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Flexible Geopolymer for Oil and Gas Well Cementing: An Experimental Study

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ABSTRACT

Conventional wellbore cementing materials used in the oil and gas industry are normally brittle, have low tensile strength and suffer from shrinkage. These properties affect the performance of these materials in downhole conditions which can lead to expensive remedial operations, lower production of reservoir fluids, environmental problems and sometimes loss of wells. Therefore, several researches have been performed to find alternative barrier materials which have the potential to substitute the conventional cements. Among these materials geopolymers have shown appealing properties.

In this thesis work, several mechanical properties of geopolymers such as Young's modulus (flexibility), uniaxial compressive strength and tensile strength have been investigated for the purpose of improving such properties for long-term and making geopolymers applicable for the use in the oil and gas fields. The material used in the experiments of this project is a geopolymer with a combination of fly ash Class F and ground granulated blast furnace slag. Two different flexible additives have been used in the geopolymer to study their effect on the flexibility and other mechanical properties of the material. In addition, two different mixing procedures, namely non-API and API have been used for the preparation of the mixtures.

Based on the experimental results, it was observed that:

- The addition of the two additives to the geopolymer mixtures led to an increase in the flexibility of all the mixtures. However, the highest flexibility was achieved in the geopolymer mixture which included both flexible additives and was prepared with the non-API mixing procedure.
- In general, for all the mixtures in both mixing procedures, the increase in the flexibility resulted in a slight reduction of the compressive strength.
- Comparing the two mixing procedures, the mixtures which were prepared with both the non-API and the API gained nearly similar tensile strength values. Thereby, with increasing flexibility, the tensile strength was reduced when the additives were added to the geopolymer mixtures separately. However, when the combination of the two additives was added to the geopolymer mixtures, the tensile strength increased with increasing flexibility.
- For both the non-API and the API mixing procedures, the geopolymer mixture which included both flexible additives showed the highest value of tensile strength to Young's modulus ratio. This higher ratio means that the geopolymer mixture has obtained better mechanical properties and as a consequence, better resistance to mechanical damage.

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NOMENCLATURE

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BHCT	Bottom Hole Circulating Temperature
BHST	Bottom Hole Static Temperature
CO ₂	Carbon Dioxide
GGBFS	Ground Granulated Blast Furnace Slag
HPHT	High-Pressure High-Temperature
HSE	Health, Safety and Environment
HSR	High Sulfate Resistance
MSR	Moderate Sulfate Resistance
OBM	Oil Based Mud
OFITE	OFI Testing Equipment
OPC	Ordinary Portland Cement
P&A	Plug and Abandonment
R&D	Research and Development
RPM	Revolutions Per Minute
SCP	Sustained Casing Pressure
UCA	Ultrasonic Cement Analyzer
UCS	Uniaxial/Unconfined Compressive Strength
UiS	University of Stavanger

1 INTRODUCTION

Conventionally, ordinary Portland cement (OPC) has been used as a wellbore barrier material in oil and gas wells (Nelson and Guillot, 2006). Generally, cement is pumped in the annulus between the formation and the casing strings with the main purpose of providing long-lasting zonal isolation and achieving a safe and profitable production of the reservoir fluids (Le Roy-Delage et al., 2000; Ravi et al., 2002). Some of the advantages of OPC are: its relatively lower price compared to other barrier materials and also the good reputation it has gained through time (Khalifeh et al., 2015). In addition, it is pumpable and there is a quite good knowledge about its chemistry. However, OPC as a barrier can face different circumstances during the lifetime of a well. Although the OPC is primarily placed in the wellbore and achieves its purpose of isolating the wellbore, variations in the downhole temperature and pressure can generate stresses which can damage the cement sheath and result in loss of zonal isolation (Bosma et al., 1999; Goodwin and Crook, 1992; Jackson and Murphey, 1993; Thiercelin et al., 1998). Among the main issues that cement can face during the lifetime of a well one can list (Le Roy-Delage et al., 2000; Nelson and Guillot, 2006; Teodoriu et al., 2012):

- Early gas migration which cannot be detected after the cement is placed,
- Debonding of cement from the casing or formation over time,
- Stresses caused during well stimulation, and
- Deterioration of cement sheath due to corrosive fluid attacks, etc.

To prevent mechanical damage to the cement sheath, it is desirable to obtain a high value of tensile strength to Young's modulus ratio as well as a lower value of cement's Young's modulus relative to that of the formation. These can be achieved by using flexible additives in the composition of the cement. The flexible additives help to reduce cement's Young's modulus and consequently increase its flexibility (Jafariesfad et al., 2017; Le Roy-Delage et al., 2000). Among these additives one can mention latex, fibers and several other polymers. The use of such additives has shown improvement in the cement's toughness and elastoplastic performance (Morris et al., 2003). As an example, Williams et al. (2011) stated that the addition of latex in the cement is of great advantage for avoiding short-term sustained casing pressure (SCP) and gas migration. However, the use of latex is not reliable for prevention of such problems in the long-term. In addition, due to the fact that oil and gas wells are getting deeper and more wells are drilled in harsh environments, the use of the mentioned additives will not provide adequate and long-lasting solution for the well integrity (De la Roij et al., 2012).

Although OPC has its advantages, different researches have been performed to investigate alternative barrier materials which have the potential to substitute the OPC (Khalifeh et al., 2015). This is because there is a demand for the use of materials which have less impact on the environment and a better performance in downhole conditions compared to OPC (Ridha and Yerikania, 2015).

Different alternative materials to OPC have been proposed and studied by several researchers. Some of these materials are such as unconsolidated sand slurries, thermosetting polymers and geopolymers (Beharie et al., 2015; Khalifeh et al., 2013; Khalifeh et al., 2014; Saasen et al., 2010). Among these materials, geopolymers have shown appealing properties (Khalifeh et al., 2019). Geopolymers are inorganic cementitious materials and due to their binding capability, they have the potential to be used as barrier materials in the oil and gas wells and consequently as a substitute to OPC (Salehi et al., 2019; Živica et al., 2015). Compared to OPC, geopolymers have lower cost, higher durability, lower energy usage and CO₂-emissions during their production (Khalifeh et al., 2016; Xu and van Deventer, 2003). However, the main current limitation is that geopolymers have not been field tested yet. In order to make geopolymers applicable for the use in oil and gas well cementing and increase their potential in substituting the OPC, long-term durability of these materials needs to be investigated. As mentioned previously, flexibility in a barrier material is of great importance. Therefore, the flexibility of geopolymers needs to be investigated and improved.

Previously, the flexibility of geopolymers has been studied by Shrotri (2006) using different flexible organic polymer additives in the geopolymer-concrete composition. Shrotri (2006) focused on the application of geopolymer in concrete for the use in the structural applications. However, in the oil and gas industry, the cement is used as a binder and does not include any aggregates. In addition, downhole conditions in the oil and gas wells are significantly different than the conditions the materials are exposed to in the structural applications. Therefore, the study of flexible geopolymers in this thesis project is considered novel in its area of application which is oil and gas well cementing.

1.1 Outline of the thesis

In order to study geopolymers' potential for oil and gas well cementing applications, it is necessary to know the challenges related to the use of OPC and also the requirements which oil and gas well cement needs to fulfill for the purpose of providing long-lasting zonal isolation. In addition, to improve the geopolymers' properties for future field applications, it is important to compare these materials with the conventional cement (OPC) which is currently used in the oil and gas industry. Therefore, Chapter 1 focuses on:

- Challenges related to the use of OPC
- Properties of conventional API Class G cement (the basic oil and gas well cement) for the purpose of comparison with geopolymers
- Most important mechanical properties of wellbore cements as well as the requirements and calculations of these properties
- Alternative barrier materials
- Geopolymers' background, chemistry, advantages and limitations and previous related studies

Further, Chapter 2 includes the detailed experimental procedure which consists of the following main subchapters:

- The description of the experimental materials
- The procedures used for preparing and testing the different samples as well as the equipment used for the experiments
- The analytical approach used to determine parameters such as Young's modulus (flexibility) of the geopolymer mixtures

In Chapter 3, the experimental results have been presented and discussed. The results illustrate the effect of the two additives as well as the two different mixing procedures on the mechanical properties of the geopolymer mixtures. The mechanical properties argued include the Young's modulus (flexibility), uniaxial compressive strength and tensile strength.

In Chapter 4, the main conclusions of this thesis work are drawn based on the results and discussions. Finally, in Chapter 5, some recommendations have been provided for improving the results of the experiments in future research works. These recommendations are based on the challenges encountered during the experiments.

1.2 Theoretical background

This section goes through the requirements and challenges related to wellbore cementing. Also, the API Class G cement which is the most common cement currently used in the oil and gas industry has been discussed. Further, the most important mechanical properties of wellbore cementing materials have been discussed, namely, Young's modulus (flexibility), uniaxial compressive strength and tensile strength. To ensure the integrity of cement and to achieve long-lasting zonal isolation in a wellbore, proper evaluation of these mechanical properties is essential. Therefore, the methods used to evaluate these properties have been argued. In addition, the required values of such properties which are necessary for long-term cement integrity have been presented based on real field cases as well as several research works. Moreover, alternative barrier materials, particularly geopolymers which have the potential to substitute conventional cement have been introduced. Also, geopolymer's chemistry, advantages and limitations as well as some prior research work on this barrier material have been reviewed.

1.2.1 Wellbore cementing requirements and challenges

In oil and gas wells, cement is placed in the annulus between the formations and casing strings and its most important purpose is to provide long-lasting zonal isolation. A proper wellbore cement should fulfill the following requirements (Paiva et al., 2018; Thiercelin et al., 1997):

- Providing hydraulic seal between different fluid-bearing zones
- Preventing the flow of the formation fluids towards the surface
- Contributing to casing support as well as supporting the surface equipment

Fig. 1.1 shows the requirements for a complete and long-lasting zonal isolation.

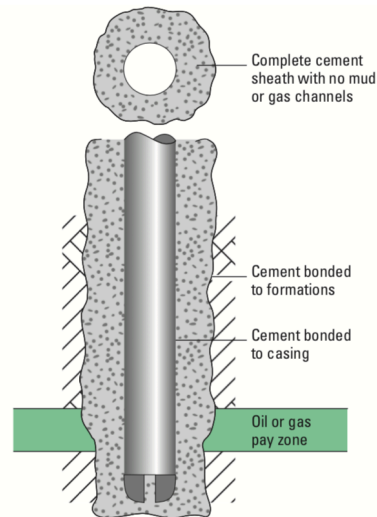


Fig. 1.1. Schematic of requirements for a complete and long-lasting zonal isolation (After Nelson and Guillot (2006)).

During the design phase of cement slurry for oil and gas well operations, several factors are required to be analyzed and taken into consideration. The performance of cement slurry is checked before use in field operations through different laboratory experiments specified by the API standards. Several parameters such as rheology, density, pumpability and fluid-loss control are usually evaluated for short-term cement slurry performance. However, a good performance of these parameters may not prove cement's potential to withstand degradation in long-term perspective through different well operations such as drilling, completion, production and plug and abandonment. Therefore, it is also important to evaluate the long-term or the thermo-mechanical properties of cement in order to achieve long-lasting zonal isolation in the well.

After the cement is placed, set and hardened, it can experience severe mechanical stresses which can result in cement failure and finally loss of zonal isolation. These stresses can include in-situ stresses caused by the formation surrounding the cement sheath as well as the stresses caused during well-operations such as hydraulic fracturing and perforating (Jimenez et al., 2016; Lyons and Plisga, 2011; Morris et al., 2003). Common cement materials used in the well cementing applications usually have some deficiencies such as being brittle and prone to shrinkage issues as well as showing low tensile strength. Such deficiencies can affect the performance of these materials in downhole conditions and lead to expensive remedial operations, lower production of reservoir fluids, environmental problems and sometimes loss of wells (Jimenez et al., 2016). In addition, temperature and loading cycles which occur during

the different well operations such as drilling, completion, hydraulic fracturing, production, etc., can present serious challenges to the well cement integrity (Shadravan et al., 2014).

To ensure the integrity of cement for its application in oil and gas wells, many researchers have studied the mechanical properties of cement such as Young's modulus, uniaxial compressive strength, tensile strength, etc. Also, they have proposed the requirements needed for such properties to provide long-lasting zonal isolation (Jafariesfad et al., 2017). These requirements are discussed in the following section.

1.2.2 API Class G cement

American Petroleum Institute (API) has defined eight classes of OPC. These classes have different chemical compositions (see Table 1.1). Each class can thus be used for a specific application. However, the API Class G is the most used cement in the petroleum industry (Nelson and Guillot, 2006). Therefore, only this class has been discussed and used as a reference further in this thesis work.

API Class G cement is designed for well-cementing operations from the wellhead to a depth of 2440 m. However, several additives such as retarders and accelerators are added to the cement to make it applicable for deeper wells such as high-pressure, high-temperature (HPHT) wells (Lyons and Plisga, 2011).

During the production of the API Class G cement, only calcium sulfate and/or water is mixed with the clinker. API Class G is manufactured with two grades, one being Moderate Sulfate Resistance (MSR) and the other High Sulfate Resistance (HSR) (Nelson and Guillot, 2006). However, the HSR-grade is the most used cement in the petroleum industry (Guner et al., 2017).

Table 1.1. Chemical requirements for different classes of API cement (After Simpson (1988)).

API Cement Classification	Sulfate Resistance*	Acceptable Maximum Concentration (%)						
		C ₃ S	C ₃ A	C ₄ AF	MgO	SO ₃	Total Alkali (as Na ₂ O)	LOI
A	Ordinary	NS**	NS	NS	6.0	3.5	NS	3.0
B	Moderate	NS	8	NS	6.0	3.0	NS	3.0
B	High	NS	3	18 to 24 [‡]	6.0	3.5	NS	3.0
C	Ordinary	NS	15	NS	6.0	4.5	NS	3.0
C	Moderate	NS	8	NS	6.0	3.5	NS	3.0
C	High	NS	3	18 to 24	6.0	3.5	NS	3.0
G,H	Moderate	58 [†]	8	NS	6.0	3.0	0.75	3.0
G,H	High	65 [†]	3	18 to 24	6.0	3.0	0.75	3.0

*An expression of the set material's resistance to attack by sulfate ions in downhole brines.
 **NS = not specified.
 † Minimum acceptable C₃/S = 48.
 ‡ Maximum C₄AF = 24 - 2 × C₃A.

1.2.2.1 Mechanical properties of cementing materials

Previously, petroleum industry performed cement integrity evaluations by concentrating particularly on one of the mechanical properties of the set-cement which is the uniaxial or unconfined compressive strength (UCS). According to API standards, the UCS is determined by crushing cubic cement samples using e.g. hydraulic testing machines. The UCS value determined is then used to predict the approximate capability of the set-cement to support the casing and withstand the perforation stresses. However, due to long-term issues which have resulted in the loss of zonal isolation, petroleum industry has realized that the UCS is not the only mechanical property that should be considered for cement integrity evaluation (Nelson and Guillot, 2006). Therefore, for achieving long-lasting zonal isolation, additional mechanical properties of set-cement such as tensile strength as well as the elastic and ductile properties such as Young's modulus should be taken into consideration (Bosma et al., 1999; di Lullo and Rae, 2000; Ravi et al., 2002; Thiercelin et al., 1997).

Currently, OPC is the most essential material used in almost all cementing activities in the construction of oil and gas wells (Nelson and Guillot, 2006). This is because the OPC has relatively lower price compared to the other materials and it has also gained good reputation through time. Nevertheless, OPC has also some disadvantages which have convinced the researchers to search for the materials which can substitute OPC for the use in the oil and gas industry. Table 1.3 illustrates the different types of barrier materials which have the potential

to substitute the OPC (Khalifeh et al., 2015). However, this thesis focuses on type A, specifically geopolymers which are setting materials similar to OPC.

Generally, the mechanical properties are important factors for the evaluation of the oil and gas well barrier materials as they define the performance of such materials against the exposure to the mechanical loads and deformations (Lavrov and Torsæter, 2016). Fig. 1.2 demonstrates the mechanical properties studied in this thesis.

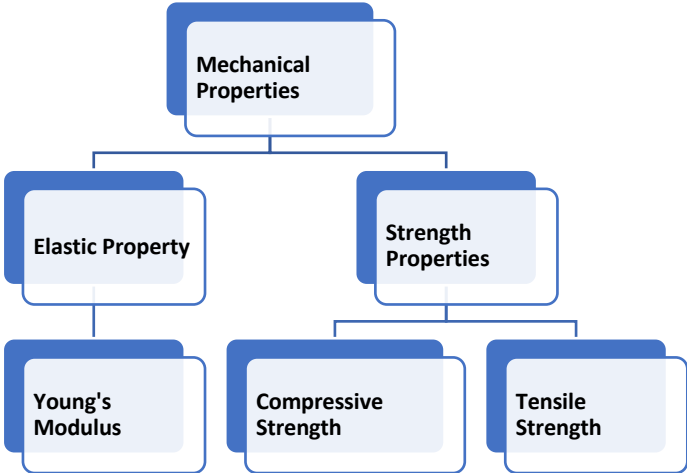


Fig. 1.2. Some of the most important mechanical properties of the cementitious material systems.

