Inorganic Chemical Technology
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Lecture - 12
Sulfur and sulfuric acid

Welcome to the MOOCs course Inorganic Chemical Technology, the title of today's lecture is Sulfur and sulfuric acid. Before going into the details of today's lecture, what we will do? We will have a kind of recapitulation of what we have discussed in the previous lecture.

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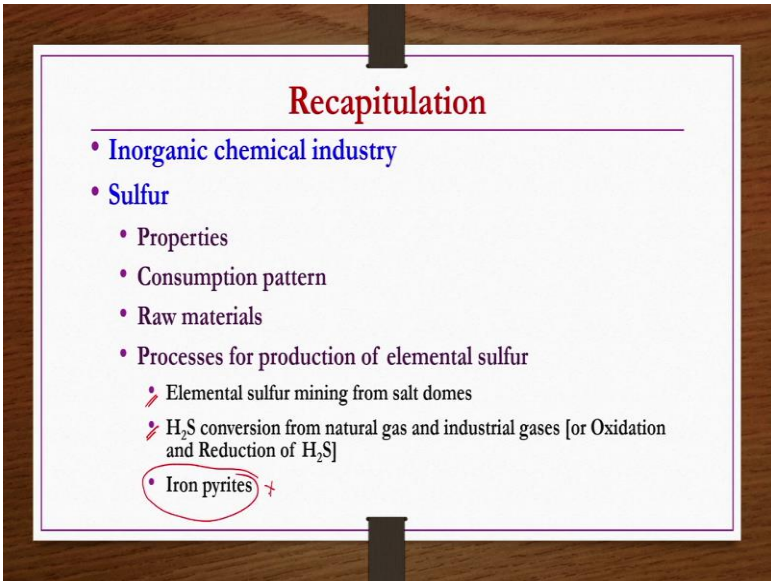

Recapitulation

- Inorganic chemical industry
- Sulfur
  - Properties
  - Consumption pattern
  - Raw materials
  - Processes for production of elemental sulfur
    - Elemental sulfur mining from salt domes
    - H_2S conversion from natural gas and industrial gases [or Oxidation and Reduction of H_2S]
    - Iron pyrites

In the previous lecture, we have seen a few basic comparison between inorganic and organic chemical industry, then we started discussing about the sulfur. Under the topic of sulfur, we started with its pertinent properties, then consumption pattern, then raw materials that are available for its production and then processes for the production of elemental sulfur.

We have seen that there are three processes for the production of a elemental sulfur. One is the elemental sulfur mining from salt domes; other one is the H 2 S conversion from natural gas and industrial gases or oxidation and reduction of H 2 S and, third one is from iron pyrites. So, out of these three methods, first two methods, we have already discussed in the previous lecture.

In today's lecture, we are going to discuss how to produce elemental sulfur from iron pyrites. That is what we are going to see now.

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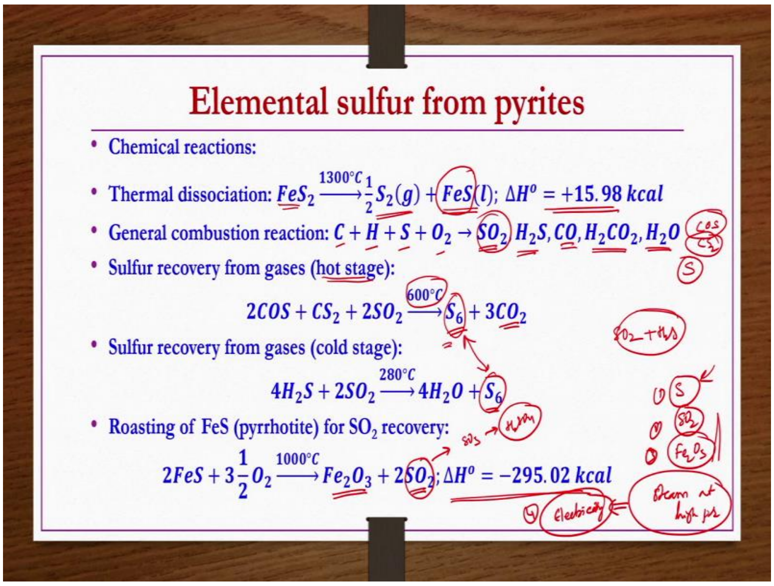

Elemental sulfur from pyrites

- Chemical reactions:
- Thermal dissociation: $FeS_2 \xrightarrow{1300°C} \frac{1}{2}S_2(g) + FeS(l)$; $\Delta H^o = +15.98\ kcal$
- General combustion reaction: $C + H + S + O_2 \rightarrow SO_2, H_2S, CO, H_2CO_2, H_2O$
- Sulfur recovery from gases (hot stage):

$$2COS + CS_2 + 2SO_2 \xrightarrow{600°C} S_6 + 3CO_2$$

- Sulfur recovery from gases (cold stage):

$$4H_2S + 2SO_2 \xrightarrow{280°C} 4H_2O + S_6$$

- Roasting of FeS (pyrrhotite) for SO_2 recovery:

$$2FeS + 3\frac{1}{2}O_2 \xrightarrow{1000°C} Fe_2O_3 + 2SO_2; \Delta H^o = -295.02\ kcal$$

Elemental sulfur from pyrites. Iron pyrites are nothing but ore, where predominantly iron disulfide component is present. When you take a ore material and then do the thermal dissociation reactions in high temperature furnaces, then several reactions takes place. So, those reactions first we start with under this third method of elemental sulfur production from iron pyrites.

Chemical reactions, thermal dissociation FeS 2, which is the primary component of iron pyrites, that is iron disulfide. If you do the thermal dissociation of this component at high temperature, something like 1300 degree centigrade, then you get a disulfur gas, which is highly active in general and also you get a iron sulfide, which is in the liquid droplet form, right.

Then this ore, whatever you take in general, that is we are getting from the natural resources. So, there may be some carbonaceous materials also or other inorganic minerals may also be present in that one. So, let us say if you take general combustion reaction between C, H, S elements reacting in the presence of oxygen, then what are the possibilities of gases that could be forming?

Sulfur dioxide, hydrogen sulfide, carbon monoxide, carboxylic acid, water, carbonyl sulfide, carbon disulfide, etcetera, these components may form, right. Most of them are in the gases or vapour form. So, now out of this, what we are going to see? We are going to see how to recover elemental sulfur S. So, this recovery of sulfur from gases takes place in two stages.

In this process, one stage is known as the hot stage, that is catalytic reaction takes place at high temperature, approximately at 600 degree centigrade, something like that. So, in this hot stage, in the catalytic converter what happens? This SO 2 reacts with carbonyl sulfide and then carbon disulfide to give sulfur vapours and then carbon dioxide. This reaction takes place around 600 degree centigrade.

Then sulfur recovery from gases will also takes place at lower temperature, that is known as the cold stage. At this stage what happen? The catalytic conversion of a SO 2 and then H 2 S takes place to get water vapour and then sulfur vapours. These sulfur vapours whatever are there, those things can be condensed using the molten sulfur and then you get the elemental sulfur, required elemental sulfur you can get.

So, now this is one of the product that you are going to see and then this is also one of the product because this iron sulfide whatever is there or pyrrhotite whatever it is there that you can granulate it and then do the roasting of it. So, if you do the roasting of this FeS, then it is possible that you can get sulfur dioxide and then iron oxide. This sulfur dioxide what you can do? You can recover it and then further convert it to the SO 3 and then further you can get sulfuric acid, right.

So, that means, not only elemental sulfur S, but also sulfur dioxide and then this iron oxide whatever is there, it can be taken as a basic ore and then sent to the steel industries for the further recovery of iron etcetera. In addition to that, one you can see the delta H though the thermal dissociation of FeS 2 is endothermic reaction.

