

Admixtures And Special Concretes

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Lecture 07 Chemical Admixtures: Introduction

Chemical admixtures (Monteiro sections 8.1 to 8.4):

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What is a chemical admixture?



- Any chemical additive to the concrete mixture that enhances the properties of concrete in the fresh or hardened state
- Does not typically include paints and protective coatings (for steel or concrete)
- ACI 116R defines the term admixture as “a material other than water, aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing”.



So primarily we are looking at additives that are included in concrete from various perspectives, primarily to make an influence on the early properties of concrete either in terms of workability or sometimes imparting properties that are required for long term performance.

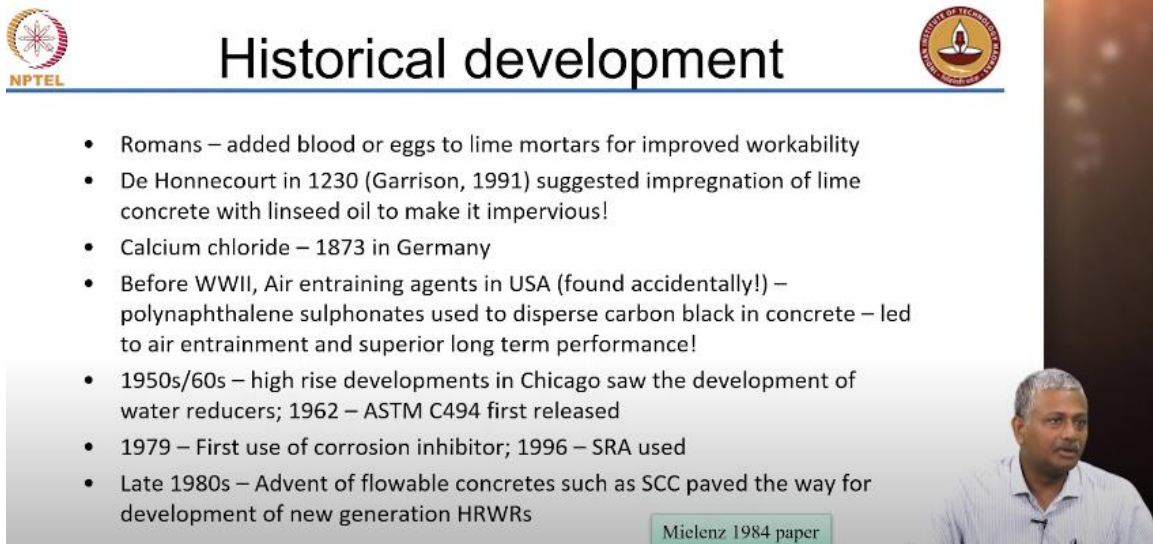
What is a chemical admixture? It is an additive to the concrete mixture that enhances the properties of concrete in the fresh or hardened state. There are functionalities that each admixture gives, which are not the same across admixtures. Nevertheless for the purposes of definition we do not include paints and coatings that are applied on the concrete surface or on the steel surface separately as an admixture.

As the name implies add - mixture means you are adding this to the concrete mixture. So if you look at the official definition by American Concrete Institute Committee 116R, it says admixture is a material other than water, aggregates, hydraulic cement and fibre

reinforcement used as an ingredient of concrete or mortar and added to the batch immediately before or during its mixing. So something that we put into the concrete. Now if you look at the class of chemicals which are waterproofing agents, there are different types of waterproofing agents. There are some chemical admixtures that you add along with the concrete itself. On the other hand there are also other waterproofing agents that are actually used as coatings on the concrete surface. You are probably aware of some of these which are used in typical households and so on. But it becomes an admixture only when it is put into the concrete mix.

Historical development:

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The slide features the NPTEL logo on the left and the IIT Bombay logo on the right. The title 'Historical development' is centered at the top. Below the title is a bulleted list of historical milestones in concrete technology. A small video inset in the bottom right corner shows a man speaking, with a caption 'Mielenz 1984 paper' below it.

