



UNIVERSITY OF ROME "LA SAPIENZA"
NANOTECHNOLOGIES ENGINEERING

SPINNING DISK REACTOR (WET CHEMICAL SYNTHESIS)

Outlook

- Operation of the chemical precipitation by SDR
- The CFD model development
- The CFD model validation
- HAP production
- Analysis by the CFD model on HAP production
- Discussion of the CFD model results
- Optimizazion of the equipment and operating conditions

Requirements for a possible precipitation reaction between two or more reactants on SDR:

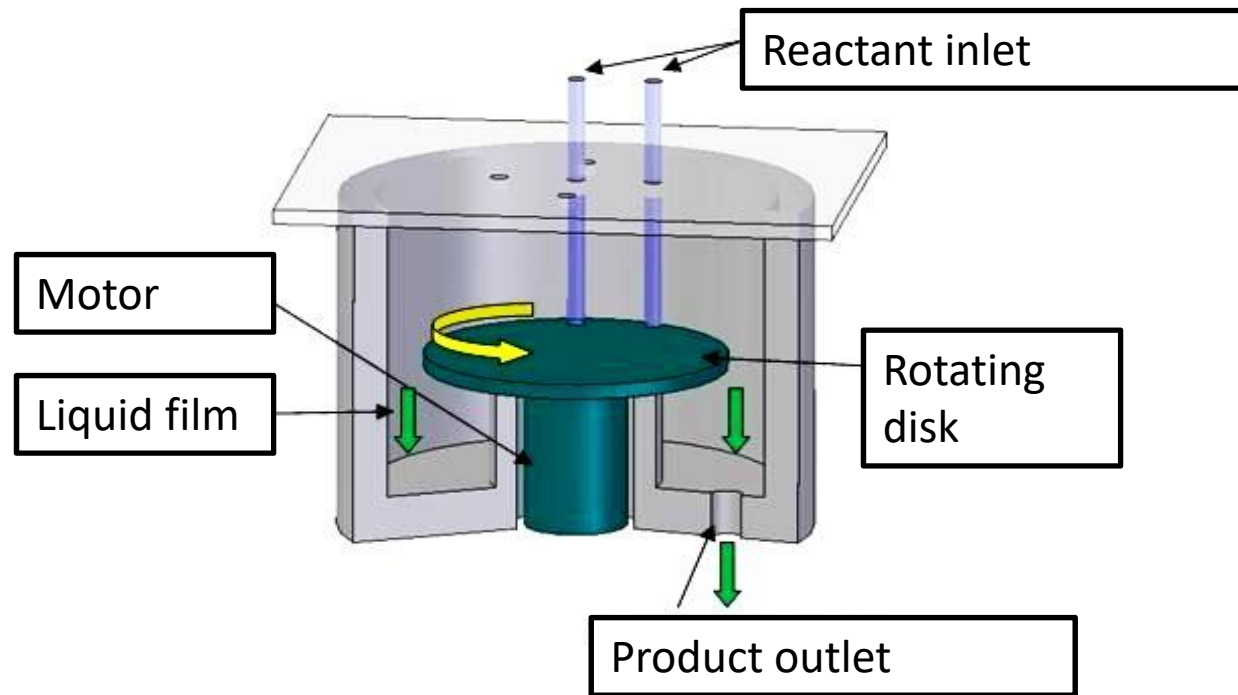
- Instantaneous reaction
- High supersaturation of the product
- High nucleation rate
- Low growth rate
- High agglomeration phenomena

Low mixing times:

$$t_m + t_r \ll t_{ind} \quad \longrightarrow \quad t_m \sim 1 \text{ ms}$$

- Highest possible product concentration

The spinning disk reactor



- Disk diameter: 8,5 cm;
- Disk surface: polymer;
- Controllable RPM (max 1400 rpm)
- Reactant injectors of 1 mm of diameter
- continous production .

CFD (*Computational Fluid Dynamics*)

Permits the simulation of the hydrodynamics and all the correlated phenomena

Fluent

- **Pre-processing: Development of the model**
(domain definition, modello definition, materials)
- **Solving**
- **Post-processing: analysis of the obtained results**

Implementation of the relevant phenomena

Velocities	Navier Stokes eq. (NS)
Materia and heat exchanges	Equations of materia and heat
Multiphase	Volume of fluids (VOF)
Turbolence	Large eddy simulation (LES)

NAVIER-STOKES EQUATIONS

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial v_\phi}{\partial \phi} + \frac{\partial v_z}{\partial z} = 0$$

$$\begin{aligned} \rho \left[\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_r}{\partial \phi} - \frac{v_\phi^2}{r} + v_z \frac{\partial v_r}{\partial z} \right] \\ = \mu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_r) \right) + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \phi^2} - \frac{2}{r^2} \frac{\partial v_\phi}{\partial \phi} + \frac{\partial^2 v_r}{\partial z^2} \right] - \frac{\partial P}{\partial r} + \rho g_r \end{aligned}$$

