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Effect of Urea Usage Rate on Thixotropic Behavior of Cementitious Systems

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Abstract: It was understood that studies investigating the use of alternative materials have increased in order to develop concrete technology, to expand sustainability and to improve the fresh and hardened state properties of cementitious systems. It was reported that one of these alternative materials is urea, which can increase both the flow performance of the mixture and the freeze-thaw resistance. In this study, the effect of the use of urea on the thixotropic behavior of Portland cement systems was investigated. In addition to the urea-free control mix, 4 different batches of paste mixes were prepared by replacing the cement with urea at a rate of 2.5%, 5% and 10% by weight. The thixotropic behavior of the mixtures was evaluated by comparing the hysteresis area values obtained from the viscosity-shear rate graphs. It was determined that the structural recovery area measured at the initial and the structural breakdown area measured at the end of the 180 second rest period decreased with the use of urea. It was determined that the optimum urea utilization rate was 2.5% in terms of the thixotropic area value of the mixtures.

Keywords: Urea, Viscosity, Hysteresiz area, Loop test, Thixotropy

Introduction

It is known that one of the most important factors affecting the durability of concrete negatively is the freeze-thaw event that occurs in cold weather conditions. It was emphasized that a 9% volume expansion occurs as a result of the water in the capillary spaces of the hardened concrete turning into ice with the decrease in temperature (Mardani Aghabaglou et al., 2019). Thus, it was reported that cracks occur in concrete samples as a result of the formation of internal tensile stresses (Erdogan, 2015).

It was declared that the water in the cavities of the concrete usually freezes at a temperature lower than 0°C due to the various salts it contains (Koefod, 2008). It was understood that the diameter of the cavity where the water is located affects the freezing temperature significantly (Berberoglu, 2011). It was reported that water freezes at 0°C in large capillary spaces, at temperatures between -15 and -20°C in very small capillary spaces, and at -78°C ingel spaces (Sahin, 2003). It was emphasized that the freezing of water in concrete occurs gradually, depending on the rate of heat transfer and the size of the void at the freezing point (Powers, 1965). It was declared that freezing starts from the water in large spaces and spreads towards small spaces (Postacıoglu, 1987). It was reported that the resulting damage starts from the spills on the surface and progresses into the concrete by fragmentation into layers (Neville, 1995).

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It was understood that the degree of saturation of concrete and its porous structure are the most important parameters affecting the freeze-thaw resistance (Baradan, 2022). In order to increase the freeze-thaw resistance of concrete, an air-entraining admixture that will create permanent air spaces is added to the mixture (Sahin, 2003). However, it was reported that the compressive strength of concrete decreases with the addition of air-entraining admixture (Guleryuz, 2020). Numerous studies were carried out to improve both the freeze-thaw resistance and the fresh state and mechanical properties of concrete (Erdem & Ozturk, 2012). In this direction, it was understood that industrial urea has been examined in various studies (Shirayama et al., 2018).

Urea was discovered by the French scientist Hillaire Rouelle (1773) but began to be synthesized in 1828. Urea, known as carbamide, is an organic compound with the chemical formula ($CO(NH_2)_2$) (Sant Ana Filho, 2012). As a bead-shaped solid product, urea has two -NH2 groups joined by a carbonyl (C=O) functional group. The compound is commercially synthesized by a reaction of ammonia (NH_3) and carbon dioxide (CO_2) under conditions dependent on the technology used in the industrial plant (Sant Ana Filho et al., 2012). It is a colorless, odorless, easily soluble substance in water and alcohol (Kim, 2017).

In the literature, it was reported that urea improves the freeze-thaw resistance of cementitious systems (Demirboga, 2014), workability (Mwaiuwinga, 1997; Demirboga, 2014), carbonation (Sadegzadeh, 1993) and drying-shrinkage (Sato, 2020) performance. It was declared that the use of urea, especially in mass concrete structures and in hot climate regions, provides a great advantage due to its lowering effect on the heat of hydration (Kim, 2021). Some research results on the subject are summarized here:

The effects of the use of rice husk ash (20%) and urea (0%, 5%, 10%, 20%) on the flow performance, compressive strength and heat of hydration properties of self-compacting concrete mixtures were investigated by Makul and Sua-iam (2017). It was reported that with the addition of urea, the heat of hydration and strength of the mixtures decrease, while the flow and strength performances increase. It was emphasized that this behavior was more evident with the increase in the urea utilization rate.

