Non-ferrous Extractive Metallurgy

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Module No. # 01

Lecture No. # 41

Review and Summary

Friends, I have finished 38 lectures on the subject of extraction of non-ferrous metals.

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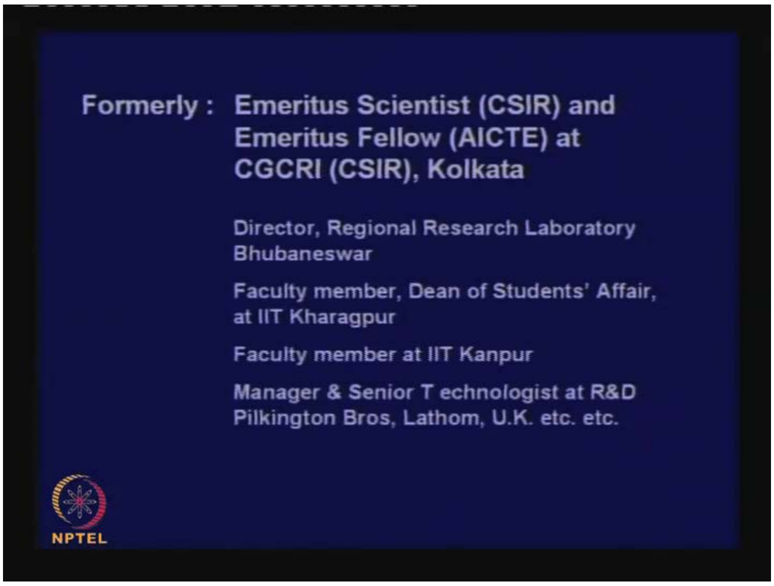

Formerly : Emeritus Scientist (CSIR) and Emeritus Fellow (AICTE) at CGCRI (CSIR), Kolkata

Director, Regional Research Laboratory Bhubaneswar

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Faculty member at IIT Kanpur

Manager & Senior T echnologist at R&D Pilkington Bros, Lathom, U.K. etc. etc.

And then I invited a good friend of mine Mr. Pugazhenthy, who has delivered two very beautiful lectures. I had specially requested him to talk about the importance of nonferrous metallurgy as regards the economy of India today.

How there is a resurges in the nonferrous industry, how it can be an attractive option from our metallurgy graduates and you will appreciate how beautifully, he has presented a subject, he holds a very important position and he is very well thought of in the nonferrous metals academia as well as the industry circle.

Fortunately, he has repeated far more effectively some of the things, I had mentioned about our history and how things are changing, I would not go into that. In the next two lectures, what I propose to do is to go through the entire set of lectures that, I have delivered and remind you of some important points.

Now, I have mentioned and I will mention it again that you always understand principles better, once you know, what actual processes are there and you understand processes better when you know the principles, they go hand in hand; so, we started the lectures with discussion of fundamental principles then, we talked about processes trying to point out how the principles apply.

But, I am sure we begin to understand the importance of the principles only, when we discussed the processes. Now that we have understood the bit, some of the principles and you have become familiar with the processes, the techniques and some details, I can now have a different kind of discussion putting them together. So, I will do that for next 2 lectures 41 and 42 lectures.

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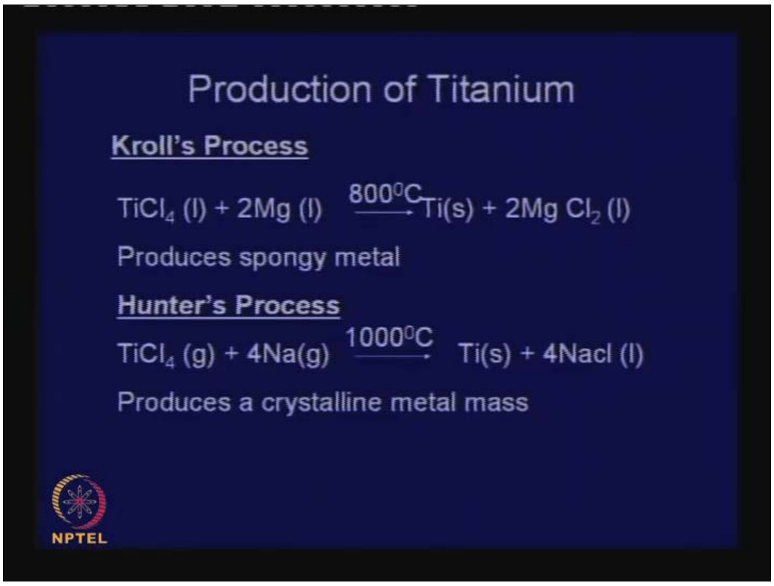

Production of Titanium

Kroll's Process

$TiCl_4\,(l) + 2Mg\,(l) \xrightarrow{800^{0}C} Ti(s) + 2Mg\,Cl_2\,(l)$

Produces spongy metal

Hunter's Process

$TiCl_4\,(g) + 4Na(g) \xrightarrow{1000^{0}C} Ti(s) + 4Nacl\,(l)$

Produces a crystalline metal mass

You would recall that, I had started my lectures by saying how non-ferrous extractive metallurgy is big different from the other under graduate metallurgy subjects. Some people think of it as more of very descriptive, not very analytical, not very quantitative.

I hope that, I have been able to show at least to some extent that, non-ferrous extractive metallurgy is really not that duller subject. There is a lot of logic, there is lot of beauty in the things that are done. It is true that there is a lot of chemistry, more of chemistry than a physics, not that much of mathematics but, certainly there is rationality and some quantification quantitative principles. I started by mentioning two equations, one on reduction of titanium tetra chloride by magnesium and sodium and another was on aluminothermic reduction.

Now, so far as this reaction is concerned in course of chemistry, we will write these two equations and that is the end of the matter. But, I mentioned in my lecture that for a metallurgist, it becomes a starting point for asking question as to how do these reactions actually take place, their mechanisms are different; and subsequently I have discussed and shown that the magnesium reduction often produces a different kind of product, a powdery titanium because of a molecular reaction, whereas the sodium reaction produces a crystalline product, because electrochemical in nature. So, the reaction mechanism is very important.

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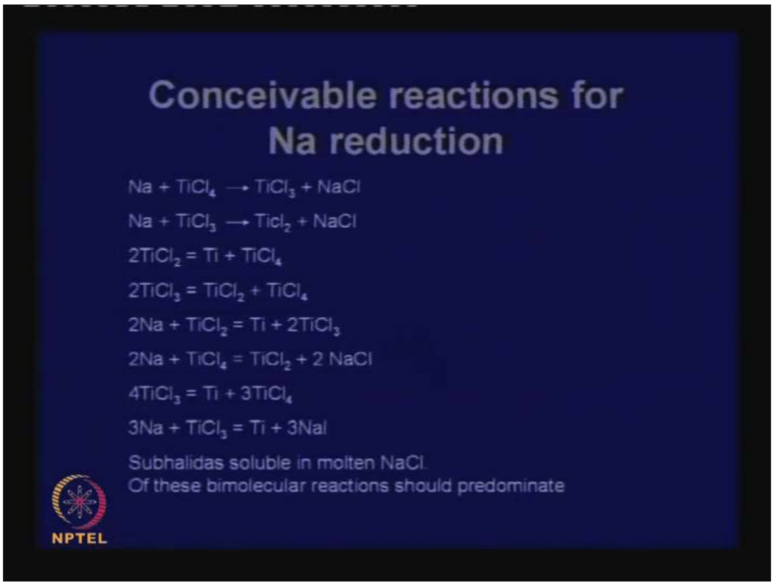

Conceivable reactions for Na reduction

$Na + TiCl_4 \rightarrow TiCl_3 + NaCl$

$Na + TiCl_3 \rightarrow Ticl_2 + NaCl$

$2TiCl_2 = Ti + TiCl_4$

$2TiCl_3 = TiCl_2 + TiCl_4$

$2Na + TiCl_2 = Ti + 2TiCl_3$

$2Na + TiCl_4 = TiCl_2 + 2\ NaCl$

$4TiCl_3 = Ti + 3TiCl_4$

$3Na + TiCl_3 = Ti + 3NaI$

Subhalidas soluble in molten NaCl.
Of these bimolecular reactions should predominate

In the second reaction, there was another reaction that that is, I will explain, why the sodium reaction in electrochemical, because there is sub halides in the sodium chloride phase, which can be detected and much of the reaction take place because of the sodium vapours reacting with sub halides in sodium chloride phase and not sodium vapours and titanium tetra chloride molecules in a gas phase, that reaction is not very probable and that was the basis of explaining how things happened at all and then I said if there is a metallic conductor then, it is conducive to electrochemical reaction that is why you must have a metallic chamber.

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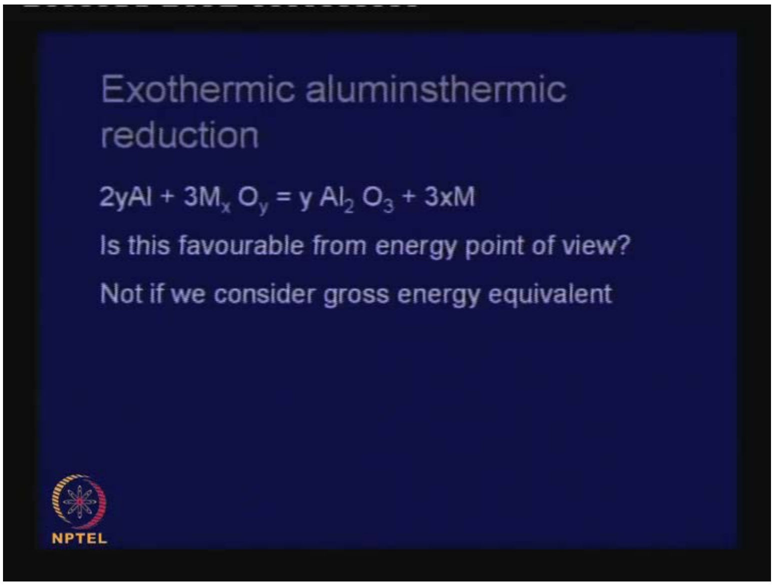

Exothermic aluminsthermic reduction

$2yAl + 3M_x O_y = y Al_2 O_3 + 3xM$

Is this favourable from energy point of view?

Not if we consider gross energy equivalent

The other reaction was aluminothermy reduction of metal oxide. This, such a reaction is exothermic, which produces a lot of heat. So, in a chemistry course, one may learn that, if this reaction is very favorable from energy point of view, because it is exothermic and its autogenous actually; once you set it off, you do not it, does not need any external heat supply. But, later on in the course, we have learned that you have to analyze energy requirements by looking at things in a holistic manner.

If you take into account the energy, that is required to produce aluminum to start with then this reaction is not necessarily favorable from energy point of view. It may generate some heat, it may not need much of an external heat supply, but it has the raw material as consumed energy in the first place and if you take that into account by taking that account you have to calculate process fuel equivalent p f e and unless that is favorable, you cannot call this favorable as a matter of fact it is really not favorable, because the aluminum needs enormous amount of energy in this production.

So, in our non-ferrous metallurgy course, we will look at reactions from a different angle in terms of mechanism and in terms of thermodynamics, in terms of kinetics and that is what I moved into subsequently.

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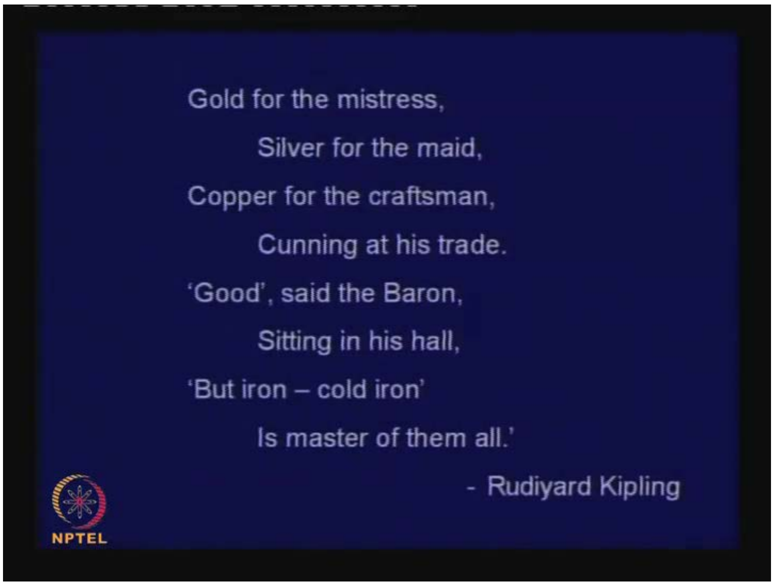

Gold for the mistress,
Silver for the maid,
Copper for the craftsman,
Cunning at his trade.
'Good', said the Baron,
Sitting in his hall,
'But iron – cold iron'
Is master of them all.'
\- Rudiyard Kipling

I did show you this poem, that says that iron is master of them all, but the non-ferrous metals are not necessarily poor cousins of steel, they have their uses and some uses are absolutely strategic and critical. You cannot think of modern age without aluminum alloys, titanium alloys, which go for aerospace applications, we cannot think of copper which go for electrical applications, we cannot think of the electronic industry without silicon and there are many, many non-ferrous metals which are vitally required for various applications. So, we can call steel, master or the iron master of them all, but the others are really not that inferior.

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Production of nonferrous metals in India (t/year)

Metal	~1980	2009
Aluminium	250,000	650,000
Copper	50,000	650,000
Zinc	100,000	585,000
Cadmium	100	40,000
Lead	35,000	61,000

Then, I had given you some figures and Mr. Pugazhenthy has given some more figures, which are, perhaps, more correct and more upto date.