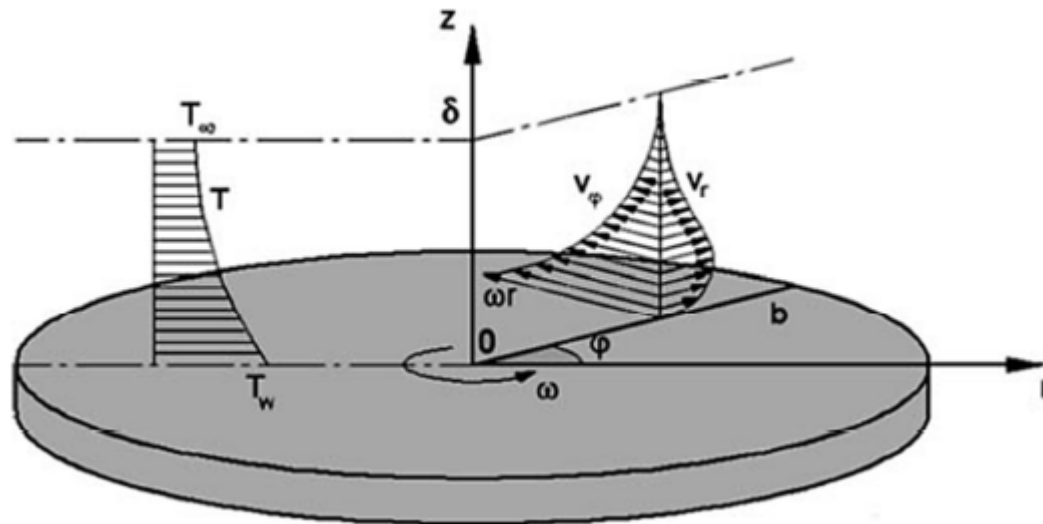
$$\begin{aligned} \rho \left[\frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_\phi}{\partial \phi} - \frac{v_r v_\phi}{r} + v_z \frac{\partial v_\phi}{\partial z} \right] \\ = \mu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_\phi) \right) + \frac{1}{r^2} \frac{\partial^2 v_\phi}{\partial \phi^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \phi} + \frac{\partial^2 v_\phi}{\partial z^2} \right] - \frac{1}{r} \frac{\partial P}{\partial \phi} + \rho g_\phi \end{aligned}$$

$$\begin{aligned} \rho \left[\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_z}{\partial \phi} + v_z \frac{\partial v_z}{\partial z} \right] \\ = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \phi^2} + \frac{\partial^2 v_z}{\partial z^2} \right] - \frac{\partial P}{\partial z} + \rho g_z \end{aligned}$$

Energy and Material Equations

$$\left[\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\phi}{r} \frac{\partial T}{\partial \phi} + v_z \frac{\partial T}{\partial z} \right] = \frac{k}{\rho c_p} \left[\left(\frac{1}{r} \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \phi^2} + \frac{\partial^2 T}{\partial z^2} \right]$$

$$\left[\frac{\partial c_A}{\partial t} + v_r \frac{\partial c_A}{\partial r} + \frac{v_\phi}{r} \frac{\partial c_A}{\partial \phi} + v_z \frac{\partial c_A}{\partial z} \right] = D_{AB} \left[\left(\frac{1}{r} \frac{\partial c_A}{\partial r} \right) + \frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 c_A}{\partial \phi^2} + \frac{\partial^2 c_A}{\partial z^2} \right]$$



OUTPUT:

**VELOCITY AND
TEMPERATURE
PROFILES ON THE
SDR SURFACE**

VOF (Volume Of Fluid)

This model is applied in presence of two or more phases that exhibits clear interfaces:

Each phase will have a volumetric fraction value in the computational cell α_i , determined locally by the simulation.

Three conditions are possible:

- $\alpha_i = 0$: phase i is not present;
- $\alpha_i = 1$: only phase i is present;
- $0 < \alpha_i < 1$: phase i is partially present together with other phases.

VOF is here necessary to take into account the gas (air) and the liquid phases in the reactor.

LES (Large Eddy Simulation)

LES



Filtering of the medium and big sized vortices from the smaller ones in the cell



The bigger ones may be calculated by NS, whereas the smaller ones are neglected and participate to the reactant conversion

Principles:

- Bigger vortices are bigger than cells and are simulated by the interaction among cells
- Smaller vortices are taken into account by internal FLUENT models in the cell

GRID

Disk diameter: 8,5 cm
Film thickness: 30-200 μm

Compromise:

