Particle Characterization

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Module No. #11
Lecture No. # 30
Nano-particle Characterization: Top-Down Synthesis Methods

Welcome to the 30th lecture in our particle characterization course. In the last lecture, we started discussing nano-particles, and in particular there are three aspects of nano-particles that we need to be concerned about, the synthesis, dispersion and characterization of nano-particles.

So, in the last lecture, we started to get into some introductory material on what is nano technology, what are the various aspects of nano technology, some applications of nano technology. And then, we started our discussion of synthesis methods of nano-particles, and in particular, the bottom-up methods. Essentially, nano-particle synthesis method can be classified as bottom-up and top-down. The bottom-up approaches require that we take precursors that are essentially in atomic form and assemble them together to form a nano dimensional material that is the definition of bottom-up. Whereas, in the case of top down, we start with materials that are of micron scale and fragment come down to nano dimensions.

So, in terms of bottom-up nano particle synthesis methods, we again sub classify them based on the nature of the precursors and we discuss several methods, where the precursors in the form of a solid which must be vaporized to generate the vapour, which can then be crystallized to form solid particles.

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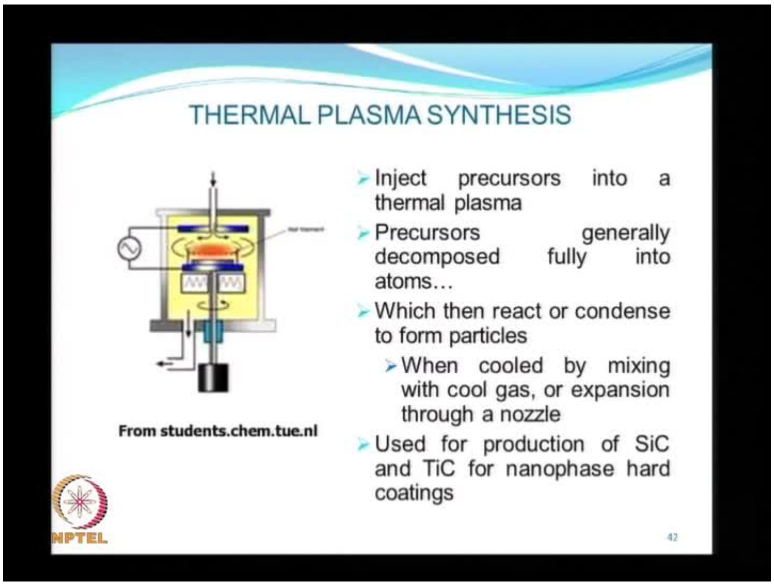

THERMAL PLASMA SYNTHESIS

From students.chem.tue.nl

- Inject precursors into a thermal plasma
- Precursors generally decomposed fully into atoms…
- Which then react or condense to form particles
    - When cooled by mixing with cool gas, or expansion through a nozzle
- Used for production of SiC and TiC for nanophase hard coatings

Now, later we also started discussing applications where the precursors are in the form of liquid droplets or vapors, so we will continue that discussion in this class. There is a method called thermal plasma synthesis, which basically requires that you take vapour precursors and introduce them into thermal plasma.

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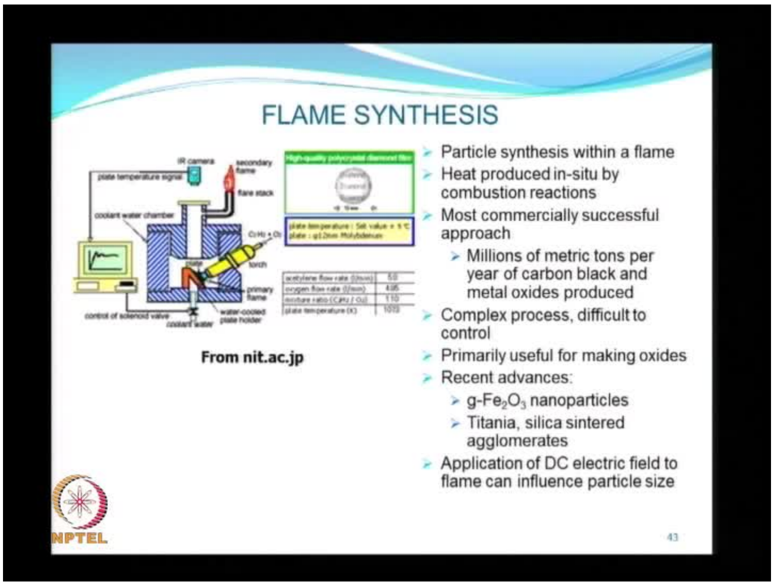

FLAME SYNTHESIS

From nit.ac.jp

- Particle synthesis within a flame
- Heat produced in-situ by combustion reactions
- Most commercially successful approach
    - Millions of metric tons per year of carbon black and metal oxides produced
- Complex process, difficult to control
- Primarily useful for making oxides
- Recent advances:
    - g-Fe_2O_3 nanoparticles
    - Titania, silica sintered agglomerates
- Application of DC electric field to flame can influence particle size

I mean, when you do that the plasma supplies additional energy to break down the precursors completely into atoms, so the precursors may be in the form of high molecular weight, molecules which using the plasma irradiation can be broken down into their constituent atoms, which then can react or condense to form particles. And this can be accomplished by providing cooling - the mixing with a cool gas - or simply expanding the vapours through a nozzle. This method is used quite widely for the production of silicon carbide and titanium carbide for nano face hot coatings.

Another technique is flame synthesis, here the primary difference is that, combustion reactions are used to generate the heat that is required, so particle synthesis here occurs literally within a flame, the flame is used to generate the energy or the heat that is required to drive the reaction to completion. It is a very successful commercial process, in fact, there are millions of tons per year of carbon black and metal oxides being produced using this method. The drawback to this method is that combustion is not an easy process to control, so it is a complex process but widely used for making oxides. And recently, we have been able to make various types of oxide nano particles as well as sintered agglomerates.

In terms of control, it is been found that if you can apply a d c field to the flame that can actually stabilize the combustion reaction and produce a more tightly controlled particle size distribution.

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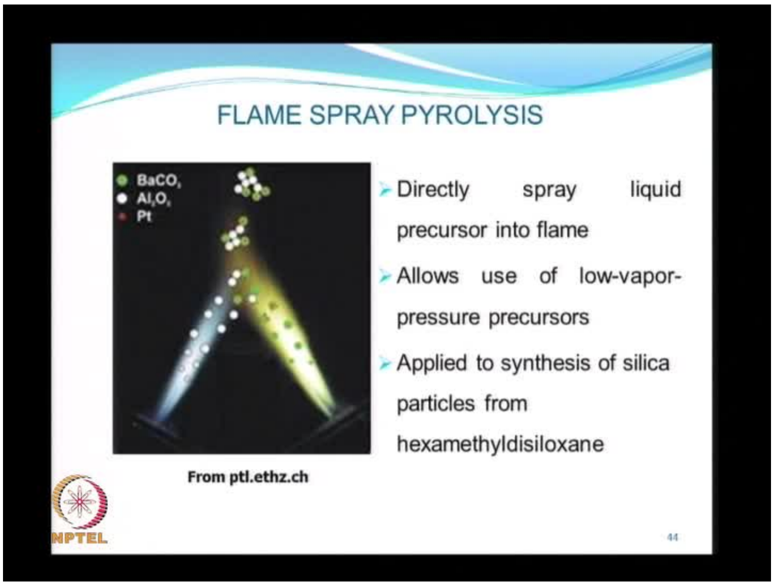

FLAME SPRAY PYROLYSIS

From ptl.ethz.ch

- Directly spray liquid precursor into flame
- Allows use of low-vapor-pressure precursors
- Applied to synthesis of silica particles from hexamethyldisiloxane

Flame spray paralysis is a combination of two methods that we have discussed earlier, flame pyrolisis and spray pyrolisis. Here, thus the liquid is sprayed directly into the flame, so the liquid precursors are injected into the flame.

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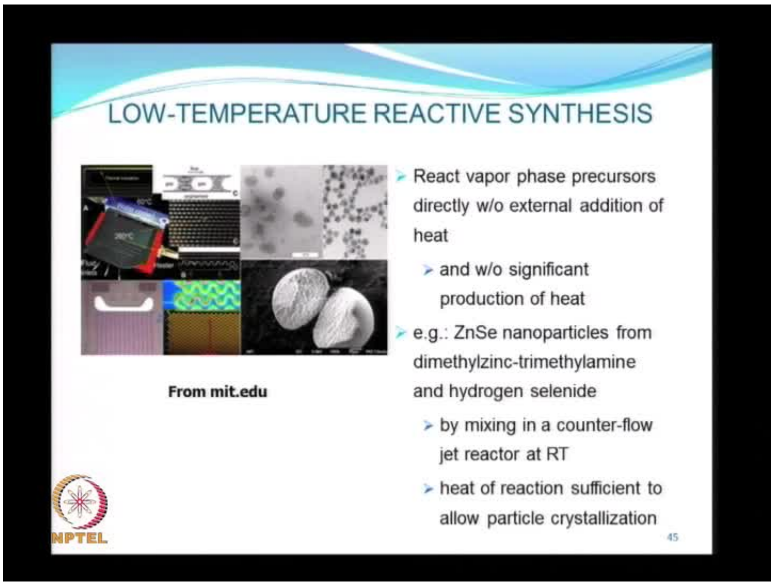

LOW-TEMPERATURE REACTIVE SYNTHESIS

From mit.edu

- React vapor phase precursors directly w/o external addition of heat
  - and w/o significant production of heat
- e.g.: ZnSe nanoparticles from dimethylzinc-trimethylamine and hydrogen selenide
  - by mixing in a counter-flow jet reactor at RT
  - heat of reaction sufficient to allow particle crystallization

The advantage of this method is that you can use low vapour pressure precursors, because the combustion process will supply sufficient heat to vaporize even low vapour pressure precursor materials and this is supplied to synthesis of silica particles. Low temperature reactive synthesis is the name given to nano particle synthesis methods that do not employ high temperatures.

Now, in most of the methods that we talked about earlier, energy is being supplied in the form of heat, and therefore there are some limitations to such method. If you are trying to make materials that are not compatible with high temperature, then you can actually bind up damaging or changing the composition of the material that you are manufacturing.

Here, we try to bring vapour phase precursors to react without adding heat and without producing heat. For example, zinc selenium nano particles can be made from dimethylzinc, trimethyleamine and hydrozen selenide, using this technique. All we do here is, provide intimate mixing, essentially, we use a counter flow jet reactor that is kept at a room temperature, but it provides very intimate mixing of the reactance, the heat of reaction itself is stuffiest to allow particles to crystallize.

So, it is a very energy efficient process because it can be run at room temperature without external addition of heat. And the fact that there is no heat generation also means that it can be essentially done in simple equipment designs, where you do not have to worry about heat generation and the heat dissipation and so on.

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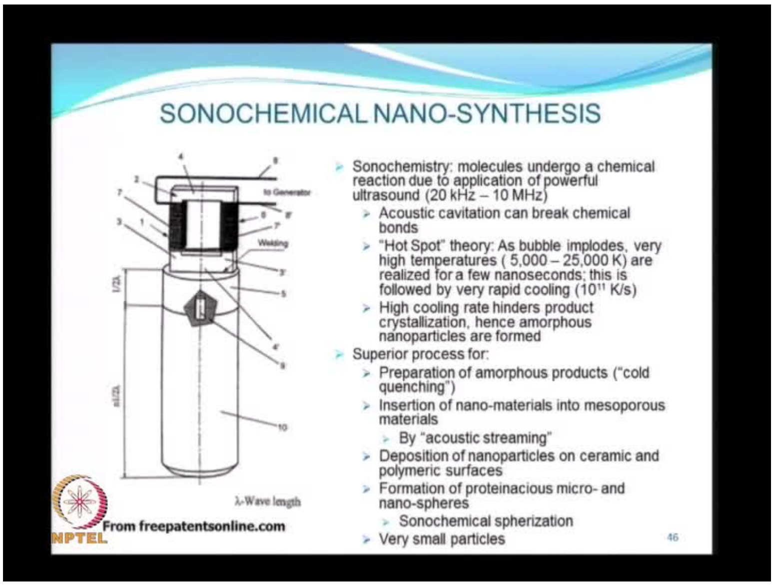

SONOCHEMICAL NANO-SYNTHESIS

- Sonochemistry: molecules undergo a chemical reaction due to application of powerful ultrasound (20 kHz – 10 MHz)
  - Acoustic cavitation can break chemical bonds
  - "Hot Spot" theory: As bubble implodes, very high temperatures (5,000 – 25,000 K) are realized for a few nanoseconds; this is followed by very rapid cooling (10^{11} K/s)
  - High cooling rate hinders product crystallization, hence amorphous nanoparticles are formed
- Superior process for:
  - Preparation of amorphous products ("cold quenching")
  - Insertion of nano-materials into mesoporous materials
    - By "acoustic streaming"
  - Deposition of nanoparticles on ceramic and polymeric surfaces
  - Formation of proteinacious micro- and nano-spheres
    - Sonochemical spherization
  - Very small particles

From freepatentsonline.com

Another method that is been widely used in the bottom-up side of manufacturing nano particles is sonochemical nano synthesis. Ultra sound is an interesting technique in the sense that it can be used to synthesize nano particles both from the bottom up approach as well as top down approach. Later, we will see how ultrasound can be used make nano particles in a top-down kind of application, but when we apply an acoustic field to a liquid, instantaneously extremely high temperature and pressures can be realized within the liquid as cavitation happens.

So, essentially, when you apply an oscillating acoustic field, you start forming bubbles in the liquid which collapse and as they do, they release high amounts of energy. And according to the hot spot theory, as bubbles implode temperatures of the order of 5000 to 25000 kelvin can be realized for a few nano seconds, which is followed by very rapid cooling. But during the time, when these high temperatures and high pressures are in effect, chemical reactions can be driven by several orders of magnitude faster than they would proceed otherwise. So, this acoustic cavitation effect can break chemical bonds and can make chemical reactions run very, very, fast and therefore, it can intensify the process by which nano particles are synthesized using chemical reactions.

The high cooling rate can be advantages in some ways, because by quenching the reaction which happens naturally in a cavitational field, you prevent crystallization of the product, so you can essentially make amorphous nano particles very easily by using the sonochemical method.

Therefore, it is considered as superior process for preparation of amorphous nano particles because of this cold quenching mechanism. Insertion of nano materials into mesoporous materials also becomes possible because, as we have discussed in one of the earlier lectures on surface cleaning, when you couple an acoustic field to a liquid two things happened, cavitation which is a mechanism of bubble implosion and acoustic streaming which is the high velocity unidirectional flow that is induced with very high frequencies when the bubbles are very fine, but bubble density is very high.

So, the net effect of these bubbles forming and collapsing is that there is no cavitational force there is significant. However, the phenomenon of bubble implosion at very small size scale leads to this process of acoustic streaming by which the fluid is directed at high velocities in one direction. So, if you can harness this acoustic streaming process, you can take the nano materials that we have fabricated and actually make them flow into porosities and materials. So, you actually insert or incorporate nano materials into a pours matrix by taking an advantage of acoustic streaming.

