

ANQUE 2010

High rate crystallisation processes: Application to softening and removal of scaling compounds for industrial wastewater re-use

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AquaFit4Use



Technology for Water



ENVIROCHEMIE



AGENDA

- **Aquafit4use context**
- **Mechanism and bibliography**
- **Context & Stakes of High Rate Softener**
- **Results on P&P wastewater : Aquafit**
- **Multiflo-Softening pilot results**
- **Conclusions**

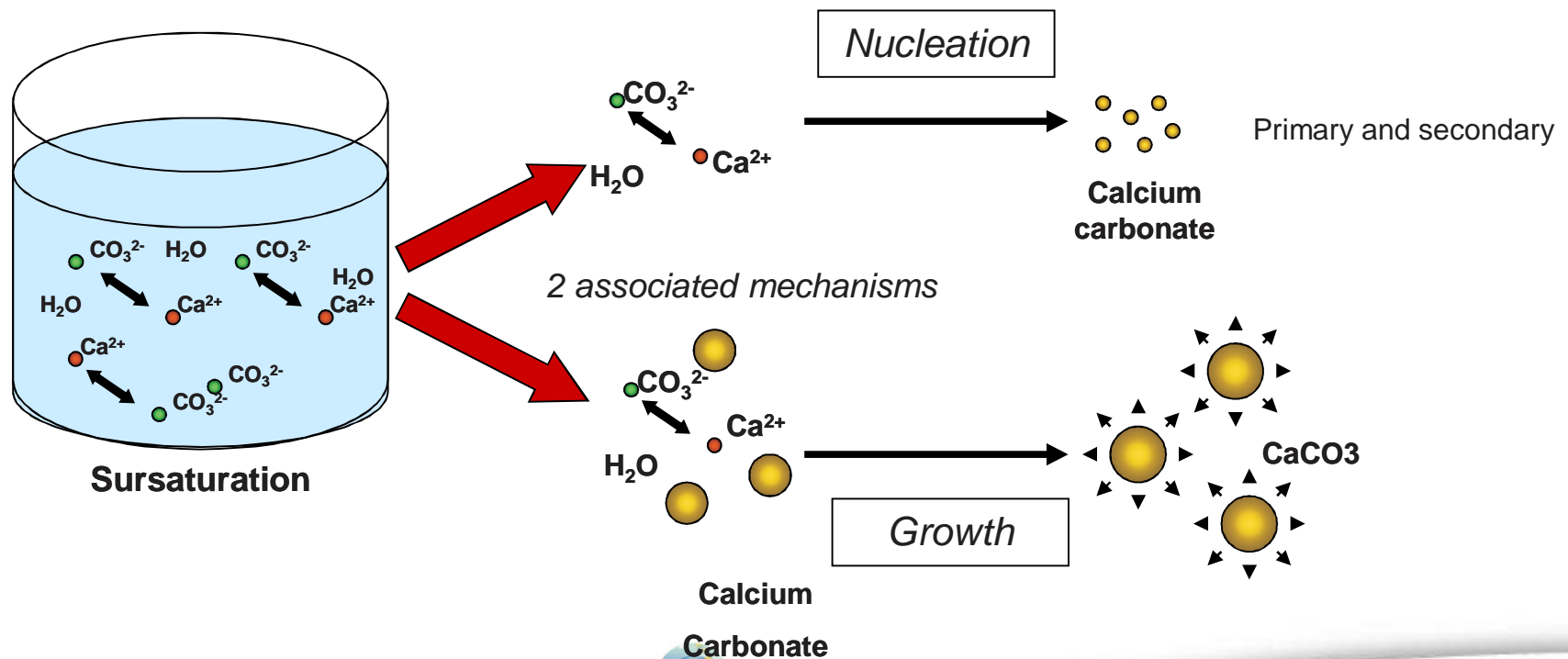
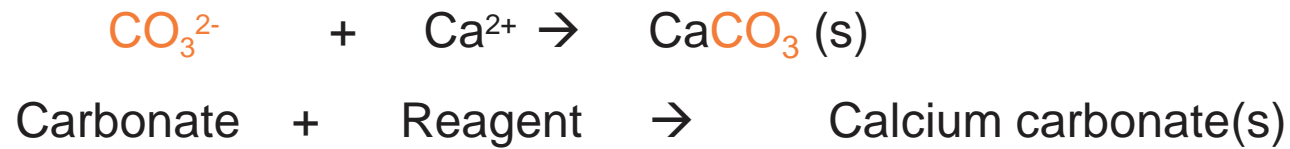
The need of advanced precipitation processes for industrial re-use

