

Mineral Resources: Geology, Exploration, Economics and Environment
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Lecture – 57
Environmental Impact of Mineral Resource Exploitation (Contd.)

Welcome to today's lecture. We just started our discussion on the environmental impact of mineral resource exploitation and today we will have a brief discussion on one of the issues, one of the known impacts of mineral resource exploitation, particularly pertaining to the multi metal sulphide deposits. Metal sulphide deposits which have been the major source of base metals like copper lead and zinc in the world, and those deposits which are essentially worked by open pit methods and in that process the environmental

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Acid Rock Drainage from Mines (including coal) and Tailing Dams

$$\text{FeS}_2 + 7/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$
$$\text{Fe}^{2+} + 1/4 \text{O}_2 + \text{H}^+ \rightleftharpoons \text{Fe}^{3+} + 1/2 \text{H}_2\text{O}$$
$$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+$$

reaction rates strongly increased by
microbial activity (e.g., *Acidithiobacillus* spp. or *Leptospirillum* spp.)

$$\text{FeS}_2 + 14 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$

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impact or the way the environment is affected is by a process, which is known as the acid rock drainage or acid mine drainage. And as we discussed before, there is such kind of situation arises, when a metal sulphide ore body is exposed during the process of open pit mining to atmosphere, and essentially the atmospheric oxygen and the moisture that leads to the oxidation of the sulphide minerals, generation of copious amount of sulphate ion and the H^+ which decreases the pH of the fluid of the water, that is how the name is derived from acid mine.

With this the water is rendered very acidic, p H becomes very low. The problem is that in addition to the fact that such acidic water when released or discharged to the surrounding water bodies in terms of stagnant water body or flowing water body. They will affect the biota, they affect the ecology of the area, and in addition to that when the water becomes very low p h, its solubility of different metals becomes high as we all know and in that process it also dissipates or it also mobilizes lots of toxic metals.

For example, if the particular deposit as a high concentration of lead and cadmium or any other heavy metals; then these metals also get dissolved in this kind of acid mine water and is dispersed into the surrounding areas contaminating the soil and water. If it happens for a good number of years then they it affects in degradation of the overall quality of the area.

And as we discussed before in the last class, the processing of such kind of metal sulphide ore bodies in a filtration process, in the concentration process, which gives rise to the waste in the form of tailings and the tailings are accumulated in structures like tailing dams. They are essentially not dam the way we know them, but their areas where the geology in terms of the topography the conditions are favourable, where this tailing could be deposited and it could sustain such kind of deposition for a good number of years for the life of the mine, and there is definitely some amount of engineering which is involved there.

So, these tailing which keeps on accumulating to quite a great thickness, by virtue of the concentration of even though lower concentration of the sulphide minerals, they do also get oxidized and the pore fluid in the in the tailing dam will percolate down eventually contaminating the groundwater. If we go just to understand the process, which is almost very similar to the one which we saw in the supergene oxidation and sulphide secondary sulphide engagement process kind of reactions,

where a pyrite molecule is oxidized within the presence of water, to give rise to Fe^{2+} plus sulphate ion plus $2H^+$, further this Fe^{2+} is again oxidized in the presence of S^{2-} give rise to Fe^{3+} and half water and is Fe^{3+} when it is oxidized. So, it gives rise to iron hydroxide, which will be in the form of either a amorphous or very cryptocrystalline form like a ferric hydrate or it could be goethite and which releases further hydrogen ions. So, if we combine these reactions we will see that

for a molecule of pyrite, when it undergoes such kind of reactions, such as chain reaction, then it gives rise to good number of hydrogen ion above one mole of pyrite will give rise to about four mole of hydrogen ion.

