Cooling Technology: Why and How utilized in Food Processing and allied Industries

Prof. Tridib Kumar Goswami
Department of Agriculture Engineering
Indian Institute of Technology, Kharagpur

Module No 11

Lecture 52
Crystallization in Freezing

Good afternoon, my dear students and dear friends. We have started application of cooling and in that we have started with freezing and we have shown that the temperature is not culprit for any change in quality. It is the transformation of water to ice that is the culprit if there be any change in quality right. So, today we come to that crystallization in freezing and how it is affecting the food material right. So, today's class we are doing crystallization in freezing and for that, we said that suspended matter or cellular components are unable to migrate and ice crystals either form around them and push them aside. Hence, in food materials, where it is having high moisture, normally food materials do have high moisture of say 80 percent, 90 percent, 95 percent, depending on the material or product right.

So, the rate of ice crystal growth is generally not limited by any mass transfer process, except during the late stage of freezing, when temperature is very low, and the viscosity is also very high, and unfrozen water is also very small, or very low. Hence, heat transfer limits the rate of crystallization, because of large latent heat of crystallization of water and growth rate is increased greatly, and with increase of heat removal, right. Then, we are lowering down the temperature, and it is forming some ice crystal, right. What is the effect will come afterwards, but, since it is forming some ice crystals, then the rate of formation of ice crystals is to be defined.

So, let us then define, and that process is that formation of ice crystal process, is known as freezing of water to ice, right. So, this transformation rate, we can say, it is slow freezing, if the rate is 1 degree centigrade to 10 degree centigrade per hour, it could be said commercial freezing, if the rate is 10 degree to 50 degree centigrade per hour, or it could be ultra-rapid freezing, if the rate is more than 100 degree centigrade per hour. In this regard let me also say that, how do you know that it is 1 degree centigrade per hour or 10 degree centigrade per hour or more than 100 degree centigrade per hour, right. Obviously, you have seen earlier. I said that, to measure the temperature, thermometers and other things are used. So, in that other things, it could be say, thermocouple, and what is thermocouple? That is junction of two dissimilar metal, right.

Junction of two dissimilar metal, that forms an EMF and that is converted into, or calibrated into temperature, and it is seen in any measuring device, right, that can be digital or anything, right. So, with the help of thermocouple, you can measure the temperature, that is one. So, if we plot time versus temperature, so what is the rate at which the freezing is going on, you can find out, and tell, whether it is 1 to 10 or 10 to 50 or above 100 degree centigrade. This is one way of knowing. Another way could be, which is of course, very difficult to measure that. You have the food material, say this, we take as the food material and say this is symmetrical, right.

So, you are cooling from both the sides, right. So, what will happen? First say, a layer of ice will be formed, in both the sides, then this layer will shift after sometime to this, and after sometime to this also, right. So, that means, the ice front is gradually going to the centre, right. Now, if you know that, how long it is taking from this layer to this layer, then you can also say what is the freezing rate, but, it is very difficult, because how you will be finding out that this layer, this layer, or this layer got frozen, right? That is why, it is always better to do with thermometer or temperature indicator.

So, we call slow freezing: 1 to 10 degree centigrade per hour, commercial freezing: 10 to 50 degree centigrade per hour, and subsequently the ultra rapid freezing or rapid freezing, which is above 100 degree centigrade per hour. During freezing of tissues, water from solution is transferred into ice crystals, of a variable, but rather, high degree of purity. Non-aqueous constituents are therefore, concentrated in a diminished quantity of unfrozen water. Unfrozen phase changes significantly in pH or rather, significantly pH, titrable acidity, ionic strength, viscosity, freezing point, surface and interfacial tensions etc. that is in unfrozen phase. Oxygen and carbon dioxide may be expelled out from solution and macromolecules are posed closer together, water structure and water solute interactions may be drastically altered.

Then, we can say that, we have already told you that, there is slow freezing, there is moderate rate of freezing, and there is quick freezing or rapid freezing, right. Definitely, we said, depending on the rate at which the temperature is being lowered. We said 1 to 10 degree is slow, 10 to 15, 50 is moderate, and above 100, is quick or rapid, right. Now, after doing it, if we look at the say, a food material under microscope. So, we have taken a section and looking into through microscope, right and for both the cases, one for slow freezing, one for slow freezing, and another for quick freezing.