■ Aquafit 4 Use context:

- By consuming several billions m³ of water a year, industry has a significant impact on available water sources. Water re-use through the treatment of their wastewater to produce water qualities according to their own specifications, can reduce significantly this impact.
 - ➔ Aquafit4Use project purpose is to propose solutions for industrial in order to produce fit-for-use water from their wastewaters.
- In industry, especially in the Pulp and Paper industry, the removal of scaling compound, especially calcium carbonate, is a key point in the perspective of a re-use of the wastewater. Indeed the recycling of water can induce salt accumulation and thus scaling issues.

Precipitation mechanism

■ Precipitation introduction:



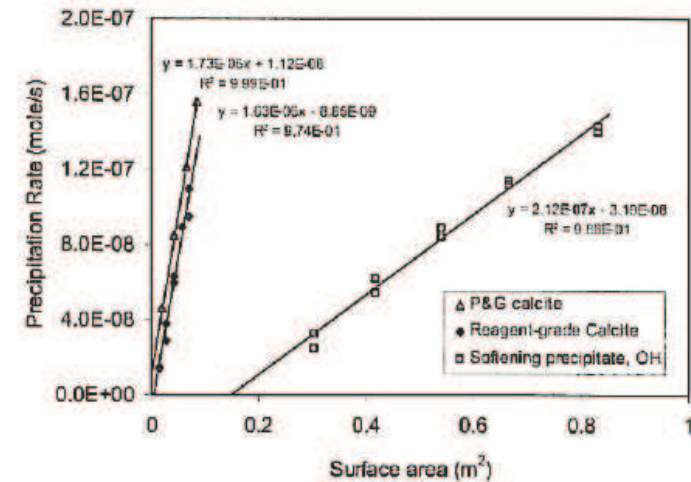
Bibliography

- Spanos and al (1998): Impact of the solid seeding on the reduction of induction times during the precipitation of calcium carbonate.

- *The induction times decreases with increasing supersaturation while the rates of precipitation increase. The induction times are shorter in the seeded precipitation experiments where the precipitation rates are higher especially at high supersaturations.*

- Nason and al. (2008) and Lin and al. (2005): Influence of the solid seeding on the processes of softening.

- *During precipitative softening, particle size distributions are shaped by three simultaneous processes: homogeneous nucleation, precipitative growth, and flocculation. The individual and relative rates of these three processes are strongly influenced by the saturation ratio, the seed concentration and the mixing intensity. Increase in the initial seed concentration prevents (or delays) the formation of new, small particles by homogeneous nucleation..*



Heterogeneous calcite precipitation rate as a function of seed surface area at 25°C
Solution composition: CT/Ca²⁺ (0.004 M), pH=7.95 (Lin and Singer, 2005)

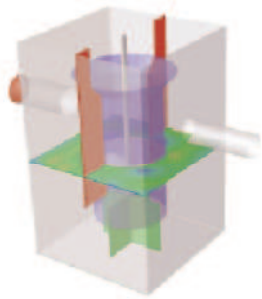
Advanced precipitation processes: High rate softening

