Non-ferrous Extractive Metallurgy

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Model No. # 01

Lecture No. # 19

Extraction of Tin

Now, friends we are still in module 5 that concerns, 'extraction of metals from oxide sources'. Now, we have discussed a good bit of detail extraction of aluminum from bauxite and earlier to that we have discussed extraction of magnesium from dolomite. Now, there are many other metals which come from oxide sources.

And these oxidic minerals may not be as rich, as say, in the case of bauxite, where we found we find bauxites very rich in aluminum in nature. Of course, you have to take out the top soil and then you have to mine from bauxite.

One can get dolomite also, good quality dolomite, good quality magnesite, without too much of other gangue associated. But there are many other oxides, which are not found, as over some minerals very rich in them.

But we can obtain the oxide concentrates by various mineral dressing techniques. Let us discuss one metal that is tin, which has very wide application, and very commonly known. Unfortunately, the word tin has come to refer to cans, only because they are coated by the tin metal. They are not made of tin. They are iron cans are coated with tin, but that makes the use of the ore tin very common.

Not many of you may know that tin is used in a surprising variety of applications. Unfortunately, India is not one country, which produces much of tin, because you do not have tin ores. But India has to consume tin, because we need tin; tin has to be imported.

So, let me start discussions on tin, by looking at the various applications of tin. Unfortunately, the slide I am going to show you, has too much of written material. Try to see what is there, or else I will help you by reading things out.

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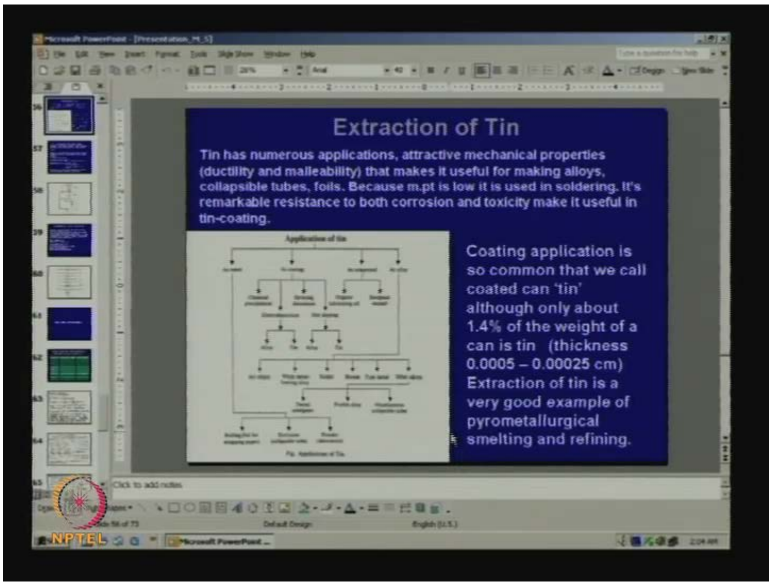

Extraction of Tin

Tin has numerous applications, attractive mechanical properties (ductility and malleability) that makes it useful for making alloys, collapsible tubes, foils. Because m.pt is low it is used in soldering. It's remarkable resistance to both corrosion and toxicity make it useful in tin-coating.

Coating application is so common that we call coated can 'tin' although only about 1.4% of the weight of a can is tin (thickness 0.0005 – 0.00025 cm) Extraction of tin is a very good example of pyrometallurgical smelting and refining.

Why is tin, an attractive metal? If I say, it is attractive because of various applications that is not the right thing to say. Actually the various applications come, because it has many attractive mechanical and chemical properties, because we have these attractive properties, we had found applications.

The attractive properties comprise mechanical properties. It is malleable, it is ductile, which means a piece of tin, can be made into a thin strip, it can be formed into many shapes. It is also very useful in making different kinds of alloys, which find wide applications, and you find tin or tin alloys in many house household consumer items, like collapsible tubes, foils, and etcetera.

One big advantage of tin is its melting point is very low, only 232 degrees, and if it is low, it can find applications in where we need some low melting alloys, like in solders for joining wires.

So, it is used in solders. It has a remarkable resistance to corrosion, and it is also resistant to toxicity, and that is why tin cans coated with tin, can be use keep beverages, food items, liquids and they will not be spoilt.

So, you see the applications. Now, look at them in little more detail. We can think of applications in four categories as metal. Now, as metal, it can be used through extrusion in making collapsible tubes. As powder, it is used in many decorative purposes. It can be rolled, made into foils, for wrapping paper; these are the uses as metal.

More important are in the form of alloys. I have listed some. Alloys to make art objects, white metal bearing alloy that contain tin solder, I have mentioned. Bronzes, that is how actually the ancient human civilizations began; copper, tin, bronzes, which are strong, which are corrosion resistant, and there was a time, when bronze was superior to steel, in terms of hardness and many properties.

Why steel become more popular, because you could produce a lot of steel, far more economically. Otherwise there are many applications where the bronze can be as good as steel, if not better. So, the bronze has also many applications; bronze sculpture, we see. There are many objects made of bronze; type metals, you know the type sets; the letters are made up bronze, because it is very hard. That type has thing has to undergo a repeated contact with the surface on which you have to print using the ink. The letters, it is made up bronze. Then there are other alloys, I need not mention them all.

Then there are tin compounds that are used, in organic lubricating oil, tin compounds have been used. There are inorganic enamels where tin compounds have used, but it finds, perhaps, maximum use as coating, on some other metal surface. This coating can be done in many ways. There can be chemical precipitation on a metal surface.

It can be electrodeposited, on an alloy, as an alloy, or as tin. As a coating, it can be spread, there can be decorative coatings or it can be simply done by hot dipping. That you have a liquid pool of tin and you put whatever you want to coat, in that liquid pool and there we can put a coating of tin alloy or pure tin.

So, there are remarkable numbers of applications are taken. Yet, perhaps the most famous application is tin coating on iron cans, which as I mentioned earlier as maders called cans tins.

Interestingly, the amount of tin, on a coated can is actually very small. There is only about 1.4 percent of the weight of the can is tin and its thickness is as small as 0.0005 to 0.00025. So, imagine how thin that coating is, tin coating is, and it is extremely effective.

It is impervious, it makes the can inside at least corrosion resistant, and it prevents degeneration, of the beverage, of the food material contained inside.

We are going to discuss the extraction of this material with such versatile uses, and we will see it is a fantastic example of pyrometallurgical smelting, and refining, and also of chemistry and it has evolved over centuries. So, many of the steps have been beautifully standardized by alchemists long ago or chemists if you can call them long ago.

