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Rheological Properties of Sodium Silicate-Formamide Grouts

Eyubhan AVCI*

Bursa Technical University, Department of Civil Engineering, 16310 Bursa, Turkey

Abstract

In this experimental study, the rheological properties of Sodium Silicate Formamide mixtures were investigated in order to determine the usability of Sodium Silicate-Formamide mixtures as grout material. While determining the rheological properties, the effect of sodium silicate percentage and ambient temperature were particularly taken into account. Experiments were started with the determination of the gelling times. Gelling times observed to be between 352 and 1650 minutes at +15 °C, between 94 and 721 minutes at +25 °C and between 26 and 648 minutes at +35 °C. The gelling times decreased as the sodium silicate percentage and temperature increased. After the determination of the gelling times, the viscosity values of the mixtures were determined. Viscosity values were observed to be between 1.98 and 11.8 cP (centipoise) at +15 °C, between 1.42 and 9.51 cP (centipoise) at +25 °C and between 1.23 (centipoise) and 8.48 cP (centipoise) at +35 °C. With an increase in the percentage of sodium silicate, the viscosity values increased, while the temperature increased, the viscosity values decreased. Finally, experiments on syneresis percentage determination were carried out. At the end of 720th day, the percentages of syneresis were found to be between 1.47% and 22.4% at +15 °C, between 2.98% and 23.7% at +25 °C and between 3.9% and 24.8% at +35 °C. In mixtures, syneresis after gelling increased in time and this increase slowed down after the 18th day. The percentage of syneresis increased up to the ratio of 50% sodium silicate with the increase in sodium silicate ratio, after which the percentage of syneresis decreased with the increase of sodium silicate ratio. In addition, the percentage of syneresis increased with the increase in temperature. Experimental studies have shown that sodium silicate-formamide mixtures show good rheological properties and an alternative grouting material.

Keywords: Sodium silicate grouts, Rheology, Gelling time, Viscosity, Syneresis

1. Introduction

In geotechnical engineering, many grouting techniques are used. Permeation grouting is the most common of them. It is defined as the injection of the grouting material into the soil in low pressures. Chemical grouting materials are the most preferred and oldest grouting materials in permeation grouting. Chemical grouting materials reduce the permeability while increasing the strength of the soils and rocks by gelling and locating in the pores in the ground and rock. There are many chemical grouting materials that are different from each other in terms of components and chemical structures throughout the world. The most common ones are Sodium Silicates, Acrylamides, Lignosulfonates, Phenoplasts and Aminoplasts [1-5].

Among the chemical injections, sodium silicate stands out as the most commonly used grouting material. Sodium silicates are highly preferred chemical grouting materials in that they are highly environmentally friendly, harmless and economical. Sodium silicates, silicate sand or any form of silicate are prepared by undergoing heat treatment at 900 °C with Na_2CO_3. After being refined, sodium silicate takes the form of a fluid solution. By adding water to this solution at various ratios, the desired concentration is obtained [6]. The prepared solution is neutralized and turned into gel by adding a material with acidic character as a reactant. Syneresis is observed over time in the gelled solutions. It is defined as the expulsion of water after syneresis reactions or deterioration of gel structure. Shrinking is observed in the gel structure as syneresis appears. Sodium silicate grouted sand was tested for unconfined compressive strength by several researchers [7-14]. In the experimental studies performed, the effect of sodium silicate percentage and ambient temperature on the rheological properties of the mixture were not investigated.

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[*] Corresponding author: Tel: +90.224.3003741 E-mail: eyubhan.avci@btu.edu.tr
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In this experimental study, it was aimed to determine the rheological properties of sodium silicate-formamide mixtures prepared at different mixing ratios. While determining the rheological properties, the effects of sodium silicate percentage and temperature on rheological properties were investigated. It was also investigated whether sodium silicate Formamide mixtures are an alternative material for grouting or not.

