New In–Line PCC filler–fiber composite opens opportunities for paper and board mills

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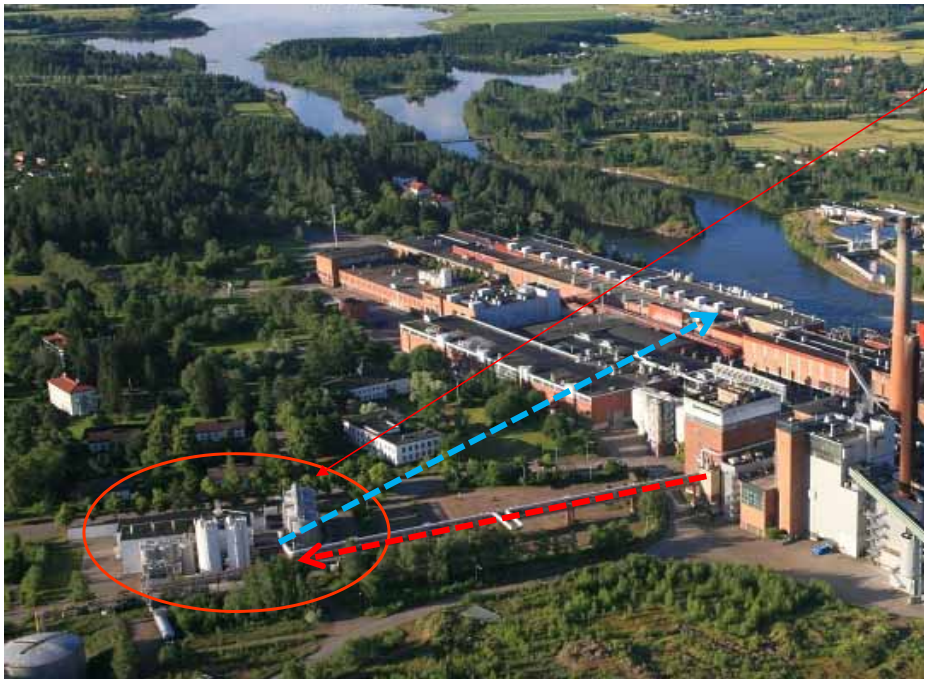
PCC technology today...

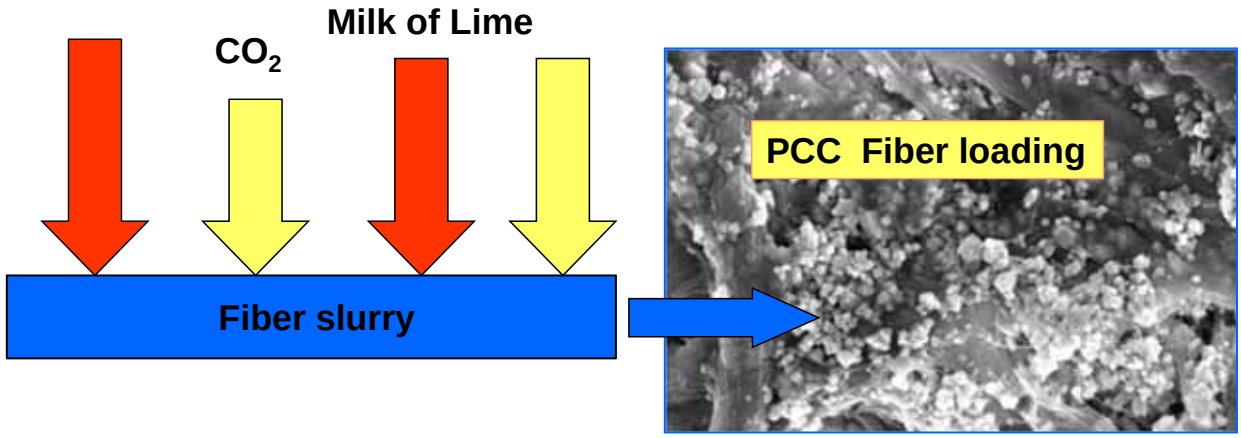
A satellite plant exploiting power plant fumes (CO_2) and quick lime (CaO)



PCC satellite plant
15 - 20 million EUR

PCC production into papermaking process

Principle is very simple



Several parties has made it to work with one way or the other in a lab .... but

In practice it has not been succeeded to develop the reaction and process to a reliable production concept and a sound integration into the papermaking process...

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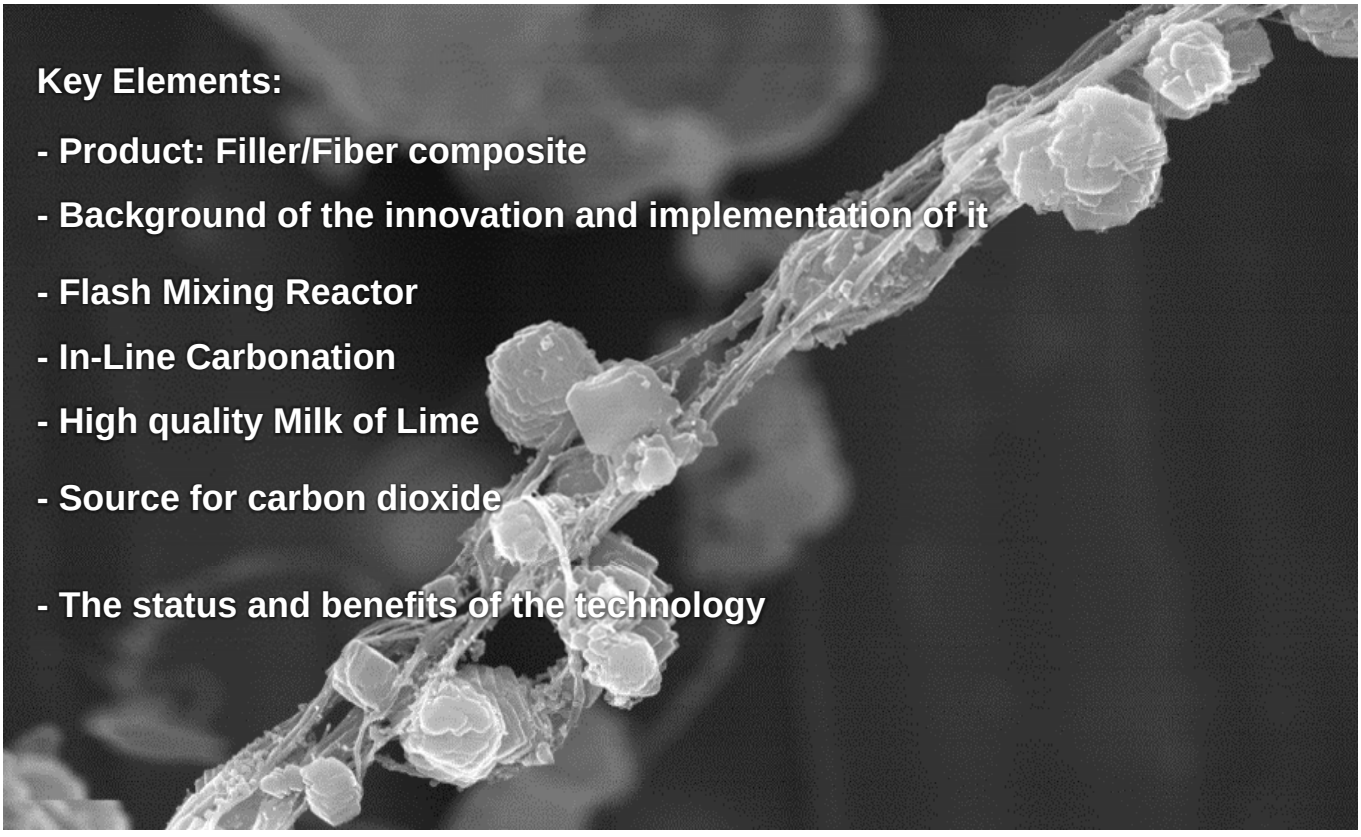
In-Line PCC™



