

Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture – 15
Graphite Ore Processing

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Graphite Ore

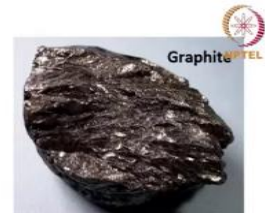
Major graphite producers: China, Brazil, India, Mozambique, Ukrain, Russia, Norway, Pakistan, Sri Lanka etc.

Graphite ores

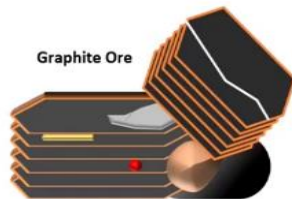
Classification based on flake size and purity:

- (i) Vein (lump) graphite (largest crystals, >98% purity, rare and expensive)
- (ii) Flake graphite (medium crystals; 80-95% purity, most commonly used)
- (iii) Amorphous graphite (powder containing very small crystals; high ash content; <85% purity; seam mineral)

- Graphite ore contains clay mineral (hydrrous rock forming minerals) impurities, which may be physically trapped between layers; or form weak bonds and get tangled due to their microtextured surface.
- We need to remove the impurities without reducing the crystal size and without inducing defects.
- Ore processing is primarily a **physical separation of impurities (benefication)**. We need to control the surface properties of different components to ensure a good mixing/ separation.



(Photo: R. Weller/ Cochise College)



Thermodynamically, Gibbs energy for mixing (m):

- $\Delta G_m = \Delta H_m - T\Delta S_m$ (at constant temperature T)
- For spontaneous mixing; $\Delta G_m < 0$ and $\frac{\partial^2 G_m}{\partial x_i^2} > 0$
 x_i is the mole fraction of component i
- For mixing and separation one can tune T, x_i



Hello everyone. In this lecture, we will move on to the processing of graphite ores. Now, you know the basic properties of carbon materials and let us now talk about natural graphite. I told you that we find this natural graphite mostly in sedimentary or metamorphic rocks. But once you get it out of the rock, what do you do?

I have mentioned a few major graphite-producing countries' names here and there may be some more countries. Now in some countries, you have graphite mines and the quality of graphite also that you find in different countries may be different. In some of the countries, the production of synthetic graphite is more and some countries will produce both. The synthetic graphite we are going to cover only in the next lecture.

Today we are going to talk about natural graphite mainly the ores. First of all, what is an ore? When you find something in the rock that complete mixture of your mineral as well

as the other impurities, so that entire mixture is an ore. The first basic material that you get from a rock or mine or wherever.

Now, are all graphite ores the same? The answer is no, we will have different types of graphite. In fact, based on the quality, based on the crystal size we can now classify these different ores. For example, the first one is known as the vein or lump graphite, this is the highest quality graphite and the quality is decided by the crystal size and the purity.

So, this kind of graphite, which is mainly found in Sri Lanka, Sri Lanka is one of the largest producer of this graphite. It is very expensive, it is very rare. The crystalline size is often above 500 micrometer means you can take a single crystal of graphite in your hand. That is already large enough. In the case of other minerals maybe you can have several centimeters long crystals. But in the case of graphite if your crystallite is in a millimeter range then that is pretty large. So, this is one of the most expensive graphite and of course, this is only used for very high-end applications, where you need very high purity and good quality and you do not care about the cost. For example, I was mentioning these nuclear reactors. So, in these kinds of high-end device applications, you will use lump graphite.

However, the most commonly used graphite for manufacturing purposes is the second type is called the flake graphite. Depending upon the mineral, you have the purity between 80 and 95 percent and the crystal size is medium, it is not very small but it is also not very large. This is the most commonly used industrial graphite mineral. And the third one is known as amorphous graphite.

Graphite is not amorphous, graphite is crystalline and we use it for all of its crystalline properties like its electrical conductivity and so on, but it is called amorphous because it is found in such small pieces that it looks like a powder. You will also hear the word powder graphite. So, this just because the crystallite size is very small and what you. It also contains a lot of impurities so it is often found in the form of a powder, any powder can be called amorphous. That is why it is commonly industrially known as amorphous graphite.

