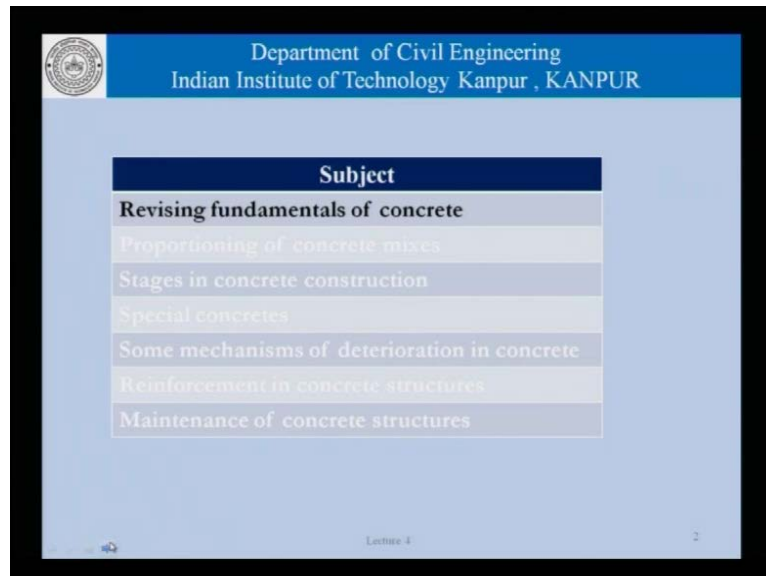


Concrete Engineering and Technology
Prof. Sudhir Misra
Department of Civil Engineering
Indian Institute of Technology, Kanpur

Lecture - 4
Admixtures in Concrete - Mineral and Chemical

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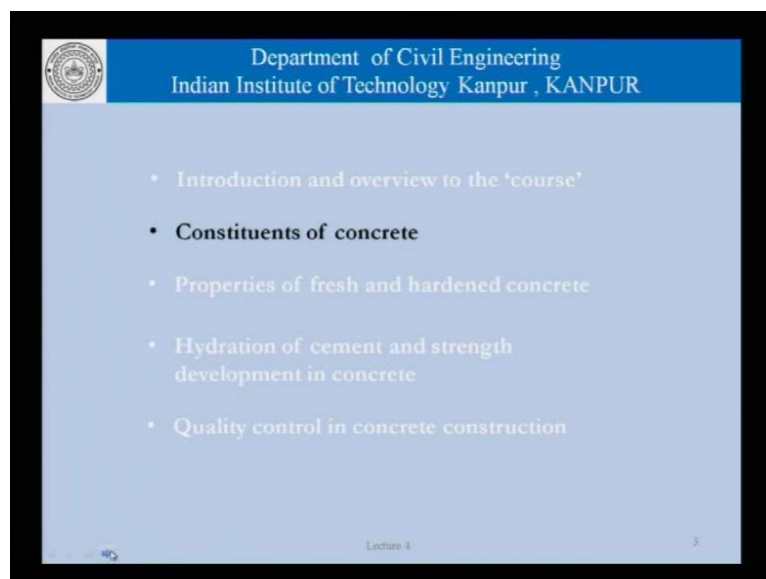


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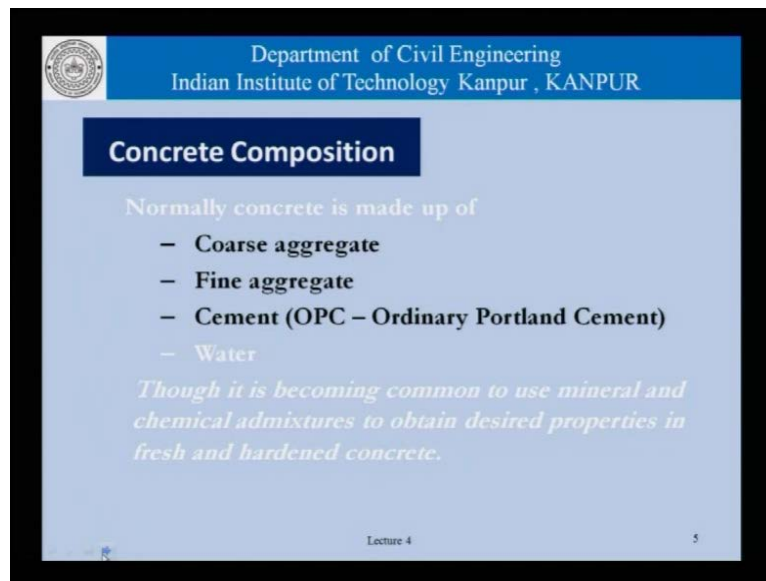
Subject
Revising fundamentals of concrete
Proportioning of concrete mixes
Stages in concrete construction
Special concretes
Some mechanisms of deterioration in concrete
Reinforcement in concrete structures
Maintenance of concrete structures

Lecture 4 2

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- 
- Department of Civil Engineering
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- Introduction and overview to the 'course'
 - **Constituents of concrete**
 - Properties of fresh and hardened concrete
 - Hydration of cement and strength development in concrete
 - Quality control in concrete construction
- Lecture 4 3

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Concrete Composition

Normally concrete is made up of

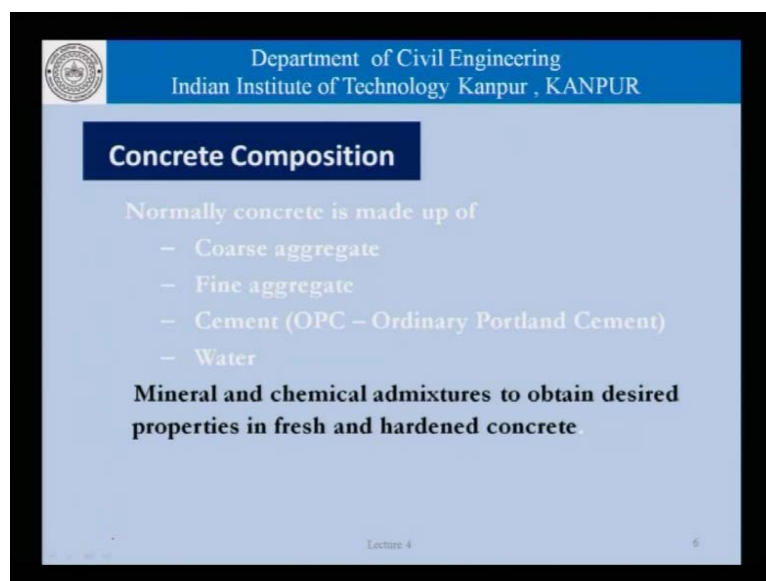
- Coarse aggregate
- Fine aggregate
- Cement (OPC – Ordinary Portland Cement)
- Water

Though it is becoming common to use mineral and chemical admixtures to obtain desired properties in fresh and hardened concrete.

Lecture 4 5

Welcome back to these series of lectures, on concrete engineering and technology. So far we were on the subject of, revising the fundamentals of concrete. and we were talking about constituents, and we had said that well normally, concrete consists of coarse aggregate, fine aggregate, cement and water in addition to mineral and chemical admixtures, which are added in certain special cases, to obtain desired properties in fresh, and hardened concrete. So out of these, we had completed the discussion on coarse and fine aggregate and ordinary Portland cement.

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Concrete Composition

Normally concrete is made up of

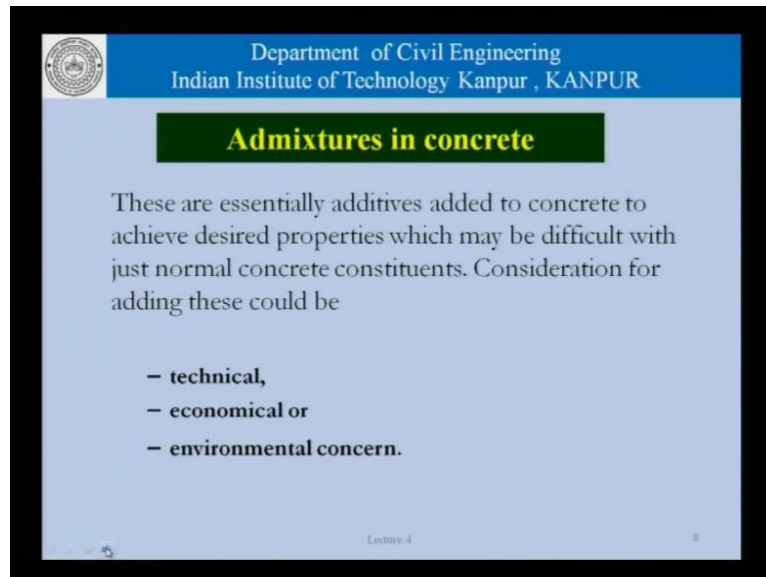
- Coarse aggregate
- Fine aggregate
- Cement (OPC – Ordinary Portland Cement)
- Water

Mineral and chemical admixtures to obtain desired properties in fresh and hardened concrete.

Lecture 4 5

So in our discussion today, we will focus on, the use of mineral and chemical admixtures, which are added to concrete, in order to modify or obtain the desired properties in fresh concrete, or in hardened concrete.