2. Material and Methods

2.1. Materials

2.1.1. Properties of Sodium Silicate and Formamide Used in the Experiment

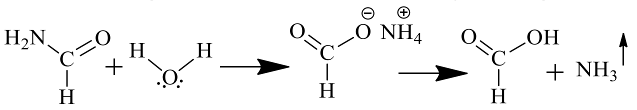
Sodium silicates are known as water glasses and are represented by the general formula Na_2 $(SiO_2)nO$. Sodium silicates are commonly used in detergents, metallurgy, furnace mortars, concrete and soil injections. Silica / alkali ratios (SiO2 / Na2O) must be between 3 and 4 in order sodium silicates to be used in soil injections. EGENAT 3203, coded sodium silicate produced by Ege Holding, was used in the determining reological properties tests, while a formamide, produced by the German Merck company, was used as the reactant. The physical and chemical properties of Sodium silicate and Formamide used in the experiments are given in Table 1.

Table 1. Physico-Chemical Properties of Sodium Silicate and Formamide

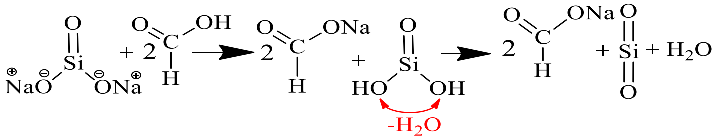
Sodium Silicate	Coloring	Colorless, clear liquid
	Formulation	Na_2SiO_3
	Weight modules (SiO_2/NaO)	3.0-3.3
	Molecular modules (SiO_2/NaO)	3.1-3.4
	Be' (20 °C)	39-41
	Density (20 °C, gr/cm^3)	1.37-1.39
	Na_2O (%)	8.5-9.5
	SiO_2 (%)	26.0-28.0
	pH (20 °C)	11.66
	Viscosity (20 °C, cP)	75-150
Formamide	Coloring	Colorless, clear liquid
	Formulation	CH_3NO
	Molar weight (gr/mol)	45.08
	Density (20 °C, gr/cm^3)	1.13
	pH (200 gr/l 20 °C)	8.0
	Viscosity (20 °C, cP)	3.75

2.1.2. Chemical Reactions

The following reaction was obtained by mixing sodium silicate with Formamide.



(R1)



(R2)

In Reaction 1 (R1), Formamide is first converted to ammonium formate salt in aqueous media. This salt, which is very unstable in the aqueous medium, is decomposed by ejecting ammonia into the media and transformed into formic acid. Formic acid, which is acidic in Reaction 2 (R2), forms the stable sodium formate salt by undergoing the neutralization reaction with sodium silicate in the basic form and is converted to silicic acid, which is the acid of the unstable silicate anion. The unstable silicic acid solution is converted into a stable silica structure by one mole of water ejection and the reaction mixture gelled after the reaction.

2.2. Methods

There are many chemical grouting materials used in the market. These materials have a wide range of different fluidity and strength properties. The first step to success in any injection application is, to select the correct injection material and determine the correct mix ratio. In this case, the rheological properties of the chemical materials are utilized. The rheological properties of a chemical injection material consist of gelling time, syneresis and viscosity.

Rheological characterization tests for sodium silicate-formamide mixtures were conducted on 8 samples and at 3 different temperatures. The mixing ratios of the solutions are presented in Table 2. While preparing the mixtures, sodium silicate solution and reactant (Formamide) were diluted with water at different ratios to try to determine the mixture ratios to be used in the grouting tests. During the preparation and mixing of the samples, airtight, plastic caps with mouth openings were used. In the mixing process, water is first mixed with the reactant material, then sodium silicate is added in the desired ratio. A magnetic stirrer is used for mixing (Figure 1).

Table 2. Grout solutions

Solution No	Water (%)	Sodium Silicate (%)	Formamide (%)
S1	5	80	15
S2	15	70	15
S3	25	60	15
S4	35	50	15
S5	45	40	15
S6	55	30	15
S7	65	20	15
S8	75	10	15

Figure 1. Mixing solutions with magnetic stirrer.