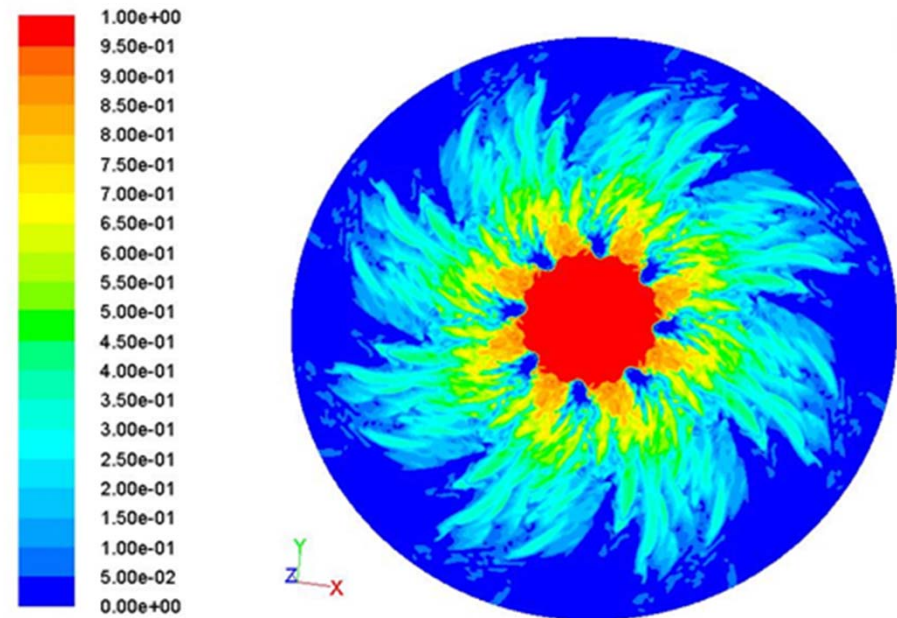
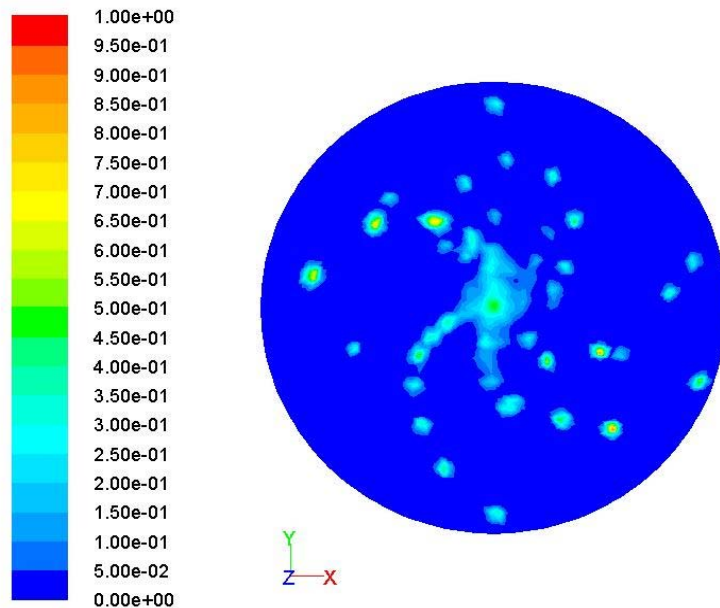


- Fine grid
- Required calculations

Difficulty

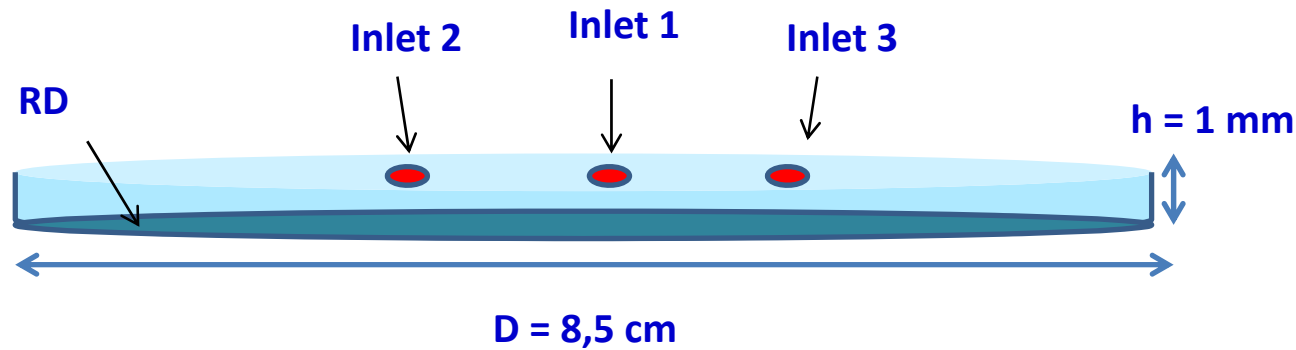


Big meshes leads to miscalculations



Optimal grid choice

System:

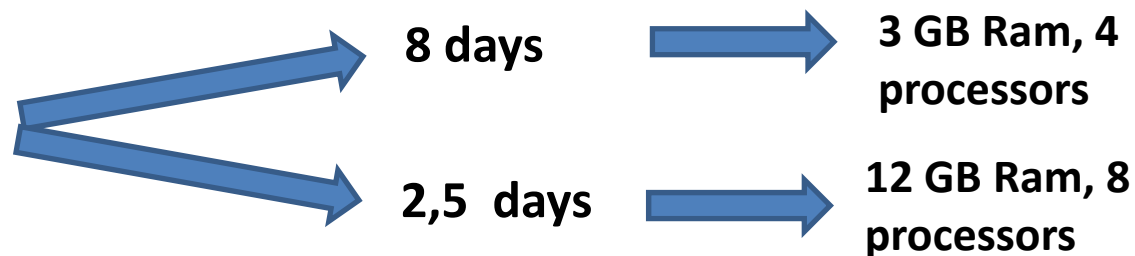


Criteria:

- Axis Z: 18 cylindric volumes of variable height (5-150 μm)
- Axis X-Y: Squared mesh of 500 μm each

538992 cells

Computational
times



EXPERIMENTAL VALIDATION

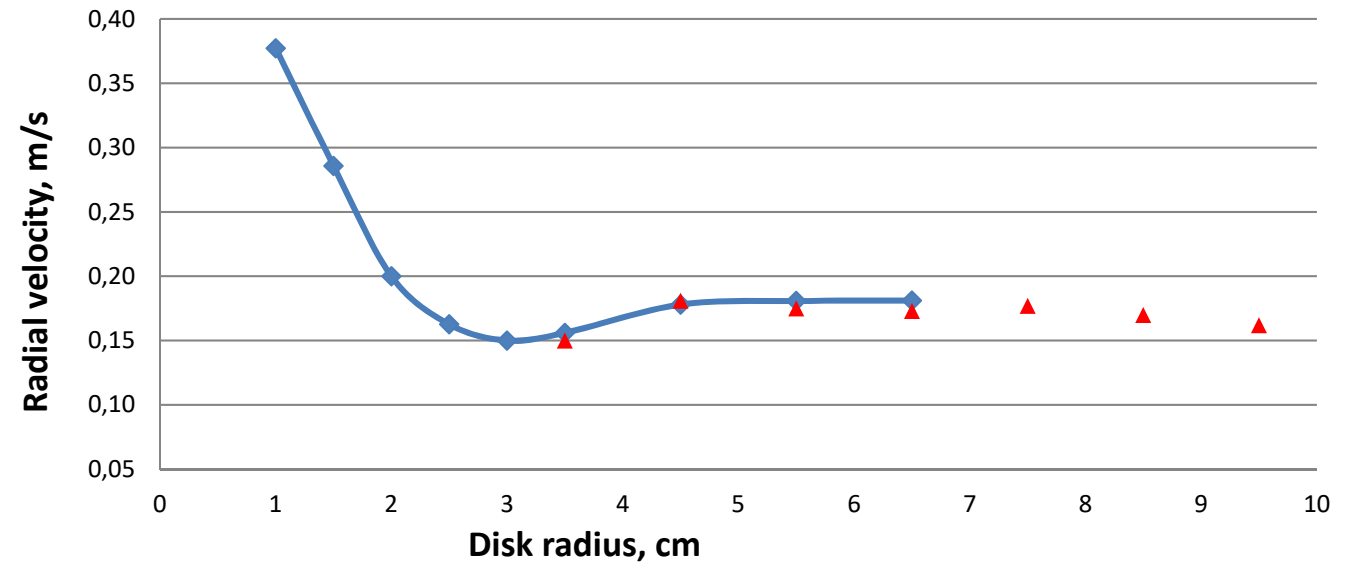
Radial velocity of
the liquid film:

$Q=0,01$ kg/s water

$\omega= 21$ rad/s

$r= 7$ cm

Burns et al. (2003)



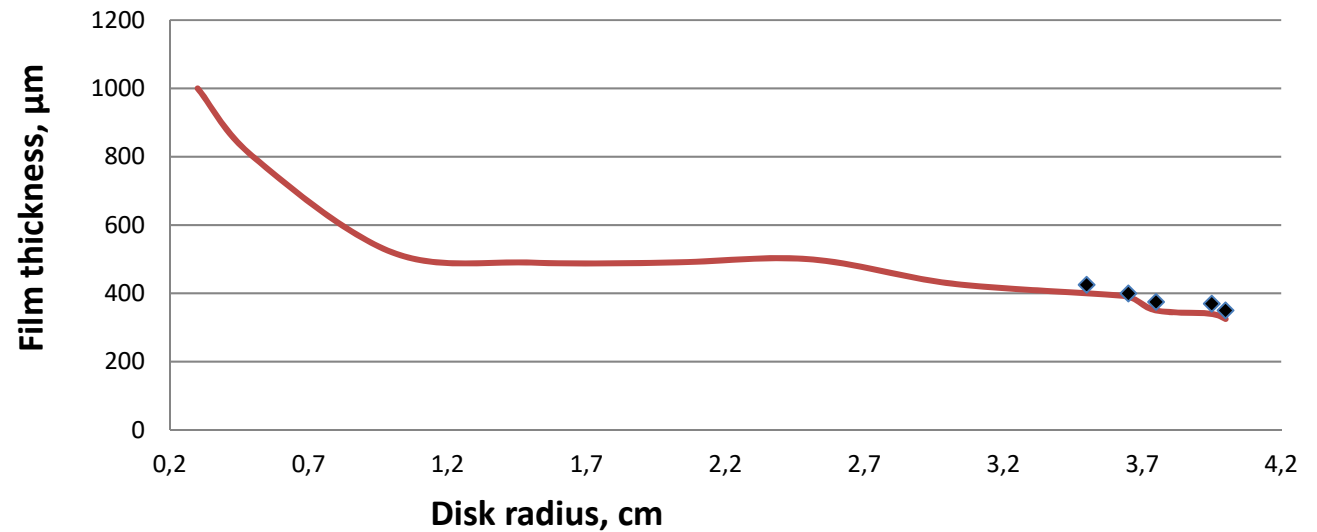
Film thickness:

$Q=0,01$ kg/s water

$\omega= 21$ rad/s

$r= 4,25$ cm

Bhatelia et al. (2009)



HAP PRODUCTION

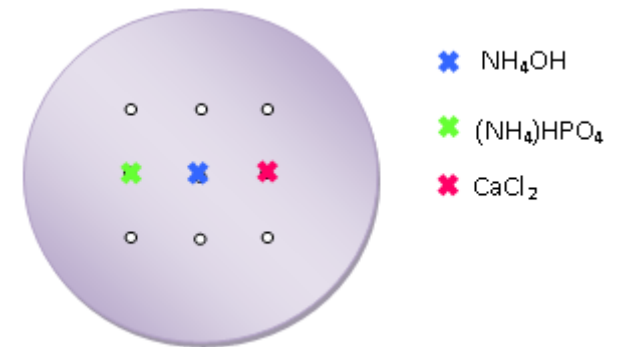


Ca/P=1.67

T ambient

pH = 10

FEED	FLOW RATE (ml/min)	COMPOSITION (g FOR 100 g OF H ₂ O)
CENTRAL	80	10 g NH ₄ OH
SIDE 1	100	5,58 g CaCl ₂
SIDE 2	100	3,49 g (NH ₄) ₂ HPO ₄



RPM OF THE DISK:

560-1400 rpm



HAP nanoparticles measurement

By DLS: Plus 90 supplied by Brookhavn

Agglomeration



Difficulty to measure PDS

A measurement protocol is required

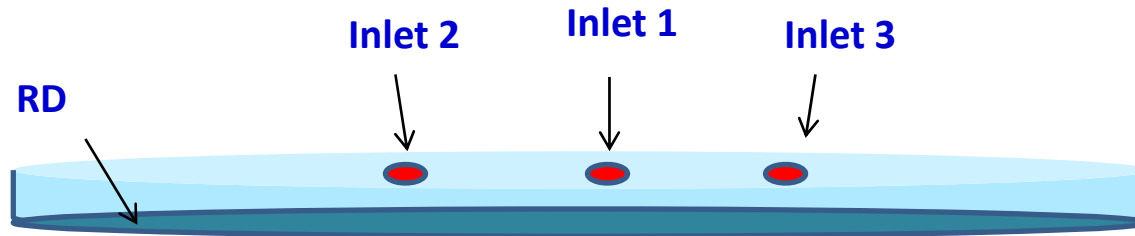
Ultrasound with addition of Tween 60

The addition of the surfactant acts as an antiagglomeration agent due to steric functionality

1) 100ml of 0,1 M di NaOH (pH = 10)
2) 0,5 g of Tween 60
3) Dissolve by ultrasound
4) Add 5 drops of sample
5) Continue the ultrasound bath for 3 minutes
6) Measurement

Implementation in FLUENT

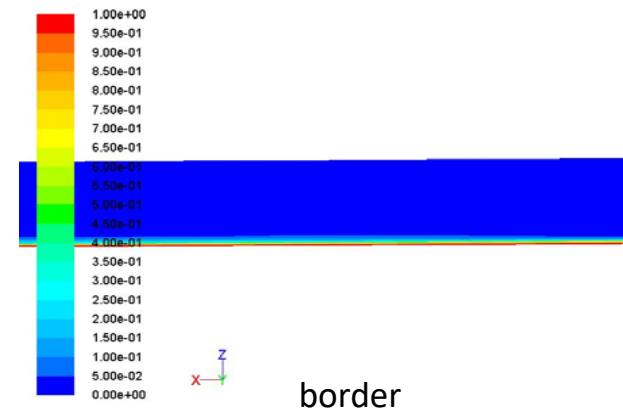
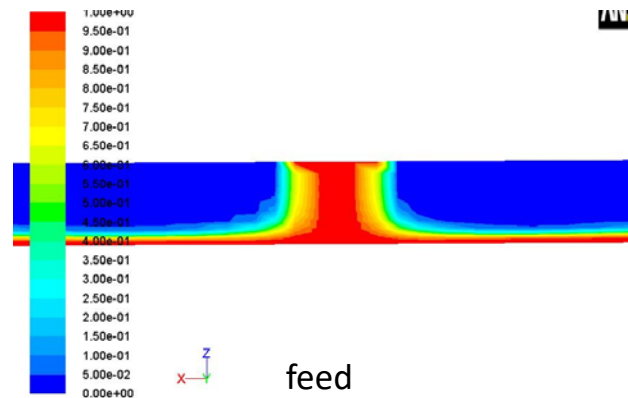
Objective:
Hydrodynamics at the injection points