- Generally, the physicochemical treatment of aqueous by-product streams from industrial operations (softening, acid waste neutralization ...) typically involves chemical precipitation of the contaminants *via* acid-base neutralization (or other means) followed by separation of the solids from the solution.
- The precipitation reaction, core of the chemical engineering in such processes, is a very unstable mechanism when poor homogenization and dispersion of the reagents are applied in the reactor. The consequences are:
 - Lower removal efficiency (hydraulic short-cut, long induction time)
 - Over-consumption of reagents (poor dispersion around the reagent input)
 - Scaling on walls and pipes / residual TSS in treated water (post precipitation)
 - Low density Sludge presenting a high moisture rate (nucleation >>> growth)
- Moreover, the size, shape, and density of the precipitated particles can have a significant impact on sludge rheology, settling rate and dewatering performance.

Context and stakes of high rate Softening

■ Objectives:

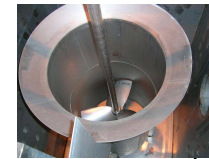
- To solve such problems, advanced precipitation and crystallization processes have been developed that address the science of particle formation and growth to improve the recovered solids properties.
- Challenge for high rated softeners is based on a reactional zone (reactor) satisfying at the same time the abilities of a CFSTR for both phases (liquid and mineral load) while minimizing energy input necessary to avoid breakage and limit energy consumption.
- As the reactor is well mixed, the total crystal surface area can be increased by increasing the slurry concentration (recirculation – as Actiflo® / Multiflo Softener™).



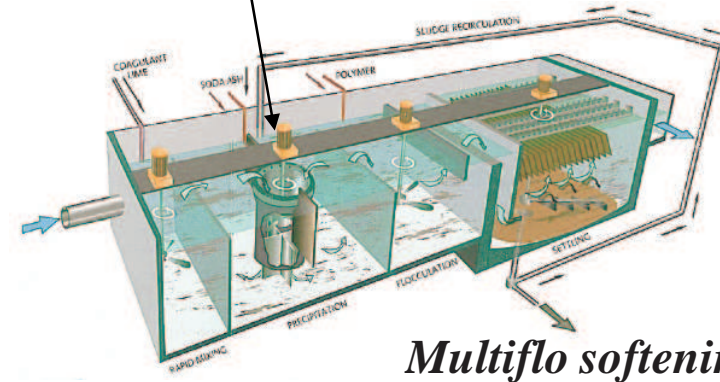
High rate softening :Multiflo/Actiflo-Softening

■ Multiflo-softening and Actiflo-softening:

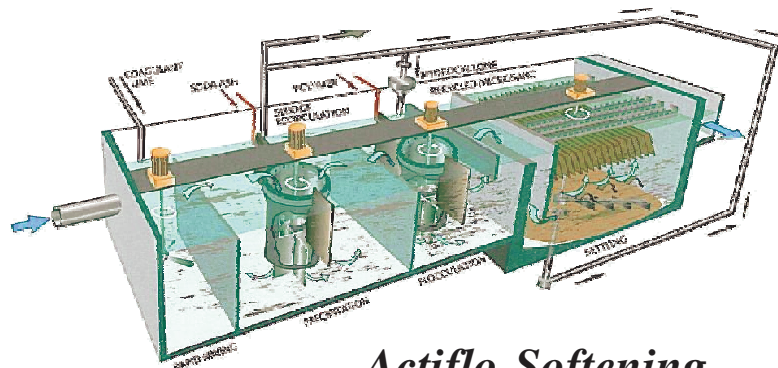
- Veolia Water Solutions & Technologies developed new softening processes (i.e. Chemical precipitation of hardness, alkalinity, and other constituents (e.g., heavy metals) from water and wastewater by the addition of lime, carbonate ions, metallic salts and polymer): Multiflo® or Actiflo®-softening processes, Hardtac®
- Compactness is one of the main advantage of High Rate Softener



