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Stress versus Strain Behavior of Geopolymer Cement under Triaxial Stress Conditions in Saline and Normal Water

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Abstract**—**Geopolymer cement was evaluated as wellbore sealing material for carbon dioxide geosequestration application. Curing of cement system in saline water and strength testing in triaxial stress state condition under lateral confinement is relevant to primary cementing in CO_2 geosequestration wellbore in saline aquifer. Geopolymer cement was cured in saline water (both at ambient conditions for 28 days and heated (60°C) conditions for 12 hours) and tested for triaxial strength at different levels of lateral confinement. Normal water and few other curing techniques were also studied both for geopolymer and API 'G' cement. Results reported were compared to evaluate the suitability of saline water for curing of geopolymer cement. Unconfined compression test results showed higher strength for curing in saline water than normal water. Besides, testing strength under lateral confinement demonstrated the material failure behavior from brittle to plastic.

Keywords**—**Fly ash, Geopolymer, Geosequestration, Saline water, Strength, Traiaxial test.

I. Introduction

GEOSEQUESTRATION of anthropogenic CO_2 has been identified as an effective mitigation option at the backdrop of growing concern over increase in concentration of atmospheric greenhouse gases. This innovative technology involves capture of CO_2 from major stationary sources such as coal fired power plant and subsequent transportation and injection into deep sedimentary rock for long-term storage. In the long term, part of this stored CO_2 get dissolved in aquifer water and undergoes complex chemical processes. For obvious reason, design and operation of different components of CO_2 geosequestration project requires consideration from different fields of engineering. These fields include geological sciences which covers geomechanical and geochemical aspects of wellbore injection as well as underground storage of CO_2. Special attention is needed in sealing the injection wellbore against potential future leakages which appear to be the prime consideration in successful operation of any such project

Currently, API (American Petroleum Institute) recommended class 'G' or 'H' cement are used for sealing annular spaces in between casing and rock formation in a geosequestration or petroleum/oil wellbore. However, sequestration of CO_2 in depleted hydrocarbon basin and/or saline aquifer has identified concerns over the long term integrity of conventional oilwell cement (API cement) seals in wellbore annulus. It has been reported [1] that the long term integrity of the wellbore cement seal is a primary performance issue in the geological sequestration of CO_2. In fact, there are complex geomechanical and geochemical processes which can cause potential failure to cement sealant placed in wellbore annulus. As a consequence, entrapped CO_2 can escape back to the atmosphere through the leakage channel created along damaged cement sheath. Evidently, any such leakage will prove the innovative technology futile and cause potential threat to the environment.

Therefore, finding an efficient cement system is the key to successful implementation of CO_2 sequestration in geological media. Other than investigating the long-term integrity of conventional oilwell cement, little effort has been made in finding an innovative primary cementing system capable of confronting extreme reservoir conditions, aggressive cement reaction and excessive mechanical stress developed. However, several studies have been reported where variation has been considered in Portland based cement using numerous additives [2], [3], [12].

Development of geopolymer as potential oilwell cement is quite recent. Geopolymer cements or alkali-activated cementitious materials are acid-resistant inorganic polymeric material with zeolitic properties [4], [5]. Over the years, this alkali-activated novel cementitious binder material has been investigated for its acid resistivity, shrinkage and compressive strength development at variable curing periods, temperatures and environments. Until today, it has been demonstrated that high temperature curing environment favors geopolymer synthesis and yields moderate to high compressive strength [6]-[8]. However, curing regime representing wellbore physical environment are more complex than mere application of high temperature. In fact, curing regime for annulus cements are multifarious and required to be thermodynamically stable against fluctuation of temperature and pressure in saline or acidic saline environment.

Placing and curing of cement in underground saline environment is one of the issues to be considered in wellbore cement application. In fact, investigation of curing of wellbore cement in saline water bears significance since terrestrial

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saline aquifer has been turned out as prospective reservoir for long-term underground CO_2 storage [9]. Besides, study on several pilot projects (e.g. Frio, Ketzin, Nagaoka) and some commercial operations (eg. Sleipner, Snφhvit, In Salah) suggest that CO_2 geological storage in saline aquifer is technologically feasible [10], [11]. Moreover, it has been found that salinity influences the hydration and strength development of wellbore sealant cement [13].

