Non-ferrous Extractive Metallurgy
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Lecture No. # 29
Extraction of Titanium

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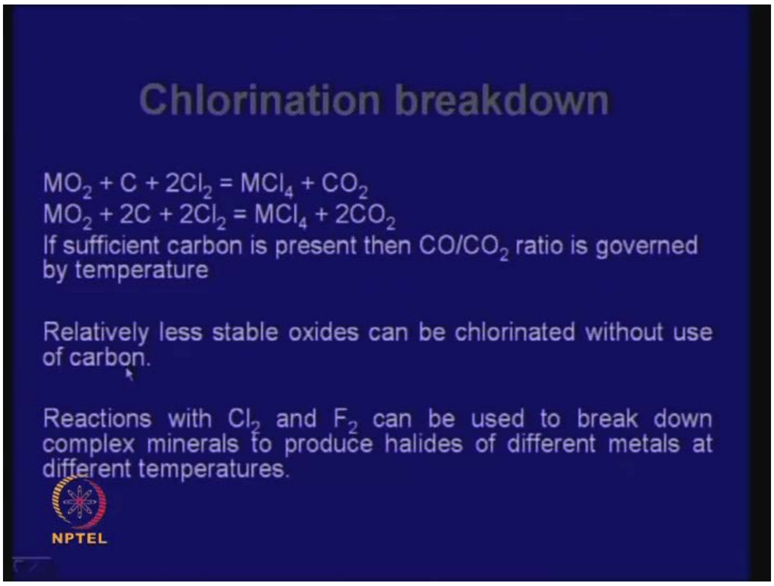

Chlorination breakdown

$MO_2 + C + 2Cl_2 = MCl_4 + CO_2$
$MO_2 + 2C + 2Cl_2 = MCl_4 + 2CO_2$
If sufficient carbon is present then CO/CO_2 ratio is governed by temperature

Relatively less stable oxides can be chlorinated without use of carbon.

Reactions with Cl_2 and F_2 can be used to break down complex minerals to produce halides of different metals at different temperatures.

Friends, we are discussing extraction of titanium from ilmenite; we have talked about 3 basic routes, one is where we smelt ilmenite in an electric furnace using carbon as a reductant, we produce pig iron. If there is some chromium and vanadium in the ore that can also go there, and the titanium part T i o 2 part will go into the slag. So, get a titaniferous slag that will have the advantage this process will have the advantage that is iron value is taken care of. And from the slag we will have to extract titanium by chlorination the other methods where, such that we were not making good use of the iron value 1 will be to partially reduce the ilmenite.

So, that only iron part is reduced, you produce metallic iron, then you rust it off reject it you have T i o 2 you do whatever you want to do with T i o 2 the other will be strong acid leaching you leach out iron part it get rejected you have T i o 2. Now you’ll find again and again we are coming back to the question of having T i o 2 then making a halide out of it, and then see how we can get titanium from it, because T i o 2 you cannot reduce by carbon to produce titanium you will produce titanium carbide. Now in the case of beryllium oxide we did a trick, we reduced beryllium oxide by carbon in presence of a lot of copper. So, that we produced a beryllium copper alloy which has very low percentages of beryllium. So, that beryllium will no longer form carbide by reaction with carbon, because the activity of beryllium is very low and, because you produced a beryllium copper alloy the activity of beryllium was low. So, the beryllium oxide reduction was driven to the right made very easy.

We also had an advantage we produced beryllium copper alloy which is what is required in the industry to make springs beryllium copper springs. This will not do for titanium oxide, because we cannot think of some other metal, which will form an alloy with titanium for which we have need. So, titanium dioxide reduction by carbon is not a feasible proposition. Now, couple of lectures ago, when I had started talking about halide formation and reduction, I said the following things which I think you can appreciate it better. When you have a metal oxide very often we reduce it in presence of carbon to produce a chloride. Why do we do that, because why do we need a carbon, because when the oxides are far too stable then without carbon they will not form the chloride thermodynamically it is not feasible, but if you bring in a reducing agent you can think of a two step process that reducing agent reduces the oxide. The metal is released and that reacts with chloride to form a chloride.

Now I put both in terms of c o 2 and this, because the two reactions feasible I think there is something wrong somewhere here, one should be 2 c o. Yeah This should be this this should not be there 2 c o. So, depending on at what temperature this is happening please correct it to 2 c o, either this reaction will predominate or this, if you go beyond nine hundred or one thousand you will have more of c o and at lower temperature more of c o 2. So, that is why saying that if sufficient carbon is present then c o by c o 2 ratio is governed by the temperature again relatively less stable oxides can be chlorinated without use of carbon, but when their oxides are stable you will need carbon. I will come back to this question in relation

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Reduction of metal halides

- Metallothermic reduction of halides allows oxygen free operation and, therefore, superior metallic product.

Choice of reduction method will depend on

- Thermodynamic feasibility and kinetics
- The heat balance
- Melting and boiling points of constituents
- Densities of metal and slag

To titanium and why do we go for metallothermic reduction of halides which you have done for uranium, plutonium, thorium and do for titanium also, because first of all in oxygen free operation if you produce the metal then there is no question of oxygen oxygen impurities which release the properties. The choice of reduction method, I am again and again saying it will not only depend on thermodynamic feasibility that is free energy change, it will also depend on the heat balance means, exothermicity. It will also depend on kinetics in which reactants and the products are there and the temperature they will define kinetics the rate at which it will happen. It will depend on melting and boiling points of constituent’s densities of metal and slag. I have given quite a few examples of this

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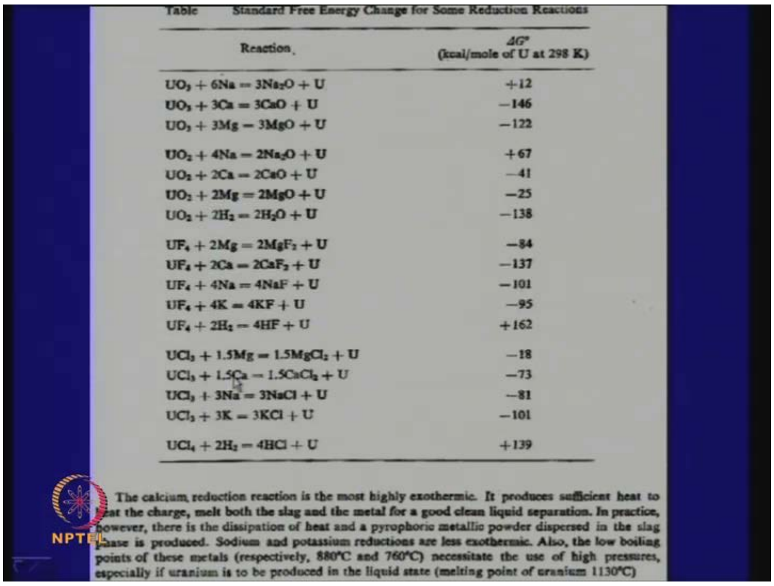

