

**Pavement Materials**  
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**Lecture 52**  
**Types of Cement, Admixtures, Geopolymers (Part-2)**

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**WHAT ARE WE GOING TO LEARN?**

- PRODUCTION OF CEMENT
- THEORY OF HYDRATION
- PHYSICAL AND CHEMICAL PROPERTIES OF CEMENT
- TYPES OF CEMENT
- POZZOLANIC MATERIALS
- GEOPOLYMERIC MATERIALS

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Hello friends, in the last class, we were discussing about the types of cement about pozzolanic materials. So, we are yet to complete our discussion on some additional materials, which are basically the chemical admixtures. And we will start our discussion with those materials. And we will try to complete the topics which you see on the screen today. And we will also complete module 5 today.

In the last class, we were discussing about mineral admixtures and now, we will start our discussion on chemical admixtures. And we will start discussing about plasticizers.

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### Other Admixtures

- **Plasticizers** ✓
  - Workability of concrete is a desirable property for easy production, placement and compaction
  - One easy method to improve workability is to increase the water content. This may affect strength and durability
  - *slump* Organic or inorganic substances which allow a reduction in water content for a given workability or give higher workability at the same water content are termed a plasticizing admixtures
  - Anionic surfactants such as lignosulphonate, their modifications and derivatives ✓
  - Salts of sulphonate hydrocarbons
  - Nonionic surfactants, such as polyglycol esters, acid of hydroxylated carboxylic acids, their modifications and derivatives
  - Other products such as carbohydrates, etc.



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Plasticizers are materials which basically alter the workability characteristics in the concrete mixture. Now, what do you mean by workability? You can think of workability as the ease with which we are able to mix all the ingredients in the concrete. These ingredients it comprises of coarse aggregate we have sand, we have cement, water and other admixtures. So, all these materials should be mixed together properly to obtain a homogeneous paste or mass which has to finally set in the respective structure.

Now, this effort which we have to give to produce this mix is defined as the workability which is a very desirable property and it is desired, because, it will define the ease with which we are able to produce the mix with which we are able to place the mix and finally, the ease with which we are able to compact the mixture.

Now, one of the easiest method to improve the workability is to increase the water content in the mixture because more is the water content, more will be the lubrication, more is the lubrication, we can work with the mix easily. However, increase in water content will also increase the water cement ratio, which basically is an important parameter to control the strength in the mixture and other characteristics related to the concrete mixture.

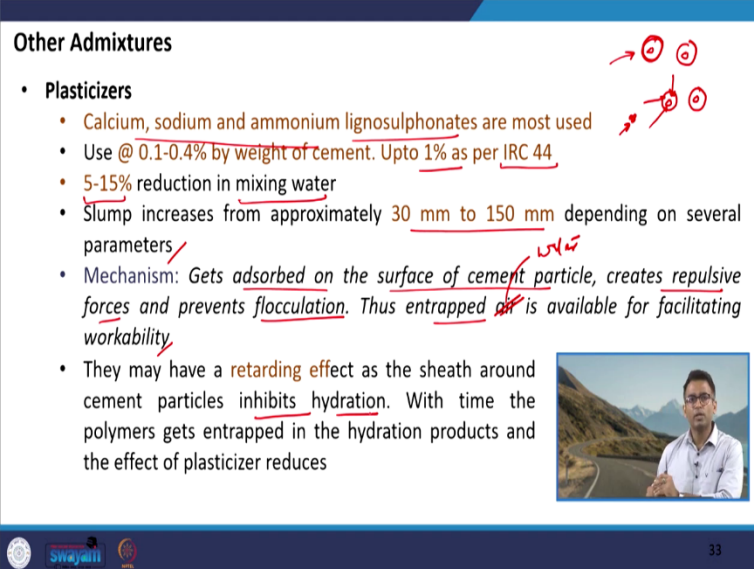
So, though increasing the water content can increase the workability of the mixture, but this may strongly affect the strength and durability characteristics of the concrete mixture and therefore, this is not a good method to improve workability. So, we have other materials which can be either from the organic origin or it can be inorganic materials, which allows us to reduce the water content for a given workability criteria. Now, this workability criteria can be defined in terms of slump of the final concrete mix which we are producing.

So, these materials it allows us to reduce the water content if we already have decided that what is the targeted slump or it can also give us higher slump or higher workability for a given water content which we have already fixed and these materials are termed or denoted as plasticizing admixtures.

Plasticizers, so, plasticizing admixtures further have several groups. So, now, we are talking about plasticizers. So, these are anionic surfactants. So, these are surfactant type of material, which you know is meant to reduce the friction between two particles. So, they are anionic surfactants which can be from the lignosulfonate origin, it can be their modification and also their derivatives.

It can also be salts of sulfonate hydrocarbons, it also can be of nonionic nature, it can be a nonionic surfactant. For example, we have polyglycol ester's we have acid of hydroxylated carboxylic acid, that is COH and we can also use their modification and derivative. So, in various ways, we can produce these surfactants or these plasticizers which can help us to improve the workability of the concrete mixtures. Other products such as carbohydrates can also be used as plasticizing agents.

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**Other Admixtures**

- **Plasticizers**
  - Calcium, sodium and ammonium lignosulphonates are most used
  - Use @ 0.1-0.4% by weight of cement. Upto 1% as per IRC 44
  - 5-15% reduction in mixing water
  - Slump increases from approximately 30 mm to 150 mm depending on several parameters
  - Mechanism: Gets adsorbed on the surface of cement particle, creates repulsive forces and prevents flocculation. Thus entrapped ~~air~~ is available for facilitating workability
  - They may have a retarding effect as the sheath around cement particles inhibits hydration. With time the polymers gets entrapped in the hydration products and the effect of plasticizer reduces

*Handwritten red annotations on the slide include arrows pointing to 'Upto 1%', '30 mm to 150 mm', 'repulsive forces', and 'entrapped air', and a small diagram of particles with arrows indicating repulsion.*

*Small video inset showing a man speaking.*

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Among all these materials else the most used material or the most popular materials falls under the category of calcium, sodium and ammonium lignosulfonates. So, these are the commonly used plasticizers for the production of concrete mixtures, talking about what should be the dosage of these plasticizers. Well, there are ways which we have to by which we can determine the optimum dose, but typically it ranges from somewhere between point 1 to point 4 percent by weight of the cement and the optimum dose as I was mentioning also depends on the other characteristics of the respective materials including the type of aggregate we are using the angularity of aggregates the type of cement we are using and so, on.

