## Electronic Waste Management - Issues and Challenges Prof. Brajesh Kumar Dubey Department of Civil Engineering Indian Institute of Technology, Kharagpur

## Lecture – 13 Recovery of Metals from Electronic Waste

So welcome back. So, we were looking at different ways of extracting those heavy metals from electronic waste. So, we looked at a few of the methods like Hydro metallurgical methods, Spyros metallurgical method. So, we will continue our Hydro metallurgical method in this particular video, as well we had if you remember in the previous video towards the end of the video; we looked, we talked about in terms of the Hydro metallurgical process.

We looked at halide, cyanide leaching and the halide leaching. So, we talked about cyanide leaching, halide leaching as well as the what is the limitations of that and now we will start talking about thiourea leaching. So, will in this particular video, we will start with thiourea some other methods and then, we will see, we will talk about some of the recovery, how the recover some of the case studies if we if we can we will see based on the time.

So, in terms of the thiourea that is another way of, another way of like a extracting the heavy metals like gold. It is a cont, it is a, it has been used quite a bit in terms of the recovery of gold from the ore.

## Thiourea leaching

□ The research on using of thiourea ((NH<sub>2</sub>)<sub>2</sub>CS) as a gold extraction agent has shown considerable promise in recovery of gold from ores.

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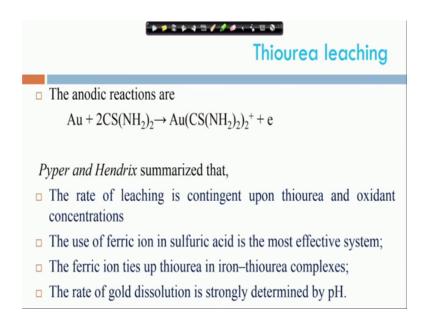
- In acidic conditions, thiourea dissolves gold, forming a cationic complex.
- The reaction is rapid and gold extractions of up to 99% can be achieved

So, it is a, as I said earlier in the previous video as well these methods are nothing new. It these have been used earlier as well, earlier mostly with the mine like ore. So, gold ore to thiourea leaching has been used; cyanide leaching has been used. So, they have been used earlier. Now we are using, we are trying to use the same technique with the electronic waste. So, rather than having the ore coming from the mine like the real mine we are doing an urban mining, you may hear the term these days urban mining. Urban mining is essentially looking at all the waste that is being produced.

And trying to recover the like a resources from there. So, that is the concept of urban mining which you may have heard in some other context too. So, in terms of the gold recovery one of the method is thiourea, pretty has been used for quite, as quite some time. Here, in what we do will work with the acidic conditions? In acidic conditions, we try to have thiourea dissolves the gold and they form a cationic complex. So, we have a thiourea which is thiourea, it is purpose the way the thiourea works; it is dissolving the gold and it is forming a cationic complex.

Cationic complex means it will be positively charged. So, and reaction happens very rapidly, gold extraction of up to 99 percent can be achieved. So, that is in terms of the mining activity that we are talking about, in terms of the smelting or the recovery of gold from the gold ore.

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So, if this is an in the anode reaction; the reaction that is taking place is you have a goal which is reacting with the thiourea and then it is getting a it is getting a positive charged complex. So, they have there have been a lot of research in this area it is the, what are the condition it works better; you have the rate of leaching. Rate of leaching means at what rate the things will move from the solid phase to the liquid phase.

Once something is charged, that means, it is in solution. So, this particular complex gold thiourea complex is in solution. So, and so, it will depend on the thiourea as well as the oxidant concentration. Now the use of ferric ion is also done, because here electron is being released.

So, there should be some this should be a electron has to be accepted as we know for any reaction, once you release an electron some there has to be a species which can take that electron. So, the ferric ion will act essentially as electron acceptor. And then, ferric ion ties up thiourea with iron-thiourea complex and also depending on the pH condition. So, pH is also important.