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Admixtures in concrete

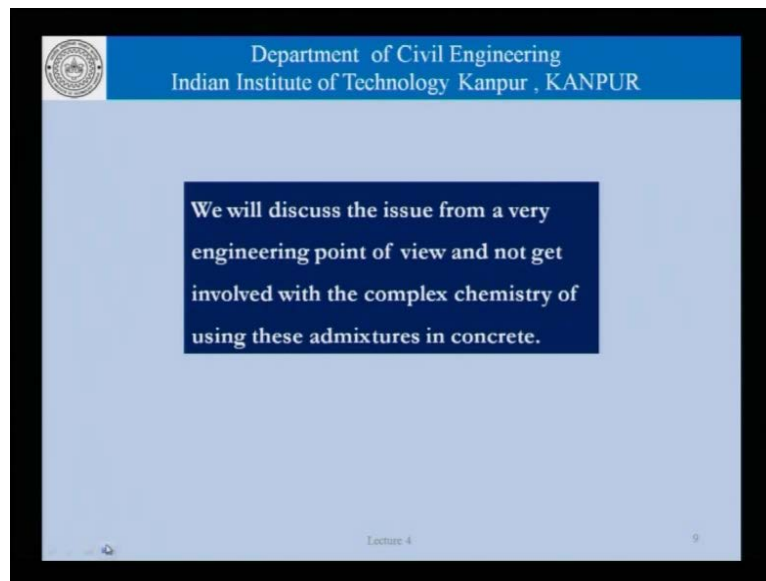
These are essentially additives added to concrete to achieve desired properties which may be difficult with just normal concrete constituents. Consideration for adding these could be

- technical,
- economical or
- environmental concern.

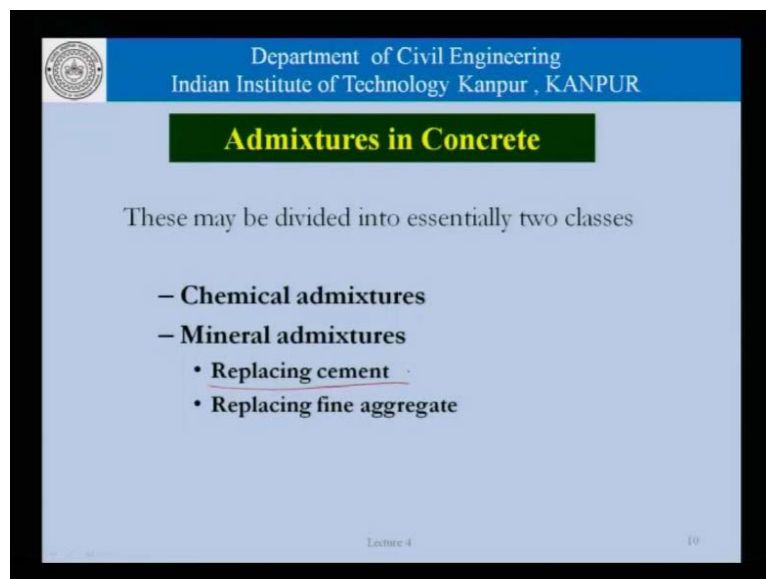
Lecture 4

Now as far as admixtures in concrete are concerned, these are essentially additives to the material; that is concrete, to achieve desired properties, which may be difficult with just the normal constituents of concrete; that is cement, water, coarse aggregated, fine aggregated. Considerations for adding these could be technical, which is basically the issue of properties. We want a certain property in the concrete, which we cannot get, and therefore we need to add admixtures. It could be economical, cement may be too expensive to use, is there a possibility of using something else instead of cement, which is cheaper, without comprising the properties of concrete, from the point of view of their specifications, or what is required. Or there could be environmental concern. There is a certain material that we produce in the industry, or somewhere, which if disposed off indiscriminately, leads to pollution and so on. If it can be gainfully used in concrete; that's the best thing that can happen. So there can be an environmental concern, which would prompt us to use that material as an admixture in concrete.

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Now we will discuss this issue of mineral and chemical admixtures, from a very engineering point of view, and not get involved with the complex chemistry, of using admixtures in concrete. Continuing our discussion, we have been talking of chemical admixtures, and mineral admixtures. These are the two broad classifications under which, admixtures would qualify. Now within mineral admixtures, we use materials, which replace cement; that is, they are so fine, that their fineness is comparable to that of cement, and therefore we try to treat them, as a part of cement in considering concrete. Other than these, there are certain other materials, which are used at times replacing fine aggregate; that is sand. Common

terminology for mineral admixtures, would include only those that replace cement of those materials also, which can be used as replacements for fine aggregate; that is sand.

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Chemical admixtures in concrete

In principle, the chemical admixtures interfere with the action of cement within concrete, including its hydration. Depending upon the desired effect, chemical could be chosen such that they act as,

- **Set regulators**
 - Accelerators
 - Retarders
- **Water reducers, and, high range water reducers**
- **Air entrainers**
- **Others (corrosion inhibitors, etc.)**

Lecture 4 12

Now, coming to the first item; that is chemical admixtures. Chemical admixtures in principle, interfere with the action of cement within concrete, and including its hydration. Depending on the desired effect, a chemical admixture is chosen could be that they act as set regulators. On account of hydration of cement, the cement sets. There is an initial setting time, there is a final setting time, the process goes on, and we get hardening of cement and so on. Now set regulation means a process, by which we either accelerate this process, or we delay this process; therefore we could have accelerators or we could have retarders. These are useful, when we are using cement or concrete in specific applications. In a repair job, where concrete is required to have early strength, we may like to use accelerators.

Whereas in a job, where concrete is to be placed at a site which is far away, we may need to use retarders. Another example could be, in hot or cold weather concrete. When the temperature is very cold, and the cement may not set normally within a reasonable period of time, we may like to use an accelerator. Similarly if we are working in hot weather, then we may use a retarder, which will give us a little more time, to work with the concrete, so that it does not set very rapidly on account of the high temperature. Other than set regulators, we will have or we have, water reducers and high range water reducers. Now what is the difference between water reducers and high range water reducers. Essentially these chemical admixtures are those, which enable us to reduce the water demand in a concrete mix.

So a water reducer, if it helps us to reduce the demand, by say 10 to 15 percent, a high range water reducer is a chemical, which enables us to reduce that water demand by say 25 to 30 percent. So it's only a matter of how much water reduction can be achieved, by using one chemical or another. Now how this reduction in water demand, is used to an engineering advantage, in proportioning concrete mixers, or in concrete engineering in general, that we shall see through examples later on in this discussion.

Then we have another class of a chemical admixtures called air entrainers. We have seen in earlier in a slide that, concrete contains certain amount of air. Now entrapped air is that which is, there in concrete without any effort; that is, it is inadvertently there. However in certain cases ,we want to entrain air; that is intentionally and consciously we want the concrete, to have a certain amount of air particles. Now those chemicals which help us achieve this objective, of entraining air in the fresh concrete, which remains there while the concrete hardens, are called air entrainers. There are other chemical admixtures as well, which are very special purpose admixtures.

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Chemical admixtures in concrete

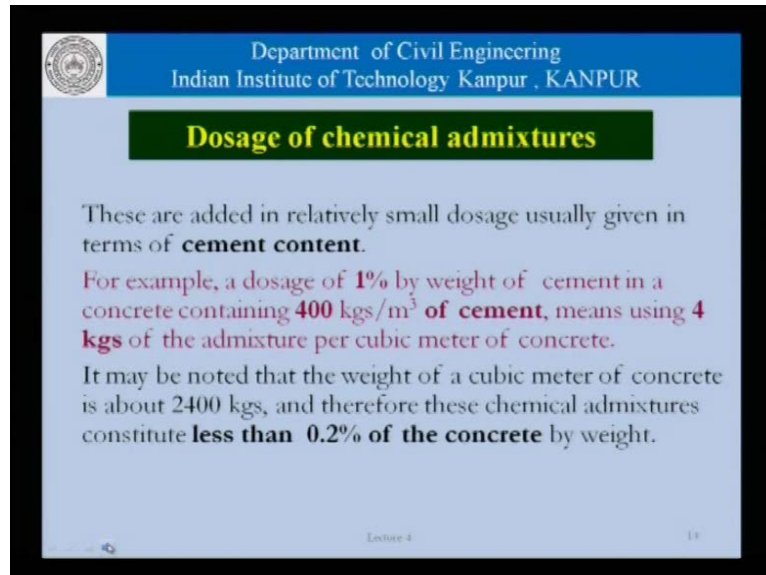
- Are usually available as liquids, and are often batched by volume.
- Since the dosage is very small special care needs to be taken a the time of batching.
- The pure admixture is often diluted with water and then added as a part of the unit water content required to be mixed, to ensure a better distribution in the concrete.

Lecture 4 13

For example corrosion inhibitors. There is literature which says, that if we use chemicals such as nitrites and so on, we get a better performance from the point of view of reinforcement corrosion. Presence of these nitrites interferes or modifies the pore solution in a manner that, the reinforcing parts is such a concrete, become more resistant to corrosion. Electrochemical process involving corrosion is slowed down and so on and so forth. So there are all these

classes of different chemical admixtures, which are used, in the concrete industry, in order to modify the properties of concrete.

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Dosage of chemical admixtures

These are added in relatively small dosage usually given in terms of **cement content**.

For example, a dosage of **1%** by weight of cement in a concrete containing **400 kg/m³ of cement**, means using **4 kgs** of the admixture per cubic meter of concrete.

It may be noted that the weight of a cubic meter of concrete is about 2400 kgs, and therefore these chemical admixtures constitute **less than 0.2% of the concrete** by weight.

Lecture 4 13

So let us try to take a look, I have some of them in greater detail. Chemical admixtures are usually available as liquids, and are often batched by volume. Since the dosage is very small, very special care needs to be taken at the time of batching. The pure admixture is often diluted with water, and then added as a part of the unit water content, required to be mixed, to ensure a better distribution in the concrete. So we do not normally batch a concentrated chemical admixture into concrete, rather we dilute it with the mixing water, part of the mixing water, is added with the chemical admixture to the concrete, and then the mixing water is added, the remaining part of it is added, so that a chemical admixture is more homogeneously mixed, throughout the concrete, mix in the mixer.