So, this could go on in an inorganic oxidation process, which will give rise to this acidity. So, whenever this surface water is flowing in form of drainage and are being pumped out of the opencast mine site. So, they will eventually be getting discharged into some local water bodies. So, what is more important to know here is, the such kind of problems are more acute in case of abundant sulphide mines than the presently working mines because of the fact that the longer the duration for which this ore bodies are getting exposed to the to the atmosphere, higher is the amount of this kind of acidic water which is being discharged.

Now, interestingly such kinds of processes are very well accentuated by the microorganisms. The microorganisms are the thiobacillus or the acidithiobacillus or the leptospirillum kind of bacterial species, which survive by the process of this oxidation of this sulphide that the energy which is liberated in this process. We of course, in this simple chemical reactions we are not representing the how much of energy is liberated in this, but it is observed that the energy in terms of calorie which is liberated in such kind of reactions is pretty significant, and it is enough for this kind of organisms for their survival.

So, essentially this overall reaction involving the iron 3 plus, as a very strong oxidant here; so then this reaction is giving rise to the iron 2 plus and sulphate plus 16 H plus. This reaction could go on with the help of these bacteria. So, since we have this kind of bacteria growing in the natural environment, such bacteria have been identified, been isolated and very well known for their role in generating this acid mine drainage.

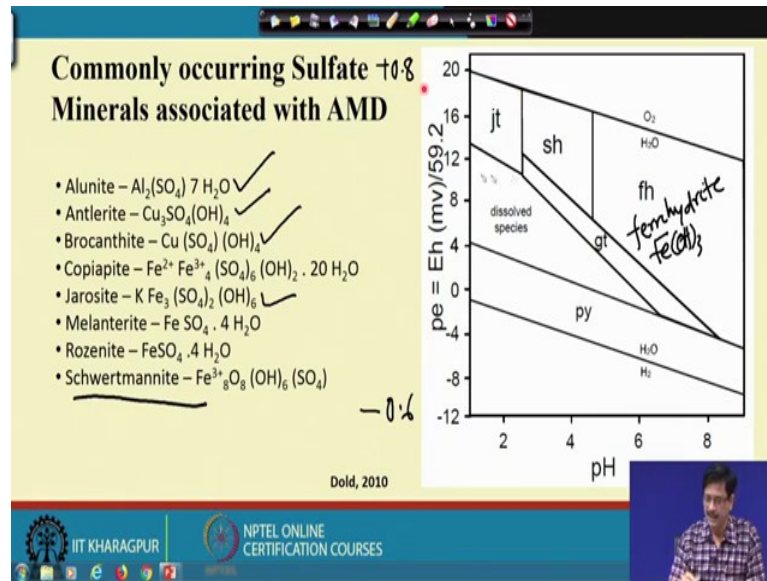
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So, these are some of the photographs which you can see here. Any abundant or any working sulphide, multi metal sulphide mine if you visit, you will see such kind of features which this water is almost getting a hue of such a yellow colour. Because of this particulate matter which is within this water called the ochre or the red ochre. In American literature they are called the yellow boys or the bad boys. So, the Ochreous precipitates are essentially constituted of so many cryptocrystalline species of iron sulphate iron oxides and much other type of different secondary mineral species which form in this kind of environment. So, essentially the p H in this environment is very low. We will see the range in which such kind of p H variation takes place and under such kind of very low p H many secondary mineral species come into existence which of course have their stabilities pretty limited, but they do play a significant role in mobilizing many of the heavy metals

and the toxic metals in the environment. So, these are some of the features and many such pictures could be seen available in public domain. Such kind of features as acid mine drainage and such kind of Ochreous precipitates.