In the next sections these mechanical properties have been discussed for zonal isolation materials such as API Class G cement and geopolymers. Also, the experimental results which show the different mechanical properties of the API Class G cement have been tabulated in Table 1.2 based on different studies by researchers such as Teodoriu et al. (2012), Alp (2012), Le Roy-Delage et al. (2000), Morris et al. (2003) and Guner et al. (2017). In addition, previous studies on geopolymers’ mechanical properties have been discussed. This is to be able to compare the results obtained for geopolymers in this thesis with the API Class G cement and other types of geopolymers.

1.2.2.1.1 Young’s modulus

Young’s modulus (flexibility) is one of the elastic properties of a material and is defined as the proportionality coefficient in the elastic region of a stress-strain curve. The Young’s modulus value can be determined from the stress-strain curve which is obtained through a UCS

test. Young's modulus is basically the slope of the elastic region of a stress-strain curve (Lavrov and Torsæter, 2016).

As mentioned in section 1.2.2.1, the uniaxial compressive strength of cement is not the only mechanical property that has to be guaranteed for a long-lasting zonal isolation and plug and abandonment (P&A). In fact, the elastic properties of cement (e.g. Young's modulus) are also important factors for ensuring lifelong well integrity.

Young's modulus is the property of a material which indicates its flexibility. The lower the Young's modulus of a material, the higher the flexibility of that material. Young's modulus for oil and gas well cements used in petroleum industry usually lies between 1 to 10 GPa (Nelson and Guillot, 2006).

Generally, in the wells where the cement has higher Young's modulus than the formation rock, the likelihood for tensile failure increases as the pressure and temperature inside the casing increase (Bosma et al., 2000). This issue was further investigated and confirmed by Thiercelin et al. (1998) and Bosma et al. (1999).

The required Young's modulus of cement systems depends on the well and formation surrounding the wellbore. As an example, 25% of the wells drilled in Marcellus shale, has experienced SCP. To reduce the SCP in such wells, flexible cement systems are required. For wells in Marcellus shale the required Young's modulus (flexibility) has been determined to range from 350000 to 900000 psi [2.4 to 6.2 GPa] (Williams et al., 2011).

Young's modulus of cement can be calculated through laboratory experiments by performing both ultrasonic cement analyzer (UCA) and UCS tests. For instance, Alp (2012) performed UCA tests on Class G cement and used the equation 1 for the calculation of Young's modulus. As the equation indicates, Young's modulus is a function of the square root of the ultrasonic velocity (shear wave velocity) which is measured from the UCA test and also the density of the cement slurry.

$$E = V^2 \times \rho \quad (1)$$

where,

- E is Young's modulus [GPa]
- V is ultrasonic velocity [m/s]
- ρ is density of slurry [kg/m³]

During the UCS tests, the standard force in Newton [N], the test time in second [s] and the deformation [mm] data are provided by the testing instrument. To find the Young's modulus, the compressive axial stress and strain are required to be calculated.

Stress is the resistance which develops within the material to balance the forces applied externally to the material. Stress is determined by dividing the average force applied to the sample by the cross-sectional area upon which the force is acting. The stress value can thus be calculated by using the equation 2.

$$\sigma_{axial} = \frac{F_{axial}}{A} \quad (2)$$

where,

- F_{axial} is the standard force obtained from the UCS tests
- A is the average cross-sectional area of the cylindrical samples

Strain can be defined as the deformation of a material as a result of the force which acts upon it. Strain is determined by dividing the change in the length of the material by its original length as shown in equation 3.

$$\varepsilon_{axial} = \frac{\Delta L}{L_{original}} = \frac{(L_{final} - L_{original})}{L_{original}} \quad (3)$$

where,

- $L_{original}$ is the length of the material before applying the external force
- L_{final} is the final length of the material after applying the external force

Young's modulus is calculated from the elastic region of the stress-strain curve obtained from the UCS test. Equation 4 can be used to calculate the Young's modulus values from the stress-strain curves (Aadnoy and Looyeh, 2011).

$$E = \frac{\sigma_{axial}}{\varepsilon_{axial}} = \frac{\frac{F_{axial}}{A}}{\frac{(L_{final} - L_{original})}{L_{original}}} \quad (4)$$

Conventionally, flexible additives with micro-sized particles have been used in the well cements in order to achieve lower Young's modulus value and as a result higher flexibility. However, in some cases, the addition of such additives in the cement has resulted in the reduction of other properties of the cement such as the compressive and tensile strength. Nevertheless, according to Jafariesfad et al. (2017), flexible additives with nanosized particles could result in increasing the flexibility of the cement and improving its tensile strength at the same time.

1.2.2.1.2 Compressive strength

A material's compressive strength can be defined as the maximum stress that the material experiences at the time of failure when it is exposed to a compressive load. The UCS test is one of the tests that can be performed in the laboratory in order to find the compressive strength of cement. In this method, the cement samples are compressed with a testing machine and the compressive strength is recorded.

Another method to measure the compressive strength is a non-destructive test using a UCA test which gives an estimation of the compressive strength. The UCA test provides the curing downhole-pressure and downhole-temperature conditions for the cement samples and records the development of the cement's compressive strength at the same time. The compressive strength is thus measured by recording the changes in the ultrasonic signal's velocity through the cement while it cures (Chandlereng.com; Fann.com; Karakaya, 2010).

Cement is a brittle-elastic material. When the cement is exposed to a compressive load, a stress will be generated and grow linearly with the strain up to a point where small cracks are created in the material. When these small cracks connect and their sizes approach a critical value, the material breaks in a complex mechanism which is influenced by the stress boundary conditions and the material's geometry (Karakaya, 2010).

In the old days, the petroleum industry relied on the cement systems with high compressive strength for the purpose of achieving good oil and gas well cementing and zonal isolation. However, due to the improvements in the technology and also the increased knowledge in this area, the industry has come to an understanding that high compressive strength can actually result in the loss of zonal isolation. In fact, to achieve proper zonal isolation, a cement system with low compressive strength and high flexibility is preferred.

The standard requirement for cement's compressive strength is about 3.5 MPa for the casing support (Nelson and Guillot, 2006). However, according to di Lullo and Rae (2000) the required

compressive strength for the highest casing weight is about 1 MPa with the assumption that just 5% of the well cement supports the casing load. Previously, a compressive strength of about 7 to 10 MPa was considered for perforating and wellbore fracturing operations. However, this range of values for the compressive strength is not needed. This is because these operations can lead to increased pressure in the wellbore and result in damaging the cement sheath. Therefore, a cement with a high compressive strength value (i.e. within the range of 7 to 10 MPa) cannot deform properly when exposed to high pressures. Consequently, a cement with a lower compressive strength and higher flexibility is required during such operations (Nelson and Guillot, 2006).

1.2.2.1.3 Tensile strength

Tensile strength is the utmost tensile stress tolerated by the material right before it starts cracking. The most accurate way to determine the tensile strength is through direct tension tests. However, these tests may need specific sample shapes (e.g. dog-bone shape) which make these types of tests inconvenient. A more convenient test which is commonly performed on brittle materials for the purpose of tensile strength measurements is the Brazilian test. This type of test is an indirect method for performing tensile tests. For Brazilian tests, cylinder-shaped samples are prepared (Lavrov and Torsæter, 2016). Fig. 1.3 illustrates the procedure of performing the Brazilian test.

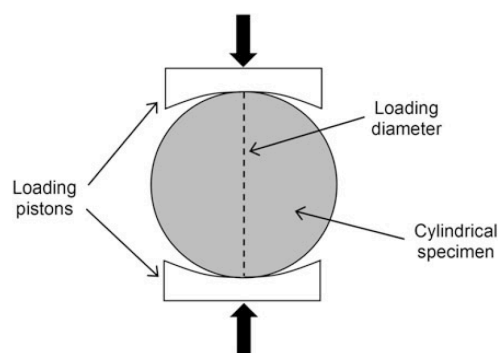


Fig. 1.3. Schematic of Brazilian test. The dashed line indicates the loading diameter and the arrows show the forces applied to the sample (After Lavrov and Torsæter (2016)).

In the oil and gas industry, the tensile strength testing of cement systems is not yet standardized and it is performed in accordance with the standards made for concrete testing in the construction industry (Heinold et al., 2003).

For a tensile strength test, the length of the cylindrical sample is normally chosen to be half of the diameter of the sample (Nelson and Guillot, 2006). However, according to the ASTM D3967-16 standard, the length to diameter ratio should be between 0.2 and 0.75. In addition, the loading rate should be between 0.05 and 0.35 MPa/s. This loading rate is controlled by the type of the rock tested and is selected such that the first crack occurs in the sample within 1 to 10 min of loading. On the other hand, according to the ASTM C496 standard, the loading rate to be applied during the Brazilian test should be a constant rate which ranges from 689 to 1380 kPa/min [0.011 to 0.023 MPa/s] until the first crack in the sample occurs.

The values of the load at failure and the sample dimensions recorded prior to the tensile test can be used in the equations 5 and 6 to calculate the tensile strength. According to the ASTM D3967-16 standard, the equation 5 should be used to calculate the tensile strength when testing instruments with flat platens are used and the equation 6 should be used for those with curved platens or jaws.

$$TS = \frac{2 \times F}{\pi \times L \times D} \quad (5)$$

$$TS = \frac{1.272 \times F}{\pi \times L \times D} \quad (6)$$

where,

- TS is the splitting tensile strength [MPa]
- F is the load at failure recorded by the machine [N]
- L is the length of the sample [mm]
- D is the diameter of the sample [mm]

According to Le Roy-Delage et al. (2000), it is also possible to calculate the tensile strength of a material using a flexion test. This test provides the flexural strength (i.e. the modulus of rupture) of the material. The tensile strength is then assumed to be half of the flexural strength by considering 50% of safety factor. The experimental results of the flexion test in this study are shown in Table 1.2. These results indicate the effect of the slurry density on the values

achieved for the mechanical properties of the material such as the tensile strength, compressive strength and Young's modulus. As it can be observed, the decrease in the slurry density results in a decrease in these properties.

When the cement sheath in a wellbore is exposed to high pressures and temperatures, several problems can occur. Among these problems one can refer to:

- The debonding of the cement from the formation or the casing
- The creation of cracks in the cement sheath due to tensile failure

Depending on the tensile strength and the shear-bond strength of the material, one of the above-mentioned problems can occur prior to the other one. According to a study performed by Parcevaux and Sault (1984), the shear-bond strength for the standard oil and gas well cements is around 7 MPa. In the case that the tensile strength of the cement sheath is higher than 7 MPa, the debonding of the cement from the casing or the formation will occur first and then lead to the creation of microannulus. On the other hand, in the case that the tensile strength of the cement sheath is lower than 7 MPa, the cement sheath will crack first before the debonding occurs (Nelson and Guillot, 2006).

Thiercelin et al. (1998) used models for predicting the occurrence of different stresses in an oil and gas well which is cased and cemented. In their study, they performed an analysis of the mechanical behavior of the set-cement under different downhole temperature and pressure conditions. This analysis was performed considering the following assumptions:

- Rock, cement and steel are materials with thermo-elastic properties
- The contact surfaces of the rock and the cement as well as the cement and the casing should be either completely bounded or have no bonding at all
- The variations in the temperature, pressure and stress are the only downhole conditions considered in the analysis and therefore, the stresses occurring internally within the set cement are not considered

In their study, Thiercelin et al. (1998) stated that the required tensile strength for the set cement is a function of the Young's modulus of both the cement and the rock. Therefore, they reported the required tensile strength of the set-cement as a function of the Young's modulus of the cement and the rock considering different wellbore pressure conditions (see Fig. 1.4 and Fig. 1.5).

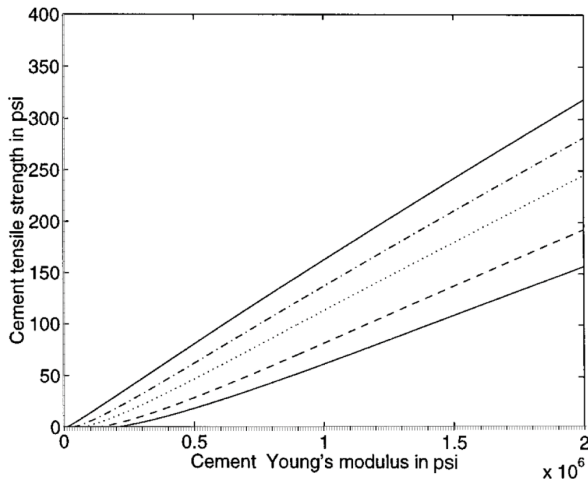


Fig. 1.4. The required tensile strength of the cement as a function of the Young's modulus of the cement and the rock for an increase in wellbore pressure of 1000 psi [68.9 bar]. The curves from the top to the bottom show the Young's modulus values of the rock in psi which are: 0.145×10^6 , 0.725×10^6 , 1.450×10^6 , 2.900×10^6 , 4.350×10^6 , respectively (After, Thiercelin et al. (1998)).

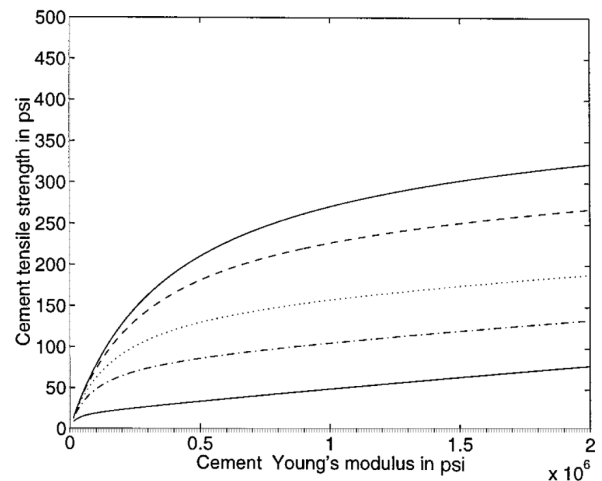


Fig. 1.5. The required tensile strength of the cement as a function of the Young's modulus of the cement and the rock for a decrease in wellbore pressure of 1000 psi [68.9 bar]. The curves from the bottom to the top show the Young's modulus values of the rock in psi which are: 0.145×10^6 , 0.725×10^6 , 1.450×10^6 , 2.900×10^6 , 4.350×10^6 , respectively (After, Thiercelin et al. (1998)).

Table 1.2 summarizes some of the values achieved for the mechanical properties of the API Class G cement such as the compressive strength, Young's modulus and tensile strength. The data is achieved based on the laboratory experiments performed by several researchers.

Table 1.2. The obtained compressive strength, Young's modulus and tensile strength values from the literature for the API Class G cement (Teodoriu et al. (2012)I, Alp (2012)II, Le Roy-Delage et al. (2000)III, Morris et al. (2003)IV, Guner et al. (2017)V).

Reference	CS (MPa)	E (GPa)	TS (Mpa)	Curing Time (days)	Curing Temperature (°C)	Curing Pressure (MPa)	Test Method	Comment
I	49.5	13.6	3.7	7	75	Ambient	UCS	-
	64	16.8	-	14	75	Ambient	UCS	-
II	43.1	-	-	1	80	Ambient	UCS	-
	44.3	-	-	7	80	Ambient	UCS	-
	19	-	-	1	80	Ambient	UCA	-
	-	17	-	1	80	-	UCA	-
	-	12	-	1	80	20.7	UCA	-
	-	15	-	7	80	-	UCA	-
III	39.2	9.04	4.53	3*	114	20.7	UCS	ρ slurry=16 lbm/gal
	36.6	6.6	4.23	3*	77	20.7	UCS	ρ slurry=15.8 lbm/gal
	22.9	3.76	3.35	3*	77	20.7	UCS	ρ slurry=14 lbm/gal
	3.21	0.5	0.6	3*	77	20.7	UCS	ρ slurry=12 lbm/gal
IV	36.9	5.48	1.9	2	84	20.7	UCS	For w/c ratio of 0.44
V	26.2	-	-	7	Ambient	Ambient	UCS	For w/c ratio of 0.4

*The samples were cured from 3 days to the time of obtaining a stable compressive strength.

