

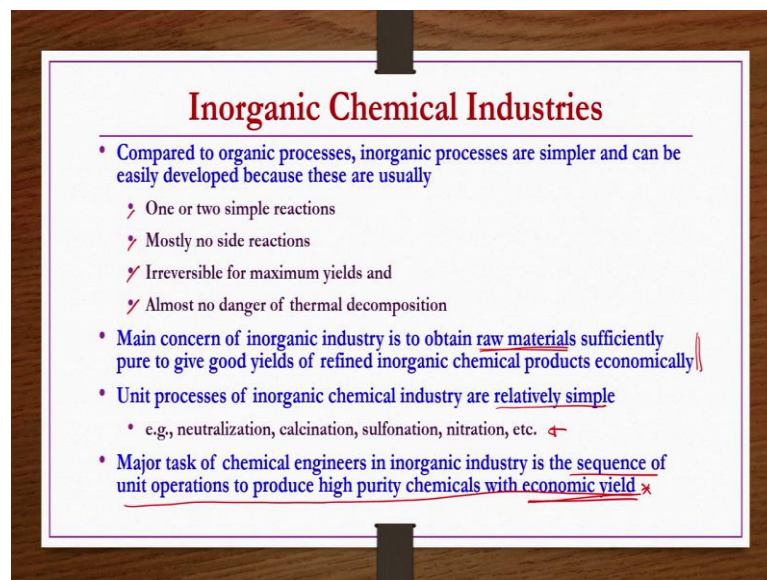
Inorganic Chemical Technology
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Lecture - 11
Sulfur Industry

Welcome to the MOOCs course Inorganic Chemical Technology, the title of today's lecture is Sulfur Industry. We have discussed until now few details about the production process of fuel and industrial gases because they are very much essential almost all chemical industries whether inorganic chemical industries or organic chemical industries right.

So, now, from today's lecture onwards what we are going to see? We are going to discuss production of different types of inorganic chemicals ok. So, before going in to the sulfur industry details we have a few comparison of inorganic chemical technology against organic chemical technology.

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Inorganic Chemical Industries

- Compared to organic processes, inorganic processes are simpler and can be easily developed because these are usually
 - One or two simple reactions
 - Mostly no side reactions
 - Irreversible for maximum yields and
 - Almost no danger of thermal decomposition
- Main concern of inorganic industry is to obtain raw materials sufficiently pure to give good yields of refined inorganic chemical products economically.
- Unit processes of inorganic chemical industry are relatively simple
 - e.g, neutralization, calcination, sulfonation, nitration, etc. ←
- Major task of chemical engineers in inorganic industry is the sequence of unit operations to produce high purity chemicals with economic yield. ✖

Inorganic chemical industries compared to organic processes inorganic processes are simpler and can be easily developed because these are usually - one or two single step reactions usually organic reactions if you take so many complicated intermediate and then intermediate steps are there before getting into the products etcetera. But coming to

the inorganic chemical reactions, inorganic chemical processes they are very simple mostly they are one or two simple step reactions only.

Then mostly there are no side reactions and then even if there are side reactions whatever the byproducts etcetera are there, they are also considered as a kind of a product. For example, if you take a zinc or copper smelting process in those processes in such metallurgical industrial processes, what happens? Large amount of H_2SO_4 is produced.

So, obviously, H_2SO_4 is very important from chemical industry point of view that it cannot be discarded, it has to be considered as a byproduct and then it should be recovered after required purification etcetera, because H_2SO_4 is a kind of barometer to measure the development of the chemical industries in general right. So, that is what happens in most of the inorganic chemical industries, there may not be by, there may not be side reactions, even if there are side reactions there would be some byproducts etcetera.

And these are irreversible for maximum yields and almost no danger of thermal decomposition. If you take a organic components, majority of organic components, they are thermal and they get thermally decomposed even its moderately high temperature like 60, 70 degrees centigrade something like that, because their boiling points may be lesser and then such kind of problems are not there in case of a majority of the inorganic chemical products.

So, these are the some of the comparisons or advantages of inorganic chemical industries if you compare with the organic chemical industries ok. If so many advantages are there compared to the organic processes, then why not the inorganic industry is dominating over the organic industry in general.

Obviously inorganic chemical industry is also used, but organic chemical industries are dominating in overall chemical industry processes. That is because concerned to this inorganic chemical industries, the main problem is that getting raw materials. Most of the raw materials required for majority of the inorganic chemical production in India are imported from other countries.

Most of the raw materials required for the production of majority of inorganic chemicals are often imported from the other countries right. So, that is one concern because of that one you know inorganic chemical industry is not dominating over organic chemical industry.

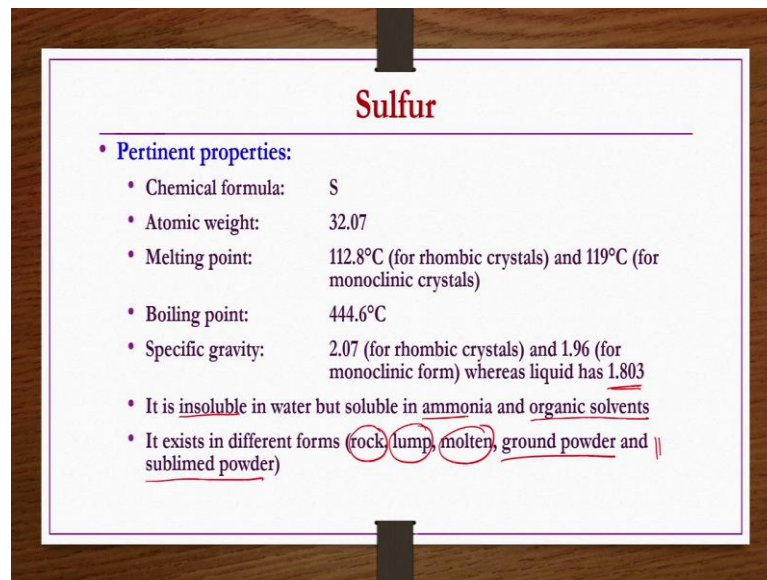
So; obviously, if you do not have raw materials sufficiently pure, then getting good yields of refined organic chemical products may not become much economically feasible. So, making them first of all getting these raw materials from the other countries and then making them to produce inorganic chemicals with economical yield etcetera is further challenge for chemical engineers in general.

Also unit processes of inorganic chemical industry are relatively simple, this is another advantage. Like if you take neutralization, calcinations, sulfonation, nitration etcetera, these reaction occur in simple kind of reactors, you know simple batch reactor etcetera one can take and then our simple CSTR reactor one can take and then do these things. So, then what is the role of chemical engineers in inorganic chemical industry?

