Hydration, Porosity and Strength of Cementitious Materials Prof. Sudhir Mishra and Prof. K. V. Harish Department of Civil Engineering Indian Institute of Technology, Kanpur

Lecture – 10 Chemical Admixtures

Hi, Good morning to one and all, I am K V Harish, assistant professor, Department of Civil Engineering, IIT Kanpur; you are watching MOOCs lecture course on hydration porosity and strength of cementitious material.

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Today we will see lecture 10 chemical admixtures the textbook and reference materials are shown overview of the course this lecture we will introduce viewers to the different types of admixtures used in concrete and understand their purpose and functions. In addition the mechanism involved while adding certain chemical admixture is discussed the topics that will be discussed are admixtures general types and some nomenclature are used chemical admixtures and specific IS specifications different types and purpose and specifically we will also see what are reducing admixtures and air entraining admixtures.

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Now, admixtures or materials that are added in concrete to modify certain properties and they usually interact with Portland cement clinker compounds through physicochemical and chemical process material such as fibers latex and other polymers are not considered as admixtures. So, in concrete we typically have cement water aggregates group together as fine aggregates and coarse aggregate and we have fifth entity which is admixture.

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The admixtures are added to concrete to modify its fresh or plastic properties early age properties and long term properties fresh properties includes setting time slump and rate of slump loss air content cohesiveness and pumpability heat of hydration.

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Early age properties may include plastic shrinkage drying shrinkage and remember drying shrinkage here refers up to 7 days.

Early age strength gain a long term properties include strength development durability and in durability we have freeze thaw durability alkali silica reaction sulfate attack and others and the third one is drying shrinkage and this is after 7 or 28 days.

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So, the different types of admixtures that we have are as follows chemical admixtures mineral admixtures and we will deal with mineral admixtures in detail at a later stage

when we discuss this one in lectures 20 to 30. So, differences between chemical and mineral admixtures are shown in the table mineral admixtures are usually in solid powder form. Whereas the chemical admixtures are an liquid form mineral admixtures are used in larger dosages typically 3 percentage to 4 percentage at a minimum chemical admixtures are used in smaller dosages usually below less than 1 percentage and the dosage of mineral and chemical admixtures are based on weight of cement.

The third difference is that mineral admixtures are added for improving fever shot term properties and more long term properties in the case of chemical admixtures they are added for improving more short term properties and few long term properties.

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Some nomenclatures that are used are as follows mineral admixtures can many times be referred as supplementary cementitious materials or supplementary cementitious material or pozzolan or pozzolanic materials mineral admixtures can be hydraulic or it can be non hydraulic typical example of mineral admixture that is hydraulic is slag and one that is non hydraulic is fly ash or silica fume remember that in the construction industry chemical admixtures are many times referred simply as just admixtures.

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So, whenever admixture word is used it is usually considered for chemical admixtures now coming onto chemical admixtures chemical admixtures are usually added during mixing operations to improve desired concrete properties chemical admixtures should be first added to water and after thorough mixing with water the combined solution that is water and chemical admixture should be added to the dry ingredients, this is to ensure uniform dispersion of chemical admixture and improve the efficiency of mixing.

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Before adding chemical admixture their compatibility with cement should be checked since admixtures can react with certain compounds in cement such as C3A and the affect certain concrete properties unknowingly.

Hence proper compatibility between chemical admixture and cement will ensure that only the targeted properties are improved or achieved.

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The Indian standard specifications for admixture chemical admixture is provided in IS 9103; the definition of chemical admixture as per IS 9103 is as follows material other than water aggregate an hydraulic cement and additives like pozzolana or slag and fiber reinforcement used as an ingredient of concrete or mortar and added to the batch immediately before or during its mixing to modify one or more of the concrete properties in the plastic or hardened state.

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Classification or types of chemical admixtures chemical admixtures are broadly categorized into set controlling admixtures water reducing admixture and admixtures for special purpose set con controlling admixture examples are retarders and accelerators water reducing admixture example is water reducer. And for special purpose we have different categories of chemical admixtures for freeze thaw resistance we use air entraining agents or air entrainers for corrosion protection we use corrosion inhibitors for alkali silica reaction mitigation we use lithium based admixtures and for shrinkage reduction we use shrinkage reducing admixtures.

