Clean Coal Technology
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Week-01
Lecture-05

Hi, I am Professor Barun Kumar Nandi. Welcome you in NPTEL online certification course on clean coal technology. We are continuing with the module 1 on coal properties. In past four classes, I have discussed different coal quality parameters and their impact on their utilization and their selection criteria for thermal power plant, cement plant and DRI plant concept and role of gross calorific value as volatile material during their utilization. So, in this class, I will be discussing types of sulfur present in coal and their impact.

So, Sulphur is always present in any type of fossil fuel whether it is solid fuel like coal, biomass or liquid fuel like petrol, diesel, kerosene as well as the gaseous fuel like natural gas. So, in coal, Sulphur can be present in three different ways. First one is pyritic sulfur, second is sulfate sulfur, and third one is organic sulfur. And apart from this, sometimes pure sulfur atoms or sulfur molecules are also present in coal. And now pyritic sulfur, if we discussed, pyritic sulfur present in coal mostly as part of mineral metal. Pyritic Sulphur present in coal as part of mineral matter or inorganic material. So different type of pyrites like iron pyrites, chalcopyrite, FeH2, FeS, galena, ZNS, FeAsS etc. in different forms pyrite compound can be present. So, these pyrite compounds are as part of soil or clay which are get mixed during the coalification process. So, these pyrites are always part of mineral matter.

They present as pyrite sulfur and they create sulfur pollution during their utilization. In case of sulphate sulfur, different type of sulphate salts also can be part of coal, mineral matter like iron sulphate, calcium sulphate, magnesium sulphate, BaSO4, etc. So different type of sulphate, this is not only these four or five sulphate, different type of sulphate salts can be present in coal as part of mineral matter. In organic sulfur, different type of organic hydrocarbons having sulfur as one of their components present in coal. Like mercaptans, disulfide, thiols, sulfide, theophanic and theocratic and similar type of hydrocarbons are always present in coal and these type of sulfur compounds are deeply attached to the coal surface and they are always part of combustible. and pyrites are frequently referred as the iron pyrites or pyrite as in whole. So, in high sulfur coal pyrites are present and very thin smaller particles may be up to 100 mm in length and 150 mm thickness. So, they are present in the coal structure in a very small fine particles or fine shape around 100 micron or 10 to 20 microns as part of octahedral crystal structure and they assemble make up like the framboids and they can be always present as part of individual crystals also which crystal size are around one to two micrometers in diameter. However, they can be found in bigger size like 40 microns also whereas the sulphate Sulphur

can be present as part of mineral matter, now we can see that their particle size or their crystal size is in the range of one to two micron. So, in Physical coal cleaning, typically we crush the coal up to 75 microns in the finest size. Mostly they are crushed up to 5 to 10 mm size or half inch, one fourth inch coal particle size. So, at this level, whether we use them in the pulverizing combustor as well as in the normal fluidized bed combustor, we cannot separate them at this level. So, it is very difficult to remove all these crystals by normal physical cold cleaning that we will not be able to get to that extent where we can expose the pyritic sulfur or sulfate sulfur. And also grinding of coal to the level of 5 micron or 10 micron is never economical and never profitable. So, both these pyritic Sulphur and sulphate Sulphur needs other type of coal cleaning. Physical coal technique does not remove such type of individual crystal as grinding to this extent is not at all profitable or techno-economically not feasible. And if we discuss about the organic sulfur, they are much more problematic than that of pyretic sulfur and sulfate sulfur. Organic sulfur in coal is as part of combustible hydrocarbons.

