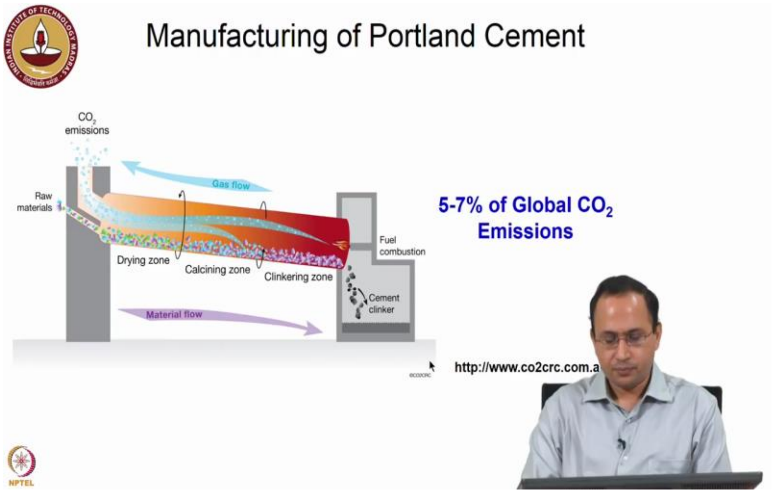
Advanced Topics in the Science and Technology of Concrete
Dr. Piyush Chaunsali
Department of Civil Engineering
Indian Institute of Technology, Madras
Calcium Sulfoaluminate Cement-Based Binder: Properties and Applications
.

(Refer Slide Time: 0:28)



Manufacturing of Portland Cement

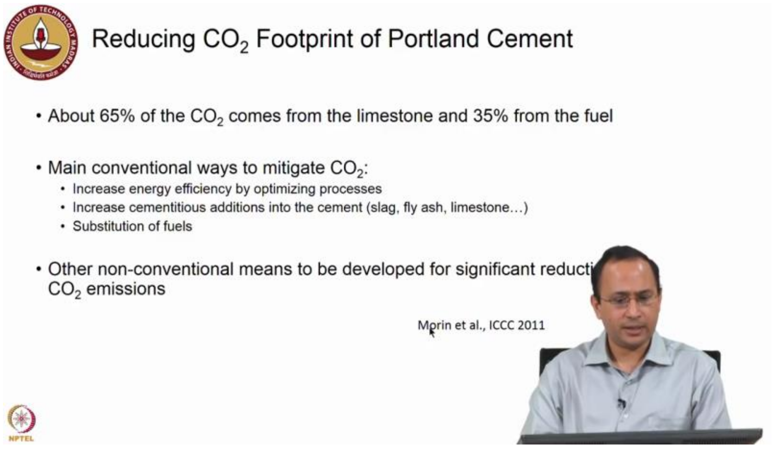
5-7% of Global CO_2 Emissions

http://www.co2crc.com.a

Good morning everyone, today we are going to discuss a next-generation of cement that is Calcium Sulfoaluminate cement-based Binder. We will look into its properties and applications.

Concrete is the most used man-made material in the world. So it is obvious that we need to look into the carbon footprint of Portland cement, which is the binding phase of Concrete. 5 to 7 percent of global CO_2 emission is attributed to Portland cement manufacturing.

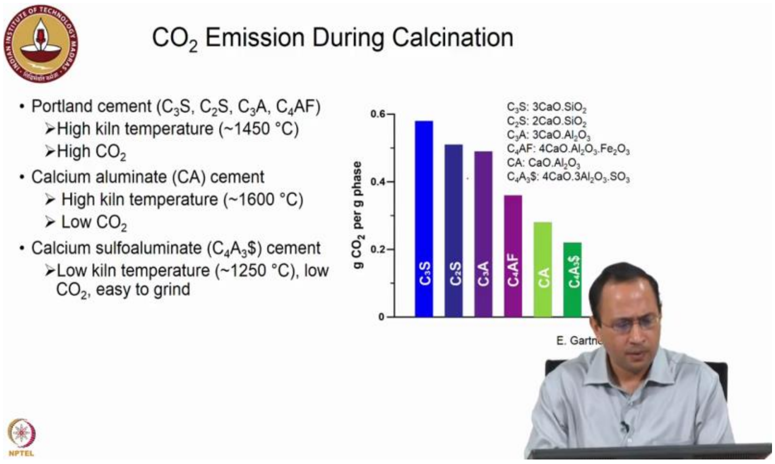
(Refer Slide Time: 0:58)



Reducing CO_2 Footprint of Portland Cement

- About 65% of the CO_2 comes from the limestone and 35% from the fuel
- Main conventional ways to mitigate CO_2:
  - Increase energy efficiency by optimizing processes
  - Increase cementitious additions into the cement (slag, fly ash, limestone…)
  - Substitution of fuels
- Other non-conventional means to be developed for significant reducti
  CO_2 emissions

Morin et al., ICCC 2011



CO_2 Emission During Calcination

- Portland cement (C_3S, C_2S, C_3A, C_4AF)
  - ➢High kiln temperature (~1450 °C)
  - ➢High CO_2
- Calcium aluminate (CA) cement
  - ➢ High kiln temperature (~1600 °C)
  - ➢ Low CO_2
- Calcium sulfoaluminate ($C_4A_3\$$) cement
  - ➢Low kiln temperature (~1250 °C), low CO_2, easy to grind

C_3S: $3CaO.SiO_2$
C_2S: $2CaO.SiO_2$
C_3A: $3CaO.Al_2O_3$
C_4AF: $4CaO.Al_2O_3.Fe_2O_3$
CA: $CaO.Al_2O_3$
$C_4A_3\$$: $4CaO.3Al_2O_3.SO_3$

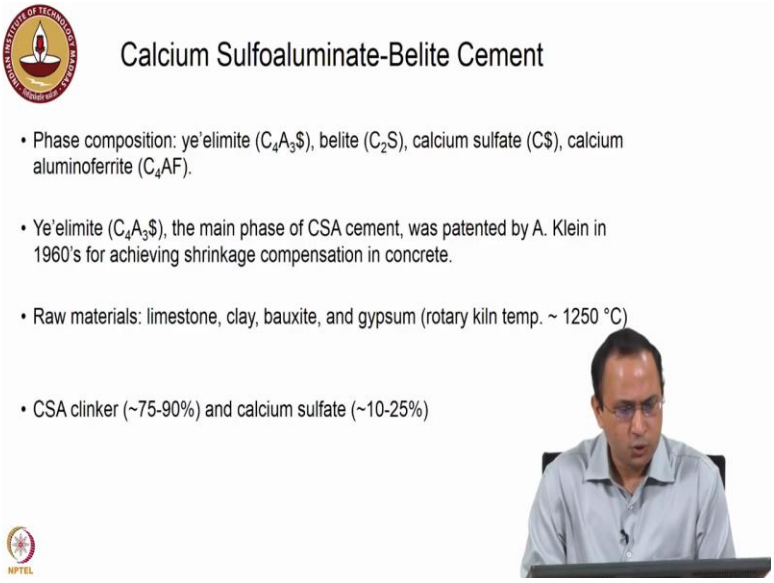
E. Gartn

Primarily it is due to the calcination of limestone which is used to manufacture Portland cement. So, how can we reduce the carbon dioxide footprint of Portland cement? Most of the CO_2 is arising from the calcination of limestone. There are conventional ways of reducing CO_2 emission like increasing energy efficiency by optimizing processes and increase the cementitious additions into cement. We have been doing that for a while, like adding slag, fly ash, limestone. Also we can think about substituting currently using fuels by environmentally friendly fuels.

But we need to think of non conventional ways if we really want to significantly reduce the CO_2 emissions during the Portland cement manufacturing. So here is the graph which compares the CO_2 emission of individual phases present in Portland cement. So let us look into the CO_2 emission of various phases does in Portland cement. C_3S has the highest CO_2 emission followed by C_2S, C_3A and C_4AF. Now if we compare it with calcium aluminate, which is the main phase of calcium aluminate cement, the carbon dioxide footprint is quite low.

And C_4A_3S, which is calcium Sulfoaluminate phase , which is the main phase of CSA based cements is the least among all these phases. Very high kiln temperature is used to manufacture Portland cement, roughly around 1450 degrees Celsius . But to make calcium Sulfoaluminate cement, we need to go only to 1250 degrees Celsius. So we can cut down the kiln temperature by 200 degrees Celsius. In addition to that we need less grinding energy because the calcium Sulfoaluminate cement clinker is more porous. So all these advantages lead to reduction in CO_2 emissions and energy requirement.

(Refer Slide Time: 3:13)



Calcium Sulfoaluminate-Belite Cement

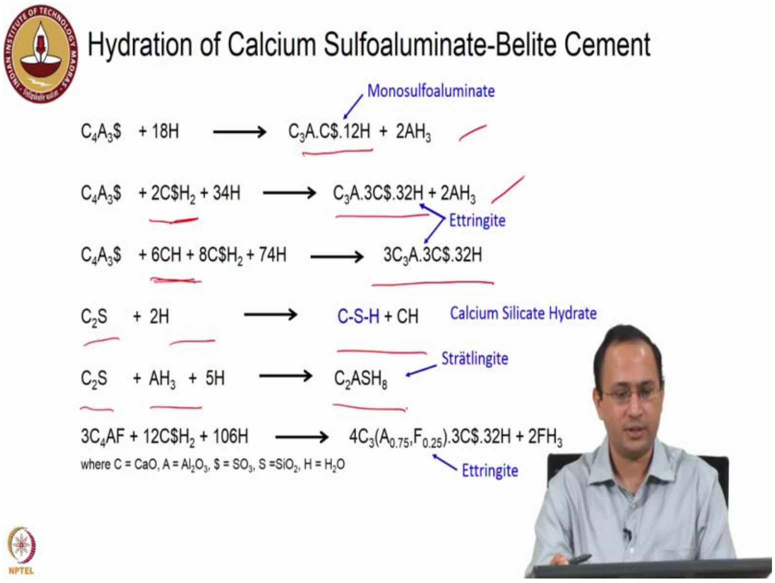
- Phase composition: ye'elimite ($C_4A_3\$$), belite (C_2S), calcium sulfate ($C\$$), calcium aluminoferrite (C_4AF).
- Ye'elimite ($C_4A_3\$$), the main phase of CSA cement, was patented by A. Klein in 1960's for achieving shrinkage compensation in concrete.
- Raw materials: limestone, clay, bauxite, and gypsum (rotary kiln temp. ~ 1250 °C)
- CSA clinker (~75-90%) and calcium sulfate (~10-25%)

So, what is Calcium Sulfoaluminate Belite cement? It comprises of Ye'elimite (C_4A_3S) also called Calcium Sulfoaluminate, Belite as you know also present in Portland cement. But it has a lot of Calcium Sulphate and Calcium Aluminate Ferrite, C_4AF. C_4A_3S is the main phase of CSA cement. It was patented by Alexander Klein in 1960s at the University of California Berkeley, but the goal was to achieve shrinkage compensation in concrete. At that time the focus was shrinkage compensation by inducing expansion in concrete. Also important thing to note is you do not need different kinds of raw materials. It is the same what is used to make Portland cement. So limestone, clay, bauxite and gypsum is used to make this Calcium Sulfoaluminate cement. But the kiln temperature has to be around 1250 degrees Celsius.

(Refer Slide Time: 4:39)

Existing CSA-Based Products

- U.S.A.
  - Buzzi CSA Cement
  - Komponent by CTS Cement
  - Calcium Sulfoaluminate Cement by Royal White Cement
- Europe
  - Zero Shrinkage Concrete Products by Primekss, Latvia
- China
  - CSA Cement by Oreworld Trade (Tangshan) Co. Ltd.



Hydration of Calcium Sulfoaluminate-Belite Cement

$C_4A_3\$ + 18H \longrightarrow \underline{C_3A.C\$.12H} + 2AH_3$ Monosulfoaluminate

$C_4A_3\$ + \underline{2C\$H_2} + 34H \longrightarrow \underline{C_3A.3C\$.32H} + 2AH_3$ Ettringite

$C_4A_3\$ + \underline{6CH} + 8C\$H_2 + 74H \longrightarrow \underline{3C_3A.3C\$.32H}$

$\underline{C_2S} + \underline{2H} \longrightarrow \underline{C\text{-}S\text{-}H + CH}$ Calcium Silicate Hydrate

$\underline{C_2S} + \underline{AH_3} + 5H \longrightarrow \underline{C_2ASH_8}$ Strätlingite

$3C_4AF + 12C\$H_2 + 106H \longrightarrow 4C_3(A_{0.75},F_{0.25}).3C\$.32H + 2FH_3$ Ettringite

where $C = CaO$, $A = Al_2O_3$, $\$ = SO_3$, $S = SiO_2$, $H = H_2O$

The CSA clinker has roughly 75 to 90 percent in clinker, rest is calcium sulphate. It is important to look into what exists. So, these are the existing CSA based products. In USA, I think there are 3 companies now which make this CSA cement Buzzi CSA cement, Komponent by CTS company and the Royal White cement company makes CSA cement. Obviously the application is different, sometimes they sell it as a rapid set cement, sometimes they sell it as zero shrinkage cement, that depends.