1.2.3 Alternative barrier materials

Nowadays, there is an increasing demand for the materials with less impact on the environment and better and long-lasting mechanical properties for the use in the field applications. Therefore, several alternative barrier materials have been studied and suggested by different researchers and engineers. Also, different laboratory experiments have been performed on these barrier materials in order to check their reliability for the use in actual oil and gas wells. Such laboratory experiments have shown that these materials have the potential to substitute the conventional cement which is currently used in the oil and gas wells. Table 1.3 lists several types of alternative barrier materials with examples. Among these materials, the geopolymers have shown many advantages (see section 1.2.4.2). Therefore, the geopolymers have been suggested to be used as potential substitutes for conventional cement by several researchers such as Khalifeh et al. (2015) and Salehi et al. (2017a).

Table 1.3. Potential or alternative barrier materials (After Khalifeh et al. (2015); Oil&GasUK (2015)).

Type	Material	Examples
A	Cements/ceramics (Setting)	Portland API class cement, slag cement, phosphate cements, hardening cement, ceramics, Pozmix and geopolymers
B	Non-setting materials (Grouts)	Sand or clay mixtures, bentonite pellets, barite plugs, calcium carbonate and other inert particle mixtures
C	Thermosetting polymers and composites	Resins, epoxy, polyester, vinylesters, including fiber reinforcements
D	Thermoplastic polymers and composites	Polyethelene, polypropelene, polyamide, PTFE, Peek, PPS, PVDF and polycarbonate, including fiber reinforcements
E	Elastomeric polymers and composites	Natural rubber, neoprene, nitrile, EPDM, FKM, FFKM, silicone rubber, polyurethane, PUE and swelling rubbers, including fiber reinforcements
F	Formation	Claystone, shale and salt
G	Gels	Polymer gels, polysaccharides, starches, silicate-based gels, clay-based gels, diesel / clay mixtures
H	Glass	-----
I	Metals	Steel, other alloys such as bismuth-based materials

1.2.4 Geopolymers as substitutes for the OPC

For decades, the OPC has been the main material used for well cementing purposes. However, several researches suggest the use of geopolymers due their many benefits. Currently, most of the researches on geopolymers have been dedicated to their application in the construction industry. In the oil and gas industry, the application of geopolymers is still in the

research and development (R&D) phase. Consequently, these materials have neither been accepted nor implemented in the oil and gas wells.

The use of OPC as wellbore cement has shown innumerable issues which have resulted in the loss of well integrity over time. Among these issues one can list mechanical failure, shrinkage, durability problems, sustained casing pressure (SCP), chemical deterioration of the cement sheath, etc. Also, the OPC's strength is reduced with time because of the exposure to high pressure and temperature conditions downhole. These issues often result in the loss of zonal isolation and lead to a lower lifetime of the well. Therefore, it is necessary to find new materials with better downhole performance than the OPC. Laboratory experiments with geopolymers have shown that these materials exhibit good performance compared to the OPC. In addition, geopolymers are cheaper to produce and have less harmful effects on the environment. Nevertheless, in order to verify the practicability of these materials in the oil and gas wells, along with the laboratory experiments, the geopolymers should also be tested in the fields in the near future (Salehi et al., 2017b).

1.2.4.1 Chemistry of geopolymers

Geopolymers are inorganic materials which have binding properties (Khalifeh et al., 2014). These materials are formed by the alkali-activation of aluminosilicate materials (solid phase) as shown in Fig. 1.6. The materials listed in Fig. 1.6 are only a few of the materials used in the geopolymers. Hence, other sources of alumina and silica can be found for the production of the geopolymers (Paiva et al., 2018).

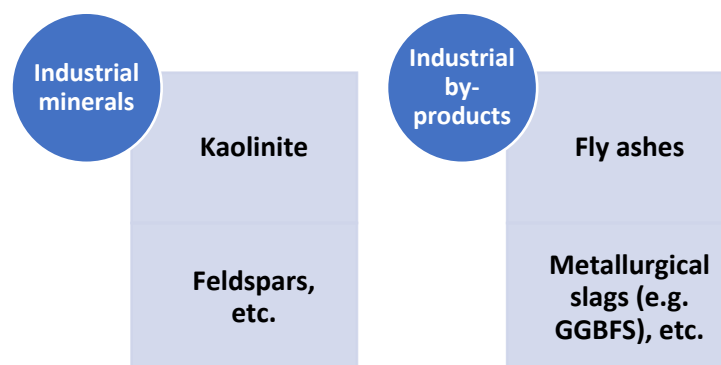


Fig. 1.6. Different materials used in the geopolymers.

Common alkaline silicate solutions (liquid phase or hardener phase) that are used in the geopolymers include (Dimas et al., 2009; Salehi et al., 2017a; Zhuang et al., 2016):

- Sodium metasilicate (Na_2SiO_3)
- Potassium Metasilicate (K_2SiO_3)

Some researchers and engineers use alkali solution as hardener. In fact, the use of alkali solution leads to production of alkali-activated cement-based materials and not geopolymers. The use of alkali solution also requires proper handling and mixing system which has special Health, Safety and Environment (HSE) consideration (Pacheco-Torgal et al., 2014).

The mechanism of making geopolymers is called geopolymerization which is associated with several processes as shown in Fig. 1.7. These processes include dissolution, nucleation, oligomerization, polymerization and curing or hardening (Zhuang et al., 2016).

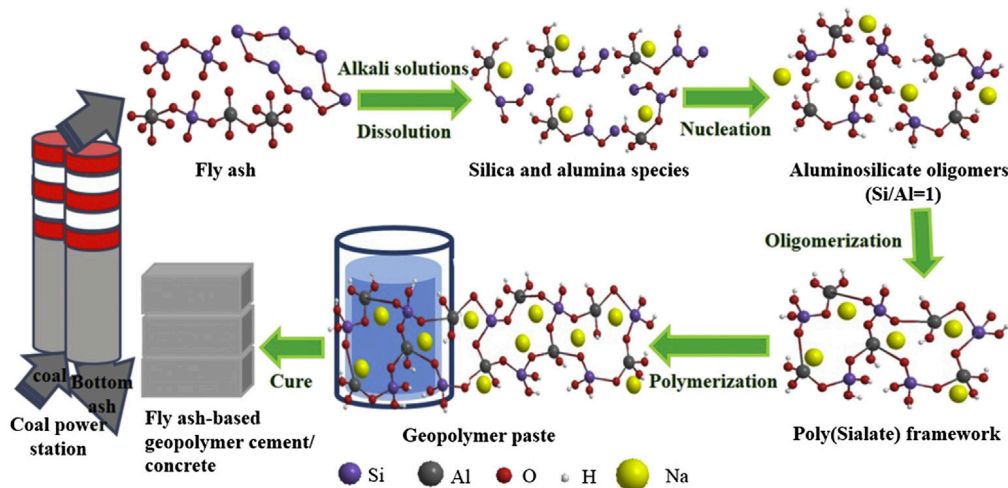


Fig. 1.7. The different processes from the production of fly ash to fly ash-based geopolymer cement (After Zhuang et al. (2016)).

When aluminosilicates are mixed with an alkaline solution, chemical bonds are created in the form of Si-O-Si or Al-O-Si through a process called hydrolysis. Later, these bonds split and discharge active aluminum ions (Al^{3+}) and silicon ions (Si^{4+}) and result in the formation of aluminosilicate monomers. In these monomers, the Si^{4+} ions are partly replaced by the Al^{3+} ions. This replacement leads to negatively charged chains of aluminosilicate. However, an equilibrium charge is achieved by the positively charged ions such as potassium (K^+) or sodium (Na^+) depending on the alkaline solution used. Further, Si^{4+} and Al^{3+} ions react and form oligomers through the processes of nucleation followed by oligomerization. Oligomers include SiO_4 and AlO_4 tetrahedrons. In addition, they can have different molecular structures which are

controlled by the Si/Al ratio. Thereafter, the oligomers react together and form a geopolymer paste through the process of polymerization. Finally, the geopolymer paste is cured which results in setting and hardening of the paste (Zhuang et al., 2016).

1.2.4.2 Advantages of geopolymers

In addition to the typical advantages of geopolymers such as being more environmentally friendly and cheaper than the OPC, these materials have several other benefits compared to the OPC. Several researchers have studied the different properties of these materials and came to the conclusion that compared to the OPC geopolymers show (Khalifeh, 2016; Khalifeh et al., 2018; Khalifeh et al., 2015; Khalifeh et al., 2017; Nasvi et al., 2014; Paiva et al., 2018; Salehi et al., 2016; Salehi et al., 2017a):

- Higher strength
- Lower chemical shrinkage
- Lower permeability
- Less contamination when exposed to oil-based mud (OBM)
- More resistance at high-pressure and high-temperature (HPHT) conditions
- Better ductility
- More durability when exposed to corrosive fluids
- Better bonding capability to casing
- Neither alkali-aggregate reaction nor carbonation

1.2.4.3 Possible limitations of the geopolymers

Currently, the use of the geopolymers has been limited to the aerospace and automotive industries, civil engineering, concrete industries, waste management, etc. (Geopolymer-Institute, 2012). As mentioned in section 1.2.4, the application of geopolymers for the purpose of oil and gas well cementing is currently in the R&D phase and therefore, the geopolymers have not been used in the oil and gas field operations yet (Salehi et al., 2017b). Other limitations with geopolymers include gelation as well as fast thickening time which lead to the necessity of using retarders to slow down the geopolymerization process. In addition, the geopolymers are brittle materials and have low tensile strength. This may result in the requirement of using additives which can improve such issues (Khalifeh et al., 2014; Paiva et al., 2018).

1.2.4.4 Prior art of geopolymers for oil and gas well cementing

Khalifeh et al. (2016) studied the ability of a type of geopolymer for the application in the oil and gas wells, namely, aplite rock-based geopolymer. In this study, several mechanical properties of this type of material were examined including the compressive, tensile and sonic strength.

GGBFS was included in the mixture's design in order to develop early geopolymer strength. In addition, micro-silica was added to the mixture's design for increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. For the purpose of increasing the setting time, they used a retarder. The liquid phase included a solution of potassium hydroxide (KOH), potassium silicate and deionized water. They used the alkali solution to adjust the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio. Geopolymer samples with different compositions (Table 1.4) were prepared and the UCS of these samples were measured using a hydraulic testing machine with a loading rate of 4000 psi/min [275.8 bar/min]. The samples were cured at a temperature of 70°C and a pressure of 2000 psi [137.9 bar] for 7 days. The UCS test-results are shown in Fig. 1.8. Khalifeh et al. (2016) concluded that the compressive strength of all the mixture designs has an increasing trend with increasing curing time. In addition, the use of sucrose as a retarder has improved the compressibility of the geopolymer material.

Table 1.4. Three mixtures of the aplite rock-based geopolymers with different wt.% of the retarder in their compositions (After Khalifeh et al. (2016)).

Mix	Total solid phase			Activator			Activator % Total solid phase
	Aplite rock % Total solid phase	GGBFS % Total solid phase	Microsilica % Total solid phase	K-silicate sol. 4M KOH	Retarder % Total solid phase	Additional water % Total solid phase	
1	70	30	0	2.32	0	4.55	51.36
2	70	30	0	2.32	1.21	4.55	52.57
3	70	30	0	2.32	1.81	4.55	53.18

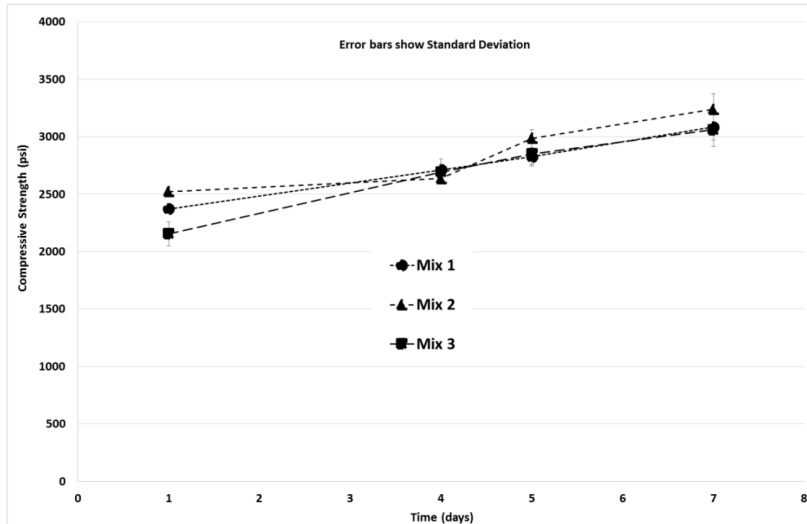


Fig. 1.8. The uniaxial compressive strength (UCS) of the aplite rock-based geopolymers cured at 70°C and 2000 psi (After Khalifeh et al. (2016)).

In this study, the tensile strength of the geopolymer samples was measured through Brazilian tests (see Fig. 1.9). The results indicated that the geopolymers' tensile strength was about 5% of their UCS for all the samples. However, in comparison with the OPC, this value was lower. Also, the addition of sucrose to the geopolymer mixtures resulted in reducing the tensile strength of the samples by about 27%. Nevertheless, as Khalifeh et al. (2016) mentioned, there are several researches which have shown that the geopolymers have higher tensile strength compared to the OPC (Sofi et al., 2007).

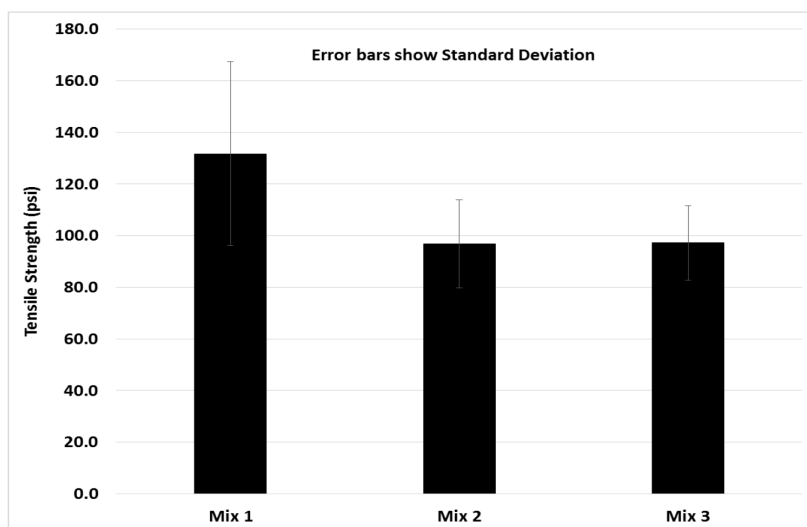


Fig. 1.9. Tensile strength measurements (Brazilian test) of the aplite rock-based geopolymers cured at 70°C and 2000 psi for 7 days (After Khalifeh et al. (2016)).

Salehi et al. (2017b) studied several aspects of the geopolymers through different experiments performed under varied laboratory and mixing conditions. The main target of these experiments was to examine the practicability of the geopolymers for the oil and gas well cementing applications. The material used was a fly ash Class F based geopolymer (i.e. a geopolymer with low calcium content) and the alkaline solution was a mixture of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). In addition, water was added to the mixture. In this study, the effect of a retarder and a plasticizer on the compressive strength of the geopolymer mixtures was studied. Further, the effect of different curing temperatures and times on the compressive strength of the geopolymer mixtures was examined as shown in Fig. 1.10.

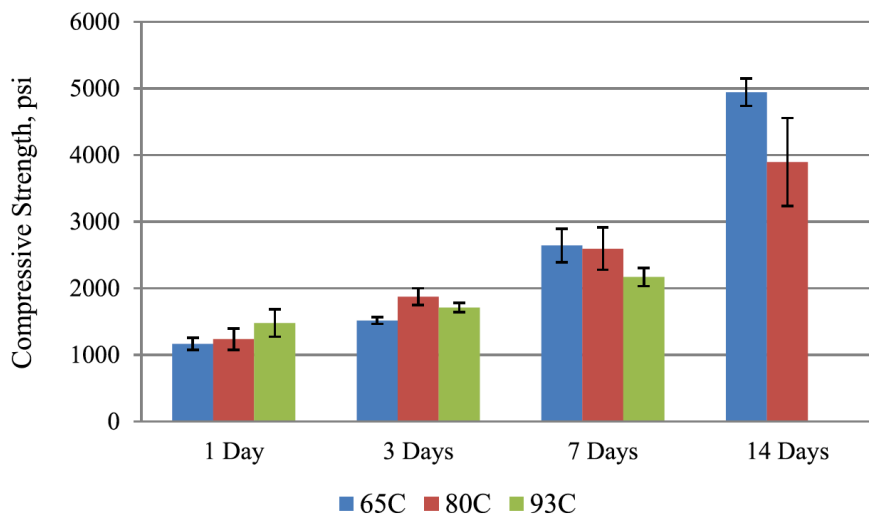


Fig. 1.10. The effect of different curing temperatures and times on the compressive strength of the fly ash Class F based geopolymer mixtures (After Salehi et al. (2017b)).

