Environmental Chemistry and Microbiology

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Module - 12
Lecture - 63
Biogeochemical Cycles - II

Welcome everyone. This is the last and final lecture of our course, the second part of Biogeochemical Cycles. This is lecture 63 of module 12.

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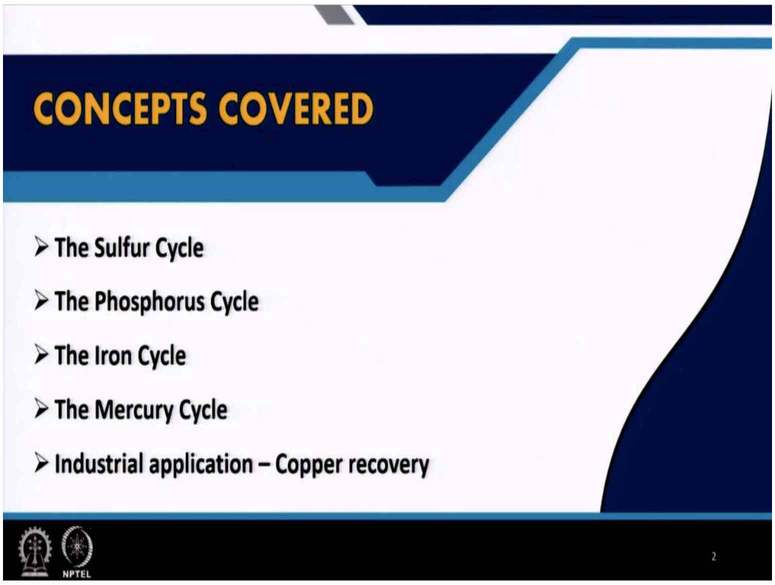

CONCEPTS COVERED

- The Sulfur Cycle
- The Phosphorus Cycle
- The Iron Cycle
- The Mercury Cycle
- Industrial application – Copper recovery

So, in this particular part, we are going to cover the sulphur cycle, phosphorus, iron, mercury and one industrial application where we are going to look at how copper can be recovered by a series of chemical and biological reactions. So, it is not a natural biogeochemical cycle, but it is a sort of imitation at the industrial level of the same kind of ideas.

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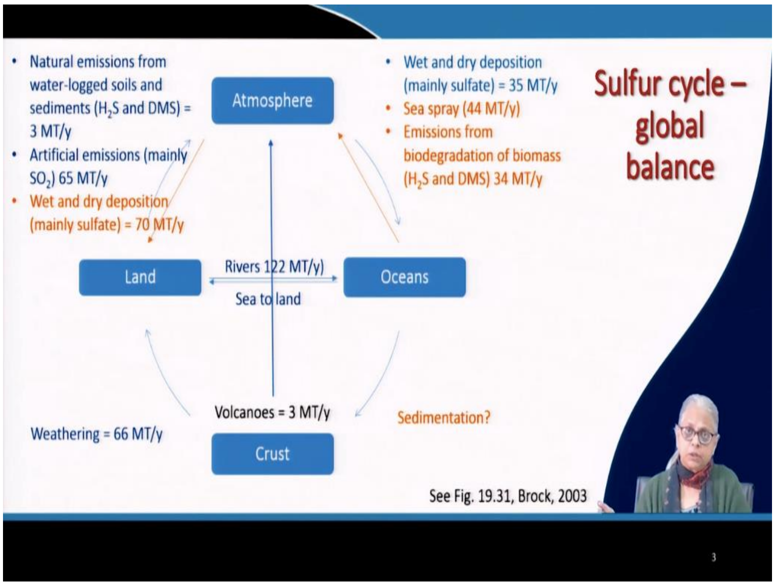

Sulfur cycle – global balance

- Natural emissions from water-logged soils and sediments (H_2S and DMS) = 3 MT/y
- Artificial emissions (mainly SO_2) 65 MT/y
- Wet and dry deposition (mainly sulfate) = 70 MT/y

Atmosphere

- Wet and dry deposition (mainly sulfate) = 35 MT/y
- Sea spray (44 MT/y)
- Emissions from biodegradation of biomass (H_2S and DMS) 34 MT/y

Land

Rivers 122 MT/y)

Sea to land

Oceans

Weathering = 66 MT/y

Volcanoes = 3 MT/y

Sedimentation?

Crust

See Fig. 19.31, Brock, 2003

Let us take a look at the sulphur cycle. So, what is the global understanding of where sulphur comes and goes from? So, let us take a look at sulphur emissions from waterlogged soils and lake sediments. Now, these are mainly in the form of hydrogen sulphide and dimethyl sulphide. You are all familiar with the stench of sulphide or ammonia. This is very common with wastewater.

If you happen to go by the seaside and you have; we normally, at least in common language, we call it this fishy smell that you get in any seaside environment. That is mainly because of these sulphur, sulphurous compounds. It is the sulphurous compounds that are, they have a stinky smell and no one really likes it; but they are all forms of sulphide.

So, the mercaptans, sulphides, these are the ones that no one really likes, and that is what the smell is all about. So, these are emissions of sulphide compounds, dimethyl sulphide, hydrogen sulphide, that come into the atmosphere from the waterlogged soils and sediments. And that is part of the decomposition process. So, when I talk about dead biomass being converted back to mineral form, whether it is CO_2 and water. So, when I use glucose as an example, that does not account for nitrogen, sulphur, phosphorus and so on. So, that is the missing point over here. So, you have sulphur as well in the biomass which is returned to the atmosphere in the form of this reduced form of sulphur. You also have artificial emissions; artificial means anthropogenic emissions; mainly in the form of sulphur dioxide (SO_2).