- **Flow rate:**
 - Equal to those adopted for the HAP production
- **Properties (ρ, μ, D):**
 - ρ, μ those of the adopted reactants
 - Diffusivity was set as for water dissolving in water (self diffusivity)
- **The chemical reaction was not taken into account**

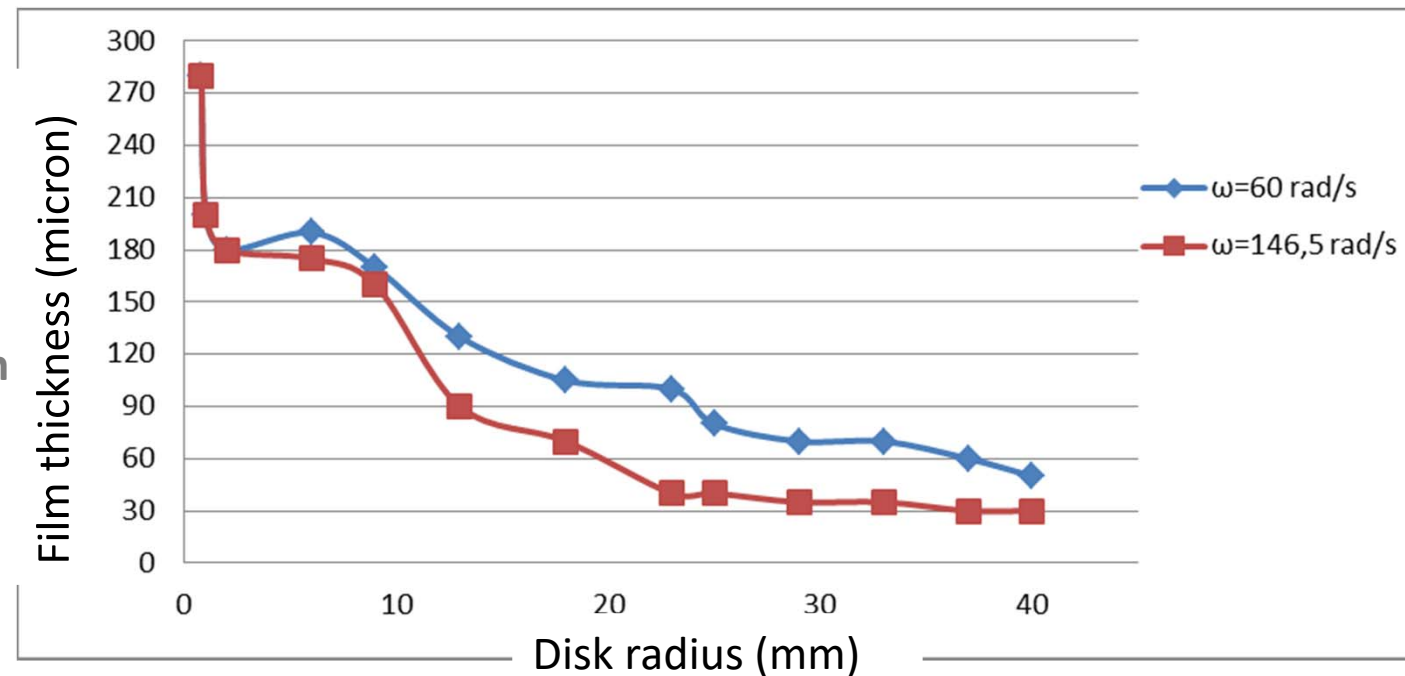
Evaluation of the film thickness – 1 center inlet

Film :
 $\omega = 146,5 \text{ rad/s}$



Min thickness:

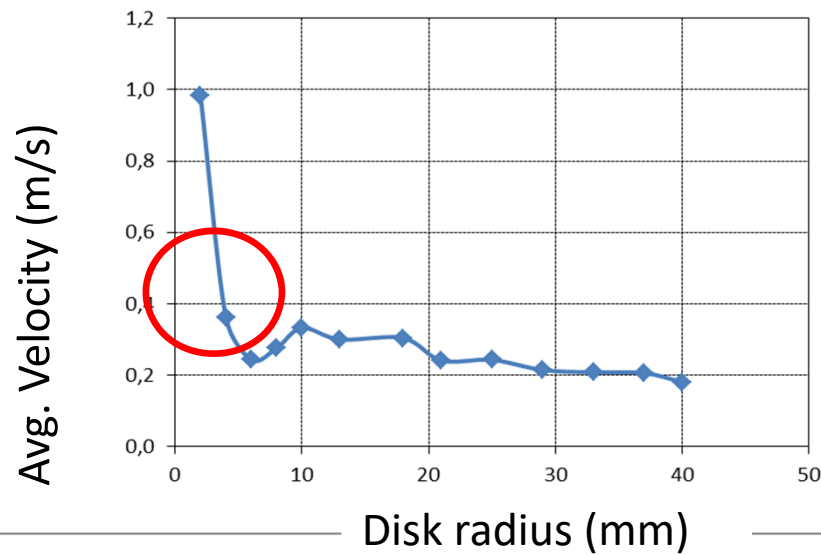
- $30 \mu\text{m} \rightarrow 1400 \text{ rpm}$
- $50 \mu\text{m} \rightarrow 560 \text{ rpm}$