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So, these are the way in which the process could be represented chemically on an E h p H diagram. There are some of the commonly occurring sulphate mineral species which are associated with acid mine drainage. Some of them which you are already quite familiar such as this alunite which we have seen the form in very low p H conditions in the advanced argillic alteration in porphyry copper deposits. So, they do form in a very low p H condition and we do also see, and such kind of mineral phases which we list even some of them and many more of them are Secondary sulphates as well as sometimes silicates and iron aluminium hydroxides when they form. So, these mineral phases are essentially identified by techniques XRD if they cannot be studied under the microscope. They have deposits with very interesting surface features

and they are identified by x ray diffractometry or some spectroscopic studies in addition to studying their surface micro features with the help of a scanning electron microscope. And this is the antlerite; hydrated copper sulphate, brochantite; this again hydrated copper sulphate. Copiapite is a very specific mineral associated with acid mine drainage, jarosite is a very interesting mineral and is a mineral of much greater interest, because of occurrence in mars and indicating presence of water and indicating the very low p H, and the Melanterite, Rozenite and Schwertmannite. Schwertmannite is also a mineral phase which is very regularly encountered in the acid mine drainage environment at very low p H. So, here it is a p e versus p H diagram, where you can translate the p H. The Eh could be something about -0.6 to plus+0.6 or +0.8 kind of value that we saw before.

So, within this E h- p H range, this different mineral species, their stabilities could be delimited. So, this is jarosite; j t is for jarosite, this is the schwertmannite, f h is for ferric hydrate, which is essentially is a cryptocrystalline amorphous form of F e OH 3 which forms and then it helps in generation of a lot of H plus ion.

So, we have seen this reaction. So, this is a natural limit of e h p H. So, this as you could see very clearly that minerals like a secondary sulphide minerals like jarosite and schwermannite and this is for goethite, which forms in this range and always we could see that the higher the oxidation state and it will very low p H which very much corresponds to the environment that prevails in an open pit sulphide mine and. So, these are the mineral species which generally are there.

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Mineral	Mole H ⁺ /Mole Mineral	Relative wt % H ⁺ /Mole mineral	Reaction with Fe(III) ⁰
Pyrite	4	0.03	2.7 x 10 ⁻⁷
Marcasite	4	0.03	1.5 x 10 ⁻⁷
Arsenopyrite	2	0.018	1.7 x 10 ⁻⁶
Chalcopyrite	?	0.011	9.6 x 10 ⁻⁹
Pyrrhotite	2-0	0.022	-
Enargite	1	0.002	-

Species	Equation	Fe ³⁺	H ⁺	log K (I = 3 M)
Fe ³⁺		1	0	0
Fe(OH) ²⁺	Fe ³⁺ + H ₂ O ⇌ Fe(OH) ²⁺ + H ⁺	1	-1	-3.05
Fe(OH) ₂ ⁺	Fe ³⁺ + 2H ₂ O ⇌ Fe(OH) ₂ ⁺ + 2H ⁺	1	-2	-6.31
Fe(OH) ₃ (aq)	Fe ³⁺ + 3H ₂ O ⇌ Fe(OH) ₃ (aq) + 3H ⁺	1	-3	-13.8
Fe(OH) ₄ ⁻	Fe ³⁺ + 4H ₂ O ⇌ Fe(OH) ₄ ⁻ + 4H ⁺	1	-4	-22.7
Fe ₂ (OH) ₆ ⁴⁺	2Fe ³⁺ + 2H ₂ O ⇌ Fe ₂ (OH) ₆ ⁴⁺ + 2H ⁺	2	-2	-2.91
Fe ₃ (OH) ₈ ⁵⁺	3Fe ³⁺ + 4H ₂ O ⇌ Fe ₃ (OH) ₈ ⁵⁺ + 4H ⁺	3	-4	-5

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So, here we could see the actual scenario. So, now, the question is whether it is only pyrite or any other sulphides. Other sulphides also do get sulphide oxidized they do generate the sulphate ion and the H plus ion but then the most important culprit in acid mine drainage is actually pyrite. So, as we saw before a pyrite one mole of pyrite will essentially be generating 4 moles of H plus.