The other important reaction is early exothermic and then many other reactions you know when this takes place steam is generated at high pressures and then this steam can be utilized to produce electricity or power. So, now what we see 1, 2, 3, 4 products are there that you can estimate or that you can get from this process.

That is the reason this process or elemental sulfur production from the iron pyrites is very famous in India because not only this sulfur you also get other three products that is SO 2 from which you can get the H 2 SO 4 and then Fe 2 O 3 and then you also generate power ok.

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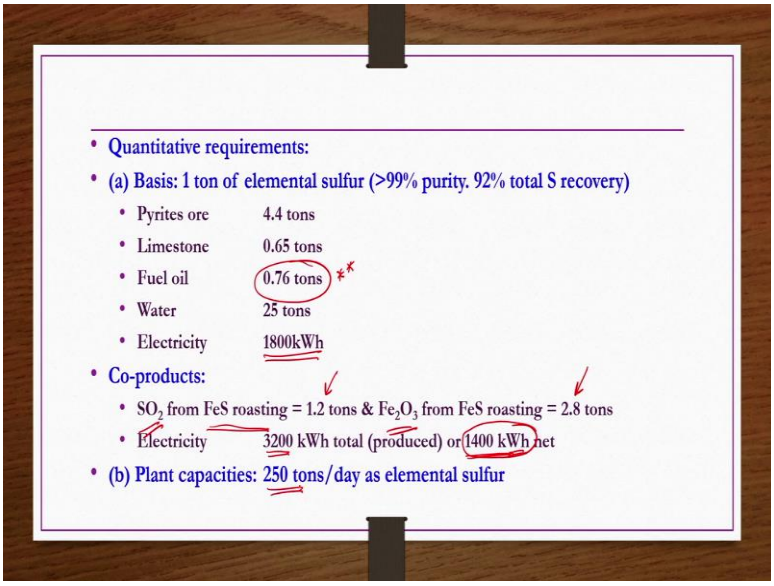

- Quantitative requirements:
- (a) Basis: 1 ton of elemental sulfur (>99% purity. 92% total S recovery)
    - Pyrites ore 4.4 tons
    - Limestone 0.65 tons
    - Fuel oil 0.76 tons **
    - Water 25 tons
    - Electricity 1800kWh
- Co-products:
    - SO_2 from FeS roasting = 1.2 tons & Fe_2O_3 from FeS roasting = 2.8 tons
    - Electricity 3200 kWh total (produced) or 1400 kWh net
- (b) Plant capacities: 250 tons/day as elemental sulfur

So, quantitative requirements if you see, if you wanted to produce 1 ton of elemental sulfur greater than 99 percent purity then pyrites ore 4.4 tons required, limestone 0.65 tons required and then fuel oil 0.76 tons required for 1 ton production of elemental sulfur which is very high quantity. So, this is one of the important economic factor.

If you can replace fuel oil with other cheaper fuel options like coal etcetera it is going to be even economically feasible. It is going to be even economically better option if you can replace fuel oil with other sources like coal etcetera, coal or pulverized coke etcetera those things if you can use.

Water requirement 25 tons, electricity 1800 kilowatt hour, right. In the reactions we have already seen that there are some byproducts or co-products are there. So, these co-products are SO 2 and then Fe 2 O 3 from FeS roasting, pyrrhotite roasting in fluidized bed roasters ok. So, how much SO 2 you get? 1.2 tons and then how much Fe 2 O 3 you get 2.8 tons.

We have also discussed that lot of steam is produced at high pressure. So, that steam can be utilized to produce electricity. How much you can produce? 3200 kilowatt hour total electricity you can produce, but you are utilizing only 1800 kilowatt hour in this process. So, 1400 kilowatt hour net electricity that is being produced in this process, ok. So, plant capacities in general 250 tons per day as elemental sulfur production.

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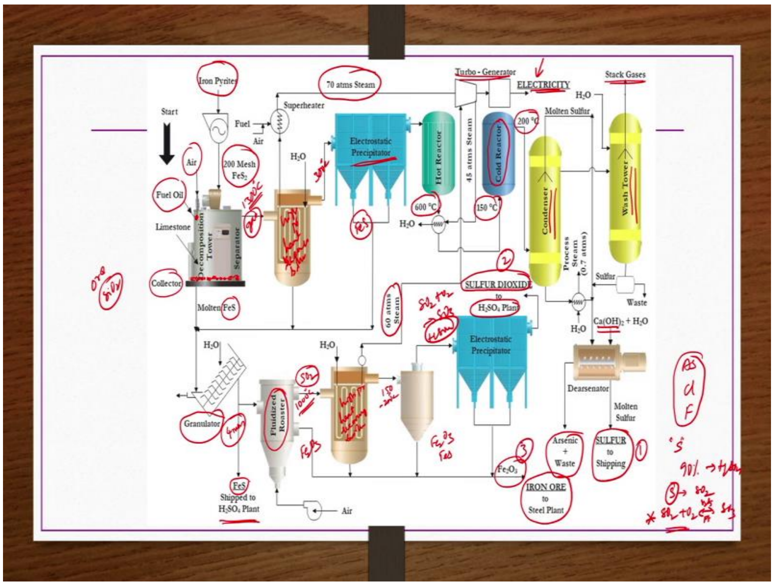

Now, we see the process by a flow sheet here that is shown here, ok. So, the iron pyrite whatever required for this process to get the elemental sulfur they should be dry enough. If they are not dry enough then what happened, whatever the moisture is there in the ores that may be interfering with the important reaction because we have seen under the chemical reaction section so many reactions are there. So, it is very essential to make the ore dry enough.

So, if it is not dry enough what you can do? You can use the flue gases in rotary kiln and then dry them. After drying them you can size reduce them to approximately 200 mesh size, right. Then what we have? We have a smelter furnace right in which different operations are taking place. At the top of the smelter what we are having? We are having oil burners, right. To this oil burner's fuel oil and then air is supplied.

When the fuel oil is combusted using the air so many combustion gases are forming here ok. So, these combustion gases would be very useful for the FeS 2 thermal dissociation, right. So, once we have these combustion gases and then ore inside the smelters. So, then what you can do? You introduce size reduced FeS 2 to this process.

Then thermal dissociation of a FeS 2 will take place and then gases would be released and then these gases would be at approximately 1300 degree centigrade because at that temperature reaction is taking place and then in the same temperature gases are coming out. So, when FeS 2 is dissociating what we have seen? We have seen FeS or pyrrhotite liquid droplets are also forming.

These droplets should be condensed at the bottom or these droplets should be collected at the bottom right in a liquid form. Let us say if the ore is having silica also in general ores definitely would be having silica whatever the purification level you do. So, then those silica may also be a kind of interfering subsequent reactions for the production of elemental sulfur or sulfur dioxide.

So, that should also be washed out or fluxed out. For that purpose we use the limestone lime solutions here to flush out the silica from here, right. So, because the silica is you know settling on the top of this molten FeS so, the flushing out this silica using the limestone is not a difficult task, right.

So, once these silica has been flushed out so, whatever molten FeS is there that is collected from the collectors and then sent to a granulator where it is being granulated to approximately 4 mm size and then it is stored or shipped to H 2 SO 4 plant as per the requirement.

Otherwise whatever these granules of FeS are there they can be taken to a fluidized roaster where roasting of FeS takes place to get SO 2 and then Fe 2 O 3, right. So, this reaction occurs at very high temperature approximately at 1000 degree centigrades So, the gases coming out from the fluidized bed roaster roasting FeS will be having temperature 1000 degree centigrades.

