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INFLUENCE OF UREA IN CONCRETE

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ABSTRACT

Urea can substantially reduce the temperature of concrete both at casting stage and during hydration process. However, not much is known about what effects urea can likely bring in concrete. In this study the influence of urea in concrete on flowability, heat of hydration, setting time, strength, shrinkage strain, and carbonation resistance are discussed. The results of the experiment show that apart from the fact that urea can reduce the hydration temperature in concrete, it can also enhance both flowability and durability of concrete. *© 1997 Elsevier Science Ltd*

Introduction

When urea is mixed with concrete, the temperature of the concrete is reduced by endothermic reaction between water and urea. By using this property, it is possible to reduce the temperature of concrete at both casting stage and during the hydration process. This can be very advantageous in mass concrete constructions and when concrete is being cast under high ambient temperature like in the summer or in hot, tropical areas. Apart from immediate reduction of temperatures at casting stage, there is also reduction of temperature during hydration process which is caused by a reaction between some parts of cement products with urea and consequently reducing the temperature of concrete. The mechanism behind seems to be that in its first reaction with water, heat is being absorbed and this reaction is accompanied by some expansion. Secondly the main product from this reaction which is carbonic acid (H_2CO_3) reacts with calcium hydroxide which is an important ingredient in the cement paste and therefore affecting hydration, setting time, and overall durability of concrete (1). The present cooling methods used to reduce the temperature in large mass concrete are very expensive. This study also investigates the influence of urea in highly flowable concrete because if high flowability without segregation is also maintained, then we shall have an additional advantage of easy discharge into forms by pumping method. Also compaction or vibration of concrete in the formwork will be minimized or completely eliminated. A research conducted by Sadegzadeh et al. (2), on the effects of urea on durability of reinforced concrete concluded that urea does not adversely affect the durability of reinforced concrete. Their experiment however was based on the influence of urea being used externally, while in this research we investigate the effects of urea in concrete by being used internally. Under normal practices, materials like fly ash, blast furnace slag, limestone powder and rice husk are currently being used as low reactive materials to reduce the heat of hydration in large

TABLE 1
The Chemical Composition of Cement

	Type of cement			
	TYPE I %	TYPE II %	TYPE III %	TYPE IV %
CaO	64.4	64	65.2	62
SiO_2	21.9	23.4	20.8	25
Al_2O_3	5.4	4.4	4.9	3.8
MgO	3.1	3.8	2.8	3.6
Fe_2O_3	1.6	1.1	1.5	0.6
SO_3	1.8	1.6	2.5	3.2
insol.	0.4	0.2	0.5	0.1
ing.loss	0.7	0.7	1	0.4
C_3S	49.17	42.44	62.57	21.92
C_2S	25.78	35.16	12.051	55.22
C_3A	9.07	5.24	8.25	3.99
C_4AF	9.42	11.55	8.51	10.94

mass concrete constructions (3). There has also been a research conducted by P.K. Mehta and D. Pirts (4) to use rice husk ash as a replacement material for cement in order to reduce heat of hydration in concrete. The use of these low reactive materials is done by replacing part of cement by these materials without changing the overall powder content in concrete which is an important factor for the mix proportions of highly flowable concrete (5). In this study limestone powder has been used to replace part of cement as a low reactive material for reasons mentioned above. Urea replaces part of water. The flowability without segregation is maintained by appropriate use of superplasticizers and segregation reducing agents. In

TABLE 2

Physical Properties of Materials

	Specific gravity	Water absorption %	Unit volume kg/m^3	F. M.	Specific area cm^2/gm
Fine aggregate	2.61	1.61	1573	2.51	
Coarse aggregate	2.75	0.74	1547	6.47	
Cement type I	3.15				2800-3100
Cement type II	3.14				2500-3150
Cement type III	3.22				3300-4230
Cement type IV	3.24				2500-3550
Limestone powder	2.73				3000-9000
Urea	1.34				

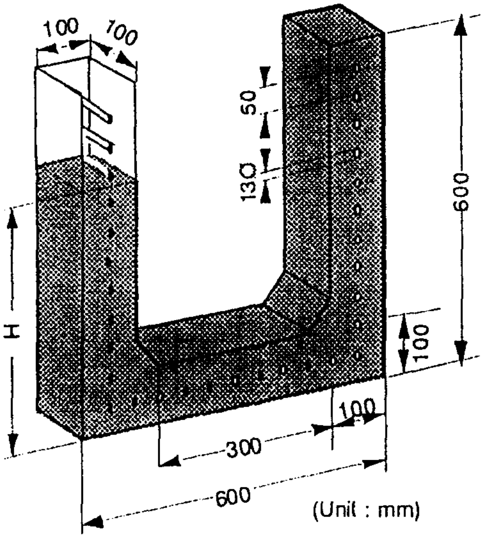

FIG. 1.
The U-apparatus.

