

The granulometric composition of NC

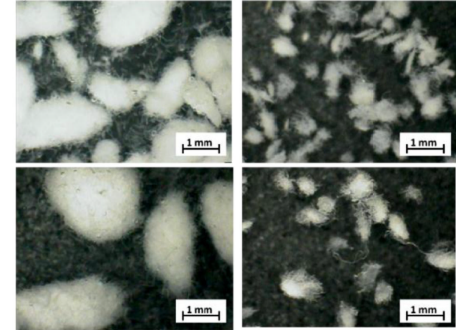
9th International Nitrocellulose Symposium

Birmingham, UK

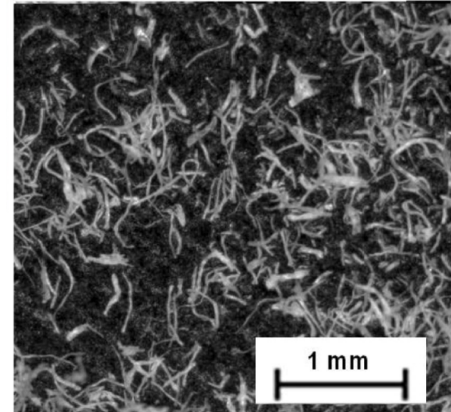
June 2023

Mario Paquet and Ian Levac

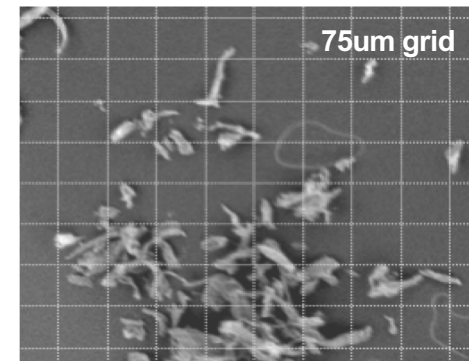
NC Aggregates NC Agglomerates



NC free fibers



NC fines



Introduction

It is well known that several types of granulometric constituents (particles) can be found in NC.

These granulometric constituents can be found in significantly different amounts with consequences depending on the type and relative quantity of constituent present, the manufacturing process and the requirements of the final applications.

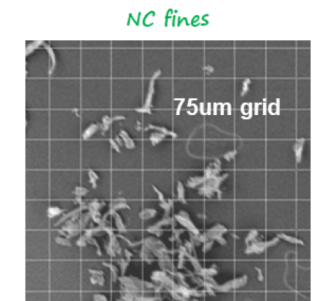
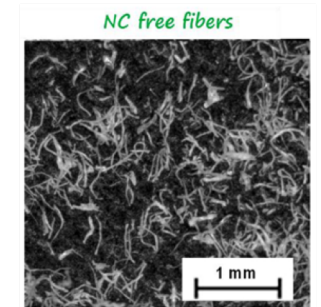
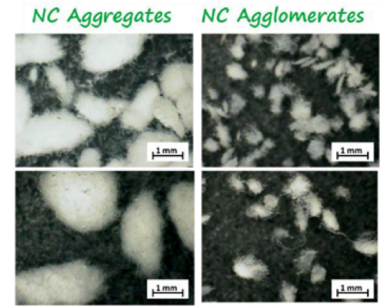
In the older MIL specifications, the only method related to granulometric composition was the fineness test.

A quantification method for agglomerates (agglom) and aggregates (aggreg) was added to the Mil-DTL at the last update (**MIL-DTL-244C 20 May 2014**). The quantification is made by counter-flow elutriation, which is a streaming fluid classification method.

A method for quantifying the fines (which are composed of fiber fragments and dust) was presented in a poster at the NC symposium in Montreal in 2016.

This more conclusive presentation integrates all granulometric aspect of NC by the introduction of the concept of granulometric composition. It offers definitions and descriptions (shape and size) of the various granulometric components which can potentially be present in NC.

It also proposes a comprehensive analytical strategy and presents analytical methods for quantification.



Granulometric composition... why do we care?

Determination of the typical granulometric composition of NC is important when:

- Changing the type of cellulose, the processing conditions and the source of raw material.
- Acquiring NC from multiple suppliers.
- Propellant is to be used for larger caliber applications, for higher precision, for challenging performance (aging, extreme temperature,...).
- Investigating new propellant applications.

Complete gravimetric composition of NC is not necessarily required for QA lot certification.

For an NC manufacturing process based on using free fibers from the start (baled cotton), the presence of agglomerates is always very low and requires less monitoring.

For an NC process based on cut sheet nitration, some methods may be required at process and/or at final certification to ensure that refining is was correctly applied

- too much refining = excess fines + short fibers
- too low refining = excess agglomerates + not many free fibers



Propellant in gun

Propellant grains



Propellant in mixer

NC in propellant



Types of constituents and comparative sizes

For the most part, the particles composing the NC are in the form of fibers. However other types of particles are always present.

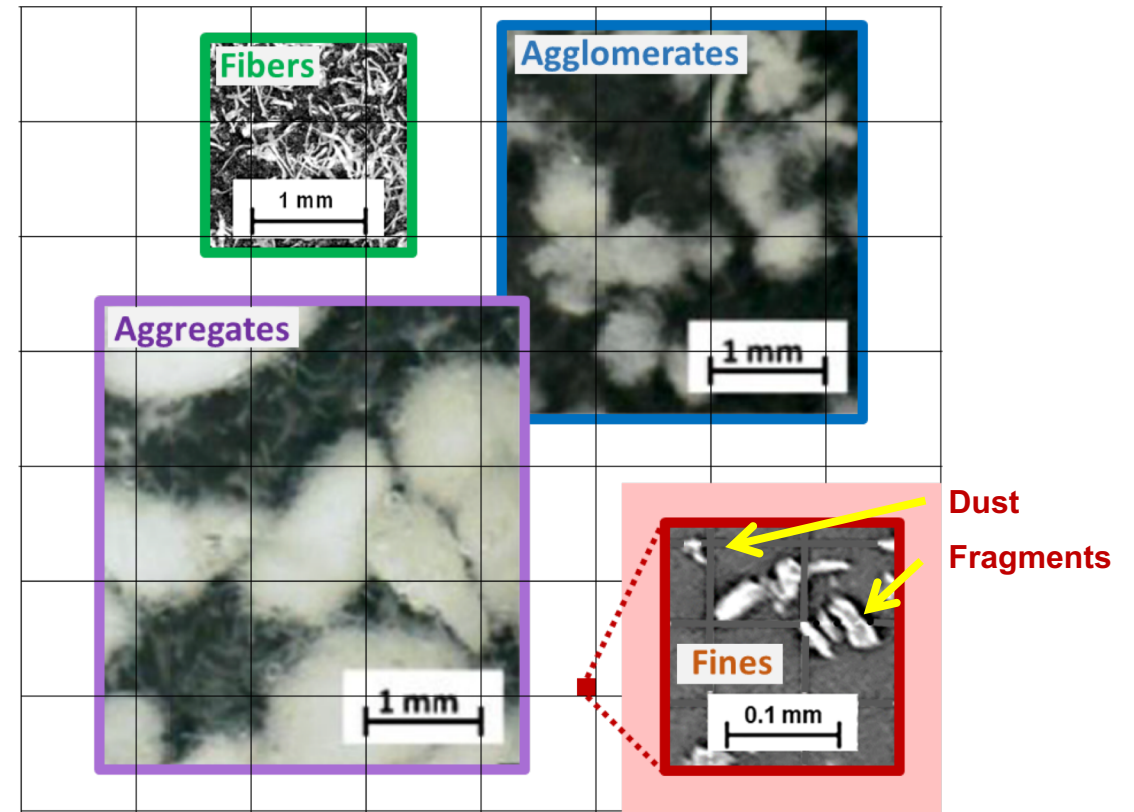
A granulometric constituent is a group of particles having similar shape and similar range in size.

The four types are identified as:

- Aggregates (*aggreg*)
- Agglomerates (*agglom*)
- Fibers
- Fines (*fragments and dust particles*)

The granulometric composition often cannot be ascertained by using only one measurement technique and/or one mathematical model.

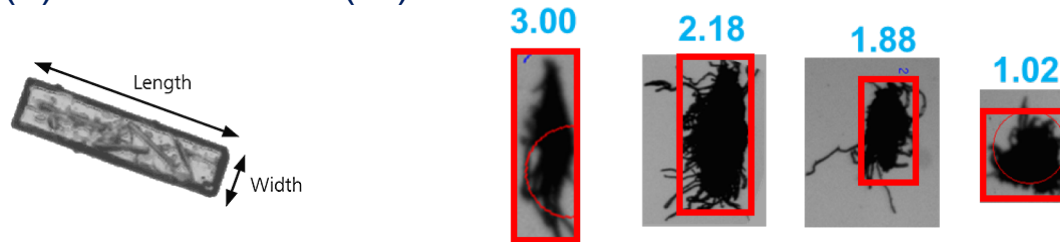
Comparing the relative size of granulometric components that may be found in NC



Typical sizes and shapes

There are several ways to define the basic shape of irregular particles.

One simple way is the description of irregular NC particles in 2 dimensions (2D) using the following two linear dimensions obtained from a bordering rectangle: the Length (L) and the Width (W).