Wang et al. (2020), the effect of using urea at different rates (5%, 10% and 15%) on the hydration process and microstructure of the concrete mixture was investigated. They reported that the use of urea reduces the heat of hydration of the concrete mixture and has a retarding effect. It was emphasized that this behavior was more evident with the increase in the urea utilization rate.

It is known that chemical and mineral additives added to cementitious systems affect their rheological and thixotropic properties. It was understood that its thixotropic properties were evaluated with different approaches (Ma et al., 2018). In this context, it was emphasized that the thixotropic behavior of cementitious systems is generally investigated through hysteresis areas (Ma et al., 2018; Ferron et al., 2007). Zhang et al. (2021) the effects of different water-cement ratio and shear stress rate on the rheological and thixotropic properties of paste mixtures were investigated. When the constant shear stress was applied, it was measured that the hysteresis loop area and the destruction energy of the agglomeration structure decreased with the increase of the water-cement ratio. In the case of constant water-cement ratio, it was emphasized that with the decrease of the shear stress rate, the destruction energy and the degree of destruction of the agglomeration structure decrease. It was emphasized that with the increase of the shear stress rate, the agglomeration structure would increase the destruction energy.

As understood from the literature, it was emphasized by various researchers that urea has a significant positive effect on mechanical and durability properties (Mwaiuwinga et al., 1997). However, no study was found on the effect of urea use on the rheological and thixotropic properties of cementitious systems. For this purpose, the effect of using different ratios of urea instead of cement on the thixotropic behavior of paste mixtures was investigated.

Material and Method

Materials

Cement

Within the scope of the study, CEM I 42.5R type cement (PC) produced by Bursa Cement was used. The chemical component, physical and mechanical properties of the cement supplied by the manufacturer are shown in Table 1. Some characteristics of the urea supplied by its manufacturer are presented in Table 2.

Table 1. Chemical composition, physical properties of cement.

Oxide	(%)	Mechanical and physical properties		
SiO_2	18.74	Compressive strength (MPa)	1-Day	2.43
Al_2O_3	5.37		28-Day	39.3
Fe_2O_3	3.04	Setting Time (min)	Initial	201
CaO	64.11		Final	321
MgO	1.21	Fineness	Blaine specific surface (cm^2/g)	3600
Na_2O	0.34		Residual on 0.090 mm sieve (%)	0.4
K_2O	0.62		Residual on 0.045 mm sieve (%)	7.4
SO_3	2.68		specific gravity	3.15
Cl^-	0.038	Volume expansion (mm)		<1

Table 2. Some properties of urea and air-entraining admixture

Admixture	Density (g/cm^3)	pH	Colour	Physical Condition	Melting point (°C)	Solids Ratio (%)
$(CO(NH_2)_2)$	1.32	9	White	Solid	133	-

Mixture Proportion

Within the scope of the study, a total of 4 different paste mixtures were produced by substituting urea at the rate of 2.5%, 5%, 10% of the cement weight into the control mixture that does not contain urea. In all mixtures, the water/cement ratio was kept constant as 0.35. The preparation of the mixtures was carried out in a room whose temperature was kept constant at 20±2°C. The denotation of the mixtures was made according to the urea usage rate. For example, the paste mixture prepared by replacing 2.5% of the cement weight with urea is called Urea_2.5%. In the preparation of the mixtures, firstly, urea and water were mixed at 62 rpm for 30 seconds, then cement was added and mixed at the same speed for another 30 seconds. Then, rheological measurements were carried out by mixing at 125 rpm for 120 seconds.

Test Methods

The thixotropic behavior of the paste mixtures prepared within the scope of the study was investigated by means of viscosity-shear stress graphs. The graphs in question were drawn through the data obtained from the Herschel Bulkley model analysis shown in Equation 1. In rheological measurements, hysteresis areas were created by increasing the shear rate from 0 s^{-1} to 60 s^{-1} and then decreasing it back to 0s^{-1} (Figure 1). The hysteresis areas are calculated using Equations 2 and 3.

$$\tau = \tau_o + b.\dot{\gamma}^P \tag{1}$$

τ_o: dynamic yield stress
b: Herschel-Bulkley coefficient,
$\dot{\gamma}$: shear rate
P: Herschel-Bulkley index

