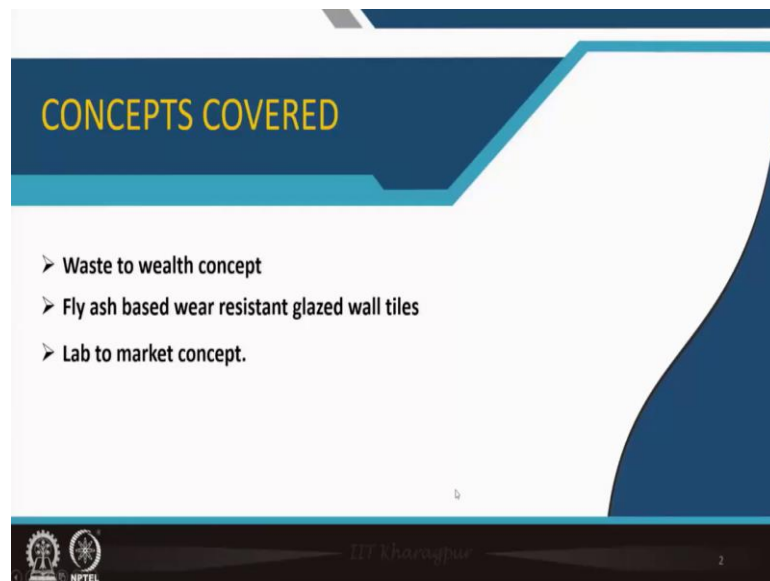


Non - Metallic Materials
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 12
Economic, Environmental and Societal Issues
Lecture - 60
Fly - Ash based glazed wall tiles: A case study

Welcome to my course Non-Metallic Materials and we are in module number 12 Economic, Environmental and Societal Issues. We are in lecture number 60 and here Fly-Ash based glazed wall tiles I will describe as a case study which will illustrate the various concepts taught in this course and how to make it a useful product out of this knowledge.


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So, this is based on waste to wealth concept and it is just a case study how you can use fly ash to make some value added product and part of it I will be describing fly ash based wear resistance glazed wall tiles, which are economic and can easily be made and the concept of lab to market the lab research translated to a valuable product that will be discussed.

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Utilization of waste material : Fly - ash



Oxide [wt%]	Fly-Ash	Pond-ash
SiO ₂	63.3	62.8
Al ₂ O ₃	24.6	28.3
Fe ₂ O ₃	4.97	3.85
FeO	0.45	--
CaO	1.23	0.70
MgO	0.56	0.58
MnO	--	0.03
TiO ₂	--	1.84
Na ₂ O	0.11	--
K ₂ O	0.64	--
Cr ₂ O ₃	--	0.04
P ₂ O ₅	--	0.32
C	0.55	1.15
LOI	1.28	0.50



Fly ash is a problem in India, where most of the electricity that is generated out of coal. So, coal is burnt to boil water and steam is used to rotate the turbine blade to generate electricity. So, ashes are generated huge quantity of ashes and this ashes are actually dumped in the form of a slurry and it forms some kind of this muddy zone and this we called a pond ash.

So, fly ash is fresh from the silo whatever we are getting from the factory of the thermal power generator factories and when it is stored, we termed this as a pond ash. So, this is a menace. So, in India particularly this is a major problem. So, and this is a good ceramic material.


If you see the composition of the fly ash and pond ash they are not very different, but depending on the coal type that is being used the major content is silicon dioxide and alumina apart from that other oxides are also there, but it does not have any cementitious property. So, it is pozzolanic in nature. So, there is no plasticity. So, you cannot make any ceramic article by simply adding water it is not plastic just like clay.

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Utilization of fly-ash

- ✦ Making bricks or concrete blocks
- ✦ Blending with cement
- ✦ Cenospheres separated from fly-ash: extenders for plastic compounds
- ✦ Synthetic foams with better mechanical properties; sports equipment; insulation, automobile and marine craft bodies, paints, fire and heat protection devices
- ✦ Production of high value products such as silicon carbide, silicon nitride, sialon, and β -cordierite

In third and fourth applications the estimated quantity of fly-ash that can be utilized is very low and so they will not help in solving the broader problem of bulk fly-ash disposal



So, it is a problem to utilize it, but people have started to utilize it and making brick by mixing it with cement and sprinkle water and press it and then sprinkle water so, that the cement gets strength. So, that is a known technology and brick and concrete blocks that is that has been used part of it is also used during cement production. So, that is the known use of fly ash.