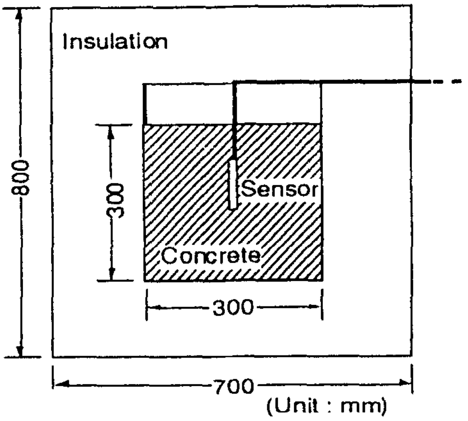

FIG. 2.
The semi-adiabatic apparatus.

this study high flowable concrete is defined as concrete whose slump is more than 25cm and whose slump flow lies between 60-70 cm (6, 8). The slump flow is defined as average diameter of the spread concrete in the slump test, provided that no segregation of aggregate occurs at tip center of the spread.

Experimental Outline

Materials. Table 2 shows the physical properties of cement, urea, limestone powder, fine and coarse aggregate used in this study. The type of superplasticizer used was naphthalene formaldehyde condensate and the type of segregation reducing agent used belongs to a group of acrylamide admixtures.

Apparatus and Methods

Figure 1 shows a U-shaped apparatus which was used to measure flowability of concrete. The concrete is poured on one side of the apparatus and left to flow on its own weight and rise to the other side of the apparatus. If it is highly flowable and self compacting it will rise on the other side but if not it won't. In case it rises, a distance "H" from the bottom corner of the apparatus is measured and is termed positive "H". In case it fails to rise to the other side and stops in between, a distance "H" is measured from the bottom corner and is termed negative. When concrete just manages to reach the bottom corner but fails to rise "H" is taken as zero. Figure 2 shows a semi-adiabatic apparatus used to measure the heat of hydration process and the rising temperature in concrete. The concrete temperatures were recorded over a period of one week time.

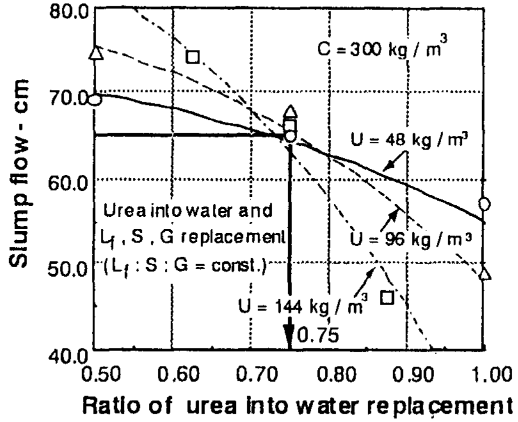

FIG. 3.
Slump flow at varying urea into water replacement ratios.

The setting and hardening process of concrete was measured by using a proctor needle penetration instrument in accordance with Japanese Industrial standards (JIS). Initial setting time of concrete is defined as the time when penetration resistance is 3.4MPa and final setting time is defined as the time when the penetration resistance is 27.7MPa. The compressive strength was measured from 10cm × 20cm cylindrical concrete specimens. The shrinkage strain was measured from 10 cm × 10 cm × 40 cm rectangular specimen. After being cured in water for 28 days the specimens were stored in a room with constant temperature and relative humidity of 19 ± 1°C and 68 ± 7% respectively. Carbonation was measured from 10cm × 20cm cylindrical specimens. After being cured in water for 27 days, they were kept in dry air for 1 day, then they were placed in a chamber with CO_2 concentration of 20%, a relative humidity of 60% and temperature of 30°C.