As per IRC 44, which is the guideline for the production of pavement quality concrete up to 1 percent can be used. So, we can use up to 1 percent plasticizer and then the respective reduction can be in the range of 5 to 15 percent reduction in the mixing water content. So, as we discussed that, ultimately the work of plasticizer is to reduce the water demand and to maintain a given range of workability which we desire.

So, for the same workability the amount of water that can be reduced can range from 5 to 15 percent depending on the type of plasticizer depending on the dosage of plasticizer. The slump of the concrete because of this addition now, if the workability improves, which means, we will have a more plastic mix, which we can easily work with.

So, you can imagine that the slump will naturally increase. So, the slump typically increases by about 30 mm to 150 mm in comparison to the you know the standard slump depending on several parameters for example, the type of plasticizer the amount of plasticizer we are using and the other properties of the mixture.

Now, how does this superplasticizer work? So, it is a form of surfactant. So, you can try to imagine in layman's terms like we have the surf with which we wash our cloth, so, if you mix it with water and you can rub your hand you will feel a slippery, you will have a slippery feeling with that, so it is like that it is a soapy material, soapy form of material.

So, how does it work? How does it improve the workability, it gets adsorbed on the surface of the cement particle? So, we have cement particle it will get adsorbed on the surface. So, ideally when we do not have a plasticizer in the mix, and when we make cement with water, what will happen the small cement particles will try to come close to each other and they will try to agglomerate.

Now, since they agglomerate they increases the you know friction between them to work with and therefore, the workability reduces they will have to apply more force to break these agglomerations and moreover, since the agglomerate the water is not able to mobilize the entire surface properly again because of this the workability reduces. So, what this plasticizer do they will get absorbed they will get (abs) adsorbed on the surface of the cement particle thereby they create some repulsive forces between the cement particles and therefore, they are not able to flocculate they are not able to agglomerate they can be you know separated from each other and it prevents flocculation.

Now, because we are able to prevent this flocculation the entrapped I think it should be watered the entrapped water is available for facilitating workability So, if the cement particles get agglomerated, there

can be water trapped inside, but this water is not available to you know provide or facilitate workability in the mix. Now, since we are able to separate the particles by the use of the surfactant materials of plasticizers this entire water is now available and it can improve the workability of the mixture.

However, the plasticizer can also have a retarding effect. Now, again you can understand the same dispersing principle that you have seen in particle there is another material which is adsorbed over the cement particle because of which water is not able to readily interact with this particle and initiate the hydration process. So, these this sheet which is created over the cement particle it will innovate the hydration process.

But of course, with time as time passes, the polymers with these materials are made of, they will get entrapped in the hydration products and the hydration will get initiated and the effect of plasticizer will reduce. So, you can say that the initial strength gain will be slow, but ultimately the hydration will take place after some time. Therefore, these plasticizers also have some retarding effect.

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**Other Admixtures**

- Superplasticizers**
  - Permits upto 30% reduction in water
  - They have powerful dispersing capability than plasticizers and are also called as high range water reducers *HRWR*
  - Use of superplasticizers in conjunction with SCMs can produced high strength concrete (as high as 120 MPa at 0.25 w-c ratio)
  - Various types of polymers can be used for producing superplasticizers
  - Used upto 2% by weight of cement. Should be added after mixing ingredients (after 3 minutes approx.)

The slide contains three graphs illustrating the effects of superplasticizer dosage:

- Slump vs. % of superplasticizer by weight of cement:** Shows a curve where slump increases from approximately 12 cm at 0% dosage to about 22 cm at 1.0% dosage, then levels off.
- Compressive Strength (MPa) vs. Superplasticizer dosage per cent by weight of cement:** Shows three curves for 1 day, 7 days, and 28 days curing. All curves show an increase in strength with dosage up to about 0.8-1.0%, followed by a slight decrease. The 28-day strength reaches approximately 48 MPa at 1.0% dosage.
- Marshall CBR vs. Superplasticizer dosage per cent by weight of cement:** Shows a curve where Marshall CBR decreases from 100% at 0% dosage to about 45% at 1.8% dosage. A 'Saturation point' is marked at approximately 1.0% dosage.

At the bottom right of the slide, there is a small video inset showing a man speaking.

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### Other Admixtures

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The figure contains three graphs illustrating the effects of superplasticizer dosage:

- Top Graph:** Shows Slump (cm) on the y-axis (10 to 24) versus % of superplasticizer by weight of cement on the x-axis (0 to 1.0). The curve shows a sharp increase in slump from approximately 11 cm at 0% to about 22 cm at 0.8% dosage, then levels off.
- Bottom-Left Graph:** Shows Water-Cement Ratio on the y-axis (40 to 110) versus Superplasticizer dosage per cent by weight of cement on the x-axis (0 to 1.8). The curve shows a sharp decrease in W/C ratio from about 100 at 0% to approximately 45 at 1.0% dosage, reaching a 'Saturation point' around 1.0%.
- Bottom-Right Graph:** Shows Compressive Strength (MPa) on the y-axis (0 to 50) versus Admixture, per cent by weight of cement on the x-axis (0 to 8). Three curves are shown for 1 day, 3 days, and 7 days curing. All curves show a peak strength around 4-5% admixture dosage, with the 28-day strength reaching approximately 48 MPa.

