Concepts of Chemistry for Engineering

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Lecture – 58

Extraction of Metals

The last chapter we have discussed about the periodic table; this is the one where we are trying to see if we can purify the metal from ores. So, usually whatever is available in the form of ore like metal oxide, metal sulphide, metal halides and so on. These are not something we want in our regular life; in daily life we want something in more of a different form, more of a pure form.

Let say we need iron bar, we need pure gold, we need pure nickel, we need pure palladium, we need pure of different metal. But these metals are not given to us by nature by default; say, it is usually existing as in in its oxidized form. Invariably, all the metal ores we see they are found as metal oxide; that means metal is in oxidized form metal sulphide.

Again, sulphide is negatively charged 2 minus and metal is usually is going to be 2 plus and so on. So, therefore what we are really looking for is a method is a technique that can reduce the oxidized form of the metal, and give us the pure reduced metal. For example, if you have iron oxide, iron oxide from iron oxide we are hoping to get pure iron; that is iron in zero form, which is utilized in regular life. Same same is true for almost every metal, whatever metal complex or metal form is available with us; we are not going to use them, we are going to purify them; and then only we can use them. As we briefly discussed in the last class.

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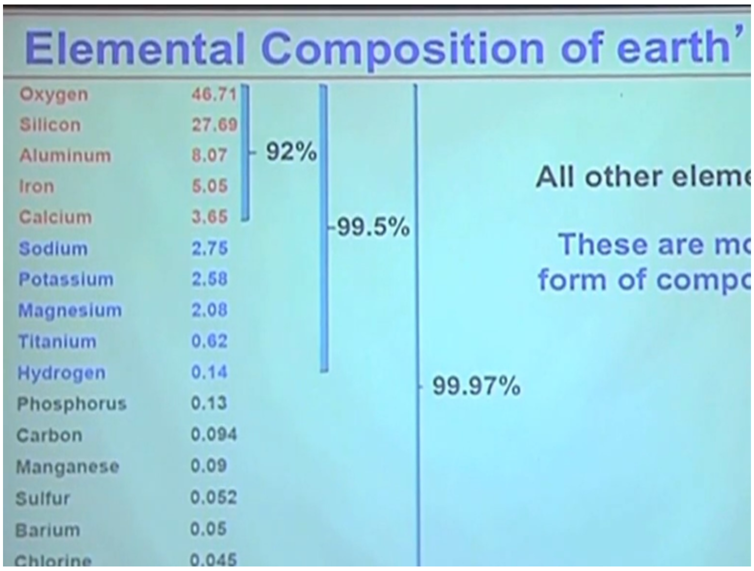

Elemental Composition of earth’

Oxygen	46.71
Silicon	27.69
Aluminum	8.07
Iron	5.05
Calcium	3.65
Sodium	2.75
Potassium	2.58
Magnesium	2.08
Titanium	0.62
Hydrogen	0.14
Phosphorus	0.13
Carbon	0.094
Manganese	0.09
Sulfur	0.052
Barium	0.05
Chlorine	0.045

92%

99.5%

99.97%

All other eleme

These are mo
form of compo

Fine, so what we are trying to say? We have 105 elements at least; more and more everyday we are discovering almost, not every day regularly. Let say in every 10 years we are discovering a new element in the periodic table; at least definitely in last few decades if you see, we have discovered something or the other.

So, that means that at least those are present in some amount on earth crust or in atmospheres, and thereby it allowed to scientist to discover them. But invariably what has happened? This is the scenario. Most often we see that only few elements are present in high quantity; all others are present in very very low quantity.

The challenge is really to get them in pure form, even if they are present in very very tiny amount. So, this is where I think chemistry becomes very handy; chemists can help the engineers to isolate the metal in pure form; and that is what we are going to discuss today.