Now if you see the microstructure, sometimes you can see the nice spherical particle which are hollow from inside. So, this is known as cenospheres.

So, this can be taken out from the fly ash and this is very good to make as a filler, it can be used to make various article including the board which block the sound wave and several other things like sport equipment, insulative material, automobile and marine craft bodies people have tried to use this cenosphere and this silica part if it can be extracted.

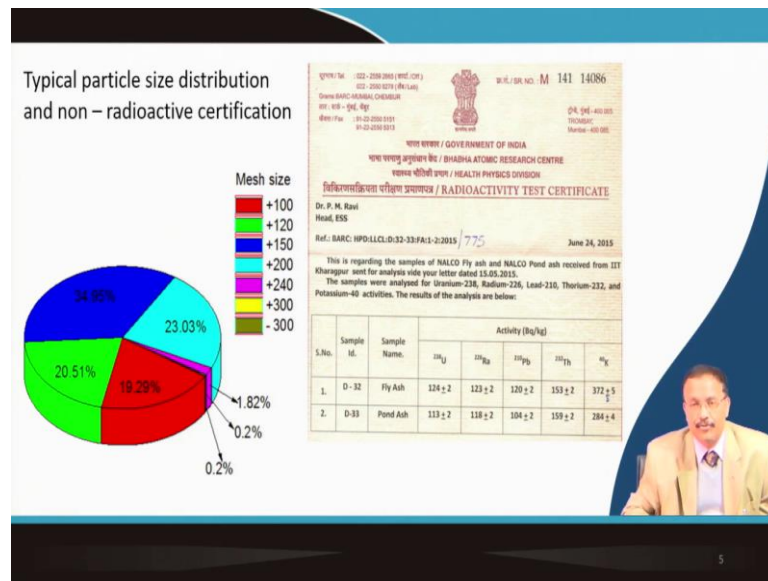
Then it can be used as glass, but that is not a proven technology, but high value product like silicon carbide, silicon nitride, Ceylon, cordierite ceramic they are being tried to make by this fly ash product. But this cenosphere or this extraction that cannot use the bulk quantity of fly ash.

So, very small quantity of fly ash can be utilized. So, major part is still being used as in a dumping for the filler material to make road etcetera. Part of it is going to the cement

industry and brick making is also quite popular nowadays, but still we have lot of raw materials. So, effort should be there so, that you can utilize more and more this waste product and you can make a value added product.

So, just using as a filler material or making simple brick or this cementitious article that will not add much value to it. So, value added product will have to be thought how to make value added product utilizing this fly ash.

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So, as a case study I will describe one of such product. So, if you see the particle size distribution of a particular type of fly ash which is an Orissa based region we collected this fly ash. So, the typical particle size distribution is having something like this. So, you know the mesh size that depends what type of particles are there in that mixture. So, there is plus 1 and minus 1.

So, minus means it passes through that and plus remains on top of that. So, that is a crude way to estimate the particle size distribution. So, different particles they are needed to be judged first so, that directly if you can use the fly ash for your ceramic article that is important for you to know.

If additional grinding etcetera is required. So, that unit operation will add up to the cost, but usually the fineness of the particle of the fly ash that is exactly very much required


what we require for normal ceramic processing. So, that is a plus point directly you can use fly ash for making some useful article.

But since it is based on fossil fuel, it is important for you to know that whether there is any radioactive element present in the fly ash. So, first and foremost thing that is required to get a certification from the concerned authority, government agency. In our country it is Bhabha Atomic Resource Centre they give the test the fly ash that is being used to give a certification that none of the radioactive element is present in the fly ash material.