It is to decide the sequence of unit operations to produce high purity chemicals with economic yield. This is very important because raw materials you are getting from the other countries especially for India there is a shortage of raw materials for the production of inorganic chemicals.

So, the problems associated with the raw materials availability would be discussed whenever we are going to discuss about a particular industry. So, for example, today we are going to discuss about the sulfur industry. So, we are going to see the difficulty of availability of sulfur raw materials or raw materials to produce elemental sulfur in India, you know those things we are going to discuss now.

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Sulfur

- **Pertinent properties:**
 - Chemical formula: S
 - Atomic weight: 32.07
 - Melting point: 112.8°C (for rhombic crystals) and 119°C (for monoclinic crystals)
 - Boiling point: 444.6°C
 - Specific gravity: 2.07 (for rhombic crystals) and 1.96 (for monoclinic form) whereas liquid has 1.803
 - It is insoluble in water but soluble in ammonia and organic solvents
 - It exists in different forms (rock, lump, molten, ground powder and sublimed powder)

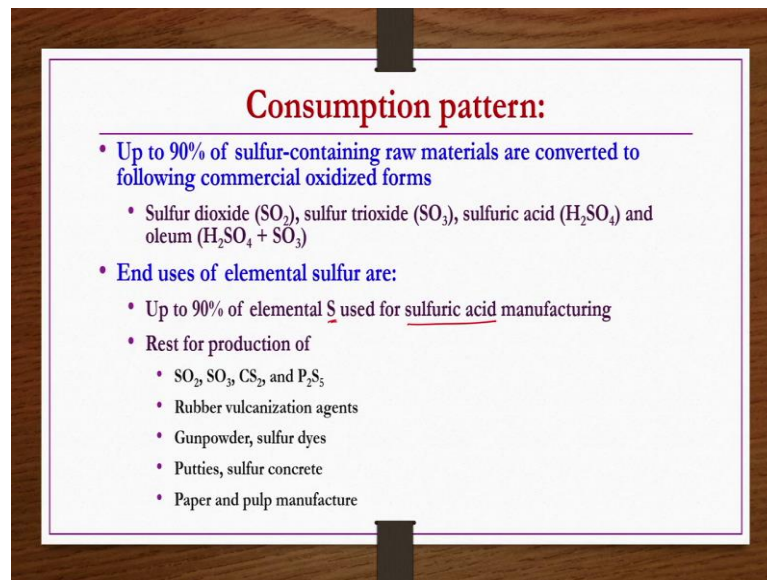
So, in sulfur industry let us start discussing about the sulfur. As we have seen for the production of fuel and industrial gases until now the similar pattern of lecture we are going to follow that is we are going to see pertinent properties of a given chemical that we are going to produce.

And then what are the quantitative requirements etcetera? Raw materials, reactions associated different types of processes available or different flow charts that are available for the production of given chemical along with them associated major engineering problems and economics we are going to discuss. So, for the sulfur if you see the properties chemical formula is S, atomic weight is 32.07.

Coming to the melting point if it is available in a rhombic crystal form then 112.8 degree centigrade, if it is available in monoclinic crystals form then 119 degree centigrade is the melting point. Boiling point is 444.6 degree centigrade and then coming to the specific gravity for rhombic crystals it is 2.07 whereas, for monoclinic form it is 1.96 whereas, the liquid form it has 1.803 specific gravity.

It is insoluble in water, but soluble in ammonia and other types of organic solvents. It exists in different forms like in rock form, in the lumps form, in the molten form, in the ground powder form and in sublimed powder form as well it is available in different forms in general.

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Consumption pattern:

- Up to 90% of sulfur-containing raw materials are converted to following commercial oxidized forms
 - Sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfuric acid (H_2SO_4) and oleum ($\text{H}_2\text{SO}_4 + \text{SO}_3$)
- End uses of elemental sulfur are:
 - Up to 90% of elemental S used for sulfuric acid manufacturing
 - Rest for production of
 - SO_2 , SO_3 , CS_2 , and P_2S_5
 - Rubber vulcanization agents
 - Gunpowder, sulfur dyes
 - Putties, sulfur concrete
 - Paper and pulp manufacture

Then consumption pattern if you see you will be surprised to know that more than 90 percent of the elemental sulfur that is produced in India is used for sulfuric acid production. So, primarily elemental sulfur is produced for the production of sulfuric acid. So; obviously, wherever there is a possibility of producing sulfuric acid as a byproduct it is better to recover them and then store them as a kind of useful byproducts like as I mentioned zinc and copper smelting processes.

Because even from the elemental sulfur 90 percent of the elemental sulfur whatever we are having we are utilizing for production of sulfuric acid. Up to 90 percent of sulfur containing raw materials are converted to the following commercial oxidized form like sulfur dioxide, sulfur trioxide, sulfuric acid and oleum. This sulfur dioxide is further oxidized to sulfur trioxide before making the sulfuric acid right. So, even sulfur dioxide, sulfur trioxide are also further being utilized for making sulfuric acid right.

Oleum is a different form of sulfuric acid where it is a mixture of sulfuric acid and sulfur trioxide. Let us say if it is 20 percent oleum means what does it mean? If you have 100 kg of oleum then out of 100 kg of oleum 80 kg should be H_2SO_4 and then remaining 20 kg should be SO_3 sulfur trioxide ok. End uses of elemental sulfur are many, but; however, primarily up to 90 percent of elemental sulfur used for sulfuric acid manufacturing. And then sulfuric acid is as I mentioned already it is a kind of barometer to measure the growth of a chemical industry.

Presently the production as well as the consumption pattern of H_2SO_4 if you see in India and compare with USA then India is on par with the United States of America. Rest of the elemental sulfur is used for the production of sulfur dioxide, sulfur trioxide, carbon disulfide and potassium pentasulfide.

These are further used for other kind of inorganic chemical productions also. Then rubber vulcanization agents for that purpose also elemental sulfur is used, gunpowder, sulfur dyes making putties sulfur concrete etcetera for these purposes also the elemental sulfur is used and then it is also used in paper and pulp manufacturing. Now, let us see availability of raw materials for production of elemental sulfur in India.