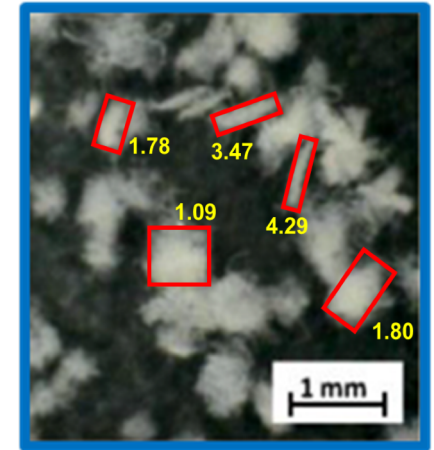
The **Aspect Ratio (AR)** is given by $AR = L / W$

It provides a quick estimate of the general shape of NC particles

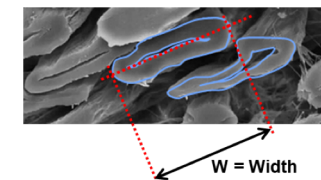
- If the aspect ratios are near 1, the shape is somewhat spherical or cubic.
- If the aspect ratios are > 1 , the shape can be rectangular, ellipsoid or short cylindrical.
- If the aspect ratios are $\gg 1$, the shape can be:
 - cylindrical or tubular (hollow cylinder) when the Width (W) equal to the Diameter (D), or
 - ribbon like (compressed tubular particles) when the Width (W) is equal to about $1.6(D)$

Since: Circumference = $\pi D = 2 W$ Thus: $W \cong 1.6(D)$

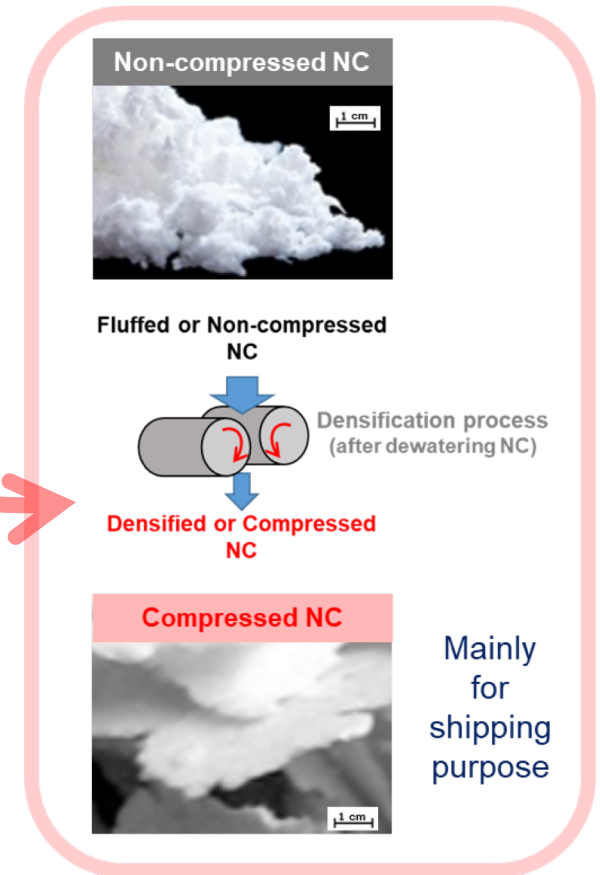
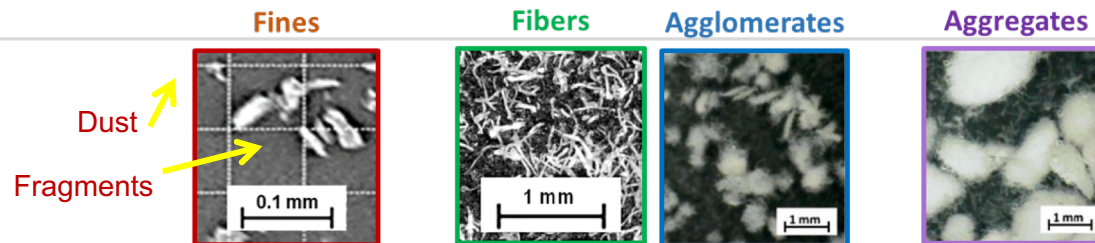
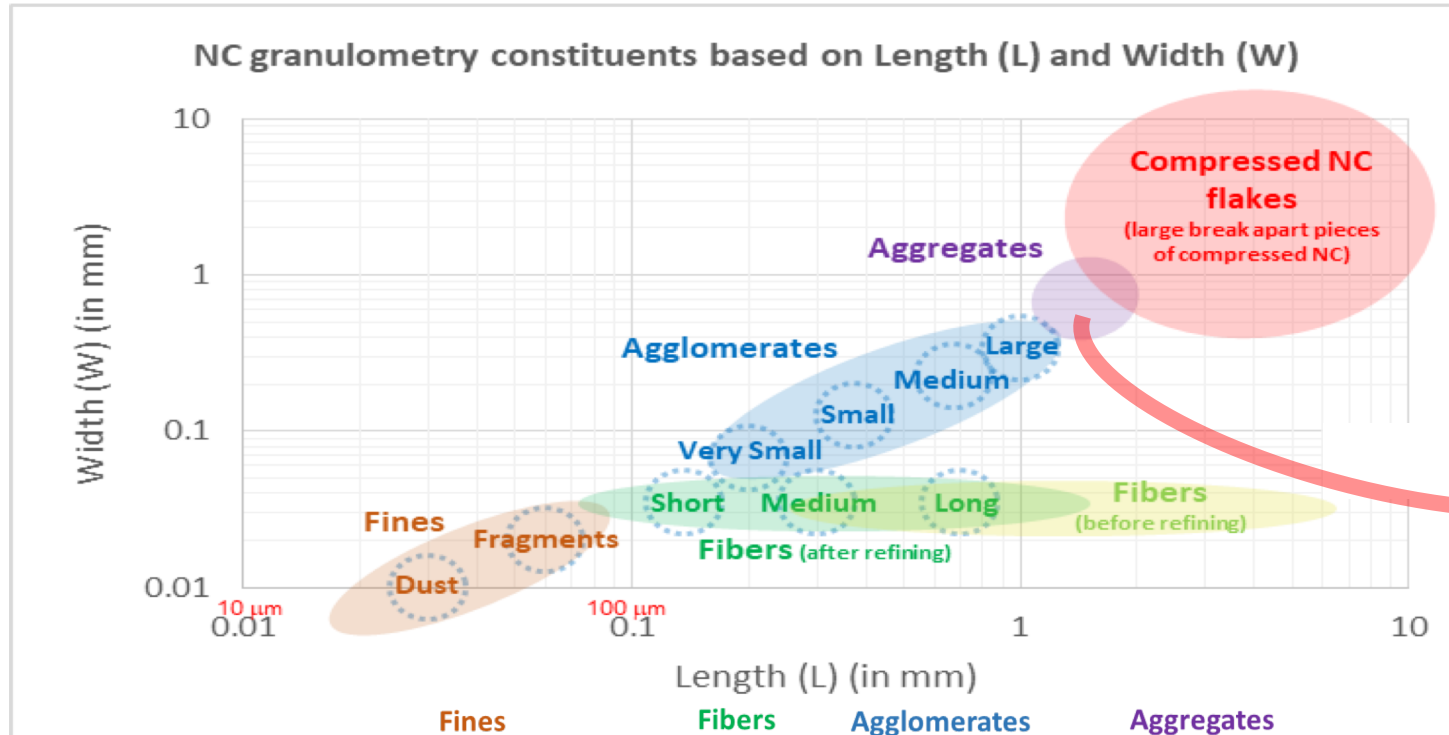
Agglomerates



L/D is > 1
Typical 1 to 5



Typical sizes and shapes



Used mainly for very high solvent formulations like spherical propellants

Granulometric components in the NC process

Aggregates (rectangular/ellipsoid) (L) =
 $>> 850 \mu\text{m}$

Agglomerates (rectangular/ellipsoid) (L) =

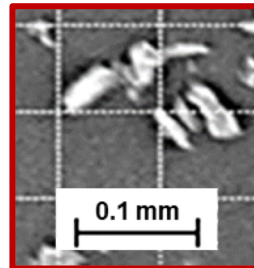
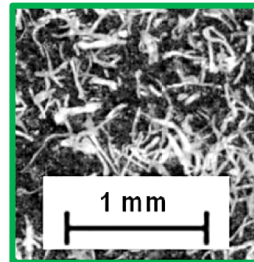
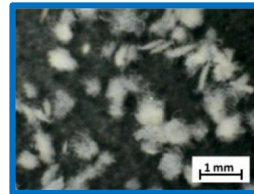
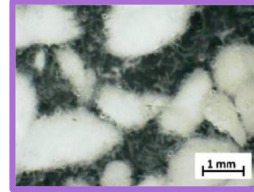
Large $> 850 \mu\text{m}$
 Medium $500 - 850 \mu\text{m}$
 Small $250 - 500 \mu\text{m}$
 Very small $150 - 250 \mu\text{m}$

Fibers (cylindrical hollow = tubular) (L) =

Long $> 400 \mu\text{m}$
 Medium $200 - 400 \mu\text{m}$
 Short $75 - 200 \mu\text{m}$

Fines (rectangular/ellipsoid/spherical) (L) =

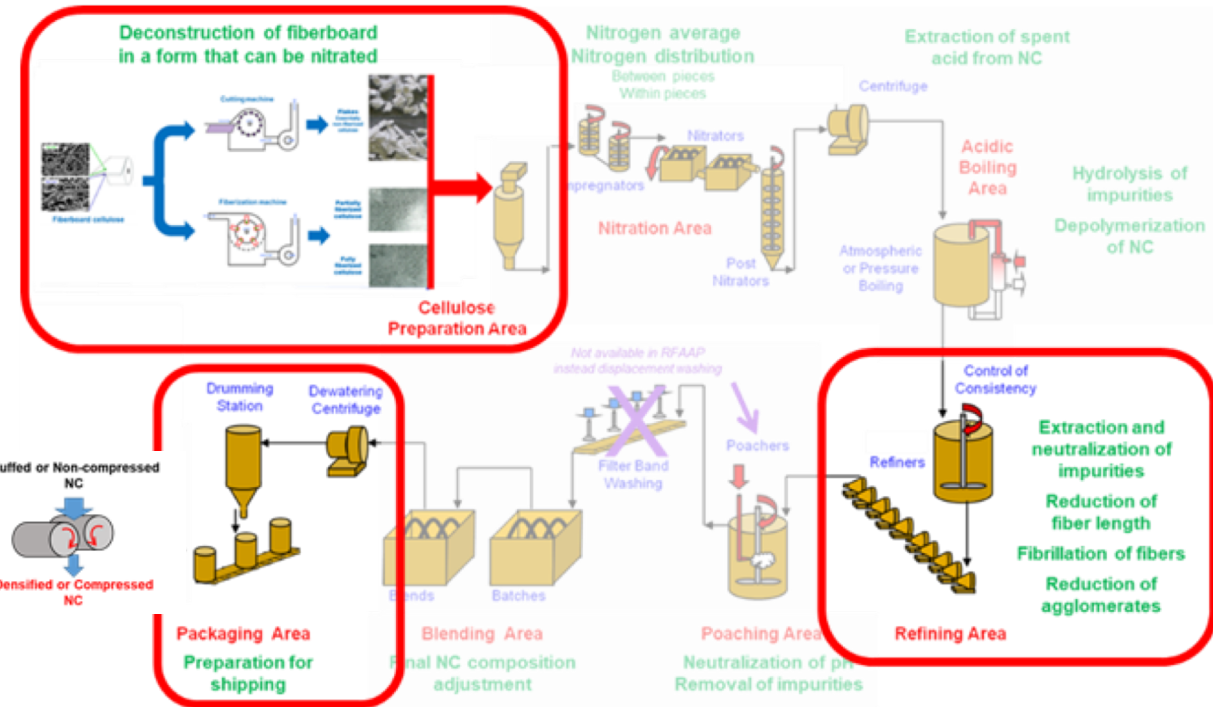
Fragments $20 - 75 \mu\text{m}$
 Dust $< 20 \mu\text{m}$