And marcasite is just a polymorph of pyrite, which is also F e s 2 in its composition and in most of the properties and in terms of it is a kinetics of oxidative reactions its almost similar to pyrite. So, pyrite and marcasite these two are the ones which generate the maximum amount of H plus ion and imparting acidity to the water. Arsenopyrite releases

two moles of H plus ions. Chalcopyrite also have seen such kind of reactions; chalcopyrite with oxidation in presence of a water which also will release copper 2 plus ion, sulphate ion, And also iron. Pyrrhotite rather has a less as a source of the generation of the acid mine drainage. It generates about almost 0 to 2 depending on what form it is, and sometimes the textural characteristics of the pyrite also are important. If there are very fine grain type of pyrite they do generate more of acids and they get oxidized much more faster quicker, and then in terms of the rate of the reactions and the generation of the p H; the acidity is concerned, and the enargite which is a silver sulphide, which gives only one mole of hydrogen.

And minerals like galena and sphalerite, they almost are very negligible contributors to acid mine drainage. So, the main culprit in acid mine drainage is pyrite and marcasite. So, any pyrite which as we saw before when it comes to a secondary supergene oxidation and sulphide enrichment process, a pyrite rich ore body will always give rise to this process much more efficiently, than a pyrite poor ore body and where the pyrite abundance will be less there the surface oxidation does not proceed to that completion and we get a lot of copper trapped in the oxidation zone.. So, these are the species and the iron bearing species are represented here.

So, the iron 3 plus, iron OH 2 plus and where the H plus ion consumption is given in terms of $12 - 3$ and the $\log k$ the equilibrium constant values, when the I is here is a ionic strength is about 3 molal and F e 3 concentration is almost 1 and here these are the iron bearing species and also as you could see the liberation of the H plus ions is shown here. F e OH 2 plus is 1, F e OH 2 plus with F e 3 plus is depending on the concentration of iron,

and the nature of the of the of the molecule and the availability to water. It also releases two moles of hydrogen ion, and in this case it is 3 mole of hydrogen ion and we see a F e OH 4 plus F e OH 4 plus. So, they are generating different amount of the H plus ions, different molarities of the H plus ions.

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Phase	Equation	moles H ⁺ /mole Fe ³⁺ hydrolyzed
amp. Fe(OH) ₃ (s)	Fe ³⁺ + 3H ₂ O ⇌ Fe(OH) ₃ (s) + 3H ⁺	3
ferrihydroxide	10 Fe ³⁺ + 60H ₂ O ⇌ 5Fe ₂ O ₃ ·9H ₂ O + 30H ⁺	3
goethite	Fe ³⁺ + 2H ₂ O ⇌ FeO(OH) + 3H ⁺	3
hematite	2Fe ³⁺ + 3H ₂ O ⇌ Fe ₂ O ₃ + 6H ⁺	3
schwermannite	8Fe ³⁺ + 50SO ₄ ²⁻ + 14H ₂ O ⇌ Fe ₈ O ₈ (OH) ₆ (SO ₄) ₃ + 22H ⁺	2.75
	16Fe ³⁺ + 3SO ₄ ²⁻ + 26H ₂ O ⇌ Fe ₁₆ O ₁₆ (OH) ₁₀ (SO ₄) ₃ + 42H ⁺	2.625
jarosite	3Fe ³⁺ + K ⁺ + 2SO ₄ ²⁻ + 6H ₂ O ⇌ KFe ₃ (SO ₄) ₂ (OH) ₆ + 6H ⁺	2

jarosite ⇒ goethite: $KFe_3(SO_4)_2(OH)_6 \Rightarrow 3FeO(OH) + K^+ + 2SO_4^{2-} + 3H^+$
 schwermannite ⇒ goethite: $Fe_{16}O_{16}(OH)_{10}(SO_4)_3 + 6H_2O \Rightarrow 16FeO(OH) + 3SO_4^{2-} + 6H^+$
 schwermannite ⇒ goethite: $Fe_8O_8(OH)_6(SO_4)_3 + 2H_2O \Rightarrow 8FeO(OH) + SO_4^{2-} + 2H^+$

So, these are the again you could see the same reaction over here, this is the amorphous iron oxide this is ferrihydroxide amorphous Fe(OH)₃ solid.