As far as dosage is concerned, these are relatively small dosages, and since the action of chemical admixtures, is relative to the amount of cement present in the system. The dosage is often given in terms of cement content; that is, if the dosage is one percent by weight of cement in a concrete it means, that if a concrete contains 400 kg's per cubic meter of cement, only 4 kg's of the admixture per cubic meter of concrete, will be added. It should be noted that, the weight of a cubic meter of concrete is about 2400 kg's, and therefore these chemical admixtures constitute a very small percentage of concrete by weight. And therefore the presence of these chemical admixtures, can be ignored, as far as the volumetric

of the concrete mix is concerned. They are usually considered, along with the volume of water, which is present in the concrete mix.

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Example:
Let the chemical admixture be available as an aqueous solution – say 4kgs is dissolved in 10 liters of water.

- 1) If 4kgs of CA is required: 10 / of 'concentrate' is added AND 10 / of water adjusted against the total water to be added.
- 2) If 6kgs of CA is required: 15 / of 'concentrate' is added AND 15 / of water adjusted against the total water to be added.

Handwritten notes:
 $W \rightarrow 180 \text{ kg/m}^3$
 10 with CA
 170 kg
 $180 \rightarrow 165$
 15

Lecture 4 15

Let us consider an example, let the chemical admixture that we want to use, be available in an aqueous solutions; say 4 kg's is dissolved in 10 liters of water. Now if 4 kg's of chemical admixture is required, the example that we saw earlier, that one percent of cement, is required and there is 400 kg's of cement in the concrete mix, we need 4 kg's of the chemical admixture. So in that situation, given that 4 kg's of this chemical admixture, is dissolved in 10 liters of water. We can use 10 liters of this concentrate, and we say that 10 liters of concentrate is added, and 10 liters of water is adjusted against the total water to be added if 6 liters of if 6 kg's of chemical admixture is required; that is about 7.5 percent of that concrete mix, then 15 liters of the concentrate is added and 15 liters of the water, adjusted against the total water required; that is if the original water demand, was 180 kg's per cubic meter.

Then in this case what we will do, is we will use 10 kg's with the chemical admixture, and only 170 kg's of water need be added to the concrete mix, and we will have a concrete mix, which has a 180 kg's of water, long, we will have a 180 kg's of water; no doubt 10 of that was used to deliver, the 4 kg's of chemical admixture which was required. In this case similarly, if the demand was again a 180 we need to use only a 165 kg's of water, and 15 kg's is already been added as given here. And therefore this mix too, contains a 180 kg's of water. No doubt 15 kg's of that was used to deliver, the 6 kg's of chemical admixture required.

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Set regulators (Accelerators or retarders)

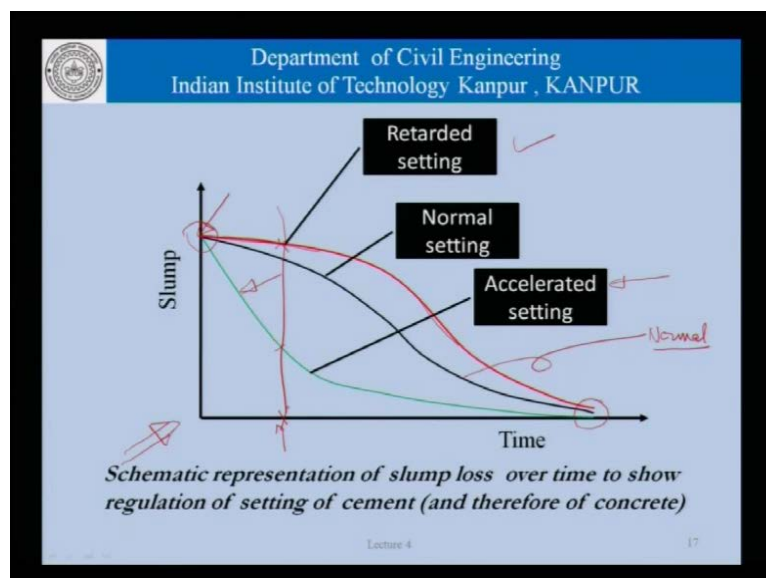
They are used under special conditions – when concrete is used in cold or hot temperatures, there could be a need to regulate the setting process – either to accelerate it or retard it !!

A retarder could also be used to prevent formation of a cold joint. Similarly, an accelerator can be used in cases when early strength is required.

Lecture 4 16

Now let us come to set regulators, they are used under special conditions as I mentioned earlier when concrete is used in hot or cold temperatures. There could be a need to regulate the setting process, either to accelerate it, or to retard it. A retarder could also be used to prevent formation of a cold joint, or a construction joint. An accelerator could be used in cases when high early strength is required.

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Let us look at schematically, what happens when we use a retarding or a setting agent. Let us see that this is the normal slump loss; that is if we have an original slump value. As the hydration process continues, the concrete continues to lose its slump, it continues to become

stiffer, and this is the process the black line here, is the process for normal concrete; that is a concrete which does not have any chemical admixture added to it. Now if I retard this; that is we have a retarder, in an appropriate dosage, within the concrete mix, what will happen is, that initially there will be no slump loss; that is the slump loss will be very small. Gradually of course as the hydration process over takes, any kind of retarding action that is there, there will be slump loss. And finally we will come to a situation, where there is no slump, and we do not require any slump at that point of time. Similarly, if we want to accelerate the process, we want the concrete to harden earlier. Then we use an accelerator, and we use, or we get rapid slump loss, if we are using a accelerator in the beginning.

Now what this picture shows, is that depending on our need, depending on the requirements of the job. We may need to specify, not only what is the initial slump of the concrete; that is measured at the concrete plant, but we may also need to specify the slump, at a certain point in time, that after the mixing has done, we want a concrete, which is almost having the same slump, or having almost the same slump, as that at plant, or we do not want the concrete to have any slump, we want the concrete to have reasonably set, or the hydration process to have or the hydration process to have reasonably progressed. So this is the importance of having, so that's the importance of understanding, the action of retarders, and accelerators, in terms of how they, alter the properties of fresh concrete in this case slump, which is measured or monitored in terms of slump loss.

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Water reducing agents (or high range water reducing agents)

- They are used to 'reduce' the water demand for a given slump (workability).
- Their effectiveness can be measured in terms of the percentage of water reduction that can be achieved for a given dosage.
- As an example, if 180kgs of water is required for a certain slump (without an admixture), and we use an admixture, which at a certain dosage, can reduce water by 20%, then we can get the same slump with $(180 - 36)$, i.e., 154 kgs.

\downarrow ? \rightarrow 5% 10% \rightarrow

\leftarrow 15%

A	180	}	Same slump.
B	154 + <		

Lecture 4
18

Now water reducing agents, or high range water reducing agents. They are used to reduce the water demand for a given slump; that is slump and water demand are linearly related. The more water we add to the concrete mix, the higher slump we get. Now in order to get the same slump, if there was another method, other than increasing water that is precisely the water reduction, or the water reducers. And their effectiveness; that is the effectiveness of a water reducer, can be measured in terms of the percentage of water reduction, that can be achieved for a given dosage. So if there is an admixture with one percent, can cause or can bring about, a reduction in water demand, to say 5 percent. And there is another admixture let us say b, which at the same dosage of one percent of cement, gives me a water reduction of 15 percent, then b is more effective as a water reducer than a.

What we have really seen, if a 180 kg's of water is required for a certain slump, without an admixture, in a normal concrete, and we use an admixture, with a certain dosage, which can reduce water demand by 20 percent. Then we get the same slump at a 180 minus 36, because 36 is 20 percent of 180 at 154 kg's; that is concrete say a made with only 180 kg's of water, and a concrete b made with 154 kg's of water, and a certain percentage in the chemical admixture, which gives us 20 percent reduction in the water demand, will have the same slump. This understanding is very important, when we are working with water reducers, and high range water reducers. There are two ways of looking at it ;one is to say that, one percent, or a certain dosage of a chemical admixture gives me 5 percent or 10 percent, reduction in water demand. The other side of the coin is, that if we want 15 percent water reduction, what should be the dosage. So with this, and this is the discussion that goes on, when we do proportioning of concrete mixes, using water reducers, or high range water reducers.

Now let us see how a water reducing agent, can be actually used in concrete engineering for different purposes. Let us consider a concrete mix, where we will basically be talking only of, the water content, the cement content, these two are given in terms of kg's per cubic meter. Water cement ratio which is a percentage, the chemical admixture, which is given as a zero or one; that is either it is present or it is not present. Let us say the slump, which is given in centimeters, strength which is given in M P A. We further assume, that water and slump, are directly related, and similarly water cement ratio, and strength are directly related. So if we increase the water content, we increase the slump. We reduce the water cement ratio, we increase the strength. So with this fundamental understanding, let us say, that we have a base mix, which has a 180 kg's of unit water content, 360 kg's of cement, which gives us a water cement ratio of 0.5.

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Example: Using a water reducer

NO	WATER	CEMENT	W/C	CA	SLUMP	STRENGTH	COMMENT
1	180	360	0.50	0	8	32	BASE
2	160	360	0.44	1	8	> 32	HIGHER STRENGTH
3	160	320	0.50	1	8	32	CEMENT SAVING
4	180	360	0.50	1	>8	32	PLASTICIZING ACTION

Lecture 4 19

We do not use the chemical admixture to begin with, because it is the base mix, and this base mix has a slump of 8 centimeters, and a strength of 32 M P A at a certain age. Now mix to, where a certain amount of chemical admixture has been added. And we are able to reduce, the water demand to a 160 kg's. Now what are the implications, if we do not change the cement content, we keep it the same 360 kg's, what have we effectively done. We have brought down, the water cement ratio from 0.5 to 0.44. Now given our understanding that a 180 kg's of water, or a 160 kg's of water plus chemical admixture, will have the same slump, the slump remains the same. However, since we have reduced the water cement ratio, the strength will increase. So what have we effectively achieved. We have achieved higher strength, in the concrete mix. So this is one way of using a water reducer, so we have used the water reducer, we have reduced the water content, and effectively what we have achieved; however, is the increase in the compressive strength of the concrete.