So, as they are part of combustible hydrocarbons, like if it has organic compounds in coal, where sulfur is also a part of this organic structure, like here, so in this case as they are part of organic hydrocarbons. They cannot be removed to any of this process whether it is a physical cleaning process or it is involved any other cleaning process because they are already part of coal structure. So, they can be present as part of aliphatic or aromatic thiols. They can be aliphatic or aromatic mixed sulfides. They can be aliphatic, aromatic or mixed disulfides or heterocyclic compounds and etc. So if we see during the coal combustion, all this pyritic sulfur and sulfate sulfur they converted to individual metal oxides forming so2 and so3 gases and organic sulfur also burned along with the hydrocarbon present in the coal and release sox gases. So, if any coal has organic sulfur. Although coal can have very less amount of mineral matter or ash, but if it has organic Sulphur, entire combustible part will have organic Sulphur or organic Sulphur rich compounds. As organic Sulphur rich compounds are present whenever we burn coal and up to what extent we get pure coal, always organic Sulphur will be present in the coal and if we burn such coal, it will cause SO2 and SO3 pollution. and in case of inorganic Sulphur like pyrite Sulphur or sulphate Sulphur or if it is some trace amount of elemental Sulphur is also present. As they are mostly part of mineral matter if we remove or if we can reduce the mineral matter or if we have coal containing very less amount of mineral matter. We can have less amount of pyrite Sulphur or sulphate Sulphur. So, distribution of organic sulfur, pyritic sulfur and sulfate sulfur in coal varies from mine to mine continuously. and is deeply correlated to the coalification process. So, whether this coal will have organic Sulphur, pyritic Sulphur or sulphate Sulphur, that depends on the origin of the coal. If the original tree or plants from which coal has been formed that contains high Sulphur compounds or Sulphur rich compounds. So, in such case the coal formed from that particular tree or plants will always have organic sulfur in its structure.

Only that its organic compound form may be modified during the coalification process. Whereas if the nearby clay or nearby, soil have some amount of sulphate or sulphide compounds. So, in such case if those clay material get mixed with the coal during the coalification process. They will always get mixed with the coal and as a result from location to location or mine to mine. content of pyritic Sulphur, sulphate Sulphur will vary. Like in one mines maybe have less amount of pyritic Sulphur and more amount of sulphate Sulphur, maybe other mines it can have more amount of sulphate Sulphur, less amount of pyritic Sulphur. But organic sulphur is correlated to the original tree or plants that has been converted. or modified to coal during this coalification process. So if organic sulfur is present, that means it is part of hydrocarbon part or combustible part. So it will be part of volatile material as well as the fixed carbon. And if pyriatic sulfur or sulfate sulfur is present, mostly it will be part of mineral matter or ash. So it is very difficult to remove or separate organic sulfur from coal as it is part of coal hydrocarbon structure. This is most important considering that their impact. Pyritic sulfur and sulfate sulfur are present. If we can separate the coal or if you can remove the mineral matter or if we can reduce the mineral matter of the coal, so we can reduce their percentage and make it below 1% as per the environmental guideline.

But if it is organic sulfur is present, it is a part of hydrocarbon part or combustible part. As we use coal for its hydrocarbons as well as combustible, we cannot remove this organic sulfur. As easily like any other process so it is very difficult to remove or reduce organic sulfur as it is part of combustible and we use this combustible from the coal so pyritic sulfur and sulfate sulfur can be removed or separated from coal using suitable coal cleaning or beneficiation process as it is mostly part of mineral matter. But organic sulfur, we cannot easily remove from this coal. So, if any coal has organic sulfur, it is very difficult to utilize that coal, even with suitable coal cleaning or coal beneficiation methods. But if pyritic sulfur and sulfate sulfur are there, we can use that coal using suitable coal cleaning and coal beneficiation method. And we can reduce their percentage because the total sulfur content should be less than 1%. Sulfate sulfur or pyritic sulfur is present. We can easily make that coal below 1%.

