Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 22
Thermochemical Cycles for Hydrogen Production

Earlier we have learned about the Hydrogen Production methods from hydrocarbon based feedstock, from biomass. Hydrogen when being produced from all these feedstock releases lot of emissions and these are released into the environment. The advantage of hydrogen as a green energy carrier is diminished if so much of emissions are released into the environment.

Now, one of the method for producing hydrogen could be producing from water, splitting up of water.

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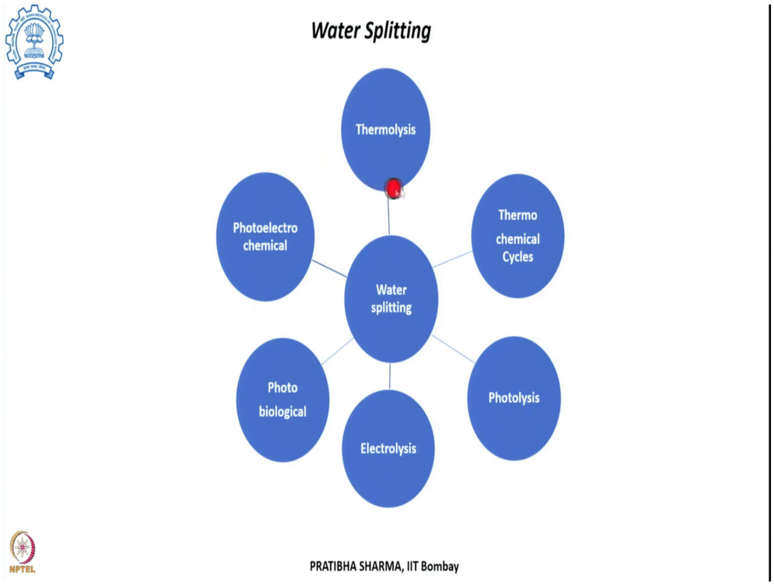

The energy which is required for water splitting can either come from heat, then the process is called thermolysis. That is the splitting up of water when subjected to heat if it occurs by means of both heat as well as certain chemical steps involved in between and thermo chemical cycles.

By means of light, that much amount of energy is being provided then photolysis. With electrical energy input electrolysis, if occur in the biological systems with the help of light photo biological. Certain electrochemical processes occurring with the help of light then photoelectro chemical processes.

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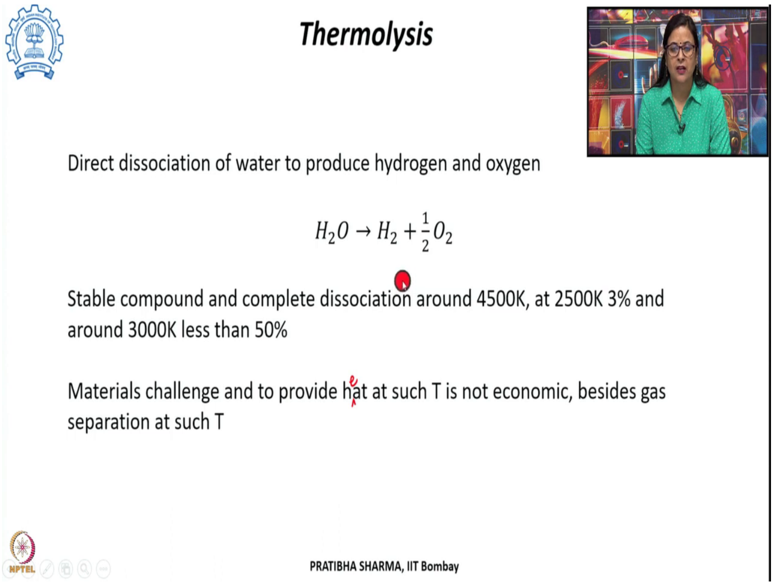

Now, when hydrogen is being produced from water splitting the only products are hydrogen and oxygen. So, the resulting emissions which were there in case of hydrocarbon based methods of production are not there when it is being produced from water, but that all depends upon where from the energy which is required for splitting the water comes from.

For example, if we look at the process which is thermolysis which involves direct dissociation of water to produce hydrogen and oxygen, a large amount of heat is required for this dissociation. The reason being water is a stable compound. It is inert. It is in a lower energy state. So, lot much amount of heat is required for it to break.

And if we want this complete dissociation of the hydrogen to occur that occurs around 4500 K temperature. At 2500 K of small amount and about 50 percent of it dissociates of the amount which has been taken dissociates around 3000 K. So, as such we can see that it is a very high amount of heat which will be required, if we want to directly spit water in one step reaction.

And that all will lead to lot many challenges which could be in terms of the materials challenge, to contain that heat and to provide that heat at such a high temperature, definitely it is not economical. Besides at that temperature when we are getting hydrogen and oxygen that separation so that it does not form an explosive mixture is also essential.

