

Clean Coal Technology
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Hi, I am Professor Barun Kumar Nandi. Welcome you to the NPTEL online certification course on clean coal technology. We are in module 3, discussing different coal cleaning methods and their industrial practices. So, we have already discussed different industrial methods like jigging, dense media cyclones, spiral concentrators, froth flotation, and oil agglomeration. So, in this lecture, I will be discussing different biochemical and chemical coal cleaning methods. Ultrasonic energy-based coal beneficiation has recently become so popular and useful.

Ultrasound energy is a very strong energy that can break different types of intermolecular bonds and bonds between mineral matter and hydrocarbons. So, actually, this ultrasound is a strong source of energy. This ultrasound energy can be used to break almost at the level of intermolecular bonds. As we know, conventional grinding or whatever size reduction method is used in different industrial units, they have some limitations like in any pulverizer, ball mill, rod mill, etc. They can grind coal up to a certain extent, mostly around 50 microns or so. In conventional pulverizers, they grind up to 75 microns. Some of the coal particles are ground to a finer size, maybe around 40 to 50 microns. As these 40 to 50 micron sizes may not be the desirable liberation size for coal particles to separate mineral matter as well as hydrocarbons. So, in conventional coal grinding, we can get a minimum of up to 40 to 50 microns, which is not the desirable size where mineral matter and hydrocarbons can be ground.

So, if we want to go for below 40 microns or 20 microns or in the range of 1 to 10 microns we have to separate the mineral matter and hydrocarbons and they can have some sulfur compounds attached to this. So, in such case conventional grinding cannot be done and in such applications ultrasound energy based grinding or breaking of coal particles are very much useful. So, ultrasound based treatments or ultrasound energy is an alternate tool in Mostly in case of desulphurization of coal as presence of sulfur in coal particles can have many major impacts.

So mostly this ultrasound based separation is very much used when we target mostly the desulphurization of coal. But it can also be used for the removal of mineral matter from the coal. As sulfur has much more environmental impact, so mostly this is used in desulfuration of coal. But theoretically, these ultrasound-based methods can be used for both reduction of mineral matter as well as the reduction of sulfur content from coal. Typically, ultrasound helps in physical breakage of coal particles and breaking bonds between sulfur and coal. So this ultrasound can break the intermolecular bonds or very at finer size level they can act to create some cracks on the coal particle. so, they can they can break the different type of physical bonds as well as they can break even some of the intermolecular bonds they can also be broken as we have seen in many literatures related to the purification of water reduction of other impurities from waters. So alternatively ultrasonic energy that can also be used in conditioning and improve the emulsion properties which is very much important in case of froth flotation and oil agglomeration, where we have seen is that in case of froth flotation and oil agglomeration. We need to properly mix the oil, other chemicals, frother, reagent etc in the water phase as it is an oil and water emulsion. Because frothers are or other chemicals create some bubbles. So, their stability, their mixing in conventional coal, conventional stirrers and other, they have some limitations in mixing, creating some very accurate or very uniform quality of froth or emulsion, which is very much required in case of froth flotation as well as agglomeration.

So, if we go for a normal mechanical agitator or mechanical stirrer, They create agglomerates, they create froths, but the quality of froths, they are not very high. Some of the bubbles can have bigger size, whereas some of the bubbles can have smaller size. Because conventional stirrer cannot properly or uniformly mix this oil and water and other chemicals. So ultrasonic energy is also used or they can also be used to prepare good quality of emulsions. As a result, overall yield of the froth flotation process or oil agglomeration process can be improved significantly. So, ultrasound based methods, they can be used in both the way first one is for breaking the intermolecular bonds to create very finer size coal particles where we can easily separate mineral matter and sulfurous particles as well as they can also be used in froth flotation as well as the oil agglomeration. So, overall ultrasonic process can be used in different type of physical separation process for better mixing or better mixing of these chemicals as well as others they can also be used in froth flotation, oil accumulation. Similarly, they can also be used for the different type of chemical treatment methods. They can also be used in different type of other applications like coal, water slurry, grinding, dewatering. So ultrasonic based

energy can be used everywhere in coal industries or coal beneficiation industries. Now how actually this ultrasonic energy works initially If any ultrasonic energy is used, typically some minor bubbles are created and they bubbles increased. So consecutively bubble growth is there and after certain times these bubbles get collapsed.