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Raw materials:

- Sulfur deposits in India are existing only in Puga valley of Kashmir
- Difficult terrain conditions mining in these areas is economically not feasible
- Alternative sources of recovering elemental S or sulfuric acid are:
 - Recovery of elemental sulfur from petroleum refineries
 - Madras Refinery Ltd. is a plant from which elemental sulfur is recovered during refining of crude petroleum
 - Production of by-product sulfuric acid from zinc and copper smelters
 - Sulfuric acid produced on large scale as by-products from Zn and Cu smelters
 - Production of sulfuric acid from pyrites *
 - From Pyrites and Phosphates Chemicals Ltd. (PPCL) plants, large volumes of H_2SO_4 is produced such that two plants for H_2SO_4 have been setup in Sindri

Sulfur deposits in India are existing only in Puga Valley of Kashmir and then we know terrain conditions are very difficult in Kashmir Valley. So, mining this elemental sulfur or sulfur deposits from the Puga Valley is not going to be economically feasible. So, what are the alternative sources of recovering elemental sulfur or sulfuric acid?

We are not only talking just about recovering elemental sulfur, but also sulfuric acid because we understand even if elemental sulfur if you recover by other alternative processes 90 percent of is this is going to be used for the production of sulfuric acid that is the reason in a process rather recovering elemental sulfur if you are directly recovering or you know producing sulfuric acid as a by production it is even better.

So, what are such kind of alternatives that is what we are going to see now. Recovery of elemental sulfur from petroleum refineries in petroleum refineries often this elemental sulfur is available, then production of byproduct sulfuric acid from zinc and copper smelting processes, then production of sulfuric acid from pyrites ok.

So, recovery of elemental sulfur from petroleum refineries if you see only Madras refinery limited is a plant from which elemental sulfur is recovered during refining of crude petroleum in Indian conditions right. And then production of byproduct sulfuric acid from zinc and copper smelters is very common because sulfuric acid produced on large scales in this smelting process.

So, these are recovered as a byproducts and then used you know and then subsequent purification of sulfuric acid is done and then sent to the consumer or utilized in within the industry if it is required ok. Then production of sulfuric acid from pyrites; from the pyrites whatever the sulfuric acid is produced that is so large in volume that pyrites and phosphates chemicals limited plants what they have done?

They have you know set up two plants for H_2SO_4 near Sindri for the production of H_2SO_4 or for the recovery of H_2SO_4 from this pyrites ok. So, these are the three alternative process or you know three alternative sources that are available for us to either recover the elemental sulfur or directly produce the sulfuric acid.

However if you see more than 50 percent of elemental sulfur available involved is produced by recovery of sulfur from the refinery gases or coke oven gases or something like this industrial fuel gases; how that is what we are going to see anyway in subsequent slides.

This is about the sources of raw materials or alternative sources of recovering elemental sulfur or sulfuric acid from the other plants and that is what we have seen. Now, let us discuss about the production of elemental sulphur. How many methods are there? Right.

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Production of elemental sulfur

- **Classification of processes:**
 - Elemental sulfur mining from salt domes (USA)
 - H₂S conversion from natural gas and industrial gases [or Oxidation and Reduction of H₂S] (USA)
 - Iron pyrites (India)

Primarily three methods are there elemental sulfur mining from salt domes. So, these are available or such process are very famous in America, Canada and some part of Europe. Then H₂S conversion from natural gas and industrial gases or oxidation and reduction of H₂S this process is also very much famous in USA and Canada and then European countries right.

Then iron pyrites process which is very famous in India ok. So, now what we are going to see? We are going to see details of each of these three processes ok. So, you will be surprised to know that H₂S conversion from natural gas to produce elemental sulfur is one of the important process because more than 50 percent of elemental sulfur that is available in the world is produced by this process.

What is this process? We have already seen production of fuel gases and industrial gases in majority of the flow sheets what you have seen? From the reactor you are getting a different types of gases like CO CO₂, H₂ H₂S etcetera. So, what we have done this H₂S? We have absorbed this H₂S by passing through that mixture of gases in a solution something like ethanol amine solution.

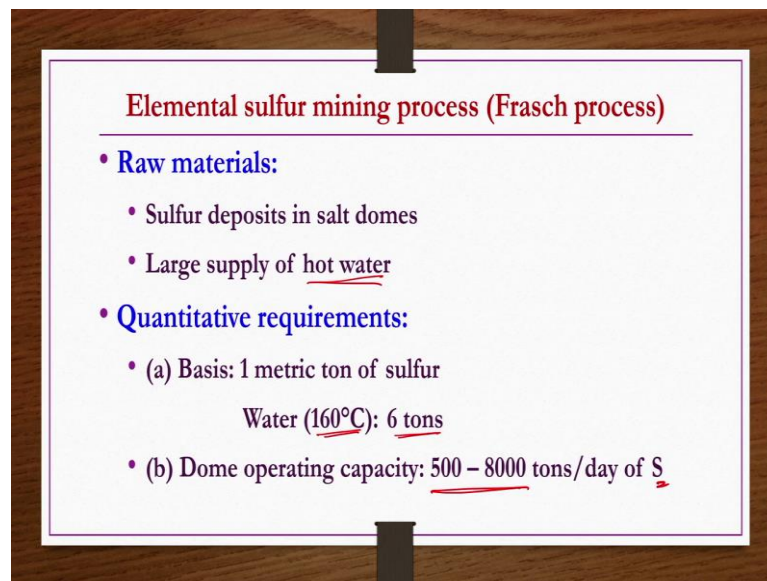
So, ethanol amine solution selectively absorbed this H₂S the conditions are operated such a way and then after absorption process what we do? We heat the solution dilute solution let us say ethanol amine which is absorbed already absorbed H₂S then when

you heat that ethanol amine dilute solution then H_2S would be released from the solution almost in a pure form.

That H_2S you take and then do the oxidation and in order to get the sulfur dioxide which further react with the H_2S to give elemental sulfur. So, that is very common and then we know that most of the refinery process or so natural gases etcetera this is there. So, then we cannot actually from industrial point of view also it is not advisable to leave it in the atmosphere, so it has to be recovered.

So, any way we have to do we are doing recovering, so then that recovered H_2S can be further utilized to produce elemental sulfur ok. So, we are going to see these three process for the production of elemental sulfur.

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Elemental sulfur mining process (Frasch process)

- **Raw materials:**
 - Sulfur deposits in salt domes
 - Large supply of hot water
- **Quantitative requirements:**
 - (a) Basis: 1 metric ton of sulfur
 - Water (160°C): 6 tons
 - (b) Dome operating capacity: 500 – 8000 tons/day of S

So, let us start with elemental sulfur mining process which is also known as the Frasch process. Raw materials: sulfur deposit in salt domes and then large supply of hot water is required. Because when you do the mining and then underground the mining wherever the sulfur rocks are found calcite sulfur containing rocks like calcite etcetera are found and what you have to do?