Some of them, principles are very easily understood. Some, one might have to think a little bit, as to why there is a step like that. Now, let us talk about its sources. The one main source of tin is cassiterite, which is SnO 2.

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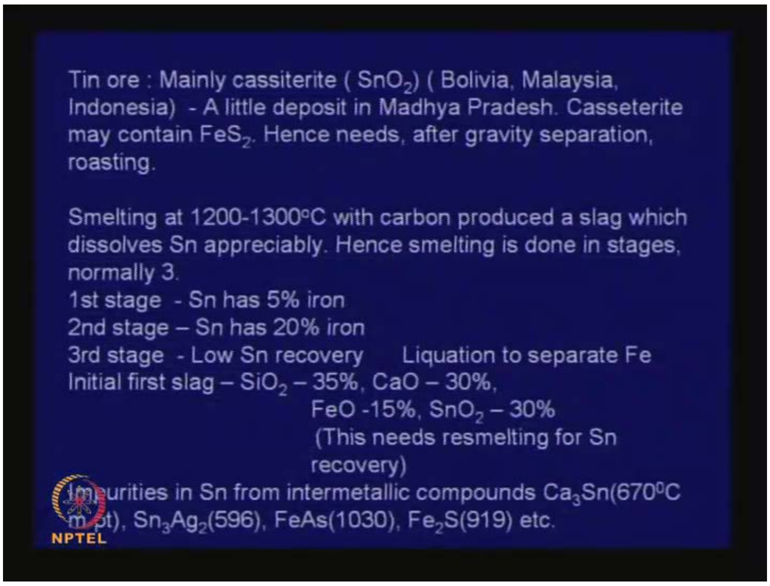

Tin ore : Mainly cassiterite (SnO_2) (Bolivia, Malaysia, Indonesia) - A little deposit in Madhya Pradesh. Casseterite may contain FeS_2. Hence needs, after gravity separation, roasting.

Smelting at 1200-1300°C with carbon produced a slag which dissolves Sn appreciably. Hence smelting is done in stages, normally 3.

1st stage - Sn has 5% iron
2nd stage – Sn has 20% iron
3rd stage - Low Sn recovery   Liquation to separate Fe
Initial first slag – SiO_2 – 35%, CaO – 30%,
FeO -15%, SnO_2 – 30%
(This needs resmelting for Sn recovery)
Impurities in Sn from intermetallic compounds Ca_3Sn(670^{0}C m pt), Sn_3Ag_2(596), FeAs(1030), Fe_2S(919) etc.

Now, there are not lumps of cassiterite found in nature, but cassiterite in combination of many other oxides and gangue materials. That is how cassiterite is found in nature. There are some countries like Bolivia, Malaysia and Indonesia which are very rich in tin deposits. So, they make a lot of money making tin, exporting and making tin.

Unfortunately, in India there are not many known deposits of tin. There is a little deposit in Madhya Pradesh and some attempts have been made, to develop flow sheets, for extraction of tin from that cassiterite that is available in Madhya Pradesh. There may be deposit elsewhere, we do not know about. The chances are that this country does not have deposits of tin. It is quite possible; we have not explored all forests and all remote areas.

But as of known data, we do not have tin in our country. That does not mean that we should not learn extraction of tin. Nobody prevents us, from importing tin ores, and producing tin adds value and produces the metal.

So, if we have the technical expertise, we can have these processes operating in our country. Say it necessary, we learn about extraction of tin, not only because it is an important metal, but because also it is a very good example of pyrometallurgical smelting and refining.

Now, it is not very difficult to reduce SnO 2 by carbon, but there is a problem in trying to do that. The problem is tin ores also contain iron. So, if you try to reduce tin ores for too much then iron would also get reduced, and we will not produce tin metal, but iron tin alloy and they form many things, which I will show you little later.

So, how do we proceed? There is another problem that SnO 2 quite easily dissolves in the slag. Now, we take advantage of that also, and how we proceed is the following. Tin dioxide will not be reduced by carbon in one go. The idea is that we will do that in stages. Why we will do that in stages? Let me explain. What we do that in the smelting at 1200 to 1300 degrees with carbon? We first try to take out some amount of tin; iron is also coming. We do not want to take too much of tin out of it, because if you want to take too much of tin out then too much of iron will also come out.

So, the aim is to have tin dioxide reduction incomplete, in the first stage and produce a metal with five percent iron. But in that process, we have to let go a lot of tin oxide in the slag; does not matter, we will collect the slag and smelt it again with carbon to produce a tin, which will now have more iron.

In the third stage, again, we will take the slag and smelt it. There the tin recovery would be rather small. Now, the first slag that will come will have silica 35 percent, calcium oxide 30 percent, FeO 15 percent, and SnO 2 as much as 30 percent, so a lot of cassiterite that we want to reduce, we do not deliberately reduce, we let it pass of into the slag, in the first stage, because we want to produce the first tin, which would not have too much of iron. So, that is why the slag needs a resmelting for tin recovery.

Now, when we get this impure tin, is not only iron that is there, it contains many other elements and most of them form inter metallic compounds like Ca 3 CSn, Sn 3 Ag 2, FeAs, Fe 2 S, etcetera.

So, the impurities in tin will be in the form of various compounds. No matter, how we produce the tin, we will have to now have an elaborate refining step, where we will need to remove all the elements impurity elements, one by one. We will see how we do that.

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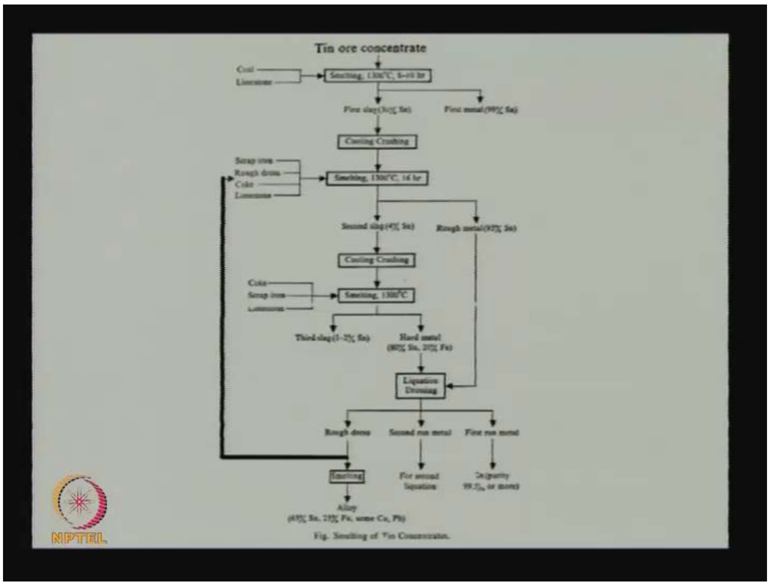

Fig. Smelting of Tin Concentrate.

