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# Lecture-44 Biohydrometallurgy

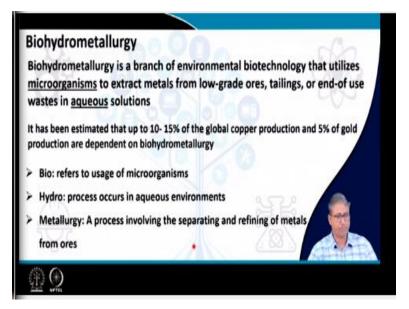
Welcome to the next lecture of our course environmental biotechnology. This is lecture number 44 and we are going to discuss about biohydrometallurgy.

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Now in this particular lecture I am going to talk about the basic concept of biohydrometallurgy. Then we will talk about the microbial principles of bioleaching, mechanisms and methods and finally different bioleaching or biohydrometallurgical approaches taken for recovery of important metals will be discussed.

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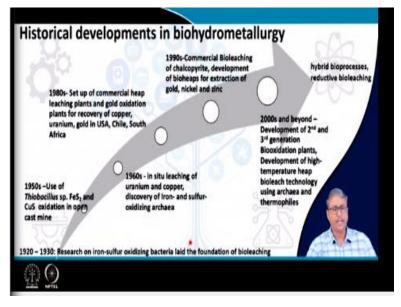
Now what is biohydrometallurgy? Biohydrometallurgy is a branch of environmental biotechnology that utilizes microorganisms to extract metals from low grade ores, tailings or end of the use waste in aqueous solution. So, it is basically a microbially catalyzed oxidation process most of the cases it oxidizes the iron and sulfur compound sulphides and it results into the soluble forms of the metals.

And within this aqueous solution which is acidic because it also generates lot of acid sulfuric acid and the metals are solubilized into that. And as of now the estimated value of the amount of this biohydrometallurgically recovered metals is very significant. And as you can see that it has been estimated that up to 15% of the global copper production and 5% of the gold production are dependent on biohydrometallurgy.

Although as we will discuss in this class biohydrometallurgical application for uranium recovery from the uranium ores are also found to be very significant. In biohydrometallurgy the term bio refers to the uses of microorganisms and as I mentioned it is actually a microbially catalyzed process. And hydro means the process occurs in aqueous environment, so essentially the presence of water is mandatory.

And metallurgy that is a process involving the separation and refining of metals from ores are involved in this process. So, over the passage of time ever since the oxidation capabilities of microorganism particularly the iron and sulfur oxidation abilities are discovered from early 1900 like 1920 onwards we see that scientists are interested on working and knowing more about this biohydrometallurgical aspects of microbial oxidation of different metals and metalliferous, ores, sulphide etcetera.

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And if you look at the historical developments in biohydrometallurgy as I was mentioning that during these early dates of 1920 to 1930 the initial research on iron sulfur oxidizing bacteria laid the foundation of the bioleaching. Because biohydrometallurgy is also considered as bio oxidation or bioleaching or bio mining, so it has actually the different nomenclatures.

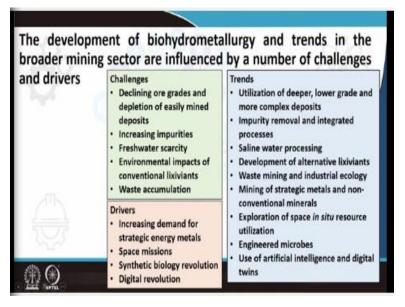
So, 1950s we see that the use of the most prominent bacterial strain or bacterium that is the Thiobacillus species who are capable of iron sulphide and copper sulphide oxidation in open cast mines. This particular strain was isolated characterized and significant developments were there. During 1960s in situ leaching of uranium and copper, discovery of iron and sulfur oxidizing archaea and many other iron sulfur oxidizing bacteria were there.

