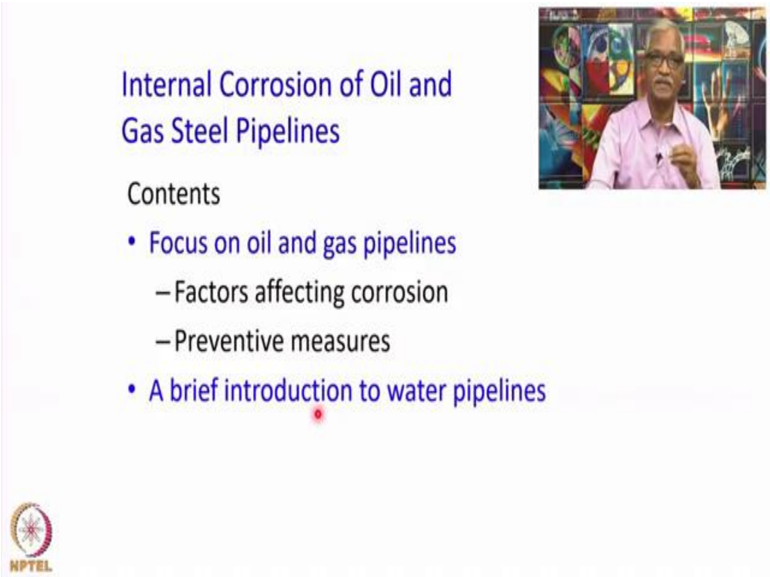
Cathodic Protection Engineering
Prof. V. S. Raja
Department of Metallurgical Engineering and Materials Science
Indian Institute of Technology, Bombay

Lecture – 13
Internal corrosion of oil and gas steel pipelines

(Refer Slide Time: 00:24)



Hi, welcome to this online course on Cathodic Protection Engineering. In this lecture, Internal corrosion of oil and gas pipeline is not directly related to cathodic protection; the methodologies adapted for cathodic protection engineering is entirely different from the methodologies to control corrosion of pipelines internal surfaces.

However, it is very relevant to these structures; because whether it is a pipeline or it is a storage tank, they face corrosion externally due to soil and internally due to the various products that they transport in the case of pipelines or stored in the case of the storage tanks.

So, a perspective of understanding the internal corrosion of these structures is somewhat useful and therefore, I will give you a broad outline of the internal corrosion of the pipelines in this lecture.

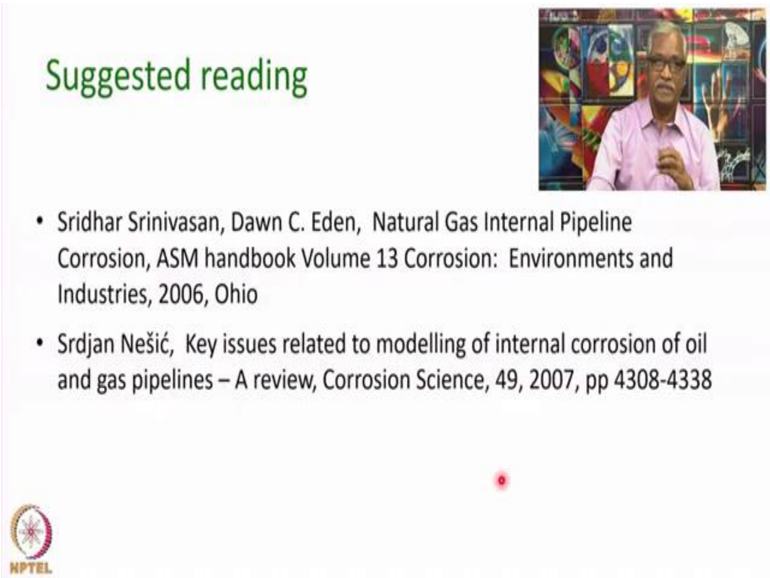
In another lecture, we will be talking about the internal corrosion control as the anodic protection methodology, especially as applicable to the sulphuric acid plants. When you talk about the internal corrosion of storage tanks; there are variety of chemicals being used, so it is not possible to cover the internal corrosion of the storage tanks.

When it comes to internal corrosion of the pipelines, the 2 major kind of pipelines are there; one the transport oil and gas, other one the transport water. The oil and gas pipelines when they corrode, the consequences are very severe; safety is involved, environment is involved.

So, a lot of measures are taken in order to control the internal corrosion of pipelines in the case of oil and gas. Not only that, because it is an oil and gas, we have the flexibility to change by adding additives; but that is not possible in the case of water.

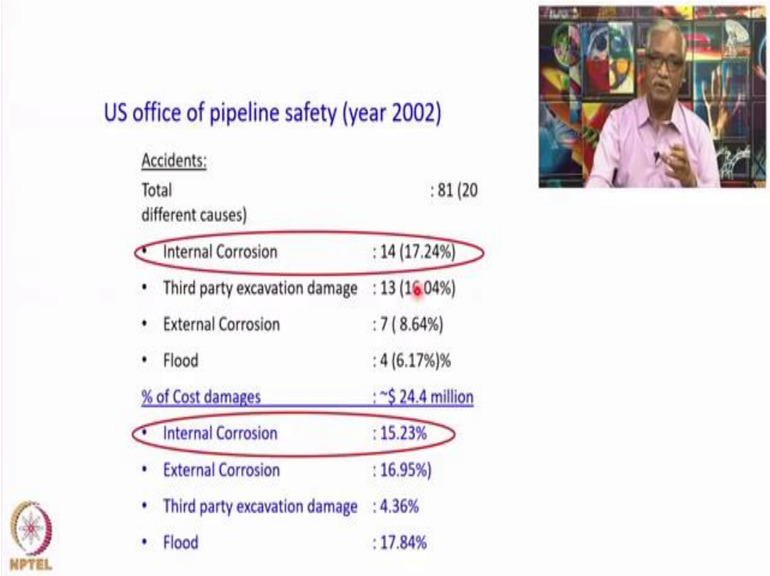
So, in this lecture, we will be briefly talking about the factors affecting corrosion as far as the oil and gas pipelines are concerned and then we briefly touch upon the preventive measures. Very briefly in about 3 or 4 slides, we will talk about what are the factors that affect the corrosion of the pipelines.