So, if we want hydrogen from water using the single step thermolysis process it has several challenges.

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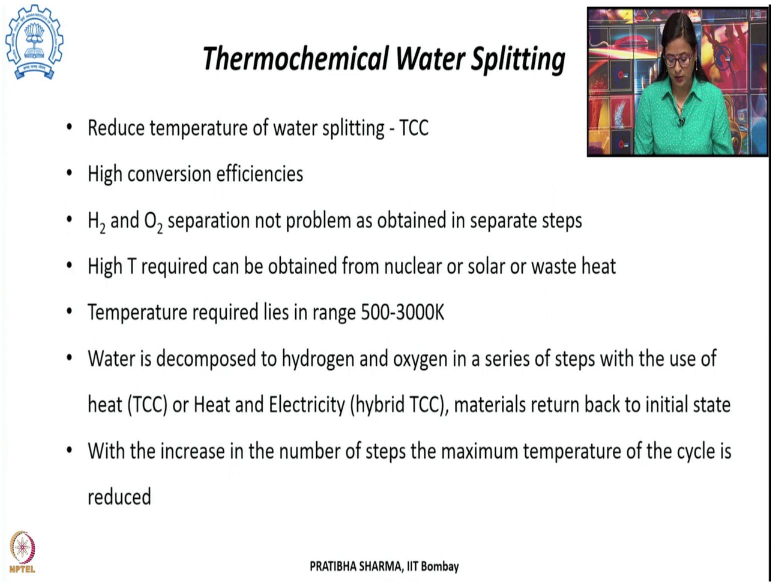

Now, what could be the alternate is thermochemical water splitting. What do we mean by thermochemical water splitting? In thermochemical water splitting there occurs a multiple step reaction, a series of reaction wherein certain chemicals, they undergo a series of processes, they are recycled back to their initial stage. However, the water which is being fed in the reaction that undergoes a splitting to form hydrogen and oxygen, that is what is thermo chemical water splitting.

With the use of thermochemical water splitting the temperature of thermolysis could be reduced. So, this thermo chemical cycles it is in short represented by TCC, these cycles are known to have higher conversion efficiencies. Although the theoretical efficiencies of these cycles are high, but when it comes to actual situations the there are many losses involved as such the efficiencies reduces.

At the same time, since the hydrogen and oxygen is being produced in separate steps as such the separation is not a problem when we are considering thermochemical water splitting. And the required heat for carrying out the reactions that can be obtained from either a nuclear reactor or from the solar thermal plant or it could be obtained from the waste heat or a process heat plant.

In fact, the temperature which is required in the processes depending on which thermochemical cycle is considered it vary between 500 to 3000 kelvin. So, the entire process is wherein water decomposes into hydrogen and oxygen through a series of step and if that involves only heat then it is thermo chemical cycle. If it involves heat and another mode of energy, whether it is electricity or photonic then it is called a hybrid thermo chemical cycle.

And in the entire process the chemical the material which is being used that comes back to its initial stage and splitting water evolving hydrogen in the process. It is also observed that as the number of steps in the thermochemical cycle increases, that step which is having a maximum temperature that maximum temperature also reduces.

So, with the increase in the number of steps in the thermochemical cycle the maximum temperature of the cycle it reduces.

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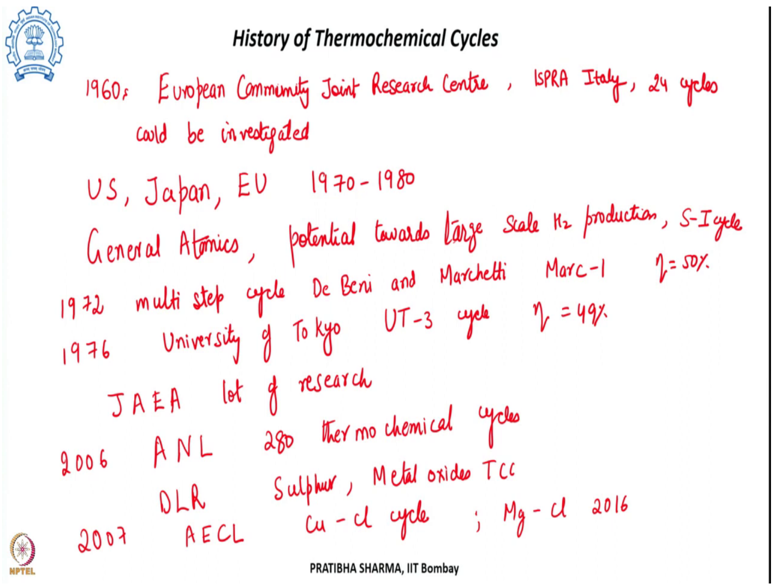

To look back, into the history of these thermo chemical cycles, so, the early work it started in somewhere 1960s, where European Community Joint Research Centre, ISPRA located in Italy. They identified proposed effect more than 200 cycles, out of that they identified about 24 cycles which could be investigated, which could be taken up for further investigation.