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Composition of the additives to make a functional value added product

Oxide (wt%)	Fly-Ash	Pond-ash	China clay	Pyrophyllite	Red Mud
SiO ₂	63.3	62.8	62	53.00	6.34
Al ₂ O ₃	24.6	28.3	20	28.14	16.6
Fe ₂ O ₃	4.97	3.85	1.5	0.61	55.4
FeO	0.45	--			
CaO	1.23	0.70	3.0	1.63	1.36
MgO	0.56	0.58	4.40	1.09	
MnO	--	0.03			
TiO ₂	--	1.84	<0.01	0.10	4.49
Na ₂ O	0.11	--	0.2	0.32	3.13
K ₂ O	0.64	--	0.35	9.21	
Cr ₂ O ₃	--	0.04			
P ₂ O ₅	--	0.32			0.07
C	0.55	1.15			
LOI	1.28	0.50		5.55	12.5



So, then you need to use this fly ash in large quantity not in small quantity. So, typically you can set a weight fraction about 60 percent of fly ash that is must inside the composition that you are make you are making for the ceramic article and you will have to select other additives so, that you can make something which is useful.

So, we can utilize the fly ash which is otherwise non plastic with some kind of plastic material like clay and also pyrophyllite and some other filler material which is also an waste like red mud. You can see the composition of this materials. So, the China clay and pyrophyllite they have China clay they have plastic mass they have good plasticity. In normal tiles only clay is used.

So, if 60 percent of the clay is replaced by the fly ash, then suddenly it will be economic. So, it is a good way to utilize about 60 percent of fly ash and another waste like red mud to make the same clay having same type of commercial properties, commercial tile property if one can make out of fly ash then suddenly it will be a value added product.

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Nature of additives

Trioctahedral
Talc $Mg_3Si_4O_{10}(OH)_2$

Dioctahedral
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$

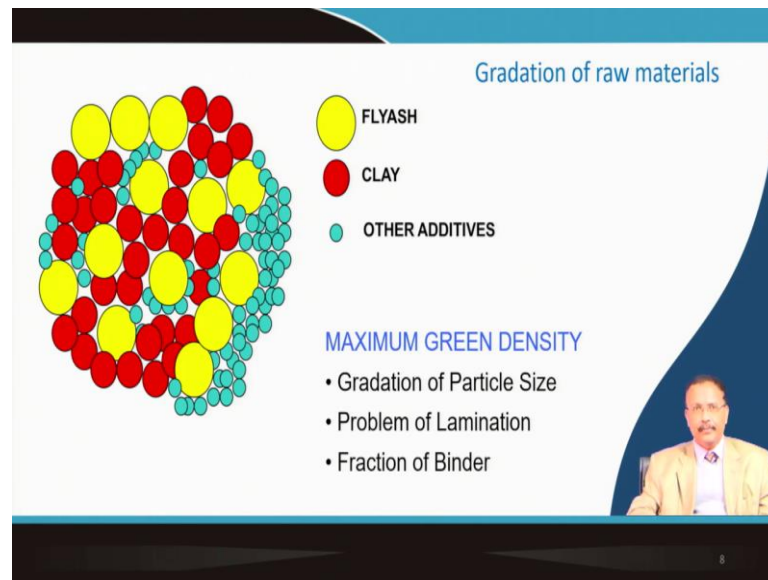
Kaolinite $Al_2Si_2O_5(OH)_4$

Pyrophyllite has a three layered structure, with a di-octahedral layer of gibbsite sandwiched between two sheets of SiO_4 tetrahedra. It has an ideal formula $Al_2Si_4O_{10}(OH)_2$

So, the pyrophyllite as you can see it has a three-layer structure. So, one is a dioctahedral layer of gibbsite, it is based on aluminium hydroxide which is sandwiched between silicon oxygen tetrahedra and ideal formula this is given by this $Al_2Si_4O_{10}(OH)_2$. So, this can be used along with the clay which is kaolinite, in the tile composition to make a dry pressed article.

Otherwise, normal fly ash if you use without this plastic agent then you cannot form any flat article out of it. So, the addition of this additives are is required.

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So, you can see that you have fly ash which is having this large particle, and you will have to judiciously select the particles of clay they are usually spherical in nature, spherical in size and other additives like pyrophyllite or red mud.