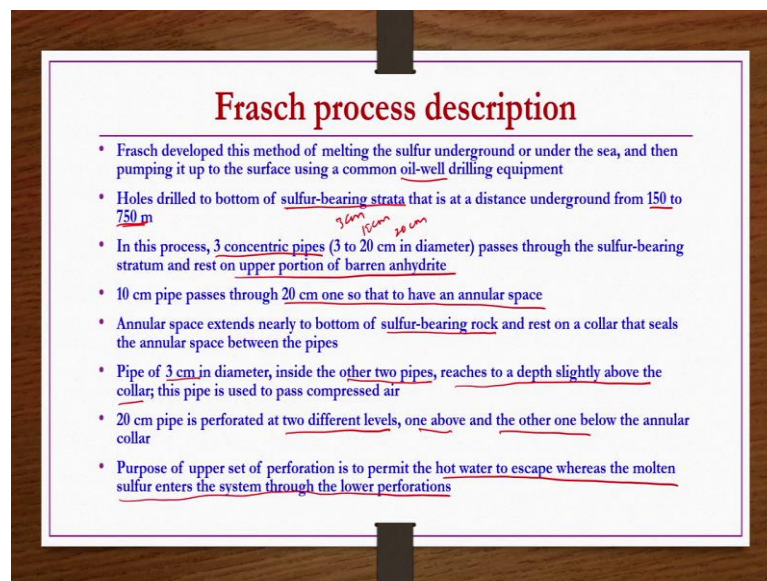
You have to provide hot water to that area, so that you know so that the rocks of sulfur you know can be melted can be melted in form of molten sulfur and then that should be

taken to the surface ground surface for the further processing or you know shipment etcetera. So, you need hot water large supply of hot water.

Quantitative requirements; let us say if you wanted to aim to produce 1 metric ton of sulfur then hot water 6 tons is required that how hot it is? 160 degree centigrade minimum it should be there 160 to 180 degree centigrade something like that why because such hot water when it goes when you do the drilling or mining when it goes to the sulfur containing rocks, then it melts the sulfur elemental sulfur and then forms the molten sulfur.

If that melt what is the melting point of the sulfur is between 112 to 119 degree centigrade depending on what crystal form it is having right. So; obviously, you have to provide a water which is higher than the 112 degree centigrade and then once it is melting, so then that elemental sulfur can be taken to the surface. The process we are going to see anyway. Dome operating capacity is 500 to 8000 tons per day of sulfur ok.

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So, what is this process? First we see the description and then we see the same thing by pictorial form also. Frasch is a scientist who developed this method of melting the sulfur underground or under the sea and then pumping it up to the surface using a common oil well drilling equipment. How it is pictorially we are going to see anyway.

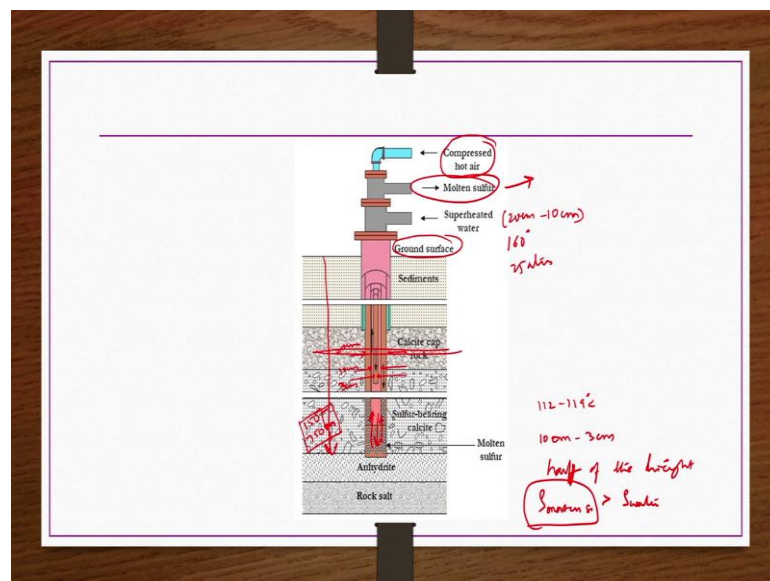
Holes drilled to the bottom of sulfur bearing strata that is at a distance underground from 150 to 750 meters ok from the surface if you drill up to minimum of 150 meters or to the maximum 750 meters then you may find this sulfur bearing strata it depends on location to location country to country ok.

In this process 3 concentric pipes having diameter 3 to 20 centimeter to be specific 3 centimeter diameter pipe 1 and then 10 centimeter diameter pipe 1 and then 20 centimeter diameter pipe 1 (Refer Time: 19:12) they are arranged such a way that they form 3 concentric pipes ok.

It passes through the sulfur bearing stratum and rest on a upper portion of barren anhydrite. Then 10 centimeter pipe passes through 20 centimeter 1 so, that to have an annular space. And then annular space extends nearly to bottom of sulfur bearing rock and rest on a collar that seals the annular space between the pipes of 10 centimeter diameter and 20 centimeter diameter.

Then a pipe of 3 centimeter diameter inside the other pipes reaches to the depth slightly above the collar this pipe is used to pass compressed air ok. 20 centimeter pipe is perforated at two different levels one above and the other one below the annular collar. Purpose of upper set of perforation is to permit the hot water to escape whereas the molten sulfur enters the system through the lower perforations.

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The same thing if you see the pictorially Frasch process this is what we are having we are at the ground surface. Now, if you drill below the ground surface, so up to 150 to 750 meters distance underground then what you have? You may find sulfur bearing calcite or sulfur bearing rocks ok. So, this distance of drilling depends on the you know location to location some countries it may be available in near distance of 150 meters also some countries this you one has to drill up to 750 meters right. So, then what you have?

So, this three concentric pipes are there right. So, we are having three pipes one is this; one having 20 centimeter dia and then other one is this one which is having 10 centimeter dia and then third one is this one which is having 3 centimeter dia right. When you drill and then you pass this 20 centimeter dia pipe goes in and then it rests on the surface here, then the second pipe is which is having 10 centimeter dia that is drilled.

So, that it goes and then rest on a sulfur bearing rock and then it the perforation is closed here. So, then what happens? From here what you do? Between the annular space of 20 centimeter to 10 centimeter pipes you allow superheated water at 160 degrees centigrade or sometimes 180 degree centigrade also at higher pressure like 25 atmospheres or something like that.