So, if you are trying to set up a thiourea leaching of gold from electronic waste, you need to look at iron sulfuric acid as well as the try to maintain the pH and, and of course, thiourea. So, those are the thing that is you need in terms of getting the leaching process done.

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**Limitation**Its commercial application has been hindered by the following three factors
It is more expensive than cyanide
Its consumption in gold processing is high because thiourea is readily oxidized in solution
The gold recovery step requires more development.

So, is it being used a lot, how it compares with other? So, it is more expensive than cyanide. So, that is why you do not see that much of thiourea leaching happening in a commercial scale, in gold recovery in the gold extraction from mine. So, it is more expensive than cyanide, but cyanide can, cyanide does produce more hazardous waste. So, that is why in terms of if you look at again, if you look at in totality. So, as I try to explain in my other classes like in other class there is another course running parallelly with this course, that course is actually 8 weeks and it is a as you some of you may have taken it was offered last year. It has been rerun this year, it is some lifecycle analysis.

So, there, so, that is where while, why those kind of concepts is important. So, here if you are looking at cyanide is cheaper than thiourea, but if you look at from a long term environmental costing, long term may be a life cycle costing, when you use cyanide the waste produced. You have to manage it as a hazardous waste. And that is more dangerous to manage them compared to what is being produced a thiourea.

So, we have to if you probably if you keep everything of those in place, we do not know like maybe we are we will be trying to find we will find out that actually thiourea comes out to be much cheaper. But again, you have to look at the big picture you have to look at the whole life cycle of that particular process rather than just looking at just like a part of it rather than looking at the whole from the very beginning to the very end.

So, it is a consumption of, it is a consumption in gold processing is high because thiourea is readily oxidized. The gold recovery steps is required some more development, is still things are in under development in this particular area. Cyanide is a older process, more established process. People have looked at that process in a more for many many years as opposed to, this one is a relatively newer process is still kind of work in progress in there.

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- Gold dissolution in ammoniacal thiosulfate solution is an electrochemical reaction catalyzed by the presence of cupric ions.
- It was proposed that Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> species present in solution acquires electrons on the cathodic portion of the gold surface and is directly reduced to Cu(NH<sub>3</sub>)<sup>2+.</sup>
- At the same time, either ammonia or thiosulfate ions react with Au+ ions on the anodic surface of gold and enter the solution to form either Au(NH<sub>3</sub>)<sup>2+</sup> or Au(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup>.

Then, the other is thiosulfate; thiosulfate leaching also happens here. The gold is dissolute the gold is dissolution happens in ammonia thiosulfate solution. So, that is what you are seeing over here the copper NH 3 4 2 plus. So, that is the solution where a copper is there and ammonia is there. And as copper has a tendency of in, actually in the presence of ammonia copper has a tendency to produce soluble complex that we have seen that in some of our other research as well.

So, it is at copper ammonia complex. They will since it is a positively charged, it will acquire electron and then, it will be it will get reduced, it will be reduced and then, at the same time either ammonium thiosulfate ion will react with gold and to produce gold ammonia complex or gold thiosulfate complex. So, it is then you have gold in solution now.

And then you can try to find out, try to find extract gold from the solution. So, any leaching this is again another leaching process. So leaching process as you know by this

time; leaching means moving of things from the solid phase to the liquid phase. So, here also our gold, our goal is to get the gold out of those electronic waste and then into the solution and then, we can recover we can try to recover gold from a solution which is enriched in gold. Right now, it is in the solid form. So, extracting that from solid to the liquid and then finally, to get the pure gold out of that.