And this was for a period between 1970 and 1983. This was the beginning of the studies on thermochemical cycles and thereafter contributions came from various studies in Japan, US and various other European Union countries in the year between 1970 and 1980. So, about 200 thermo chemical cycles were identified by general atomics and only few of them had the potential towards carrying them forward for large scale hydrogen production.

By general atomics one of the most well known cycle, which is the sulphur iodine cycle was being proposed and it was identified that this can be integrated with the nuclear reactors, which could supply heat at about 900 degree centigrade. It was in 1972 that the first multi step cycle was identified by De Beni and Marchetti. These were called Marc cycles and they had a theoretical efficiency of about 50 percent. In 1976, University of Tokyo they came up with UT-3 cycle that was predicted to have an efficiency of 49 percent having calcium, bromine and iron.

It was in by Japan Atomic Energy Agency, lot of research was being carried out. So, most of the research which was carried out on thermochemical cycles that was at the time of 1970s in when oil price shocks were seen, thereafter when the prices of fossil fuels reduced, so the interest went down.

However, certain institutions like in Japan they kept on doing lot of activities on to the thermo chemical cycles. And also in the earlier time the integration for of these thermochemical cycles for getting the required heat was considered towards nuclear energy.

But later with the certain nuclear accidents, so, the interest was towards getting that energy from the solar. It was in 2006 by Argonne National Lab they reported about 280 thermochemical cycles for further studies. It was also in DLR Germany; the German Aerospace Research Centre they worked for two decades on the sulphur base cycles as well as for metal oxide thermochemical cycle.

In 2007, the Atomic Energy of Canada Limited and University of Ontario they along with the Argonne National Lab, they started with the project of the copper chlorine cycle. Ontario Tech they have also demonstrated magnesium chlorine cycle in the year 2016 and there has been numerous research which has been carried out on the various thermochemical cycles.

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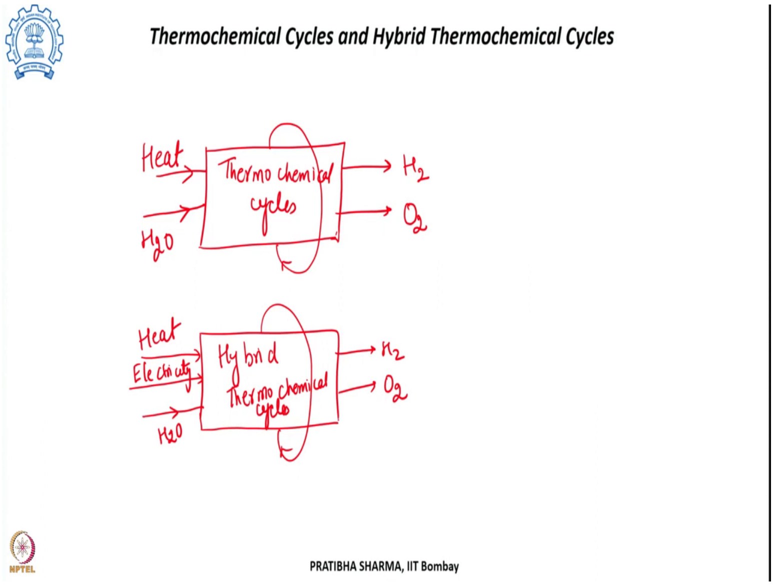

Now, let us understand these thermochemical cycles little better. In the thermochemical cycles, the input which is supplied is heat, it could be either from the nuclear reactor or it could come from the concentrated solar power and water. The materials or chemicals water whatever are being used they get recycled back to their initial stage producing the two products which is hydrogen and oxygen.

So, this is a pure thermo chemical cycle, however if this required input also comes in the form of heat, electricity along with water and we get output as hydrogen and oxygen again the materials undergo a complete cycle. Then these are known as hybrid thermo chemical cycles.