In Europe that this Primekss, a company based in Latvia, it does not sell cement per se but itself concrete products. They sell it zero shrinkage concrete products. In China this company has been manufacturing for decades actually. So, Oreworld Trade Co. So, these are the existing products on the market. It is good to know that there is something which exists which is based on CSA cement.

Now we will look into hydration of calcium Sulfoaluminate based cement. I will use Ye'elimite and calcium Sulfoaluminate at the interchangeably. Ye'elimite which is C_4A_3S can hydrate just in presence of water and gives monosulphate. You have mono sulphate and aluminum hydroxide, also called gypsite. When there is the presence of gypsum, you have a formation of Ettringite. And again you will have aluminum hydroxide. Now, when there is enough lime in the system, which may be the case when you have enough of C_2S in CSA cement or it is used with Portland cement, you have only Ettringite forming, so no aluminum hydroxide. C_2S can react with water and form CSH, calcium silicate hydrate. And the C_2S can also react with this aluminum hydroxide which is coming from these two reactions and form stratlingite. So these are the possible reactions which may take place depending on obviously composition of CSA cement. Although C_4AF is in minor amount but it can also hydrate in presence of gypsum and form Ettringite.

$$C_4A_3S + 18H \rightarrow C_3A.C\$.12H + 2AH_3$$

$$C_4A_3S + 2CSH_2 + 34H \rightarrow C_3A.3C\$.32H + 2AH_3$$

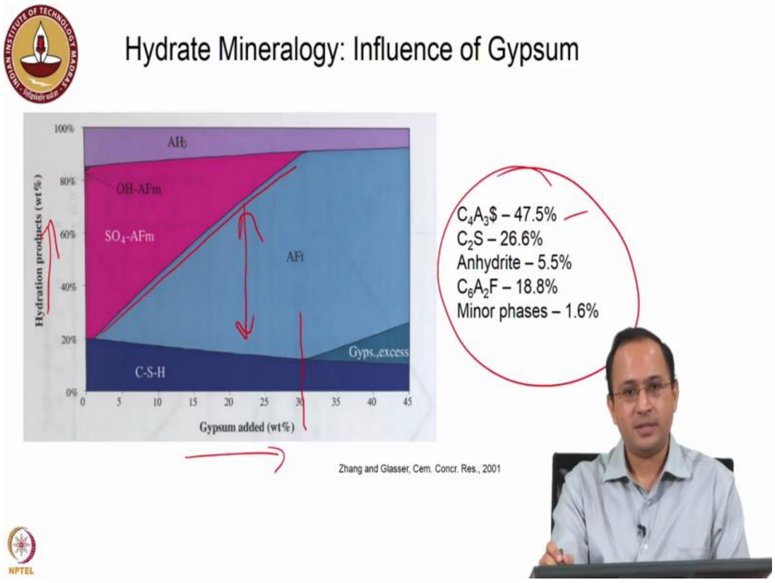
$$C_4A_3S + 6CH + 8C\$H_2 + 74H \rightarrow C_3A.3C\$.32H$$

$$C_2S + 2H \rightarrow C\text{-}S\text{-}H + CH$$

$$C_2S + AH_3 + 5H \rightarrow C_2ASH_8$$

$$C_4AF + 12C\$H_2 + 106H \rightarrow 4C_3(A_{0.75,}F_{0.25}).3C\$.32H + 2FH_3$$

(Refer Slide Time: 7:37)



Hydrate Mineralogy: Influence of Gypsum

$C_4A_3\$$ – 47.5%
C_2S – 26.6%
Anhydrite – 5.5%
C_6A_2F – 18.8%
Minor phases – 1.6%

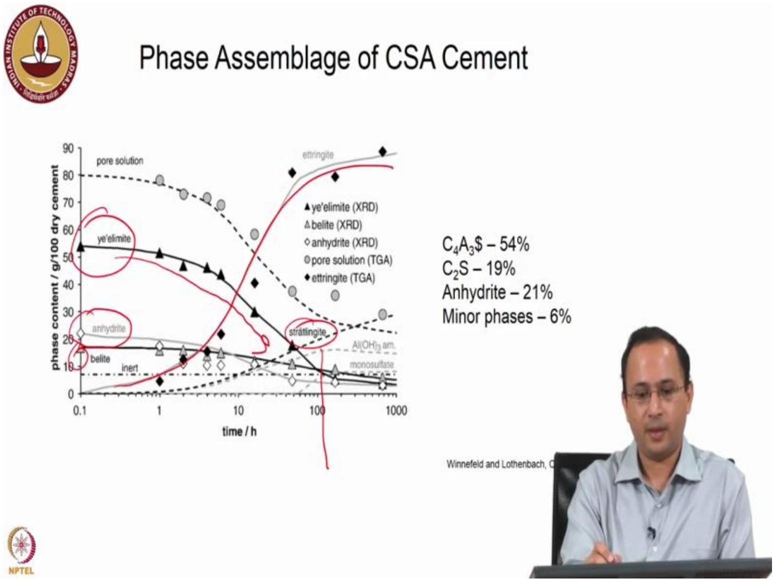
Zhang and Glasser, Cem. Concr. Res., 2001

So, these reactions are important to always look into. And we know that whenever we have formation of Ettringite, the reaction can be expensive. We will come down to this point later. How can be leverage this expansion in making concrete durable? Here is the study done by Zhang and Glasser in early 2000. If you look into the hydration products, Y axis we have hydration products and what happens when you increase the amount of gypsum.

When there is no gypsum, you will have formation of monosulphate. But as you increase the amount of gypsum, you form a AFT phase or Ettringite, that is what it is showing basically. So with the increase in gypsum you see AFT phase is increasing. But beyond a point, like here in this case we see this 30 percent limit, you will have excess gypsum. Also we see formation of aluminum hydroxide. So, this study was done on this particular type of cement, here is the phase composition, you have 48 percent of Ye'elimite, 27 percent of C_2S, very small amount of Anhydrite.

It depends, what is a form of your calcium sulphate. It could be in form of anhydrite, could be in form of gypsum and dihydrite, could be in form of hemi-hydrite. So the dissolution kinetics of these individual phrases will also influence the hydration of Ye'elimite.

(Refer Slide Time: 9:07)



Phase Assemblage of CSA Cement

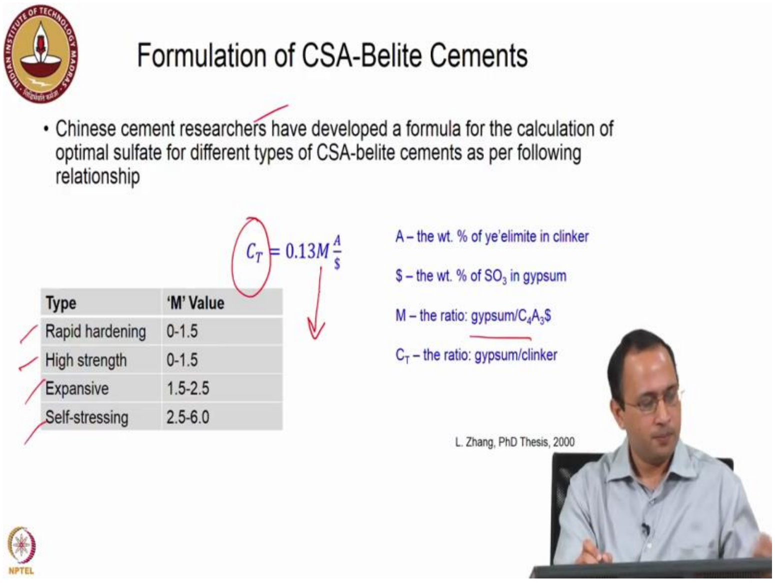
$C_4A_3\$$ – 54%
C_2S – 19%
Anhydrite – 21%
Minor phases – 6%

Winnefeld and Lothenbach, C

If you look into now phase content, you start with Ye'elimite, particularly Ye'elimite, suppose this clinker had anhydrite, some Belite. So, as the reaction proceeds, you see reaction of Ye'elimite. And what is important to note is just in like 4 days, 100 hours, roughly, most of the Ye'elimite is reacted. It tells us that the reaction is fast and we can expect reaction to complete in 7 to 10 days completely. And as Ye'elimite is decreasing in amount, we see increase in the amount of Ettringite.

Again that will depend upon the amount of anhydrite or gypsum. And depending on the C_2S content, we can also see a presence of stratlingite. We have seen earlier in one of the slides, C_2S can react with aluminum hydroxide and form stratlingite. So here basically the data points, discrete data points are the measurements and the solid lines, solid and dashed lines are the simulated plot using thermodynamic modelling.

(Refer Slide Time: 10:26)



Formulation of CSA-Belite Cements

- Chinese cement researchers have developed a formula for the calculation of optimal sulfate for different types of CSA-belite cements as per following relationship

$$C_T = 0.13M\frac{A}{\$}$$

Type	'M' Value
Rapid hardening	0-1.5
High strength	0-1.5
Expansive	1.5-2.5
Self-stressing	2.5-6.0

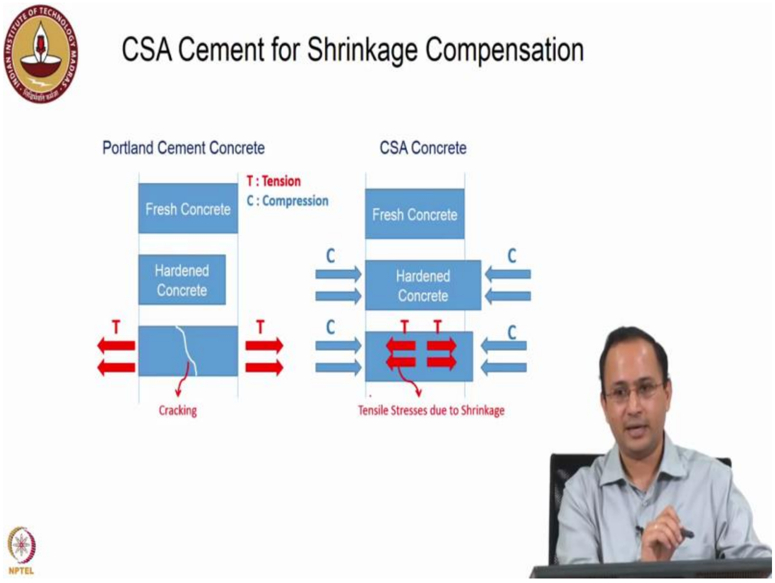
A – the wt. % of ye'elimite in clinker

$\$$ – the wt. % of SO_3 in gypsum

M – the ratio: gypsum/$C_4A_3\$$

C_T – the ratio: gypsum/clinker

L. Zhang, PhD Thesis, 2000



CSA Cement for Shrinkage Compensation

Portland Cement Concrete

CSA Concrete

T : Tension

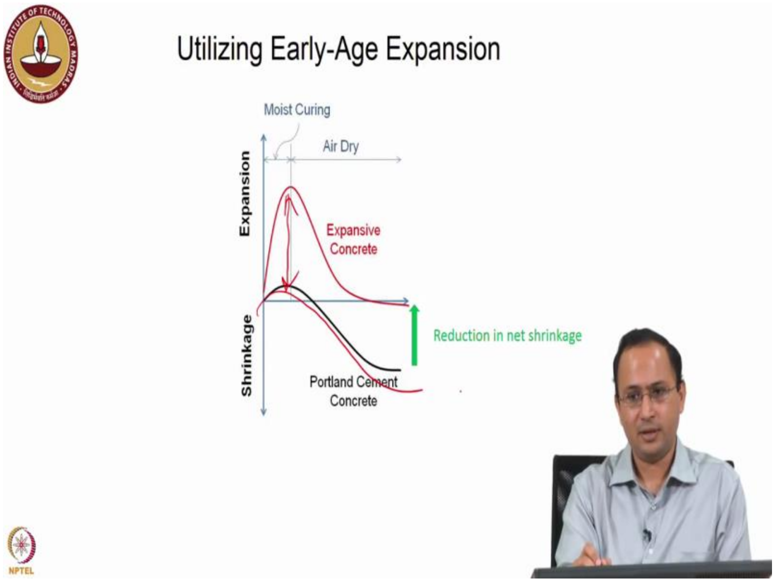
C : Compression

So, now we know that Gypsum plays a big role, depending on the amount of gypsum we can either form monosulphate or ettringite or both of those. So Chinese researchers have developed this formula. Basically what it says is like based on this M, M is the molar ratio of gypsum to Ye'elimite, we can develop different types of cements, rapid hardening cement, high-strength cement, spans of cement, self stressing cement.