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Thiosulfate leaching

Both the Cu(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub><sup>5-</sup> species and the Cu(NH<sub>3</sub>)<sup>2+</sup> species in solution are then oxidized to Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> with oxygen.
 Au + 5S<sub>2</sub>O<sub>3</sub><sup>2-</sup>+Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> → Au(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup>+4NH<sub>3</sub>+Cu(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub><sup>5-</sup>
 2Cu(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub><sup>5-</sup>+8NH<sub>3</sub>+1/2O<sub>2</sub>+H<sub>2</sub>O → 2Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>+2OH<sup>-</sup>+6S<sub>2</sub>O<sub>3</sub><sup>2-</sup>

So, it is depending on the thiosulfate or the ammonia copper complex you may have either it will convert to copper thiosulfate or and ammonium. So, in the presence of thiosulfate and ammonia copper complex what happens is essentially a change of place. So, copper will thiosulfate will react with copper and then, it will make a complex with copper thiosulfate complex and. So, ammonia will be free and then, it will be ammonium that it will make complex with gold and then, it will bring it to solution.

So, and at the end both the copper thiosulfate and the copper ammonia species, they oxidize to copper ammonia complex again. So, that is how the process works. Here the reaction has been presented. Again, these reactions and other stuff I am not expecting you to memorize. It is not that, this is not a memorization test. So, you do not have to memorize even if you those of you are planning to take an exam on this one, you do not have to memorize all these equations. You try to understand, what is the process that is happening there?

Depending on the concentration of  $S_2O_3^{2-}$ ,  $Cu(NH_3)^{2+}$  converts to  $Cu(S_2O_3)_3^{5-}$  ions and likewise for  $Au(NH_3)^{2+}$ .

So, just to give you an idea that things, what are the complexity which goes into recovery of gold from electronic waste and those of you who are from a chemistry by a background or a chemical background or and possibly wants to set up or anybody who once possibly wants to set up a like a process, where we can recover this goal because right now, what is happening in terms of the US management, I was trying to explain the earlier, most of it goes to informal sector and formal sector does not cannot actually manage it in a properly. There are lot of environmental impact, a human health impact.

So, if there is a nice merger of informal and formal and if we can set up some of these plans in a formal at most in the formal sector, which we can recover some of these gold and other stuff which will be which can be done in more efficiently. So, these are the, how it needs to be done, how things have been being done, in other countries and other places. So, this is just to give you an idea of how, what are the different methods we looked at different types of extraction. So, this is a either you go for urea, thiourea, thiosulfate, cyanide, halide all these are different methods. They work under different pH conditions.

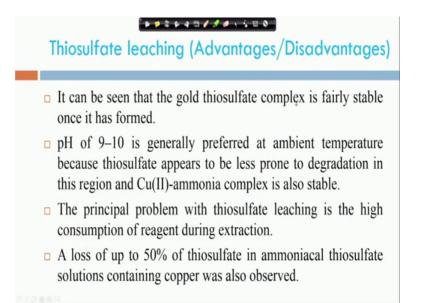
They worked under different operating conditions and then, they have different efficiencies as well. So, if you are if. So, if say if we want to decide which one to use? Of course, we have to look at the efficiency of the process, the cost of the process and then, when we say the cost, my request to all of you from now on that whenever you look at the cost of any anything, look at total lifecycle cost; do not just look at the cost of a short term. Because, the short term cost is not the real cost and does not matter whether that is I am talking about in general, not only for e waste for.

In general, when you look at the cost, look at the total lifecycle cost of that particular process, of particular product. So, it because environmental degradation, resource depletion, they are all it is because the that will be that is a big thing actually in today's world, with all these the climate change, sustainable development goal and all those things that we talk about. Unless we start implementing that in our day to day practices, we are not going to go anywhere in terms of the environmental betterment of environmental performance.

So, so, the again we were looking to this long reaction, I am not expecting you to remember of this reaction. I just want you to understand that how the things work. So,

enterprises of you will have thiosulfate and copper ammonia complex; there will be exchange of ions for that matter and sulfate thiosulfate will go with copper ammonia will get free. Ammonia reacts with silver and the sorry gold and it brings gold and ammonia complex in solution. And then, we can re recover our goal from there. So, this is how typically the scenario work in terms of thiosulfate leaching.