But if this total sulfate contains mostly contribute by the organic sulfur, then it is very difficult because organic sulfur is not removed easily from the coal. And during organic sulfur, as it is a part of combustible, it also contributes to some of the GCV. Any sulfur-rich compounds, when it is part of organic sulfur, they significantly contribute or improve the GCV of coal. There is another reason. In most of the cases, we can find that organic sulfur-rich coal has very good gross calorific value. And conversion of pyritic sulfur to individual carbon SOX compounds. These reactions can be endothermic and exothermic as per the reaction stoichiometry or reaction kinetics. So, this part is also important as what we can identify from this information is that if pyritic sulfur is present or if sulfate sulfur is present and during their decomposition it needs some amount of energy for their decomposition like if there is sodium

sulfate is present during their decomposition. It will form sodium oxide plus so2 but this reaction may need some heat. So, if they need some heat so that heat will be collected from the coal combustion. So, in such case effective heat available for utilization may be less that's why this conversion of pyritic sulfur or sulfate sulfur to individual SOX gases may be exothermic or may be endothermic. May be that sodium sulphate decomposition is endothermic or calcium sulphate decomposition is exothermic, etc. So, it depends on the individual types of Sulphur present, particularly in case of sulphate Sulphur. Whereas in case of pyritic Sulphur, this similar phenomenon is there. But if it has organic Sulphur, we get mostly some amount of additional energy from such gases. So, if we see the effect of sulfur in coal mines, sulfur along with water during the natural reaction occurs in the presence of sulfur along with water and microbial activity or natural reaction can generate water with H2SO4 if any sulfur is present any sulfur rich compounds are present in coal mines and if coal mines have some good amount of moisture content present in that particular coal mines. some microbial activity can happen. So, some microbes or microorganisms can decompose this organic sulfur as well as pyritic sulfur to their individual acids level like sulfuric acid, phosphorus may be decomposed to phosphoric acids and etc.

So, as a result, any sulfur-rich coal mines or any pyritic sulfur-rich coal mines, it has the probability of generating H2SO4 in the coal mines due to the microbial activity. So, if any coal mines have some microbial activity and produce some H2SO4 and in coal mines as it is linked with the groundwater and it is always below the earth surface maybe 50- or 100-meters depth, there is always some groundwater or surface water is available. So, surface water along with mixed with sulfuric acid always creates an extremely low pH water. which is highly corrosive environment. So, this environment is highly corrosive and highly toxic environment. Such condition is known as acid mine drainage like any mine that has acids present and that acid may be draining or flowing through some river or maybe some water tunnels and etc. so this AMD condition is extremely dangerous condition for mining corrosive for both human as well as the mining equipment as this AMD condition it has some H2SO4 present so this H2SO4. This pH can be extremely low maybe up to pH2 or pH 1.5, pH 2.5 at this level. So at this level, water is extremely corrosive in nature and they can dissolve any type of metals or inorganic compounds as sulfuric acid is a very good reactant or highly reactant to all these things. So if in any coal mines or any similar coal mines having AMD is there. It is very dangerous to do the mining in such location and it is extremely corrosive like any mining equipment, mining heavy equipment or any human or worker or engineer working in the coal mines. They will be always exposed to this corrosive environment and their body can get damaged by exposure of this sulfuric acid in different ways.

So high sulfur coal mining and their utilization is very difficult and not environmentally friendly. So, if any coal mines have sulfur exceeding percentage of one percent per minute. So

in such case, it is extremely dangerous to do the mining of this coal and such coal cannot be used even after mining as it will create sox gases So, if any coal have Sulphur present, either it is organic Sulphur, pyritic Sulphur or sulphate Sulphur, if their total combination is more than 1 percentage or nearby 1%, our present environmental guideline doesn't allow this coal to be used in any of the thermal power plant or not to be mined without any proper protection or safety guidelines. So, these are the typical reactions what happens during this acid mine drainage formation like weathering of pyrites in presence of water which creates acids. Similarly in oxidation of Fe2 to Fe3 and it also creates some number of acids and it can expose make it to Fe3.