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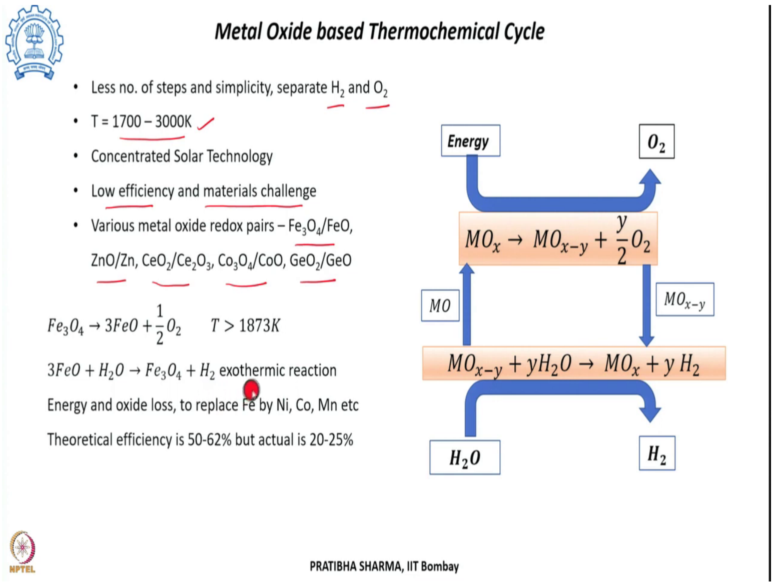

Let us start with the simplest thermochemical cycle which is a two step process involving various metal oxides. The interest in these metal oxide based thermo chemical cycles is because the number of steps involved in the process are only two these are simple. And they produce hydrogen and oxygen separately as such the separation of the two gases is not a problem.

However if we see the temperature of operation for these cycles is high; 1700 to 3000 kelvin temperature and this temperature could be obtained from concentrated solar technology using, heliostats various heliostats concentrating on to a receiver with a tower on the receiver cavity. And that could be used for undergoing these type of thermochemical cycles.

But since the temperatures involved are very high there will be losses involved heat losses, the efficiency is relatively lower. And then there are materials challenges when it comes to getting so, such a high temperature. For this particular cycle there are various metal oxide redox pairs which have been studied; iron oxide, zinc oxide, cerium oxide, cobalt oxide, germanium oxide.

Now, let us understand the process first. The metal oxide in its higher oxidation state or higher valence state, it undergoes a reaction in such that it goes into its lower oxidation state and producing oxygen. So, it undergoes a sort of reduction producing oxygen in the process this is basically the endothermic process and usually the limiting process wherein energy is required and oxygen is being produced in the process.

Now, this metal oxide which is in its lower valence state, it undergoes a hydrolysis reaction wherein oxidation occurs and the metal oxide it comes back to its initial stage. So, it reaches its, to its initial higher valence state producing hydrogen in the process. So, the input here is water and what we are getting out is hydrogen. So, the material which is metal oxide completes its full cycle coming back to its initial state producing oxygen and hydrogen in the process.

Now, among the various metal oxide redox pairs which are known and well studied includes the iron oxide pair where Fe_3O_4, it converts into either FeO or elemental metallic iron and produces oxygen. The temperature of this reaction is high 1873 kelvin. The FeO again reacts with H_2O, to produce Fe_3O_4 back and hydrogen, this is slightly exothermic reaction.

Now, the major issues with this reaction are that since it involves very high temperature there are energy losses, at the same time there are oxide the materials related losses. So, the possible variations could be to replace iron by means of either zinc, nickel, cobalt or manganese.

Although the theoretical efficiency of this cycle is high 50 to 62 percent, but in actual practice this is because of these losses involved, it is restricted to 20 to 25 percent. The another metal oxide based thermochemical cycle which is studied and known is a zinc oxide based cycle.

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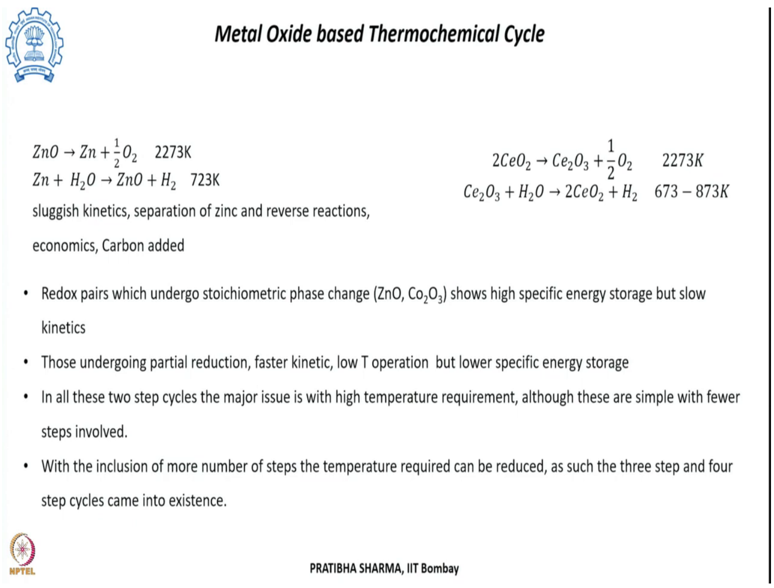

Wherein the zinc oxide at a temperature of 2273 kelvin converts into zinc metal producing oxygen in the process. Now, this zinc undergoes hydrolysis to produce zinc oxide. So, it undergoes an oxidation process producing hydrogen in the second step. The second step is a lower temperature step taking place at 723 kelvin.