In this lecture some information about water reduces and air entraining agents alone are provided more information about retarders and accelerators will be dealt at a later stage.

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Now, set controlling admixture again you have two categories accelerating admixture and retarding admixtures the definitions from IS 9103 are as follows an oscillating admixture is an admixture which when added to concrete mortar or grout increases the rate of hydration of hydraulic cement shortens the time of set or increases the rate of hardening or strength development a retarding admixture is defined as an admixture which delays the setting of cement paste and hence of mixtures such as mortar or concrete containing cement remember that we will see more information about accelerators and retarders in other lectures dealing with hydration of cement.

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For now we are heading on with the second category water reducing admixtures the definition of water reducing admixture as per IS 9103 is as follows water reducing admixture is an atmosphere which either increases workability of freshly mix concrete or mortar without increasing water content or maintains workability with a reduced amount of water other names such as water reduces or water reducing agents are also used instead of water reducing admixtures what does water reducing admixture contain they are usually surfactant chemicals and may include solves of lignosulfonic acids or lignins they can also have souls of hydroxylated carboxylic acids.

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And how do we understand the different functions. So, for this in the next slide we will see a table. So, let me first brief down the 3 main functions of water reducing admixtures the first function is that lower the water to cement or water to cementitious material ratio are the same slump level and this is primarily done to achieve higher strength. The second one is lower the cement content to achieve a given stand and this will lead to more economical mixture increase slump at a given water and cement content and this will help in giving more consistent and easier placement.

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Functions							
					Compressive strength (MPa)		
Test series		(kg/m ³)	water-cement ratio	Slump (mm)	7 days	28 days	
A—Reference cone (no admixture)	rete	300	0.62	50	25	37	
Water-reducing ac is added for the p	lmixture purpose of:						
B-Consistency in	icrease	300	0.62	100	26	38	
C-Strength incre	ase	300	0.56	50	34	46	
D-Cement saving	g	270	0.62	50	25.5	37.5	

So, the explanation of these is provided in the table that follows in this table we have 5 or 6 columns in the left side we have mixture A, B, C and D mixture, A is a reference mixture which does not contain admixture mixture B, C and D contains water reducing admixtures. Now the proportions of these mixtures are shown to understand what are the 3 main functions of chemical admixtures. So, in the next column what you see is cement content expressed in k g per meter cube water to cement ratio no unit slump in mm and in the last column what you have is compressive strength that can be achieved in 7 days and 28 days. So, if you take a reference mixture that do not contain chemical admixture the cement content here is taken as 300 for a water to cement ratio of 0.62 and the slump that is achieved for the reference mixture is 50 mm and the strength at 7 and 20 days or 25 and 37 mega Pascal or Newton per mm square respectively.

Now, in the first case when we are using water reducing admixture and if you want a consistency increase then we have to use the same cement content which is 300 kg per meter cube and we have to use the same water to cement ratio except that we will be adding water reducing admixture to this entire mixture and in that case what you get is that you get a higher slump compared to the reference mixture 7 days strength is approximately equal slightly higher. And the 28 days strength is also either equal or slightly higher than the reference mixture in the second case where we use it for increasing strength we have the same cement content as that of the reference mixture 300 kg per meter cube, but the water to cement ratio is lowered. So, from 0.62 to 0.56 what

this will give is you will get a the same slump that you got with the reference mixture and because you reduced the water to cement ratio you get much higher strength compared to the reference mixture.

In this case mixture c provides a 7 days strength of 34 MPA and forty 6 MPA which are substantially higher than the reference concretes now in the third case where we will see mixturority the cement content is substantially lowered. So, instead of 300 we are using 270 where as the water to cement ratio is the same 0.62 and the slump is also the same and you see that the 7 day and 28 days strengths are 25 and 37 MPA which are approximately the same as the reference concrete and this mixture d is primarily seeing from economical perspective.

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Now, what does the water reducing admixture actually do when it is used in concrete typically water reducing admixtures or either acids or. So, here the example is taken as citric acid or gluconic acid.

