

**Industrial Inorganic Chemistry**  
**Prof. Debashis Ray**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 23**  
**Fluorine and Inorganic Fluorides**

Hello and welcome back to this class of Inorganic Industrial Chemistry, where we are talking about the production as well as utilization of Fluorine compounds.

(Refer Slide Time: 00:36)

**Fluorspar Quality and Utilization**

Manufacture of aluminum, bricks, cement, glass, glass fibers, enamel and in the metal working industry (foundries).

**Metallurgical fluorspar (met grade) as a coarse to lumpy material or briquetted (CaF<sub>2</sub> content: 60-85%).**

Utilized as a flux in steel manufacture (lowering of the melting point and viscosity of the slag) and aluminum manufacture.

The slide features a yellow background with a blue header and footer. The footer contains logos for IIT Kharagpur, SWAYAM, and the Ministry of Education, Government of India. A small video inset in the bottom right corner shows Prof. Debashis Ray speaking.

And we have started our discussion from where we see that the composition of the different minerals, because we will be talking about the natural resources. You must have the very useful natural resources in your hand so, that we can process for some useful material or compound or some other converted species.

So, one of the fluorine bearing compound, because we are with this halogen the first member of the halogen family the fluorine. So, fluorspar is a useful material or useful mineral or ore, which we can utilize for getting is different types of fluorine based compounds up to the different organ of fluorine compounds. So, what is the fluorspar that we have seen earlier in our previous classes, that it is the calcium fluoride. So, depending upon its different amount of content; that means, throughout the globe we can have the different resources or the different places where we can go for the mineral expedition of fluorspar.

So, this fluorspar may not have the equal amount of your calcium fluoride content. So, the calcium fluoride content can be different. So, since we are handling one of the major constituent of it would be the 50 50. If you consider that one is the calcium part the cationic part is calcium and the anionic part is fluoride, from where we try to get the fluorine based compounds in the hydrofluoric acid itself.

So, directly this particular material; that means, fluorspar can be very useful for the manufacture of aluminum how you can co relate it? If I say that fluorspar which is nothing, but your calcium fluoride and can be utilized in the manufacture of aluminum. So; that means, there should be some process where we can utilize the fluorine or the fluoride ion present in calcium fluoride, to treat the corresponding aluminum ore which is your bauxite is well known the alumina  $Al_2O_3$ . So, if the  $Al_2O_3$  can be converted to  $AlF_3$  or any other species where from we can get very easily very quickly the corresponding aluminum as the metallic aluminum part.

So, you should use the fluoride ion other fluoride anion or any other fluoride salt or even the hydrofluoric acid, which can be obtained from your fluorspar to get a production of your aluminum. To aluminum industry basically therefore, will be dependent on the availability of the fluorspar, that will see afterwards how we can get these that utilization of this fluorine based compound for aluminum production industrially. Similarly we also know that in while making the brick the one of the major constituent of is the corresponding calcium oxides and calcium based material.

So, the source of these calcium is calcium fluoride can be utilized for making bricks also. In a similar way it can also be a good constituent for cement, glass, glass fibers, enamels and in metalworking industry; that means, the foundries; that means, we if we are going for a particular type of foundry where we can extract aluminum or any other metal. Then we can take help of the these anions; that means, the corresponding salts you can have or the complex basis can have from the thing where we get the corresponding oxides, sulphides or any other through mining.

So, that particular one can also be utilizing; you never know that where phosphor will be utilized for the production of the aluminum to glass fibers. So, one of the other quality is your metallurgical quality or the metallurgical grade fluorspar, still calcium fluoride you have in your hand which is known as metallurgical grade met grade. So, met grade is

nothing, but it is having a bigger sizes of materials. So, is a coarse to lumpy material or sometime the briquetted material; we know that the coar briquetted to all we know.

So, that sort of briquetted; so, it is sum if it is moistened and then if you apply some high amount of pressure. So, high pressurized thing which can be your calcium fluoride a content is up to 85 percent 60 to 85 percent content of calcium fluoride, but you can get it in briquetted form and that briquetted form can be utilized for metallurgical engineering purposes, which is beyond the scope of this particular class which is nothing, but we are talking about the inorganic chemistry which can be utilized in industry. And sometimes our more useful material is corresponding utilization of this particular calcium fluoride as a flux in steel manufacturing industry.