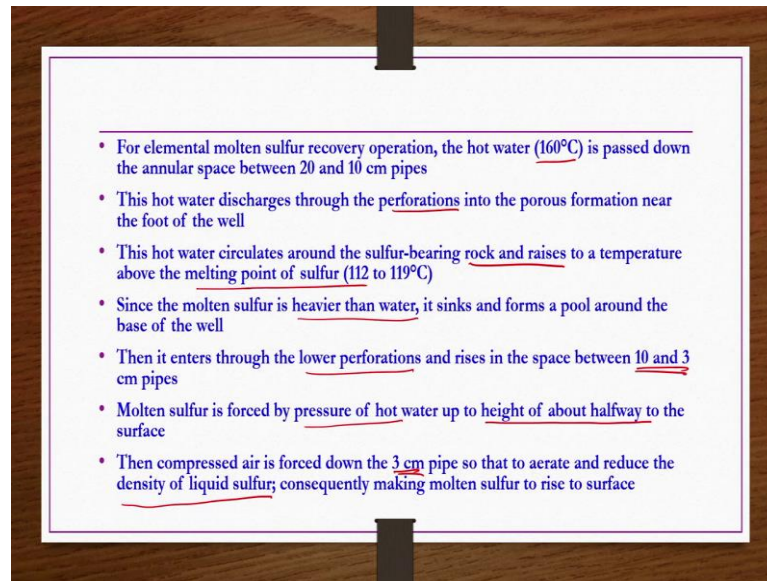
So, that it goes here and then moment it comes here it interacts with the this whatever the sulfur bearing rocks and then what happens? This sulfur gets melted up because the melting point of sulfur is between 112 to 119 degree centigrades. So, then what happens? This molten sulfur it tries to pass through the space between 10 centimeters dia pipe to 3 centimeter dia pipe right and then it raises only to the half of the distance half of the height of this pipes because you know the density of molten sulfur is greater than the density of water.

So, the pressure that is exerted because of the hot water is only is marginally sufficient to lift the molten sulfur to the half of this distance maybe up to this point or something like that. So, then further it has to go up to the ground surface then only you can recover. So, further for that purpose what you do?

You send compressed hot air through the 3 centimeter dia pipe. So, then when it goes here, so then what it does? It does it reduces the density of the molten sulfur, so that its surface elevates further to the ground surface and then from here you collect the you collect the molten sulfur whatever you are looking for.

So, this is the Frasch process ok. So, this only mining part the entire flow sheet part we can take. So, then this molten sulfur let us say if there are some impurities you can do the filtration etcetera or directly you can take it to the sulfur or molten sulfur storage vessels or you can take to the sulfur drying or you know for the drying of molten sulfur, so that you get the dry sulfur.

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For elemental molten sulfur recovery operation the hot water approximately 160 degree centigrade is passed down the annular space between 20 and 10 centimeter pipes. This hot water discharges through the perforation into the porous formation near the foot of the well. This hot water circulates around the sulfur bearing rock and raises to a temperature above the melting point of sulfur between 112 to 119 degree centigrade.

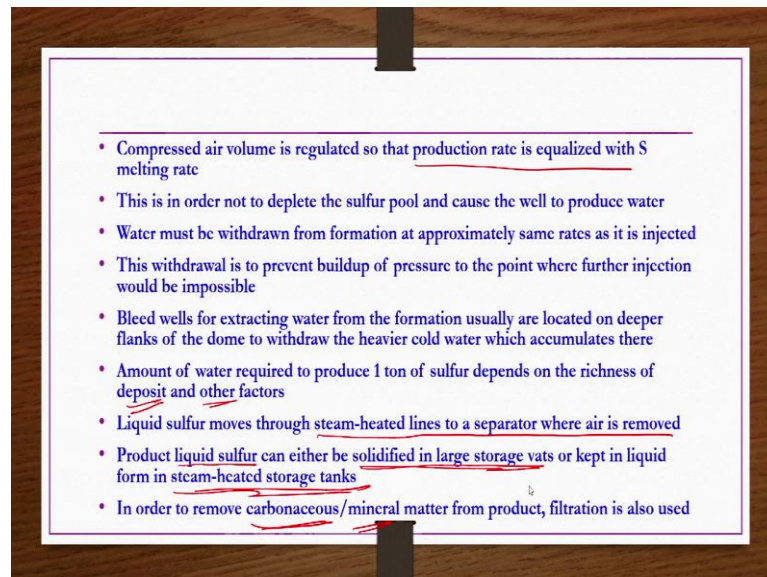
Once it crosses the temperature of the rocks sulfur bearing rocks raises to the more than 112 to 119 degree centigrade the sulfur will melt. Since the molten sulfur is heavier than water it sinks and forms a pool around the base of the well, then it enters through the lower perforation and raises in the space between 10 centimeter and 3 centimeter pipes.

Molten sulfur is forced by pressure of water up to height of about half way to the surface only. Then compressed air is forced down the 3 centimeter pipe. So, that to aerate and reduce the density of liquid sulfur consequently making molten sulfur to raise to surface, ground surface.

Now, in this process two important things are there other than the drilling; one is the allowing the water allowing the hot water to go into the deeper level almost up to the sulfur bearing rocks and then sending the compressed air. So, at what rate should this hot water should be sent?

At what rate this compressed air or what volume of the compressed air should be sent? These are the kind of engineering parameters one has to carefully calculate depending on the rocks depending on the distance at which rocks are available underground from the surface from the ground surface. So, one has to be very careful in this calculations.

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So, but basic principle what has to follow while doing this calculation that compressed air volume is regulated, so that production rate is equalized with sulfur melting rate. This is in order not to deplete the sulfur pool and cause the well to produce water. If you send the compressed air at a higher rate than the melting rate of the sulfur, then what happens?