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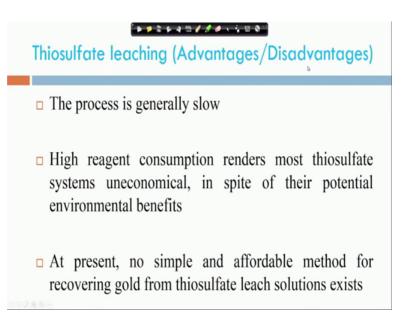
In terms of say any process, has certain advantages, certain disadvantages. So, it is a gold thiosulfate complex is fairly stable, which is a like you can it is a stable complex; pH of around 9 and 10 is preferred, because that is the this because it is a and generally preferred especially at ambient temperature because thiosulfate appears to be less prone to degradation as well as the copper, copper ammonia complex is more a stable. Ammonia as you probably know, ammonia typically you will see at the pH of 9, anything below pH 9, you will see that in ammonium. You will see in NH 4 plus when you look at when you try to see NH 3 that will happen only when the pH is above 9.

So, that is where that is why you would typically you see the pH of 9 and 10. So, again if you have to, do not try to memorize things, try to understand that why pH 9 and 10 will be preferred. It because the copper ammonia complex is more stable, ammonia will be in the form of ammonia only where when the pH is above 9 or around that particular pH. Anything below that it is mostly in ammonium NH 4 plus.

So, you will not see it and if you know that ammonia ammonia-ammonium chemistry, it is obvious for that you will say the of course, you need to have pH 9 and 10. Otherwise you will not see copper ammonia complex. So, that is how you need it to use, you should approach rather than trying to memorize and then, of course, if you try to memorize something without understanding, it does not stay for long in your head. So, the and then, what are the those are the kind of advantages point of view.

In the terms of disadvantage the principle problem is it is a high conjunction of reagent during extraction. So, you need a lot of thiosulfate and there is a loss because there is around 50 percent of the thiosulfate. It is a copper ammonical thiosulfate solution; copper also has some reactions going on. So, 50 percent of the thiosulfate kind of goes there and. So, it is not a very efficient process. So, that is it is a loss of around 50 percent of there.

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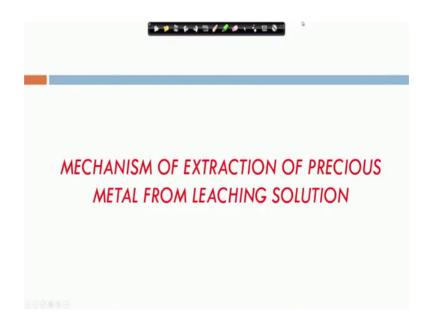


So, and it is a slow, it is a slow process and it is a lot of consumption of so, it becomes uneconomical in spite of their potential environmental benefit. So, although it is better from environmental point of view compared to cyanide leaching.

But since it is a lot of reagent consumption that makes it the things are uneconomical. So, again you have to look at the lifecycle cost. Here the bullet 2nd bullet which you see over here, I am not sure whether that incorporates the lifecycle cost; because we have to look at the how much money that goes into managing that cyanide containing waste because that may be much higher than rather than going for this thiosulfate leaching.

And there is a in terms of at present there is no simple and affordable method recovery gold from thiosulfate leach; although we are bringing it to the thiosulfate solution. Now how to get it out from thiosulfate solution that also is a question, that also because ultimately our goal is to get the pure gold. So, to get the pure gold, I have to take it out of that thiosulfate solution. So, the method the process for that is also under kind of a lot of where its there is no simple and affordable method of doing that as well.

