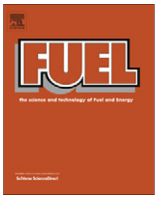
Fuel 107 (2013) 34–39

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Strength of geopolymer cured in saline water in ambient conditions

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HIGHLIGHTS

- ▶ Oil well cements have durability issues in CO_2 geo-sequestration in saline aquifer.
- ▶ Curing of a new cement, geopolymer, was examined in saline and normal water.
- ▶ Saline water cured geopolymers showed better properties than normal water samples.
- ▶ The reason for this behaviour is investigated by microstructural and other tests.
- ▶ It is found that leaching to curing media rather than ingress caused these results.

ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 15 January 2013
Accepted 16 January 2013
Available online 31 January 2013

Keywords:
Geopolymer
Geo-sequestration
Saline water
Strength
Ambient conditions

ABSTRACT

Results of geopolymer cement tests in saline water curing are reported. Saline water exposed curing is relevant to wellbore cements used for geo-sequestration of CO_2 in saline aquifer. The conventional Portland cement based oil well cements have unfavourable results when cured in saline water. However, geopolymer based cements cured in saline water showed higher strength results than the ones cured in normal water. The reason for this behaviour is not readily apparent, and hence microstructure investigations, namely, scanning electron microscopy, Energy-dispersive X-ray spectroscopy and X-ray diffraction were performed. Saline water cured geopolymer samples also were found to have lower sorptivity test results than normal water cured samples. Improved properties of geopolymers when cured in saline water is found to be related to reduced leaching of reactants from the samples rather than the result of ingress of saline water into the samples. Geopolymers tested are made from fly ash with small amount of slag (9%), and were cured at room temperature.

1. Introduction

Geo-sequestration of anthropogenic CO_2 provides an effective mitigation option against increasing concentration of atmospheric greenhouse gases. Worldwide, there have been 18 demonstration and commercial geological storage projects in successful operation since 1996 [1]. However, long-term sustainability of such projects depends largely on potential leakage of stored CO_2 due to wellbore integrity loss associated to failure and degradation of sealant material. In fact, Carey et al. [2] reported that the long term integrity of the well bore seal is a primary performance issue in the geological sequestration of CO_2.

Currently, API recommended class ‘G’ or ‘H’ cement has been in use for sealing geo-sequestration or petroleum/oil wellbore. However, it has been demonstrated by several studies that traditional materials are not entirely capable of providing a viable solution to the risks linked to the potential wellbore leakage [3–7]. Therefore, it is imperative that an innovative wellbore sealing material be devised which can withstand extreme reservoir conditions, aggressive cement reaction and excessive mechanical stress developed.

In the quest for finding suitable cements, this study investigates geopolymer, a new class of cements which may be effective in confronting the prevailing subterranean conditions in geo-sequestration wellbore. Geopolymer cements or alkali-activated cementitious materials are acid-resistant inorganic polymeric material with zeolitic properties [8,9]. Davidovits [10], who introduced the name geopolymer to these materials, reported the structure of geopolymer of poly-sialates as: $M_n\{-(SiO_2)_z-AlO_2\}.\,wH_2O$, where M is a cation such as K^+, Na^+ or Ca^{2+}; n is the degree of polycondensation and z is 1, 2 or 3. Although this amorphous alkaline aluminosilicate hydrates [N–A–S–H] refers to the main reacted polymeric component in the system, reaction kinetic model [11] suggests crystalline zeolitic phases as well. Study carried out on alkali activated fly ash [12] identified that final reaction products

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http://dx.doi.org/10.1016/j.fuel.2013.01.035

contains Na-Herschelite ($NaAlSi_2O_6$. $3H_2O$) – type of zeolite and hydroxysodalite. On the other hand, network of sialate (silicon–oxo–aluminate) in amorphous phase consist SiO_4 and AlO_4 tetrahedra linked alternatively in 4-fold coordination with oxygen. In such a three dimensional framework, positive ions such as Na^+, K^+, and Ca^{2+} are required to be present in the cavities to balance the electric charge generated by the substitution of Al^{3+} for Si^{4+} [8,13].