TABLE 3

Mix Proportions of Concrete

W	C	L_f	U	S	G	S.P	S.R.
162 153 144	300	182 185 187	48(36)	686 697 706	980 993 1006	7.05	7
144 126 106	300	177 182 187	96(72)	670 688 706	955 980 1006	7.05	7
113 99 86	300	176 180 183	144(108)	655 679 692	948 967 987	7.05	7

Lf : Limestone powder U : Urea
S.R. : Segregation reducing agent ( ): volume in litres
S.P. : Superplasticizer (SNF) Units in kg/m^3

Results and Discussion

Preliminary investigations were first made to determine the influence of urea on slump flow of concrete when it replaces water. Figure 3 shows relationship between slump flow of concrete with varying ratios of urea into water replacement. Three different urea contents 48 kg/m^3, 96 kg/m^3 and 144 kg/m^3 were considered. The cement content was kept constant at 300 kg/m^3. It is evident from the figure that when the urea to water replacement ratio is 0.75, the slump flow of concrete lies between 60~70 cm and is almost the same regardless of variation of the urea content. Table 3 shows the mix proportion of those concrete used. In a similar manner, the optimum replacement ratio of 0.6 and 0.9 at corresponding cement contents of 388 kg/m^3 and 250 kg/m^3, respectively were established. Table 4 shows the considered mix proportions of concrete at respective optimum replacement ratios. The concretes of these mixes with an exception of normal concrete have a slump more than 25cm and slump flow between 60~70cm which is a basic requirement of highly flowable concrete as already discussed. The amount of superplasticizer in these concrete was kept at 2.35% of cement. The amount of segregation reducing agent depended on sand/aggregate ratio and water cement ratio (6).

The following show chemical reactions of the alite, belite, and other elements of the cement paste.

TABLE 4

Mix Proportions of Concrete

W	C	L_f	U	S	G	S.P	S.R.
155	388	179	0	709	1006	9.12	7
143		177	27(20)	698	995		
131		175	53(43)	690	983		
119		173	80(60)	682	972		
107		171	107(80)	674	960		
180	300	187	0	706	1006	7.05	7
165		186	27(20)	701	999		
150		184	53(43)	696	992		
135		183	80(60)	691	985		
120		182	107(80)	686	977		
200	250	176	0	706	1006	5.88	7
182		175	27(20)	704	1003		
164		175	53(43)	702	997		
146		174	80(60)	700	995		
128		174	107(80)	698	987		

Lf : Limestone powder U : Urea

S.R. : Segregation reducing agent . ( ): volume in litres

S.P. : Superplasticizer (SNF) Units in kg/m^3

Hydration Reaction

(1) $2C_3S + 6H \rightarrow C_3S_2H_3 + \mathbf{3Ca(OH)_2}$
(100) (24) (75) **(49)**

(2) $2C_2S + 4H \rightarrow C_3S_2H_3 + \mathbf{Ca(OH)_2}$
(100) (21) (99) **(22)**

Urea Reaction with Water

(3) $(NH_2)_2CO + 2H_2O \rightarrow H_2CO_3 + 2NH_3$
(100) (60) (103) (57)

(4) $H_2CO_3 + \mathbf{Ca(OH)_2} \rightarrow CaCO_3 + 2H_2O$
(100) **(119.4)** (161.3) (58.1)

Where: $(NH_2)_2CO$ = 60(GMF), H_2CO_3 = 62(GMF), $2NH_3$ = 34(GMF), $Ca(OH)_2$ = 74(GMF), $CaCO_3$ = 100(GMF)
GMF = Gram mass formular

Equations (1) and (2) shows hydration reaction between alite, belite with water. The alite and belite reaction with water produce calcium hydroxide and the gel. Equation (3) shows the reaction between urea and water. Ammonia gas and carbonic acid are produced from this reaction. This reaction is fast and absorbs heat which in turn causes the cooling effect in concrete. The ammonia gas quickly disappears in air but carbonic acid remains and it reacts with calcium hydroxide which is produced from the hydration reaction. The authors are in opinion that the possibility for carbonic acid to react with the gel is small because the gel is a more stable compound than calcium hydroxide (1). The amount of calcium hydroxide used in this reaction is larger as compared to the total amount produced from the hydration reaction. It is about 1.7 times much bigger. This is evident when observing the molecular

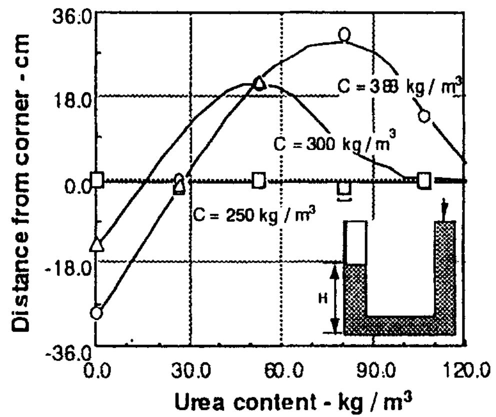

FIG. 4.
Dependence of flowability on weight of urea.