During 1980s and subsequent time we see that the setup of commercial heap leaching plants and gold extraction and gold oxidation plants for the recovery of copper, uranium, gold in USA Chile, South Africa and subsequently in Australia and many other countries South Africa of

course are there. In 1990s so on commercial biology of chalcopyrites that is the copper ore and the development of bio heaps for extraction of gold, nickel and zinc were practiced.

2000s and beyond the development of 2nd and 3rd generation bio oxidation plants, development of high temperature heap bioleaching technologies using archaea and thermophilic bacteria both. And subsequently the hybrid bioprocesses and reductive bioleaches were also developed and currently under practice.

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Now the development of this biohydrometallurgy or recovery of useful metals from low grade ores. And the trends in the broader mining sector are influenced by a number of challenges and drivers. So, in this particular infographics we can see that a number of challenges were actually found to be responsible for defining the different objectives of the biohydrometallurgical research and developments. So, within these challenges we see that declining ore grades and depletion of easily mined deposits remain in the top of the list.

Because as the good quality ores where the percentage of the target or the desired metals are at high as they are exhausted. The companies and the mining industries were forced to work with lower grades of ores. And also the ores which are deeply hosted within the earth crust and with declining ore quality the impurities were also higher in the ores. And also the scarcity of the fresh water, because fresh water is one of the fundamental requirements in the ore processing industries, so as the fresh water becomes more scarce.

So, the recycling of water was found to be very important. Environmental impacts of the conventional lixiviants, lixiviants means the chemical compounds which are produced and used during for the leaching or the oxidation of the elements and waste accumulation. So, these fundamental challenges were possibly responsible for driving a more research and developments on biohydrometallurgy.

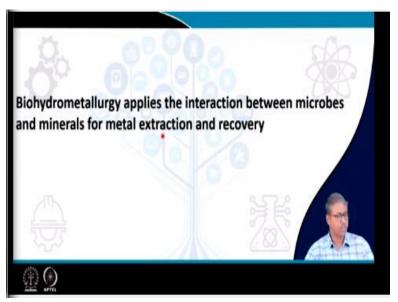
And these challenges led to the following trends like utilization of deeper, lower grade and more complex deposits. Impurity removal and integrated process development, saline water processing and development of alternative lixiviants and waste mining and industrial ecology. There were a number of drivers also, drivers in the sense these factors actually motivated the researchers and the industry increasing demand for strategic energy metals.

Because of the increased reliance on renewable energy sources and declining interest on the fossil fuel based technologies, production of different strategic materials were found to be very important and the demand for those metals were also high. Space missions, synthetic biology revolution and digital revolution all these factors were considered to be further drivers for expediting and improving the biohydrometallurgical processes.

And we see that approximately 100 billion tons of solid wastes from mining and mineral productions are produced each year. And biohydrometallurgy is commonly applied for the recovery of metal values from materials that would otherwise be considered waste. So, apart from the low grade ores which are not suitable for conventional mining, milling process and recovering the target metals?

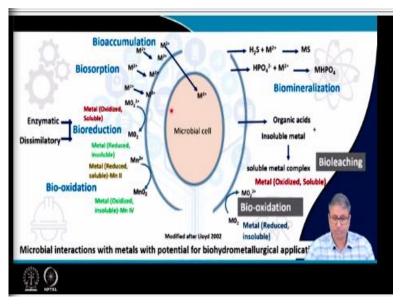
The wastes generated from the mining industries are also considered as the target for the biohydrometallurgical processes. Because during this biohydrometallurgical processes we are developing technologies wherein the waste materials which are generated from mining can be subjected to further recovery process, so that the useful metals can be recovered from that.

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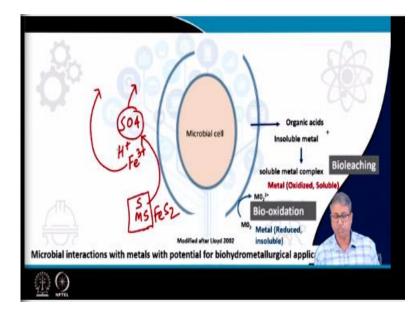
Now biohydrometallurgy applies the interaction between the microbes and minerals for metal extraction and recovery. As I mentioned in the beginning that this is a metal this is catalyzed by microorganisms, so microbial interaction with metals are found to be very critical.