M/S Shetty

Now, other than plasticizers we also have superplasticizers. So, these are materials which are more popularly used these days because of their additional advantages in comparison to the plasticizer because, these superplasticizers are able to provide you know higher reduction in water content which can be up to 30 percent. They have powerful dispersing capability the mechanism remains the same, which we have discussed in case of plasticizer. But, they are more powerful in comparison to the plasticizers, because of this powerful capacity, they are also called as high range water reducers HR WR.

Superplasticizers also facilitate production of high strength concrete specially when they are used in conjunction with SCMs or the supplementary cementitious materials like pozzolanic material like silica fume, metacholin or fly ash or GGBFs or we have rice husk ash and so, on. When these materials especially silica fume, so, as we have already discussed at silica fume are very fine, it increases the water demand and it also reduces the workability but it provides high strength.

Now superplasticizers in those mixtures can maintain the workability of the mixture allow the silica fume to do its work and you get a high strength concrete. So, it can be used in conjunction with other SCMs specially those SCMs which are very fine and this facilitates production of high strength concrete.

So, even at a water cement ratio of 0.25 which is a very low water cement ratio specially in the in respect to the workability characteristic without superplasticizer if you use a 0.25 water cement ratio for the production of concrete mixture, it will be a very dry mix and you know it will be very difficult to work with that mix you have to apply a lot of force. But just by adding the superplasticizer material, we are able to maintain the workability similar to what we have in conventional concrete let us say at a water with a water cement ratio of 0.35 or 0.4 which is used normally and then you get a very high strength because as water cement ratio is reduces the strength of the concrete will increase.

Talking about the products that are used as superplasticizers there are various types of polymers that can be used for manufacturing of superplasticizers. Typically, for example, we have you know polycarboxylate ether as one of the product that is popularly used as a superplasticizer. Talking about their dosage, again, there are ways to determine the dosage optimum dosage of these superplasticizers because, you know excessive dosage cannot be used, if you use excessive dosage, it will retard the hydration process which can be detrimental especially to the strength gain in the concrete mixtures.

So, we cannot go beyond a particular limit, but there should be some minimum dosage again, which will provide us the adequate workability. Typically, it is used up to 2 percent by weight of the cement. And again, the mixing process the how you are mixing the superplasticizer also affect its working characteristics, it is recommended that it should be added after mixing the ingredients.

So, you have the aggregates, sand, cement and some and water, you mix them up and then you apply the superplasticizer and again we mix the sample or sometimes what is done that a portion of the water is kept separately and with the remaining portion of the water you make the concrete mix properly. And then, you add this water which you have reserved along with the superplasticizer finally, in the mix and then mix it for a few more minutes.

So, that way the superplasticizers work better and instead of if you add the superplasticizer initially in the mix. So, if we look at some of the variations here with the use of superplasticizer for example, you see how the slump increases, but you see the slump stabilizes after some time. So this chart can also be used to select the percentage of superplasticizer base on the targeted slump.

Then we have some other variations here. For example, if you see this so this is the marsh cone time in second. So, Marsh cone is a simple apparatus, it is a simple mold, you can say a mold, which has opening from both the sides a conical mold. So you take the marsh cone, you prepare a, a mixture of cement water and the plasticizing agent. And then and then you allow the space to move in that marsh cone.

So marsh cone looks something like this. So this is the opening here. So first, we will close this opening, we will put our entire mix here taking a standard weight, and then we will open this, we will just open this opening and because this will be the plastic state the mix will start flowing. So, you can try to understand that more workable the mix is or the paste is the flow will be fast. So, depending on how quickly this material comes out of this marsh cone, we can indirectly quantify the workability of the paste.


So, you can see in this particular variation, that how with increase in superplasticizer, the marsh cone time, gradually decreases. So, there is one particular point which is also called a saturation point beyond which

you do not see further reduction in the marsh cone timing and this graph will be different for different types of water cement ratio. So, this is for a water cement ratio of 0.35, and based on this, you can again select the appropriate dosage of the superplasticizer.




Here is another variation which shows that how at different days the compressive strength varies by the addition of these agents. So, you can see that let us see the 28-day graph. So, you see how it varies when you have one person that makes sure the strength is somewhere here, it gradually increases with increasing percentage of the admixture, but after a particular point, you also see a decrease. So, you have to select again the superplasticizer dosage, so that you are not affecting the compressive strength of the final concrete mix.

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### Other Admixtures



- **Air Entraining Admixtures**
  - Air entraining admixture refers to the admixture that entrains a large number of uniform, stable and closed tiny bubbles in the process of mixing concrete
  - They reduce segregation of concrete mixture, improve the workability, and also enhance anti-freeze ability and durability of concrete
  - Air entrainment will reduce concrete strength. As a general rule, a 1% increase in the concrete air content will decrease the 28-day compressive strength by about 3 to 5%
  - In cold weather climates, water within the concrete capillary pores will freeze and expand when the temperature drops below freezing. The expansion of ice exerts pressure within the hardened concrete) and will cause cracking if the tensile strength of the concrete is exceeded
  - Entrained air voids spaced within the concrete provide a place for the freezing / expanding water to move into, which relieves the pressure and thereby prevents cracking
  - They are typically used in an amount of about 0.001–0.1 wt%, based on the weight of dry cement. The size of bubbles created are about 0.01-1 mm 4.5%.




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We also have air entraining admixtures again, these are very special admixtures required for specific construction purposes. So, what are air entraining admixtures it refers to the admixture that entrains a large number of uniform stable and closely and closed tiny bubbles. So, you will have a concrete with small tiny bubbles here, some air spaces will be created. The question is why do I need to produce a concrete with so much of airspace, what is the benefit? What are the advantages and say what are the disadvantages?

Their main purpose their main the main aim of using these agents is to produce a concrete which has to be used at a location where we are anticipating, freezing and thawing cycles, let us say. So, these tiny bubbles which you create it act as a space as a living space for those the phenomena of freezing and thawing which means the water will first freeze it will then melt.