So, you will have chemical formulas like this and sometimes there are also lignosulphonate polymers which have this formula these structures basically come from pure chemistries. So, I am not getting into that now what we have to know is that the cement grains have positive charges on the surfaces and why do they have positive charges primarily because the calcium oxide content is much higher. So, the calcium oxide has positive charges and when you have the water reduces in the mixture they are usually negative charges and they usually occupy the surfaces of each and every grain each and every cement grain and what happens is before water reduces or added what you will see is that the cement grains or approximately very close to each other and they are not dispersed.

So, the movement you add water reduces the negative charges get attracted because of the positive charges of the cement grains and they lubricate or they occupy the surface of the cement grains. And in this figure what is shown is you have some 3 cement grains and you have a negative charge on the surface of one cement grain and you have another negative charge on the surface of another cement grain and negative and negative charges ripple each other and because of this repulsion you see that the cement grains are well dispersed in the mixture.

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Another simple example is shown this is a photomicrograph of flocculated cement particles. So, in the first figure what you see is that you have the cement grains and water and you see that the cement grains are shown in black color water is shown in white color and in the first figure you do not have chemical admixtures and if you have a closer look at the cement grains you will see that the cement grains are flocculated and the water is not uniformly dispersed in the matrix and you have cement grains on the surface and the water is inside and it is not properly dispersed.

The moment you add water reduces you get a photomicrograph of this sort where you can see that the water and cement grains are completely dispersed well and what you see is that because the cement particles have negative charges on their surface is because of the addition of water reduces they get dispersed and finally, you get a much more uniform mixture.

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The second important chemical admixture that we will see in this lecture is air entraining agents or air entraining admixtures the definition of air entraining admixture as per IS 9103 is as follows air entraining agent is an admixture for concrete or mortar which causes air to be incorporated in the form of minute bubbles in the concrete or mortar during mixing usually to increase workability and resistance freezing and thawing and disruptive actions of de icing salts.

The surfactant chemicals that are present in air entraining agent are as follows salts of would resins proteinaceous materials and fatty acids and synthetic detergents.

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The purpose and function of air entraining agent can be understood by knowing the mechanisms that are involved in freeze thaw damage because the principle purpose of using air entraining agent is to offer resistance to concrete against freeze thaw damage air entraining agent are used in concrete exposed to freeze thaw attacks the purpose of adding air entraining agent can be understood by knowing the mechanism involved in freeze thaw damage of concrete which is explained a little later.

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Now, assume that we are going to use concrete in a freezing and thawing condition. So, in that case what usually happens is concrete usually contains pores and it also has water in it and when the temperature goes to the freezing stage the water in the pores are basically frozen and the when it is frozen the volume is approximately nine percentage higher compared to the volume of water in the liquid form.

So, basically the pores try to expand and the condition of concrete remains like that for some period and once the temperature increases automatically it goes to thawing stage and the frozen water now comes back to the liquid form and now the volume decreases and again the concrete may be subjected to freezing. So, multiple cycles of freezing and thawing may cause crystal pressures primarily due to the ice formation and this will initiate expansion through the pore boundaries.

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So, the hydraulic pressure that is built in concrete will depend on permeability of paste and permeability of aggregate and this is especially around the pores saturation condition whether there is substantial water present inside concrete presence of cavity from the nearest escape boundary do you have any voids or cavity close to the boundary of the pores.

Pressure can be relieved if the water can escape from the pore to a free space by diffusing through the unfrozen pores on unfrozen pores can be created by entraining air voids using air entraining agents if you do not use air entraining agent then you do not

have unfrozen pores and hence the entire concrete is subjected to freezing thaw cycles and finally, expansion and finally, cracking.

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Mechanism of air entraining agent is important to understand how the admixture is capable of producing air bubbles inside concrete air entraining agent has non polar chain with hydrophobic end hydrophobic means disliking water. So, air entraining agent is added an appropriate dosages. So, that air content in the mixture is in the range of 3.5 to 7 percent this is important to resist freezing and thawing air entraining agent may increase slump slightly.