In-Line PCC technology development

Mile stones of Wetend Technologies Ltd

- 2003 PCC mixing and production tests – mixing is the key
- 2004 - 2005 Preliminary development work
- 2006 Concepts and Development agreements with parties for the technology
- 2007 - 2010 Process Pilot plant at a paper mill in Finland,

  Full Mill scale production test runs, mill A

  Full Mill scale production test runs, mill B
- 2010 - Development of In-Line PCC composite products
- 2011 Mill scale tests, mill C
- 2012 Fine paper, In-line PCC system in full scale production
- 2012 Full scale Pilot machine In-Line PCC system in production
- 2013 SC-paper, In-line PCC system in full scale production

Tools of development

Wetend In-Line PCC Reactor

- For laboratory carbonations
- Flexible and easy tool to make several carbonations per day
- Mixing speed max 6000 rpm, power max 30 kW
- Reaction time <1 second
- The results are visible immediately

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Tools of development

Wetend In-Line PCC pilot

- Moveable unit to run trials at the customer site
- Process and application tests in relevant conditions
- Continuous runs, if necessary several weeks

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Tools of development

In-Line PCC pilot paper machine installation

- Pilot paper machine with In-Line PCC reactor
- R&D and In-Line PCC Feasibility studies
- Access to paper quality results prior operation in full scale production

Tools of development

Cooperation with Paper and Board mills and related parties for full scale production trials of In-Line PCC

- SC paper
- Fine paper
- Board application
- In close cooperation with paper and board making companies
- In close cooperation with specialized suppliers

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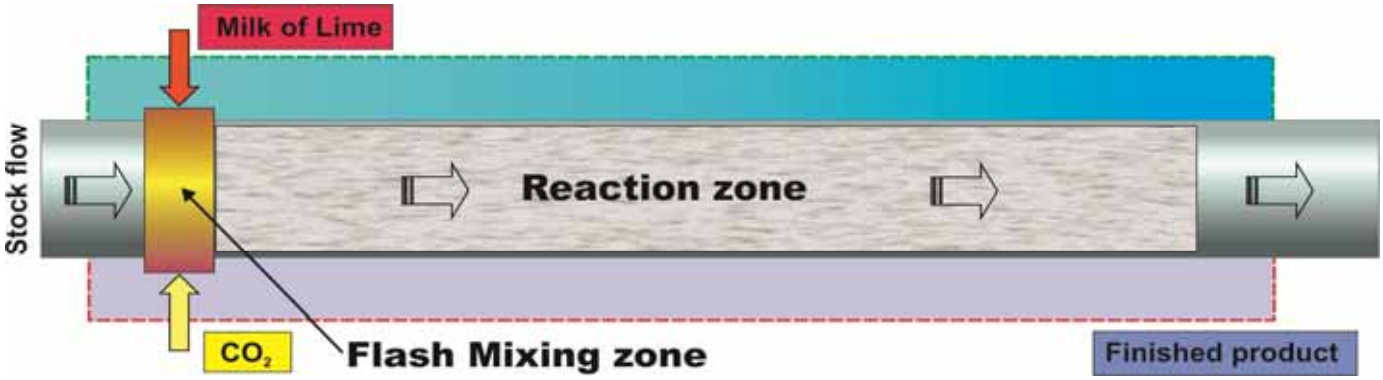
Filler/Fiber composite

- In In-Line PCC technology calcium carbonate crystalls (Precipitated Calcium Carbonate) are precipitated on the surfaces of fibrills and fibers in a Flash Mixing Reactor that forms a special part of PM Approach system pipe line of a paper machine
- The process will produce Filler/Fiber composite particles
- It is essential that both milk of lime and CO_2 gas are thoroughly mixed at the pipe to make the carbonation reaction extremely fast
- A portion of precipitation will take place also on surfaces of the fines and colloidal material of stock

In-Line PCC process

Flash Mixing Reactor; Principle of operation

- Milk of Lime ($Ca(OH)_2$) and gaseous carbon dioxide (CO_2) are Flash mixed into the stock flow through Reactor
- Flash Mixing will complete the precipitation reaction in time less than one (1) second. In a traditional precipitation process the reaction will take at least tens of minutes or hours
- The reaction is completed at the reaction zone (see below)
- Precipitation takes place on and around fibers, fibrils and fines of stock
- Precipitation on the surfaces of the reactor is prevented



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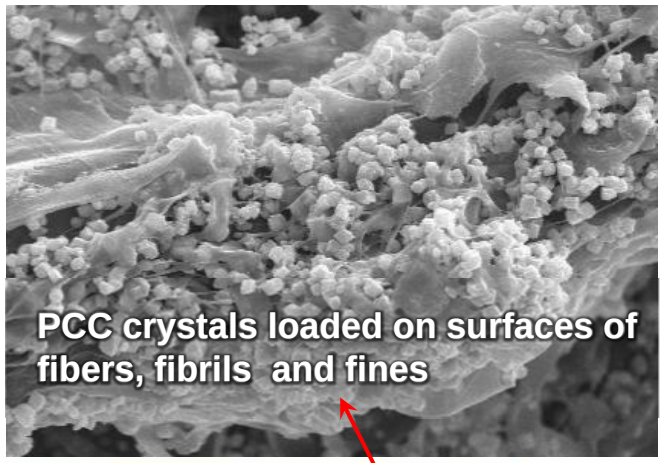
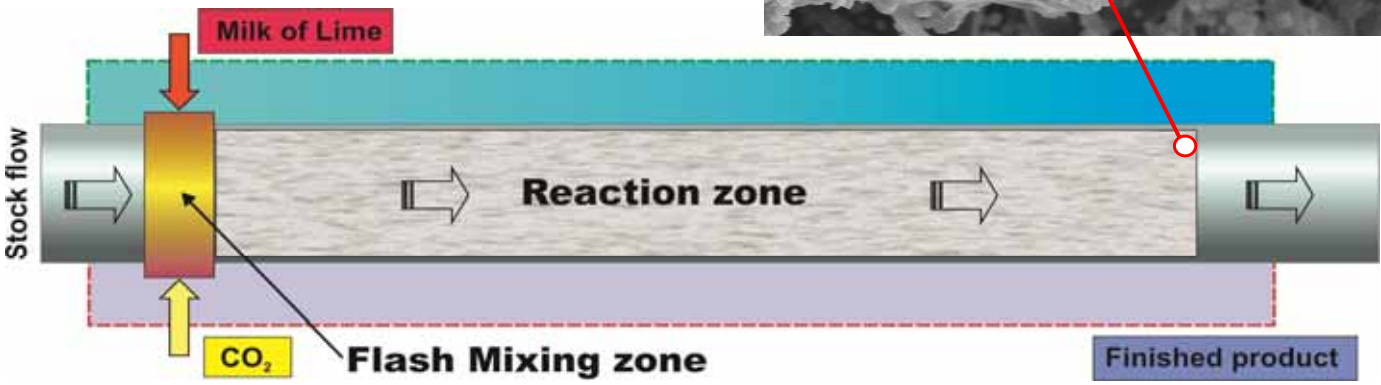
In-Line PCC process