So, this zinc oxide based step this is the zinc oxide based cycle this is efficiency which is higher, but then there are challenges like the kinetics of the process is slow. And then the separation of the zinc is a problem then there are reverse reactions that can also occur. So, the economics also is not very favourable.

So, the suggestion was that if carbon can be introduced in the cycle in that case there could be certain some of these challenges could be addressed. Cerium oxide based metal oxide, when it undergoes the reduction reaction produces Ce_2O_3 and oxygen. This first step occurs again at 2273 kelvin, this Ce_2O_3 again comes back to its initial stage when reacting with water and producing hydrogen.

So, this second step occurs at 673 to 873 kelvin. So, these are some of the representative metal oxide based thermochemical cycles which involves two step. These are oxidation reduction type of reactions. But the temperatures involved in the one of the cycles which is the endothermic cycle are substantially high.

Now, it was observed that some of the redox pairs of these metal oxide, which undergoes complete stoichiometric phase change. Like in case of zinc oxide or cobalt oxide there is a high specific energy storage obtained, but the kinetics is slower. For those metal oxides which undergo partial reduction the kinetics although is faster, these are involve low temperature operation, but then the specific energy storage is comparatively lower.

In these two step cycles the major challenge is the high temperature step. One of the step involves very high temperature. And the advantages being that these are simple in nature and the number of steps involved is few. With the inclusion of more number of steps, now this disadvantage which is the high temperature step existing, this can be addressed if number of steps are increased.

And it is observed that if more number of steps are there then the temperature requirement of the endothermic reaction or the maximum temperature of the cycle can be reduced. So, because of that various other cycles came into existence. So, the other cycles which were having either three steps or four steps or five steps or more they came into existence because of addressing this disadvantage of the two step process.

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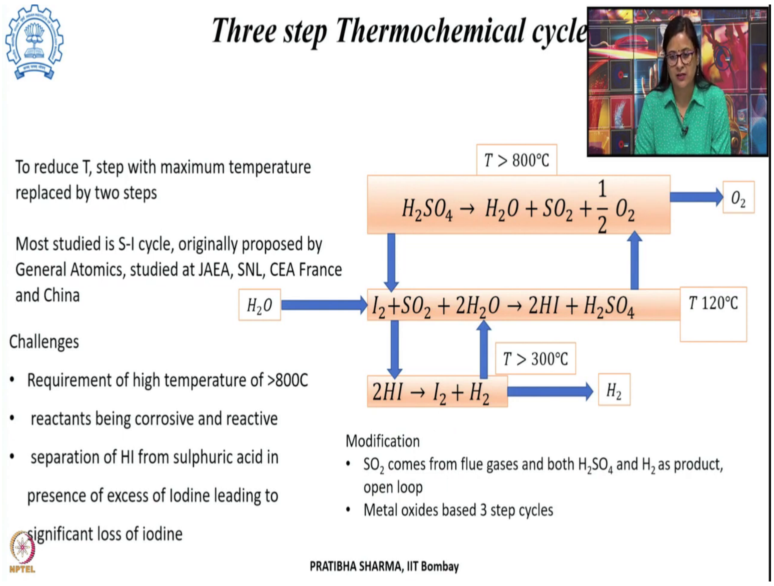

If we look at the three step thermochemical cycle again the reason is that the maximum temperature involved in the two step process was very high. To reduce that this three step thermochemical cycle was identified. There are various such thermochemical cycles and the most studied one is the sulphur iodine cycle.

This was actually being proposed by the general atomics, but later on it was studied by Japan Atomic Energy Agencies, Sandia National Lab and the Centre for Atomic Energy France and China. In the process, if we try to understand in the first step wherein sulfuric acid formation occurs from iodine SO2 and H2, it forms hydrogen iodide and sulfuric acid.

So, this is the low temperature process, where the temperature is about 120 degree centigrade producing sulfuric acid as well as hydrogen iodide. Now, this sulfuric acid which is produced this undergoes a decomposition step, that is the second step producing water, SO2 and oxygen.

So, this is actually the oxygen evolution step or oxygen generation step wherein sulfuric acid at a very high temperature, above 800 degree centigrade it disintegrates to produce SO2 and oxygen. Now, there is a third step wherein the hydrogen iodide which is being produced in the second step that decomposes to give iodine and hydrogen. This step occurs at a temperature higher than 300 degree centigrade. Now, this is the hydrogen evolution step where hydrogen is being produced.

So, overall the maximum temperature of the endothermic step has reduced, but still this is higher when it comes to providing that heat input. So, the major challenges associated with three step cycle is, that the temperature involved is still higher, higher than 800 degree centigrade. The reactants which are involved in the process they are corrosive and reactive, so their handling is a problem.