So, the forces which are created during this cycle, they can be relieved by the presence of these pores. So, they reduce segregation of the concrete mixture, I mean these are some of the benefits, they improve the workability, they enhance the antifreeze ability and they also improve the durability of the concrete. However, air entrainment, because we are creating some additional space, which would have been filled by cement paste otherwise, if we would have used a normal concrete. So, air entrainment will reduce the concrete strength.

So, a thumb rule is that 1 percent increase in the concrete air content will decrease the 28-day compressive strength by about 3 to 5 percent. So, with every 1 percent increase in the percentage of air or air entrainment, you will do the reduction will be about 3 to 5 percent. So, again we have for even for the special purpose if we have to use we have to see that the strength a does not fall beyond our desirable minimum value.

So what happens usually that especially in cold Whether climates, water within the concrete capillary pores it will freeze as you can imagine, and it will expand when the temperature drops below the freezing point. So, the expansion of this ice it will exert some forces within the hardened concrete, which can lead to cracking of the concrete, if the tensile strength of the concrete is exceeded, I mean the forces are the stresses which are induced exceeds the strength of the material.

Now, these entrained air voids spaces which we create within the concrete, it provides this place for the freezing expanding water to move into which relieves the pressure and thereby prevents cracking. So, this is the basic phenomena or this is the basic reason why air entrainment is important, but, in special cases especially when the construction has to be done in a very cold weather climate where freezing and thawing cycles are anticipated.


Now, talking about the dosage that what should be the dosage, the dosage of the air in training agent is about 0.001 to 0.1 percentage by weight of the cement and the size of the bubbles which you see here which are created the size of this air entrained bubble they range from 0.01 to 1 mm and the amount of air entrainment that is required is typically around like 4 to 5 percent which we require.




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## Other Admixtures

- **Air Entraining Admixtures**
  - Air-entraining admixtures are surface-active chemicals (surfactants) that consist of a water-repelling chain (nonpolar hydrocarbon) with a water-attractive chain (anionic polar)

Wood-Derived Acid Salts ✓	Synthetic Resins ✓
<ul style="list-style-type: none"> <li>• Develop good bubble structures ✓</li> <li>• Used for more than 60 years ✓</li> <li>• Work well with low water-cementitious mixtures. ✓</li> <li>• Tend to <u>lose air with time/haul distance</u> ✓</li> <li>• Due to supply issues, <u>wood rosins</u> have replaced <u>vincol resins</u> in most markets ✓</li> </ul>	<ul style="list-style-type: none"> <li>• Can be <u>detergents, fatty acids, gum resins, and tall oils</u> ✓</li> <li>• Have been in the marketplace since the mid-1980's ✓</li> <li>• Can produce smaller bubbles that are spaced closer together relative to bubbles formed by <u>(vincol resins and wood rosins)</u>; thus, offering greater durability under <u>freeze/thaw conditions</u> ✓</li> <li>• Can lead to increased air contents with delayed additions of water ✓</li> </ul>






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Now, talking about these admixtures I mean what are those materials that are used as air entraining admixtures they are usually surface active chemicals or also again a type of surfactant and this surfactant has two parts one part consists of a water repelling chain. So, this is a nonpolar hydrocarbon usually, which is more of hydrophobic in nature and then we have a hydrophilic part and these are an ionic polar groups.

And having discussed about the basic characteristic of the air entraining admixtures there are various products that are available, we have wood derived acid salts, and we have synthetic resins both of which can be used as air entraining admixtures. So, some of the characteristics of let us say would derive acid salts are that they develop good bubble structures, they are being used in the production of air entrained concrete since a very-very long time.


However, presently there is a supply issue, because it is a wood derived product we do not get food easily and therefore, these products are not readily available. And this would rosins with which a typical the notion again. So, this would rosins have replaced the winsol resins in most of the markets. Again, one of the characteristic is that they tend to lose air with time. So, with time the amount of entrained air it reduces. Then also this type of material is more useful when we have a concrete mixture with low water cement ratio. So, this wood derive acid salts work better with those concrete.

We have synthetic resins these can be detergents, it can be fatty acids, it can be gum resins, it can be tall oils. Again a very old product or the knowledge of this material is not very new now, it can produce smaller bubbles that are spaced close together related to the bubbles which are formed by the word derived acid salts and therefore, they offer greater durability and you know, especially under the freeze thaw conditions, they can lead to increased air content with delayed editions of water.

So, these are some of the characteristics under both the categories of air entraining admixtures. This is a typical picture of an air entrained concrete you can see the size of the bubbles here how small it is, and this is not a usual surface which we get in a normal concrete mix as you can see very clearly.

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### Other Admixtures



- **Retarders**
  - Used to delay the initial setting time of the concrete upto an hour
  - They are generally used in the hot weather condition to counter the rapid hardening due to high temperature, thus allowing the time for mixing, transporting and placing
  - Adding a retarder, dissolved in the mixing water or sprayed on the surface of the concrete, temporarily interrupts the hydration reactions, which creates a longer dormant period
  - After a predictable period, the effects of the mechanisms disappear and the hydration continues
  - Possible mechanisms
    - Retarders adsorb on the surface of cement particles and thus hinders the movement of water to unhydrated cement
    - Retarding mixture is adsorbed by the surface of  $\text{Ca(OH)}_2$  nuclei and prevents its growth
    - It increases the concentration of calcium and hydroxyl ions which delays formation of  $\text{Ca(OH)}_2$

So, let us now discuss about the next chemical admixtures which are retarders. So, as the name suggests, what do they actually do? They delay the initial setting time of the concrete up to let us say an hour. So, this is the function of the retarder. Now, the question is why do we want to delay the initial setting time? So, try to imagine that you are doing a construction maybe in a very high temperature area in a very complex location or maybe the plant or the site is very far away from the plant where you are actually producing this mix.