Flash Mixing Reactor; Principle of operation

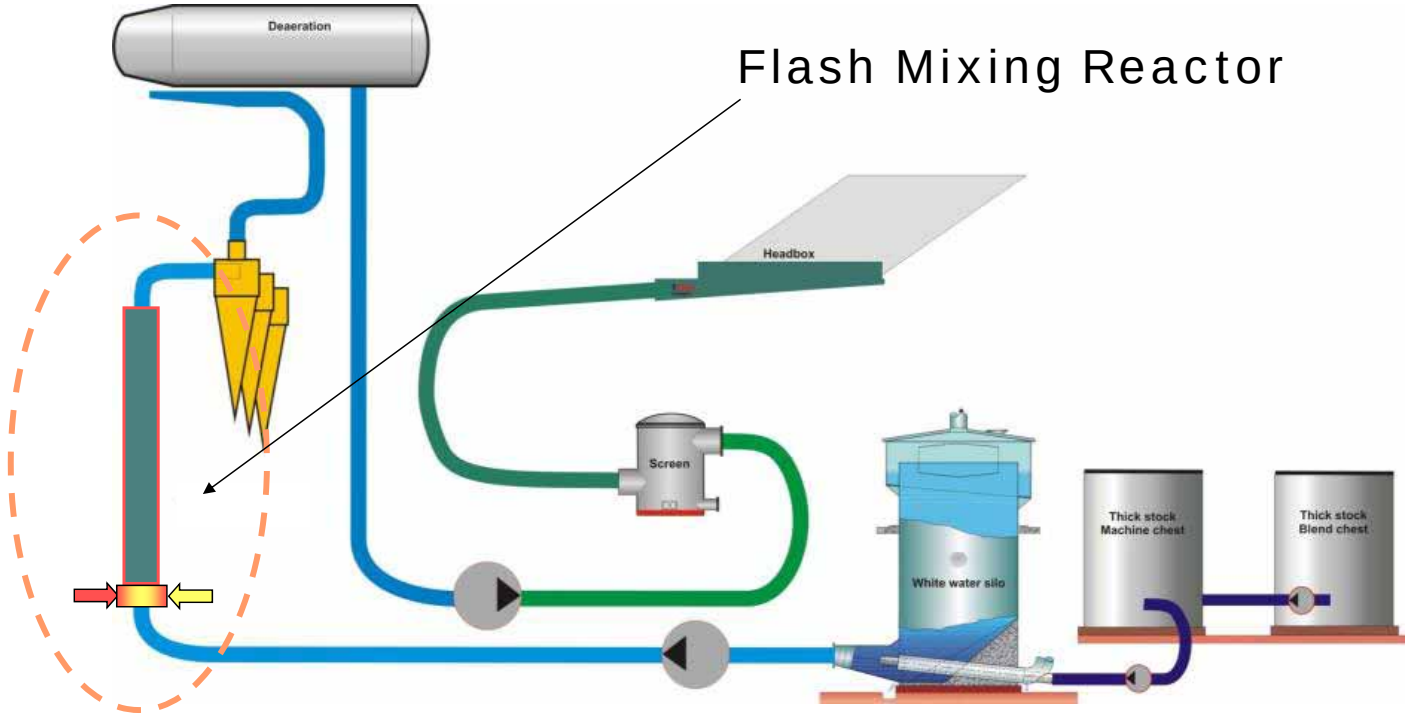
Flash Mixing Reactor





In-Line PCC process

Flash Mixing Reactor installed into PM Approach system



In-Line carbonation

- **Precipitation of calcium carbonate takes place in water phase according to the following equation:**

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

- **Intermediate stages of the reaction are:**

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

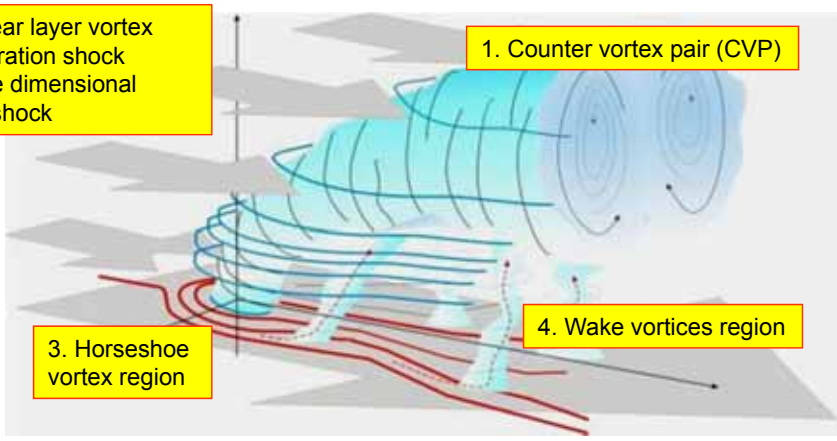
$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + 2\ OH^- \rightarrow 2\ H_2O + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