So, the steel company or the company which are producing steel good quality steel or the iron ore for starting from the iron ore to steel manufacturing process we use basically the flux which basically utilized for lowering the melting point and viscosity of the slag because we all know that the corresponding unwanted material unwanted part from the iron we use something; that means, calcium fluoride can be utilized. So, calcium oxide, calcium carbonate and all the other thing which is the unwanted material during the steel manufacturing industry or the steel industry, which can be taken away as the slag material.

So, for the typical processing; that means, we want to get good quality of iron because the iron content should be higher as we go for the production. So, we should have a corresponding melting point lowering basically. So, you add the flux, that is we sometimes we consider it as the fusion mixture. When we have your ore and mineral in our hand and if we try to get a melt out of that, we had some amount of fusion mixture and if calcium fluoride is given to eat.

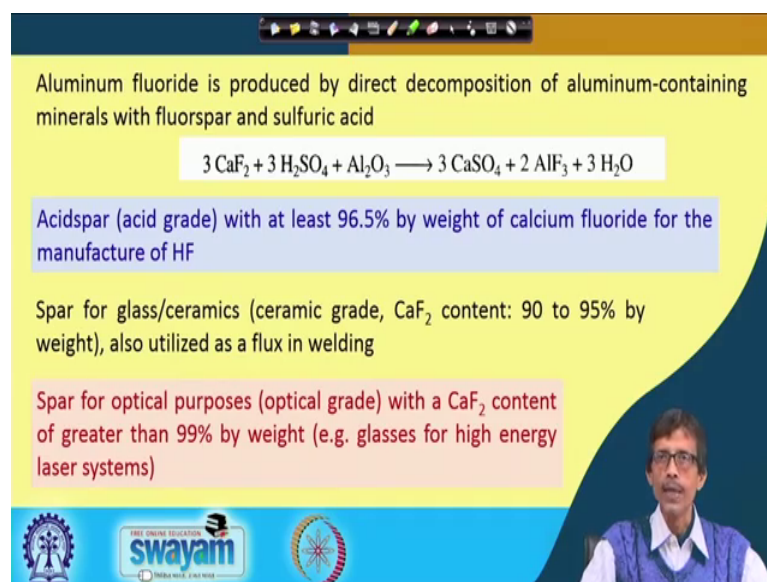
So, it is basically functioning as a flux which basically giving a low melting point for the ore material. So, we can lower the melting point; that means, your expenditure for getting the temperature higher temperature would be less and also the viscosity of the slag is also reduced. So, lowering into both of these two cases, the melting point as well as the viscosity of the slag so, that it is very easy to remove the slag material from the pure iron material, that is the molten iron you have in on our hand. So, if the slag material is lighter than your molten iron. So, it will be floated at the top of the molten

iron. So, you can have some (Refer Time: 08:04) or you can have some exit pathway through which the slag can be removed.

So, the production of slag you can add some other additives for the production of slag material in steel manufacturing process is dependent on the material what we are supplying as calcium or some time as typically the calcium fluoride. So, it will be utilized as the flux material for the production of steel as well as I told you in the previous first line, that it is also utilized in the manufacture of aluminum because you get aluminum trifluoride or  $AlF_3$  then we convert that  $AlF_3$  to cryolite which is  $Na_3AlF_6$  will see also that how cryolite. So, from cryolite we directly get the aluminum or cryolite can be utilized for the production of aluminum.

So, this fluorspar will therefore, be dependent we depend on this fluorspar quality fluorspar quantity and we can utilize it for two major industrial sector one is a steel manufacturing sector and another is the aluminum manufacturing sector. We are also very active our country is also very much active in manufacturing all these things. So, we are definitely dependent on your fluorspar or the availability of the fluorspar.

(Refer Slide Time: 09:24)



Aluminum fluoride is produced by direct decomposition of aluminum-containing minerals with fluorspar and sulfuric acid

$$3 CaF_2 + 3 H_2SO_4 + Al_2O_3 \longrightarrow 3 CaSO_4 + 2 AlF_3 + 3 H_2O$$

Acidspar (acid grade) with at least 96.5% by weight of calcium fluoride for the manufacture of HF

Spar for glass/ceramics (ceramic grade,  $CaF_2$  content: 90 to 95% by weight), also utilized as a flux in welding

Spar for optical purposes (optical grade) with a  $CaF_2$  content of greater than 99% by weight (e.g. glasses for high energy laser systems)

swayam  
FREE ONLINE EDUCATION  
EMPOWERING CHANGING

So, if we get that aluminum fluoride out of this calcium fluoride, which is nothing only we are simply converting the raw material has ore, what we are getting as aluminum fluoride to convert it to typically (Refer Time: 09:42) the ore; that means, the bauxite and we get this one; that means, the aluminum containing mineral we have to de composite.

