Admixtures And Special Concretes

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Lecture -47

Mineral Admixtures: Agricultural ashes - Part 2 : Rice husk ash

Rice husk ash:

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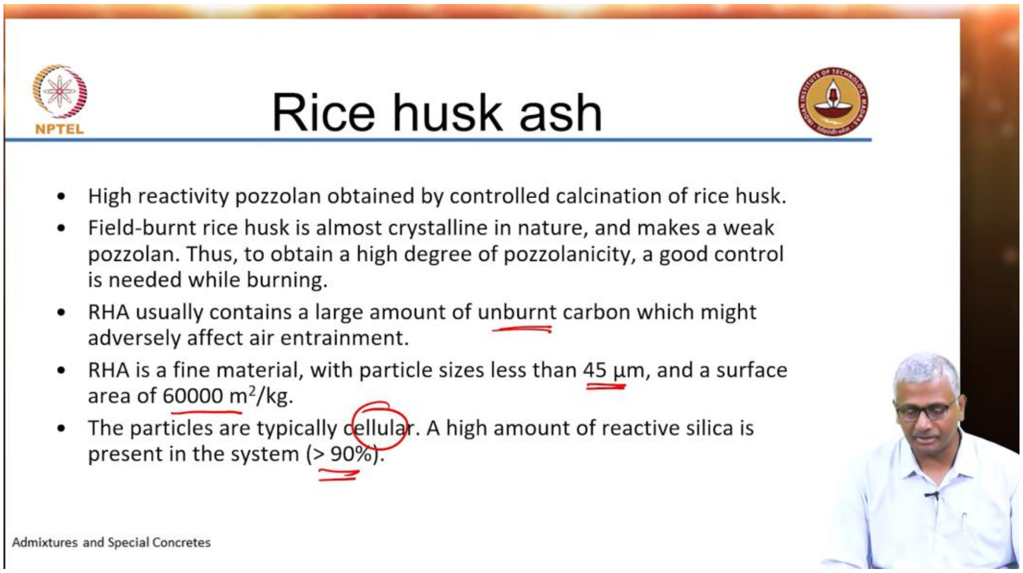

Rice husk ash

- High reactivity pozzolan obtained by controlled calcination of rice husk.
- Field-burnt rice husk is almost crystalline in nature, and makes a weak pozzolan. Thus, to obtain a high degree of pozzolanicity, a good control is needed while burning.
- RHA usually contains a large amount of unburnt carbon which might adversely affect air entrainment.
- RHA is a fine material, with particle sizes less than 45 µm, and a surface area of 60000 m^2/kg.
- The particles are typically cellular. A high amount of reactive silica is present in the system (> 90%).

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So we have been talking about the structure of agricultural ashes. We primarily saw that bagasse ash had a range of different types of particles depending upon how the bagasse was being burnt, the particles were either irregular or prismatic or spherical which indicates that there is some degree of crystallinity that is crept in because of the differences in temperature during burning. And we also saw that certain levels of processing techniques could help in actually ideally separating out the ingredients that are reactive and producing a material that is highly pozzolanic. Well at least normally pozzolanic. On the other hand, rice husk ash we have started to look at what the structure was which made rice husk ash such a highly pozzolanic material and this essentially is because of the very high surface area available for reaction. Although particle size of rice husk ash is not significantly large but surface area is significantly more than cement particles which leads to a large amount of surface available for pozzolanic reaction and the fact that this is high purity amorphous silica leads RHA to become a very highly pozzolanic material just like silica fume.

Typical composition of rice husk ash:

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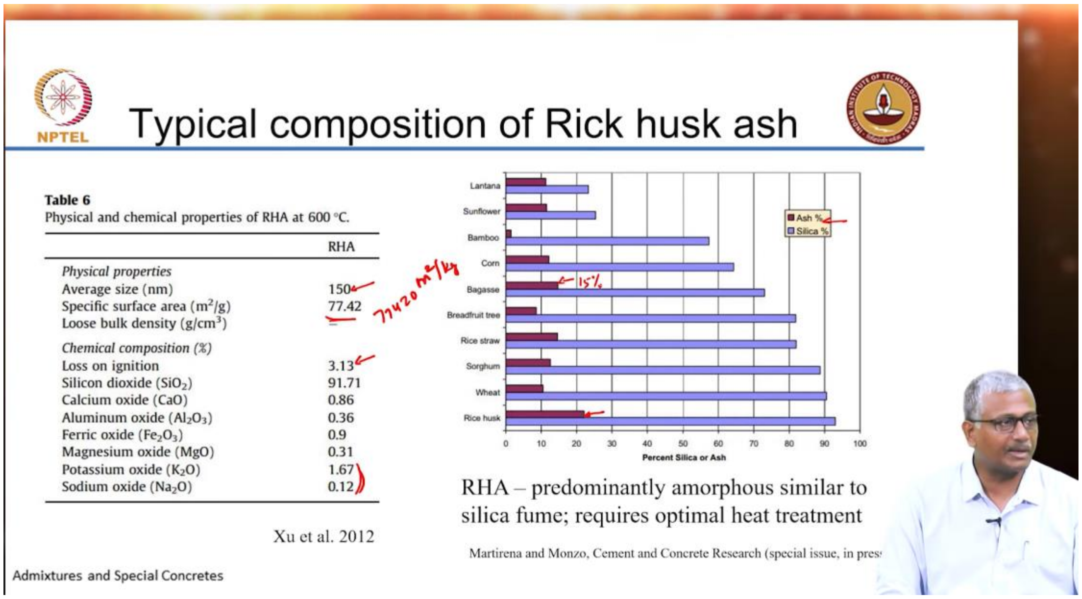

Typical composition of Rick husk ash

Table 6
Physical and chemical properties of RHA at 600 °C.

	RHA
Physical properties	
Average size (nm)	150
Specific surface area (m^2/g)	77.42
Loose bulk density (g/cm^3)	–
Chemical composition (%)	
Loss on ignition	3.13
Silicon dioxide (SiO_2)	91.71
Calcium oxide (CaO)	0.86
Aluminum oxide (Al_2O_3)	0.36
Ferric oxide (Fe_2O_3)	0.9
Magnesium oxide (MgO)	0.31
Potassium oxide (K_2O)	1.67
Sodium oxide (Na_2O)	0.12

77420 m^2/kg

Xu et al. 2012

RHA – predominantly amorphous similar to silica fume; requires optimal heat treatment

Martirena and Monzo, Cement and Concrete Research (special issue, in pres

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Now in terms of composition if you look at the sizes given here, now of course the particles which are measured by your laser particle size analysis may indicate a surface area or rather particle size of less than 45 micron. In general, this is because of 45 micron sieve type analysis but if you do a proper laser diffraction or an alternative analysis with very fine powders you may actually see RHA which has been processed to even have a much lower average size. So it is 150 nanometers here. I do not think most RHA's that are processed by controlled burning will achieve that size.

This particular study had an RHA which had 150 nanometer size. 150 nanometers almost in a nanoparticle size range when we have like from nanometers to tens of nanometer sizes typically, we call them nanoparticles. So, 150 is not really a microparticle which we are used to a cement replacement. So, this is not really the bulk of what you will find in other research studies. Many other research studies will have rice husk ash which has particle sizes which appear to be similar to that of your cement particles except that because of the highly cellular nature of these particles, you get extremely large surfaces and here also the surface is 77.4 meter square per gram that means 77000 meter square per kilogram. So it is a very large surface area. Here you can again see the fact that this is a processed silica in terms of the low loss and ignition that is there only about 3 percent. If you collect rice husk ash from just after a burning process you may actually find the LOI to be much higher than that. You can see that silica is very rich 90 plus.