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And as we have already studied microbes are able to interact with these metals in a diverse ways including the bioaccumulation, biosorption, bioreduction and bio-oxidation where the metals are converted into mostly insoluble form and these insoluble forms or sequester forms were of interest from removal point of view.

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But when we look at the recovery point of view, that if we want to recover the metals, so we need to solubilize the metals. So, this solubilization process can be done by basically 3 means. So, one of the means is considered to be using the organic acids which are produced by different microorganisms and these organic acids when they interact with the insoluble metal they produce the soluble metal complexes.

So, these soluble metal complexes are then leached out from the ore bodies or from the waste mining mine waste materials and can be recovered and processed. The second and most prominent one is the direct and indirect oxidation of the metals including the metal sulphides and iron in particular. So, the metals which are reduced and insoluble are oxidized by the microbes and these oxidized forms of the metals are solubilized or soluble.

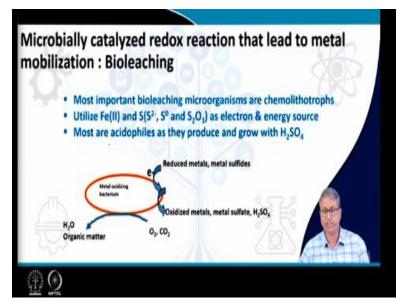
And they are mobilized and they leach out from the waste materials or the ore bodies. There is another important process which is not directly linked with metal transformation but that could be indirectly linked to the metal transformation as well which is basically the microbial ability to oxidize sulfur. So, both the metal sulphides as well as the sulfur compounds are oxidized by microbes to produce the sulphates.

So, these sulfates which are produced, the metal sulphates are produced for example. So, these sulphates which are in the form of basically sulfuric acid and they have also produce the proton

and often they also produce another very interesting thing that is called Fe 3+. So, this Fe S 2 when that is oxidized eventually Fe 3+ is also produced and as we will see this sulphate which is in the form of sulfuric acid helps the leaching of the metals which are present in the waste materials.

Because under strongly acidic conditions many metals are solubilized. The Fe 3+ acts as a kind of important electron accepting molecule, it accepts the electron from reduced molecules and thereby it also facilitates in the leaching of the process. So, basically if we look at the sulfur and sulphide metabolism process, we find that microorganisms oxidize these sulfur metal sulphides or iron sulphides in order to produce this sulphate and proton. And along with that it often produce also either Fe 3 or Fe 2 those also play very important roles.

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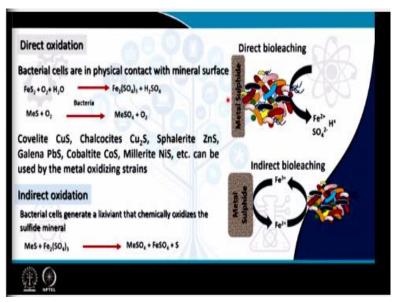
So, now if we look at the microbially catalyzed important redox reactions that lead to the metal mobilization will be able to understand this thing more clearly. So, here is the microbial cell for example, the microbial cells this particular microbial cell for example is a iron or sulfur oxidizing bacteria or we can call it a metal oxidizing bacteria. So, these bacterial strains they are capable of oxidizing the reduced metals or the metal sulphides.

For example the Fe, FeS 2 or sulphides or thiosulfates all these things are oxidized by these bacteria and they produce the oxidized metals like form Fe 2+ is produced or the sulphates are

produced. And many of these bacteria were rather the most important microorganisms who are involved in the bioleaching process are found to be chemolithotrophs. These chemolithotropic bacteria they utilize the iron that is Fe 2+ and sulfur, so in a sulphide or elemental sulfur or thiosulfate form as electron and energy source.