Content, Size and Density of Agglomerates

Content of Fibers

Content in Fines



Content and Size of Aggregates

Content in Densification Chunks

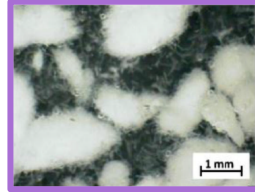
Content and Size of Agglomerates

Content and Size of Fibers

Content in Fines

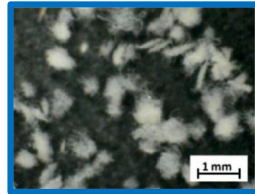
Typical weight contents that can be observed (% W/W)

Aggregates (rectangular/ellipsoid) (L) =
 >> 850 μm



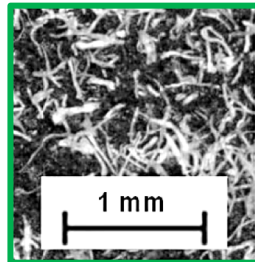
Between
0 % and 5 %

Agglomerates (rectangular/ellipsoid) (L) =
Large > 850 μm
Medium 500 - 850 μm
Small 250 - 500 μm
Very small 150 - 250 μm



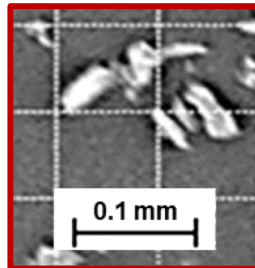
Between
0 % and 65 %

Fibers (cylindrical hollow = tubular) (L) =
Long > 400 μm
Medium 200 - 400 μm
Short 75 - 200 μm



Between
25 % and 97 %

Fines (rectangular/ellipsoid/spherical) (L) =
Fragments 20 - 75 μm
Dust < 20 μm



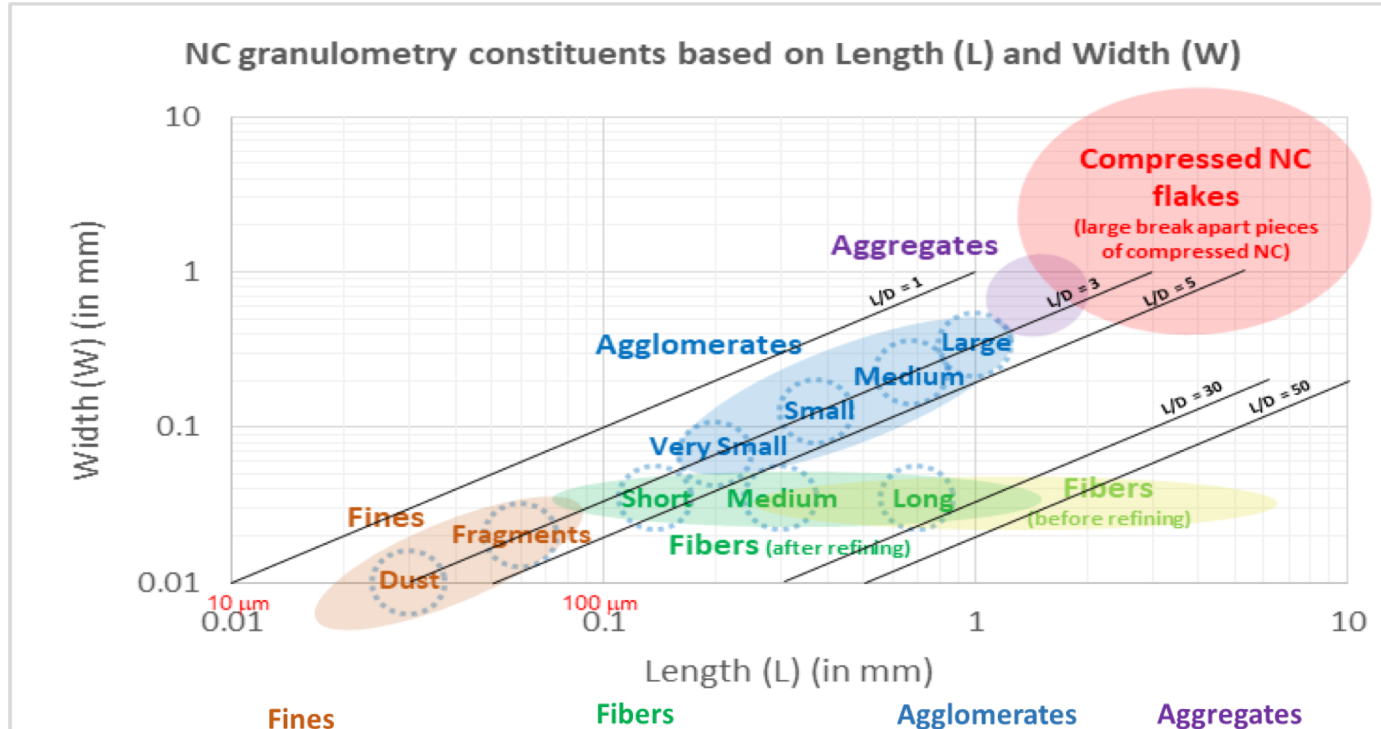
Between
3 and 10 %

How to express the content in constituents for a material like this?

Weight content is usually preferred.
A count number is useless except if a weight can be associated to the count.

Meaningful quantitative assessment requires different analytical approaches because there are 4 types of constituents having very different shapes, sizes and densities.

Typical L/D values for the granulometric components

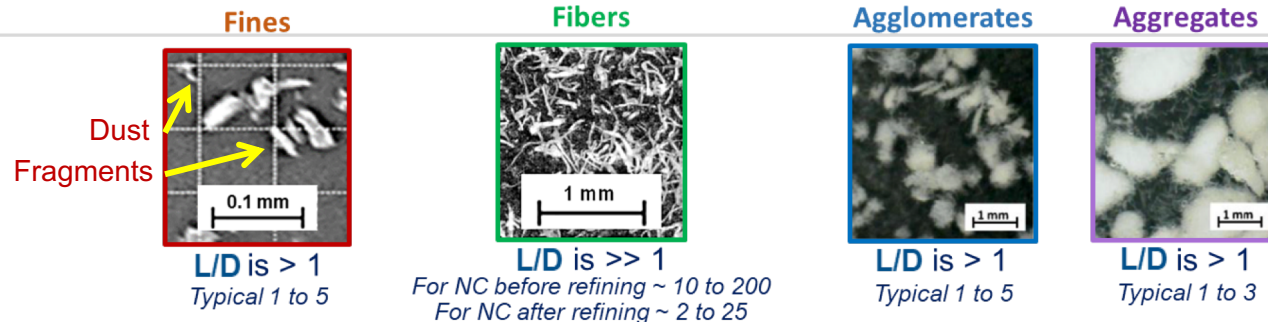


Fines / Agglomerates / Aggregates have similar shape (with L/D near 1) but very different densities.

The density of fines is about 1.66 g/cc, which is that of the NC fiber wall.

However, the density of aggreg and agglom are not constant and cannot be predicted (compressed or fused fibers with various degree of compression).

Fibers are very different, with $L/D \gg 1$. Density of fiber wall is about 1.66 g/cc but the wall thickness and fiber diameter are not specifically predictable from one fiber to the next.



Comparing Length (L) to falling velocity in water

Aggregates (L) =
>> 850 μm

Agglomerates (L) =
Large > 850 μm
Medium 500 - 850 μm
Small 250 - 500 μm
Very small 150 - 250 μm

Fibers (L) =
Long > 400 μm
Medium 200 - 400 μm
Short 75 - 200 μm

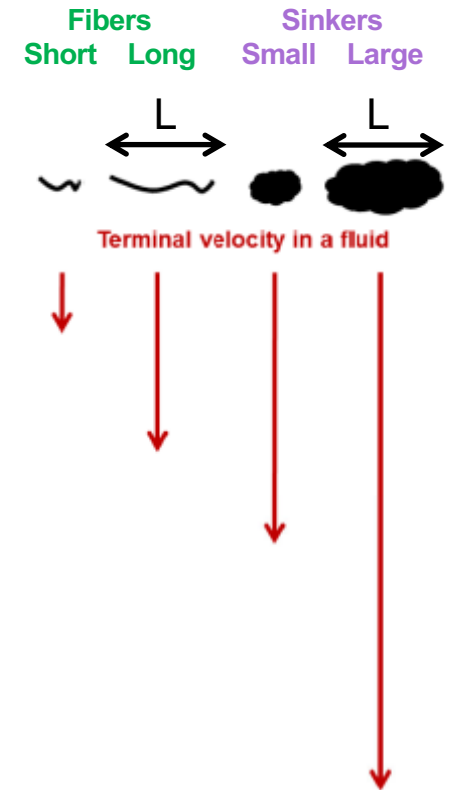
Fines (L) =
Fragments 20 - 75 μm
Dust < 20 μm

Particles in a fluid settle due to gravity acting on the particle, against the buoyancy of water and other drag forces acting against the settling particles.

This relationship is expressed by Stokes' law, which is valid only for particles settling under conditions of terminal velocity and non-turbulent flow.

The terminal velocity is reached very rapidly and in a very short travel distance.

Very fine particles below 10 μm , will stay suspended for extremely long period of time. Below 0.5 μm , Brownian motion will tend to keep the fines suspended almost indefinitely.