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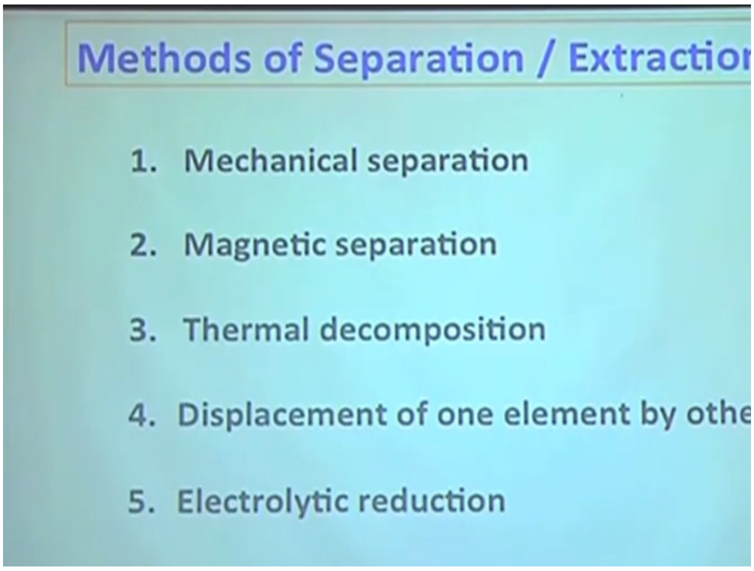

Methods of Separation / Extractio

1. Mechanical separation
2. Magnetic separation
3. Thermal decomposition
4. Displacement of one element by othe
5. Electrolytic reduction

We were discussing there are different techniques, not necessarily each or any technique are going to be only useful; it is a combination of things. We need to utilize a number of or series of experiments, by which from a impure mixture, impure metal ores or mixture of ores; we will be able to get a pure form of the metal.

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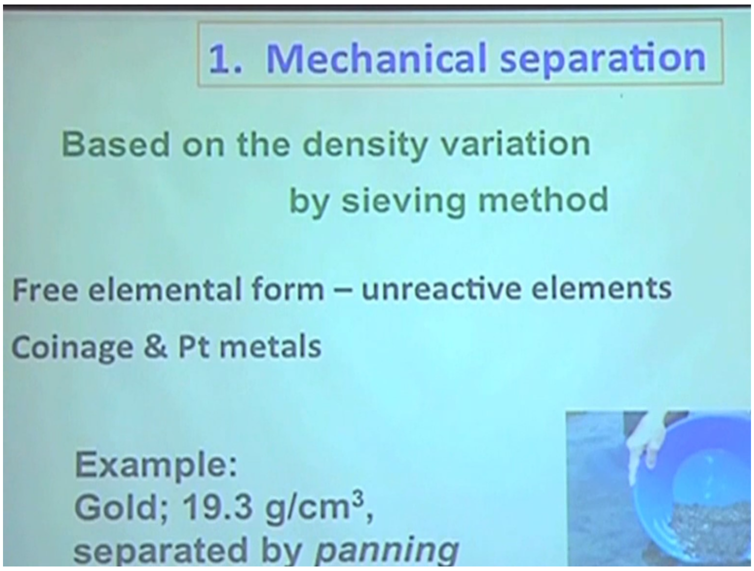

1. Mechanical separation

Based on the density variation
by sieving method

Free elemental form – unreactive elements

Coinage & Pt metals

Example:
Gold; 19.3 g/cm^3,
separated by *panning*

The easiest one is the mechanical separation as we were discussing in the last class. You just (())(03:51) off, you just wash it off. So, for example over here as it shown, you just wash off with some solvent; let say water is a usually water is a something which is usually used. You just wash it off, so unwanted material maybe going off; or the important materials maybe coming out. Whatever it is, you will be able to wash off some of the material that you do not want.

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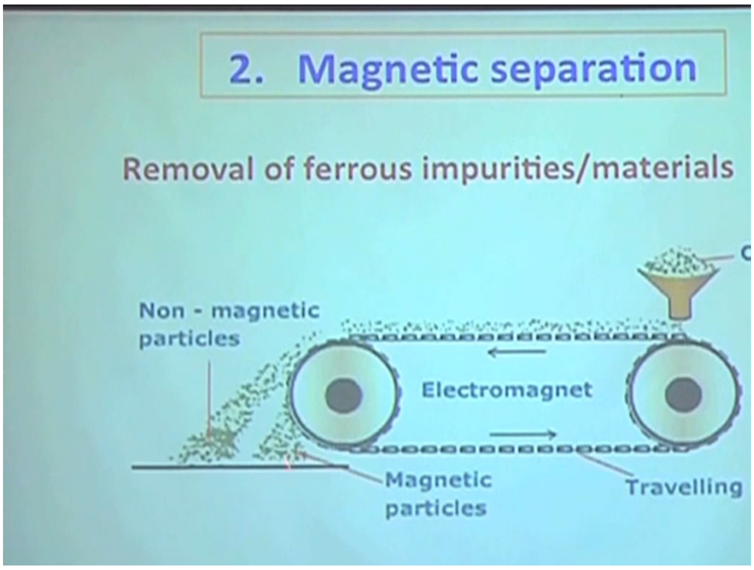