Consider another example, here when we reduced the water content, or where we could reduce the water content to 160, we did not want the strength to go up. We were happy with this strength of 32 M P A. So we let, in order that this 32 M P A strength be preserved, or since we did not want higher strength, what we need to do, is to keep the water cement ratio at the same level of 0.5. And that can be done, if we keep the cement level at 320, because our water cement ratio is 0.5, and the water content in this mix is 160. So what have we effectively achieved, cement saving, so instead of using 360 kg's of cement, we are now able to get the same 32 M P A strength, with just 320 kg's of cement. Of course, like in the

previous example, the slump is the same 8 centimeters, because we are still working with a 160 kg's of the water, and a certain amount of chemical admixture. In the third form of using water reducer would be, where we do not reduce the water content, we keep it at 180 and yet we use a chemical admixture at certain dosage. We do not alter the cement content either, it is still retained at 360 kg's, what is the characteristics of this mix.

The water cement ratio is 0.5, and therefore the strength will still be 32 M P A, what will happen to the slump a slump value, which was there at 8 at a level of 8 centimeters. When we were using a 160 kg's, with the chemical admixture, will go up, because now instead of 160, we are using a 180 kg's of water. A 160 kg's plus chemical admixture, was giving me 8 centimeters of slump. Now if I push my water content up to 180 the slump will go up. So effectively what I have achieved is plasticizing action; that is a concrete has become more workable.

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Air entraining admixtures

These are used in air entrained concrete *AE concrete*

Air entrainment is accompanied by increase in workability and hence it may be required that the unit water content (may have to) be reduced for a certain workability.

Air entrained concrete is recommended for use in environments with cyclic freezing and thawing

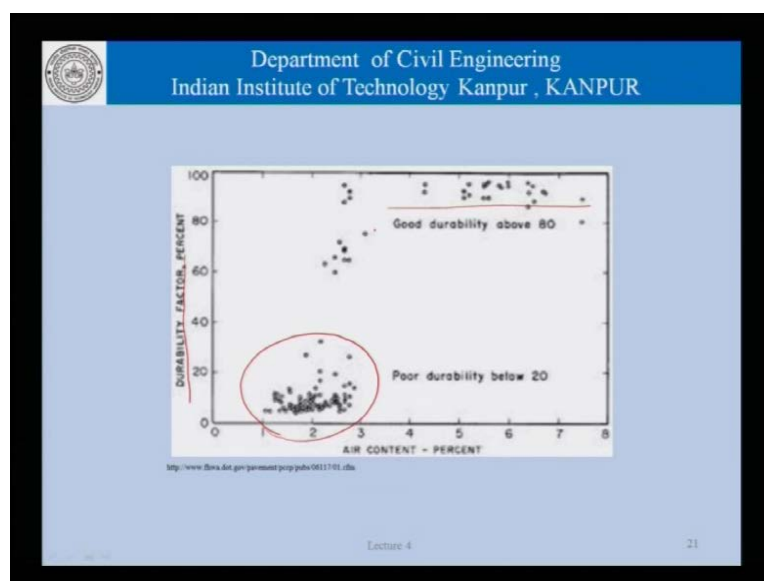
Lecture 4 29

So depending on how we use, whether we choose to save cement, whether we choose to increase the strength, or we choose to plasticize the concrete mix. All these three actions are possible, when we are using a water reducer, or a high range water reducer, or a super plasticizer. Of course I must caution that, this is a very simplified picture, a simplistic picture as a matter of fact, where an assertion is made, that the slump is depending only on the water content. It is independent of the cement content, which is really is not, but it is an illustrative example, to show how the huge of water reducers, can be an effective way to adjust, modify

your engineer the properties of concrete, whether it is the fresh concrete in terms of slump, or its the harden concrete in terms of strength.

Now let us come to air entraining admixtures. These are used in air entrained concrete, we sometimes call concrete as A E concrete, and non A E concrete, and our A E concrete is air entrained concrete; that is that concrete where an admixture has been added, to consciously entrain air into the system. Whereas a non air entrained concrete is one, where air may be still present, but it is the entrapped air, and not entrained air, and it is there only unintentionally and not entrained. Air entrainment is accompanied by increase in workability, and hence it may be required, that the unit water content may have to be reduced for a certain workability. What happens is, that when we entrain air in fresh concrete, air gets entrained in the form of minute bubbles.

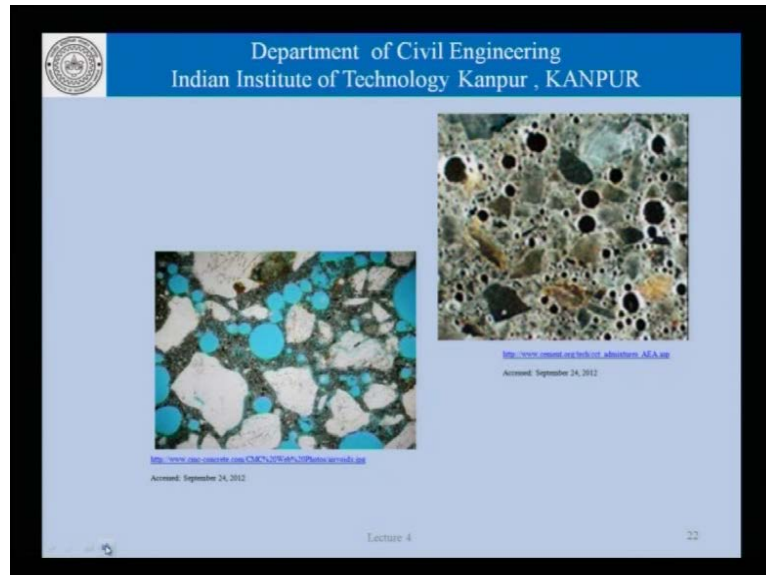
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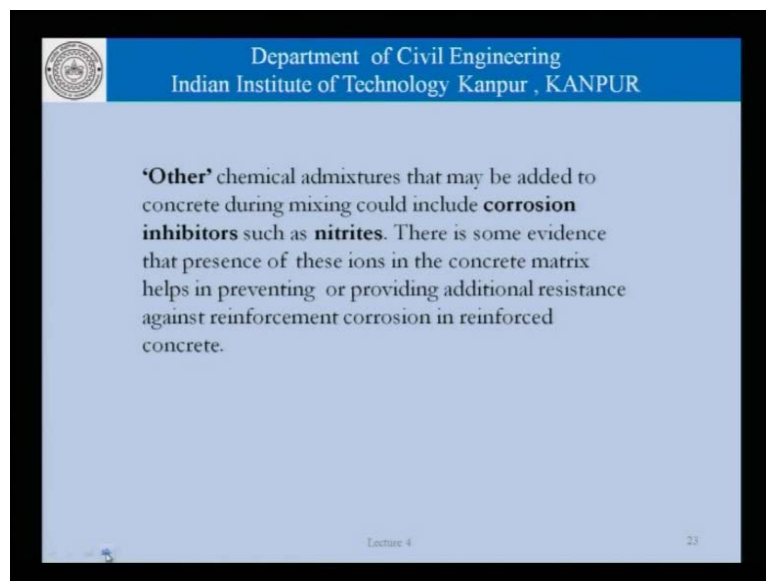
Now these bubbles act as ball bearings, and improve the workability of concrete. And therefore once we are using air entrainment, for some purpose, we may need to reduce the water content of the concrete mix, in order to preserve the workability. So that's something which we must keep at the back of our mind, when proportioning concretes with air entrainers. Air entrained concrete is recommended for use in environments with cyclic freezing and thawing. We have mentioned earlier, that cyclic freezing and thawing means, concrete structures built-in environments, where the temperatures vary over the year in a range, that causes the concrete, or the water in concrete, to freeze and thaw. And once the concrete, or the water in concrete freezes and thaws, that causes distress to the pore structure,

and it has been found that, having air entrained concrete in such environments, is one of the options, that an engineer can use to increase the durability.

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This is what is being said, that if the air content in concrete, is in the range of one one and a half two to 3 percent, then what is called the durability factor; that is how durable the concrete is, in the freezing and thawing environment the durability factor is very small. However if the concrete is in the range, having 4 to 6 percent of air, then the durability factor is very high, and that is what is being said, when we state that, in the case where concrete is exposed to cyclic freezing and thawing, having a certain amount of entrained air, is a very

good idea, to increase the durability of the concrete. These pictures here, show the presence of air voids, within the hardened concrete matrix. Please remember that, the blue color or the red color and so on, are always just illustrative, and the air in the concrete does not have any specific color. Apart from all these admixtures set regulators, water reducers, and air entrainers, there are other chemical admixtures which we talked about, and these are also added to concrete in the time of mixing, for other action; such as corrosion inhibitors, like nitrites, and there is evidence that the presence of these ions in the concrete matrix, helps in preventing or providing, additional resistance against reinforcement corrosion and reinforced concrete.