As it can be seen in Fig. 1.10, the compressive strength at the curing temperature of 65°C demonstrates a considerable increasing trend throughout the 14 curing days. The same conclusion has also been made for the curing temperature of 80°C. However, in this case, the compressive strength between 7 and 14 curing days has not improved as much as in the case of 65°C. For the curing temperature of 93°C, an increase in the compressive strength can mainly be noticed after 3 days of curing. In this case, the samples which were cured for 14 days contained too many cracks due to shrinkage which resulted from the high curing temperature. The creation of the cracks in the samples led to unsuccessful results which were thus excluded from the other results. Salehi et al. (2017b) added that at 93°C, the insignificant buildup in the compressive strength between 1 to 3 curing days could be due to the high curing temperature.

This is because a high curing temperature can act as a catalyst for the chemical reaction between the fly ash and the alkaline solution. Therefore, it was concluded that a curing temperature of 65°C was preferable for these types of geopolymer mixtures.

Salehi et al. (2017b) also examined the effect of barite on the compressive strength of the geopolymer. As it can be seen from Fig. 1.11, adding barite to the geopolymer mixture improved the compressive strength of the samples throughout a curing time of 7 days. However, between 7 to 14 days, the barite did not lead to any improvement in the compressive strength of the geopolymer.

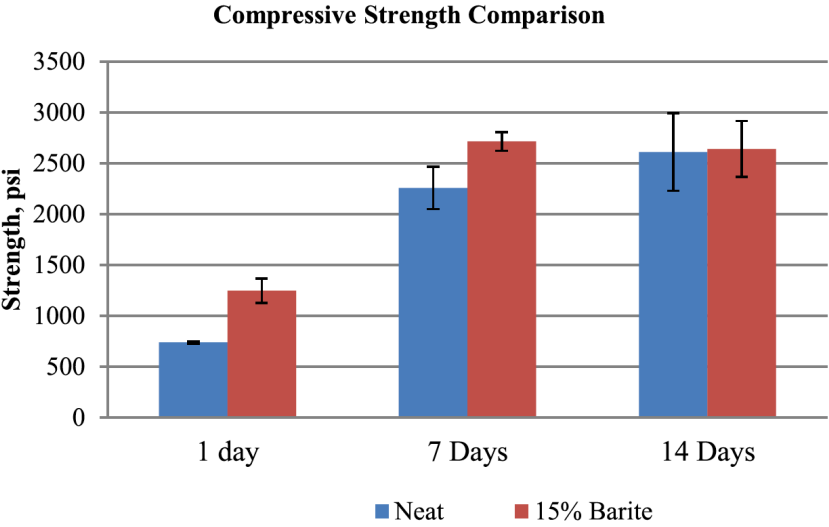


Fig. 1.11. The effect of barite on the compressive strength of the mixtures at 65°C (After Salehi et al. (2017b)).

1.3 Objectives and problem formulation

As the geopolymers have shown interesting properties according to the prior art publications, this thesis will consider them as a candidate for further investigation. The main focus is a possible optimization of the flexibility of a type of geopolymer which includes a combination of fly ash Class F and ground granulated blast furnace slag (GGBFS).

The flexibility of a wellbore barrier material is of great significance as it can increase the lifetime of the barrier material and secure the well integrity during various operations (di Lullo and Rae, 2000; Jafariesfad et al., 2017; Thiercelin et al., 1997; Thiercelin et al., 1998). In this thesis, the flexibility is studied through several experiments in the cement laboratory at the University of Stavanger (UiS). Two different organic polymer additives have been added to the geopolymer samples both separately and also in combination. Also, two different mixing procedures, namely, non-API and API were used to prepare the geopolymer samples. Further, the effect of the additives and the mixing procedures on the mechanical properties of the geopolymer has been investigated. These properties include the Young's modulus (flexibility), compressive strength and tensile strength.

Moreover, this thesis work aims to answer the following questions:

- Do the two additives have any effect on the flexibility of the geopolymer?
- If flexibility is achieved, which additive gives the highest flexibility in the geopolymer?
- Does flexibility influence the other mechanical properties (i.e. compressive strength and tensile strength) of the geopolymer?
- Is there any difference in the results which will be achieved for the two different mixing procedures?
- Which mixing procedure gives a better overall result with respect to the mentioned mechanical properties of the geopolymer?

2 EXPERIMENTAL PROCEDURES

During the experiments in this project, two different mixing procedures were used to prepare the required mixtures. For each mixing procedure, four different geopolymer mixtures were prepared both with and without the addition of the flexible additives. In addition, one mixture of API Class G cement was prepared and used as a reference in order to compare its mechanical properties with the geopolymer mixtures. This was done because the API Class G cement is the main material used in the oil and gas well cementing. It is thus interesting to see how the pure geopolymer and the geopolymers containing flexible additives behave compared to the API Class G cement.

This section gives an overview of the following:

- Materials used to prepare the different mixtures
- The preparation procedure of the mixtures
- The equipment used during the experiments
- The tests performed to investigate the mechanical properties of the mixtures
- The analytical approach used to determine the values of the mechanical properties (i.e. UCS and Young's modulus)

2.1 Materials

The compositions of the five different mixtures used for the experiments are summarized in Table 2.1. As it can be seen, the base material used in the geopolymer mixtures contains equal amount of fly ash Class F and GGBFS (product name "Merit 5000"). The function of the GGBFS is to provide early strength in the geopolymer mixtures (Khalifeh et al., 2016).

Table 2.1. The materials used in the five different mixtures which were cured for 7 days at a BHST of 70°C. K-silicate stands for potassium silicate.

		Solid Phase			Activator			
		[wt.% of total solid phase]			[wt.% of total solid phase]			
		Fly ash Class F	GGBFS	API Class G	K-silicate solution	Deionized water	Additives	
						A1	A2	
Mixture Design	MG	0	0	100	0	43.94	0	0
	M1	50	50	0	44.14	11.14	0	0
	M2	50	50	0	44.14	11.14	0.21	0
	M3	50	50	0	44.14	11.14	0	1
	M4	50	50	0	44.14	11.14	0.21	1

2.2 Mixture designs, equipment and testing procedures

This section describes the following:

- The preparation sequence of the different mixtures
- The conditioning procedure of the mixtures
- The molding and curing procedure of the mixtures
- The cutting and flattening procedure of the samples and
- The UCS and the tensile strength testing procedures along with the equipment used for performing these tests

All the mixtures were prepared twice through two different mixing procedures, namely, non-API and API. This was performed to examine whether the two mixing procedures have any effect on the mechanical properties of the mixtures. The non-API mixing procedure was performed without following the API standard while the API mixing procedure was performed according to the API RP 10B-2 standard.

In the API procedure, an OFITE WARING commercial blender (Fig. 2.5) was used to prepare the slurries. The commercial blender has a high rotational speed and consequently, exhibits high mixing energy to the slurries. Since organic polymer additives were used in some of the mixtures, the polymer chains could be damaged due to the high mixing energy and the sharp blades (Fig. 2.3) used in the blender. On the other hand, in the non-API procedure, a single-speed Hamilton Beach mud mixer (Fig. 2.4) was used for mixing the slurries. The mud mixer does not have sharp blades (Fig. 2.2) and its speed is quite lower than the commercial blender used in the API procedure. Therefore, it could prevent the damage to the polymer chains.

According to Yong (2013), polymer-mixing needs special mixing equipment and procedures. Preferably, the polymers should be mixed with an initial high mixing energy followed by a low mixing energy. Starting with the high mixing energy prevents the formation of fisheyes which are formed due to the initial lack of proper wetting. Further, the low mixing energy prevents the damage to the polymer chains (see Fig. 2.1).

In this project, the polymer additives were added to the liquid phase of the mixtures one day prior to performing the mixing of the slurries. This was done to let the additives to dissolve properly in the liquid phase and to avoid the formation of the fisheyes in the mixtures.

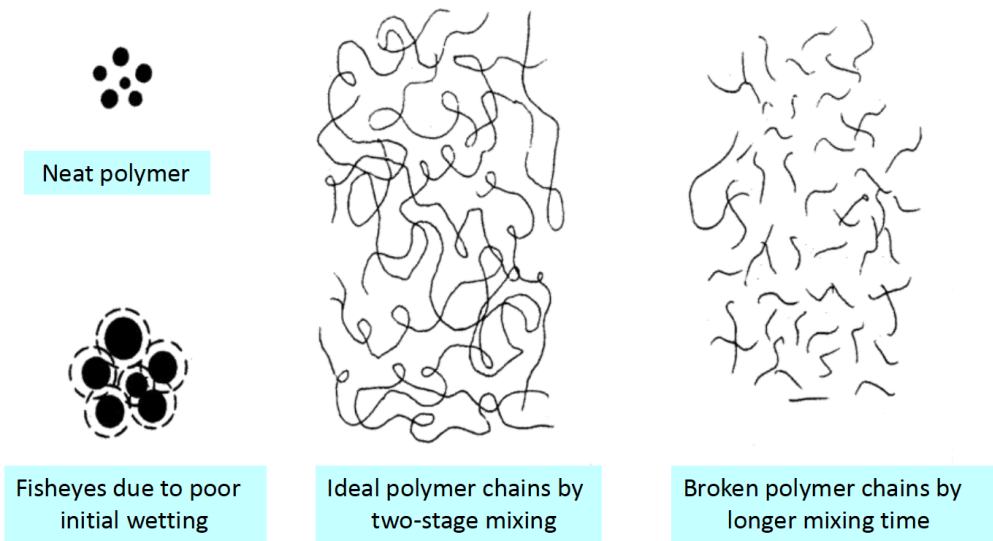


Fig. 2.1. The various forms of polymer solution (After Yong (2013)).



Fig. 2.2. The blades of the Hamilton Beach mud mixer used for mixtures prepared with the non-API mixing procedure.



Fig. 2.3. The blades of the OFITE WARING commercial blender used for mixtures prepared with the API mixing procedure.

2.2.1 Slurry preparation

As shown in Table 2.1, five different mixtures were prepared for the experiments. These mixtures include:

- MG (API Class G cement)
- M1 (pure geopolymers)

- M2 (geopolymer including additive A1)
- M3 (geopolymer including additive A2)
- M4 (geopolymer including both additives A1 and A2)

The liquid phases were the same in all the geopolymer mixtures and composed of 44.14 wt.% of potassium silicate solution as well as 11.14 wt.% of deionized water. The only difference was the sequence of adding the two different additives to the liquid phase of the mixtures M2, M3 and M4. The additive A1 which was included in the mixtures M2 and M4 was water-soluble. Therefore, it was added to the water one day before the preparation of the mixtures in order to dissolve properly before being added to the potassium silicate solution. However, the additive A2 which was included in the mixtures M3 and M4 was not water-soluble. It was thus added to the potassium silicate solution one day before the preparation of the mixtures.

The solid phase was prepared similarly for all the geopolymer mixtures and included 50 wt.% of fly ash Class F as well as 50 wt.% of GGBFS. A bucket was used in order to mix the two materials properly.

Once the final solid and liquid phases were prepared, they were poured into separate beakers. Further, the slurries were prepared using both the non-API and API mixing procedures.

2.2.1.1 Preparation sequence of the different mixtures

In this section, the five different mixtures have been discussed with respect to their compositions. Also, the preparation sequence of the liquid and solid phases of the mixtures has been explained.

2.2.1.1.1 MG (API Class G cement)

For the preparation of the mixture MG, 100 wt.% of API Class G cement provided by the Dyckerhoff company was used as the solid phase. Also, 43.94 wt.% of deionized water was used as the liquid phase. The solid phase and the liquid phase were weighed separately in different beakers.

2.2.1.1.2 M1 (pure geopolymer)

The mixture M1 was pure geopolymer without the addition of the two flexible additives. The solid phase included 50 wt.% of fly ash Class F and 50 wt.% of GGBFS. The liquid phase

contained 44.14 wt.% of potassium silicate solution as well as 11.14 wt.% of deionized water. The liquids were then mixed for 3 seconds before adding the solid phase.

2.2.1.1.3 M2 (geopolymer including additive A1)

To prepare the mixture M2, the same composition as the mixture M1 was used plus the addition of the additive A1. In a beaker, 0.21 wt.% of A1 was added to 64.1 wt.% of the total weighed water one day before preparing the mixtures. The beaker was then sealed with Parafilm in order to avoid evaporation of the liquid. Once the A1 was properly dissolved in the water, the solution was poured into a beaker which contained the potassium silicate solution. The residual water which was 35.9 wt.% of the total weighed water was then used to wash the beaker used for dissolving A1. Further, it was poured back again into the beaker which contained the potassium silicate solution. The liquids were then mixed for 3 seconds before adding the solid phase.

2.2.1.1.4 M3 (geopolymer including additive A2)

To prepare the mixture M3, the same composition as the mixture M1 was used plus the addition of the additive A2. In a beaker, 1 wt.% of A2 was added to the potassium silicate solution. The beaker was then sealed with Parafilm and put aside for one day in order for the A2 to dissolve in the solution. Once the A2 was properly dissolved in the solution, the total water of 11.14 wt.% was added and the liquids were mixed for 3 seconds before adding the solid phase.

2.2.1.1.5 M4 (geopolymer including both additives A1 and A2)

The mixture M4 had again the same composition of the mixture M1 plus the addition of both additives. Therefore, its liquid phase was prepared following both the M2's and M3's procedures. Shortly said, A1 was added to the water and A2 to the potassium silicate solution and finally, both liquids were added together and mixed for 3 seconds before adding the solid phase.

2.2.1.2 Non-API mixing procedure

When the solid and liquid phases were prepared according to the procedures explained in the previous section, the solid phases were in steps added to the liquid phases and mixed properly using a spatula (rubber scraper). For each mixture, once the whole solid phase was added and mixed with the liquid phase, the mud mixer (Fig. 2.4) was used to mix the slurry for 50 seconds.

2.2.1.3 API mixing procedure

For the mixtures prepared following the API mixing procedure, the slurries were mixed using an OFITE WARING commercial blender (Fig. 2.5) which mixes the slurries according to the guidelines covered in the API RP 10B-2 standard. The solid phases were added to the liquid phases under 15 seconds at a rotational speed of 4000 rpm and then mixed for 35 additional seconds at a rotational speed of 12000 rpm.

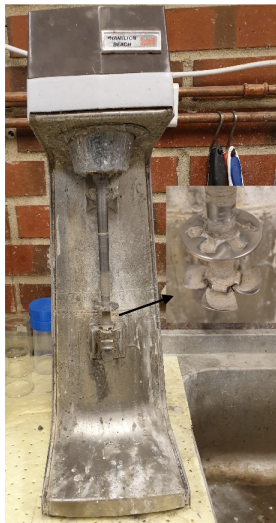


Fig. 2.4. The mud mixer (Hamilton Beach type) which was used in the non-API mixing procedure.



Fig. 2.5. The OFITE WARING commercial blender used for the mixtures prepared with the API mixing procedure.

2.2.2 Conditioning of the slurries

Usually, consistent laboratory tests are required to check the physical properties and the performance of cement slurries before applying them in field applications (Ofite.com, 2017). Conditioning is performed in order to create a simulation of the downhole conditions to which the cement slurries are exposed as they are pumped and placed inside the wellbore. To achieve well-represented simulations, the conditioning of the cement slurries should be performed in accordance with a schedule which follows the known or estimated wellbore conditions. If the circumstances permit, the wellbore pressures and temperatures should be included in the schedule. Otherwise, the conditioning of the cement slurries can be performed at atmospheric pressure (API, 2013).

In this thesis, the conditioning of the slurries was performed using an OFITE model 60 atmospheric consistometer (Fig. 2.6). All the slurries were conditioned with the same procedure which is explained in detail later in this section. Each slurry mixture was prepared twice in order to have enough slurry for the preparation of six samples. The reason for preparing six samples was to provide more measurements of the mechanical properties and consequently, reduce the error in the data.

The consistometer is designed to comply with the API Spec 10A/10B2 standards (Ofite.com, 2017). It has two main functions. One is to provide conditioning of the slurries to prepare them prior to the laboratory measurements of properties such as:

- Viscosity
- Rheological properties
- Compressive strength using the UCA
- Compressive strength using the UCS (after molding and curing of the mixtures), etc.

The other is to take measurements of the thickening time, consistency and pumpability of the slurries (Fann.com).

Thickening time is a valuable slurry property which implies how long the slurries are pumpable during wellbore cementing operations (Salehi et al., 2018). In this thesis work, the thickening time was measured through the software LabVIEW2018 which was installed on a computer connected to the consistometer. Although the thickening time of all the slurries was recorded, the consistometer was mainly used for conditioning to achieve more homogeneous slurries.

The pressure in the consistometer is not adjustable and is equal to the atmospheric pressure. The only parameter that can be adjusted is temperature. However, the highest allowable

temperature by the consistometer is limited to a value between 88 to 93°C (API, 2013; Fann.com).