(Refer Slide Time: 03:01)



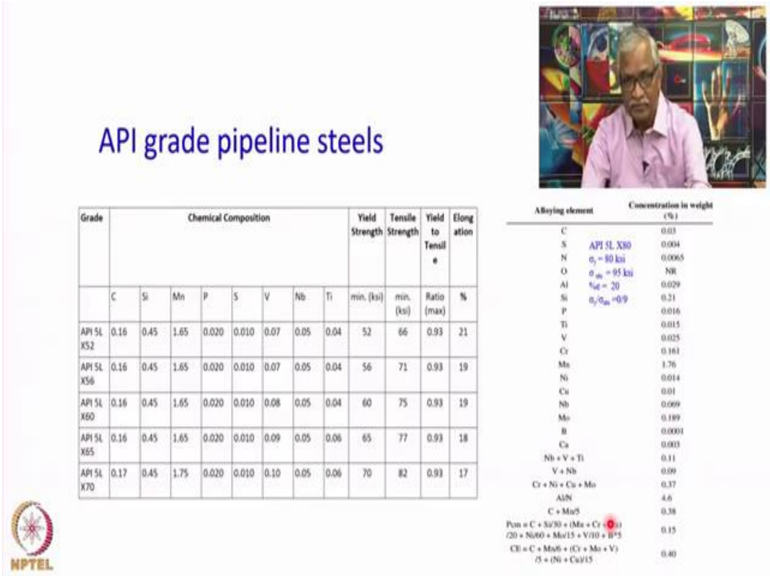
These are the suggested readings for the oil and gas corrosion of pipelines. One is the excellent chapter by Sridhar Srinivasan and Dawn C Eden; you can find them in the ASM handbook Volume 13 C of Corrosion handbook. There is a nice review by Professor Nesic on the internal corrosion of oil and gas pipelines; he focuses, he gives focus on the modeling aspect of the internal corrosion and as well as monitoring of the internal corrosion of the pipelines.

(Refer Slide Time: 03:47)



Let us look at how important it is the internal corrosion pipelines, we have seen this in the earlier lecture as well. If you look at the number of cases appearing in terms of failures attributable to internal corrosion, it is about 17.24 percent as per the US office of pipeline safety, that appeared in the year 2002. However, if you look at the cost of damages occurring due to internal corrosion pipelines, it is about 15.23 percent. So, its a significant amount of loss that happens because of the internal corrosion of the pipelines.

(Refer Slide Time: 04:39)



Now, before we go into the internal corrosion of the pipelines, it is better to have some brief idea about what are the materials used in the pipelines. When I say pipelines, I refer this pipelines by default to oil and gas pipelines.

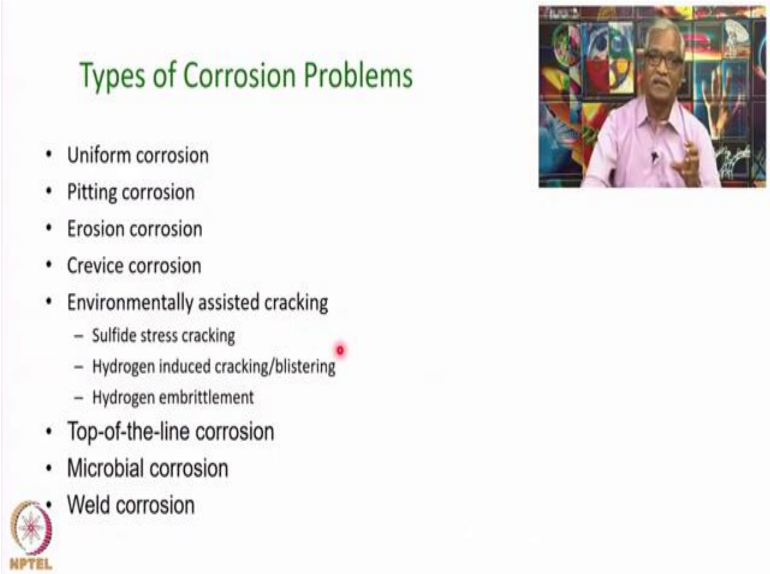
The oil and gas pipelines are given this API grades and you see here API for example, X 52; it this 52 refers to the yield strength given in terms of ksi strength units. So, the pipelines of various strength levels have been developed in order to make them lighter, in order to save the weight of the steel required for making the pipelines.

In all these cases you would notice that, the chemistry of the steels that are employed here, there is not very significant change. Since the chemistry is not changed very significantly, you will see later that all these pipelines would have a similar corrosion behavior in the oil and gas sector. Subsequently, there has been another steel API 5L X80, where the strength level has gone to 80 ksi and uts value has gone to 95 ksi.

Even over here, there are micro alloying elements in order to increase the strength; metallurgies add to refine the grind structures and also to bring in the phases which are providing higher strength and ductility. Over here too if you look at the composition of the steel; there is hardly significant increase in terms of elements like chromium, which offers passivation.

So, as a consequence, the corrosion behavior of all these steels are very much identical. And so, when you are going to talk about corrosion of oil and gas pipelines, we are not going to distinguish significantly between these steels; there are of course some cases we will see later, certain aspect of corrosion failures they are related to the strength of the pipelines.

(Refer Slide Time: 07:08)

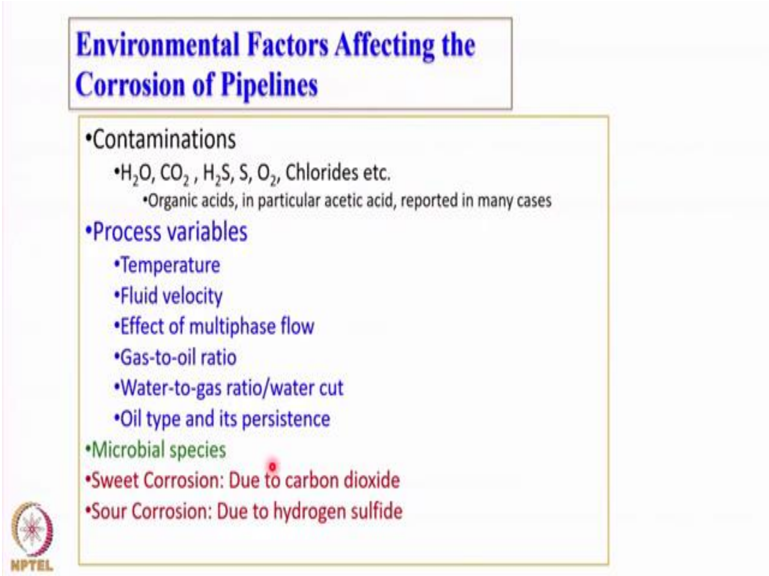


So, these pipelines suffer the variety of corrosion problems and these problems like as simple as uniform corrosion, pitting corrosion, erosion corrosion, crevice corrosion and we also have 3 different types of environmentally assisted cracking. And in this case, the cracking is mainly due to the sulfide stresses; of course in the case of hydrogen induced cracking, we do not require any external stresses for the pipeline to crack. The hydrogen so entered in the steel, produces the pressure and cracking really occurs.

Whereas, in the case of sulfide stress cracking and hydrogen embrittlement, the applied stresses play a dominant role in deciding the susceptibility of the pipeline towards cracking. In addition to these kind of failures, we also have some failures which are specific to pipelines, which are called as top of the line corrosion failure.

And addition to that, we also have microbial corrosion and weld related corrosions; these pipelines are welded and these weldments can suffer preferential attack as compared to the remaining areas of the pipelines.