Now before we close the discussion, on chemical admixtures, I would like to point out, that the effectiveness, or the dosage of a chemical admixture, is related to the properties of cement. Finer cements, coarser cements, cements with higher $c_3 a$, or a higher $c_3 s$, and so on. They will need to be handled differently, when we are trying to adjust the dosage of a chemical admixture for any purpose, whether it's set regulation, or it is water reduction, or it is air entrainment and so on. So one has to be very careful, when using chemical admixtures, in terms of determining the compatibility, of the chemical admixtures with the cement which is used. It's a good practice that, whenever this lot of cement changes, or the batch of the chemical admixtures changes, then simple tests should be carried out in the laboratory, to ensure that the compatibility still exists, and a minor adjustment, in the dosage of the chemical admixture, is appropriately made.

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Admixtures in Concrete

- Chemical admixtures
- Mineral admixtures
 - Replacing cement
 - Replacing fine aggregate

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Motivation to use mineral admixtures

Motivation to use mineral admixtures in concrete comes from one or more of the following:

- Industrial by product utilization
- Environmental concern (Sustainable Development)
- Economy in cement consumption
- Reduced heat of hydration
- Durability considerations
- (High) strength requirements

Lecture 4

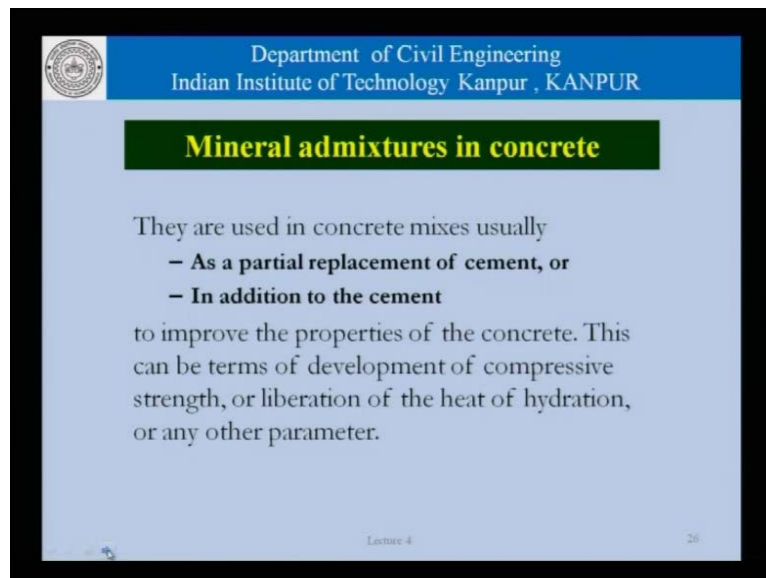
Let us continue the discussion on admixtures in concrete, having completed chemical admixtures, let us now come to mineral admixtures, especially in the role of replacing cement. Now the motivation for using mineral admixtures in a concrete, could come from one or more of the following. Industrial by product utilization, we have the steel industry, or the thermal power plants, which are classically cited as examples, where we get large amounts of blast furnace slag, or fly ash, which are used in concrete as mineral admixtures. We have the copper industry, which gives copper slag, which again is a potential candidate for using concrete as a mineral admixtures and so on.

So there is this issue of industrial by product utilization in concrete. There is environmental concern in terms of sustainable development, which is related to industrial by product utilization, where we want that certain products from the industry, or by products waste from the industry, which can be gainfully used, in the concrete. Then we have ratio of economy, in cement consumption. Cement is the most expensive of the concrete constituents, and even if you are able to say if a k g of cement in a cubic metre, that translates to into a lot of savings, as far the project, as far as the carbon foot print and so on is concerned.

The reduced heat of hydration, using cement is not only uneconomical, but it also gives us large amount of heat of hydration, which is, which in certain cases becomes an issue, in case of mass concrete and so on. And therefore we may like to reduce, the cement consumption in concrete, not only from the point of view of economy, but also from the point of view of handling, or controlling the heat of hydration. Durability issues, certain times if we use fly

ash, or we use blast furnace slag, or silica fume. We enhance the durability of the concrete structure, because the pore structure of the concrete containing these admixtures, is finer, a concrete is less permeable, and therefore more durable. So durability concerns, or considerations often drive us to use, mineral admixtures, along with cement, in a concrete mix. There may be strength requirements.

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Mineral admixtures in concrete

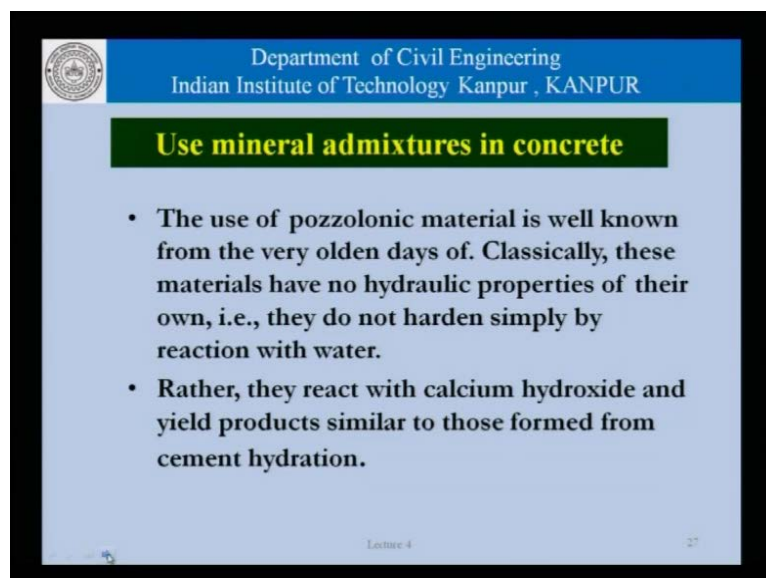
They are used in concrete mixes usually

- As a partial replacement of cement, or
- In addition to the cement

to improve the properties of the concrete. This can be terms of development of compressive strength, or liberation of the heat of hydration, or any other parameter.

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Use mineral admixtures in concrete

- The use of pozzolonic material is well known from the very olden days of. Classically, these materials have no hydraulic properties of their own, i.e., they do not harden simply by reaction with water.
- Rather, they react with calcium hydroxide and yield products similar to those formed from cement hydration.

Lecture 4 27

At times it may be not possible, to achieve a certain strength, or a certain level of strength, by using only the traditional ordinary portland cements, at least in an economical manner or in a manner that the concrete still continues to satisfy the specifications in terms of heat of

hydration or the maximum temperature and so on and therefore for even strength considerations we may need to use mineral admixtures. Now they are used in concrete, usually as a partial replacement of cement, or they are used in addition to the cement. Now this is done in order to improve the properties of concrete obviously, and can be in terms of compressive strength, liberation of heat of hydration, or any other parameter that we choose to identify, specify, and monitor.

Historically the use of pozzolonic material is very well known, and these materials have no hydraulic properties of their own, and they do not simply and they do not simply harden by adding water, rather they react with calcium hydroxide, and yield products, similar to those formed during cement hydration. So what these mineral admixtures do. They do not react with water; that is added to the concrete. However the water and the cement, when they react they form large amounts of calcium hydroxide, and this calcium hydroxide is what ,the mineral admixtures react with, to give hydration products, or products of that reaction, or similar to the products formed on account of normal cement hydration.

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Mineral admixtures used in concrete

In recent years, the following have emerged as the primary mineral admixtures used in concrete (as replacements of OPC)

- Ground granulated blast furnace slag
- Fly ash
- Silica fume

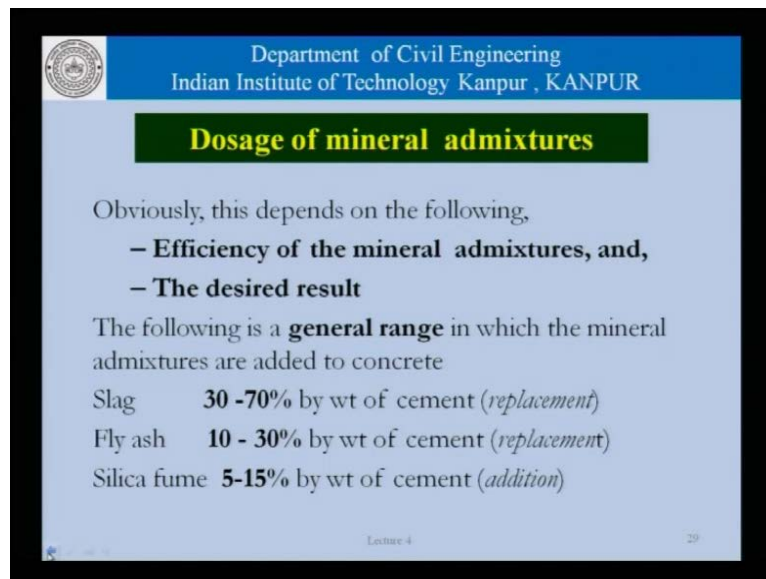
Other than these, **metakaoline** and **rice husk ash**, may also be used as a mineral admixture.

Lecture 4 28

In recent years, the following have emerged as the primary mineral admixtures used in concrete, as far as replacement of cement is concerned, ground granulated blast furnace slag, fly ash, and silica fume. Please note that, this is not all kinds of ash that we get from the thermal power plants. The thermal power plants produce primarily two kinds of ash; one is pond ash, and the other is fly ash. Pond ash does not find too much of use in concrete, even though there is effort being made, to use pond ash as well, at least as a concrete material or as

a constituent of concrete, even if not considering it as a part of cement. But fly ash is the one that has, found wide spread use, as far as the mineral admixture is concerned, and then there is silica fume of course. Other materials such as metakaoline, a rice husk ash, may also be used as mineral admixtures, provided the satisfied, whatever is the requirement that, a client or a code may choose to impose, on the use of mineral admixtures and concrete.