2.2.1. Gelling Time

The process that lasts until the injection material loses its fluidity and starts to solidify, is called gelling time [15]. In the literature, gelling time is defined as the time between the moment the mixture enters the reaction and the time when the viscosity value is 100 cP (centipoise). When the mixture starts to reach this viscosity value, the mixture begins to solidify and flowing stops when horizontally turned [16]. All chemical mixtures of the Newtonian type have more or less some viscous properties and while the time-dependent viscosity of some of these mixtures is constant for some time (silicates, lingosulphonates, etc.), this viscosity starts to increase after a period of time and in some cases, the constant viscosity does not change for a while as in organic resins and then a sudden solidification occurs (Figure 2). Control of the gelling time is crucial for chemical injections, and whichever material is chosen, this time period must be clearly set by selecting suitable catalysts [17]. Gelling time is a function of the injection materials, primarily reactants, inhibitors and catalysts added to mixture and varies depending on the mixing ratios of these elements [4].

Injection materials, by which a wide range and reproducible gelling times, are obtained are characterized as good or excellent in terms of control of the gelling time, while injection materials with narrow-range and difficult-to-reproduce gelling times, in are regarded as moderate or poor injection materials [5]. Other factors affecting the gelling time are the temperature, the solution rate and the dilution that occurs during the injection process [18]. The injection material begins to gain strength rapidly after gelling, and the time between the moment of gelling and the moment the neutralization reaction is completed is called the curing period [4].

In order to determine the gelling time, gelling time determination experiments were carried out on 8 different mixtures at different temperatures (+15 ℃, +25 ℃ and +35 ℃) (Figure 3). The variation of the gelling times with temperature is given in Figure 4.

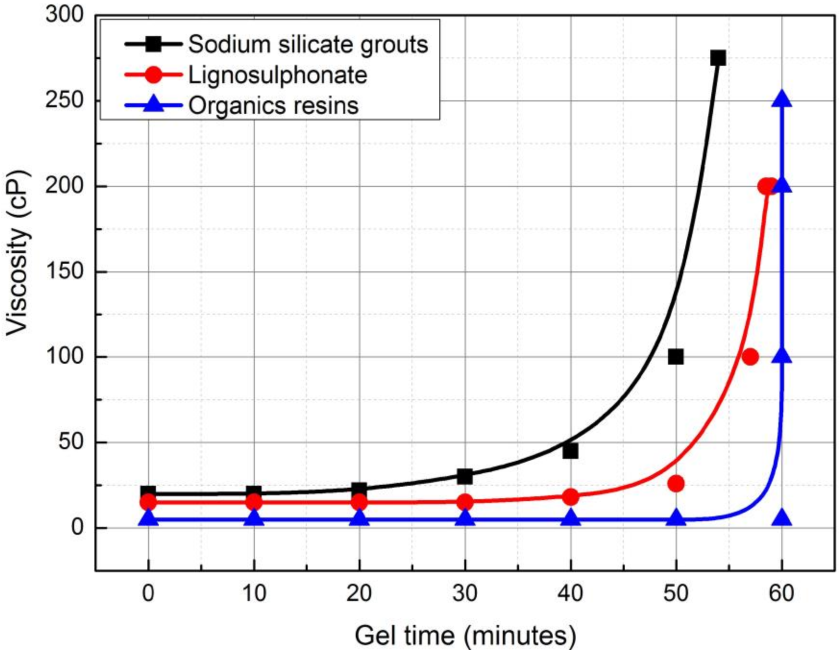


Figure 2. Viscosity and Sodium gel time relationship of grouts (Verfel, 1989).