So basically if M is from 1.5 to 2.5, the cement will be expansive. That means there will be increase in volume. And self stressing system, you have significant expansion that leads to significant compression. But the important point to note is this M plays a big role in governing the volume change. This is a conventional way of looking into the shrinkage cracking of the Portland cement concrete. You have a fresh concrete, when it dries, due to restrain there is a tensile stresses developed. And that the stress exceeds strength, there is cracking.

Now in CSA concrete, if you want to leverage the expansion, suppose you are trying to formulate mix which expands, this expansion will lead to some compression and that compression can then counteract the themselves stresses developed due to shrinkage. So, like in self stressing system, you have the residual compression, the level of compression will be higher than just expansive system.

(Refer Slide Time: 12:25)



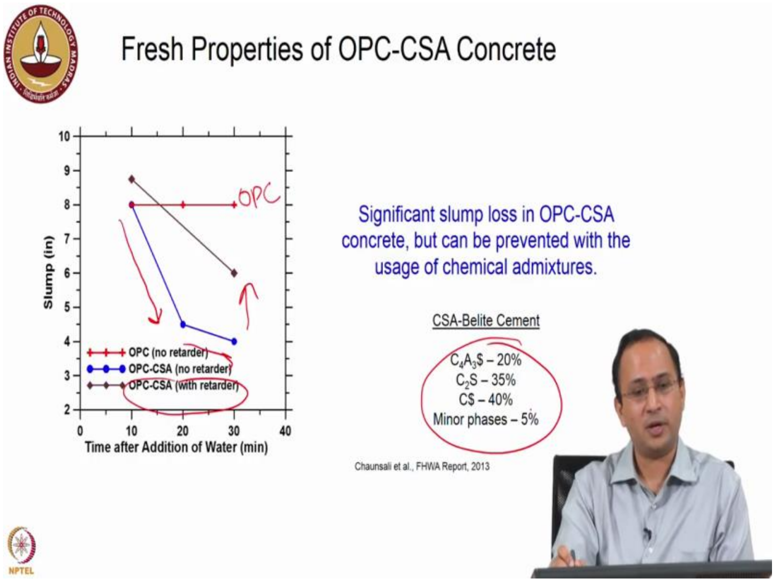
Utilizing Early-Age Expansion

Sustainability and Durability

So, now if we look into this typical shrinkage versus time plot, in Portland cement we see some level of shrinkage. It could be 500 to 600 microns, micro strain depending on the drying conditions. But in the expansive systems based on CSA, because of this expansion at early-age, basically we are reducing the net shrinkage. So, there is a reduction in net shrinkage when you CSA cement as an expansive agent. We know that there are advantages in terms of reducing CO_2 footprint, less limestone is needed to make this cement, kiln temperature is 200 degrees Celsius lower than what you use for Portland cement, the grinding energy is low and

(Refer Slide Time: 13:37)

Early-Age and Hardened Properties of CSA-Based Binder



Fresh Properties of OPC-CSA Concrete

Significant slump loss in OPC-CSA concrete, but can be prevented with the usage of chemical admixtures.

CSA-Belite Cement

$C_4A_3\$$ – 20%
C_2S – 35%
$C\$$ – 40%
Minor phases – 5%

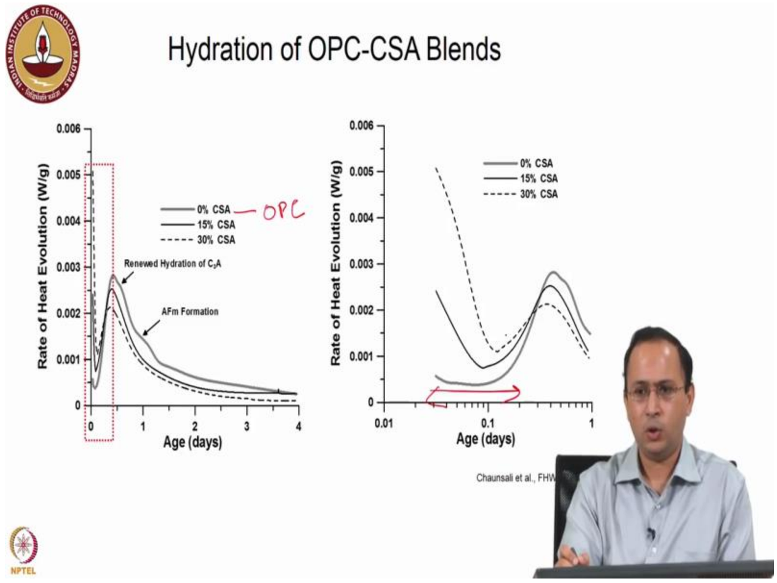
Chaunsali et al., FHWA Report, 2013

also by leveraging this early age expansion, we can make this cement shrinkage resistant. So it can be used to address both issues sustainability and durability. Now we will go over early age and hydration properties, hardened properties of CSA based binders. We will look into fresh properties, how does it compare with conventional concrete based on Portland cement, mechanical properties, early-age volume change, how do we model this early-age volume change. Eventually we will see one application.

If you make a concrete using CSA cement because of the formation of Ettringite crystals, there is a loss in slump. And if you compare with OPC, when you have a CSA in the system, there is a significant loss in slump. And obviously in this study no admixture was used initially. But we see that when you use a retarder with CSA, you can reduce this slump loss. And this is the conventional retarder which people use for Portland cement.

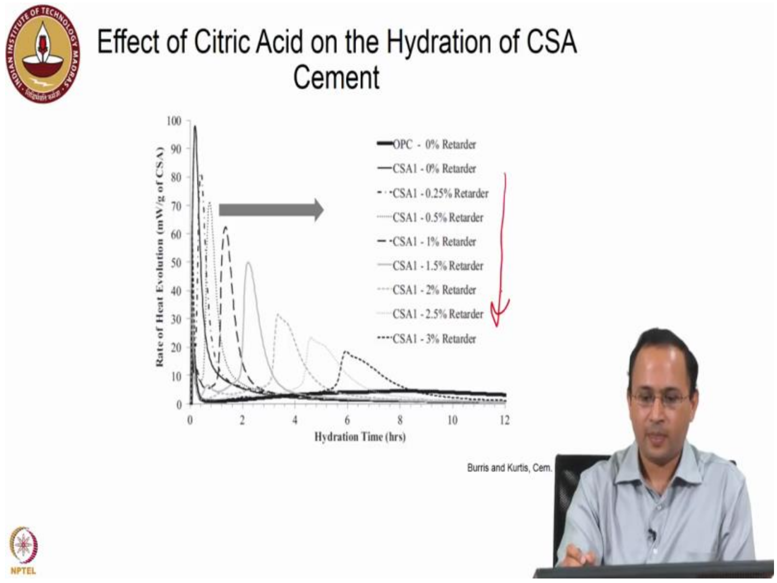
And also this study was done in which only 15 percent of OPC was replaced. So it was OPC-CSA blend. And the CSA cement which was used in the study had this phase composition 20 percent Ye'elimite, 35 percent C_2S, Belite, and calcium sulphate in all forms was around 40 percent. So, there is a loss in workability but can be reduced.

(Refer Slide Time: 15:30)



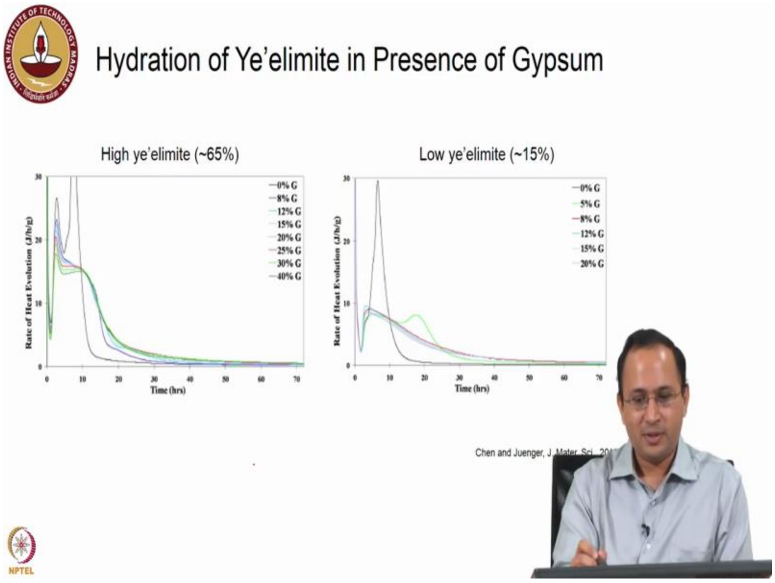
Hydration of OPC-CSA Blends

Chaunsali et al., FHW



Effect of Citric Acid on the Hydration of CSA Cement

Burris and Kurtis, Cem.



Hydration of Ye'elimite in Presence of Gypsum

High ye'elimite (~65%)

Low ye'elimite (~15%)

Chen and Juenger, J. Mater. Sci., 20

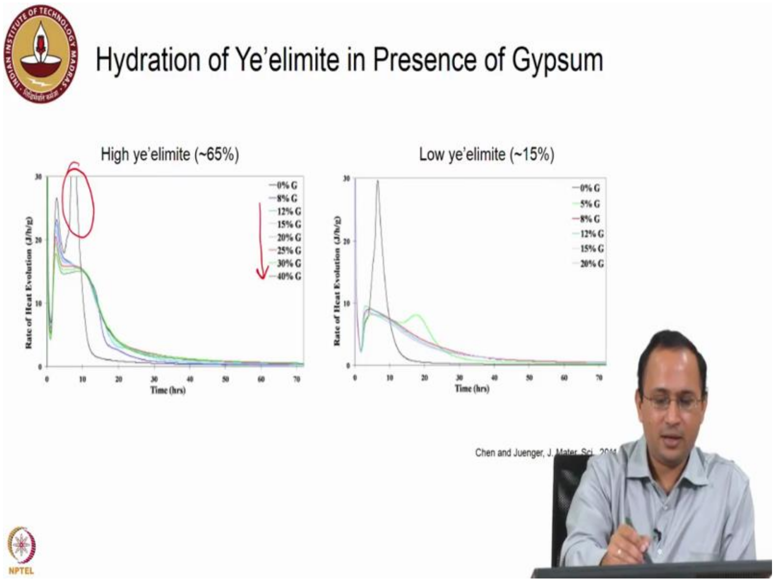
Now if you want to examine, we can use isothermal calorimetry to look into this closely. So, here is the rate of heat evolution in 3 different binders. 0 percent CSA corresponds to plain OPC, now what happens when you add CSA, 15 percent CSA, 30 percent CSA? What happens in early few hours, we see that in OPC a dormant period, which is very useful when you have to transfer the concrete by some time.

But in cement, when you have CSA, you have a shorter dormant period. Again, in the study, no chemical admixture was used. And as you increase the amount of CSA, we can see the further reducing the dormant period. This study was published in 2007 addressed the issue of this shorter dormant period by adding citric acid. Citric acid basically what you can see that is a good retarder for CSA cement. As you increase the amount of citric acid in this system CSA, you are delaying the peak.

Isothermal calorimetry is a good tool to look into this early-age hydration kinetics. Now we know that in the system with 3 percent retarder, we have delayed the hydration by 4 to 6 hours. So this is only one example, there are other examples also. So there are ways you can retard the CSA, the hydration of CSA cement. Now, since Gypsum is integral part of this the cement.