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The mechanism of air entraining agent is shown here now what you see in the figure is difference cement particles and remember that the cement particles of positively charged and the air entraining agent has already discussed has a non polar chain. And the negative ion negative ion or a anion and so the negative ion is attracted toward the positive charge of the cement grain and basically this provides a coat around the cement grey like what we saw in water reducing admixture. Now many particles surround the cement and you see that or the non polar chain of the individual particles of the air entraining agent they club together and they form a air they actually form a bubble air bubble and at a later stage say after 2 or 3 days, these air bubbles break and finally, you have a air void that is created and this air void provides the additional void for the expansion of water inside concrete.

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Det	ermination of air content of concrete
0	Pressure method
0	Volumetric method
0	Gravimetric method
0	Air indicator method
0	Microscopic determination
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Air content is determined using different methods pressure method volumetric method gravimetric method air indicator method and microscopic determination they will not get into each of the methods for this lecture.

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SI No.	Requirements	Accele- rating Admixture	Retarding Admixture	Water Reducing Admixture	Air-Entrain- ing Admixture	Supery Admixtur Reduced	plasticizing e (for Water- Concrete Mix)	Test Ref
						Normal	Retarding Type	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
i)	Water content, percent of control sample, Max	-	-	95	-	80	80	7.2.5
ii)	Slump	-	-	-	-	Not more than 15 mm below that of the control mix concrete		7.2.
iii)	Time of setting, allowable deviation from control sample hours:							7.2.
	Initial					D		
	Max	- 3	+ 3	± 1	_	-	+ 4	
	Min	- 1	+ 1	-	-	+ 1.5	+ 1	
	Final							
	Max	- 2	+ 3	*1	-	± 1.5	+3	
	Min	- 1	+1	-	-		-	

Now, some of the provisions for chemical admixtures are provided in IS 9103 under physical requirements. So, there are about 9 to 10 physical requirements in this slide 3 of them are shown and we will see the others in the subsequent slides. So, in this table what we have is we have water content which is expressed as percentage of control sample

and the water content maximum value is provided for each of the cases the second one we have a slump the third one we have is time of setting and time of setting in expressed in hours allowable deviation from control sample. So, in other columns what you have is the requirements for different chemical admixtures.

So, in one column you have accelerating admixtures the other one you have retarding admixture the other one you have water reducing admixture air entraining admixture and super plasticizing admixture. So, if you take the first requirement water content we have provisions only for water reducing admixture which is 95; that means, when you compare a control mixture which do not have water reducing admixture and the if the water content in that is expressed as hundred percentage then if you use a water reducing admixture in that mixture you should get a water content of 95. This is maximum value likewise for a super plasticizing admixture you have to get 80 in super plasticizing admixture we again have two categories one is normal the other one is retarding type and both of them should give a maximum of 80 percentage more information is available in clause 7.2.5.

For slump usually for different chemical admixtures there are not much values provided, but for super plasticizing admixture it is stated as not more than 15 mm below that of the control mix concrete more information is available in clause 7.2.1 time of setting. So, again time of setting as we all know that we have both initial and final setting time assuming the control sample expressed in hours the initial setting value maximum and minimum are shown here. So, for accelerating admixture it is minus 3 for retarding admixtures it is plus 3 for water reducing admixture it is plus or minus one percent plus or minus one hour air entraining agent no provision is given super plasticizing admixture for normal no provision is given whereas, for retarding plus 4 is given.

What does this value actually indicate? So, if you take control sample the control sample has the minimum initial setting time is should be 30 minutes maximum final setting time should be 10 hours. So, these values provide the deviation of initial and final setting time values mentioned for the control mixer. So, here you see that the variation is from 1 percentage to about 3 percent.