You can deposit nano particles on ceramic surfaces and polymer surfaces and you can form essentially spherical nano particles. Sonochemical reactions are particularly suited to make spherical nano particles; indeed, we will see later that when you use sono-fragmentation that also has the effect of making spherical nano particles.

So, there are applications which require sphericity in the nano materials and for that sonochemistry is a good process to use. You can also make very small particles because of this rapid quenching effect, as the particle starts to form, if you can quench the formation process then you do not provide time for the nano particles to grow to larger sizes, so sonochemistry can be very effectively deployed to control the size.

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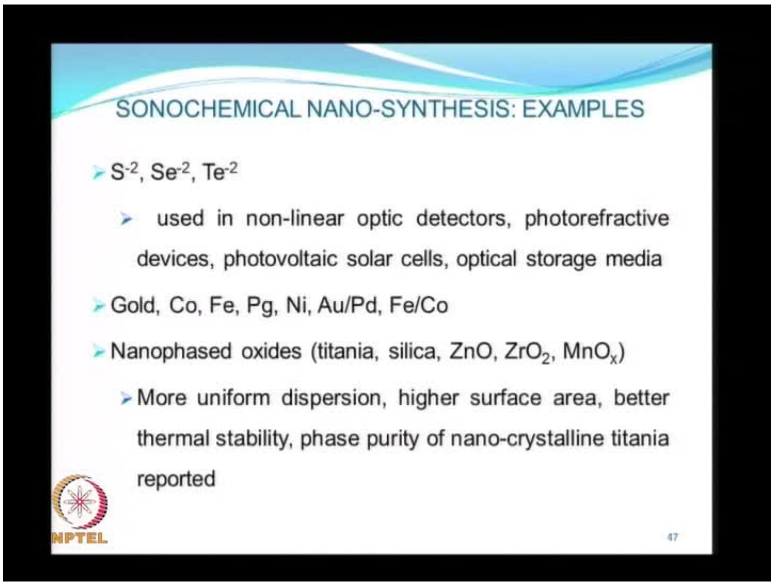

SONOCHEMICAL NANO-SYNTHESIS: EXAMPLES

- S^{-2}, Se^{-2}, Te^{-2}
  - used in non-linear optic detectors, photorefractive devices, photovoltaic solar cells, optical storage media
- Gold, Co, Fe, Pg, Ni, Au/Pd, Fe/Co
- Nanophased oxides (titania, silica, ZnO, ZrO_2, MnO_x)
  - More uniform dispersion, higher surface area, better thermal stability, phase purity of nano-crystalline titania reported

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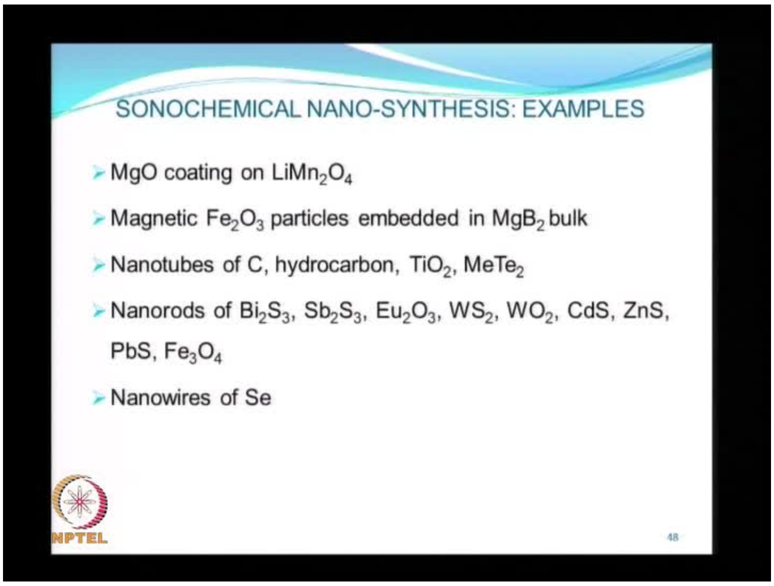

SONOCHEMICAL NANO-SYNTHESIS: EXAMPLES

- MgO coating on $LiMn_2O_4$
- Magnetic Fe_2O_3 particles embedded in MgB_2 bulk
- Nanotubes of C, hydrocarbon, TiO_2, $MeTe_2$
- Nanorods of Bi_2S_3, Sb_2S_3, Eu_2O_3, WS_2, WO_2, CdS, ZnS, PbS, Fe_3O_4
- Nanowires of Se

Some examples of materials that are synthesized using sonochemical methods are shown here and other materials are listed here. So, there is a huge variety of materials and compounds that are commercially manufactured using sonochemical nano synthesis techniques.

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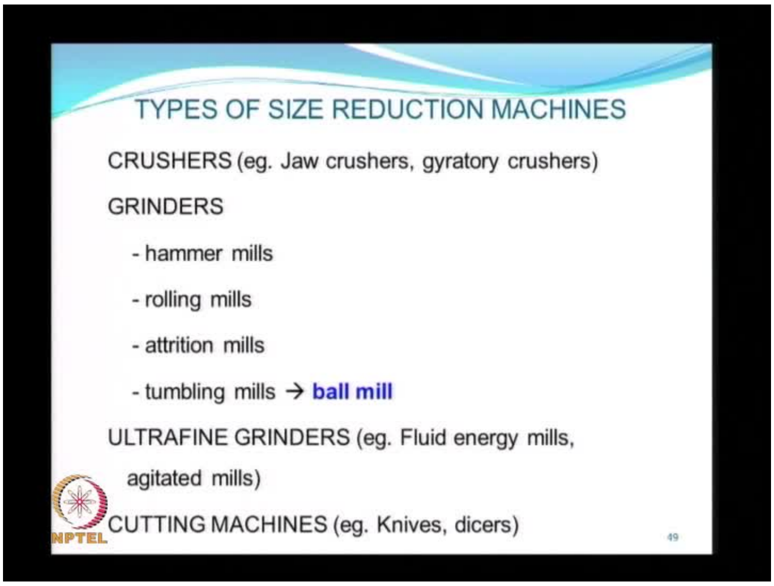

TYPES OF SIZE REDUCTION MACHINES

CRUSHERS (eg. Jaw crushers, gyratory crushers)

GRINDERS

- hammer mills
- rolling mills
- attrition mills
- tumbling mills → **ball mill**

ULTRAFINE GRINDERS (eg. Fluid energy mills, agitated mills)

CUTTING MACHINES (eg. Knives, dicers)

Now, moving over from bottom-up to top-down methods of nano particle synthesis, size reduction is the primary mechanism by which we can make nano particles starting from larger sized particulate material crushes, grinders, ultra-fine grinders, cutting machines you are familiar with all of these tools from your courses and labs in industrial processing mechanical operations.

They can actually be used quite affectively to do size reduction; however, reaching nano dimensions is very difficult with many of these machines. Crushes, grinders are only good for reducing particle size from, say, millimeters down to possibly 10s or 100s of microns.

A ball bearing as well as ultra-fine grinders is effective in making particles down to roughly 10 microns, but when you try to the size below 10 microns to 1 micron or less, there is a huge energy penalty. Some of these size reduction techniques do not work very well and that has somewhat limited their application to synthesis of nano particles.

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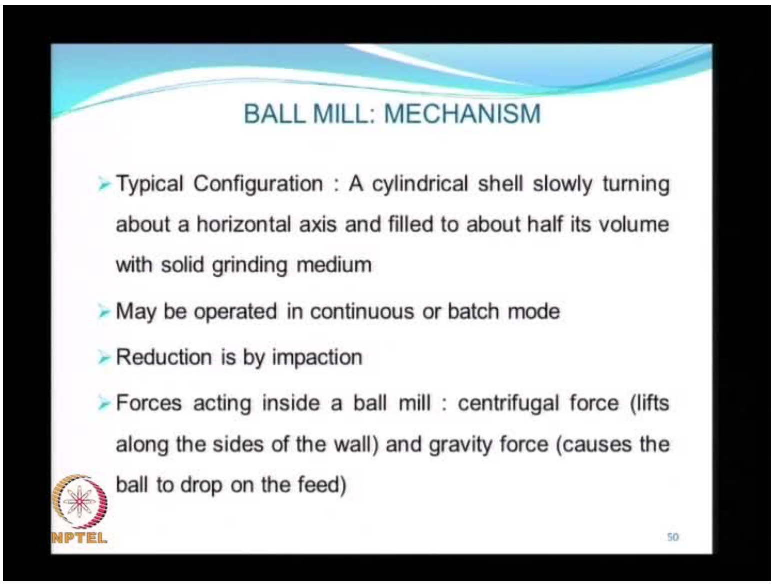

BALL MILL: MECHANISM

- Typical Configuration : A cylindrical shell slowly turning about a horizontal axis and filled to about half its volume with solid grinding medium
- May be operated in continuous or batch mode
- Reduction is by impaction
- Forces acting inside a ball mill : centrifugal force (lifts along the sides of the wall) and gravity force (causes the ball to drop on the feed)

A ball mill which I am sure everyone has familiar with, is basically a cylindrical shell that slowly turns about a horizontal axis, it is filled with about half the volume with a solid grinding medium and essentially, as it rotates the balls that are in the grinding chamber reach a maximum height and then drop and as they do the impact on the material being size reduced and break it to a smaller size.

The advantage for ball mill is that it can be operated in continuous mode or batch mode size reduction happens by a simple impaction process. If you look at the forces acting inside a ball mill, you have centrifugal force which is lifting particles along the sides and gravity force which then causes the ball to drop on the feed and crush it.

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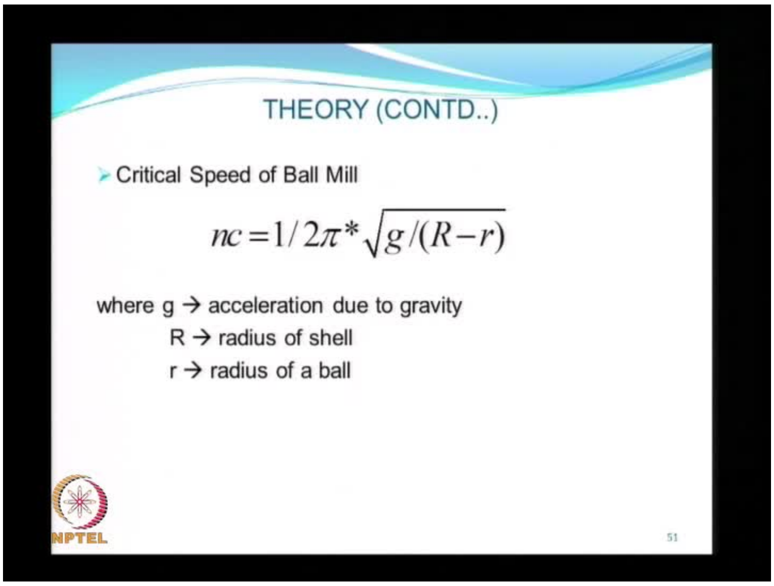

THEORY (CONTD..)

- Critical Speed of Ball Mill

$$nc = 1/2\pi * \sqrt{g/(R-r)}$$

where g → acceleration due to gravity
R → radius of shell
r → radius of a ball

And you can establish a critical speed of the ball mill n c which is related to the acceleration due to gravity, the radius of the shell and the radius of a ball. You want to keep the actual operating speed of the ball mill to no more than 75 to 80 percent of the critical speed, otherwise essentially all the balls will become entrained and just keep following the circumferential motion of the grinding chamber rather than dropping on the material to the crushed.

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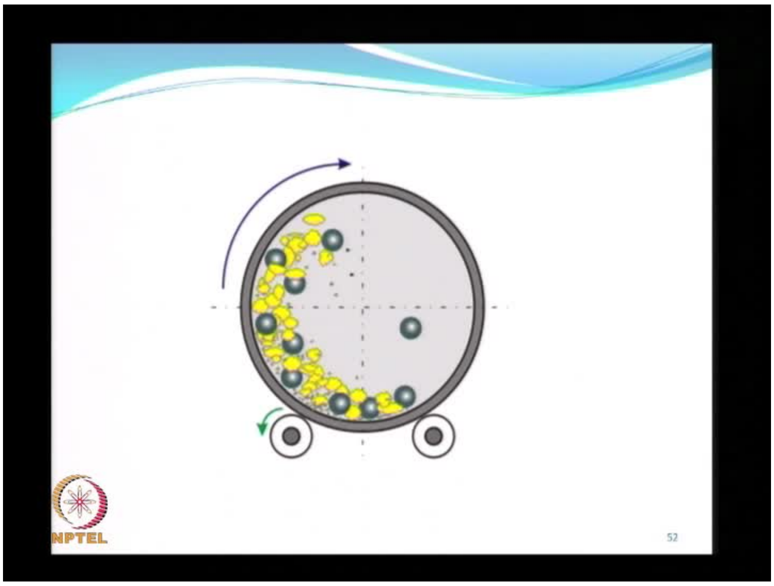

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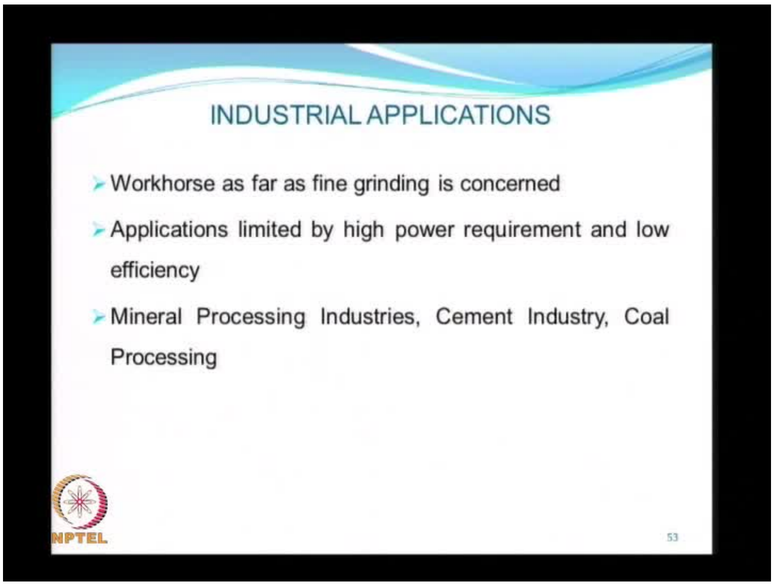

INDUSTRIAL APPLICATIONS

- Workhorse as far as fine grinding is concerned
- Applications limited by high power requirement and low efficiency
- Mineral Processing Industries, Cement Industry, Coal Processing

So, this is a schematic of how the inside of the grinding chamber looks, the yellow popcorn like things or the material that are being crushed and the spherical balls or the grinding media. The ball mill is the workhorse in industry, as far as fine grinding is concerned.

Applications are limited by high power requirement and low efficiency, I am sure you all recall the lab experiments you have done which demonstrates that, as the effective particle size decreases you have to keep supplying more and more energy to produce new surface area. So, it is essentially a self-limiting process, as the surface becomes finer, it becomes more and more difficult to reduce its size further. However, it is widely used in many mineral processing industries, cement industry, in coal processing and so on.