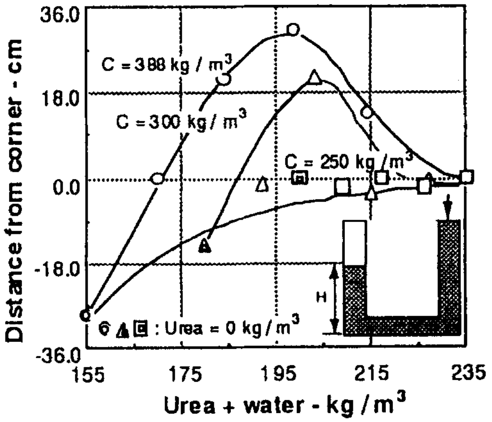

FIG. 5.
Dependence of flowability on water plus urea.

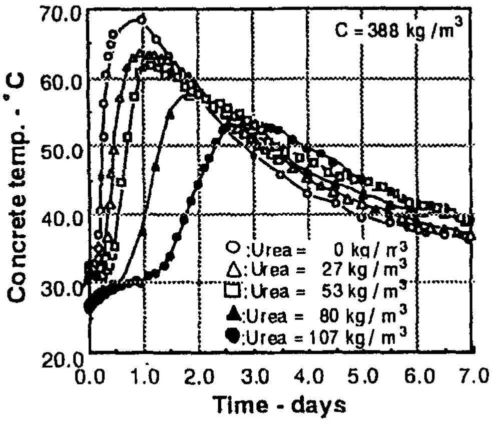

FIG. 6.
The rising temperature in concrete.

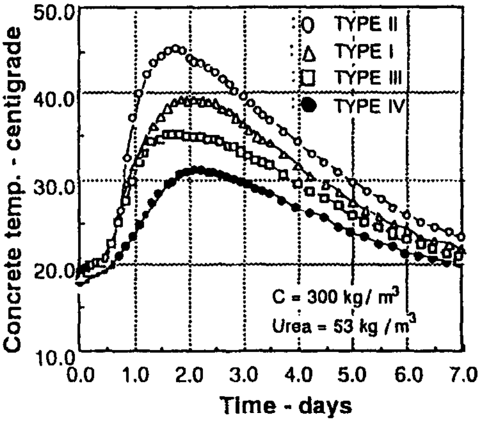

FIG. 7.
Rising temperature for different cement types.

weights of the equations above. Briefly, the reaction between urea and concrete leads to two main things; one is the temperature reduction which is caused by endorthemic reaction and therefore initial cooling of concrete, second is the gradual decrease of calcium hydroxide content in concrete due to the fact that more is being consumed than what is being produced. These are important governing factors which help to explain some of urea influence in concrete.

Influence on Flowability of Concrete. Figure 4 shows the flowability of concrete measured by U-shaped apparatus. A value of "H" above zero means the concrete is highly flowable and is self compacting. It is clear from the graph that at higher cement content levels of 388 kg/m^3 and 300 kg/m^3, urea is able to influence or increase the flowability of concrete up to a point after which a negative effect occur. At lower cement content of 250 kg/m^3, there is no change in flowability of concrete even though urea content is increased. The influence of urea on flowability therefore seems to be greater when the cement content is high. The water

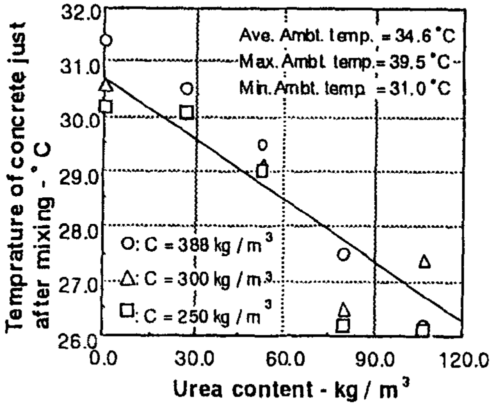

FIG. 8.
Temperature of concrete just after mixing.

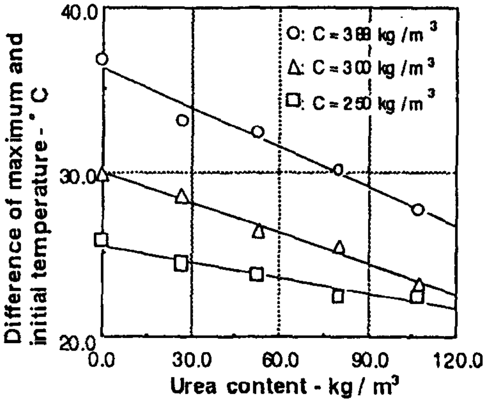

FIG. 9.
Difference between max and min.