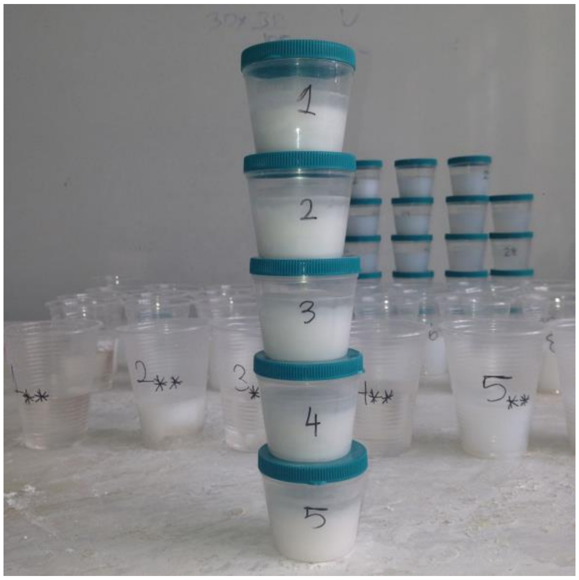


Figure 3. Observation of gelation times

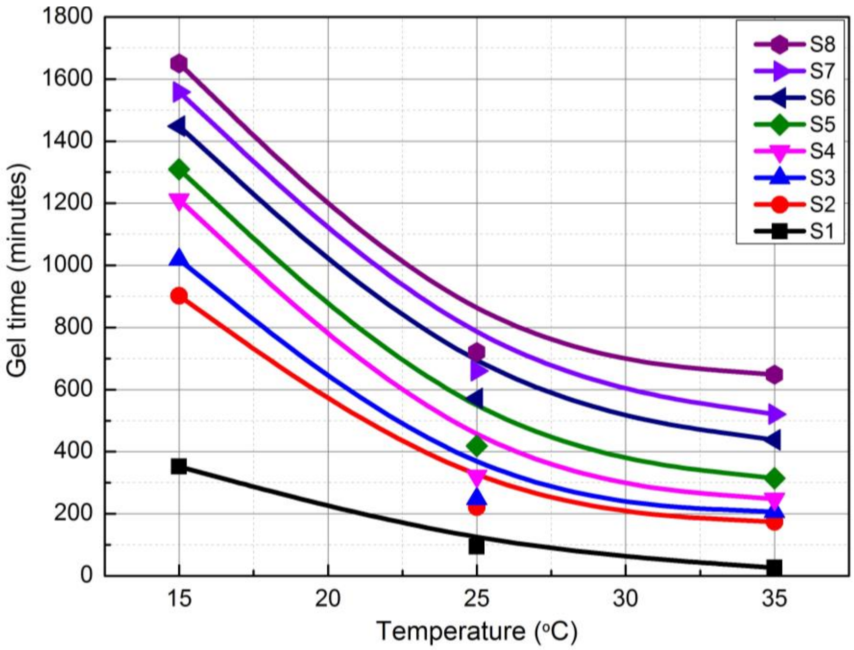


Figure 4. Gel time and Temperature relationship.

2.2.2. Viscosity

The most important parameter affecting groutability among chemical injections is viscosity. Viscosity can be defined as the resistance of a fluid to flow or the resistance to internal shear stress [4]. In addition, it can also be defined as a tangential force acting on a unit field in two horizontal layers mixed with space filling matter, one of which is fixed and the other of which is moving at a constant speed and away from each other [5]. Viscosity is expressed in dyne-seconds or poisses units in cm2. It is desirable that the water viscosity at 20 °C is 1 cP (centipoise) and that the viscosity of an ideal material is close to this value. With this low viscosity value, the injection material can easily fill the voids as a penetrate into the soils [15]. When a solid is subjected to shear force, deformation occurs and internal stresses form in the material until it reaches static equilibrium. These internal stresses within the elastic limits of the material are proportional to shear deformations. The ability of a material to reach a static balance instead of a continuous deformation is due to the shear strength property. The liquids do not have such a shear strength as in the case of solids, and they resist deformation due to molecular friction in the liquids. Despite this, the deformation continues indefinitely with shear force effect. The property defined as viscosity is a measure of internal friction against shear forces. The viscosity of liquids is generally not measured directly. A specific relationship is used to obtain the true value by measurement of a viscosity-related parameter [5].

Brookfield DV III rheometer device was used to determine the viscosity of sodium silicate-formamide mixtures. Experiments were carried out on 8 mixtures at 3 different temperatures. The tests were carried out according to ASTM D 2196 15 standard. The variation of the viscosity values with temperature is given in Figure 5.