Here is the flow sheet. We will have a tin ore concentrate. How we are going to produce this concentrate, I am not discussing, but please note that SnO 2, cassiterite is a fairly heavy oxide, you know silica gangue etcetera density of about 2, SnO 2 has a density more than 7.

So, we can employ gravity separation techniques, and there are all kinds of gravity separation techniques, which exploit the differences in density, particle size, and shape. It is possible to produce a fairly rich tin ore concentrate, which would have very high percentages of SnO 2, not pure SnO 2; there will be other gangue materials also.

Then we smelt, say at 1300 degrees, for 8 to 10 hours. We put coal, we add limestone to make a slag, because the limestone will combine with gangue and which would have SiO 2 produce a fluid slag. In that fluid slag, 30 percent SnO 2 will dissolve. If you want we can reduce it, if you make it more reducing condition, if you have add more carbon, if you are allow more time; tin will come out, but iron will also come out, we do not want that.

Initially, we allow an incomplete smelting, precisely, because we want the first metal to be as pure as possible, and we might get as much as 99 percent tin in that step with only 1 percent impurities, slightly different from what I have mentioned, bit earlier. Then the slag is not something that we are discarding, it becomes our raw material. This slag will be cooled, crushed, again smelt it, and in the smelting process, we will again add coke again we would have limestone and would have lot of scrap iron.

Why we will add scrap iron? Because iron will dissolve tin and it will help in the reduction process. Aim now is not to produce tin, but to recover tin, and tin will be dissolved in iron. So, in the next process, we are producing a second slag, which would have only 4 percent tin, as against 30 percent tin here, and we produce a rough metal which will have 95 percent tin, as against initially 99 percent tin.

The second slag would again be cooled, crushed. It goes through a 3rd smelting operation. All these smelting operations will be in the reverberatory furnace. I have shown pictures of this reverberatory furnace earlier. I will show it again, when I start discussing copper metallurgy. So, you go through a third step, again add, coke, limestone scrap iron. In the third step, what are produced are only 80 percent tin and 20 percent iron because you added iron to dissolve tin.

We will get a third slag, this slag now can be discarded because it is only 1 to 2 percent tin, and we can let that go. So, you see how complicated the process becomes, the idea is to recover tin, also recover three kinds of tin. One which is really pure, and next step less pure, third step not at all pure, but on the whole, we have recovered almost 99 percent of the tin, in the charge.

Now, this rough metal, which is ninety five percent tin, we mix with this third smelting metal which is 80 percent tin and twenty percent iron and it will go for, “Liquation

Drowsing”. What is Liquation Drowsing? When you have discussing general principles of refining, I happen to mention a process called Liquation.

Now, let me give you a specific example, as is applied for tin. The process of liquation makes use of the phase diagram. I hope you are able to see this phase diagram here, if not, it is in my book in extraction of nonferrous metals, when I am discussing tin where; let me say, what it says. You know this is a phase diagram for tin; you have iron in this side, pure iron, and tin on this side.

You see, how complicated this phase diagram is, all kinds of phases are forming. There are also, some are around 75 percent tin. FeSn, there is an intermetallic compound; there is also Fe Sn 2, an intermetallic compound. But the point to notice this that if we have an alloy, which has iron and tin, if you can hold it around 600 degrees or so, then it will separate into two phases. One phase will be almost pure tin; other will be iron with some amount of tin. This is what is done by liquation.

That you simply take that alloy, which contains iron and tin, take it to a temperature about 600 or so, and there it will have two layers. Now, tin will float up because it is lighter than iron tin alloy, that iron tin alloy has only a small amount of tin, but what is floating up is almost pure tin that can be taking out.

So, this is the principles of liquation that is what we will done in liquation drowsing. Liquation drowsing means constantly you get something floating up and you remove it. Now, this will give us rough drowse, second run metal, first run metal, means various stages. This will go for another liquation; the rough drowse that has tin iron etcetera will go back recalculated for total tin recovery.

The first run metal, the first layer that will come out will be very pure tin, 99.5 percent tin, but as you take out purer pure tin, you are changing a composition of what you are purifying. In the second step it will not be. So, pure tin in the third step, it will not be very pure, it will only have 65 percent tin. It will have 25 percent iron and copper and lead. This will have to be recalculated back.

So, this is a classic metallurgy of tin where things are very much interconnected, but now equally interesting is, how you purify that the impure tin that you have produced. I will spend little bit of time on that.

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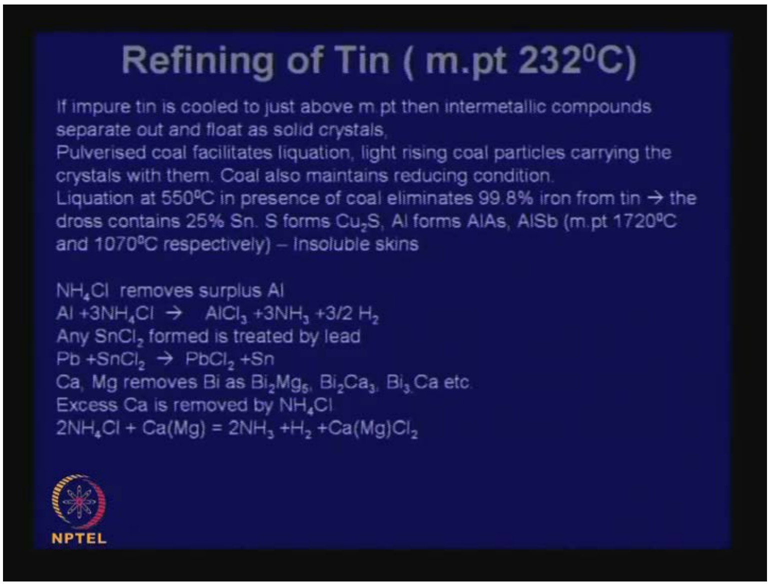

Refining of Tin (m.pt 232^{0}C)

If impure tin is cooled to just above m.pt then intermetallic compounds separate out and float as solid crystals,
Pulverised coal facilitates liquation, light rising coal particles carrying the crystals with them. Coal also maintains reducing condition.
Liquation at 550^{0}C in presence of coal eliminates 99.8% iron from tin → the dross contains 25% Sn. S forms Cu_2S, Al forms AlAs, AlSb (m.pt 1720^{0}C and 1070^{0}C respectively) – Insoluble skins

NH_4Cl removes surplus Al
$Al + 3NH_4Cl \rightarrow AlCl_3 + 3NH_3 + 3/2\ H_2$
Any $SnCl_2$ formed is treated by lead
$Pb + SnCl_2 \rightarrow PbCl_2 + Sn$
Ca, Mg removes Bi as Bi_2Mg_5, Bi_2Ca_3, Bi_3Ca etc.
Excess Ca is removed by NH_4Cl
$2NH_4Cl + Ca(Mg) = 2NH_3 + H_2 + Ca(Mg)Cl_2$

Now, this you should understand. If impure tin is cooled to just above the melting point then many intermediate intermetallic compounds that exist as impurities, will separate out and float as solid crystals.