(Refer Slide Time: 08:41)



Let us move on to understanding what are the factors that affect corrosion of oil and gas pipelines. We all know that the oil and gas, especially let us say crude or maybe the finished products like kerosene or a diesel or a pure natural gas; they are not very corrosive, they are non-polar. How the pipelines suffer corrosion is due to the contaminants present in these products; especially in the crude, you will see significant amount of water, carbon dioxide, hydrogen sulfide, sulfur, oxygen content, and chlorides

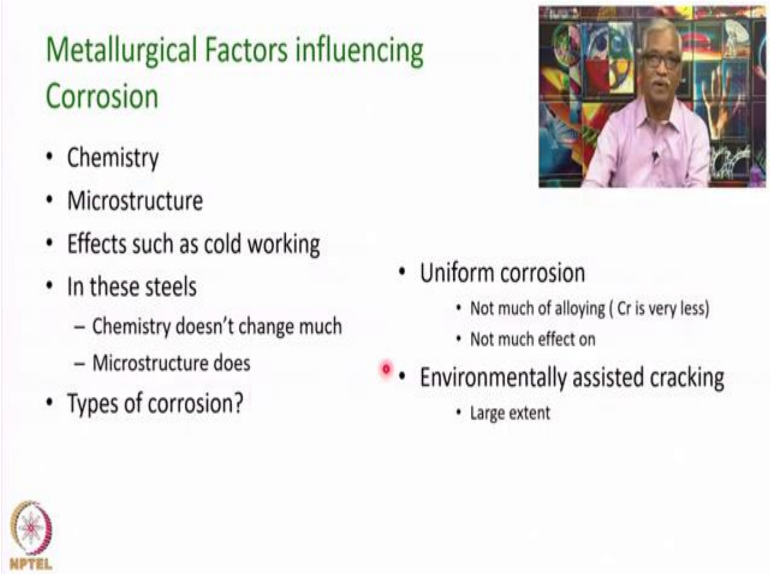
So, these species significantly change the corrosive behavior of so called the crude actually I would say. In addition to these species, sometimes you find some organic acids, which are present may be the result of decomposition of these hydrocarbons, can also affect the corrosion of the pipelines. These are about the contaminants present in the crude.

There are process variables, they also can significantly affect the corrosion, involved the temperature of the product being transferred, fluid velocity and you also have sometimes multi phase flow; it could be gas and a crude or sometimes water the crude, sometimes there are other phases like the acids present in the crude.

Gas to oil ratios and what is the ratio of gas and oil. Water to gas ratios is defined in terms of water cut and the oil type; and how long the oil will persist on the surface of the pipeline? So, these are process variables they significantly affect the corrosion of the pipelines.

The microbes that are carried through these products; they cause significant amount of corrosion, they are called as microbially assisted corrosion, microbial assisted corrosion. There are 2 types of terminologies very commonly used in the pipeline corrosion, which are which is called as sweet corrosion due to carbon dioxide and the sour corrosion that is due to hydrogen sulfide.

(Refer Slide Time: 11:25)



Let us look at the role of metallurgy, how it can affect the corrosion of the pipelines? I would like to look at metallurgy in terms of these parameters; simply the chemistry of the steel, what are the alloying elements added to it; the micro structures, what are the type of phases present; the morphology, the grain size. So, they all constitute the micro structures.

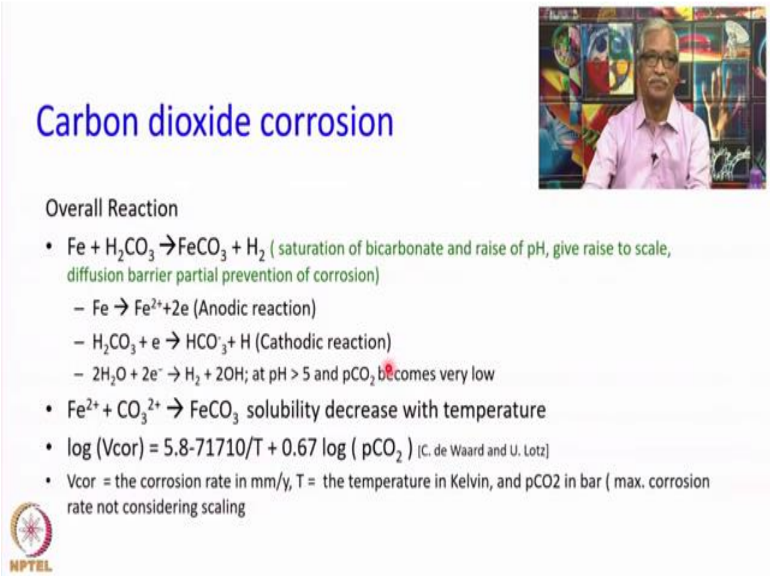
If this is cold worked and deformed for example. And so, these are the factors, we constitute overall we called the metallurgical factors. In this interestingly, if the chemistry does not change significantly; even the microstructures would not affect the corrosion very significantly.

However, there are cases we will see later that, microstructures can affect the other forms of corrosion, the localized forms of corrosion. For example, let us take the uniform corrosion of the steels, not much effect as long as the alloying elements are not changed, ok.

But when you take when you, but when you look at the environmental assisted cracking, we discussed before; like sulfide stress cracking, hydrogen induced cracking or hydrogen blistering or hydrogen embrittlement, microstructures significantly affect the integrity of the pipelines.

The composition may play; the microstructures play a significant role in deciding the resistance of the pipelines towards cracking. We shall now move on to understanding the role of carbon dioxide and the hydrogen sulfide on the corrosion of the pipelines.

(Refer Slide Time: 13:43)



The carbon dioxide corrosion is generally termed as sweet corrosion. And the carbon dioxide, the dry carbon dioxide is not corrosive to steel; however when it dissolves in water, it forms a carbonic acid and the carbonic acid reacts with the steel and forms iron carbonate. The iron carbonate it reaches the saturation and forms a scale on the surface; the scale is a barrier for corrosion and so it offers a reasonable protection against corrosion.

But this is the overall corrosion reaction between the carbonic acid and the iron; but you can also look at the partial reactions that are involved in the corrosion process. The anodic reaction we call an oxidation of the steel is simply iron is getting into Fe 2 plus plus 2 electrons.

$$Fe \rightarrow Fe^{2+} + 2e$$

And the predominant cathodic reaction is the carbonic acid is getting reduced to bicarbonate and then hydrogen gas is liberated.

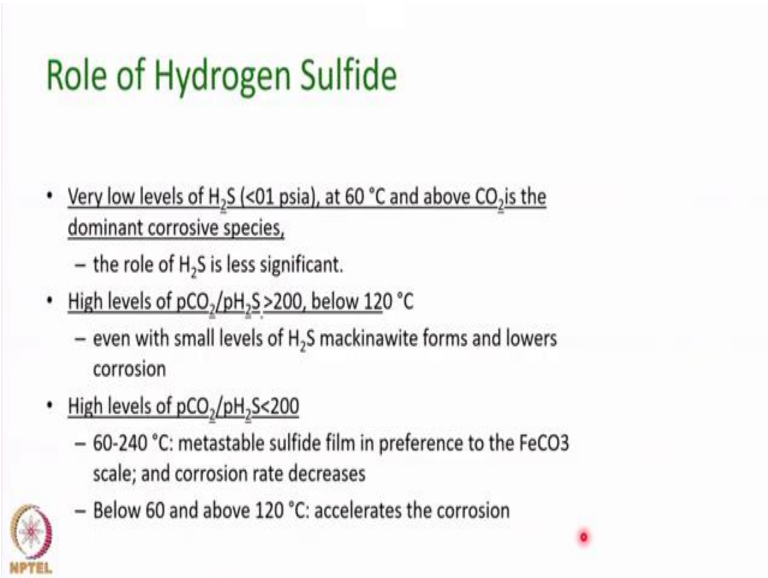
But the pH is going to be higher that happens in the crude; the carbonic acid reduction reaction becomes very low, the predominant reaction in that case becomes the water is getting reduced to form hydroxide and the hydrogen is liberated.