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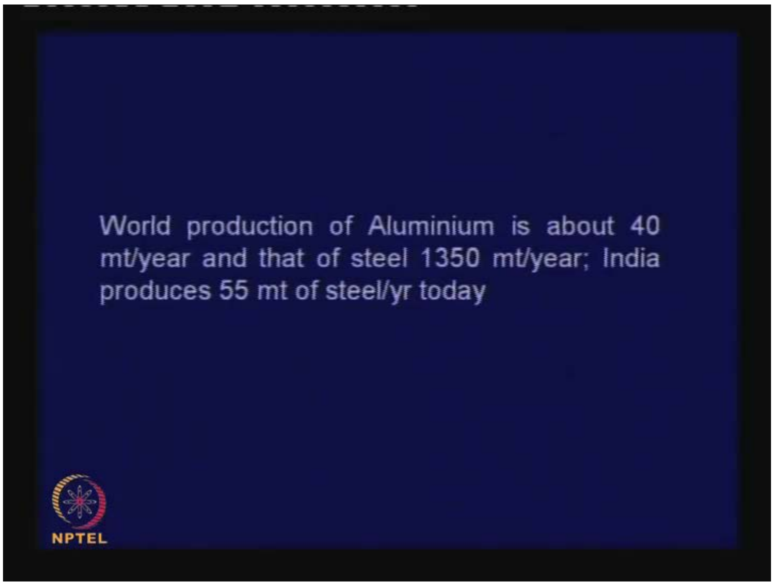

World production of Aluminium is about 40 mt/year and that of steel 1350 mt/year; India produces 55 mt of steel/yr today

The idea was to show that the non-ferrous metals industry in our country is expanding but, even then we are far behind the international scenario, particularly if you look at aluminum which is so, very important for India’s economy that industry has to expand in a big way and all metallurgy graduates will have a very important role to play, if we want to sustain the growth and expansion of a non-ferrous metals industry.

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Learning Objectives of this course

- To discuss past, present and future of nonferrous metals production in India
- To discuss fundamental principals of extraction and refining of nonferrous metals
- To understand application of thermodynamics and kinetics
- To discuss extraction of groups of metals according to modes of occurrence or nature of main starting compounds
- To discuss energy and environment related issues in metal production

Now, having said that, I went back into the history, because in our learning objectives, it was there to discuss past also.

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Learning objectives of the first module of 2-3 lectures

- Brief history of nonferrous metals production in India and some remarkable achievements
- Sources of nonferrous metals, minerals wealth of India
- Classification of metals in terms of reactivities

And so, what we did, we discussed very briefly about the history of non-ferrous metal production in India and we; I mentioned that our history was something very enviable. In ancient world seven or eight metals were known and from ancient times India was producing them, but India had something which no other nation had, until very recent times, it was zinc, India learn to produce zinc very early by 4th or 5th century AD and the industry came to almost a peak by eleventh and twelfth century until after the Muslim invasion things began to decline.

There is a reason why Indians are so crazy about zinc because zinc is one thing for making brass, which was almost a substitute for gold. Indians have always been crazy about gold. So, there were alchemists like Nagarjuna, who was trying to make gold.

And very often the brass they made was just as good as gold and when kings and emperors ran out of gold to cover their temples and monuments then fell back on brass. Brass was, and also for the ordinary public who could not afford gold, good because it also shine like shown like gold.

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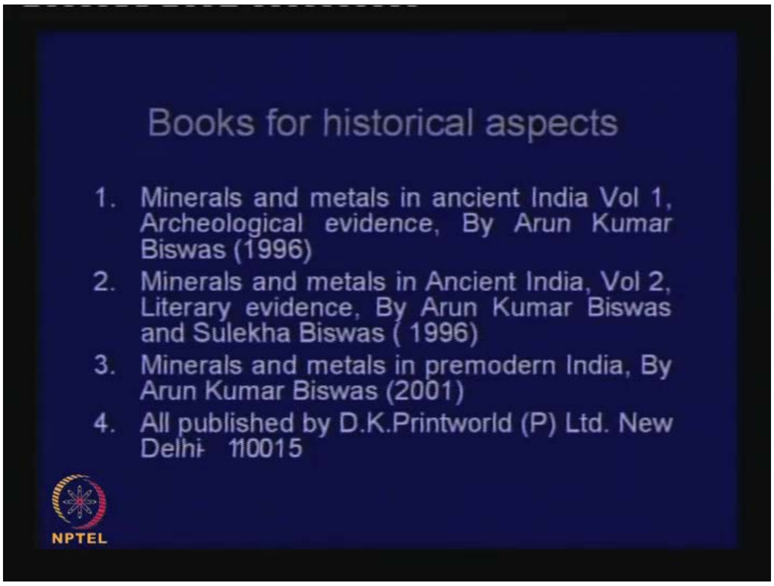

Books for historical aspects

1. Minerals and metals in ancient India Vol 1, Archeological evidence, By Arun Kumar Biswas (1996)
2. Minerals and metals in Ancient India, Vol 2, Literary evidence, By Arun Kumar Biswas and Sulekha Biswas (1996)
3. Minerals and metals in premodern India, By Arun Kumar Biswas (2001)
4. All published by D.K.Printworld (P) Ltd. New Delhi 110015

Now, after having discussed the history and we showed some very good nice pictures also I have referred to this couple of books which I recommend you read sometime, may be after your graduation, to know about how are the minerals and metals in ancient India.

There are two volumes. One volume is on archaeological evidence the other is on literary evidence, for all our texts, we know about, what was there, to what extent they were there. There’s another book on minerals and metals in pre-modern India, just when the Britishers came, that also gives us a lot of things about what was happening in the area of non-ferrous metals.

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A brief history

- Upto about 5000 BC
  Paleolithic (Old Stone) Age – Hunting and food gathering from forests
- ~5000 B.C Beginning of Neolithic
  (New Stone) Age
  Settlements beginning through learning of farming and domestication of animals that ensure ready food supply
  Discovery of fire, baked pottery and cooked food
- ~ 3500 B.C. Beginning of ancient civilization in Egypt, Mesopotemia, Indus Valley (Mohenjo daro, Harappa), China spread of Harappa civilization far and wide in north west India

And then, we went through some. I will go through them quickly over the development of the metals by mankind, over the millennia. Actually things began to happen in Egypt, Mesopotamia, then Indus valley, and then China also started. Many of them started independently or they have been exchange of information.

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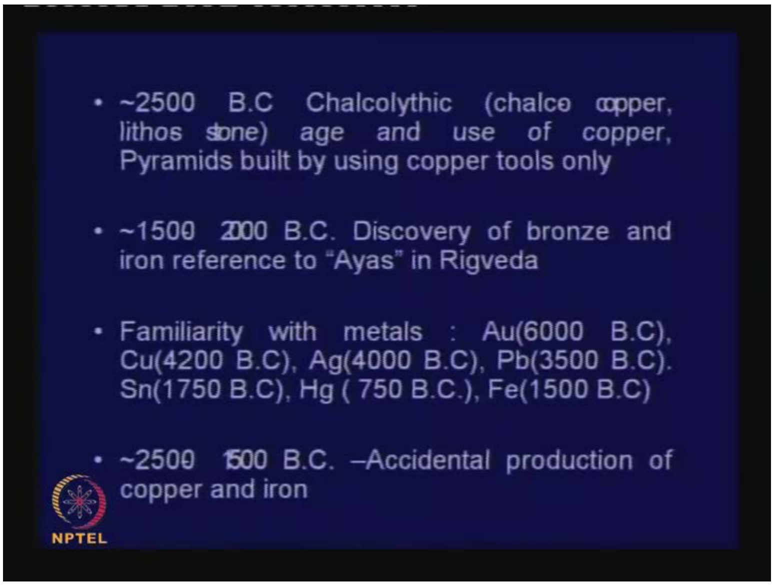

- ~2500 B.C Chalcolythic (chalco copper, lithos stone) age and use of copper, Pyramids built by using copper tools only
- ~1500 2000 B.C. Discovery of bronze and iron reference to "Ayas" in Rigveda
- Familiarity with metals : Au(6000 B.C), Cu(4200 B.C), Ag(4000 B.C), Pb(3500 B.C). Sn(1750 B.C), Hg (750 B.C.), Fe(1500 B.C)
- ~2500 1500 B.C. –Accidental production of copper and iron

But, we know that around 2500 B C there was unset of Chalcolithic age which meant copper and stone people are beginning to come from stone age to use of copper and first came bronze because tin has a lower melting point and bronze had beautiful properties and very often we say ayas that is referred to Veda. This is not necessarily aya, ayas could mean bronze also. People became familiar with gold, copper, silver, lead, tin, mercury, iron, antimony also.

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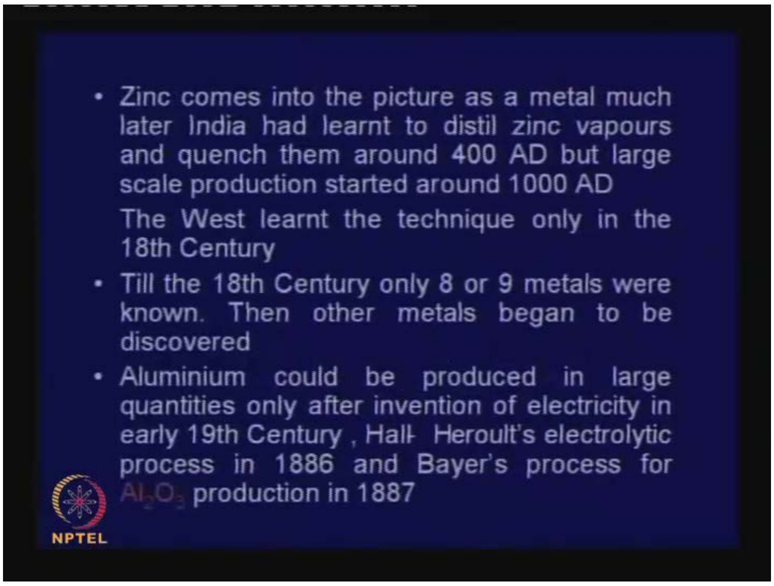

- Zinc comes into the picture as a metal much later India had learnt to distil zinc vapours and quench them around 400 AD but large scale production started around 1000 AD
  The West learnt the technique only in the 18th Century
- Till the 18th Century only 8 or 9 metals were known. Then other metals began to be discovered
- Aluminium could be produced in large quantities only after invention of electricity in early 19th Century , Hall- Heroult's electrolytic process in 1886 and Bayer's process for Al_2O_3 production in 1887

Then, how copper and iron came? There may have been kind of accidental, there are many conjectures I have talked about them. The point to note is that zinc came into the picture as a metal much later and India was a first country to learn this around 400 A D. West learnt the technique only in the eighteenth century because the Indian producers had kept their technique hidden, from rest of the world.

Only from the end of eighteenth century, many newer metals were beginning to be discovered. Before that they were only a handful of metals and strangely aluminum could not be produced. It was produced in smaller, small quantities by chemistry but, it could be produced in bulk, because three things happened together. We had the invention of electricity. Electricity could be used for electrolysis and a process was invented simultaneously in America and France, they are called Hall Heroult's process which was possible because there was electricity. But it was also made possible, because huge quantities of pure alumina could be produced by Bares process.

The Bares process was not there, it would not be possible to produce aluminium in bulk, because you cannot electrolyze bauxite as it is. You have to purify, you have to produce pure alumina for that, you need Bares process. So, in technology many advancements have taken place, because two, three things have happened simultaneously and they have helped each, aluminum is an example.

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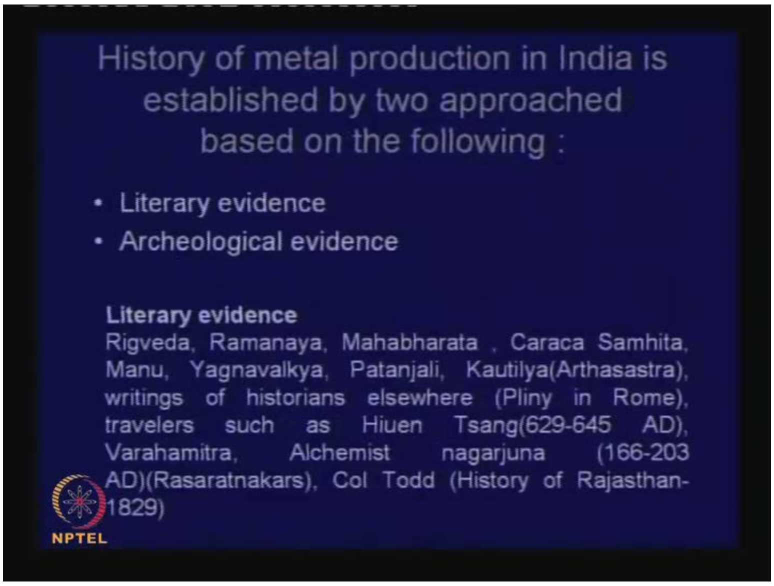

History of metal production in India is established by two approached based on the following :

- Literary evidence
- Archeological evidence

Literary evidence

Rigveda, Ramanaya, Mahabharata , Caraca Samhita, Manu, Yagnavalkya, Patanjali, Kautilya(Arthasastra), writings of historians elsewhere (Pliny in Rome), travelers such as Hiuen Tsang(629-645 AD), Varahamitra, Alchemist nagarjuna (166-203 AD)(Rasaratnakars), Col Todd (History of Rajasthan-1829)

I have talked in detail about the literary evidence in our ancient texts starting from Rig-Veda mention of various metals and alloys.