So, these hot gases what they will be done next? They will be taken to a high pressure heat recovery boilers where heat would be recovered and then they will be reduced to temperature something like 150 or 200 degree centigrade something like that. So, when the temperature is reduced so much so, what happens? Steam at high pressure would be released and then that steam may be collected and sent to turbo generator for the electricity generation.

After cooling the gases if at all gases are having traces of Fe_2O_3 or unreacted FeS etcetera they would be separated in cyclone separator followed by electrostatic precipitator and then almost pure sulfur dioxide whatever is there that is collected and then sent to H_2SO_4 plant. This SO_2 would be further oxidized to SO_3 and then this SO_3 when you dissolve in water you get H_2SO_4.

So, in the production of sulfuric acid lecture we are going to see these details anyway in the subsequent lectures. So, whatever Fe_2O_3 that is present in the gases they will be separated out from the cyclone separator and then electrostatic precipitator and then collected as Fe_2O_3 and then that is sent as iron ore to steel plants. So, this is another product ok.

Now, whatever the gases coming out from this smelter they are at high temperature of 1300 degree centigrade those gases will also be taken to high pressure heat recovery boiler where the temperature is reduced to 300 degree centigrade. So, when the temperature is reduced from 1300 degree centigrade to 300 degree centigrade. So, lot of steam is generated that would be approximately at 70 atmospheric pressures and then that can also be taken to turbo generator for electricity production, right.

So, cooled gases which are at 300 degree centigrade, they would be further sent to electrostatic precipitator to check if any droplets of FeS or dust of FeS is present in the gases. If at all there, so, those would be separated out in the electrostatic precipitator and then those droplets or dust of FeS is mixed with the molten sulfur and then further granulation is done.

These cooled gases which are at 300 degree centigrade, then sent to a hot stage or hot reactor where catalytic reactions take place at 600 degree centigrade. Here most of the SO_2 react with the COS and then CS_2 to get the S_6 and then carbon dioxide, ok. So, if at all some H_2S or SO_2 are still unreacted they will be reacted into a separate reactor which is cold stage reactor or cold catalytic reactor which occurs at approximately 200 degree centigrade, right.

Before sending the gases of hot reactor to the cold reactor those gases again cooled in a low pressure heat recovery boiler and then here again the steam approximately 45 atmospheres generated that can also be taken for the electricity production, alright. So, now after cooling these gases from the hot stage they will be at approximately 150 degree centigrades and then these gases are sent further taken in a cold stage catalytic reactor where reaction occurs at the approximately 200 degree centigrade where SO 2 and then H 2 S reacts to give water and then sulfur vapour.

Those sulfur vapour now would be at 200 degree centigrade, they will be taken to a condenser where molten sulfur drops are sprayed from the top in order to condense the sulfur vapour, alright. If at all some uncondensed sulfur vapours are there or if unreacted SO 2 or other gases are there in order to remove them.

These gases would be further taken to wash tower these exit gases taken to the wash tower where water is sprayed from the top so that if any sulfur is there that would be collected from the bottom and then wastes are separated out. Whereas, the stack gases which are having permissible limits of SO 2 etcetera they can be sent to the atmosphere, alright.

See the molten sulfur that you collected from this process after the condenser and then after the wash tower you know that may be having some impurities like arsenic or it may be having some chlorides or it may be having some fluorides etcetera. Having these component is not good for the subsequent use of you know this S because this S elemental sulfur whatever is there 90 percent of it is being used for a H 2 SO 4 production only.

That is what we have seen in the previous lecture, right. So, this S would be converted to the SO 2 and then this SO 2 will be further oxidized to give SO 3 which is a reversible reaction. It occurs using some catalyst V 2 O 5 or platinum or iron oxide these kind of catalyst are there, right.

So, when you do these catalytic reactions later stage if this sulfur is having this arsenic or something this kind of components they will be present along with the SO 2 gases also. And, then this when SO 2 is being oxidized using the catalyst to SO 3 this impurities may be deactivating this catalyst etcetera. So, that is the reason it is very essential to remove this arsenic components etcetera.

That can be done by taking them in a continuous autoclave in which calcium hydroxide solution is present. So, after this dearsenator, you can remove arsenic and other kind of waste and then get almost pure sulfur to ship. This is the entire process that is happening in the case of elemental sulfur production from the iron pyrites.

So, now you can see here elemental sulfur is one product and then sulfur dioxide is second product, third product is iron oxide and then fourth product is electricity, ok. Now, whatever we have seen in the flow sheet the same thing is presented as a notes here.

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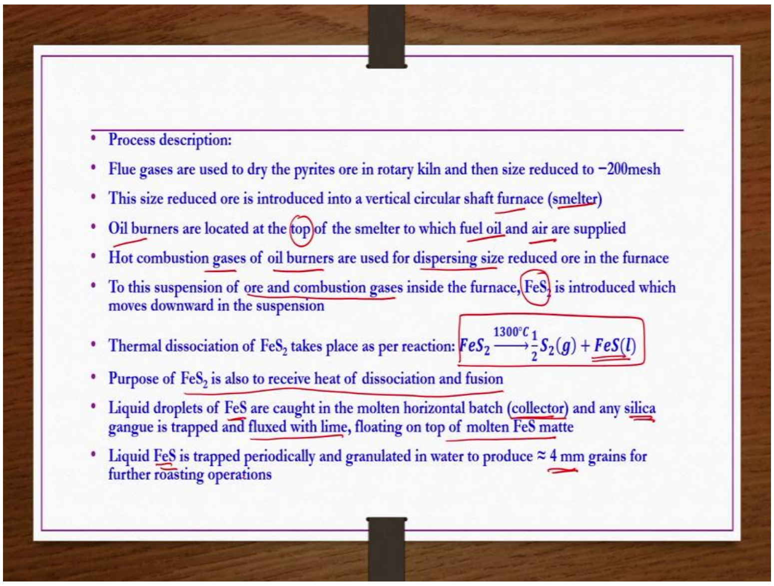

- Process description:
- Flue gases are used to dry the pyrites ore in rotary kiln and then size reduced to −200mesh
- This size reduced ore is introduced into a vertical circular shaft furnace (smelter)
- Oil burners are located at the top of the smelter to which fuel oil and air are supplied
- Hot combustion gases of oil burners are used for dispersing size reduced ore in the furnace
- To this suspension of ore and combustion gases inside the furnace, FeS_2 is introduced which moves downward in the suspension
- Thermal dissociation of FeS_2 takes place as per reaction: $\boxed{FeS_2 \xrightarrow{1300°C} \frac{1}{2} S_2(g) + FeS(l)}$
- Purpose of FeS_2 is also to receive heat of dissociation and fusion
- Liquid droplets of FeS are caught in the molten horizontal batch (collector) and any silica gangue is trapped and fluxed with lime, floating on top of molten FeS matte
- Liquid FeS is trapped periodically and granulated in water to produce ≈ 4 mm grains for further roasting operations

The process description: Flue gases are used to dry the pyrites ore in the rotary kiln and then size reduced to 200 mesh size. This size reduced ore is introduced into a vertical circular shaft furnace which is smelter. Oil burners are located at the top of the smelter to which fuel oil and then air are supplied. Hot combustion gases of oil burners are used for dispersing size reduced ore in the furnace.

To this suspension of ore and combustion gases inside the furnace, introduce FeS 2 from the top which moves downward in the suspension. Then thermal dissociation of this iron disulfide takes place at 1300 degree centigrade and then give disulfur gases which is highly active and then Pyrrhotite that is iron sulfide a liquid droplets, ok.

So, purpose of FeS 2 is also to receive heat of dissociation and fusion not only production of these two components. Liquid droplets of FeS are caught in the molten horizontal batch which is called as collector and if any silica is present that is trapped and fluxed with lime which is floating on the top of molten FeS matte. This silica is floating on the top of molten FeS.