So, they derive the electrons they oxidize these iron and sulfur compounds and also they fix carbon dioxide. So, fixing carbon dioxide under aerobic condition they produce the organic matter and that might be helpful for the other microorganisms. So, basically these microorganisms are chemolithotropic autotroph and they rely only on the availability of the reduced metal or the metal sulphides.

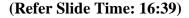
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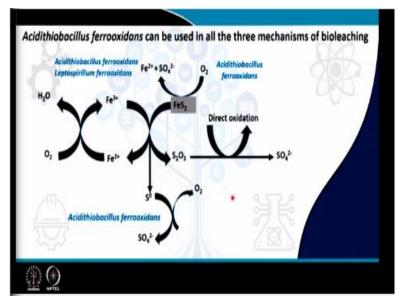


Now the oxidation process can be of 2 types, one is called direct oxidation where the bacterial cells are in physical contact with the mineral surface for example in this case. So, the bacterial cells are in direct contact with the metal sulphides for example and they are capable of oxidizing the metal sulphides, allowing the production of this lixiviant molecule that is Fe 2 S 4 O 3 and sulfuric acid.

Alternatively they can oxidize the metal size like copper sulphide or zinc sulphide and produce the copper sulphate and this copper sulphate becomes soluble and it leaches out from the ore body or the waste material. So, many of the minerals which are listed here are subjected to these metal oxidizing strains and we found that the bacterial strains like thiobacillus etcetera, they are capable of oxidizing the metals or the iron sulphides.

And facilitate the leaching or the oxidation of these metals and sulfur to sulphate. Whereas in case of indirect oxidation, bacterial cells generate a lixivant, now what is lixivant? Lixivant is the Fe 3+, so these bacteria they do not come in direct contact with the metal sulphides rather they utilize the soluble Fe 2+ and the Fe 2+ as used as electron donor and Fe 2+ is oxidized to Fe 3. Now Fe 3 acts as an electron accepting molecule and facilitates the oxidation of the metal sulphides further producing more sulphate and Fe SO 4 from the metal sulphide deposits.



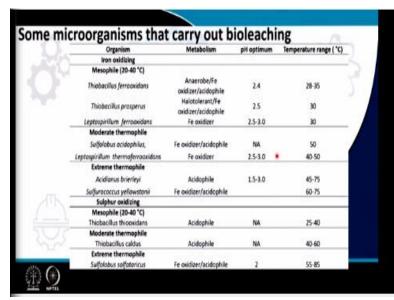


Sometimes these processes are also these bacteria they produce copious amount of exopolysaccharides and they work through this exopolysaccharide based matrix as well. Now here we see the acidithiobacillus ferroxidase which is found to be one of the most important and catalytically the most robust bacterial strain for catalyzing all different types of like direct oxidation, indirect oxidation of metals and oxidation of sulfur compounds as well.

As you can see here this bacteria is capable of oxidizing FeS 2 producing Fe 2+ and sulphate. It also produces thiosulfate; the thiosulfate can be subjected to direct oxidation to sulphate. It can also facilitate the production of the conversion of Fe 2 and Fe 3 conversion. So, Fe 2 is basically oxidized to produce Fe 3 and Fe 3 actually adds into this Fe S 2 oxidation process.

And so that the cycle of events continued and the production of sulphate is the essential outcome which solubilizes all the metal deposits, metal sulphides and essentially enables the production of the metal sulphates, like the copper sulphate, zinc sulphate, cadmium sulphate. And all these sulfates are soluble, so that they leach out from the ore bodies or the mine waste materials.