The equipment contains a stainless-steel bath filled with mineral oil. The mineral oil is heated when the temperature is increased. The mineral oil bath helps to transfer the heat through the slurry container into the slurry and maintains the set-temperature.

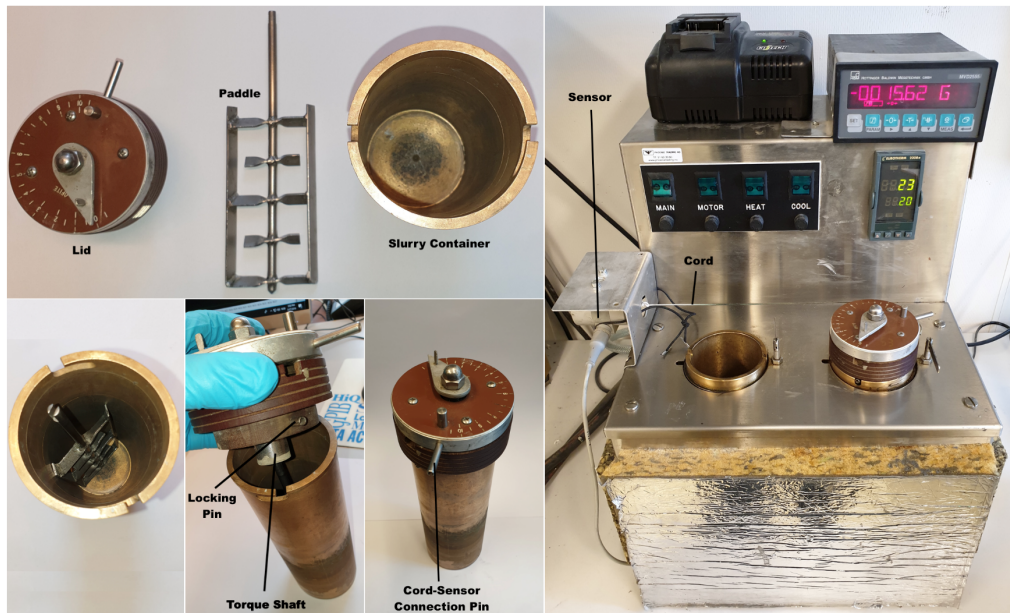


Fig. 2.6. The OFITE model 60 atmospheric consistometer used for preconditioning of the mixtures.

The setup assembly and conditioning procedure of each slurry mixture after the two mixing procedures was as follows:

1. The paddle was placed into the slurry container and secured at the center by lowering its pointed tip into the hole carved at the bottom of the slurry container.
2. The mixed slurry was poured into the slurry container up to the highest allowable point marked inside the container.
3. Further, the lid was put on top of the slurry container and secured in place by inserting the top point of the paddle into the torque shaft of the lid and then the locking pin into the pin slot located on the top end of the container.
4. Then, the slurry container was lowered into the mineral oil bath inside the atmospheric consistometer and locked in place.

5. Further, the cord-sensor connection pin on the side of the lid was connected to the torque sensor by the attached cord in order to measure and record the consistency of the slurry on the computer.
6. Then, the main, motor and heat switches were turned on prior to running the software on the computer to start recording the consistency. Once the consistometer was turned on, the slurry cup started rotating at a constant rotational speed of 150 rpm.
7. The temperature was set to 25°C with a waiting time of 5 min. Further, the temperature was increased to 30°C which represented the bottom hole circulating temperature (BHCT) with a waiting time of an additional 5 min until the actual temperature in the slurry was reached to 30°C. Moreover, the temperature was kept constant at 30°C for an additional 20 min. All in all, the slurry was conditioned for 30 min.

2.2.3 Molding and curing of the slurries

After conditioning, the slurry container was removed from the consistometer and the slurry was molded in cylinder-shaped molds (Fig. 2.7). Six molds were used for the preparation of the samples for the UCS tests and three for the tensile tests. After pouring the slurries in the molds, some of the air bubbles trapped in the slurries were removed by tapping on the molds by the use of a screwdriver. Further, a small amount of deionized water was poured on top of the slurries in order to prevent dehydration of the mixtures during curing. Then, the molds were placed in an atmospheric-pressure curing-oven and cured for 7 days at a curing temperature of 70°C which represented the bottom hole static temperature (BHST).

For the UCS tests, it is common in rock mechanics to have cylindrical samples with a height to diameter ratio of 2 to 3. This is due to the fact that lower ratios can result in increasing the friction between the samples and the platen of the UCS-machine (Lavrov and Torsæter, 2016). However, the samples achieved from the molds used in this project had a geometry with an approximate height of 80 mm and a diameter of 50 mm which gave a lower height to diameter ratio than the one mentioned above. This could result in high friction during the UCS tests. Nevertheless, since appropriate molds were not available, the tests were performed using these molds. The three samples for the tensile strength tests were also prepared using the same molds. According to the ASTM D3967-16 standard, the length to diameter ratios of the samples prepared for the tensile strength tests should be between 0.2 and 0.75. Therefore, the three

prepared samples were then cut into two pieces each and made into a total of six samples with the required values of the length to diameter ratio.

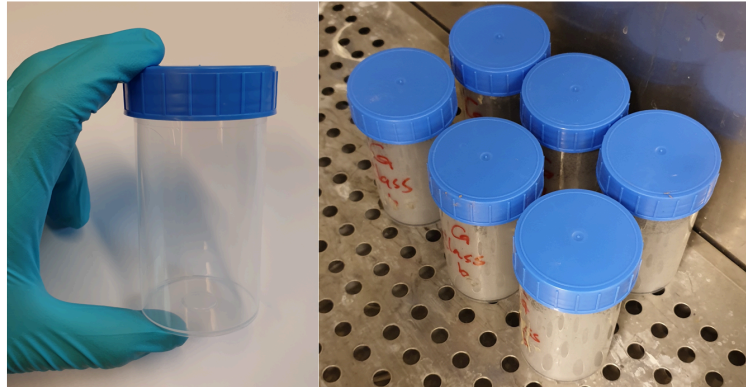


Fig. 2.7. The cylindrical plastic molds used for sampling of the different mixtures which resulted in an average sample diameter of ca. 50 mm and an average sample length of ca 85 mm.

2.2.4 Preparation of the samples for the UCS and tensile strength tests

After the curing period, the samples were removed from the oven. To avoid thermal shock in the samples, the molds were placed into a bath of hot tap water with an approximate temperature of 53°C and put aside in order to cool down slowly at room conditions. After approximately four hours of cool-down time, the samples were demolded. Since demolding agent was not used prior to pouring the slurries into the molds, the cured samples made bonding with the molds. This resulted in difficulties during the demolding of the samples.

The following steps were then performed for the removal of the samples from the molds:

1. The mold's lid was removed.
2. A force was applied by the use of a hand against the bottom of the mold to create a small void space between the bottom of the sample and the mold.
3. The bottom of the mold was perforated carefully with a screw to create a small hole.
4. Compressed air was then led through the hole via an air nozzle in order to force the sample out of the mold.

For the UCS tests, the demolded samples were cut at both ends using a cutting machine (Fig. 2.8). The cutting was performed in order to flatten the samples' ends. This was necessary for achieving an evenly distributed force on the samples' surface area during the tests. After cutting, the approximate length to diameter ratios of the samples prepared for the UCS and the tensile strength tests were 1.7 and 0.6, respectively. Prior to the UCS and the tensile strength

tests, the prepared samples were kept in water to prevent drying. This was done because drying may lead to the creation of cracks in the samples.



Fig. 2.8. The cutting machine used for cutting and flattening the ends of the samples for the UCS and the tensile strength tests.

2.2.5 UCS testing procedure

After cutting the samples, the UCS tests were performed using a Toni Technik-H hydraulic press machine (Fig. 2.9) with a loading rate of 72 kN/min according to the API RP 10B-2 standard. The UCS data were recorded with the help of the TestXpert v7.11 software.

Each sample was removed from the water one at a time before running the test. The sample was then dried with tissue. Further, the sample's length as well as its diameter at both ends were measured using a caliper. The reason for measuring the sample's diameter at both ends was that the molds used for the experiments did not have a uniform diameter along their length. The molds' diameter gradually increased from the bottom to the top end. Therefore, an average diameter was used for the calculations of the mechanical properties of the samples. Afterwards, the sample was placed at the center of the machine and a constant force of 72 kN/min was applied to the sample until it crushed. Different parameters such as compressive load, test-time and axial deformation were recorded automatically by the software. Further, the recorded data was used for the calculation of the UCS and Young's modulus (flexibility) of the samples.

The recorded deformation is basically the displacement of the platen of the machine which comes into contact with the sample's surface area. The displacement is thus measured and recorded by the software as soon as the machine's platen touches the sample and exerts a force upon it. Although the recorded deformation gives a nearly representative value of the sample's

deformation, it is better to use an extensometer to obtain more accurate measurements. However, due to the unavailability of a suitable extensometer, it was decided to use the deformation data recorded by the machine.

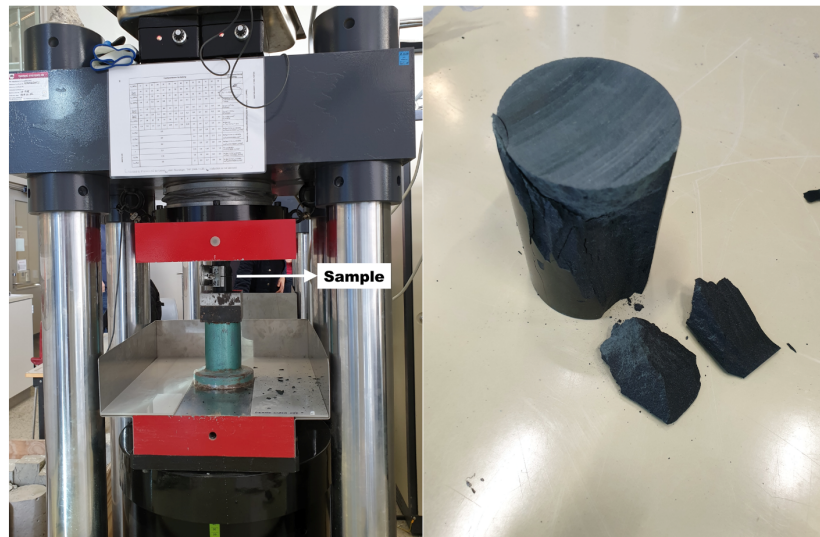


Fig. 2.9. The Toni Technik-H hydraulic press machine used for the UCS tests (left) and an example of a sample after crushing (right).

2.2.6 Brazilian tensile strength testing procedure

After cutting the samples, the tensile strength tests were performed using a Zwick/Z020 mechanical testing machine. The tensile strength data were recorded with the help of the TestXpert II v3.2 software. A constant loading rate of 50 N/s was chosen for the tests. Since the average circumferential area of the samples was measured to be 1500 mm², a 50 N/s loading rate was equivalent to 0.03 MPa/s. This loading rate resulted in cracking the samples between 1 to 5 minutes. For the purpose of the tests, it was decided to use curved jaws instead of the flat platens of the machine (Fig. 2.10). According to ASTM (2016), the curved jaws help to lower the contact stresses on the sample. Each sample was placed in the middle of the curved jaws in order for the load to be evenly distributed on the samples. A preloading of 2 N was set on hold for 5 seconds before the constant loading rate of 50 N/s started for each test. When the first crack occurred, the test was stopped and the maximum load at the time of failure was recorded. This load was then used in the equation 6 to calculate the tensile strength of each sample. At the end, the average tensile strength values of all the six samples were calculated for each mixture.

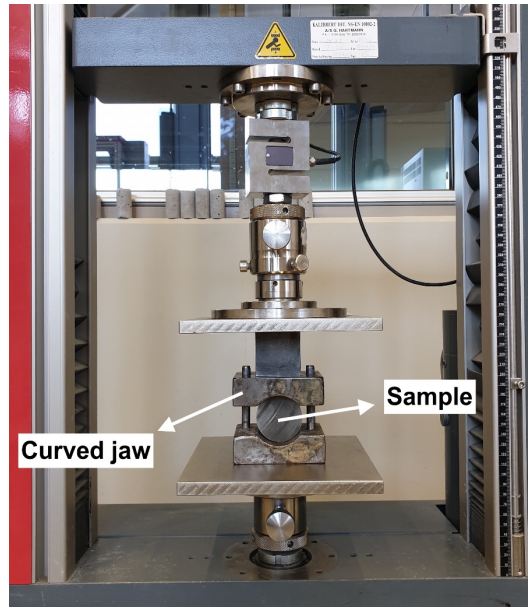


Fig. 2.10. The Zwick/Z200 mechanical testing machine used for the Brazilian tests.

2.3 Analytical approach

For the calculation of the UCS, the axial stress of each sample was first calculated using the equation 2. Further, the maximum value of the axial stress was chosen as the UCS of each sample. Also, for each mixture, the average value of the UCS of the six samples was calculated. In addition, the axial strain values of the samples were calculated using the equation 3. As shown in Fig. 2.11, the axial stress values were thus plotted versus the axial strain values for the purpose of determining the Young's modulus of the samples.

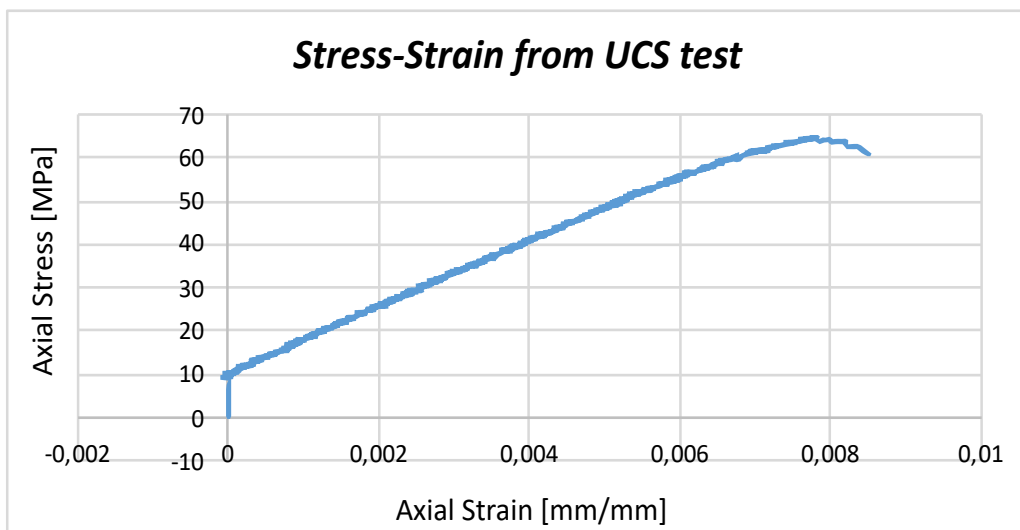


Fig. 2.11. Axial stress-strain curve plotted in Excel using the data obtained from the UCS tests.

The Young's modulus was then determined according to the following steps:

1. The nearly linear part of the stress-strain curve was identified as shown in Fig. 2.12.
2. The nonlinear section of the curve was removed.
3. The linear trendline function on Excel was used to find the slope of the curve.
4. By using the trendline function, an equation was generated which provided the slope and the intercept of the curve. Generally, the slope of the curve indicates the Young's modulus. An example is provided in Fig. 2.13 in which the slope of the line (i.e. the Young's modulus) is 7624.1 MPa or 7.62 GPa.

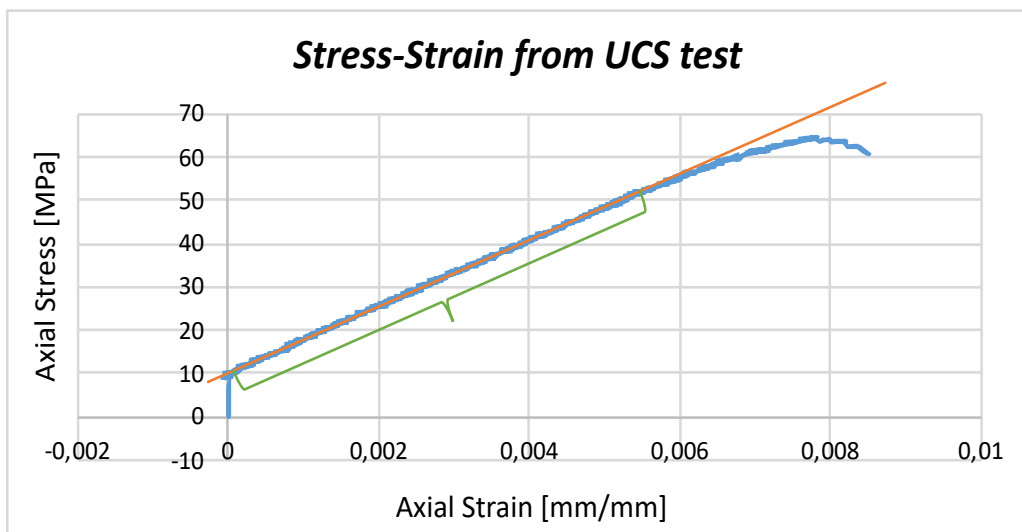


Fig. 2.12. The figure shows the methodology used to select the linear part of the stress-strain curves in order to find the Young's modulus for each of the samples.