Besides in this step, the separation of hydrogen iodide from the sulfuric acid when it is occurring in the presence of excess of iodine that leads to significant loss in the iodine. Now, this cycle however can be modified and the modifications that were suggested is that this process which is leading to sulfuric acid decomposition which is taking place at a higher temperature can be made such that this input SO2 which is required in the process can come from flue gases.

So, in that case the sulfuric acid may come up as a product along with hydrogen and the required SO2 can come from the flue gases. So, the cycle becomes instead of closed cycle it becomes an open loop. Other than that the other modification suggested is that we can also introduce a third step in the two step processes, that we have seen that was metal oxide based.

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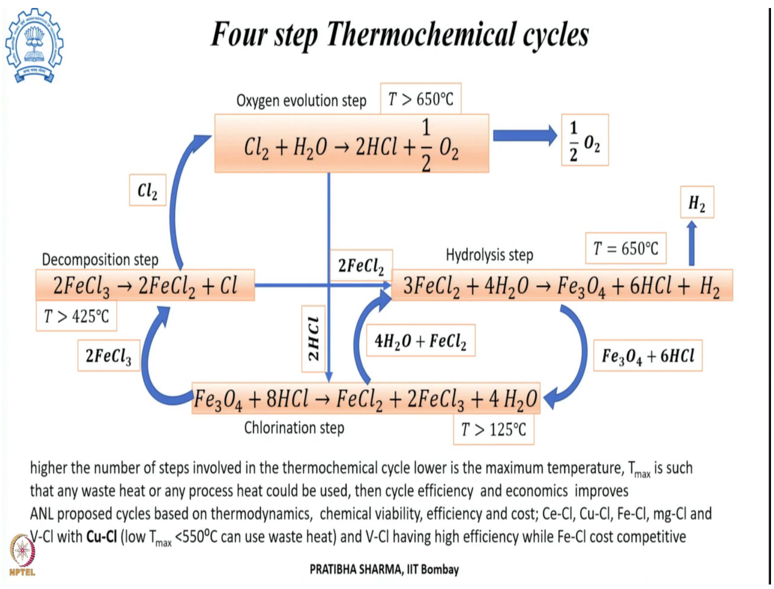

Now, if we include one more step then, so, we know that higher the number of steps involved in the thermochemical cycle lower will be the maximum temperature required in the endothermic step. And if it gets so much lower that if any waste heat or process heat which is available, the industrial waste heat in any of industrial processes, if that could be used for the thermo chemical cycle then the economics as well as the efficiency works very well.

Let us look at one of these such four step cycles. So, there are several such four step cycles, which have been studied, identified and some of these demonstrated already. The FeCl2 which is being produced is from Fe3O4, so that is the chlorination step reacting with HCl produce FeCl2, FeCl3 and H2O. This is however, a lower temperature step which takes place at slightly higher than 125 degree centigrade.

Now, the FeCl2 which is produced undergoes a hydrolysis step producing Fe3O4 and HCl and producing hydrogen. So, the first step is chlorination step, second step is this hydrolysis step. The FeCl3 which is produced undergoes a decomposition step reducing FeCl2 and chlorine.

This occurs at a temperature higher than 425 degree centigrade. The chlorine which is being produced undergoes oxygen evaluation step to convert into HCl and oxygen. And in this process oxygen is being produced. This process occurs at temperature higher than 650 degree centigrade.

So, if we can see in this way the maximum temperature of the step is lower compared to the three step cycle. Now, Argonne National Laboratory they proposed many cycles based on the thermodynamics, their chemical viability whatever chemicals we are using, so, how viable is the cycle based on those, based on the efficiency, based on the cost. Some of these cycles are like cerium chlorine cycle, copper chlorine cycle, iron chlorine cycle, magnesium chlorine cycle and vanadium chlorine cycle.

Now, if we look at these among these cycles iron chlorine cycle that we have just now seen, this is economical the cost involved is lower. The vanadium chlorine cycle, the efficiency for vanadium chlorine cycle is higher. And for copper chlorine cycle, the required maximum temperature is lower, it is less than 550 degree centigrade. Such that any of the waste heat from any industrial plant can be utilized for undergoing the copper chlorine cycle.

So, that is the biggest advantage of this process.