Again, just like other agricultural ashes, there is a potential to have quite a bit of alkalis in the form of potassium oxide just like what we saw in sugarcane bagasse ash. So if you look at the percent silica or ash depending upon the type of agricultural residues you can have different levels of ashes that are obtained from these systems. So if you look at the ash fraction present in all these materials or ash percentage rice husk is possibly one of the largest ash percentages. Only 25 percent of the rice husk becomes ash. So that means the potential to use rice's husk ash is significantly large.

If you look at wheat straw is only about 10 percent. If you look at bagasse it is about 15 percent. So, depending upon the type of plant that is getting processed to form the ash you can get the varying quantities of ashes. So, you need to have optimal heat treatment in order to get the right reactivity from rice husk ash. That is what we discussed previously that controlled burning is required in terms of control of temperature and time of burning to obtain the right level of reactivity.

RHA particles:

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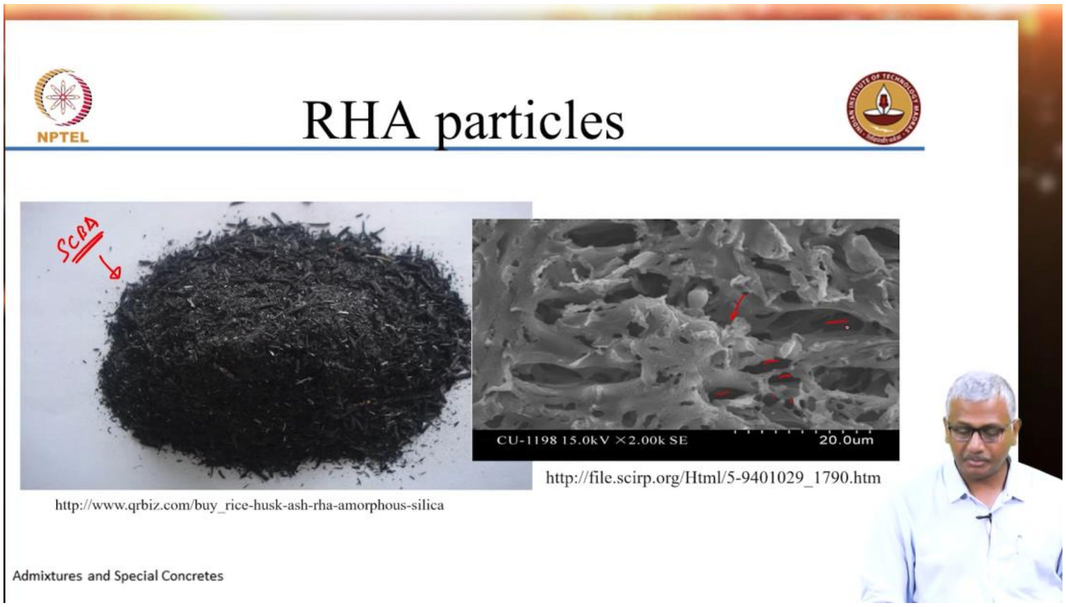

RHA particles

http://www.qrbiz.com/buy_rice-husk-ash-rha-amorphous-silica

http://file.scirp.org/Html/5-9401029_1790.htm

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So, you can see the rice husk ash particles. This photograph obviously appears quite similar to your sugarcane bagasse ash. If somebody gave you two samples of rice husk ash and bagasse ash you will probably not be able to distinguish easily. But when you start looking at the structure of the particles you can see here this scale is 20 microns and you can see the kind of particles that you have. So many vesicles and cavities that you see inside.

Highly cellular nature of the particles. You really do not see a solid particle but a very high surface that is present in these particles. So, this rice husk ash has a distinctly cellular nature as compared to the other solid particles that we are used to from the other types of pozzolanic materials.

Burning temperature:

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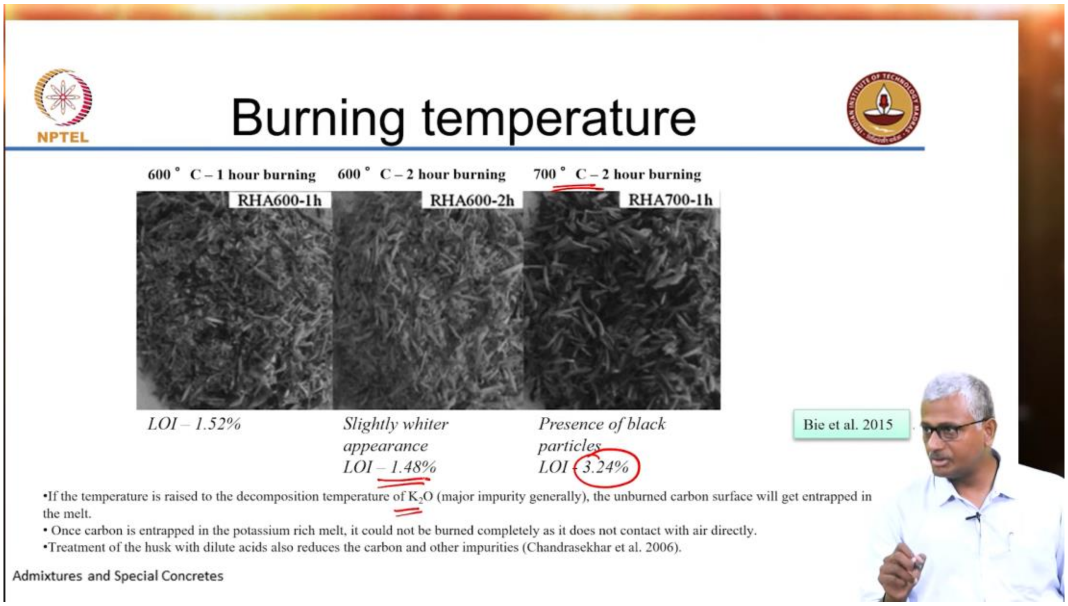

Burning temperature

LOI – 1.52%

Slightly whiter appearance
LOI – 1.48%

Presence of black particles
LOI – 3.24%

Bie et al. 2015

- If the temperature is raised to the decomposition temperature of K_2O (major impurity generally), the unburned carbon surface will get entrapped in the melt.
- Once carbon is entrapped in the potassium rich melt, it could not be burned completely as it does not contact with air directly.
- Treatment of the husk with dilute acids also reduces the carbon and other impurities (Chandrasekhar et al. 2006).

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And what happens if you burn at different temperatures at different times? So what really happens is at some temperatures you are able to produce the right combination of LOI and reactivity. Now what can also happen is at very high temperatures you could reach the decomposition temperature of potassium oxide.

And what will happen is the unburned carbon surface will get entrapped in the melt. The melt basically appears when the entire product starts burning as a single mass. So your unburned carbon surface which has these alkalis may actually start getting entrapped in the mass. Once it is entrapped in the potassium rich melt it cannot be burnt completely. So some LOI will remain in the system because when you are reaching this decomposition temperature of the potassium you are not able to react out the carbon dioxide or carbon into CO_2 completely.

