Inorganic Chemical Technology
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Lecture - 13
Sulfuric Acid

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is 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 couple of lectures. In the previous couple of lectures, we started with discussion on a comparison between inorganic chemical industry and organic chemical industry.

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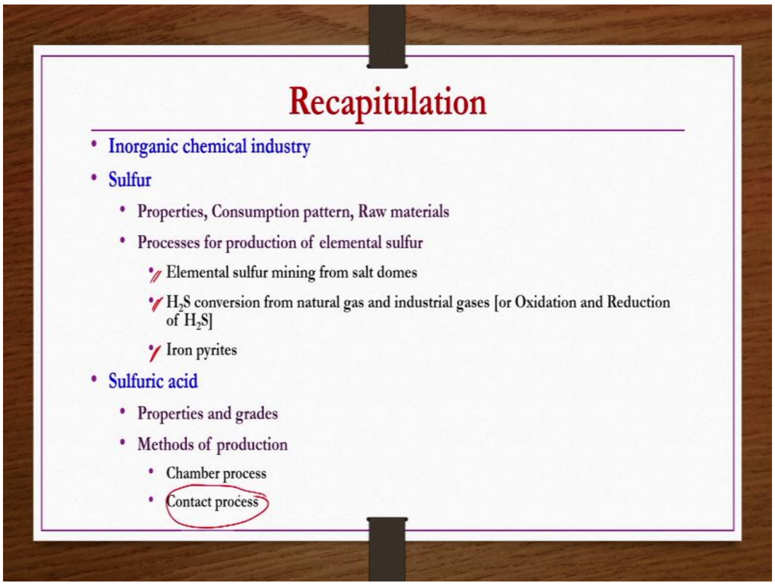

Recapitulation

- 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
- Sulfuric acid
  - Properties and grades
  - Methods of production
    - Chamber process
    - Contact process

Then, we started our discussions on sulfur with its properties, consumption pattern, raw materials followed by processes for production of elemental sulphur, where we have seen three different types of processes are available for production of elemental sulfur. The first one is elemental sulfur mining from salt domes. The second one is H 2 S or hydrogen sulfide conversion from natural gas and industrial gas or oxidation and reduction of hydrogen sulfide. And then iron pyrites.

So, all these three processes we have discussed with the possible raw materials, chemical reactions if any, and then bases, quantitative requirements etcetera with a proper flow chart, with a proper flow sheet and process description followed by major engineering problems if any. Those things we have already seen.

Then, we started discussing about sulfuric acid; we started with its properties and grades. Then, we started discussing types of methods of production, how many types of methods available for the production of sulfuric acid. We have seen conventional older chamber process and then modern contact process. These two types of processes are available.

In today's lecture, we are going to discuss production of sulfuric acid using contact processes, right.

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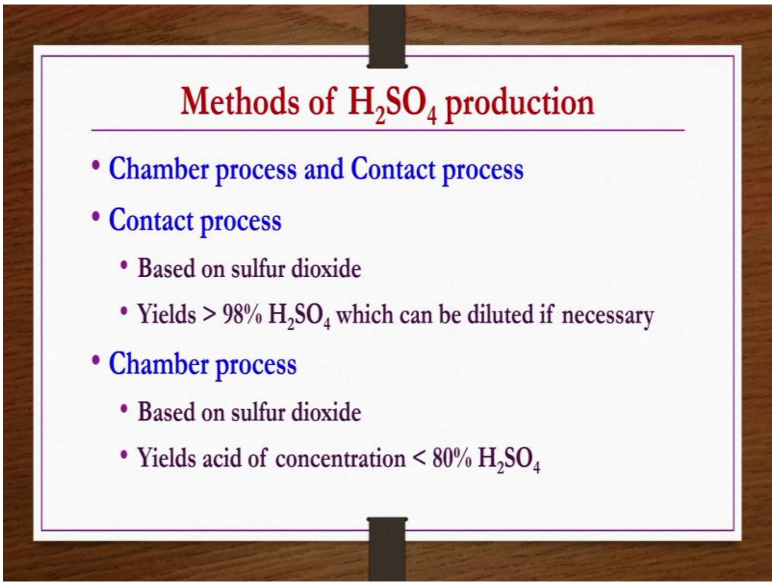

Methods of H_2SO_4 production

- Chamber process and Contact process
- 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

So, methods of sulfuric acid production, chamber process and contact process are two very famous processes. Contact process is based on sulfur dioxide. It yields acid of concentration more than 98 percent, if required which can be diluted. Whereas, the chamber process is also based on sulfur dioxide, but it yields acid of concentration less than 80 percent H 2 SO 4, ok.

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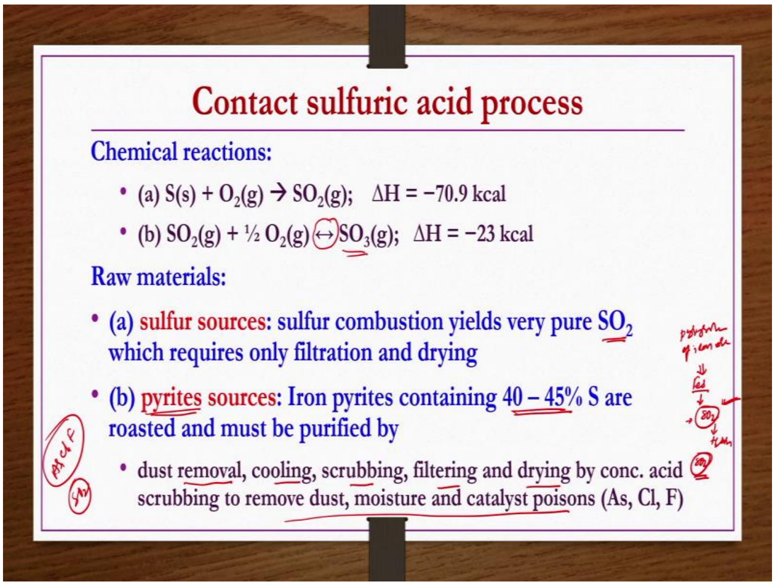

Contact sulfuric acid process

Chemical reactions:

- (a) $S(s) + O_2(g) \rightarrow SO_2(g)$; $\Delta H = -70.9$ kcal
- (b) $SO_2(g) + ½ O_2(g) \leftrightarrow SO_3(g)$; $\Delta H = -23$ kcal

Raw materials:

- (a) sulfur sources: sulfur combustion yields very pure SO_2 which requires only filtration and drying
- (b) pyrites sources: Iron pyrites containing 40 – 45% S are roasted and must be purified by
  - dust removal, cooling, scrubbing, filtering and drying by conc. acid scrubbing to remove dust, moisture and catalyst poisons (As, Cl, F)

As Cl F

FeS

SO_2

SO_3

So, now we see details of contact sulfuric acid process. Chemical reactions, elemental sulfur whatever is there that will be oxidized to give sulfur dioxide. This sulfur dioxide will be further oxidized to give sulfur trioxide, this sulfur trioxide would be dissolved in water to get the sulfuric acid.

This reaction we can see is a reversible reaction. So, wherever there are reversible reactions, then kinetics and thermodynamic parameters play vital role as the engineering problems, engineering issues so, one should be careful about the such processes.

Then, raw materials, raw materials, natural sulfur, elemental sulfur whatever if it is available that can be used. So, sulfur combustion yields usually very pure, sulfur dioxide, which requires only filtration and drying. However, not many countries are having sulfur resources or you know elemental sulfur can be mined, such kind of resources are not there in many countries including in India. So, what we do? We depend on sulfur by other different types of processes, available processes.

Like in the previous lecture, what we have seen? We have seen pyrites of iron ore or iron pyrites. Here in this process, what we have seen? When thermal dissociation of iron pyrites expressed in pyrrhotite or iron sulphide forms in a molten liquid form and then that can be granulated. And then, this if you do the roasting in fluidized bed reactors then you can get a sulfur dioxide. And then, this sulfur dioxide you can purify to get H 2 SO 4 after oxidizing followed by you know absorption in water, ok.

So, this is a source. Like that, there are smelting process of non-ferrous metals also like zinc lead etcetera. In such kind of processes also, sulfur sources may be there and sulfur sources will be there, and then because of those sulfur sources in ores then sulfur dioxide would form there also.

So, then that can be that can also be utilized, similar like you know roasting of iron pyrites, pyrrhotite. Similar like you know roasting of iron pyrrhotite processes, ok. Now, but whatever sulfur dioxide you get from these sources, they will be having impurities usually 40 to 45 percent sulfur only would be there and then that must be roasted and then purified.

So, so that to remove dust and then followed by cooling, scrubbing, filtering, drying by concentrated acid to remove dust, moisture and catalyst poisons etcetera. All these processes has to be done before taking this sulfur dioxide to contact process as a feed to produce the sulfur trioxide followed by sulfuric acid, right.

So, since we are getting from ores, the sulfur source for the sulfur is some kind of ores. Here now iron pyrites. So, then in ores so many minerals and then inorganic impurities may be there. So, like silica, arsenic, chlorides etcetera may be there. So, if arsenic or chlorides etcetera are there in sulfur sources, then they will be deactivating the catalyst as we have seen in the previous lecture as well.

So, all those thing should be removed either from the sulfur or from the sulfur dioxide gases, ok. So, pyrites would also be a kind of source for the sulfur dioxide which can be further oxidized and then produced sulfuric acid.