Now, this is a seam mineral. I told you that you can find graphite in coal seams. These kinds of graphite are generally found with other forms of carbon or petroleum. So, they are often formed under high-temperature conditions and that is why you also can find some ash. Whatever is left after your material is burnt, this is the definition of ash. When you

use a high-temperature process for processing your carbon material which we will learn which we will use multiple times and we are going to talk about that. When we convert organic material into carbon by getting rid of the non-carbon impurities and we do that by heating it. So, often when you are heating something in a furnace people end up calling it burning.

So, just make sure that you do not do that because burning can only take place in the presence of oxygen. What is burning? Burning means oxidation. So, if you are heating something in the furnace in the absence of oxygen then that should not be called burning.

Burning leads to ash formation and in some cases where if you end up by mistake or for any particular reason you end up having some oxygen in your furnace then you often get a lot of ash content which can also clog your systems and this can also be a problem anyway.

So, these are the three types of graphite that we have. Now, what are the type of impurities that our graphite minerals contain? If you find something in a rock how will it look like? It will contain some of these what are known as clay minerals. You have sand, of course, you have certain silicates.

Now, you will also have clay minerals actually they are rock-forming minerals in very general terms. And however, they are often formed in the presence of waters. They are hydrous rock-forming minerals. So, you will find these kinds so these minerals maybe they may actually be trapped inside the layers of graphite.

Sometimes they may create a stacking fault or they may create any other types of defects. Sometimes you have two small crystallites of graphite and you will have the impurities trapped between them, sometimes they will be sticking on top of the surface.

However, in most of these cases, they are physically attached to graphite and not chemically. So, when you are doing the processing of graphite you will only use the physical separation methods and not the chemical process.

For example, in the case of iron, you will have sulfites or calcium in the form of calcium carbonate. You will have carbonates and sulfates and so on. Then you have to utilize

chemical processes to remove these things. But in the case of graphite, it is very simple you only have the physical separation processes.

However, one thing that you need to ensure that you do not end up reducing the size of your crystal very much because graphite value is because of its crystal size. In some mine, you find really large crystals and then you end up making them very small then that should not happen.

So, this is something that we need to make sure that we do not induce defects because that also influences the properties of your material. All these separation methods will move from the ore to your pure metal.

Whatever processes that you use they are known as beneficiation. So, you are actually improving the value of your ore at each individual step and at the end, you get your metal. Graphite is not metal, it is called semi-metal. This beneficiation process is what we are going to learn in our next couple of slides.

For most of the physical separation methods, one property becomes very important for you i.e the surface property of your material for example, if something is hydrophobic or something is hydrophilic then you can easily separate them in one medium.

For example, if you have just water and you have a mixture of something that is hydrophilic then you just mix it then something will settle down and something will float. So, we use these kinds of methods very often and that is why the surface properties become very important.

Now, quickly thermodynamically speaking what is your Gibbs function or what is this process? When you are separating two things, that means things are mixed. Sometimes you will also intentionally mix them, not any additional impurities but basically, you will make a very fine powder of whatever rock you get.

And now, you want that powder to mix very well within itself. Why? So that in whatever system you are using, you want the distribution of all the particles to be uniform. So, you are doing mixing and afterward, you are also doing separation.

So, what is separation? Separation is the opposite of mixing. So, if you want to consider the enthalpy of a certain reaction, let us say this is a mixing reaction well the opposite of

it would be separation. So, your the Gibbs free energy of mixing will be $\Delta G = \Delta H - T\Delta S$. I have not written the ΔT term because the constant we are doing this at constant temperature.

Now, for spontaneous mixing, you have your $\Delta G(\text{reaction}) < 0$. It should be negative and also the second derivative of your delta G should be greater than 0 with respect to the mole fraction of your different components so these are the two conditions. Now you can play with these things. This is your thermodynamic reaction or thermodynamic relationship.

And now what are the things that you can vary? You can vary the temperature and another variable is the mole fraction. Mole fraction may not always be in your control because it depends on the mineral that your mineral contains. But sometimes you can also additionally have certain minerals or certain impurity if you want to play with this relationship and if you want to you want to purify your material or your ore.