Turbomix reactor

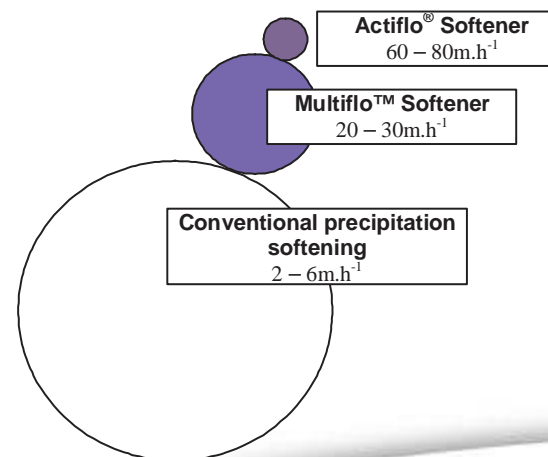


Multiflo softening



Actiflo-Softening

Research & Innovation

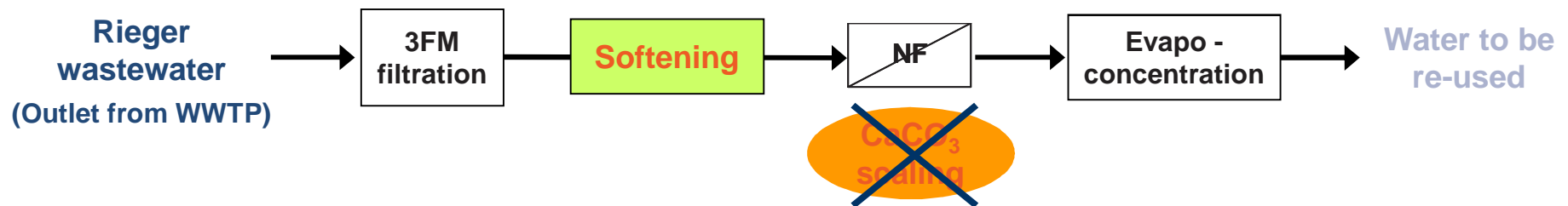


Comparison of processes compactness

Aquafit softening tests

Context:

- Treatment of wastewater from P&P industry:



- **Problem during NF treatment:** CaCO₃ scaling due to high concentration of carbonate !!!
 - ✓ 80% recovery at pH = 6.5 with use of anti-scalant

SOFTENING → Removal of carbonate before NF treatment

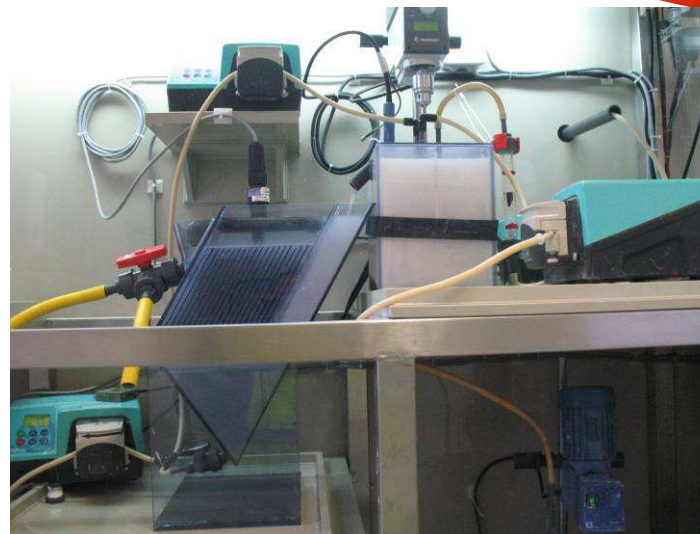
➤ Addition of calcium chloride and lime

- ✓ Calcium chloride → Calcium contribution
- ✓ Lime (Ca(OH)₂) → To reach a basic pH to allow CaCO₃ precipitation

Aquafit softening tests

■ Bench scale tests on P&P wastewater:

- Continuous bench-scale unit
- 5 Liters turbomix reactor + lamellar settler
- Flow rate: 10 l/h
- Ts: 30 min
- Sludge recirculation ratio: 10:1
- No coagulant and no flocculant