Comparing Length (L) to falling velocity in water

Sinkers (fast falling velocities constituents)

Aggregates (L)

>>850 μm >150 cm/min

Agglomerates (L)

Large	> 850 μm	>75 cm/min
Medium	500 - 850 μm	30 - 75 cm/min
Small	250 - 500 μm	9 - 30 cm/min
Very small	150 - 250 μm	

..... Threshold velocity
9 cm/min

Fibers (slow falling velocities constituents)

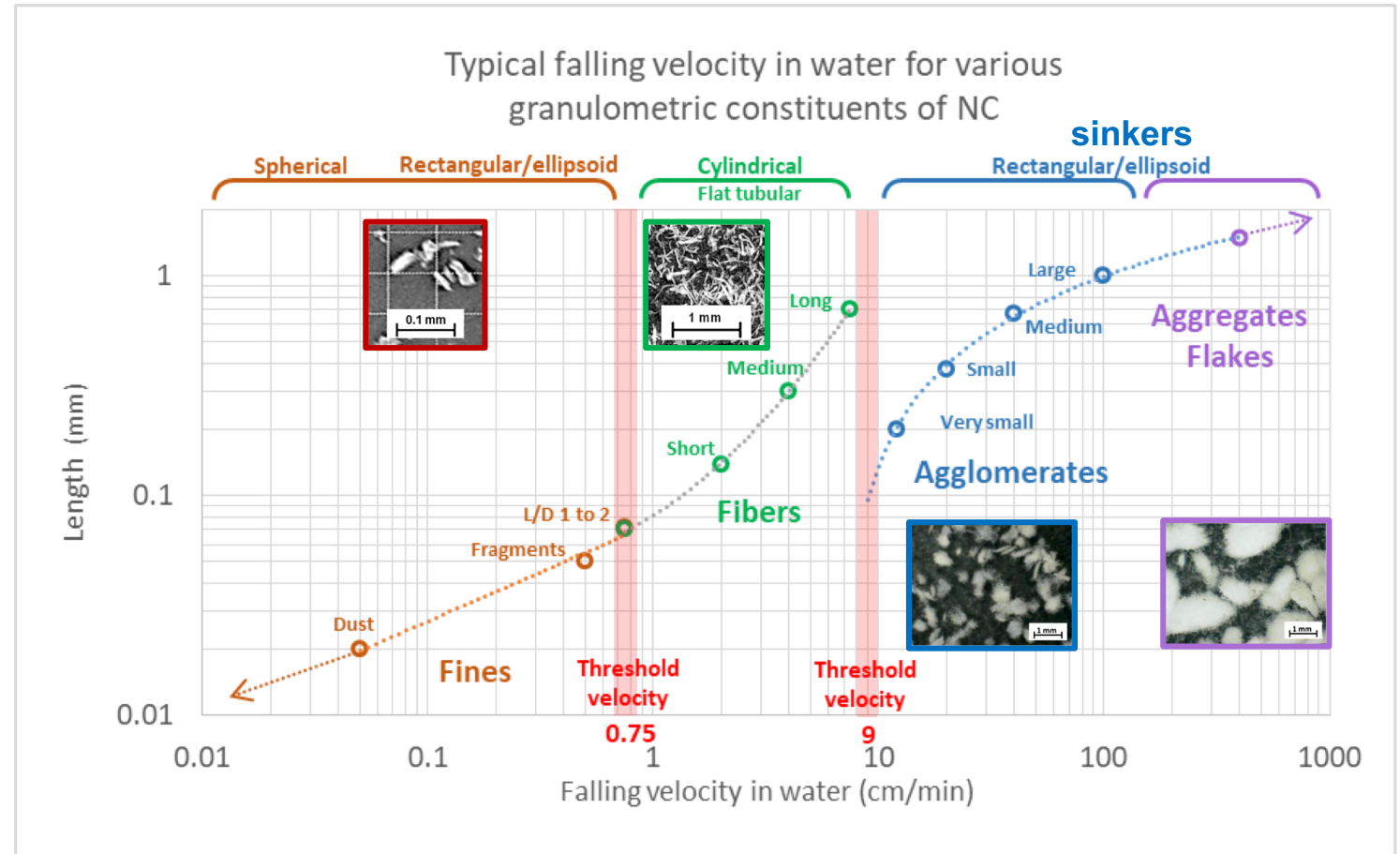
Long	> 400 μm	5 - 9 cm/min
Medium	200 - 400 μm	0.75 - 5 cm/min
Short	75 - 200 μm	

..... Threshold velocity
0.75 cm/min

Fines (very slow falling velocities constituents)

Fragments	20 - 75 μm	0.1-0.75 cm/min
Dust	< 20 μm	< 0.10 cm/min

Using the falling velocity, the granulometric composition is divided in 3 groups of constituents: the **fines**, the **free fibers** and the **sinkers**



Main analytical methods for quantification

Sinkers (fast falling velocities constituents)

Aggregates (L)

>>850 μm >150 cm/min

Agglomerates (L)

Large	> 850 μm	>75 cm/min
Medium	500 - 850 μm	30 - 75 cm/min
Small	250 - 500 μm	9 - 30 cm/min
Very small	150 - 250 μm	

..... Threshold velocity
9 cm/min

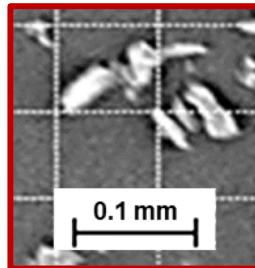
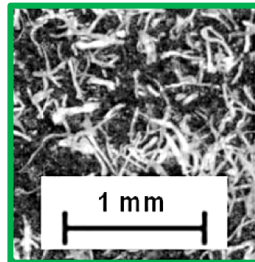
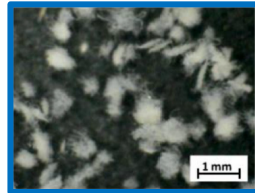
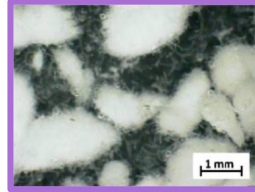
Fibers (slow falling velocities constituents)

Long	> 400 μm	5 - 9 cm/min
Medium	200 - 400 μm	0.75 - 5 cm/min
Short	75 - 200 μm	

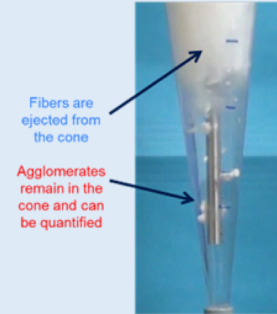
..... Threshold velocity
0.75 cm/min

Fines (very slow falling velocities constituents)

Fragments	20 - 75 μm	0.1-0.75 cm/min
Dust	< 20 μm	< 0.10 cm/min

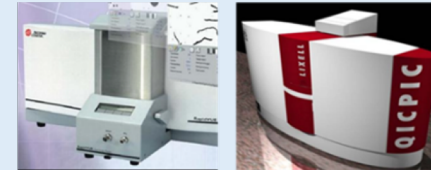


Counter-flow elutriation



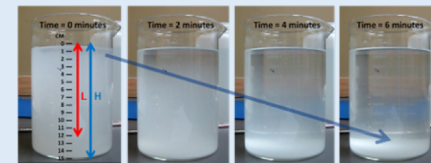
Primary methods to obtain the % by weight content of
Aggregates,
Agglomerates,
Free fibers

Image analysis



Main method to obtain the fiber length distribution and the average fiber length L_w .

Gravitational sedimentation (repeated decanting method)



Main method to obtain the % by weight content of fines.

Main analytical methods for quantification: The Counter-Flow Elutriation method

Sinkers (fast falling velocities constituents)

Aggregates (L)

>>850 μm >150 cm/min

Agglomerates (L)

Large	> 850 μm	>75 cm/min
Medium	500 - 850 μm	30 - 75 cm/min
Small	250 - 500 μm	9 - 30 cm/min
Very small	150 - 250 μm	

Threshold velocity

9 cm/min

Fibers (slow falling velocities constituents)

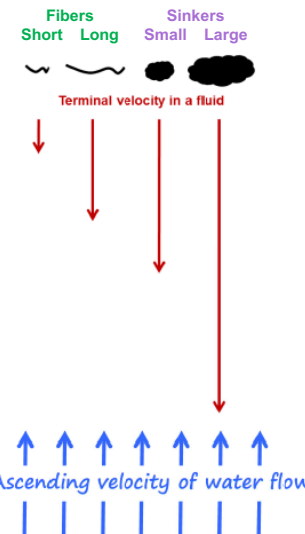
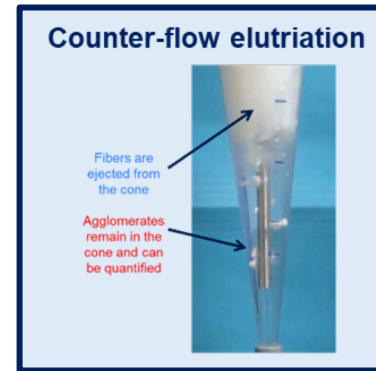
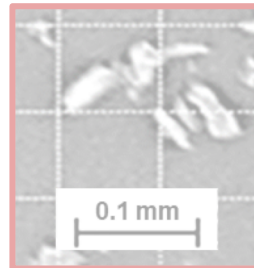
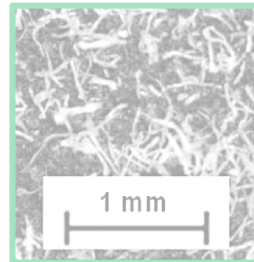
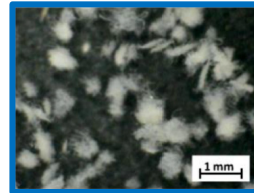
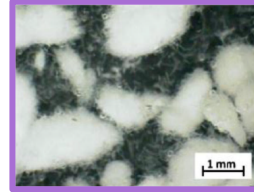
Long	> 400 μm	5 - 9 cm/min
Medium	200 - 400 μm	0.75 - 5 cm/min
Short	75 - 200 μm	

Threshold velocity

0.75 cm/min

Fines (very slow falling velocities constituents)

Fragments	20 - 75 μm	0.1-0.75 cm/min
Dust	< 20 μm	< 0.10 cm/min



-Using a Imhoff sedimentation cone, a stable ascending velocity gradient of water is created by feeding water from the bottom of the cone.

-Granulometric components falling in water quickly reach the height in the cone equivalent to their terminal falling velocity, causing separation to occur.

-The fractions can thus be separated for quantification.