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INDUSTRIAL BALL MILLS

Here are some examples of industrial ball mills; you can see the scale of the equipment. These are huge chambers that are used to make thousands of tons of material on a weekly basis, so you know it is difficult to think of these machines in the context of nano technology, where or production rates are much more modest and so many of these industrial ball mills really do not lend themselves to making nano particles.

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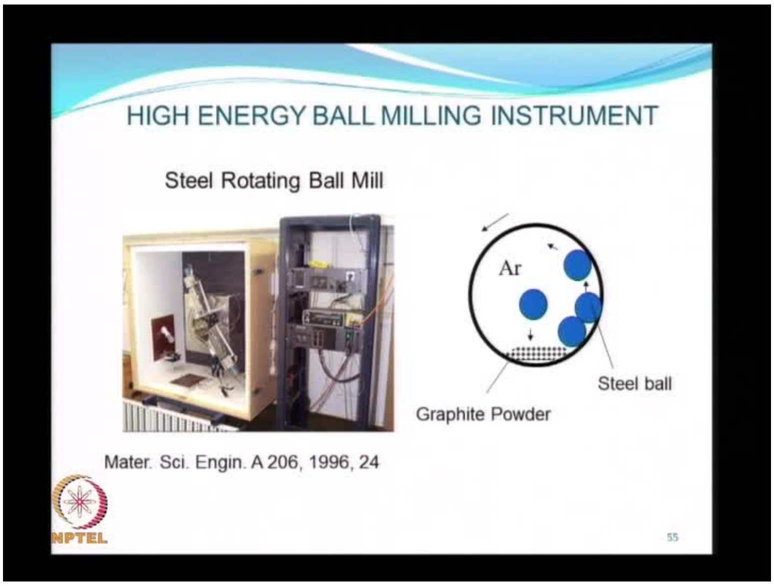

HIGH ENERGY BALL MILLING INSTRUMENT

Steel Rotating Ball Mill

Mater. Sci. Engin. A 206, 1996, 24

However, more recently they have been advances in ball milling technology, in particular, the high energy ball mill which is an improvement over the conventional ball mill in the sense that it is a much, it is a more controlled operating environment. So, you can actually control the temperature inside the milling chamber, you can control the pressure, you can even control the chemistry of the ball milling chamber in order to produce product that you need. This is again a schematic of how high energy ball mill might look.

Essentially, the mechanism remains the same, you are still taking material to be size reduced putting it a chamber and allowing the grinding media to impact on the material with some force which causes a size reduction to happen. However, in this example you can see that the inside of the chamber is filled with organ an inert material to prevent oxidation. So, for example, if you have aluminum or copper that you are trying to produce, if you do this is the ambient environment air itself is sufficient to cause aluminum and copper to oxidize.

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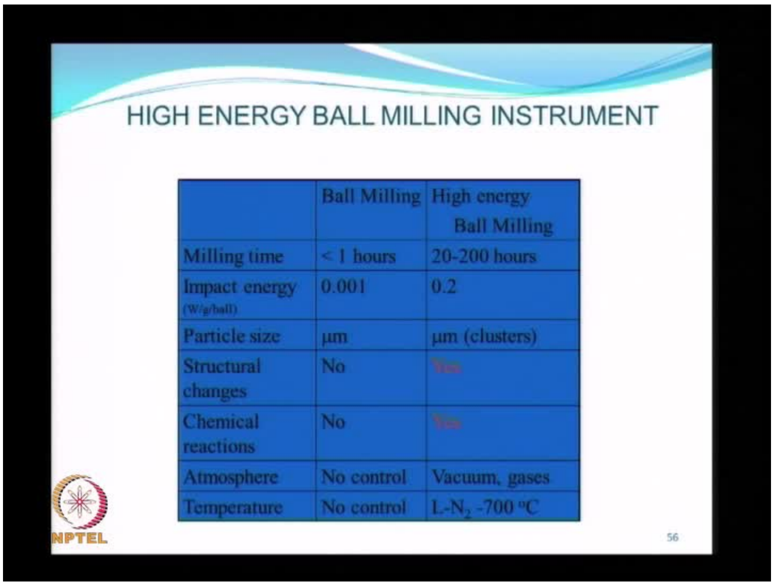

HIGH ENERGY BALL MILLING INSTRUMENT

	Ball Milling	High energy Ball Milling
Milling time	< 1 hours	20-200 hours
Impact energy (W/g/ball)	0.001	0.2
Particle size	µm	µm (clusters)
Structural changes	No	Yes
Chemical reactions	No	Yes
Atmosphere	No control	Vacuum, gases
Temperature	No control	L-N_2 -700 °C

So, if you want to make sure that you synthesize the metal nano particle without any oxide being taken up then you have to provide an inert environment. This table shows that differences between ball milling and high energy ball milling.

One of the key differences is in a high energy ball mill is, you run the mill for much longer. Essentially, the mean size will keep decreasing as you run the mill longer and longer, so while in a ball mill with a milling time of one hour or less you can achieve particles that are, say, 10 microns mean size. In a high energy ball mill just by running it much longer, you can achieve much smaller sizes also the impact energy is designed to be much higher in a higher energy ball mill.

The particle size that is produced, well actually, if you take a look at the output from the high energy ball mill looks not very different from the output from a conventional ball mill, that is because even though you may be size reducing too much smaller sizes, because you are running the process for so long agglomeration sets in. So, the final product that you get from a high energy ball mill is a kind of a powdery substance that has agglomerates or clusters that are micron in size. Now, it is possible to take these clusters and then disperse them, so that extra step is required after high energy ball milling to the material that you have produced and disperse it into the sub-micron sized individual particles. In a high energy ball mills structural changes and chemical reactions can be induced.

The atmosphere can be vacuum or it can be gas field in a high energy ball mill, and the temperature can be controlled all the way from subzero temperatures that are achieved using cryogenic fluids to 700 degree centigrade, so a very wide temperature ranges possible in a high energy ball mill.

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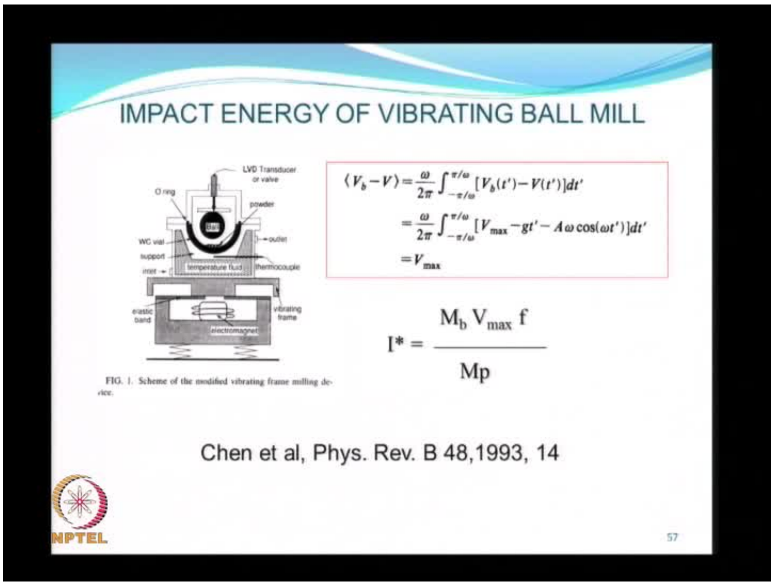

IMPACT ENERGY OF VIBRATING BALL MILL

FIG. 1. Scheme of the modified vibrating frame milling device.

$$\begin{aligned}\langle V_b - V\rangle &= \frac{\omega}{2\pi}\int_{-\pi/\omega}^{\pi/\omega}[V_b(t') - V(t')]dt' \\ &= \frac{\omega}{2\pi}\int_{-\pi/\omega}^{\pi/\omega}[V_{\max} - gt' - A\omega\cos(\omega t')]dt' \\ &= V_{\max}\end{aligned}$$

$$I^* = \frac{M_b V_{max} f}{Mp}$$

Chen et al, Phys. Rev. B 48,1993, 14

The impact energy of a vibrating ball mill can be calculated based on the operating conditions, in particular, the frequency of the vibrating ball mill. The vibrating ball mill is an alternative to the impact ball mill, where the balls drop by the force of gravity, and it is another method for making fine particles from coarser field.

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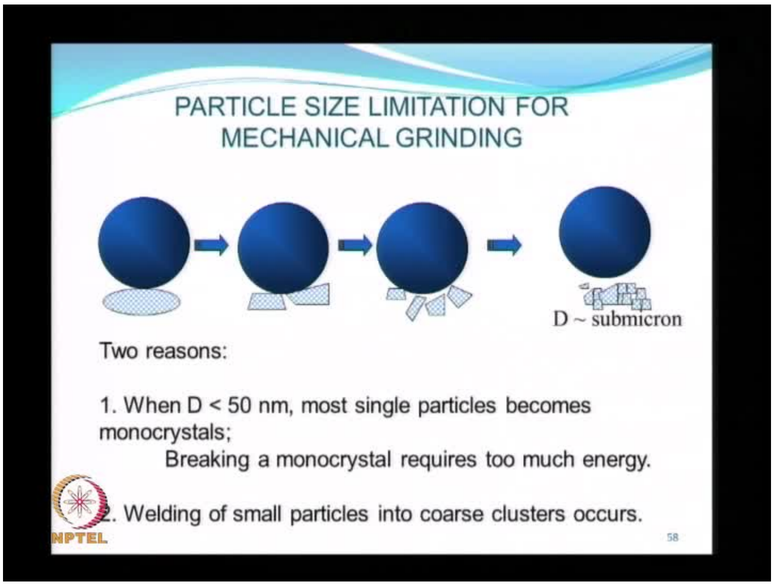

PARTICLE SIZE LIMITATION FOR MECHANICAL GRINDING

Two reasons:

1. When D < 50 nm, most single particles becomes monocrystals;
   Breaking a monocrystal requires too much energy.
2. Welding of small particles into coarse clusters occurs.

However, vibrating ball mills are not widely used in industry compared to the impact based ball mills that are more conventionally used. Now, why is there a size limit in mechanical grinding? There are really two reasons, one is that as the size decreases particles become mono crystalline in nature, and as they do, the energy requirement to break the particle keeps increasing. So, essentially the particle itself becomes more and more un-breakable as it gets smaller.

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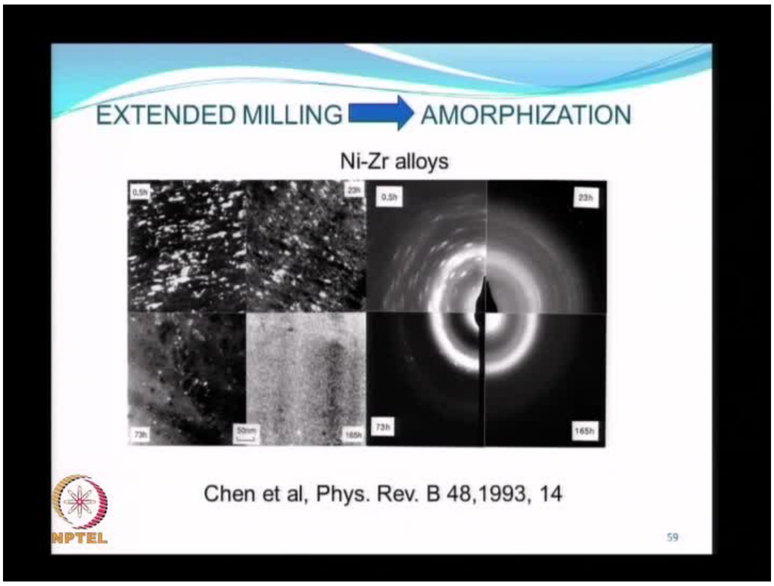

EXTENDED MILLING → AMORPHIZATION

Ni-Zr alloys

Chen et al, Phys. Rev. B 48,1993, 14

In addition agglomeration begins to happen; welding of small particles into clusters begins to happen. And again, the longer you run it, the stronger are these inter particle cohesive forces, and essentially, sintering begins to happen after some period of time. And these clusters that form over long period of operation can be very difficult to break down into their component materials.

Extended milling also leads to amorphization this is shown here in a series of graphs that are taken at various time intervals ranging from 23 hours to 73 hours to 165 hours. And you can see that what started out as very crystalline material, where the structure can be easily identified. Soon reaches an amorphous form, where it is very difficult to really identify the shape of the individual particles. Essentially, you get an amorphous powder, which if you were to test it using x-ray difraction would basically tell you that it is a highly non-crystalline material.

So, one of the problems with extended time high energy ball milling to make nano-particles is that, it is very difficult to get crystalline materials using this process, there is over time and amporphization that happens which is very difficult to avoid.

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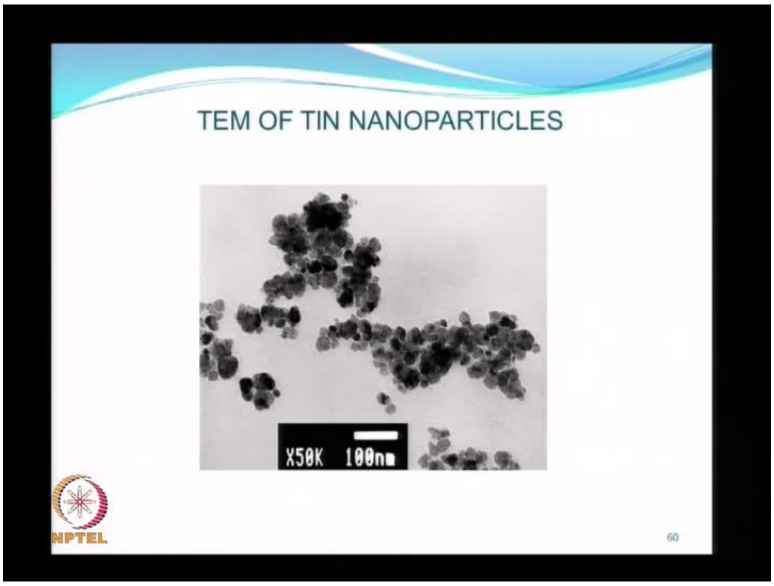

TEM OF TIN NANOPARTICLES

It is T E M pictures of titanium nitrite nano-particles that are produced by high energy ball milling and here you can see the clustering that is happening. This is a good example of characterization of nano particles using tunneling electron microscopy. You can see that the resolution is fantastic, you can actually see particles that are nano meters in size and you can actually resolve particles that are nearby which are about a nano meter apart. So, the primary advantage of the T E M over scanning electron microscopy is its ability to sensitively detect as well as resolve particles that are in the nano size range and the clustering is very apparent in this picture.