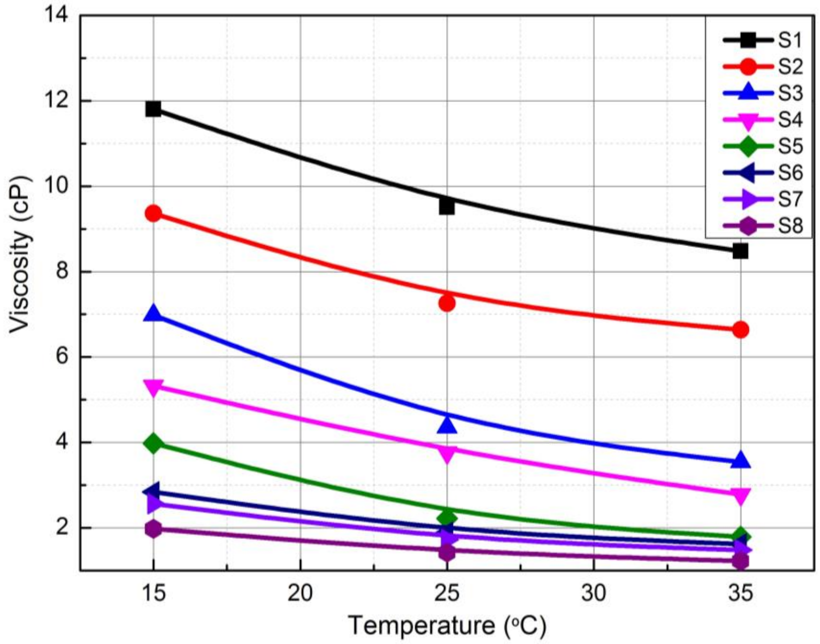
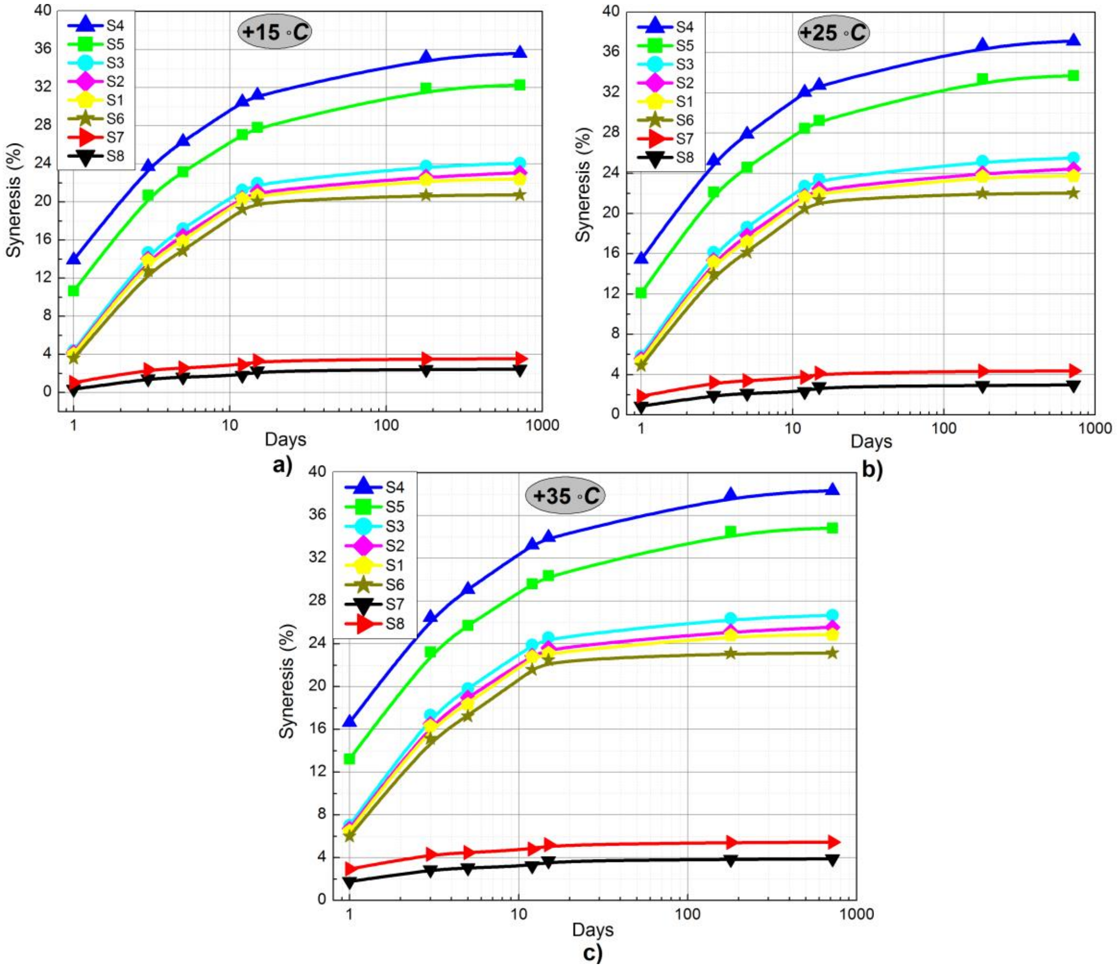