2. Magnetic separation

Removal of ferrous impurities/materials

Next another technique you can use; most often you need to use, is that is you pass the ore through the through this electromagnetic separation. Depending on the nature of the materials you have, some of those materials will be isolated completely, when you are passing through the electromagnet. Those magnetic materials which are having some attraction for the magnet will be isolated or separated out in a in a separate place compared to the non magnetic material. These are very easy technique and easy to understand.

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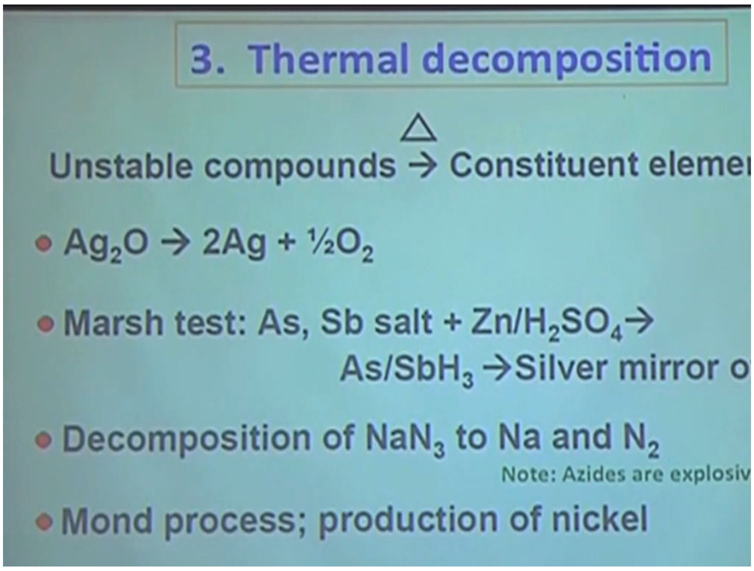

3. Thermal decomposition

Unstable compounds $\xrightarrow{\Delta}$ Constituent eleme

- $Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$
- Marsh test: As, Sb salt + $Zn/H_2SO_4 \rightarrow$
  $As/SbH_3 \rightarrow$ Silver mirror o
- Decomposition of NaN_3 to Na and N_2
  Note: Azides are explosiv
- Mond process; production of nickel

Of course, it is not going to be all is that easy; some more techniques are there, such as heating. Just you take the ore, you heat it. What will happen if some of the metal oxide, metal sulphide which are not stable; you can just heat it and decompose it to corresponding metal, so, that is I guess the easiest.

But, then there also could be problem, even if you are able to heat it and break the metal oxide. Still if the metal is found to be solid usually it is, those solid will be really mixed with other metal oxide or metal sulphide; still your job may not be full done. But some time this is still can be a good approach.

For example, silver oxide not every metal oxide you can heat it at a very low temperature or 50 to 100 degree C, you cannot break it. For that I will come to that Ellingham diagram, where you can heat the metal and thereby you can get it. But, usually something like silver oxide, you can heat it; and get it also sodium azide; from there you can get sodium in pure form.