Then you have; whatever goes into the atmosphere is going to come back into either the terrestrial or aquatic environment. And we use 2 words, dry deposition and wet deposition. So, dry deposition is when the sulphur containing aerosols you might say are adsorbing to particles, and then the particles come down. They can come down in 2 ways: either by the weight of the particles or when there is rain or hail or snow or whatever it is, any form of precipitation, if it brings these particles or aerosols down, then it becomes wet deposition.

So, you have dry and wet deposition. Most of this is in the form of sulphate, because by now, sulphur has been converted to its most oxidised form which is sulphate (in the presence of oxygen in the atmosphere). Now, this is dry and wet deposition over land. The same thing happens over the oceans as well.

You also get certain amount of emissions from volcanoes. That is a natural source. And there is a lot of soluble sulphur that goes into rivers and streams, which is then carried to the oceans. Now, the ocean spray, again that smelly stench of sulphur; that is the sea spray. So, that sea spray contains sulphur, and that sends it back into the atmosphere. So, you have emissions from biological decay, mainly hydrogen sulphide, dimethyl sulphide, all of that. So, whatever is happening on land is also happening on sea, on the oceans; and that is the complete cycle.

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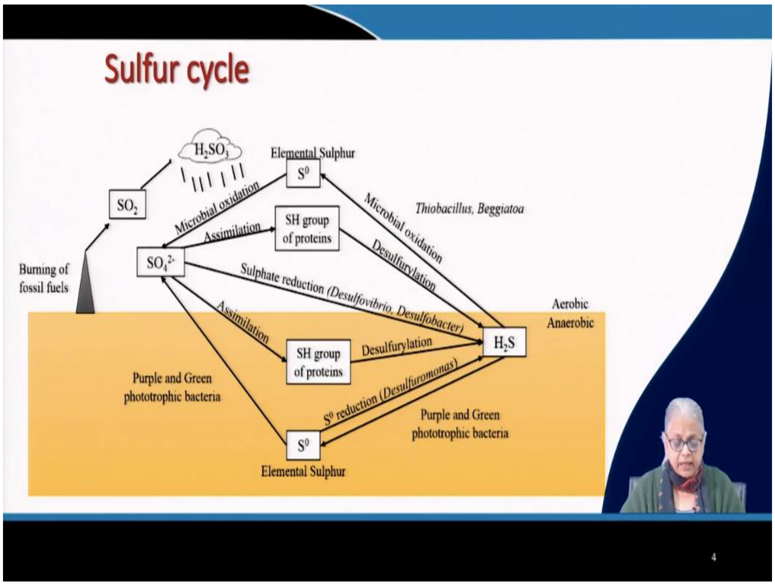

Sulfur cycle

H_2SO_3
Elemental Sulphur
S^0
SO_2
Microbial oxidation
Assimilation
SH group of proteins
Thiobacillus, Beggiatoa
Microbial oxidation
Desulfurylation
Burning of fossil fuels
SO_4^{2-}
Sulphate reduction (*Desulfovibrio, Desulfobacter*)
Aerobic
Anaerobic
Assimilation
SH group of proteins
Desulfurylation
H_2S
Purple and Green phototrophic bacteria
S^0 reduction (*Desulfuromonas*)
Purple and Green phototrophic bacteria
S^0
Elemental Sulphur

Here are examples of individual bacterial species that are responsible for mediating the redox reactions: the oxidation-reduction reactions where you get the conversion of sulphur from one oxidation state to another oxidation state. So, let us take a look at the most reduced form of sulphur. So, the most reduced form of sulphur is hydrogen sulphide. So, you have H_2S. It then gets converted to either elemental sulphur in both oxic as well as anoxic environments.

This elemental sulphur is further oxidised to sulphate. So, H_2SO_4 which is familiar to all of you is one form of sulphate, but there are several other forms. Now, in nature, these reactions are all mediated by specific species of bacteria. So, you have the first one, sulphide or sulphur oxidation; so, whether it is aerobic or anaerobic. So, let us take a look at the anaerobic; let us go with oxic first.

H_2S - chemolithotrophic oxidation is done by sulphur chemolithotrophs like *Thiobacillus, Beggiatoa* and many other species. Under anaerobic conditions, the same reactions are mediated by purple and green phototrophic bacteria as well as chemolithotrophs. Then you have sulphate reduction under anaerobic conditions: sulphate to sulphide. So, you have sulphate going back to sulphide, and sulphate reduction by anaerobic bacteria like *Desulphovibrio* and *Desulphobacter.* That was sulphate reduction.

Here we have elemental sulphur being converted to hydrogen sulphide, *Desulfuromonas* and many other hyperthermophilic archaeabacteria. Sulphur disproportionation thiosulphate can be converted to two forms, sulphate and sulphide. Now, here we have a similar situation like the fermentation of organic compounds, where you get a reduced form and an oxidised form.

So, thiosulphate has an oxidation state that is somewhere between H_2S and sulphate. So, this thiosulphate is getting partly reduced and partly oxidized and *Desulphovibrio* is the mediating species. You can also have organic sulphur compound oxidation or reduction. So, you have sulphur in certain amino acids like cysteine that can be converted to CO_2 and sulphide.

You have DMSO, dimethyl sulphur oxide, which can be converted to dimethyl sulphide. Then desulfurylation, organic sulphur is converted directly to hydrogen sulphide; and several organisms are involved in it. Wastewater is a very good example of many of these reactions; it has many of these species. Depending on how much oxygen there is in the water, you will get many of these reactions. Municipal wastewater is what I am talking about.