- Romans – added blood or eggs to lime mortars for improved workability
- De Honnecourt in 1230 (Garrison, 1991) suggested impregnation of lime concrete with linseed oil to make it impervious!
- Calcium chloride – 1873 in Germany
- Before WWII, Air entraining agents in USA (found accidentally!) – polynaphthalene sulphonates used to disperse carbon black in concrete – led to air entrainment and superior long term performance!
- 1950s/60s – high rise developments in Chicago saw the development of water reducers; 1962 – ASTM C494 first released
- 1979 – First use of corrosion inhibitor; 1996 – SRA used
- Late 1980s – Advent of flowable concretes such as SCC paved the way for development of new generation HRWRs

Mielenz 1984 paper

Now there has been historical evidence of use of chemicals of different forms for centuries. For instance if you look at the Roman times, they had added blood or eggs to lime water for improved workability. A lot of Chinese heritage structures they have actually found traces of having used blood as an ingredient. Blood is quite interesting from the perspective of its ability to actually make the mixture more cohesive. And of course it does not mean that we cut open our bodies to put blood into concrete. Nowadays we have chemicals available but in the past I presume it was animal blood and not the person's blood who was actually using the mixing himself. So yeah, eggs are quite common in India also in several locations of India especially in the decorative plasters that were made with lime. Eggs were a common feature. If you go to the Chettinad type of construction in southern Tamil Nadu that is also incorporating the egg white as an ingredient in the lime water. And that egg white basically gives a nice glassy finish to the exterior surface of lime waters.

In 1230 you have De Honnecourt who suggested impregnation of lime concrete with linseed oil to make it impervious. It is probably one of the first documented uses of a

waterproofing agent. Linseed oil is of course most oils are water repelling. They do not mix with water. So if you impregnate concrete with this kind of wax or an oil, it is not going to allow water to come in. So that is probably one of the first uses of waterproofing agents.

Calcium chloride which is well known as a very good accelerator for concrete, setting accelerator for concrete. The first use was described in 1873 in Germany and before World War II, air-entraining agents were used in the US and this was found accidentally based upon certain types of chemicals that were being used.

And again what these chemicals were essentially these chemicals led to the development of the later age water reducers. Polynaphthalene sulphonates which are well known as water reducing agents were actually used to disperse carbon black and concrete just before World War II. And that it was determined that these were actually giving rise to the air entrainment. Now air entrainment is typically required in concrete when we want resistance to freezing and thawing. So again this gave birth to a different class of chemicals which we wanted to use for specific purposes to make concrete durable in certain environments.

Now a lot of high rise developments in Chicago led to the development of the first water reducing chemicals. So already polynaphthalene sulphonates had been used previously and they found that using these polynaphthalene sulphonates they could cut back on the water also to produce concrete that was workable enough and in doing so they were able to enhance the strength of the concrete. Now obviously the primary use of high strength concrete would have come about for the high rise buildings. I do not know how many of you are familiar with the skyline of Chicago. Many of you may have seen pictures of it. It has got the most amazing set of high rise buildings that you can find in a city even better than New York because each building is an architectural marvel. But that is where a lot of the initial technologies for high rise buildings were investigated and this first usage of water reducers officially documented was with the high rise buildings in Chicago.

And soon after that in 1962 the standard for chemical admixtures ASTM C494 which is now the benchmark worldwide with respect to standards on different types of chemical additives that was first released.

In 1979 first use of corrosion inhibitor in concrete and today of course corrosion inhibitors are still trying to find inroads into the market they are not as prevalent as they need to be but yes people have started realizing that you can use corrosion inhibitors in concrete as a protection mechanism against corrosion instead of trying to protect the reinforcing steel which is a much more expensive proposition.



And in 1996 the shrinkage reducing admixture started getting used. Now shrinkage is a major problem with concrete as we discussed earlier. You can add additives to the concrete mixture to take care of shrinkage also and first use was documented in 1996.

Late 1980s there was the advent of flowable concrete in Japan, people started using self-compacting concrete. People had been experimenting with trying to make concrete very workable and in the late 80's the first set of official applications of self-compacting concrete came into being one of those that were quite popular in the bridge which we call as Akashi Kaikyū bridge in Japan. In any literature in self-compacting concrete that is one example that you will get to read. So from then on SCC became quite popular and from then we came to a new era of high range water reducers that are specifically formulated for the purpose of concrete usage.