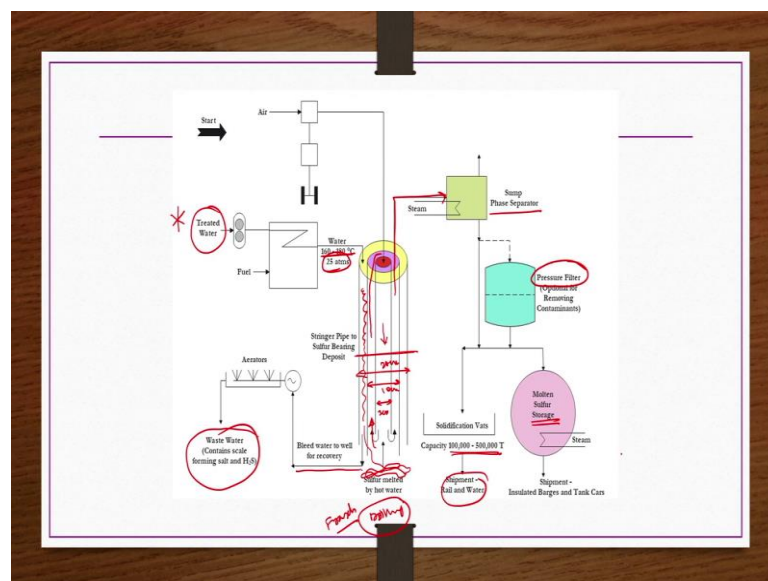
Depletion of the sulfur will take place and then well, start producing the water. You do not want you do not want that hot water to be getting onto the surface as your product that has to be taken in a different route ok. Then water must be withdrawn from formation at approximately same rates as it is injected. Let us say 10 kg per hour is the water feed rate hot water feed rate, so approximately at the same rate you have to withdraw also.

This withdrawal is to prevent build up of pressure of the point where further injection would be impossible. If you do not if you do not withdraw at the same level or at the same mass rate or volumetric flow rate then what happen? Because of this water hot water pressure would be build up in the underground area and then the further injection of hot water may not be possible. So, then if it is not possible it will not be able to you know you are not able to take the sulfur out efficiently.

Bleed wells for extracting water from the perforation usually are located on deeper flanks of the dome to withdraw the heavier cold water which accumulates there. Amount of water required to produce one ton of sulfur depends on the richness of deposits and other factors obviously. So, one has to be careful about how much sulfur is available underground accordingly one has to calculate the water requirement water requirement; obviously, ok.

Liquid sulfur moves through steam heated lines to separator where air is removed. The product liquid sulfur after removing air can either be solidified in large storage vats or kept in liquid form in steam-jacketed store storage tanks either way. If there are some carbonaceous or mineral matter present in the molten sulfur, then what you do? You can do filtration process to remove those contaminants. So, now if this entire process if you see in a flowchart form what you have? You have you know this is what you have ok.

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So, what you have here? So, this is the drilling equipment drilling part or Frasch process whatever we have seen here in the previous things and then rest other things are you know to completely flow sheet. So, now here this is you know 20 centimeters dia pipe and this is 10 centimeters dia pipe and this is 3 centimeters dia pipe ok.

The concentric space between 20 and 10 centimeters dia area is used for pumping the hot water which is at around 160 to 180 degree centigrade and then pressure at which this is allowed is approximately 25 atmosphere. It reaches the bottom area where this sulfur containing rocks are present.

So, then when this hot water comes here, so whatever this sulfur rocks are there you know the temperature here gradually raises and then once the temperature raises to 112 to 119 degree 119 degree centigrade it start melting. Once it is start melting it will pass through the space between 10 centimeter and then 3 centimeter pipe diameter between the space of 2 pipes having 10 centimeter and then 3 centimeter diameters right.

But the hot water pressure is created that much that it can force the molten sulfur approximately about half of the half the way of you know this distance whatever to the surface distance right. So, then what you have to do? You have to give compressed air from the 3 centimeter dia pipe, so then when the compressed air comes in it reduces the density of the sulfur. So, that the sulfur further raises to the surface and then that can be collected in a some phase separator.

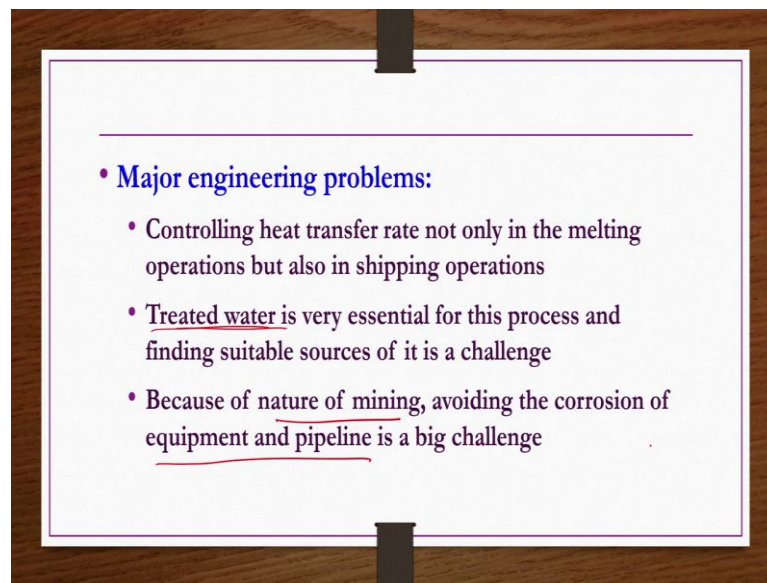
Whatever the bleed water to well is there that can be recovered from the bottom here from here itself and then aerators can be used and then after that one waste water or contains scale forming salt and H_2S whatever are there, so they can be separated out. So, now you can understand the same water you cannot reuse that is the reason treated water whatever is there its requirement is very large in this process that is one of the engineering problem right.

So, this treated water is sent to the well around at 160 to 180 degree centigrade and 25 atmosphere ok. So, now whatever the molten sulfur you got on the surface if it is not having any impurities, then you can take to the molten sulfur storage if you wanted to store in the liquid form where you know the steam heated containers are used for storing in liquid form.

If you wanted to do the if you wanted to do the solidification it can be taken after solidification it can be taken to the solidification vats having the capacity of 1 lakh to 5 lakhs tons and then from there to shipment etcetera it can be done. Let us say if there are let us say if the molten sulfur is having some kind of impurities.

So, then you can opt for the pressure filtration process in order to remove this carbonaceous or mineral impurities that are present in the molten sulfur. This is the process ok; this is the elemental sulfur recovery process from the salt domes.

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If you see the major engineering problems; obviously, what you understand the heat transfer rate heat transfer rate is very essential not only in the drilling area, but also in the you know shipping operation also because the drilling area because the sulfur rocks are there at different levels in different locations. Some are at just 150 meters distance some are even up to 700, 750 meters you have to drill. So, then; obviously, heat transfer calculations are going to be affected by the distance.

So, the controlling heat transfer rate not only in the melting operation, but also in shipping operations is one of the important engineering problem that one should be concerned about because of presence of these H₂S and then flakes forming salts etcetera in the recovered water the same cannot be used further as a treated water for the process ok, that is, the reason requirement of treated water is very large.