Now, its very interesting to see how this reaction affects the corrosion in relation to the temperature. If you raise the temperature of the process fluid, then the solubility of iron carbonate changes; in fact it becomes retrograde solubility, the solubility decreases when the temperature increases.

So, what happens is, on one hand the rise in temperature increases the corrosion rate; in the other hand the increase in temperature lowers the solubility. So, there are 2 opposing processes happening on the metal surfaces and so, the corrosion goes through the maxima and then the corrosion drops.

The earliest, you know relationship between the corrosion rate of the steel and the carbon dioxide and temperature was given by de Waard and Milliams and then later it was modified by de Waard and Lotz. The equation given here is an empirical relationship obtained by experimental, experiments carried out at the laboratory actually. And you find it is the it is inversely related to temperature and directly related to the carbon dioxide.

(Refer Slide Time: 16:46)



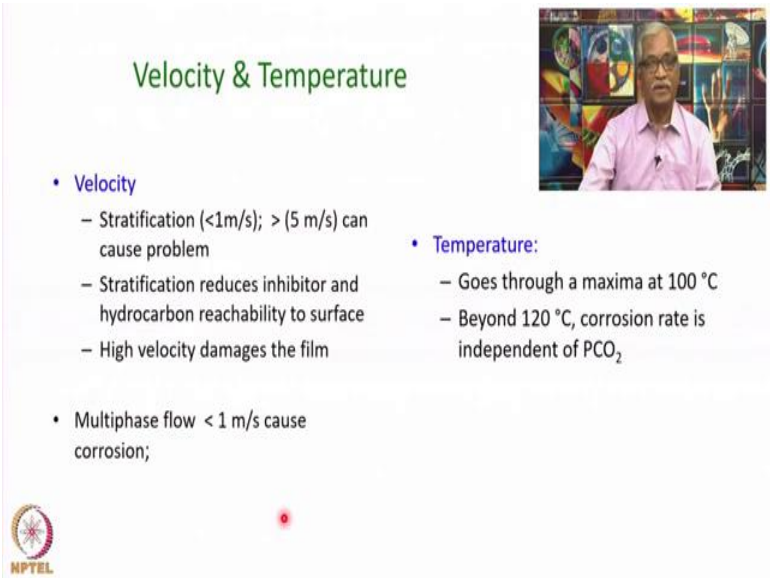
Let us now look at the role of hydrogen sulfide on the corrosion of oil and gas pipelines. As opposed to carbon dioxide, the hydrogen sulfide influences corrosion of pipelines depending upon the concentration of hydrogen sulfide in relation to the carbon dioxide.

At very low levels of hydrogen sulfide at 60 degree Celsius and above, carbon dioxide is very dominant and hydrogen sulfide does not play any significant role in affecting the corrosion of the pipelines.

However, if the carbon dioxide partial pressure is increased and if the ratio of the partial pressure of carbon dioxide to hydrogen sulfide increases beyond 200 and if the temperature is below 120 Celsius, even the small amount of hydrogen sulfide leads to the formation of a phase called as mackinawite. And this is a stable phase forms on the surface and thereby, lowers the corrosion of the pipelines.

Should the ratio of the partial pressure of carbon dioxide and hydrogen sulfide decreases below 200; then these metastable film is formed in preference to the iron carbonate, especially in the range of 60 - 240 degree Celsius and as a consequence the corrosion rate decreases. However, below 60 degree Celsius and above 120 degree Celsius that is in this range ok; the corrosion is accelerated due to the presence of hydrogen sulfide.

(Refer Slide Time: 18:38)



The process parameter namely the velocity and temperature, they have a significant influence on the corrosion of the pipelines. When the flow is closed stratification; that happens when the velocity is less than 1 meter per second or if the velocity is quite large goes beyond 5 meter per second, in both cases the pipeline suffers severe corrosion.

In the case of stratification, that is below 1 meter per second; the increase in corrosion rate is mainly because of the fact that, the added inhibitors they do not reach the surface. And the additional reason is that, the hydrocarbons which prevent the corrosion ok, they also reach less on the surfaces, ok. The formation of a film of hydrocarbon, lowers the corrosion. So, stratification lowers the tendency of the formation of hydrocarbon film on the pipeline surfaces.

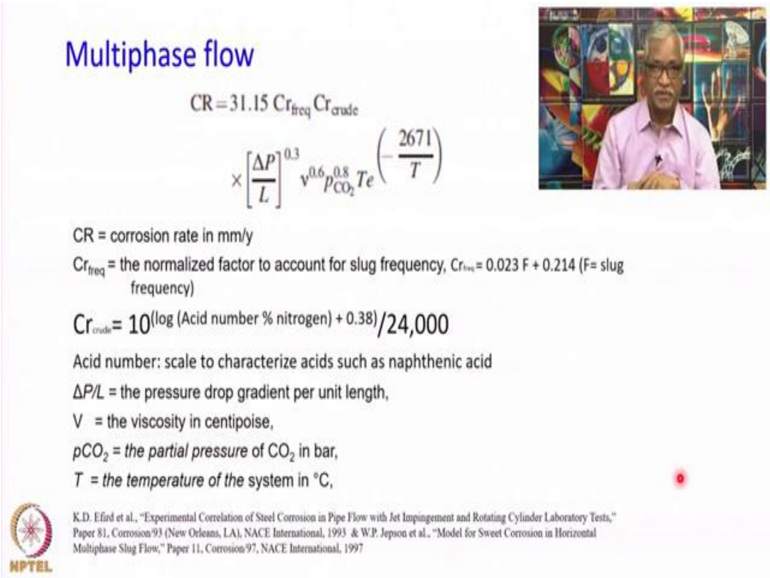
At a higher velocity, of course you will have more tendency for inhibitor to reach the surface so as hydrocarbon; however the velocity is significantly large, it damages the protective films formed on the metal surfaces.

When the flow is multi phase flow, it has got you know gas and as well as the; as well as the liquid; then even the 1 meter per second can cause the corrosion. So, depending upon whether it is a single phase flow or 2 phase flow, the velocity has a significant role in affecting the corrosion of the pipelines.

As we discussed earlier that, the temperature has a very interesting effect, the corrosion rate goes through a maxima; because when you raise the temperature, the solubility of iron carbonate decreases. On the other hand, the rate of any chemical reaction so as corrosion reaction, increases with temperatures. So, when the solubility of iron carbonate decreases with temperature, it has more tendency to form a scale on the surface, so that retards the corrosion process.