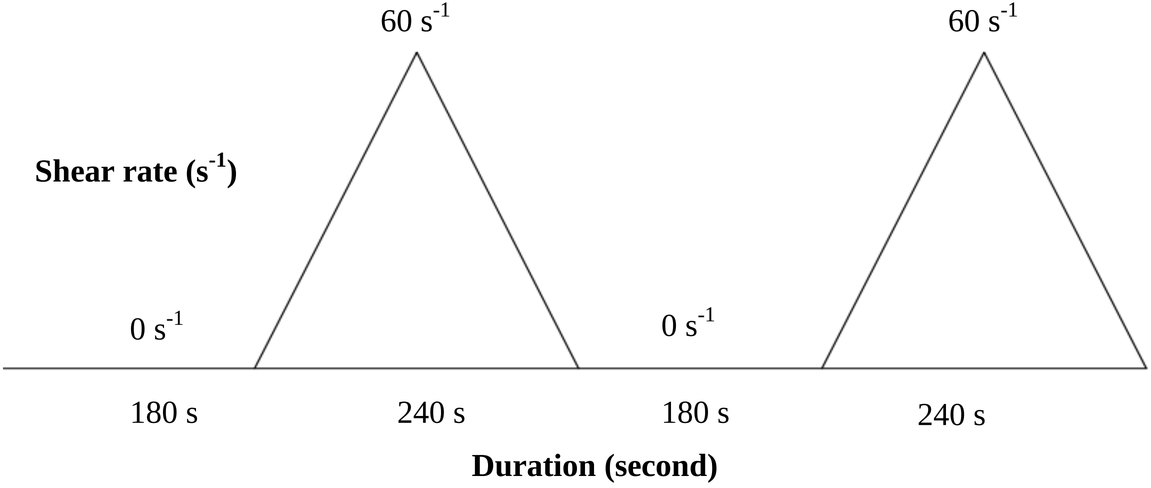


Figure 1. Rheological measurement process

$$A_{viscosity} = \left[\sum_{i=1}^{n-1} A_{i.viscosity\_up}\right] - \left[\sum_{i=1}^{n-1} A_{i.viscosity\_down}\right] \tag{2}$$

$$A_i = \frac{1}{2}\left[\left(\dot{\gamma}_i - \dot{\gamma}_{i+1}\right).\left(\eta_{\ i} + \eta_{\ i+1}\right)\right] \tag{3}$$

n: number of data

$\dot{\gamma}_i$: shear rate (s^{-1})

$A_{viscosity}$: hysteresis area (Pa) formed in the viscosity-shear rate graph.

$A_{i.viscosity\_up}$: area under the up curve

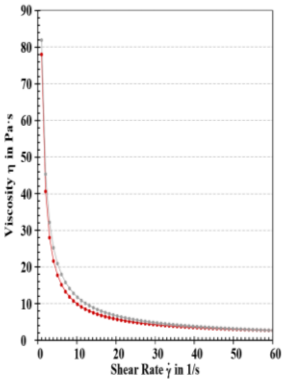
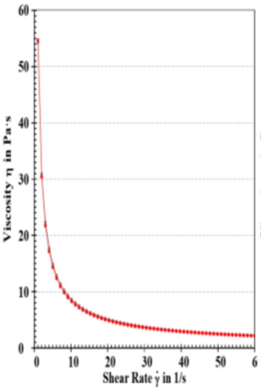
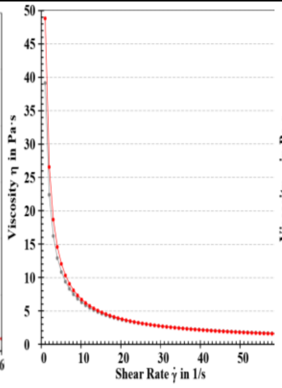
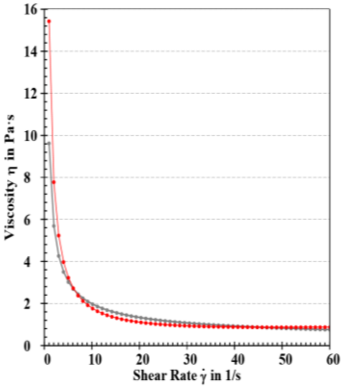
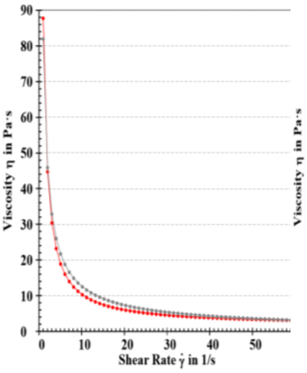
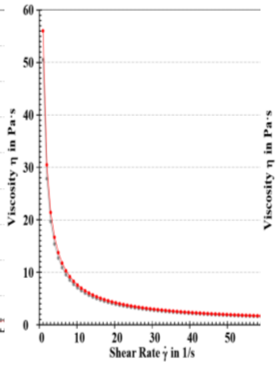
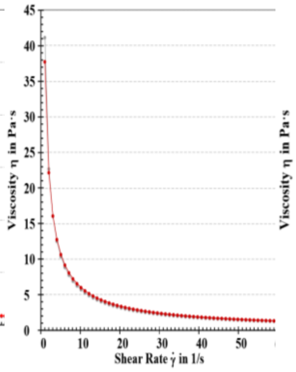
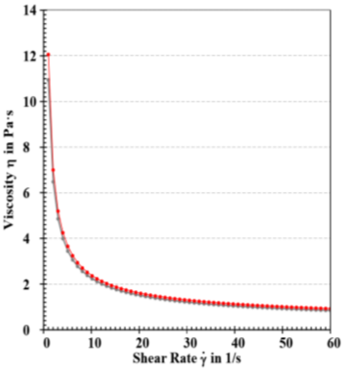
$A_{i.viscosity\_down}$: area under the down curve (Pa)