Where you have the aluminum containing mineral; the aluminum containing mineral is nothing, but your bauxite and that bauxite is treated with fluorspar; that means, calcium fluoride and sulfuric acid. So, if we have a mixture, it can be a very high temperature one because we do all these in the industrial reactors not in your test tube, not in your beaker or not in your round bottom flask.

So, if we have all these things and if we put a higher temperature over that. So, we should carefully look at the reaction, what will be happening over there. So, that is also very simple reaction, but sometimes the bulk of the material, the quantity of the material can also guide the reaction for a particular course of reaction because you can have the corresponding mass action reactions.

So, simply your bauxite, the third component is your bauxite which is your  $\text{Al}_2\text{O}_3$ . As I told you that it treat with fluorspar have a very good amount of calcium fluoride from 60 to 85 percent. So, it is with calcium fluoride and then sulfuric acid. So, it is a acid base reaction which will be utilized for the production of  $\text{AlF}_3$ . So, is not the direct reaction of calcium fluoride with aluminum will give you aluminum fluoride you require, sulfuric acid because some amount of your oxygen what is available in alumina; that means, three oxygen atoms of alumina per unit or per mole or per molecule of alumina  $\text{Al}_2\text{O}_3$ . So, these three oxygen's or neither utilized for any anion formation will be directly utilized to take out it as water molecule.

So, we use protons or you use hydrogen ions as a source of heat; for sulfuric acid and that sulfuric acid is basically. So, this ratio that three sulfuric acid will produce three water molecules. So, that is the simple stoichiometry of the reaction, which will tell you that how much sulfuric acid we require that will depend on the amount of bauxite what you are handling. So, that equivalent amount of that the three oxygen atoms of the aluminum will be taken care of by supply of six protons.

So, 6 h plus from the sulfuric acid otherwise the reaction is very simple calcium fluoride will be converted to the calcium sulphate of sulfuric acid. So, sulphate ions will be coming from your sulfuric acid. So, apart from your met grade fluorspar we can have another one which is known as acidspar which is also known as like metallurgical grade is acid grade with at least having a higher quantity of calcium fluoride which is 96.5 percent by weight of calcium fluoride, for the manufacture of hydrofluoric acid now .

If you have a poor grade or lower grade of fluorspar, which is your metallurgical grade we are utilizing it for say aluminum production through aluminum trifluoride formation. But if your content is good one, we considered it as some acid grade because we will be utilizing this as the corresponding production of hydrofluoric acid. Even if you have some amount of trapped hydrofluoric or HF in calcium fluoride.

So, this spar also can be used for some other purposes which are for making glass and ceramics. So, they have another category basically we considered these are the spar, such that we can have the metallurgy metal spar. The acid spar now spar for glass and ceramic production or ceramic making thing. So, you have a ceramic grade calcium fluoride where content will lie between 90 and 95. So, which is less than your acid spar and you also utilized as a flux in welding.

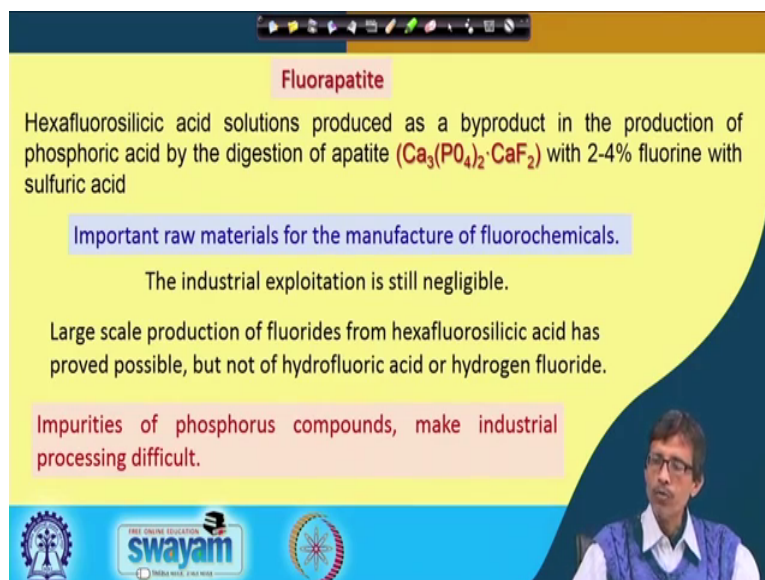
As we have seen just now that when we add the flux it is basically utilized for lowering the melting point. So, during the welding purpose we know that we use some good amount of the different types of flame such as your oxyacetylene flame or other flame that is oxygen is being burnt with your LPG with your CNG, with your acetylene, with your butane or any other gases. So, for that particular welding process we know that these for these cases we required temperature above 2200 2400 or 2500, sometimes it can reach temperature up to 3000 degree centigrade or more than 3000 degree centigrade.