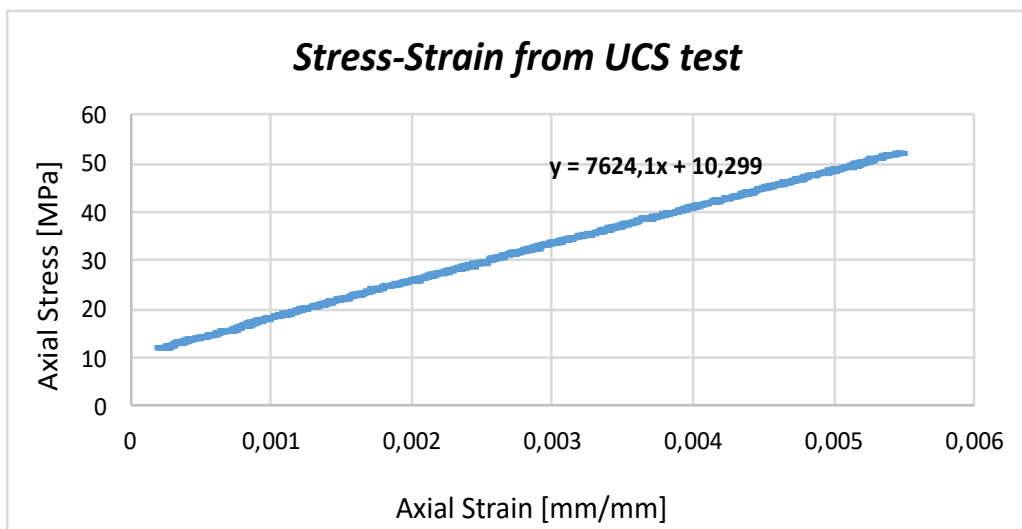


Fig. 2.13. The figure shows the data points of the linear part of the stress-strain curves. The linear trendline function is used to find the slope of the curves which indicates the Young's modulus of each sample. The first value in the equation shows the Young's modulus in MPa.

According to the API RP 10B-2 standard, at least three samples had to be prepared for the UCS tests. However, it was decided to prepare six samples for each mixture design in order to reduce the standard deviation in the data. After plotting the average values of the UCS, Young's modulus and tensile strength for each mixture, high standard deviation was observed. Therefore, to reduce the standard deviation, the average of the three closest values for each mixture design was calculated. Consequently, this led to better interpretation of the results.

3 RESULTS AND DISCUSSION

In this section, the results of the experiments are presented and further discussed. The parameters which are investigated include:

- The consistency of the different mixtures
- The effect of the two additives on:
 - The Young’s modulus (flexibility) of the samples
 - The UCS of the samples
 - The tensile strength of the samples

3.1 Consistency

During conditioning, the consistency values of the mixtures prepared according to both non-API and API mixing procedures were measured and recorded for 30 minutes at a BHCT of 30°C. Fig. 3.1 and Fig. 3.2 show the plots of consistency versus time for the non-API and API mixing procedures, respectively. As it can be observed, the consistency values of the mixtures prepared using the API mixing procedure are more spread than those prepared using the non-API. However, the consistency values in both cases range between 10 to 25 Bc (Bc stands for Bearden units of consistency). Therefore, there is not a significant difference between the consistency of the two mixing procedures during the 30 minutes of conditioning time.

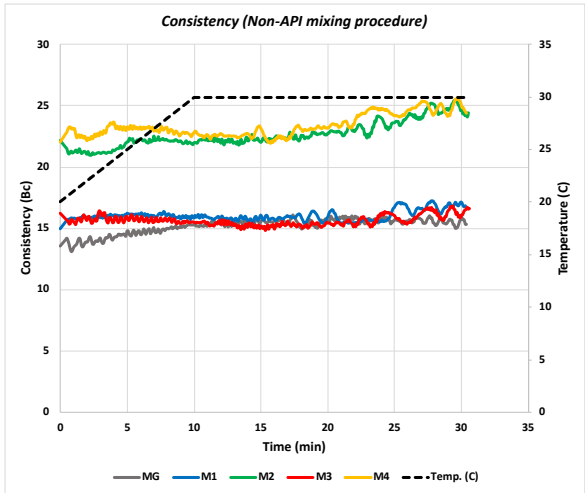


Fig. 3.1. The consistency of the mixtures prepared using the non-API mixing procedure at a BHCT of 30°C and atmospheric pressure for a conditioning time of 30 min.

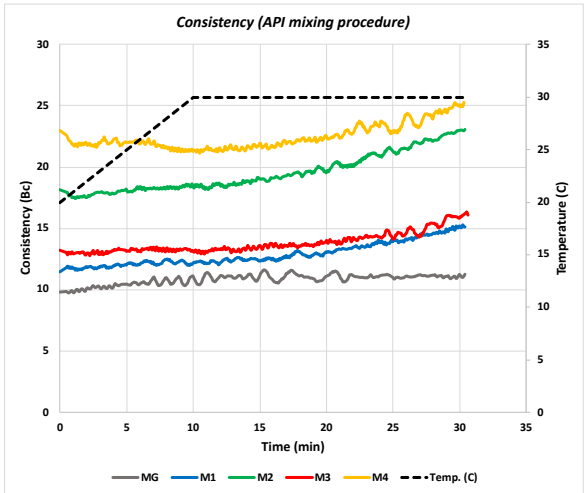


Fig. 3.2. The consistency of the mixtures prepared using the API mixing procedure at a BHCT of 30°C and atmospheric pressure for a conditioning time of 30 min.

3.2 Effect of the additives and the two different mixing procedures on the mechanical properties of the different mixtures

In this section, the effect of the two additives on the mechanical properties of the geopolymer mixtures has been discussed. These mechanical properties include the Young's modulus, compressive strength and tensile strength. In addition, the effect of the two different mixing procedures on the mechanical properties has been investigated. This has been done to observe whether these procedures have any effect on the performance of the polymer additives in the geopolymer mixtures. Further, the results of the mechanical properties of the mixtures have been compared with the requirements provided by several research works.

3.2.1 Effect of the additives and the mixing procedures on the Young's modulus

The average Young's modulus (flexibility) values of the mixtures which were prepared with the non-API and the API mixing procedures are shown in Fig. 3.3. As it can be observed, the error bars which show the standard deviation in the data are quite low. This low standard deviation is because of the method used for the selection of the three closest data out of the six recorded data as mentioned in section 2.3.

As mentioned in section 1.2.4.2, the geopolymers have shown good mechanical properties compared to the API Class G cement. From Fig. 3.3 it can be seen that M1 (pure geopolymer) shows a lower Young's modulus and as a result a higher flexibility than MG (API Class G cement) in both mixing procedures.

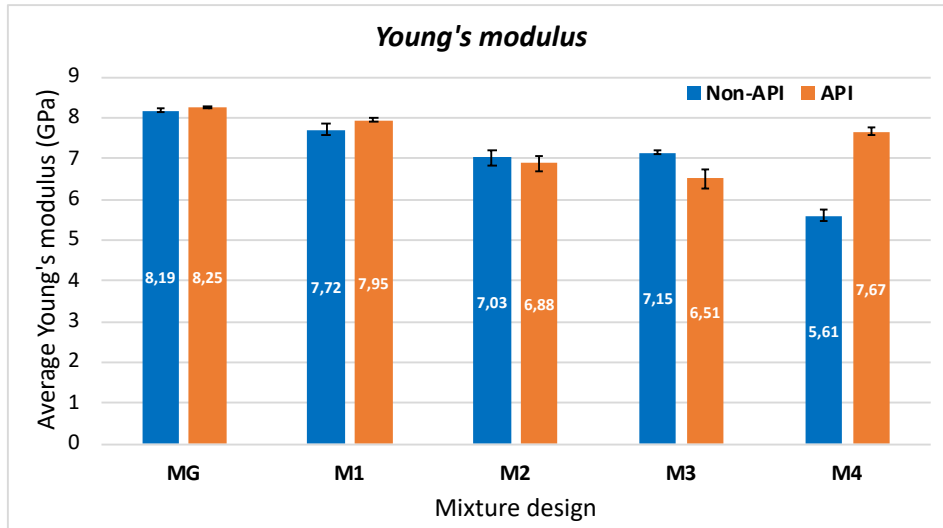


Fig. 3.3. The Young's modulus values obtained for all the mixtures with both the non-API and the API mixing procedures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

M1 is considered as the base case with which the flexibility of the geopolymer mixtures M2, M3 and M4 are compared. Table 3.1 shows the average percentage increase in the flexibility of the geopolymer mixtures compared to the base case for the two mixing procedures.

Table 3.1. The numbers show the average Young's modulus decrease (flexibility increase) in percentage. The increase in flexibility of the mixtures M2, M3 and M4 are shown relative to the pure geopolymer mixture M1.

	Average Flexibility Increase [%]	
	Non-API	API
From M1 to M2	8.93	13.43
From M1 to M3	7.36	18.13
From M1 to M4	27.38	3.48

As it can be observed from Fig. 3.3 and Table 3.1, for the non-API mixing procedure, the change in the Young's modulus (flexibility) of the geopolymer mixtures compared to the base case is according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), the Young's modulus decreases from an average value of 7.72 to 7.03 GPa. This indicates a flexibility increase of 8.93%.
- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), the Young's modulus decreases from an average value of 7.72 to 7.15 GPa. This indicates a flexibility increase of 7.36%.

- With the addition of both additives to the geopolymer (i.e. mixture M4), the Young's modulus decreases from an average value of 7.72 to 5.61 GPa. This indicates a flexibility increase of 27.38%.

Similarly, for the API mixing procedure, the same comparison with respect to the base case is made according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), the Young's modulus decreases from an average value of 7.95 to 6.88 GPa. This indicates a flexibility increase of 13.43%.
- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), the Young's modulus decreases from an average value of 7.95 to 6.51 GPa. This indicates a flexibility increase of 18.13%.
- With the addition of both additives to the geopolymer (i.e. mixture M4), the Young's modulus decreases from an average value of 7.95 to 7.67 GPa. This indicates a flexibility increase of 3.48%.

In the non-API case, the results of the flexibility increase of the mixtures with respect to the base case indicate that the addition of the additive A1 to the mixture M2 results in a higher flexibility increase compared to the additive A2 in mixture M3. The concentrations of the additives A1 and A2 in the mixtures M2 and M3 were 0.21 and 1 wt.%, respectively. A1 with a much lower concentration compared to A2 results in a much higher flexibility in the geopolymer mixtures. However, in the API case, the additive A1 results in a slightly lower flexibility compared to the additive A2. Nevertheless, a flexibility increase of 13.43% in the mixture M2 is still high taking into account the concentration of the additive A1 (i.e. 0.21 wt.%) compared to the concentration of the additive A2 (i.e. 1 wt.%) in the mixture M3.

The reason behind the higher flexibility achievement with the additive A1 could be due to its solubility in water. This is opposite to the additive A2 which is only soluble in the geopolymer activator i.e. the potassium silicate solution. Generally, the role of the water during the geopolymerization process of the geopolymer materials is mainly to serve as a medium which helps the transportation of the ions. Some of this water is excess water and thus evaporates during the curing period of the geopolymer mixtures (Park and Pour-Ghaz, 2018). Since the additive A1 is water-soluble, it may keep the water bounded inside the geopolymer structure and therefore, result in a higher flexibility. Further, from Table 1.2 (reference III), it is obvious that higher water content results in lower slurry density. This means that the lower

the slurry density is, the lower the Young's modulus or the higher the flexibility of the material is.

In both mixing procedures, a higher flexibility was expected for the mixture M4 which included both additives A1 and A2. This was because the presence of both additives in this mixture led to a higher concentration of flexible additives which could result in a higher flexibility. However, as shown in Fig. 3.3, this turned as expected only for the mixture M4 prepared with the non-API mixing procedure. On the other hand, the M4 prepared with the API mixing procedure showed lower flexibility increase compared to the mixtures M2 and M3 which both included only one of the additives. This indicates that something happened to the polymer structures when both additives were added to the M4 in the API case. As mentioned in section 2.2, there were concerns that the commercial blender used in the API mixing procedure might damage the polymer additives and result in less flexibility in the mixtures which included the additives. However, as it can be observed from Fig. 3.3, the mixtures M2 and M3 prepared with the API mixing procedure showed even higher flexibility than the same mixtures prepared with the non-API. The reason behind this might be that the polymer chains were broken down into smaller pieces by the sharp blades used in the blender. This could thus increase the number of the polymer chains in the mixtures and lead to an even higher flexibility. However, the reason for the low flexibility increase of the M4 in the API case should be investigated in the future research works.

To make it easier to compare the effect of the two mixing procedures on the flexibility of the geopolymer mixtures, Fig. 3.4 was created. As it can be observed, the Young's modulus has a decreasing trend up to mixture M2 for both mixing procedures. However, the trend is different from the mixture M2 to M4 for both mixing procedures. For the non-API case, the Young's modulus first increases and then decreases. However, for the API case, it first decreases and then increases. Further, these trends show that in order to get lower Young's modulus (i.e. higher flexibility) in the mixtures, the non-API mixing procedure is more suitable for the mixtures MG, M1 and M4. On the other hand, the API mixing procedure results in higher flexibility in the mixtures M2 and M3.

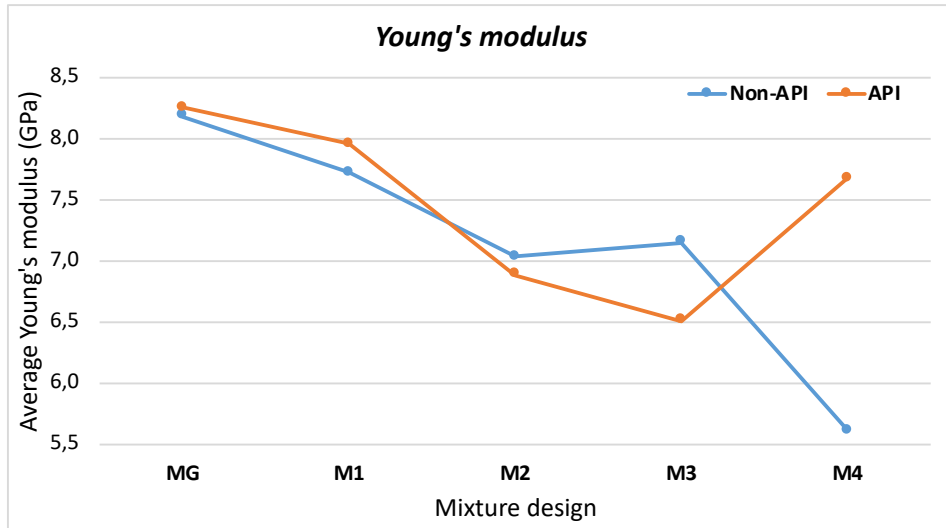


Fig. 3.4. The lines show the trends of Young's modulus values achieved for the different samples. These trends show the difference between using the non-API and the API mixing procedures for the preparation of the mixtures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

For both mixing procedures, the addition of the additives in the geopolymer mixtures M2, M3 and M4 has resulted in an increase in their flexibility. The only difference in the two mixing procedures is that in the non-API case, adding both additives into the geopolymer mixture has resulted in a higher flexibility increase than when the additives were separately added to the mixtures. For the API case, this behavior is exactly the opposite i.e. the additives have resulted in higher flexibility increase in the geopolymer when each of them was separately added to the mixtures (see Table 3.1).

3.2.1.1 Comparison of the Young's modulus values achieved with the oil and gas well cement requirements

As mentioned in section 1.2.2.1.1, the Young's modulus values for oil and gas well cements used in the petroleum industry usually lies between 1 to 10 GPa (Nelson and Guillot, 2006). This is the case for all the Young's modulus values achieved in the experiments in this thesis. Also, one example of the Young's modulus requirements in the wells drilled in Marcellus shale was presented in section 1.2.2.1.1. The required Young's modulus values in these wells for reducing the SCP problems were between 2.4 to 6.2 GPa. As it can be observed from Fig. 3.3, the mixture M4 prepared with the non-API mixing procedure has a Young's modulus value of 5.61 GPa which lies within the required range for the wells in Marcellus shale.

3.2.2 Effect of the additives and the mixing procedures on the uniaxial compressive strength

The results from the UCS tests performed on the mixtures prepared with both the non-API and the API mixing procedures are shown in Fig. 3.5. As it can be observed, M1 (pure geopolymer) exhibits higher compressive strength compared to MG (API Class G cement) in both mixing procedures.