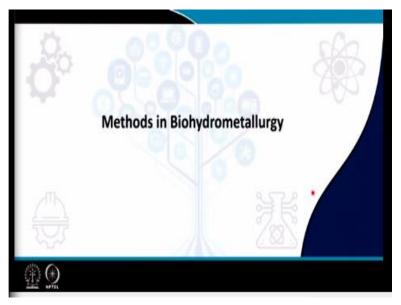


So, here are the list of some of the bacterial strains which are found to be very effective and their respective metabolism. So, the name of the bacteria includes the Thiobacillus ferrooxidans or Acidithiobacillus ferrooxidans. The name of Thiobacillus has been changed in the later time. So, some of them are mesophilic, some of them are moderately thermophilic and some of them are found to be extremely thermophilic bacteria.

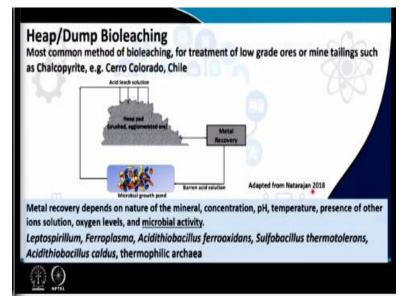
And their metabolisms include anaerobic to aerobic, iron oxidizing bacteria, acidophilic or they are some of them are iron oxidizing and most of them are we see that they are iron and sulfur oxidizing and most of them are acidophiles also. And many of them are actually truly extremophilic bacteria because they live in or they are capable of living in very low pH high metal concentration, high sulphate concentration environment.

As you can see the pH regime which they generally operate is very acidic because it can grow at 1.5 to 3 or even less than that also. And the temperature ranges also vary from neutrophilic conditions to moderate the thermophilic conditions.

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Now we will talk about the different methods in biohydrometallurgy.



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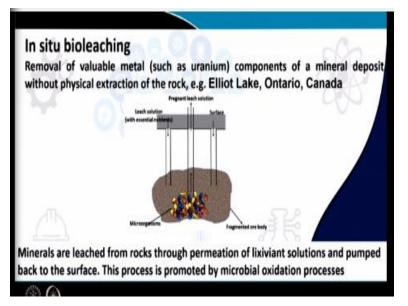
These biohydrometallurgical processes where bioleaching or the oxidations of the metals or the metal sulphides are practiced can be done with firstly the heap or dump leaching. This is one of the most common methods of biology for the treatment of the low grade ores or the mind tailings such as Chalcopyrite etcetera. And it has been practiced in many of the mines even in the Chile

and other places. So, what it does basically? Here we see that the heap of crust aggregates of the low grade ore, so the mine tailings are there.

The specialized microbial cells are grown and then they are added into this heap of the waste materials that are low grade ore or the tailings. And they are allowed to interact intermittently water is also added into that. And eventually within a few weeks or so, micro microorganisms they act on the metal sulphides and other iron present in that and they produce the aqueous solution which contains the high concentration of the metals. And the metals come in the form of the leachates. The leachates are collected and it is used for the recovery of the metal.

Now the metal recovery through these process like the heap or dump leaching where the microorganisms are added and it is kind of a open heap where the microbes are allowed to act on that. Depends on the nature of the minerals, concentration of the particular element which is targeted pH, temperature presence of other ions present in that, oxygen level and of course the microbial activity responsible for catalyzing this oxidative metabolism. Mainly the organisms like Leptospirillum, Ferroplasma, Acidithiobacillus ferrooxidans, Sulfobacillus, Acidithiobacillus caldus etcetera. And many thermophilic archaea are found to be involved in this kind of heap or dump bioleaching.

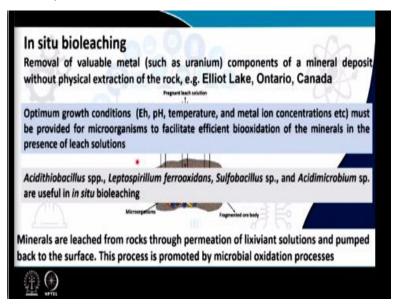
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The next type of bioleaching is called the in situ biology, where the removal of valuable metals such as uranium particularly is done while the ore body remains underground itself. So, no excavation is involved here, so physical excavation of the rocks or the ores are not done. It is only from the surface the appropriate solutions and the nutrients are added into that, the indigenous microorganisms are allowed to act on the uranium.