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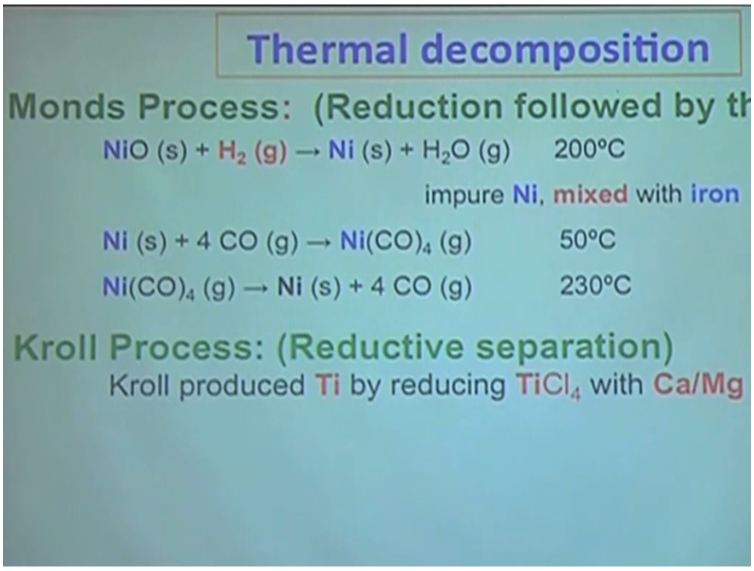

Thermal decomposition

Monds Process: (Reduction followed by th

$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$ 200°C

impure Ni, mixed with iron

$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$ 50°C

$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$ 230°C

Kroll Process: (Reductive separation)

Kroll produced Ti by reducing $TiCl_4$ with Ca/Mg

Other processes are there, such as Monds process and van Arkel process, which is also mainly dependent on thermal decomposition; but here you have to take care of the chemistry as well. What we are talking about is there is a mixture of at least three, four compounds or ten compounds. From there if you react those mixture of compounds with something like hydrogen; not every metal will be converted to corresponding, metal oxide will be correspond converted to corresponding metal and water. But, only few of them will be converted to metal and correspond water.

So, from a mixture of a lot of compounds you will be able to reduce some of the metal oxide with hydrogen at a given temperature. And thereby you will have a mixture of reduced metal, few of the reduced metal, and few of the metal oxide which is remained unreactive under that condition. You take that mixture react with carbon monoxide.

For example, in this process Monds process, selectively only few metal will react with carbon monoxide. And thereby for example, this nickel will be reacting to give nickel tetra carbonyl. This nickel tetra carbonyl being gas, you will be able to collect it in a different container. And then you heat it at 230 degree C; selectively you can get nickel in pure form.

So, what we have learned just that it is a generalized approach; it is not just a Monds process. What we are trying to see is we will select a reaction, that reaction will be somewhat selective for one, two or three metals. It will not going to be useful at least not under this reaction condition, let say 200 degree C; not every metal oxide will react with hydrogen.

Therefore, only out of let say ten metal oxide present, only one or two metal oxide will be converted to their corresponding metallic form. Now, still you are left with a mixture of metals; what you do with it? You then try to do yet another selective reaction, such as you react it with carbonyl. You do that reaction or carbon monoxide; you do that reaction at a temperature.

For example, only one of the metal will react with that carbonyl or carbon monoxide. Only one metal will react under this condition; thereby only selectively from a mixture of lot of solid. You selectively get, let say in this case nickel carbonyl which is gas; not every metal carbonyls are coming out.

Selectively only one metal carbonyl is compound is coming out; it is a gas, you collect it and then you heat it at 230 degree C. So, basically what it is telling you is you need to know the chemistry. If you want to apply your knowledge chemistry knowledge, then the things are going to be much more simpler; it is not complex any more.

Just one technique may not be good enough; you have to use a series of techniques. But slowly what will happen is let say you are having only one percent of nickel. If you keep on doing this thing like mechanical separation, electromagnetic separation and then thermal process; slowly slowly that one percent material will be accumulated.

And overall, from 1 kg of ore, you can get 1 gram of pure nickel, which is a lot for you. It is going to be a lots. Imagine instead of 1 gram of nickel 1 gram of gold; now it is making sense more sense. Instead of 1 kg of ore, you have hundred kg of ore; you get 1 kg of gold that is going to be much more attractive method.