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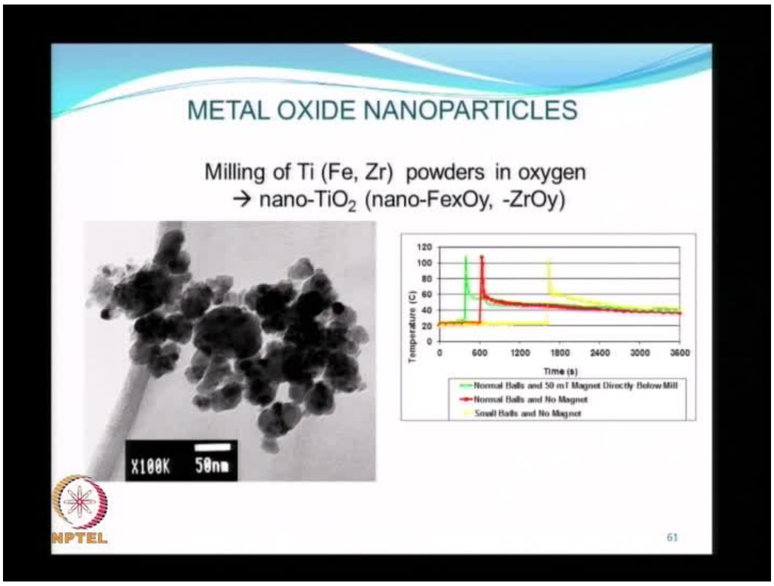

METAL OXIDE NANOPARTICLES

Milling of Ti (Fe, Zr) powders in oxygen
→ nano-TiO_2 (nano-FexOy, -ZrOy)

Now, these are examples of metal oxide nano particles that are produced by milling of various powders titanium, iron, and zirconium in an oxygen environment. Again, this is done in a high energy ball mill, where the interior of the mill can be made to be oxygen rich and what you produce is nano titania, nano F e x O y and nano Z r O y. And here again, when you look at the T E M picture at the bottom, you can see the extent of clustering that is happening. Clearly, nano particles are being produced, but by the time you take them out of the mill they have essentially clustered into agglomerate that is of the order of several hundred nano meters in dimension. So, they have to be broken up somehow, before you can employ them for further processing.

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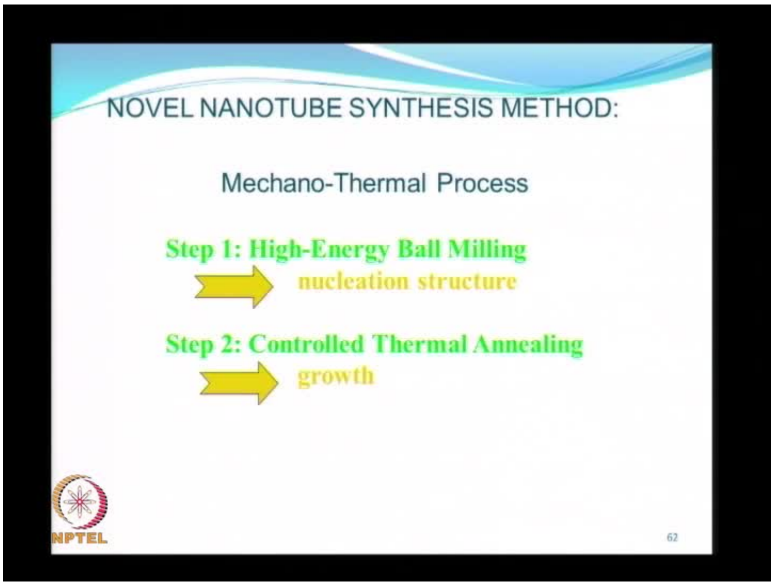

NOVEL NANOTUBE SYNTHESIS METHOD:

Mechano-Thermal Process

Step 1: High-Energy Ball Milling

➡ nucleation structure

Step 2: Controlled Thermal Annealing

➡ growth

So, this process that is labeled as mechano-thermal process, which involves at two stage procedures; in step 1, you use high energy ball milling to produce a structure that is a nucleate structure; step 2 is to then produce a controlled thermal annealing process which leads to growth.

Now, thermal annealing is essentially taking a nano material that you have produced and exposing it to high temperatures in a controlled manner in order to obtain a certain structure and size that you are interested in. Typically, thermal annealing is do get a more sintered a harder structure compared to the amorphous structure that are high energy ball mill would normally produce. So, if you want to take the output from a high energy ball mill and give it more of a crystalline structure, then thermal annealing is a process that is highly recommended.

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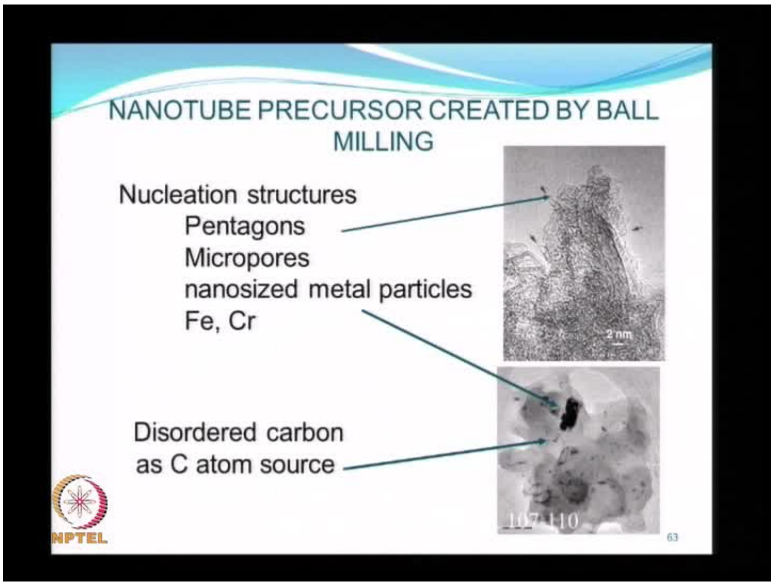

NANOTUBE PRECURSOR CREATED BY BALL MILLING

Nucleation structures
  Pentagons
  Micropores
  nanosized metal particles
  Fe, Cr

Disordered carbon
as C atom source

These are examples of nano tubes that are produced by ball milling. Here, you can see that ball milling is been able to produce the precursors for nano tubes. So, the nucleations structures are there, that are pentagons, micropores as well as the nano sized metal particles. And you can see that carbon is being incorporated as the source of carbon atoms.

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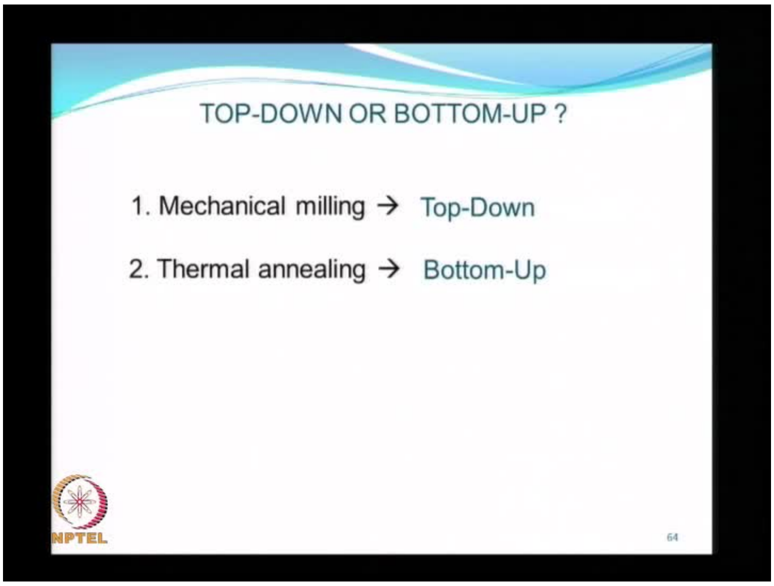

TOP-DOWN OR BOTTOM-UP ?

1. Mechanical milling → Top-Down
2. Thermal annealing → Bottom-Up

Now, when you look at this process that combines mechanical milling and thermal annealing, it is actually difficult to decide whether you should label it as a top-down process or a bottom-up process. Because the mechanical milling itself is a top-down process obviously, but thermal annealing is where you are essentially taking loose fragments that you have generated by the mechanical milling and bonding them together to produce a crystalline structure. So, it is kind of a combination of top-down and bottom-up methodologies just like the liquid gel technique was that we talked about earlier.

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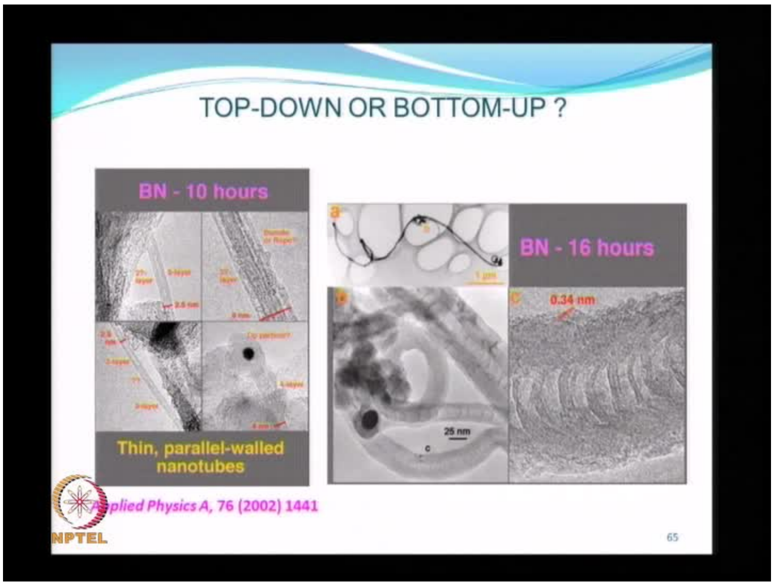

TOP-DOWN OR BOTTOM-UP ?

BN - 10 hours

Thin, parallel-walled nanotubes

BN - 16 hours

Applied Physics A, 76 (2002) 1441

65

So, here is some output from this combined process boron nitrite; nano tubes can be produced using this process and you can see the structure of the nano material that results after 10 hours and after 16 hours.

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THE FIRST COMMERCIAL SOURCE FOR BN NANOTUBES

http://www.anutech.com.au/TD
http://www.rsphysse.anu.edu.au/nanotube/
http://www.pa.msu.edu/cmp/csc/nanotube.html

PRICE LIST

Quantity	Price US$/gram
1g	US$400/g
2g - 5g	US$350/g
6g - 10g	US$300/g

In fact, a high energy ball milling combined with the thermal annealing was the first commercial process to be used for the production of boron nitrite nano tubes. And cost wise, actually this is very competitive with bottom-up approaches, you can see some prices listed here for grams of material. In comparison, if you were trying to make the same materials using a bottom up process, it would cost you at least 3 to 4 times as much.

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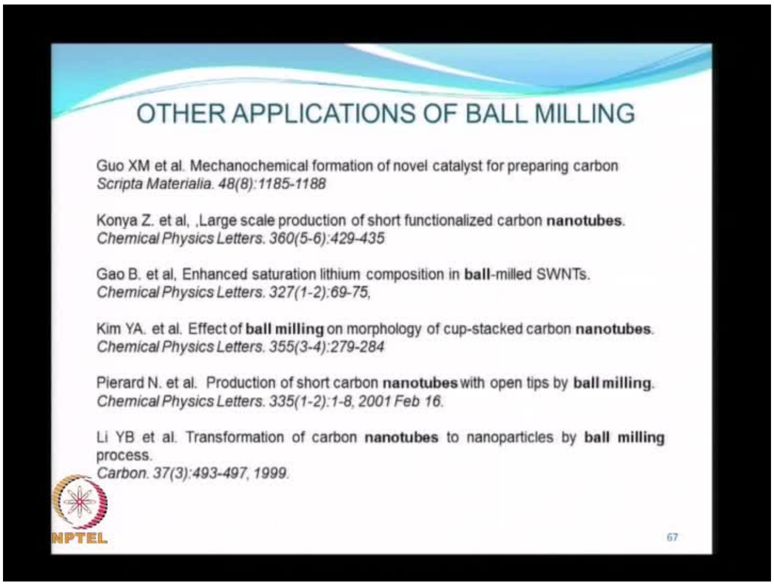

OTHER APPLICATIONS OF BALL MILLING

Guo XM et al. Mechanochemical formation of novel catalyst for preparing carbon
Scripta Materialia. 48(8):1185-1188

Konya Z. et al, ,Large scale production of short functionalized carbon **nanotubes**.
Chemical Physics Letters. 360(5-6):429-435

Gao B. et al, Enhanced saturation lithium composition in **ball**-milled SWNTs.
Chemical Physics Letters. 327(1-2):69-75,

Kim YA. et al. Effect of **ball milling** on morphology of cup-stacked carbon **nanotubes**.
Chemical Physics Letters. 355(3-4):279-284

Pierard N. et al. Production of short carbon **nanotubes** with open tips by **ball milling**.
Chemical Physics Letters. 335(1-2):1-8, 2001 Feb 16.

Li YB et al. Transformation of carbon **nanotubes** to nanoparticles by **ball milling** process.
Carbon. 37(3):493-497, 1999.

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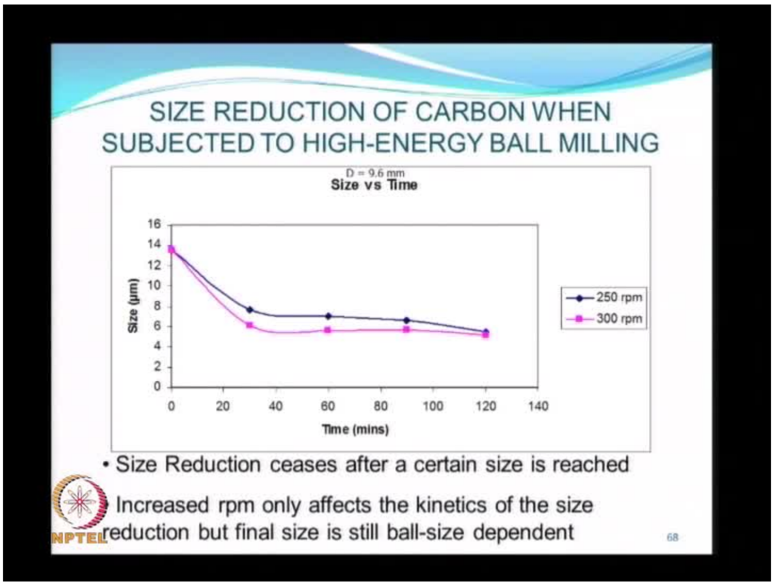

SIZE REDUCTION OF CARBON WHEN SUBJECTED TO HIGH-ENERGY BALL MILLING

- Size Reduction ceases after a certain size is reached
- Increased rpm only affects the kinetics of the size reduction but final size is still ball-size dependent

As There is in literature many, many, applications of ball milling for the synthesis of nano particles and you can see that there is a large variety of materials that are made using the ball milling process, particularly popular for making nano tubes.

Now, these are some results from our laboratory, where we have taken carbon and do and try to do size reduction using various techniques. So, when we do this in a high energy ball mill and you plot the mean size has a function of time. You can see that there is a leveling of effect or an asymptotic effect which in this case is reached about 6 micron or so. And the size reduction stops happening after this limiting size is reached. When you increase the r p m of the ball mill, it really does not affect the asymptotic size that is reached, what it affect is, the rate at which the size is approached.