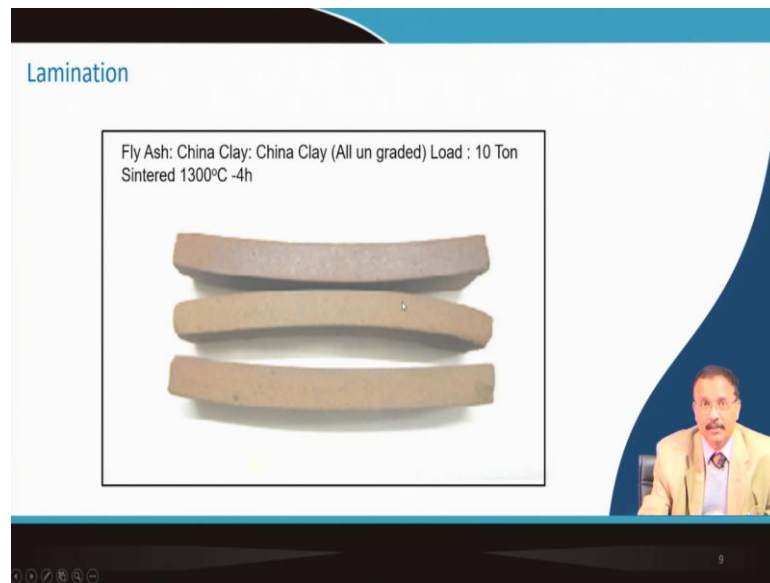
So, you will have to first grade this particle size so, that the finer the coarser particle they will have voids and this void will be adopted by the medium size particle, and the void in the medium size particle will be adopted by the small size particle. So, that you will have a green density good green density achievable by this way.

There is a standard solid state ceramic process, the gradation first it is done, and you cannot use too much fine fraction because that will lead to a problem of lamination because when you are pressing this article this mix, then with the pressure the heavier particle will go down to the mould and the finer particle will be on the top.

So, it is difficult to sinter. So, once its sinter, then you will see that the layer structure usually forms and there will be a lamination and part of it will be just chipped off after the sintering process.

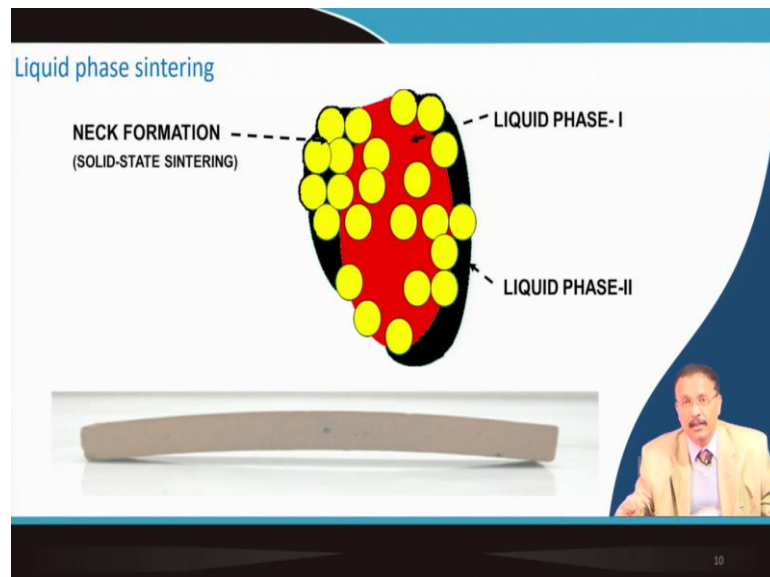
The fraction of the binder initially is important because that will give you the green strength because otherwise even handling a pressed article from the press to the dryer or the furnace it is difficult. So, you need to have a good quality binder which is also cheap for industrial purpose to identify that.

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So, the lamination is something similar to this, you can see that after sintering the sample that was made out of this fly ash they just bent like this. So, gradation was not done for this samples. So, the finer particle they were floated on top during pressing and after sintering they are laminated.