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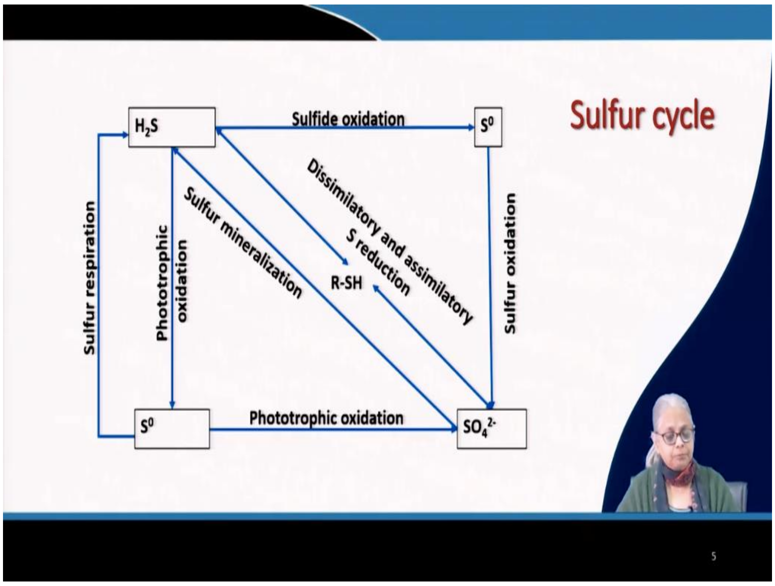

Sulfur cycle

So, in a nutshell, this is how sulphur is recycled through nature by nature. So, H_2S, elemental sulphur, sulphate back to elemental sulphur and then back to hydrogen sulphide. So, you have sulphur oxidation reactions; you have sulphur reduction; you have dissimilatory as well as assimilatory sulphur reactions; you have organic sulphur; you have phototrophic oxidation of elemental sulphur; and you have sulphur respiration. So, the number of processes that are present in nature, that allow sulphur to be recycled through all these different parts is any; I mean, the diversity of bacterial species is enormous.

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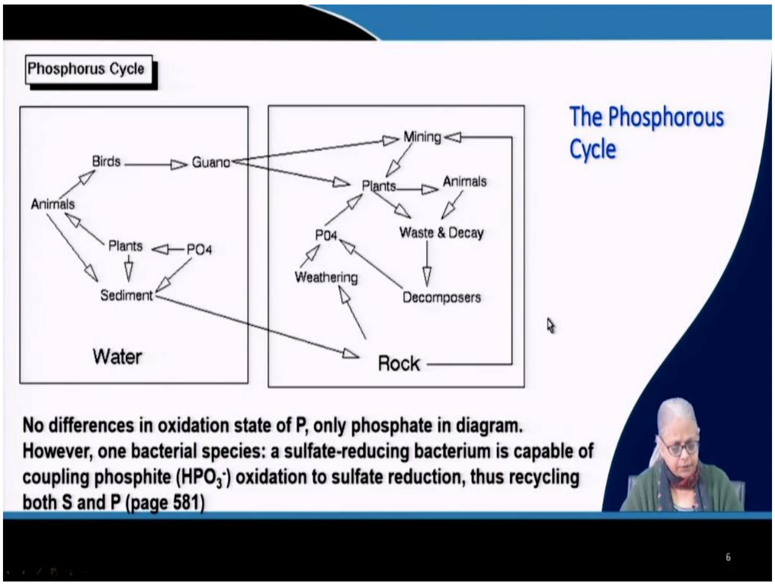

The Phosphorous Cycle

No differences in oxidation state of P, only phosphate in diagram.
However, one bacterial species: a sulfate-reducing bacterium is capable of coupling phosphite (HPO_3^-) oxidation to sulfate reduction, thus recycling both S and P (page 581)

Let us then come to the next essential macronutrient and that is phosphorus. Phosphorus in general does not change its oxidation state. Unlike all the other elements, if you notice carbon, nitrogen, sulphur, all of them, the biogeochemical cycles are dependent on the change in oxidation state and that change in oxidation state is entirely due to different species. Different bacterial species are capable of mediating these oxidation reduction reactions.

Now, phosphorus is very strange, it is very stable (chemically speaking). The phosphate part of any compound is the most oxidised form of phosphorus and therefore, it is extremely stable and very few other oxidation states have ever been observed. So, in terms of the biogeochemical cycles, most of the phosphorus is in the faeces of seabirds. And for some reason, seabirds have very high phosphate content in their faecal matter, and that is what the guano deposits are all about.

So, these guano deposits have been mined. And that is how we get our phosphate fertiliser, and we get phosphate in the environment by the dissolution of these deposits. This phosphorus which is taken up by plants and then is eaten; these plants are eaten by animals; both types of biomass are going to die and decompose. And the decomposing organisms which include bacteria, fungi and so on, will bring organic phosphate back into soluble form. And some of it will end up in the rocks; and if it is in the rocks, it will also be weathered and dissolved and brought back into the water. So, that cycling of phosphorus from different parts of the environment will always be there.

And the same thing, whatever I said about the land area, will also be happening in the aquatic systems. So, that is how phosphorus is recycled in both parts, whether it is the lithosphere or the hydrosphere; in both parts, it is more or less the same. There is no oxidation-reduction reaction, except one bacterial species that have been observed and is noted in the text, and I think I have covered it in the previous lecture. There are one bacterial species, is a sulfate-reducing bacterium that can couple phosphite; phosphite is a reduced form of phosphorus, and it can couple phosphite oxidation to sulphate reduction, thus recycling both sulphur and phosphorus.