Tin melts only at 232 degrees. So, we take the impure tin to slightly above the melting. You have now molten mass inside the impurity that we have as intermetallic compounds. There melting points are higher, remember, I have shown that.

You see at the bottom of this slide, if you see, right at the bottom (Refer Slide Time: 25:50). You have Ca 3 Sn 670 degrees, you have an intermetallic compound with silver 596, FeAs (1030), Fe 2 S (919).

So, there are these impurities, which are very high melting. So, when there is a bulk of molten impure tin, impurities inside are not melting so they will float up, and there are some age old techniques, to help these crystals float up. It is done by adding charcoal because if you add charcoal to the bath, the charcoal is a very light material, charcoal particles will float, and in that process, they will carry those impurity intermetallic compounds to the surface also.

These things have been evolved thousands of years ago, more than centuries, 2000 years ago. Somebody has found how to do these techniques. So, you just above the melting point intermetallic compound separate out, float as crystals.

Now, pulverized coal facilitates liquation, light rising coal particles carrying the crystals with them, coal also ensures maintaining a reducing condition. So, the impure metal, you are trying to purify will not get oxidized. So, there is a reducing condition.

Now, if we go, as I mentioned bit earlier, to slightly above higher temperature of 550 degrees, in presence of coal, 99.8 percent of iron from tin will get separated by liquation. Thanks to the phase diagram, there is a complete separation of pure tin and iron containing small amounts of tin; that is how the phase diagram tells us.

The drowse contains 25 percent tin; of course it depends on the temperature, at which operating. If you have in liquation at 550 you will get pure tin and you will get iron tin alloy containing 25 percent tin.

Then we can remove copper by adding sulphur. We can add aluminum to reduce arsenic as aluminum arsenide, also we can import antimony impurities by adding aluminum, and see the impurity the melting point is 1720 degrees they will come out as crystals, 1720 degrees for this and seventeen ten 1070 degrees for this (Refer Slide Time: 28:51). So, if we add aluminum powder we will form insoluble skins that contain these solids.

Then there comes pure chemistry; in that impure tin, we can add this ammonium chloride to remove surplus aluminum that we have added. We may have added too much of aluminum. Aluminum reacts with ammonium chloride to produce Al Cl 3 vapors, ammonia and hydrogen, they all gases and SnCl 2 formed is treated by lead, if during this process of treatment of with ammonium chloride, we produce SnCl 2.

Then by adding lead, we can recover tin, lead will form into lead chloride. These are the chemistry; chemicals steps, I will give a flow sheet, but you must understand how the flow sheet has evolved.

One will add to impure tin, calcium and magnesium, to remove bismuth, as a bismuth magnesium compound, bismuth calcium compound. There are two of them and since you are adding excess calcium, you may add excess, so calcium will be removed again by adding ammonium chloride.

So, the impure tin has to undergo all these so that we can finally, produce pure tin. These are various steps and there is flow sheet that should make it clearer.

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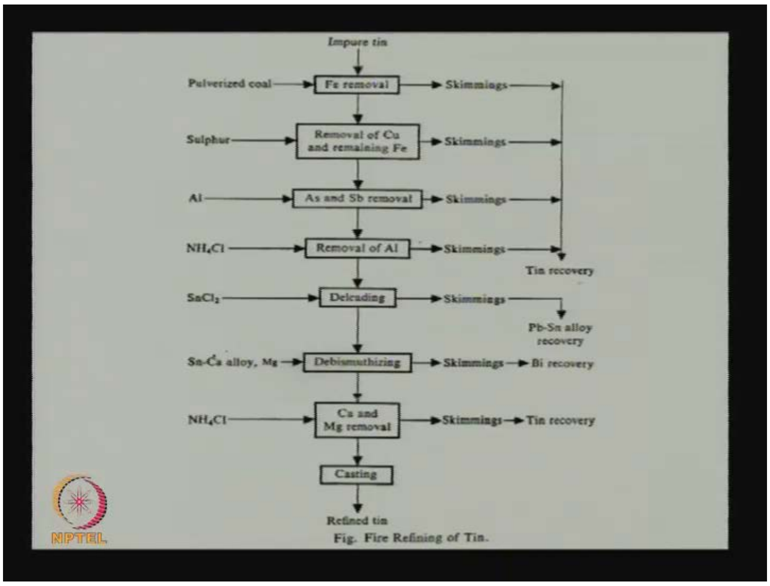

Fig. Fire Refining of Tin.

This is the flow sheet. We want to purify impure tin. How would you remove iron? We will remove by liquation around 550 degrees; pulverized coal will be added.

Then there will be a skim formed, skimming will be separated out. We will add sulphur that will remove copper, remaining iron. These will all be skimming, these will all the solids that will come out and removed.

We will add aluminum, skimming should have arsenic and antimony, ammonium chloride for removal of excess aluminum skimming. All the skimming's will go again for tin recovery because they will all have some interruptive.

We will have SnCl 2 for recovery. After removing lead, the skimming will have lead tin alloy that will also go for recovery steps. Then we can add SnCa alloy, Mg to remove bismuth skimming go for bismuth recovery, again ammonium chloride goes for tin recovery, etcetera finally, we get fire refined tin.

Now, these are chemical reactions that have been perfected, over long time, and that is how tin is produced. The interesting thing to remember here is that although it looks very easy that SnO 2, why you cannot reduce simply by carbon? That would have been possible if you could produce absolutely pure SnO 2, it is not that you cannot do that.

But it is not worth all that trouble. The best is to have the concentrate, do exactly as have been indicated. So, that initially you let go some tin in the slag, produce fairly fine pure tin, second step, third step, then all kinds of steps that have indicated. So, this is how we produce tin.