So, when this bubble gets collapsed at it creates a very high amount of pressure and high amount of energy is released. So, from starting from a normal amount of energy but when this ultrasonic bubbles blast, so creates a very higher amount of energy so if that higher amount of energy is exposed or get in contact with the coal particle, very fine coal particle. So, coal particle initially may have side like this shape so over the surface some small amount of bubbles are typically placed or generated. So, these bubbles transport energy higher amount of energy to this coal particle. So, as a result coal particle can breaks they can create some cracks and they can ultimately break to very finer size. So entirely particle fragmentation can occur so this particular this particle fragmentation this is very much required for reaching the desired size where we can separate the mineral matter as well as the hydrocarbon rich particles. As this coal conventional coal grinding we cannot go beyond this size like it may be 75 micron. So, in conventional grinding we have to beneficiate the coal up to at this 75 micron size but if we use ultrasonic energy or ultrasound energy along with the conventional process. We can crush we can grind the coal up to at this level so which can be 1 micron, 10 micron or 5 micron. So, in this shape size we can effectively reach the desired liberation size for this coal particle which can easily get broken and we can easily separate them by the conventional oil agglomeration as well as the froth flotation method. So, In case of froth flotation, same thing happens. Whatever the bubbles are created, they are created even in the micro or nano emulsion sites. Like in conventional froth flotation, we can create bubbles which may be of in the range of 0.5 mm or 100 micron or maybe 2 mm 3 mm size. So, this can be the bigger size. So only some bigger size coal particle, very less amount of coal particle can be attached to this, but if you can create a very small amount of bubbles or very uniform very smaller size bubbles effectively we can improve the surface area of the bubbles available from multiple bubbles from these multiple bubbles as well as only a single bubble.

So, in case of multiple bubbles created during the froth flotation as well as oil agglomeration, their surface area is improved significantly So, many more quantities of coal particles can be attached to this. So, overall yield of the process. Typically, in the froth flotation, their limitation is that we cannot get very high yield. Like we can get only 10% to 15% of coal particles as the clean coal as it has limitation in terms of quality of bubbles.

But if we can increase the number of bubbles, increase their surface area, and etc. Overall yield can be improved from only 10 percent reporting to the clean coal and 90 percent reporting to the reject coal but if in such case we can get that yield may be increased up to 50 to 60 percent without any deficiency in the clean coal quality. So, if we use ultrasound and in the froth flotation, oil agglomeration. Similarly in other process Better mixing of chemicals or reagents occurs. As a result, overall yield of the process improves significantly along with some improvements in the quality of the coal. So, this ultrasonic based method is nowadays getting much more and more utilized in different practice as the cost of this ultrasound energy is significantly high so most of the industry is doing their economic analysis technical economic analysis whether using ultrasound energy will improve their performance improve their profitability and others so finally they are at present doing their techno economic analysis whether utilization of ultrasound energy will be profitable how much they can profit as For ultrasound energy generation a significant amount of electricity is consumed. So, all are under process. So maybe very soon or maybe in near future we can see many industrial practice or many coal industries are using ultrasound energy. They are incorporating their ultrasound energy in their plants.