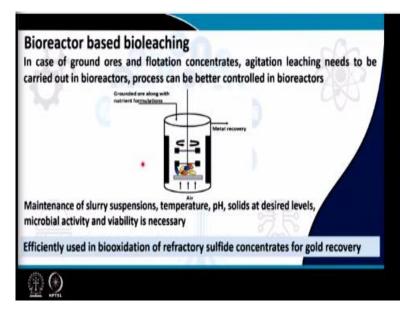
And uranium once these oxidized the oxidized uranium is soluble in water and that is called the pregnant leach solution, it is then recovered from the underground ore bodies or the underground crust. So, minerals are leached from the rocks through the permeation of the leaks event solutions and pumped back to the surface, this process is promoted by mine. So, it is all about the microbial catalytic activities which are allowed in the underground ore deposits and it has been found to be quite effective for recovering the uranium.

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Now optimum growth conditions including the Redox potential pH temperature metal ion concentration etcetera must be provided for microorganism to facilitate efficient biooxidation of the minerals in the presence of the leach solutions. Acidithiobacillus species Leptospirillum ferrooxidans, Sulfobacillus, Acidimicrobium are found to be useful for this type of in situ biology.

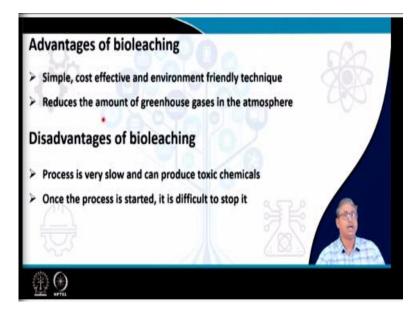
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The third one is the bioreactor based biology. In case of ground ores and flotation concentrates which are available in the mining industries. Agitation leaching needs to be carried out in bioreactors and process can be better controlled in bioreactors as well. So, the grounded ore along with the nutrient formulations are added and they are mixed while air is purged and the microbes are allowed to grow in that.

And the microbes catalyze the desirable reactions and the metals are leached and the leachates are collected and used for metal recovery. Now maintenance of slurry suspension temperature, pH, solids at desired levels microbial activity and viability are important parameters for the performance of this type of bioreactor based bioleaching. Efficiently this type of bioreactors based biology has been found to be effective in refractory sulphide concentrates of gold particularly.

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Now the advantages of bioleaching. It is considered to be simple as it is microbially driven, cost effective and environment friendly technique. Reduces the amount of greenhouse gases in the atmosphere, it does not utilize electricity or the otherwise the infrastructure requirements are very, very nominal. The disadvantage of the bioleaching is mainly that it is a microbially dependent microbially driven process.

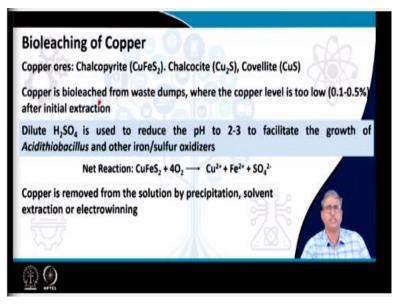
So, the process is sometimes found to be quite slow and also it can produce other toxic metals and if it is not controlled appropriately then because it is difficult to stop once particularly for in situ type of leaching process. So, it is difficult to stop this type of process, so a strict monitoring of the activities are essentially required.

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Now in the last phase of this lecture we will discuss about the bioleaching of some of the important metals.