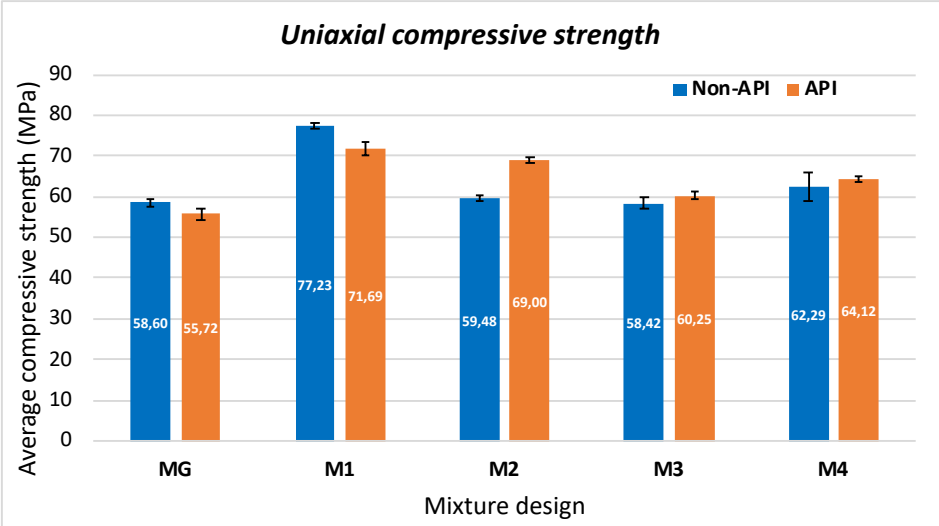


Fig. 3.5. The UCS values obtained for all the mixtures with both the non-API and the API mixing procedures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

Similar to the previous section, M1 is again considered as the base case with which the compressive strength of the geopolymer mixtures M2, M3 and M4 are compared. Table 3.2 shows the average percentage decrease in the compressive strength of the geopolymer mixtures compared to the base case for the two mixing procedures.

Table 3.2. The numbers show the average decrease in the UCS in percentage. The decrease in the UCS of the mixtures M2, M3 and M4 are shown relative to the pure geopolymer mixture M1.

	Average Decrease in Uniaxial Compressive Strength [%]	
	Non-API	API
From M1 to M2	22.98	3.76
From M1 to M3	24.36	15.96
From M1 to M4	19.34	10.57

As it can be observed from Fig. 3.5 and Table 3.2, for the non-API mixing procedure, the change in the compressive strength of the geopolymer mixtures compared to the base case is according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), an increase in flexibility of 8.93% was achieved. This resulted in a decrease in the compressive strength by 22.98% from 77.23 to 59.48 MPa.
- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), an increase in flexibility of 7.36% was achieved. This resulted in a decrease in the compressive strength by 24.36% from 77.23 to 58.42 MPa.
- With the addition of both additives to the geopolymer (i.e. mixture M4), an increase in flexibility of 27.38% was achieved. This resulted in a decrease in the compressive strength by 19.34% from 77.23 to 62.29 MPa.

Similarly, for the API mixing procedure, the same comparison with respect to the base case is made according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), an increase in flexibility of 13.43% was achieved. This resulted in a decrease in the compressive strength by 3.76% from 71.69 to 69 MPa.
- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), an increase in flexibility of 18.13% was achieved. This resulted in a decrease in the compressive strength by 15.96% from 71.69 to 60.25 MPa.
- With the addition of both additives to the geopolymer (i.e. mixture M4), an increase in flexibility of 3.48% was achieved. This resulted in a decrease in the compressive strength by 10.57% from 71.69 to 64.12 MPa.

According to Le Roy-Delage et al. (2000), an increase in the flexibility of cement due to the addition of flexible additives can result in a decrease in its compressive strength. Also, the results from the experiments in this project indicate that the compressive strength of all the geopolymer mixtures slightly decreases as their flexibility increases in both mixing procedures.

Between the mixtures M2, M3 and M4 which were prepared with the non-API mixing procedure and included flexible additives, the M4 showed the highest flexibility increase by a value of 27.38% as well as the lowest reduction in the compressive strength by a value of

19.34%. This indicates that the combination of the two additives gives better mechanical properties in the non-API case.

For the API case, the mixture M2 had a flexibility increase of 13.43% which was high taking into account the low concentration of the flexible additive used in this mixture compared to M3 and M4. In addition, M2 had the lowest reduction in compressive strength which was 3.76%. This indicates that between all the three mixtures which include flexible additives, the mixture M2 achieves better mechanical properties.

Fig. 3.6 shows that the two mixing procedures have similar trends of compressive strength despite the fact that each mixture has different values of compressive strength for each mixing procedure. For both mixing procedures, the compressive strength decreases from the mixture M1 towards M3, and then slightly increases from M3 towards M4. Nevertheless, from the data, it can be seen that a higher compressive strength can be achieved with mixing the mixtures MG and M1 with the non-API mixing procedure. However, the API mixing procedure can provide higher compressive strength in the mixtures M2, M3 and M4.

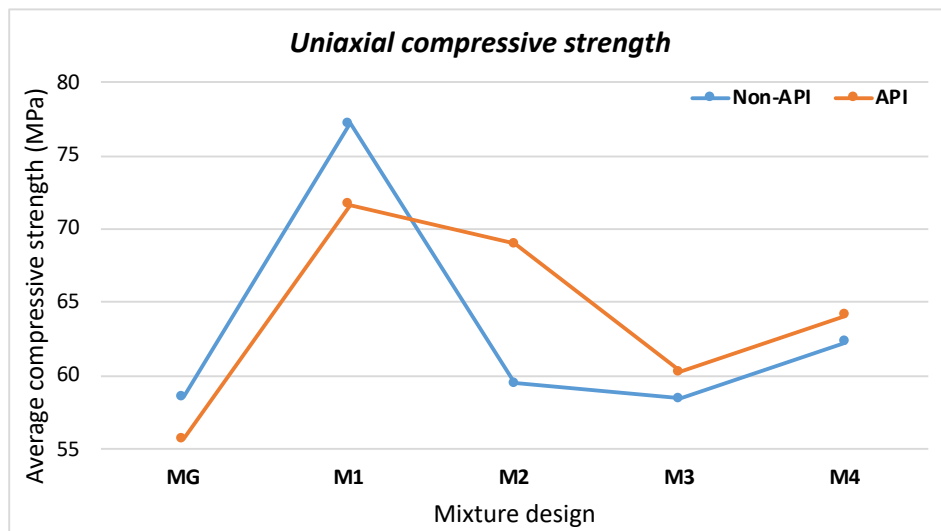


Fig. 3.6. The lines show the trends of the UCS values achieved for the different mixtures. These trends show the difference between using the non-API and the API mixing procedures for the preparation of the mixtures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymers), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

3.2.2.1 Comparison of the UCS values achieved with the oil and gas well cement requirements

As mentioned in section 1.2.2.1.2, according to Nelson and Guillot (2006), the standard requirement for cement's compressive strength is about 3.5 MPa for the casing support and

within the range of 7 to 10 MPa for the perforating and wellbore fracturing operations. As it can be seen in Fig. 3.5, the values obtained for the compressive strength fulfill the standard requirement mentioned above. Therefore, the use of the organic polymers (i.e. flexible additives) in the geopolymers is of advantage since it results in higher flexibility and yet fulfills the requirements of compressive strength for the use in field applications. In addition, it should be kept in mind that the higher the flexibility gets, the lower the compressive strength requirements get (Jafariesfad et al., 2017). Since all the geopolymer mixtures prepared in this thesis have higher compressive strength than the requirements mentioned above, the best mixture would be the one which provides the highest flexibility. In this case, the mixture with the highest flexibility was M4 which was prepared with the non-API mixing procedure and achieved a flexibility increase of 27.38%.

3.2.3 Effect of the additives and the mixing procedures on the tensile strength

The tensile strength of the mixtures which were prepared with the non-API and the API mixing procedures were measured through Brazilian tests. Fig. 3.7 shows the tensile strength values achieved through these tests. As observed in the results in sections 3.2.1 and 3.2.2, the pure geopolymer mixtures (M1) showed higher flexibility as well as higher compressive strength than the API Class G mixtures (MG). However, as shown in Fig. 3.7, the mixtures M1 shows lower tensile strength compared to the mixture MG. Nevertheless, according to Jafariesfad et al. (2017), the tensile strength requirements decrease with a higher flexibility in the cement systems. Therefore, the lower tensile strength value in M1 compared to MG can be justified by the fact that M1 has a higher flexibility than MG.

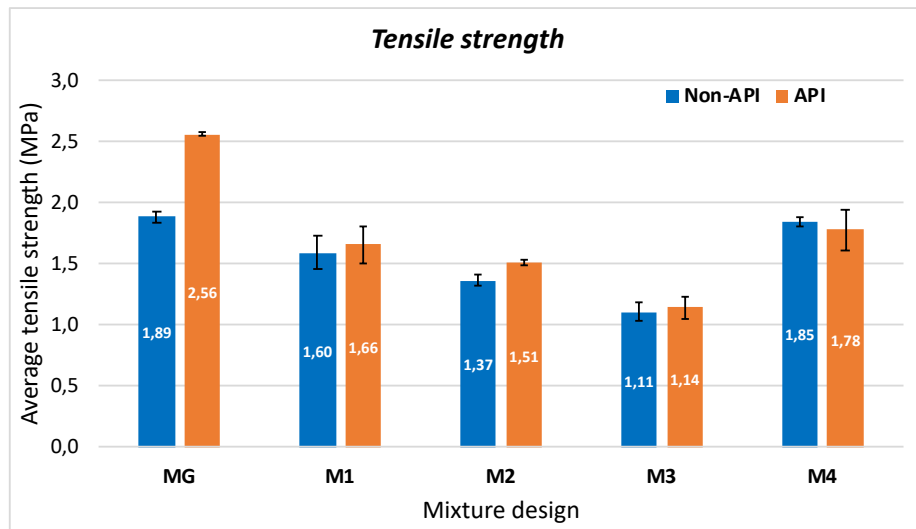


Fig. 3.7. The tensile strength values obtained for all the mixtures prepared with both the non-API and the API mixing procedures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

Similar to sections 3.2.1 and 3.2.2, M1 is again considered as the base case with which the tensile strength of the geopolymer mixtures M2, M3 and M4 are compared. Table 3.3 shows the average percentage decrease and increase in the tensile strength of the geopolymer mixtures compared to the base case for the two mixing procedures.

Table 3.3. The numbers show the average decrease (negative sign) and increase (positive sign) in the tensile strength in percentage. The decrease or increase in the tensile strength of the mixture M2, M3 and M4 are shown relative to the pure geopolymer mixture M1.

	Average Decrease (-) or Increase (+) in Tensile Strength [%]	
	Non-API	API
From M1 to M2	-14.32	-8.81
From M1 to M3	-30.31	-31.03
From M1 to M4	16.15	7.33

As it can be observed from Fig. 3.7 and Table 3.3, for the non-API mixing procedure, the change in the tensile strength of the geopolymer mixtures compared to the base case is according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), an increase in flexibility of 8.93% was achieved. This resulted in a decrease in the tensile strength by 14.32% from 1.60 to 1.37 MPa.

- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), an increase in flexibility of 7.36% was achieved. This resulted in a decrease in the tensile strength by 30.31% from 1.60 to 1.11 MPa.
- With the addition of both additives to the geopolymer (i.e. mixture M4), an increase in flexibility of 27.38% was achieved. This resulted in an increase in the tensile strength by 16.15% from 1.60 to 1.85 MPa.

Similarly, for the API mixing procedure, the same comparison with respect to the base case is made according to the following:

- With the addition of the additive A1 to the geopolymer (i.e. mixture M2), an increase in flexibility of 13.43% was achieved. This resulted in a decrease in the tensile strength by 8.81% from 1.66 to 1.51 MPa.
- With the addition of the additive A2 to the geopolymer (i.e. mixture M3), an increase in flexibility of 18.13% was achieved. This resulted in a decrease in the tensile strength by 31.03% from 1.66 to 1.14 MPa.
- With the addition of both additives to the geopolymer (i.e. mixture M4), an increase in flexibility of 3.48% was achieved. This resulted in an increase in the tensile strength by 7.33% from 1.66 to 1.78 MPa.

For both mixing procedures, the addition of the flexible additives in the mixtures M2 and M3 resulted in an increase in their flexibility and a decrease in their tensile strength. In the non-API case, the mixture M2 showed a higher flexibility increase and a lower decrease in tensile strength than the mixture M3. In the API case, the mixture M3 showed a higher flexibility increase compared to the mixture M2. However, the mixture M2 showed a lower decrease in tensile strength than the mixture M3.

In the non-API case, the mixture M4 which included both additives showed even a much higher flexibility achievement compared to the mixtures M2 and M3. Despite the higher flexibility in the mixture M4, its tensile strength increased by 16.15% compared to the base case. On the other hand, in the API case, the mixture M4 showed the lowest flexibility increase compared to mixtures M2 and M3. However, the tensile strength of M4 increased by 7.33% with the increase in flexibility. This means that in the mixtures which included both additives, the increase in the flexibility led to an increase in the tensile strength with respect to the base case. A possible explanation for this behavior could be that a chemical reaction occurred

between the two flexible additives which resulted in an increase in the tensile strength. However, in this case, further research is required to investigate the actual reason.

According to Jafariesfad et al. (2017), the use of some flexible additives for the purpose of increasing the flexibility in the cement may result in reducing the other mechanical properties of the cement such as compressive and tensile strength. However, the results of the tensile strength tests in this project indicated that an increase in the flexibility of the geopolymer may not always result in the reduction of the tensile strength. Therefore, to increase the flexibility and the tensile strength in a geopolymer mixture, the following requirements should be met:

- With respect to the base material, proper flexible additives should be chosen.
- If several flexible additives are used, a right combination should be selected.
- Based on the chemical and physical properties of the flexible additives, a right mixing procedure should be chosen.

Fig. 3.8 shows that the two different mixing procedures have similar trends of tensile strength. This means that both mixing procedures may be used for the preparation of the mixtures. However, using the API mixing procedure may result in higher tensile strength values for the mixtures MG, M1, M2 and M3.

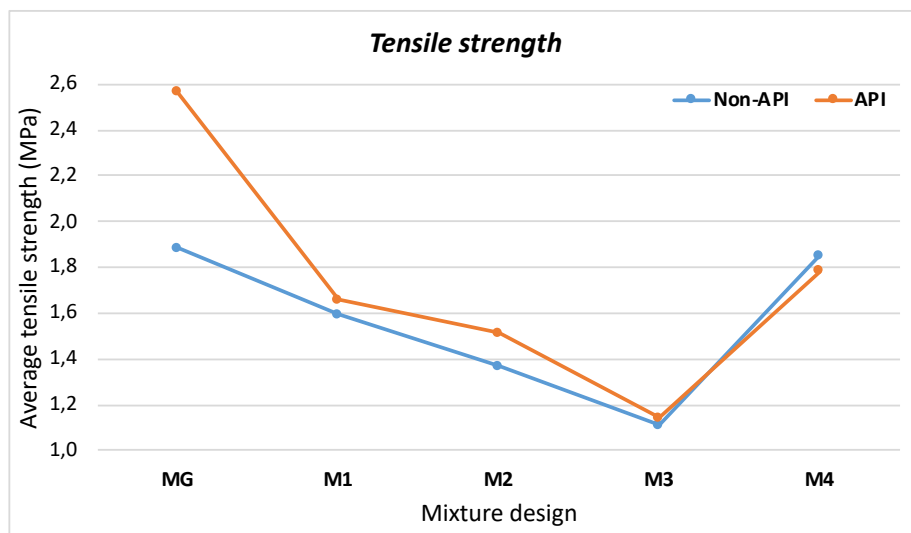


Fig. 3.8. The lines show the trends of the tensile strength values achieved for the different mixtures. These trends show the difference between using the non-API and the API mixing procedures for the preparation of the mixtures. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

3.2.3.1 Comparison of the tensile strength values achieved with the requirements presented in previous research works

In order to check the reliability of the tensile strength values achieved for the mixtures prepared in this thesis, an example of tensile strength requirements from the literature has been provided and discussed.

As mentioned in section 1.2.2.1.1, in a study by Bosma et al. (2000), it was stated that in general, in wells where the cement has higher Young's modulus than the formation rock, the likelihood for tensile failure of the cement increases as the pressure and temperature inside the casing increase. Previously, this issue was also investigated and confirmed by Thiercelin et al. (1998) and Bosma et al. (1999). However, the tensile failure of the cement may be prevented by the use of cement systems with high tensile strength.