-Only the fibers and sinkers fractions can be separated by this method.

-The sinkers (agglom and aggreg) left over are filtered in a prepared crucible to obtain the % by weight of sinkers in the NC.

Main analytical methods for quantification: The Counter-Flow Elutriation and **Sedimentation** methods

Sinkers (fast falling velocities constituents)

Aggregates (L)

>>850 μm >150 cm/min

Agglomerates (L)

Large	> 850 μm	>75 cm/min
Medium	500 - 850 μm	30 - 75 cm/min
Small	250 - 500 μm	} 9 - 30 cm/min
Very small	150 - 250 μm	

..... Threshold velocity
9 cm/min

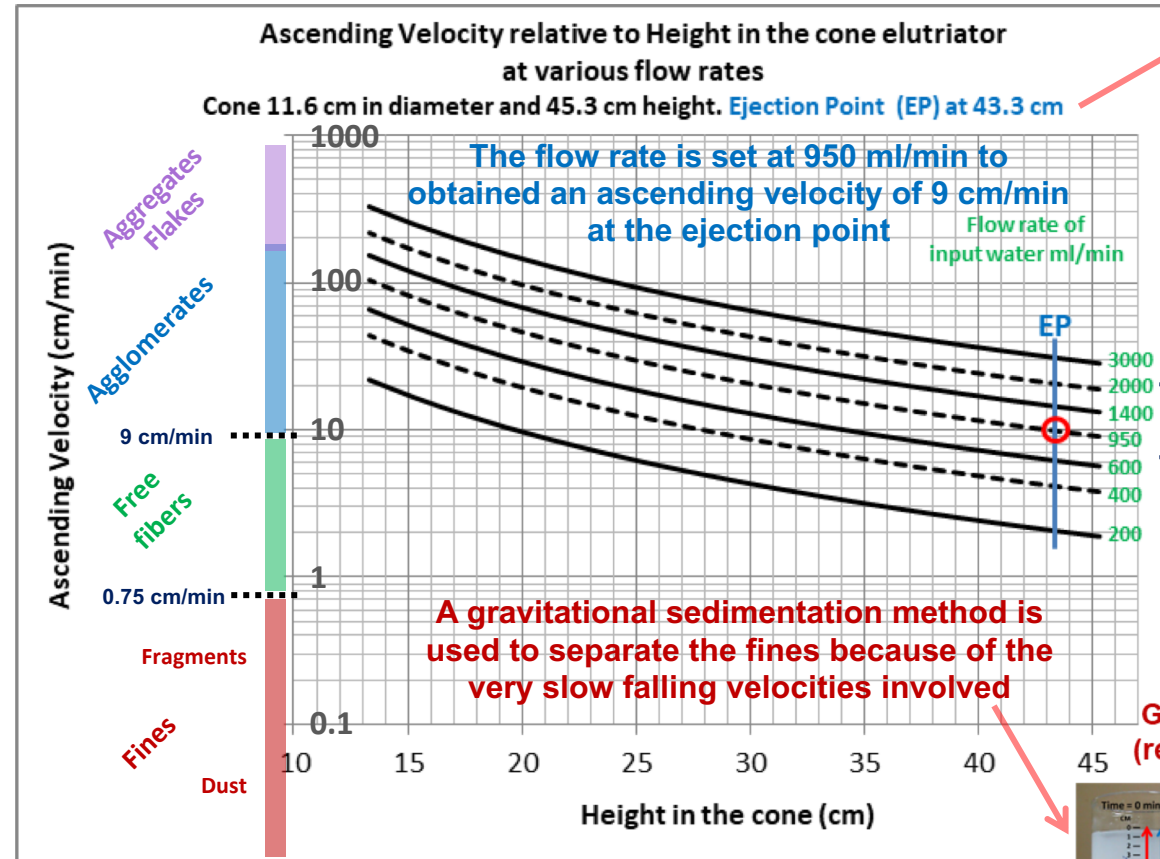
Fibers (slow falling velocities constituents)

Long	> 400 μm	5 - 9 cm/min
Medium	200 - 400 μm	} 0.75 - 5 cm/min
Short	75 - 200 μm	

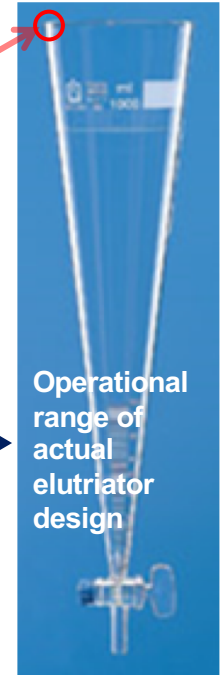
..... Threshold velocity
0.75 cm/min

Fines (very slow falling velocities constituents)

Fragments	20 - 75 μm	0.1-0.75 cm/min
Dust	< 20 μm	< 0.10 cm/min

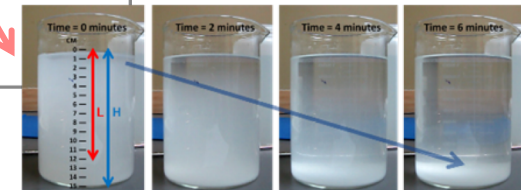


Counter-flow elutriation

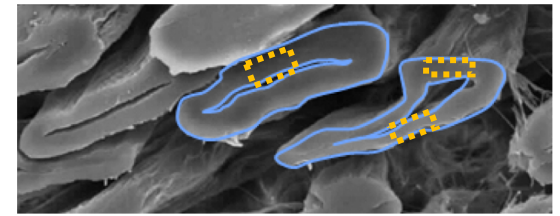


Operational range of actual elutriator design

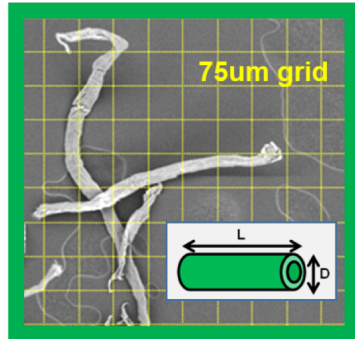
Gravitational sedimentation (repeated decanting method)



Fibers as Flat Tubular Cylinder (Hollow Cylinder)



NC fibers



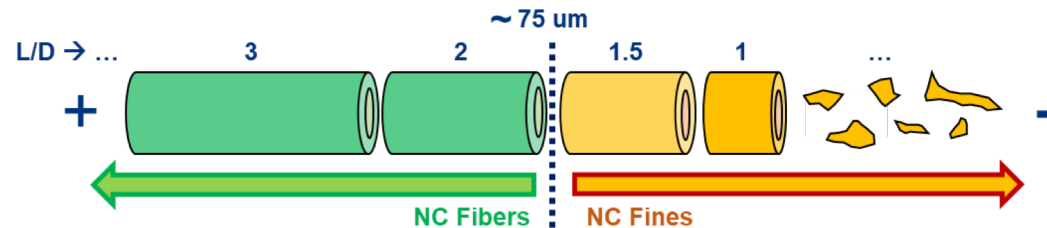
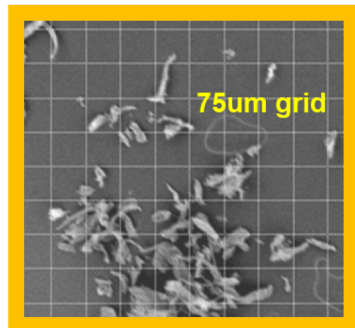
Cellulose fibers, typical diameter (D) between 25-45 μm
(average 35 μm)

NC fibers, typical D between 30-45 μm due to nitration swelling
(average about 37.5 μm)

To be considered a fiber, the particle must have a L/D of 2 or more.

Since average D is ~ 37.5 μm , the threshold length is set at 75 μm
(or as close as possible)

NC fines (fragments / dust)



NC fibers (long + mid + short) are
above the length of about 75 μm

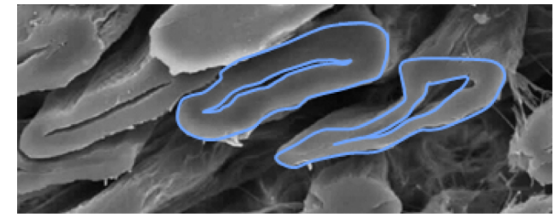
Fines (fragments + dust) are below
the length of about 75 μm

Type of wood	Typical		
	External Diameter μm	Wall Thickness μm	Ratio Ext Dia / Wall Thick
Douglas Fir	40	4.0	10
Hemlock	40	2.5	16
Spruce/Pine	30	2.0	15
Western Red Cedar	30	1.5	20
White Spruce	30	2.0	15
Lodgepole Pine	30	2.0	15
Alpine Fir	35	2.0	18
Southern Pine	45	5.0	9
Scandinavian Pine	35	3.0	12
Total Average	35	2.7	14.4

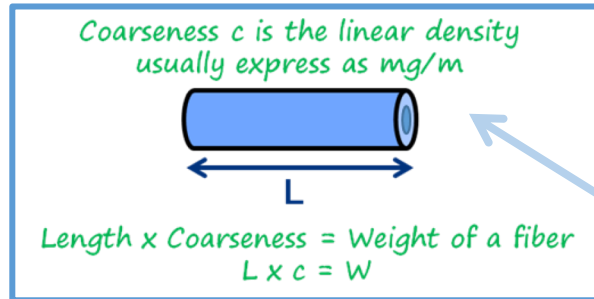
The physical properties of NC depend more on the mass of the fractions than on the *number* of particles of the fractions.
By itself, knowing the length of a fibers does not provide information about its mass.

To estimate the *average length based on mass*, assumptions specific to NC are required

From Number distribution to Weight distribution



The number average length (L_n) ...when a dust particle (a pebble) and a large fiber (a bus) each count for one.



$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i}$$

To estimate the average length (L_n) based on mass, information is required on the **coarseness** of fibers of various length.