So, as a consequence, the corrosion rate goes through a maxima closely about 100 degree Celsius; beyond 120 degree Celsius in fact, it appears that the corrosion rate of the pipeline is independent of the partial pressure of carbon dioxide.

(Refer Slide Time: 21:30)

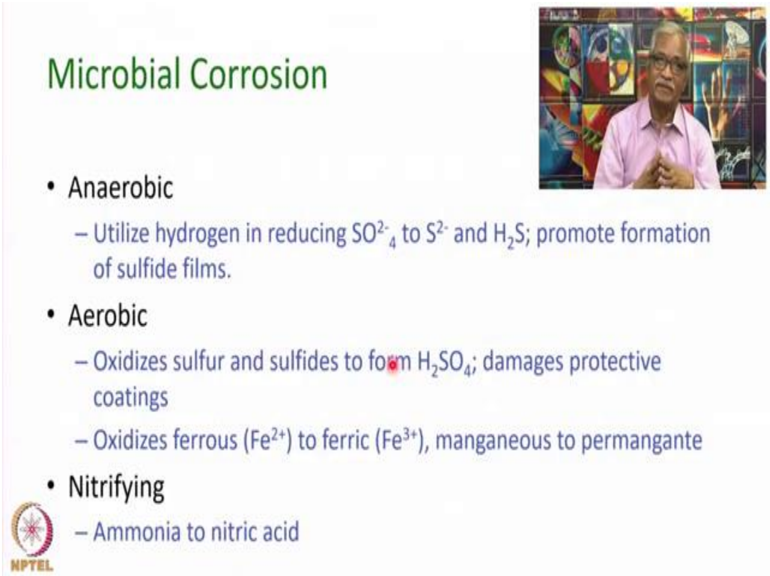


The role of velocity changes depending upon is a multi-phase flow or a single phase flow. This equation that is given here, the corrosion rate is related to the 2 parameters; the parameter Cr_{freq} corresponds to the slug frequency, the Cr_{crude} corresponds to the acid number of the crude.

In addition to these parameters, the partial pressure of carbon dioxide plays an important role and as well as the pressure drop gradient per unit length and of course, the temperature, ok. The viscosity also plays an important role in deciding the corrosion rate of the pipelines.

So, coming to this Cr_{crude} ok, which is related to the acid number of the crude; the acid number means, it characterizes the acid present, acids such as naphthenic acid they increase the acid acidity, they bring down the pH of the crude and so the corrosion rate of the pipeline increases.

(Refer Slide Time: 22:49)

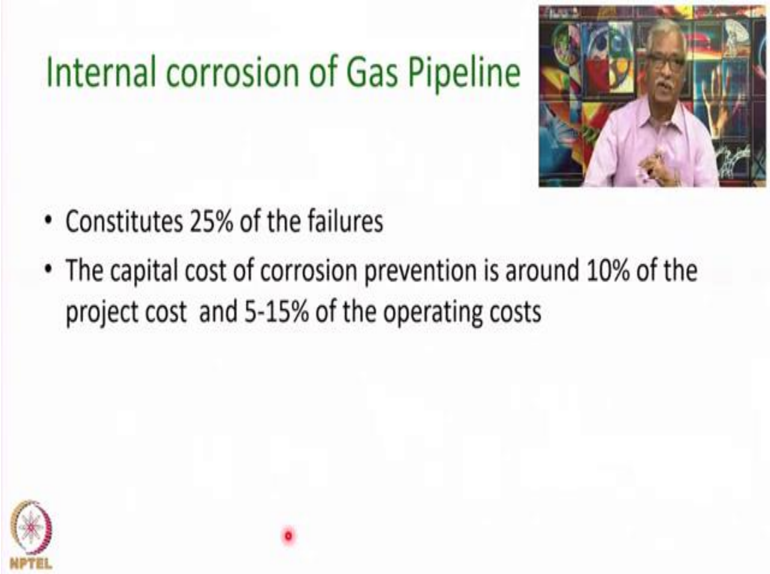


So, we have looked at the chemistry of the crude, how it can affect the corrosion. The other factor that affects the crude oil pipeline is the microbial corrosion. Microbial corrosion is a big subject, we will just briefly look at the 3 important microbes which are responsible for the corrosion of the pipelines. The anaerobic bacteria, that is mostly the sulfate reducing bacteria, it reduces the sulfate to sulfide; it promotes the formation of hydrogen sulfide films on the surface.

Or you can also have aerobic bacteria, which can oxidize sulfur and hydrogen sulfide to sulfuric acid and so can increase the corrosion rate of the pipelines. There are other kinds of aerobic bacteria, one among them is converting ferrous to ferric, and another one is the manganese to permanganate.

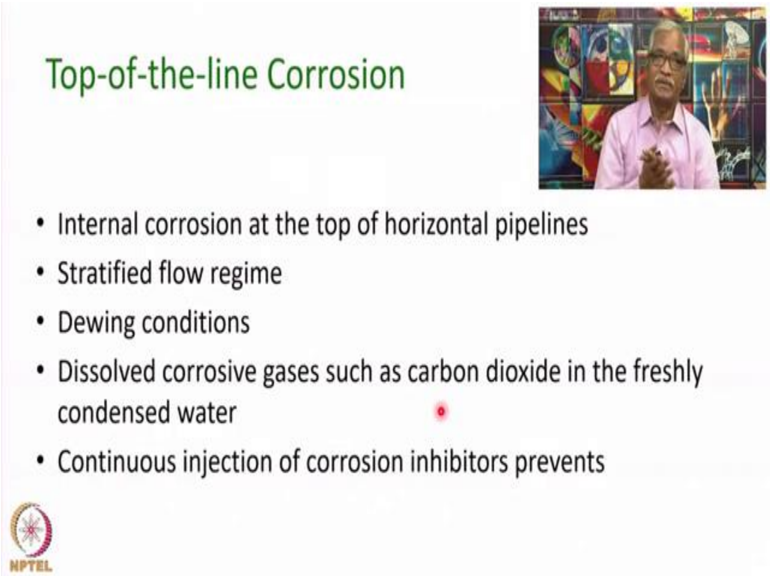
So, these are the predominant ones they affect the corrosion of the pipelines; should there be ammonia present in any of these pipelines, then these bacteria called nitrifying bacteria, they convert ammonia into nitric acid. So, the microbial corrosion is one of the important forms of corrosion affecting the crude oil pipelines or oil and gas pipelines to be called in general.

(Refer Slide Time: 24:23)



So, we talked about the oil gas pipelines. The internal corrosion of gas pipelines are also equally important; in fact in the gas pipelines, the 25 percent of the failures are related to internal corrosion of the gas pipelines. So, the corrosion becomes very important; not only that, the capital cost of corrosion prevention is on about 10 percent of the project cost and 5 to 15 percent of the operating cost, that means internal corrosion of the gas pipelines are very important and that has to be addressed.

