Clean Coal Technology

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Week-08

Lecture-36

Hi, I am Professor Barun Kumar Nandi, welcoming you to the NPTEL online certification course on clean coal technology. From today, we will start Module 8 with the broad topic of emission control from combustion utilities. In this module, I will be discussing SOx, NOx control and their reduction strategies during combustion and after combustion from different utilities, oxy-fuel combustion, carbon dioxide capture and storage. So, let's start with Lecture 1, discussing SOx control strategies. Now, if we see the generation of SOx during combustion or from combustion-based utilities.

SOx, that means sulfur dioxide, sulfur trioxide, and similar sulfur-rich gases in the flue gas, are originated from sulfur present in the fuel. So typically, if we see any amount of sulfur oxides in the gaseous stream, whether it is sulfur dioxide, sulfur trioxide, or any other similar sulfur-rich gases, they typically originate from the sulfur present in the fuel. So, if it is combustion utilities, we can get oxides like sulfur dioxide and sulfur trioxide. If it is a gasification-based unit, we can get H2S and maybe some sulfur compounds or sulfur in elemental sulfur, which can also be present there, depending on the reaction conditions. So, any amount of sulfur and its gaseous compounds originate from the sulfur present in the fuel or coal.

So, if we have seen in our previous chapters, like as part of coal analysis, CHNSO or ultimate analysis, there is always some amount of sulfur present, and this sulfur can be organic sulfur, pyritic sulfur, or sulfate sulfur. So, what we have to ensure is that if we want any flue gases released from these combustion utilities, as well as gasification-based utilities, in all such cases, the sulfur present in the feed coal, or we can say in the source, should be within the permissible limit. Typically, it is one percent. So, it is like source control. If we can eliminate the sulfur present in the fuel or reduce it, we can easily maintain a lower amount of sulfur dioxide or sulfur trioxide in the flue gas.

So, first of all we have to ensure that we should use any of the fuel which has lower quantity of sulphur for coal or biomass or solid fuel. This percentage is typically one weight percentage. as we see in the ultimate analysis report. In case of liquid fuel and gaseous fuel, they have their corresponding BS4, BS6 and similar guidelines about the sulfur content present in all those types of fuels. So, first method is that if sulfur is present in the fuel and we know that still we have to use this coal for combustion purpose like in the case where sulfur percentage is nearby one percent so we can do the pre-utilization cleaning like before utilization of coal or before burning the coal in the coal combustor we can reduce the sulfur content present in the coal so first method if we say it is the source control that we should use coal with less amount of sulfur in the second case if sulfur is there and still we have to use that amount of fuel that means if the sulfur content is nearby one percentage So in such case, we can remove or reduce the sulfur content present in the coal before utilization like before sending it to the combustor or before sending it to the coal carbonization unit or the coal gasification unit. We can do the coal desulphurization using the various methods of coal cleaning. or to switch to the low sulfur coal.

So, all these discussions on the coal cleaning about the amount of sulfur present and how to reduce the sulfur present in coal, we have discussed in the chapters of coal washing and coal cleaning. So, first method is we should remove the sulfur. from the coal before its utilization that is the first method using different methods of sulfur reduction like froth flotation, oil agglomeration, conventional coal washing as well as any other type of method like physical coal cleaning whatever is suitable for that type of coal, second method is that during the utilization when we are burning coal or when we are gasifying the coal, we can trap the sulfur compounds present in the combustion units using limestone or similar type of material. what we have discussed in the fluidized bed combustion methods or similarly we will be discussing in the fluidized bed gasification methods.

And third, or it is the final stage, is the post-combustion, post-gasification, or you can say the post-utilization cleaning. Like, we can guarantee that we are not able to remove the sulfur. Present in the coal either during the pre-utilization or during the utilization due to different reasons, that means if sulfur is present in the coal, but the sulfur content cannot be removed to certain limits using conventional coal washing or coal cleaning, neither can we utilize the fluidized bed combustor as it is very good quality coal. We may have to use it in the pulverized coal combustion units. So, if both cases are not applicable, we can still capture the sulfur dioxide after the coal combustion and before releasing the flue gas to the environment. That is called flue gas desulfurization or FGD. So, this is selected or utilized to reduce the sulfur oxides from the flue gas, or we can say to capture the sulfur oxides from the flue gas.