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Dosage of mineral admixtures

Obviously, this depends on the following,

- **Efficiency of the mineral admixtures, and,**
- **The desired result**

The following is a **general range** in which the mineral admixtures are added to concrete

Slag	30 -70%	by wt of cement	(<i>replacement</i>)
Fly ash	10 - 30%	by wt of cement	(<i>replacement</i>)
Silica fume	5-15%	by wt of cement	(<i>addition</i>)

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Now as far as the dosage of these mineral admixtures has concerned, it obviously depends on the efficiency of the mineral admixture, now what is the inefficiency of a mineral admixture. It basically is the ability of the admixture or that material, to replace cement. If to replace a k g of cement, we require more material, then the efficiency is lower. If lesser amount of material can be used, to replace the k g of cement, it is more efficient. The dosage of a mineral admixture obviously depends on the efficiency of the mineral admixture, now what is the efficiency of a mineral admixture. It is the ability of a mineral admixture, to replace cement.

If there are two mineral admixtures a and b, such that in order to replace a k g of cement, less of a is required. Then a is more efficient as a mineral admixture than b. Of course the second part of it is the desired result, what do we expect from the concrete, and that will determine what the dosage of the mineral admixture is, or how much of the mineral admixture is required to be used, in a cubic meter of concrete. The following is a general range, in which the mineral admixtures are added to concrete, as far as fly ash slag in silica fume are concerned. Now slag is used to the extent of 30 to 70 percent by weight of cement, under

replacement. Similarly fly ash is used up to 10 to 30 percent by weight of cement, again as replacement, and silica fume is usually added, in a range of 5 to 15 percent by weight of cement, in the mode of addition.

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MIX	CEMENT	MIN ADM	COMMENT
1	350	0	BASE
2	300	80	REPLACEMENT
3	350	80	ADDITION

Note: 80 kgs of MA replaces 50 kgs of cement in Mix (2)

Now let me just give an example of what replacement and addition means. If we consider a base concrete mix, which has say 350 kg's of cement per cubic meter, without any mineral admixture. Now if there is mix 2, where we have 300 kg's of cement, and 80 kg's of the mineral admixture, what has happened effectively is that, 50 kg's of cement has been replaced by, 80 kg's of the mineral admixture. In another case, if we use the same amount of cement ;that is 350 kg's, but we use 80 kg's of mineral admixture, in addition to the 350 kg's of cement.

Then this concrete mix has a mineral admixture, in addition to the cement content, or in addition to the cement. Whereas in this case, the mineral admixture is in partial replacement of cement. So if we have an example like this, where 80 kg's of mineral admixture has replaced 50 kg's of cement, then we can talk, we can we can try to define the efficiency one admixture, versus another admixture. As stated in the previous slides, fly ash and slag are typically used, in replacement, or partial replacement of cement. Whereas silica fume is often used in, addition to the cement that is there in the concrete mix.

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Dosage of mineral admixtures - Comments

- A 50% replacement by slag in a mix containing $400\text{kg}/\text{m}^3$ of cement, will thus mean a mix that has only $200\text{ kgs}/\text{m}^3$ of cement and $200\text{ kgs}/\text{m}^3$ of slag.
- Use of 5% additional silica in a similar mix, would mean a mix containing $20\text{kg}/\text{m}^3$ of silica fume in addition to the $400\text{kg}/\text{m}^3$ of the cement.

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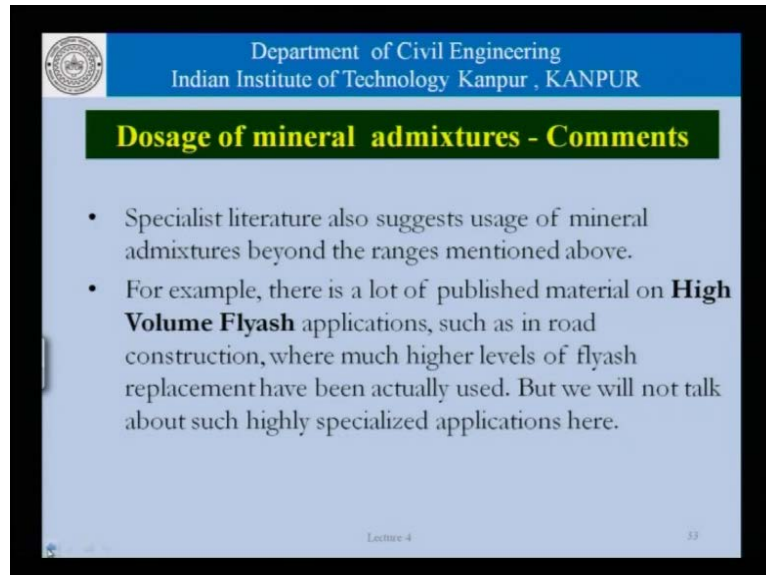
Another example that's given here, is a 50 replace. Another example given in this slide here says, a 50 percent replacement by slag in a concrete mix containing 400 kg's of cubic meter of cement, will thus mean that the mix now has 200 kg's of cement, and 200 kg's of slag. Similarly use of 5 percent additional silica in a similar mix would mean that, the mix contains 20 kg's per cubic meter of silica fume, in addition to the 400 kg's of cement per cubic meter of that concrete. Of course, we have to keep in mind that, what is the property, that's going to change.

For example in this case, if the replacement given here is a one to one replacement; that is 200 kg's of cement has been replaced by 200 kg's of slag, without any change in the properties of concrete, whether it is fresh concrete or harden concrete. Then the efficiency of the slag is one; that is it has replaced unit to unit k g to k g of the cement. It may not usually happen, we may need to use a little more of the mineral admixture, whether it is slag or it is fly ash or whatever it is, to replace a k g of cement, and that is what we will see later is the idea of the efficiency of a mineral admixture.

Of course when I say that 5 to 15 percent of silica fume can be used, or 10 to 30 percent of fly ash can be used, or 30 to 70 percent of slag can be used; that is just the normal figures. A specialist literature also suggest usage of mineral admixtures, beyond these ranges. For example there is a lot of published material on high volume fly ash, in applications such as roads, where the replacement levels for fly ash in concrete, that is much higher and has been actually used, but these are something's which we will not talk about, in this discussion in

our. But those applications which are specialized in nature are not, within the view of our discussion in this, set of lectures.

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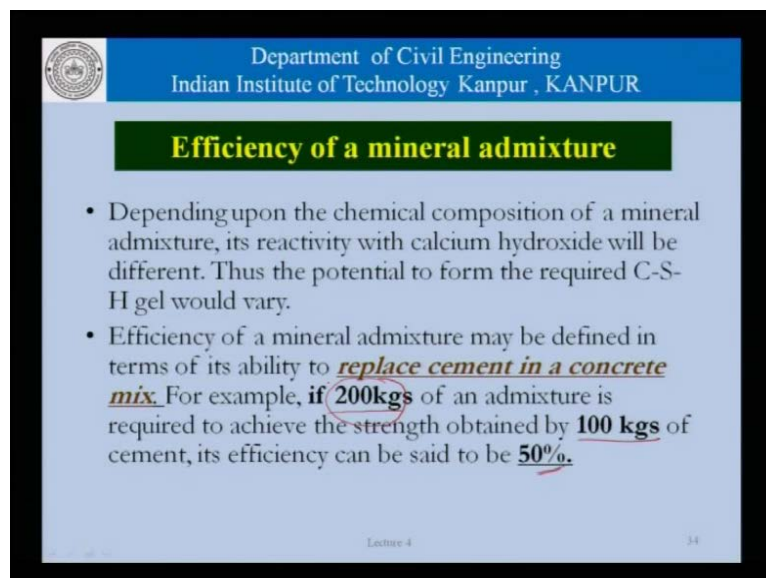
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Dosage of mineral admixtures - Comments

- Specialist literature also suggests usage of mineral admixtures beyond the ranges mentioned above.
- For example, there is a lot of published material on **High Volume Flyash** applications, such as in road construction, where much higher levels of flyash replacement have been actually used. But we will not talk about such highly specialized applications here.

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Efficiency of a mineral admixture

- Depending upon the chemical composition of a mineral admixture, its reactivity with calcium hydroxide will be different. Thus the potential to form the required C-S-H gel would vary.
- Efficiency of a mineral admixture may be defined in terms of its ability to *replace cement in a concrete mix*. For example, if 200kgs of an admixture is required to achieve the strength obtained by 100 kgs of cement, its efficiency can be said to be 50%.

Lecture 4 34

Now coming to the efficiency once again, depending on the chemical composition of the mineral admixture. Its reactivity with calcium hydroxide will be different, and thus the potential to form the required calcium silicate hydrate gel would vary. See how does a mineral admixture work. The mineral admixture works through reacting with calcium hydroxide, and if the mineral admixture is such, that it is able to react very effectively with calcium hydroxide, produce the same amount of calcium silicate hydrates or hydration

products, then it is a very efficient mineral admixture. Whereas in certain cases, for chemical composition, for any other reason, the mineral admixture may not be a very effective admixture, and therefore its efficiency will be lower.

The efficiency of a mineral admixture may therefore be defined in terms of, its ability to replace cement in a concrete mix. As I have said earlier, that if 200 kg's of an admixture is required to achieve the strength, and in this example we are using strength as the parameter, to achieve the strength obtained by 100 kg's of cement, then it's efficiency is 50 percent, because 100 kg of cement has been replaced by 200 kg's of mineral admixture, or 200 kg's of the mineral admixture were required to be used, in order to get the same output, which we were getting with 100 kg's of cement, and therefore the efficiency of that mineral admixture is 50 percent. In other words if you are given the mineral admixtures efficiency, then we know how much of that mineral admixture we should be using in a concrete mix, in order that the quality of concrete, or the desired parameter that we have; that is not compromised, by using the mineral admixture.