Figure 5. Relationship between Viscosity and Temperature.

2.2.3. Syneresis

Syneresis is defined as ejection of water due to shrinking over time after gelling. Syneresis occurs at the thickest state of gelling following fluid and plastic phases in the most solid state following gelling, and is expressed as the ratio of the volume of seperating water to the initial volume of gel [16]. While syneresis is much more effective in gels possessing low silicate content and long solidification time, the effect is negligible for sands from fine to medium [5]. Factors affecting syneresis are the ratio of dissolved SiO2 and the degree of neutralization. The syneresis percentage are used when the synereses of the materials after grouting are compared. In the reaction after gelling, silanol groups transform into siloxane bonds and there emerges water. The formation of syneresis after injection, significantly affects the engineering properties of the grouted soil sample. As the percentage of syneresis increases, the strength decreases and permeability increases [5]. 8 samples were measured for syneresis percentages on 1st, 3rd, 5th, 12th, 15th, 180th and 720th days. In the determination of syneresis percentages, the amount of water released after the reaction in the closed cups after the gelling was measured depending on the time and the percentage of syneresis was calculated by dividing the total volume. Syneresis percentages were measured at 3 different temperatures (+15 °C, +25 °C and 35 °C). The change in the percentage of syneresis over time is given in Figure 6. The change in the percentage of syneresis with sodium silicate is given in Figure 7.



a) b)

c)

Figure 6. Variation of Sodium silicate-Formamide syneresis with time; a) +15 °C, b) +25 °C, c) +35 °C

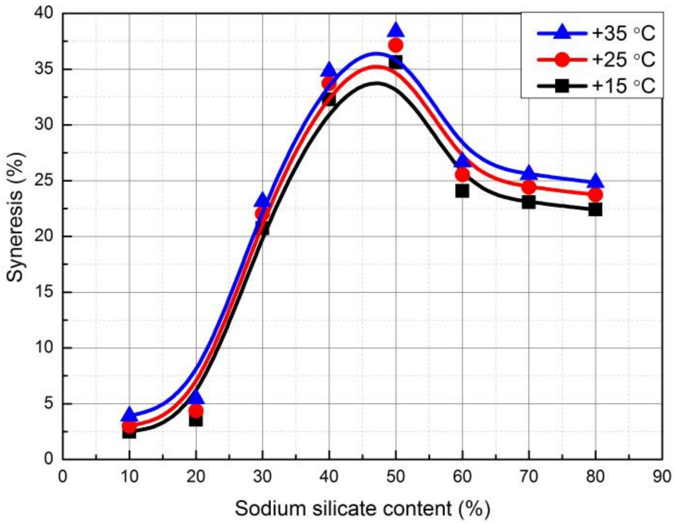


Figure 7. The effect of sodium silicate content on the syneresis of grout gels for 720th day

3. Results and Discussion

3.1. Gelling time

The gelling times of the sodium silicate Formamide mixtures are 352, 902, 1018, 1211, 1310, 1448, 1558 and 1650 minutes respectively, for mixture ratios S1, S2, S3, S4, S5, S6, S7 and S8 at + 15 °C. The gelling times of the sodium silicate Formamide mixtures are 94, 221, 248, 322, 419, 571, 660 and 721 minutes respectively, for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at + 25 °C. The gelling times of Sodium Silicate Formamide mixtures are also 26, 174, 206, 248, 315, 438, 521 and 648 minutes respectively, for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at + 35 °C (Figure 4). Gelling times were shortened with the increasing temperature. While the amount of this shortening has an average of 68% between +15 °C and +25 °C, it has an average of 27% between +25 °C and +35 °C (Figure 4).