If you look at under microscope, then you will see that, the food materials having, as we have just said, cells and tissues, and there are intercellular or intracellular food material also, because if this is a cell, and if this is a cell in between, there could be intracellular or intercellular materials, and intra means inside also there are materials, right, of course, this is magnified. So, those cell materials, both inter and intra, they will gradually freeze, the solvent, that is water, and say, an ice crystal has formed, right, and again, you are lowering down the temperature at the same rate. So, as we said earlier that, if one ice crystal is formed, and if surrounding water molecules, they find that, forming another ice crystal is not possible for them under that condition, it is also slow freezing, right, under that condition, it is not possible to form another crystal by them. So, they will go and join already formed crystal. So, the size of the crystal will go up, that is what it is happening here, right, size of that crystal is going up, going up, and it may be to that extent that, these cell materials, like say, you 10 people are standing in one place, and if another person and you are standing very closely, very closely, and if another person comes there, then you have to adjust between you, right, keeping the boundary, that may be, you cannot cross this boundary, either this side, or that side, you cannot cross the boundary.

So, what will happen? You all have to adjust, right and accommodate the new entrant, right. So that is what these cells have been doing, with lowering of the temperature. So, the cells are getting shattered, getting deformed, and ultimately may be ruptured, right, because of the increase of the size of the crystal, right. Now, if that be true, then, it is happening in this case, one more thing, I should say, I don't know how many of you know that, volume of ice is bigger than that of the same water right. There is, if 9 volume of water is transformed into ice, it forms 11 volume of ice, that means, 2 volume is increased, it is 9 -11, right.

So, that 9 -11 factor is coming. If it is more, like say, 90 then 110, if it is 900, then 1100 right. So, as much you can think of, this is one way, another way is that, this is increasing, if we have the decrease, right, you had 0.9, right and now it has become 1.1 right, increase, 1.1. So, if it is 0.09, then it is 0.11, like that, you go down as much as you can think of. So, increase in size, as you could think of 9 – 11; to 9,000 to 90000 to 9 lakhs, right, the decrease also you can think of like 0.9, or 0.09, then, 0.0000009. So, that will be very minute. So, this is what is happening in the this, 9 -11, is happening in the slow freezing, right. So, that 11 has become very very high, right, and the cells, either got deformed, or got fractured, right, now, if we look at the other one, where rapid freezing is happening, then the lower one which we said say, 0.099 or 0.0009. So, there, the size of the ice crystal is very small, and here it was size of the ice crystal is very high, but number of ice crystals are also very low. As in the rapid freezing, where it is more than 100 degree centigrade per hour, right. So, there, what happened your ice crystals size is very low, and number of ice crystals formed are also very high, right. So, in slow freezing, you have less number of ice crystal size is very high, or big whereas, in this, number of ice crystals forms are very high, and the size of the ice crystal is very very low, right. So, what will happen? That same 9 -11, you have 0.0009 and that converted into 11 equivalent, right, and you see, for their small one this is under frozen condition. So, when you are thawing, right, that is, you are defrosting or thawing. So, that time this part will get again converted into ice. Now, 11 part of ice is converted to 9 part of water, right. So, volume requirement is less, but already by this process, you have deformed the cells, and tissues. So, what will happen? Those cells and tissues are not elastic.

So, it will not be possible for them to come back to the original. So, that is why, when this 11 is getting converted to 9, that liquid is getting out of the food material and this is called drip loss, DRIP, drip loss, right, to the tune of 10 to 15 percent drip loss may occur for slow freezing, right. Since, our time is not there, let me tell a very very, I mean a story, a little, that may be useful to understand. The prime minister of India wanted to give some gift to the prime minister of or president of USA. So, he said that, "I would like to send you, say, 100 kg of frozen prawn", prawn is, maybe 1000 rupees a kg at the moment, right. So, 100 kg or maybe 1000 kg whatever, I would like to present you if you like then the other side said yes, fine, you send. Now, the other side, I mean our prime minister sent that 1000 kg to the president of United States.