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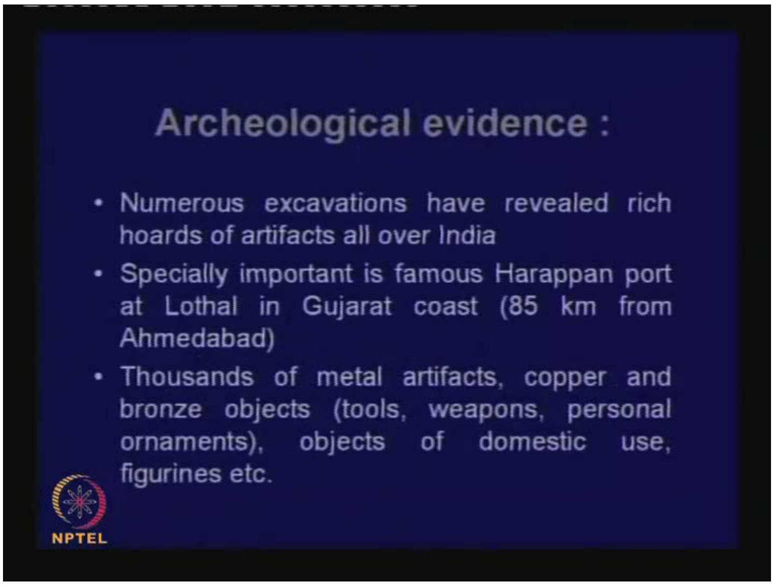

Archeological evidence :

- Numerous excavations have revealed rich hoards of artifacts all over India
- Specially important is famous Harappan port at Lothal in Gujarat coast (85 km from Ahmedabad)
- Thousands of metal artifacts, copper and bronze objects (tools, weapons, personal ornaments), objects of domestic use, figurines etc.

I have talked about archeological evidences from numerous excavations which have yielded thousands of artefacts of all kinds of metals and alloys, not only sculptures but, tools, weapons, personal ornaments, objects of domestic uses, everything are there. They are distributed all over India, there is a large concentration in western India, but then things spread to the south, down to the east.

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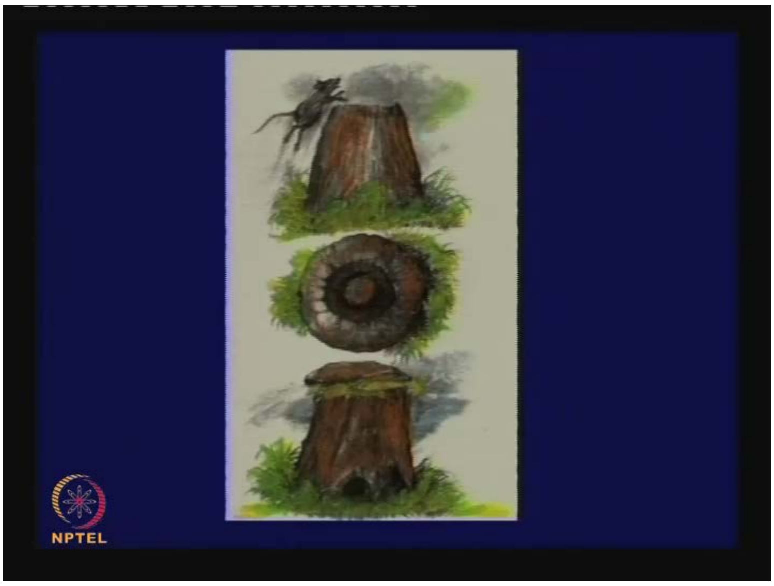

So, there are numerous sites in India where these things were produced. Here is the story as to how the ancients learnt iron production.

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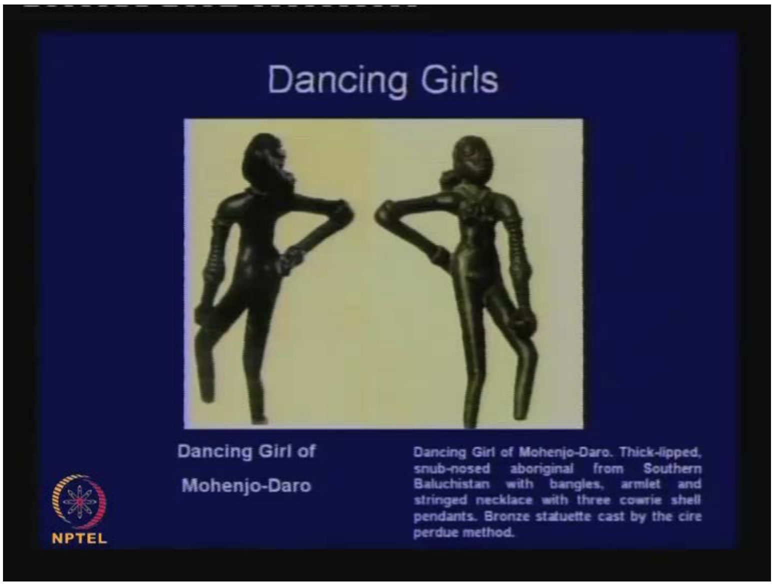

Dancing Girls

Dancing Girl of Mohenjo-Daro

Dancing Girl of Mohenjo-Daro. Thick-lipped, snub-nosed aboriginal from Southern Baluchistan with bangles, armlet and stringed necklace with three cowrie shell pendants. Bronze statuette cast by the cire perdue method.

Then this is one of the oldest examples of a non-ferrous metal figure in India, the dancing girl of Mohenjo Daro. It is a small sculpture with very interesting features bangles only in the left arm. Unfortunately this is Mohenjo Daro is no longer in India, it is in Pakistan now.

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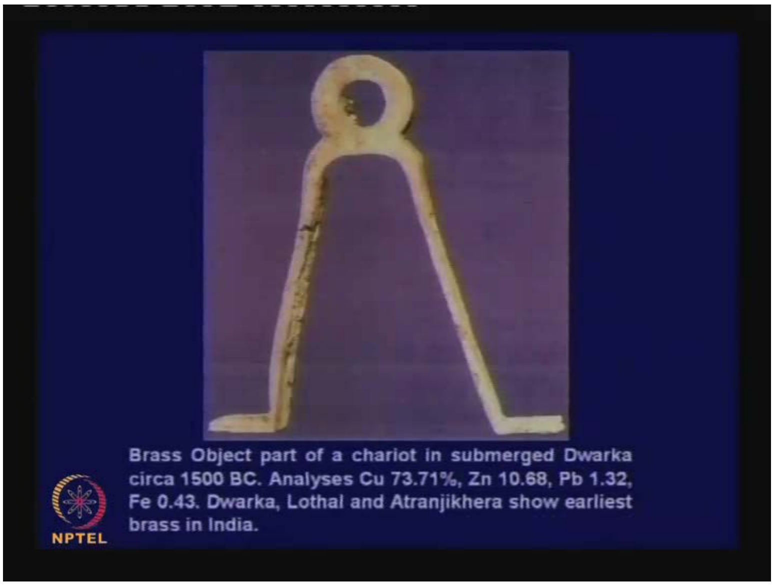

Brass Object part of a chariot in submerged Dwarka circa 1500 BC. Analyses Cu 73.71%, Zn 10.68, Pb 1.32, Fe 0.43. Dwarka, Lothal and Atranjikhera show earliest brass in India.

But then from the submerged Dwarka of the coast of Gujarath, lots of objects have been found which were made of copper, zinc, lead and all kinds of alloys.

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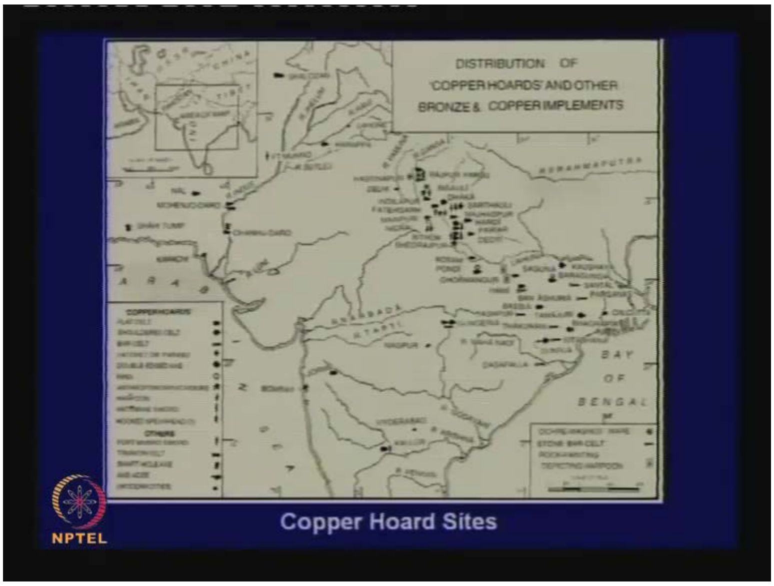

Copper Hoard Sites

And here is a picture showing were all were archeological sites have been found that are yielded many, many non-ferrous metal objects

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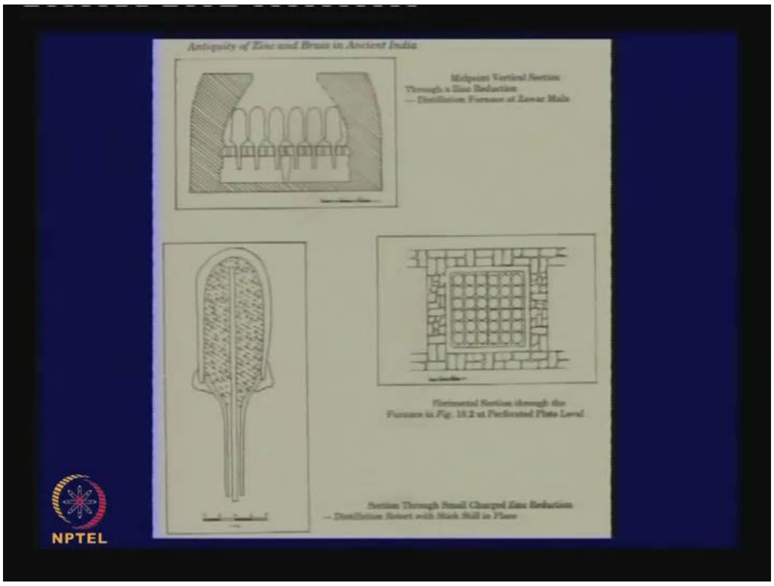

Antiquity of Zinc and Brass in Ancient India

Midpoint Vertical Section
Through a Zinc Reduction
— Distillation Furnace at Zawar Mala

Horizontal Section through the
Furnace in *Fig.* 18.2 at Perforated Plate Level

Section Through Small Charged Zinc Reduction
— Distillation Retort with Stick Still in Place

I showed pictures of some ancient copper making furnaces also distillation units for a zinc, many of them are still intact in the hills sides in Rajasthan. Because it almost looks like when the distillation units were all charged and ready for production, may be they were flooded and those who were to operate them, they left the area.

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Retort walls, Zawar

And they are found intact on the hill sides you find these retorts Indians used both horizontal retorts as well as vertical retorts Mr. Pugazhenthy is showing some pictures.

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Naṭarāja from Kankoduttavanitam (South India), Cola, Eleventh century AD. One of the important large bronzes in the collection, Madras, Govt. Museum.

Then I showed some beautiful sculptures starting from early, as early as seventh or eighth century. There were brasses, bronzes and they were astounding not only because of the quality of the alloy that was produced in India but, also the beauty and the aesthetics the craftsmanship, the high skill of the artisans and one of the techniques they must advise the lost wax process, where actually things that were made, they are really not solid, they are all very hollow. So, there is a thin layer of metal which make these things.

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Naṭarāja. Early Cola period, *circa* 950 AD.

The famous Nataraja which, its beauty, has an international impact and so many books have been written on it. There is a book called The Tao of Physics, where there is a big chapter on this Nataraja concept, what all symbols are there, what all it means and the author thinks that is one of the most beautiful things. This is Ardhanareshwara, this is also another sculpture

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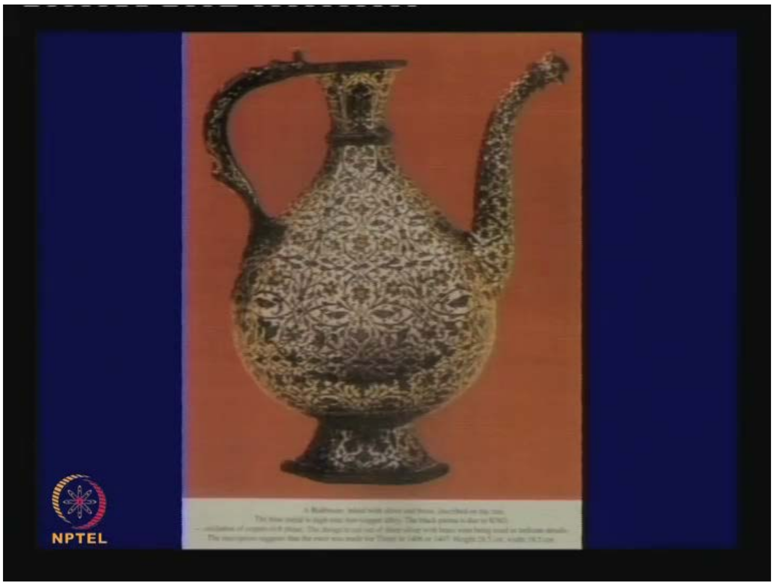

Then in recent time, pre-modern times when the Mughals were declining, they made this beautiful bidriware. It was another special kind of alloy and special kind of craftsmanship.