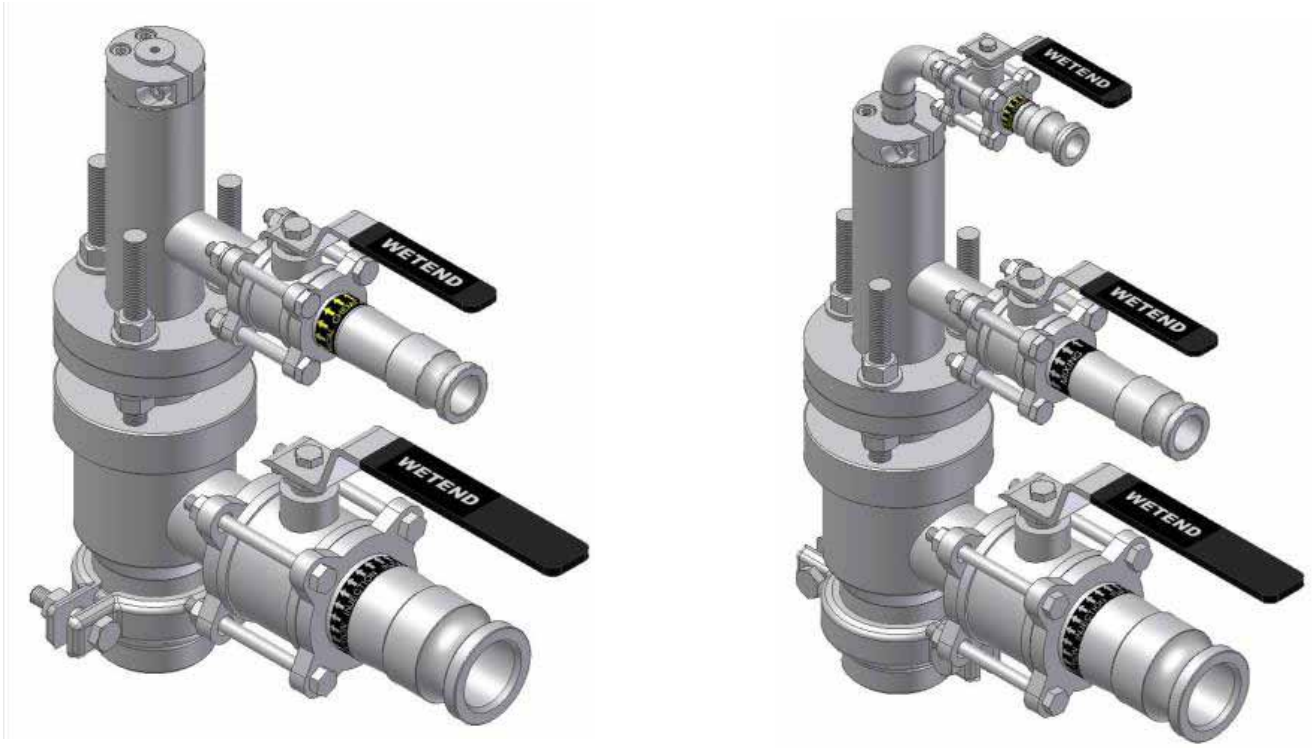
Mass transfer

- **Precipitation reaction is *fast*. Mass transfer from solid and gas phase to liquid phase is *slow***
- **Mixing and dissolving of feed materials exploits high water flow volume of PM Approach procces**
- **Precipitation is accelerated by Flash Mixing process. Generated, numerous high volume, counter rotating vortex pairs give the immediate mixing power**

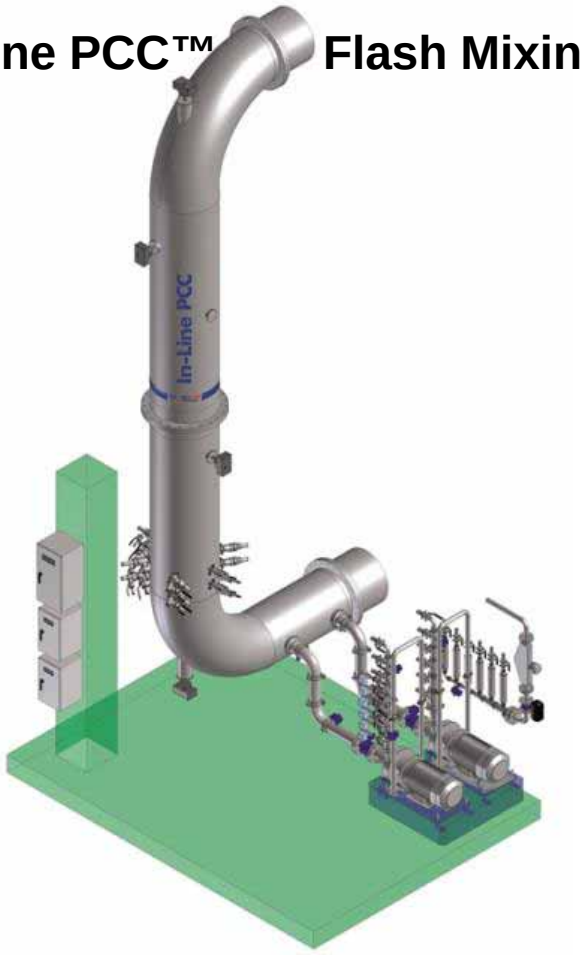


Transverse Jet Shear Layer Instabilities.
S. MEGERIAN, J. DAVITIAN, L. S. de B. ALVES, A. R. KARAGOZ IAN †
University of California, Los Angeles, 2006

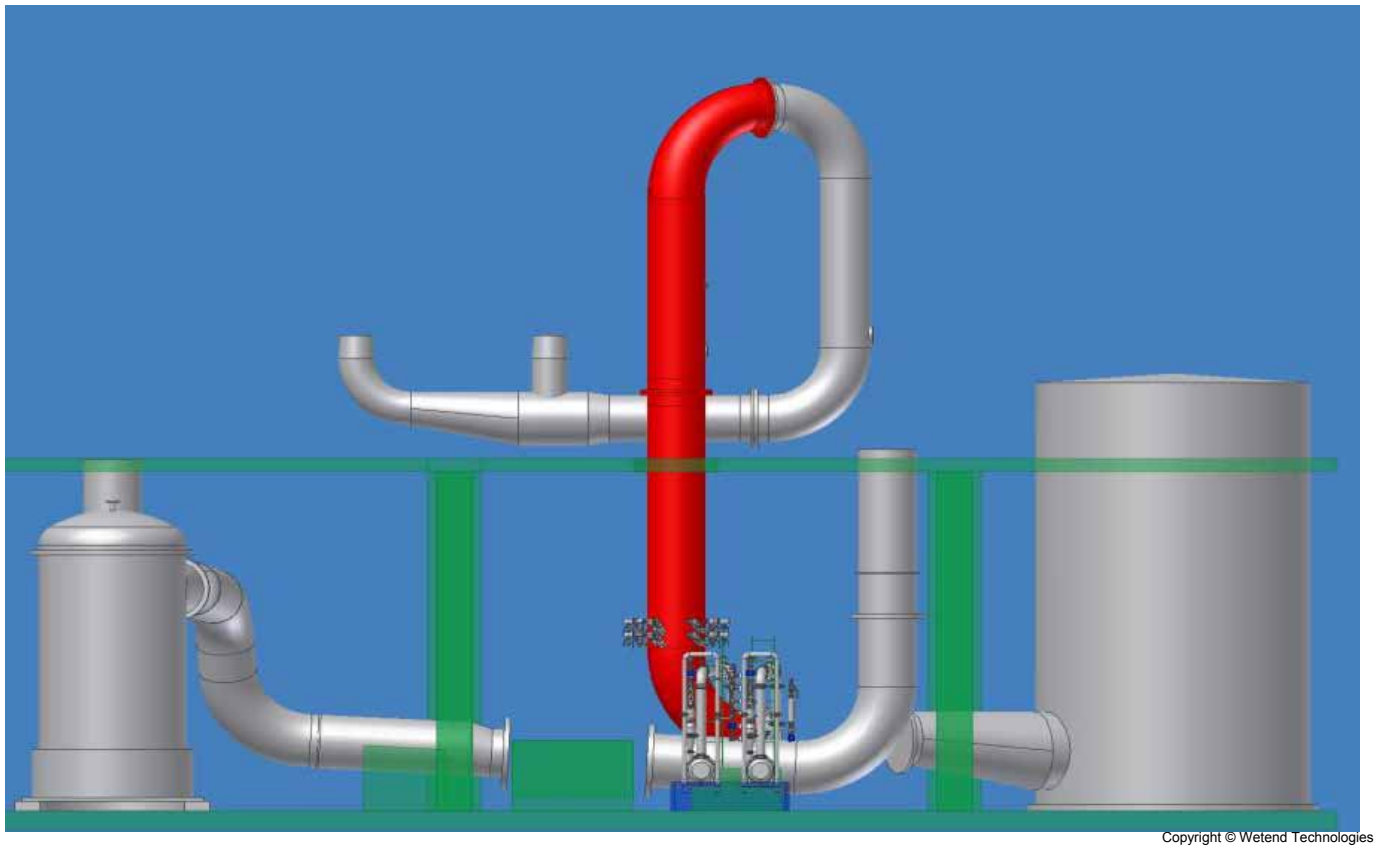
In-Line PCC™ Flash Mixing Reactor with TrumpJet® Mixers for CO_2 gas and milk of lime