cement ratios of the concretes used in this experiment as shown in Table 4 are equal or less than 0.4, 0.6, and 0.8 for 388 kg/m^3, 300 kg/m^3, and 250 kg/m^3 cement contents, respectively. This also indicates that the influence of urea in concrete depends on its water cement ratio. The smaller the ratio is, the larger the influence. Figure 5 shows the flowability of concrete when water plus urea content is considered. It is clear from the figure that flowability of concrete is also influenced by the urea plus water content. The figure shows that at higher cement contents 388 kg/m^3 and 300 kg/m^3, flowability of concrete increases with the increase of urea plus water weight. At lower cement contents 250 kg/m^3 there is no change in either flowability or volume. The bottom curve in the graph represents the influence of water only. While the influence of urea in concrete is that of increasing and decreasing the flowability, that of water is a continuous increase up to a certain limit in which no further changes occur. It is not possible to obtain a self compacting concrete under the influence of water alone.

Influence on Concrete Temperature. Figure 6 shows the influence of urea on concrete temperature. The cement content of concrete as shown in this figure is 388 kg/m^3. It is clear from the figure that the maximum temperature is reduced by the effect of urea. In the initial hours of hydration, the temperature of concrete is affected by urea but at ending hours of hydration, concrete temperature is almost the same regardless of urea content. On the other hand we can observe that, the time taken to reach maximum temperature is delayed by urea. The larger the amounts of urea in concrete the more the delay. It has been found out that other levels of cement content show similar results. Fig. 7 shows the heat of hydration of concrete for different types of cements when 53 kg/m^3 of urea is added. The maximum temperatures reached for TYPE II, TYPE I, and TYPE IV cements are 46°C, 39°C, 31°C, when no urea has been added the maximum temperatures are in the order of 55°C, 48°C, and 34°C respectively. The addition of urea shows an average decrease in temperature of concrete up to about 16%. Figure 8 shows the rate of decrease of temperature just after mixing. A temperature drop up to 5°C just after mixing of concrete can be obtained when high amount of urea is used.

Figure 9 shows the differences between maximum and initial temperatures of concrete at different cement content levels. A minimum temperature difference of about 23°C can be obtained when lower levels of cement content are used. The difference between maximum and initial temperatures of concrete is decreased linearly with the increase of urea content.

Influence on Setting Time of Concrete. Figure 10(a-e) shows the penetration resistance of concrete against time when different amounts of urea content are mixed with concrete. Three different levels of cement content have been considered. The results clearly show that urea slows down the setting time of concrete.

The effect is more if both the cement content and amount of urea content in concrete is large. With increasing amounts of urea content the situation becomes even more worse (Fig. 10(d)). The concretes with high cement content are delayed more comparable to those with low cement content. This delay in setting time of concrete is a complex thing and is not easy to explain. However the authors think it is probably caused by the decrease in amount of calcium hydroxide which as already explained keeps on diminishing as the reaction between urea and concrete continues. Fig. 10(c) establishes the optimum amount of urea in concrete in which the setting time is almost the same regardless of the amount of the cement content. This amount is about 53 kg/m^3. Beyond this amount the influence of cement content in delaying the setting time of concrete becomes big as its content increases.