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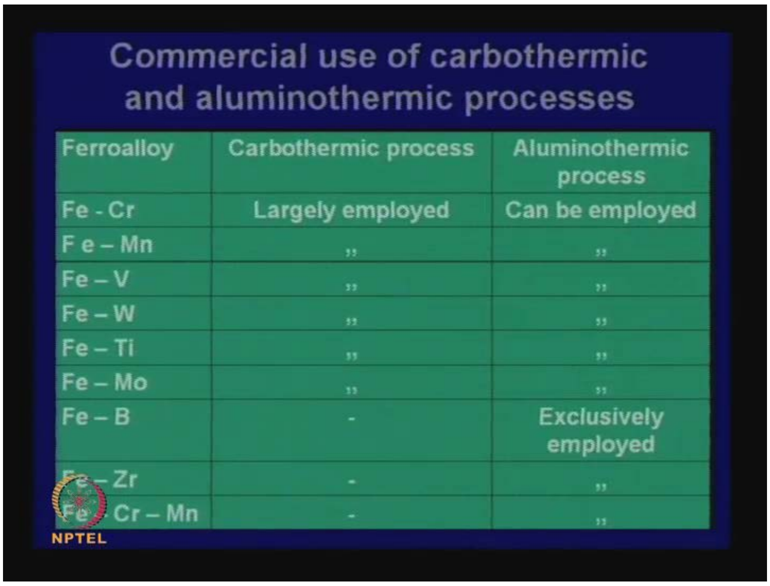

Commercial use of carbothermic and aluminothermic processes

Ferroalloy	Carbothermic process	Aluminothermic process
Fe - Cr	Largely employed	Can be employed
F e – Mn	„	„
Fe – V	„	„
Fe – W	„	„
Fe – Ti	„	„
Fe – Mo	„	„
Fe – B	-	Exclusively employed
Fe – Zr	-	„
Fe – Cr – Mn	-	„

Let me now go to one or two other elements, and this will be in connection with production of Ferro-alloys. Now, I have told you, quite some time ago that ferroalloys are alloys that contain iron and some ferroalloying element, and these are the examples of ferroalloying elements that are extensively required in today’s world. In the industry ferrochrome, ferromanganese, ferrovanadium, ferrotungsten, ferrotitanium ferromolybdenum, ferro boron, ferrozirconium, ferrochromium manganese, most of these ferroalloys, are used for adding these elements into steel. These are called ferroalloying element and it is much easier to add them into steel in the form of ferroalloys, firstly.

Secondly, it is easier to produce these ferroalloys, than these elements, these elements in elemental form. If we need them in elemental form then of course, we have to produce and there are times when we need chromium as metal, pure metal. Manganese is a pure metal or vanadium is a pure metal. Then there are methods to produce.

So, I will mix up this sometimes how we produce elemental things and sometimes as in the form of ferroalloys. Now, let me first talk about the ferroalloys one or two general things.

In theory and I have, I am again repeat something that I have mentioned many times earlier. In theory, you can reduce any oxide by aluminum or calcium, which form very stable oxide, aluminothermic reduction or calciothermic reduction.

In theory, all oxides can be reduced by carbon, because as temperature increases oxides becomes unstable, but CO becomes very stable, but for carbon reduction the problem is you may end up not with the metal, but a combination of metal and metal carbide. If you reduce the oxide by a metal, such as aluminum or calcium, then there is no question of having a carbon, in the metal that you produce.

There is another advantage of metallothermic reaction that is metallothermic reactions are often highly exothermic. Once initiated, the charge may not need any more heating whereas, carbothermic reduction are endothermic. You have to supply heat for carbon reduction.

So, there are advantages and disadvantages, either way. carbon reduction will something simpler, carbon is a cheap reducing agent, but it will need energy, it will need a carbide in the metal, but then we can think of a refining step that we produce a metal, which has carbon, but refine it and get the pure ferroalloy or go for calcium or aluminum reduction and produce ferroalloy, which does not have come.

Now, here I have indicated that this carbothermic process is largely employed. It should be here actually, it is ferrochrome production, ferromanganese production, ferrovanadium, ferrotungsten, ferrotitanium, ferromolybdenum. This will not work for the boron, zirconium or Fe-Cr-Mn.

Whereas, aluminothermic process means reduction by aluminum, can be employed in all the cases, it can be universal planned, and there are two examples. There is one example, ferro-boron exclusively employed; it is only by aluminothermic reduction.

Whereas in the other cases, either there are many places, where there is carbon reduction, subsequent refining, or aluminothermic or calicothermic reduction, both processes are employed. Again, to repeat, why we produce ferroalloys? The reason is ferroalloys are easier to produce than ferroalloy elements. Usually used for alloying iron where a ferroalloy dissolves more easily.

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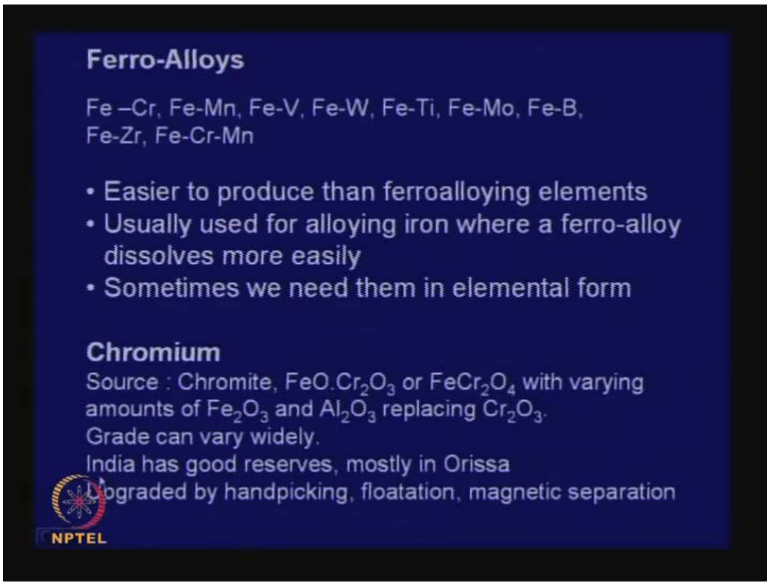

Ferro-Alloys

Fe –Cr, Fe-Mn, Fe-V, Fe-W, Fe-Ti, Fe-Mo, Fe-B,
Fe-Zr, Fe-Cr-Mn

- Easier to produce than ferroalloying elements
- Usually used for alloying iron where a ferro-alloy dissolves more easily
- Sometimes we need them in elemental form

Chromium

Source : Chromite, $FeO.Cr_2O_3$ or $FeCr_2O_4$ with varying amounts of Fe_2O_3 and Al_2O_3 replacing Cr_2O_3.
Grade can vary widely.
India has good reserves, mostly in Orissa
Upgraded by handpicking, floatation, magnetic separation

Sometimes, we need them in elemental form. Suppose, want to talk about production of a ferroalloying element in elemental form. We can take as example, chromium. There will be a method for producing chromium metal. The source is chromite which is FeO.Cr 2 O 3 or you can write it has Fe Cr 2 O 4 with varying amounts of Fe 2 O 3 and Al 2 O 3 replacing Cr 2 O 3; the grades can vary.