At the same time, mechanical behavior of wellbore cement system is important because once placed and cured in subterranean environment; this cement experiences variable stress scenarios. Reservoir re-pressurization and subsequent expansion cause sealant cement to undergo varying stress states. This dictates the necessity to investigate mechanical strength of wellbore cement under confinement rather than having only the uniaxial compressive strength. In such context, this study explores the curing of fly ash based geopolymer in saline water compared to normal water at ambient conditions. Apart from uniaxial strength testing for each of the samples, mechanical strength of geopolymer cured in saline water has been evaluated in triaxial stress state condition as well.

However, it has already been detailed that in most cases, cement slurry placed in geo-sequestration or petroleum/oil wellbore will confront high temperature and high pressure down hole environment even during initial curing period, notwithstanding the possibility of encountering highly acidic fluid. However, it is important to study the effect of each condition separately so that we have a comprehensive understanding of the material behavior in such extreme conditions. Further, study of geopolymer curing at ambient conditions (temperature range 20-22°C) is relevant to the borehole conditions when the uppermost casing is inserted and cemented at the onset of overall construction. Also, satisfactory performance of geopolymer material cured in saline water at ambient conditions is a pre-condition for geosequestration application, since high temperatures and pressures cannot always be guaranteed.

II. Materials

ASTM Class ‘F’ fly ash was used as aluminosilicate source material for synthesization of geopolymeric cement. Besides, small percentage of ground granulated slag (Australian standard AS 3972) was blended with fly ash as an additive. As already revealed by literature [14], [15], the objective of slag addition was twofold – to accelerate the initial hardening of fly ash slurry at room temperature and also to get higher strength by delivering more calcium to the system. The chemical composition of fly ash and ground granulated slag used in this study are presented in Table I.

Sodium silicate (Na_2SiO_3) solution of specific gravity 1.53 and sodium hydroxide (NaOH) flakes of 98% purity (PQ Australia) were mixed together one day prior to usage. The chemical composition of the sodium silicate solution was Na_2O =14.7%, SiO_2 =29.4% and water =55.9% by mass. In parallel, oil well cement (class G cement) was used for strength testing.

TABLE I
CHEMICAL COMPOSITION OF FLY ASH AND SLAG

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Loss on ignition
Fly ash	2.8	48.3	30.5	12.1	1.2	0.3	0.2	0.4	1.7
Slag	42.1	32.5	13	0.22	5.47	4.1	0.21	0.25	0.35

III. Methods

A. Specimen Preparation

The geopolymer was synthesized from mixture of fly ash and slag in the proportion of 9:1. The blended fly ash and slag particles were mixed with an amalgamated solution of sodium silicate and 8M sodium hydroxide at a ratio of 2.5:1. The materials were proportioned by weight and the slurry was prepared by using a liquid to solid ratio of 0.4. The mixing was conducted in a mechanical mixture operated at 80rpm for 5 minutes. Cylindrical specimens were made by means of molds of 38mm diameter and 76mm height. All molds were filled with slurry and compacted in layers with vibration. The molds filled with slurry were kept in room temperature for 10~12 hours to allow sufficient hardening and easy remolding. After remolding, specimens were immersed in different curing media for subsequent curing. For oil well cement (Class G cement), water cement ratio of 0.44 was adopted as specified in API 10B specification.

B. Specimen Curing

After taking out from the molds, cylindrical samples were immersed in two types of curing media – saline water and normal water. Tap water was used as normal water, which from here onwards will be referred to as water. Saline water was prepared by adding sodium chloride (NaCl) with water in different concentrations. Geopolymer samples were cured for 28 days in water, 15%, 8% saline water at room temperature in atmospheric conditions. In addition, a series of samples were cured in air, saline water and normal water at 60°C for a period of 12 hours inside an oven. Few samples were also cured in sealed condition for the same period where the sample surfaces were coated by silicon layers and then wrapped by thin plastic sheets. These samples were then kept in a closed airtight container for 28 days. Oil well cement was also cured in the same manner.