Liquid FeS is trapped periodically and granulated in water to produce approximately 4 mm grains for further roasting operations in fluidized bed reactors.

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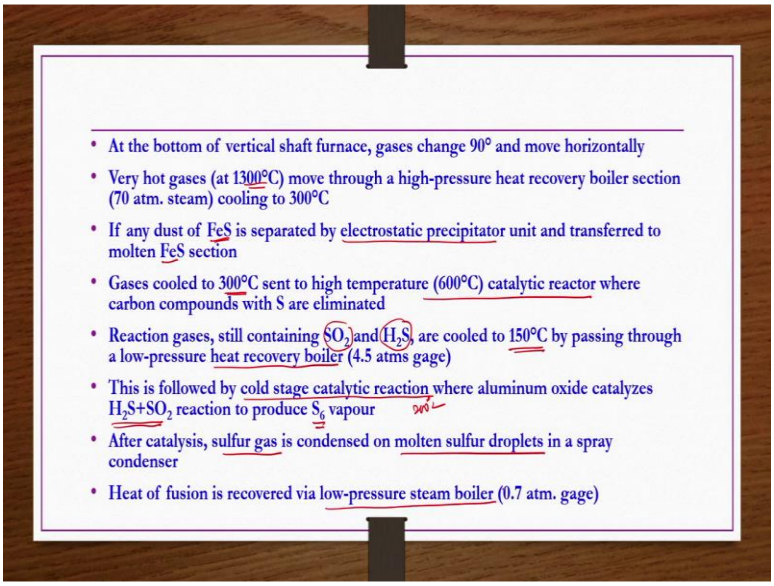

- At the bottom of vertical shaft furnace, gases change 90° and move horizontally
- Very hot gases (at 1300°C) move through a high-pressure heat recovery boiler section (70 atm. steam) cooling to 300°C
- If any dust of FeS is separated by electrostatic precipitator unit and transferred to molten FeS section
- Gases cooled to 300°C sent to high temperature (600°C) catalytic reactor where carbon compounds with S are eliminated
- Reaction gases, still containing SO_2 and H_2S, are cooled to 150°C by passing through a low-pressure heat recovery boiler (4.5 atms gage)
- This is followed by cold stage catalytic reaction where aluminum oxide catalyzes H_2S+SO_2 reaction to produce S_6 vapour 200
- After catalysis, sulfur gas is condensed on molten sulfur droplets in a spray condenser
- Heat of fusion is recovered via low-pressure steam boiler (0.7 atm. gage)

At the bottom of vertical shaft furnace, gases change 90 degrees and more horizontally. Very hot gases which are at 1300 degree centigrade move through a high-pressure heat recovery boiler section and get cold to 300 degree centigrades. If any dust of FeS is there that would be separated by the electrostatic precipitator unit and transfer to the molten FeS section. Cooled gases to 300 degree centigrade sent to high temperature catalytic reactor where carbon compounds with S are eliminated.

Reaction gases, if at all still containing SO 2 and H 2 S are cooled to 150 degree centigrade by passing through a low pressure heat recovery boiler. This followed by cold stage catalytic reaction which occurs at approximately 200 degree centigrade where aluminum oxide catalyzes H 2 S and then SO 2 reaction to produce sulfur vapour and water vapour.

After catalysis, sulfur gas is condensed on molten sulfur droplets in a spray condenser and then heat of fusion is recovered via low pressure steam boilers.

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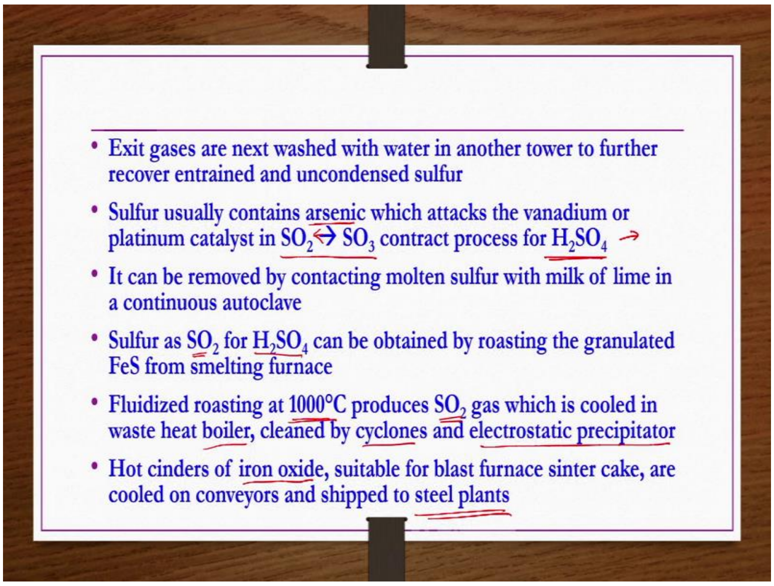

- Exit gases are next washed with water in another tower to further recover entrained and uncondensed sulfur
- Sulfur usually contains arsenic which attacks the vanadium or platinum catalyst in $SO_2 \leftrightarrow SO_3$ contract process for H_2SO_4 →
- It can be removed by contacting molten sulfur with milk of lime in a continuous autoclave
- Sulfur as SO_2 for H_2SO_4 can be obtained by roasting the granulated FeS from smelting furnace
- Fluidized roasting at 1000°C produces SO_2 gas which is cooled in waste heat boiler, cleaned by cyclones and electrostatic precipitator
- Hot cinders of iron oxide, suitable for blast furnace sinter cake, are cooled on conveyors and shipped to steel plants

Then exit gases are next washed with water in another tower to further recover entrained and uncondensed sulfur. Sulfur usually contains arsenic which attacks the vanadium or platinum catalyst in SO 2 giving rise to SO 3 in contact process for H 2 S production. This we are going to see in subsequent lectures. It can be removed by contactings molten sulfur with milk of lime in a continuous autoclave. Sulfur as SO 2 for H 2 SO 4 can be obtained by roasting the granulated FeS from smelting furnace.

Fluidized roasting at 1000 degree centigrade produces sulfur dioxide which is cooled in a waste heat boiler, followed by cleaning in cyclones and then electrostatic precipitators. Hot cinders of iron oxide, suitable for blast furnace sinter cake are cooled, on conveyors and shipped to steel plants. This is about the process.

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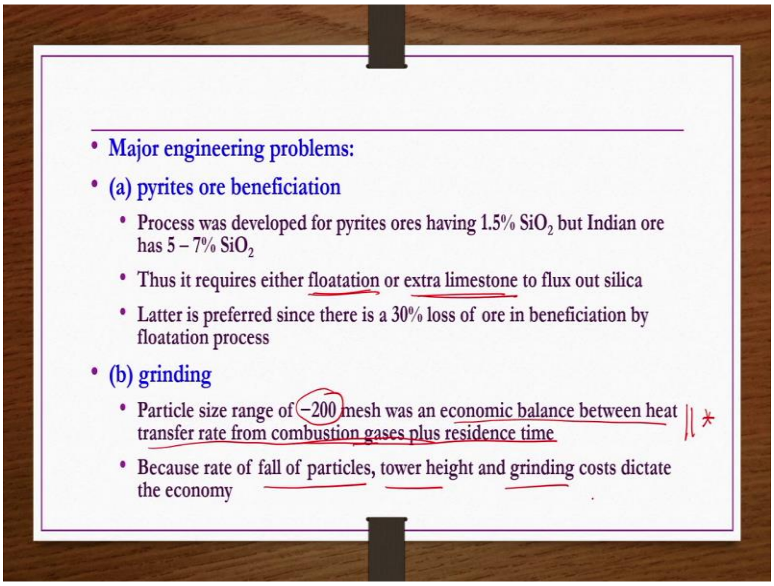

- Major engineering problems:
- (a) pyrites ore beneficiation
  - Process was developed for pyrites ores having 1.5% SiO_2 but Indian ore has 5 – 7% SiO_2
  - Thus it requires either floatation or extra limestone to flux out silica
  - Latter is preferred since there is a 30% loss of ore in beneficiation by floatation process
- (b) grinding
  - Particle size range of −200 mesh was an economic balance between heat transfer rate from combustion gases plus residence time || *
  - Because rate of fall of particles, tower height and grinding costs dictate the economy

Now, we see if at all any engineering problems what are the problems you know they are very essential from engineering point of view to consider? So, major engineering problems: pyrites ore beneficiation. Ores in general include so many kind of impurities, dust, mud etcetera, not only that one other metallic ferrous, non-ferrous ingredients may also be present in or other inorganic may also be present.