So, if we can use some flux that means the fusion will take place at low temperature for the particular welding purpose, we use simply this calcium fluoride. Then higher grade or very usefully utilized for higher calcium fluoride content material is for optical purposes. So, different optical lenses, optical material for lasers and the spectrometers we use for this because you have to make the corresponding windows out of those glasses sometimes the quartz glasses also. So, the glasses for the best way of knowing it is or remembering it is also; the sometime we use some of these glasses as the glasses for high energy laser systems.

So, you use a special quality of glass, such that you use now the optical grade spar now that optical grade calcium fluoride. So, that question can be with you also similar to that that what sort of calcium fluoride you material or the spar fluorspar. What fluorspar you can use for making that optical grade glasses or optical grade material for say laser

system. So, this is that material which is level, because its calcium fluoride content or the spar content is higher up to almost 99 percent.

(Refer Slide Time: 16:07)



**Fluorapatite**

Hexafluorosilicic acid solutions produced as a byproduct in the production of phosphoric acid by the digestion of apatite ( $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ) with 2-4% fluorine with sulfuric acid

**Important raw materials for the manufacture of fluorochemicals.**

The industrial exploitation is still negligible.

Large scale production of fluorides from hexafluorosilicic acid has proved possible, but not of hydrofluoric acid or hydrogen fluoride.

**Impurities of phosphorus compounds, make industrial processing difficult.**

swayam

Then we go for another material as ore which is fluorapatite. So, after fluorspar if we have fluorapatite you all know that this is also a constituent for your biomaterials because our teeth our bone or also appetite material. So, when you talk in terms of these appetite materials, where you have selectively the fluorine is present. So, fluorine can either increase your strength of the material or decrease your strength of the materials.

So, the optimum concentration of fluorine is required such that you do not have the cavities in teeth. So, these are basically the fluorine materials. So, that is why use the fluorine toothpaste, the fluoride toothpaste you use, but you must know that the corresponding concentration of the available fluoride ion should be limited such that it will not degraded or decay your fluorapatite of the enamel of your teeth.

So, one of the species what we can get while making or utilizing this appetite, when you have the fluorine to be considered as the fluorapatite which is nothing, but calcium phosphate and calcium fluoride is double salt again, where we are just now we are seeing that it is only calcium fluoride, but now we are bringing calcium phosphate in it. So, calcium phosphate calcium fluoride double salt is your appetite and if you have the fluorine (Refer Time: 17:37) known as fluorapatite.

And our goal is to make the hexafluorosilicic acid something else where you have 6 fluoride groups or 6 fluoride as ligands, the fluorides very good ligands we consider as is very small ligands system around the metal ion. So, you have if you have the silicon center. So, silicon centre will be covered octahedrally by six fluoride groups giving you the corresponding  $\text{Si F}_6$  anion what is that anion and how you get the corresponding acid; that means, some amount of  $\text{H}_2\text{SiF}_6$  will be there.

So, it is the byproduct basically what will get it in the production of phosphoric acid from apatite because if you look at the molecular formula of this double salt of apatite, you just simply see that phosphate in it. So, along with fluoride we have phosphate. So, it is this possible to make both these two; that means, if we are able to get it as  $\text{HF}$  or  $\text{H}_3\text{PO}_4$ . So, this particular material can supply you or through the production you get it as the corresponding production of hydrofluoric acid as well as phosphoric acid.