So, this is a generalized approach; same approach is applicable for Kroll’s process, where we see that titanium oxide is converted selectively to titanium chloride, by reacting with charcoal and chlorine gas. And this Titanium tetrachloride again has to react with calcium or magnesium mixture to get back to the titanium. It is not like we are directly going to the reduced form of the metal from the oxidized; we can go to reduced form of the metal, oxidize it back, and then reduce it again. Or go to the reduced form, do some other reaction and then somehow figure out a technique to selectively identify or isolate that compound; and then do the thermal decomposition or some other technique.

So, it is going to be always going to be a mixture of approaches; you have to have different approach, you cannot have a generalized approach. As you can see ore available in Mumbai will I mean certain mixture from for nickel separation will be different; that is available in Rajasthan, it is going to be different. So, you have to know what are the elements present in your ore; and thereby you have to choose what are the techniques you are goings to use.

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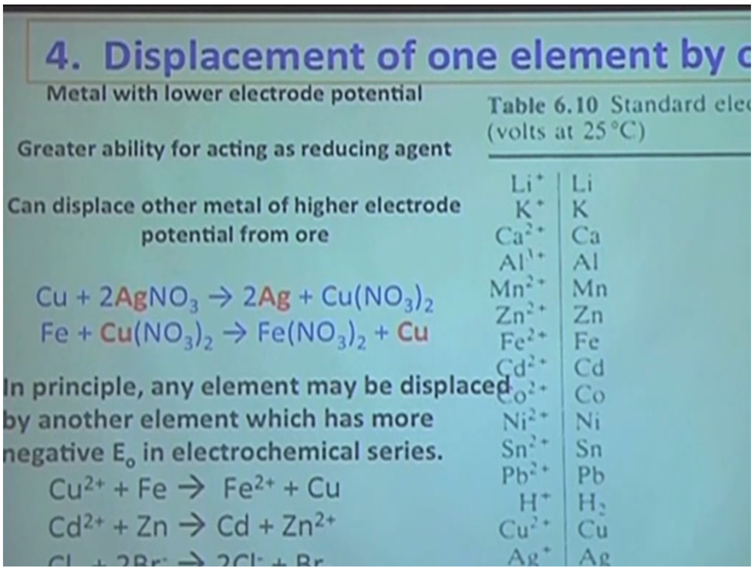

4. Displacement of one element by

Metal with lower electrode potential

Greater ability for acting as reducing agent

Can displace other metal of higher electrode potential from ore

$Cu + 2AgNO_3 \rightarrow 2Ag + Cu(NO_3)_2$

$Fe + Cu(NO_3)_2 \rightarrow Fe(NO_3)_2 + Cu$

In principle, any element may be displaced by another element which has more negative E_o in electrochemical series.

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

$Cd^{2+} + Zn \rightarrow Cd + Zn^{2+}$

$Cl + 2Br^- \rightarrow 2Cl^- + Br$

Table 6.10 Standard

(volts at 25 °C)

Li^+	Li
K^+	K
Ca^{2+}	Ca
Al^{3+}	Al
Mn^{2+}	Mn
Zn^{2+}	Zn
Fe^{2+}	Fe
Cd^{2+}	Cd
Co^{2+}	Co
Ni^{2+}	Ni
Sn^{2+}	Sn
Pb^{2+}	Pb
H^+	H_2
Cu^{2+}	Cu
Ag^+	Ag

Anyway, let us go on another approach which is stands very attractive is that of a use of one metal to get another metal; it is a sacrificial method. You sacrificed one metal to get another metal; of course your that another metal has to be very very important or precious. You cannot sacrifice gold to get 1 gram of iron. So, it is other way around if it is true, then of course you are going to use it.

So, what determines which metal you are going to sacrifice? And this is what is all about these electrochemical series. What it tells you? The one which is at the bottom let say gold, silver, copper; these are going to get reduced very easily. So, you take a oxidized form of those metals that is going to get reduced very easily.

If you have the metal oxide or sulphide of this element, you will be able to reduce those elements pretty easily; their reduction potential is very high. Reduction potential high means they will be going to reduced form; that is what exactly you are looking for. You want to have the reduced form of these precious metals. So, what you do?

In order to do that you take anything from top of this series; and use those of the reduced form of these metals; and oxidized form of the metal at the lower part. And you just do a oxidation reduction chemistry. For example, you take iron just iron with silver, so iron will be oxidized to iron t plus 2 plus; and silver plus will get reduced to silver that is all you are going to do.