So, if you have to carry in in such situations if you have to carry the mixture and to the site, it will take some time and during this process the loose concrete or the plastic concrete will continuously lose its plasticity it will try it will stiffen with time, but you also desire some level of workability before placing it before compacting it at the site. So, in those situations, you need that the setting time of the concrete should be delayed by some time. So, that you have the appropriate amount of slump requirement when you are placing the mixture at the site. So, using of retarders it allows additional time for mixing transporting and placing.

You can add the retarder either in the mixing water or it can also be sprayed directly on the surface of the concrete, if it is sprayed directly on the surface of the concrete let us say if this is the concrete structure, you are spraying it here then the surface to some depth it will basically set later, but the core of the concrete will set at its usual time and then if you are dissolving it in the mixing water and then you are producing the concrete then it delays the setting time of the entire mixture.

So, these materials they will they temporarily interrupt dehydration reactions. And this helps to create a longer dormant period. So, the interference is temporary in nature, after a predictable period the effect of mechanism it disappears and dehydration will continue as usual. Now, there are various possible mechanisms that have been proposed, which tells us about the working process of these retarders.

Some of these mechanisms are as follows that retarders adsorbed on the surface of the cement particles, similar to what we have discussed in case of plasticizers. That if you know make a sheet of any material around the cement particle, this cement particle is not able to come in contact with water directly, because this sheet this additional layer it prevents it from interacting with the cement particle once you are preventing it from interacting, you can imagine that the process of hydration will be delayed. So, it hinders the movement of water to the un-hydrated cement and therefore, the process gets delayed and this is what plasticizers and superplasticizers also tend to do.


Now retarding mixture, this is another way of understanding this that the retarding mixture is absorbed by the surface of calcium hydroxide nuclei and prevents its growth. Now, the hydration has begun and then the production of calcium hydroxide has started. Now, these material they will get adsorbed on the surface of the calcium hydroxide nuclei and it will prevent its growth in the other sense it will delay the hydration process.


Another way of understanding this is that these material increases the concentration of calcium and hydroxyl ions. Now, the more is the concentration the late will be the formation of calcium hydroxide, does the hydration process and this is how the setting time can be delayed.

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**Other Admixtures**

- **Retarders**
  - Types
    - **Organic:** Lignosulphonates, Hydroxycarboxylic acids, and their salts  
Phosphonates, Sugars
    - **Inorganic and Chemical Retarders:** Phosphonates, Borates, Salts of Pb, Zn, Cu, As, Sb
  - **Dosage:** About 0.5% by weight of cementitious materials



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Now, there are various type of materials that can be used as retarders it can be classified under organic group or it can be classified under inorganic and chemical retarders group. Under organic group, we have several options for example, we have lignosulfonates again something which is typically used as plasticizers, we have hydroxycarboxylic acids again something which is used as plasticizers and they are salt, we have phosphonate we have sugars. Under the inorganic category we can have phosphonates we can have borates we can also have salts of various elements for example, zinc, copper and so on.

Talking about the dosage of retarders that are typically used for the production of concrete for delaying the initial setting time is about 0.5 percent by weight of the cementitious material. So, now, let us jump to the next topic, which is the effect the last topic in this module, which we will discuss and that is talking briefly about geopolymeric cement or let us say in general geopolymeric concrete.

Now, the question which we have to answer before we start discussing about the geopolymeric cement is why do we need a new type of cement, which we call as geopolymeric cement, what is the need of using this cement, why the present options available in the category of cement cannot be utilized or what is the problem associated with those cements that you know we are talking about this new product.

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**Alternate Cement: Geopolymeric cement** Geopolymer concrete: A review of some recent developments, Singh et al. 2015


- Use of Portland cement has **increased the use of natural resources and leads to emission of CO<sub>2</sub> gases**
- Increase in demand of construction and concerning **environmental issues** have prompted researchers and industries to look for **alternate binding materials for construction**
- Search for several alternatives such as **alkali-activated cement**, **calcium sulphoaluminate cement**, **magnesium oxy carbonate cement (carbon negative cement)**, **supersulphated cement** etc. are being made
- Use of **Geopolymer** has recently attracted attention due to several advantages such as **early compressive strength**, **low permeability**, **good chemical resistance** and **excellent fire resistance behavior**
- Geopolymer is an amorphous alkali aluminosilicate which is a type of inorganic polymer
- It consists of a repeating unit of silicate monomer  $(-Si-O-Al-O-)$

Alumino silicate + activation → Geopolymer

$$(SiO_2, Al_2O_3)_n + H_2O + OH^- \rightarrow Si(OH)_4 + Al(OH)_4^-$$

$$\rightarrow (-Si-O-Al-O-)_n + H_2O$$

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## Alternate Cement: Geopolymeric cement

Geopolymer concrete: A review of some recent developments, Singh et al. 2015

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- Search for several alternatives such as alkali-activated cement, calcium sulphoaluminate cement, magnesium oxy carbonate cement (carbon negative cement), supersulphated cement etc. are being made
- Use of Geopolymer has recently attracted attention due to several advantages such as early compressive strength, low permeability, good chemical resistance and excellent fire resistance behavior
- Geopolymer is an amorphous alkali aluminosilicate which is a type of inorganic polymer
- It consists of a repeating unit of silicate monomer (-Si-O-Al-O-)
- The source materials should be highly amorphous and possess sufficient reactive glassy content, low water demand and be able to release aluminium easily
- The alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and potassium silicate (K<sub>2</sub>SiO<sub>3</sub>) are used to activate aluminosilicate materials



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## Alternate Cement: Geopolymeric cement