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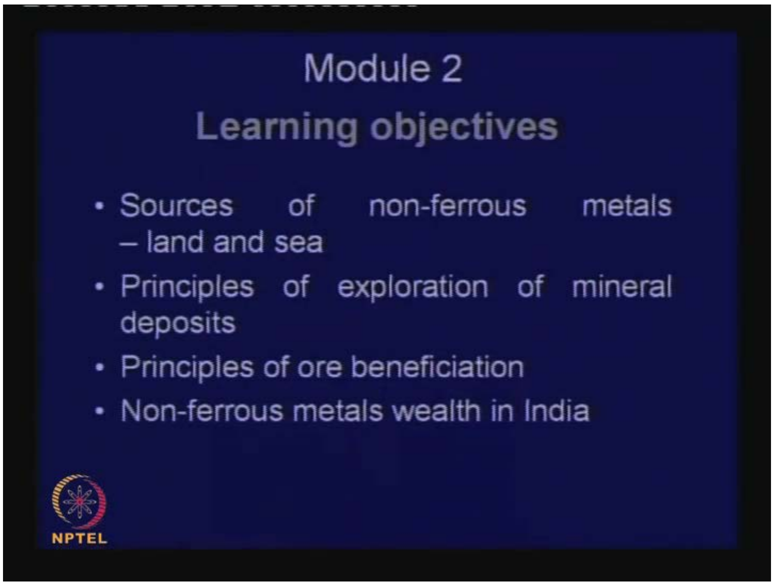

Module 2

Learning objectives

- Sources of non-ferrous metals – land and sea
- Principles of exploration of mineral deposits
- Principles of ore beneficiation
- Non-ferrous metals wealth in India

So, I have discussed all. This was the first module, which was kind of introductive to the course, then I came to the second module, which were little more on the dull side with descriptive but, it had to be done. It was the learning objectives was sources of nonferrous metals, land and sea, principles of exploration, principles of all beneficiation and something about the non-ferrous metal wealth.

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Factors that govern economy of extraction

- Percentage of metal values in ore
- Nature of the occurrence i.e. form of occurrence
- Percentage of impurities and their association
- Physical conditioning of ore
- Location and magnitude of deposits
- Proximity to transport facilities and other services
- Market value of metal(s)
- Value of land, cost of rehabilitation
- Environmental and social concerns etc.

The point to note in this, was that metals do not come from land alone, there are metals in the sea also, and I have given you some data on their distributions. So far as the land is concerned, we can extract metals only from the surface of earth. That surface includes sea also when we say crust of the earth, it is about a few kilometers is what we can normally take samples out, from.

So, the average things, percentages have been shown and that I have discussed at the end of the lectures also that we have shown that oxygen, silicon, aluminum these are there in plenty and that is why we find oxide silicates. There is also calcium, is also there some of the other metals, we are very familiar with like base metals copper, lead, zinc, there abundance is very low. So, had they been distributed uniformly all over the crust, it will be very difficult to extract them. Fortunately there are pockets where they are concentrated that what helps us to get them, extract them.

So, we have discussed the nature of occurrence, that different metals because of their difference in reactivities, occur in different forms, some in some form, they are more stable, some minerals are more stable, they are difficult to decompose, some other minerals are not so stable. I have given you some tables about that and then I have said that an extraction process. We will have to take into account the percentage of impurities, their association, physical conditioning of the ore, location and magnitude, proximity to transport facilities, market value of the metal, if at all extracted.

Then, value of land, cost of rehabilitation, environmental and social concerns, all these to set up the non-ferrous metal industry.

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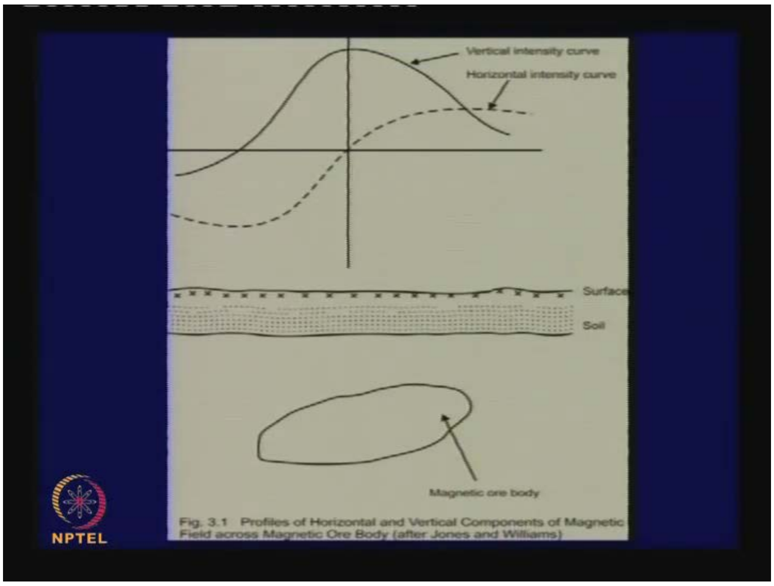

Fig. 3.1 Profiles of Horizontal and Vertical Components of Magnetic Field across Magnetic Ore Body (after Jones and Williams)

So many, many factors go into the production of non-ferrous metals. It start with the exploration that are based on magnetic studies on land, studies on electrical resistivity.

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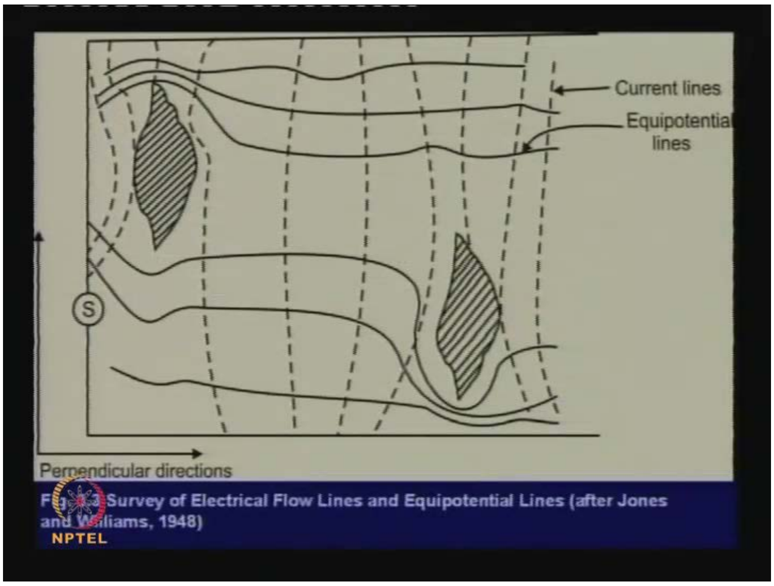

Fig. 3.3 Survey of Electrical Flow Lines and Equipotential Lines (after Jones and Williams, 1948)

These things tell us where water bodies are there, some of such things can be done from air also. Aero planes flow according to some grids and electrical flow lines or equipotential lines are drawn

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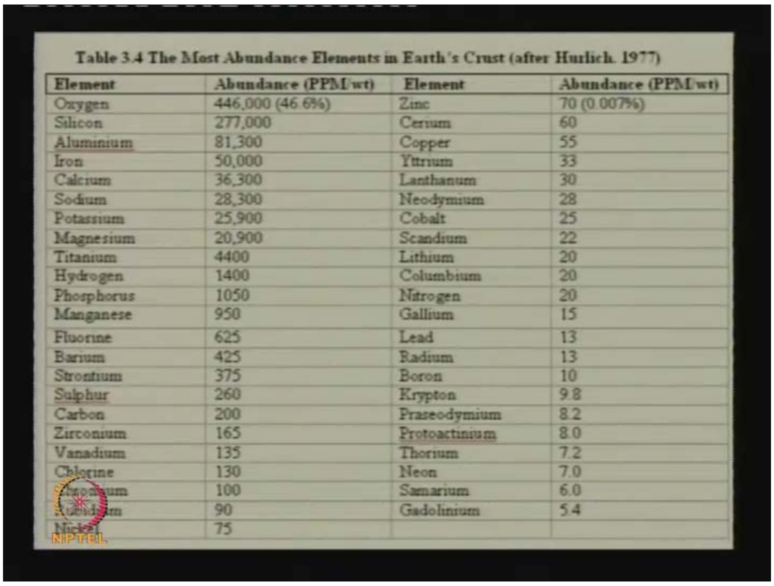

Table 3.4 The Most Abundance Elements in Earth's Crust (after Hurlich. 1977)

Element	Abundance (PPM/wt)	Element	Abundance (PPM/wt)
Oxygen	446,000 (46.6%)	Zinc	70 (0.007%)
Silicon	277,000	Cerium	60
Aluminium	81,300	Copper	55
Iron	50,000	Yttrium	33
Calcium	36,300	Lanthanum	30
Sodium	28,300	Neodymium	28
Potassium	25,900	Cobalt	25
Magnesium	20,900	Scandium	22
Titanium	4400	Lithium	20
Hydrogen	1400	Columbium	20
Phosphorus	1050	Nitrogen	20
Manganese	950	Gallium	15
Fluorine	625	Lead	13
Barium	425	Radium	13
Strontium	375	Boron	10
Sulphur	260	Krypton	9.8
Carbon	200	Praseodymium	8.2
Zirconium	165	Protoactinium	8.0
Vanadium	135	Thorium	7.2
Chlorine	130	Neon	7.0
Chromium	100	Samarium	6.0
Rubidium	90	Gadolinium	5.4
Nickel	75		

Which indicate where water bodies may be there and then detailed explorations are done, where actual samples are taken out, the samples analyzed, doing all this only people go for exploration.

Now, if we take the world average, the average composition of the crust, this is the list of abundance. The elements on top are oxygen, silicon, aluminum, iron, calcium, and then there is, after magnesium, there is a drastic drop and I have said a few elements account for more than ninety five percent of the abundance, but still we manage to get many, many elements, which are the average, shows very low figures but, fortunately they are found concentrated in certain areas, that is why we are able to extract that.

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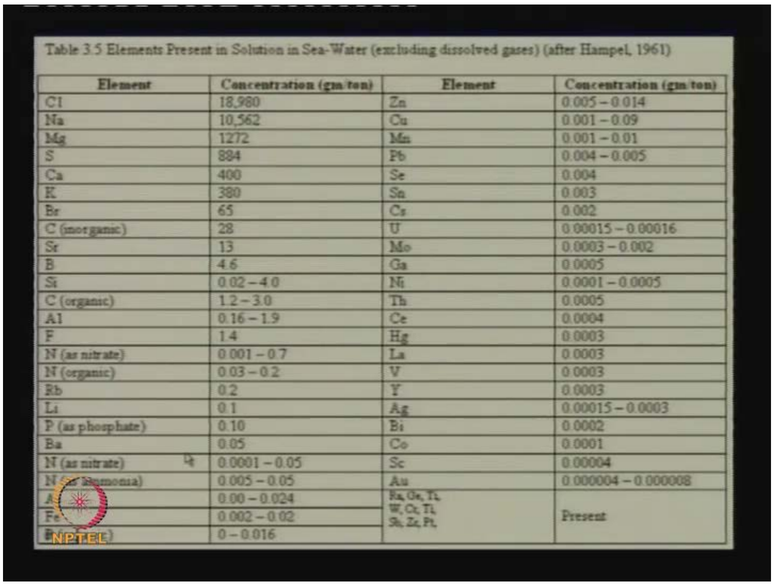

Table 3.5 Elements Present in Solution in Sea-Water (excluding dissolved gases) (after Hampel, 1961)

Element	Concentration (gm/ton)	Element	Concentration (gm/ton)
Cl	18,980	Zn	0.005 – 0.014
Na	10,562	Cu	0.001 – 0.09
Mg	1272	Mn	0.001 – 0.01
S	884	Pb	0.004 – 0.005
Ca	400	Se	0.004
K	380	Sn	0.003
Br	65	Cs	0.002
C (inorganic)	28	U	0.00015 – 0.00016
Sr	13	Mo	0.0003 – 0.002
B	4.6	Ga	0.0005
Si	0.02 – 4.0	Ni	0.0001 – 0.0005
C (organic)	1.2 – 3.0	Th	0.0005
Al	0.16 – 1.9	Ce	0.0004
F	1.4	Hg	0.0003
N (as nitrate)	0.001 – 0.7	La	0.0003
N (organic)	0.03 – 0.2	V	0.0003
Rb	0.2	Y	0.0003
Li	0.1	Ag	0.00015 – 0.0003
P (as phosphate)	0.10	Bi	0.0002
Ba	0.05	Co	0.0001
N (as nitrate)	0.0001 – 0.05	Sc	0.00004
N (as ammonia)	0.005 – 0.05	Au	0.000004 – 0.000008
A[illegible]	0.00 – 0.024	Ra, Ge, Ti, W, Cr, Tl, Sb, Zr, Pt	Present
Fe	0.002 – 0.02		
[illegible]	0 – 0.016		

Interestingly, we should not, we should remember that sea also contains all elements, it is over the millennia, rivers have washed down things or from all corners of the earth surface and dissolved them, elements come from the bottom of the sea, also through under sea cracks or volcanoes, through which things are constantly coming out. On an average, these are the relative abundance, of course, chlorine is maximum that is why we have chloride salts, you have sodium and magnesium, these are sodium chloride and magnesium chloride. There are also other things – sulphur, calcium, whole lot of things.