In the past whatever people were using where chemicals from other industries that were applied just by trial and error tried to find out whether these could be useful for concrete but later with the advent of new generation HRWR that is when people started actually developing these chemicals for concrete usage. Most of the historical development is captured in this paper by Malins 1984 paper in Concrete International which is one of the interesting journals from American Concrete Institute. Now this journal of course is not very academic in nature, it emphasizes a lot on concrete practice and also deals a lot with the current developments in the concrete industry presented to a wider audience than actual researchers.

Classification of chemical admixtures:

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Classification

- Water reducers
- Set-controlling chemicals
- Air entrainers
- Specialty admixtures
 - Viscosity modifiers
 - Corrosion inhibitors
 - Shrinkage reducing admixtures
 - SBR latexes
 - Others
- Specialty coatings including curing compounds (technically not chemical admixtures!)

Common characteristics of chemical admixtures:

1. Water soluble
2. (Mostly) Organic

Helpful to understand polymer structure



Now for the purposes of modern day construction we divide chemical admixtures into various categories the most common categories are the water reducers. Then we have set controlling chemicals either set acceleration or set retardation. And then we have air entraining chemicals which are introducing air wantedly to the concrete for the purposes of providing durability and freezing conditions. Specialty admixtures are of different types,

sometimes you want to make your concrete thixotropic or stabilize high flowing concrete and prevent segregation, so we use viscosity modifiers.

To protect the steel from corrosion by inhibiting the corrosion from happening inside the concrete which can be a mechanism both affecting the steel or the concrete. So in this case we call it corrosion inhibition or corrosion inhibitors are the admixtures that are used. Shrinkage reducing admixtures for the obvious purpose of reducing the extent of shrinkage that happens in concrete. There are also polymeric materials like latexes which are used in concrete primarily for providing some flexibility and better bonding ability to repair materials that are applied to concrete. Now every time you do patch work with mortars when concrete is broken off or spalled off from a section of the building we use these special mortars to patch up these locations and to produce patches that bond well with the substrate and also have very little shrinkage, One of the common ingredients that we use in such mortars is latex. Latex is basically rubber, polymer which is basically derived from rubber and there are other specialty chemicals which we can use for other purposes which we will talk about later in the course of this chapter.

Now specialty coatings also include curing compounds. Now curing compounds are technically not chemical admixtures but we will still have a discussion of those because they are getting increasingly important in this day and age when we have little access to good quality water for construction. We of course need water for making concrete. There is no doubt about it but the water for curing can be avoided to some extent if we apply these curing compounds in a proper manner.

Now if you look at all the classes of chemical admixtures there are some common characteristics that we have. One very important characteristic is all of these are water soluble. All the admixtures that are added in the concrete have to be water soluble because if they are not then they will not get mixed up in the overall concrete system. They will remain as such if they do not mix in the water, if they do not dissolve in the water they will not get distributed evenly in the structure of the concrete. Mostly these chemicals are organic of course that does not mean inorganic chemicals are not used like I already told you about calcium chloride which is a very effective accelerator. There are inorganic chemicals also but for the most part most chemical admixtures are organic and as a result of them being organic it is obviously helpful for us to understand the polymer structure because organic chemicals are basically polymeric in nature and water soluble polymers.

Polymer Structures:

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The slide, titled "Polymer structures", features the NPTEL logo on the left and the Indian Institute of Technology Bombay logo on the right. The main title "Polymer structures" is centered at the top. Below it, the subtitle "Synthetic Water-Soluble Polyelectrolytes" is displayed. The slide illustrates five types of polymer structures:

- Type of monomer:** Represented by three building blocks: a light blue square, a black square, and a black circle.
- Length (Mw):** A linear chain of ten light blue squares.
- Branching, cross-linking:** A central light blue square connected to four other light blue squares in a cross shape.
- Charge, counter-ions:** A linear chain of ten light blue squares, each with a negative charge symbol ($-$). To the right, a counter-ion M^{+n} is shown.
- Co-polymers:** A linear chain of ten squares, alternating between light blue and black squares, with a black circle in the middle.