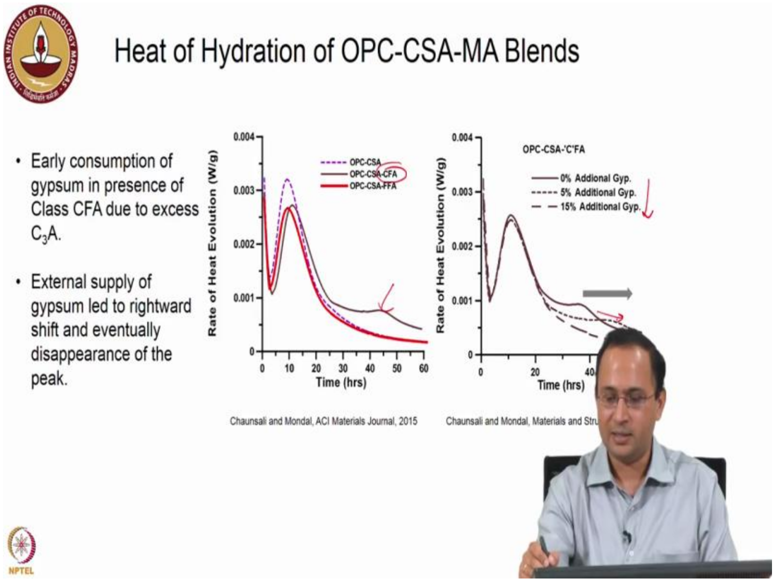
It is important to calculate the optimal Gypsum. We all know that optimal Gypsum for Portland cement is roughly around 3 to 5 percent. So, again isothermal calorimetry can be used to determine this optimal Gypsum. So, you see 1st this peak, it is because of Gypsum depletion. When the Gypsum is depleted, this C_4A_3S or Ye'elimite hydrates very fast and releases a lot of heat. Same phenomena happens in Portland cement when you are run out of Gypsum, your C_3A can hydrate very fast and their reaction way, so you want to control that.

(Refer Slide Time: 18:29)



Hydration of Ye'elimite in Presence of Gypsum

Chen and Juenger, J. Mater. Sci., 2011



Heat of Hydration of OPC-CSA-MA Blends

- Early consumption of gypsum in presence of Class CFA due to excess C_3A.
- External supply of gypsum led to rightward shift and eventually disappearance of the peak.

Chaunsali and Mondal, ACI Materials Journal, 2015

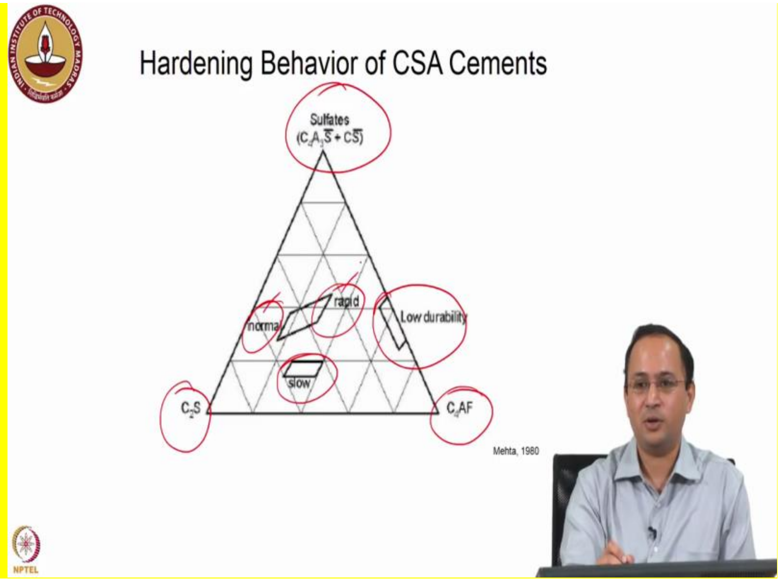
Chaunsali and Mondal, Materials and Stru

As we increase the amount of Gypsum, we are basically delaying this peak and basically the optimal Gypsum is a content beyond which the isothermal calometry curve does not change. It is more clear in the later one, if you see the right plot, so the initial gypsum depletion peak is here and when we add 5 percent of Gypsum, then beyond that we do not see any change. So it tells you that the optimal Gypsum for this cement is around 8 percent.

Similar thing also can happen when you have mineral admixtures. So, here is the example, what happens, when you have Portland cement, you have CSA cement and class C fly ash and class F fly ash. So, depending on the chemistry you will see very different behaviour. So you notice that this shoulder occurring only in the mix where you have class C fly ash. So as we saw earlier, usually any shoulder after the main peak can be attributed to gypsum depletion.

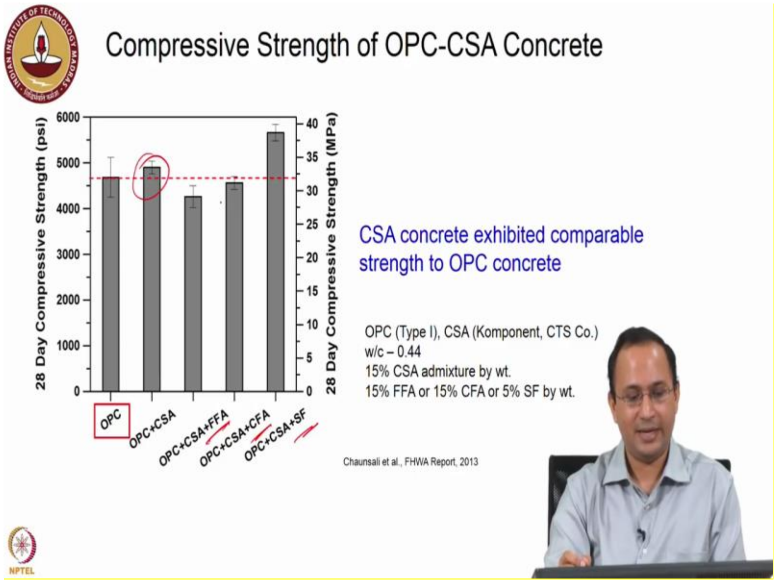
Now, if you want to verify, is it because of only gypsum depletion? You can simply add additional Gypsum. So, with 5 percent additional Gypsum, you delay this peak and eventually add 15 percent, we do not even see that peak. So it was confirmed that this peak was due to the depletion of Gypsum. Now what caused that depletion? The class C fly ash basically has C_3A tricalcium aluminate. So that also competes for the Gypsum.

(Refer Slide Time: 20:39)



Hardening Behavior of CSA Cements

Mehta, 1980

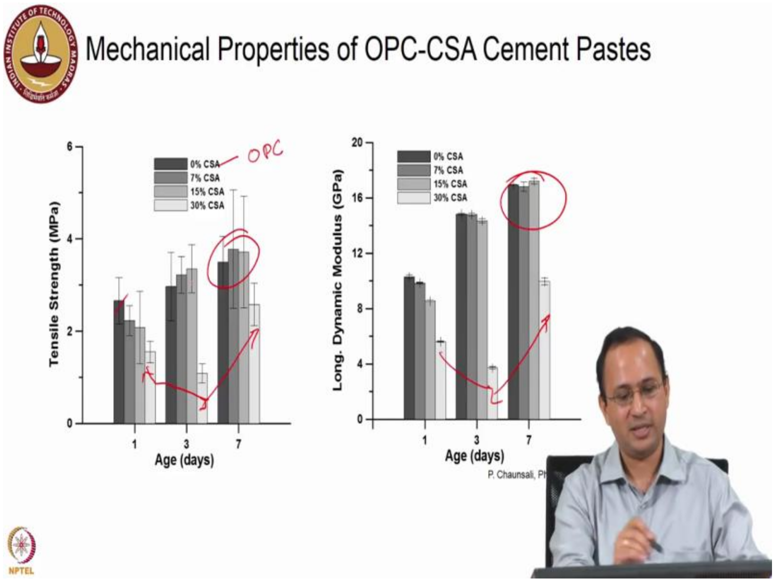


Compressive Strength of OPC-CSA Concrete

CSA concrete exhibited comparable strength to OPC concrete

OPC (Type I), CSA (Komponent, CTS Co.)
w/c – 0.44
15% CSA admixture by wt.
15% FFA or 15% CFA or 5% SF by wt.

Chaunsali et al., FHWA Report, 2013



Mechanical Properties of OPC-CSA Cement Pastes

P. Chaunsali, Ph

So, obviously if you compare with the class F fly ash which does not have C_3A, you will see early depletion of Gypsum in the mix with class C fly ash. If we look into this ternary diagram, where we put all sulphates in one corner, like in the form of Ye'elimite and calcium sulphates, you can combine C_4A_3S and calcium sulphate, here is C_2S, silicate phase and ferrite phase, C_4AF. So, it gives a very good idea like where do you want to be. You do not want to be in this region (near right side corner, shown as low durability) because you do not have enough C_2S, you do not have enough binding phase.

if you are somewhere here (the region shown as slow in the diagram, near to C2S corner), so very far away from C_4A_3S corner, that means you have a very small amount of C_4A_3S, the hardening will be slow. So this just gives you an idea about the sweet spot you want to be in. If you want normal hardening, you want to be somewhere here (the region shown as normal in the diagram), if you want rapid hardening, you want to be somewhere here the region shown as rapid in the diagram).

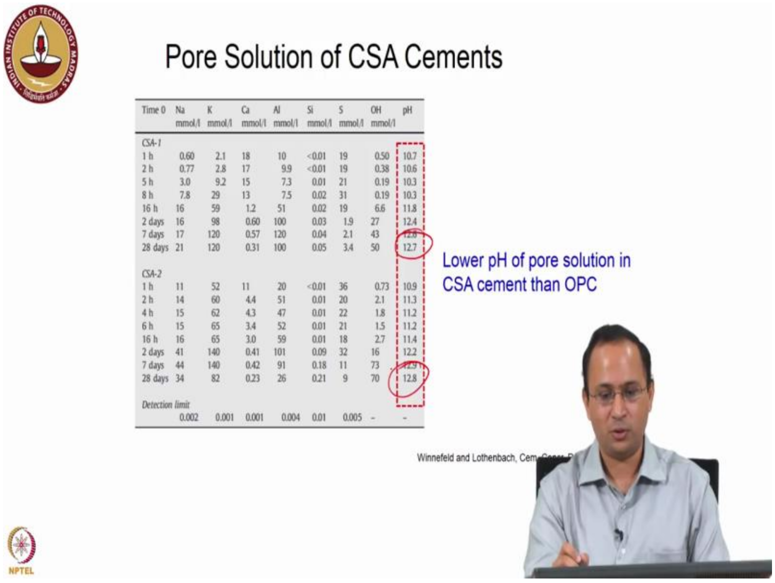
Now coming back to the strength of CSA concrete, at least in the study was comparable to Portland cement concrete, and many researchers, many studies have reported that. So, here is the Portland cement concrete and 28 days compressive strength. When you just replace OPC with CSA, in this case the replacement was 15 percent, small increase but we can get comparable strength to Portland cement concrete. Further, you can also look into the effect of these mineral admixtures. What happens when you add class F Fly ash, class C Fly ash and Silica fume?

Obviously these are the mineral admixtures, take time to hydrate. The pozzolanic reaction is slow. So this is 28 days strength, although it is little bit lower, we expected to be higher if we test it at later ages. Again, now coming back to other mechanical properties. If you look into the tensile strength, 0 percent CSA again corresponds to plain OPC, 7 percent OPC means 93 percent OPC, 7 percent CSA. So with that age you see increase in strength. Hydration is occurring and pores are being filled, so you see continuous increase in strength.

For OPC with CSA, when you add lot of CSA, like in this case you got 30 percent CSA, there was a cracking because there was a lot of expansion which took place that led to this drop. But again the hydration is happening, so your cracks are being filled and then you see again strength increases. Same behaviour we see when we try to monitor the dynamic modulus.

So you can see increase in dynamic modulus for all other systems, except 30 percent CSA at early-age. But then because of this continuous hydration, which fills the pores, cracks, you see increase in strength. But in general, comparable strength, will look into this, 7 days comparable strength of OPC CSA cement paste. This study was done on paste and not concrete.