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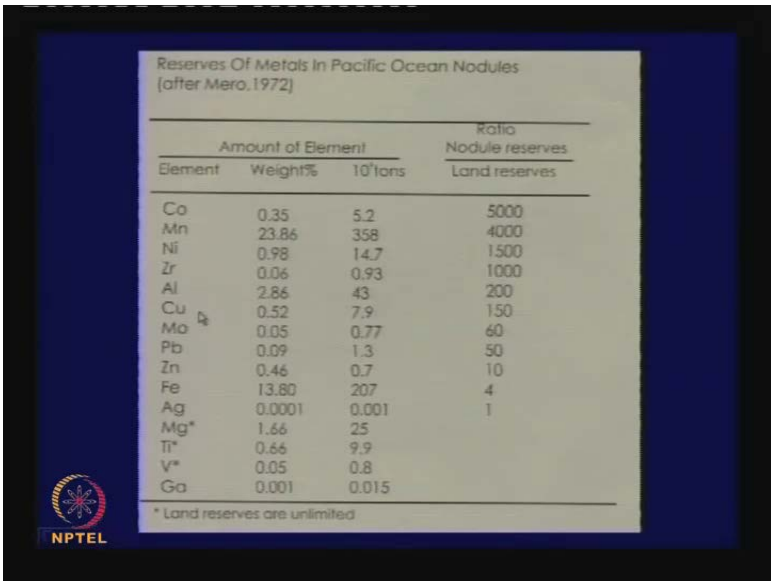

Reserves Of Metals In Pacific Ocean Nodules
(after Mero, 1972)

	Amount of Element		Ratio
Element	Weight%	10^9 tons	Nodule reserves / Land reserves
Co	0.35	5.2	5000
Mn	23.86	358	4000
Ni	0.98	14.7	1500
Zr	0.06	0.93	1000
Al	2.86	43	200
Cu	0.52	7.9	150
Mo	0.05	0.77	60
Pb	0.09	1.3	50
Zn	0.46	0.7	10
Fe	13.80	207	4
Ag	0.0001	0.001	1
Mg*	1.66	25	
Ti*	0.66	9.9	
V*	0.05	0.8	
Ga	0.001	0.015	

* Land reserves are unlimited

And if you go down, you can find there are also precious metals like, you have gold, silver. All that is there, but then because their percentage is so small, even uranium is there, it is not easy to extract those things from sea water. Fortunately there is some concentrated source of things in the sea in the form of manganese and nodules, solid nodules which are continuously forming and getting distributed in sea floors, not in a uniform manner. Some sea floors have more, some have less. They are very rich in manganese because it is in the highest concentration, we call them manganese nodules. It might look like a very good source of manganese, but unfortunately on land also, we have very rich manganese.

But it is more attractive point of view, cobalt, zinc which compare to what is available on land is very attractive and people are interested in extracting cobalt, zinc, nickel, etc from those manganese nodules, but then extracting manganese nodules from the bottom of the sea, which could be several kilometers down, it is not an easy proposition.

There are fortunately some shallows seas, which also have these manganese nodules. So, extraction has to start from there. India is very much in this game in National Metallurgical Laboratory, Hindustan Zinc Ltd., which is now Sterlite. In Regional Research Laboratory, which is now called Institute of Minerals and Materials Technology, a program has been going on for twenty years and it has gone to a pilot plant scale, but it is basically for the future that if you really have to get cobalt, zinc, nickel, we can get from the manganese nodules.

But the process would become better, more economical when we extract also manganese and iron, which are in good quantities.

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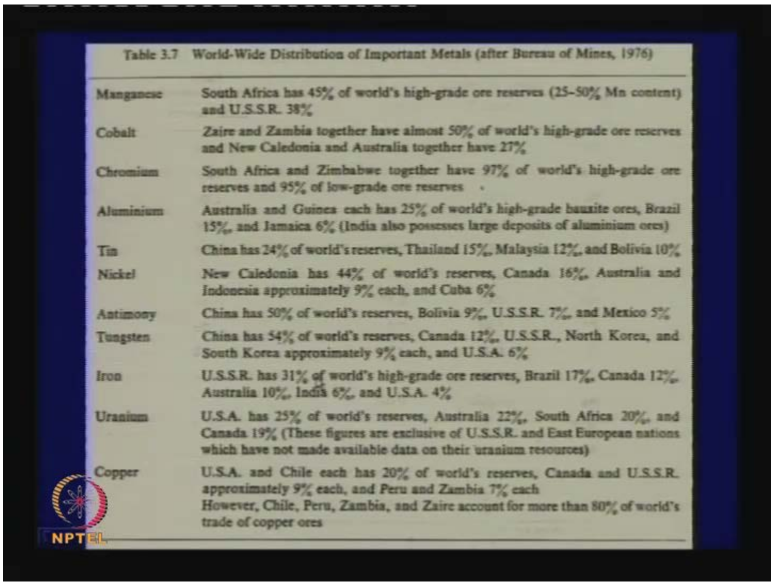

Table 3.7 World-Wide Distribution of Important Metals (after Bureau of Mines, 1976)

Manganese	South Africa has 45% of world's high-grade ore reserves (25–50% Mn content) and U.S.S.R. 38%
Cobalt	Zaire and Zambia together have almost 50% of world's high-grade ore reserves and New Caledonia and Australia together have 27%
Chromium	South Africa and Zimbabwe together have 97% of world's high-grade ore reserves and 95% of low-grade ore reserves
Aluminium	Australia and Guinea each has 25% of world's high-grade bauxite ores, Brazil 15%, and Jamaica 6% (India also possesses large deposits of aluminium ores)
Tin	China has 24% of world's reserves, Thailand 15%, Malaysia 12%, and Bolivia 10%
Nickel	New Caledonia has 44% of world's reserves, Canada 16%, Australia and Indonesia approximately 9% each, and Cuba 6%
Antimony	China has 50% of world's reserves, Bolivia 9%, U.S.S.R. 7%, and Mexico 5%
Tungsten	China has 54% of world's reserves, Canada 12%, U.S.S.R., North Korea, and South Korea approximately 9% each, and U.S.A. 6%
Iron	U.S.S.R. has 31% of world's high-grade ore reserves, Brazil 17%, Canada 12%, Australia 10%, India 6%, and U.S.A. 4%
Uranium	U.S.A. has 25% of world's reserves, Australia 22%, South Africa 20%, and Canada 19% (These figures are exclusive of U.S.S.R. and East European nations which have not made available data on their uranium resources)
Copper	U.S.A. and Chile each has 20% of world's reserves, Canada and U.S.S.R. approximately 9% each, and Peru and Zambia 7% each However, Chile, Peru, Zambia, and Zaire account for more than 80% of world's trade of copper ores

Then the total, on the on the whole, the economics will be better. We have talked about worldwide distribution of important metals which country is richer. God has not been kind to every country in the same manner; some countries are very rich in mineral deposits America, South Africa, parts of Soviet Union, Australia very rich in mineral wealth.

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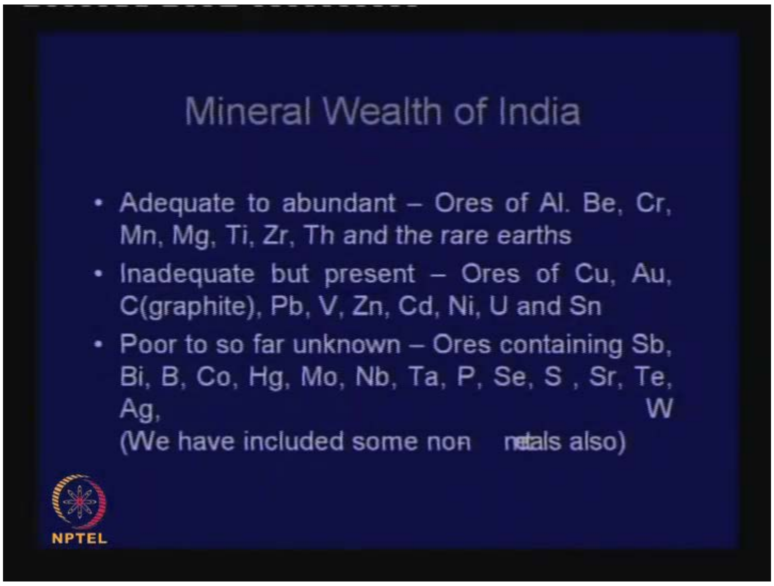

Mineral Wealth of India

- Adequate to abundant – Ores of Al. Be, Cr, Mn, Mg, Ti, Zr, Th and the rare earths
- Inadequate but present – Ores of Cu, Au, C(graphite), Pb, V, Zn, Cd, Ni, U and Sn
- Poor to so far unknown – Ores containing Sb, Bi, B, Co, Hg, Mo, Nb, Ta, P, Se, S , Sr, Te, Ag, W
  (We have included some non metals also)

India is rich in some, but not rich in some others, we would have liked it. For example the mineral wealth of India, is adequate to abundance. So, far as ores are aluminum, beryllium, chromium, manganese, magnesium, titanium, zirconium, thorium and for the rare earths are concerned, we say that we are inadequate, but we have some, definitely ores of copper, gold. I have put graphite also here, because it is an important thing though it is not a metal, lead, vanadium, zinc, cadmium, nickel, uranium, tin, we have.

But, poor to, not known, so far they also include in many metals – antimony, bismuth, boron, cobalt, mercury,molybdenum etc silver, tungsten, they are not there. So, Indian metal industry, non-ferrous metal industry, has to depend a great deal on where we have adequate or abundant resources.

It does not mean, we should ignore the others, because if we have the skill, if we have the knowledge, we can always import concentrates from elsewhere and process them and produce, add value. You can get concentrates of those metals which are available in other countries and if they are willing to sell, we can add value, extract those metals.

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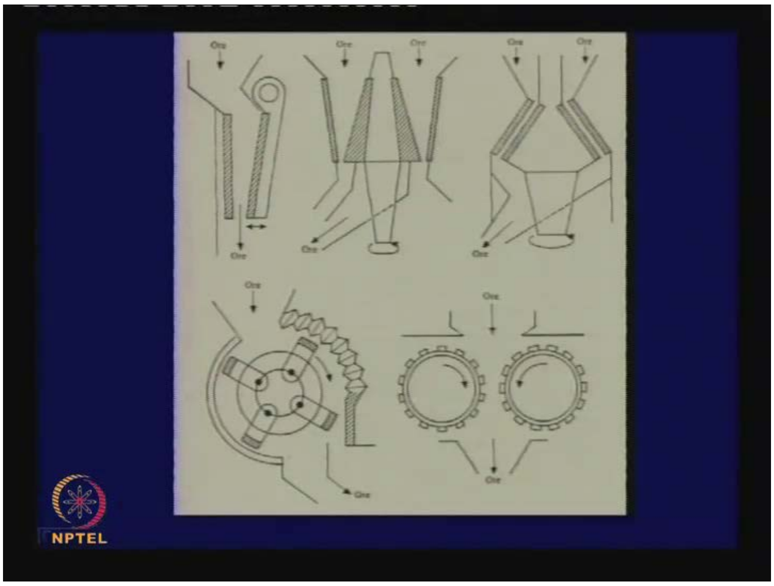

Then we went into the subject of mineral beneficiation, which very often starts with crushing and grinding. There are some pictures of grinders, say this grinding always has the ore particles, go through a gap where we have the grinding surfaces, rotating to force the particles to go through and that is when size reduction takes place.

There are different kinds of mills, these are self explanatory. But, towards the end of my lectures, I mentioned these days the subject of crushing and grinding is becoming very important because it is extremely energy consuming step. In the entire process of mineral beneficiation, we saw that in copper extraction processes seventy five percent of the energy is going into the very first step of crushing and grinding to produce an ore fine ore from which, through floatation will get a copper concentrate.

So, there is now tremendous urge to develop newer kind of crushers and grinders and we have talked about high pressure grinding mills where, suppose if this is the kind of grinder, these two rolls will be pressing from two directions as the particles go through, they are not fixed. So, this high pressure grinding mills are more efficient, they save on energy.

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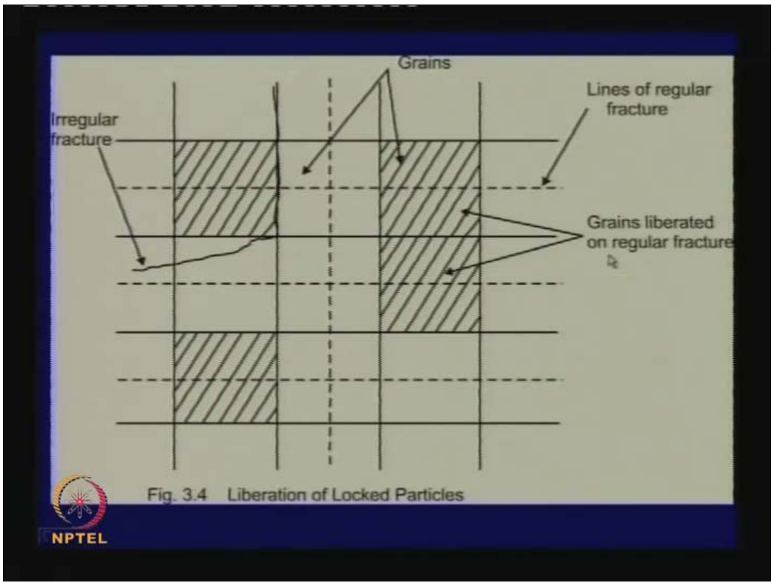

Fig. 3.4 Liberation of Locked Particles

This is regarding how particles fracture, they can fracture around the grains, they can fracture across the grains. Then, I have talked about what kind of particle size that different particles have.