At the bottom left, the text reads: "P.K. Mehta and P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials". At the bottom right, it says: "Courtesy from Carmel JOLI". A small inset video of a man speaking is visible in the bottom right corner of the slide area.

Polymers are composed of many units of individual components which we call as monomers or sometimes we just call it mer, single block is a mer. And there are different ways of polymerizing. You have obviously the addition polymerization in which the same unit keeps joining together under some conditions of temperature and pressure. Alternatively you may have two different mer units which come and join together in a reaction which we call as condensation. So you have either addition polymers or condensation polymers. Now of course when you go through admixture chemistry in more detail you will see that most polymers are produced by the condensation mechanism and usually to have this condensation happen you have additional chemicals that you need to actually pump into the system for enabling this condensation to happen.

So one important aspect as far as the effectiveness of the polymer is concerned is the length of the polymer. The length obviously means how many units are joined together to make the chain. The length obviously also affects the molecular weight of the polymer. The greater the length the greater the molecular weight.

So when you start looking at the mechanism by which these polymers interact inside the concrete system then you will start appreciating why this particular aspect of length of the polymer is important. Now the structure of the polymer could be different. Some polymers are long chain polymers, some other polymers may be branched and you may have side chains of the main polymer that are quite large and bulky. When we look at the mechanism of action of some of the water reducing chemicals you will understand how these polymer structures tend to affect the overall performance of your polymer. Some polymers may

carry a charge, there may be some counter ions present; either a positively charged or negatively charged system may be present in the polymers. Again this influences the way that these charged particles or charged polymeric chains interact with the cement to lead to certain properties in the cementitious system. Copolymers have more than one type of unit to make the polymer. So all of these aspects need to be understood in a much more detailed fashion if you want to go into chemical admixture manufacture because controlling the proportions of the individual components, controlling temperature, controlling the pressure, all of these are critical in trying to get an understanding of what type of ultimate chemical you end up producing.

Water Reducers:

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Water Reducers

- Normal (plasticizers) ←
- High-range (Superplasticizers)



Water reducers typically are classified either as plasticizers or normal water reducers and super plasticizers or high range water reducers. Now what do you think could be the meaning of a water reducer? It reduces water obviously. What is the benefit of reducing water? When you reduce water in concrete, you automatically increase the strength. That is the primary impact of water reducers and as I said the major development happened in the high rise building industry where the purpose was to produce higher strengths without using too much water in the system. If you are pumping this concrete to higher elevations, if you keep on adding more water obviously strength is going to drop. So you need to increase the workability without adding water.

Broad Classification of water reducers:

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Broad classification

Water Reducers

- Normal
5 - 8% water reduction
- Mid-range
8 - 15% water reduction
- High range
15 - 25% water reduction

Up to 40% possible!

Water reduction??

- For a given workability, the water demand is reduced, thus resulting in higher strength and durability.
- For a given w/c and strength, workability can be increased.
- For a given w/c, strength and workability, the quantity of cement can be reduced

Apart from normal and high range there is also a mid-range water reducer. So all these names are derived from the fact that you can reduce water content to a certain extent with each of these chemicals. With a normal water reducer you can get 5 to 8% water reduction. With mid-range you can get 8 to 15%. Well it depends about what people usually use as mid ranges but most mid ranges will go up to 15% water reduction. High range typically what is required is 15 to 25 but these days you have up to 40% water can be reduced, significant amounts of water can be reduced to produce workable concrete.

So what is water reduction? Basically for a given workability that means without changing the slump of your concrete you can reduce some water by the addition of these admixtures and reduction of that water leads to a higher strength and because your water cement ratio is low it also leads to higher durability.

So strength and durability are enhanced but your workability is constant. Now what if I do not want to change my water cement ratio? I keep my water cement ratio constant. I simply add this plasticizer then it increases my workability and makes my concrete more flowable. So I am using these chemicals in concrete by keeping the water cement ratio constant.