(Refer Slide Time: 25:10)

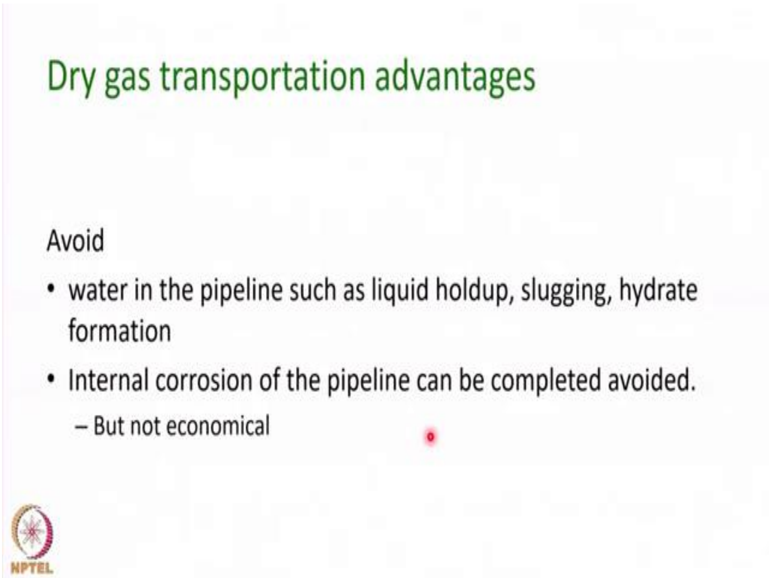


One of the problems that occur in the gas pipeline is the top of the line pipelines. The gases carry, so water, humidity for example, and this humidity they settle on the top surfaces. And along with the humidity and if you have gases like carbon dioxide or hydrogen sulfide;

they dissolved in this moisture, they dissolved in water. So, the moisture when they settle on the top of the pipeline, the inner surface of the pipeline; then they become severely corrosive.

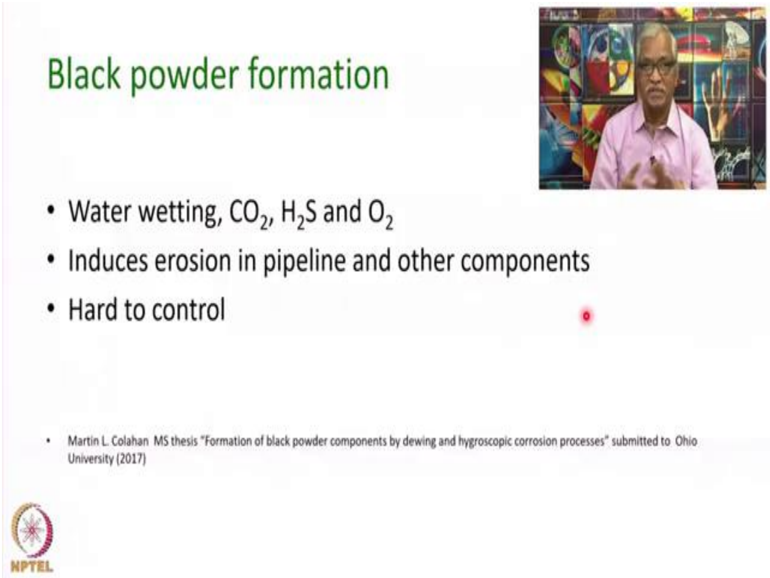
And this becomes even more severe if the flow is stratified you know, so and if the due conditions favor; for example, if the temperature of the pipeline is lowered ok, so the condensation becomes favorable. So, causes more corrosion problem. One of the ways to control the top of the light corrosion is injecting inhibitors; the inhibitors will dissolve in water and then they deposit along with the gases on the top of the line pipelines and lower the corrosion of the pipelines.

(Refer Slide Time: 26:35)



Of course, making the gas dry is surest way to control the corrosion of the gas pipelines. However, that is not practicable; because you want to make the gas completely dry, it is not very economical. And so, water is going to be present in the pipeline. But, however, if one can avoid holdup of water, slugging for example; then the localized corrosion can be significantly reduced in the gas pipelines.

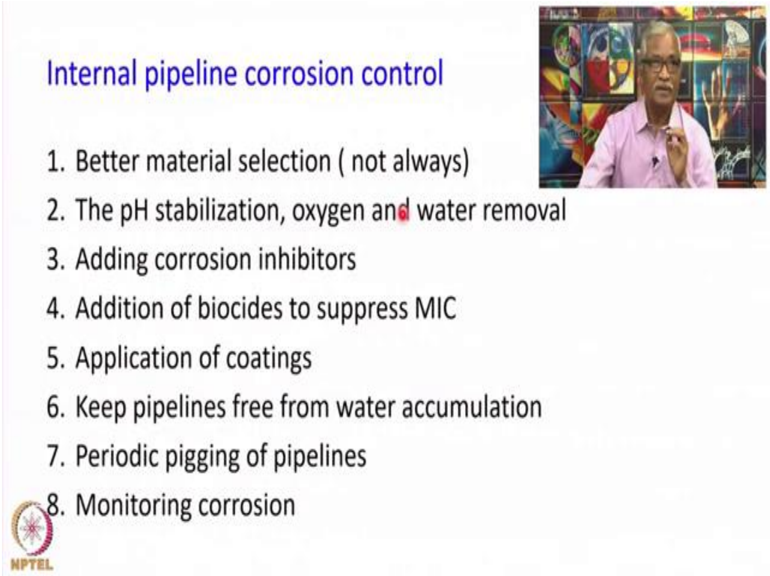
(Refer Slide Time: 27:16)



Gas pipelines are known to suffer one form of problem that is called black powder formation. The black powder formation, in fact lowers the thickness of the pipelines; it also causes in you know erosion of the pipelines. These black particles when they dislodged from the surface and they can erode the pipelines; in fact this these gases when they are transported to some of the units industrial units, industrial units can suffer significant erosion damages.

And this black powder formation as I indicated before is mainly because of the water presence in the gas along with the carbon dioxide, hydrogen sulfide; the presence of oxygen of course it becomes an oxidizer, it increases the oxidation or the corrosion of the metal. It is really hard to control; unless you control the water, carbon dioxide, hydrogen sulfide, and the oxygen content of the gases.

(Refer Slide Time: 28:23)



The internal corrosion control of the pipeline involves these broad categories, ok. As a metallurgist a material scientist, you suggest good materials; but that is hardly not possible, ok. You have seen earlier that all the API grade steels, there is nothing in that that suggests that these steels can resist corrosion. So, the process control is one of the most important one in controlling the internal corrosion of the pipelines.