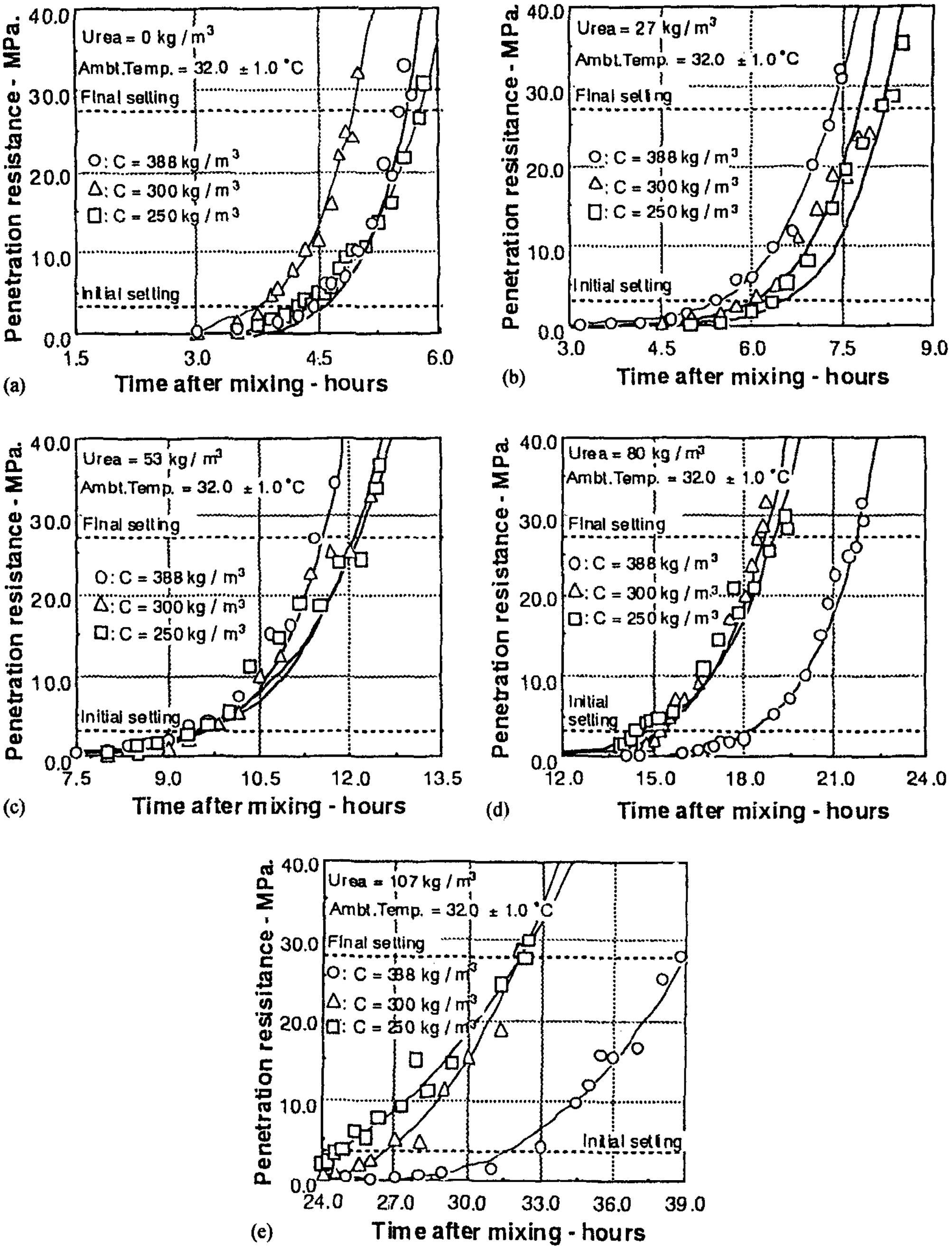

FIG. 10.

(a) Penetration resistance U = 0 kg/m^3; (b) Penetration resistance U = 27 kg/m^3; (c) Penetration resistance U = 53 kg/m^3; (d) Penetration resistance U = 80 kg/m^3 (e) Penetration resistance U = 107 kg/m^3.

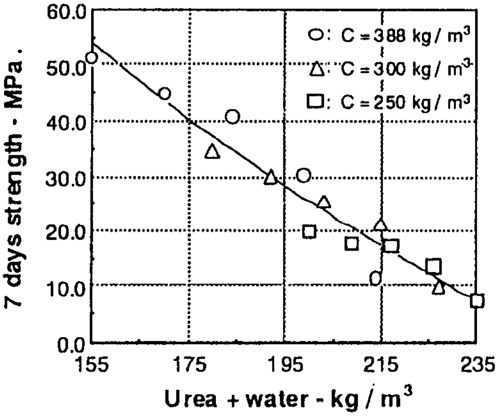

FIG. 11.
7 days strength against urea plus water.

Influence on Strength of Concrete. The 7 days strength of concrete depending on the content of urea and water content is shown in Figure 11. The result shows that the 7 days strength against urea plus water can be represented moreless by a straight curve regardless of the cement content and that the strength decreases as urea plus water content increases. Fig. 12 shows 91 days strength of concrete against urea plus water content. In this figure the different levels of cement content are clearly distinguished. Similar results are possible for plain concrete under the influence of water only. This is a clear indication that the influence of urea on concrete strength is dependent on the age of concrete and that there is very little effect of urea on strength of concrete at 91 days. Fig. 13 shows the 91 days strength of concrete represented by cement to urea plus water ratio. It is clear from this figure that the relationship between 91 days strength and the cement to urea plus water ratio is linear. Again a similar behavior is observed by concrete which is under the influence of water only. This leads us to think that the effect of urea on 91 days strength of concrete is same as that concrete which is under the influence of water only. Or rather by preceding the 91 days strength

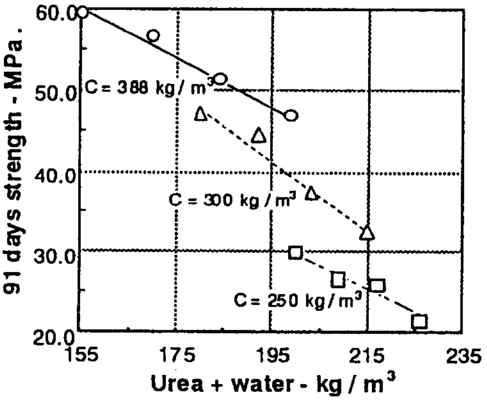

FIG. 12.
91 days strength against urea plus water.