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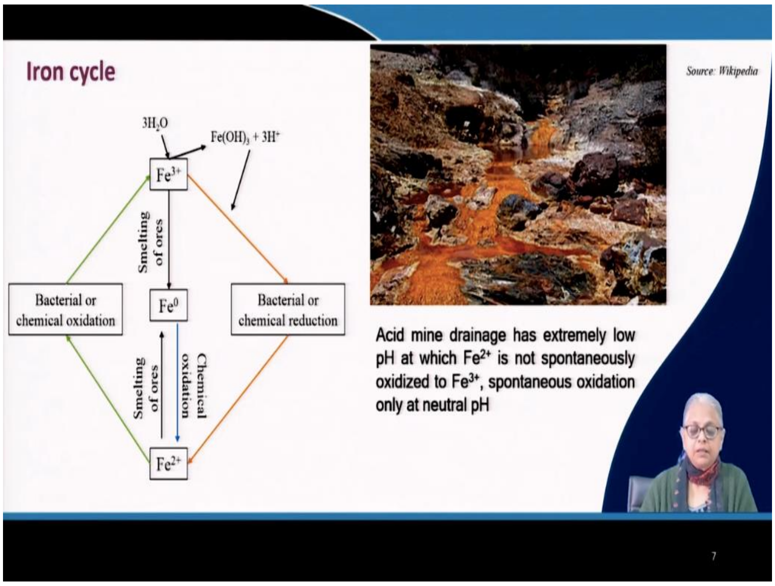

Iron cycle

Source: Wikipedia

Acid mine drainage has extremely low pH at which Fe^{2+} is not spontaneously oxidized to Fe^{3+}, spontaneous oxidation only at neutral pH

Let us now come to another element. The next element is iron. Iron is not a macronutrient, it is a micronutrient, but it is an essential micronutrient. So, this is the first graphic; (it) shows you the redox cycle of iron in the environment. You are all familiar with the fact that iron exists in 3 major forms. The most oxidised form is Fe^{3+} which is ferric iron; the next form is reduced Fe^{2+} which is ferrous iron; and Fe^0 which is the elemental form.

Now, the elemental form is found only by anthropogenic means. You have to smelt the ores to create elemental iron. What is found in nature is ferric and ferrous iron. Now, ferrous iron can be either reduced or oxidised; it can be done bacterially or it can be done chemically. Let us take a look at something that is very interesting. Now, we all know that if you have iron in your environment; assuming that you are not in any extreme environment, in the normal environment; you know that iron, when it is in dissolved form, will spontaneously get oxidised from Fe^{2+} to Fe^{3+}; and Fe^{3+} is highly insoluble, it precipitates. So, you get these black precipitates, and that is what we call rust. So, if you have anything that contains iron, like steel or any alloy of iron and so on, so you get this rust and precipitation of ferric iron.

What is happening in acid mine drainage is very different from what we see in our normal environment. Our normal environment when iron-containing material is in contact with water, the pH is 7. And under neutral pH conditions, Fe^{2+} gets spontaneously oxidized to Fe^{3+}. But acid mine drainage is a different game altogether. Here, the pH is less than 2 and under these low pH conditions, Fe^{2+} does not get spontaneously oxidized to Fe^{3+}. It is highly soluble and it remains soluble, it does not get oxidised. For that oxidation to happen, you need a bacterial species which is an acidophilic species and that is what is done in the environment.

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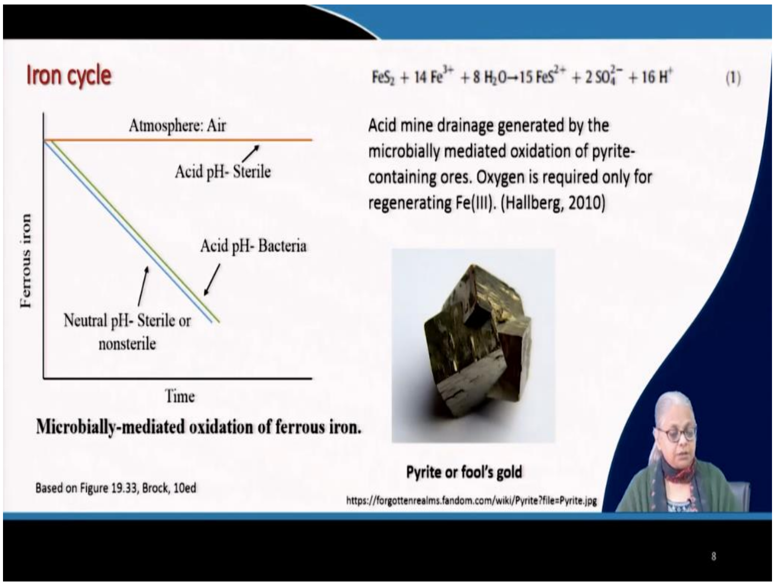

Iron cycle

$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,FeS^{2+} + 2\,SO_4^{2-} + 16\,H^+$ (1)

Acid mine drainage generated by the microbially mediated oxidation of pyrite-containing ores. Oxygen is required only for regenerating Fe(III). (Hallberg, 2010)

Microbially-mediated oxidation of ferrous iron.