C. Experimental Setup

Triaxial setup used for testing cylindrical samples consisted of a triaxial cell combined with two deformation devices

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(LVTDs) set internally along the axial direction. Each LVDT consisted of a coil assembly and a core both coupled electromagnetically. Average axial strains are measured by taking average of the values obtained from the two LVDTs. A compression frame assembly with a load cell capacity of 3000 kN was used with the test set up to apply a deviator stress to the sample. Confining pressure to the triaxial cell is applied with the aid of a confining pressure system which operates on a piston assembly driven by air pressure. The whole assembly was connected to computer aided data acquisition software through a SCON-1600 universal signal conditioning and control unit.

IV. Experimental Results

A. Uniaxial Compressive Strength

Compressive strength testing of fly ash for 28 days cured samples in different media showed higher strengths for saline water curing (66 ±1.45MPa for 15% salinity and 61.5 ±1.41MPa for 8% salinity) and lowest strength for water curing (47.5 ±1.05MPa) (Fig. 1). On the other hand, strength results for oil well cement (class G cement) showed higher strength for water curing (52 ±1.65MPa) and lower strength for saline water curing (30.5 ±1.08MPa for 8% salinity and 28.5 ±0.93MPa for 15% salinity) (Fig. 1). The oil well cement tests were done for benchmarking purposes.

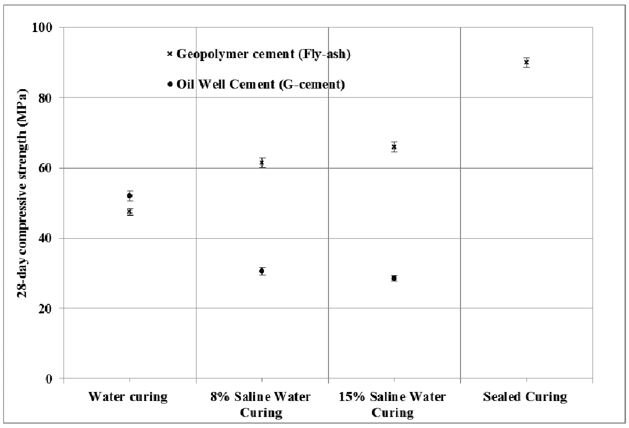

Fig. 1 Strength of geopolymer and oil well cement cured for 28 days in different media

In order to examine the effect of temperature together with water and saline water on strength development of geopolymer, samples were cured in air, normal water and 15% saline water, all kept inside a preheated oven at 60°C for 12 hours. Compressive strengths for samples cured in air, normal water and saline water are presented in Fig. 2. It is observed that all samples have gained almost same compressive strength (53.08 ±1.16MPa for temperature cured, 53.79 ±2.19 MPa for heated water cured samples and 55.57 ±1.77MPa for 15% heated saline water cured samples).

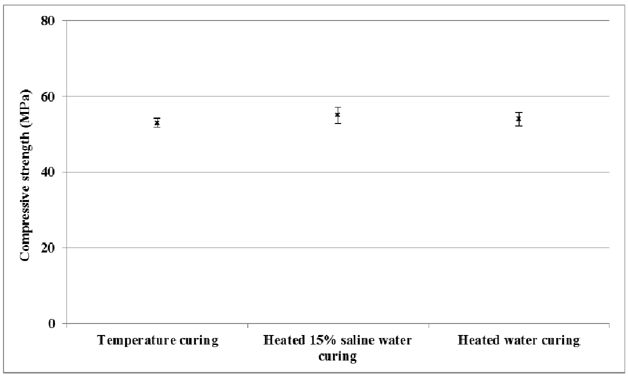

Fig. 2 Strength of geopolymer cured in 60°C temperature, preheated water and 15% saline water at 60°C for 12 hours

B. Triaxial Compressive Strength

Geopolymer samples tested at low confining pressure (<20MPa) showed more pronounced peak than samples tested under high confining pressure. From Fig. 3 it is evident that failure of samples under 35MPa and 25MPa lateral pressures shows plastic deformation at failure. However, failure of samples under confining pressure of 10MPa and 15MPa shows brittle failure.