Table Standard Free Energy Change for Some Reduction Reactions

Reaction	ΔG° (kcal/mole of U at 298 K)
$UO_3 + 6Na = 3Na_2O + U$	+12
$UO_3 + 3Ca = 3CaO + U$	−146
$UO_3 + 3Mg = 3MgO + U$	−122
$UO_2 + 4Na = 2Na_2O + U$	+67
$UO_2 + 2Ca = 2CaO + U$	−41
$UO_2 + 2Mg = 2MgO + U$	−25
$UO_2 + 2H_2 = 2H_2O + U$	−138
$UF_4 + 2Mg = 2MgF_2 + U$	−84
$UF_4 + 2Ca = 2CaF_2 + U$	−137
$UF_4 + 4Na = 4NaF + U$	−101
$UF_4 + 4K = 4KF + U$	−95
$UF_4 + 2H_2 = 4HF + U$	+162
$UCl_3 + 1.5Mg = 1.5MgCl_2 + U$	−18
$UCl_3 + 1.5Ca = 1.5CaCl_2 + U$	−73
$UCl_3 + 3Na = 3NaCl + U$	−81
$UCl_3 + 3K = 3KCl + U$	−101
$UCl_4 + 2H_2 = 4HCl + U$	+139

The calcium reduction reaction is the most highly exothermic. It produces sufficient heat to heat the charge, melt both the slag and the metal for a good clean liquid separation. In practice, however, there is the dissipation of heat and a pyrophoric metallic powder dispersed in the slag phase is produced. Sodium and potassium reductions are less exothermic. Also, the low boiling points of these metals (respectively, 880°C and 760°C) necessitate the use of high pressures, especially if uranium is to be produced in the liquid state (melting point of uranium 1130°C)

This and again and again you see in the case of uranium we found that uranium oxide can also be reduced, but there are lots halides and very often it is the calcium reduction of an halide which helps us sometimes we use the booster reaction.

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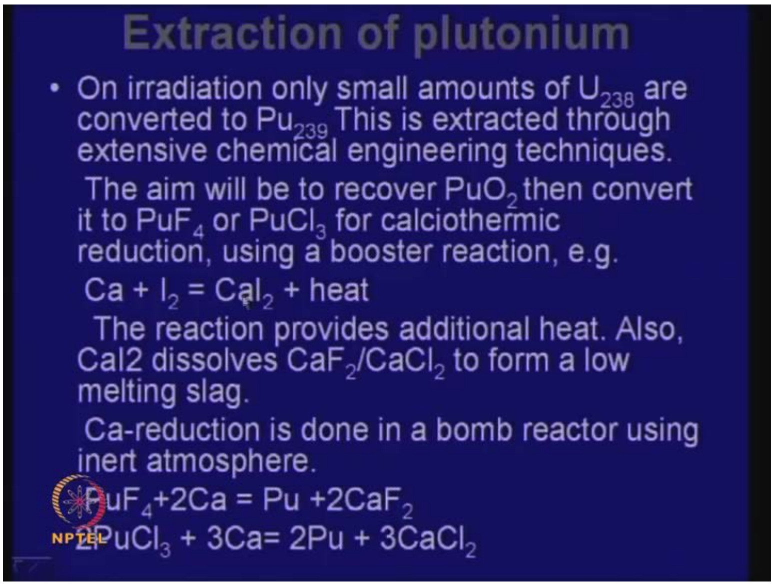

Extraction of plutonium

- On irradiation only small amounts of U_{238} are converted to Pu_{239} This is extracted through extensive chemical engineering techniques.

  The aim will be to recover PuO_2 then convert it to PuF_4 or $PuCl_3$ for calciothermic reduction, using a booster reaction, e.g.

  $Ca + I_2 = CaI_2$ + heat

  The reaction provides additional heat. Also, CaI2 dissolves $CaF_2/CaCl_2$ to form a low melting slag.

  Ca-reduction is done in a bomb reactor using inert atmosphere.

  $PuF_4 + 2Ca = Pu + 2CaF_2$

  $2PuCl_3 + 3Ca = 2Pu + 3CaCl_2$

Which provides heat and also it provides a constituent which mixes with the slag to produce a low melting slag. So, the reaction is driven to the right in the case of plutonium we have also calculated this reduction. Then you come in the case of thorium again fluorides and chlorides can be reduced by calcium and magnesium all very similar, in this case, we are using calcium chloride. So, that we have the flux at a lower melting point.

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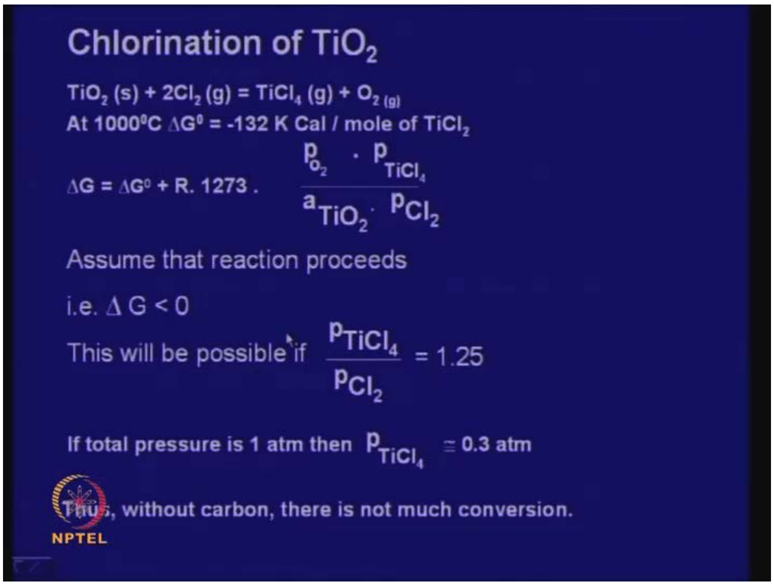