That is why when you see the 700 degrees at 2 hours of burning it actually leads to a higher LOI as compared to 600 degrees at 2 hours. So, at 700 degrees you are closer to the decomposition temperature of potassium oxide and that captures this unburned carbon and does not allow it to actually oxidize as CO_2. And because of this you may have to again have a very clear-cut control on the rate at which you are cooling or burning, temperature to which you are burning and so on. So, all of these factors have to be paid particular attention when you are actually trying to process rice husk ash.

Microstructure:

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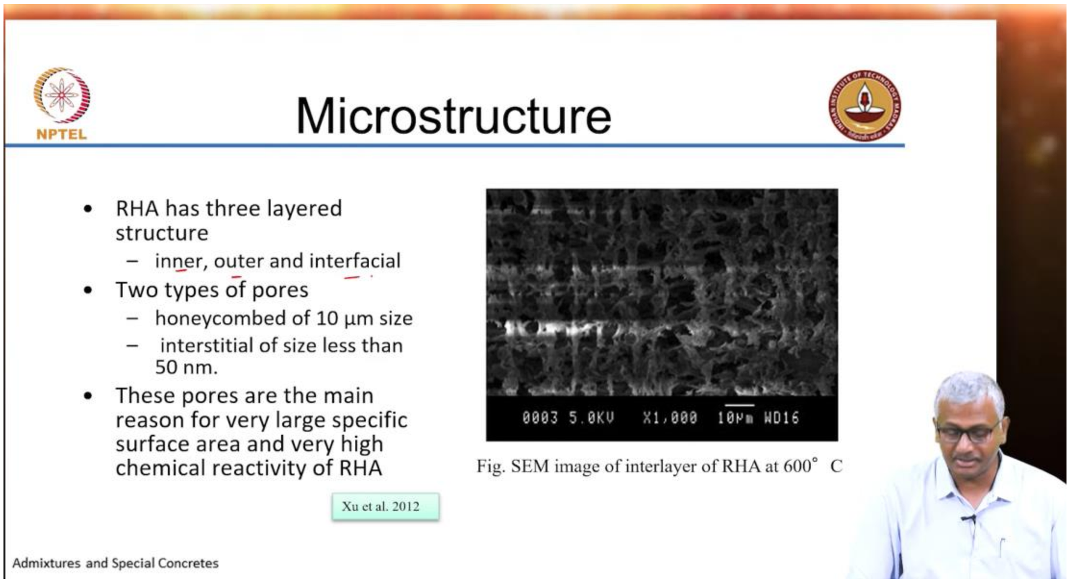

Microstructure

- RHA has three layered structure
  - inner, outer and interfacial
- Two types of pores
  - honeycombed of 10 µm size
  - interstitial of size less than 50 nm.
- These pores are the main reason for very large specific surface area and very high chemical reactivity of RHA

Xu et al. 2012

Fig. SEM image of interlayer of RHA at 600° C

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Again microstructure, I am sorry this is not such a great picture because you can see that you are not seeing the image clearly there are some white bands and dark regions that is because of what we call in scanning electron microscopy as charging of the specimen.

So, generally if you look at RHA or rice husk ash particles closely you have a three layered structure you have inner, outer and interfacial structure. And you will have two types of pores which are based on their size ranges you have honeycombed pores of nearly 10 micron size.

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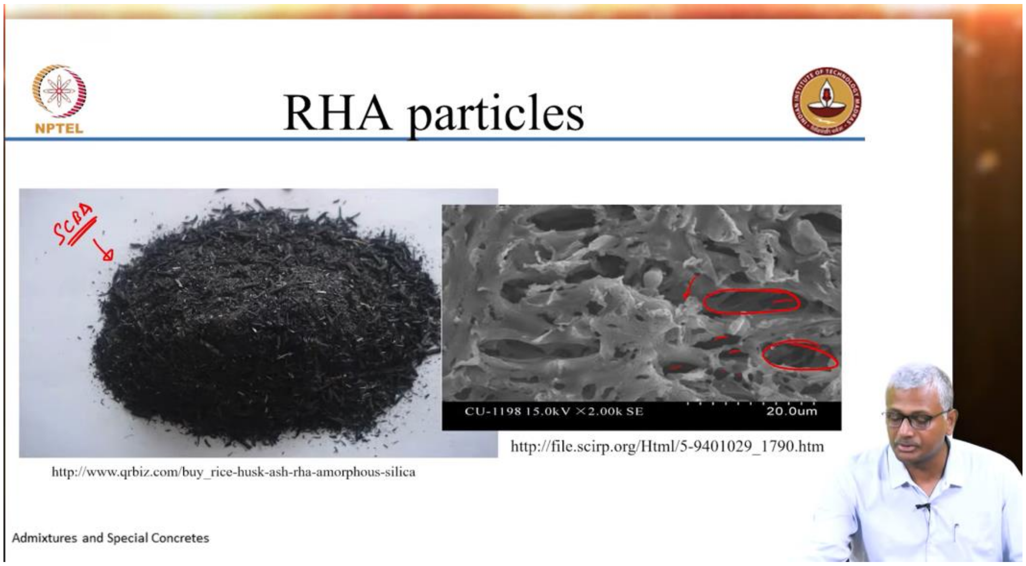

RHA particles

http://www.qrbiz.com/buy_rice-husk-ash-rha-amorphous-silica

http://file.scirp.org/Html/5-9401029_1790.htm

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So, if you look at this picture you have these large honeycomb pores which may be about more than 10 micron size and then you have interstitial pores of less than 50 nanometers.

So, again the presence of these pores and vesicles is the reason for the very high specific surface available on the particles of rice husk ash.

Effect on fresh properties:

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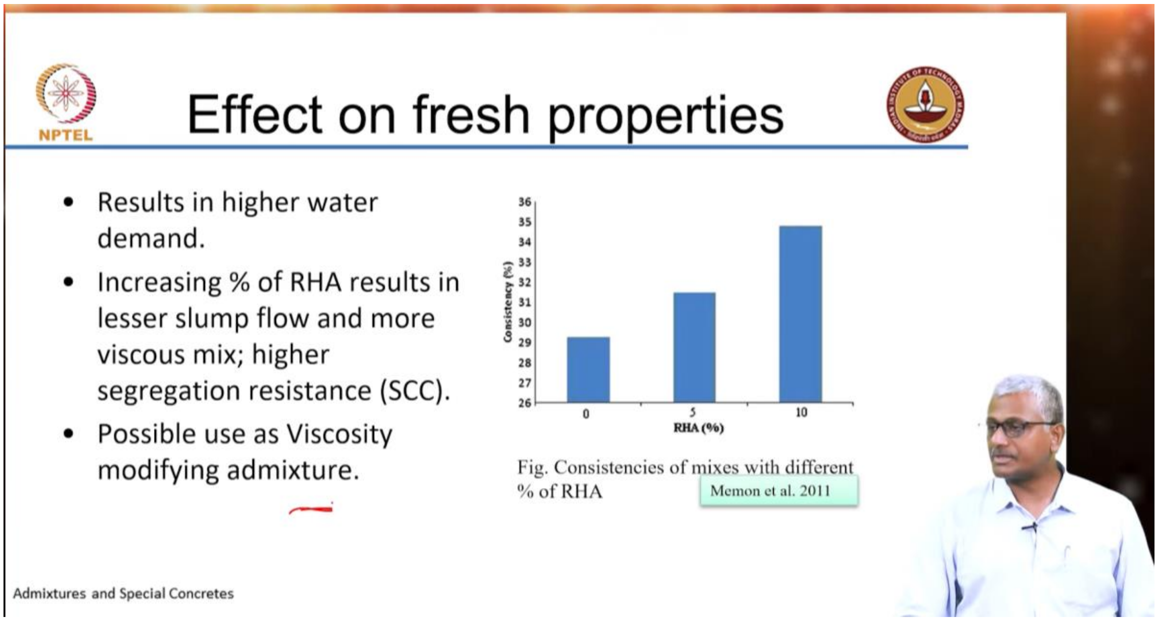

Effect on fresh properties

- Results in higher water demand.
- Increasing % of RHA results in lesser slump flow and more viscous mix; higher segregation resistance (SCC).
- Possible use as Viscosity modifying admixture.