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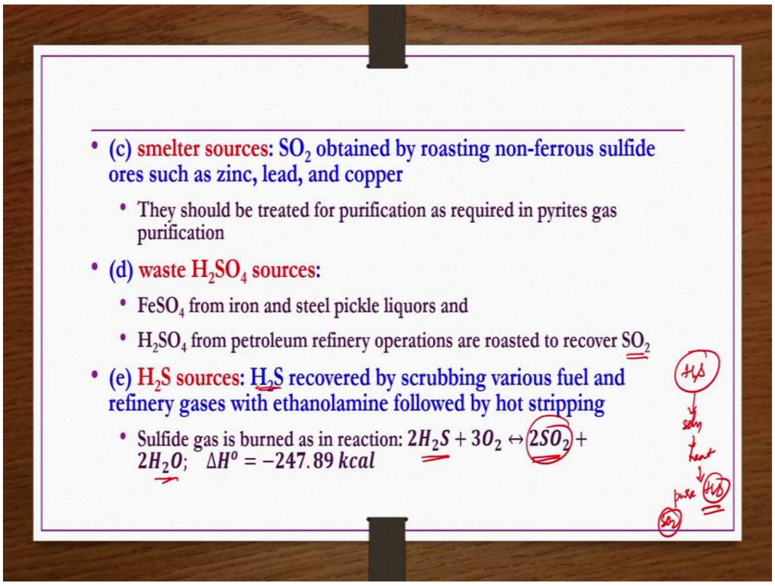

- (c) smelter sources: SO_2 obtained by roasting non-ferrous sulfide ores such as zinc, lead, and copper
  - They should be treated for purification as required in pyrites gas purification
- (d) waste H_2SO_4 sources:
  - $FeSO_4$ from iron and steel pickle liquors and
  - H_2SO_4 from petroleum refinery operations are roasted to recover SO_2
- (e) H_2S sources: H_2S recovered by scrubbing various fuel and refinery gases with ethanolamine followed by hot stripping
  - Sulfide gas is burned as in reaction: $2H_2S + 3O_2 \leftrightarrow \boxed{2SO_2} + 2H_2O$; $\Delta H^o = -247.89\ kcal$

H_2S → soln → heat → H_2S

pure SO_2

Likewise, smelter sources SO 2 obtained by roasting non-ferrous sulfide ores also such as zinc, lead and copper. And then, here also whatever the sulfur dioxide you get that will not be pure enough. So, then, proper purification should be done as has been done in the case of a iron pyrites ok.

Waste sulfuric acid sources, actually sulfuric acid is also used as a catalyst for many reactions. So, when it is used as a catalyst you know only a fraction of it would be used and then it would be diluted, slightly diluted or slightly contaminated and would be treated as a waste sulfuric acid.

But even if it is slightly diluted, the concentration would be above the 70 percent in general, for majority of the waste sulfuric acid. So, such concentrated sulfuric acid you cannot throw because of the pollution concerns as well. And then rather discarding it you know or even let us say if you wanted to do the neutralization before discarding or different applications that would be very expensive.

So, then better what you do, you can do the purification of such waste acids and then reuse for the applications wherever this sulfuric acid is required because people have found purification of such waste sulfuric acid is going to be much cheaper than producing the virgin sulfuric acid from the pure sulfur sources.

Some of the waste H 2 SO 4 sources are listed below. Like iron sulfate from iron and steel pickle liquors, and then H 2 SO 4 from petroleum refinery operations are usually roasted to recover SO 2, and then from SO 2 you get SO 3 and then sulfuric acid. Then, H 2 S sources also, as we have already seen you know in production of fuel gases as well as in many refinery gases, this H 2 S is present as a impurity.

And then, it has to be removed for the proper applications of you know those gases, mixtures as fuel gases or refinery gases whatever may be the application. So, how do you remove? We have seen like ethanolamine kind of solutions may be used to absorb this H 2 S and then that dilute solution would be heated or hot stripping would be done to liberate pure H 2 S.

And then, this pure H 2 S can be taken and then oxidized and followed by reduction to get sulfur, elemental sulfur or sulfur dioxide and then that can be again used as a kind of source for the production of sulfuric acid. For example, H 2 S oxidation if you do you get sulfur dioxide along with the water, ok.

So, there is a source of sulfur here as well. So, like that even though if you do not have elemental sulfur resources from the mining, you have either sulfur sources or sulfur dioxide sources from different possible ways like you know pyrite ores, smelting process waste, H 2 SO 4, H 2 S sources etcetera .

Catalyst, previously platinum and iron kind of catalyst were used, but they were having different problems like poisoning or rapid deactivation because of the heat, such kind of problems were there.

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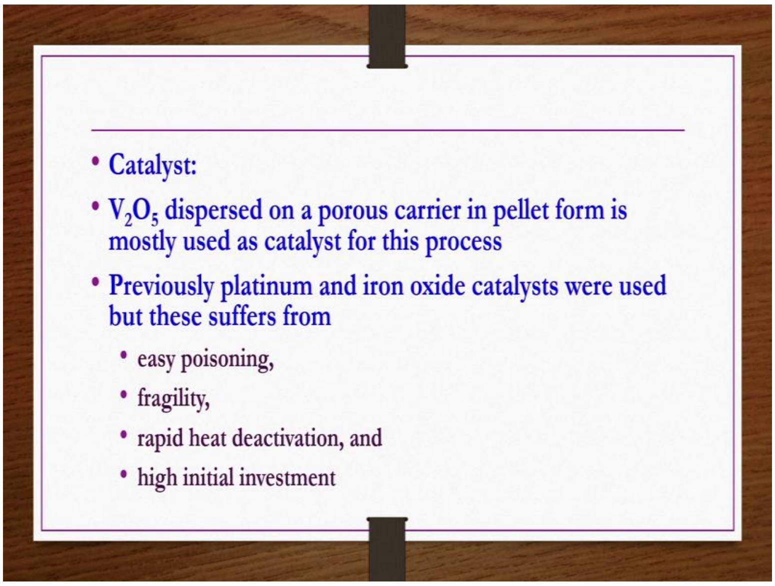

- Catalyst:
- V_2O_5 dispersed on a porous carrier in pellet form is mostly used as catalyst for this process
- Previously platinum and iron oxide catalysts were used but these suffers from
  - easy poisoning,
  - fragility,
  - rapid heat deactivation, and
  - high initial investment

Then, people found V 2 O 5, vanadium pentoxide as a very best catalyst for the production of sulfuric acid. This catalyst is actually used for the conversion of SO 2 to SO 3, ok. So, V 2 O 5 dispersed on a porous carrier in pellet form is mostly used as catalyst for this purpose.

Older chamber process etcetera, used to have platinum and iron oxide catalyst as well, but they suffer from different problems like poisoning, fragility, rapid heat deactivation, and then high initial investment because platinum etcetera these kind of metals are expensive, ok.

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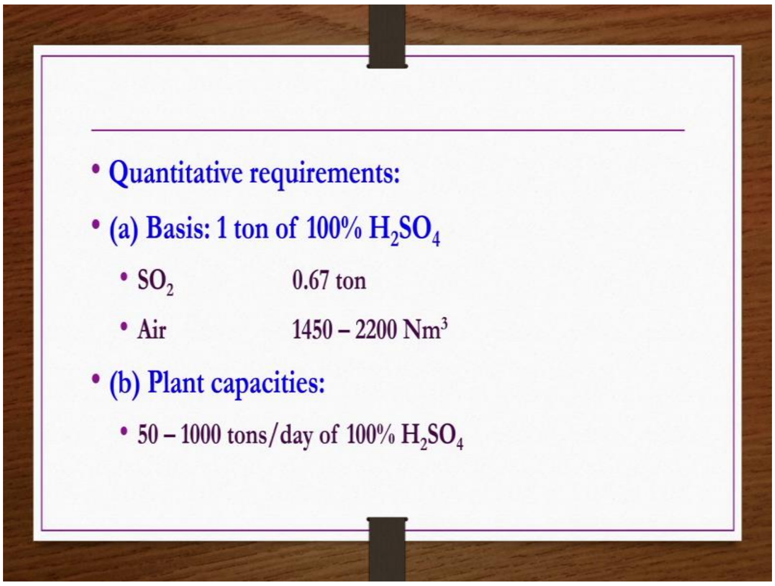

- Quantitative requirements:
- (a) Basis: 1 ton of 100% H_2SO_4
  - SO_2 0.67 ton
  - Air 1450 – 2200 Nm^3
- (b) Plant capacities:
  - 50 – 1000 tons/day of 100% H_2SO_4

Quantitative requirements if you see, if you wanted to produce 1 ton of 100 percent sulfuric acid, then you need 0.67 tons of sulfur dioxide and air 1450 to 2200 normal cubic meters of air is required. Plant capacities, vary between 50 to 1000 tons per day of 100 percent pure H 2 SO 4 sulfuric acid.