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Graphite Ore Processing



Graphite ore processing steps: We utilize physicochemical properties such as specific gravity, magnetism and surface characteristics (e.g. hydrophilicity) of the ore and the impurities.

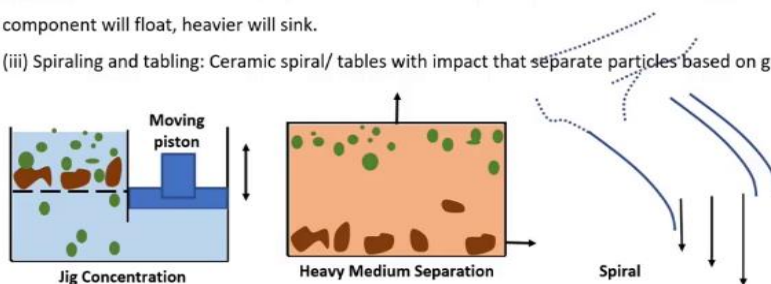
Benefication may involve the following steps, depending upon the composition of the ore

Step-I: Communion

- (i) **Crushing:** Converting the rock into smaller pieces by mechanical force (compression, impact, shear, etc).
- (ii) **Grinding, milling:** with increased shear stress and lower compressive stress to avoid damage to anisotropic crystals
 - Milling may be done using water. Attrition milling and tumbling are also used.

Step-I: Impurity separation

- (i) **Gravity concentration-jigging:** a method to separate components based on specific gravity. A jig screen and layer of larger particles
- (ii) **Heavy media (sink-and-float) separation:** Immersing the sample in a liquid with intermediate gravity (between the components). Lighter component will float, heavier will sink.
- (iii) **Spiraling and tabling:** Ceramic spiral/ tables with impact that separate particles based on gravity.



Now we will move on to the actual processing steps for graphite ore. As I mentioned before we use the surface properties of the material and impurities like hydrophilicity and so on. But other than that what is important? If you have any magnetic impurity, for example,

iron impurities, then that is very easy, you can utilize magnetic forces to separate it out. You can also use certain electrostatic forces to separate out the impurities.

You are also using physical separation using water or other kinds of solvents or liquids. In that case, one more property that becomes very important is the specific gravity. What is heavy, what is light that becomes very important for us. So, these are the important properties.

Now, I am going to list a lot of processes that are used for the beneficiation of graphite. But remember that not all these processes are used in all cases. So, for example, somebody can choose a certain type of separation method and leave out the rest. Not all of them will be used together, but I am listing all of them so you know all of them. Maybe one company is using one set of techniques and the other is using another. However one common thing is that you will mainly have three stages of this beneficiation.

Logically if I give you a piece of rock and I say that this is graphite rock and they are filled with impurities all the way inside even. They are trapped between the layers of your crystals. What are you going to do? First, you will make a powder of that of your rock.

Why do you want to make a powder? Because in order to clean these impurities from deep inside you need to increase the surface area of your material. First, you will make the powder and then you will then do the actual separation and then you will do the refining steps. So, these are the three primary stages.

So, stage number one is known as comminution. Comminution is basically powder making or size reduction of your rocks. If you find big lumps of your ore then you can do things like crushing, grinding, milling and common techniques that are used for size reduction.

So, milling can be also offered in different types; you can use ball milling, you can also use water as medium during your milling if you want to make sure that you do not want to damage your sample very much or damage your mineral very much crystals.

And you can also use attrition milling, you can also use tumbling. These are all combination techniques and these are used for graphite for making the powder out of the rocks. That part is simple. The second part is where you are actually doing the separation of your impurities.

So, what do you have in graphite? You have sand, you have silicates and you also have clay minerals. Also, you may have ash if you have you know amorphous graphite. So, the first method that we are going to discuss is known as gravity concentration or jigging concentration.

This is jigging commonly known as the jigging process. What is it? This is a method where you separate things based on the specific gravity with a medium like water. So, I will show this with this picture. Here I have shown on a moving piston. You see there are like two chambers and water is filled inside it.

Now in water what do you have? You have one moving piston which is constantly moving up and down, up and down and that action is known as the jigging action. Now, on the other side you see that there is some sort of a filter. It is a kind of barrier from where only a certain size of the particle can pass through and others will stay on top.