So, the overall purpose is that whatever sulfur oxides are released to the atmosphere or to the environment, that sulfur concentration should be within the permissible limits or permissible guidelines as per the environmental law. So, this sulfur quantity or SOx emission guidelines vary or change periodically by different types of environmental agencies or as per the government guidelines. So, each and every plant has to follow those sulfur emission guidelines or SOx emission guidelines as applicable from time to time. Typically, it is getting more stringent with time, that the permissible limit of SOx in the environment will be less in the future days. So, to achieve that lower limit of SOx in the flue gas, there are many flue gas desulfurization systems or flue gas desulfurization units. They are currently in use. And many other new technologies are under development under the R&D wing of different bodies. So, at present, some of the flue gas desulfurization units are there, they are working, and in the future, we may get some more technologies, new technologies, so that we can reduce the entire SOx emissions from the coal combustion utilities. One of the methods as being currently followed in different industries are the blending with the low sulfur fuel as we can get it that overall sulfur quantity should be less than one percentage. So, this sulfur quantity should be one percentage in the fuel what is being charged or what is being sent to the combustor So in any case, if some of the fuel has higher amount of sulfur content, like it may have just above 1%, maybe 1.2% of sulfur present. And whereas if we can have other type of coal, which has 0.5% or 0.3% sulfur present in coal. So typically, nowadays most of the plants or most of the utilities, they blend the coal. that high sulfur coal in lower percentage with the low sulfur coal in the higher percentage, so that the blended coal or the final coal they gets that overall sulfur percentage in the combined fuel or mixed coal that should be less than one percentage that is to reduce the consumption of high sulfur fuel that is not burning entirely the high sulfur fuel but along with the high sulfur fuel blending with some amount of fuel which has lower amount of sulfur. So that overall amount of sulfur emission per unit mass of coal is reduced and that can be within the permissible limit. And in other cases, some of the industries also used high excess air to dilute the SOX in the flue gas. Like if they know that the SOX concentration in the flue gas like above 100 ppm. Like if it is the 100 ppm is the guideline, so maybe they are having the flue gas concentration of 150 ppm. So, in such case, if they increase the excess air concentration or excess air amount, so overall as the volume of air is increased, so number of SOX will be decreased per unit volume of the gases.

But in both the cases, like blending or whatever, total amount of SOX emission, it will remain same. Like, whatever is the sulfur emission or sulfur dioxide emission coming to the environment, the total amount of SOx emission is same, but only we are doing some of the mathematical calculations to show that the SOx emission in the environment is less. So, in the, although in both the cases, we can achieve lower percentage of sulfur oxides in the environment and may pass the permissible guideline but all these things is does not reduce the actual total amount of sulfur oxides emission to the environment so these they are not the good technologies or good practice to be followed in the industries they this such practice should be avoided And we should go for the sulfur capture or sulfur reduction either using the pre-utilization cleaning or during utilization or post combustion.

We should reduce sulfur emissions by only these three methods, as applicable. Not going through this type of method where, by mathematical calculations alone, we can show that sulfur oxides are within permissible limits, but the total amount of sulfur emissions remains the same. Typically, if we go for flue gas desulfurization units, these units are generally classified by wet methods as well as dry methods. That means the reduction or capture of SOx from the flue gas can be done by two different methods. One is the wet method.

And another is the dry method. In the wet method, there will be some water involved. So, in such cases, we will get some liquid waste or slurry. In the case of the dry method, some dry chemicals will be used. So, there will not be any heat loss or other issues.

But they have their inherent advantages and disadvantages. And they can also be categorized as wet scrubbers or spray dryers. They can be by dry injection, or some processes can be regenerable processes. And in most cases, whatever chemicals are used, either in wet scrubbers or dry methods, those chemical reactions are only one reaction—a chemical reaction. So, they are not reversible chemical reactions.

So as a result, there is regular consumption of chemicals in this process. So, we have to on a regular basis we have to procure or we have to get some amount of adsorbent or capturing material which will capture sulphur through some chemical reaction and those chemical reactions will be irreversible. So, to avoid that Some of the regenerable process are also there and some of the processes are still under development under R&D. So, broadly they can be by wet method, dry method as well as the regenerable method.

Typically, regenerable method is under process. So, not so many units' plants are utilizing these methods. So, all these things can be applied using a circulating fluid bed method where some amount of liquid is circulated throughout the chamber so that that liquid or that fluid can capture the SOx from the flue gas. And in some of the cases, in some of the design, it can have combined SOx emission control, NOx emission control, dust particle emission control may be there. they may not remove or trap only one of the pollutant work materials they can capture multi-component like in the same unit. Here SOx, NOx as well as the dry particle can be removed as we have seen in case of settling tank or wet settling tank there that in the settling tank method of dust particle removal in our previous module. We can see that the dust particles can be captured by water where we can add some chemicals which will capture SO2 as well as you know NO2 and NOx gases typically by the wet method we get a slurry waste or that slurry will typically contain H2SO4. So, if we use the wet method, so it has water involved in this process. So, as water is there and sulfur dioxide or sulfur trioxide is getting absorbed there, so as a result we will get some acidic solution either sulfuric acid or sulfurous acid H2SO4 or H2SO3 whatever depending on the condition.