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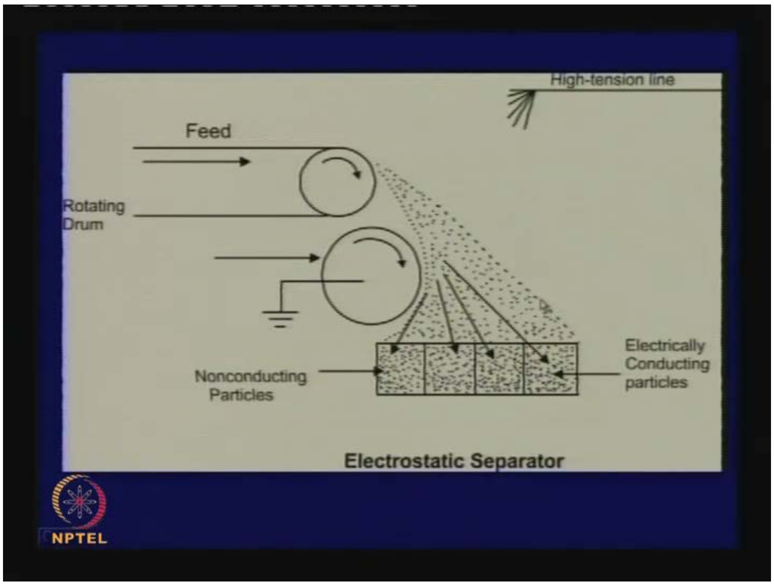

They we have come to various methods of concentration and there are the central thing to remember is different minerals have different kinds of properties, magnetic susceptibility or one mineral is different from the other, electrical susceptibility, their density, size, shape are different. So, these properties will be exploited and electrostatic separator exploits electrical conduction properties, like if we have a rotating drum that attracts particles, which are most attracted that fraction will go here, no the other way, the electrically conducting particles will go there, no conducting particles will go there.

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Unit Operations

Process	Properties to be exploited
Comminution (crushings, grinding)	Brittleness
Sizing (handpicking,screening)	Size difference
Sizing by hydraulic classification	Size and density
Concentration using pulp (Tabling, Jigging, spiral heavy media separation)	Size, density,shape etc.
Magnetic separation	Magnetic permeability and Susceptibility
Electrostatic separation	Conductivity, charge retention characteristics
Flotation	Surface properties

Other methods, coagulation, Adsorption, Filtration, Drying, Agglomeration etc.

So, these are the kind of properties we exploit brittleness just by crushing and grinding you can separate fractions size difference size and density magnetic permeability susceptibility conductivity surface properties in floatation surface properties (( )).

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Spiral concentrator

Beach Sands

- Very heavy minerals (VHM) – Ilmenite, rutile, zircon, monazite etc.
- Heavy minerals (HM0 Garnet, sillimanite
- Lighter minerals – Silica

I have given you one interesting example, which is used in processing of beach sands, which have come again and again, when we talked about monazite concentrate, we have talked about ilmenite processing, processing of beach sands in general and because it is such an important area, processing of beach sands I took in the beginning only. One concentration divide that was spiral concentrator which is used for beach sands which has many, many minerals, very heavy minerals, ilmenite, rutile, zircon monazite, heavy minerals like garnet and sillimanite, lighter minerals like silica. We need to fractionate we need to separate all this and then they will go for their different circuits.

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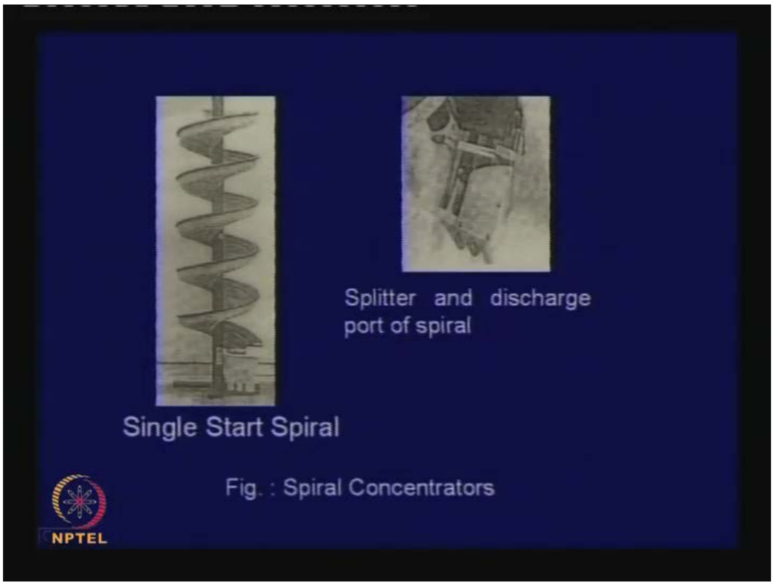

Splitter and discharge port of spiral

Single Start Spiral

Fig. : Spiral Concentrators

And how does it function? We have shown you a picture, a slurry will come down from the top, it will come at increasing velocity, rotating and during the process of rotation, the particles minerals will get separated depending on their density,

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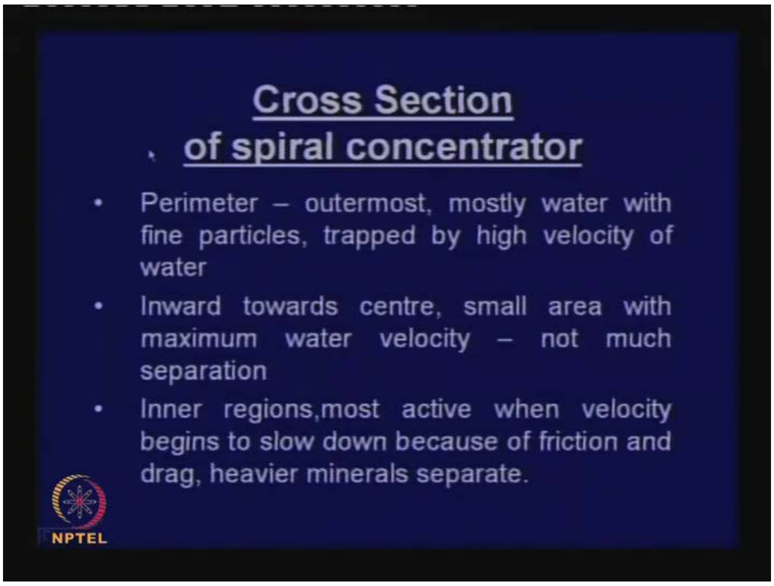

Cross Section of spiral concentrator

- Perimeter – outermost, mostly water with fine particles, trapped by high velocity of water
- Inward towards centre, small area with maximum water velocity – not much separation
- Inner regions,most active when velocity begins to slow down because of friction and drag, heavier minerals separate.

and shape and we have explained how this happens that. In the parimeter outer most, mostly water with fine particles will go, that can be collected separately, that is where just out, inside the perimeter, the velocity will be high and there cannot be not much separation, maximum separation will be inner regions, which is where the velocity drops and begins to slow down and heavier minerals separate there.

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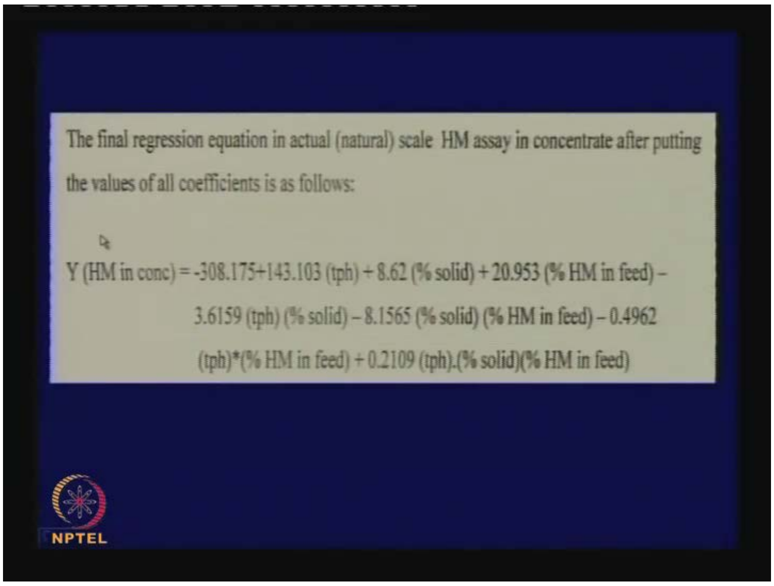

The final regression equation in actual (natural) scale HM assay in concentrate after putting the values of all coefficients is as follows:

Y (HM in conc) = -308.175+143.103 (tph) + 8.62 (% solid) + 20.953 (% HM in feed) – 3.6159 (tph) (% solid) – 8.1565 (% solid) (% HM in feed) – 0.4962 (tph)*(% HM in feed) + 0.2109 (tph).(% solid)(% HM in feed)

Then I have said, the whole thing is really not very descriptive, we can now put in mathematical models, we can bring in computer applications, we can do optimization, we can consider a particular, say a fraction, heavy metal concentrate and we can do experiments and use design of experiment to set up empirical equations

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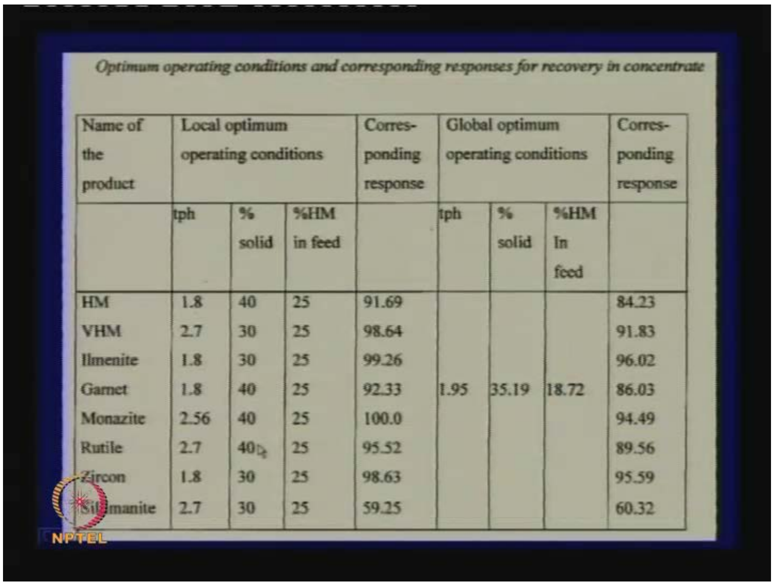

Optimum operating conditions and corresponding responses for recovery in concentrate

Name of the product	Local optimum operating conditions			Corres-ponding response	Global optimum operating conditions			Corres-ponding response
	tph	% solid	%HM in feed		tph	% solid	%HM In feed	
HM	1.8	40	25	91.69	1.95	35.19	18.72	84.23
VHM	2.7	30	25	98.64				91.83
Ilmenite	1.8	30	25	99.26				96.02
Garnet	1.8	40	25	92.33				86.03
Monazite	2.56	40	25	100.0				94.49
Rutile	2.7	40	25	95.52				89.56
Zircon	1.8	30	25	98.63				95.59
Sillimanite	2.7	30	25	59.25				60.32

from which we can optimize things to find what are the waste conditions of getting one fraction out, in quantity or quality, something that the industry traditionally use, to do by lot of trial and error over years. Now, today they can be done in a matter of days using computer packages.

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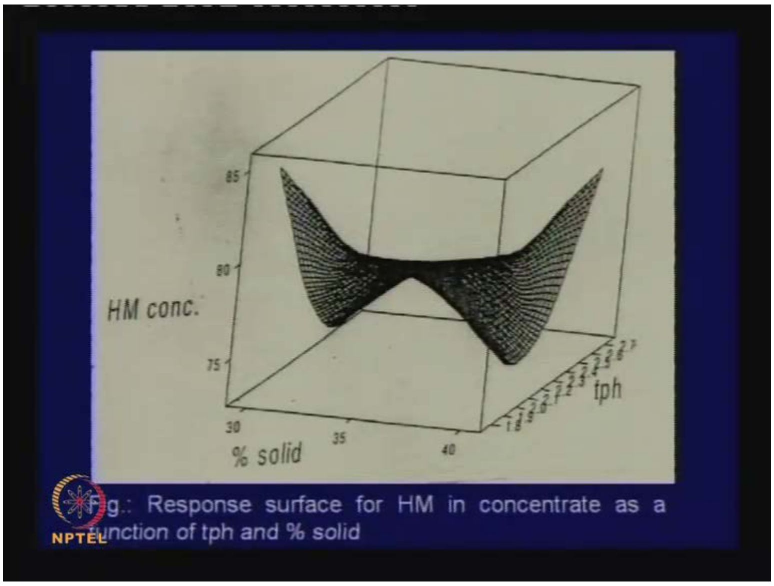

Fig.: Response surface for HM in concentrate as a function of tph and % solid

And then we have done this in Indian rare earths and we have made lot of predictions plotted this sort of waste found surfaces, using standard computer packages to show under which conditions you get maximum concentrate etcetera etcetera and they have been found useful in the industry.