India has very good resource of chromites, almost 80 percent of that is in Orissa. Chromites are very easily upgraded; because one can selectively pickup pieces and one can tell which are rich in chromite. They can be upgraded by floatation. They can be, that will be by the gangue is floated up; they can be also upgraded by magnetic separation.

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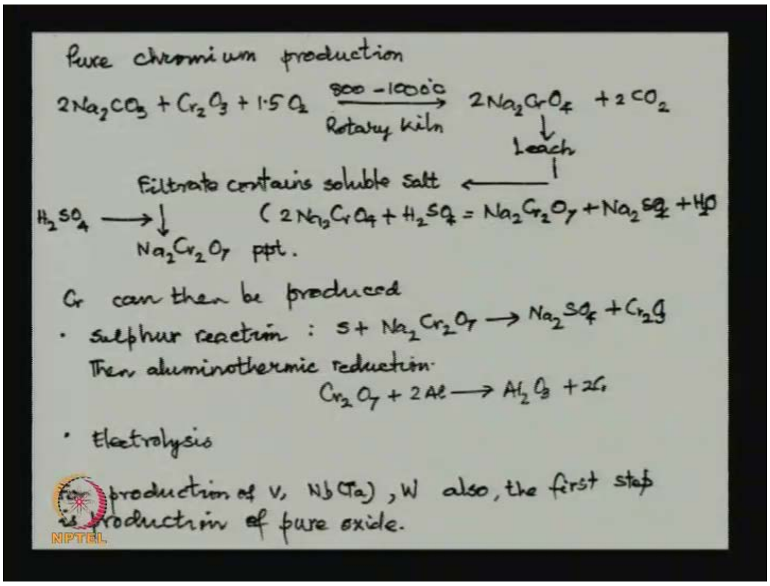

Pure chromium production

$2Na_2CO_3 + Cr_2O_3 + 1{\cdot}5\,O_2 \xrightarrow[\text{Rotary kiln}]{800-1000^\circ C} 2Na_2CrO_4 + 2CO_2$

↓ Leach

Filtrate contains soluble salt ←

$H_2SO_4 \longrightarrow \downarrow$ $(2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7$ ppt.

Cr can then be produced

- sulphur reaction : $S + Na_2Cr_2O_7 \rightarrow Na_2SO_4 + Cr_2O_3$

  Then aluminothermic reduction:

  $Cr_2O_7 + 2Al \longrightarrow Al_2O_3 + 2Cr$

- Electrolysis

For production of V, Nb(Ta), W also, the first step is production of pure oxide.

Now, I will come to ferrochrome production later on. Let us see how it goes for elemental production of element, but to produce pure chromium, a standard technique is to go through a rotary kiln reaction of sodium carbon into Cr 2 O 3, to form leachable sodium chromate, sodium dichromate.

This reaction takes place in a rotary kiln, 800 to 1000 degrees. Then once that is leached, you have Na2Cr2O7 in solution; by hydro hydrosulphuric acid treatment we can precipitate Na 2 Cr 2 O 7. This is how we do that, 2 Na 2 CrO 7 plus H 2 SO 4, will precipitate Na 2 Cr 2 O, this will be in solution.

Now, once you get a precipitate, which is a very pure compound of chromium. Chromium can then be produced in many ways. It can be made to react with sulphur to produce Cr 2 O 3 pure, in this form. Then we go for aluminothermic reduction, produce pure chromium or Cr 2 O 3 can be dissolved in a suitable electrolyte and we can go for electrolysis.

Actually, for production of any of these ferroalloying elements in elemental form, we have to start with the pure oxide. But let us go back to discussing ferroalloys as we started.

I think there is some confusion, excuse me, let us let us come here. So, we were here, and I have mentioned that aluminothermic process seems to be applicable universally whereas, carbothermic process would be largely employed for some, but not exclusively employed.

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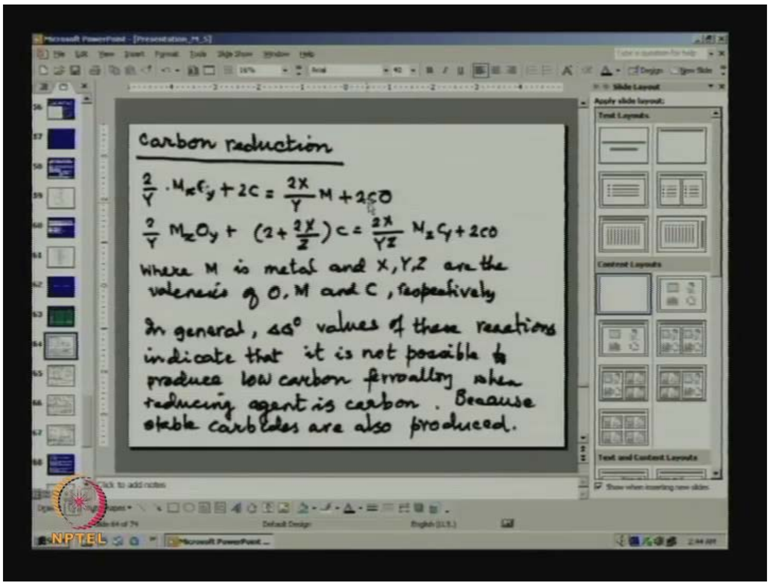

Carbon reduction

$$\frac{2}{Y} \cdot M_xO_y + 2C = \frac{2X}{Y} M + 2CO$$

$$\frac{2}{Y} M_xO_y + \left(2 + \frac{2X}{Z}\right) C = \frac{2X}{YZ} M_zC_y + 2CO$$

Where M is metal and X, Y, Z are the valencies of O, M and C, respectively

In general, ΔG^0 values of these reactions indicate that it is not possible to produce low carbon ferroalloy when reducing agent is carbon. Because stable carbides are also produced.