So, many purifications steps are done using different types of mechanical unit operation and then almost pure, almost clean enough ore is used in a smelter process, right. So, but this process whatever we discuss that is developed for the process where ore is having only 1.5 percent silica, but Indian ore has in general 5 to 7 percent silica.

So, then you know this removal is very essential. Thus it requires either flotation or extra limestone to flux out silica. But, however, if you use the flotation then what happened? It has been found that approximately 30 percent of loss of ore is there if you use the flotation.

So, that is the reason it is better to go for extra limestone solution to flux out the silica which is floating on the surface of molten FeS. Then grinding, whatever the size reduced FeS to that is there 200 mesh size that is based on the economic balance between heat transfer rate from combustion gases plus residence time, right. So, this size is you know that much important, right. It is because of this balance, right.

Why it is so much important? In general, fall of particles or the settling velocity of the particles, tower height and then grinding cost etcetera dictate the economy, ok.

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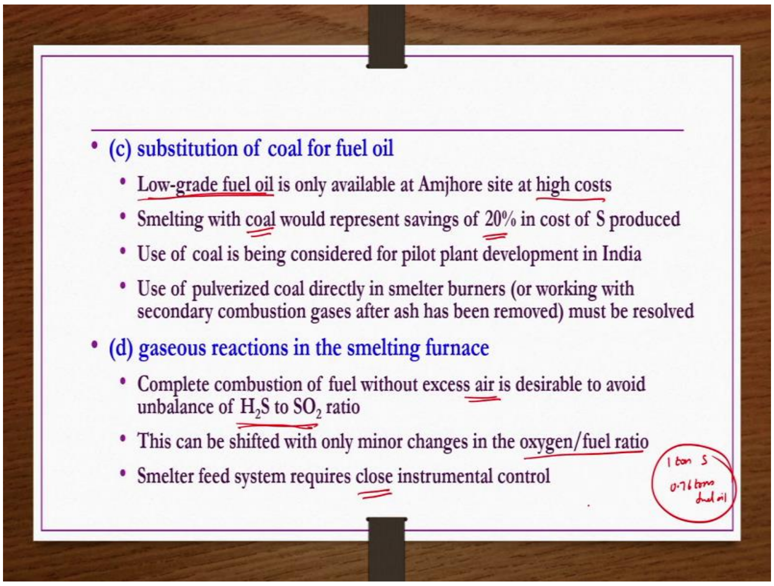

- (c) substitution of coal for fuel oil
  - Low-grade fuel oil is only available at Amjhore site at high costs
  - Smelting with coal would represent savings of 20% in cost of S produced
  - Use of coal is being considered for pilot plant development in India
  - Use of pulverized coal directly in smelter burners (or working with secondary combustion gases after ash has been removed) must be resolved
- (d) gaseous reactions in the smelting furnace
  - Complete combustion of fuel without excess air is desirable to avoid unbalance of H_2S to SO_2 ratio
  - This can be shifted with only minor changes in the oxygen/fuel ratio
  - Smelter feed system requires close instrumental control

1 ton S
0.76 tons fuel oil

Then substitution of coal for fuel oil, fuel oil is very expensive. Actually we have seen in quantitative requirement section what we have seen, if you want to produce one ton of elemental sulfur you need 0.76 tons of fuel oil which is very high large quantity, right and then these fuel oils are expensive in general.

Especially in India they are available in limited locations like Amjhore site, but it at high cost, right. So, that also low-grade fuel oil. Low grade fuel oil itself is available only at one site and that also at high cost. So, then it is better to use coal rather than using the fuel oil and then it has been found. In place of fuel oil if you use coal there is a 20 percent saving in the cost of sulfur production. So, obviously, it is better to use coal and then some research is going on, I hope hopefully it must be available now.

Gaseous reaction in the smelting furnace: Complete combustion of fuel without excess air is desirable to avoid H 2 S to SO 2 ratio because if this ratio is not maintained properly what happen? The reaction at hot stage and then cold stage whatever the degree of reaction conversion to take place that may not take place. This can be shifted with only minor changes in the oxygen and then fuel ratio.

Smelter feed system requires close instrumental control because of the specified settling velocity of the 200 mesh size etcetera those things.

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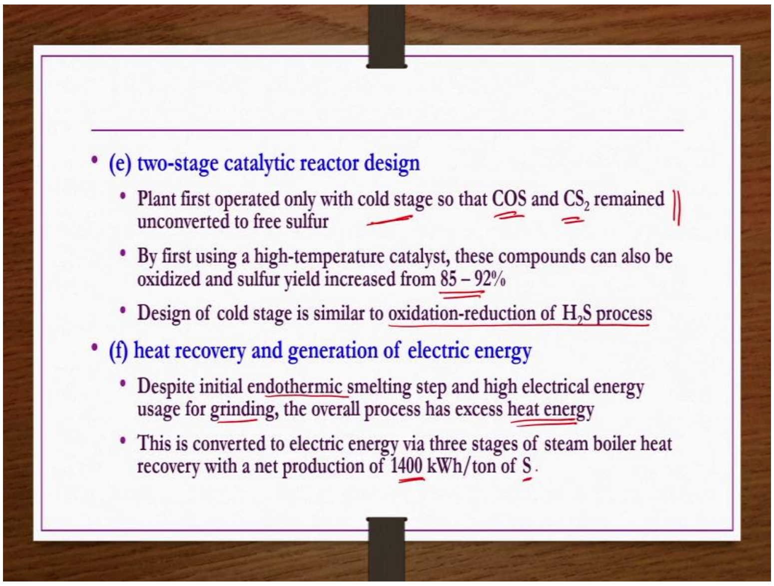

- (e) two-stage catalytic reactor design
  - Plant first operated only with cold stage so that COS and CS_2 remained unconverted to free sulfur
  - By first using a high-temperature catalyst, these compounds can also be oxidized and sulfur yield increased from 85 – 92%
  - Design of cold stage is similar to oxidation-reduction of H_2S process
- (f) heat recovery and generation of electric energy
  - Despite initial endothermic smelting step and high electrical energy usage for grinding, the overall process has excess heat energy
  - This is converted to electric energy via three stages of steam boiler heat recovery with a net production of 1400 kWh/ton of S.

Then two-stage catalytic reactor is designed. Actually initially single stage catalytic reactor was designed where it was assumed that COS and then CS 2 will remain unconverted to free sulfur. But, however, later on high temperature catalysts utilization found that this can also be oxidized and then sulfur yield would be increasing to 85 to 92 percent. So, otherwise initial plants whatever having they were having only cold stage operations using aluminum oxide catalyst, ok.

Later on this high temperature catalytic converter has been found because of which conversion or the yield of sulfur has increased up to 92 percent. Then design of cold stage is similar to the so called oxidation reduction of H 2 S process that we have discussed in the previous lecture.