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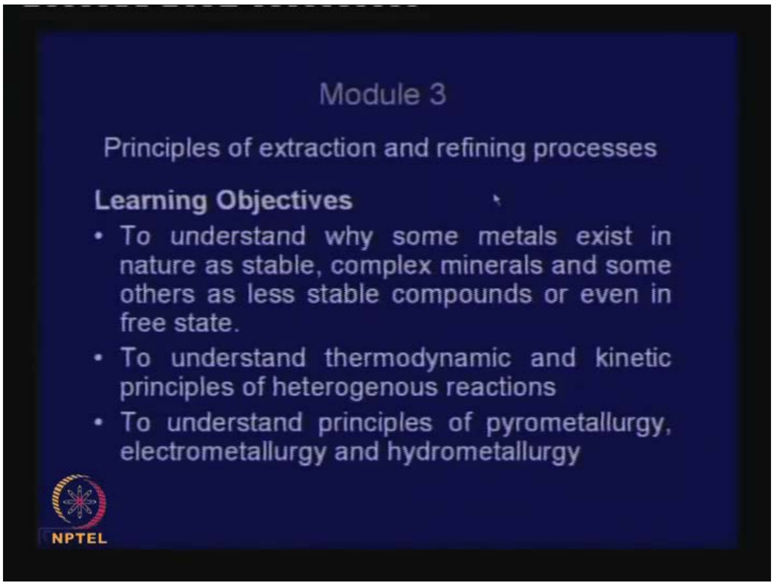

Module 3

Principles of extraction and refining processes

Learning Objectives

- To understand why some metals exist in nature as stable, complex minerals and some others as less stable compounds or even in free state.
- To understand thermodynamic and kinetic principles of heterogenous reactions
- To understand principles of pyrometallurgy, electrometallurgy and hydrometallurgy

Then, we moved to module three, which was principles of extraction and refining processes and that was a fairly long thing. Now in many Universities there can be a full one semester course, only on extraction processes, there can be a course only on principles of refining.

Now, I have squeezed all that into a few lectures taking something from here, something from there and these lectures can never be a substitute for your learning by really going and reading various books which are available Now, in the in the days of internet on any subject you can get so much of information. So, essentially if you have a at least some ideas to what is what, you can always go to a source, where you will get lot more details when you need it.

Now, in this module our learning objectives, was to understand why some metals exist in nature as stable complex, minerals, and some do not. We wanted to understand some thermodynamic and kinetic principles of heterogeneous reactions, because in metallurgy most reactions are heterogeneous. Heterogeneous means either solid, liquid used gases or gases and solids in contact or solids and liquids in contact, very rarely wherein example of something happening in a homogenous gas phase or a homogenous liquid phase. So, you have always talked about heterogeneous reactions where more than one phase is involved. Then we went to understand principles of pyrometallurgy, electrometallurgy and hydrometallurgy

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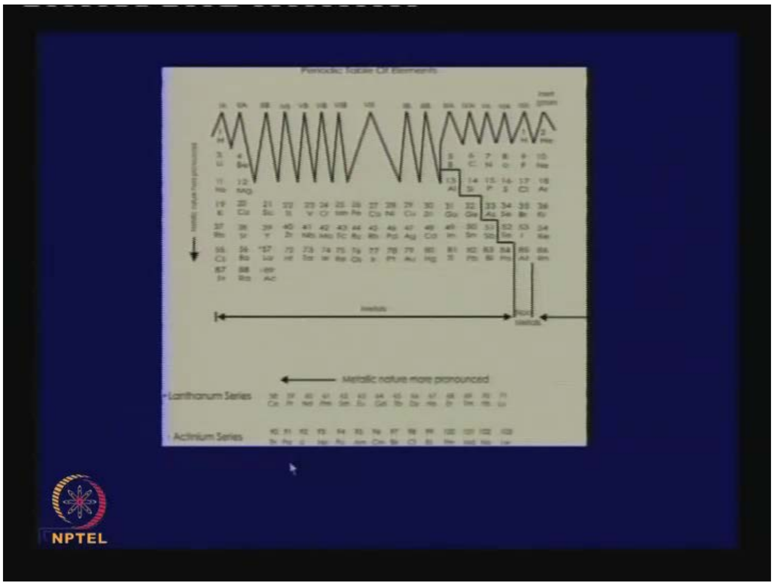

This was where I showed a periodic table to tell you where we find metals, non-ferrous metals. I told you that there are so, many non-ferrous metals, variety of them because all are non-ferrous metals if you leave aside iron, the halogens and some elements which are solids, but they are not metals because metals are supposed to have some properties like lustre, some strength, but then there are some exceptions, graphite has lustre, but, it is not a metal, mercury is not a solid, it has lustre, but it is a metal. Why we call them a metal because metals are supposed to have some reactivity.

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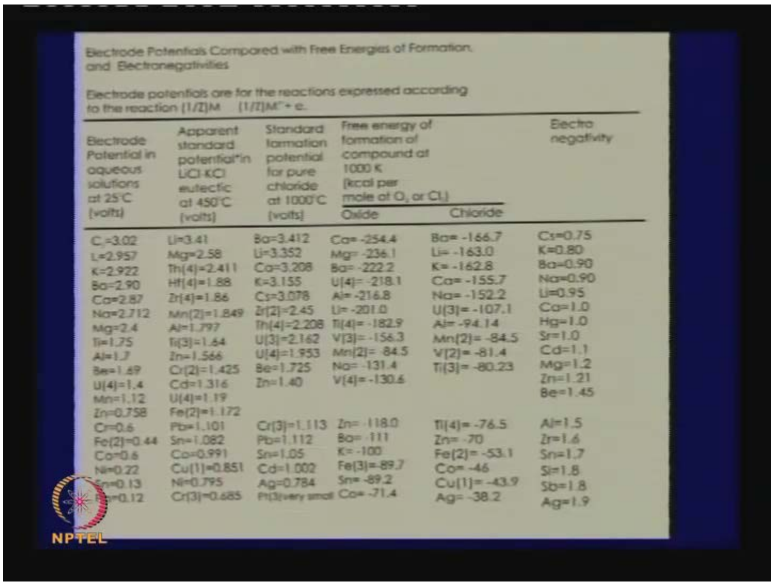

Electrode Potentials Compared with Free Energies of Formation, and Electronegativities

Electrode potentials are for the reactions expressed according to the reaction (1/Z)M (1/Z)M^{Z+} + e.

Electrode Potential in aqueous solutions at 25°C (volts)	Apparent standard potential* in LiCl-KCl eutectic at 450°C (volts)	Standard formation potential for pure chloride at 1000°C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O_2 or Cl_2)		Electro negativity
			Oxide	Chloride	
Cs=3.02	Li=3.41	Ba=3.412	Ca= -254.4	Ba= -166.7	Cs=0.75
Li=2.957	Mg=2.58	Li=3.352	Mg= -236.1	Li= -163.0	K=0.80
K=2.922	Th(4)=2.411	Ca=3.208	Ba= -222.2	K= -162.8	Ba=0.90
Ba=2.90	Hf(4)=1.88	K=3.155	U(4)= -218.1	Ca= -155.7	Na=0.90
Ca=2.87	Zr(4)=1.86	Cs=3.078	Al= -216.8	Na= -152.2	Li=0.95
Na=2.712	Mn(2)=1.849	Zr(2)=2.45	Li= -201.0	U(3)= -107.1	Ca=1.0
Mg=2.4	Al=1.797	Th(4)=2.208	Ti(4)= -182.9	Al= -94.14	Hg=1.0
Ti=1.75	Ti(3)=1.64	U(3)=2.162	V(3)= -156.3	Mn(2)= -84.5	Sr=1.0
Al=1.7	Zn=1.566	U(4)=1.953	Mn(2)= -84.5	V(2)= -81.4	Cd=1.1
Be=1.69	Cr(2)=1.425	Be=1.725	Na= -131.4	Ti(3)= -80.23	Mg=1.2
U(4)=1.4	Cd=1.316	Zn=1.40	V(4)= -130.6		Zn=1.21
Mn=1.12	U(4)=1.19				Be=1.45
Zn=0.758	Fe(2)=1.172				
Cr=0.6	Pb=1.101	Cr(3)=1.113	Zn= -118.0	Ti(4)= -76.5	Al=1.5
Fe(2)=0.44	Sn=1.082	Pb=1.112	Ba= -111	Zn= -70	Zr=1.6
Co=0.6	Co=0.991	Sn=1.05	K= -100	Fe(2)= -53.1	Sn=1.7
Ni=0.22	Cu(1)=0.851	Cd=1.002	Fe(3)= -89.7	Co= -46	Si=1.8
Sn=0.13	Ni=0.795	Ag=0.784	Sn= -89.2	Cu(1)= -43.9	Sb=1.8
=0.12	Cr(3)=0.685	Pt(3) very small	Co= -71.4	Ag= -38.2	Ag=1.9

And to that to show, I showed you a table where metals have been listed in terms of their reactivities now, what is the criterion of reactivity. There are many criteria I have listed. Here electrode potentials apparent, standard potentials, standard formation of potential of P O chlorides, free energy formations of oxides and chlorides electro negativity. I have not gone far too deep in the subject, but I should mention this, there are different fundamental principles behind all such listing.

The list we get using different criteria, do not give identical listing means which is on top here, may not be on top there. But then by and large, you will find some metals are coming to the top means they are very reactive, they are very reactive towards halogens, oxygen and things like that, like cesium, potassium, beryllium, sodium, lithium, calcium. You will find them all at the top everywhere, whereas, some metals like platinum gold, silver, etc. they will all be at the bottom, they are not at all reactive.

Metals like copper also would be towards the bottom, things like lead, tin, iron, zinc, manganese, they would be somewhat at the in the middle. By electro negativity, we mean these are electropositive, metals going down is electro negative, those which are electro positive, we will have greater negative values of free energies of formation of either oxides or chlorides means, they make very stable compounds and when they have stable compounds, it will be very difficult to dissociate and get the metal same in terms of electrode potential electrode potentials are with reference to hydrogenous one.

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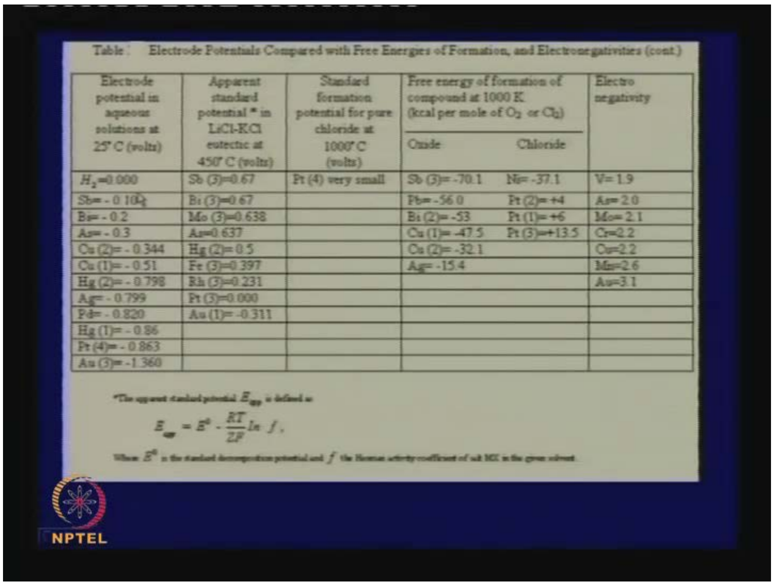

Table : Electrode Potentials Compared with Free Energies of Formation, and Electronegativities (cont.)

Electrode potential in aqueous solutions at 25° C (volts)	Apparent standard potential * in LiCl-KCl eutectic at 450° C (volts)	Standard formation potential for pure chloride at 1000° C (volts)	Free energy of formation of compound at 1000 K (kcal per mole of O_2 or Cl_2)		Electro negativity
			Oxide	Chloride	
H_2=0.000	Sb (3)=0.67	Pt (4) very small	Sb (3)= -70.1	Ni= -37.1	V= 1.9
Sb= - 0.10	Bi (3)=0.67		Pb= -56.0	Pt (2)= +4	As= 2.0
Bi= - 0.2	Mo (3)=0.638		Bi (2)= -53	Pt (1)= +6	Mo= 2.1
As= - 0.3	As=0.637		Cu (1)= -47.5	Pt (3)= +13.5	Cr=2.2
Cu (2)= - 0.344	Hg (2)= 0.5		Cu (2)= -32.1		Cu=2.2
Cu (1)= - 0.51	Fe (3)=0.397		Ag= -15.4		Mn=2.6
Hg (2)= - 0.798	Rh (3)=0.231				Au=3.1
Ag= - 0.799	Pt (3)=0.000				
Pd= - 0.820	Au (1)= -0.311				
Hg (1)= - 0.86					
Pt (4)= - 0.863					
Au (3)= -1.360					

*The apparent standard potential E_{app} is defined as

$$E_{app} = E^0 - \frac{RT}{ZF} ln\ f ,$$

Where E^0 is the standard decomposition potential and f the Henrian activity coefficient of salt MX in the given solvent.

Now, electrode potential tells us there is a line we can draw at hydrogen. With reference to hydrogen, taken as zero, all below elements, below that metal, below that are electro negative all above that are electro positive which means these metals should not normally be obtained from ecos media by electrolysis. Because if that comes it will immediately react with water and liberate hydrogen, like if you have somehow get magnesium out of water, it will not be magnesium, it will react with water immediately, liberate hydrogen, normally that would happen for zinc also, zinc in an acid medium will liberate hydrogen.

But when we pass a current, there are some phenomena and that we have discussed, called activation over potential, which changes these electrode potentials because of certain reasons, which I will discuss a little later. And that is why under the condition of some passing of current, this listing changes and hydrogen will come on top of zinc and sometimes it can be done from manganese also - means up to manganese all metals below that, can be produced by electrolysis of eco solutions acid, solutions these the ones above cannot be.