Based on Figure 19.33, Brock, 10ed

Pyrite or fool's gold

https://forgottenrealms.fandom.com/wiki/Pyrite?file=Pyrite.jpg

So, here is an example of this particular iron-oxidizing species *Thiobacillus ferrooxidans*. This is a very neat experiment that shows you how iron is being converted under neutral conditions from ferrous iron to ferric iron. So, under neutral pH, whether the sample has bacteria or no bacteria, there is spontaneous oxidation to Fe^{3+}. In acidic conditions, no bacteria, there is no change, ferrous iron remains stable, no spontaneous oxidation happens. Only when this particular bacterium *Thiobacillus* is present, it can convert ferrous iron to ferric iron. And this is, like I said, an indicator; this is again extremophilic conditions. This bacterium is again an extremophile, because it is capable of living under extremely low pH conditions.

So, pyrite and coal can be oxidized by sulphur and iron-oxidizing bacteria. So, this is a coal seam and you can see the gold-coloured discs. Some of you may be knowing that pyrite is called fool's gold. So, we have FeS_2 and because it has a gold or shiny colour; sometimes it looks shiny, sometimes it looks golden-coloured; so, many times, people who do not know better, often mistake it for gold, but it is really pyrite FeS_2. That is why it used to be called fool's gold. So, here is an experiment that; what I showed you was the natural environment, but this is another experiment to show you the same thing.

So, you have acid mine drainage which has very low pH. And the spontaneous oxidation happens only at neutral pH, not at low pH conditions. So, you can see the precipitation of iron. So, all this coloured is because of the precipitation of iron; otherwise, it is soluble and it just keeps going into the water. Now, how does this work? This is an aerobic autotrophic reaction. So, we have the electron donor which is Fe(II) to Fe^{3+}, and the electron acceptor is oxygen. So, you require aerobic conditions and iron for this reaction to happen.

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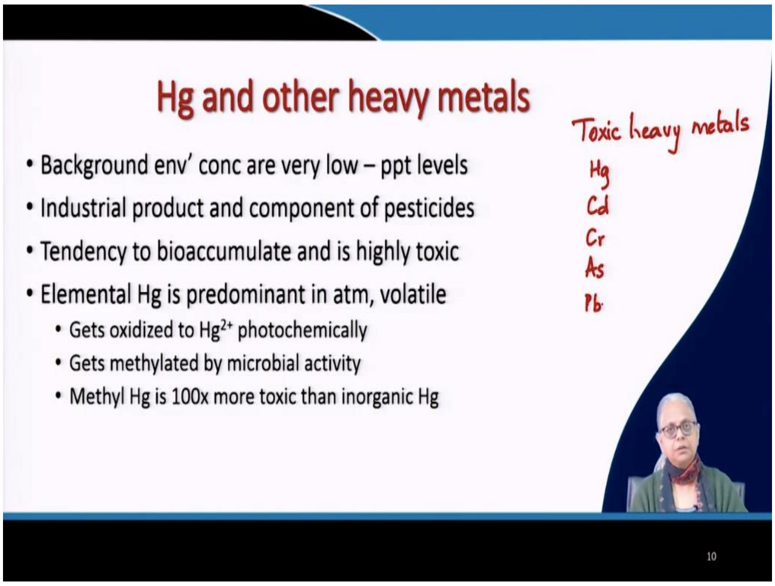

Hg and other heavy metals

- Background env' conc are very low – ppt levels
- Industrial product and component of pesticides
- Tendency to bioaccumulate and is highly toxic
- Elemental Hg is predominant in atm, volatile
  - Gets oxidized to Hg^{2+} photochemically
  - Gets methylated by microbial activity
  - Methyl Hg is 100x more toxic than inorganic Hg

Toxic heavy metals
Hg
Cd
Cr
As
Pb

Let us come to another metal and that is mercury. Now, you might say that mercury is not a nutrient. That is true. Mercury is extremely toxic. It is one of the most; yes. There are 5 toxic metals that are considered to have no beneficial properties, and mercury is definitely one of them. So, I will just list the toxic heavy metals. So, these are considered the 5 toxic heavy metals which have no beneficial properties.

So, we will go through the cycle for mercury. So, looking at mercury and some of the other toxic heavy metals, let us just focus on mercury. It has been studied to a much greater extent, perhaps than the other metals. In natural conditions, the background environmental concentration of mercury is very low. So, it is ppt level; ppt stands for parts per trillion. So, it is an industrial product, we know that. And it is often used in pesticides. It has a tendency to bioaccumulate, it is also known to be extremely toxic. Like I said, it has no beneficial properties, and it is extremely toxic. It is a neurotoxin. Now, elemental mercury is predominant in the atmosphere. And if you are wondering why, it comes from thermal power plants which burn coal. So, coal is something that contains a large number of heavy metals and when it is burned, all these heavy metals will rise with the hot gases. And mercury has a very low boiling point compared to all the other heavy metals. So, because the boiling point of mercury is much lower, it rises along with the flue gases, it goes into the atmosphere. It is a volatile compound at the temperature of the flue gases, and it is emitted into the atmosphere. So, that is the reason why elemental mercury is predominant in the atmosphere.

The other thing that it has a tendency to do is, as the flue gases are cooling down; when they go into the atmosphere, the flue gases start cooling down, and this volatile or gaseous form of mercury starts adsorbing to the (ash) particles. So, when these particles come down by wet and dry deposition, that is how mercury comes back on land or water. In the atmosphere, it can also get oxidised to Hg(II) and that is a photochemical reaction.

Another possible reaction is methylation of mercury. Now, we know that in aquatic environments, if you have Hg(II), Hg^{2+}, it is quite likely to form what are called organometal complexes. So, mercury will tie up with methyl groups and form methylated mercury. Now, methylated mercury has much higher solubility compared to elemental mercury. Elemental mercury has very poor solubility.