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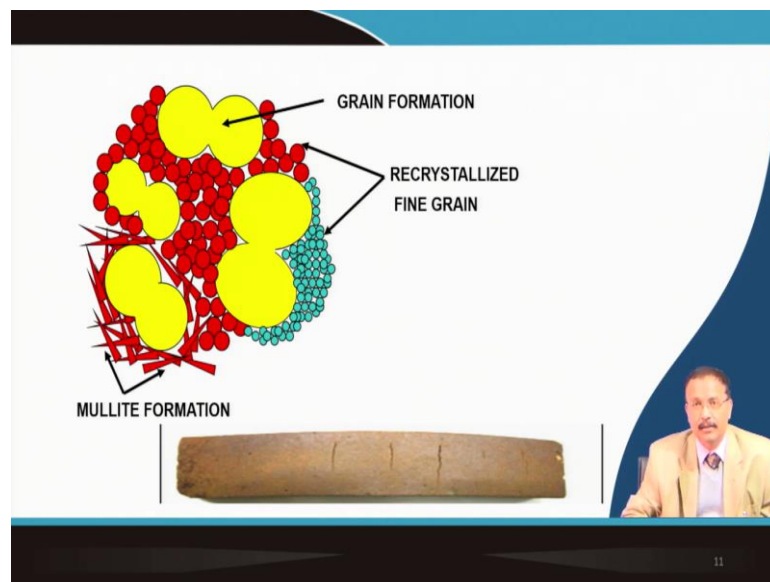


So, you know the liquid phase sintering. So, the composition is chosen such that part of the additives, clay, pyrophyllite they form a liquid. So, you have a liquid phase which due to the capillary action that goes inside the particle to wet the particle surface and

partially dissolve the material into the liquid and finally, it recrystallize. So, it removes the porosity and liquid phase sintering and also recrystallization that other crystalline phase may have larger good mechanical property that is important.

So, how much fraction the liquid? Usually it should be less than 15 percent that also will have to be judiciously selected otherwise the sample shape which was a rectangular block that cannot be maintained properly. So, the composition optimization is very important to make not only a strong material, but also maintaining the shape, get rid of the lamination, and get rid of this large liquid fraction so, that it sag due to its own weight. So, those kind of problem will be there.

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So, the final microstructure is something like this. So, you know the sintering will take place, although it is a schematic it will form a grain and then you will have a recrystallized fine grain where the liquid was there.

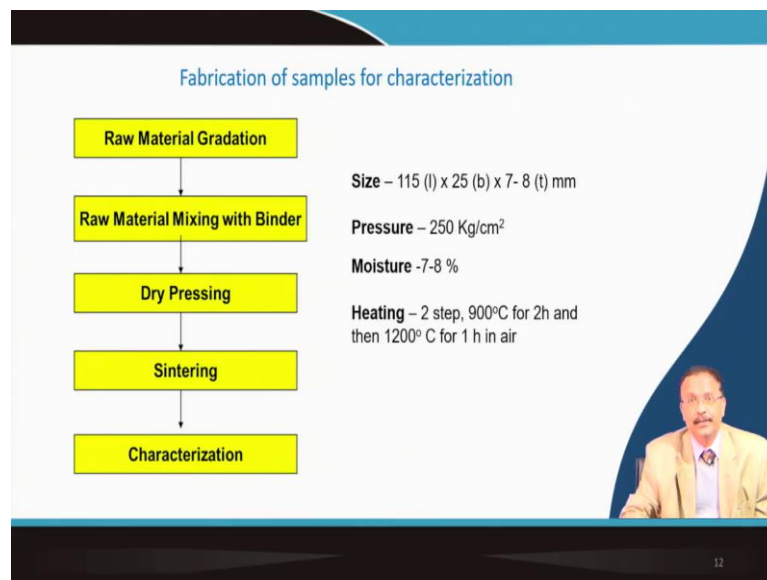
So, this kind of recrystallized area will also be there and some alumina silicate they will have a composition of mullite which is alumina silica in different proportion. So, they are very strong material. So, if the recrystallized product this mullite is crystallized, then the stress fracture stress will be manifold increase for this kind of tile.

So, usually if it is not process optimized then as you can see that for the liquid phase sintered material the formation of the surface crack bending they are very common

problem and that needs to be eliminated by trial and error process, but not fully trial and error because you will have to understand the liquid phase sintering, you will have to understand the formation of the composition whatever you are using whether the mullite formation will be there, how much fraction of liquid will be there, then whether you have graded the particles to have a large green density.