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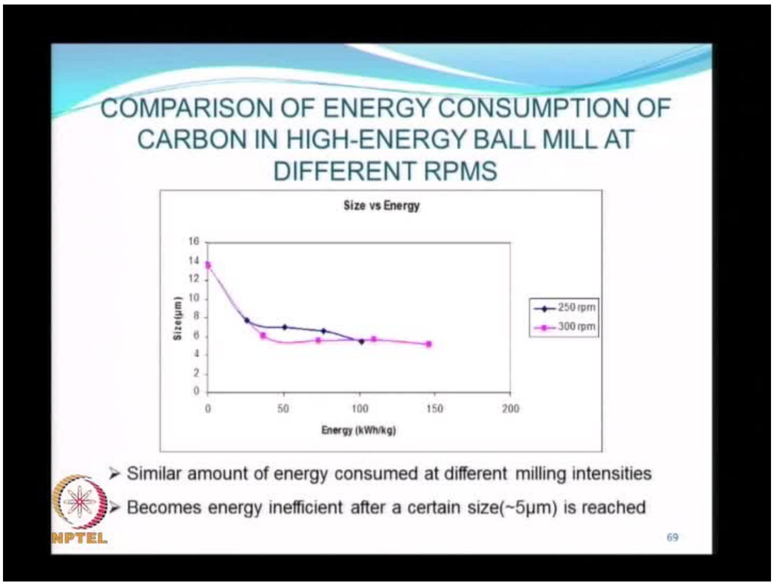

COMPARISON OF ENERGY CONSUMPTION OF CARBON IN HIGH-ENERGY BALL MILL AT DIFFERENT RPMS

- Similar amount of energy consumed at different milling intensities
- Becomes energy inefficient after a certain size(~5μm) is reached

So, by increasing the r p m, you can increase the kinetics of the size reduction process, but you really cannot do anything about the final size, which is more dependent on the dynamics of the mill itself, such as the size of the ball, the size of the chamber. And ultimately, the size reduction process itself will stop after a certain minimum size is reached; this is a comparison by size verses energy.

So, if you look at energy, there is being input and the size there is achieved as a result of the energy input, you can see that there is a similar amount of energy being consumed at various milling intensities. In other words, even if you change the r p m as long as the input energy remains the same, the final size that is achieved also remains the same. And again, you can see that the process of size reduction by ball milling essentially becomes energy inefficient after about 5 microns is reached. Because you can keep increasing the amount of energy that you input without causing any change in the mean size after roughly in this case about 50 kilowatt hours per kilogram.

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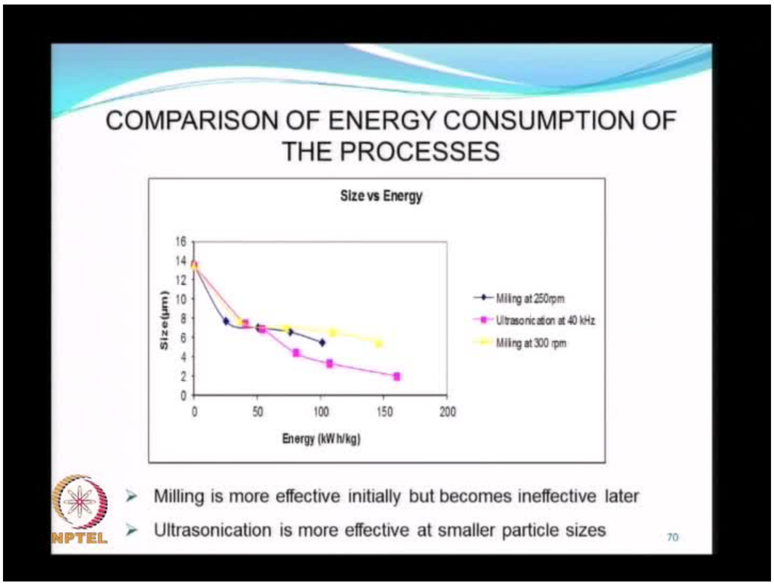

COMPARISON OF ENERGY CONSUMPTION OF THE PROCESSES

- Milling is more effective initially but becomes ineffective later
- Ultrasonication is more effective at smaller particle sizes

Here, we compare the ball milling processes with ultrasonication to look at the energy efficiency of these processes. As we have seen in the previous pictures, milling at various r p m's starts to show a leveling of tendency around 6 microns. Whereas, if you did the size reduction using sono-fragmentation as a technology at in this case at 40 kilo hertz, you can keep driving the size much lower than you can with conventional size reduction processes such as ball milling.

In fact, if you look at this figure more closely, you can see that actually milling is a more energy efficient process until, a size of roughly 5 microns is reached after which sonication becomes the more energy efficient process. So, if you are trying to do nano particle synthesis by size reduction, then you are probably better off using a combination of techniques. So, to get from an initial size that is, let us say around 70 to 100 microns to about 5 microns, you should use ball mill to reach that size and after that you start sonicating the particles to do further size reduction.

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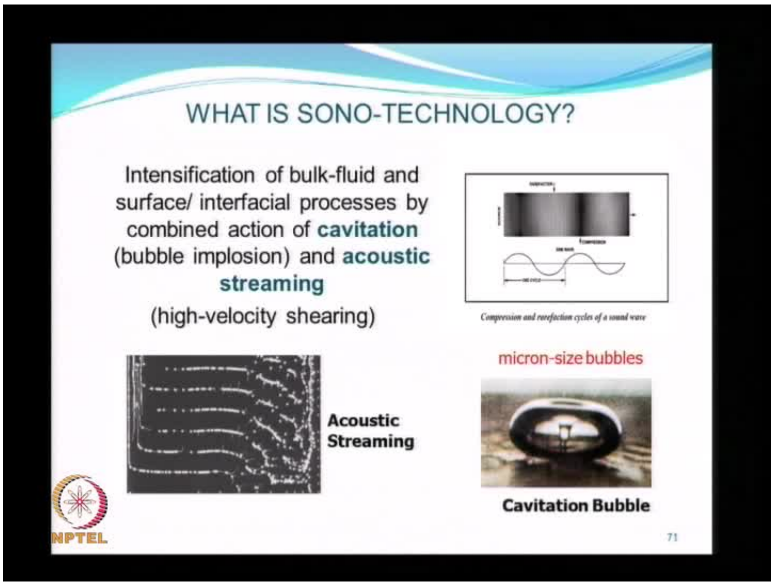

WHAT IS SONO-TECHNOLOGY?

Intensification of bulk-fluid and surface/ interfacial processes by combined action of **cavitation** (bubble implosion) and **acoustic streaming** (high-velocity shearing)

Compression and rarefaction cycles of a sound wave

micron-size bubbles

Acoustic Streaming

Cavitation Bubble

So, let us quickly recap what is sono-technology? We have discussed this in the context of surface cleaning earlier. Sono-technology refers to intensification of bulk fluid as well as surface and interfacial processors by the combined action of cavitation and acoustic streaming. And here, we see schematics of what a cavitation bubble looks like just before it implodes. We see a typical acoustic streaming pattern which is essentially unidirectional in nature. And at the top, we see the typical compression and rarefaction cycle of a sound wave, here of course, the bubbles will be forming during the rarefaction cycle and they will be collapsing during the compression cycle.

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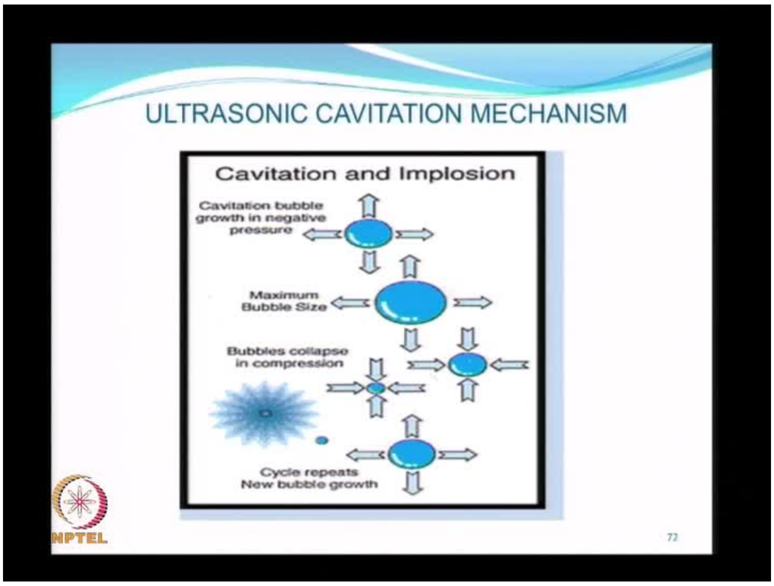

ULTRASONIC CAVITATION MECHANISM

This is how the cavitation actually happens, there is a bubble growth which leads to a maximum bubble size at which point, the bubbles collapse in the compression cycle and releases energy as a shock wave that propagates though the liquid medium and either impacts on particles that are suspended in the liquid or it impacts on a surface that the liquid is adjacent to. And the energy there is transferred due to this shock wave impaction causes physical changes or chemical changes to happen and then, this cycle keeps repeating itself as new bubbles form and implored.

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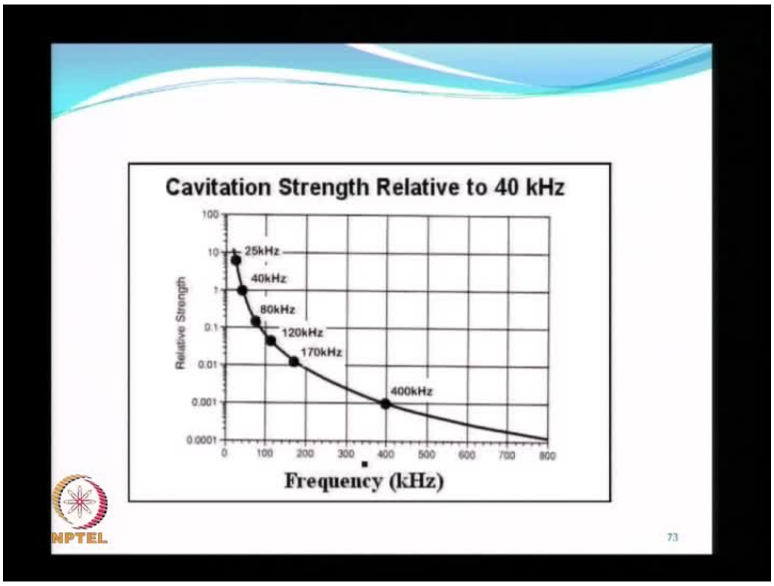

Frequency is a major player in this, as you increase the frequency of the acoustic field, the cavitation intensity drops quickly. Actually, there is over f cubed dependence, cavitation strength decreases with frequency as 1 over the cube of the frequency.

So, you can see here that as you approach 400 kilo hertz, 800 kilo hertz or close to 1 mega hertz, cavitation is virtually absent. And at its most significant levels for ultrasonic frequencies that are less than 100 microns, that 25 kilo hertz to 100 kilo hertz range is where you get the most intense cavitation.

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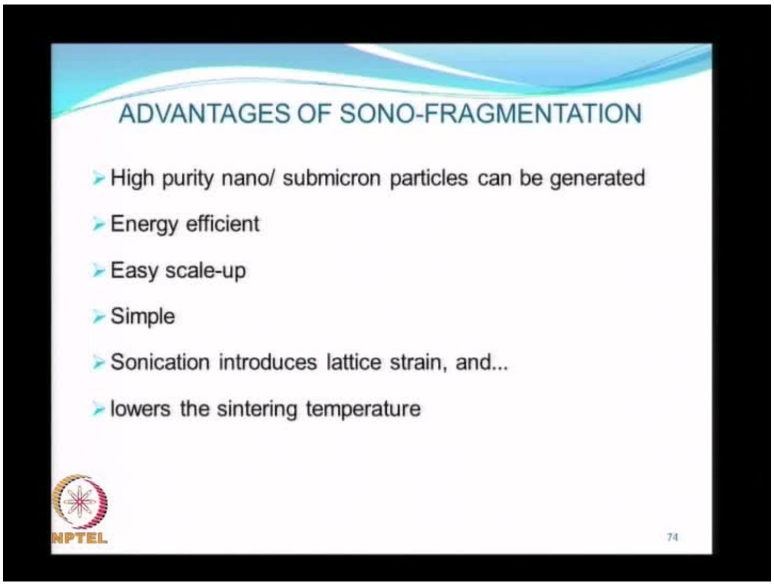

ADVANTAGES OF SONO-FRAGMENTATION

- High purity nano/ submicron particles can be generated
- Energy efficient
- Easy scale-up
- Simple
- Sonication introduces lattice strain, and...
- lowers the sintering temperature

Some of the advantages of sono-fragmentation for synthesizing nano particles are; high purity, because essentially you are taking the base material. If you are trying to make nano alumina, you are taking micron sized alumina, so there is no additional chemical involved and all you use is high purity water typically. So, you immerse the micron sized particles in high purity water, turn on the acoustic field and you start fragmenting the particles. So, it is very simple process, energy efficient, easy to scale up, and also it does some interesting things to the crystalline structure of the material.

The sonication introduces what is known as lattice strain. So, the crystallinity of the particle is maintained, it does not become an amorphous with extended exposure like, high energy ball milling does, but there are certain subtle changes in the crystallinity. Effectively, from a physical view point use what you see is a rounding of the corne, so that the material or a particle that subjected to long term sonication becomes increasingly spherical with a passage of time.

It also lowers a sintering temperature, now that is an advantage when you are using these particles in an application that requires them to be sintered and the ability to use a lower temperature is advantages from an energy efficiency view point. Ofcourse, the reason that the sintering temperatures are lower is because the process of sonication increases the surface energy of the particle. So, the natural adhesiveness or cohesiveness of the particle is greatly increased by the process of sonication.

This is actually true for all top-down methods, but in particular ultra sound because it imports such a high energy to the particles to fragment them, leaves behind a residue of the energy which is much higher compare to, for example, high energy ball milling. So, the particles - nano particles - that are synthesized using sono-fragmentation or essentially much more reactive, much more adhesive, and much more conformable to a process compared to nano materials that are made by other techniques.

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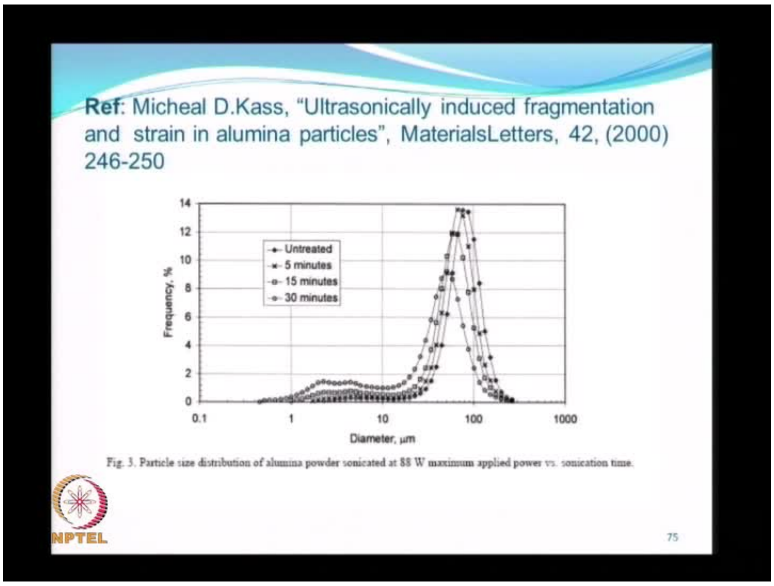

Ref: Micheal D.Kass, "Ultrasonically induced fragmentation and strain in alumina particles", MaterialsLetters, 42, (2000) 246-250

Fig. 3. Particle size distribution of alumina powder sonicated at 88 W maximum applied power vs. sonication time.