Now, let us do a bit of thermodynamic analysis. Suppose we have a metal oxide M x O y. This is O and you want to reduce by carbon, you know depending on the temperature either you produce CO or CO 2.

Let us assume that we are going to fairly high temperatures, because they are stable oxide. These ferroalloying elements from stable oxide; so we will produce CO, carbon giving you CO. It can also produce metal carbide. M x O y, reduced by carbon produces metal or M x O y reduced by carbon can also produce M x C y. So, we have to see which reaction is going to predominate.

Now, in general the Delta G naught values of these reactions indicate that it is not possible to reduce produce low carbon ferroalloy when reducing agent is carbon, because stable carbides are also produced.

It will not be all carbide; it will not be all metal, will produce metal with substantial amount of carbides. So, carbon reduction would always do that. You should know that even in the case of production of pig iron in the blast furnace what we get is not pure iron it has carbon in it, up to 4 percent of carbon in iron, Fe 3 C in iron that is what makes it pig iron, it is not pure iron.

So, in the case of iron also, it forms carbide. So, all these metals produce carbide.

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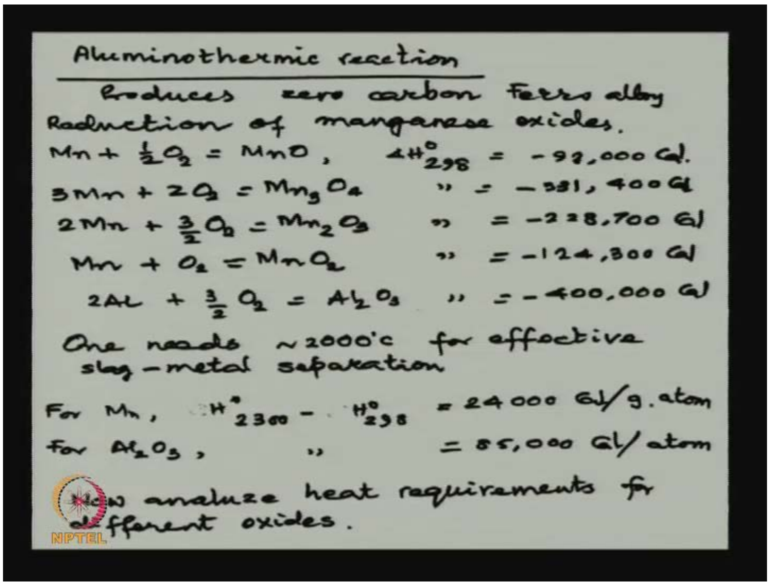

Aluminothermic reaction

Produces zero carbon Ferro alloy

Reduction of manganese oxides.

$Mn + \frac{1}{2}O_2 = MnO$, $\Delta H^{\circ}_{298} = -92{,}000$ Cal.

$3Mn + 2O_2 = Mn_3O_4$ ″ $= -331{,}400$ Cal

$2Mn + \frac{3}{2}O_2 = Mn_2O_3$ ″ $= -228{,}700$ Cal

$Mn + O_2 = MnO_2$ ″ $= -124{,}300$ Cal

$2Al + \frac{3}{2}O_2 = Al_2O_3$ ″ $= -400{,}000$ Cal

One needs ~2000°C for effective slag-metal separation

For Mn, $H^{\circ}_{2300} - H^{\circ}_{298} = 24000$ Cal/g.atom

For Al_2O_3, ″ $= 85{,}000$ Cal/atom

Now analyze heat requirements for different oxides.

But let us look at aluminothermic reduction and do an analysis of this reaction. Look at it from the point of view of heat. Let us consider reduction of manganese oxide by aluminum. Now manganese oxide can be found in many forms. It can be MnO, it can be MnO 4, it can be Mn 2 O 3, and it can be MnO 2. I would like to ask this question that which of these oxides will be ideally suitable for aluminothermic reduction. This is a question we are asking. We have a problem ok.

Now, I have mentioned that aluminothermic reduction is exothermic. So, I would like to do a heat balance to find out how much of heat is available for aluminothermic reduction for each of these oxides, and then find out which will be just right for production of that metal by aluminothermic reduction. Consider the formation reaction of MnO, Mn plus half O 2, the enthalpy change is this much, and I had long ago I have said that this standard enthalpy change does not change very much of temperature. Almost at all temperatures will be the same minus 92000 calories (Refer Slide Time: 47:59).

For this reaction, it is more they are both exothermic where the sign is minus for Mn 2 O 3, we have another figure, and for MnO2 we have also another figure. The free energy of formation of aluminum is written like this for one mole of O 2. Three by two mole of O 2, it is minus 400000 calories. Now, one needs at around 2000 degrees for efficient slag metal separation, we have to find how much heat do we need for clear separation between metal and slag. We have to heat the manganese metal from room temperature to 2000 degrees, for that the data is this much, we can get from the specific heat and melting points and the enthalpy of melting.

For Al 2 O 3, the heat required to heat from room temperature, this is this. Basically what we are saying, we assume the reaction is taking place at this temperature, then we taking the products at high temperature. So, we need extra heat supply so that we get a clear separation between metal and slag.

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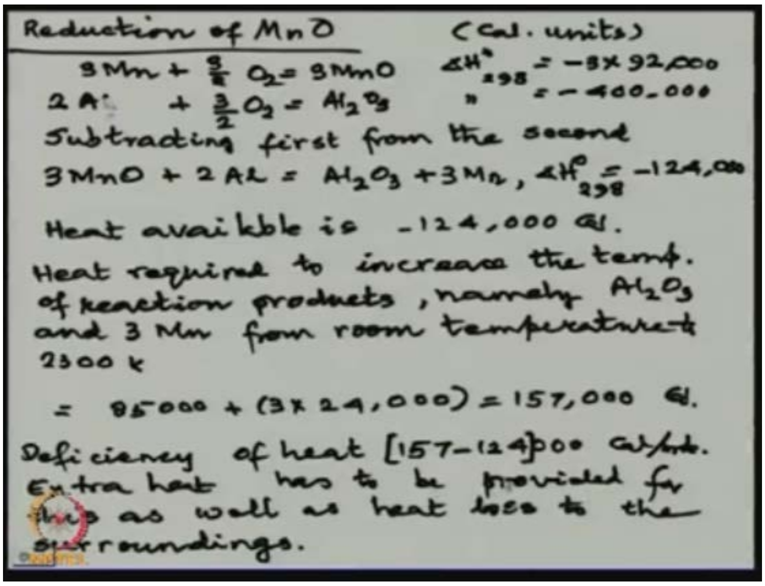

Reduction of MnO (Cal. units)

$3Mn + \frac{3}{2}O_2 = 3MnO \quad \Delta H^\circ_{298} = -3 \times 92{,}000$

$2Al + \frac{3}{2}O_2 = Al_2O_3 \quad " = -400{,}000$

Subtracting first from the second

$3MnO + 2Al = Al_2O_3 + 3Mn, \quad \Delta H^\circ_{298} = -124{,}000$

Heat availble is -124,000 Cal.