Aquafit softening tests

■ Results:

- Sludge concentration: 50 g/l (reactor)

	Before softening	After softening
pH	8.09	9.0
Ca (mg/L)	120	40
Alkalinity (mg CaCO ₃ /L)	992	363
Na (mg/L)	460	369

■ Impact on membrane treatment:

- Higher recovery
- Higher permeability
- Better quality of permeate
- No use of acid → Positive effect for re-use

Parameter	Unit	Rieger effluent pH 6.5 + Antiscalant	Rieger effluent Softened + Antiscalant
Permeability @ 80 % recovery	[L/(m ² ·h·bar)]	2.24	4.15
Max. Recovery	[%]	max. 90 [#]	93

Perm. Conc. @ recovery	[%]	80	93
El. Cond.	[mS/cm]	300 – 350*	160
Ca	[mg/L]	2 – 14*	< 0.1
Na	[mg/L]	30 – 70*	28
Cl	[mg/L]	50 – 80* (400)	32
SO ₄	[mg/L]	< 5*	< 5
DOC	[mg/L]	1 – 2*	2
COD	[mg/L]	< 15* (24)	< 5

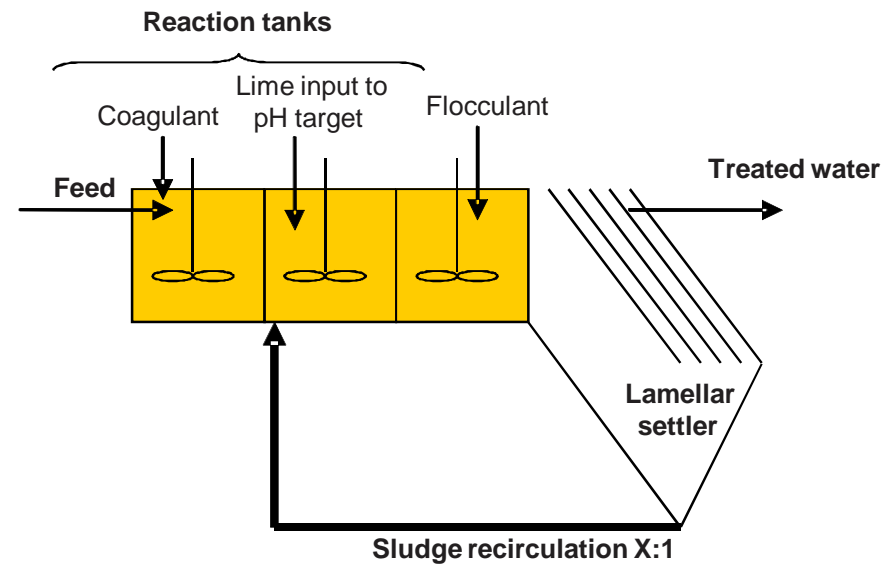
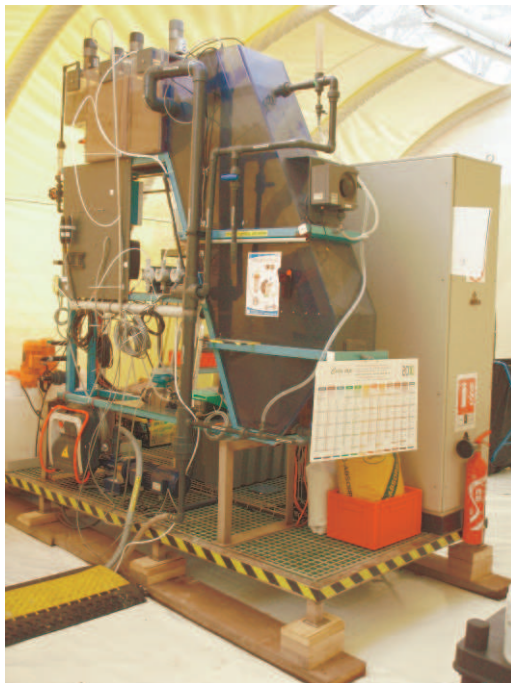
[#] visible scaling detected