Fig. Consistencies of mixes with different % of RHA

Memon et al. 2011

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Now for obvious reasons because of this high surface there is also going to be a larger water demand and increase in RHA percentage will reduce the workability properties of your concrete that is quite clear that is going to happen.

It will also result in a more viscous mix, your RHA particles because of the fact that your surface is increasing will also lead to a higher viscosity of the mix and mixes with RHA because they are trapping the water will have higher segregation resistance water will not be able to come out easily. People have also experimented the use of RHA as a viscosity modifying admixture to try and control the rate of settlement of the particulate species inside concrete by adopting RHA as a viscosity modifying admixture. But of course, that is not the primary use because of its pozzolanic reactivity it has to be used primarily as a mineral additive.

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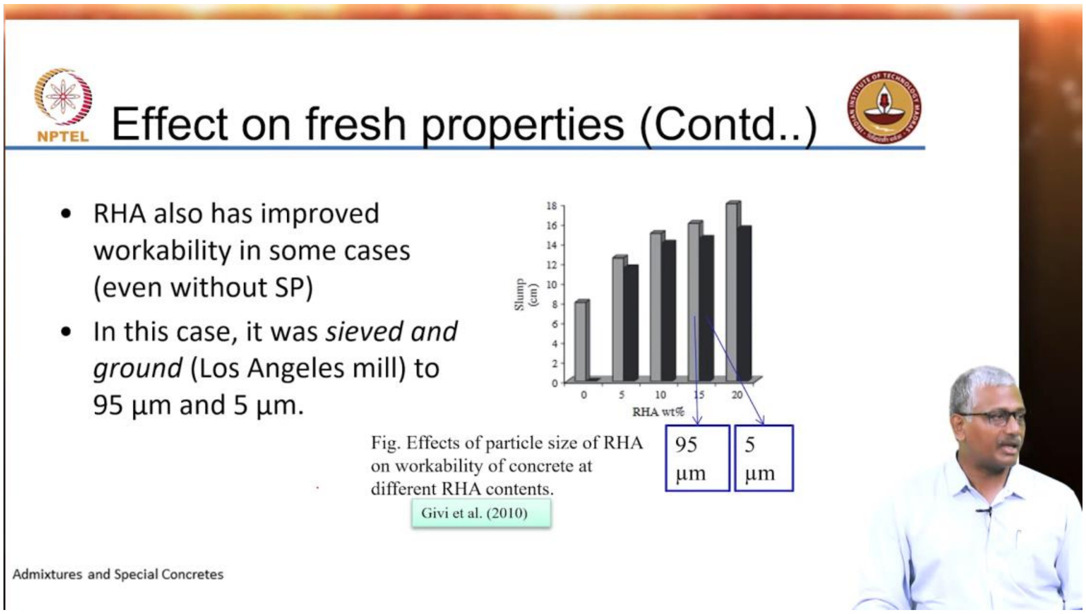

Effect on fresh properties (Contd..)

- RHA also has improved workability in some cases (even without SP)
- In this case, it was *sieved and ground* (Los Angeles mill) to 95 µm and 5 µm.

Fig. Effects of particle size of RHA on workability of concrete at different RHA contents.

Givi et al. (2010)

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Now of course results can vary significantly based on what type of work and what type of particle sizes have been used. So it turns out in some instances there has also been a reported increase in slump with RHA.

Now such results have to be obviously taken with a pinch of salt because you need to have a clear-cut understanding of how they prepared the concrete mixes whether the absorption of RHA was accounted for? Whether additional superplasticizer was taken to actually counter the effect of increased surface that RHA provides? So what you should do is try to look at the conflicting data and literature and try to figure out for yourself. But primarily what one would think is that because the cellular nature you can expect that there will be greater water entrapment and you will have a loss of workability.

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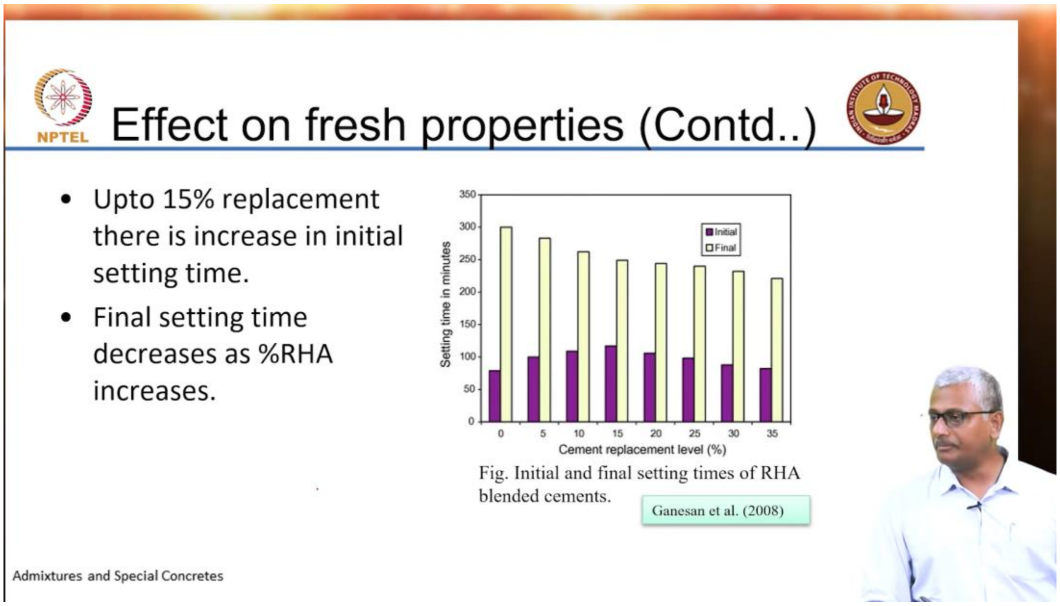

Effect on fresh properties (Contd..)

- Upto 15% replacement there is increase in initial setting time.
- Final setting time decreases as %RHA increases.

Fig. Initial and final setting times of RHA blended cements.

Ganesan et al. (2008)

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And in terms of setting time more or less you really do not get a major change in performance. You can see that there is some variation, but I would not really call it very significant more or less it is in the ballpark that you estimate for most common cementitious materials.

So, although in research papers people may try to make much out of this result in reality there is really not much that we can say about the result here.