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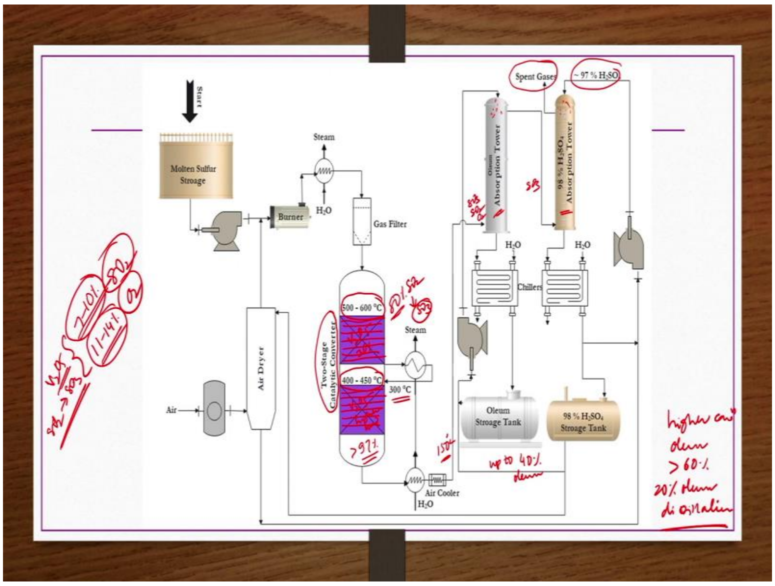

So, now we see contact process by a flowchart. So, whatever the gases, actually for the contact process SO 2 and then oxygen are the primary raw materials, ok. These are actually fed to a catalytic converter, right. These gases have to be dry enough, if they are not dried enough, so then what can be done these gases can be dried and mixed and then sent to catalytic converter, ok.

So, the percentage of mixture whatever the mixture of gas that you are going to feed to the reactor that should have 7 to 10 percent of SO 2 and then 11 to 14 percent of O 2. These are based on the many reasons are there, V 2 O 5 actually it is a slow catalyst. It is does not catalyze the reactions very rapidly. So, that is the reason you cannot have high concentrations of sulfur dioxide in the mixture.

The conversion of SO 2 to SO 3 should be as much high as possible. But however, in this process, in the single contact process what happened? The conversion is not much it is only 80 percent, right. Also, what happens? This gases, when they come out of the reactor lot of heat is liberating, actually during the absorption as well as before the absorption also that heat has to be recovered.

So, like that several reasons are there why should we go for you know only this much percentage of SO 2 and then O 2. We are going to see those details in the section of major engineering problems anyway. So, whatever the dried gases of SO 2 and then O 2 are there, they will be sent to a two stage catalytic converter, right. Two stages are there.

So, one stage is the high temperature stage, ok. So, which is packed with catalyst whatever the catalyst we have taken. Usually, 30 percent load is there as taken here. So, then when these gases comes here, by the time the catalytic bed is maintained at 50 to 600 degree centigrade. So, then, up to 80 percent of SO 2 is being converted to SO 3. Yield of SO 2 is only 80 percent. SO 2 to SO 3 conversion takes place partially, does not take completely.

So, then what we do? In order to increase the conversion of SO 2 to SO 3, these hot gases because the reaction is occurring approximately at between 500 to 600 degree centigrade. The gases coming out from here would be at high temperature up to 600 degree centigrade. These gases would be cooled to 300 degree centigrade and then sent to a low temperature catalytic converter stage here which is also having the same V 2 O 5 catalyst. But having higher load of catalyst would be there, ok.

So, but the reaction temperature is low temperature, around 400, 400 to 450 degree centigrade. Low high is with reference to each other, right. So, the range of temperature is in the topper section is higher compared to the lower section that is the reason it is called high temperature. Though, the 400 degree centigrade reaction temperature it is called as low temperature stage, because the temperature is lower compared to the previous you know top section, right.

So, here the conversion of SO 2 to SO 3 is more than 97 percent or up 97 to 98 percent by the completion of the second stage reaction ok. So, these gases would be again at high temperature, they will be cooled by water and air coolers to approximately 150 degree centigrades.

Then, these gases would be sent to a oleum absorption tower, where oleum droplets are sprayed from the top in order to absorb these SO 3 gases because these gases are having primarily now SO 3 unreacted SO 2 if I need and then unreacted oxygen anything. Those things only will be there.

Here, in oleum absorption tower, SO 3 will be absorbed because from the top oleum droplets are sprayed from here, from the top. And then, this rate of absorption is maintained such a way that acid concentration should not trace more than 1 percent of the acid concentration.

Let us say, if you wanted to produce 30 percent oleum only, right So, then you have to make the flow rates and then absorption conditions such a way that the output oleum whatever you are getting that should not be having more than 31 percent concentration ok. So, like that you have to operate the conditions, right.

In this process, if at all any SO 3 that is not absorbed along with the other impurities like SO 2 O 2, they would be sent to another absorption tower which is sulfuric acid absorption tower to which 97 percent H 2 SO 4 is sprayed from the top. And then, these gases are coming from the bottom.

So, here remaining whatever the SO 3 that is not being absorbed in the oleum absorption tower that would be absorbed here. And then, acid concentration increases to 98 percent like this. Whereas, the spent gases SO 2 O 2 and etcetera would be taken out ok. So, now here in this process you can get up to 40 percent oleum, right.

You can even get up to 60, 65 percent oleum also, but that is not economically feasible. If you wanted to have higher, if you wanted to have, if you wanted to have a higher concentration of oleum or greater than 60 percent or something like that it is better to take 20 percent oleum and do the distillation to increase its concentration.

That is a that is a more economically feasible process compared to the preparing the higher concentrated oleum by this process, ok.

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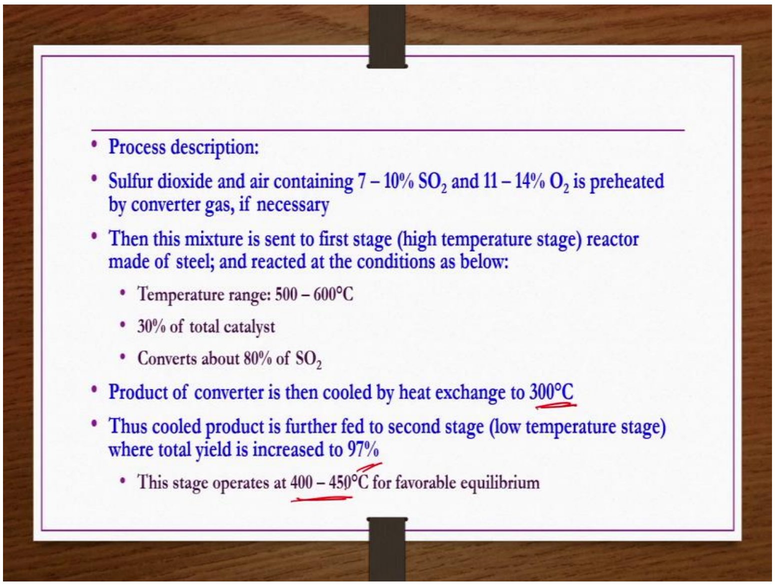

- Process description:
- Sulfur dioxide and air containing 7 – 10% SO_2 and 11 – 14% O_2 is preheated by converter gas, if necessary
- Then this mixture is sent to first stage (high temperature stage) reactor made of steel; and reacted at the conditions as below:
  - Temperature range: 500 – 600°C
  - 30% of total catalyst
  - Converts about 80% of SO_2
- Product of converter is then cooled by heat exchange to 300°C
- Thus cooled product is further fed to second stage (low temperature stage) where total yield is increased to 97%
  - This stage operates at 400 – 450°C for favorable equilibrium

So, this process whatever we have discussed the same thing is provided as a text here. Sulfur dioxide and air containing 7 to 10 percent SO 2 and 11 to 14 percent O 2 is preheated by converter gas if necessary. If necessary in the sense, if the gases are not dry enough then this process is required.

Then, this gas mixture is sent to first stage that is high temperature catalytic reactor stage. The reactor is made up of steel and reacted at the conditions as below 500 to 600 degree centigrades, 30 percent catalyst load, conversion of SO 2 takes place up to 80 percent.

Then, product of converter is then cooled by heat exchange to 300 degree centigrade. Thus, cooled product is further fed to second stage which is low temperature stage where total yield of SO 2 is increased to 97 percent. This stage operates approximately at 400 to 450 degree centigrade for favorable equilibrium.

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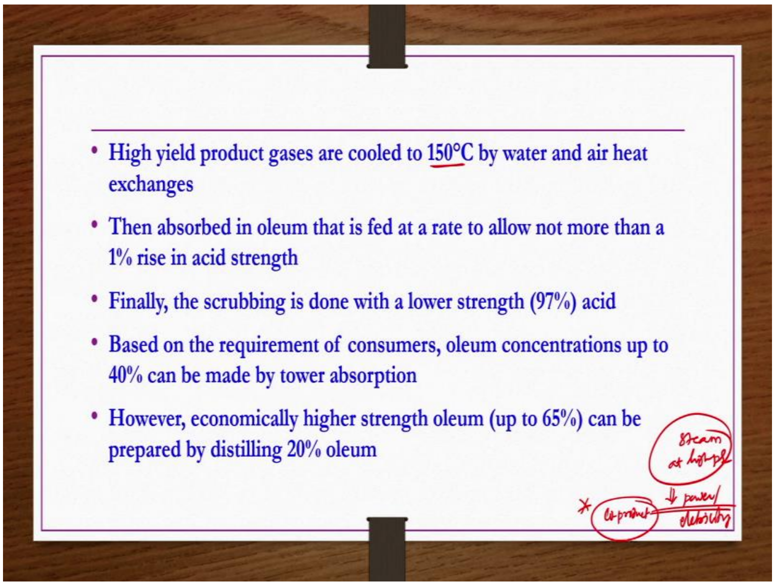

- High yield product gases are cooled to 150°C by water and air heat exchanges
- Then absorbed in oleum that is fed at a rate to allow not more than a 1% rise in acid strength
- Finally, the scrubbing is done with a lower strength (97%) acid
- Based on the requirement of consumers, oleum concentrations up to 40% can be made by tower absorption
- However, economically higher strength oleum (up to 65%) can be prepared by distilling 20% oleum

Steam at high p.
↓ power/ electricity
* co-product

High yield product gases whatever are there after second stage or cold stage. They are cooled to 150 degree centigrade by water and air heat exchanges. Then, absorbed in oleum that is fed at a rate to allow not more than a 1 percent rise in acid strength.