Geopolymer concrete: A review of some recent developments, Singh et al. 2015

- Use of Portland cement has increased the use of natural resources and leads to emission of CO<sub>2</sub> gases
- Increase in demand of construction and concerning environmental issues have prompted researchers and industries to look for alternate binding materials for construction
- Search for several alternatives such as alkali-activated cement, calcium sulphoaluminate cement, magnesium oxy carbonate cement (carbon negative cement), supersulphated cement etc. are being made
- Use of Geopolymer has recently attracted attention due to several advantages such as early compressive strength, low permeability, good chemical resistance and excellent fire resistance behavior
- Geopolymer is an amorphous alkali aluminosilicate which is a type of inorganic polymer
- It consists of a repeating unit of silicate monomer (-Si-O-Al-O-)
- The source materials should be highly amorphous and possess sufficient reactive glassy content, low water demand and be able to release aluminium easily
- The alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) and potassium silicate (K<sub>2</sub>SiO<sub>3</sub>) are used to activate aluminosilicate materials



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So, use of Portland cement, though has given many benefits in the construction of various structures, it utilizes various natural resources, it also leads to emission of carbon dioxide gases by now. However, though, there are problems environmental issues associated with the use of cement, but we cannot neglect its use, because the demand of construction is increasing, we cannot stop construction we need to build infrastructure for the development of the nation for the development of the community.

However, this demand parallelly also increases the demand of using new materials also increases the demand of using binding agents such as cement, which also has implications related to the carbon footprint. So, it has concerning environmental issues and these environmental issues and the unavailability of the raw materials have prompted researchers and industries to look for alternative binding materials for construction and geopolymer concrete is one such material, which can satisfy the present demand and also can be used as an alternative.

Now, search for several alternative materials as I said geopolymeric material is one such you know material, there are various alternatives which researchers have discussed for example, we have alkali activated cement this is something like a geopolymeric cement, another name for geopolymeric cement, we have calcium sulphoaluminate cement, we have magnesium oxy carbonate cement or carbon negative cement, we have super sulphated cement etcetera. There are similar products that are being made that are being used.

Now, use of geopolymer concrete has attracted attention because of its additional advantages such as a early gaining the compressive strength of the final mix which we produce or geopolymeric concrete, which we produced. Low permeability in these structures in these mixes, good chemical resistance and excellent fire resistance behavior. So, these benefits have attracted the attention of researcher, scientist and also people from the industry and government agencies on the use of geopolymer.

So, what is a geopolymer? Geopolymer is an amorphous alkali illuminous aluminosilicate which is a type of inorganic polymer. It consists of a repeating unit of silate monomer which can be represented as  $\text{Si}-\text{O}-\text{Al}-\text{O}$ . So, what do you need for the production of geopolymeric concrete is that you need aluminosilicate and then you need some activators to remove the auto dissolve the alumina and silica that are present and then upon doing this you get a geopolymeric chain.

Let me give you an example. For example, you need material having alumina and silica. So, we have already discussed about various materials various waste byproducts that have these characteristics. For example, we have fly ash having alumina silica, we have GGBFs having alumina silica and so on we have metakeolin and so on.

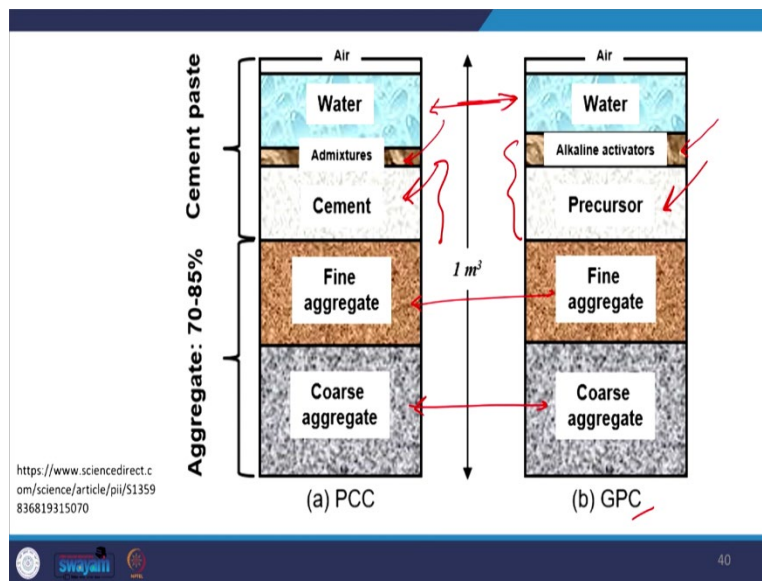
So, let me give you the example of fly ash. Suppose, you have a fly ash having you know let us say this is the fly ash. So, when it is reacts with water and we have some activators So, activators are in our alkaline solutions basically. So, if we have an alkali. So, this will dissolve it or this will break up the components of the fly ash. So, we will get it will break up in this form. And finally, this will create a polymeric chain having silica along with sharing oxygen ions with alumina. And finally the water will get liberated this liberated water will also help in the workability of the mixture.

So, this is a typical polymeric chain you can see this this is n says that depends on the numbers that are created. So, similar to what we call like a monomer inside a polymer, so, this is the monomer which will have repetitive units and this is something which we call as geopolymer here, which will bind the particles and will create a cementing effect.

Now, the source of material should be highly amorphous. So, this is desirable that the raw material which has the source of silica and alumina should be highly amorphous or glassy in nature and it should possess sufficient reactive glassy content, it should have low water demand and it should be able to release aluminum easily. So, these are some of the desirable requirements of the source material.

Now, the activator that are used to create an alkaline environment it can consist of several options, but the common options are use of sodium hydroxide, potassium hydroxide, sodium silicate and potassium silicate. So, they are basically used to activate the aluminosilicate materials such as fly ash or GGBFS. Now, among these materials usually sodium hydroxide and sodium silicate are preferred because they are able to extract aluminum more easily from the alumina silicate material that is why they are more preferred.

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This picture shows you a typical difference between the presence of different materials in a normal concrete and in a geopolymeric concrete. So, we have coarse aggregate in both these type of concrete, we have fine aggregate in both these types of concrete in case of a let us say a normal concrete we have cement, as the binding agent here we have a precursor which are aluminosilicate materials, this precursor they are activated using alkaline activators here we can have admixtures additionally and then water is present in both the type of concrete.