Chlorination of TiO_2

$TiO_2\,(s) + 2Cl_2\,(g) = TiCl_4\,(g) + O_{2\,(g)}$

At 1000°C $\Delta G^0 = -132$ K Cal / mole of $TiCl_2$

$$\Delta G = \Delta G^0 + R.\,1273\,.\,\frac{p_{O_2}\cdot p_{TiCl_4}}{a_{TiO_2}\cdot p_{Cl_2}}$$

Assume that reaction proceeds

i.e. $\Delta G < 0$

This will be possible if $\dfrac{p_{TiCl_4}}{p_{Cl_2}} = 1.25$

If total pressure is 1 atm then $p_{TiCl_4} \cong 0.3$ atm

Thus, without carbon, there is not much conversion.

Now let us come to this question. Why we want carbon sometimes for chlorination or sometimes we do not need carbon I have I have said and I will repeat it. When the oxide is very stable it is very difficult to chlorinate it without presence of carbon. If it is unstable it may be possible, you can look at it from the free energy point of view through a very simple analysis. Now in this thing, I am sorry you will often find that I have not been able to use the same kind of style of lettering, because too complicated. You know sometimes o is small o is large, and there could be some other mistakes also, please you should understand what I am trying to say there could be some errors. All the p’s are small p’s, because they are partial pressures if anywhere there is a capital p its wrong I think in 1 or 2 places it is there.

Let us consider reaction of T i o 2 with chlorine to produce titanium tetrachloride vapor. And the reaction is T i o 2 plus 2 c l 2 producing T i c l 4 and oxygen gas. So, oxygen comes out chlorine attaches itself to titanium. This is a simple reaction that we can write. Now at one thousand degrees we know that the standard free energy change is minus one hundred and thirty two kilo calories per mole of T i c l 4 sorry this should be 4 not T i c l 2 this is 4 I am correcting again. We also know from thermodynamics that delta g is written as delta g naught, plus r t let us consider the reaction at one thousand degrees l n k there should be a lawn here, the lawn is missing l n sorry lawn k r t lawn l n k. So, this is p o 2 into p T i c l 4 activity of T i o 2 p c l 2. Under standard conditions this will be 1 and it 1 atmosphere is 1. Now assume that the reaction takes place that is happens, supposing this is happening which means, delta g naught is less than 0

Now we can find out that the condition for this turns out to be p t c i 4 by p c l to be 1.25. Means, you will produce a ratio of p T i c l 4 by p c l 2 1.25. If the total pressure is 1 atmosphere then this calculates to be 0.13 atmosphere. You can easily find this by simple calculations. That you know in the product you have total pressure of these, if you take 1 atmosphere this will come out to be 0.3 atmospheres. Thus without carbon there is not much conversion, because you are producing a titanium tetrachloride this you make it 4 which is only 0.3 atmosphere and this would be lawn correct it lawn.

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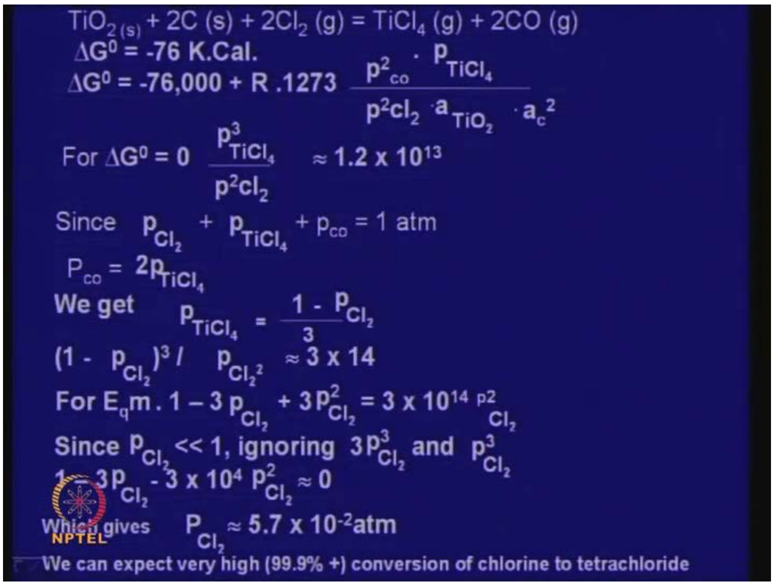

$TiO_{2\,(s)} + 2C\ (s) + 2Cl_2\ (g) = TiCl_4\ (g) + 2CO\ (g)$

$\Delta G^0 = -76$ K.Cal.

$$\Delta G^0 = -76{,}000 + R\ .1273\ \frac{p^2_{co} \cdot p_{TiCl_4}}{p^2cl_2 \cdot a_{TiO_2} \cdot a_c^2}$$

For $\Delta G^0 = 0$ $\quad \frac{p^3_{TiCl_4}}{p^2cl_2} \approx 1.2 \times 10^{13}$

Since $p_{Cl_2} + p_{TiCl_4} + p_{co} = 1$ atm

$P_{co} = 2p_{TiCl_4}$

We get $p_{TiCl_4} = \frac{1 - p_{Cl_2}}{3}$

$(1 - p_{Cl_2})^3 / p_{Cl_2^2} \approx 3 \times 14$

For E$_q$m. $1 - 3p_{Cl_2} + 3P^2_{Cl_2} = 3 \times 10^{14}\ p2_{Cl_2}$

Since $P_{Cl_2} << 1$, ignoring $3P^3_{Cl_2}$ and $p^3_{Cl_2}$

$1 - 3P_{Cl_2} - 3 \times 10^4\ P^2_{Cl_2} \approx 0$

Which gives $P_{Cl_2} \approx 5.7 \times 10^{-2}$atm

We can expect very high (99.9% +) conversion of chlorine to tetrachloride

Sorry there is a mistake there should be lawn here also l n l n correct it now consider a reaction where T i o 2 is being chlorinated in presence of carbon. For this delta g naught is minus 76 kilocalories delta g naught can be written as r t lawn there will be lawn here. And obviously p c o square p t s c l 4 p square c l 2 a T i o 2 and a c square. We can take this activity as 1 this activity as 1 will be reduced to three partial pressure terms.