* Results of test runs on semi-technical scale at 80 % recovery

Veolia Softening pilot test on surface water

■ Pilot Unit: Multiflo-Softening

- Pilot-scale unit of 150-300 l/h



Veolia Softening pilot test on surface water

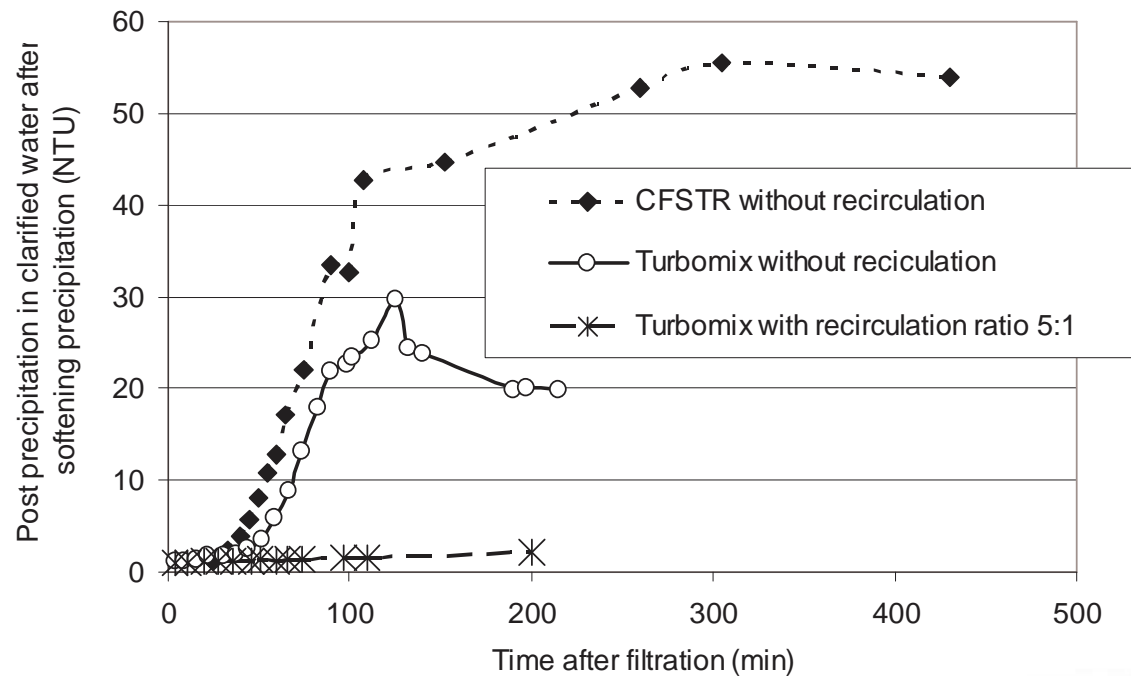
■ Pilot scale tests on surface water:

	Surface water	Config1	Config2	Config3
Chemical input (coag + Flocc)		no	no	yes
Sludge recirculation ratio		0:1	5:1	5:1
Total calcium (mgCa/L)	82 - 100	57	42	37
Total Alkalinity (mg CaCO ₃ eq/L)	130 - 170	60	45	26
pH	7.8 – 8.3	10.5	10.5	10.5

Veolia Softening pilot test on surface water

■ Impact of process configuration on post-precipitation:

- Impact of reactor design
- Impact of recirculation:
 - ✓ Turbomix and sludge recirculation have a strong positive impact to reduce post precipitation