Heat recovery and generation of electric energy, we have seen that you know 1400 kilowatt hour of net electricity is generated in this one. So, that is very much essential to pay attention to collection of steam and then sending to the turbo generators. Despite initial endothermic smelting step and high electric energy usage for grinding because grinding we understand operating grinding equipment consumes lot of power rather than you know.

Let us say if you give 100 kilowatt hour of power for grinding operation so that ore is reduced to 200 mesh size. Out of that 100 kilowatt hour approximately 70-80 or even more kilowatt hours of power is utilized for the operation of the grinding equipment itself. So, these grinding equipments are very inefficients in terms of the power requirements, alright.

So, you know lot of electrical energy is utilized for grinding as well. Despite of that one overall process has excess of heat energy and that must be properly collected for the electricity production. This is converted to electric energy via three stages of steam boiler heat recovery with a net production of 1400 kilowatt hour per ton of elemental sulfur produced.

So, this is all about the sulfur production. In this lecture we have seen one process, in the previous lecture we have seen two other processes.

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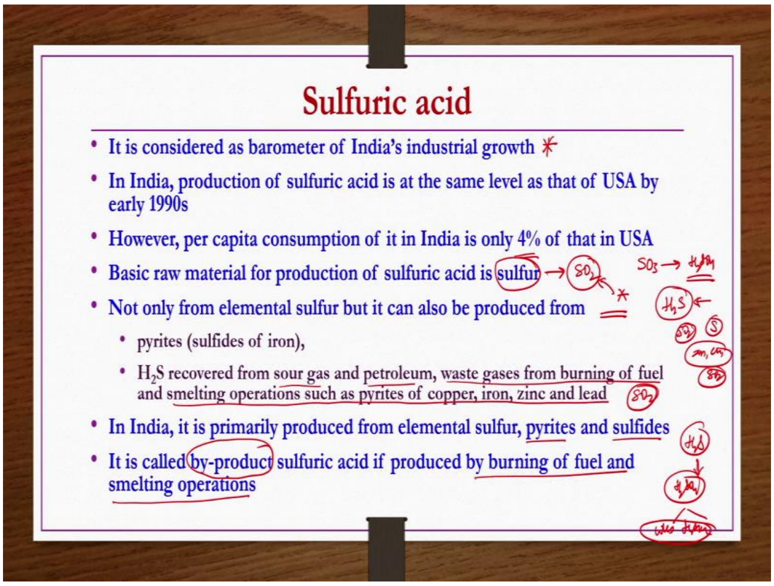

Sulfuric acid

- It is considered as barometer of India's industrial growth *
- In India, production of sulfuric acid is at the same level as that of USA by early 1990s
- However, per capita consumption of it in India is only 4% of that in USA
- Basic raw material for production of sulfuric acid is sulfur → SO_2
- Not only from elemental sulfur but it can also be produced from
  - pyrites (sulfides of iron),
  - H_2S recovered from sour gas and petroleum, waste gases from burning of fuel and smelting operations such as pyrites of copper, iron, zinc and lead
- In India, it is primarily produced from elemental sulfur, pyrites and sulfides
- It is called by-product sulfuric acid if produced by burning of fuel and smelting operations

Now, what we are going to see? We are going to see production of sulfuric acid. Before going into the production details of sulfuric acid, we see a few basics utilization, consumption pattern, different grades of sulfuric acid etcetera. In general, sulfuric acid is considered as barometer of India's industrial growth initially and then by early 1990s India's production of sulfuric acid is almost on par with the what USA was producing.

However, per capita consumption of it in India was only 4 percent compared to that of USA. Basic raw material for production of sulfuric acid is sulfur. This sulfur would be converted to the sulfur dioxide and then sulfur dioxide would be further converted to the sulfur trioxide and then from the sulfur trioxide you get H 2 SO 4.

Not only from elemental sulfur, but it can also be produced from different other sources because this sulfur is ultimately being converted to the SO 2. What if this SO 2 itself we are getting from other sources? Like previous just now we have seen elemental sulfur production from iron pyrites, there also we produced SO 2 that can be utilized for H 2 SO 4 production, right.

And, in previous lecture we have seen elemental sulfur from H 2 S. H 2 S is impurity in many of the fuel gases etcetera. Petroleum refinery gases etcetera right. In those production processes of fuel gases or in refinery gases whatever H 2 S is there as impurity that can be dissolved in solutions like ethanol amine and then the dilute solution you further heat it at high temperature to liberate pure H 2 S.

This H 2 S can be oxidized and then reduced in order to get the sulfur elemental sulfur. This we have seen in the previous lecture. In this process also we have seen SO 2 is being produced. So, why cannot we utilize this one? So, like in the just previous slide we have seen elemental sulfur from iron pyrites there smelting has been done.

Similar smelting of Zn copper etcetera, zinc copper etcetera may also be taking place and then there also this SO 2 is being produced. So, we can use that SO 2 also for production of H 2 SO 4. Like that there are different sources are there for the production of H 2 SO 4, those we are going to see now here.

One is the pyrites or sulfides of iron that we have just seen and then H 2 S recovered from sour gas and petroleum or waste gases from burning of fuel and then smelting operations such as pyrites of copper, iron, zinc and lead. In India, it is primarily produced from elemental sulfur, pyrites and then sulfides only. If it is produced by burning of fuel and then smelting operations then this sulfuric acid is known as the by-product sulfuric acid.

In fact, in one of the previous lecture where H 2 S is oxidized and reduced to get the elements of sulfur in that process where we have seen you know one of the plant is producing so much of large amount of H 2 SO 4, they constructed two sites for H 2 S production that is what we have seen. That much of H 2 SO 4 is in general produced as a co-product or byproduct in some processes.

So, such H 2 SO 4 directly you are getting that is known as the byproduct sulfuric acid which would be at moderately high concentration not very high concentration may be 60 percent, 65 percent H 2 SO 4 like that.

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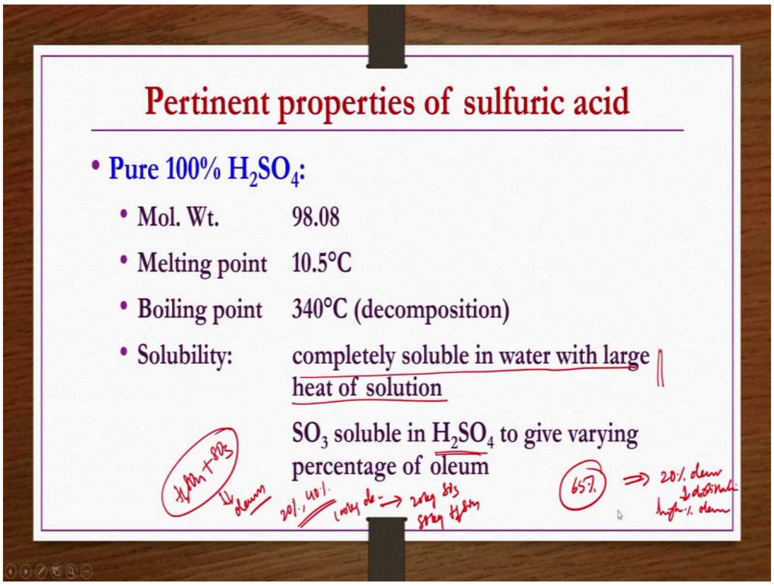

Pertinent properties of sulfuric acid

- Pure 100% H_2SO_4:
  - Mol. Wt. 98.08
  - Melting point 10.5°C
  - Boiling point 340°C (decomposition)
  - Solubility: completely soluble in water with large heat of solution

    SO_3 soluble in H_2SO_4 to give varying percentage of oleum

Pertinent properties of sulfuric acid if you see different grades or different degrees or different concentration of H 2 SO 4 are available in the market for different applications, right. So, this properties what we do? We see for pure 100 percent H 2 SO 4 first molecular weight 98.08, melting point 10.5 degree centigrade, boiling point or decomposition temperature is 340 degree centigrade.