η : apparent viscosity (Pa.s)

Discussion and Conclusion

The viscosity-shear rate graph of the mixtures and the 'structural breakdown area' (SBDA) and 'structural build-up area' (SBUA) values obtained from this graph are given in Figure 3.

Table 2. Viscosity-shear rate graphs of mixtures

Mix	Control	Urea_2.5%	Urea_5%	Urea_10%
Initial Graph				
Area	SBDA(Pa)= 0 SBUA(Pa)=54.5	SBDA (Pa)=0 SBUA (Pa)=8.5	SBDA(Pa)=12,7 SBUA(Pa)=1.1	SBDA (Pa)= 3,6 SBUA (Pa)= 5.5
180 Second after graph				
Area	SBDA (Pa)=0 SBUA (Pa)= 58.7	SBDA(Pa)= 18.6 SBUA(Pa)=0	SBDA (Pa)= 8.3 SBUA (Pa)= 0	SBDA (Pa)= 6.9 SBUA (Pa)= 0

Note: ● up SBDA:Structural breakdown area
● down SBUA:Structural buildup area

With the addition of 2.5% and 5% urea to the control mixture, it was understood that the SBDA value decreased by 84% and 98%, respectively. However, it was measured that the SBUA value increased 5 times with an increase in the urea utilization rate from 5% to 10%. Despite the mentioned increase, it was understood that the mixture containing 10% urea had 90% and 35% lower SBUA values compared to the control and mixtures containing 2.5% urea. Thus, it was understood that the SBUA values generally decreased with the use of urea, but after a certain value (10% for this study), this decreasing trend changed to an increasing trend. While the SBDA value was measured as 0 for the control and Urea_2.5% mixtures, the said value was measured as 12.7 Pa and 3.6 Pa for the Urea_5% and Urea_10% mixtures, respectively. Thus, it was understood that the Urea_5% mixture had the highest SBDA (thixotropic area) value and the said value started to decrease with 10% urea usage rate.

As can be seen from Table 4, an 8% increase in the SBUA value of the control mixture was detected after resting for 180 seconds. In the mixtures containing urea, the SBUA values were measured as 0. When the measurements at the end of 180 seconds were evaluated among themselves, the SBDA values decreased with the increase in the use of urea. The highest and lowest SBDA values were observed in Urea_2.5% and Urea_10% mixtures, respectively. Thus, it was understood that the optimum urea usage rate for portland cement mixtures is 2.5% in terms of thixotropic area value.

Conclusion

The results obtained in accordance with the materials and methods used in the study are presented below.

- Compared to initial, the SBUA value measured after the 180 second rest period increased in the control mixture and decreased in the mixtures containing urea.
- SBUA values measured at the initial generally decreased with the use of urea, and were measured as 0 after a rest period of 180 seconds.
- It was understood that the SBDA values measured after the 180 second rest period decreased with the use of urea.
- In terms of thixotropic area value, it was determined that the optimum urea usage rate for portland cement mixtures is 2.5%.

Conflicts of Interest/Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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***** All data, models, and code generated or used during the study appear in the submitted article.

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