Now for delta g naught equal to 0 for equilibrium, we will calculate p cube t c i 4 bar p square c l 2 would be this value. And since all these sums up to one atmosphere we can say that p c o would be 2 p c l 4, because these two must have the same partial pressure if you see here. Anyway finally, if you go through all these you follow that and only make this correction lawn I will correct it by typing. We will finally, find that p c l 2 value comes out to be 5.10 to the minus 2 atmosphere which means, all that chlorine that has that you have reacted 99.9 percent has conversion of chlorine to tetrachloride. So, after the reaction if there is hardly any chlorine left means, all all has converted to tetra chloride. So, you can do it yourself and show that if you put in carbon in the system the conversion of T i o 2 T i c l 4 is far more.

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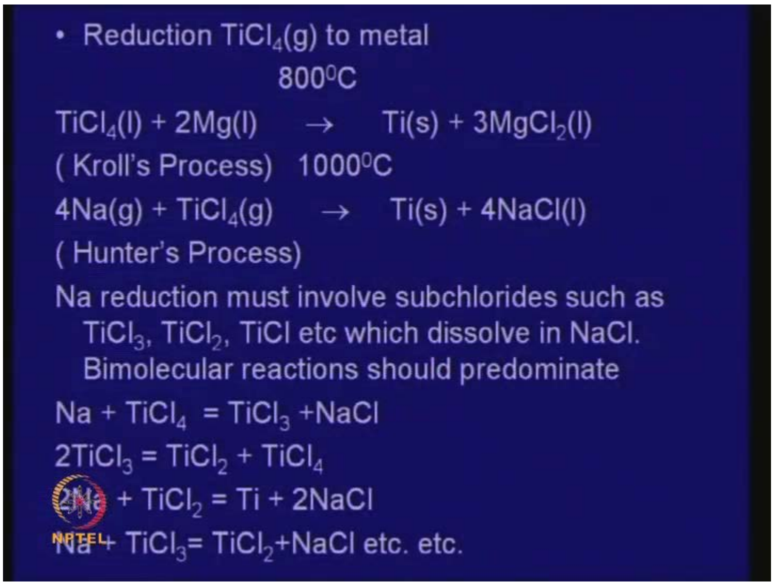

- Reduction $TiCl_4(g)$ to metal

$800^{0}C$

$TiCl_4(l) + 2Mg(l) \rightarrow Ti(s) + 3MgCl_2(l)$

(Kroll's Process) $1000^{0}C$

$4Na(g) + TiCl_4(g) \rightarrow Ti(s) + 4NaCl(l)$

(Hunter's Process)

Na reduction must involve subchlorides such as $TiCl_3$, $TiCl_2$, TiCl etc which dissolve in NaCl. Bimolecular reactions should predominate

$Na + TiCl_4 = TiCl_3 + NaCl$

$2TiCl_3 = TiCl_2 + TiCl_4$

$2Na + TiCl_2 = Ti + 2NaCl$

$Na + TiCl_3 = TiCl_2 + NaCl$ etc. etc.

Now I'm showing you a slide now a reactions, which I remember mentioning in my very first lecture, when I started the series of lectures. I had given this example to indicate how in metallurgy when you write a reaction. We look at things differently from than when we write the reaction in a course in chemistry. See in a chemistry class we can write t I c l 4 reacts with magnesium to produce titanium, and m g c l 2 we can write sodium reacts with t I c l 4 t I solid and 4 n a c l that is the end of the matter. We cannot do that in metallurgy we have to understand how these reactions take place, because the fact of the matter is when 1 reduces t i c l 4 liquid by magnesium liquid you produce a solid titanium solid which is powder in nature, its physical characteristics very unsatisfactory powder in nature it has to be consolidated again by vacuum melting. Whereas when we reduce titanium tetrachloride vapor by sodium vapors at one thousand degrees this takes place at eight hundred degrees.

We get a metal which is crystalline; it is almost like what happens in electro deposition. In an electro deposition when a metal is deposited from its iron irons are discharged then when another iron is discharged it builds on to the metal and it goes in to the crystal lattice it produce a solid metallic layer which you call a crystalline product. Of course, there are some situations where it does not happen we got metallic particles it is also a powdery deposite, but ideally you should be able to produce the crystalline cathode product if there is a proper electro chemical reaction under correct conditions. So, in chemically you are reducing this by magnesium reducing agent you are reducing titanium tetrachloride by sodium, but the products are very different. In 1 case it is a crystalline product in one case it is a powdery product.

So, in metallurgy in process metallurgy, we have to stop here to think why it happens can we control it can we try to produce in this reaction something which is not powdery or here, what should we do to ensure that we the crystalline product is crystalline things like that. So, hunter’s process which was the first process they were superior product, but kroll’s process has its advantages. Advantage here, is it will be at lower temperature we are dealing with liquids the 2 liquids another liquid is solid. Whereas here we are dealing with gaseous reactants 1 solid 1 liquid the moment you have gaseous reactants your entire reactor shape and details change. So, we will rather have magnesium reduction, but the product is not very good this is the problem. Now lot of work now has been done to analyze why why we have this difference. Now first of all now this I had mentioned in first lecture itself. We can write an overall reaction like this, but this can never be the reaction simple logic tells us why it cannot be the reaction what does this imply it implies four atoms of sodium. Gas phase is reacting with 1 molecule of titanium tetrachloride in the gas phase

Imagine a reactor full of gaseous sodium atoms and gaseous titanium tetrachloride atoms they are moving around these gas particles. For four atoms of sodium to react with one molecule of titanium tetrachloride, they have to come at 1 point even if they do not have to hit exactly at one point they have to be in the vicinity for a reaction to take place. The probability of this is almost zero. Imagine it is so difficult in the gas phase for two particles to come and come at one point, because they are flowing all over the place to have 5 of them come to one point probability is almost zero. This means, such penta molecular reaction in gas phase we cannot accept by common sense. Then what what then can we say the reaction does take place well, we can propose and then find out whether what we are proposing is correct. What you propose is that the sodium reduction involves sub chlorides sub chlorides means, this is not the reaction this the overall reaction.