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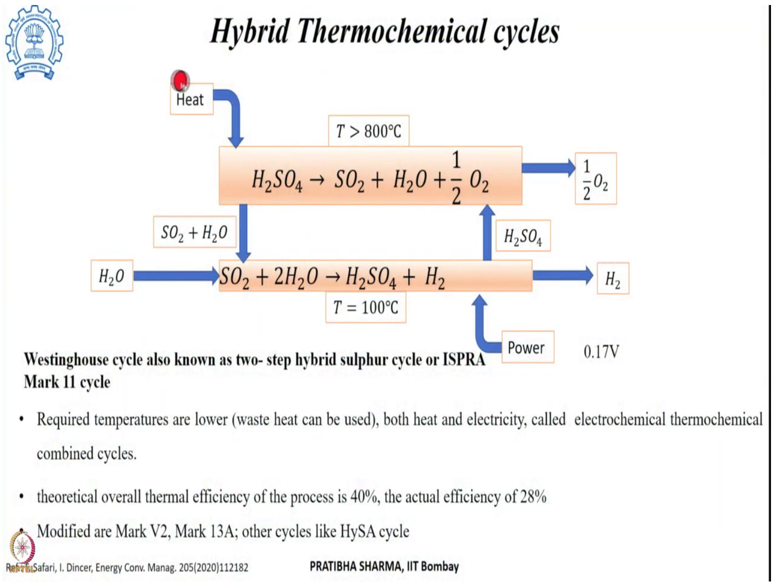

If you look at the hybrid thermal thermochemical cycle as I mentioned that other than the heat input, there could be input in terms of either electrical energy input or it could be photonic also with terms of from light. So, here this is one of the modified sulfuric acid cycle which involves only two steps. The first step where sulfuric acid it decomposes to give SO2, H2O and evolves oxygen, so producing oxygen.

This step occurs for temperatures higher than 800 degree centigrade and the SO2 which is produced in the first step that undergoes a hydrolysis to produce sulfuric acid again and hydrogen is being evolved. Now, this is the power requirement. The electrical power requirement is very low as against the requirement in case of electrolysis. It is a voltage of 0.17 volt as against 1.23 volt in case of electrolysis.

The second step is taking place at very low temperature. It is about 100 degree centigrade and this cycle is also a two step hybrid sulphur cycle, which is also known as Westinghouse cycle or ISPRA Mark 11 cycle. This requires temperature which is lower and waste heat can be used both heat and electricity since are being used in the cycle, that is why this is also known as electrochemical thermochemical combined cycle.

The theoretical efficiency of this process is 40 percent; however, the actual efficiency obtained was 28 percent. There were modifications to this cycle which was in terms of Mark V2 and Mark 13A. In Mark V2 other than hydrogen sulphide, hydrogen bromide was used, while in Mark 13A cycle SO2 it came from the flue gases that was an open cycle and various other hybrid cycles are existing.

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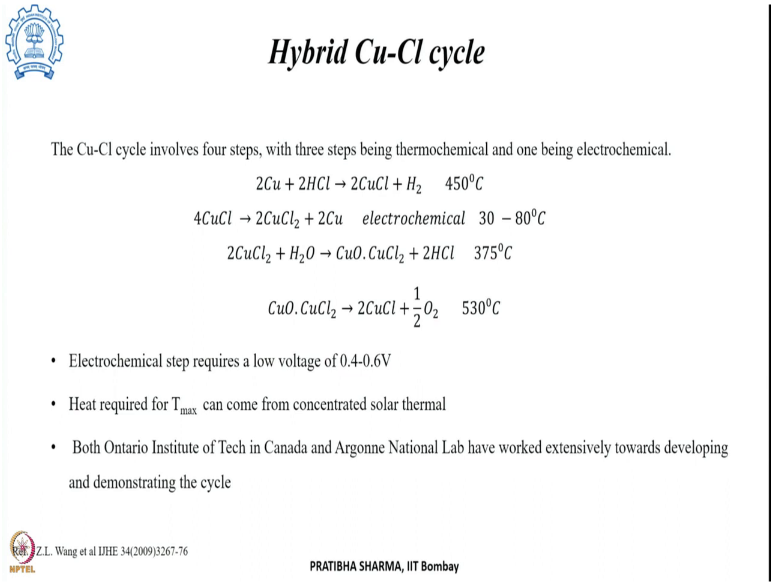

One of such cycle is the hybrid copper chlorine cycle. This involves four steps and these out of these three step one, three and four these are thermochemical steps and the second one is an electrochemical step. So, copper reacting with HCl produce CuCl, this occurs at a temperature of 450 degree centigrade.

This undergoes a reaction to produce CuCl2. This is an electrochemical reaction taking place between 30 to 80 degree centigrade. The CuCl2 reacts with water to produce CuO CuCl2 and HCl taking place at 375 degree centigrade. This compound again produces CuCl and oxygen at a temperature of 530 degree centigrade. So, the first step is the hydrogen evolution step and the last step is the oxygen evolution step. Now, this electrochemical energy input requires a very low voltage of 0.4 to 0.6 volt.

And the maximum temperature we can see is low; 530 degree centigrade and this can come from a concentrated solar thermal power. Both Ontario Institute of Technology in Canada and Argonne National Lab they have worked extensively towards developing and demonstrating this cycle.