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Efficiency of a mineral admixture

In other words, the strength of the following two concrete mixes should be the same:

Mix A: With say 350 kgs/m³ of cement, and,
Mix B: With 300 kgs/m³ of cement and 100 kgs/m³ of MA with an efficiency of 50%.

In the example of the last slide, where we assumed that 80kg of a MA will replace 50kg of OPC, the efficiency of the MA may be taken to be about 62.5 % (50/80) .

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In other words, the strength of the following two concrete mixes should be the same, 350 kg per cubic meter of cement, or 300 kg's of cement with 100 kg's of mineral admixture, having an efficiency of 50 percent.

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Implications of MA addition

Increase in powder content of concrete [assuming that the efficiency is less than 100%, and therefore the MA added will be more than the cement (replaced)]

Increase in paste and/or mortar content of concrete

Example: Sp gr of cement and MA is 3.12 and 2.2; η of MA = 60%

Note: W, C and MA in kg/m³; Powder and paste content in liters/m³

Mix	W	C	MA	Powder	Paste
1	175 ✓	350 ✓	0	112.18	287.18
2	175 ✓	300 ✓	80 ✓	132.52	307.52

50
80 kg

Lecture 4
36

These two will produce identical strengths. If we have strength as the parameter, and we know that the mineral admixture that we are using, has an efficiency of 50 percent. In another example when we have talked about 50 kg's of cement being replaced by 80 kg's of the mineral admixture, there the efficiency can be taken to be 50 upon 80, which is 62 percent. Another implication of using mineral admixtures in concrete, is the increase in the powder content of concrete. This of course assumes, that the efficiency of the mineral admixture, is less than 100 percent, and therefore to replace any amount of cement, more of the mineral admixture is required.

This causes an increase in the paste or the mortar content of the concrete. If for example, the specific gravity of cement, and the mineral admixture, are known to be 3.12 and 2.2, and the efficiency of the mineral admixture, is known to be 60 percent. Then if we have a concrete mix here, which has water content of 175, a water cement ratio of 50 percent, and therefore you use 350 kg's of cement. So in another mix, if we want to go get the same level, we will need a 175 five kg's of water, with 300 kg's of cement but 80 kg's of mineral admixtures, instead of the 50 kg's. Now this 50 kg's of cement, is being replaced by 80 kg's of the mineral admixture. Now, since the mineral admixture is lighter, than the cement, then the volume is more. The volume is any case more, because 50 kg's is becoming 80 kg's on account of the efficiency, and then the volume is further increasing, because the densities are lower. So what is effectively happening is, that if we do a calculation, we will find that the powder content in the concrete mix, is a 112 liters, in the first case. And in the second case, it

has gone to 132 liters. The paste content therefore, which is the sum of the powder content; that is water, and the powder, is 287.18 in one case, and in the other case it is 375.2. So we have added more powder, and therefore we have caused the paste content to increase.

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In concrete engineering, the following definitions apply

- Cement + water = Paste
- Paste + sand = Mortar
- Mortar + CA = Concrete

(CA is Coarse aggregate)

What is the need to change or reiterate them ??

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Now, let us go back to a very old slide, which we saw in the first lecture. Where we had defined cement and water to be paste, paste and sand to be mortar, and mortar and coarse aggregate to be concrete.

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Implications of MA addition

Increase in powder content of concrete [assuming that the efficiency is less than 100%, and therefore the MA added will be more than the cement (replaced)]

Increase in paste and/or mortar content of concrete

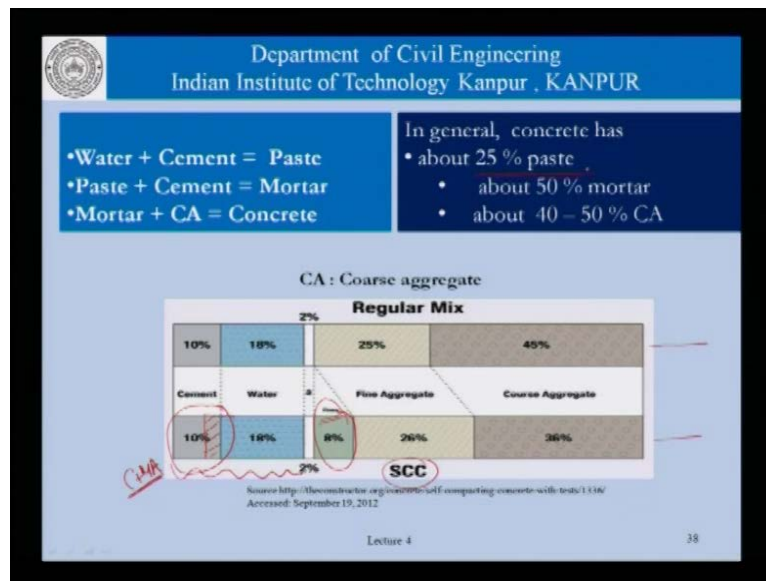
Example: Sp gr of cement and MA is 3.12 and 2.2; η of MA = 60%

Note: W, C and MA in kg/m^3 ; Powder and paste content in liters/m^3

Mix	W	C	MA	Powder	Paste
1	175	350	0	112.18	287.18
2	175	300	80	132.52	307.52

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And we had asked a question as to what is the need to change, or reiterate those definitions, in the context of modern day concrete engineering. And now we have the answer, that it is not only the cement content, which constitutes or provides the powder, as far as the concrete mix is concerned. In addition to cement, there could be mineral admixtures, whether they take part in the hydration reaction or not. Those powders, they definitely would constitute, or play a role, similar to that of cement paste, as far as the properties of fresh concrete are concerned, and therefore we need to keep this in back, and we must keep this aspect at the back of our mind, when we analyze modern concrete mixes, or we design modern concrete mixes for specific applications. And let us straight away example is already shown here. We have seen this picture before, and we talk in terms of a self consolidating concrete.

It depends on these fines, whether they are part of the fine aggregate, or they could be part of the cement, or they could be, in addition to the cement. So basically the paste content, is getting added. So we have seen this slide earlier, which is a pictorial representation, of the volumetric of a normal mix, or a regular concrete mix, and a special purpose concrete mix. The role of these fines, is what has to be understood in terms of the properties in the fresh concrete. These fines can be, considered a part of the fine aggregate, depending on what the nature of the fines is, or as far as mineral admixtures are concerned, they could be considered a part of cement plus mineral admixtures, is what constitutes the paste content, which is this much.

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Implications of MA addition

Increase in powder content of concrete [assuming that the efficiency is less than 100%, and therefore the MA added will be more than the cement (replaced)]

Increase in paste and/or mortar content of concrete

Example: Sp gr of cement and MA is 3.12 and 2.2; η of MA = 60%


Note: W, C and MA in kg/m³; Powder and paste content in liters/m³

Mix	W	C	MA	Powder	Paste
1	175	350	0	112.18	287.18
2	175	300	80	132.52	307.52

50
 80 kg
 ←

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Basic mechanism of mineral admixture action

$$\begin{array}{l}
 \text{C}_3\text{S} + \text{H}_2\text{O} \rightarrow \text{C-S-H} + \text{Ca(OH)}_2 \\
 \text{C}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{C-S-H} + \text{Ca(OH)}_2
 \end{array}$$

The above two are the basic hydration reactions for the silicates in cement. It can be seen that C-S-H gel and calcium hydroxide are direct products of the hydration reaction.

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Hydration reactions of pozzolonic material

In a classical pozzolonic reaction, calcium hydroxide formed during hydration of cement is consumed by the reactive silica (SiO_2) in the pozzolona to form the C-S-H gel, as shown below:

$$\text{S} + \text{CH} \longrightarrow \text{C-S-H (gel)}$$

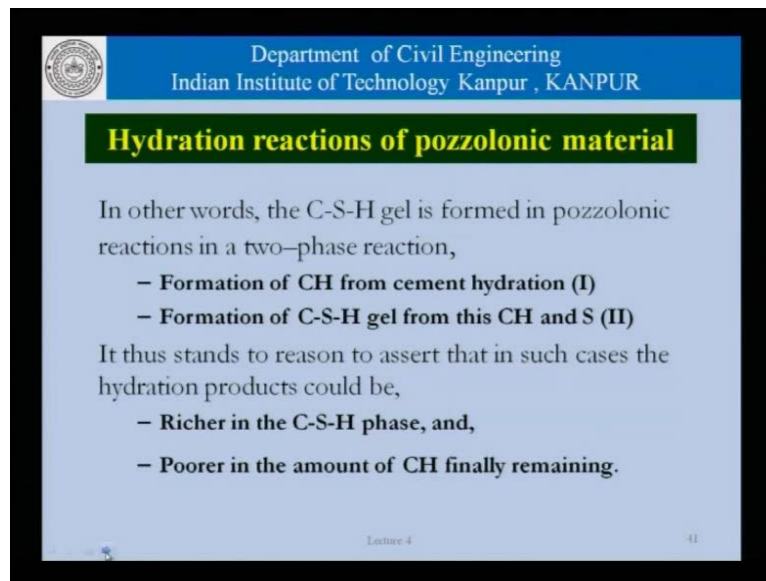
The above shows the basic pozzolonic reaction, and the fact that the pozzolonic material is not hydraulic (does not react with water), and needs CH to form the binding C-S-H gel (which is similar to the one formed during hydration of cement).