The average fiber length L_w (also called the Length Weighted Average Length)

$$L_w = \frac{\sum_{i=1}^n N_i L_i^2 c_i}{\sum_{i=1}^n N_i L_i c_i}$$

At this point, an assumption must be made about coarseness c_i

$$L_w = \frac{\sum_{i=1}^n N_i L_i^2 \cancel{c_i}}{\sum_{i=1}^n N_i L_i \cancel{c_i}} = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i}$$

Usually labeled:

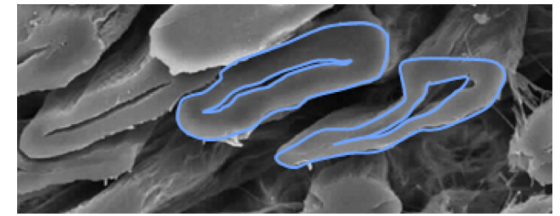
$L_L \rightarrow$ Length Weighted Average Length
or $L_{WAFL} \rightarrow$ Length Weighted Average Fiber Length

For intact cellulose fibers, the coarseness typically increases somewhat with fibers length.
Cellulose fibers can be several mm long.

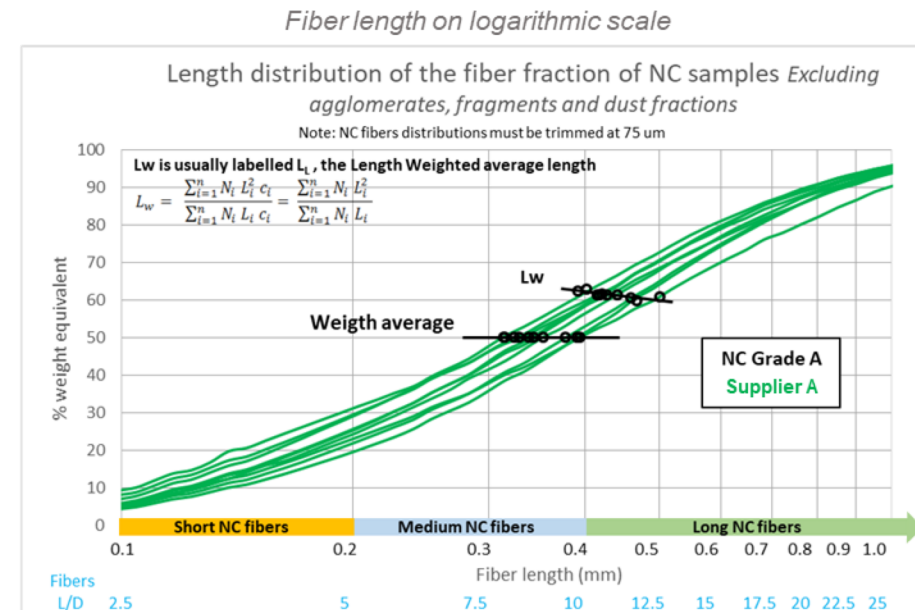
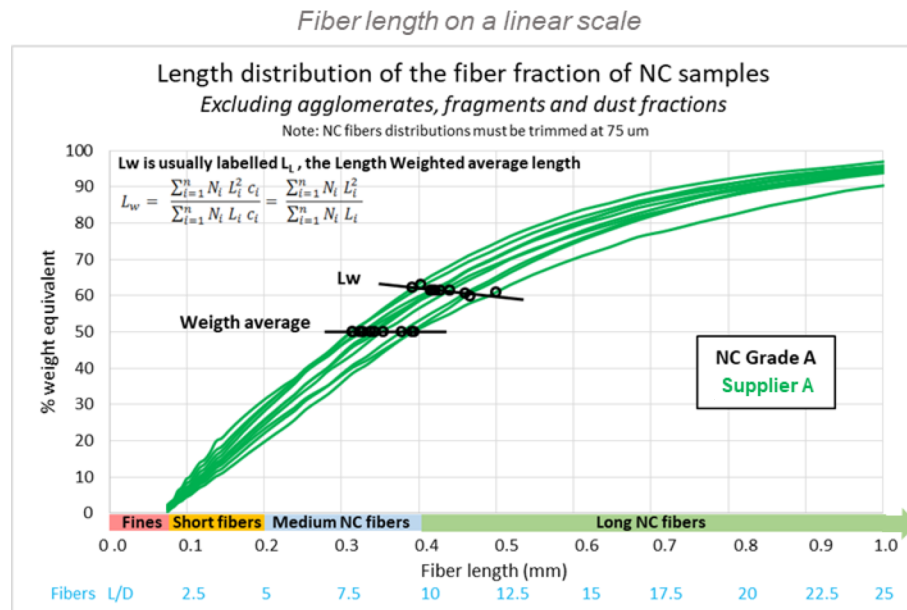
For NC after refining, long fibers are cut down to much shorter fibers from several mm long down to between 0.1-1 mm (typically 90% w/w are less than 1 mm long).
These shorts fibers populate the lower size classes, leveling the average coarseness to nearly a constant value.
Since the coarseness c is nearly constant, it cancels out...

Nitrocellulose fiber length distribution

Example: Grade A (from wood pulp)



Graphs of Grade A lots, trimmed at 75µm and showing the L_w and 50% w/w average



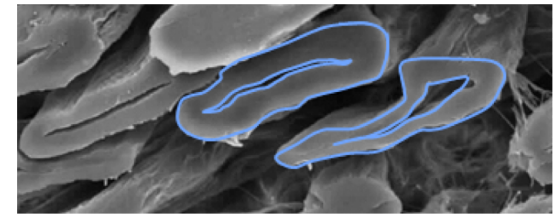
Beware:

L_w , the Length Weighted Average Length **is not the same as** the Length at 50% w/w (length at average weight)

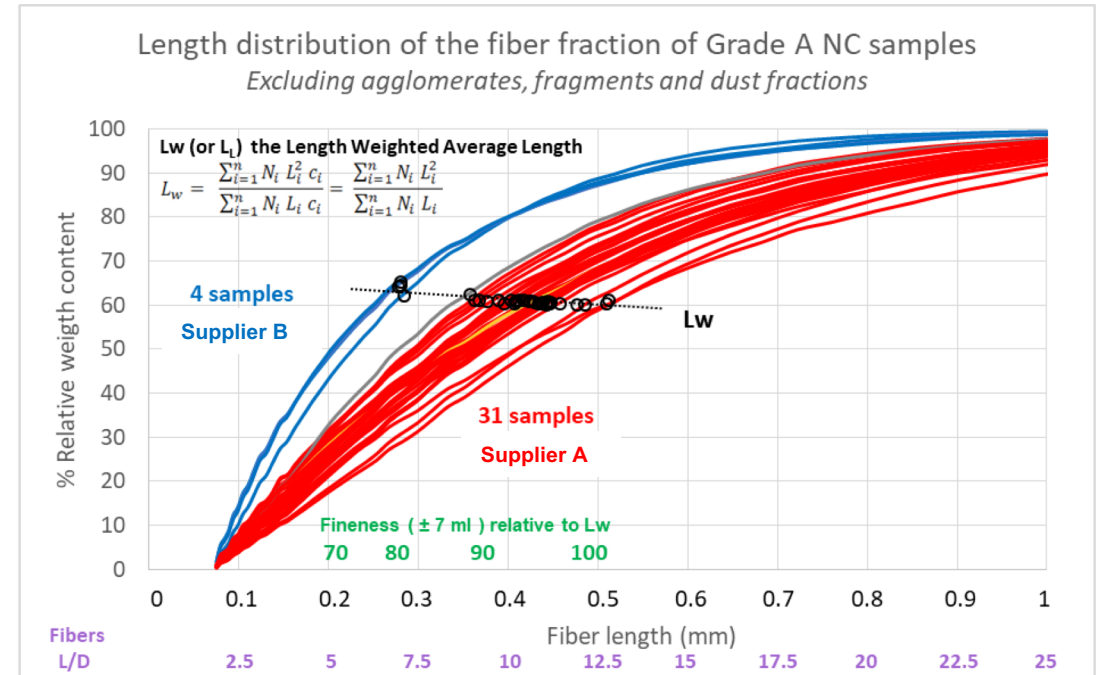
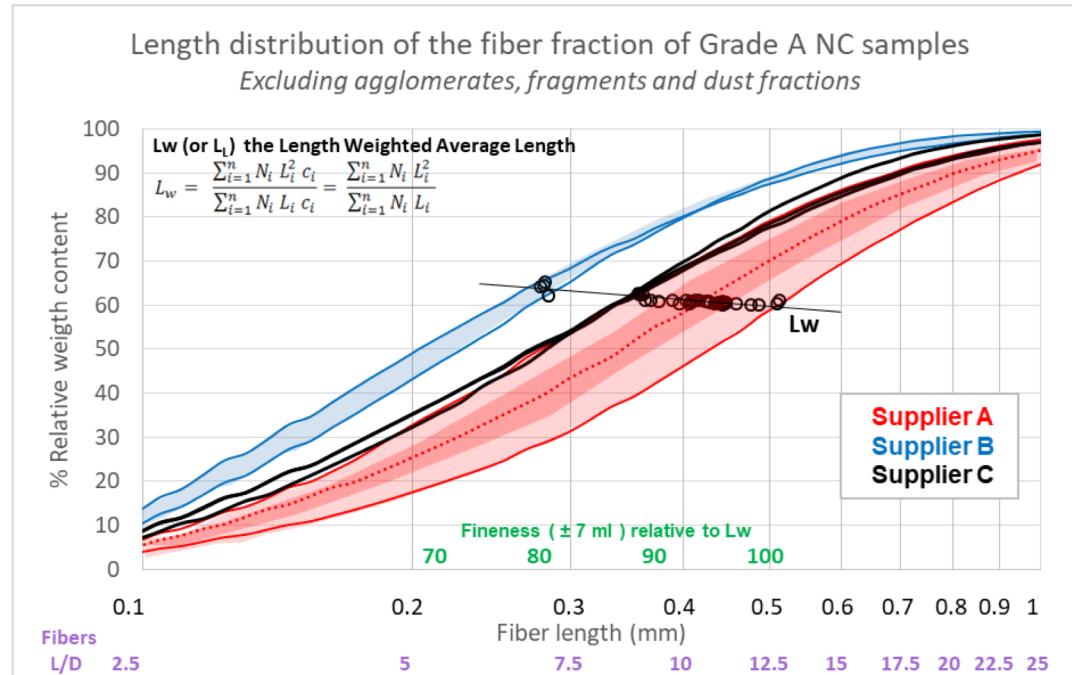
L_w is affected by the overall shape of the distribution. It can shift up and down typically between 60 and 65% w/w for NC fibers

Nitrocellulose fiber length distribution

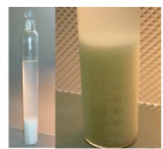
NC Average fiber length by gravitational sedimentation (Fineness)



Graphs of Grade A lots, trimmed at 75µm and showing the L_w

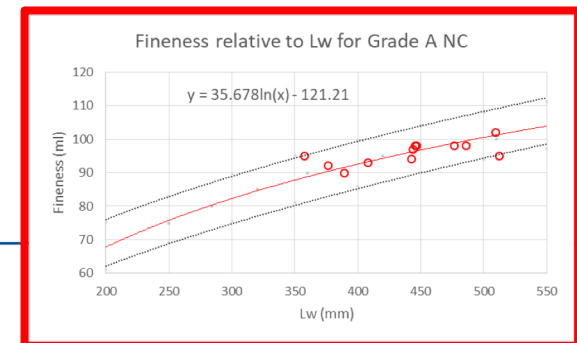


Gravitational sedimentation
(Fineness settling method)



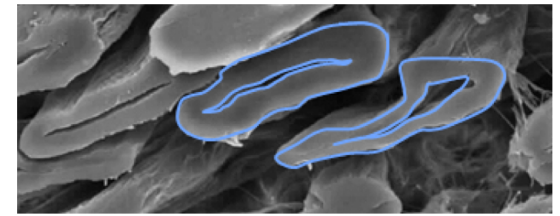
Fineness of NC with low agglomerates

NC fibers shorter than L/D of 5 tend to exhibit a different behavior to solvent system when manufacturing propellant.