Gelling times were shortened by increasing the percentage of sodium silicate. For example, at +35 °C the gelling time in the S8 mix was 721 minutes, while in the S1 mix the gelling time is 26 minutes. The highest gelling times are seen in the S8 mixture, while the lowest gelling series is seen in the S1 mixture (Figure 4.) Figure 2 shows that the gelling is white and completely homogeneous (Figure 3).

3.2. Viscosity

The viscosity values of sodium silicate-formamide mixtures are 11,8, 9.36, 6.98, 5.32, 3.98, 2.56 and 1.98 cP (centipoise) for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at + 15 °C respectively. The viscosity values of the sodium silicate-formamide mixtures are 9.51, 7.26, 4.35, 3.76, 2.22, 1.89, 1.72 and 1.42 cP (centipoise) for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at + 25 °C. Sodium silicate-Formamide mixtures have viscosity values of 8.48, 6.64, 3.54, 2.78, .1.79, 1.62, 1.48 and 1.23 cP (centipoise) respectively, for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at + 35 °C (Figure 5).

Viscosity values were seen to decrease with the increasing temperature. While this decrease is 31% on avarage between +15 °C and +25 °C, it has an average of 16% between +25 °C and +35 °C (Figure 5). Viscosity values increased with the increasing sodium silicate ratio. For example, at +35 °C, the viscosity of the S1 mixture is 8.48 cP (centipoise) while the viscosity of the S8 mixture is 1.23 cP (centipoise). The highest viscosity values are seen in the S8 mixture while the lowest viscosity values appear in the S1 mixture. The viscosity values of the S1 mixture are very close to the water viscosity values (1 cP at + 20 °C) (Figure 5).

3.3. Syneresis

The syneresis percentages of sodium silicate Formamide mixtures kept at + 15 °C were 22.4%, 23.1%, 24.1%, 35.6%, 32.3%, 20.7%, 3.55% and 2.47% respectively, for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at the end of 720th day. The syneresis percentages of Sodium silicate Formamide mixtures kept at + 25 °C were 23.7%, 24.4%, 25.5%, 37.1% and 33.7%, 22.0%, 4.35% and 2.98%, respectively, for mixture ratios of S1, S2, S3, S4, S5, S6, S7 and S8 at the end of 720th day. The syneresis percentages of Sodium silicate Formamide mixtures which were similarly kept at + 35 °C were 24.8%, 25.6%, 38.4%, 34.8%, 23.1%, 5.4% and 3.9%, respectively for S1, S2, S3, S4, S5, S6, S7 and S8 mixture ratios at the end of 720th day (Figures 6 and 7).

The percentage of syneresis were observed as increased by increasing sodium silicate ratio in the sodium silicate-formamide mixtures, and the maximum percentage of sodium silicate was increased by 50%, after which the percentage of syneresis decreased with the increasing sodium silicate ratio (Figure 7), While the highest percentages of syneresis are observed in S4 mixtures, the lowest ones are observed in S8 mixtures.

The increase in temperature, increased the percentage of syneresis. An increase of 9% occured in the percentage of syneresis between + 15 °C and + 25 °C, while an increase of 11% occurred in the percentage of syneresis between + 25 °C and + 35 °C (Figs.5 and 6). The percentage of syneresis increased with time. This increase slowed down after the 15th day (Figure 6).

4. Conclusions

The main results obtained from this study are:

- Gelling times were shortened by increasing the percentage of sodium silicate and the temperature.
- Completely homogeneous gelling was observed in the prepared mixtures.
- As the percentage of sodium silicate increased, the viscosity values increased and as the temperature increased, the viscosity values decreased.
- Post-gelling syneresis in mixtures increased with time, and this increase slowed down after day 18.
- The percentage of syneresis increased with the increasing sodium silicate ratio, and this percentage increased to a maximum value at 50% sodium silicate ratio, after which the percentage of syneresis decreased with the increasing sodium silicate ratio.
- The percentage of syneresis increased with the increasing temperature.
- Experimental studies have shown that sodium silicate-formamide mixtures are alternative injection materials with their good rheological properties they have.

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