Now, you have your impurities. The moment you put your piston down the water level on the other side will go up. Then you remove the piston the water level goes down. This water level is going up and down up and down; what is happening? Now if you have your mineral in it which contains some light impurities and some heavy ones also. And within the light and heavy you will have the different particle sizes of the impurity also not all the impurities will be of same size.

So, what will happen the lighter ones will float and they will not be able to come back when your water level settles. They will not be able to come back, only a certain size or the optimum size and optimum weight will go down. Again when the water level is going up and down up and down very fast, the lighter impurities will continue to float they may not be able to come back that fast.

In the end, you will get whatever is the desired either impurity or it can also be your graphite crystal, you can remove. Typically in the case of graphite, this is done for impurities that also you use water as the medium.

Another method is known as heavy media separation and one form of it which is most commonly used is also known as the sink and float separation method. Here what do you do? Instead of water if I use an oil or if I use alcohol or if I use anything which has different properties which is either lighter than water or heavier than water; then what will happen?

Again you are playing with the specific gravity of the medium. this is a heavy heavy medium, in this case, certain impurities which were floating in the case of water will also get settled.

Now you do not need a piston, here you do not have anything else. You just have a very simple device where you have a big chamber and you need to optimize the specific gravity of your medium so you will have certain things settling and certain floating.

I have shown the inlets and out with these arrows. In the case of jig concentration, the lighter ones you get on the top and you will remove it, whatever you get on the bottom you remove it. These are very simplified diagrams so I am not really showing you the actual equipment at all.

I have just made chambers, but you can often you will have conical shapes. You will optimize the design of your chamber such that it is easier to remove and easier to perform these operations. And that also helps the concentration of the of what you get at the bottom. But this is just a very simplistic view.

What else? You can also have spirals. Spirals you know how spirals look like. If you can think of a spiral slide on what children slide onto or sometimes they have these rides in some parks. So, those kinds of slides you will have also for the powder of your mineral.

What will happen? You will have different inclinations in the slide and depending upon the speed and that speed will be decided by the weight and size of the particles. So, depending upon that you can collect different particles from different parts of the slide.

I have made three arrows on the diagram, typically you can collect different types of particles in different parts of the slide. This is also very similar to many techniques which are used in separating the agricultural produce.

You will see that if you have some dal then you can separate it out of the husk based on it is weight. So, these are particle separation techniques and you will also use them for the graphite powders. This picture that I have shown is just one part or one very small part of your spiral which goes on like that.

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(iv) Air classification: Separation based on the aerodynamic behaviour of the particles. Floating particles in a chamber with rising air flow (bottom to top). Air flow can be pulsed. Based on the weight/ drag, particles separate.

(v) Magnetic separation: Use of magnets for separation.

(vi) Froth flotation: Floating impurities using suitable frothing agents. Separation based on hydrophilicity.

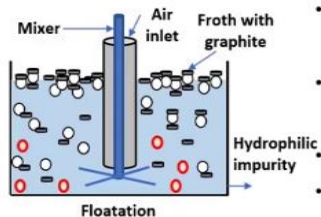
If air bubbles are passed through a suspension (with mixed impurities), the hydrophobic impurities will get attached to the bubbles and float.

Frothing agents: A material that promotes bubble formation (e.g. in soaps). Examples: sodium laureth sulfate, sodium lauryl sulfate, etc.

Step-III: Refining

After separation of primary impurities using one or more of these methods (i-vi), mineral is cleaned via physical or chemical processes.

- Acid leaching
- Roasting
- Microwave treatment.
- Other processes: Electrostatic separation, film floatation, flushing etc.
- Industrial requirements of graphite cannot be fulfilled by natural graphite.
- Natural graphite may contain large amounts of impurity; beneficiation may be expensive.
- There is no control over the crystallite size, defects etc.
- One can obtain graphite from carbonaceous materials.



Now, the fourth method is known as air classification. We were using water as the medium or some liquid as a medium till now for the separation. Now we are going to use air, so we can say that this method is based on the aerodynamic behaviour of the particles.