Now next part of this coal cleaning is the chemical coal cleaning. what is the chemical coal cleaning in the chemical coal cleaning we use chemical reaction but we do the chemical reactions between the coal and added chemicals so we add different type of chemicals to do some chemical reactions Among the added chemicals and coal particles. So that's why they are called the chemical coal cleaning, not like that physical coal cleaning. In case of physical coal cleaning like dense media cyclone, oil agglomeration, etc. As such, apparent no chemical reactions are there. So, coal properties, coal remains as it is like coal. But in case of chemical coal cleaning, there are some chemical reactions happens between the coal particle and the added chemicals. What type of chemicals we can add? We can add like concentrated acids like hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoric acid, etc. We add concentrated acid or we can add concentrated base like high-concentration sodium hydroxide solution, potassium hydroxide solution, or calcium hydroxide solutions. They are also used, and sometimes other Organic materials like other reactive materials, such as ozone or hydrogen peroxide, are also used in some cases to improve the efficiency. In another method, some organic solvents like aniline, dimethylformamide, and many more similar organic solvents are also used in these chemical coal-cleaning methods. So, we can use either acids, bases, or different types of organic solvents.

So, what is the role of these added chemicals? Typically, these materials react with the coal particles. Some of the materials can react with the mineral matter, whereas other chemicals can react with the hydrocarbon part of the coal. So, either mineral matter That will react with the mineral matter, as they are inorganic in nature. So, mostly they react with the acid or base. And as the hydrocarbons are typically organic compounds, So, typically they are dissolved. They react very well with different types of organic solvents, like aniline and dimethylformamide. So, either they will react, or they may get dissolved or solubilized in the added chemicals in the aqueous medium or maybe in the pure solvent medium.

So, in case of chemical coal cleaning, typically mineral matter as they are Containing different type of inorganic salts. So, this mineral matter reacts with the acid or base. Suitable acid or base at suitable temperature, pressure and environmental condition. So, what will happen once they react with the acid? So they after reacting with the acids, they will soluble in the water phase or in the liquid phase. So once this mineral matter get reacts with the acids, they soluble in the water phase or mineral matter, water phase or in the solvents. So, they will easily get removed or come out from the coal structure. so mineral matter they can easily get removed from the coal as this initially this mineral matter were insoluble in the medium but once they are reacting with the acids they create some soluble inorganic salts as a result they will come out from the solid coal particle and they will get dissolved in the acidic phase and we can easily remove all of them similarly In case of organic hydrocarbons, as these organic hydrocarbons like benzene, toluene and similar bigger size only hydrocarbons are there, they are very well or they get soluble in the organic solvents. Typically, we use any of the inorganic solvents, they will not get dissolved because of formation of hydrogen-hydrogen bonds and other bonds. Typically, inorganic solvents are very well suitable for the inorganic compounds, and organic solvents are used for the organic compounds. So, all these organic solvents, they dissolve the hydrocarbon part of this coal. So, entire hydrocarbon will come to the liquid phase at they are getting dissolved in this organic solvent. So, mineral matter they will remain as a solid particle. So, they can be easily separated by normal filtration or other methods. We can use in case of acids and base we can use water as a liquid medium in case of hydrocarbon we have to use that organic solvent as a liquid medium and further we have to recover the organic solvents or acid or base whatever is available so after the reaction One part either mineral matter or hydrocarbon depending on whether we are adding acid base or we are adding solvent. So, one part will remain as solid phase and other part will be in the liquid phase. So, suitable separation techniques are used along with recovery of solvents and chemicals. So, after this, once they are

mixed and one part gets soluble in the liquid phase, we use suitable type of filter. separation method like we can use normal filtration or we can use other type of filtration technique we can use even different type of phase separation techniques etc to separate the soluble phase as well as the insoluble phase and later we recover the solvents or chemical used and if their reaction is not happening at normal environmental condition like maybe possible that mineral matter is not reacting very well or that whatever organic solvent is there as the solubility improves upon the temperature or maybe at the high pressure so sometimes high pressure and high temperature is also used. So, this entire chemical reactions happens maybe at higher temperature of 400 degree centigrade 300 degree centigrade may be at higher pressure at 50 bar, 1 bar, 2 bar, maybe 100 bar as per the types of coal and as per the chemicals used. Overall, if we see, this method is very much expensive in nature as the cost of all these acid, base and others, they are too much high and if we consider the cost of coal, they are on the much lower side. So, overall, this is a very much expensive method and may not be Sometimes environment friendly because all these acid base and others sometimes creates environmental pollution, creates distress to the environment.