Finally, the scrubbing is done with a lower strength 97 percent sulfuric acid. Based on the requirement of consumers, oleum concentrations up to 40 percent can be made by tower absorption. However, economically higher strength oleum up to 65 percent can be prepared by distilling 20 percent oleum, right.

So, in this process absorption is taking place and this reactions are exothermic lot of heat is being evolved. So, when this heat exchange taking place, steam is generated at high pressures usually. So, this steam is sufficient enough to generate power or electricity. So, that means, in this process also electricity or power is a co-product.

You know elemental sulfur production from iron, pyrites whatever we have seen, there also a lot of steam is generated. So, electricity could electricity is produced there. Here also lot of steam is generated. So, that steam can be utilized for the internal heating requirement within the plant. After that also, sufficiently large amount of steam is remaining, so that can be utilized for production of electricity.

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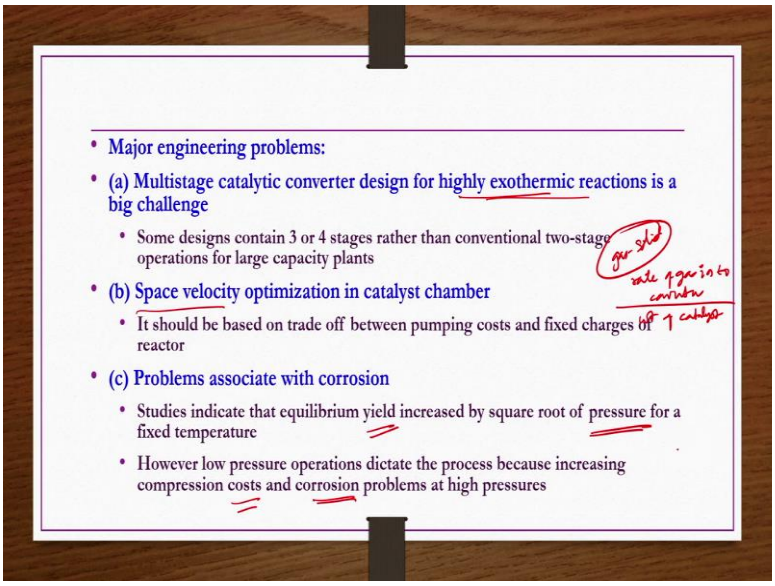

- Major engineering problems:
- (a) Multistage catalytic converter design for highly exothermic reactions is a big challenge
  - Some designs contain 3 or 4 stages rather than conventional two-stage operations for large capacity plants
- (b) Space velocity optimization in catalyst chamber
  - It should be based on trade off between pumping costs and fixed charges of reactor
- (c) Problems associate with corrosion
  - Studies indicate that equilibrium yield increased by square root of pressure for a fixed temperature
  - However low pressure operations dictate the process because increasing compression costs and corrosion problems at high pressures

gas solid

$\frac{\text{rate of gas in to convertor}}{\text{wt of catalyst}}$

Major engineering problems. First problem is the design of multi-stage converters. Here we have seen only two-stage converters, high temperature and low temperature converters only. But in general, some plants where the capacity is very large up to 1000 tons per day. In such cases, the plant may be having 3-4 stages as well.

So, designing such multi catalytic, such multi-stage catalytic converter is very difficult challenging task, especially when the reactions are highly exothermic ok. So, some designs contain even 3 or 4 stages rather than the conventional two-stage operations for large capacity plants. Then, space velocity optimization in catalyst chamber also.

Space velocity is nothing, but rate of gas in to converter or catalytic converter divided by the weight of catalyst. This is actually space velocity, right. It is having the time inverse units, right. This is a very important parameter in majority of the gas solid reactions, ok. Or reactions taking place on solid surface something like that, as in packed beds or fluidized beds etcetera.

So, then under such conditions space velocity has to be optimized. So, if you have the highest space velocity sometimes good, if you have lower space velocity sometimes, it is good depends on the operation. But it also you know adds cost, right. So, if you go for the highest space velocity then pumping cost etcetera, may be increasing.

So, there should be a trade-off between pumping cost and fixed charges of the reactor also. Based on that one this optimization has been, based on those criteria optimization of the space velocity has to be done. Then, problems associated with corrosion. Actually, in so many studies indicated that the yield of SO 3 increases by square root of pressure for a fixed temperature. Let us say if you are doing reaction at a fixed temperature of 500 degree centigrade. If you increase the pressure, the yield increases.

But however, when you increase the pressure what happens? The not only compression cost increases, you know are the units required for the such high pressure compression, they incur additional cost plus in addition to that one corrosion is also an issue ok. So, because of these two problems not because of these two problems though higher pressure is good for the higher yield usually they are not preferred, ok.

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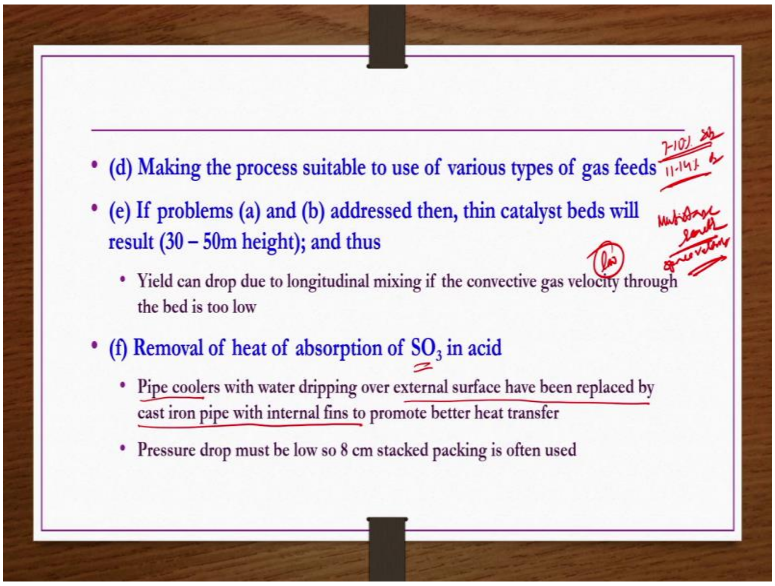

- (d) Making the process suitable to use of various types of gas feeds
- (e) If problems (a) and (b) addressed then, thin catalyst beds will result (30 – 50m height); and thus
  - Yield can drop due to longitudinal mixing if the convective gas velocity through the bed is too low
- (f) Removal of heat of absorption of SO_3 in acid
  - Pipe coolers with water dripping over external surface have been replaced by cast iron pipe with internal fins to promote better heat transfer
  - Pressure drop must be low so 8 cm stacked packing is often used

7-10% SO_2
11-14% O_2
Multistage
length
space velocity
low

Then, making the process suitable to use of various types of gas feeds. Now, gas feeds in this process what we have seen 7 to 10 percent of SO 2 and then 11 to 14 percent of O 2 only. Why not other percentages? Right. So, such kind of issues should be properly addressed.

Obviously, these again depends on the catalyst and then size of the reactor, and then what flow rate are you allowing these gases to the reactor, and then what is the rate of heat transfer when you cool the gases coming out from the first stage of the converter.

Then, what is the rate of heat transfer when they are entering to the second stage or cold stage.

Then, what is the rate of heat transfer when the gases are being cooled when after coming out from the second stage. All these parameter should be taken into the considerations, ok. So, let us say, if you address both the problems of a multi-stage reactors, catalytic reactors that is step a and then space velocity optimization is the point b. When you have these things, what happens? You supposed to go and then you will be having low space velocity.

When the space velocity is low and then multi stages are there. Especially, when multi-stages are there, then what happened? The catalytic bed whatever is there that will become very thin. When the catalytic bed becomes thin and then space velocity is very low, then what happen? A kind of back mixing takes place and then because of that back mixing you know yield may be dropping substantially ok.

So, again you cannot completely focus on points a and b. If you completely focus on point a and b, then such kind of problems reduction of problem may be there. So, all these problems you have to take and address such a way that yield is not affected. Then, removal of heat of absorption of SO 3 in acid when the absorption of SO 3 is taken place not only in the acid tower, sulfuric acid tower, but also in oleum tower, lot of heat is being liberated.

Lot of heat is being liberated. That you do the absorption then what you do you get lot of steam you get lot of steam and then that steam can be utilized for the electricity production. So, you have to have proper mechanism to recover it. So, then what has been done usually, pipe coolers with water dripping over external surface have been replaced by cast iron pipe with internal fins to promote better heat transfer.

And then pressure drop must be low, so that 8 centimeter stacked packing is often used. So, that is about a contact process for the production of sulfuric acid.