Again this will depend on what kind of powder do you have and what kind of impurities do you have. And that is why I said that not in all cases you will use the same types of techniques. If you have ash then it is much easier to separate it out using the using floating. Or if you have iron it is easier to do it using a magnet.

In the case of air classification, what do we have? We have sort of a chamber and that chamber has air coming from the bottom. It is rising air and sometimes you may even have pulsating rising air. And you have your particle, since your powder inside sometimes in the form of dry powder, sometimes also as a stream or jet, you will spray your slurry. So, you have the particles there and some particles will float and some will settle down. So, these are this is the aerodynamic behaviour and again a lot of agricultural products are also separated using this method. You may have seen that you know husk separation also. You can just drop them from a very high place, if you have heavy and light things mixed and then just blow air and the lighter things will just be removed. So, something very similar, but it is done in a chamber.

One important thing that I would like to discuss in more detail is known as froth flotation. So, flotation you understand the impurities should float or sometimes in the case of graphite often because graphite is hydrophobic and graphite is light so your graphite will float.

So, often it happens that the impurities that are mixed are heavier and when you are doing any kind of separation your graphite is the one that is actually floating. So, then you can separate it out. However, what is a froth? Froth is a foam, foam that you get in your soap when you wash your hands, that is froth.

So you are going to create a froth and if you have noticed that when you have froth and when you have bubbles in the water. The hydrophobic impurities, the impurities that want to go away from water, often get attached to the surface of these bubbles. So, this is the fundamental principle that we are going to use here.

Now you need some frothing agents typically to promote or to make sure that you have the sufficient number of bubbles in your water. So, that is number one, you need the frothing agents and then you may supply air separately. But you want to create this foam-like material and then which will take your material away. This is how it looks like, again this is not a real image this is just a representation.

You see that there is a chamber where you have water and in water you have this air inlet. You have a frothing agent and you supply air and you have foam. And you see that the white ones are the air bubbles here and the black ones could be graphite flakes, as I mentioned is hydrophobic so that gets stuck to your air bubbles. And because air bubbles float. So, this whole process is known as the froth flotation process. Of course, you are constantly mixing it and you remove the froth from time to time and then you further clean it.

The last steps are refining steps. Some impurities that are still leftover like some oily content or some leftover organic compounds in your rock. So in order to remove them, you can clean the entire material with acid. If that still does not help you can do roasting or you can basically heat your material. You can also do roasting both in the presence of air and in the absence of air.

So, if you want to burn out the impurities then you can do not heat it to a very high temperature so it does not damage the graphite itself. You can heat it in the presence of

oxygen at a reasonably low temperature. So, your impurities from the surface will get burnt.

You can sometimes make sure that the temperatures are very high in that case you need to also control the amount of air that you provide so that you do not damage your graphite. Typically graphite is very stable so it is not a problem. You can also do certain microwave treatments in order to get rid of the impurities.

Other than these things, you can also do electrostatic separation, the froth flotation also have different variants. There is something called film floatation, you can also read more about it. And then there is flushing. There are many other techniques that can be so for refining or for processing of the graphite mineral.

However, what is important for us and what takes us to our next lecture is the fact that natural graphite is reasonably expensive because it's cleaning and its beneficial can actually be reasonably expensive.

So, natural graphite is very expensive and we also do not have much control over its properties. So, if we have flake graphite then that is what we have. If we have very large crystallite then that is what we have. We do not have very much control over the properties of natural graphite. So, in that case, we need alternatives. The applications are so many, but we do not have enough graphite. So, the alternative is synthetic graphite.

Now, synthetically it is easy to produce other types of carbons. Graphite because of its unique crystal structure, because you need the 3D arrangement that is relatively difficult, but we have processes that can be used for this purpose. So, in fact, even making graphene is much easier compared to graphite.

Because you will always get carbon flakes that are separated from each other. What is difficult is to give them this 3D crystal arrangement; for that, you need to provide it certain energy. So, in the next few lectures, we are going to discuss how do we make synthetic graphite.

So, as I mentioned to you you can get your graphite from carbonaceous materials, organic materials and from many different precursors and polymers. But not all polymers will work. So, this is something we are going to discuss in our next lecture.