In-Line PCC™ Flash Mixing Reactor



In-Line PCC Reactor installes



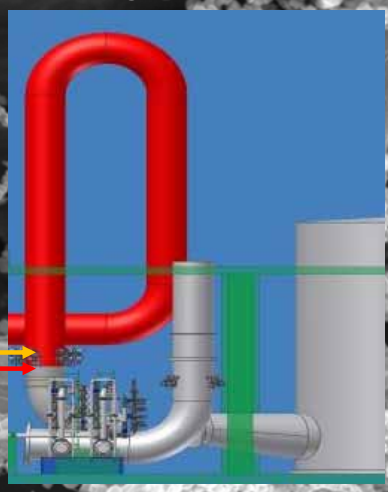
In-Line PCC™ process

Production of CO_2

or

Production of Filler-Fiber Composite

Flash Mixing Reactor



CO_2

Production of Milk of Lime

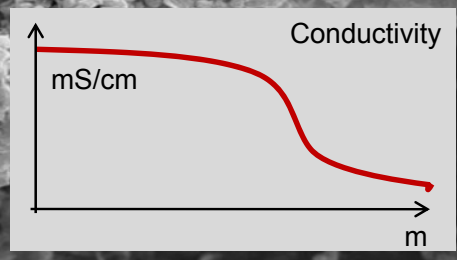
Quick lime CaO

Wetend Milk of Lime Production plant at mill site

Calcium hydroxide slurry

Carbonation

- Crystallization begins from a solid nucleus present in the process - often on a particulate or on a surface of a particle
- Stock includes a lot of fines, fibrils and fibers where the crystallization instantly begins to grow
- Average particel size: 0,8 µm



- When the conversion of the reaction approaches 100 %, both pH and conductivity decreases and settle rapidly on desired level

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Carbonation

Lumen loading… by accident

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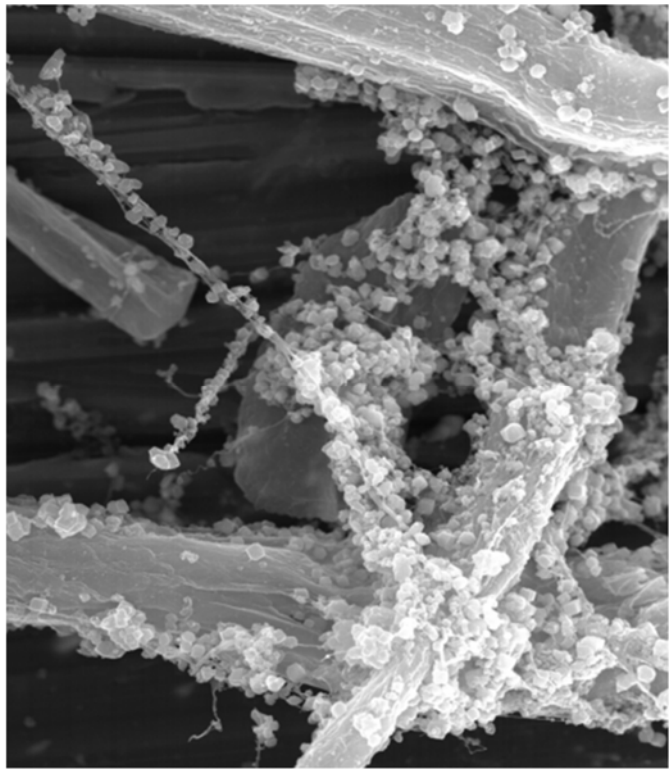
Milk of Lime, Calcium Hydroxide

- The quality of the milk of lime has an impact both on crystallization process and on the quality of the filler/fiber composite
- The average particle size has an impact on reaction speed
- The mean particle size has an impact also on the quality of the composite and structure of the paper
- Quality of Milk of lime has an essential role for both in runnability of the technology and on the nature of the composite produced



Dosing of the milk of lime and carbon dioxide

- The components of the crystallization are fed to the process in a correct stoichiometric relationship
- If the carbon dioxide is overdosed, the pH will decrease and calcium ion concentration will increase
- If calcium hydroxide is overdosed, the pH will increase

Carbon dioxide is transported and stored in about 20 bars pressure and -10 °C temperature

In-Line PCC™ technology status at the moment

- UPM Jämsankoski PM5
- SC Magazine paper
- In-Line PCC investment completed after thorough mill trials since 2009.
- In continuous production Q1/2013

- Stora Enso Varkaus PM3
- Wood Free Paper (fine paper)
- In-Line PCC investment completed
- On production since Q1/2012

- Stora Enso Imatra
- Pilot paper machine
- In-Line PCC investment completed
- In operation since Q2/2012

Printing paper production and testrun results

In-line PCC on full scale production

Paper quality and sheet characteristics are the same or better

Draw of sheet develops positively

With In-Line PCC PM Approach system stays clean:

- **COD decreased**
- **Turbidity decreased**
- **Amount of Na-ions and Cl-ions in circulation decreased**

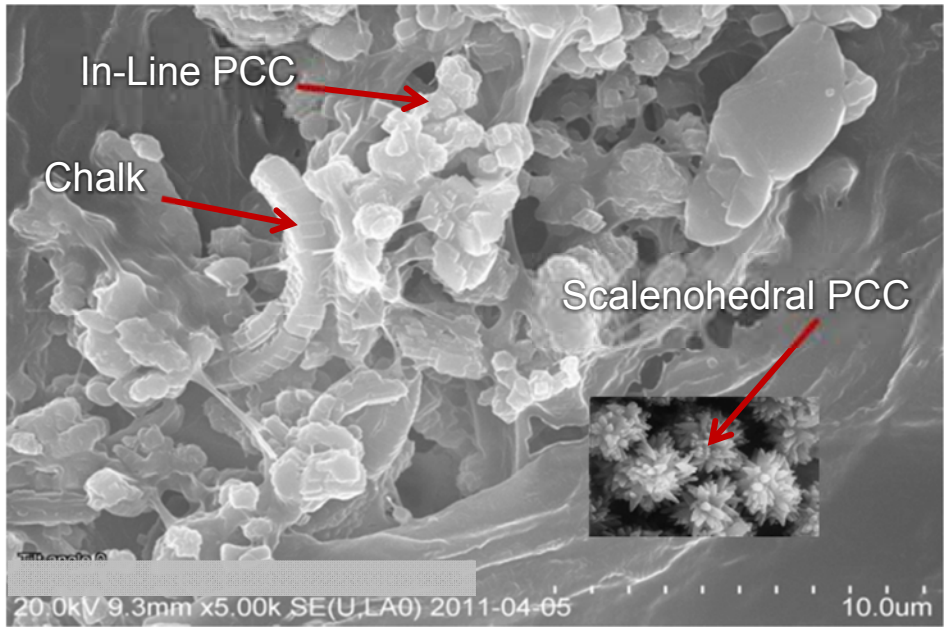
Improved retention

- **Decreased CPAM retention aid polymer consumption**
- **Decreased APAM micro polymer consumption**