Lecture 4 40

So instead of 25 percent paste in the normal conditions, the amount of paste could go slightly higher, as we have seen for example in this case, instead of 287 liters per cubic meter is about 28 percent, it goes to about 30 percent or 32 percent. So this change of 2 percent 3 percent is not insignificant, and must be kept in mind when we are designing concrete mixes. Now let us come to the basic mechanism of mineral admixture action. normally tri calcium silicate, and the di calcium silicates, they react with water to form C S H, which is the calcium silicate hydrate, which is the normal or the most common hydration product, and a lot of calcium hydroxide.

These two are the direct products of the hydration reaction, and you have seen earlier, that the tri calcium silicate, and the di calcium silicates are the bulk, of the ordinary portland cement, and therefore these are the most common, and most voluminous kind of reaction products. As far as the classic pozzolonic reaction is concerned, the silica which is SiO_2 reacts with the calcium hydroxide, and forms the same C S H; that is the calcium silicate hydrate, and we get the mineral admixtures, reacting with the calcium hydroxide, to form the C S H, even though this silica itself is not hydraulic. It does not react with the water, and needs the calcium hydroxide, to form the binding C S H.

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Hydration reactions of pozzolonic material

In other words, the C-S-H gel is formed in pozzolonic reactions in a two-phase reaction,

- Formation of CH from cement hydration (I)
- Formation of C-S-H gel from this CH and S (II)

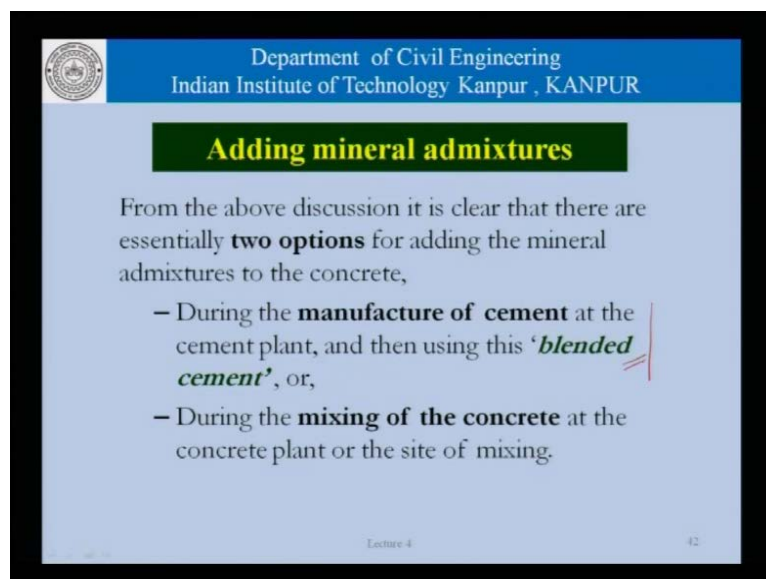
It thus stands to reason to assert that in such cases the hydration products could be,

- Richer in the C-S-H phase, and,
- Poorer in the amount of CH finally remaining.

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In other words the C S H formed in pozzolonic reactions, is really a two phase reaction in the first phase. We have the formation of calcium hydroxide from the hydration of cement. And in the second phase, we have the formation of C S H from this calcium hydroxide and the silica. It thus stands to reason, to assert that in such cases, the hydration products could be, richer in the C S H phase, and poorer in the amount of calcium hydroxide finally remaining, because part of this calcium hydroxide has been used, in the pozzolonic reaction.

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Adding mineral admixtures

From the above discussion it is clear that there are essentially **two options** for adding the mineral admixtures to the concrete,

- During the **manufacture of cement** at the cement plant, and then using this '*blended cement*', or,
- During the **mixing of the concrete** at the concrete plant or the site of mixing.

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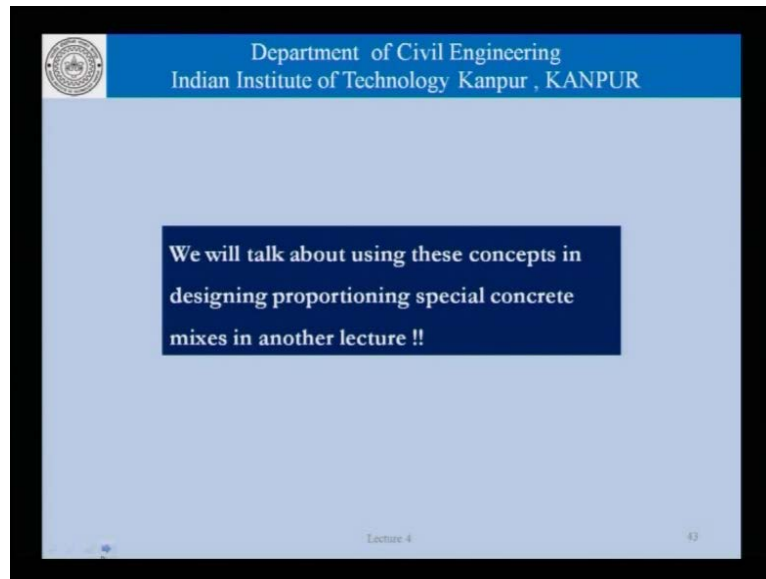
So whereas we have more C S H sitting in the concrete mix, we might have lesser amount of calcium hydroxide. And this has some implications, in concrete engineering, in certain applications, as the literature suggests.

Now, how are mineral admixtures added to the concrete mix. There are basically two options that we have; one is during the manufacture of the cement, and that happens at the cement plant, and there, and what do we get, blended cements; that is this mineral admixture is added to the cement at the cement plant, and the cement is not O P C, what the product of the cement plant now, is not ordinary Portland cement, it is blended cement, because the mineral admixture has already been added, to the O P C. The other option of course, is to add the mineral admixture, during the mixing of the concrete, at the concrete plant, or at the site of mixing. in this case, the cement used is O P C, and the mineral admixture is added, in an appropriate dosage in the plant.

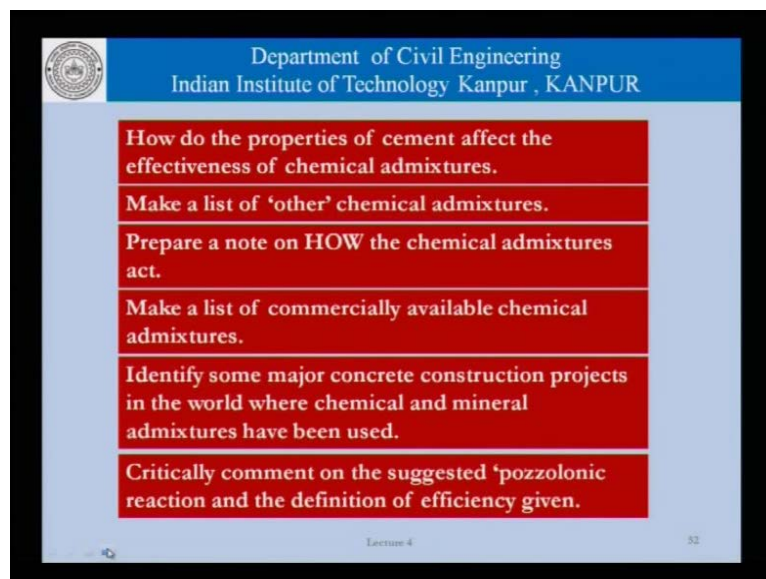
So in this case, the cement manufacturer, takes responsibility for the addition of mineral admixtures, and ensures and assures the user, that the blended cement meet certain specifications and so on, and very often, the amount or the exact amount at least, of the mineral admixture, used is not known. What we know, is the performance of the blended cement, that yes it has a certain initial setting time, or certain final setting time, it has certain strength development characteristics. Though it is not o p c alone, it is a pozzolonic or a blended cement. In the later case, where the mineral admixture is added to the concrete at the batching plant. The batching plant or the concrete manufacture, takes responsibility to make sure that, a concrete produced has the required properties, in terms of strength, workability and so on, and must use only the right amount of mineral admixtures.

We will talk about some of these concepts once again, when we are proportioning, special concrete mixes at another time. With this we come to an end of the discussion today, where we have talked about, chemical admixtures added to concrete, and the mineral admixtures added to concrete, also eluded to the manufacture of blended cements, where the mineral admixtures are added to the, cement at the time of cement manufacture, at the cement plant.

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Now before we close, as usual we will have some questions. How do the properties of cement affect the effectiveness of chemical admixtures. I would like you to make a list of the other chemical admixtures; that is we talked about just one; that is the corrosion inhibitors, there are several others, and if you see the literature, you will find other chemical admixtures which are used, which have reported history, where these admixtures have been used for special purposes in concrete construction. I would like you to prepare a note, on how the chemical admixtures actually act. We would not get involved with the mechanism of action of, either the set regulator, or a water reducer or the air entrainer, but it's an interesting area,

which you would like to see, and see how cement chemists actually work, or how chemist, how chemistry, and cement technology comes together in this very interesting area. I would like you to make a list of commercially available chemical admixtures, in a region.

There are different chemical admixtures, there are different chemicals which are used as chemical admixtures, in different parts of the world, and that will be an education, for anybody who tries to understand this a little more. I would like you to identify, some major concrete construction projects in the world, where chemical and mineral admixtures have been used, and I would like you to critically comment, on the suggested pozzolonic reaction, and the definition of the efficiency of mineral admixtures that we have talked about. Specifically please try to see, how this reaction is different, in the case of blast furnace slag, or silica fume, or fly ash, in terms of their reaction with calcium hydroxide, and what is the definition of efficiency which is given. We defined efficiency in terms of, effectiveness of a effectiveness of a mineral admixture to replace the cement, how does it work for the different mineral admixtures, and with that, we come to a close of the discussion today.

Thank you