(Refer Slide Time: 24:30)

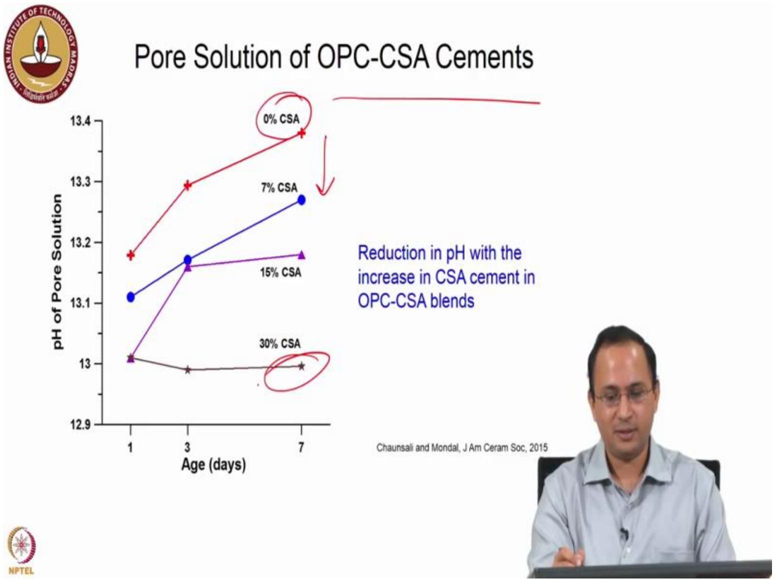


Pore Solution of CSA Cements

Time 0	Na mmol/l	K mmol/l	Ca mmol/l	Al mmol/l	Si mmol/l	S mmol/l	OH mmol/l	pH
CSA-1								
1 h	0.60	2.1	18	10	<0.01	19	0.50	10.7
2 h	0.77	2.8	17	9.9	<0.01	19	0.38	10.6
5 h	3.0	9.2	15	7.3	0.01	21	0.19	10.3
8 h	7.8	29	13	7.5	0.02	31	0.19	10.3
16 h	16	59	1.2	51	0.02	19	6.6	11.8
2 days	16	98	0.60	100	0.03	1.9	27	12.4
7 days	17	120	0.57	120	0.04	2.1	43	[illegible]
28 days	21	120	0.31	100	0.05	3.4	50	12.7
CSA-2								
1 h	11	52	11	20	<0.01	36	0.73	10.9
2 h	14	60	4.4	51	0.01	20	2.1	11.3
4 h	15	62	4.3	47	0.01	22	1.8	11.2
6 h	15	65	3.4	52	0.01	21	1.5	11.2
16 h	16	65	3.0	59	0.01	18	2.7	11.4
2 days	41	140	0.41	101	0.09	32	16	12.2
7 days	44	140	0.42	91	0.18	11	73	12.9
28 days	34	82	0.23	26	0.21	9	70	12.8
Detection limit								
	0.002	0.001	0.001	0.004	0.01	0.005	-	-

Lower pH of pore solution in CSA cement than OPC

Winnefeld and Lothenbach, Cem. Concr. R



Pore Solution of OPC-CSA Cements

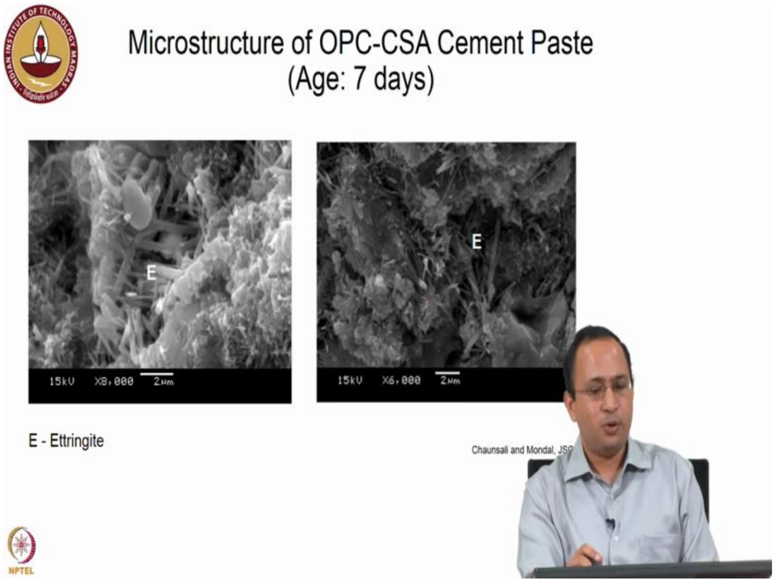
Reduction in pH with the increase in CSA cement in OPC-CSA blends

Chaunsali and Mondal, J Am Ceram Soc, 2015

Also it is important to look into the pore solution, because the pH of pore solution dictates a lot of things like corrosion for an example. CSA cement have lower pH than OPC, but you can see that, at least in the study they reported around 12.6 to 7 pH. I have not seen any study where it was lower than 12 basically. So, it is lower than OPC but not very low to cause corrosion.

This was the study done when CSA was replaced. A zero percent CSA is OPC, the pH in the range of 13.324 at the end of 7 days. As you increase the amount of CSA, there is a reduction in pH. But even at 30 percent CSA, what we see that around 13 pH. There is a reduction in pH with increasing CSA cement but it is not too low. Look into the microstructure, we know that there is a formation of Ettringite and the crystal. And a lot of formation of Ettringite and we see that there is a lot of crystal needle extractions.

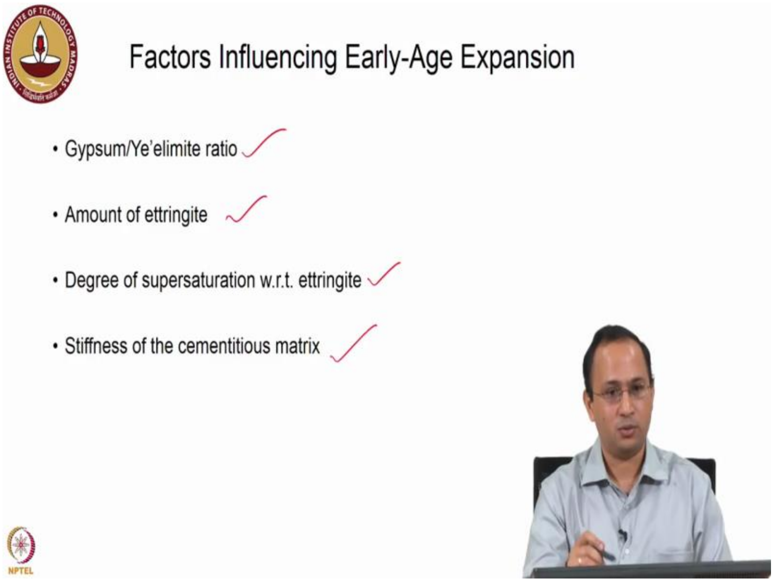
(Refer Slide Time: 26:12)



Microstructure of OPC-CSA Cement Paste
(Age: 7 days)

E - Ettringite

Chaunsali and Mondal, JSC



Factors Influencing Early-Age Expansion

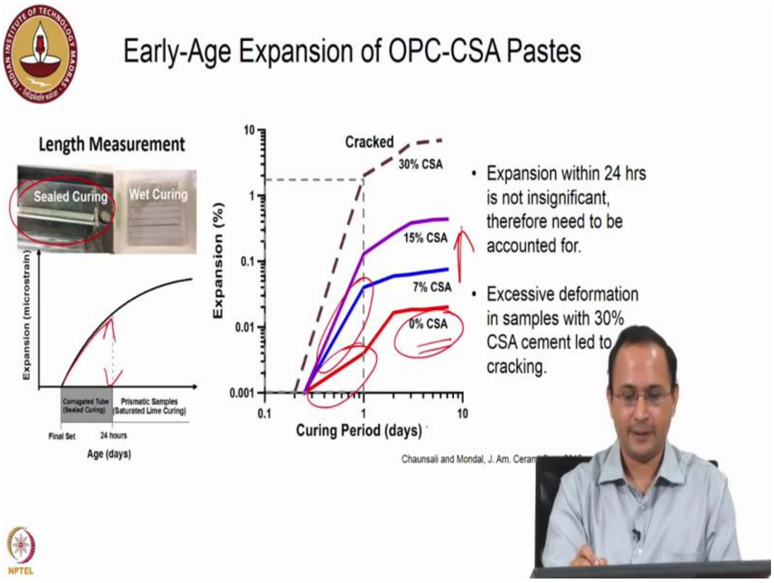
- Gypsum/Ye'elimite ratio ✓
- Amount of ettringite ✓
- Degree of supersaturation w.r.t. ettringite ✓
- Stiffness of the cementitious matrix ✓

These are the micrographs seven-day old sample. So, we see a lot of needle structures in both. Now it is important to look into, because this is the phase that is giving you expansion. If you have a lot of Ettringite, you will see expansion. We want expansion just enough to contract shrinkage. So it is important to look into factors which influence early-age expansion. How can we quantify? How can we predict basically?

So we know that Gypsum to Ye'elimite ratio is one of the factors governing early-age expansion. When you do not have enough Gypsum, you will not have expansion. Then amount of Ettringite, obvious choice. Degree of super saturation with respect to Ettringite is also an important factor. So it depends, what is the saturation level of your sulphates. And these can be estimated, if we know the composition of pore solution and using thermodynamic modelling we can calculate the degree of saturation.

Apart from these chemical factors, we need to also pay attention to stiffness of the cementitious matrix. It is like, if you compare a stone versus rubber, same amount of expansion happening in rubber will cause greater expansion compared to stone. So we need to pay attention to the stiffness of the cementitious matrix.

(Refer Slide Time: 27:38)



Early-Age Expansion of OPC-CSA Pastes

- Expansion within 24 hrs is not insignificant, therefore need to be accounted for.
- Excessive deformation in samples with 30% CSA cement led to cracking.

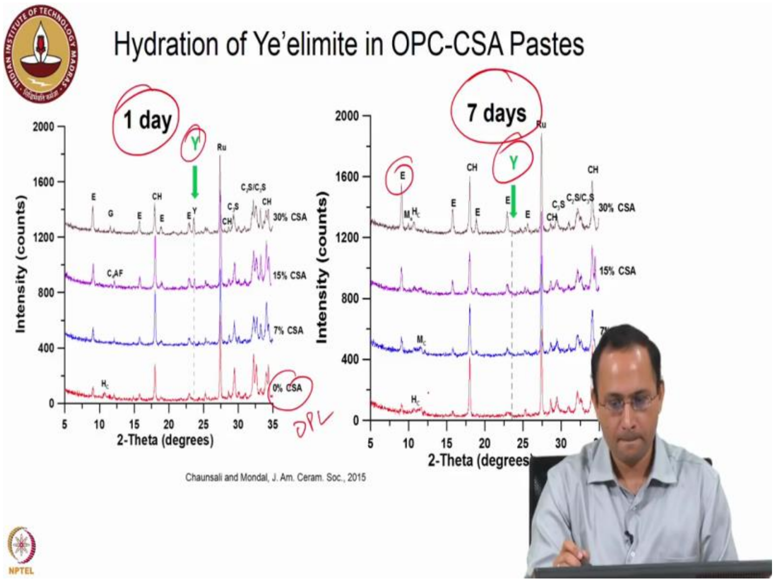
Chaunsali and Mondal, J. Am. Ceram

Now if you look into early-age expansion, here again we are seeing the effect of CSA addition. It is also important to capture this expansion very early on, a lot of conventional way of measuring expansion or shrinkage is relying on the one-day datapoint. So you cast your sample demould it after 24 hours. But we know that C_4A_3S starts reacting immediately and you have formation of Ettringite, you will see expansions occurring within 24 hours. So it is very important to capture that.

For that we can use this corrugated tube, which allows you to take measurements immediately after casting. So basically you fill your tube with cement slurry and using this gauge you can monitor the change in length. And what is important is then you can cast the parallel samples, the prisms which you do and then add this data. But here is an evidence that the expansion occurring within 24 hours is not insignificant.

So depending on your CSA content, you may have significant expansion occurring within 24 hours. Obviously as we increase the amount of CSA cement, we see the increase in expansion. And order of magnitude difference, 0 percent CSA is OPC, plain OPC, when you add 7 percent CSA n order increase, 15 percent n order increase, 30 percent CSA, the samples cracked. Because we saw that earlier in mechanical properties also, there was a reduction in tensile strength and dynamic modulus and samples cracked.