So, it is forming through this reaction liberating 3 moles of H⁺ plus ion, and when its form a cryptocrystalline ferrihydroxide forming from iron 3 plus, it is giving rise to a form of a hydrated iron oxide limonite and generating H⁺ plus ion. Goethite is again similarly generating the H⁺ plus ion, hematite and this one is the schwermannite. When this schwermannite forms also it generates H⁺ plus ion. So, we can see that in a very strongly acidic environment, such kind of minerals they are forming. So, schwermannite can be written in two different ways. So, this is jarosite.

Now, what exactly happens we can see through this kind of reaction that, suppose this is the formation of goethite from this compound, which is alunite, jarosite. So, there you have seen before in the diagram, with increasing p H a jarosite gets converted to ferrihydroxide with increasing p H. So, this jarosite with increase in the p H is getting converted to a goethite. This is a goethite and again this is same this schwermannite, which is again when it is getting converted to goethite it also releases H⁺ plus ion, and again the same depending on what the way we are writing the formula and availability of water.

So, the diagram that we saw before in the Eh - p H diagram in the stability, we can understand that this minerals like jarosite and schwermannite with increasing p H get

changed over to iron hydroxide phases. The important thing about them is that, this can also happen with decreasing moisture or the situation becoming more drier or even temperature is higher and also the p H of the surrounding is changing by interaction with the surrounding rock.

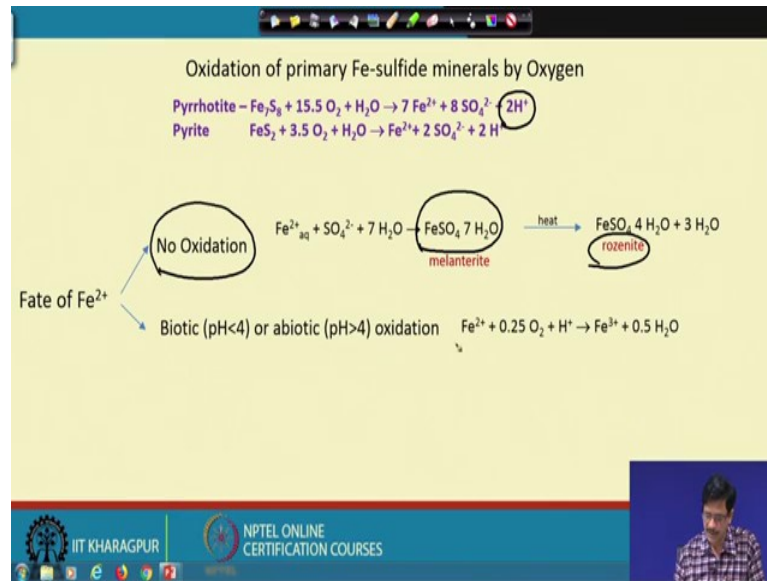
So, what happens is that, such kind of minerals like jarosite and schwertmannite, they are very fine grained. So, with a lot of available surface area and their typical surface features they do have lots of other heavy metals adsorbed onto their surfaces. So, as and when such kind of mineral phases are getting transformed to iron hydroxide phases, the adsorbed heavy metals get released. So, this minerals they even though they themselves are not the culprit, but they are very much responsible for generating toxic materials.

So, when they are generated at the acid mine drainage generation site, and when these are the secondary minerals that are forming from or precipitating from the fluid and carried in solution or the in the form of suspension in cryptocrystalline state a very fine grain state. They do have lots of other toxic metals, heavy metals, adsorbed onto their surfaces.

So, when they get converted to the iron hydroxide phases like ferrihydrite or goethite, this ferrihydrite and goethite cannot accommodate these toxic metals on the surface, the way these minerals are able to accommodate through the process of adsorption.