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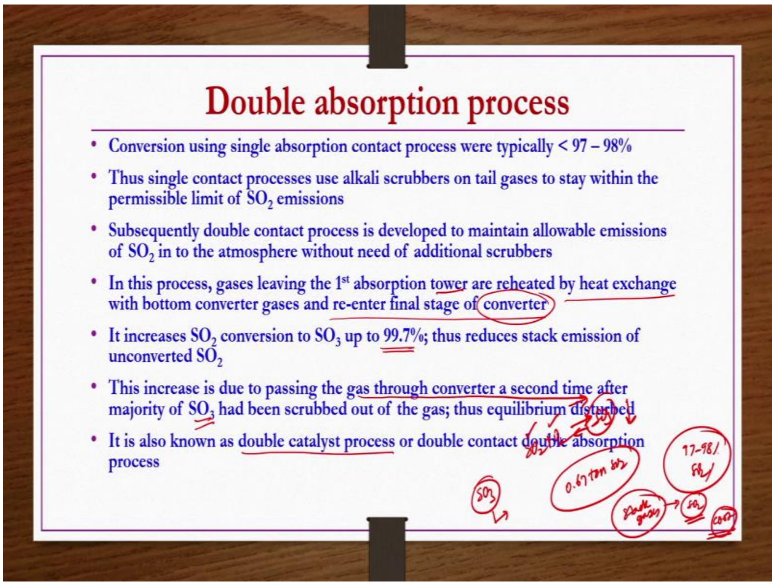

Double absorption process

- Conversion using single absorption contact process were typically < 97 – 98%
- Thus single contact processes use alkali scrubbers on tail gases to stay within the permissible limit of SO_2 emissions
- Subsequently double contact process is developed to maintain allowable emissions of SO_2 in to the atmosphere without need of additional scrubbers
- In this process, gases leaving the 1st absorption tower are reheated by heat exchange with bottom converter gases and re-enter final stage of converter
- It increases SO_2 conversion to SO_3 up to 99.7%; thus reduces stack emission of unconverted SO_2
- This increase is due to passing the gas through converter a second time after majority of SO_3 had been scrubbed out of the gas; thus equilibrium disturbed
- It is also known as double catalyst process or double contact double absorption process

But in this process what we have seen? Up to 97 or 98 percent of SO 2 conversion is only taking place, right. So, then what happens? Because of you know environmental concerns; you cannot leave such large amount of SO 2 in the environment. So, from the stack gases, what you have to do? You have to absorb this SO 2 in some solutions, alright. Alkalis are usually used.

So, then that add some cost, addition of the cost, right. So, since it is increasing the cost, you cannot leave SO 2 or exit. You cannot release this SO 2 because it is having high percent of SO 2, 3 percent is high percent actually. Unreacted SO 2, it is a high percent because the plants are producing you know so many tons, per 1 ton of sulfuric acid you need 0.67 tons of a you know SO 2.

Now, you take 3 percent of 0.67 tons of SO 2 that much is remaining, right That much is unreacted and this is we are taking 1 ton. Let us say if you have 100 tons, so then multiplied by 3, multiplied by 100. So, you can calculate how much SO 2 is there. That much SO 2 you cannot release, you cannot release into the atmosphere because of the pollution concern. So, you must absorb it or otherwise you have to go for the other alternative options.

So, in order to reduce the absorption cost because large this amount is very large. Though it looks like 3 percent or 2 percent or something like that, but when you take in terms of tons it is large quantity. So, such large quantity of SO 2 for if you wanted to do absorption, so then absorption cost increases drastically.

So, for that reason people, what have done? They try to look out for different options and then people come out with the double contact process, where whatever the unreacted SO 3 is there, SO 3 from the stack gases are the last section of sulfuric acid absorption tower. They will be taken to you know first converter again after you know passing through a heating section like that, right.

So, since SO 3 most of it is most of this SO 3 is absorbed, so then SO 3 content should be less. So, SO 2 plus O 2 giving rise to SO 3, if this content is gradually decreasing so then it is concentration is less whereas, the reactants SO 2 and O 2 concentrations are more. So, then positive or you know right hand side reactions will progress faster and then equilibrium conversion gradually increases because of this process.

Thus, double absorption process or double contact double absorption process has been developed. That is what we are going to see now.

Conversion using single absorption contact process were typically 97 to 98 percent. Thus, single contact processes use alkali scrubbers on tail gases to stay within the permissible limits of SO 2 emissions as per the pollution concerns. So, subsequently double contact process is developed to maintain allowable emissions of SO 2 into the atmosphere without need of additional scrubbers.

In this process gases, leaving the first absorption tower are reheated by heat exchange with bottom converter gases and re-enter the final stage converter ok. After the first tower of absorption you know what happens? Lot of SO 3, SO 2 and O 2 are not being absorbed. So, then they will be reheated by heat exchange with bottom converter gases and then re-enter the final stage of converter, right.

It increases SO 2 conversion to SO 3 up to 99.7 percent almost complete conversion. Thus, reduces stack emission of unconverted SO 2 into the atmosphere. This increase is due to passing the gas through converter a second time after majority of SO 3 had been scrubbed out of the gas thus equilibrium is disturbed. It is not because of the increased catalytic activity because of resending the gases for the second time to the converter.

It is also known as the double catalyst process or double contact double absorption process.

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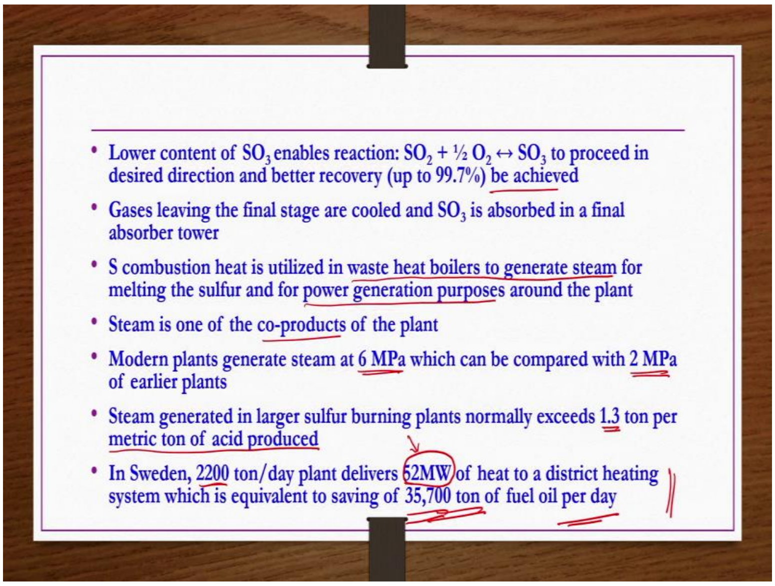

- Lower content of SO_3 enables reaction: $SO_2 + \frac{1}{2} O_2 \leftrightarrow SO_3$ to proceed in desired direction and better recovery (up to 99.7%) be achieved
- Gases leaving the final stage are cooled and SO_3 is absorbed in a final absorber tower
- S combustion heat is utilized in waste heat boilers to generate steam for melting the sulfur and for power generation purposes around the plant
- Steam is one of the co-products of the plant
- Modern plants generate steam at 6 MPa which can be compared with 2 MPa of earlier plants
- Steam generated in larger sulfur burning plants normally exceeds 1.3 ton per metric ton of acid produced
- In Sweden, 2200 ton/day plant delivers 52MW of heat to a district heating system which is equivalent to saving of 35,700 ton of fuel oil per day

So, lower content of SO 3 enables this reaction to move in a positive right-hand side direction to produce more SO 3, and then better recovery or better conversion of SO 2 can be achieved. Or almost complete conversion of SO 2 can be achieved. Gases leaving the final stage are cooled and SO 3 is absorbed in a final absorber tower. Further, sulfur combustion heat whatever is there it is utilized in waste heat boilers to generate steam for melting the sulfur and for power generation purposes around the plant, ok.

So, waste heat when you do this waste heat boilers to generate heat lot of steam is being generated, ok. So, steam is co-product of the plant. Modern plants generate up to 6 mega pascals of steam which can be compared with 2 mega pascals of steam, right. Steam generated in large sulfur burning plants normally exceeds 1.3 ton per metric ton of acid production which is quite high quantity.

In terms of numbers if you see, for example, in Sweden 2200 tons per day plant delivers 52 megawatts of heat to a district heating system which is equivalent to saving of 35,700 tons of fuel oil per day. Per day this much fuel oil you are consuming to get whatever the heating requirement, those heating requirement could be fulfilled with this 52 megawatts of heat that is being you know because of the steam that is being generated in a plant in Sweden, ok.

Such is the importance of the steam that is produced in the sulfuric acid production process as a co-product.