(Refer Slide Time: 29:46)



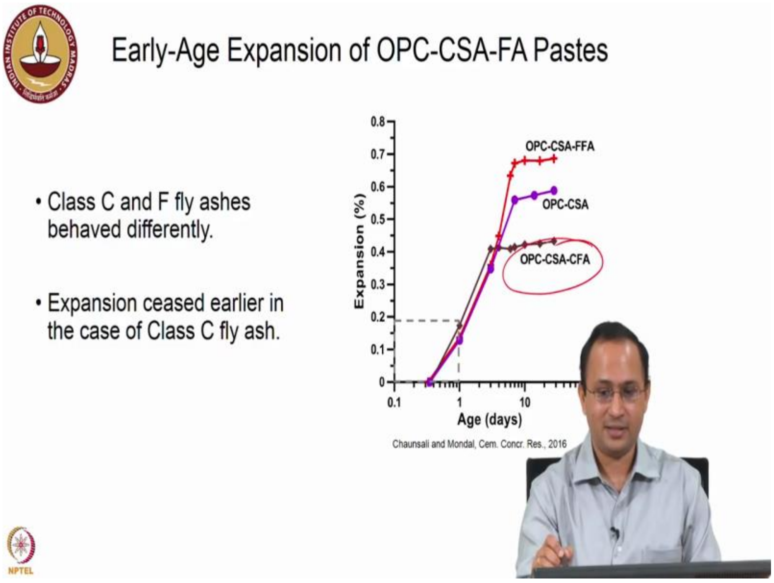
Hydration of Ye'elimite in OPC-CSA Pastes

Chaunsali and Mondal, J. Am. Ceram. Soc., 2015

So expansion within 24 hours is not insignificant, one thing to note and there are ways to capture that. Now, we look into the hydration of Ye'elimite, because that is what is causing the expansion and that is what leads to the formation of Ettringite, monosulphate and other phases. So here again, comparing the 4 different samples OPC and sample with CSA. So you see presence of Ye'elimite, why? It gives you peak at around 23.4 degree in XRD. And you can see that as you increase the amount of CSA, this peak is more intense. This is picture, what happens in one day.

So you still have underrated Ye'elimite after one day. But now if you look at 7 days, basically Ye'elimite is consumed, there is no Ye'elimite. So all Ye'elimite has reacted and led to the formation of Ettringite. And in addition to Ettringite, you have other phases like mono sulphate also. And hemi-carbonate may form depending on the conditions. So important thing to note is that in 7 days, the hydration of Ye'elimite is complete.

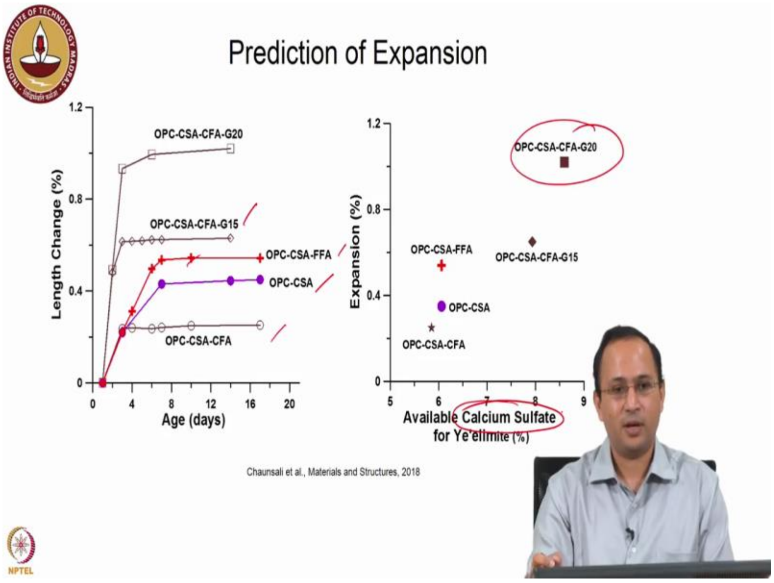
(Refer Slide Time: 31:11)



Early-Age Expansion of OPC-CSA-FA Pastes

- Class C and F fly ashes behaved differently.
- Expansion ceased earlier in the case of Class C fly ash.

Chaunsali and Mondal, Cem. Concr. Res., 2016



Prediction of Expansion

Chaunsali et al., Materials and Structures, 2018

Now, depending on the use of mineral admixtures. We saw earlier that in isothermal calorimetry, that class C fly ash behave differently, because there was the Gypsum depletion in class C fly ash. So, the effect of that on expansion is also, is shown here basically. So when you have class C fly ash in system, the expansion was less compared to the plane system. But when you have class F fly ash, the expansion, there was increase in expansion.

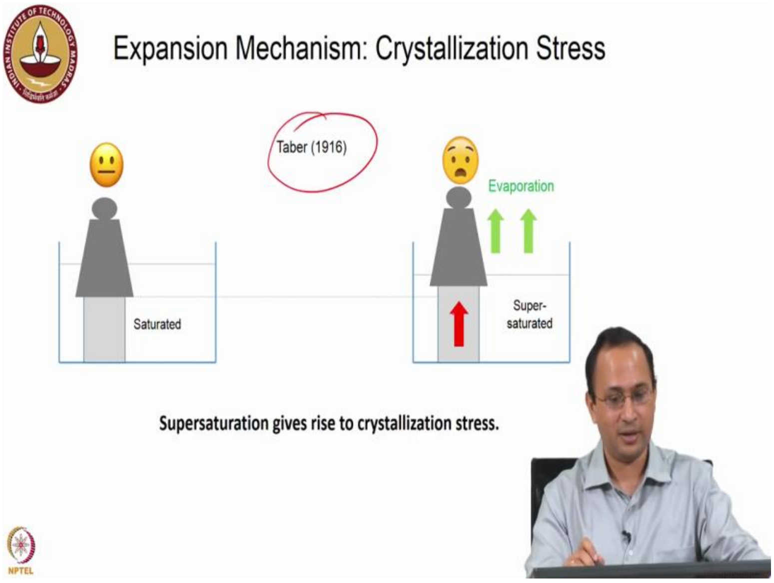
It again ties back to isothermal calorimetry data. So these other techniques can be used to understand what is happening, what is the cause of this expansion behaviour. Again here we see that the expansion occurring within 24 hours is not insignificant. So we all want to predict the expansion depending on the phase completion. We want to know like how much it system will expand. So this we have already seen when you have class C, class F, this is a plot shown in the earlier slide.

Now we know that class C fly ash, again going back to isothermal calorimetry, we found that when we added the Gypsum, the shoulder peak disappear. So, that led to again this increase in expansion. When you had 15 percent Gypsum, you see increase in expansion, 20 percent, further increase. So this is one of the ways to mitigate this loss in expansion. Suppose your target is to achieve a level of expansion, suppose you want your system to expand like as class F fly ash but you have class C fly ash, then you can add Gypsum basically.

You know that there is going to be Gypsum depletion in class C fly ash, so we can add Gypsum and get that expansion back. And when we try to calculate this calcium, available calcium sulphate, we can calculate that based on the stoichiometry, we can calculate how much calcium sulphate is available for the hydration of Ye'elimite. And we saw that it was very interesting to that, it was a very nice correlation basically. So the system which expanded most, as you see has the highest amount of calcium sulphate available for Ye'elimite.

These are the simple calculations you can do to predict or compare 2 systems. Because we know that Ye'elimite is reacting with calcium sulphate and forming Ettringite, that is causing expansion. So, this availability of calcium sulphate can also give you an idea about the expansion.

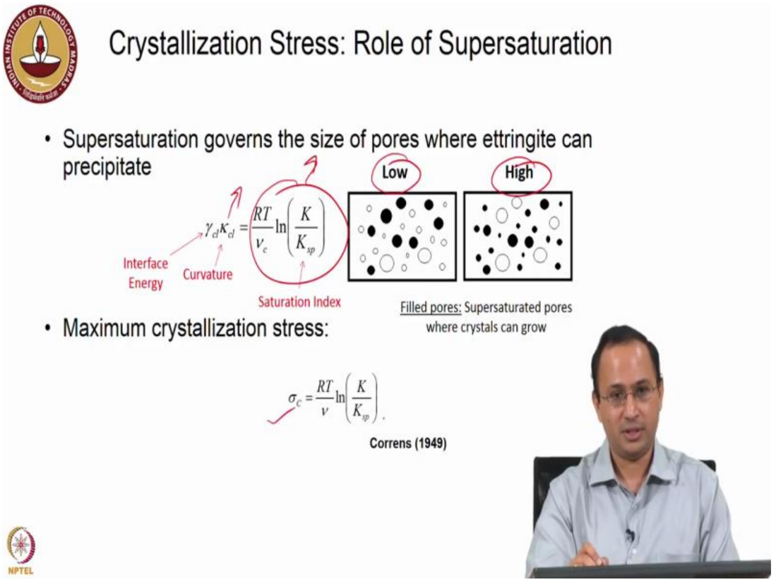
(Refer Slide Time: 34:16)



Expansion Mechanism: Crystallization Stress

Taber (1916)

Supersaturation gives rise to crystallization stress.



Crystallization Stress: Role of Supersaturation

- Supersaturation governs the size of pores where ettringite can precipitate

$$\gamma_{cl}\kappa_{cl} = \frac{RT}{v_c}\ln\left(\frac{K}{K_{sp}}\right)$$

Filled pores: Supersaturated pores where crystals can grow

- Maximum crystallization stress:

$$\sigma_c = \frac{RT}{v}\ln\left(\frac{K}{K_{sp}}\right)$$

Correns (1949)

$$\gamma dKd = \frac{RT}{vd}\ln\left(\frac{K}{Ksp}\right)$$

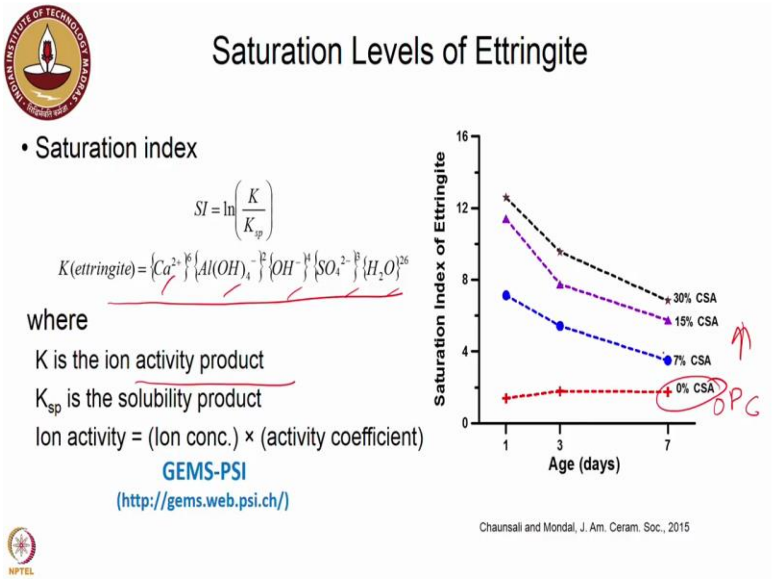
$$\sigma c = \frac{RT}{v}\ln\left(\frac{K}{Ksp}\right)$$

Since we are talking about the expansion, it is important to look into the mechanism, what is that causing this expansion? what is the origin of it? So, long time ago, Taber did a very interesting experiment in 1916, where he had a salt in its saturated solution and you put a weight on it. Then due to evaporation yours salt your saturated solution will become supersaturated. And that led to the growth in Crystal and that lifted the weight.

The simple experiment tells us that the super saturation gives rise to crystallization stress. This test was done long time back and we can calculate this crystallization stress. So what does super saturation do? Here are the 2 systems, the low and high super saturation. First of all we see that super saturation can be linked to the curvature. And we see when you have high super saturation, it allows crystals to grow in smaller pores. High super saturation means higher curvature, higher curvature means lower radii.

So when you have high super saturation, that means your crystals can form in smaller pores. But when you have low super saturation, that will not happen. So these 2 schematics depict that. In high we see the pores being filled, the smaller pores being filled. Now, this maximum crystallization stress can be calculated, if we know the super saturation. This gives us the upper bound of the stress.