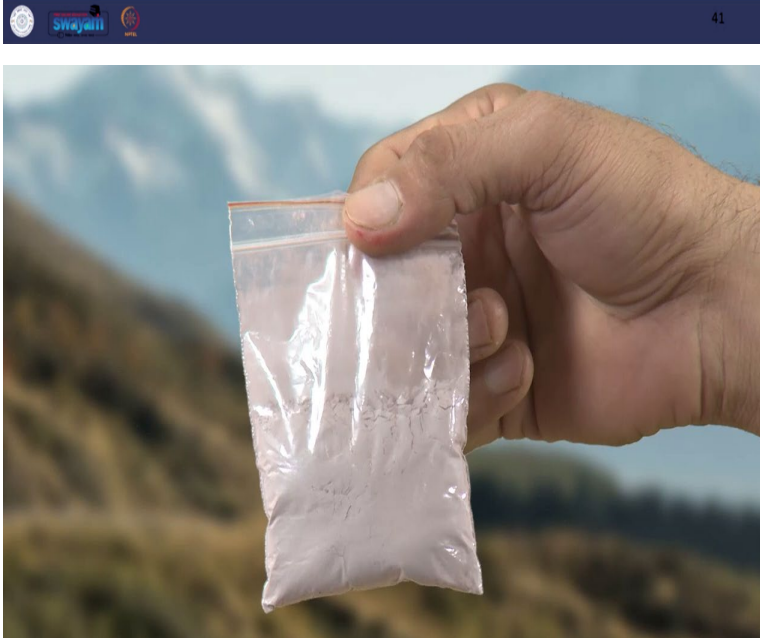
So, the main difference being here on in a normal concrete we are using a cement as the binding agent whereas in the geopolymeric concrete we have a combination of precursor and alkaline activators.

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## Alternate Cement: Geopolymeric cement

- Geopolymers are synthesized by the reaction of a solid aluminosilicate powder with alkali hydroxide/alkali silicate
- Polymerisation takes place when reactive aluminosilicates are rapidly dissolved and free  $[\text{SiO}_4]^-$  and  $[\text{AlO}_4]^-$  tetrahedral units are released in solution. The tetrahedral units are alternatively linked to polymeric precursor by sharing oxygen atom, thus forming polymeric Si-O-Al-O bonds
- Expelled water provides workability and is used in dissolution process
- **Sources of Aluminosilicates:** Flyash, GGBFS, Metakaolin, Rice Husk Ash, etc.
- **Alkali Activators:** Sodium hydroxide (NaOH), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), potassium hydroxide (KOH), and potassium silicate ( $\text{K}_2\text{SiO}_3$ ) are incorporated in GPC for dissolving Al and Si oxides





## Alternate Cement: Geopolymeric cement

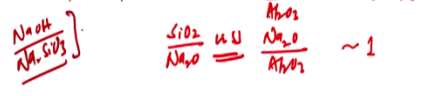
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- The most important factors affecting the properties of geopolymer paste are:  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio,  $\text{R}_2\text{O}/\text{Al}_2\text{O}_3$  ratio,  $\text{SiO}_2/\text{R}_2\text{O}$  ratio ( $\text{R} = \text{Na}^+$  or  $\text{K}^+$ ) and liquid-solid ratio

## Alternate Cement: Geopolymeric cement

*he. ni alkali and geopolymer ni solvent  
me. the strength*

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*NaOH | Mol of Silicate  
| Lit*



## Alternate Cement: Geopolymeric cement

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- Curing range: 40 °C to 85 °C for 24 hours
- Selection of molarity of NaOH and ratio of  $\text{Na}_2\text{SiO}_3$  to NaOH is critical
- A standard mix design procedure is yet to be developed



So, geopolymers they are synthetic synthesized by the reaction of solid aluminum silicate powder with alkali hydroxide or alkali silicate. So, this alkali silicate can be sodium silicate sodium hydroxide or it can be a potassium hydroxide potassium silicate. Now, polymerization it will take place when reactive aluminosilicates they get rapidly dissolved. So, we have to separate this alumina silicate bond.

So, they will be rapidly dissolved and we have free  $\text{SiO}_4$  minus and we have free  $\text{AlO}_4$  minus So, the silica and the alumina part they will get separated and they will form tetrahedral unit. So, these tetrahedral unit they are alternatively linked to polymeric precursor by sharing oxygen atom does forming Si-O-Al-O bonds. So, this is what typically happens during the production of geopolymeric material.

As I discussed in the previous slide that a certain quantity of water will get released. So, the expel water it will provide workability and is also used in the dissolution process of aluminum during the reactions. Now, various sources of Alumina silicate can include flyash, GGBFS, metakaolin, rice husk ash, etc. I have few of these materials with me.

For example, this is flyash which you see in my hand alright. So, this is flyash very fine material from thermal power plant. We have GGBFS which you see again in my hand. Now, this is a product which you get from the iron industry. We have rice husk ash, which you get after processing in the rice mill. And this is how the ash looks like.

Now talking about the alchemy activators this can include sodium hydroxide, sodium silicate. So, usually a combination of sodium hydroxide and sodium silicate is preferred, which you know and again the ratio of what should be the percentage of sodium hydroxide and sodium silicate depends on the targeted properties.

So, this is also the, a property of the sodium hydroxide and sodium silicate from where we have procured it, what is the molarity of the solution in both the cases. So, these parameters need to be optimized before we can finalize the proportions of various constituents in the geopolymeric concrete. Similarly, we can also use potassium hydroxide and potassium silicate. So, they are as I mentioned, they are used for dissolving the aluminum and silica oxide that get generated.

Now, there are various aspects related to geopolymeric concrete which can be discussed for example, what are the factors affecting the strength, what should be proportion of different constituents that can be used and so, on. So, this will take a lot of time to discuss because this being a very new area where people are exploring. So, let us see some of the important factors that that affect the properties of geopolymeric paste, which has been cited in the literature.