In fact, often when kids end up ingesting the mercury in thermometers and so on, it gets excreted out of the digestive system because it is not very soluble. Methylated mercury which can be present in fish tissue, it can be present in other foods. In fact, if you have heard about the Minamata disaster or the Minamata disease; that is because of the presence of methylated mercury in the tissue of fish. And I can go on and on about that.

But just remember that, in Minamata, where there was a fertiliser corporation that was operating, they were releasing a large amount of wastewater, and the catalyst in the fertiliser production process was a mercury compound. So, this wastewater had high amounts of mercury in it and when it was released into the aquatic environment, it got into the fish, in methylated form. So, this methylated form of mercury was being ingested by people who were eating the fish in this area. So, Minamata is a village on the coast of Japan, where the fishermen and their families were using this fish. And over a period of time, they developed neurological problems. And it was not just the human beings, but the cats, the birds, the fish, everything was behaving in a ‘not sane’ fashion. And therefore, that is when people started realising that the methylated form of mercury is a neurotoxin, and it is highly problematic, it is highly toxic, it can be fatal.

So, this methylation is also mediated by microorganisms. And I can give you another example. In previous experiments that I myself was part of, we used mercury chloride as a biocide to prevent microbial activity. But now it is well known that certain microorganisms have the ability to convert Hg^{2+}, which is $HgCl_2$ in dissolved form, will give you Hg^{2+}. Now, this Hg^{2+} can be methylated and form organic methyl-Hg. So, this methyl mercury is 100 times more toxic than the inorganic form. So, whether it is elemental or Hg^{2+}, they are not as toxic as the methylated form.

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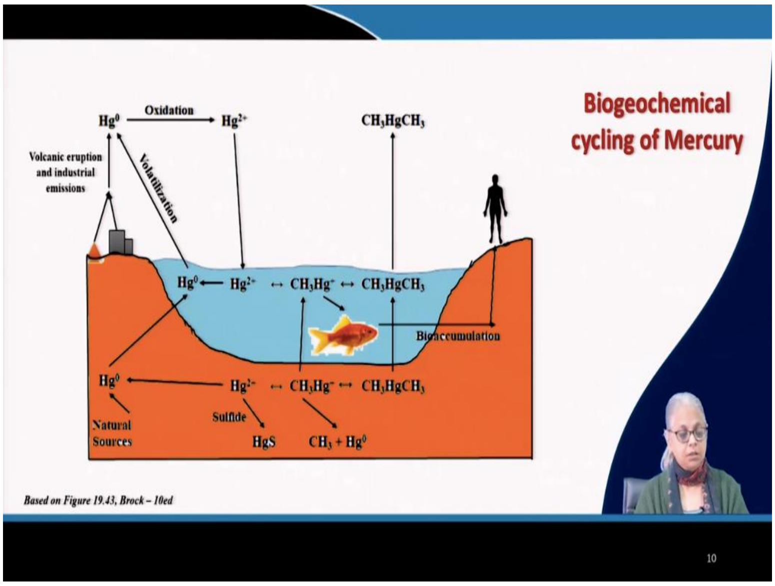

Biogeochemical cycling of Mercury

Based on Figure 19.43, Brock – 10ed

So, here we have the biogeochemical cycling of mercury. So, what is released into the air is mostly elemental mercury. It gets photochemically converted to Hg^{2+}. Hg^{2+} will adsorb to particles in air, absorb in water (aerosols). It will come down through the water, through the sediment, through the air, wet and dry deposition; all this will bring it down. It will come into the sediment, and there it will form complexes with both organic as well as inorganic compounds. So, you get methylation of mercury as well as mercury sulphide. And like I said, it is the methylated form of mercury that is dangerous.

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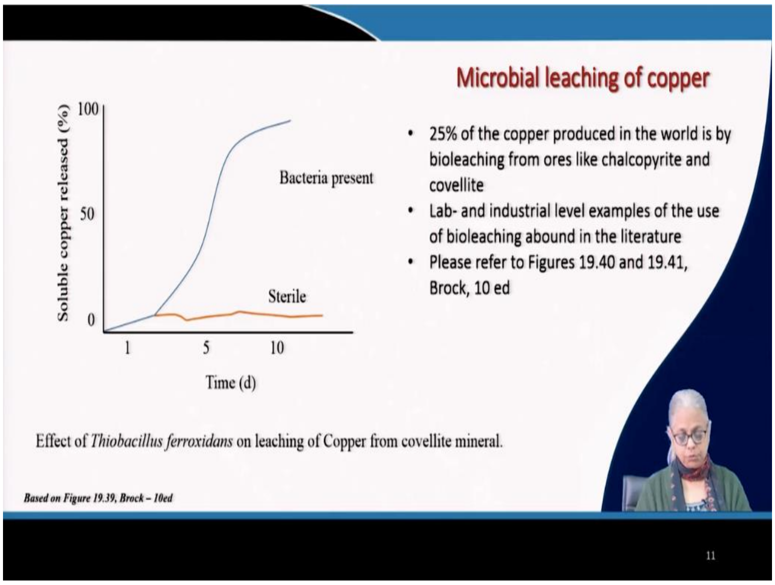

Microbial leaching of copper

- 25% of the copper produced in the world is by bioleaching from ores like chalcopyrite and covellite
- Lab- and industrial level examples of the use of bioleaching abound in the literature
- Please refer to Figures 19.40 and 19.41, Brock, 10 ed

Effect of *Thiobacillus ferroxidans* on leaching of Copper from covellite mineral.

Based on Figure 19.39, Brock – 10ed

Let us come to the last part of this lecture and that is the industrial application of our understanding of how you can use certain bacterial reactions, certain biochemical reactions and chemical reactions to cycle and recover certain types of metals. So, here is an example of how copper can be recovered from the ore form. So, here we have the same bacterium, *Thiobacillus ferrooxidans*, where the leaching of copper from a mineral covellite has been shown.