We have other reactions like sodium one atom reacts with one molecular titanium tetrachloride. I am not writing the gas phases now, these are in gas phases it produce a tri chloride. This reaction is possible yes in the gas phase 2 of them come and collide and produce this then 2 t I c I 3 2 molecules of this can come together and produce t i c l 2 and t I c l 4 to generate t I c l 4. 2 sodium can react with 1 t i c l 2 it is term molecular reactions definitely much better than a penta molecular reaction. We can think of another by bimolecular reaction sodium titanium tri chloride titanium dichloride and sodium chloride do you understand what I am trying to say here. Now there is something more to this if you go back to this reaction we have 1 liquid phase sodium chloride. Now careful analysis of this sodium chloride during reaction has shown that it does contain trace amounts of this tri chloride dichloride. So, essentially what happens once two of them react and produce a tri chloride molecule it dissolves in sodium chloride?

Now sodium can react with the liquid phase where there is titanium tri chloride they reduce it to titanium. If there is a dichloride it also dissolves in sodium chloride liquid phase it has been detected. So, sodium can react with the dichloride produce titanium and sodium chloride. Sodium can react with traces of titanium tri chloride to generate dichloride sodium chloride etcetera etcetera. So, essentially it is a beautiful concept that you sodium initially somehow produces certain amount a reaction tri chloride dichloride which are now in sodium chloride. Now the sodium atom’s vapor phase are reacting with that liquid and reducing. So, they do not have to search around in the in the chamber looking for a a gas molecule of titanium tetra chloride.

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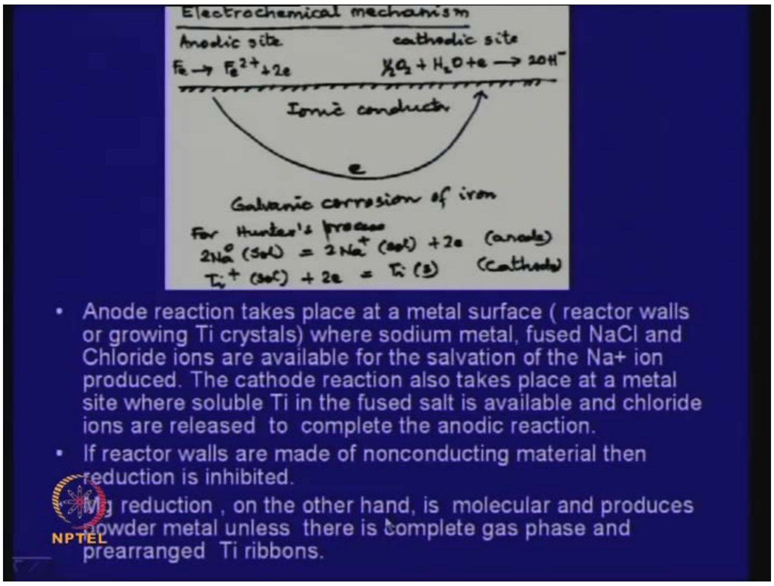

Electrochemical mechanism

Anodic site

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

cathodic site

$\frac{1}{2}O_2 + H_2O + e \rightarrow 2OH^-$

Galvanic corrosion of iron

For Hunter's process

$2Na^0\ (sol) = 2Na^+\ (sol) + 2e$ (anode)

$Ti^+\ (sol) + 2e = Ti\ (s)$ (cathode)

- Anode reaction takes place at a metal surface (reactor walls or growing Ti crystals) where sodium metal, fused NaCl and Chloride ions are available for the salvation of the Na+ ion produced. The cathode reaction also takes place at a metal site where soluble Ti in the fused salt is available and chloride ions are released to complete the anodic reaction.
- If reactor walls are made of nonconducting material then reduction is inhibited.
- Mg reduction , on the other hand, is molecular and produces powder metal unless there is complete gas phase and prearranged Ti ribbons.

And a proof of that is that those phases have been detected, those phases have been detected in small quantities in sodium chloride. So, you see here is the here is the explanation or something which looks so illogical if you do not go deep into the so called mechanism. Now when it comes to magnesium reaction, well it is a term molecular reaction, but here everything is taking place in liquid state. Titanium is producing one particle at a time the reaction takes place titanium is produced another place titanium is produced and they do they produce a dispersion of titanium. Now coming back to sodium reaction I have explained how it cannot be a penta molecular reaction, but why should it may give it crystalline product that question we mention. So, let me go back to that question. Now it has been shown now that sodium reactions with titanium tri chloride vapor to give titanium solid and sodium chloride liquid and actually is an electro chemical reaction.

Now, what is an electrochemical reaction? Consider the electrochemical the corrosion of iron we call it galvanic corrosion in that there is a cathodic side there is an anodic side. In the anodic side iron forms ferrous iron produces electrons there is an there is a, this is not ironic conductor this should be electronic conductor. So, the electrons can go there and these electrons reacts with h 2 o and half o 2 to produce 2 o h. So, iron reacts with water and oxygen to produce ferrous iron and o h irons, please change it is electronic conductor there is a metallic body through which electrons are going. So, in the hunters process they say there is a similar, electronic ah electrochemical mechanism. That sodium in solution in it produces sodium ions, and the it will go to another side reactive titanium to produce titanium solid. In other words, if you have a chamber which is not made of a metal this kind of thing does not happen. So, in the case of sodium reduction we need metallic conductors. So, that titanium can grow as a crystal in those sites where titanium is being deposited.

So, the anode reaction in the case of sodium reaction takes place at a metal surface, reactor walls or growing titanium crystals they themselves can be the anode sites. Where sodium metal fuse n a c l and chloride ions are available for salvation of the sodium plus ions produced. The cathode reaction also takes place at metal sites, elsewhere where soluble titanium in the fused salt is available and chloride ions are realized to complete the anodic reaction. This titanium has to be now available in the fused salt media as sub halides, and that is why the anodic reactions are possible. If the reactor walls are made of non conducting material then reduction is that is the proof that there is an electro chemical mechanism, which is adding sodium reduction. Now magnesium reduction on the other hand is molecular, and it produces powder metal unless there is complete gas phase and prearranged titanium ribbons.

We can help the magnesium reduction by putting in the bath titanium ribbons. And if we go into the complete gas phase we can have on titanium ribbons similarly, titanium depositing and producing crystalline product, but in the liquid phase it will not be possible you have to go to a this phase.