Effect on compressive strength:

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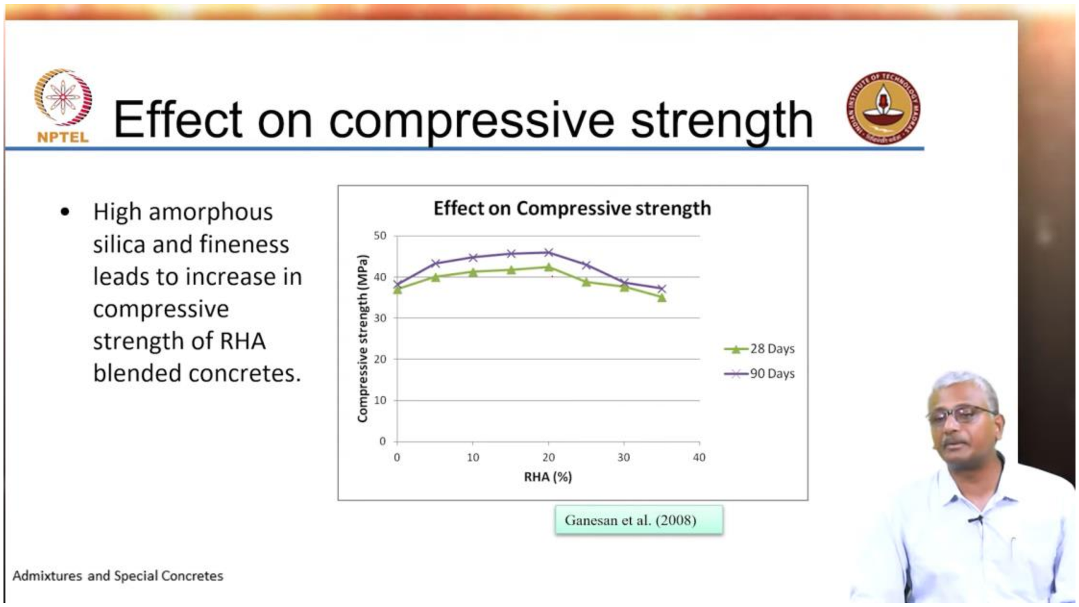

Effect on compressive strength

- High amorphous silica and fineness leads to increase in compressive strength of RHA blended concretes.

Ganesan et al. (2008)

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Again with respect to compressive strength we know that because of the high reactivity replacement of cement by RHA can have a good influence on the ultimate strength. But what will happen is if you keep on increasing the extent of percentage replacement of cement by RHA you are going to reach a stage where you will start losing the benefit of increasing the RHA content because you do not have sufficient lime to react. You are not really making the use of pozzolanic reactivity of the RHA and because of its size of the particle it is not really functioning very well as a filler also. It is not like silica fume.

Silica fume does not really need to react to provide you an enhancement in strength. It can still provide strength by simply acting as a filler. In RHA you do not really get that benefit. The primary benefit in RHA is because of the reactivity provided by the high surface available. So that is where you need to have a clear distinction between how silica fume would react and how RHA would react.

That is why beyond a certain percentage you really do not see an improvement. Of course, in silica fume beyond a certain percentage your improvement may be restricted because of the fact that your water demand goes up so much that it is nearly impractical to make the concrete.

Durability results:

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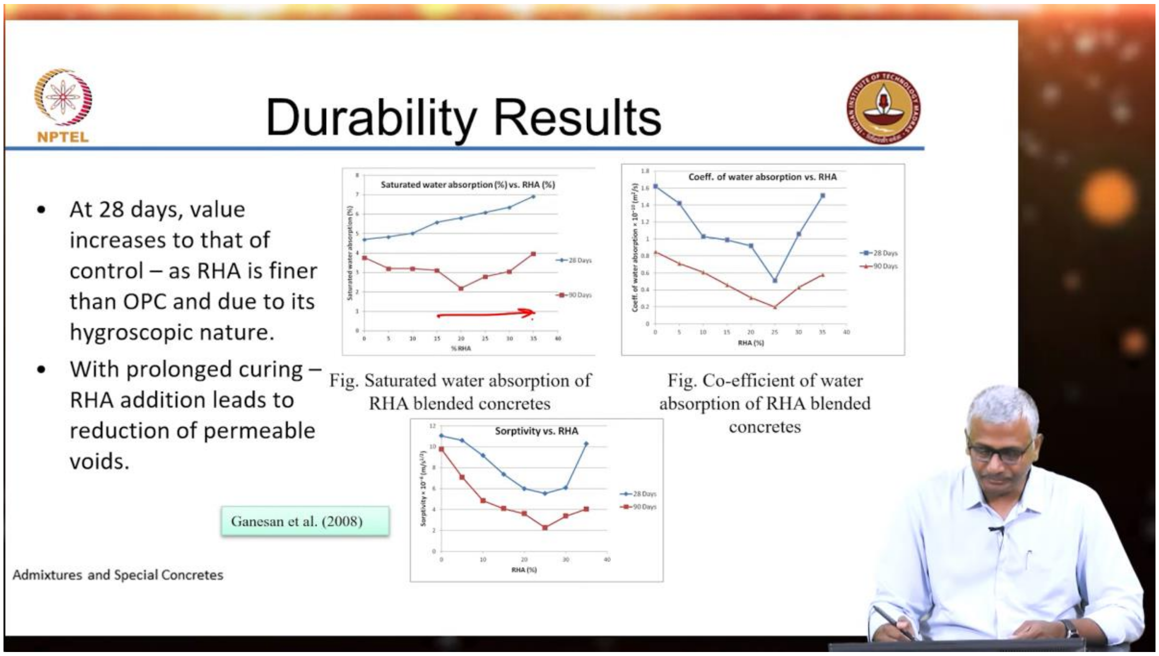

Durability Results

- At 28 days, value increases to that of control – as RHA is finer than OPC and due to its hygroscopic nature.
- With prolonged curing – RHA addition leads to reduction of permeable voids.

Fig. Saturated water absorption of RHA blended concretes

Fig. Co-efficient of water absorption of RHA blended concretes

Ganesan et al. (2008)

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In terms of durability of course what results that are presented here because there is not too many well-controlled studies that have been done on RHA that if you are working in the common regime of replacement of about 10% the durability with RHA is always better than for plain OPC. Again, this goes to the credit obviously goes to the pozzolanic reaction which results in a finer microstructure and produces less permeability of the concrete. So, beyond that if you look at these high percentage replacements I do not think the results are going to be very reliable because it is a moot point whether the RHA is providing any assistance to the system at all beyond about 10 to 20% and even 20% would be stretching the use of RHA a bit too far.

You would rather restrict it to something like 10% because beyond that you are not really relying on the pozzolanic reactivity that much. You do not really have sufficient lime in the system to interact with the RHA at that level.