So, water will have some strong acidic solution which has to be taken care of with some precautions at a later stage. In the case of the dry method. Whatever solid waste is there, it is easy to transport and dispose of easily as it is solid material in the dry method compared to the wet method. The wet method needs some pond, tank, or particular water chamber, which can also contaminate the groundwater and other sources. So particularly, this wet method needs much more processing or handling compared to the dry method. In the dry method, we can similarly dispose of the calcium sulfate-rich solids in some locations and even utilize this calcium sulfate for other purposes. In the regenerative flue gas desulfurization process, it produces a concentrated sulfuric acid SO2 byproduct, usually H2SO4 or elemental sulfur. In the case of the regenerable process, typically water along with some chemicals in the liquid phase is used.

So, after the process is over, typically that chemical is recycled back or recovered back by the reversible chemical reaction, so water will react with sulfur dioxide and can typically form either sulfuric acid or, if we are using some reducing agent, we can get some amount of elemental sulfur. So, in both cases, we can recover the amount of sulfur dioxide captured and utilize it for producing some byproduct which can be marketed by the plant. Recently, there has been much more focus on other types of pollutants from coal combustion utilities, like emissions of mercury, lead, selenium, or any other heavy metals. Recently, there has also been a focus on capturing or reducing other types of heavy metals from the flue gas, using flue gas desulfurization units like in the flue gas desulfurization unit, can also capture mercury and other heavy metals from the system. Typically, the adsorbent used by the wet scrubber includes the oxides of calcium. So typically, these calcium oxides, magnesium oxides, potassium oxide, or sodium-based oxides are mostly used to capture sulfur dioxide. As these oxides of calcium, potassium, sodium, and magnesium can react with sulfur dioxide to create corresponding sulfate salts. Mostly, calcium carbonate or calcium oxide, magnesium carbonate, sodium carbonate or sodium oxide are typically used. So, the final selection is based on their availability as well as the cost of the process. Whereas in some processes, ammonia is also used because ammonia can react with sulfur to form ammonium sulfates. And sometimes, as seawater has different types of other salts available, in many cases, seawater is also used as a suitable adsorbent or absorbent to capture different types of pollutants from combustion utilities. If SO2 is used and reacts with calcium, it typically forms calcium sulfate, also known as gypsum. So, this gypsum has some market value and can be used in cement factories as well as other utilities. So, in most cases, calcium-based salts are used as they have very good market value on a large scale. So, in most cases, calcium-based material is used in both the dry method as well as in the wet method. If ammonia is used in such cases, we can get ammonium sulfate as the byproduct. Typically, sulfate is preferred from sulfur as these sulfate salts, whether calcium sulfate or sodium sulfate, can have good nutritional value for vegetables and crops, and ammonium sulfate is an ideal sulfate compound for soil supplementation. So, if we dispose of these two materials, typically the environmental pollution is less; rather, they can be used as nutrients or fertilizers for crops and other purposes, so they have very good market value. That is the reason in most cases either calcium or ammonia these two base materials are used in the flue gas desulfurization unit, and typically the use of ammonium sulfate, as this ammonium sulfate is a ready-made fertilizer compared to calcium sulfate, which has limited use only in the cement industries. So, the use of ammonium sulfate in large-scale fertilizers or large-scale plants is employed so that they can also get fertilizers along with sulfur dioxide capture. So, it has a very good market value, and that's why it is growing gradually day by day. This growth provides a market for flue gas desulfurization products and could make the flue gas desulfurization process based on ammonia much more attractive as an alternative process than calcium carbonate and calcium oxides. And if we discuss these two points, if we see the coal combustion utilities, they have sulfur emissions of sulfur dioxide emissions, and if they want to capture the sulfur dioxide emissions by any of these methods, there is some cost involved in this process. So, if the cost of this desulfurization is significantly high, that makes the entire plant economically unprofitable, meaning whatever profit they can get by burning coal and generating electricity or making other products, a significant amount of that profit will go to the flue gas desulfurization units. So typically, these plants or most plants do not want to install such units, as that will create problems in their financial sector, as the profitability of the plant will be under question. So, in such cases, if they can obtain this ammonium sulfate, which is a very good fertilizer and also has very good market value, from where they can at least recover the cost of the flue gas desulfurization.