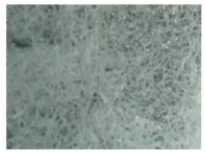
Nitrocellulose fiber length distribution

Grade A from 3 suppliers *NC from wood pulp (A, B, C)*

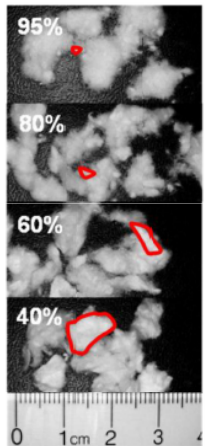


Type of cellulose used and mode of preparation for nitration

% by weight of the total available free fiber



Baled cellulose



Fully fiberized cellulose

Partially fiberized cellulose



Flakes cellulose

Supplier A

Short fibers → about 25%
Long fibers → about 30-55% w/w

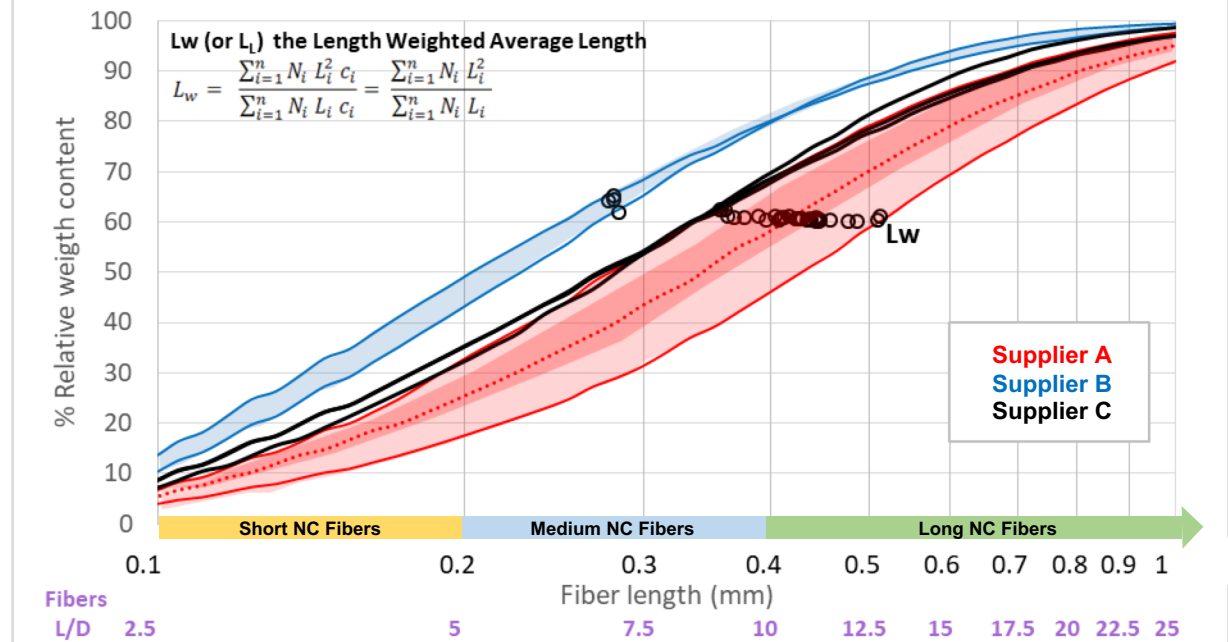
Supplier C

Short fibers → about 30% w/w
Long fibers → about 30% w/w

Supplier B

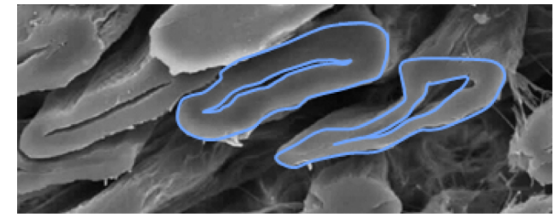
Short fibers → about 45% w/w
Long fibers → about 20% w/w

Length distribution of the fiber fraction of Grade A NC samples
Excluding agglomerates, fragments and dust fractions



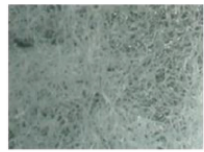
Nitrocellulose fiber length distribution

Grade A from 3 suppliers *NC from wood pulp (A, B) and cotton (D)*



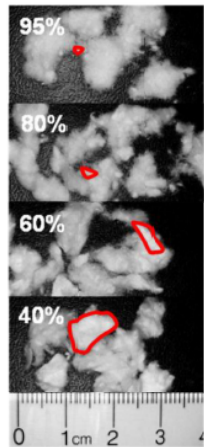
Type of cellulose used and mode of preparation for nitration

% by weight of the total available free fiber



Baled cellulose

Supplier D
Short fibers → about 27%
Long fibers → about 40% w/w



Fully fiberized cellulose

Supplier A
Short fibers → about 25%
Long fibers → about 30-55% w/w

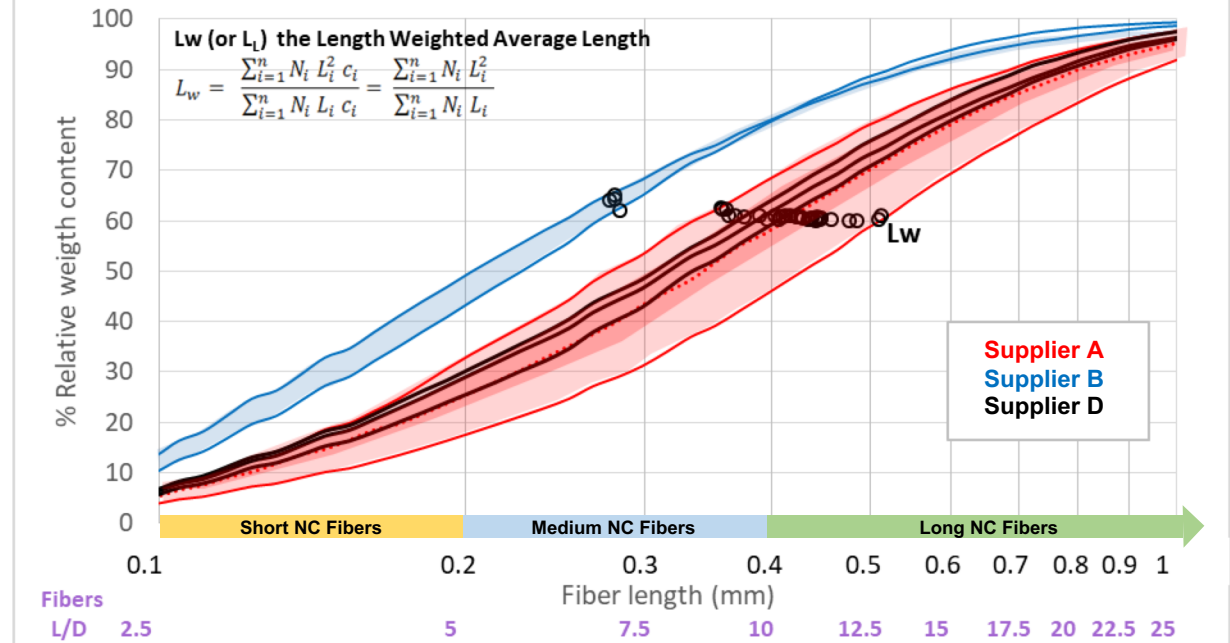
Partially fiberized cellulose



Flakes cellulose

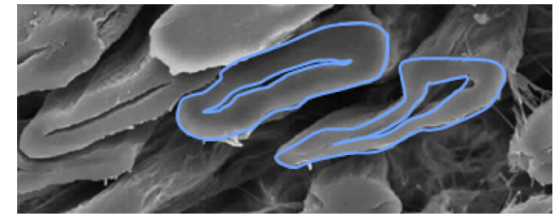
Supplier B
Short fibers → about 45% w/w
Long fibers → about 20% w/w

Length distribution of the fiber fraction of Grade A NC samples
Excluding agglomerates, fragments and dust fractions



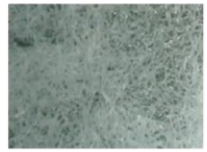
Nitrocellulose fiber length distribution