Stuff like that you will have to work it on throughout the course I have talked about various aspects of the processing. So, you will have to put all your knowledge so, that this lamination bending then surface crack formation this kind of thing does not occur.

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So, this is the step usually you follow raw material gradation, then mixing with binder, then you do dry pressing, then you sinter and then finally, you characterize mostly in terms of its water absorption and the strength these are the two parameters which is important for the tile.


So, you optimize this process heating schedule, heating temperature, time of heating all these things basically you need to optimize.

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Sl. No.	Pond / Fly ash	Clay	Pyrophyllite	Water	Strength (MPa)	SEM IMAGES
A7	60%	30%	10%	1.91	18.86	
A14	60%	25%	15%	2.03	25.17	
A18	60%	15%	25%	2.34	45.11	
A20	60%	15%	25%	2.40	51.00	
A26	60%	10%	30%	2.31	50.00	

Selected composition, density, flexural strength and fractured microstructure of the fly and pond ash based sintered tile samples

- Clay: pyrophyllite ratio has been increased from 1: 0.33 (A7) to 1:3 (A 26)
- With the increase of pyrophyllite the **liquid phase sintering** is more prevalent with more densification and higher flexural strength values.



And you optimize certain composition of the fly ash, clay, pyrophyllite and look at its microstructure at different stages and different compositions and finally, you select that which one is good in terms of the mechanical properties.

So, this is a structure and property relationship so, that you need to identify that how much fly ash, how much pyrophyllite, how much clay and what is this microstructure and how this microstructure affects the ultimate strength for this material which is sintered by a liquid phase sintering process.



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Laboratory made fly – ash tiles

Process Flow Diagram

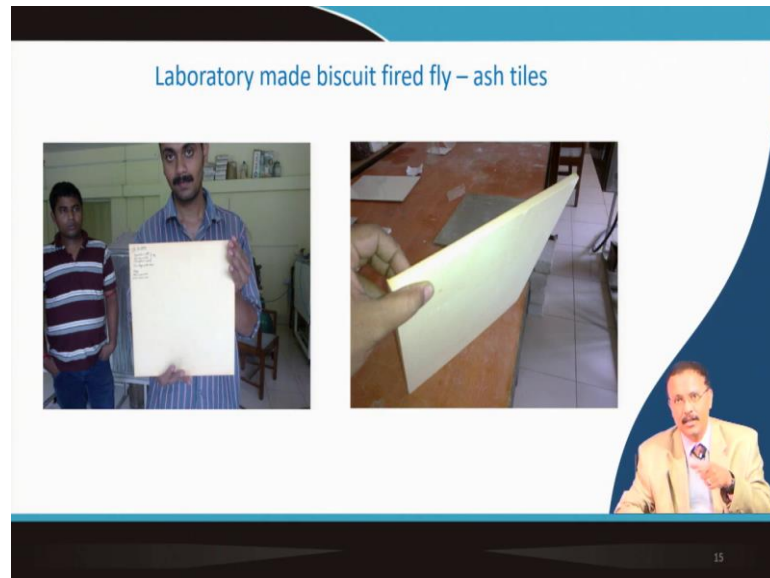
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    graph TD
      A[Raw Material Gradation] --> B[Raw Material Mixing with Binder]
      B --> C[Dry Pressing]
      C --> D[Sintering]
      D --> E[Characterization]
  