For example, over here, you take copper; copper is above silver, copper is just above silver. So, you take copper, copper is in metal form metallic copper; so copper to copper oxidation is more favourable. What is more favourable in this case is silver plus to silver reduction; because reduction potential is very is high for silver compared to copper.

Now, so silver plus will get reduced to silver, so silver nitrate where silver is in 1 plus will get reduced to silver zero; and copper which is in reduced form will get oxidized to copper 2 plus. So, this gives you the basis what you are going to choose or which metal you are going to choose.

So, anything that is below or that is existing at the lower part of this electrochemical series that is what you will use in its oxidized form, to get the corresponding metal in pure form or in reduced form. The one which is going to be sacrificed is the one on the top, clear; anything with almost any metal combination you can take.

For example, with gold and lithium you can take technically. Anything that is above, anything that is below you can take any combination of these things; and in principle you should have an opportunity to do that. But of course you have to think about cost and safety, which one you are going to choose?

Of course, you have to choose judiciously which is available in large quantity; not that very expensive you are going to choose for such reduction. So, electrochemical series gives you an idea what reaction is favourable what is not? Sometimes that I was trying to tell you in the last class. So, it seems like these this to this thus would go; but this to this go; that is basically because you have to look at the potential.

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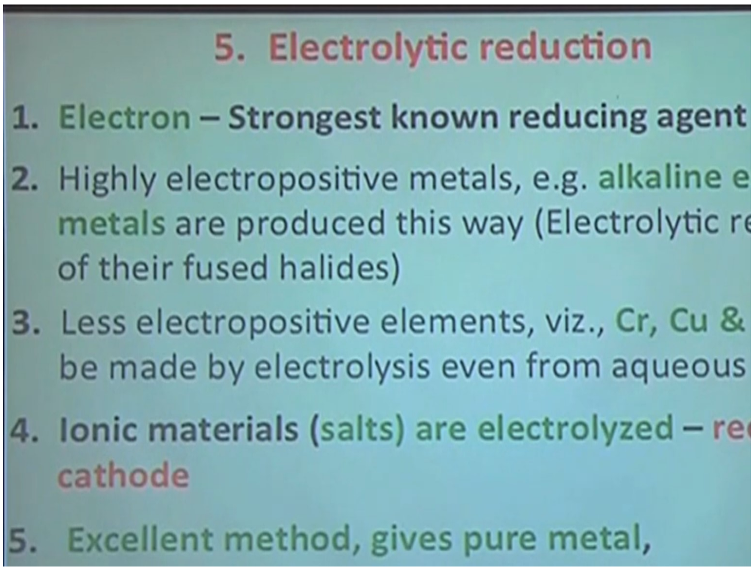
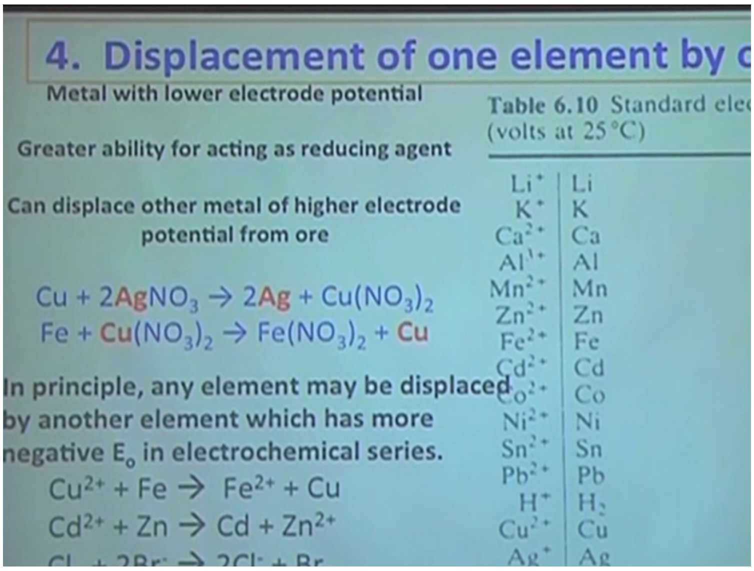