Heat required to increase the temp. of reaction products, namely Al_2O_3 and 3 Mn from room temperature to 2300 K

$= 85000 + (3 \times 24{,}000) = 157{,}000$ Cal.

Deficiency of heat [157-124]000 Cal/mole.

Extra heat has to be provided for this as well as heat loss to the surroundings.

Now, we will analyze the heat requirements for different oxides. Reduction of MnO, we can write three Mn plus three by two O 2, three MnO, enthalpy change is this, because in terms of MnO, it was 92 multiplied by three. For aluminum oxide formation it is aluminum, it is this, so if we subtract this from that we get for this reaction three MnO plus two Al gives Al 2 O 3 plus 3 Mn. The delta, it is not value to be like this. So, this is the amount of heat available with us, if this is the reaction that takes place whereas, how much of heat we actually would need we will find that out.

Now, the heat available is this much. Now, heat required to increase the temperature of reaction products namely Al 2 O 3 and Mn, from room temperature to 2300 degrees k that is where the final temperature, we are aiming at for clear slag metal separation, would be, we can find out from here.

This into this is the amount of heat that we really need. So, this is the amount of heat that is being made available by the reaction, but manganese and Al 2 O 3, if we look at there, the amount of heat that we require for them to be heated from room temperature to 2000 degrees is this much.

So, there is a deficiency of heat means we need this much amount of heat to take the products up to 2300 k, but the reaction is giving us only this much of heat. So, there is a deficiency of heat. So, if we want to produce manganese by aluminothermic reduction of MnO, then we need to supply heat externally; otherwise the reaction will not be spontaneous.

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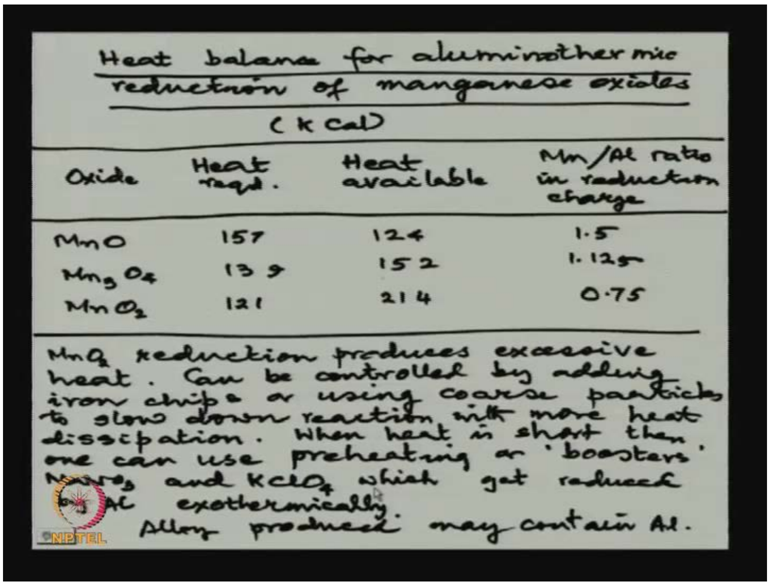

Heat balance for aluminothermic reduction of manganese oxides

(k cal)

Oxide	Heat reqd.	Heat available	Mn/Al ratio in reduction charge
MnO	157	124	1.5
Mn_3O_4	139	152	1.125
MnO_2	121	214	0.75

MnO_2 reduction produces excessive heat. Can be controlled by adding iron chips or using coarse particles to slow down reaction with more heat dissipation. When heat is short then one can use preheating or 'boosters' $NaNO_3$ and $KClO_4$ which get reduced by Al exothermically.

Alloy produced may contain Al.

We can do similar calculations and do the heat balance for the aluminothermic reduction of manganese oxides and we will find that heat available and heat required, if we compare for MnO being reduced by aluminum, heat required would be 157 to take the products to 2000 degrees. Heat available by the reaction is 125, for Mn O 4, heat required is less because of the enthalpy considerations heat available is more. If we take Mn O 2 the heat available is much more than what is required to take the products to 121degrees and it all depends on the Mn- alumina of ratio in the reduction charge.

So, the conclusion of this kind of analysis will be that it will be very risky to take Mn O 2 and try to reduce it by aluminum to produce manganese, because there will be excessive heat and it can be exclusive. Of course, when the charge is becoming too hot it can be controlled also by adding iron chips. We can put iron chips to dissolve manganese and also take that heat to get heated up from room temperature to that temperature.

So, we can produce ferromanganese that way, control the reaction. So, we are reducing MnO 2 by aluminum, we find there is too much of excess heat. We add iron chips which will absorb the heat produce ferromanganese will not allow any explosive reactions.

On the other hand when heat is short like in this case heat available is less than heat required, we can help the charge, by what we call a "Booster reaction", like if we add some sodium nitrate or potassium chloride, they will get reduced by aluminum exothermically and there is no harm done because what will remain KCl, it will go into the slag and it will heat up the charge.

So, in the industry, if you want to apply aluminothermic reduction for production of a metal from its oxide, all these kind of heat balance calculations are done to see what the right kind of charge is. If there is an excess heat it has to be absorbed, it can be absorbed by adding iron if you do not mind producing a ferromanganese, or else if we do not want ferromanganese, you want manganese, then you add some manganese. You already add cold manganese which will they absorb and mix with the manganese that you are producing. So, there it will be diluents, it is diluents.

On the other hand if you find the heat available is less than heat you require then you have to put in booster reactions. Add chemicals like sodium nitrate, potassium chloride to which you will get reduce by aluminum exothermically.

Now, in all these cases, when you are using aluminum, as a reducing agent, the alloy produced may contain aluminum. So, we have to worry about that as to what we do if it contains aluminum.

I will not discuss this now. There are ways and means of ensuring like this does not happen or if it happens how to get rid of the aluminum, but I will stop it here now and I will continue next time with ferroalloys. Thank you very much.