- **Improvement in process runnability and efficiency**

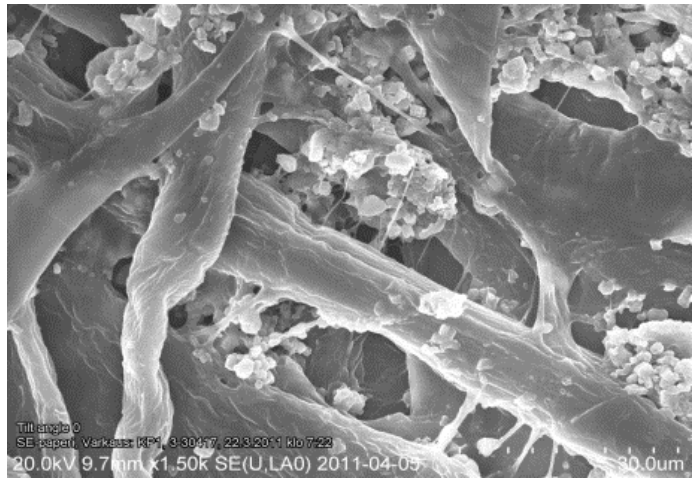
Optical Properties, Light Scattering

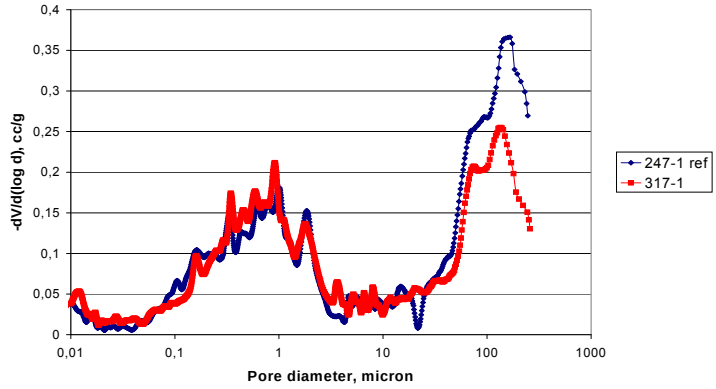
- PSD_{50} for In-Line PCC is about **0,8 µm**
- For Scalenohedral PCC about **3,0 µm**
- For chalk choccolites partiles can be up to **90 µm**
- Knowing that optimal light scattering is reached with 250–500 nm particles and that **In-Line PCC** is evenly distributed in a paper web, **one can achieve excellent light scattering**
- A papermaker can take the advantage of high light scattering several ways, eg. lower grammage, less OBA etc.



Web forming process

- 50−70% of In-Line PCC particles are attached to the fibers and fibrils during the carbonation process without any retention aid after shear of process elements
- A conventional way to retain the filler particles is to flocculate the fiber & filler slurry with retention aid
- A single crystal is more effective in light scattering, in paper strength and paper structure (bulk)
- **Paper porosity is developed, less big "holes", i.e. less print through**

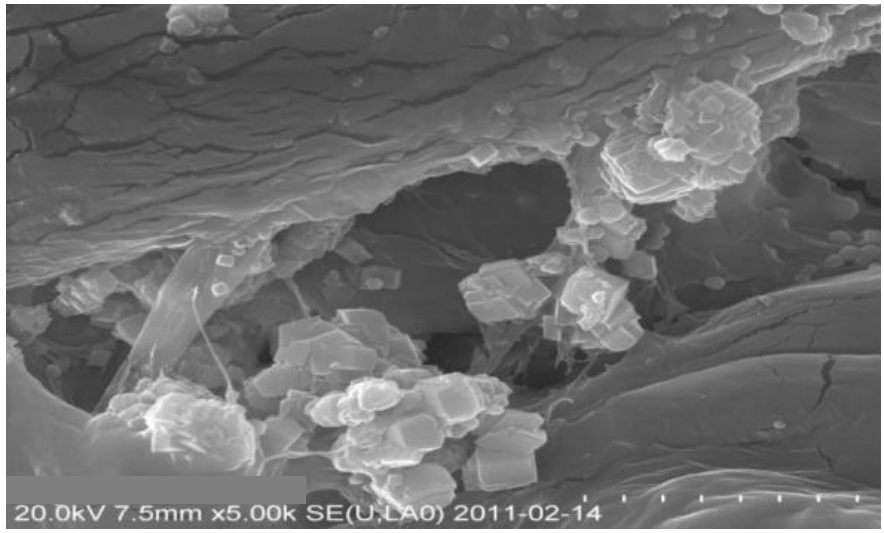




Web Structure

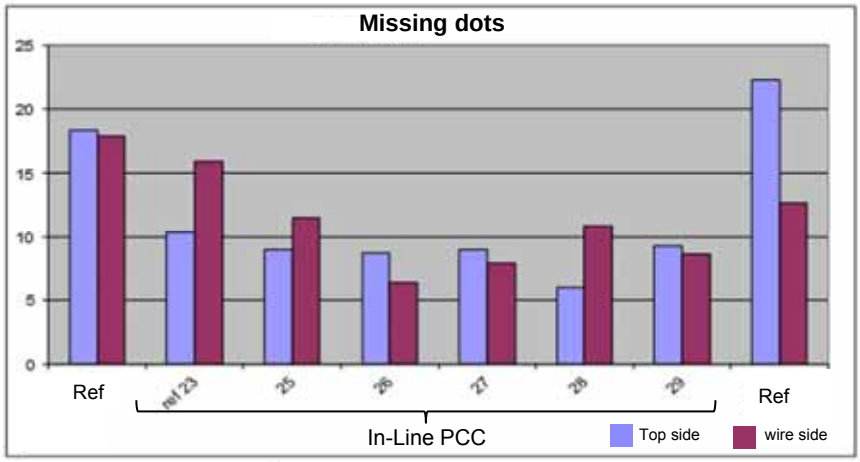
- PCC crystals are evenly distributed in the web and mainly attached to the fibrils.
- This will open up the structure of the web and will have a positive effect of the bulk and porosity of the paper – along with the amount of fibrils
- Fibers with fibrils and PCC crystals slides less between each others, which increases wet strength of the paper – less draw at a paper machine.
- This can be exploited e.g. by

