggregates in surface saturated dry condition (SSD) were used to prepare the mortar. The activator solution of different molarities was made at least twenty-four hours prior to its use. The ratio of sodium silicates and sodium hydroxide by mass was maintained as 0.4 throughout the work.

Geopolymer mortar composites were considered in this investigation. Natural sand as fine aggregate along with fly ash was mixed in dry condition in the ratio of 1:1. Mortar cubes of 50 mm size were cast and they were immediately transferred to an oven maintained at a temperature of 60°C for 48 hours. At the end of the curing period, the mortar cubes were removed and kept in air in the laboratory to cool to ambient temperature before testing for their compressive strength. The cubes were tested at the age of 3 and 7 days. Several mortar cubes were cast and cured in oven as specified. The mortar prepared for a fluid-binder ratio of less than 0.3 requires compaction. Hence the range of fluid-binder ratio in this investigation is 0.3 and 0.6. Beyond 0.6, bleeding was observed.

6. Development of the phenomenological model

In this section, Portland cement concrete is considered for the analysis as reported by Nagaraj et al. (1993). Later the data generated by the author is considered for geopolymer mortars.

6.1 Strength analysis of cement concrete

The strength data generated for different cement concrete using different grades of cement as shown in Fig. 2. The data is extracted from the publication by Nagaraj et al. (1993). It can be observed that compressive strength decreases as the water to cement ratio increases, as per the Abrams’ Law.

When this data is transformed by considering the variation of the compressive strength with respect to cement to water ratio the paths are linear for all the mixtures (Fig. 3). This is in accordance with Bolomey’s Law. The variation of compressive strength with respect to cement to water ratio can be normalized taking strength at $S_{cw=2.0}$ as a reference value. Figure 4 shows the linear relationship of the generalized strength ratio $S/S_{cw=2.0}$ as cement to water ratio varies with a correlation coefficient of 0.94.

The resulting phenomenological model for the ce-

$$\{S/S_{0.5}\} = -0.2 + 0.6\{c/w\} \text{ for } S_{0.5} \geq 30\text{MPa}$$

$$\{S/S_{0.5}\} = -0.73 + 0.865\{c/w\} \text{ for } S_{0.5} \leq 30\text{MPa}$$

Fig. 1 Generalization of strength data (Nagaraj and Banu 1996).
ment based composites would be as in Eq. (2).

\[
\frac{S}{S_{ref}} = 0.6 \left(\frac{c}{w}\right) - 0.26
\]  (2)

The predicted strength values according to the phenomenological model in Eq. (2) for the data from Road Note No. 4 (Road Research Laboratory 1950) are shown in Fig. 5.

6.2 Strength analysis of geopolymer mortar

Figure 6 shows the strength data generated for geopolymer mortars. In this figure, (as well as in Figs. 7, 8, 9 and 11 that follow), “M” indicates the molarity of the alkaline solution and the numbers before “Days” indicate the age of the specimen tested. It is observed that the variation of compressive strength is inversely proportional to the fluid to fly ash ratio. The fly ash can be regarded as binder too. This is also in accordance with Abrams’ Law.

Figure 7 is a transformed plot according to Bolomey’s Law. It is interesting to note that the variation of the compressive strength with respect to the fly ash to fluid ratio variation is also linear even in case of the geopolymer mortars (Fig. 7). Figure 8 is the graphical representation of phenomenological model for the generalized strength data.

\[
\frac{S}{S_{ref}} = 0.62 \left(\frac{FA}{F}\right) - 0.29
\]  (3)
The experimental and predicted strength data for 3 days is shown in Figure 9. One possibility for such close agreement in both the cases of Portland cement concrete and geopolymer mortars is that the strength ratios considered might indirectly reflect the same microstructure for different combinations. Since microstructure is a geometrical parameter this possibility merits examination by a different consideration.

6.3 Strength analysis of cement concrete and geopolymer mortar

For a constant strength of 15 MPa the corresponding values of the binder to fluid ratio \( \frac{B}{F_{S=15MPa}} \) for various curves in Figs. 3 and 7 as reference values and normalized B/F ratios \( \frac{B}{F_{S=15MPa}} \) versus strength are plotted as shown in Fig. 10. Here binder refers to both cement or fly ash and fluid to water and alkaline solution. The variation of generalized ratios of cement to water at compressive strength of 15 MPa with respect to the compressive strength is linear. This is due to the fact that the parameter \( \frac{S}{B/F_{S=15MPa}} \) represents a geometrical parameter thereby indirectly reflecting the microstructure of the cement concrete and geopolymer mortars (Fig. 10).