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. Although, the material characteristics of geopolymer known so far seemingly indicate its suitability as wellbore sealant [14–16], laboratory and field scale simulations are required to be carried out to establish the capability of the proposed binding material in enduring geo-sequestration environment. It is also important that before exploring for long-term durability, issues articulated to short term cement performance such as curing together with hydration are needed to be addressed.

Investigating curing of wellbore cement in saline water bears significance since terrestrial saline aquifer has been turned out as prospective reservoir for long-term underground CO_2 storage [17]. Besides, study on several pilot projects (e.g. Frio, Ketzin, Nagaoka) and some commercial operations (e.g. Sleipner, Snφhvit, In Salah) suggest that CO_2 geological storage in saline aquifer is technologically feasible [18,19]. Moreover, it has been found that salinity influences the hydration and strength development of wellbore sealant cement. The investigation made by Zhou et al. [20] on the hydration of saline oil well cement at elevated temperatures and pressures, tested cement slurry mixed with saline water at four different concentrations as 0%, 5%, 15%, 25%, and 36% of NaCl by weight of water. The salt concentration of curing water was also the same as mixing water. The results revealed that low salt concentration accelerates hydration and high salt content retard hydration. Besides, the strengths of saline cement slurries decrease with increasing salt content.

On the other hand, no studies have been found yet which investigates curing of geopolymer cement in saline water. However, Lee and van Deventer [21] tested the fly ash mixed with small quantity of chloride salt (0.08 mol of salts per 450 g of fly ash) and found that inorganic salt contamination adversely affected the strength and durability. As stated [20], salt contaminated cement slurry are preferred in cementation of wellbore in saline aquifer because fresh water slurry absorbs salts from the adjoining formation pores and thereby damage wellbore stability. Hence, considering results of Lee and van Deventer [21] and the fact of salt intrusion, saline water curing of geopolymer cement would be considered enduring if the scale of the likely salt intrusion during hydration is such that it does not affect adversely the strength and long-term durability.

As mentioned before, moderate range of temperature based curing regime has already been demonstrated and established as a favourable curing condition for geopolymer cement [15,16,22–26]. On the contrary, synthesization of geopolymer at ambient conditions has not been explored as much as at elevated temperature. Of late, Somna et al. [27] examined the ambient temperature curing of ground fly ash geopolymer activated by NaOH and obtained geopolymer with compressive strength varying from 20.0 to 23.0 MPa for NaOH concentration ranging from 9.5 to 14 M.

In such a context, this study explores the effect of curing of fly ash based geopolymer in saline water compared to normal water at ambient conditions. 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 [5,28,29], 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 behaviour in such extreme conditions. Further, study of geopolymer curing at ambient conditions (temperature range 20–22 °C) is relevant to the bore-hole 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 geo-sequestration application, since high temperatures and pressures cannot always be guaranteed.

2. 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 [23,30], 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, as determined by X-ray fluorescence (XRF) analysis, are presented in Table 1.

Sodium silicate (Na_2SiO_3) solution of specific gravity 1.53 and sodium hydroxide (NaOH) flakes of 98% purity (PQ Australia) were mixed together 1 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. For benchmarking purposes, oil well cement (class G cement) was also used for strength testing.

3. Methods

3.1. Specimen preparation

The geopolymer was synthesized from mixture of fly ash and slag in the proportion of 10:1. The blended fly ash and slag particles were mixed with an amalgamated solution of sodium silicate and 8 M 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 80 rpm for 5 min. Cylindrical specimens were made by means of moulds of 23 mm diameter and 46 mm height. All moulds were filled with slurry and compacted in layers with vibration. The moulds filled with slurry were kept in room temperature for 10–12 h to allow sufficient hardening and easy remoulding. After remoulding, specimens were immersed in different curing waters for subsequent curing. For oil well cement (Class G cement), water cement ratio of 0.44 was adopted as specified in API 10B specification.

3.2. Specimen curing

After taking out from moulds, 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

Table 1
Chemical composition of fly ash and slag (mass%).

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