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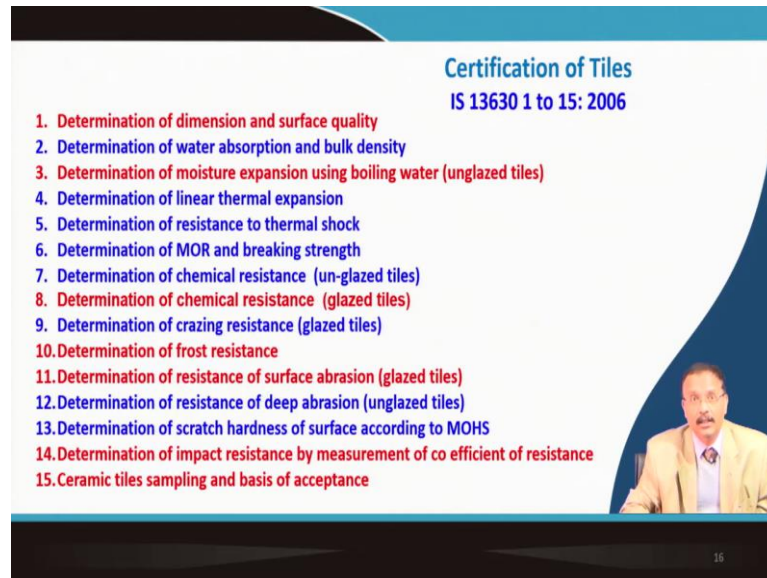
So, that optimization will take little bit more time, but finally, in the laboratory it is possible for you to make a flat tile which is crack free. So, initial stage it may bent like this, it may have crack usually we use a mixture like this one and then it is pressed in a big hydraulic press and then it is sintered. So, sometimes it is sintered like this which is useless and in the process optimize step you will get a flat tile something like this.

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So, this is the flat tile that can be made in the laboratory which is uniform in thickness and quite big in shape we are testing small samples, but the optimized parameter it is sufficient to make a large tile these are not coated it is not glazed. So, call it is a biscuit fired tile made out of fly ash.

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Certification of Tiles
IS 13630 1 to 15: 2006

1. Determination of dimension and surface quality
2. Determination of water absorption and bulk density
3. Determination of moisture expansion using boiling water (unglazed tiles)
4. Determination of linear thermal expansion
5. Determination of resistance to thermal shock
6. Determination of MOR and breaking strength
7. Determination of chemical resistance (un-glazed tiles)
8. Determination of chemical resistance (glazed tiles)
9. Determination of crazing resistance (glazed tiles)
10. Determination of frost resistance
11. Determination of resistance of surface abrasion (glazed tiles)
12. Determination of resistance of deep abrasion (unglazed tiles)
13. Determination of scratch hardness of surface according to MOHS
14. Determination of impact resistance by measurement of coefficient of resistance
15. Ceramic tiles sampling and basis of acceptance

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So, once the fly ash base tiles are made, then there are about 15 tests that you will have to do. First the dimension quality absorption of water, absorption of moisture, then linear thermal expansion coefficient, resistance to thermal shock modulus of rupture which tells the strength, chemical resistance both in glazed and unglazed condition then the frost resistance which is not very important for our purpose surface abrasion.

So, all this standard test that is required to be done so, that if it passes then only it is industrially adaptable process. So, all this test need to be done under this strict ASTM specification.

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So, once you are ready with your recipe the composition, you are confident that you can make tile in the laboratory premises and then you have tested, you have characterized all the standard properties and they are at par with the commercial tiles, then you will have to see whether your process is adaptable to the industry we usually make this kind of tile.

So, there are many tile making industries in western part of India and this recipe can be transferred to any one of those industries and you can see that there are big press not a small laboratory press. So, about 500 kilogram of the mix mixture fly ash, pyrophyllite, kaolinite, red mud. So, that mixture you can feed it here and continuously the tile will be pressed and with the conveyor belt it will be moved after pressing towards the furnace for drying and sintering.

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So, before that we need to glaze it. So, glaze as I told that fly that this tiles need to be glazed because intrinsic porosity is quite high for this type of fly ash this thing about 14 percent porosity is there. For all practical purpose you do not allow the porous ceramic. So, you will have to make a glass layer we call it glaze.

So, glaze is usually done by a something similar to the tape casting you remember we talked about the raindrop type of tape casting where the slip is slip of glaze; that means, the suspension of the glaze that is falling like a waterfall and your tile just passes through it so, that it forms a very uniform coated layer. So, that glazing is required to be done for the biscuit fire tiles and then you can print on top of this glaze by a computer printer.

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So, the tile is something like a paper and any kind of design you can make out of this computer type printer and on the glaze surface on the glaze surface it will print the design that you want on the tile surface.