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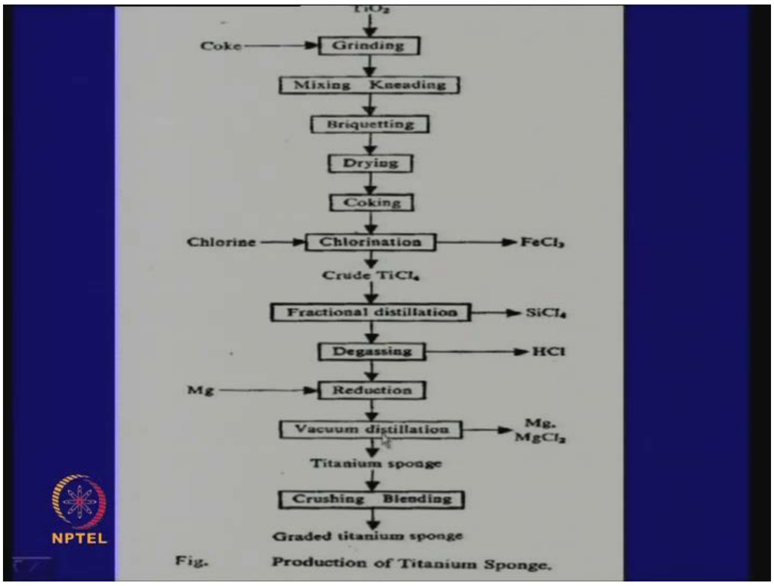

Fig. Production of Titanium Sponge.

So, this now let us move on with titanium production. How do we produce titanium sponge we produce T i o 2 you have to mix coke, because we are going to chlorinate in presence of carbon, mixing kneading briquetting drying coking chlorination, will get crude t c i 4 fractional distillation will remove any s i c l for that may have been produced, during chlorination ferric chloride is very easily removed we degas take out h c l. Now we go for magnesium reduction which is now the process. We do vacuum distillation finally, we produce titanium sponge, and it goes for crushing blending and grading titanium sponge. So, today’s industry has discarded the sodium process, because magnesium is a more convenient medium. Even if you do not produce a beautiful product it can always go for vacuum distillation and consolidation to produce titanium sponge.

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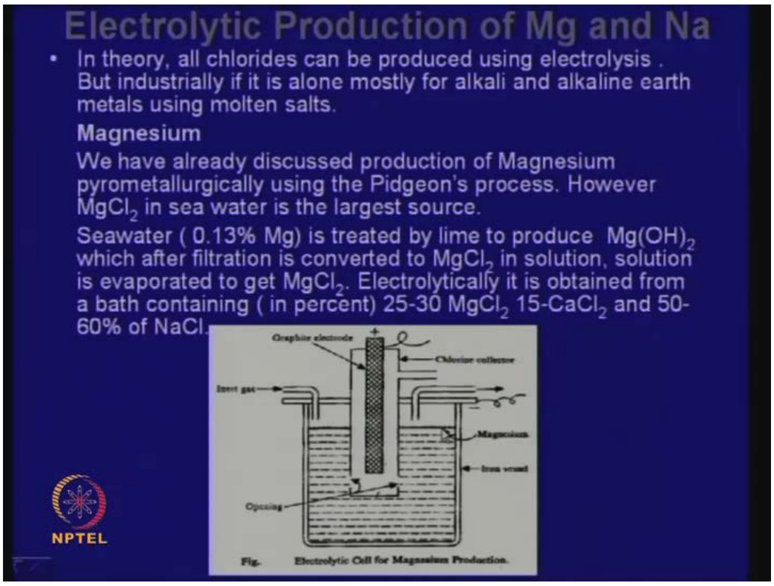

Electrolytic Production of Mg and Na

- In theory, all chlorides can be produced using electrolysis . But industrially if it is alone mostly for alkali and alkaline earth metals using molten salts.

Magnesium

We have already discussed production of Magnesium pyrometallurgically using the Pidgeon's process. However $MgCl_2$ in sea water is the largest source.

Seawater (0.13% Mg) is treated by lime to produce $Mg(OH)_2$ which after filtration is converted to $MgCl_2$ in solution, solution is evaporated to get $MgCl_2$. Electrolytically it is obtained from a bath containing (in percent) 25-30 $MgCl_2$ 15-$CaCl_2$ and 50-60% of NaCl.

Fig. Electrolytic Cell for Magnesium Production.

We have so far discussed, initially reactor metals that are metals which found applications in nuclear reactors. We talked about uranium is fissionable isotope u 235 then the fertile isotope u 238. We talked about u 38 converted to plutonium 239 which is a fissionable material we talked about thorium converting t h 232 to an isotope of uranium 233 which is a fissionable material. Then we said we also consider zirconium to be a reactor metal, because we need it in the reactors, as a cladding element zirconium alloys which allows the neutrons to pass through. It will be very difficult to produce a critical mass, if we had some other material that will absorb neutrons it allow the neutrons to go through we also, brought in beryllium which is a moderator which can slowdown neutrons.

Now there are some other metals which are not nuclear reactor metals, titanium is 1 of them we do not use titanium in reactors, it is a reactive metal all the same. Sometimes some of these are called rare metals. Titanium is not a rare metal, but uranium plutonium thorium these are rare metals, but titanium is a reactive metal we will talk about 2 other reactive metals which also come from halides, in this case naturally occurring halides you do not have to make halides out of oxides. The first that comes to my mind is magnesium. Now do not forget that we have talked about magnesium in the very beginning when we were talking about metals from oxides, magnesium is produced by pigeon's process by reduction of m g o produced by decomposition of dolomite or magnesite. The magnesite will produce m g o dolomite will produce m g o c e o reduce that by ferrosilicon and it produced magnesium vapor which were condensed and collected. That was reduction metallothermic reduction of magnesium oxide we dint go for halide, but a lot of magnesium is also produced through the halide route. I am not going to talk about importance of magnesium this we have discussed when we were talking about pigeon process, how important magnesium is as a metal, not only for all kinds of alloying it finds even use in the in the steel industry that without magnesium we cannot go for nodular cast iron is faradizations of graphite.