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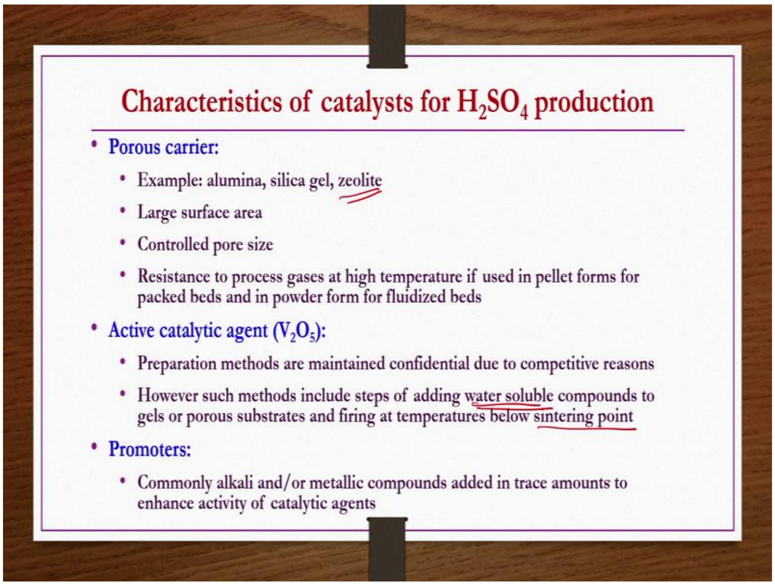

Characteristics of catalysts for H_2SO_4 production

- Porous carrier:
  - Example: alumina, silica gel, zeolite
  - Large surface area
  - Controlled pore size
  - Resistance to process gases at high temperature if used in pellet forms for packed beds and in powder form for fluidized beds
- Active catalytic agent (V_2O_5):
  - Preparation methods are maintained confidential due to competitive reasons
  - However such methods include steps of adding water soluble compounds to gels or porous substrates and firing at temperatures below sintering point
- Promoters:
  - Commonly alkali and/or metallic compounds added in trace amounts to enhance activity of catalytic agents

Now, we see characteristics of catalyst for sulfuric acid production. Porous carrier it should have a carrier which is sufficiently porous in nature. For example, alumina, silica, gel, zeolite etcetera. And then, large surface area should be there and then controlled pore size should be there. In zeolites, usually pore size is very much controlled.

Further, resistance to process gases, process gases are up to 700, 600 degree centigrade and as we have seen in the flow chart. At high temperature if we use if these carriers are used you know they should be thermally resistant enough. So, that is resistant to process gases at high temperature, if used in the pellet forms for packed beds are in powder form for fluidized beds.

Active catalytic agent, in this case vanadium pentoxide is active agent. Preparation methods are confidential because of the competitive market. However, generally, in general the V 2 O 5 preparation methods include adding water soluble compounds to gels or porous substrates and firing at high temperatures however, below this sintering point, ok.

Promoters are also in general added commonly alkali or metallic compounds added in trace amounts to enhance the activity of catalytic agents.

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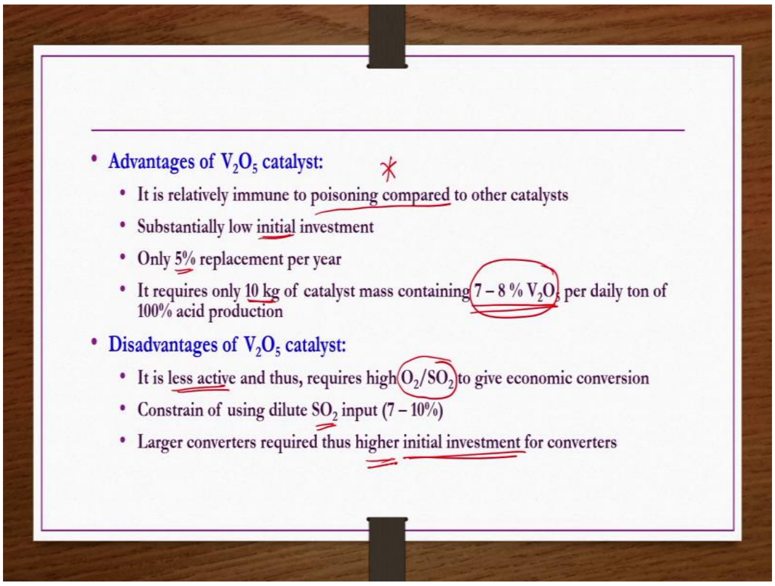

- Advantages of V_2O_5 catalyst:
  - It is relatively immune to poisoning compared to other catalysts
  - Substantially low initial investment
  - Only 5% replacement per year
  - It requires only 10 kg of catalyst mass containing 7 – 8 % V_2O_5 per daily ton of 100% acid production
- Disadvantages of V_2O_5 catalyst:
  - It is less active and thus, requires high O_2/SO_2 to give economic conversion
  - Constrain of using dilute SO_2 input (7 – 10%)
  - Larger converters required thus higher initial investment for converters

Advantages of V 2 O 5 catalyst if you take, it is relatively immune to poisoning compared to other catalysts. It is one of the major important thing. Because if it is poisoning either you have to go for the reactivation or you know you have to replace with the fresh catalyst. So, and then, this not only hampers the continuous production process, but also adds of the cost

So, if you have a catalyst which gets less poisoned in general, so then it is obviously, better compared to the catalyst which can get easily poisoned ok. It is having substantially low initial investment. Compared to the platinum, obviously, it is much cheaper. And then only 5 percent replacement per year is required. You can see how much it is having you know immunity towards the poisoning, ok. Only 5 percent replacement per year is required.

It requires only 10 kg of catalyst mass containing 7 to 8 percent V 2 O 5 per daily ton of 100 percent acid production. If you have a plant where you are producing 1 ton of acid, then you need only 10 kgs of catalyst. This catalyst is including the precursors and then if any promoters including the active agents.

So, all these 3 weights together 10 kgs, out of which only 7 to 8 percent of V 2 O 5 is there such low quantity of V 2 O 5 is required per daily ton of 100 percent acid production ok. However, it has some disadvantages. What are the disadvantages? It is less active actually.

However, actually such kind of reactions where highly exothermic it is better to have a catalyst which is less active, ok. And thus, but what is the disadvantage of havingly less active catalyst in this process? Then, you have to use high O 2 to SO 2 gas mixture to give economic conversion.

Then, constrain of using dilute SO 2 input only. You cannot use highly concentrated SO 2. You can use only up to 7 to 10 percent of SO 2 in the reactor ok. Whatever the gaseous mixture you are taking in that mixture, you can have only 7 to 10 percent of SO 2. Larger converters required because of such reasons and thus higher initial investment for converters are required, ok.

So, though it is cheaper catalyst because of its less activeness and then because of its constrain that it cannot take higher concentrations of SO 2 input higher size of reactors or larger size of the converters are required, which adds to the initial cost, initial investment.

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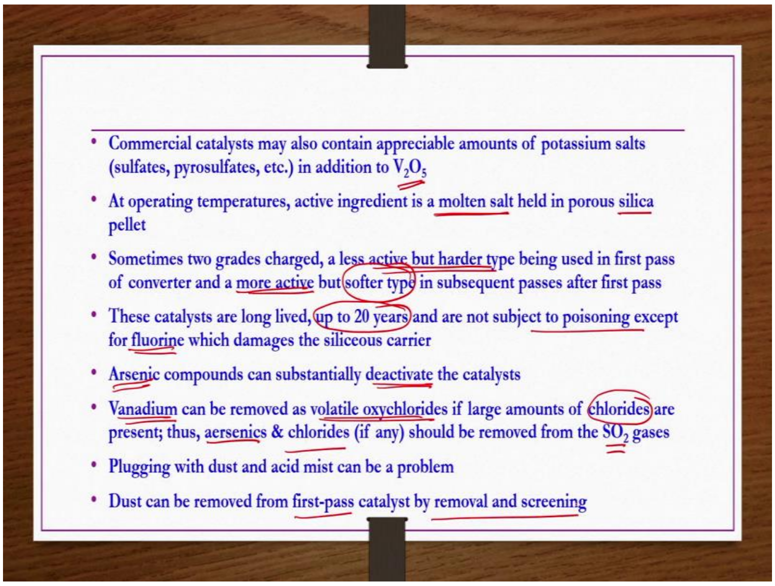

- Commercial catalysts may also contain appreciable amounts of potassium salts (sulfates, pyrosulfates, etc.) in addition to V_2O_5
- At operating temperatures, active ingredient is a molten salt held in porous silica pellet
- Sometimes two grades charged, a less active but harder type being used in first pass of converter and a more active but softer type in subsequent passes after first pass
- These catalysts are long lived, up to 20 years and are not subject to poisoning except for fluorine which damages the siliceous carrier
- Arsenic compounds can substantially deactivate the catalysts
- Vanadium can be removed as volatile oxychlorides if large amounts of chlorides are present; thus, aersenics & chlorides (if any) should be removed from the SO_2 gases
- Plugging with dust and acid mist can be a problem
- Dust can be removed from first-pass catalyst by removal and screening

Some more characteristics of this V 2 O 5, with respect to the sulfuric acid production if you see commercial catalyst may also contain appreciable amounts of potassium sulfate, potassium salts in addition to V 2 O 5. At operating temperatures, active ingredients are in general in a molten salt form held in porous silica pellets if you are using silica as base or as carrier or the supporter.

Sometimes two grades charged, a less active but harder type catalyst being used in the first pass of converter and a more active, but softer type of catalyst in subsequent passes after the first pass. These are based on the economic conversion and then balance, economic balance for against the heat transfer and other parameters of the processes. These catalyst are long lived up to 20 years.

So, such high is their life period. Up to 20 years you can use them, because it is less poisoning and you need only small amount of V 2 O 5 in general and are not subject to poisoning, except for fluorine, which damages the siliceous carrier. Arsenic components if at all they are present, they will also substantially deactivate the catalyst. Similarly, if halogens are there, so then vanadium may be removed as volatile oxychlorides, right.

So, that is the reason. If you have large amount of halogens or halides like you know chlorides etcetera, if you have large amount of chlorides then they should also be removed. So, any arsenics and chlorides are there they should be removed either from the elemental sulfur or from the SO 2 gases wherever it is possible. Before feeding to the catalytic converter they should be removed.

Otherwise they will be greatly deactivating the catalyst. Plugging with dust and acid mist can also be a problem in general. Dust can be removed from the first pass catalyst by removal and screening.