So, if you have only very small quantity of fluorine you need; so, 2 to 4 percent of fluorine; so, digestion of apatite with 2 to 4 percent of fluorine with sulfuric acid. So, that will give you the corresponding hexafluorosilicic acid formation because we have this supply silica in it, because the silica will be there then this fluorapatite is also an important raw material for the manufacture of different fluorochemicals what is those fluorochemical? Because the industrially very important fluorochemicals are there some of them are fluoro organic chemicals; that means, the organic part is there; that means, you have the carbon backbone of the hydrogen atoms are also attached to it; that means, the fluorohydrocarbons.

Fluorine based hydrocarbons were some of the hydrogen center for the hydrogen atoms will be replaced by the fluorine.

But what about the other species if you consider that other fluoro chemicals you can have. So, we can have one such in example I can give you as the  $\text{BrF}_5$ . So, this  $\text{BrF}_5$  which can be utilized for treating many material like your quartz or silica  $\text{Si O}_2$ . Because just now what we see here that you can produce hexafluorosilicic acid; that means, the Si center or the silicon center on silica  $\text{Si O}_2$  has a good affinity for forming your corresponding  $\text{Si F}_4$  the tetra fluoride silicon tetra fluoride  $\text{Si F}_4$ , when it goes for the corresponding hexafluoro one you get it as  $\text{H}_2\text{SiF}_6$ .



So, you get this. So, this particular ones in  $\text{BrF}_5$  or  $\text{BrF}_3$  or sometimes  $\text{ClF}_3$  where enter halogen compound which can be utilize as a good source of fluorine. So, you get it for making some very useful compound; that means, something we go for this compound that will also see that you have ethylene which is nothing, but  $\text{C}_2\text{H}_4$  or  $\text{CH}_2=\text{CH}_2$  double bonded carbon you have and on the two ends of the carbon you have two hydrogen center. And if I want to substitute all four hydrogen centers or hydrogen atoms of ethylene by fluorine, you have the think for some reaction and that would be your the most simplest fluoro organic chemicals which can be utilized for Teflon preparation.

So, that will see how you go for that utilization for Teflon preparation. So, this fluorapatite you use it for some material, but phosphoric acid what we have seen earlier than making of phosphoric acid for it then you can use it as a source of calcium; that means, for the brick making or the cement making proceed yours, but has been utilized to a lesser extent to get the fluorine out of it. So, if your fluorine content is less if you do not have a good quality of this fluorapatite you may not use it for only the fluorine based compound preparations. So, industrial exploitation of this material is still negligible. So, we can have good processes, good procedures which is industrial available which will be cheaper also and you can have a very good access of the raw material.

So, large scale production of fluorides basically now once you make this hexafluorosilicic acid form silica as well as HFC giving you  $\text{SiF}_4$  than  $\text{SiF}_4$  with extra HF giving you  $\text{H}_2\text{F}_6$ . So, it is possible to get the different fluoride because this hexafluorosilic acid if it immediately loses the fluoride ions it has extra fluoride content, because the silicon center can have some affinity for giving you the corresponding octahedral species; that means, the hexa species the hexa fluoride species, but not the hydrofluoric acid or hydrogen fluoride. So, you can help other fluoride the metallic fluorides sodium fluorides.

And ammonium fluorides, but this particular procedure is not very useful for the preparation of HF and that hydrofluoric acid or hydrogen fluoride as gas because you have huge amount of phosphorus present in it. So, you have the phosphorous content in it. So, impurity is which will be coming from your phosphorus compounds a phosphoric acid make industrial processing difficult out of your fluorapatite. So, fluorapatite can be utilized mostly for calcium and phosphorus not for your fluorine content.

(Refer Slide Time: 23:42)

**Fluorine and Inorganic Fluorides**

Fluorine is manufactured electrochemically from a salt melt, which consists of a mixture of KF and HF in a molar ratio of 1:2.0 to 1:2.2.  
The temperature of the salt melt is ca. 70 to 130°C.

**Electrolysis Cell**

$$2 \text{ HF} \xrightarrow{56.3 \text{ Ah}} \text{ H}_2 + \text{ F}_2$$

The cathodes and cell are usually made of Monel alloys or steel, the anodes of degraphitized carbon.

The cathodic and anodic compartments are not separated by a diaphragm, but by 'steel skirts' suspended from the lid into the melt.

The slide also features logos for Swamyam and other educational institutions, and a small video inset of a man speaking.