So, adsorption desorption plays a very important role in mobility of the heavy metals and their dispersal in the surroundings. So, the moment these minerals are getting converted to such iron or hydroxide phases, these heavy metals are again released into the surrounding.

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So, you can see through this schematic reaction as to what exactly happens or the chemical control. So, this gives us some of the idea as to the process of oxidation of the primary iron sulphide minerals by oxygen, where you could see that pyrrhotite where it gives rise to 2 H plus. So, it is basically is an incomplete reaction which is written for pyrite, but this again we know that this is a Fe 2 plus will be acted upon by Fe 3 plus and then the amount of total hydrogen that will be released will be 4 H plus.

So, now we can see that, what will happen to this iron 2 plus that is released here. In the process of the oxidation, the iron 2 plus that is released in this reaction what happens to them. So, one is that, it may be that there is no further oxidation to the iron and in that case the iron will only get combined with the sulphate, to form the hydrated sulphide which is melanterite is one of the secondary sulphate which we reached before and such kind of phases like melanterite if the situation is becoming little drier or the temperature increases, they get converted to phases like rozenite, where you could see that its iron sulphate 4 H 2 O and 3 water molecule is released.

If this particular iron 2 plus undergoes oxidation either by biotic with the help of the bacteria which are surviving at pH very low, pH less than four and abiotic where pH is greater than 4 slightly less acidic condition than biotic condition. So, we can write the reaction like Fe 2 plus plus oxygen plus water is Fe 3 plus + 0.5 water.

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So, what happens to the fate of iron 3 plus, which is coming out by the oxidation process of this Fe 2 plus. Means this Fe 2 plus which is liberated here may not be further oxidized depending on the prevailing environment or it can get oxidized either in biotic or in abiotic better give it a Fe 3 plus. So, what happens to the fate of Fe 3 plus. So, either it could undergo some precipitation of salt, ferric or mixed valence state, which we just saw the mineral copiapite, which forms just from the Fe 3 plus ion in a situation which could be represented by the action like this.

So, this is a simple salt precipitation in which it could be in both 2 plus and 3 plus states. So, it could be mixed valence state. It could also undergo a hydrolysis and ochre precipitation. So, what we represented as ochre, is a combination. As I told you, that ochre which is the suspended particulate metal which is present in the water which is coming at acid mine drainage with this typical color that we saw from the photographs.

So, these are the ochreous precipitates or the phases which are in jarosites shwertmannite and ferrihydrite. So, these are the situations in which if the sulphate concentration is more than 3000 microgram per millilitre and if there are some availability of potash ions from the silicates in the surrounding rock, then it forms the jarosite.

So, the essential condition for formation of jarosite is definitely p H should be very low almost about 1.5 to 3 and under such kind of a very low p H, with availability of potassium from this common rocks it forms jarosite.

If the p H is a little high between 3 to 4 and the sulphate concentration is something between 1000 to 3000 microgram per m l, then it will form and a mineral which is the shwertmannite which we just saw before the composition.

And if the p H is greater than 5 and the sulphate concentration is falling down much less than even 1000 microgram per m l then there is formation of ferrihydrite. So, the secondary minerals which form in the acid mine drainage, the mechanism of the formation could be explained in this way, and they are very much dependent on the p H of the fluid that is essentially coming out from the what we saw is that such kind of processes are so very expedited and facilitated by microorganisms like bacteria.

So, in which there is copious amount of H plus ion that is released to the solution and the p H can fall down to as low as 1.5 to 3, favouring formation of mineral phases like jarosite or shwertmannite and if the p H is increasing with reaction with the rock and sink available for the H plus ion, then the ferrihydrite will form. They also do form when the situation becomes less hydrous and that is how the they lose their water molecules and form this.

So, we will continue discussing on the issue of acid mine drainage a little further and then take up some other environmental impact issues related to mineral resource exploitation in the next class.

Thank you.