Here are some examples of particles that are produced using sono-fragmentation. And again, from a particle characterization view point what you see here all data that are produced using a particle size analyzer. In this chart, you can see that compare to the un-treated alumina particles, as you expose them to sonication for various periods of time and this is using fairly low power ultra sound 88 watts, you can see that the mean size keeps shifting to a smaller size range.

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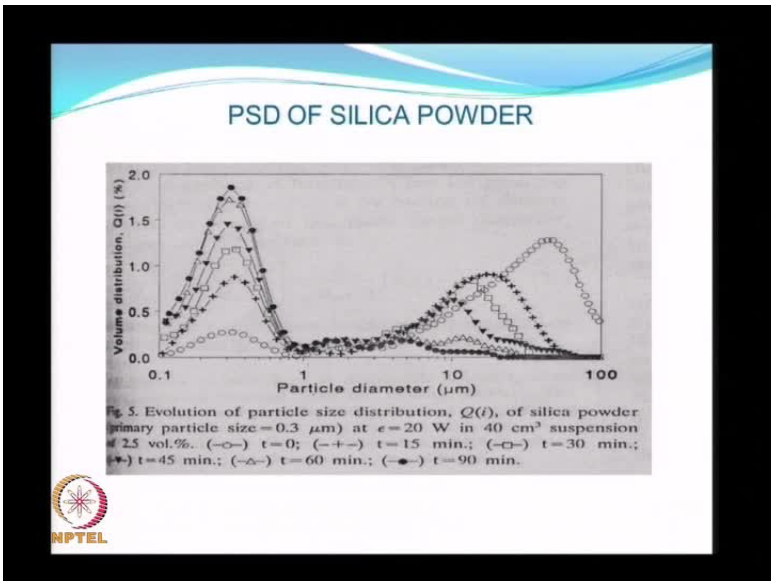

PSD OF SILICA POWDER

Fig. 5. Evolution of particle size distribution, $Q(i)$, of silica powder primary particle size = 0.3 μm) at $\epsilon = 20$ W in 40 cm^3 suspension 2.5 vol.%. (–○–) t = 0; (–+–) t = 15 min.; (–□–) t = 30 min.; –▼–) t = 45 min.; (–△–) t = 60 min.; (–●–) t = 90 min.

This is an illustration of a silica particle or silica powder that has been exposed to ultrasound and you can see here that a very characteristic by model distribution develops over time. And here again, what you see is, a reduction in the mean size of particles and also an increase in the volume fraction of particles in the finer size range. So, you can see that there is a significant enrichment of particles in the sub 1-micron size range as you subject the powder to sonication over an extended period of time.

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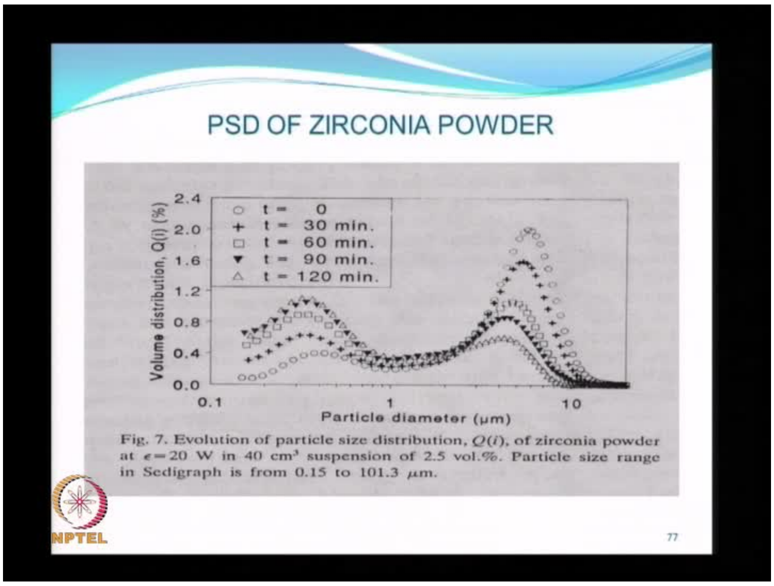

PSD OF ZIRCONIA POWDER

Fig. 7. Evolution of particle size distribution, $Q(i)$, of zirconia powder at $\epsilon = 20$ W in 40 cm^3 suspension of 2.5 vol.%. Particle size range in Sedigraph is from 0.15 to 101.3 μm.

This is a sample of zirconia powder that has been subjected to ultrasound. And again you see the same trend, the volume fraction of particles in the larger size range decreases with increasing sonication time and the volume fraction of particles in the sub-micron size range increase with increase in sonication time, so the mean size decreases as well.

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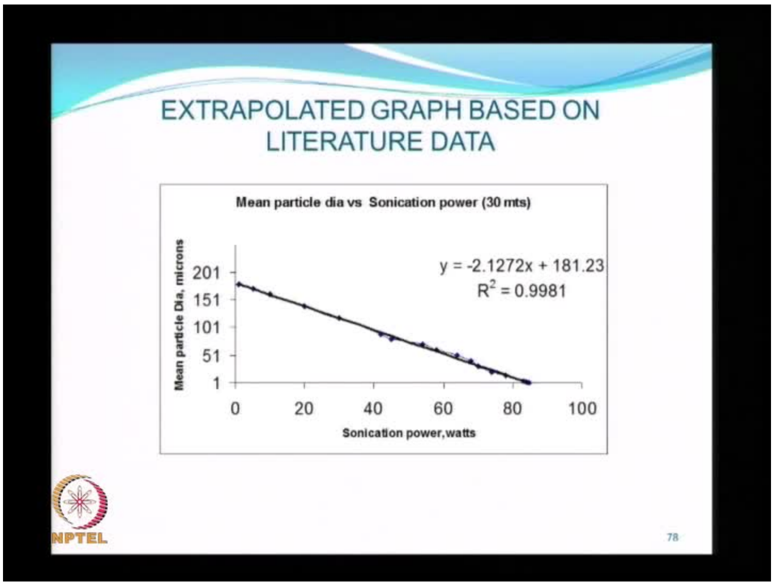

EXTRAPOLATED GRAPH BASED ON LITERATURE DATA

So, if you actually took all the data that is in literature and plotted it as mean particle diameter verses sonication power in watts, you see a very interesting trend that with increasing sonication power, you can drive the mean particle diameter after 30 minutes of sonication down to 1 micron.

However, if you look at the literature data that is not much work reported for particles that are smaller than 1 micron. It is reasonable to expect that this line cannot simply be extrapolated to sub-micron sizes, there will be a leveling of effect even with sono-fragmentation; however, based on these it is reasonable to expect that sonication will remain a viable technology even for particles that are smaller than a micron.

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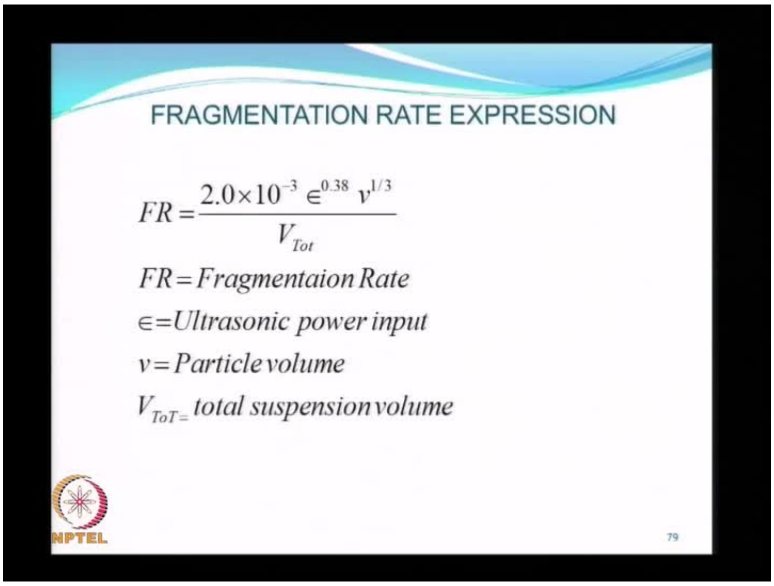

FRAGMENTATION RATE EXPRESSION

$$FR = \frac{2.0\times 10^{-3} \in^{0.38} v^{1/3}}{V_{Tot}}$$

$FR = Fragmentaion\ Rate$

$\in = Ultrasonic\ power\ input$

$v = Particle\ volume$

$V_{ToT=}\ total\ suspension\ volume$

79

If you look at the fragmentation rate expression reported in literature, the fragmentation rate in sono-fragmentation is related to the ultrasonic power input with an exponent of 0.38, particle volume with an exponent of one-third and total suspension volume which is in the denominator. This is an interesting expression, what it implies is that as the total suspension volume increases, the fragmentation rate will decrease reciprocally.

The reason for that is, that sono-fragmentation is a volumetric effect; you are supplying a constant power if you increase the volume of the liquid, then the power per unit volume decreases and that result in reduced fragmentation. It is reasonable to expect that power input will be in the numerator, but an interesting finding is that particle volume is in the numerator. What that implies is, as the concentration of particles in the suspension increases sono-fragmentation efficiency will increase, that is somewhat counter intuitive, because what that says is that if you process more material, the process will be more efficient.

Thus, usually the reverse of what happens with most chemical processes as you try to pump in more material your efficiency will decrease. The fact that in this particular case the particle volume or concentration is in the numerator gives us a lot of hope that scale up would not be that difficult, because in scaling up what you are trying to do is, essentially, process more material. At least, this expression would indicate that fragmentation rate will not decrease when you do that if anything it will increase as the particle volume to the power one-third.

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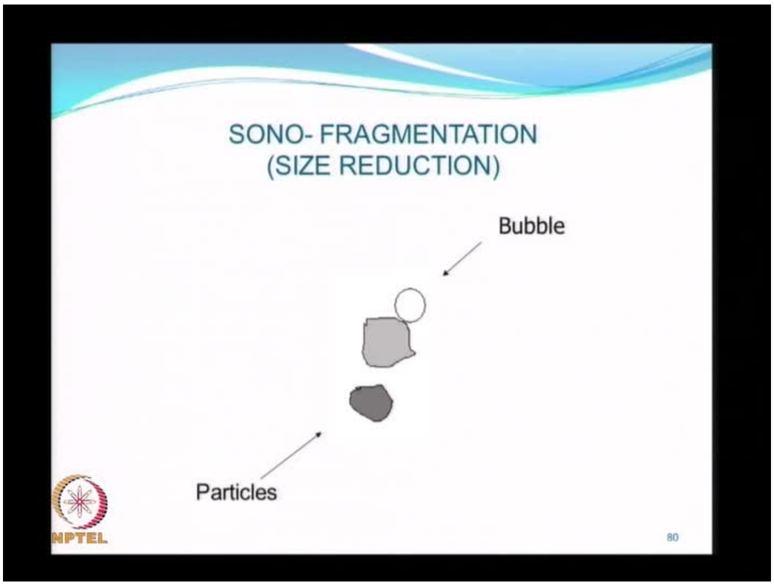

SONO- FRAGMENTATION
(SIZE REDUCTION)

Bubble

Particles

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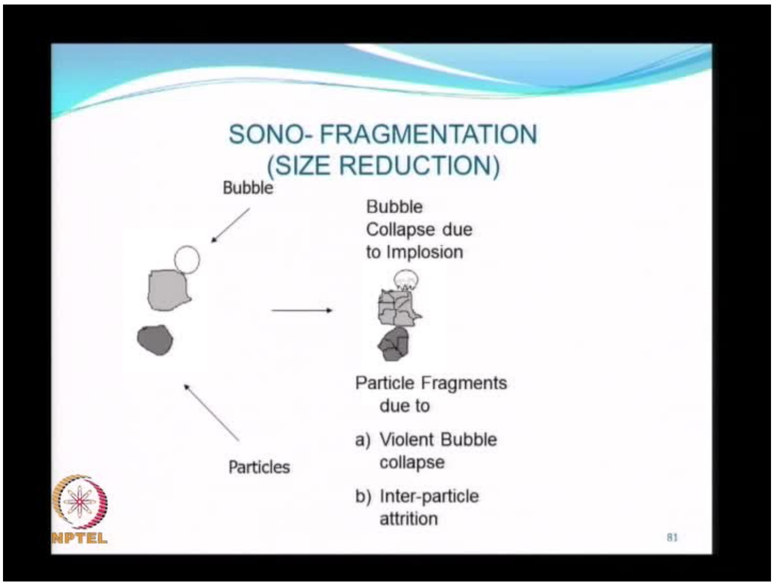

SONO- FRAGMENTATION
(SIZE REDUCTION)

Bubble

Bubble
Collapse due
to Implosion

Particle Fragments
due to

a) Violent Bubble collapse
b) Inter-particle attrition

Particles

Now, if you look at the mechanism of sono-fragmentation, there are actually two mechanisms by which particle fragmentation happens, there is direct interaction of the bubble with a particle and also interaction between two adjacent particles that are being accelerated by the bubble explosion.

So, in this particular case, the bubble collapse due to implosion is one of the mechanisms, with the other mechanism is simple particle to particle impact. So, particle fragmentations here occur due to the violent bubble collapse as well as inter particle collisions and the resulting attrition in the particles. So, this is basically what happens, the bubbles impact on the particle, particles impact on each other and the net result is a fragmented population of particles.