And mostly, they are used to get high-quality, carbon-rich material. Typically, not for coal cleaning for industrial combustion and other units, but where from coal we prepare high-quality, carbon-rich material like the preparation of graphite, some anodes, electrodes, etc. Where high-quality, carbon-rich material is required, but the origin starts from coal. Mostly, all these methods are used only in those applications. So, if we go for the chemical reactions, how do these chemical reactions happen? Alkali treatment methods are used for the reduction of sulfur as well. Like if coal has some amount of sulfur present, sulfur also reacts whether it is organic sulfur or part of pyritic or sulfate sulfur. They also react with the solvent. So, as a result, sulfur can also be reduced by this method. So, the effectiveness of such methods depends on the reactivity of the coal and alkali—what type of alkali or acids we should use, and what is the reactivity of coal. Accordingly, we have to consider whether we will use HCl, H₂SO₄, nitric acid, or it may need some additional oxidative material like ozone, hydrogen peroxide, and others. If we see silica and alumina and their similar materials, they react with the base to form different types of silicates. So, if we see like silica is used, it reacts with NaOH, creating some sodium silicates, which are water-soluble. Similarly, if alumina is there, then it also reacts with NaOH, creating some sodium aluminate. Similarly, if we—this sodium—both of these materials in the presence of NaOH, Anyways, they can use sodium alumina silicate material, which is also water-soluble, and we can easily separate them. Similarly, if we go for the sulfur

present in coal, this pyrite sulfur reacts with sodium hydroxide, and sodium sulfide reacts with water to create some of these gases. So, FeH_2 also reacts in the presence of oxygen as an oxidative medium in terms of water. So, as a result, sulfur can also be removed by this method or such chemical methods. Similarly, if we see the organic solvent, different types of organic materials or oxidizing agents like Air is used, oxygen is used, ferric salt is used, nitrogen oxides and chlorine are also used to convert ferritic sulfur and part of organic sulfur to make it water-soluble sulfates and to remove it from the coal structure.

So, these reagents or these oxidizing agents are used additionally along with different types of acids, bases, or organic solvents. They are very effective for the reduction of both pyritic sulfur as well as organic sulfur from coal. So, if coal has a higher quantity of sulfur present and conventional coal cleaning cannot remove the sulfur percentage from coal, particularly if it is organic sulfur in nature, which is very difficult to remove by conventional physical coal cleaning. So, in such cases, we can use this Chemical coal cleaning method for the reduction of both pyritic sulfur as well as organic sulfur from coal, which are difficult By conventional physical separation processes. So, if we see that different types of chemical reactions, like if iron sulfides are there, they react with oxygen in the presence of ammonia, oxygen, and others. They can also react with oxygen, water, and even different types of alcohols like methanol, ethanol, Sometimes they are also used in such reactions. So, all this, the entire coal particle having sulfur presence as part of hydrocarbon, can react with alcohol in the presence of all these materials. So, by this, we can replace sulfur present in this coal with the oxygen group. So, as a result, we can easily remove this Sulfur compound from this coal. Now, if we see all these coal cleaning methods, comparing them like organic chemicals, different types of Solvents like dimethyl formamide, aniline, as well as different types of acids and others.

So, they are very much effective in reducing sulfur content primarily sulfur content from coal but they can also be used for reduction of mineral matter from the coal. But what disadvantage from all these method is that they are very much costly method. If we see the cost of coal, if we see that cost of coal is very less as we have seen in our previous modules. Cost of coal in an industrial scale varies like rupees 4000 per ton. That means if we consider it in terms of kg. maybe Rs 4 to 5 per kg for non-coking coal or thermal coal or even for the metallurgical coal it is like rupees 10 000 to 15 000 per ton that means rupees 10 to 15 per kg of coal and if we see the cost of chemicals used here typically these acids and base they are cost like one liters cost like 100 or 200 and some of the organic solvent maybe for one liter cost is around thousand so overall it is a very much expensive method and as the finally price of coal depends on the