So, those are the limitations also once you know or understand all this things very easily or very nicely, we can help some comments on it that which particular material can be utilized for making your organ fluoro compounds or inorganic fluorine compounds or a HF or sodium fluoride. So, we now move to your inorganic fluoride compound one such good example is your ammonium fluoride or sodium fluoride and elemental fluorine; that means, F<sub>2</sub> as gas. When we go in our future classes to chlorine as well as fluorine because, you have huge demand of all these gases; that means, the fluorine gas, the chlorine gas, the bromine gas and iodine gas as we all know it is also available in the solid form.

So, the fluorine gas F<sub>2</sub> and inorganic fluoride how we make it. So, electrochemical process we have utilized from its salt melt. So, we only from a melting thing; that means, you have either the ammonium fluoride melt or the sodium fluoride or the potassium fluoride melt, which has this particular mixture is giving is not that all other, but you just most preferred one is your potassium fluoride and HF in a molar ratio of 1 is to 2. So, if you have in 1 mole of KF then 2 mole of HF. So, what we get therefore, if we consider that these ratios of 1 is to 2; that means, if we use it into one is to one we get KHF<sub>2</sub>, that is potassium by fluoride has the salt that will also see how we make these has the potassium by fluoride salt, but when you have double amount of HF. So, you have the courtesy on by fluoride; that means, KHF<sub>2</sub> to dot HF.

Then it can be considered as a double salt of potassium by fluoride, but you can still use a further higher mole ratio of 2.2, so, 1 is to 2.2. So, it is in the HF side and at the temperature range of 70 130 degree centigrade, you get this melt and the salt made is utilized for your electrochemical production. So, what we use? Use the electrolysis cell. So, we will go for the electrolysis as we have seen long back for our production of hydrogen and oxygen from the electrolysis of water we all know. So, the typical makeup of this when (Refer Time: 26:13) have the electrochemical cell.

Because the most of the time we use this electrochemical cell because the material what is being produced at the expense of electricity may be it can be a costly affair, but the purity, purity of the material what you will be getting out of that will be highest. So, you have to have the electrolysis cell; that means, it should have a corresponding anode and cathode for the production of hydrogen as well as fluorine if you are utilizing only HF.

So, if we have the melt also as I told above that if you have a melt of KF and HF it is giving you a potassium by fluoride as well as your salt of HF, but if you go for the electrolysis out of that melt, the potential is set in such a fashion that only that oxidation of fluoride ion and the reduction of the hydrogen ion. If you considered HF from its electro negativity difference H will be remain as a H plus in the course of the melt medium or F will be remain as a minus.

So, the fluoride and will undergo oxidation and H plus will accept those electrons out of this fluorides to giving the production of hydrogen. So, this particular procedure will therefore, be very useful for not only production of fluorine, but it can also produce hydrogen if we have some mechanism, such that we can separate the hydrogen gas also from the fluorine gas what is being produced.

So, a rating of that particular electrolysis sale is also given you which is 56.3 ampere hour. So, the cathodes what you have are utilized and cell are used usually made of the monel alloys steel, the monel alloy steel alloys or steel (Refer Time: 28:06) is very top container the anodes are of different materials. So, anodes are graphitized carbons. So, is the carbon based materials as we know the typical cell the battery cells what we use the container is something is a anode and the cathode is something different which is there as the carbon rod.

So, anode cathode material is important. So, you have the alloy and steel material as the cathode or the cell itself whole cell whole cell can be your cathode material and anode is your corresponding carbon. So, on that two cases on these two cases you get this. So, what we basically get? So, you can have the corresponding once you see what we are assembling, what we are trying to assemble around that particular cell. So, what are the materials you can have? So, you have to have the cathodic and anodic compartments why you are calling this as the compartment?

Because the two products like the electrolysis of water molecule is the electrolysis of HF is also giving the fluorine and H<sub>2</sub>, but unlike O<sub>2</sub> and H<sub>2</sub> these two are highly reactive. So, if you just mix at a particular temperature of 700 more than hundred or less than 100 degrees centigrade. They are highly reactive they can again react back and combine in the form of HF back.

So, you must have the corresponding separators spaces the separation should be there. So, cathodic and anodic compartments are there and obviously, they are not separated by the use of any diaphragms, only steels skirt something hanging from the top. So, steels are skirts suspended from the lid that in the cover of the cell into the melt.

So, melt will be at the bottom of the cell, you have the anode and cathodes and they are separated by steels skirts. So, when you see the flow diagram in our next class, will now have to have good idea how these two are separated and we can have some past passages for taking out the hydrogen as well as the fluorine ok.

Thank you very much.