Change in porosity:

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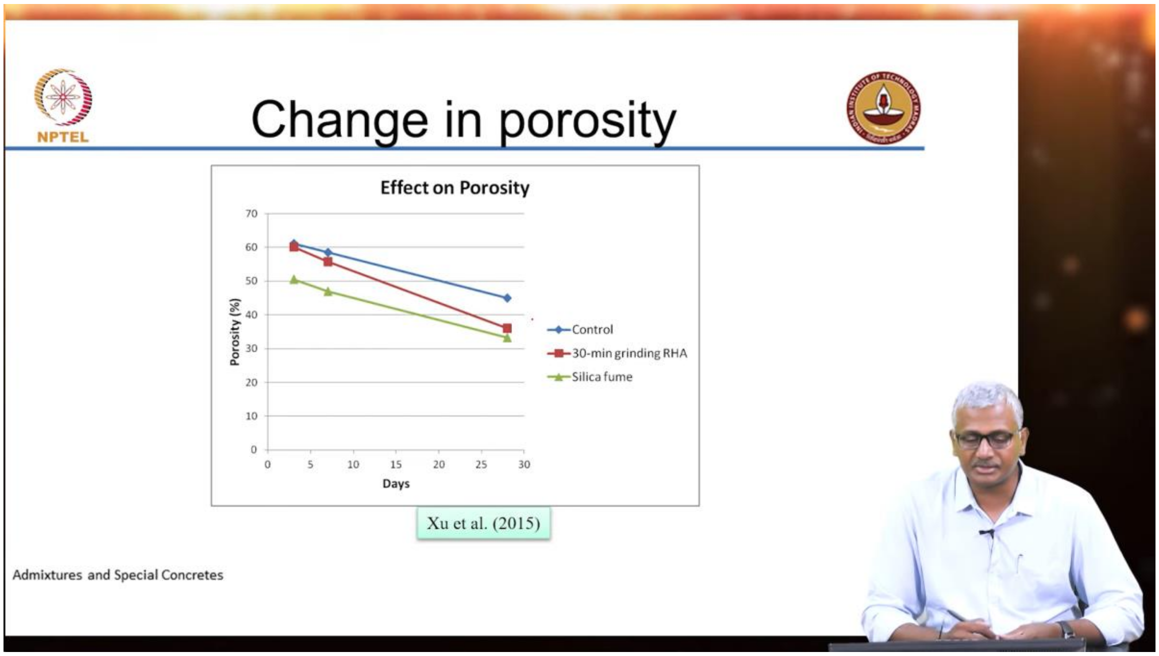

Change in porosity

Xu et al. (2015)

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Again, your change in porosity is reflected in this picture this is porosity of paste that is why the porosity content seems to be too high. This is porosity of paste and depending upon the days of curing obviously porosity reduces it turns out that the porosity with rice husk ash-based systems is reducing to the level of silica fume-based systems if you are curing for a long enough time primarily because you are getting the pozzolanic effect with silica fume from the beginning itself you are getting the filler effect. So porosity reduction is almost immediately seen as you can see from this result.

Chloride-based tests:

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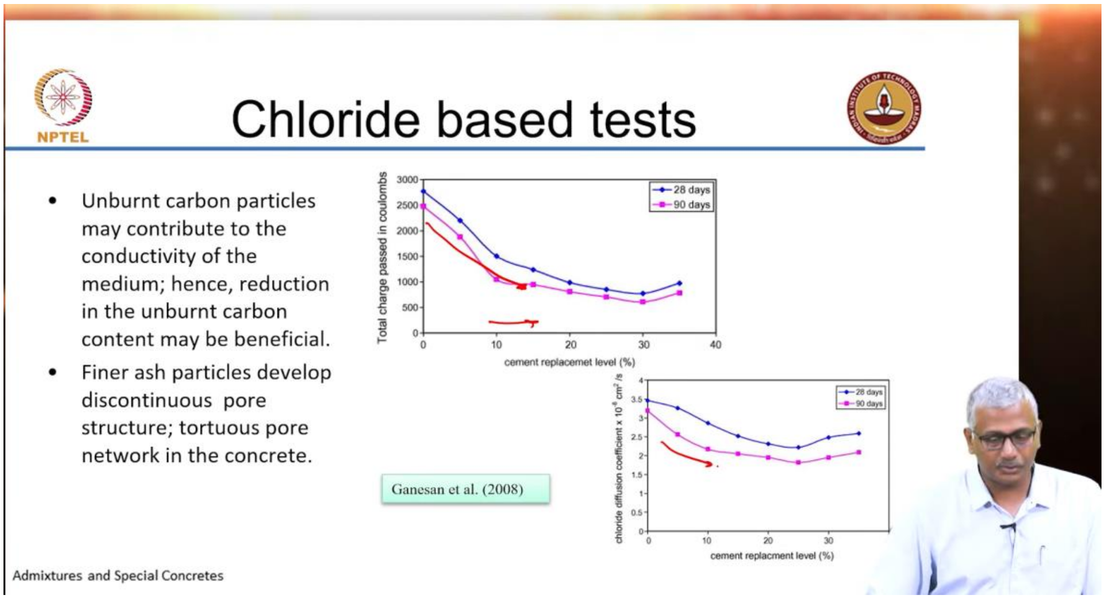

Chloride based tests

- Unburnt carbon particles may contribute to the conductivity of the medium; hence, reduction in the unburnt carbon content may be beneficial.
- Finer ash particles develop discontinuous pore structure; tortuous pore network in the concrete.

Ganesan et al. (2008)

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In most cases utilization of rice husk ash as a cement replacement is going to obviously improve the resistance to chloride penetration more from the fact that you are now causing a denser microstructure to form and again tortuosity of the pore structure just like what you get in other mineral admixture-based systems is going to restrict the increase of chloride ions. So most chloride-based tests will show that as the replacement level increases your charge passed in RCPT is decreasing and actually chloride diffusion coefficient is also decreasing as you increase the replacement level. Now charge passed in RCPT again please remember it has to be attributed not just to the reduction in permeability but also to the fact that you are binding the alkali ion concentration which is otherwise going to increase the conductivity of the pore solution.

Agro-based ash (mixed source)

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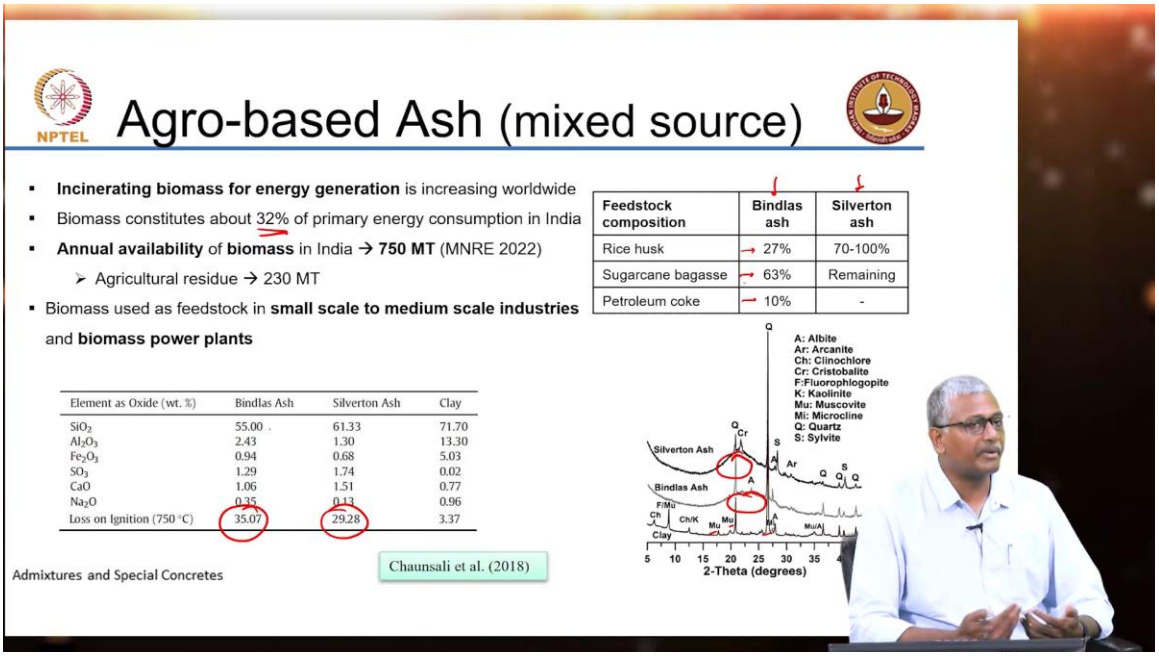