So, magnesium also is required in all kinds of light metals used in photography this and that. So, we will not we will not mention again the uses, but we will talk about magnesium from a chloride route now in theory all chlorides can be produced using electrolytes, all chlorides and all the things that we talked about nuclear metals and then titanium all the halides in theory we can produce by electrolysis in a suitable halide bath. But, the methods I have discussed are more convenient and that is why there is no industrial process based on electrolysis of the halide, but the next two metals I am going to discuss magnesium and sodium they are produced by halide reduction, because they are very stable halides themselves you cannot think of a metallothermic reduction and that you know calcium or magnesium you know the halides will be electrolyzed. Now halide electrolysis industrially is mostly used only for alkali and alkaline earth metals using molten salts and I give you only two examples first is magnesium.

We are now going to talk about the pidgeon’s process, but let us come to where is magnesium chloride coming from. Now magnesium chloride is available plenty in sea water, sea water contains magnesium chloride 0.13 percent magnesium in sea water is a huge amount of magnesium. If you imagine how much of sea water we have and magnesium there is as magnesium chloride. There are some natural deposits of some salts where there is magnesium in a exposed sea beds. So, this the water has dried out and you have the salts that contain magnesium we are not going to talk about that we will talk about industrial process for producing magnesium from sea water. Basically I can mention that right in the very beginning I had given the availability of metals in sea water. Every metal you can think of is available in the sea, because for millennia rivers have been flowing over land and going into the sea they have carried down from hills and plateaus and land all kinds of material into the sea. From the bottom of the sea also many metals are coming through cracks at the bottom of the sea from under sea volcanoes all elements are there, and if you take the volume of the sea their quantities are enormous. In France actually a company tried to extract gold from sea water they almost successful, because the amount you go by percent is very small, but looking at the huge volume of sea the amount of gold layer is unbelievable they try to extract almost made it, but economically it was not sustained. I have also talked about a peculiar source of metals in the sea floor they were the manganese nodules which are very very rich in nickel cobalt copper zinc etcetera but, basically very rich in manganese.

If they had gold the gold prices would crash, but magnesium is found dissolved in water and almost the entire sea everywhere has around 0.13 percent magnesium, because the seas are connected and that is not a small percentage that can be extracted it is not in parts per million or parts per billion. It is 0.13 percent magnesium in sea water. So, there is a very simple way of getting that magnesium out it is the sea water is treated by lime, and you produce magnesium hydroxide which is precipitate and which after filtration is converted to magnesium chloride in solution. You know you can chlorinate the magnesium chloride in solution, this evaporated to get h g c 2. So, how magnesium is there in sea water it could be we cannot say you know after all it could be chloride or whatever, but magnesium is in solution magnesium ions it precipitate as hydroxide this is very easy then chlorinate magnesium chloride and then get pure magnesium chloride it has to be now electrolytic ally decomposed.

It is decomposed using a bath twenty five to thirty percent magnesium chloride fifteen percent calcium chloride and fifty to sixty percent sodium chloride. We need a mixture of salts so that the melting point is low, and calcium chloride and sodium chloride are more stable than magnesium chloride during electrolysis otherwise these will get electrolyzed. So, that is not a problem magnesium chloride will get decomposed a cell is like this and try to understand why this cell is like this. This is a graphite electrode which is a standard electrode for for chlorine this electrode has to be isolated, because we do not want that the magnesium will be produced and will react with again chlorine which is the anode product we have to keep the cathode product magnesium and the anode product chlorine separately. So, during electrolysis chlorine will evolve around the graphite electrode and it will escape by this place. Whereas magnesium will be deposited in this cathode which is the iron vessel all around that magnesium will be deposited and magnesium very being very light will float up it will float up.

Now this magnesium which is floating is completely separated from the chlorine which is being evolved. So, there is no question of back reaction, and this whole chamber is flushed with inert gas. So, that magnesium produced is collected under inert atmosphere and there is a way of collecting that magnesium out. So, this is a very important principle here, that you are keeping the cathode product and anode product separate from each other. We will always need it when there is a question of back reaction, if you go for aluminum electrolysis we will also find that aluminum is deposited below the electrolyte the the things are so adjusted that there will be no back reaction between aluminum and c o c o 2 that is coming out. So, all kinds of tricks have to be played.

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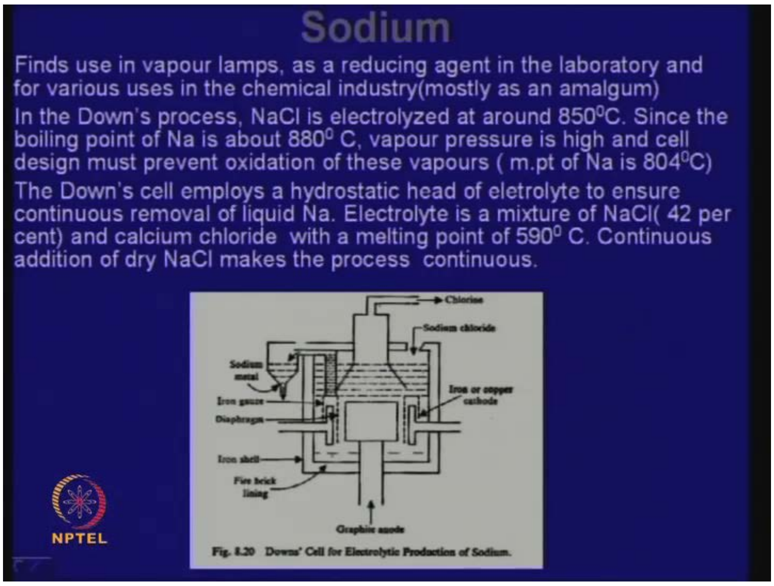

Sodium

Finds use in vapour lamps, as a reducing agent in the laboratory and for various uses in the chemical industry(mostly as an amalgum)

In the Down's process, NaCl is electrolyzed at around 850^{0}C. Since the boiling point of Na is about 880^0 C, vapour pressure is high and cell design must prevent oxidation of these vapours (m.pt of Na is 804^{0}C)

The Down's cell employs a hydrostatic head of eletrolyte to ensure continuous removal of liquid Na. Electrolyte is a mixture of NaCl(42 per cent) and calcium chloride with a melting point of 590^0 C. Continuous addition of dry NaCl makes the process continuous.

Fig. 8.20 Downs' Cell for Electrolytic Production of Sodium.