But the most important is the third one, the most important application of super plasticizers in modern day understanding of concrete should be taken as a third one which says that for a given water to cement ratio and for the same strength and workability level the quantity of cement can be reduced. Now how can this happen? We have designed concrete with a particular cement content with a particular water cement ratio. Now I am telling you that if you use a chemical admixture you can cut down on the cement. How can that happen? So just for an example let us say there are two concrete mixtures.

Mix 1 has 400 kilograms of cement and 200 kilograms of water.

Mix 2 I have used a water reducer which cuts 20% of my water. I have 160 kg of water content here. Now I want to maintain the same water to cement ratio which is 0.5, 200 by 400 0.5. So technically I should be able to produce this concrete with 320 cement content. So with a water reducer.

Does this mean that I can cut down my water to 120 kg and cut down my cement to 240 kg? Probably not. You may not get the same effectiveness out of that system but what you can get out of 400 kg you can get quite easily out of 320 kg also.

So what does this mean? You have used some chemical which may add to the cost of your concrete perhaps but that cost enhancement due to the chemical is easily offset by the cost reduction by using less cement but more important than cost? Carbon footprint.

Today we need to increasingly talk about sustainability, carbon footprint. Less cement you have in your concrete the less is the carbon footprint of the concrete. Less CO₂ emission from the concrete, less energy utilization, embodied energy of the concrete is also lower. So this is a very impactful statement that you can make by convincing people to start using water reducing chemicals. Now interestingly in our country there are still a lot of jobs where water reducers are not even permitted. After nearly about 70 years of research data have been published in water reducers there are still organizations that will not permit you to use water reducers. That is really unfortunate because for M20 concrete, I have seen examples where people have been using 400 kilograms of cement per cubic meter for M20 concrete. Why do they do that? Because they want to get workability, they push up their water content significantly to 200 or 220 kilograms because without a water reducer you need to have sufficient amount of water to get workability. So if you do not have that much water it would not be workable. So you push up your water so you also have to push up your cement because your water cement ratio is what is determining the strength.

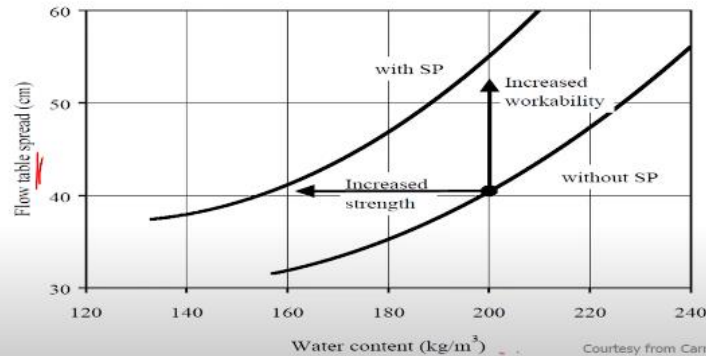
So as a result I have seen several applications for low grade concrete like M20, M25 where people are using as much as 400 kilograms of cement and that is really a criminal wastage of resources. We have to really put a stop to this. So whatever you learn from this course, at least learn this one thing to convince your management to use super plasticizers to cut down the cement in the concrete rather than to make concrete workable or anything which is obviously important but the most important aspect is cutting down cement usage in concrete. There is no other means of reducing CO₂ footprint and embodied energy in concrete as much as utilization of less cement in concrete. Cement is the single largest contributor to CO₂ emissions from concrete. So cut down cement you get that and chemical admixtures can help you do that.

Effect of water reducers:

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Effect of water reducers



P.K. Mehta and P.J.M. Monteiro, Concrete: Microstructure, Properties, and Materials

Courtesy from Carmel JOLICOEUR

Now this is a very simple way of looking at it about looking at water reducers. So this is the workability in terms of spread measured in a flow table test and that is the water content of the x axis. So what does this say? This says that as you increase the water content the workability increases, flow table spread increases. If you add a super plasticizer to a concrete you shift this curve towards the left. In other words if you choose a given water content the choice of inclusion of super plasticizers leads to increased workability. If you choose the same level of workability you can reduce your water content to get increased strength and durability.