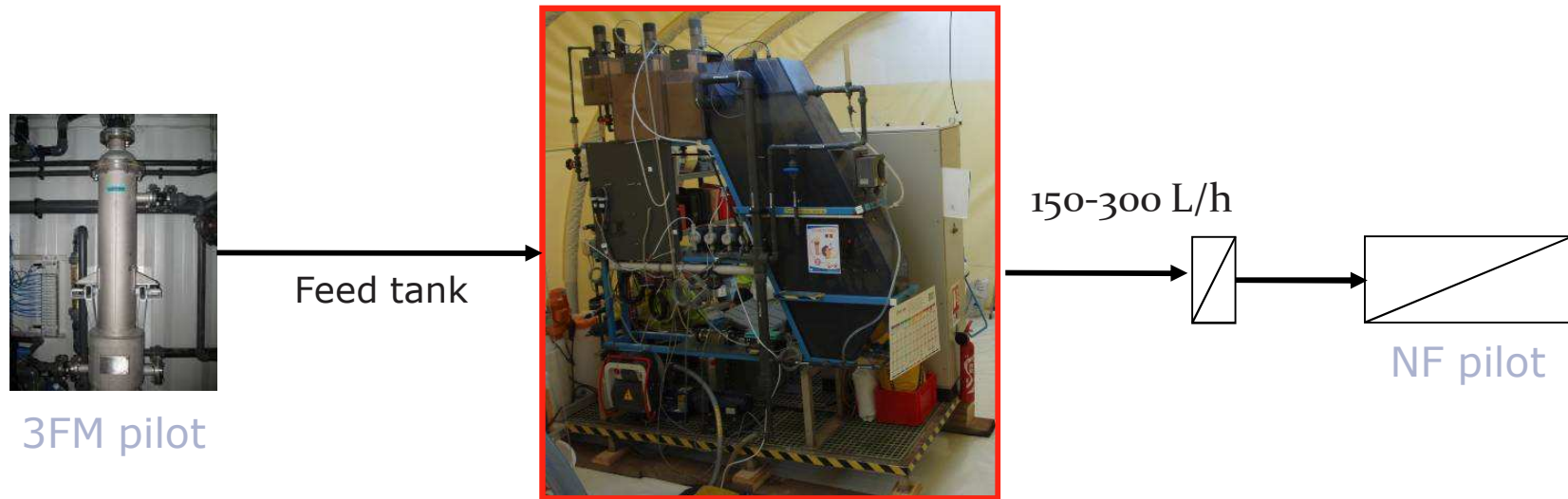
Conclusions and perspectives

- **Draft tube flow reactor allows to reach high rate of sludge recirculation in order to:**
 - Reduce induction time
 - Control the supersaturation
 - Improve particle size distribution
 - Avoid or limit scaling and post-precipitation
 - Improve solid/liquid separation and limits additional chemicals for settling

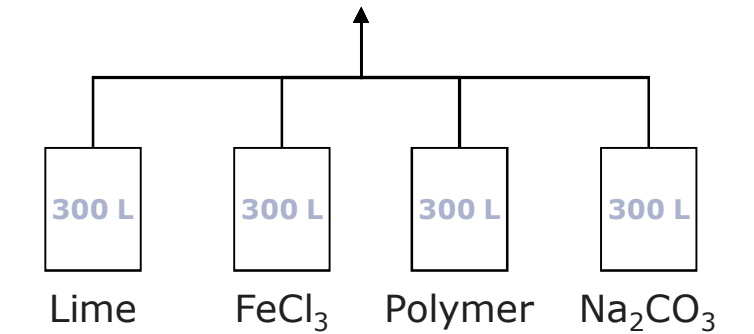
- **To prevent scaling issues in industrial re-use applications:**
 - Multiflo-Softening test shows very good results regarding Ca and alkalinity abatement with 67% and 60% respectively.
 - Lab-scale test on NF filtration with this treated water allowed to reach a conversion rate of 93% instead of 80% without pre-softening.
 - ✓ These results should be confirmed at pilot scale which are going to be performed on site within the coming year of the AquaFit4Use project.

Conclusions and perspectives

- To be tested on industrial P&P site:



Softening



**High rate crystallisation processes:
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wastewater re-use**

Thank you for your attention !

Any questions?