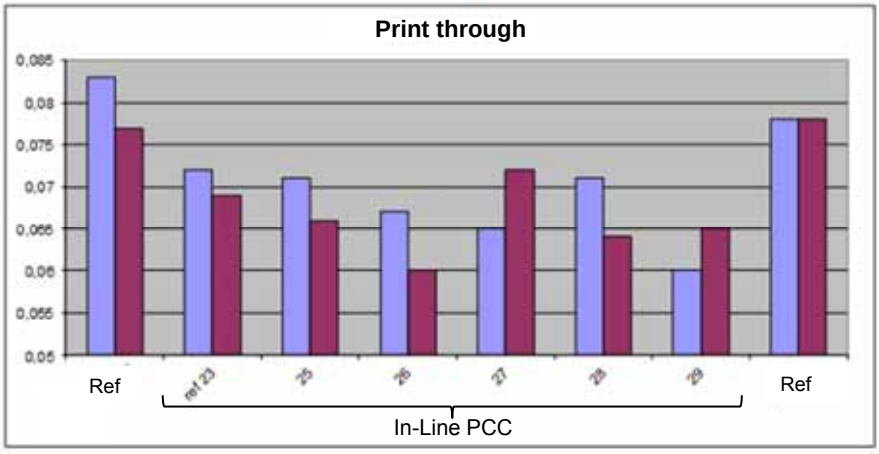
  increasing sheet filler content

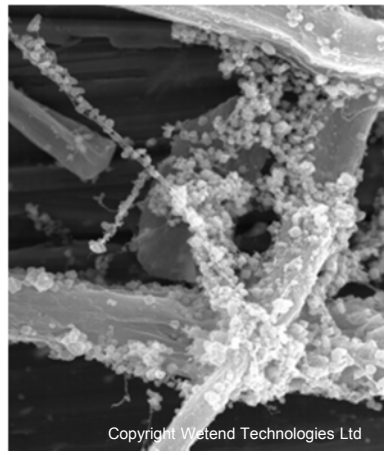


Printability

- **In-Line PCC vs. reference produced**
  - less missing dots and
  - print through
- **This results from**
  - different pore size distribution and
  - structure to reference





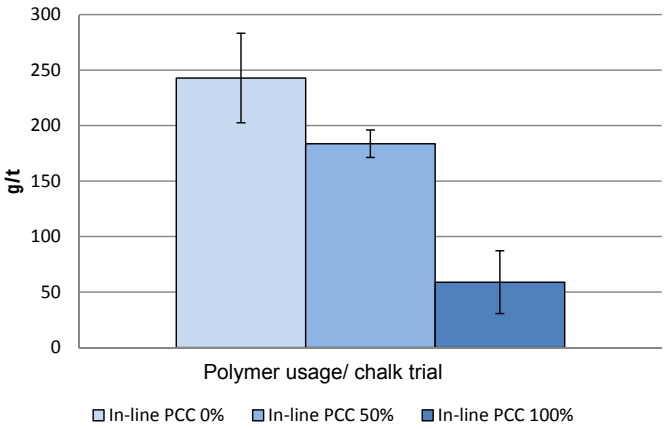


Printing paper production testrun results

Improved retention

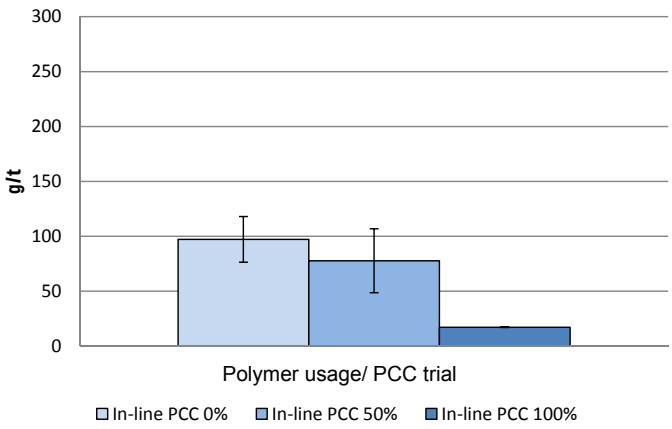
Trial with In-line PCC (85% PCC , chalk 15%)

Retention polymer -76%

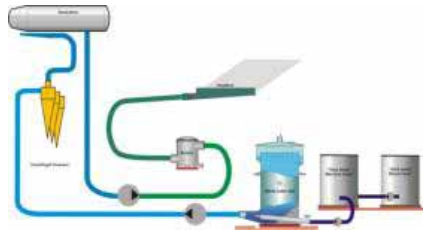


Trial with In-line PCC (100% PCC)

Retention polymer -82%



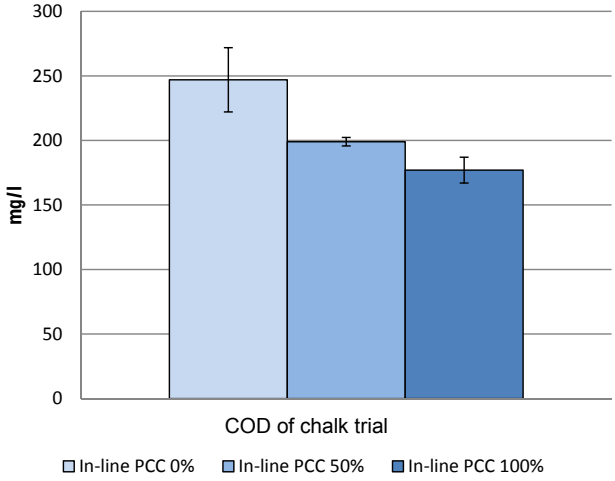
Printing paper production testrun results



Cleaner PM Approach system

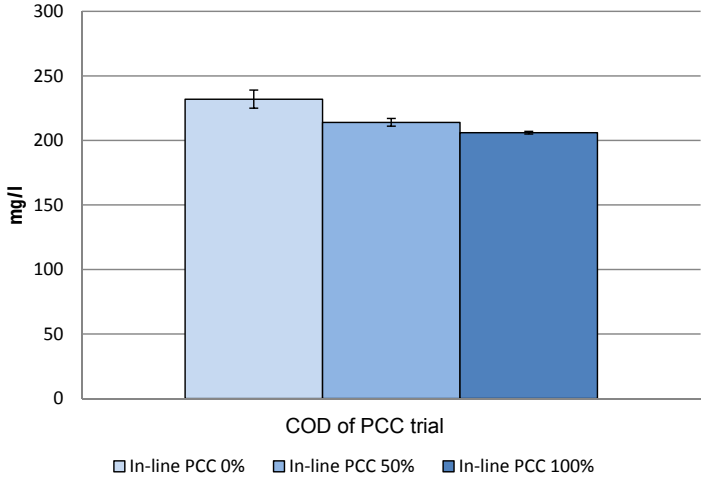
In-Line PCC (85% PCC, chalk 15%)

COD -28%



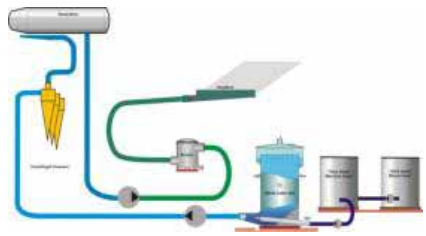
In-Line PCC (100% PCC)