Let’s come to production of sodium. Now sodium is a very useful metal I have just mentioned a few uses, it is used in sodium vapor lamps, it is a reducing agent in the laboratory, and it has a lot of applications in the chemical industry mostly as an amalgam. A standard method of sodium production is the downs process, downs process is based on electrolysis of sodium chloride around 850 degrees why eight hundred and fifty degrees, because sodium will boil at 88 degrees. So, it has to be below the boiling point of sodium even at 850 it will have very high vapor pressure, but there are many reasons why we cannot bring down the temperature far to down, but it certainly has to be below the boiling point. Vapor pressure is high and cell design must prevent oxidation off these vapors there are sodium vapors fairly high at 850 degrees, but they have to be completely separated from. Now the reason is we cannot bring down the temperature too low if the melting point of sodium is 804. It is very tricky it melts at eight hundred and four and it boils at eight hundred and eighty degree. So, your window is very small just about eighty degrees so we put it somewhere in between.

So, we are producing sodium which is liquid, but it had a high vapor pressure, because it is not too far from the boiling point. Now all these things have to be kept in mind in the design of the cell. Now and also the design of the electrolyte the electrolyte is a mixture of sodium chloride forty two percent and calcium chloride whose melting point is 590 degree. So, we bring down the melting point. So, you are sure there is a a liquid electrolyte and we have enough sodium in that and only sodium chloride and calcium chloride. And the downs process is a continuous reactor that is continuous addition of dry n a c l and there is a continuous retrieval of sodium metal being produced. How do we do that here is the cell. Now here in the case of magnesium we had graphite electrode coming from the top remember and there was a chamber all around for collection of chlorine. Here we have a graphite anode, which is where chlorine will be evolved this is the electrolyte so when the chlorine is evolved the chlorine straight away after release goes into the wood and the chlorine will go up. There is you will find a diaphragm that prevents chlorine to move out of the anode chamber and it has no chance of attacking the sodium.

The sodium will deposit at iron or copper cathodes see how they are placed with a hydrostatic device the moment sodium is produced. Now being very light it will float up the sodium metal will produce this is a cylindrical thing. So, we do not have to show it on this side this thing does not have to be showed on this side. There is a diaphragm the sodium produce cannot move into the electrolyte. It only has to float up through the electrolyte same thing here, it will also float up to the electrolyte and there is a hydrostatic device sodium metal will come out here, and it is usually kept under kerosene. So, here also we have a design of a cell which ensures that the anode product chlorine and the cathode product the metal they are completely separate. In this case chlorine deposited here moves out, metal deposited here floats up through this a hydrostatic device and collected.

In the case of magnesium chlorine deposited here went out magnesium fortunately had no problem it floated here and from there it could be collected. Now this is a continuous process because the sodium chloride is continuously added here, nothing is happening to the calcium chloride part it is just a supporting electrolyte. So, sodium chloride is continuously deposited chlorine is continuously taken out, and sodium that floats up the hydrostatic device is collected somewhere it is a continuous process. Now there are also other metals like potassium and sodium can may be there are other metals also, but I need not cover each and every thing in this course. I think I have talked enough about reactor metals and non reactor metals which are produced from the halide route I will I will end it there.

So, we have discussed about metals from oxides metals from sulphide sources metals form halides natural halides, like in the case of magnesium or sodium and synthetic halides, of uranium plutonium thorium titanium which come from oxidic sources you must understand that, but I thought it was logical to put them in this category, because there is they are so similar, things are so similar. There is only one category of metal left and I will may be, I will just cover it in one lecture, rather two categories one is that noble metals that essentially exist in free state. Like you know precious metals, gold, platinum series metals, silver silver does occur as weak compounds I will discuss, but not gold not platinum they are essentially all free that is how at in ancient times they could get gold chunks of gold here and there or particles of gold from river

Then there is another category you must not ignore from where we can produce metals. And they are called secondary metals from metal scrap. All the metals that we are producing going for some use either in industry or to the consumers what happens to them after months or years every use every item has a life after the life what do you do with the scrap. If you do not do something about it then you have an environmental problem. So, we will have to recalculate them. So, we have to extract metals from these scraps and metals extracted like that would be called secondary metals. Now obviously we have been talking about beneficiation of ores and minerals getting into so much of trouble to bring bring up the percentages from far less than 1 percent to an acceptable level level so that it can go for extraction processes. When you talk about a scrap it may be dirty, but imagine its metallic value is so high whatever scrap aluminum copper zinc lead all that iron all that we have used and you have thrown away its very rich in that metal.

So, it is far better than time to extract metals from ores and minerals and that is why if we process such scrap we need far less energy. So, they are from energy point of view far more favorable, because most of the metals have been extracted anyway you just have to do a little bit to clean up the things produce them again to the purity level you want.

So, you will save on energy and you will also save the environment, because they would not be lying around in the environment. So, secondary metals also form a very important category of metals actually you can think of a day when we will not need this methods of producing primary metals almost very little, because whatever is there as scrap will be recalculated. And then again we produce fresh metals for various uses they will be consumed again there will be some scrap we will reintroduce them of course, it cannot be a total recirculation you might have to produce metals to a much lower level. This actually has happened in the case of say steel, may be forty to fifty or more percentages of steel in united states is coming from scrap. Particularly the huge numbers of cars they produced and after the cars are discarded after three to four years they take out all the non metallic things everything is goes into a press made into a small box that goes for steel making. So it is recalculated, now it is not easy in all the cases, but in cases many cases recalculate is is a distinct possibility and as there is more development there will be more recirculation.

The problem in our country is we are not that developed. We have not made available consumer goods to all our people. Elsewhere the per capita consumption of metals all kinds of metals at a much higher level than that in India? So, we have to produce more and more of the all the metals have been talking about. So, that our people are developed they have more goods and services. We need to make available more copper lead zinc aluminum to more and more people. And the industry would also develop they will need more and more of this. So, we will come to the question of recirculation may be twenty years from. Now you should understand why the process metallurgy operations have shifted from the advanced countries to countries like ours. There are two reasons for it first of all the metallurgical extraction processes are quite dirty, they are lab our intensive they have an impact on environment. So, the advance countries have passed these on to us they have gone into high technologies into software.

Advanced electronic equipments planes spacecrafts they have gone into high technology and left the so called lower technologies to us, but we have no choice we need more metals we have to produce in ourselves and our industry will depend on how we develop our metal extraction processes. So, we will move into next time discussing precious metals and secondary metals. Thank you very much .