(Refer Slide Time: 36:07)



Saturation Levels of Ettringite

- Saturation index

$$SI = \ln\left(\frac{K}{K_{sp}}\right)$$

$$K(ettringite) = \{Ca^{2+}\}^6\{Al(OH)_4^-\}^2\{OH^-\}^4\{SO_4^{2-}\}^3\{H_2O\}^{26}$$

where

K is the ion activity product

K_{sp} is the solubility product

Ion activity = (Ion conc.) × (activity coefficient)

GEMS-PSI

(http://gems.web.psi.ch/)

Chaunsali and Mondal, J. Am. Ceram. Soc., 2015

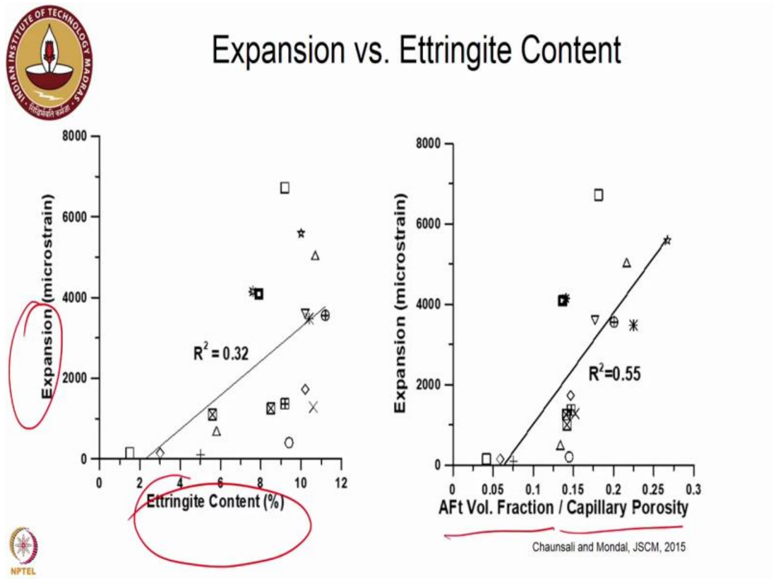
$$\mathrm{SI} = \ln\left(\frac{K}{Ksp}\right)$$

$$K(ettringite) = \{Ca^{2+}\}^6\{Al(OH)_4^{\ -}\}^2\{OH^-\}^4\{SO_4^{\ 2-}\}^3\{H_2O\}^{26}$$

If we know the composition of pore solution, and we know the concentration of various ionic species, we can calculate the saturation index for any phase. In this case it was calculated for Ettringite, which is the expansion causing phase. So, you write the what is the ion activity product. Because the super saturation gives the ratio of ion activity product and solubility product. So, now if you know these concentrations, using any thermodynamic modelling software, you can calculate the ion activity.

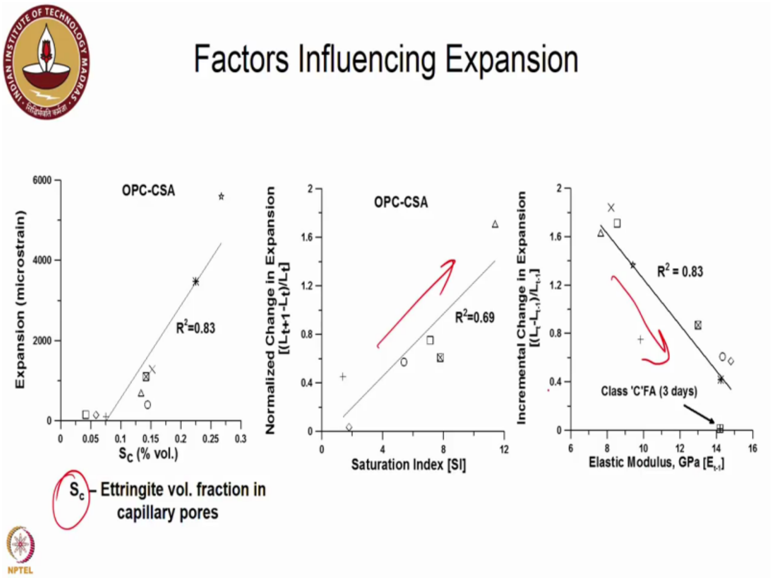
And basically this GEMS is a software, relies on the minimization of Gibbs free energy can give you saturation index of individual face. But the input is concentration. And we see here now that what happens as you increase the amounts of CSA, you see the increase in super saturation. So we saw that super saturation gives rise to crystallization stress. So when you have higher fraction of CSA, you see increase in saturation index of Ettringite.

(Refer Slide Time: 37:27)



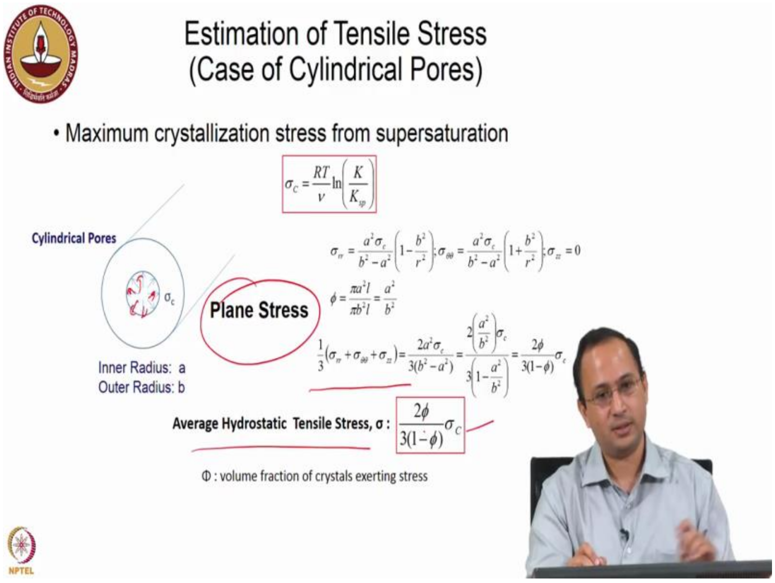
Expansion vs. Ettringite Content

Chaunsali and Mondal, JSCM, 2015



Factors Influencing Expansion

S_c – Ettringite vol. fraction in capillary pores



Estimation of Tensile Stress (Case of Cylindrical Pores)

- Maximum crystallization stress from supersaturation

$$\boxed{\sigma_C = \frac{RT}{v}\ln\left(\frac{K}{K_{sp}}\right)}$$

Cylindrical Pores

Inner Radius: a
Outer Radius: b

Plane Stress

$$\sigma_{rr} = \frac{a^2\sigma_c}{b^2-a^2}\left(1-\frac{b^2}{r^2}\right);\sigma_{\theta\theta} = \frac{a^2\sigma_c}{b^2-a^2}\left(1+\frac{b^2}{r^2}\right);\sigma_{zz} = 0$$

$$\phi = \frac{\pi a^2 l}{\pi b^2 l} = \frac{a^2}{b^2}$$

$$\frac{1}{3}(\sigma_{rr}+\sigma_{\theta\theta}+\sigma_{zz}) = \frac{2a^2\sigma_c}{3(b^2-a^2)} = \frac{2\left(\frac{a^2}{b^2}\right)\sigma_c}{3\left(1-\frac{a^2}{b^2}\right)} = \frac{2\phi}{3(1-\phi)}\sigma_c$$

Average Hydrostatic Tensile Stress, σ : $\boxed{\frac{2\phi}{3(1-\phi)}\sigma_C}$

Φ : volume fraction of crystals exerting stress

$$\sigma c = \frac{RT}{v} \ln\left(\frac{K}{Ksp}\right)$$

Error! Reference source not found. ;Error! Reference source not found.; Error! Reference source not found.

$$\varphi = \frac{\pi a^2 l}{\pi b^2 l} = \frac{a^2}{b^2}$$

$$\frac{1}{3}(\sigma rr + \sigma\theta\theta + \sigma zz) = \frac{2a^2\sigma c}{3(b^2 - a^2)} = \frac{2\left(\frac{a^2}{b^2}\right)\sigma c}{3\left(1 - \frac{a^2}{b^2}\right)} = \frac{2\varphi}{3(1-\varphi)}\sigma c$$

Average hydrostatic tensile stress,**Error! Reference source not found. Error! Reference source not found.**

People have been relating expansion to just Ettringite content. But the correlation is very weak. If you look into any problem related to sulphate attack, delayed Ettringite formation, even in this case when you have early-age expansion. So you see these are the data points, each data point is one mix. But same Ettringite content if it is plotted this way, like when you normalize it by capillary porosity, you see better correlation . We will come back to this point why we did this.

But same thing if we know the volume fraction of Ettringite and we know capillary porosity, that correlation improves. So, here are some factors which influence the expansion. We saw this again, SC, Ettringite volume fraction in capillary pores can also be called SC and the correlation is better. And there is a good correlation between saturation index and expansion. Increase in saturation index leads to increased in expansion. What is interesting here is what we saw is elastic modulus.

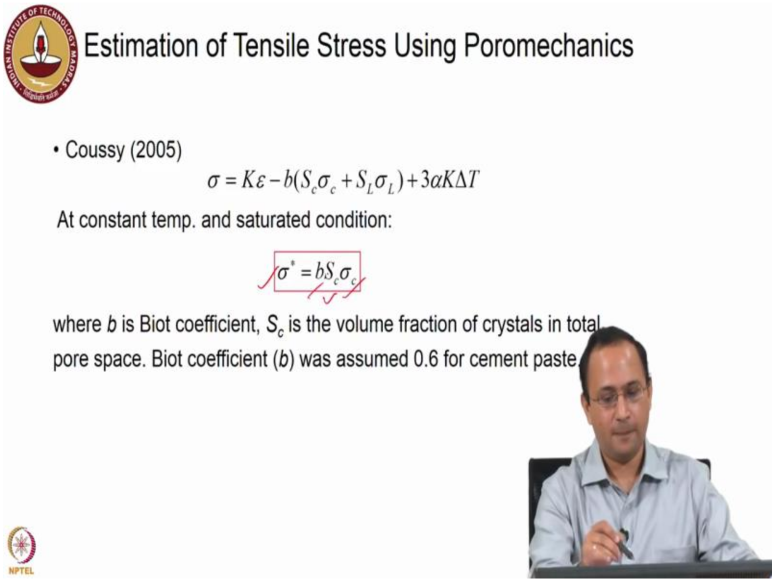
It is very important to pay attention to the stiffness of the matrix. A matrix which is less stiff will expand more. So as you increase the elastic modulus, you see reduction in expansion. Now, there are simple ways, obviously there are a lot of assumptions like matrix being isotropic and homogeneous, or elastic, we can estimate the tensile stresses. This is a case of cylindrical pores basically. And for plain stress condition, what you can calculate is average hydrostatic tensile stresses.

In cylindrical pores we are assuming these are the crystals right here causing these stresses. So the Sigma C is the maximum crystallization stress from thermodynamics. Now, based on the volume fraction of crystals, you can estimate this, average hydrostatic tensile strength.

(Refer Slide Time: 39:56)

$$\sigma = K\epsilon - b(Sc\ \sigma c + SL\ \sigma L) + 3\alpha K\Delta T$$

$$\sigma^* = b\ Sc\ \sigma c$$



Estimation of Tensile Stress Using Poromechanics

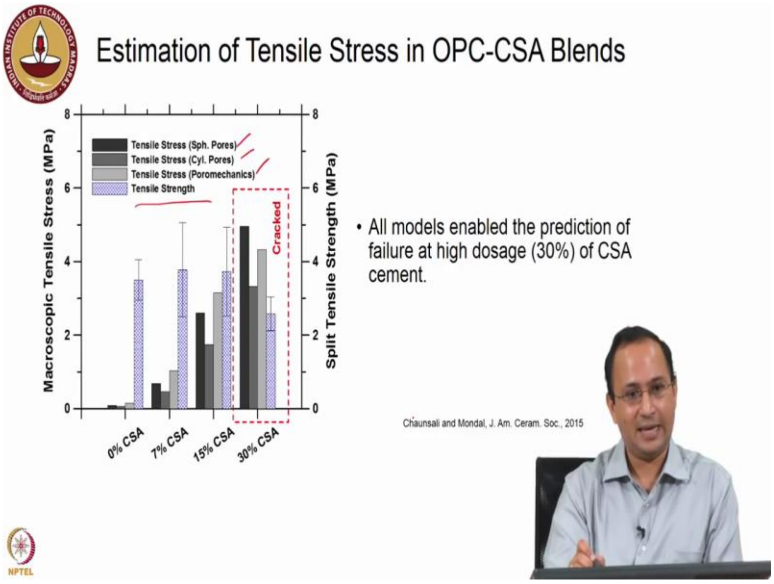
- Coussy (2005)

$$\sigma = K\varepsilon - b(S_c\sigma_c + S_L\sigma_L) + 3\alpha K\Delta T$$

At constant temp. and saturated condition:

$$\boxed{\sigma^* = bS_c\sigma_c}$$

where b is Biot coefficient, S_c is the volume fraction of crystals in total pore space. Biot coefficient (b) was assumed 0.6 for cement paste.