The generalized relation with the above parameter is of the form shown below.

\[
\frac{S}{B/F_{S=15MPa}} = 0.325 + 0.39S
\]

(4)

The combined data of cement concrete and geopolymer mortars for the development of the phenomenological model are presented in Fig. 11. As mentioned earlier, “M” in this figure indicates the molarity of the alkaline solution and the numbers before “Days” indicate the age of the specimen tested. With reference value of strength at \( S_{B/F=2.0} \) corresponding to each of the linear paths, the data is normalized. This results in the phenomenological model of the form (Equation 5) with a correlation coefficient of 0.95 (see Fig. 12).

\[
S = 0.65 \left( \frac{B}{F_{S=15MPa}} \right) - 0.33
\]

(5)

It is needless to stress that reference value is not unique for all combinations. It is different for various
combinations of ingredients and that corresponding strength value reflects the synergy between the different constituents in strength development at any specified age irrespective of strength gain is either by chemical or thermal bonding. As such this can be regarded as a phenomenological model with underlying principle being Abrams’ Law (Abrams 1918) represented by linear relation according to Bolomey’s Law (Bolomey 1927). The use of this model requires an input reference strength data in the denominator of left hand side of expression in Equation 5, for any specific combination of ingredients for use of the above phenomenological relation (Equation 5) to determine the \( B/F \) ratios for any level of strength development envisaged.

7. Validation of the model with the data of independent researchers

It is interesting to note that the model was used to predict the data generated by different independent researchers both for conventional concrete and geopolymer composites. Rangan (2008) has reported the variation of compressive strength of geopolymer concrete with fluid to binder ratio (F/B). In this case, fluid is alkaline solution and binder is fly ash. The strength for F/B of 0.5 was extrapolated and used to predict various compressive strengths. The predicted strength values were in line with the experimental values (Table 1). The maximum error was less than 11.6%. This reinforces the possibility of using this model for any geopolymer composites.

In another case, the equations developed by Kargari et al. (2018) were used to validate the model. This data is taken from Kargari et al. (2018), wherein compressive strength was found at various ratios of \( B/F \) for geopolymer concrete. The values are listed in Table 2. It can be observed that the error is between 0.6 and 25.2%, and that the error is significantly less at lower strength (20 to 30 MPa). This error is also equivalent to the correlation coefficient, \( R \) as indicated by Kargari et al. (2018).

The method of prediction of compressive strength confidently adopted for the range of strength 20 to 30 MPa for both conventional and geopolymer composites, as the majority of structural concrete lies in this range across the world. It is seen that the strength development in OPC and geopolymer composites follow the same pattern. This can be used in re-proportioning these composites irrespective of the type of binder.

8. Concluding remarks

The following broad conclusions can be drawn from this investigation.

A phenomenological model within the basic framework of Abrams’ Law, extensively used in concrete technology, can be advanced for analysis and assessment of the strength of geopolymer composites. The analysis of combined data of Portland cement concrete and geopolymer mortars reinforces this possibility. This is further strengthened by validation by an independent
set of data and developed by different researchers. Since this phenomenological model is based on the experimental data analyzed, the constants in the functional relationship can be further refined by incorporating additional data in the analysis to encompass a still wider range of combinations of ingredients. The form of relationship would remain the same since the development of the relationship is based on the basic framework of Abrams’ and Bolomey’s Laws. To use this relation, it is necessary to determine the strength data for reference SB/F = 2.0 and use the same as input parameter for assessment of binder/fluid (B/F) ratios for different strength values. It is also possible to determine the range of strength that can be obtained in the working range of B/F ratios.

Acknowledgements
The author thanks the authorities of RSST, and RV College of Engineering Bengaluru for extending facilities to carry out the research work at RV-Centre for Alternative Construction Materials and Technologies (RV-Caltech), RVCE, Bangalore, India.

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