So overall we can see by most of this reaction always some amount of H plus ion or acids are formed. So, if such number of acids are formed. Any sulfur rich coal mines, it is very dangerous and if during the rain or any heavy water flooding, it is very common that such mine water or surface water is flown through the nearby land or nearby agricultural land or nearby road or nearby hills etc., where color you can see it yellow color or almost reddish color is there which shows that it has a very extremely acidic pH and this is very much dangerous. So nearby localities also get exposed to such strong sulfuric acid and maybe the nearby forest and other also get damaged by these sulfuric acids.

So, if any coal has sulphate Sulphur, pyritic Sulphur or organic Sulphur, it is very dangerous to do the mining of this coal and such coal cannot be used for any purpose. Typically, if Sulphur percentage is nearby 1%, then such coal can be used with some other process or maybe some beneficiation process can be used to reduce the sulfur percentage make it to nearby or below the safety guidelines but if it is above one percent or above two to three percent like northeast coal available in the Assam, Meghalaya, Manipur, Mizoram, Nagaland or natural produce most of the cases all this coal has high sulfur content starting from three percent four percent even in some cases goes up to ten percent. So, such coal although, they can have very good amount of gross calorific value, lower ash content and very good combustible content, very good coking properties is there but such coal cannot be used and their utilization is very much limited due to their high sulfur content in rare cases. Some of the coals are used in cement plants as cement plants can accept some amount of sulfur as it converted to gypsum which is a part of cement.

So, if we conclude overall from this sulfur containing chapters, so sulfur in coal can be different based on their composition. So, if we say some coal has some sulfur content, it does not mention the true type of sulfur present. We have to identify whether it is organic sulfur or it is pyritic Sulphur or if it is the sulphate Sulphur. So we have to identify the exact type of Sulphur present in coal as it will be useful to kind of pathways to utilize such coal and high sulfur coal cannot be used in any industrial or even in the domestic application even if we use them in a domestic application in smaller cases if we use them in domestic application with smaller content of coal

reduced released sulfur dioxide or SOX gases can very soon converted to smog, fog as well as the acid rain can happen to nearby areas. And acid mine drainage can be generated in high sulfur coal mines. If sulfur content is very high, like 3%, 4%, it will always create some acid mine drainage. And particularly with the location, having very good quantity of relative humidity or moisture or nearby water body is there where coal mines is exposed to water sources.

Either from air or from water so acid mine can be generated in high sulfur coal mines easily if sulfur is on borderline value of about one percentage. So, we can go for some sulfur removal or sulfur reduction techniques can be tried but if sulfur removal reduction methods will be dependent on types of sulfur present. You have to identify whether it is an organic sulfur in such case, their treatment or their beneficiation process will be different. If it is pyritic sulfur, their beneficiation process, their utilization strategies will be different. And if it is sulfur, sulfate sulfur, its utilization and beneficiation methods will be different. We have to first identify what type of sulphurs are present in coal and for that purpose we have to go for detailed characterization of coal to identify whether it is organic sulphur, whether it is pyritic Sulphur or it is sulphate Sulphur.

So, for this process, we can do some FTIR analysis or we can do some NMR analysis. So, which will show us whether any sulfur rich compounds or sulfur types of hydrocarbons are present in coal hydrocarbon structure or not. If it is in pyrite sulfur or sulfate sulfur, we can go for some XRF analysis or XRD analysis or similar type of analysis we can do. to see whether what type of Sulphur is present and as per the ASTM guideline there are different methods or separate methods are already available to analyze this type of Sulphur present in coal and regarding ultimate analysis. In ultimate analysis we need sulfur containing probes as part of CHNS analyzer because in the CHNS analyzer different modules are available whether it can have some only CHN or CHS different combinations are available. So, we have to see that equipment have sulfur containing probe is there or sulfur containing detector is there, it should have CHNS mode and sulfur should be detected even at the lower level so that we can identify trace amount of sulfur is present. If sulfur is present in coal, then it will create so much environmental problems and we will not be able to utilize such coal. If there is other type of elements is there, we can use such coal.

Thank you.