So, if you have bacteria; this particular bacterium, when it was added to the solution containing this mineral, you can see the amount of soluble copper released, as compared to the sterile form. So, this mineral without any bacteria will not release copper in soluble form. So, this is one example. And I will show you the next one which is far more interesting.

So, you know that most of the metals in their natural form are very minor fractions of the total amount of ore containing that metal and so on. So, it takes a lot of effort to take the ore out of the ground and then extract the useful metal from it. So, here you have low-grade copper ore which is piled up in such a way that you have a huge amount of surface area. And this has been crushed. So, you can see the crushing of the ore; it has been crushed into smaller parts to provide larger surface area and then, acidic leach water is spread. You can see the spreading, the spraying of acidic leach water over the ore. So, the acid will dissolve the ore and this effluent; this is the effluent that you see coming out of the leaching dump. And this acidic water is slowly coming out and the green colour is because of the soluble copper in it. And the effluent; like I said, it is rich in dissolved copper. And here, in the last case, it is being passed, this water is being passed over metallic iron. So, these are large flumes, these are flumes with metallic iron, and the copper is being passed over it. At the end of the process, you get a huge pile of copper metal. And I will show you how this works.

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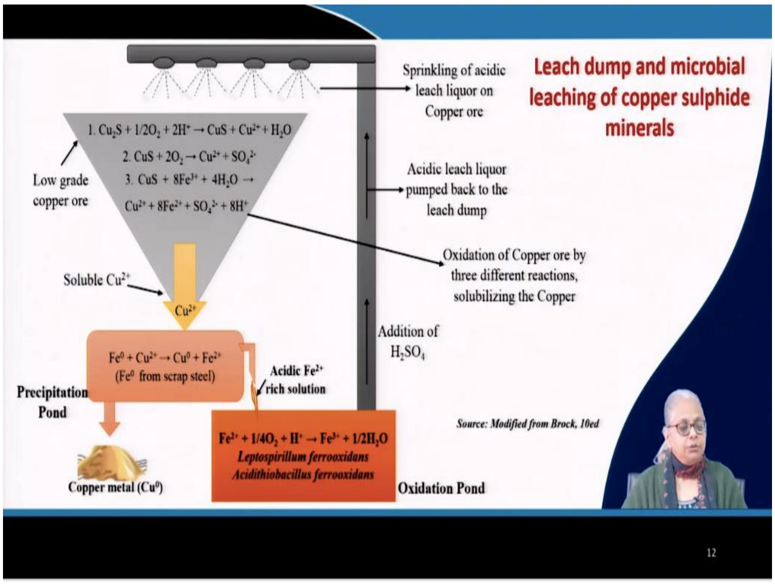

Leach dump and microbial leaching of copper sulphide minerals

Sprinkling of acidic leach liquor on Copper ore

Low grade copper ore

1. $Cu_2S + 1/2O_2 + 2H^+ \rightarrow CuS + Cu^{2+} + H_2O$
2. $CuS + 2O_2 \rightarrow Cu^{2+} + SO_4^{2-}$
3. $CuS + 8Fe^{3+} + 4H_2O \rightarrow Cu^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+$

Acidic leach liquor pumped back to the leach dump

Oxidation of Copper ore by three different reactions, solubilizing the Copper

Soluble Cu^{2+}

Cu^{2+}

Addition of H_2SO_4

$Fe^0 + Cu^{2+} \rightarrow Cu^0 + Fe^{2+}$

(Fe^0 from scrap steel)

Precipitation Pond

Acidic Fe^{2+} rich solution

Copper metal (Cu^0)

$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$

Leptospirillum ferrooxidans

Acidithiobacillus ferrooxidans

Oxidation Pond

Source: Modified from Brock, 10ed

So, let us start with the sprinkling of acidic water or leach liquor on the copper ore. So, at this point, sulphuric acid is part of the leach liquor and it has been sprayed all over the copper ore.

3 types of major reactions are happening at this point. The first reaction is a bacterially mediated reaction; the second one is both biological as well as chemical; and the last one is a chemical reaction. So, the copper in the ore is associated with sulphur.

So, you have Cu_2S, CuS that are present. The first one under aerobic conditions - Cu_2S is being converted to CuS and Cu^{2+}. Cu^{2+} is soluble. So, that is why the effluent from the spraying of this leach liquor is going to give you an effluent that is highly rich in copper. So, this copper is then either converted chemically with the catalysis of Fe^{3+}. So, here you have an oxidation-reduction reaction.

So, you have CuS in the presence of ferric iron. Ferric iron is being reduced to Fe^{2+}, and CuS is dissolving as Cu^{2+}. So, you get more dissolution of copper from the ore. Now, this Cu^{2+} has to be recovered in elemental form. So, how to do that? So, again you have another oxidation-reduction reaction, where elemental iron from steel cans; so, this is what you see over here. These are the metal filings, iron metal filings from steel cans or any other source.

So, Fe^0, elemental iron along with the soluble form of copper which is there in the effluent, by redox reaction is being converted to elemental copper and Fe^{2+}. At the end of this process, you get this copper. And the next step is, you have to convert Fe^{2+} which is a product of this reaction, has to be converted back to Fe^{3+}. So, this Fe^{2+} in the presence of oxygen will go back to Fe^{3+} under acidic conditions by the same bacteria, *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. So, that is an oxidation pond. So, you have complete cycling of iron, and extraction of copper-based on these principles.