Agro-based Ash (mixed source)

- **Incinerating biomass for energy generation** is increasing worldwide
- Biomass constitutes about 32% of primary energy consumption in India
- **Annual availability** of **biomass** in India → **750 MT** (MNRE 2022)
  - Agricultural residue → 230 MT
- Biomass used as feedstock in **small scale to medium scale industries** and **biomass power plants**

Feedstock composition	**Bindlas ash**	**Silverton ash**
Rice husk	27%	70-100%
Sugarcane bagasse	63%	Remaining
Petroleum coke	10%	-

Element as Oxide (wt. %)	Bindlas Ash	Silverton Ash	Clay
SiO_2	55.00	61.33	71.70
Al_2O_3	2.43	1.30	13.30
Fe_2O_3	0.94	0.68	5.03
SO_3	1.29	1.74	0.02
CaO	1.06	1.51	0.77
Na_2O	0.35	0.13	0.96
Loss on Ignition (750 °C)	35.07	29.28	3.37

Chaunsali et al. (2018)

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Now in many instances as I said you may not get agro ashes from a single source. People may collect agricultural residues from various different farms and bring it to a common source to do the incineration.

So, in general this aspect is increasing worldwide and in India biomass is a major energy source about 32% of primary energy consumption in India is from biomass. So it is a significant amount probably second only to coal. Coal is the primary source but biomass could be the second largest source. In India about 750 tons of sorry 750 million tons of biomass is available and that leads to an agricultural residue totally of about 230 million tons. We saw that rice husk ash, bagasse ash they are available to about 20 million, 2 million, 3 million like that.

So overall if you total up all the different types of agricultural residue and the ash derived there in overall quantity will be close to about 200 plus million tons which is equivalent to that of fly ash. Fly ash is also about 200 plus million tons overall. Now biomass itself before burning is typically used in small-scale to medium-scale industries and biomass power plants. From the biomass power plants obviously you are able to generate the agricultural ashes. So as I said this particular study which was done by Professor Piyush before he joined IIT Madras.

So in this case there were two sources of ashes that were looked at and these two sources had mixed ashes. So for instance this one had rice husk, sugarcane bagasse and petroleum coke or pet coke which was present in the burning mass which could lead to the generation of different of a mixed ash and silver tan ash basically was a mixture of rice husk and sugarcane bagasse alone. So again in terms of the oxide compositions you can see the differences here. For the Bindlas ash, your SiO2 content was 55 percent whereas silverton was about 61 percent. If you can look at the alumina content which is fairly low in both these cases loss and ignition is extremely high indicating there is a lot of unburned carbon that is still present in these systems.

They also had a nearby clay which was being used in a brick manufacturing unit. So this project was about whether the ashes that are produced from this mixed ash burning or mixed agri-based burning could be used towards processing of bricks. So they compared it with the clay that was available nearby and this is the chemical composition of the clay. And you can see the X-ray diffraction pattern and with respect to the ashes you can see the amorphous regions exhibited by the ashes also. And from the clay you can see that there are specific phases present in the clay like mullite, quartz and so on.

So clay obviously is used as it is and then it is burnt inside the sintering furnace where it transforms into the brick because of the formation of silica alumina bonds. The ash obviously will need a binder it cannot react on its own with water so it will need a binder like lime or cement.

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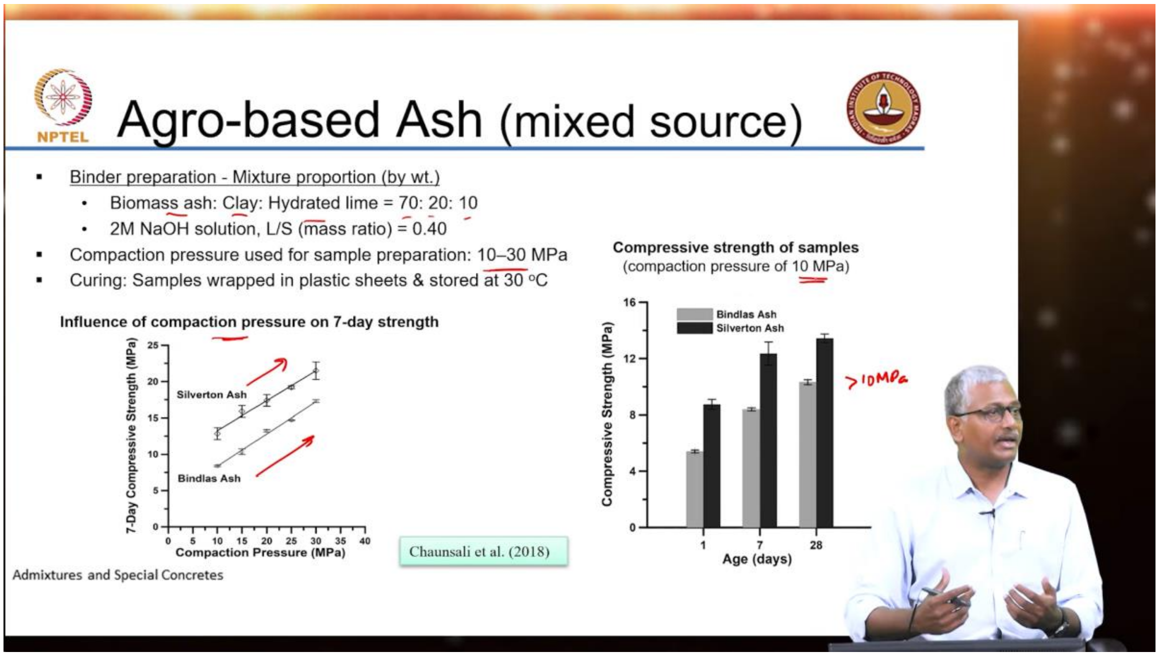

Agro-based Ash (mixed source)

- Binder preparation - Mixture proportion (by wt.)
  - Biomass ash: Clay: Hydrated lime = 70: 20: 10
  - 2M NaOH solution, L/S (mass ratio) = 0.40
- Compaction pressure used for sample preparation: 10–30 MPa
- Curing: Samples wrapped in plastic sheets & stored at 30 °C

Influence of compaction pressure on 7-day strength

Chaunsali et al. (2018)

Compressive strength of samples
(compaction pressure of 10 MPa)

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So in this case the binder preparation was by using the biomass ash and clay in combination with hydrated lime in the ratio 70 is to 20 is to 10. So instead of using plain clay for the production of the bricks they substituted large part of the clay by biomass ash and hydrated lime as a binder or as a cementing agent. And in this case, they also used a geopolymeric system, highly alkaline solution of 2 molar sodium hydroxide was used and with a liquid-to-solid mass ratio of 0.4.