So, that is one important challenge. So, another one is because of nature of mining; obviously, corrosion of equipment and then pipeline is going to be taking place and then avoiding or reducing such corrosion is another important challenge from the chemical engineering point of view.

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Elemental S by Oxidation and Reduction of H₂S Process:

- Chemical reactions:**
 - (a) $2H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O$; $\Delta H^\circ = -247.89 \text{ kcal}$
 - (b) $4H_2S + 2SO_2 \xrightarrow{Al_2O_3} S_8(g) + 4H_2O$; $\Delta H^\circ = -42.24 \text{ kcal}$
- Raw materials:**
 - H₂S from natural (sour) gas and petroleum refinery streams (recovered by scrubbing with ethanolamines and high T stripping)
- Quantitative requirements:**
 - (a) Basis: 1 metric ton of sulfur and 100% yield
H₂S: 1.2 tons and Air: 1,700Nm³
 - (b) Plant capacities: 20 – 600 tons/day

Handwritten notes:
 - A circle around 'H₂S' in reaction (b) with an arrow pointing to 'ethanolamine'.
 - An arrow pointing from 'Mile' to reaction (a).
 - A signature 'm/s' at the bottom left.

So, next process is elemental S by oxidation and reduction of H₂S process. Chemical reactions if you see H₂S reacting with the oxygen to give sulfur dioxide and then water. The sulfur dioxide may be further oxidized to give sulfur trioxide and then when the sulfur trioxide dissolved into water one can get the you know sulfuric acid, but what happens?

The reactions or conditions such a way that in this process this SO₂ sulfur dioxide further react with the hydrogen sulphide H₂S to give the elemental sulfur when appropriate catalyst are is been used Al₂O₃ or Fe₂O₃ sometimes iron catalyst are also used ok.

And then what you see these reactions are exothermic because enthalpy of the reactants is higher than the enthalpy of the products, so that is another issue ok. So, now raw materials; obviously, what you see? H₂S is the raw material one of the raw material along with the air and air or oxygen ok. So, this H₂S from where are we getting?

We get from natural sour gases or petroleum refinery streams or in the production of you know producer gas, coke oven gas etcetera all this fuel gases production what we have seen? We have seen H_2S right. In such processes this H_2S is impurity, so it has to be removed right.

After removing because of the pollution concern you cannot discard it into the environment, so it has to be properly recovered and then subsequent chemical operation one has to do. So, what we do? We what we have seen? In production of fuel gases section the mixture of gases passes through ethanol, amine or potassium carbonate solutions. So, that this H_2S is being absorbed by the solutions.

One whatever once this H_2S is absorbed, so then remaining gases whatever the purified gases or gases free from H_2S are taken from the taken for the subsequent processes, but whatever this dilute solution is there it is heated up to elevate a temperature to release or relieve almost pure H_2S this is what we have seen.

And then once it is released pure almost pure solution is again reused for absorbing additional H_2S from the incoming mixture gases again. So, this is what we have seen in the production of fuel gases section previously in last couple of weeks several times we have seen. So, this recovered H_2S can be used as a you know source for production of elemental sulfur by this process ok.

Recovered by scrubbing with ethanol amines and high temperature stripping one can get the H_2S and then that can be oxidized to get required elemental sulfur as per the reactions A and B right. Quantitative requirements if you see let us say if you wanted to produce 1 metric ton of sulfur at 100 percent yield then 1.2 tons of H_2S is required and then air 1,700 normal cubic meters are required. Plant capacities is usually low 20 to 600 tons per day.

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Process description

- Large volumes of H_2S is being removed during purification of sour natural gas, coke-oven gas and from petroleum refinery gas
- It is recovered by dissolving the H_2S rich vent gases in potassium carbonate solution or ethanolamine followed by heating to regenerate almost pure H_2S
- Thus produced H_2S is burned to give sulfur dioxide for sulfuric acid
- But majority is converted to elemental S by various modifications of original Claus process as per reactions (a) & (b)
- Recovery of sulfur components from the fuel and industrial gases is also required from the pollution regulations viewpoint as well
- Thus several process developed and approximately one-half of the world production of elemental S is made by gas treatment
- Other sources of sulfur include coke-oven gas and synthetic crude oils from tar sands or shale oils; very little sulfur is presently recovered from coal

Process description if you see - large volumes of H_2S is being removed during purification of sour natural gas, coke oven gas and from petroleum refinery gas. It is recovered by dissolving the H_2S rich vent gases in potassium carbonate solution or ethanol amine solution followed by heating to regenerate almost pure H_2S , right.

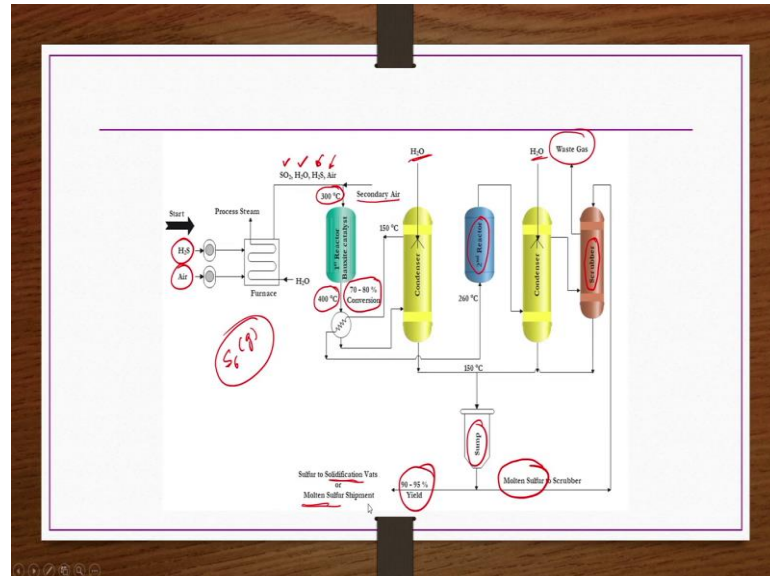
So, once you remove the H_2S from the solution that solution can be reused for absorbing more H_2S from the incoming mixed gases ok. Thus produced H_2S is burned to give sulfur dioxide for sulfuric acid production. But majority is converted to elemental as by various modifications of original Claus process as per reactions a and b that we have seen in the previous slide.

This H_2S when oxidized it gives the sulfur dioxide. So, this sulfur dioxide further react with the H_2S to give the elemental sulfur this is what we have seen right. So, recovery of sulfur components from the fuel and industrial gases is also required from the pollution regulations viewpoint as well. Thus several processes developed and approximately one half of the world production of elemental sulfur is made by gas treatment.