Now, as you know, both this is true, both in India as well as in any other countries, when anything is getting imported, then that is first checked, its quality is checked with all respects, and then, it is sent to the person. Now, when they thawed it, this 1000 kg, they saw that, it is not 1000 kg, 10 percent of it means, 100, so, it is 900 kg is there. So, they reported to their president, and their president called our prime minister and said, "you said that 1000 kg you have sent, but I got 900 kg, where this 100 kg went up, but, our prime minister said that, "believe me, I have seen it by my own eyes, when it was being weighed, and it was 1000 kg. It was never 900 kg", but the other side said, "no, it is 900 kg I received. Now, the thing is that, none of them were saying wrong, or lying. Both were correct, because, yes, 1000 kg was given, and 900 kg was received, because if the freezing method used was commercial one, where it was 50 degree centigrade, 10 to 50 degree centigrade per hour, where the drip loss was 10 to 15 percent. So, when they thawed it to check, that time, this 10 to 15 percent say,10 percent, that is 100 kg went out by drip loss.

So, actually they received 900 kg, whereas, our prime minister sent really, 1000 kg, but they did not receive. This is only because of the freezing method applied, right ok. This I had said jokingly, so that it is in your mind right. Now, after this the major point which is required to be kept in mind is that, ice crystals are relatively pure, even when they originate from a complex system, and proper to assign an expansion value approximately 9 percent to the quantity of water that freezes, which I said, 9 -11, right. System changes is not uniform throughout the food material, because most other constituents, contract as the temperature is lowered leading to localized areas of expansion, that is formation of ice crystals and localized areas of contraction, that is likelihood to be, because of the stresses, and possibility of mechanical damage. So, more likely in plant tissues, with its rigid structure and poorly aligned cells, than in muscle that is animal, that unlike plant tissues, animal tissues are more pliable, having more pliable consistency, and parallel arrangements of cells or fibers are there.

Then, this also should have been white however, you see that effect of initial concentration on the decrease in volume, and the increase in molality of the unfrozen phase. So, if you consider that you have one, where 5 solutes are there, and you have another, where, say 15 solutes are there, right, and in the unfrozen phase of 1 litre, it is like that. Now, after that, if you are freezing it, then what is happening, that frozen 1 litre, this part is that, this part has been frozen into ice, and the unfrozen part contain the solutes. This is also same, unfortunately this solutes are not seen here, because of the colour masking, right. So, here also 15 solutes are there, and here 5 solutes are there, right.

So, if that be true, then after analysis, what you can see? You can see that, the concentration of the unfrozen phase, it was 5 solute per litre, and it was 15 solute per litre. In this case, 15 solute in this case 5 solute, right. In unfrozen phase of solution, it was 30 solutes per litre, in this case, like one fifth, it is 5/6, if it is one sixth, 5/6 are frozen. So, 30 solutes per litre in this case, and 30 solutes per litre also in this case. So, increase in concentration by freezing is 6 times and here it is 2 times. Then, volume of unfrozen phase after freezing, that is one sixth of litre, this part one sixth of litre, and this is half a litre, this part right, this is half a litre.

Then what we can say finally, the amount of ice formed in this case is 5/6 of a litre, this is the 5/6 of a litre and in this case, this is the half of a litre, right. So, amount of ice, which is formed is 5/6 of a litre, and this is half a litre. That means, if you remember, at some time, we said that, the law, which is governing this, that was Raoult's law. So, Raoult's law as it says, as the concentration is increasing in the unfrozen phase, the lowering of temperature or the freezing point is decreasing, as well the melting point, or not melting point, as well the boiling point is increasing. So, this is corroborating that Raoult's law, and this we will be using in some case.

And that this information is very useful. So, we will use it in some case, and that time we will also give some reference to this, ok. So, today our time is over, and we are running with freezing, which is the, one of the best application of low temperature, one of the best application will come in the next class, and try to finish the freezing part as much as we can ok. If it is possible, we will try to cover up a little quickly, and then subsequent things, we will also go into. Thank you. So, nice of you.