coal quality as per the coal grading so these methods or this chemical coal cleaning method cannot be used as the primary method for coal cleaning only these methods can be used for at the last stage for fine tuning the sulphur presence or other compound present in coal as their cost is significantly on the higher side. So, these methods, acid base, acid cleaning, NaOH methods and organic methods are typically not used in industrial practice where coal is used as a source of fuel. but they can be used in other applications where coal is used to prepare or produce some valuable materials or high price and material like preparing some carbon rich material so carbon rich materials are required in many high ends applications. So where high quality carbon is required and as there is no as such pure carbon source available in many cases.

Coal is used as the starting material and from that coal after processing or going through different type of purification process, high carbon rich material is used to as in getting an carbon anode, carbon electrodes and graphites and others and even for the preparation of printer ink, cartridge ink, Xerox machine ink and others where high carbon rich materials are required. That means where the market value of carbon rich particles is on the higher side. not like a low end application like using it as a fuel so if we see the utilizing coal for fuel purpose means it is a low market value applications we get less amount of equal price if we use it as fuel but if we can use this carbon rich material as an chemicals or as a value added applications where Price of this carbon rich material will be on the higher side, maybe Rs. 1000 per kg or maybe Rs.10,000 or Rs. 1 lakh per kg. In all those applications, we can use this chemical coal-cleaning method involving acid, base, and organic materials. Also, if we use all these acid, base, and organic solvents in higher quantities, their availability is also a major concern. For industrial practice, we may need gallons of acids and bases. There may not be such high quantities of acids or bases available for industrial utilization. There are not as many high-quantity resources available from which we can regularly obtain higher quantities of acids and bases, particularly in high concentrations. Because HCl, H₂SO₄, and HNO₃ are only used in high concentrations—like 90% sulfuric acid, 98% nitric acid, or other very high-concentration acids—they are not used in dilute form, as their reactivity would be lower. So, the availability of these and their environmental impact all affect the final coal-cleaning method. Typically, this chemical coal-cleaning is used only for high-end applications to obtain high-quality, pure carbon-rich material, not for conventional thermal power plants, coal washeries, or coke-making industries where we have to beneficiate the coal for use as a fuel source. If we combine ultrasound-based energy with these reactions, like chemical coal-cleaning, even if we use

ultrasound energy, overall, we can achieve very good separation of coal from the coal surface, mineral matter, as well as hydrocarbons.

They will be directly exposed to this and can be broken down to very fine sizes or even at the molecular level. So, by combining ultrasound-based energy with the chemical cleaning method, we can obtain almost pure carbon particles or pure hydrocarbon-rich particles. Similarly, if we combine ultrasound-based conditioning methods during oil agglomeration or the froth flotation process—even for other methods—we can improve the efficiency and yield. Typically, the limitation of froth flotation and oil agglomeration is high oil consumption due to creating smaller droplets. Whatever froth is produced is not of good quality and is in larger sizes. With conventional mixing, we can only get larger-sized froths. So, they have some limitations in terms of yield, not in terms of quality.

So, ultrasonic-assisted froth flotation and ultrasonic-assisted oil agglomeration processes are nowadays getting implemented in many coal washeries. To get the high yield of the process and to obtain a higher quantity of clean coal with a very low amount of ash. So, overall, this entire ultrasonic-assisted method, as well as the chemical coal cleaning method, if we see, their cost is on the higher side. So, the industry is making some techno-economic decisions on whether they should apply this or not apply this method during their chemical coal cleaning. So, if we see overall at their final level, the physical coal cleaning method will continue to be used in the coal washeries, whereas the chemical coal cleaning and ultrasonic methods will be used as a top-up or an add-on option to their different units for fine-tuning the properties of clean coal or eliminating some of the harmful compounds from the coal structure.

Thank you.