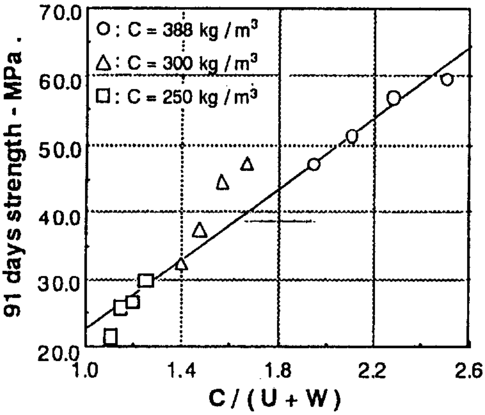

FIG. 13.
91 days strength against (C/U + W) ratio.

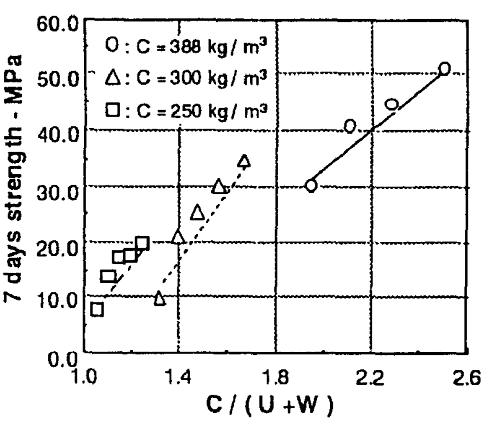

FIG. 14.
7 days strength against (C/U + W) ratio.

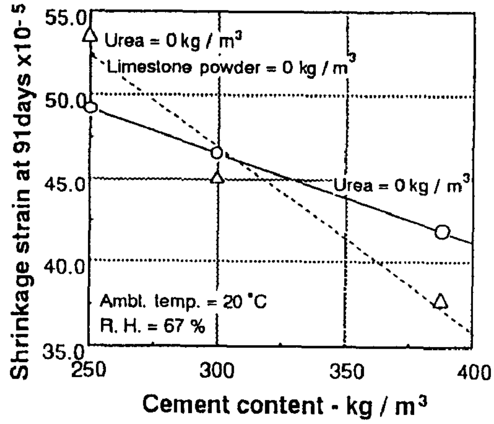

FIG. 15.
Shrinkage with/without limestone powder.

as a function of the ratio between cement and urea with water, similar linear behavior is observed like that of plain concrete. Fig. 14 shows the 7 days strength of concrete represented by the cement to urea plus water ratio, in this figure the linear relationship can not be confirmed.

Influence on Shrinkage of Concrete. Fig. 15 shows the relationship between shrinkage strain of concrete at 91 days and variation in cement content. It is clear from the figure that limestone powder reduces the rate of shrinkage in concrete. Fig. 16 shows the shrinkage strain of concrete with varying time when cement content is kept constant at 300 kg/m³. The results clearly show that as increasing amounts of urea are mixed with concrete, shrinkage strain of concrete is reduced. Up to nearly 50% reduction can be reached at the age of 91days when large amounts of urea are used as compared to normal concrete. There are two possible

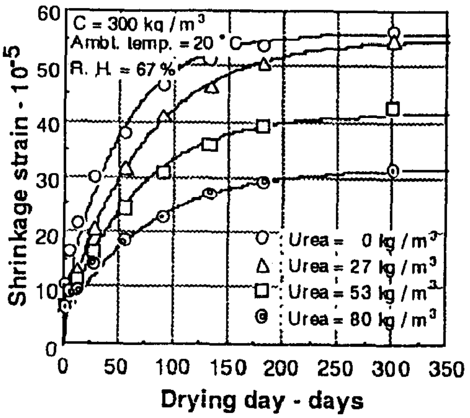

FIG. 16.
Shrinkage strain of concrete at 300 kg/m³.