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And then finally, it will have to be sintered at high temperature. So, instead of a small furnace, you have a tunnel kiln very large furnace where this biscuit fired and glazed material will go in and they will undergo at different temperature regime so, that

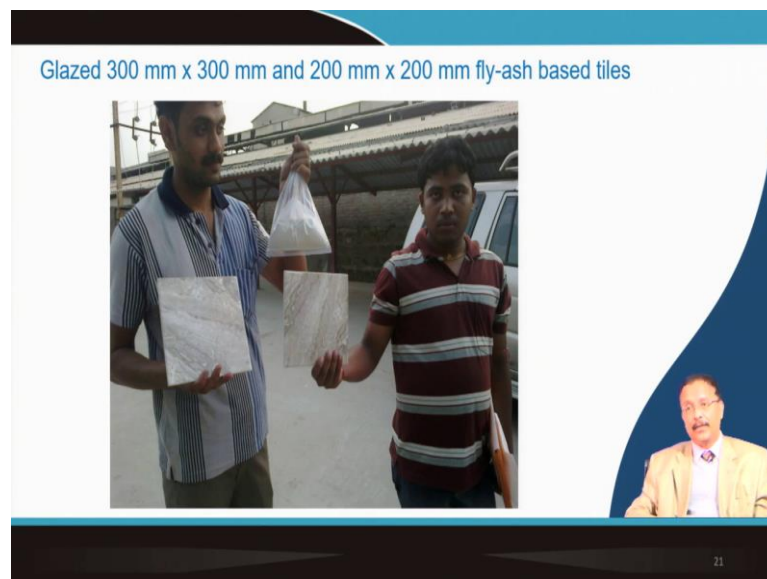
eventually the glass will form and here the thermal expansion mismatch is a very critical parameter.

So, if there is a huge thermal expansion mismatch between the crystalline glaze and your biscuit fire tile, then all the glaze will be cracked and it is useless. So, again the glaze composition that needs to be properly optimized. So, that it is having slightly lower thermal expansion coefficient as compared to your underlying biscuit fire tiles. And it is fired inside a tunnel kiln and you can get this kind of tiles.

So, from fly ash this technology normally they use clay to make this kind of commercial tile which all of you are aware of Kazzaria of Johnson tile and I am talking about the wall tile where the strength is not of that importance and not like float tile. Usually the float tile they are they are made this is a vitreous tile.

So, polishing is required to have the surface gloss and the porosity is much less in case of the float tiles, but fly ash based tiles they are very good adaptable for wall tile which is eventually glazed and made it in a industrial environment.

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So, finally, as you can see that this is the kind of glaze that is used which is liquid and which eventually was coated on top of the biscuit fire tiles of different size and shape different shape was all square, but different size of this tiles were made, you can see different types of designs that was made on top of the glazing.

So, this is the original glaze and this is the fly ash base tile which were glazed and this is a finished product and certain characterization is also required once you do this finished product in terms of its industrial adaptability that is required for you to undertake it. But this is a doable technology. So, doable technology and it is much more economic because 60 percent you are replacing the raw material.

So, you can imagine that the price reduction will be very very small and it will have in fact, it is tested that this properties are at par or better than the commercial tiles available in the market commercial wall tiles. So, it is a very lucrative technology that one can develop out of the knowledge of the non-metallic ceramic course which has been covered in this particular series of lectures.

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So, the study material for this type is of course, two chapters are important one is the processing part how to shape the ceramic article chapter 10, and also chapter 11 where it is described in terms of densification along with the book by Barsuam, already we covered it in earlier lecture. So, this is a good study material to understand the powder processing of ceramic heat treatment gradation.

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CONCLUSION

- Concept of Lab to market
- Waste utilization : Use of fly and pond ash in making value added glazed wear resistant wall tiles.
- Raw material characterization
- Optimization of process parameters
- Laboratory made tiles
- Certification on the properties for Industrial adaptability
- Field trial to judge the process feasibility

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So, this is important and in this particular lecture we introduce the concept from lab based research to market whether it is possible or how it is possible. Waste utilization is important for fly ash several other possible material, value added material that needs to be explored. So, I have just cited one example where we have used the this fly ash as a replacement of the clay which is important in most of the cases and we have tremendous use here in India.

So, that is demonstrated that the wall tiles can be made out of this. A raw material characterization is important, optimization of the process parameter is important to make this laboratory tiles in the laboratory and then you need to have proper certification as far as this property is concerned and then finally, field trial to see if your technology is industrially viable.

Thank you for your attention.