So, one of that parameter is the ratio of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the raw material will also finally affect the geopolymeric concrete strength. Then the ratio of alkali oxide are being here the sodium or potassium whatever alkali product we are using. So, the ratio of  $\text{R}_2\text{O}$  divided by  $\text{Al}_2\text{O}_3$  also affects the strength of the final geopolymeric concrete.

So, this ratio also needs to be optimized the ratio of  $\text{SiO}_2$  to  $\text{R}_2\text{O}$  which is the ratio of silicon oxide to the alkali oxide, it also affects the final property of the geopolymeric concrete. And then what is the liquid to solid ratio in the mix. So, usually it is seen that the increase in the alkali content and reduction in the silicate content it increases the compressive strength, it increases the strength talking about these ratios typically, the ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  it ranges from 3 to 3.8 the ratio of  $\text{NA}_2\text{O}$  to  $\text{Al}_2\text{O}_3$  which is again an important factor is somewhere around 1.

And then we also have to see that what is the molarity in case of the sodium hydroxide solution which we are preparing and we are I hope we understand that molarity tells us about the number of moles of solute per liter of solution, which we are preparing. Also the ratio of as we have discussed  $\text{SiO}_2$  to  $\text{NA}_2\text{O}$  in the sodium silicate will affect the property of the final geopolymeric concrete which we have which we make.

And during the production we also have to appropriately select the proportion of if you are let us say you are using sodium hydroxide and sodium silicate, then the ratio of sodium hydroxide to sodium silicate which we are using to create the alkaline environment will affect the properties of the final geopolymer concrete which we are producing. So, these parameters need to be selected we have to do iterations in the lab with the materials which we are using before deciding the final proportion.

Now, curing is an important factor here. Usually the curing required is the appropriate curing temperature ranges from 40 to 85 degrees Celsius and the duration is approximately 24 hours because whatever strength gain has to take place it will take at the early stages. As I said selection of molarity of NaOH and ratio of  $\text{Na}_2\text{SiO}_3$  to NaOH is critical. So, this has to be decided depending on the source from where we are procuring these materials.

So NaOH can be prepared in the lab selecting different molarity every time and  $\text{Na}_2\text{SiO}_3$  can be taken from the industry. Again when they are taken from the industry we have to specifically check them that what are the typical characteristics of an  $\text{Na}_2\text{SiO}_3$  which they are supplying.

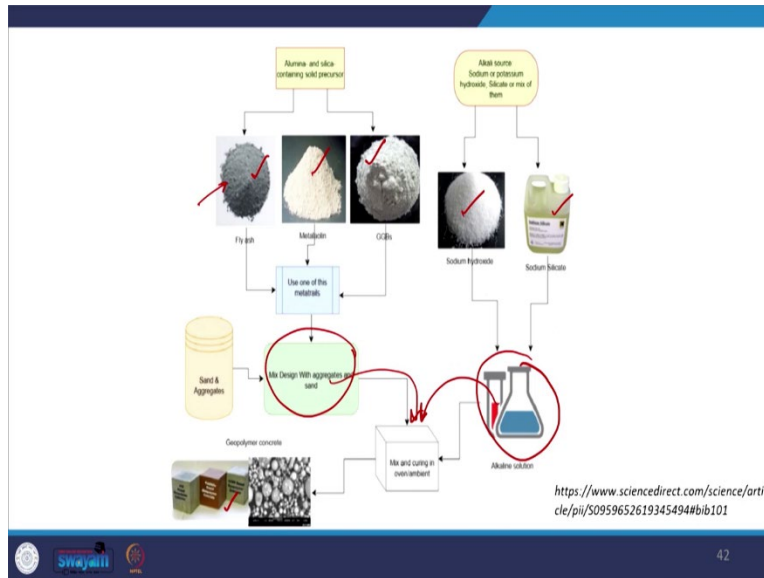
Presently we do not have a specific mixed design process for geopolymeric concrete but this is being developed various researchers have and reports have talked about some preliminary mix design procedure to be adopted and the large scale construction using geopolymeric concrete is yet to be done specially in India and there are various researches which are going on presently on understanding or on exploring the use of geopolymeric concrete especially in pavement constructions.

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So, before I stop here today, and I discuss this slide, which gives us an overview for the production of geopolymeric concrete, let me show you a sample in my hand this is a geopolymeric concrete and by looking at it, you would not be able to figure out whether this is a normal concrete or a geopolymeric concrete, but this is a typical cube which was fabricated by some of the researchers here at IIT, Roorkee. This I just wanted to show you for reference and also to tell you that the appearance of this concrete is very-very similar than a normal concrete mix which I produce in the laboratory using cement.

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So, we will wind up today by discussing this last slide which gives an overview for the production of geopolymeric concrete. So, you can use different sources of aluminosilicates you can use flyash we have metakolin we have GGBFS and so on. So, you have to first select the appropriate source in these sources it is important what is the ratio of  $Al_2O_3$  to  $SiO_2$ .

So, you have to do a chemical characterization then you have to choose the source for activators. So, you can choose a mixture of let us say sodium hydroxide and sodium silicate. So, this is sodium hydroxide and sodium silicate they have to be mixed in appropriate proportion. So, they need to be mixed in appropriate proportion to create an alkaline solution.

Now, you can use any of these materials, you mix it with the other ingredients that is sand and aggregates and then you combine this alkaline solution with the raw materials that we are using cure it for the appropriate period of time and then what you get is a geopolymeric concrete the strength of which can be assessed using the laboratory investigations. So, this is a very simple flowchart. I think, it must be clear to you that how geopolymeric concrete can be produced.

With this we will stop here and today we have completed our discussion on module 5 and in the next class we will start discussing about the mixed design of concrete mixtures that to typically focusing on these standards that are used in India for pavement construction. Thank you.