So, this gives us an ideas to what this listing is all about, if we go little further these reactivities, will also tell us how they should exist in nature, those which are up here will form very stable oxides, silicates, aluminates, halides in nature, very stable compounds at the bottom, where we have platinum group metals, gold, silver etcetera. The reactivity is very low, they will not form compounds, they can exist in free state, the ones which are near the bottom like lead, tin, nickel, etcetera will form compounds but, very weak compounds, there are very easy to dissociate, no problem at all, little bit of reducing atmosphere, will reduce them.

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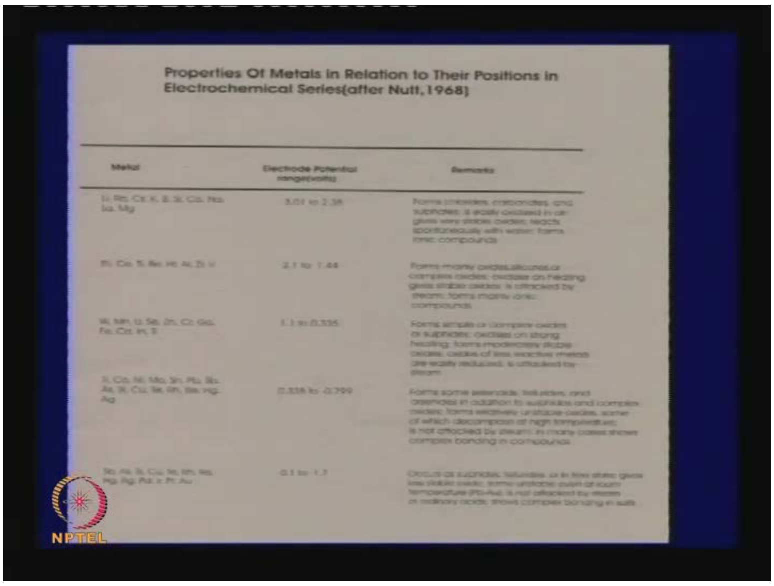

Properties Of Metals in Relation to Their Positions in Electrochemical Series(after Nutt,1968)

So, we made a category of metals, we put them into four categories, depending on electrode potential those which are very high, we said they form chlorides, carbonates sulphates etcetera etcetera, very stable compounds. Then gradually they also have the other property, those which are very stable compounds, they form they will spontaneously react with water. They will form ionic compounds those below, will form also stable compounds but, they will not oxidize unless we heat them.

They will not oxidize spontaneously in air like sodium if you take it out in air it will oxidize but, these metals which are slightly less reactive will get oxidize only when you heat and they will be attacked by steam they will not be attacked by water because their reactivity is slightly less.

If you go further down, they will form simple or complex oxides or sulphides, they will oxidize, only if there is a strong heating or there is a strong oxidizing agent, ores are easily reduced. Below that we are coming to elements, which form weak compounds, they will form selenides, tellurides, arsenides, which are very easy to reduce and, of course, which will decompose at high temperatures, only by heating. Such metals will not be attacked by steam, in many cases it will show complex bonding in compounds and then at the bottom, we have elements many of them will occur in free state or will occur as weak sulphide, tellurides, etcetera, etcetera.

Many will not be attacked by acids at all, unless it is a very special kind of acid like aqua regia, some things like that. So, as the reactivities go down, the nature of compounds also become different, weaker compounds here, stronger compounds on top, accordingly our extraction processes also change.

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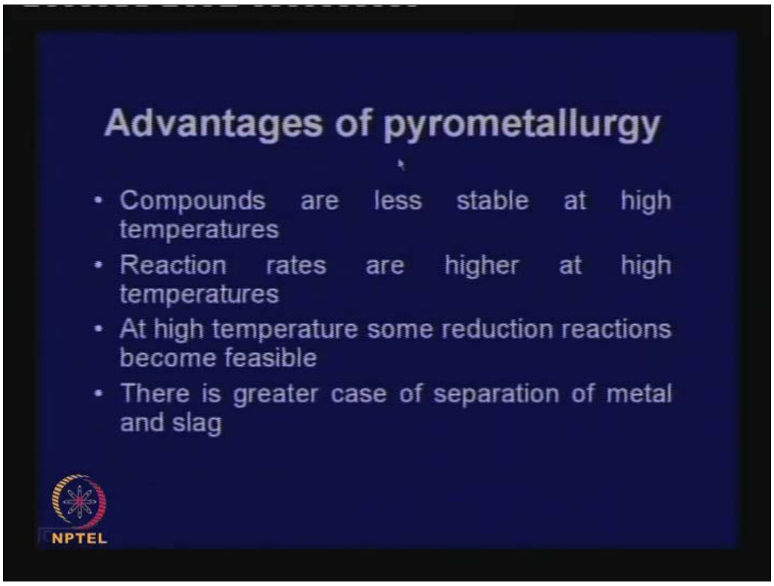

Advantages of pyrometallurgy

- Compounds are less stable at high temperatures
- Reaction rates are higher at high temperatures
- At high temperature some reduction reactions become feasible
- There is greater case of separation of metal and slag

Then, you started with pyrometallurgy, which was the ancients method, because men human when first invented fire, they experimented a great deal with fire. Starting with cooking of food, roasting of animals, then they saw the effect of fire on mud. Mud became clay, when it was heated to a certain temperature, the clay was much stronger, it did not dissolve in water. So, clay pots could be made into pots which are very stable. Then they found accidently some metals, elements, some mineral decompose like if those, mercury sulphide it decomposes to produce mercury.

Then accidently or by design or by trial and error, they learn to apply pyrometallurgy in the production of bronze, in the production of lead, in the production of iron, in the production of various alloys. Advantages of pyrometallurgy are that compounds become less stable at high temperatures. So, even if you have stable compounds, compounds become unstable. So, we have to bring in a reducing agents, if the element will get separated from whatever, it is combining reaction rates, will be high because in kinetics, you know temperatures, I mean reactions is so high.

Then at high temperature, some reduction reaction becomes feasible which cannot be done at room temperatures, can be done at high temperature and there is a greater ease of separation of metal and slag. So, clean liquid metal can be separated out.

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Different kinds of roasting

- Oxidising roasting
- Volatilizing roasting
- Caloridising roasting
- Reduction roasting etc.

Now, there are many, many steps in any roasting operation, oxidizing first is roasting. You roast. In roasting there is necessarily release of some gaseous substances oxidizing. Roasting means you change, say carbonate into an oxide. Volatilizing roasting means you take out some volatiles. Caloridising roasting means you make a chloride reduction. Roasting means you reduce.

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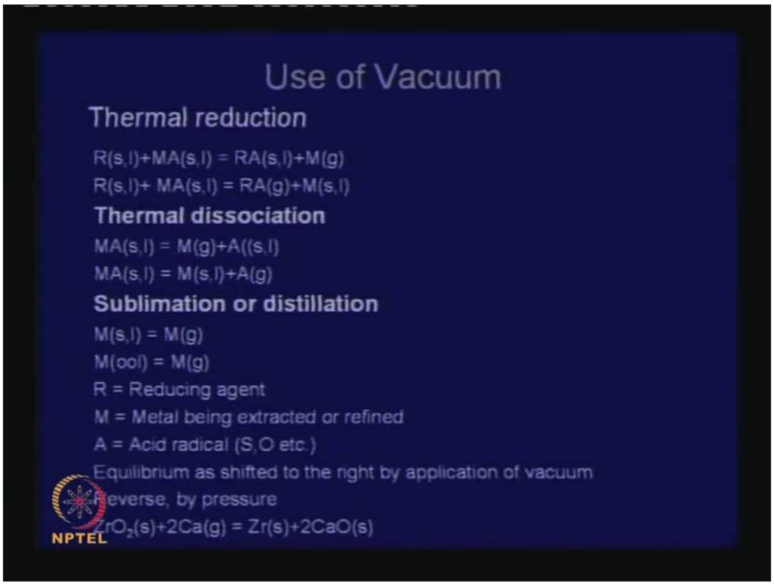

Use of Vacuum

Thermal reduction

$R(s,l)+MA(s,l) = RA(s,l)+M(g)$

$R(s,l)+ MA(s,l) = RA(g)+M(s,l)$

Thermal dissociation

$MA(s,l) = M(g)+A((s,l)$

$MA(s,l) = M(s,l)+A(g)$

Sublimation or distillation

$M(s,l) = M(g)$

$M(ool) = M(g)$

R = Reducing agent

M = Metal being extracted or refined

A = Acid radical (S,O etc.)

Equilibrium as shifted to the right by application of vacuum

Reverse, by pressure

$ZrO_2(s)+2Ca(g) = Zr(s)+2CaO(s)$

There are different kinds of reduction techniques in pyrometallurgy. One can reduce by carbon, one can reduce by metals, one can reduce simply by heating. There are some reactions that you know; a reducing agent reacting with a compound will release the reducing agent. Sometimes reducing the metal that terms out this gas, sometimes it can be solid or liquid, sometimes what you form by the combination of the reducing agent and what was there with the metal, that can be gas, that can be solid, there all kinds of combinations.

Thermal dissociation, as I said, mercury sulphide, sometimes simply by heating we can recover the metal and you know that sometimes vacuum has a role to play, in all this if there is a gaseous substance. In the right, vacuum would drive the reaction to the right, if there is a gaseous substance in the left hand side, reaction can be driven by use of pressure.

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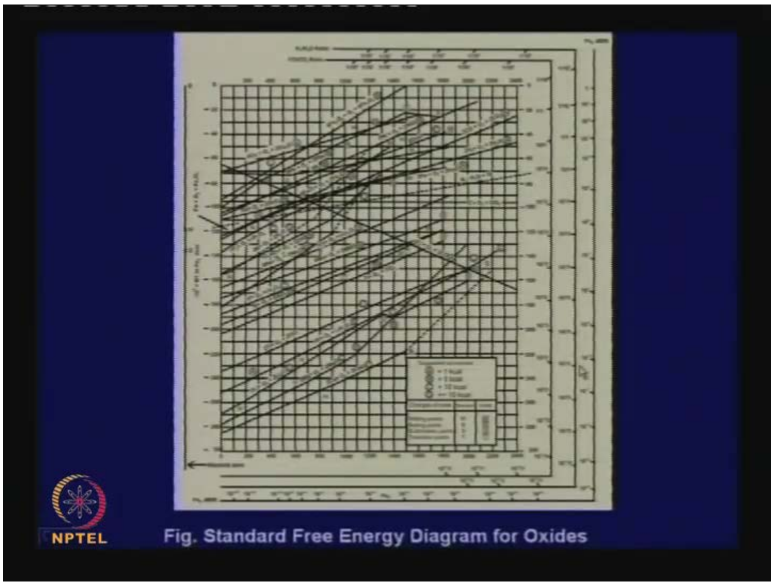

Fig. Standard Free Energy Diagram for Oxides

I gave you refer to some books that might find useful. There are many other books. Then we came to a very important subject, this is the basis of pyrometallurgy. The standard free energy diagram for oxides, also known as Ellingham diagram, which plot free energies of formation against temperature and this plots are always with reference to one molecule of oxygen because that helps us, in our, when we associate two reactions. We can add or divide, we can subtract one from the other, and very easily one HO2 and 1O 2 would get cancelled out.

Now, in these plots, the thing to notice for all oxides, all metal oxides, the plot goes upward which means the free energy of formation becomes less negative with temperature. All metals and that becoming less negative means they are becoming less stable. On the other hand when carbon reacts to form CO 2 the free energy of formation hardly changes with temperature. But when we consider formation of CO, we find it has a negative slope, these had a positive slope, the line for CO 2 has zero slope line, for C O has negative slope, the slope is related to change in entropy.

All these have a reaction indicating metal with one molecule of oxygen forming the oxide and all these reactions imply disappearance of one molecule of oxygen and that is what gives a change in entropy. It is just same for all in the case of C plus O 2 give you CO 2, same amount of gas in the left hand side, same number of moles on the right hand side, slope is zero here, it is the other way around, you will find C 2 C plus O 2 is 2 C O.

So, when one molecule of oxygen disappears two molecules of CO are produced. So, we have a negative slope and this is of great importance in pyrometallurgy.

It shows that this line crosses all the lines for the oxides. So, there is always a point where carbon monoxide becomes more stable, compare to the line for the metal oxide and when that happens, carbon can reduce the oxide to form, release the metal and from carbon monoxide. Now, for metals which are more stable like aluminum, zirconium etcetera etcetera, the crossing point is at a much higher temperature, you have to go to much higher temperature, whereas, when the metals are so stable, the oxides are not so stable. They can be reduced by carbon to form, when it form CO at much lower temperature. So, essentially everything can be reduced by carbon.

But there is a problem. Oxides which are very stable and according to Ellingham diagram, can be reduced at very high temperature, also form stable carbides. So, very often, carbon reduction will not be applicable to this. We have to find something else to do it. So, if we have BEO, which is very stable you will find the line for BEO's fairly low down - BEO plus carbon, if you do, will produce beryllium with carbide, but we do the reaction in presence of copper. So, we produce a beryllium copper alloy, where the beryllium activity is very low, having copper drives the reaction not to the right.

Now having the copper produces beryllium copper, activity of beryllium is low. Therefore, the reaction is driven to the right activity. Low means it will not form a carbide, another advantage is here, in the industry, we want beryllium carbide, but it is not applicable in all cases. We like to avoid carbide formation. I will stop here now and proceed further because I would like to review the entire course very quickly. Thank you very much.