So, in such cases, overall, this flue gas desulfurization or FGD unit process makes the process somehow much more economical. So, it will not make any economic burden to the plant or to the coal combustion utilities. That's why the growth of ammonium sulfate-based flue gas desulfurization units is nowadays much more popular and gaining much more popularity. So, in the future, we can see many more units using this ammonia-based process compared to the conventional calcium-based process, where we utilize calcium oxide or calcium carbonate and this process can be further classified as regenerative and non-regenerative, depending on whether the chemical used to remove or cover the sulfur can be regenerated. If we can recover those chemicals, the process is called regenerative; if we are not able to recover them, it is the non-regenerative process. In the wet process, we have already discussed that we can get either elemental sulfur or sulfuric acid. In the wet non-regenerable process, we can add lime or limestone, where we can get calcium sulfate sludge, which is either disposed of or maybe utilized in the cement plant.

And in the wet scrubbing method, even if we go for the wet scrubbing method, where flue gas will be captured or reacted with the solution, which mostly contains calcium oxides or sodium dioxides, we will remove the sulfur dioxide in the wet methods. So, this is the typical flow sheet or process used in different plants, like if we see the wet method from this side. Flue gas enters, so this is another chamber or flue gas desulfurization unit that works on the wet method. So, from this side, if we frame the flue gas, and from this part, we spray the nozzle containing calcium-based salts like calcium oxide or sodium oxide, so they are sprayed from the top. As a result, they will have very good contact, and there will be very good mass transfer of sulfur oxides or sulfur dioxides to the calcium oxides, and a chemical reaction will occur, or you can say chemical absorption will occur. In this phase, we will get that it will be converted to H2SO3 or H2SO4, and whatever unused calcium salt or sodium salt will be there.

We can recirculate it through this chamber and reduce the or you remove any of the water droplets and other particles. There, we have a spray chamber available which will remove any excess amount of water molecules or vapor containing sulfuric acid in the gaseous phase. This mist eliminator removes any type of acidic gases going out from the flue gas. So effectively, the flue gas released from this chamber will contain a lower amount of sulfur dioxide and other gases. Thus, we obtain clean flue gas with the lowest quantity of sulfur oxides or within the permissible limit of sulfur oxides from this unit. This is how wet-based units typically work. The water finally goes to the hydro-cyclone, where we capture solid particles, removing elemental sulfur or any fly ash trapped by this water method. or water spraying method. These are removed by hydro-cyclones, yielding pure water that can be discharged to nearby plants or locations or treated further. We can also recover gypsum or fly ash particles as byproducts from these units.

In real-time plants or coal combustion utilities, this is how they are used. For example, this boiler burns coal in the presence of air. Water and air are sent to the boiler along with coal, producing bottom ash and boiler slag. Typically, these gases contain CO2, H2O, SOx, and NOx. These are the four gaseous materials presents, while fly ash also contains some gaseous material. These are removed either by ESP or baghouse to collect fly ash and other particles.

The gaseous material contains carbon dioxide, moisture, SOx, and NOx. Here, using the scrubbing method, we can add calcium oxide or calcium carbonate in the water scrubbing method, which is sent to this unit. After this unit, all SOx will be removed. Any remaining fly ash particles can be captured by the wet scrubbing method, resulting in clean flue gas released into the atmosphere, containing H2O, some carbon dioxide, and possibly NOx. From these circuits, we obtain flue gas desulfurization byproducts, such as synthetic gypsum or gypsum. This is the flow sheet or method by which conventional thermal power plants remove dust particles and sulfur oxides from flue gas, typically in the dry method. We use lime or limestone slurry.

If we go for the dry method, in case of dry method, typically lime or limestone-based spray from the top of the chamber and these dry sorbents injection occurs from the, maybe inside some of the furnace if possible or technically feasible. In some of the cases this is feasible even in pulverized combustion units but not all the units. So, in some of the cases it is possible that we can spray very fine powders of calcium oxide or limestone which will capture in the combustion utilities like the case of fluidized bed combustion. In case of fluidized bed combustion, we are already doing the same thing. So in case of other plants also this is possible subject to that technically it is okay and we can add it in the economizer duct or hybrid methods that means we should allow that contact with this limestone or calcium oxides to be present in the combustion if it is through which flue gas will pass, so that can even start from the combustion chamber or from the path wherever just flue gas is coming out of these units. So, the in the entire path, we can spray or we can keep some amount of dry calcium oxides or limestone there. So that they can capture the sulfur oxides during their path. Typically, in this process, dry waste product can generally easier to dispose compared to the wet method. If we use the dry powders of calcium oxides or calcium limestone, so as they are the solid particles, they can easily get transported and easily get disposed to any of the locations. If we are using the wet method, as it contains some sulfuric acids and other pollutants, it is typically some difficult and some many more technical challenges are there.