Solubility – completely soluble in water, but with large heat of solution evolution. Lot of heat is being evaluated while H 2 SO 4 is dissolved in water. So, that is the reason when you make dilute H 2 SO 4 solution you take water and then drop by a dripper, drop by drop you add H 2 SO 4 to the water and then dilute it because lot of heat is evolved. You cannot add water to the H 2 SO 4 to make it dilute. Such large amount of heat of solution is liberated when you dilute the H 2 SO 4.

Other thing that SO 3 soluble in H 2 SO 4 to give varying percentage of volume. Actually, if you mix or dissolve SO 3 in H 2 SO 4 whatever the product is coming that is called as oleum and then different degrees or grades of oleum are available like 20 percent oleum, 40 percent oleum etcetera. 20 percent oleum in the sense if you have 100 kg of oleum out of which you will be having 20 kg of SO 3 and then 80 kg of H 2 SO 4, ok. So, like that 40 percent whatever they require percentage oleum you can prepare.

If you wanted to produce very high percent of oleum like 63, 65 percent something like that what you do? You take this 20 percent oleum and do the distillation to get high percentage oleum that is more economically better rather than producing by dissolving SO 3 in H 2 SO 4.

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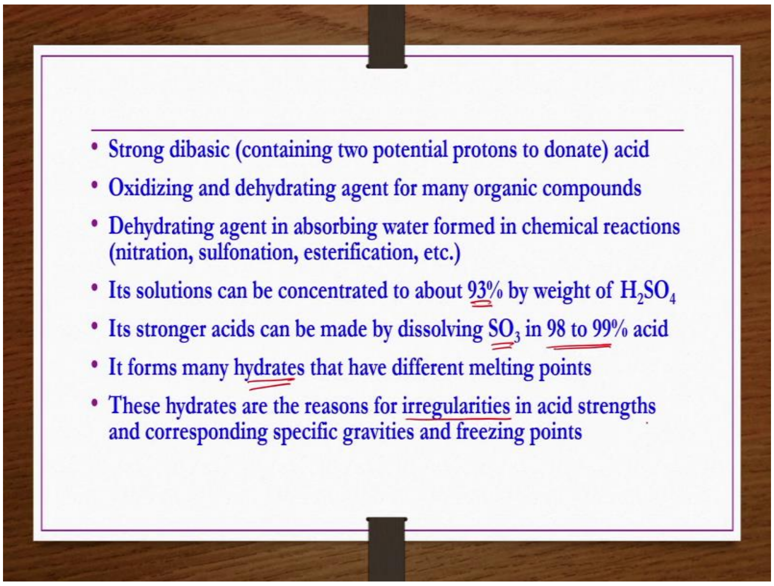

- Strong dibasic (containing two potential protons to donate) acid
- Oxidizing and dehydrating agent for many organic compounds
- Dehydrating agent in absorbing water formed in chemical reactions (nitration, sulfonation, esterification, etc.)
- Its solutions can be concentrated to about 93% by weight of H_2SO_4
- Its stronger acids can be made by dissolving SO_3 in 98 to 99% acid
- It forms many hydrates that have different melting points
- These hydrates are the reasons for irregularities in acid strengths and corresponding specific gravities and freezing points

It is strong dibasic acid which is containing two potential protons to donate and then it is also a very good oxidizing and dehydrating agent for many organic components. Not only many organic components, but also many inorganic chemical reactions like nitration, sulfation etcetera; some organic reaction like esterific reactions etcetera when takes place water vapour is produced and in that water vapour has to be separated out.

So, then if you wanted to absorb that water formed in such kind of reactions, then also this dehydrating agent H 2 SO 4 can be utilized. Its solution can be concentrated to about 93 percent by weight of H 2 SO 4. Its stronger acids can be made by dissolving SO 3 in 98 to 99 percent acid, sulfuric acid.

It forms many hydrates that have different melting points. This hydrates that you know we have 63 percent H 2 SO 4, 90 percent H 2 SO 4, 98 percent H 2 SO 4; when you dissolve in water and then make 100 percent mono hydrate H 2 SO 4 then there you know melting points are different – that is because of the these hydrates. These hydrates are the reason for irregularities in acid strength and corresponding specific gravities and freezing points in general.

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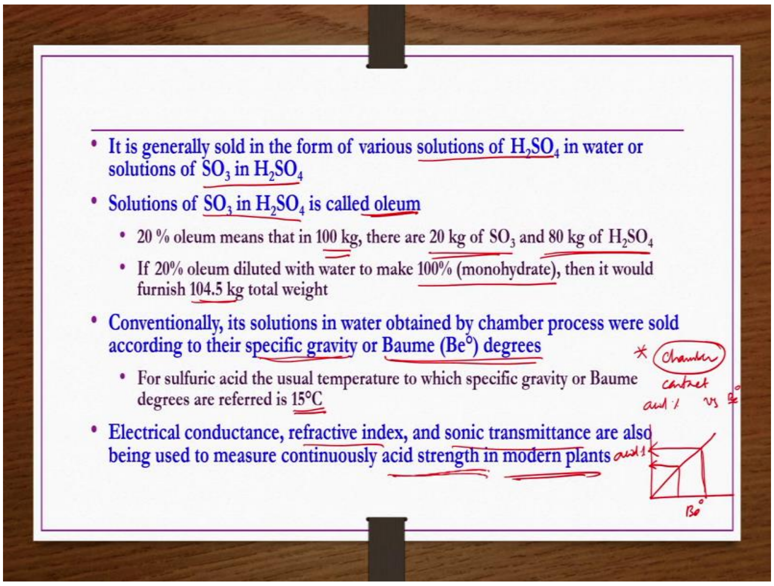

- It is generally sold in the form of various solutions of H_2SO_4 in water or solutions of SO_3 in H_2SO_4
- Solutions of SO_3 in H_2SO_4 is called oleum
  - 20 % oleum means that in 100 kg, there are 20 kg of SO_3 and 80 kg of H_2SO_4
  - If 20% oleum diluted with water to make 100% (monohydrate), then it would furnish 104.5 kg total weight
- Conventionally, its solutions in water obtained by chamber process were sold according to their specific gravity or Baume (Be°) degrees
  - For sulfuric acid the usual temperature to which specific gravity or Baume degrees are referred is 15°C
- Electrical conductance, refractive index, and sonic transmittance are also being used to measure continuously acid strength in modern plants

It is generally sold in the form of various solutions of sulfuric acid in water or solutions of SO 3 in H 2 SO 4. Solution of SO 3 in H 2 SO 4 is called oleum. 20 percent oleum means in 100 kg, you have 20 kg of SO 3 and then 80 kg of H 2 SO 4. If you dilute it with water to make 100 percent monohydrate sulfuric acid, then it would furnish 104 kgs of total weight.

Conventionally, its solutions in water obtained by chamber process; actually for the production of H 2 SO 4 two main processes are there – chamber process and then contact process. Chamber process is one of the oldest process right or conventional process. In production of H 2 SO 4 by using this chamber process, the percentage of acid has to be monitored continuously and then you cannot do the titration etcetera you know to find out the strength of acid periodically in the plant.

So, then for that reason, you know specific gravity of the acid is periodically measured and then you know accordingly acid strength is defined. The specific gravity or Baume degrees are often utilized or used as a kind of reference to measure the degree of or the strength of the acid, ok. How it is done? You know, initially you take different acids prepared and then you make a acid concentration versus Baume degree and then you make a chart, right.