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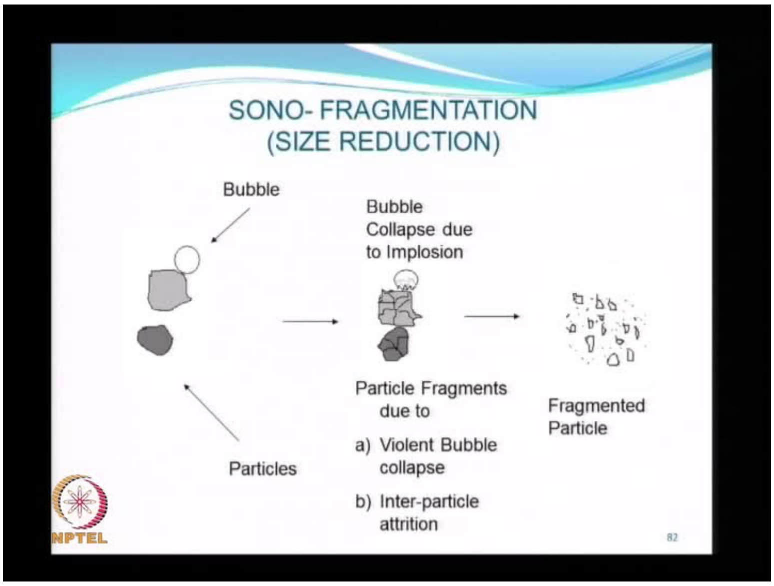

SONO- FRAGMENTATION (SIZE REDUCTION)

Bubble

Particles

Bubble Collapse due to Implosion

Particle Fragments due to
a) Violent Bubble collapse
b) Inter-particle attrition

Fragmented Particle

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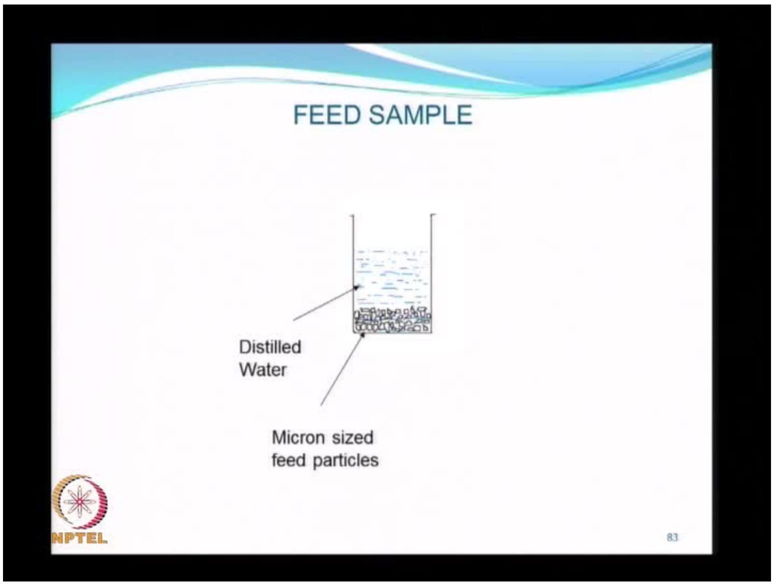

FEED SAMPLE

Distilled Water

Micron sized feed particles

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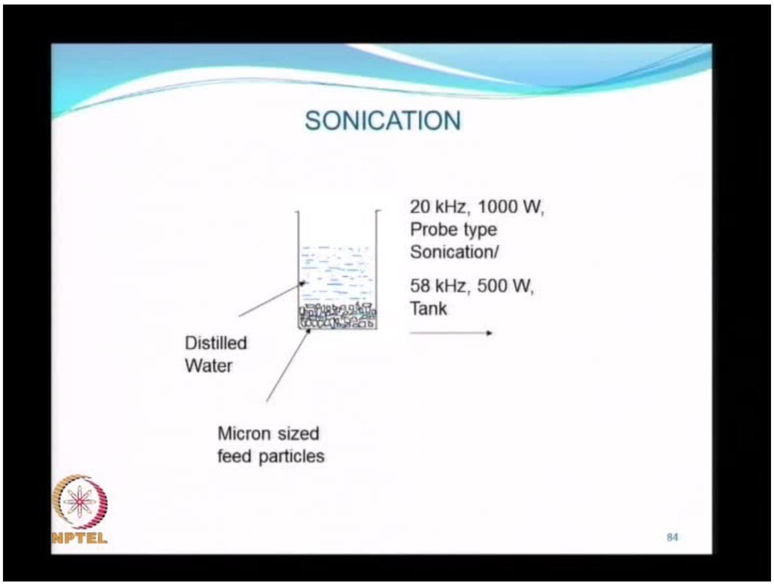

SONICATION

20 kHz, 1000 W,
Probe type
Sonication/

58 kHz, 500 W,
Tank

So, in a laboratory setting, this can be easily simulated by taking a beaker with distilled water, put some micron sized field particles into it and subjected to ultrasound which can be in the form of a tank with bottom mounted transducers or it can be in the form of a horn or a nozzle through which the ultrasonic energy is transmitted.

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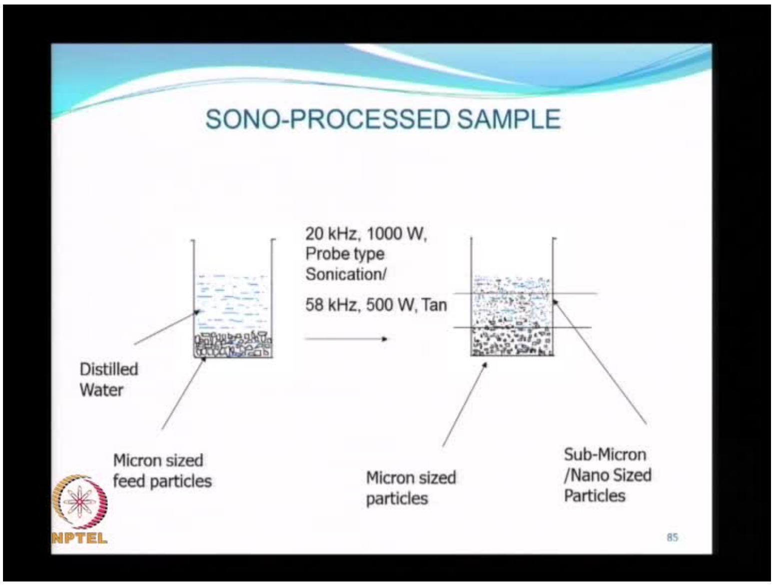

SONO-PROCESSED SAMPLE

20 kHz, 1000 W,
Probe type
Sonication/

58 kHz, 500 W, Tan

And if you look at what happens in the beaker now, you will see that you have essentially three layers that show up. The bottom most layer will contain the un-fragmented particles, mostly the feed particles that have escaped the process of sono-fragmentation. The top most layers will show the fragmented particles that have been reduced from micron size to nano size, because of the sono-fragmentation mechanism.

Then, there will be a middle layer which is a mix of both, it will have a fraction of the particles being the size reduced - nano dimensional particles - and it will have a fraction of the particles being the original micron size particles. So, this gives us a clue that if you were to combine this sono process with kind of a beaker decantation process, you can not only make nano particles, but you can also quickly collect them by a process that is based upon the sedimentation characteristics of the various sized fragments.

If you have a beaker decantation type of setup, you can simply take the top layer off and drain it in to a collector and that will be enriched in nano particles whereas, a bottom most layer can be recycled, so that it can be size reduced further.

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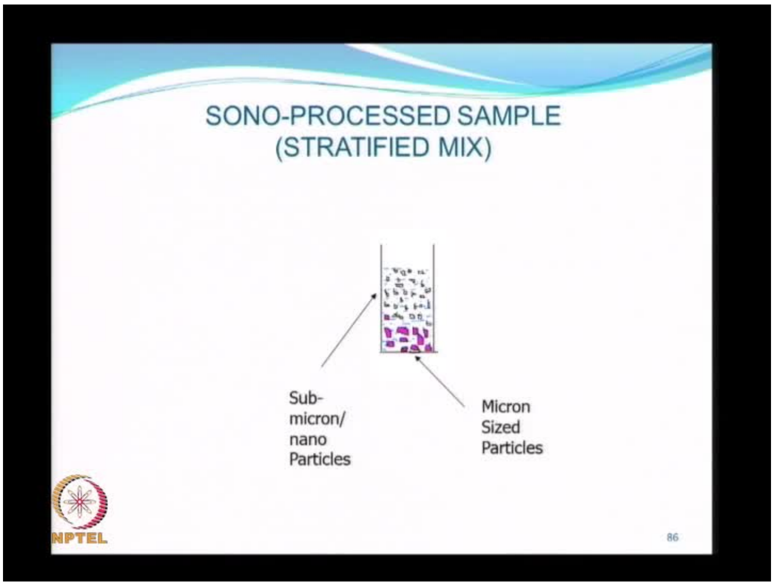

SONO-PROCESSED SAMPLE
(STRATIFIED MIX)

But you can also do is, take this sample which is stratified with three different size distributions and you can actually mix them up again. Now, that may be important in some applications where you need a range of particle sizes rather than a particle size in a particular size range. So, it is very easy to take this stratified layer of sub-micron, micron and nano sized particles and remix them to produce a homogenous suspension.

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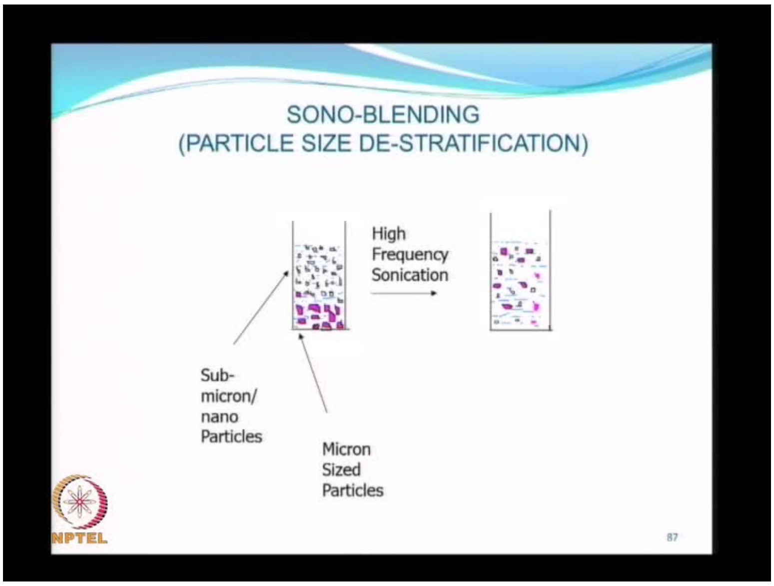

SONO-BLENDING
(PARTICLE SIZE DE-STRATIFICATION)

High
Frequency
Sonication

Sub-
micron/
nano
Particles

Micron
Sized
Particles

So, in this particular case, it is possible to take particles that have been produced by sono blending as this is called an essentially make a uniform composition of nano sized sub-micron sized and micron sized particles, which can then be used to make composites.

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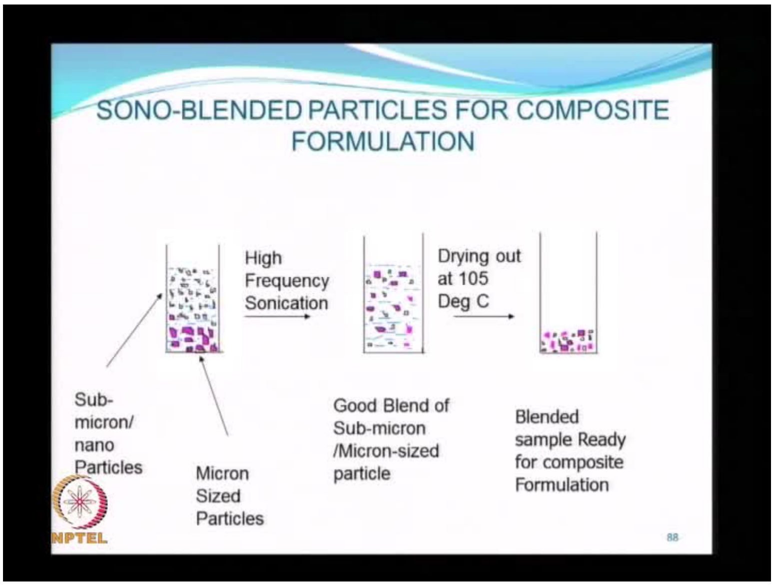


SONO-BLENDED PARTICLES FOR COMPOSITE
FORMULATION

High
Frequency
Sonication

Drying out
at 105
Deg C

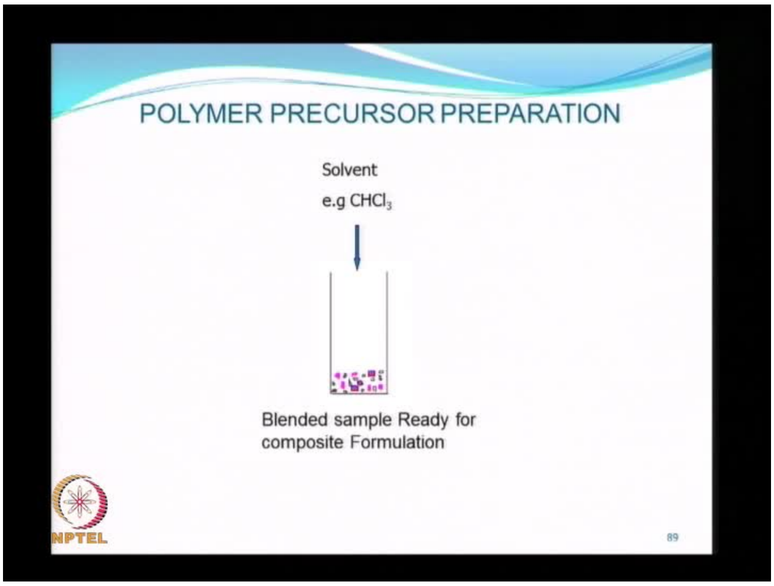
Sub-
micron/
nano
Particles

Micron
Sized
Particles

Good Blend of
Sub-micron
/Micron-sized
particle

Blended
sample Ready
for composite
Formulation

(Refer Slide Time: 42:30)



POLYMER PRECURSOR PREPARATION

Solvent

e.g $CHCl_3$

Blended sample Ready for composite Formulation

One of the major applications of sono technology is not only to synthesize nano particles, but also to incorporate them into polymers and other materials to make composite materials. So, the way that works is, you take this blend of various sized particles, dry them out and keep the blended sample ready to make into composites. The polymer precursor itself has to be prepared by dissolving it in a solvent.

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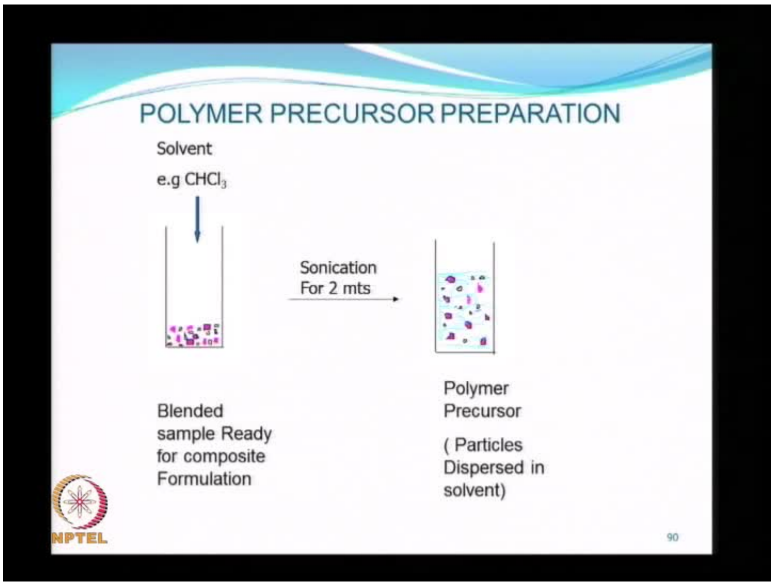

POLYMER PRECURSOR PREPARATION

Solvent

e.g $CHCl_3$

Sonication For 2 mts

Blended sample Ready for composite Formulation

Polymer Precursor

(Particles Dispersed in solvent)

And then, you take the nano materials that you have prepared by your nano your sono-fragmentation process and blend them into the polymer that you have prepared by dissolving in a solvent, and then, you can again use sonication to uniformly mix the particles into the polymer.