Estimation of Tensile Stress in OPC-CSA Blends

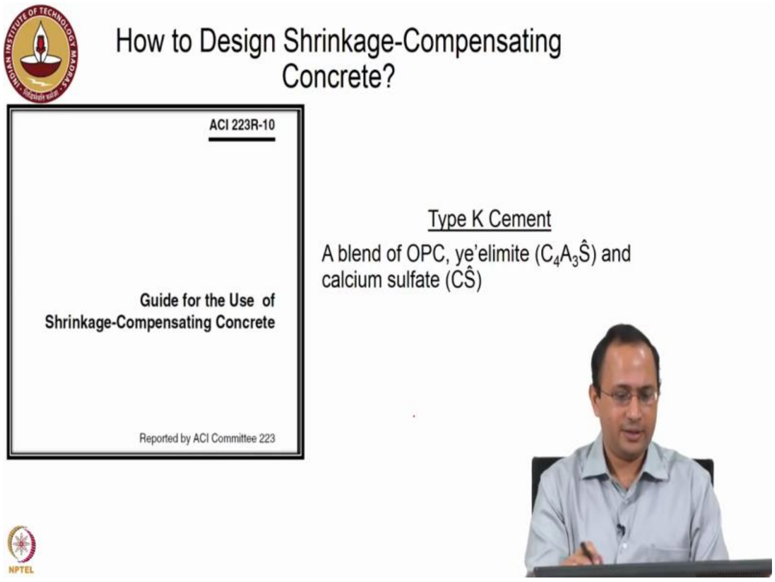
- All models enabled the prediction of failure at high dosage (30%) of CSA cement.

Chaunsali and Mondal, J. Am. Ceram. Soc., 2015

Using poromechanics also we can relate this stress to this S_c factor. We talked, there was better correlation of expansion with the S_c factor, we can calculate the tensile stress. So, now what happens when we try to plot? So, here is a graph which compares the tensile stresses for spherical pores, cylindrical pores and poromechanics, like these are the 3 models used to predict the tensile stresses. And here is the tensile strength. So basically the 30 percent CSA, we are seeing significant amount of tensile stress, they exceed strength.

So, these are simplistic models but can be useful to predict, so all models in this case enables the prediction of failure, especially at high dosage of CSA, that is what we also verified experimentally when we measure the length change, we saw cracking in the sample with 30 percent CSA. If you want to design concrete, where you want to leverage early-age expansion due to the formation of Ettringite, how can you do that?

(Refer Slide Time: 41:17)



How to Design Shrinkage-Compensating Concrete?

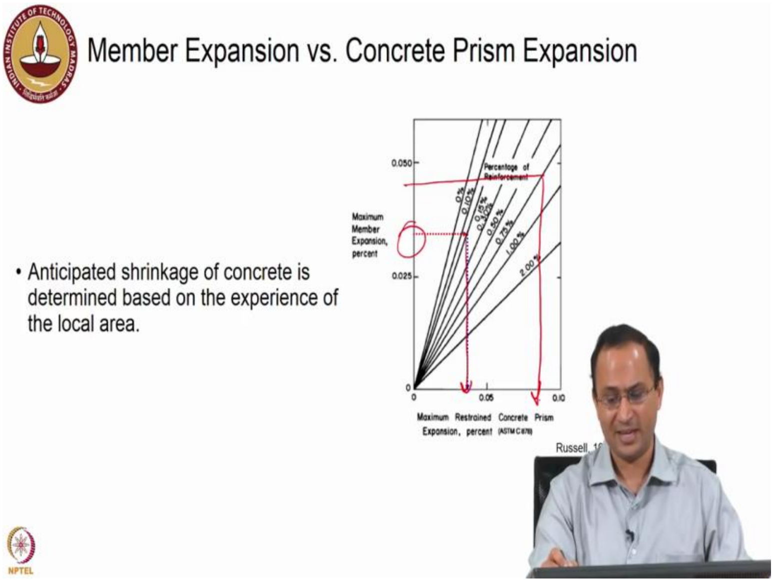
ACI 223R-10

Guide for the Use of Shrinkage-Compensating Concrete

Reported by ACI Committee 223

Type K Cement

A blend of OPC, ye'elimite ($C_4A_3\hat{S}$) and calcium sulfate ($C\hat{S}$)



Member Expansion vs. Concrete Prism Expansion

- Anticipated shrinkage of concrete is determined based on the experience of the local area.

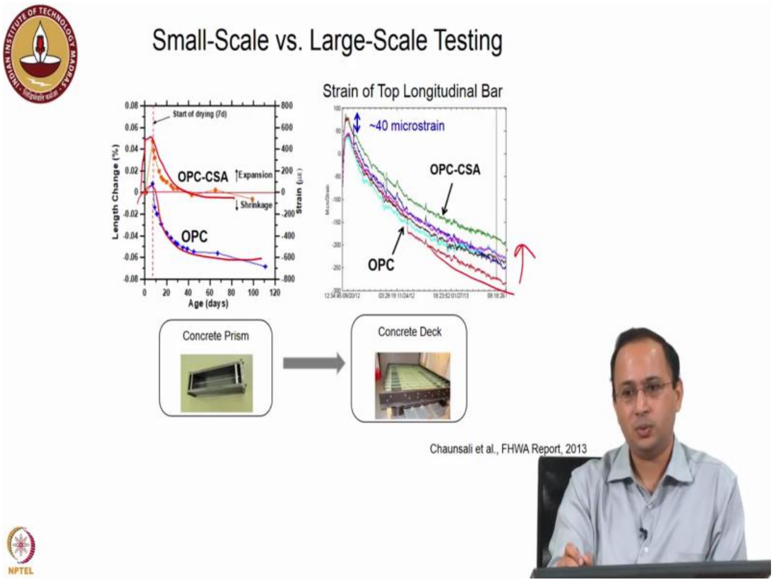
Russell, 1

So this is a guide, this is from American concrete Institute 223R, guide for the use of shrinkage compensating concrete. And in that also they mention type K cement basically, it is a blend of OPC, Ye'elimite and calcium sulphate. So, how do you do it? Basically first we anticipate the shrinkage of concrete, based on the experience of the local area. Depending on where you are, what are the conditions, you know what is the member shrinkage. So you know suppose this is the shrinkage, particular region.

Now this is a curve where you can get based on the percentage of reinforcement, based on the percentage of reinforcement you can calculate how much maximum restraint, how much expansion you want in the maximum in the restraint concrete prism. So, based on this area you can calculate the maximum expansion in restraint concrete prism. And how do you do this concrete prism test? It is basically according to ASTM 878, you have this reinforcing bar.

When we pour the concrete and then measure the early-age expansion. We can see the expansion from 0.04 percent 0.06 percent, depending on what you have. Again you can calculate it if you are somewhere here (approximately 0.040% in y-axis) and your percentage of the enforcement is here, then you would like to be here (approximately 0.090% in x-axis), so you want expansion, your expansion of your concrete prism, restraint concrete prism somewhere here. So, this is a guide, you can use it.

(Refer Slide Time: 43:12)



Small-Scale vs. Large-Scale Testing

Chaunsali et al., FHWA Report, 2013

Application of CSA-Based Binder

Field Application of CSA Concrete (Illinois, USA)

Successful implementation of CSA concrete in a bridge deck!

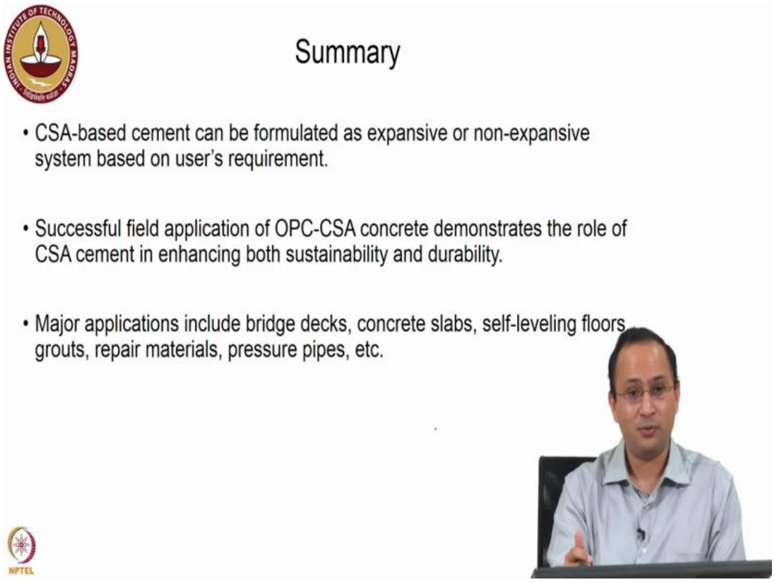
Now will look into the small scale versus large-scale. In a small-scale test, when you do this concrete prism test, it compares, you have seen similar plot before, so this is a conventional concrete, when you do not have any expansion agent. There is a shrinkage of the order, in this case 600 to 700 micro strain. And you add the calcium Sulfoaluminate cement, this early-age expansion and the net shrinkage is close to 0. But because of this restraint, now if you look into the strain level in slab, the degree of restraint is different, it is high.

Although we see some difference but we are not seeing like zero net shrinkage. There is a difference, like OPC is here, we are able to reduce the net shrinkage. So that is why it is important to pay attention to the degree of restraint, percentage level of your reinforcement in the slab, when you want to predict. Now, coming back to the application of CSA base binder, this was a field application done using OPC CSA cement in Illinois, where 2 decks were cast side-by-side.

You see normal deck with Portland cement and when we replace Portland cement with CSA. And what was interesting to see that the deck with CSA did not crack in early-age. So, there was no cracking, no sign of shrinkage cracking. So it was a successful implementation of CSA concrete.

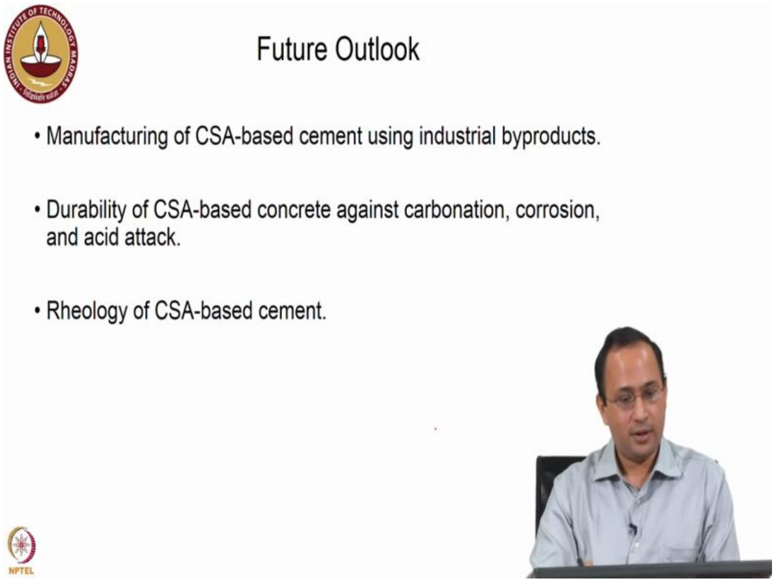
(Refer Slide Time: 44:57)

Bridge Deck Pour: OPC-CSA Concrete



Summary

- CSA-based cement can be formulated as expansive or non-expansive system based on user's requirement.
- Successful field application of OPC-CSA concrete demonstrates the role of CSA cement in enhancing both sustainability and durability.
- Major applications include bridge decks, concrete slabs, self-leveling floors grouts, repair materials, pressure pipes, etc.



Future Outlook

- Manufacturing of CSA-based cement using industrial byproducts.
- Durability of CSA-based concrete against carbonation, corrosion, and acid attack.
- Rheology of CSA-based cement.

This is the deck pour, the concrete was fluid, workable, no issue. So again this was a blend of OPC and CSA cement. And there was no issue in terms of pouring it in heavy reinforced areas.

So, in summary, CSA cement can be formulated as expansive or non-expansive cement system based on users requirement. If you want to reduce your shrinkage, then you will leverage the early-age expansion. And successful field application of the OPC CSA concrete demonstrates its role in enhancing both sustainability and durability.

And the major applications of this cement include in bridge decks, concrete slabs, self-levelling floors, grouts, repair materials, pressure pipes, etc. So where we stand now in terms of research? So, now we need to think about the manufacturing of the CSA based cement using industrial byproducts, because that will drastically reduce the cost. Also durability of CSA based concrete against carbonation, corrosion and acid attack is an active area of research. As we see the rheology is very important, how can we come up with the new chemical admixtures that can control the workability of the CSA based cement. So these are the future possible areas of research.

Thank you for your attention.