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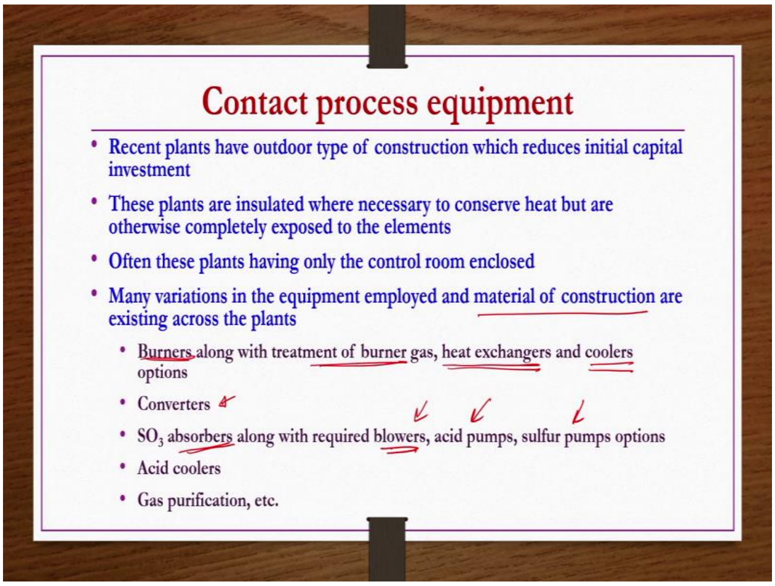

Contact process equipment

- Recent plants have outdoor type of construction which reduces initial capital investment
- These plants are insulated where necessary to conserve heat but are otherwise completely exposed to the elements
- Often these plants having only the control room enclosed
- Many variations in the equipment employed and material of construction are existing across the plants
    - Burners along with treatment of burner gas, heat exchangers and coolers options
    - Converters
    - SO_3 absorbers along with required blowers, acid pumps, sulfur pumps options
    - Acid coolers
    - Gas purification, etc.

Now, we see what are the options of contact process equipment. Actually, this process has been developed so much that, so much research has been done on almost each and every aspect, each and every component of the process, right. So, some of the options we list them here.

Recent plants have outdoor type of construction, which reduces initial capital investment. And then these plants are usually insulated wherever necessary to conserve the heat, but or otherwise completely exposed to the atmosphere. Mostly, the modern plants they are having only control room enclosed. Rest all the plant is you know open to the atmosphere.

Many variations in the equipment employed and then material of construction are existing across the plants. Different plants are having, different commercial plants are having, but the process is same. So, they have different types of equipments used actually.

Let us say burners along with the treatment of burner gas, what types of burners you wanted to use. Let us say burner gases are there, how many ways that are there to treat these burner gases. Heat exchangers are obviously we have seen, what type of heat exchangers you wanted to do. You wanted to use similarly coolers.

So, there are several options, right. So, people have used different heat exchangers different coolers from one plant to the another plant like that. Like that converters also. Single you know single contact process or double contact process like you know how many stages you wanted to have all those things you know several options are there.

Also, some people used packed bed, some people used fluidized bed reactors. So, different options are there. Then, SO 3 absorbers along with the required blowers, what types of absorbers you wanted to use, what is the MOC, then blowers are there, acid pumps are there, sulfur pumps are there.

So, all these are having different options. One has to do the proper economic calculation without overlooking the safety aspects and then select accordingly these equipments. Acid coolers, gas purifications, etcetera so many options are there.

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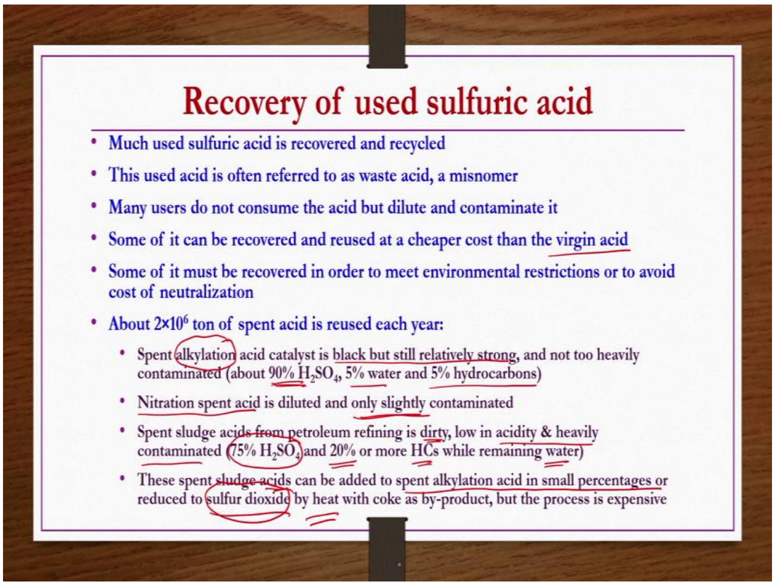

Recovery of used sulfuric acid

- Much used sulfuric acid is recovered and recycled
- This used acid is often referred to as waste acid, a misnomer
- Many users do not consume the acid but dilute and contaminate it
- Some of it can be recovered and reused at a cheaper cost than the virgin acid
- Some of it must be recovered in order to meet environmental restrictions or to avoid cost of neutralization
- About 2×10^6 ton of spent acid is reused each year:
    - Spent alkylation acid catalyst is black but still relatively strong, and not too heavily contaminated (about 90% H_2SO_4, 5% water and 5% hydrocarbons)
    - Nitration spent acid is diluted and only slightly contaminated
    - Spent sludge acids from petroleum refining is dirty, low in acidity & heavily contaminated (75% H_2SO_4 and 20% or more HCs while remaining water)
    - These spent sludge acids can be added to spent alkylation acid in small percentages or reduced to sulfur dioxide by heat with coke as by-product, but the process is expensive

Now, recovery of used sulfuric acid: Sulfuric acid actually for example, it is also used for catalyst purpose. We have seen in the previous lecture, it is a good oxidizing agent, it is also good dehydrating agent etcetera. But it is also used as a catalyst for several organic reactions also, something like alkylation etcetera.

Whatever the sulfuric acid that you have taken for the reaction, to catalyze the reaction, after the reaction if you take the if you take the sulfuric acid you can see that acid is only marginally diluted. Maybe you take 98 percent H 2 SO 4, and then after the reaction when you use this H 2 SO 4 as catalyst. After the reaction you take the H 2 SO 4 and check its acid strength you may be having more than 90 percent, 90-92 percent H 2 SO 4. So, it is only marginally diluted.

So, when have such kind of acid sources, rather producing acid from the virgin sources of sulfur or sulfur dioxide, it is better to recover or re-concentrate it to the higher concentration and reuse it. Such kind of things are there, ok. That is one use. Another use is that you know sulfuric acid is a very strong acid as we have discussed yesterday. So, such strong acid if you want to neutralize, you need lot of basic solutions etcetera base. You need lot of base solutions. And then process may be expensive, right.

If you do not do the neutralization, you cannot discard into the atmosphere as it is. So, those are the other problems, even if the acid is highly diluted after the process. So, then it is better to find out a way how you can utilize or recover the sulfuric acid and then use it.

So, first what we do? We see or we enlist a few points where recovery of sulfuric acid is required and then how it is being recovered, those things we are going to see now. Much used sulfuric acid is recovered and recycled in general. This used acid is often referred to as waste acid, a misnomer. Many users do not consume the acid, but dilute and contaminate it.

Some of it can be recovered and reused at a cheaper cost than the virgin acid. Let us say, alkylation reaction if you take 98 percent H 2 SO 4 as the catalyst, after the reaction you are getting 92 percent of H 2 SO 4. So, rather discarding it and then buying or producing the new one, the same one, you can concentrate it and reuse it. It will be much cheaper compared to the virgin acid.

Some of it must be recovered in order to meet environmental restrictions or to avoid cost of neutralization ok. About 2 multiplied by 10 power 6 tons of spent acid is reused each year. Spent alkylation acid catalyst is black, but still relatively strong and not too heavily contaminated. See, after the reaction actually some kind of alkylation reactions are taking place in the presence of sulfuric acid.

So, after the reaction, whatever the sulfuric acid is there that is called as spent alkylation acid catalyst. This is spent diluted, but still it is strong enough. Why? Because you can see 90 percent H 2 SO 4 is there in spent alkylation acid catalyst only 5 percent water and 5 percent other hydrocarbons of the reactions.

So, rather going for a new acid or rather going for a fresh acid for the subsequent batches or sequences of the reactions, you can concentrate this acid and then reuse it. That would be more economically better. Nitration spent acid is diluted and only slightly contaminated up to 73, 75 percent H 2 SO 4 would be there in the nitration spent acid catalyst.

It is also nitration spent acid catalyst in the sense, you have a nitration reaction in the presence of sulfuric acid only it is taking place. After the reaction whatever the sulfuric acid is there, that spent sulfuric acid is known as the nitration spent acid ok, which is usually diluted, but still you know strong enough, if it is not very strong.

Spent sludge acids from petroleum refining are dirty usually, low in acidity and heavily contaminated. See, you are calling 75 percent H 2 SO 4 is there in the sludge, but still you are calling it is a heavily contaminated. Because usually acid of 90 percent or higher is usually used for majority of the process, ok.