So instead of mixing this system with water they mixed it with an alkaline solution with 2 molar sodium hydroxide concentration. So the idea was not just to get the pozzolanic reaction but also possibly some level of geopolymerization from the aluminosilicate that is present in the system. Now in bricks, we mold them in specific sizes and shapes. So in this case for sample preparation they also applied a compaction pressure of about 10 to 30 MPa. So these systems were actually compressed into the mold and wrapped in plastic sheets and stored at 30 degrees Celsius because they wanted to produce this reactivity at regular temperatures rather than heating at a very high temperature.

Clay obviously has to be burnt or sintered at extremely high temperatures to harden into the brick. So, the idea was to show that even without burning which consumes a lot of energy you could still lead to the production of bricks with sufficient strengths. So obviously when you increase the compaction pressure the strength increases because you are getting much better packing of the particles and the reactivity is also improved because particles are now closer together there is no excess voids that are present inside the system. So, as you increase the compaction pressure irrespective of the type of ash your system is increasing in its strength. And in terms of compressive strength itself very clearly you are seeing that most of these all these systems are approaching a strength of more than 10 MPa at 28 days even at a compaction pressure of just 10 MPa.

The compaction pressure is 10 MPa and the strength achieved by the brick at 28 days is more than 10 MPa easily qualifies as a class 1 brick. Instead of burning clay what they have just used is directly the clay and the unprocessed ash mind you this ash had 30% or more LOI and this was used in the as collected state without any processing. One of this carbon was removed all this carbon was present within the system. So they actually used these to form bricks directly mixing a little bit with the clay and hydrated lime and also used a highly alkaline solution. The resultant effect of pozzolanicity and geopolymerization together led to the formation of a hardened structure that was good enough to give you a strength of a class 1 brick.

So very clearly agro-based ashes can be processed near the source of collection itself after burning to form construction products like bricks or if you are in close proximity to a cement plant and if you can do a little bit more processing you can use this as a replacement of fly ash just in case the thermal power plant is too far away to give the right quality fly ash to the cement plant.

References:

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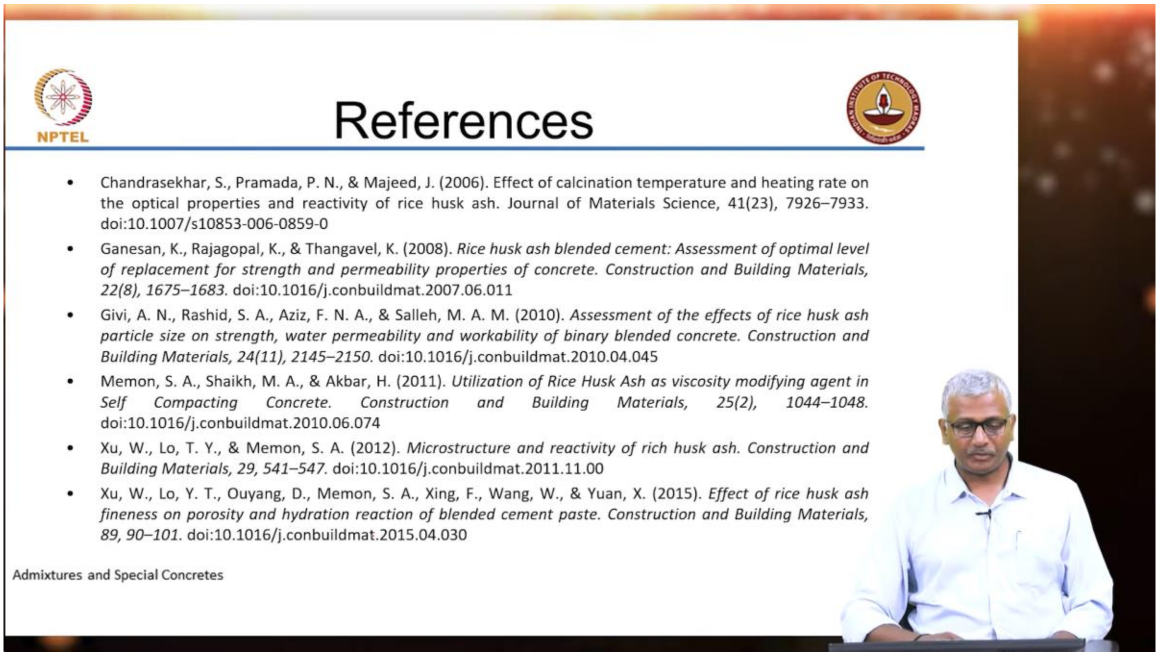

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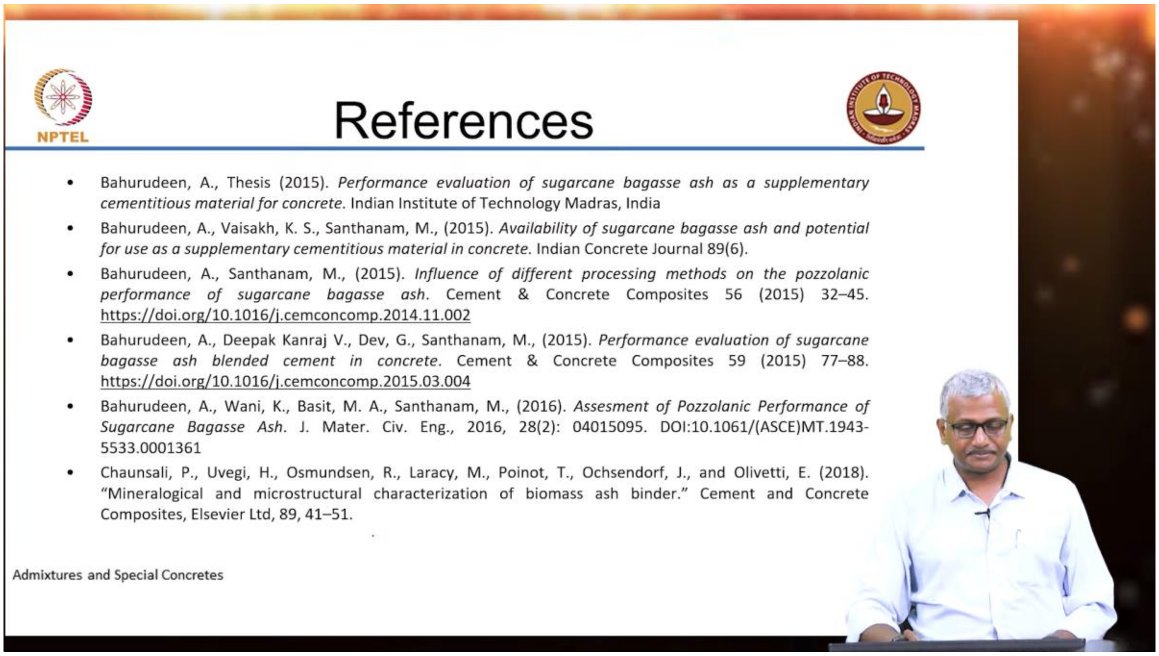

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So with that we come to a close of this chapter on agricultural ashes if you have any specific questions and the references from which all of those examples are given are shown here.