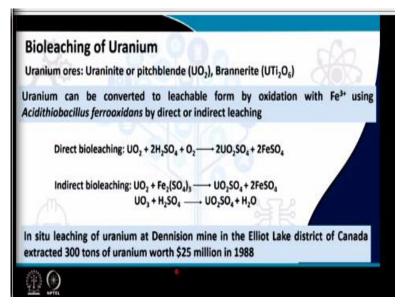
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For example the bioleaching of copper, copper ores like Chalcopyrites, Chalcocites or Covellite are particularly subjected to the bioleaching. Copper is bioleach from waste, dump where the copper level is too low like 0.1 to 0.5% after initial extraction. So, in most of the copper mines they have large amount of these waste dump sites where these very low concentration copper is present in the waste materials.

Dilute sulfuric acid is used to reduce the pH to further to 2 to 3 pH to facilitate the growth of the Acidithiobacillus and other iron sulfur oxidizers which essentially oxidize the Fe CuFeS 2 with in presence of oxygen to produce the copper sulphate. And copper is removed from the solution by precipitation solvent destruction or electrowinning.

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Bioleaching of uranium as I mentioned earlier, uranium can be recovered is converted to leachable form by oxidation with iron 3 using Acidithiobacillus ferrooxidans by direct or indirect leaching. So, uranium can be oxidized by bacteria, some bacteria can directly oxidize like acidithiobacillus ferrooxidans can directly oxidize uranium producing uranium sulphate which is soluble.

Or indirectly through this Fe 3+ which is produced by the action of iron sulphide oxidation process. And UO 2 can be oxidized further by this Fe 2 SO 4 whole 3 to produce again the uranium sulphate and FeSO4 and the produced sulfuric acid can further oxidize and solubilize the uranium present in the ore body. In situ leaching of uranium in Dennison mine in the Elliot lake district of Canada was most important from industrial point of view. Because the reported values are like about 300 tons of uranium worth rupees 25 million US dollar was possible in 1988.

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And finally the bioleaching of gold. Gold ores like Calaverite and Petzite etcetera are subjected to bioleaching. Generally gold ores are treated with cyanide and the cyanide treated gold is extracted with carbon. However some of the gold ores are enmeshed in FeS 2 or FeAsS is recalcitrant to cyanide treatment. And these ores particularly are initially bioleached because wherever the iron or arsenopyrite kind of stuffs are there.

So, the bioleaching is first done with Acidithiobacillus ferrooxidans in a series of bioreactors and then the treated ore is further extracted using the cyanide extraction process under aerobic or anaerobic condition. Cyanide is subsequently removed from the ores by chemical or biological oxidation with So 2, H 2 O 2 or otherwise with microorganisms. There are several cyanide utilizing microorganisms including Actinomyces, Arthrobacter, Pseudomonas, Thiobacillus etcetera, are reported who can actually utilize the degrade the cyanide.

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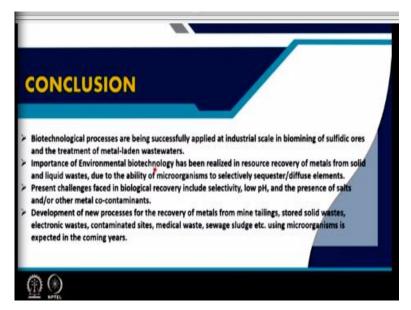
So, these are some of the screenshots of some of the important papers which I found to be very relevant for knowing more about this biohydrometallurgy and bioleaching process recovery of important ores.

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So, the following papers are used as the reference material for this lecture.

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And in conclusion the biotechnological processes are being successfully applied at industrial scale in biomining of sulfidic ores and the treatment of metal laden waste water or waste materials. Importance of environmental biotechnology has been realized in resource recovery of metals from solid and liquid waste. And due to the ability of natural microorganisms to selectively sequester or diffuse elements, these bio hydro metallurgical processes have been found to be very useful for developing green technologies.

So, present challenges faced in biological recovery include the selectivity low pH and the presence of salts and other metals and co-contaminants. And development of new processes for the recovery of metals from mine tailings, stored solid waste, electronic waste, contaminated site, medical waste etcetera, are practiced or incorporated in this research as well and we will see that in coming years. More interesting findings and processes are being developed using those improved understanding. Thank you so much.