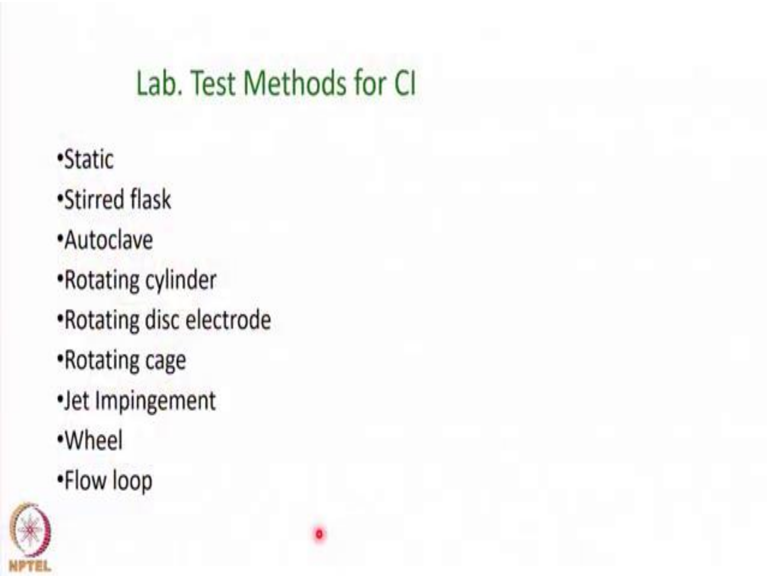
Now, the pH stabilization right; you lower the pH, you know that corrosion rate drops, oxygen reduction of oxygen content and the water removal. And along with that adding the inhibitors, the corrosion inhibitors is a good strategy to do that. In order to reduce the microbial corrosion, the biocides are added; where the corrosion becomes very severe ok, the applications of coatings is done ok.

There in fact, many cases people do cladding ok; that is with stainless steels, so that the corrosion rate can be really brought down. The other strategy as we discussed here is to keep the pipelines free from water accumulation and periodic pigging of pipelines; because any deposition that is taking place will induce under film corrosion or crevice corrosion, ok.

And monitoring corrosion is one of the most important ways of assessing the corrosion of the process fluid; whether you have added enough amount of inhibitors, whether the pH has been controlled, whether the oxygen has been adequately scavenged, all can be monitored indirectly using corrosion monitoring technique.

Of course, in corrosion, monitoring technique is a big subject; some of them like weight loss measurements cannot detect the instantaneous changes in the pH, oxygen content, water removal. And there are the other techniques like linear polarization probe, you one can use to determine the corrosion rate; of course the linear polarization probe is not applicable for gas pipelines.

(Refer Slide Time: 31:22)



Corrosion inhibitors are the most important part of or strategy for controlling corrosion, internal corrosion of the pipelines. And so, lot of techniques have been developed; it is not very easy to tailor a corrosion inhibitors. Unlike the normal cases like you add inhibitors to cooling water system; the developing inhibitors for oil and gas applications are very very difficult, especially the crude applications very difficult, because the corrosion occurs because of water. But the amount of water present is very small.

So, the inhibitor that are added to the process fluid, should able to dissolve in water; but the fraction of water is very less in the crude. So, there are various strategies in tailoring, the inhibitors and there are also different type of techniques to determine the efficacy of the corrosion impetus. I just listed here some of these techniques and for more details, you can refer the a literature.

(Refer Slide Time: 32:19)

Let me spend a couple of minutes about the role of metallurgy on corrosion of the pipelines. Stress corrosion cracking is one form of corrosion failures, especially the inner surface of the pipelines can suffer due to the presence of hydrogen sulfide. When you have hydrogen sulfide, it facilitates the hydrogen entry into the material causing the problems, such as hydrogen embrittlement, and hydrogen induced cracking.

(Refer Slide Time: 33:01)

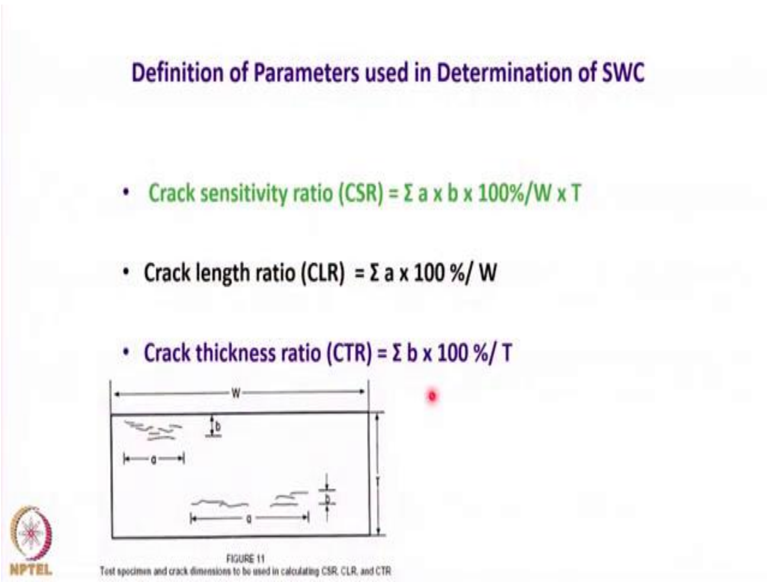
The metallurgy of this alloy is very very important and as you notice here, this is the microstructure of a steel pipeline used for transporting the refinery product between 2 cities. And very you know and very interestingly, this pipeline suffered severe failure within a short duration of the commissioning.

Mainly, because the pipeline had the features what you see here is the inclusions long inclusions, which facilitate the hydrogen blistering. And it is very difficult to overcome the hydrogen induced cracking; if we are not taking care of selecting steel that is free from these kind of inclusions.

(Refer Slide Time: 34:03)

So, in order to do this, there are standard tests available NACE TM0284 in the year 2003; it describes the method to qualify steel to avoid stepwise cracking or hydrogen induced cracking or hydrogen blistering, they are all referring to same kind of failure.

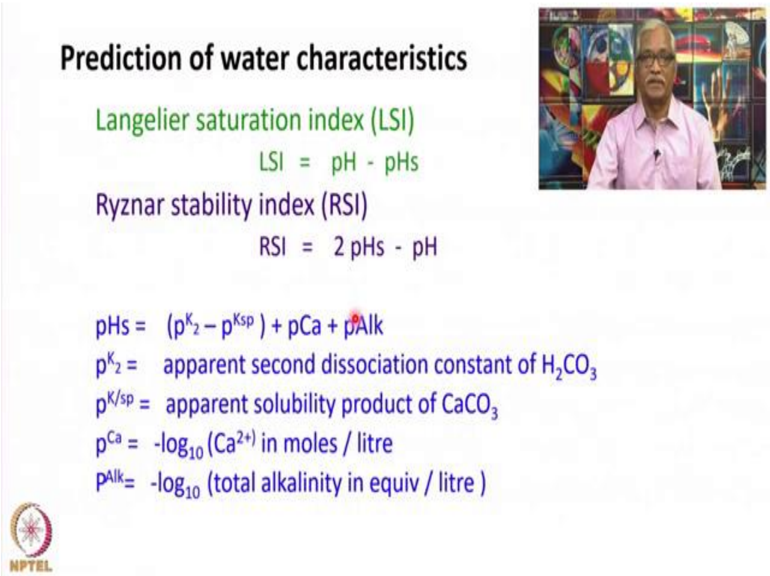
(Refer Slide Time: 34:29)



And again there are calculations, I would not go into details; standard that I have shown here can be referred to understand how one qualifies a material against step wise cracking. There are 3 types of cracking parameters called crack sensitivity ratio CSR, crack length ratio, and crack thickness ratios; they are all talk about how the material is susceptible to micro cracking. The stepwise cracking is nothing, but you know colony of cracks appearing in steel, because of hydrogen entry into the steel.