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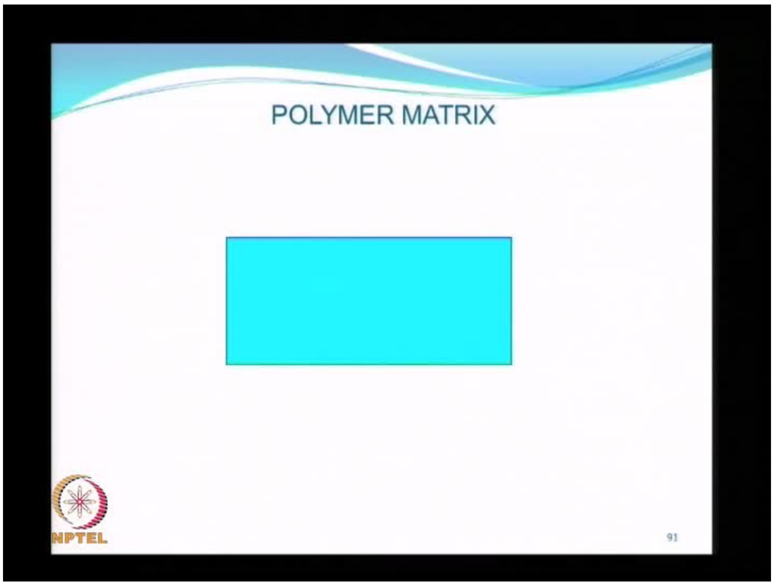

POLYMER MATRIX

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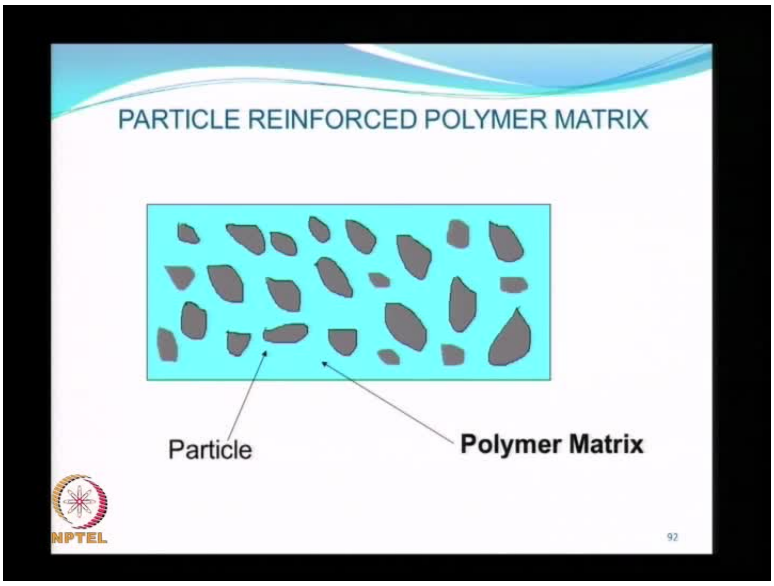

PARTICLE REINFORCED POLYMER MATRIX

And the polymer matrix that you have prepared in this fashion will essentially look like this; you will have the polymer material within which the nano particles are incorporated. Now, there are two important things here; the particles should be non-agglomerated, so they should be dispersed very well, they should also be distributed. We will see later on when we talk about nano particle dispersion that these are two different characteristics, dispersion and distribution. They are both very important in preparing a high quality polymer composite material.

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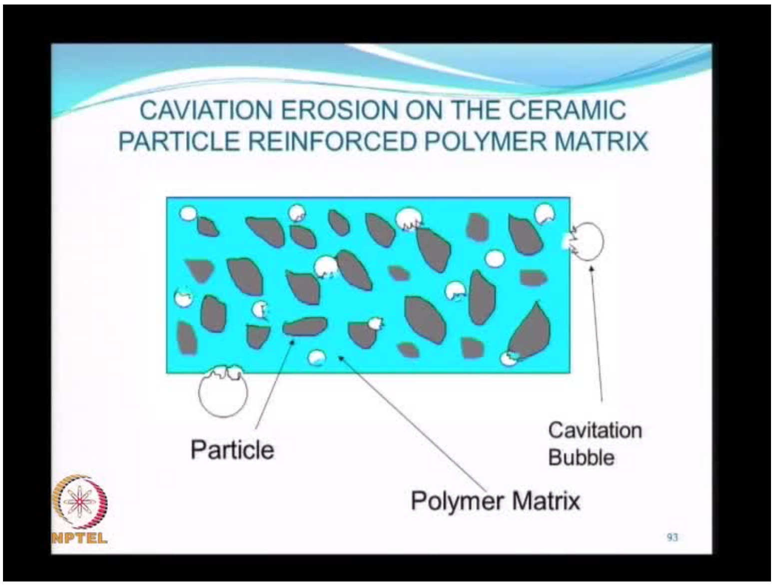

CAVIATION EROSION ON THE CERAMIC PARTICLE REINFORCED POLYMER MATRIX

The strength of these nano composites can also be tested by subjecting them to cavitation erosion. For example, you can take this composite material that you have prepared and expose it to an ultrasonic field and look for weight loss. And as the material becomes stronger, there will be less weight loss due to cavitation erosion. So, ultrasonic processing can be used very effectively to synthesize nano particles, to prepare nano composites and also to test the cavitation resistance or strength of the nano composites.

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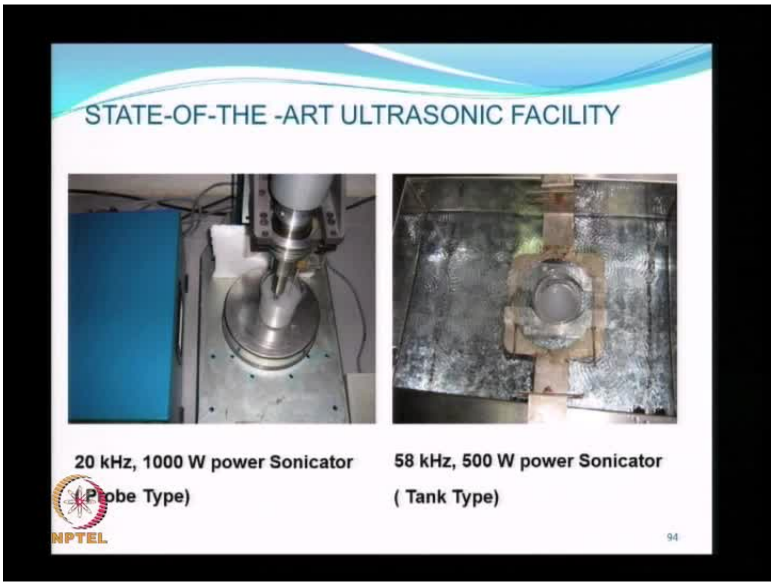

STATE-OF-THE -ART ULTRASONIC FACILITY

20 kHz, 1000 W power Sonicator
(Probe Type)

58 kHz, 500 W power Sonicator
(Tank Type)

In our laboratory, we have some state of the art ultrasonic facilities that we used to make nano particles, as well as the nano composites. You can see our 20 kilo hertz probe type sonicator here on the left hand side and 58 kilo hertz tank type sonicator on the right hand side. On the right hand side picture, if you look down on the water you see that the ultrasonic field is very uniform over the entire surface. That is in fact, the primary advantage of the tank type sono-fragmentation process that you produce very uniform cavitation patterns over the entire liquid whereas, in the probe type sonicator the acoustic field is highly localized. So, you get very high intensities the immediate vicinity of the probe, but as you move farther away from the probe, the energy intensity drops off very rapidly.

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ANALYZERS USED

Sound the analyzers that are used for testing particle compositions and sizes and counts are shown here. The left hand side top picture shows at turbidity meter, you may recall that we discuss this in the context of measuring particle concentrations in suspensions, turbidities are measure of the total scattering intensity of particles in suspension. So, it can be used as a qualitative measure of particle size as well as particle concentration in liquids.

The top picture on the right hand side shows a laser particle counter, which works by the principle of laser scattering which we also discussed in one of the earlier lectures. This particular laser particle counter can count particles in liquids down to 1micron. And at the bottom you have a particle size analyzer, which works by the principle of acoustic attenuation spectroscopy which we also discussed earlier in one of the lectures. So, these are the three instruments that are very widely used in our laboratory as well as the many other laboratories to characterize particles sizes and particle counts in liquid suspensions.

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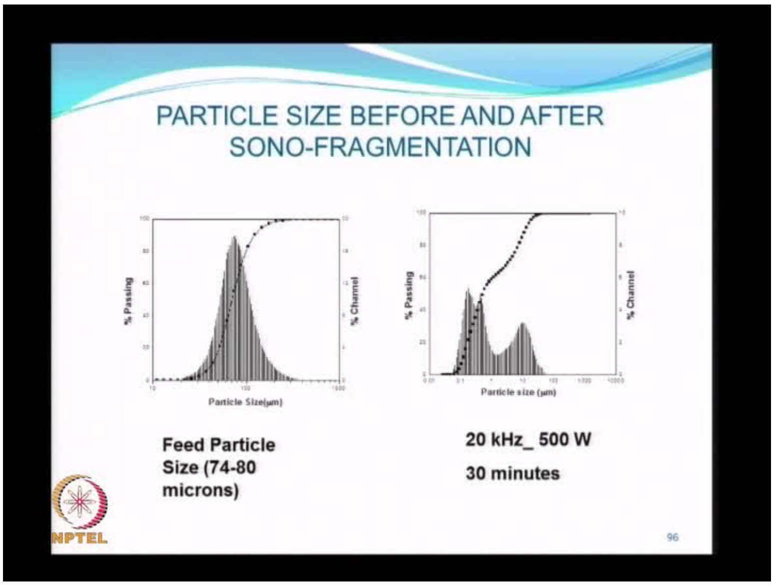
PARTICLE SIZE BEFORE AND AFTER SONO-FRAGMENTATION

Feed Particle Size (74-80 microns)

20 kHz_ 500 W

30 minutes

The data that we will be reviewing here are taken from one or the other of these instruments. So, here we see what happens to feed particles of alumina that are subjected to sono-fragmentation. So, the feed size that shown on the left hand side graph is 74 to 80 microns, when you expose it to 20 kilo hertz ultrasonics at 500 watts for 30 minutes you can see that there is a substantial reduction in size and the particle mean size is now close to 1 micron and you can see, there are substantial fraction of the particles are less than a micron.

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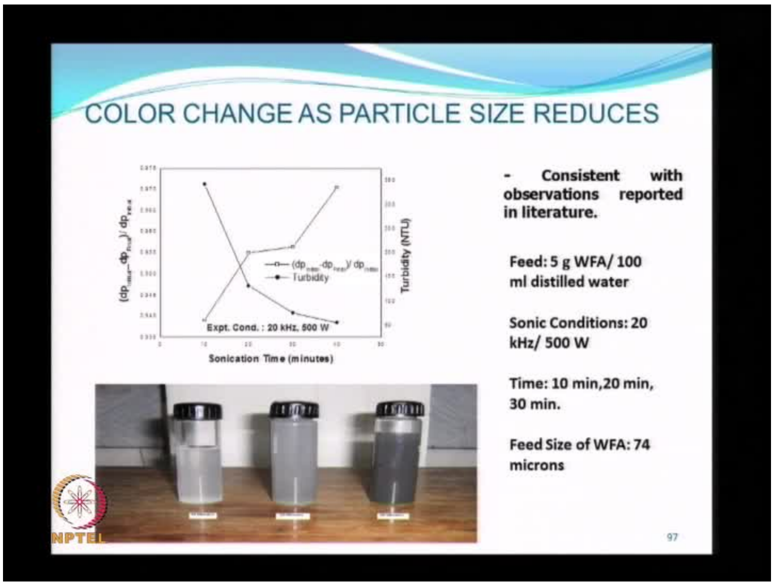
COLOR CHANGE AS PARTICLE SIZE REDUCES

- Consistent with observations reported in literature.

Feed: 5 g WFA/ 100 ml distilled water

Sonic Conditions: 20 kHz/ 500 W

Time: 10 min,20 min, 30 min.

Feed Size of WFA: 74 microns

So, even a fairly short duration sonication is sufficient to make a sizable number of sub-micron particles. Another indicator of size reduction is the color change, you will find that for the same material in this case wide fused alumina, which is being size reduced the color of the suspension changes as particle size decreases, which actually gives us an idea that if you can monitor the turbidity or the color of the suspension quantitatively that can actually be used to track size reduction without having to use more sophisticated technique such as a particle analyzer. So, the graph shows sonication times in minutes, and on the left hand side vertical axis we see the particle size that results after sono-fragmentation and you can see that decreases to a very low value.

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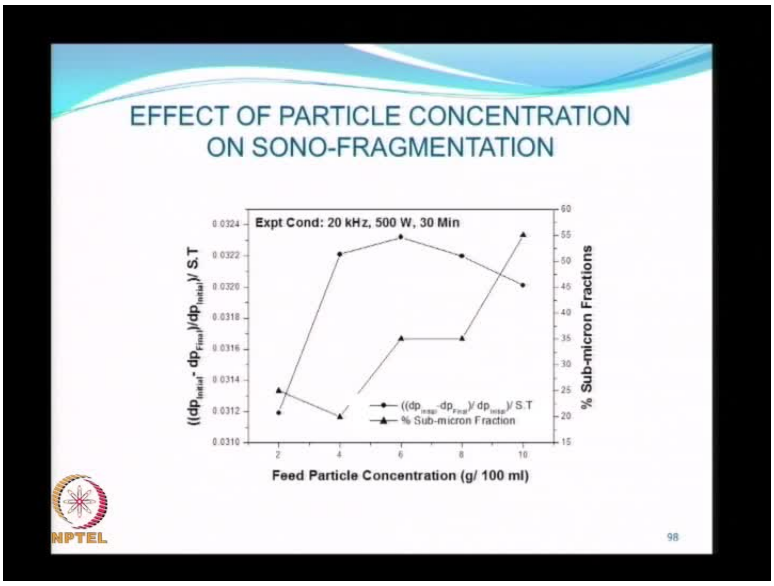

EFFECT OF PARTICLE CONCENTRATION
ON SONO-FRAGMENTATION

On the right hand side, vertical axis that is the data are plotted in terms of turbidity, which are the measure of particle suspension in the liquid and also the particle color of the suspension. And you can see that with sonication time, the color essentially becomes darker and darker, which is indication that we have many, many, more particles now in suspension but of smaller sizes. So, this is an interesting plot that says that color change can actually be correlated to size reduction, when you subject a suspension to sonication in order to achieve size reduction.

Here, we are showing the effect of feed particle concentration on size reduction. The interesting thing here is, that it is actually not a monotonic relationship, the fragmentation rate expression that I showed earlier seem to suggest that, as particle concentration increased the size reduction efficiency will keep increasing.

However, you will see from this figure that is not necessarily the case that is actually an optimum value of particle concentration at which you have the best size reduction efficiency, but if the concentration increases beyond that the size reduction efficiency actually starts to drop and the reasons for that are interesting. And we will pick up the discussion from this point in the next lecture, and we will highlight the influence of feed particle concentration on size reduction efficiency. Are there any questions on what we have talked about today? So, see you at the next lecture.