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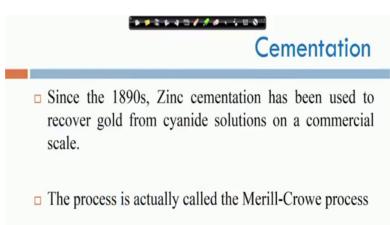
So, that gives you some idea about in terms of the different extraction methods. Then we will look at some of these extractions of precious metals from the leaching solution. So, far we have been talking about how to get this into the leaching solution. So, if you remember in terms of the extraction, of the precious metal one the step 1 is to because everything is in the solid form. So, the step 1 is let us bring this the precious metal from the solid form in e waste to the liquid form. So, let us bring them in solution.

So, let us say try to get them in solution by all these Hydro metallurgical process, Spiro metallurgical process. So, and that that is how these processes works anyway. So, you bring it into the liquid form. Now when they are in the liquid form, we try to next obvious step is to now let us get these individual metals extracted from this liquid form which is called the leaching solution, because what we have been doing.

So, far is the Hydro metallurgical leaching or the Spiro metallurgical leaching. Now we want to get things from there were liquid form into the pure solid form. So, that is let us look at some of the mechanism some of the examples of how that is done because that is also an important that is like an important follow up is step.

So, in terms of getting the precious metals from the leaching solution there are different ways you can go about it. Again similar things have been done by the metallurgical friends for different applications. So, you either you can go for cementation, you can try to same we will go over each one of them, go for solvent extraction, adsorption on activated carbon that is another one and then, ion exchange. So, those are 4 mechanism which potentially you can go for. Now, what is the cementation? It is a there has been it is a pretty old method.

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The major reactions are the cathodic deposition of gold and anodic corrosion of zinc.

Since almost 1040 years ago, 1030 years ago, Zinc cementation has been used. So, once you have the cyanide solution in which, we from the gold ore when you have the gold in the cyanide solution now. So, Zinc cementation is used to recover the gold from the cyanide solution on a commercial scale. This process has been explained nicely, but Merill and Crowe. So, that is called Merill-Crowe process. The major reaction here in especially in cathodic deposition is a goal and anodic corrosion of zinc. So, in cathode we say the gold gets deposited.

So, that is how the reaction takes place. So, that is the cementation, cementation reaction for zinc cementation is used to recover gold from it is a pretty old method.

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Cementation

□ The major reactions are

 $2Au(CN)^{2-}+2e \rightarrow 2Au + 4CN Zn + 4CN^{-} \rightarrow Zn(CN)_{4}^{2-}+2e$ 

- □ Cementation of gold is practically constant over the pH range 8–11.
- Impurities such as lead, copper, nickel, arsenic, antimony and sulfur are most deleterious for gold cementation.

So, a major reaction here is we have the gold with the cyanide complex, as you can see on the first reaction. Gold and the cyanide complex is there and then you add. So, you basically have a reaction where it is gets further reduced, where you have the gold gets separated with cyanide. So, cyanide ion and then, the zinc reacts with the cyanide ion and make zinc cyanide and. So, that is how the process works. So, the cementation of gold is practically constant you work at the pH range of 8 - 11. Here or So, it is a, but some problematic is also there in terms of if you have impurities of lead, copper, nickel, arsenic, antimony and sulfur. They have a chance to they actually they are deleterious for gold cementation.

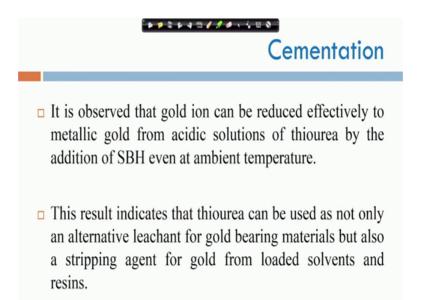
So, they also react in this particular scenario and they create some impurities. So, that is one process in terms of cementation and it has been deported that goal from thiourea thiosulfate thiocyanate solution you can use that. (Refer Slide Time: 19:54)

Cementation

- Awadalla and Ritcey (1991) reported that the recovery of gold from thiourea, thiosulfate or thiocyanate solutions by reduction-precipitation with a stabilized form of sodium borohydride (SBH).
- Sodium borohydride containing 12% by weight NaBH<sub>4</sub> and 40% NaOH.