So, if we see in terms of handling method, dry methods are much more advantageous to handle or to dispose of the dry limestone or lime as well as the calcium sulfate. In case of spray tire, they are the second most widely used method to control the SO2 emission. Typically, in many thermal power plants, they go for the dry methods where they spray the lime or limestone. In the dry chamber, where flue gas will get passed and this from the flue gas, sulfur oxides will react with the lime or limestone to create the gypsum. It is mostly used where high temperature is there and practically wet method is little bit difficult to apply.

And prior to the 1980s, SO2 removal by absorption was usually performed using the wet scrubber. And in the earlier stage, typically the weight method was used to capture the SO2 gases. But nowadays... This dry method is also getting popular, as wet scrubbing requires many pieces of equipment to control the sulfuric acid, water spray, and others. Compared to the spray scrubber, dry scrubbers typically have lower costs. And mostly, calcium oxide is also used in the spray or drying methods, but in some cases, hydrated lime or calcium hydroxide is also used.

They are like the semi-dry method if you are using calcium hydroxide in this method. And they can be used in retrofit applications wherein the new installation in both cases, calcium hydroxide can also be used to capture this. So overall, if we see, if we add water to this, it will create calcium hydroxide, and this calcium hydroxide will be used to capture the sulfur oxides. These sulfur oxides in the flue gas are typically absorbed in the slurry and react with the lime and fly ash to form calcium sulfate or gypsum. So, the reactions are almost similar in nature in all cases, whether we are using calcium oxide, calcium carbonate, or calcium hydroxide. In all cases, we can get the calcium sulfate as the product.

The only difference is that the method can be wet, dry, or semi-dry. So, in this case also, from this chamber, we can spray the calcium hydroxide compound from here, which will capture the sulfur-rich compound from the flue gas. So, if we see the overall advantages and disadvantages of the different methods compared to the wet method, this dry flue gas system requires lower capital. If we see the wet method, as it involves water, it has to have some pump, water collection system, water purification system, and sulfuric acid handling system, which is extremely corrosive. So, all these things need many, many pieces of equipment, many manpower, and many technical challenges, which are typically in the wet method. But if we go for the dry method, it requires lower capital cost. Only the limestone has to be ground to almost the shape of fine powders, like pulverized coal. It has to be ground to the lowest possible size so that the overall absorption efficiency or SOx removal efficiency is comparatively higher. In addition, this dry method does not produce any liquid waste. This liquid is sulfuric acid, which is one of the most corrosive materials and is very difficult to discharge from any thermal power plant. So, thermal power plants prefer to go for the dry methods. The liquid method was very popular earlier, but nowadays, it is not so popular, but still in some cases, it is being used where, in combination, we can remove both SO2 and NO2 or NOx gases from the flue gas. However, the reagent utilization efficiency of the dry method is on the lower side. If we consider the overall mass transfer and chemical reaction involved in this process. For example, if we perform this reaction in the wet method, the same amount of liquid is recycled many times until all the absorbent has reacted with the sulfur dioxide. Therefore, we can achieve much better reagent utilization efficiency with the wet method. In contrast, in the dry method, since solid calcium oxide particles react with gaseous sulfur dioxide or sulfur trioxide, their mass transfer and reaction rate are slightly lower. Overall, the efficiency of the dry method is on the lower side. On the other hand, in the wet method, the utilization efficiency is much better, as the mass transfer coefficient from the gas to the liquid phase is higher. Additionally, we can recycle this water multiple times in the same unit until all the adsorbents have reacted with the sulfur oxide. Overall, in terms of utilization efficiency, the dry method has lower efficiency, while the wet method has much higher efficiency. However, wet methods are more expensive and require more equipment to be installed and managed. They also handle corrosive H2SO4 gases, whereas the dry method is simpler, producing only dry calcium sulfate powder, which can be used in cement plants or disposed of nearby. If we use ammonia-based adsorbent, the product can be converted into fertilizer. This fertilizer can be marketed as a value-added product from the plant, making the flue gas desulfurization unit more economical and profitable.

In real-time applications, the final choice between the dry method, wet method, or ammonia-based method depends on the plant's requirements, considering factors such as flue gas temperature and concentration. If the SOx concentration is low, the dry method may be acceptable. If the concentration is high, ensuring complete SO2 removal may require the wet method, which is more technically sound, as it can remove higher amounts of SOx from the flue gas system.

Thank you.