Because many countries are not having sources natural resources of this sulfur containing salt, domes etcetera, so then they are depending on this gas treatment process to get this elemental sulfur. Other sources of sulfur include coke oven gas and synthetic

crude oils from tar sands or shale oils. It was also available previously from coal, but nowadays only very little sulfur is presently recovered from the coal.

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So, the recovery of molten sulfur or elemental sulfur from H_2S by this process is having you know two step reactions. So, what are these two steps, that we are going to see now through the flow sheets. Now, the almost pure H_2S recovered from the petroleum refineries etcetera or while production of fuel gas etcetera whatever the H_2S , almost pure H_2S that recovered that along with the air you pass through a furnace which is you know maintained by the this furnace is nothing but steam heated furnace right.

So, depending on the economics different types of furnace can also be utilized anyway. So, once this H_2S and air pass through furnace; obviously, oxidation of H_2S takes place and then SO_2 water forms there may be some impurities of H_2S as because of unreacted H_2S as well as air would be there. The products coming from this furnace would be at certain temperature like 300 degree centigrade and then this gases mixture is sent to first reactor where bauxite catalyst is used.

Catalysts is also an option here. So, Al_2O_3 can also be used Fe_2O_3 can also be used by different processes different these things catalyst are used. For this reaction first step reaction to take place here are the for this conversion of SO_2 to sulfur or elemental sulfur more air is required let us say in case then secondary air can also be sent. So, the

product that is coming out from the reactor is at 400 degree centigrade and then conversion is 70 to 80 percent only.

This mixture what we do? You pass through a condenser right and then in the condenser the H₂O is spread. So, that the temperature reduces to 150 degree centigrade whatever the molten sulfur is there that can be taken to the sump right. But; however, if you wanted to increase the conversion, so then temperature reduced gases are sent back to the are sent to the another reactor second reactor which is operating around 250 to 300 degree centigrade.

So, again here now the further conversion takes place and then the yield is going to be increased right. So, then this from this reactor whatever the effluents are coming so, they are taken to the another condenser where again water is spread and then temperature is reduced to 150 degree centigrade and then molten sulfur is taken to the sumps right. Whatever the waste gases are there they are scrubbed in a scrubber using the molten sulfur before taking out the waste gases.

Because waste gases may also contain this elemental sulfur because this elemental sulfur in this process whatever is there that is S₆ we are getting that we get in gases from as per the reaction that we have seen. So, you do not want any sulfur gases to pass through along with the waste gases. So, then before taking out the waste gases those waste gases has to be processed through a scrubber where molten sulfur is used to observe the elemental S₆ gases right.

So, actually these reactors are inbuilt with the internal condensing and cooling options, but; however, for the easier understanding they are shown like this ok. So, now the products from the condenser are taken to the sumps right from here molten sulfur can be taken to the scrubber. So, that to recover more S₆ from the waste gases before releasing the waste gases to the vent ok.

Once the S₆ is also absorbed on this scrubber, so they will be back taken back to the sump again and then if you wanted to do the solidification this molten sulfur would be taken to the such respective units or if you wanted to store it in a molten sulfur form then they will be taken to a molten sulfur container, which is steam heated equipment ok. By this process here because of these two reaction because of the two reactors using the yield is 90 to 95 percent ok.

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• H_2S and air burned as per reaction: $H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O$

• This SO_2 further oxidizes H_2S by reaction: $4H_2S + 2SO_2 \xrightarrow{Al_2O_3} S_6(g) + 4H_2O$

• For above reaction, a two-stage catalytic converter with intercooling and condensing provision is often used

• Final waste gas is scrubbed with molten sulfur

• Major engineering problems:

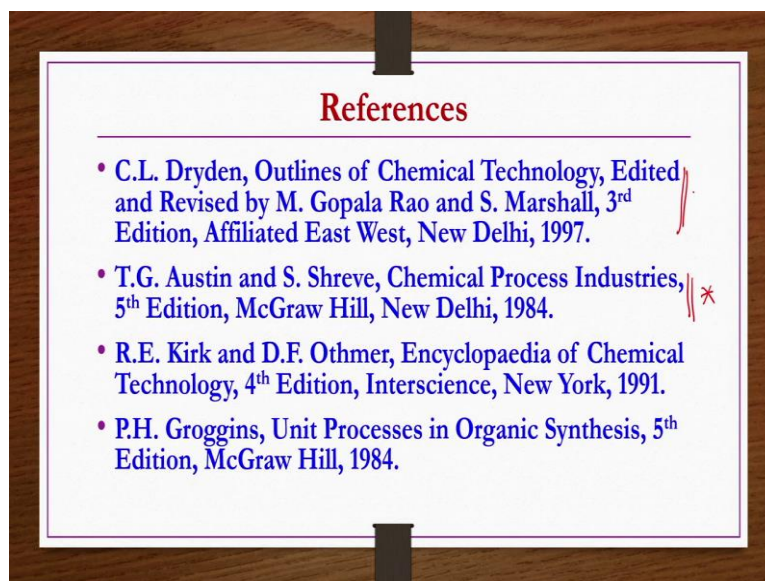
- (a) two-stage reactor design for exothermic SO_2 oxidation of H_2S ✖
70 – 80% conversion in first stage at 300 - 400°C followed by 250 - 300°C operation in second reactor to obtain favorable equilibrium
- (b) heat exchange for molten sulfur handling
- (c) corrosion of equipments
- (d) final clean-up of stack gases

So, if you recapitulate what we have seen elemental sulfur recovery by oxidation of H_2S process. H_2S and air burned as per reactions this one first reaction A and then this SO_2 further oxidizes H_2S by this reaction to give elemental sulfur S_6 in gases form. For above reaction two-stage catalytic converter with inter cooling and condensing provisions are often used.

Final waste gas is scrubbed with molten sulphur, then engineering problems two-stage reactor design for exothermic SO_2 oxidation of H_2S is very much challenging problem. 70 to 80 percent conversion in first stage occurs at around 300 to 400 degree centigrade followed by 250 to 300 degree centigrade operation in the second reactor to obtain favorable equilibrium. This is one important challenge accordingly one has to do the calculations.

Then heat exchange for molten sulfur handling is another problem then; obviously, corrosion of equipments wherever this kind of components like sulfur, sulfuric acids are there, so corrosion is very big problem. Then final cleanup of stack gases is another engineering problem one has to take care.

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Coming to the references for this lecture are provided here, but; however, all these details can be found in these two references.

Thank you.