Grade A from 2 suppliers *NC from wood pulp (A, B)*

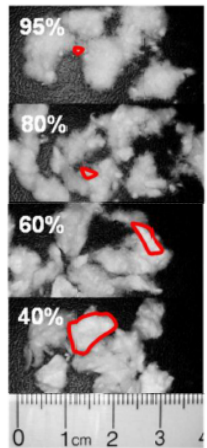


Type of cellulose used and mode of preparation for nitration

% by weight of the total available free fiber



Baled cellulose



Fully fiberized cellulose

Partially fiberized cellulose



Flakes cellulose

Supplier A

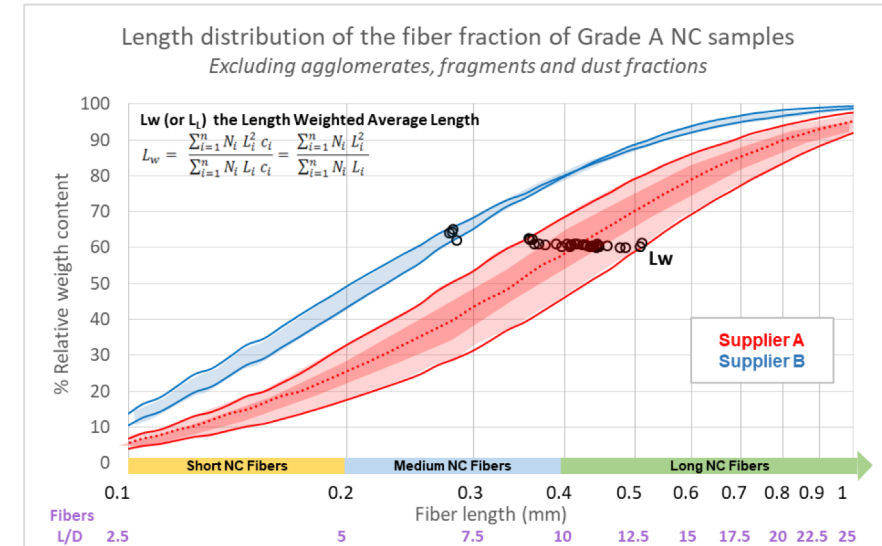
Short fibers → about 25%
Long fibers → about 30-55% w/w

% w/w free fibers by elutriation
85-95%

Supplier B

Short fibers → about 30-45% w/w
Long fibers → about 20-30% w/w

% w/w free fibers by elutriation
50-75%



% Fibers	Sample B			Sample A		
	Image analyzer	Elutriation	% w/w Fibers	Image analyzer	Elutriation	% w/w Fibers
Total	100	53.7	53.7	100	96.3	96.3
Short	45		24.2	25		24.1
Mid	30		16.1	30		28.9
Long	25		13.4	45		43.3

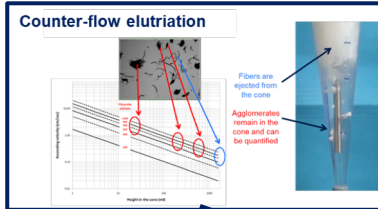
Analytical strategy summary

Aggregates (L) =
 >> 850 μm

Agglomerates (L) =
Large > 850 μm
Medium 500 - 850 μm
Small 250 - 500 μm
Very small 150 - 250 μm

Fibers (L) =
Long > 400 μm
Medium 200 - 400 μm
Short 75 - 200 μm

Fines (L) =
Fragments 20 - 75 μm
Dust < 20 μm



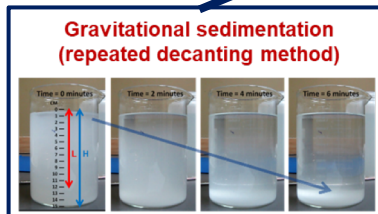
The image fiber analyzer results provide information only about the fiber fraction of the sample.

By elutriation:
% w/w Agglomerates
% w/w Free fibers



By image analysis:
Relative weight content
of fiber fractions
and
Average fiber length L_w

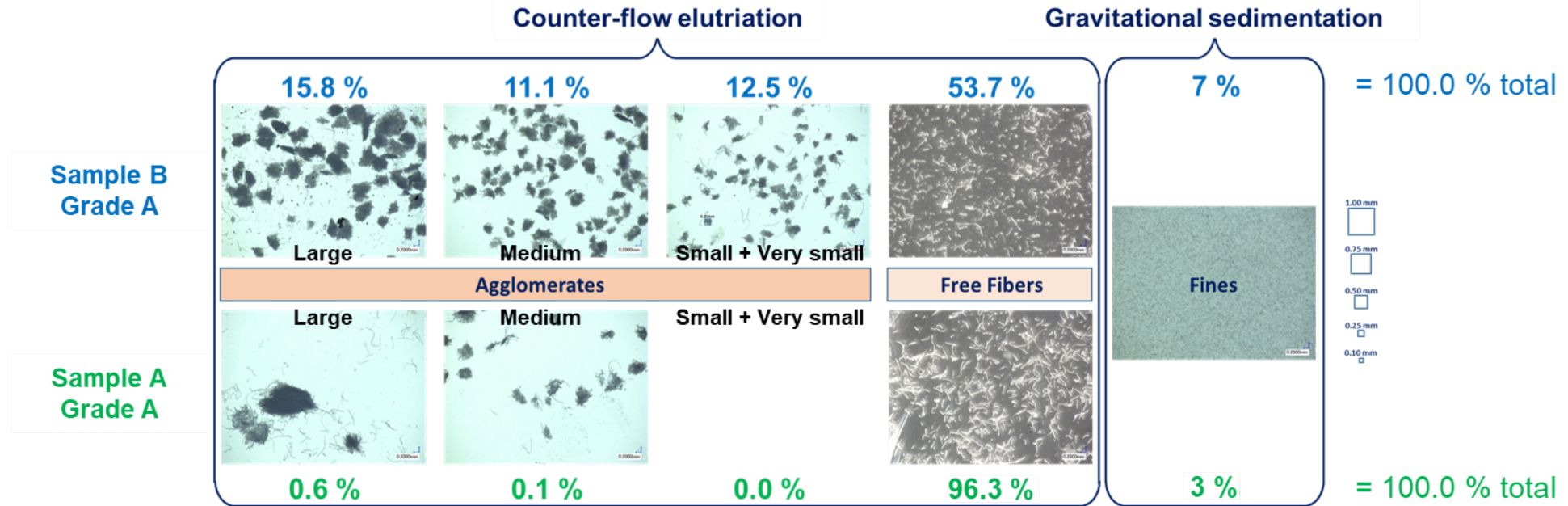
By sedimentation:
% w/w Fines



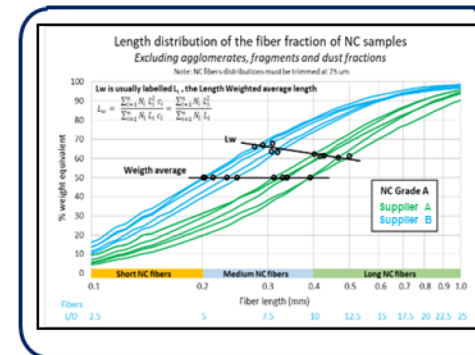
The image analyzer results must be combined with the % w/w free fibers obtained by the falling velocity methods (elutriation and sedimentation) to get the complete granulometric composition of NC

Using information from
Elutriation
Sedimentation
Image analysis
%w/w of
short/mid/long fibers

Finding the % w/w granulometric composition



% Fibers	Sample B			Sample A		
	Image analyzer	Elutriation	% w/w Fibers	Image analyzer	Elutriation	% w/w Fibers
Total	100	53.7	53.7	100	96.3	96.3
% Short	45		24.17	25		24.1
% Mid	30		16.11	30		28.9
% Long	25		13.43	45		43.3

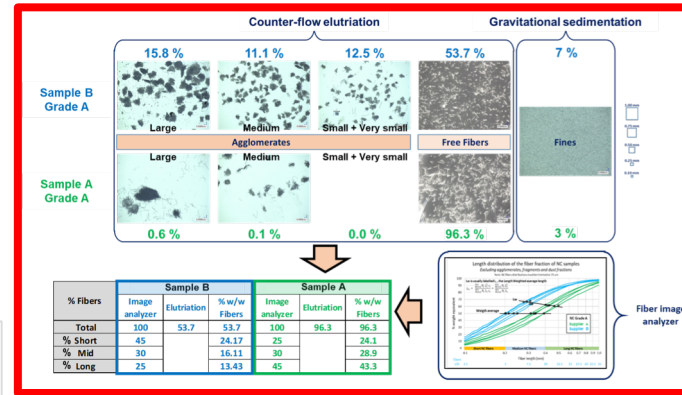
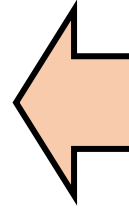


Fiber image analyzer

Finding the % w/w granulometric composition and expressing the results

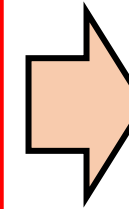
Combining elutriator results and FQA results

Granulometric constituent	Sample B	Sample A
	% w/w	%w/w
Fines (fragments/dust)	7	3
Short fibers (<0.2mm)	24.2	24.1
Mid fibers (0.2-0.4mm)	16.1	28.9
Long fibers (>0.4mm)	13.4	43.3
Small agglomerates	12.5	0.0
Medium agglomerates	11.1	0.1
Large agglomerates	15.8	0.6

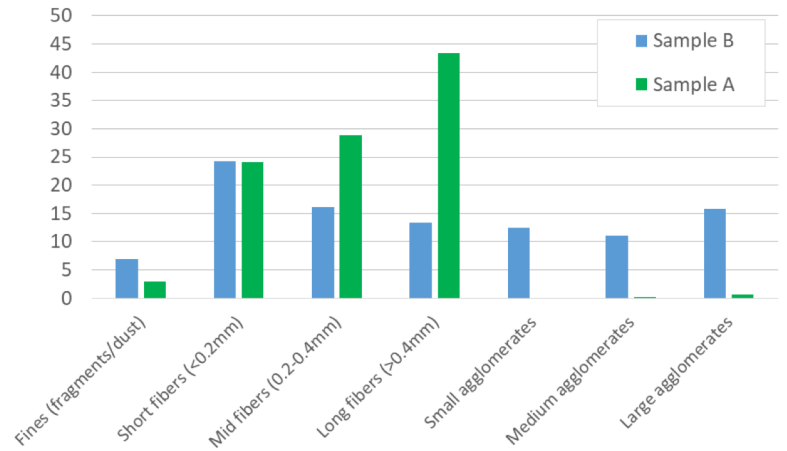


Separation of elutriator results from FQA results

Granulometric constituent	Sample B	Sample A
	% w/w	%w/w
Fines	7	3
Free Fibers	53.7	96
Lw	0.281 mm	0.425 mm
Agglomerates	39.4	0.7



Granulometric constituents of Grade A NC



Granulometric constituents of Grade A NC