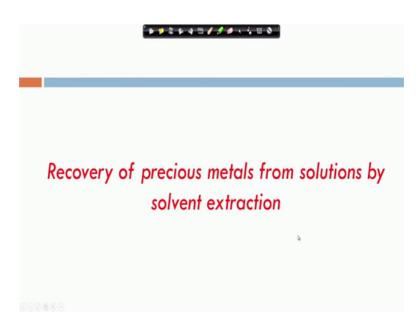
And you can also use the reduction precipitation with the sodium borohydride. So, sodium borohydride is also used which is 12 percent above weight of sodium borohydride and 40 percent sodium hydroxide. So, that is also bused as one of the recovery of gold.

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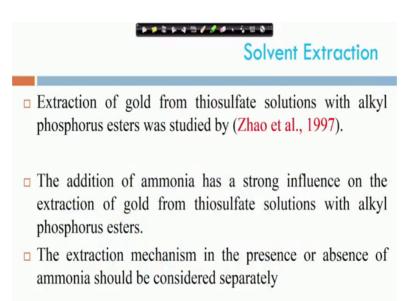
So, it is a, it is it can be reduce effectively to a metallic gold from an addition of sodium borohydride at ambient temperature. So, it is a thiourea, it is a alternative leaching from gold bearing, but also it is stripping agent for goal from loaded solvents and resins. So, thiourea does happen very, thiourea is kind of works good along with cementations for recovery of gold from the electronic waste.

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So, that is in terms of in terms of looking at how to get the precious metal, out from the solution; that is one we saw what we saw so far is in terms of getting things in this into the solution. The other a same thing we can do by solvent extraction as well. So, we can do some sort of solvent extraction, we will look at some of the example.

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So, it is there are they have been studies, where they have tried to have the gold in thiosulfate solution, extracted with alkaline phosphor ester. So, you can have alkaline phosphorous esters being used which in use which can. So, if the goal is more soluble in that particular ester alkaline phosphorous ester the gold will get more solubalize over there and then it will go from thiosulfate solution.

So, ammonia has also a effects gold from thiosulfate solution with alkaline phosphorous ester. So, that is there and the you there is a mechanism the extraction mechanism is there in the presence of ammonia and also in the absence of ammonia, both mechanisms are is available in the literature.

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**Solvent Extraction** 

■ For the system with no ammonia, the extraction reaction is  $iNa++2Au^++jS_2O_3^{2-}+OH^-+mTBP_{(0)} = Na_iAu_2(S_2O_3^{2-})_j(OH^-)\cdot mTBP_{(0)}$ 

□ The addition of ammonia into thiosulfate solutions, the extraction reaction is  $iNa++2Au++jS_2O_3^{2-}+OH^-+2NH_3+mTBP_{(o)} = Na_iAu_2(S_2O_3^{2-})_i(OH^-)(NH_3)_2 \cdot mTBP]_{(o)}$ 

Where i (i = 3-5) varies with j (j = 2-3), and the TBP coefficients m in the two equations are in the ranges of 1.5-2.5 and 6-9 respectively.

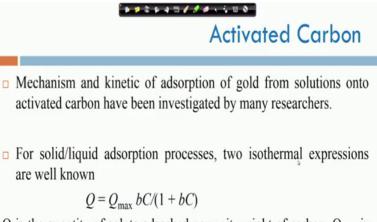
So the system with the no ammonium you will see some sort of the reaction as you see on the first bullet.

So, you will have sodium is there, then you have gold and then thiosulfate hydroxide and you have take a in terms of your, what would we say, like a precious metal by that by the solvent which is using the alkaline phosphorous ester. So, that is what you see like phosphorous ester as being used and you make a complex which is a sodium gold thiosulfate and hydroxide with some ester which is there and. So we, that is one in terms of; so, like a complex and if you in the absence of ammonium.