So, for a given Baume degree, what is the corresponding acid strength you can easily find out? This is how it is measured in the plant without any interruption or stopping the production. For sulfuric acid, the usual temperature to be specific gravity or Baume degrees are referred is 15 degree centigrade. Some people measure it at 15 degree centigrade, some people also measure it at 18 degree centigrades.

But however, modern plants, electrical conductance, refractive index and sonic transmittance are also being used to measure continuously the acid strength how much it is, ok.

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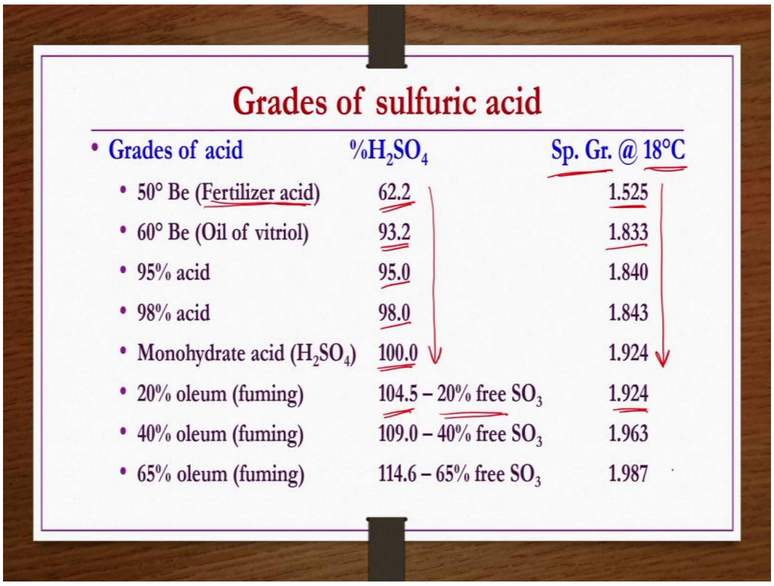

Grades of sulfuric acid

Grades of acid	$\%H_2SO_4$	Sp. Gr. @ 18°C
50° Be (Fertilizer acid)	62.2	1.525
60° Be (Oil of vitriol)	93.2	1.833
95% acid	95.0	1.840
98% acid	98.0	1.843
Monohydrate acid (H_2SO_4)	100.0	1.924
20% oleum (fuming)	104.5 – 20% free SO_3	1.924
40% oleum (fuming)	109.0 – 40% free SO_3	1.963
65% oleum (fuming)	114.6 – 65% free SO_3	1.987

Now, grades of sulfuric acid, if you see each grade of acid having certain percent of H 2 SO 4 and then what is corresponding specific gravity at 18 degree centigrade that we are having now. Let us say if you have 50 Baume degrees sulfuric acid, then that is also known as the fertilizer acid which is utilized for this fertilizer production. It is having 62.2 percent of sulfuric acid specific gravity is 1.525.

60 Baume degree sulfuric acid whatever is there that is known as the oil of withdrawal which is having 93.2 percent of H 2 SO 4 and then specific gravity 1.833. Like that 95 percent acid; that means, H 2 SO 4 is 95 percent and then 98 percent acid means it is having 98 percent H 2 SO 4 and then monohydrate acid H 2 SO 4 means 100 percent H 2 SO 4. And, then as you can see as this degrees increasing or the concentration or the acid strength is increasing, this specific gravity is increasing at a fixed temperature, alright.

If you have 20 percent oleum fuming then; that means, it is having 20 percent free SO 3 in that one and then it is making overall 104.5 kgs specific gravity is 1.924 like that 40 percent and then 65 percent oleum etcetera also the properties provided here.

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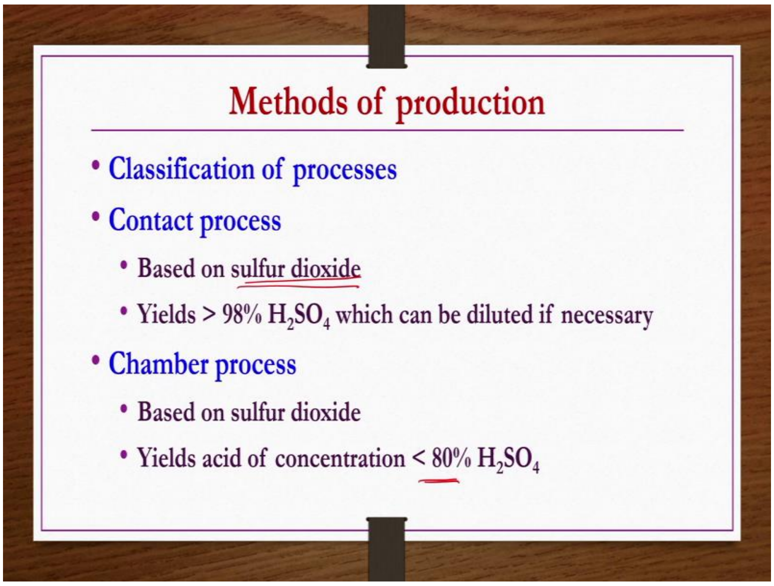

Methods of production

- Classification of processes
- Contact process
  - Based on sulfur dioxide
  - Yields > 98% H_2SO_4 which can be diluted if necessary
- Chamber process
  - Based on sulfur dioxide
  - Yields acid of concentration < 80% H_2SO_4

Now, we see methods of production of sulfuric acid. So, classification of methods if you see there are two methods. One is the contact process, another one is the chamber process. Chamber process is the old process, contact process is newer process or almost all the modern plants are based on the contact process methodology, right.

This contact process is based on SO 2 sulfur dioxide that is feed material is not elemental sulfur, but sulfur dioxide directly you are using as a feed and then it produce or it yields acid of strength up to 98 percent or even more H 2 SO 4 such high yields are produced in this process. Chamber process it is also based on the sulfur dioxide. However, it yields acid of concentration less than 80 percent H 2 SO 4. Ok.

In the next lecture, we will be discussing details of a contact processes for the production of sulfuric acid.

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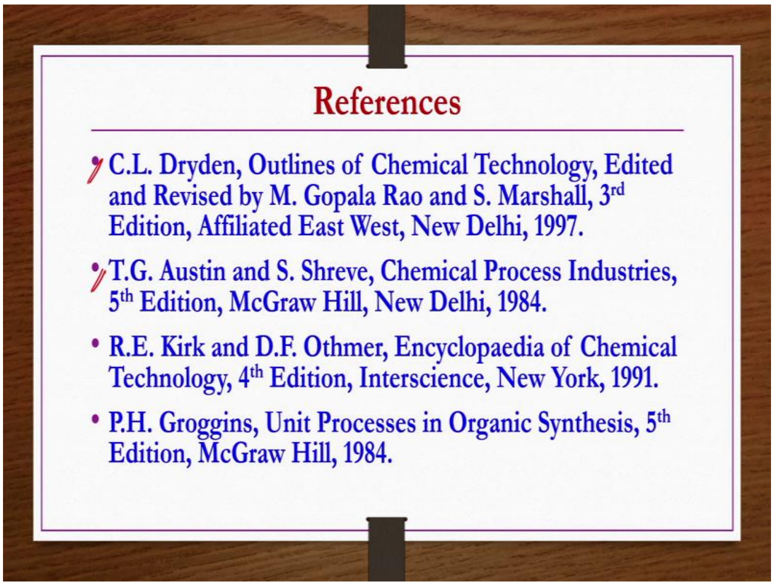

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References for today's lecture are provided here. However, most of the details can be found from these two reference books that is Outlines of Chemical Technology by Dryden and Chemical Process Industries by Austin and Shreve.

Thank you.