5. Electrolytic reduction

1. Electron – Strongest known reducing agent
2. Highly electropositive metals, e.g. alkaline e metals are produced this way (Electrolytic re of their fused halides)
3. Less electropositive elements, viz., Cr, Cu & be made by electrolysis even from aqueous
4. Ionic materials (salts) are electrolyzed – re cathode
5. Excellent method, gives pure metal,



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Ni^{2+}	Ni
Sn^{2+}	Sn
Pb^{2+}	Pb
H^+	H_2
Cu^{2+}	Cu
Ag^+	Ag

Anyway, another technique which is very effective is that electrolytic reduction. What is that? It is nothing; you just take a electrochemical cell, where you have a cathode and anode. In this case you are not using a sacrificial reducing agent; the reducing agent is your electron. So, you take gold solution, gold whatever gold let say gold chloride, Au3 plus.

Now, that gold you want to get that gold in cathode, because gold is cationic form is in cationic form; that is going to be at cathode and going to get reduced from gold 3 plus to gold, or silver plus to silver, or lithium plus to lithium. So, those reducing agents are provided or reducing equivalents are provided by electron.

Of course, it is not that very popular method, not everything you are going to get in this way. When you have no option, when you have no option left; then you are going to turn to this electro catalytic reduction. For example, you want to synthesize lithium; lithium plus to lithium as you have seen in the previous one. This this is a electro positive metal, it is try to stay in plus form electro positive; it does not want to get reduced.

So, you need some very strong reducing agent; the strongest possible reducing agent perhaps would be this electron. There is almost no sacrificial reagent available chemical available, that can chemically reduced lithium plus to lithium. So, this is when you need to use electrolytic reduction; so, of course it is a very good method.

It is applicable all across the board any metal in plus form in oxidized form, you can reduce; but it is very very expensive. It is it is excellent method; it gives you pure metal that is for sure; but it is going to be very very expensive. So, you need to use it only at a advance stage when you have the one or two metal possible; not lot of mixture of things are possible because mixture of things are going to complicate your life.

It is an expensive process, you do not want to use a mixture of just you do not want to take ore; and want to apply cathode and electrochemical reduction, you are not going to do that electrolytic reduction. When things are in very pure form, then only you are thinking to do it; or when you do not have any other option to do it, then you are going to so it.

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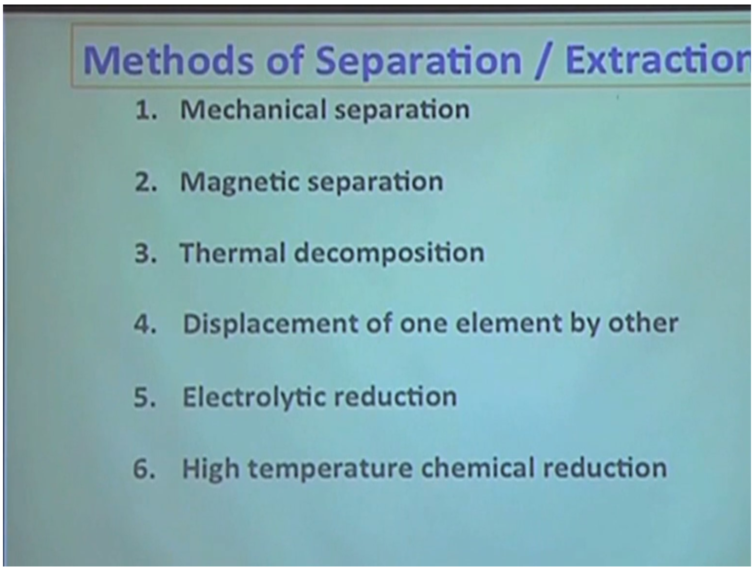

Methods of Separation / Extractio

1. Mechanical separation
2. Magnetic separation
3. Thermal decomposition
4. Displacement of one element by other
5. Electrolytic reduction
6. High temperature chemical reduction

So, I think I have covered so far or we have covered so for mechanical separation, magnetic separation, thermal decomposition these are very kind of easy; and then displacement of one element by other, and also electrolytic reduction.