As discussed in section 1.2.2.1.3, Thiercelin et al. (1998) reported the required tensile strength of the set-cement as a function of the Young's modulus of the cement and the rock for different wellbore pressure conditions. As shown in Fig. 3.9 and Fig. 3.10, the results of the tensile strength values achieved in this project have been compared with those provided by Thiercelin et al. (1998).

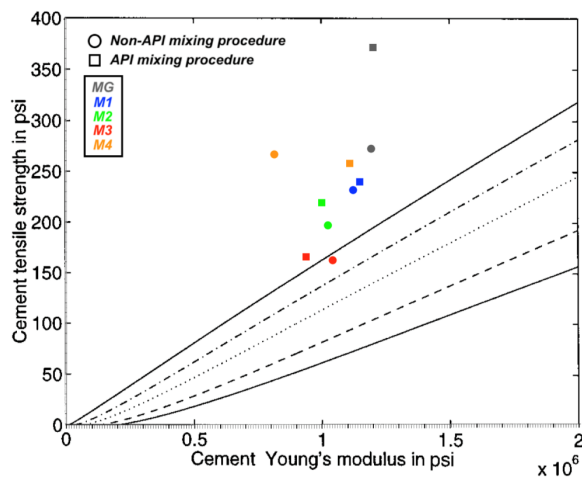


Fig. 3.9. The required tensile strength of cement as a function of the Young's modulus of cement and the Young's modulus of rock for an increase in wellbore pressure by 1000 psi [68.9 bar]. The curves from top to bottom show the Young's modulus values of the rock in psi which are: 0.145×10^6 , 0.725×10^6 , 1.450×10^6 , 2.900×10^6 , 4.350×10^6 , respectively (After, Thiercelin et al. (1998)).

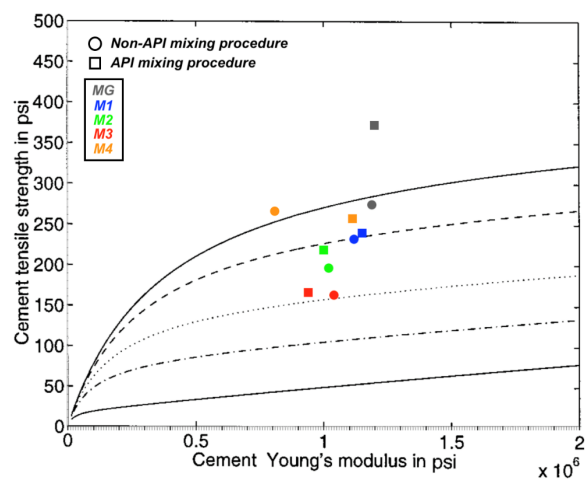


Fig. 3.10. The required tensile strength of cement as a function of the Young's modulus of cement and the Young's modulus of rock for a decrease in wellbore pressure by 1000 psi [68.9 bar]. The curves from bottom to top show the Young's modulus values of the rock in psi which are: 0.145×10^6 , 0.725×10^6 , 1.450×10^6 , 2.900×10^6 , 4.350×10^6 , respectively (After, Thiercelin et al. (1998)).

Fig. 3.9 shows that in the case of a wellbore pressure increase by 1000 psi [68.9 bar], the higher the Young's modulus of the rock and the lower the Young's modulus of the cement are, the lower the tensile strength requirements for the cement are. This means that in order for the cement to have lower tensile strength, it should obtain a higher flexibility than the rock. This also reduces the chances of tensile failure of the cement due to increased wellbore pressures.

As it can be observed from Fig. 3.9, with the exclusion of the mixture M3 which was prepared with the non-API mixing procedure, the tensile strength values of all the other mixtures satisfy the cement tensile strength requirements for all of the values specified for the Young's modulus of the confining rock. Nevertheless, the mixture M3 still satisfies most of the tensile strength requirements. A tensile failure in the case of the mixture M3 may only happen if the Young's modulus of the rock is equal to a value of 0.145×10^6 psi.

Fig. 3.10 shows that in the case of a wellbore pressure decrease by 1000 psi [68.9 bar], the lower the Young's modulus of the rock and the cement is, the lower the tensile strength requirements for the cement are.

As shown in Fig. 3.10, only two of the mixtures, namely, M4 in the non-API case and MG in the API case satisfy the cement tensile strength requirements for all of the values specified for the Young's modulus of the confining rock. However, for the rock's Young's modulus of 1.450×10^6 psi and lower (i.e. the three bottom curves), all the mixtures satisfy the requirements. This means that all the mixtures are safe with respect to tensile failure when they are confined with a formation which has a rock's Young's modulus value of 1.450×10^6 psi and lower. Therefore, it is important to check the Young's modulus of the cement with respect to the that of the rock as well as the tensile strength requirements in actual oil and gas wells.

3.2.4 Tensile strength to Young's modulus ratio

As mentioned in Chapter 1, according to Le Roy-Delage et al. (2000), to prevent mechanical damage to the cement sheath, it is desirable to obtain a high value of tensile strength to Young's modulus ratio. An increase in the value of this ratio means that the tensile strength of the material has increased and/or the Young's modulus of the material has decreased. Also, the increased value of the ratio indicates an improvement in the mechanical properties of the material. Fig. 3.11 and Fig. 3.12 show the values of the tensile strength to Young's modulus ratio achieved for the mixtures prepared with the non-API and the API mixing procedures, respectively. As it can be observed, among the geopolymer mixtures (i.e. mixtures M1, M2,

M3 and M4), the highest value of the tensile strength to Young’s modulus ratio is achieved in mixture M4 which contains both flexible additives.

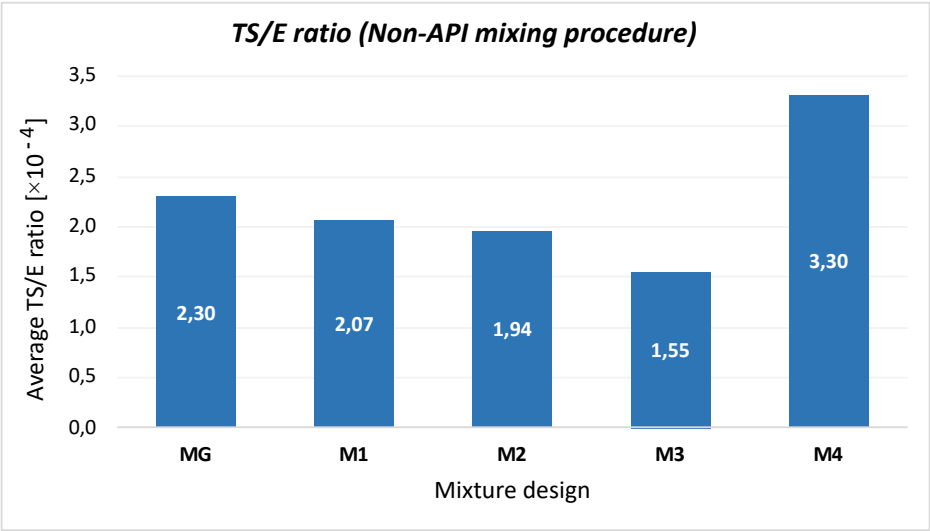


Fig. 3.11. The values of the tensile strength (TS) to Young’s modulus (E) ratio for mixtures prepared with the non-API mixing procedure. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

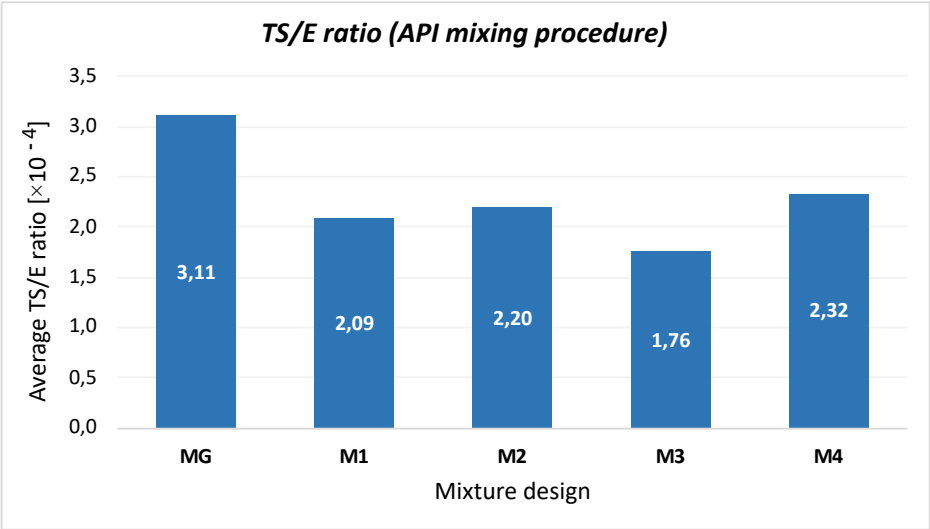


Fig. 3.12. The values of the tensile strength (TS) to Young’s modulus (E) ratio for mixtures prepared with the API mixing procedure. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

3.2.5 Uniaxial compressive strength to Young’s modulus ratio

An increase in the value of the compressive strength to Young’s modulus ratio means that the compressive strength of the material has increased and/or the Young’s modulus of the material has decreased. Also, the increased value of the ratio indicates an improvement in the mechanical properties of the material.

Fig. 3.13 and Fig. 3.14 show the values of the compressive strength to Young’s modulus ratio achieved for the mixtures prepared with the non-API and the API mixing procedures, respectively. In the non-API case (Fig. 3.13), among the geopolymer mixtures (i.e. mixtures M1, M2, M3 and M4), the highest value of the compressive strength to Young’s modulus ratio is achieved in mixture M4 which contains both flexible additives. However, in the API case (Fig. 3.14), the highest value of this ratio is achieved for mixture M2 which contains only additive A1.

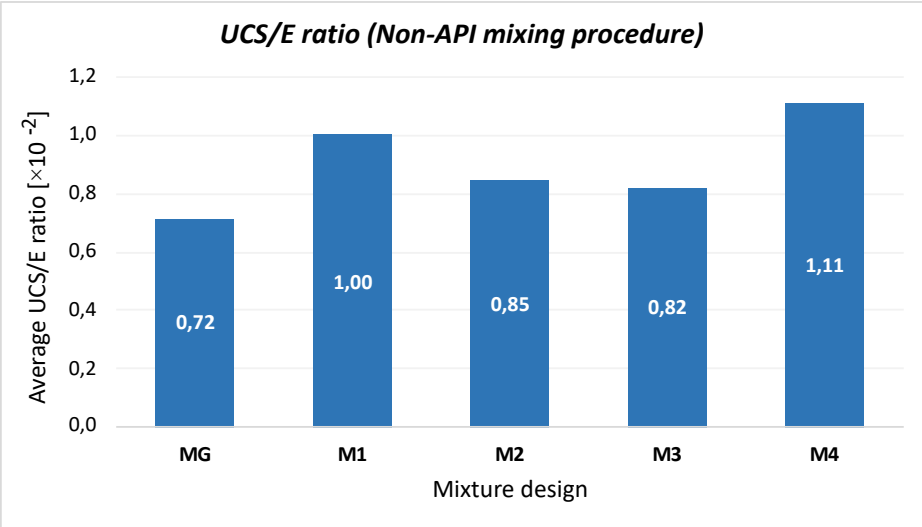


Fig. 3.13. The values of the uniaxial compressive strength (UCS) to Young’s modulus (E) ratio for mixtures prepared with the non-API mixing procedure. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

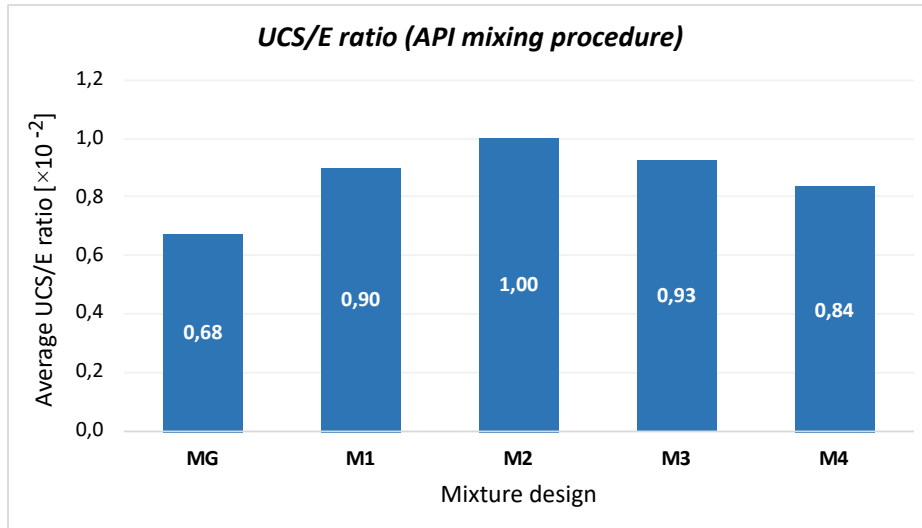


Fig. 3.14. The values of the uniaxial compressive strength (UCS) to Young's modulus (E) ratio for mixtures prepared with the API mixing procedure. From left to right the mixtures are: MG (API Class G cement), M1 (pure geopolymer), M2 (geopolymer including additive A1), M3 (geopolymer including additive A2) and M4 (geopolymer including both additives A1 and A2).

4 CONCLUSION

Based on the results and discussion, it can be concluded that:

- The pure geopolymer (M1) has higher flexibility and compressive strength compared to the API Class G cement (MG). However, the tensile strength of the pure geopolymer is lower than the API Class G cement. Nevertheless, this lower value of tensile strength may be acceptable since with higher flexibility the tensile strength requirements decreases.
- The use of the two flexible additives A1 and A2 results in increasing the flexibility of the geopolymer. However, by using the non-API mixing procedure, a higher flexibility is achieved when both additives are combined and added to the geopolymer. This is the opposite when the API mixing procedure is used. By using this procedure, a higher flexibility is achieved when the additives are separately added to the geopolymer.
- For both mixing procedures, as the flexibility increases in the geopolymer mixtures M2, M3 and M4, the compressive strength slightly decreases. However, the obtained compressive strength values of all the mixtures satisfy the compressive strength requirements of actual oil and gas wells.
- For both mixing procedures, as the flexibility increases in the geopolymer mixtures M2 and M3 which include a single flexible additive each, the tensile strength decreases. However, in the case of the mixture M4 which includes both additives, the increase in flexibility results in an increase in the tensile strength of the geopolymer.
- Taking into account the overall mechanical properties (i.e. Young's modulus, compressive and tensile strength) of the geopolymer mixtures which include flexible additives, the comparison of the two mixing procedures indicates that:
 - The API mixing procedure seems to give better results for the mixtures M2 and M3 which include a single flexible additive each.
 - The non-API mixing procedure results in better mechanical properties in the mixture M4 which includes a combination of both flexible additives.
- To prevent mechanical damage to the cement sheath in a wellbore, it is advantageous to obtain a high value of tensile strength to Young's modulus ratio. This indicates that the Young's modulus and the tensile strength are the most important mechanical properties of oil and gas well cement systems. Based on the results of the experiments, for both mixing procedures, mixture M4 shows the highest tensile strength to Young's modulus ratio.

5 FUTURE WORK

Based on the overall work of this thesis project as well the results achieved, the following recommendations have been suggested which require future research work:

- The concentration of each flexible additive should be increased in the geopolymer mixtures. This is to investigate whether higher concentrations of such additives can result in higher flexibility achievements. Also, in this case, both mixing procedures should be used to observe their effect on the mechanical properties of the mixtures.
- Cylindrical molds with uniform diameter along their length should be used in order to simplify the cutting and flattening of the samples and obtain more horizontal contact surfaces. This is because the non-uniformity of the molds used for the experiments in this thesis resulted in sample surfaces with some deviation from the horizontal during cutting. During the UCS tests, this deviation may affect the results by causing the force to be distributed unevenly on the surface of the sample.
- The mixtures in this thesis work were only conditioned for 30 min at a BHCT of 30°C. Future works could include a pumpability analysis of the mixtures where consistency versus time at different BHCTs is measured until the mixtures set. This is to see how long the mixtures are pumpable and to check whether their pumpability is in accordance with the requirements in actual oil and gas wells. Further, the mixtures could be cured at different curing temperatures and time. This is to investigate the effect of curing temperature on the mixtures which include the flexible additives A1 and A2 as these additives may be damaged at high temperatures. Longer curing time may give different results of the mechanical properties. Therefore, different curing times could be also included in the future experiments.
- In order to find the compressive strength and Young's modulus of the samples, it is preferable to perform the required tests using an equipment which provides confining pressures rather than using UCS machines. This is to be able to simulate the actual wellbore conditions, since the cement in the oil and gas wells is surrounded by the formation rock and thus exposed to confined pressures. Therefore, performing confined compressive strength tests provides more representative results which can be compared with the actual field cases.

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