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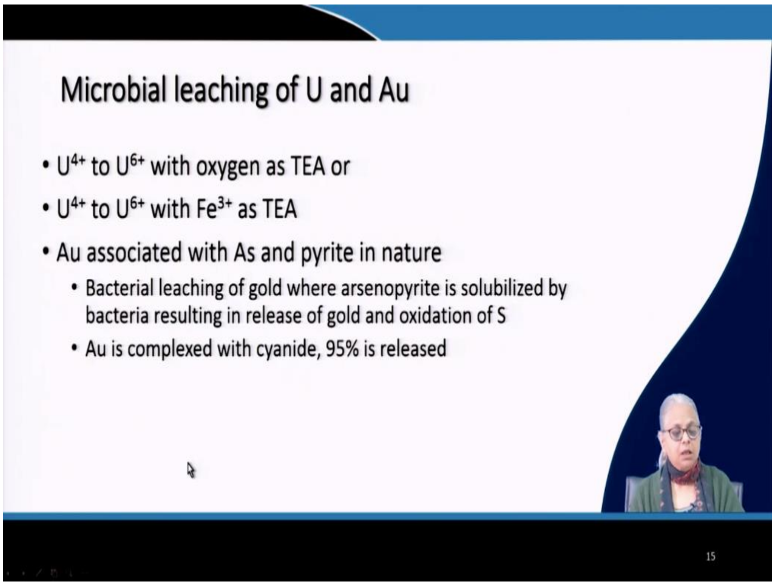

Microbial leaching of U and Au

- U^{4+} to U^{6+} with oxygen as TEA or
- U^{4+} to U^{6+} with Fe^{3+} as TEA
- Au associated with As and pyrite in nature
  - Bacterial leaching of gold where arsenopyrite is solubilized by bacteria resulting in release of gold and oxidation of S
  - Au is complexed with cyanide, 95% is released

This can be done. Microbial leaching can be done for uranium as well as gold. Remember that in nature, the concentrations of uranium and gold in the ore form is very small. So, huge amounts of ore have to be processed before you can extract these metals. So, uranium, U^{4+} to U^{6+} can be extracted with oxygen as a terminal electron acceptor using microbes or with Fe^{3+} as the terminal electron acceptor.

Gold in general is associated with arsenic and pyrite in nature and bacterial leaching of gold, where arsenopyrite is solubilized by bacteria, will result in the release of gold and oxidation of sulphur. Gold is often complexed with cyanide, and you get 95% recovery of gold from the ore.

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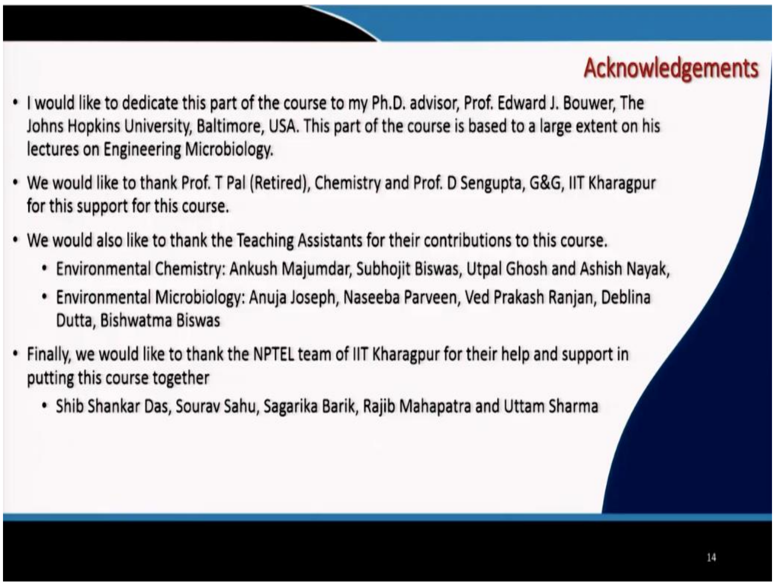

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    - Shib Shankar Das, Sourav Sahu, Sagarika Barik, Rajib Mahapatra and Uttam Sharma

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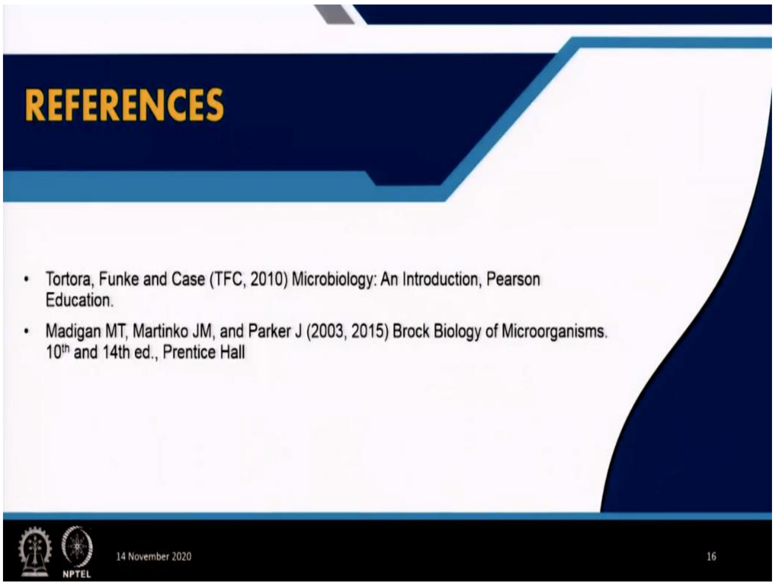

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All right. Thank you. I will end this topic over here. Thank you.