Water is largely transported through pipelines and water is corrosive. And the problem with respect to the water pipelines is that, it is not easy to modify or choose any kind of inhibitor to control the corrosion. To look at what makes the corrosion a given water; we shall now look, at in this lecture, we shall briefly look at what are the characteristics of water that influence the corrosion of the pipeline.

(Refer Slide Time: 35:52)



The corrosion tendency of water can be predicted using 2 type of indices; the Langelier saturation index and the Ryznar stability index. In both indices they use 2 parameters, pH and pHs. The pH is nothing, but a negative logarithm of hydrogen concentration, and pHs is given by this equation here.

These 2 indices while they represent the corrodibility of the water ok; what makes the difference between these 2 are that, the Langelier saturation index can go from a negative value to a positive value, whereas the Ryznar stability index it has got only a positive value. So, otherwise both represent the same relationship between pHs and the pH.

(Refer Slide Time: 36:53)

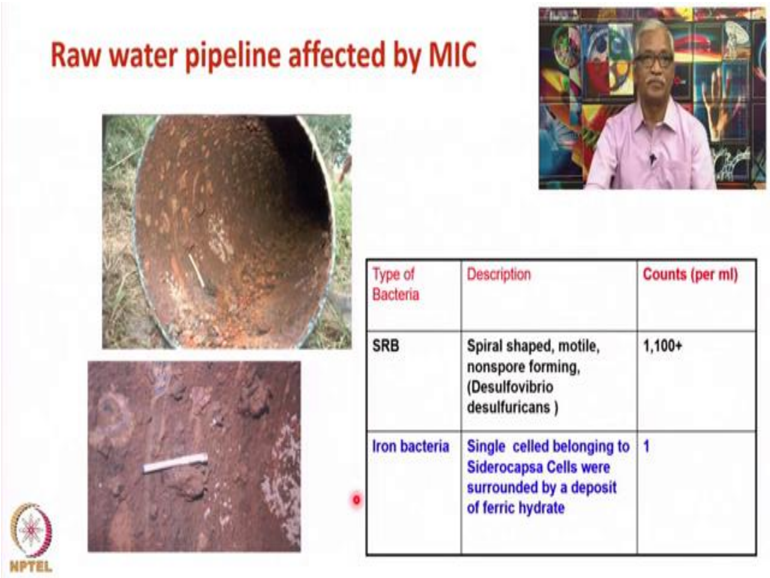
Prediction of water characteristics by LSI and RSI

LSI	RSI	Tendency of water
2.0	<4	Heavy scale forming, non aggressive
0.5	5-6	Slightly scale forming, mildly aggressive
0	6-6.5	Balanced or at $CaCO_3$ saturation
-0.5	6.5-7	Non scaling and slightly aggressive
-2.0	>8	Under saturated Very aggressive

The table that is given here outlines the relationship between the LSI, RSI and the corrosion tendency of the water. We all know that whenever the water has a tendency to form scales right, then it becomes non aggressive; that means the LSI value is 2 and RSI value is less than 4, the water has got scale forming tendency and so it is less corrosive. But as the LSI value becomes low and the RSI value becomes higher; you see that the scale forming tendency of the water becomes lower and it becomes mildly aggressive.

And when a LSI becomes 0 and RSI lies between 6 and 6.5 and the carbon dioxide is just in a saturation level and the pipelines do not form the scales or the water does not form the scale. And so, the water becomes more corrosive. As the LSI value tend to become, as the LSI value tends to become more negative; the water becomes very aggressive, because the calcium carbonate is not having sufficient concentration to form the scale.

(Refer Slide Time: 38:20)



The other reason why these water pipelines fail is due to microbially induced corrosion. What I have shown here is one of the pipelines corroded due to microbial species present in the water; this is a raw water pipeline that was used in Maharashtra actually, which I have investigated personally. And you see that inside microbes have been colonizing there and you see a lot of tubercles, right.

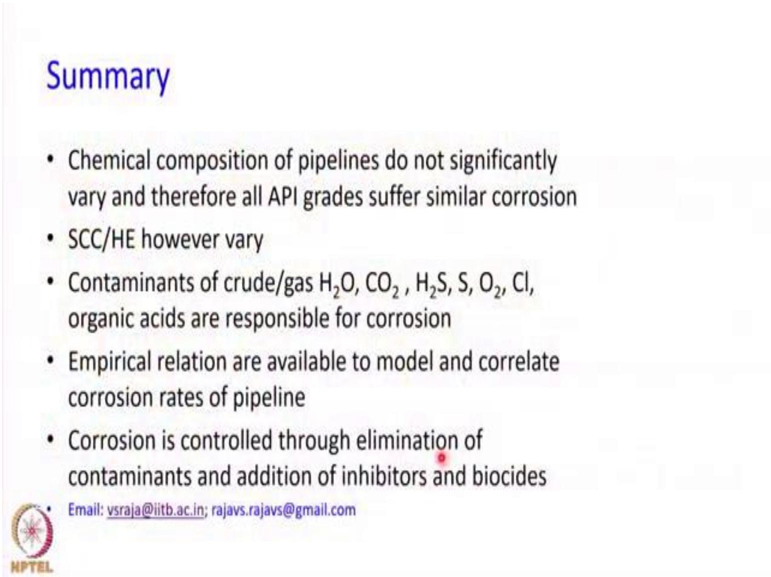
And these are tubercles that if you see them very closely; there are large tubercles and if you break open these tubercles, the microbes present in that. And inside these tubercles, you will have SRB sulfate reducing bacteria and outside this tubercle, you have an iron bacteria. So, both cause the corrosion of the pipelines.

(Refer Slide Time: 39:19)

It is not only the water pipelines, it also happens in pipelines that are used for utilities for example, ok. And microbes are present; what is seen here is a booster chiller pipeline used for building utility due to microbial corrosion.

You can see that, there is a leak the external wall; you can see this here, you open up and see the dark silvery kind of appearance indicative of sulfate reducing bacteria. So, we have seen so far 2 aspects; one is the corrosion of the oil and gas pipelines and we see various briefly the corrosion related to water.

(Refer Slide Time: 40:17)



So, before we close, we will summarize what you have seen so far. It is to be realized that the pipelines used in oil and gas industries that, the API grades; the chemical composition does not significantly vary and as a consequence, they almost have same corrosion behavior, irrespective of the grades of steels. However, these steels they vary with respect to stress corrosion cracking and hydrogen embrittlement.

With respect to the process fluid ok, say in crude or maybe gases, natural gases; the contaminants they decide the corrosivity of the crude or gas. These contaminants such as hydrogen sulfide, carbon dioxide, water, sulfur, oxygen, chloride, organic acids are responsible. Empirical relationships have been developed to model the corrosion of the pipelines. And corrosion in all these cases are mostly controlled by the addition of inhibitors and the biocides.

And thank you very much.