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	Table 1	A of I	S 910	3 - Pł	nysical	Requ	iremer	nts
SI No.	Requirements	Accele- rating Admixture	Retarding Admixture	Water Reducing Admixture	Air-Entrain- ing Admixture	Supery Admixtur Reduced	plasticizing e (for Water- Concrete Mix)	Test Ref
						Normal	Retarding Type	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
iv)	Compressive strength, percent of control sample, Min							8.2.1
	1 day		_	_	-	140	-	
	3 days	125	90	110	90	125	125	
	7 days	100	90	110	90	125	125	
	28 days	100	90	110	90	115	115	
	6 months	90	90	100	90	100	100	
	1 year	90	90	100	90	100	100	
v)	Flexural strength, percent of control sample, Min							8.2.2
	3 days	b 110	90	100	90	110	110	
	7 days	100	90	100	90	100	100	
	28 days	90	90	100	90	100	100	
vi)	Length change, percent increase over control sample, Max							8.2.3
	28 days	0.010	0.010	0.010	0.010	0.010	0.010	
	6 months	0.010	0.010	0.010	0.010	0.010	0.010	
	1 year	0.010	0.010	0.010	0.010	0.010	0.010	-

So, the fourth, fifth and sixth physical requirement are compressive strength flexural strength and length change and assuming that the control value has hundred percentage strength the corresponding values when you use different admixtures are shown which ranges from ninety percentage to about 140 and remember that you also have different periods mentioned.

So, compressive strength for 1 days, 3 days, 7 days, 28 days, 6 months and 1 year is provided in a case of flexural strength at different periods like 3 days, 7 days and 28 days the percentage ranges from 9,210, similarly lengths change the maximum values are provided for 28 days, 6 months and 1 year and the maximum value should be 0.01 for all of them.

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No.	Requirements	Accele- rating Admixture	Retarding Admixture	Water Reducing Admixture	Air-Entrain- ing Admixture	Superp Admixture Reduced (lasticizing (for Water- Concrete Mix)	Test Ref
						Normal	Retarding Type	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
viļ)	Bleeding, percent increase over control sample, Max	5	5	5	5	5	5	7.2.4
viii)	Loss of workability	-	-	,—	-	At 45 min the slump shall be not less than that of control mix concrete at 15 min	At 2 b, the slump shall be not less than that of control mix concrete at 15 min	7.2.1.2
ix)	Air content (%) Max, over control	-	-	-	-	1.5	1.5	
ix)	Air content (%) Max, over control	-	-	-	-	at 15 min 1.5	at 15 mir 1.5	1

Last 3 bleeding percentage values are shown loss of workability and maximum air content. So, they are shown here. So, for bleeding percentage, 5 percentage is specified for any of the chemical admixture used loss of workability we do not have value specified for the first 4 admixtures for super plasticizing admixture at 45 minute, the slump shall be not less than that of the control mix concrete at 15 minutes this is for the normal case for the retarding case at two hours the slump shall be not less than that of the control mix the slump shall be not less than that of the slump shall be not less than tha

Finally for the air content which is expressed in percentage no provisions are given for the first 4 admixture and for super plasticizing admixture one percentage and one percentage for normal and retarding type.

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SI No.	Requirements	Type of Superpla	Test Reference	
(1)	(2)	Normal (3)	Retarding Type (4)	(5)
i)	Flow	510 mm - 620 mm	510 mm - 620 mm	7.2.1.1
й)	Loss of workability on standing	At 45 min the slump shall be not less than that of control mix concrete at 15 min	At 2 h the slump shall be not less than that of control mix concrete at 15 min	7.2.1.2
iii)	Minimum compressive strength, percent of control mix concrete			8.2.1
	7 days	90	90	
	28 days	90	90	
	6 months 1 year	90 90	90 90	
_				

There are also special requirements that are given for mixtures that require higher workability higher workability can be achieved by using super plasticizing admixtures which are many times referred as high range water reduces. So, here in this table you see requirements flow loss of workability on standing minimum compressive strength expressed as percentage of control mix concrete and under a type of super plasticizing admixture we have this normal and retarding type.

So, for flow we have fined and 10 mm to 620 mm and the same for and retarding type for loss of workability on standing at forty minutes the slump shall be not less than that of control mix concrete at 15 minutes and for retarding type we have 2 hours the slump shall be not less than that of the control mixture at 15 days more information are given in clause 7.2.1.1 and 7.2.1.2 respectively minimum compressive strength it is stated for both of these admixture type at least 90 percentage strength have to be obtained. With this we come to an end for this lecture.

Thank you.