So, now though it is heavily diluted or contaminated, you can use it or you can recycle and then recover and then reuse again ok. Remaining in this process in this sludge, petroleum sludge usually remaining is 20 percent or more hydrocarbons and then about you know 5 percent or 10 percent remaining is the water.

These spent sludge acids can be added to spent alkylation acid in small percentages or reduced to sulfur dioxide. These acids whatever are there, if you are not able to concentrate to 98 percent H 2 SO 4, you can what you can do? You can heat it or reduce it to the sulfur dioxide by heating, right. This sulfur dioxide you can use as a by product, ok. But however, this process is slightly expensive.

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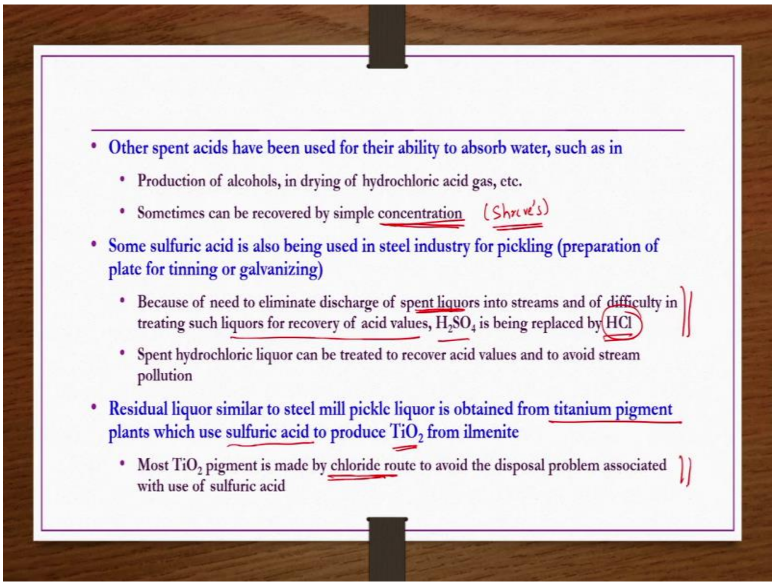

- Other spent acids have been used for their ability to absorb water, such as in
  - Production of alcohols, in drying of hydrochloric acid gas, etc.
  - Sometimes can be recovered by simple concentration (Shreve's)
- Some sulfuric acid is also being used in steel industry for pickling (preparation of plate for tinning or galvanizing)
  - Because of need to eliminate discharge of spent liquors into streams and of difficulty in treating such liquors for recovery of acid values, H_2SO_4 is being replaced by HCl
  - Spent hydrochloric liquor can be treated to recover acid values and to avoid stream pollution
- Residual liquor similar to steel mill pickle liquor is obtained from titanium pigment plants which use sulfuric acid to produce TiO_2 from ilmenite
  - Most TiO_2 pigment is made by chloride route to avoid the disposal problem associated with use of sulfuric acid

Other spent acids have been used for their ability to absorb water. Depending on the percentage of acid strength whether it is 70 percent 80 percent or 90 percent, they can also be used for absorbing water. Let us say you have some kind of nitration reactions and then alcohol productions, in those processes, what happens? You know some moisture would be there, if you wanted to absorb that moisture the spent acid catalyst can be used, ok.

Sometimes can be recovered by simple concentration. Concentrating sulfuric acid or weak concentrating weak sulfuric acid is also a separate process. We are not discussing anyway if somebody interested, they can go to the reference book while Shreve's Chemical Engineering, that one of the reference that we are following and then understand the process.

Some sulfuric acid is also being used in steel industry for pickling that is known as the preparation of plate for tinning or galvanizing. So, here also you get the you know spent liquors which is you know having a lot of sulfuric acid. Because of need to eliminate discharge of spent liquors into streams and of difficulty treating such liquors, such liquors for recovery of acid values H 2 SO 4 is being replaced by HCI.

Earlier people were using H 2 SO 4 for such kind of process, but you know recovery and then subsequent treating of spent acid, spent sulfuric acid is much difficult compared to that of hydrochloric acid. Because of that people are moving towards hydrochloric acid. Because spent hydrochloric acid liquor can be treated to recover acid values and to avoid stream pollution, much easily compared to the case of spent sulfuric acid.

A residual liquor similar to steel mill pickle liquor is obtained from titanium pigment plants, which uses sulfuric acid to produce titanium dioxide from ilmenite, right. So, most titanium dioxide pigment is made by chloride route to avoid the disposal problem associated with the use of sulfuric acid, same as in the previous case here.

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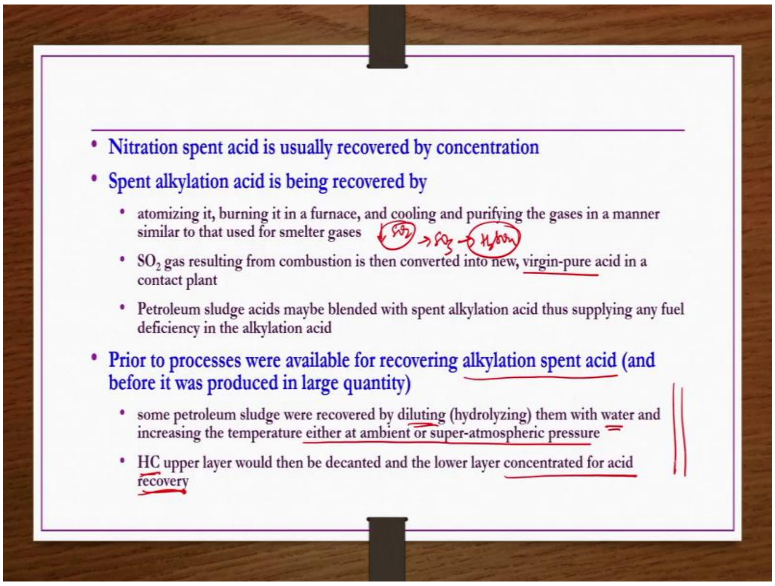

- Nitration spent acid is usually recovered by concentration
- Spent alkylation acid is being recovered by
  - atomizing it, burning it in a furnace, and cooling and purifying the gases in a manner similar to that used for smelter gases
  - SO_2 gas resulting from combustion is then converted into new, virgin-pure acid in a contact plant
  - Petroleum sludge acids maybe blended with spent alkylation acid thus supplying any fuel deficiency in the alkylation acid
- Prior to processes were available for recovering alkylation spent acid (and before it was produced in large quantity)
  - some petroleum sludge were recovered by diluting (hydrolyzing) them with water and increasing the temperature either at ambient or super-atmospheric pressure
  - HC upper layer would then be decanted and the lower layer concentrated for acid recovery

$SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

Further, nitration spent acid is usually recovered by the concentration process. Spent alkylation acid is being recovered by automizing it, burning it in a furnace, and cooling and purifying the gases in a manner similar to that used for smelting purposes or smelters or smelter gases.

S O 2 gas resulting from combustion is then converted into new, virgin-pure acid in a contact process. From here whatever S O 2 you get, this process, that can be you know converted to the S O 3, and then from here you can get H 2 SO 4 as in the contact process as we have discussed.

Once you have S O 2, then purify it and then follow the contact process. Only thing that you have to check whether is it economically feasible or economically you know profitable or not. Petroleum sludge acids may be blended with spent alkylation acid which can supply any fuel deficiency that is required for the alkylation acids.

Prior to processes were available for recovering alkylation spent acid and before it was produced in large quantity. That is you know in previous days, in law in decades before, people used to take the petroleum sludge and then diluting it or hydrolyzing it with water and increasing the temperature either at ambient or super atmospheric pressure.

So, that the upper layer which is hydrocarbon layer would be decanted and the lower layer which would be having the mostly acid. So, that can be concentrated for the acid recovery. So, this is what people were following previously as well. So, this is all about sulfuric acid production, consumption pattern, and then engineering problems, and then requirement catalysts characteristics etcetera and then recycling or reuse of recovery of spent acid etcetera, those things.

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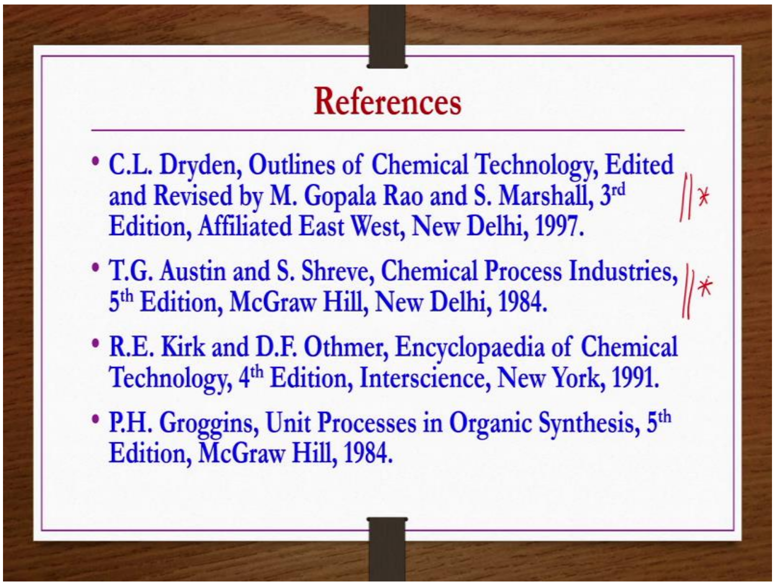

References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997. ||*
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984. ||*
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

The references for this lecture are provided here. However, most of the contents may be found from these two books.

Thank you.