COD -11%



COD/ PCC trial

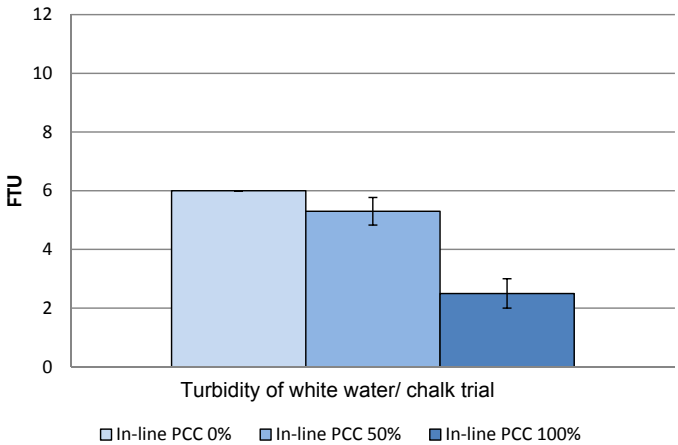
Printing paper production testrun results



Cleaner PM Approach system

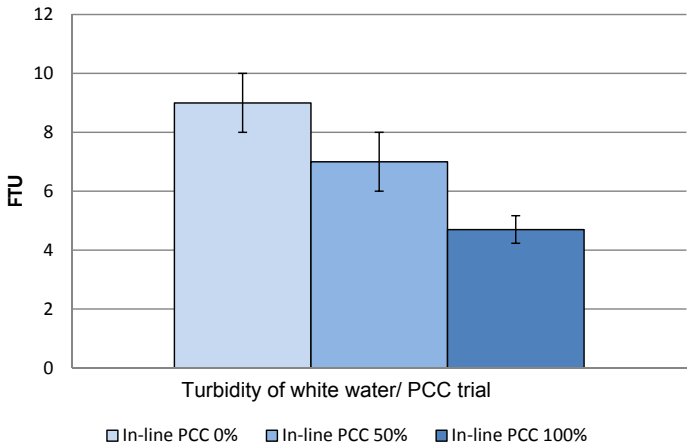
In-Line PCC (85% PCC, chalk 15%)

Turbidity -58%



In-Line PCC (100% PCC)

Turbidity -48%



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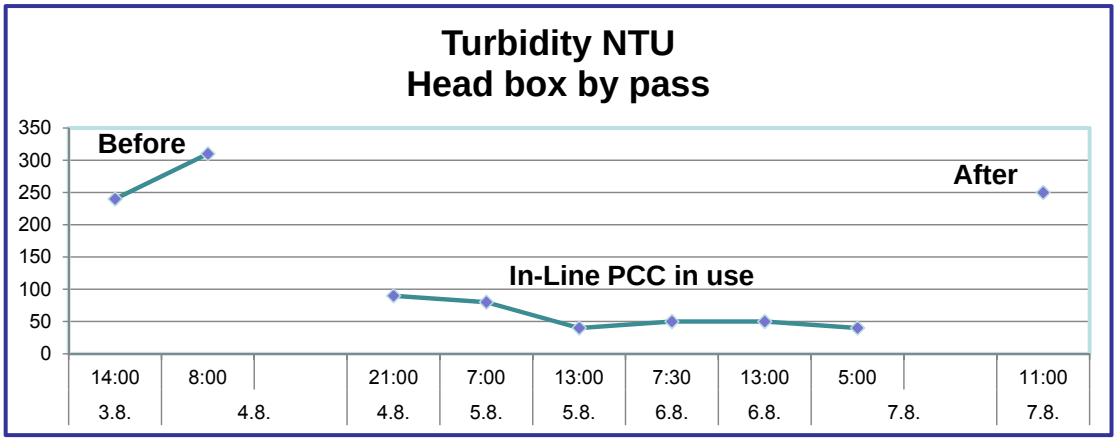
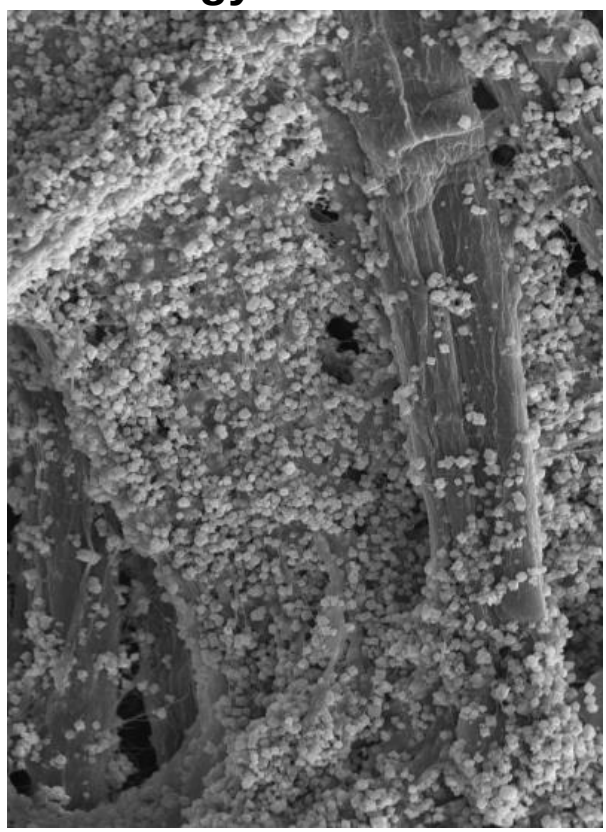
Runnability of a paper machine with mechanical fiber

- In in-line precipitation of calcium carbonate extracts and anionic trash is precipitated into the paper web with generated filler
- This can be seen in clear purification of water circulations of a paper machine
- Clean circulation water has correlated with an excellent runnability
- Better filler retention means less filler penetration through wire, which means less wire wear and longer life of fabrics



Potential benefits of the In-Line PCC technology

- Powerful fiber loading effect
- Good sheet and optical characteristics
- Very high retention of filler and fines
  - Better retention means that less filler is penetrated through the wires
    → less wire wear
    → longer lifetime of wire fabric
- Less retention aid means better formation
- Binds and eliminates interfering substances resulting to a much cleaner process, reduced solids and COD of white water
- Improves efficiency of other additives
- Opportunity to develop quality of paper and cost structure of production
- Modest investment cost
- A price competitive new raw material



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Summary:

- In-Line PCC technology is a simple and straight forward filler manufacturing process integrated directly into the main process
- A new production method with a key technology of very fast TrumpJet Flash Mixing process
- Even filler distribution in a paper web means better formation and good paper strength properties, which also gives opportunity to increase filler content in the paper or board; saving potential is significant.
- Can exploit carbon dioxide recovered from fumes of boiler plant or lime kiln
- The result is achieved through good and open co-operation with end users and through close work with several partners in the operating network

The In-Line PCC technology is protected with patents and patent applications

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In-Line PCC™ – filler fiber fibril composite

Thank You ...

Fiber&PCC COMPOSITE
-PAPER & BOARD STRUCTURE
FOR THE FUTURE