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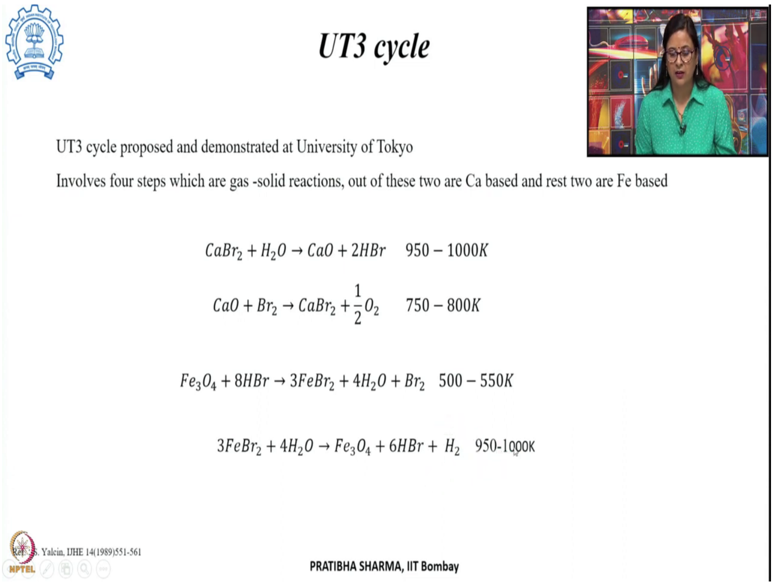

Another cycle is UT3 which was proposed and demonstrated by University of Tokyo as such the name comes from the University of Tokyo UT. So, UT3 cycle this involves four steps and these are gas solid reactions. Out of these two are based on calcium and rest are based on iron. So, calcium bromide CaBr2 reacting with water to produce calcium oxide and HBr at 950 to 1000 K.

This CaO produced reacts with bromine to produce CaBr2 and oxygen. So, oxygen is being released at a temperature of 750 to 800 kelvin and calcium bromide is again produced back. Iron oxide Fe3O4 reacting with the HBr to produce 3FeBr2, H2O and Br2 taking place at 500 to 550 kelvin. And this FeBr2 reacts with H2O to produce back Fe3O4, 6HBr and H2. This is the hydrogen evolution step taking place at 950 to 1000 kelvin.

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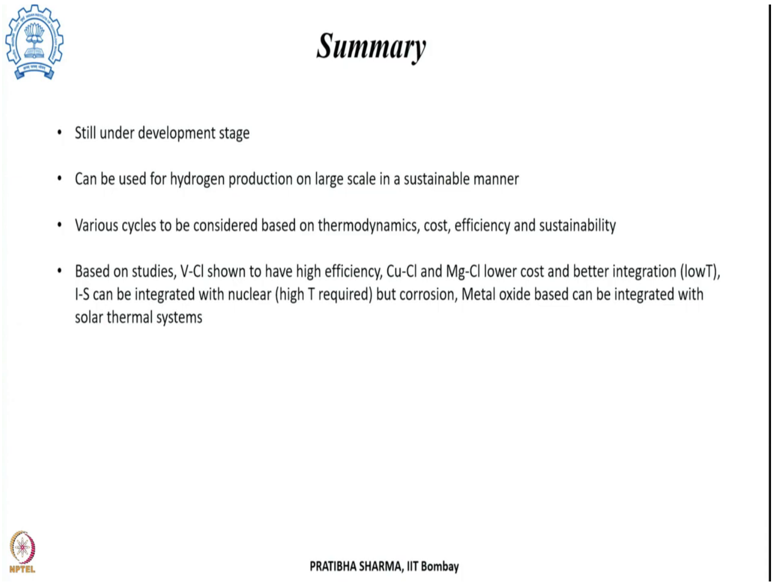

So, these are some of the thermochemical cycles. Although we know that there are large number of cycles which have been proposed, some of them they have got to the developmental stage some of them they have also been demonstrated experimentally. These thermochemical cycles they have an advantage that they can be integrated with renewable energy input and then hydrogen can be produced on a large scale in a sustainable manner.

Now, when we consider the various cycles involved this needs to be considered on the basis of what is the thermodynamics of the process, what is the cost associated with the materials with the systems involved, what is the efficiency that could be obtained and how much sustainable these cycles are. Now based on the various studies that have been carried out, the vanadium chlorine cycle is known for its higher efficiency, copper chlorine, magnesium chlorine they are cost effective.

At the same time since the temperatures involved are lower, so they can be integrated with the renewable energy. Either they can be integrated with solar thermal, iodine sulphur, this the temperature requirement since it is higher these can be possibly integrated with nuclear power plants. But then there are challenges like the corrosion involved and then the metal oxide cycles that we have seen they can be integrated with the solar thermal system.

So, this is about the thermo chemical cycles.

Thank you.