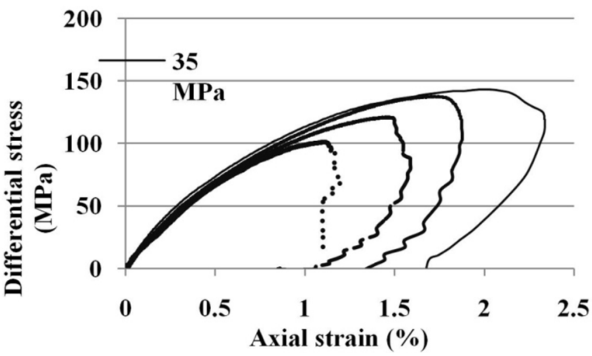

Fig. 3 Differential stress versus axial strain (%) plot for geopolymer cured in 15% saline water at ambient conditions at different confining pressure

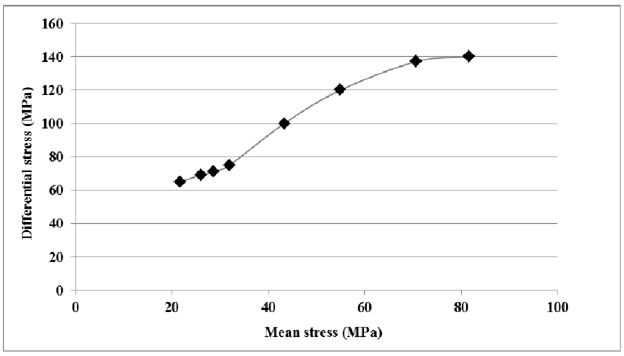

Fig. 4 Failure envelope for geopolymer cured in 15% saline water at ambient conditions

Failure envelope of geopolymer under triaxial stress state conditions is depicted in Fig. 4. The failure path initially shows an inclined straight line (for confining pressures up to 7MPa), then followed a non-linear path for confining pressures up to 25MPa. After that it turns into a flat line.

V. Discussion on Results

Results obtained from strength testing showed that curing of geopolymer samples for 28 days in saline water provides an increase in strength as compared to water cured samples. Conversely, compressive strength decreases for oil well cement (G cement) cured in saline water as compared to normal water for equal period of curing. The results for oil well cement are consistent with the outcome reported by Zhou et al. [13]. However, the contrasting result of geopolymer samples cured in saline water is, to some extent, explained by the compressive strength developed in sealed samples. In fact, sealing prevented early dissolving of unreacted components out of the geopolymer samples to the surrounding curing water. It also turns out from the strength attainment scenario of differently cured samples that concentrated saline water prevents more easily early dissolution of activator components than water.

All samples cured in air (60°C), heated saline water and normal water at 60^0C temperature for a period of 12 hours achieved nearly same strength. This obviously dictates that short interval (12 hours) temperature curing exhibited same strength as heated saline water and water curing because type of water (either saline water or water) did not influence the strength gain of geopolymer. Rather, temperature accelerated the reaction mechanism and appeared to be the only cause for strength gain. It can also be stated that there is no adverse effect in curing of geopolymers at high temperature (60°C) with saline water. Hence, it is understandable that higher strength achievement in saline water curing is due to the lowered leaching out of reactants to the surrounding liquid during prolonged curing period (28 days). Apart from that 53°C can be considered as common exposure temperature in most geosequestration wellbores. Compressive strength obtained (53-55MPa) from geopolymers cured at this temperature (60°C) can also be considered reasonable taking into account the wellbore stress scenarios.

From triaxial stress results it is observed that at 10MPa and 15MPa confining pressures, saline water cured geopolymer showed brittle failure and above that it showed plastic failure. Such failure behaviour has already been identified for conventional cement [16], [17]. Additionally, failure envelope obtained for saline water cured geopolymer under lateral confinement showed that under confining pressures up to 7MPa, stress path is inclined linear which finally turns back to linear (flat). However, in between the failure line is non-linear. At the beginning, the transition from linear to non-linear elucidates the fact that the cement gets compacted at this point due to hydrostatic compression. Obviously, this compression brings in closing of microcracks and pores. In general, this coalescence of microcracks may lead to shear localization and development of fracture for materials like cement (porosity 30~40%). Apart from that, there is a second transition at the end of failure envelope and it appears that the material enters into the plastic state at this stage. In summary, it can be stated from the plastic yield envelope (Fig. 4) that geopolymer cement can withstand high mean stresses without any macroscopic failure or porosity increase. Therefore it turns out that geopolymer cement cured in saline water follow the same failure behaviour as conventional cement under lateral confinement.

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