If the ammonia is present again similar reaction takes place and then we have ammonia also in solution over here. So, ammonia also is in the complex. So, here the i and j can vary as we can know what that coefficient like ester coefficient in the 2 equations in the range of 1.5 to 2.5 and pH is around 6 and 9 or something like that. So, that is it is based on that we use this particular solution for extraction and. So, that is it how you can do some recovery of gold from different places liquid.

So, as I said earlier we have this liquid which 1st we have the groups on e waste which is in the solid form. We have some of this basis metal 1st step; we try to bring this basis metal into the liquid phase. In the next step from the liquid phase, we try to bring it back into a solid phase, but more in a pure form. So, that is the goal in terms of these method that we have been talking right now.

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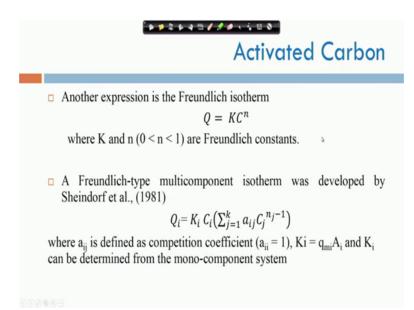
Q is the quantity of solute adsorbed per unit weight of carbon,  $Q_{max}$  is the maximum sorption capacity, C is the equilibrium concentration of the adsorbate in solution and b is the adsorption equilibrium constant

So, other ways activated, carbon activated carbon again it will work with the adsorption because that is what it does. Activated carbon is has good say like a particle like a small particle size, bigger surface area and good adsorption site. So, there is a mechanism of kinetics of goal from solution has been investigated, many people have looked at. So they have isothermal expression where the Q is equal to Q max where, the Q times certain factor which is bC upon 1 plus bC which is explained over here.

So, what is Q and Q max and all that. So, Q is the quantity of solute absorbed per unit weight of carbon. Q max is the maximum sufficient capacity. C is the equilibrium

concentration and a and b are the adsorption equilibrium constant. So, they are the factors which we need, which we use. So, this is activated carbon as we know it is a works on the principles of adsorption and different isotherms and that is what we have been looking at here. So, it is another expression we can explain this either of the Freundlich isotherm.

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So, Freundlich isotherm, again some of you may be assume that many of you will be familiar with that. So, you can put another expression we can put is the Freundlich isotherm; Freundlich type multi component isotherm is also there. So, which is presented in the small bullet? Again, you do not have to memorize all of these; what I am trying to say is just trying to show you that whatever you we have we learned in different courses.

So, with their different courses that we take whatever we learn, they do get applied somewhere. So, if you remember that these like activated carbon isotherm, Freundlich isotherm and other like a in terms of the multi component isotherm. So, all these things you have taken this especially if you are a masters or a PhD student you already have done this kind of like basics of some of these terminology in some other courses. But, what I am trying to show you here is all these concepts that we learn in different courses are actually really applied.

So, always think 1 thing if you can trust me like whatever we learn, whatever we learn from say high school or even from before that from my middle school and all the way to say college and other stuff, most of the stuff that you learn is for some purpose it is not for fun. So, you it is there to make you learn some of the new stuff, which you will use it at some point or the other you may not realize it when and but, you will use that knowledge in some form or the other. So, that is with that message let us close this particular video.

So, we will continue our discussion in the next video, where we will talk about more in terms of these leaching processes and essentially how to get this gold and precious metal which is there in the liquid phase now. It was only the solid phase in the e waste; we brought it to the liquid phase by different extraction methods which we explained so far. Now, we want to get it back into the solid phase and in a pure form. So how we can do that? So, we will keep on talking about it in the next video as well.

Thank you, keep watching, keep following up; they put do put questions, concerns or whatever you want to communicate with us on discussion forum, we will be more than happy to answer.

Thank you.