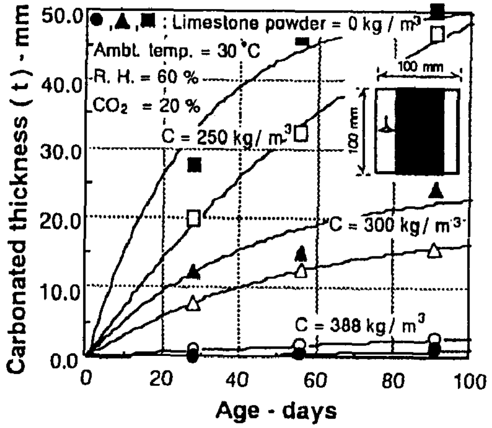

FIG. 17.
Carbonation thickness with/without limestone.

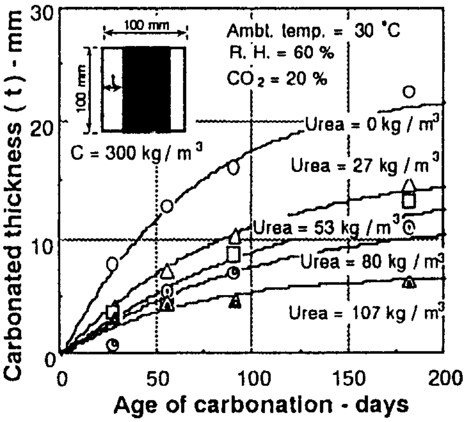

FIG. 18.
Carbonation thickness at varying urea content.

explanations as to why urea seems to reduce shrinkage of concrete. One is that since urea replaces part of water in the mix proportions of concrete and cement is kept constant, the water cement ratio reduces as amount of urea increases. This reduces shrinkage strain since as we know shrinkage reduces with decreasing water cement ratios. The other explanation is that the reaction between urea and hydration products amounts to reduction of calcium hydroxide which in turn leads to unfinished hydration causing both capillary and gel pores to be filled with solid or insoluble ingredients and therefore reducing shrinkage.

Influence on Carbonation Resistance of Concrete. Fig. 17 shows the carbonated thickness of three different kinds of concretes with or without limestone powder at 7, 28, and 91 days. The results show that limestone powder reduces carbonation resistance of concrete especially when the water cement ratio is low. Fig. 18 shows the relationship between carbonated thickness of concrete with age at constant cement content. Different amounts of urea are added in concrete and the result show that as the amount of urea in concrete increases

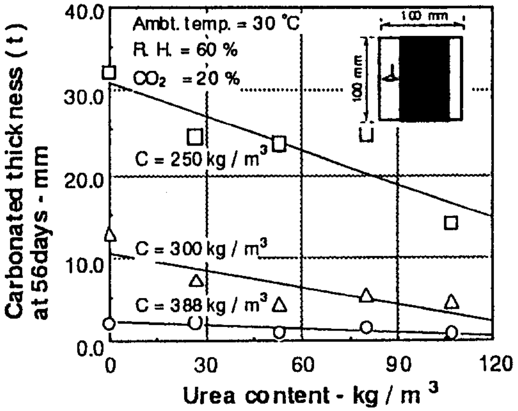

FIG. 19.
56 days carbonated thickness of concrete.

carbonation thickness of concrete is reduced. Fig. 19 shows the relationship between carbonated thickness of concrete at the age of 56 days with varying urea content at three different levels of cement content. The results clearly show that carbonated thickness decreases with increasing amounts of urea contents and with the increase of cement content. Furthermore it shows that the rate of reduction is a linear relationship and is bigger when the cement content is low.

The explanation to this is that the amount of calcium hydroxide which normally combines with CO_2 to facilitate carbonation keeps on reducing because of the reaction between urea and concrete and therefore carbonation is hindered from taking place thus being reduced.

Conclusion

There seems to be no adverse effects when urea is mixed with concrete. Flowability and durability are generally improved. Generally the influence of urea is large or significant especially when cement content is high. The main product from this reaction which is carbonic acid (H_2CO_3) reacts with calcium hydroxide which is an important ingredient affecting hydration reaction, setting time, and overall durability of concrete. Due to that, heat of hydration is reduced, shrinkage strain and carbonation resistance are greatly improved. Though setting time and compressive strengths are reduced, this can still be advantageous in places where setting of concrete has to be delayed due to technical or contractual reasons and in case of its low strength it can be used in places where strength is not an important factor like filling in the inner parts of the large mass concrete constructions. The effect of urea on concrete strength is dependent on the concrete age. At the age of 91 days, the effect is almost same as that if water only was used. It can be concluded that the effect of urea in concrete at this age has ended. But at the age of 7 days, and especially when big amounts of urea are used, strength development is very low and even hardening becomes very slow. Since urea is a new material in concrete, further research is needed especially for long term conditions. The authors are currently investigating the effects of urea on sulphate attack and on freezing and thawing.

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