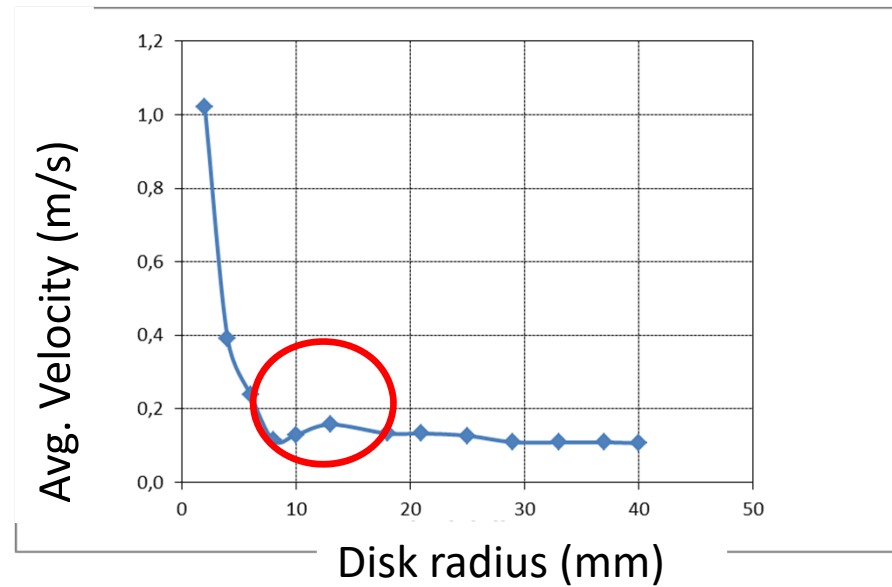
Increase of RPM \longrightarrow REDUCTION OF FILM THICKNESS

Radial velocity profile

$\omega = 1400$ rpm



$\omega = 560$ rpm



Similar to the experimental observation:

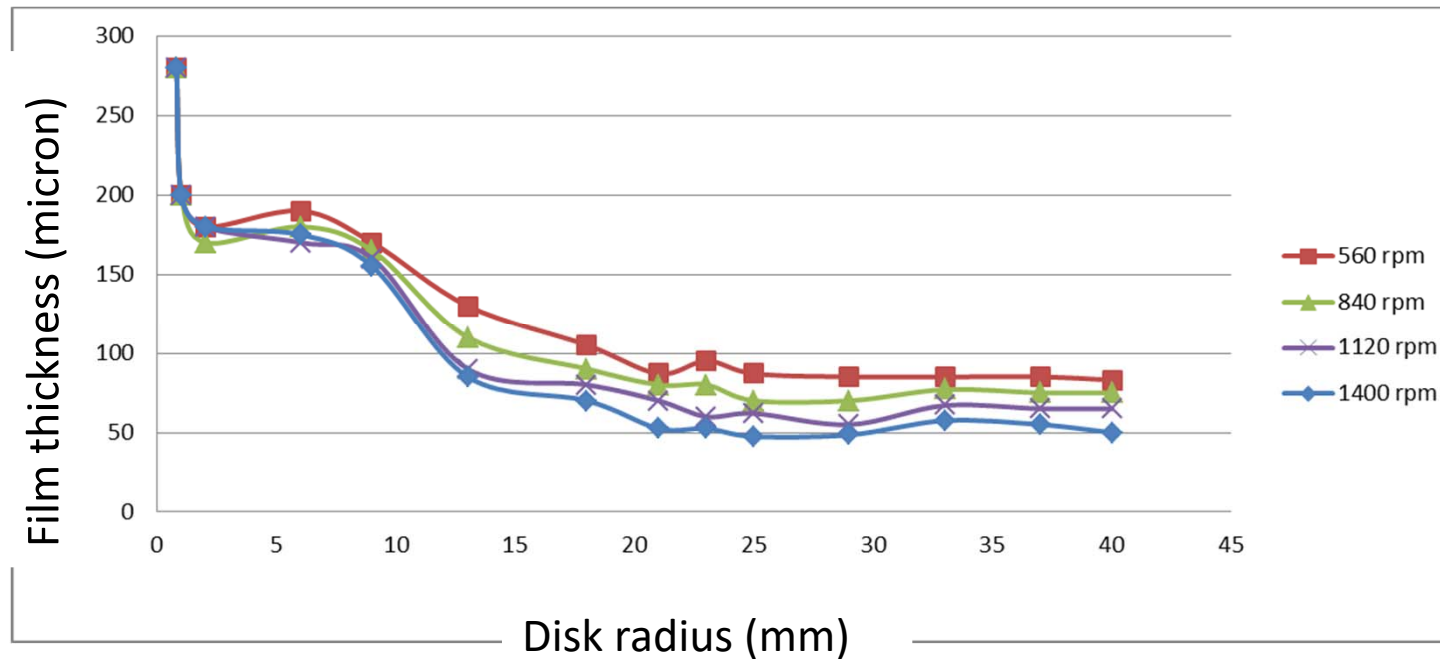
There are three different sectors

- Injection sector
- Acceleration sector
- Synchronization sector

Simulation with 3 injection points

The side streams are added to the central one

Film thickness as a function of the disk radius



ω	h , min
560 rpm	83 μm
840 rpm	75 μm
1120 rpm	65 μm
1400 rpm	50 μm

Increase of RPM



Reduction of the thickness

The synchronization sector appears to start independent from RPM

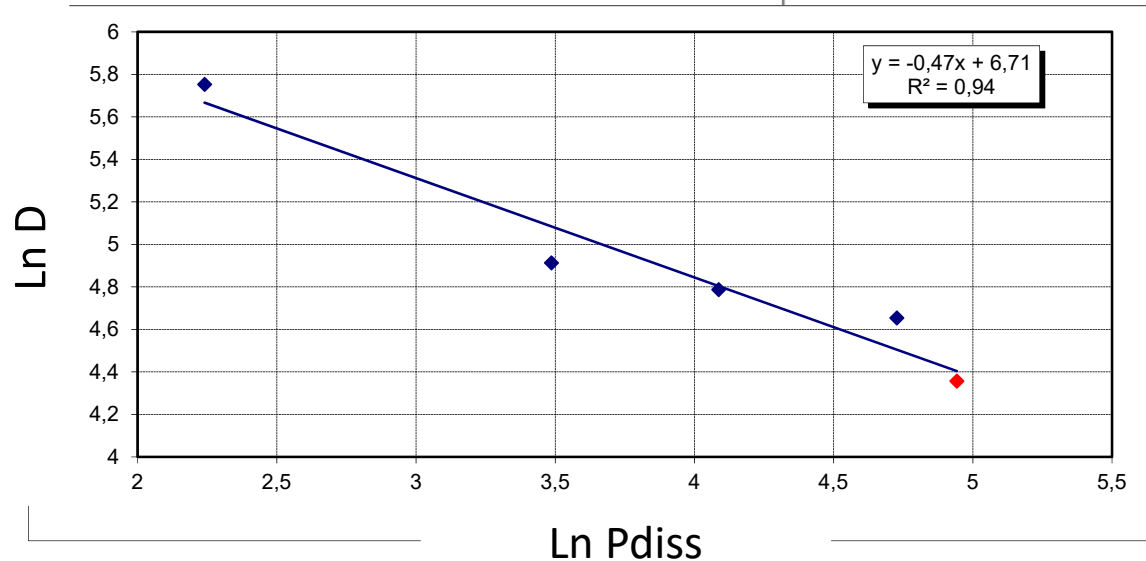
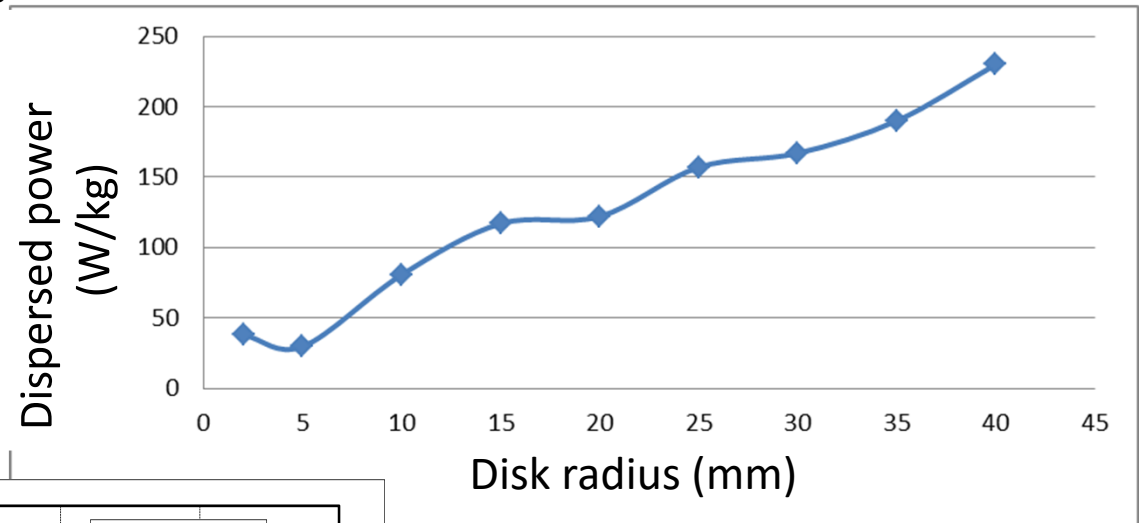
Dispersed energy evaluation

Dispersed power

$$P_{diss} = \frac{1}{2 \cdot t_{res}} \left((r_e^2 \cdot \omega^2 + v_{r_e}^2) - (r_i^2 \cdot \omega^2 + v_{r_i}^2) \right)$$

Increases as a function
of RPM and r

$\omega = 1400$ rpm
Center flow



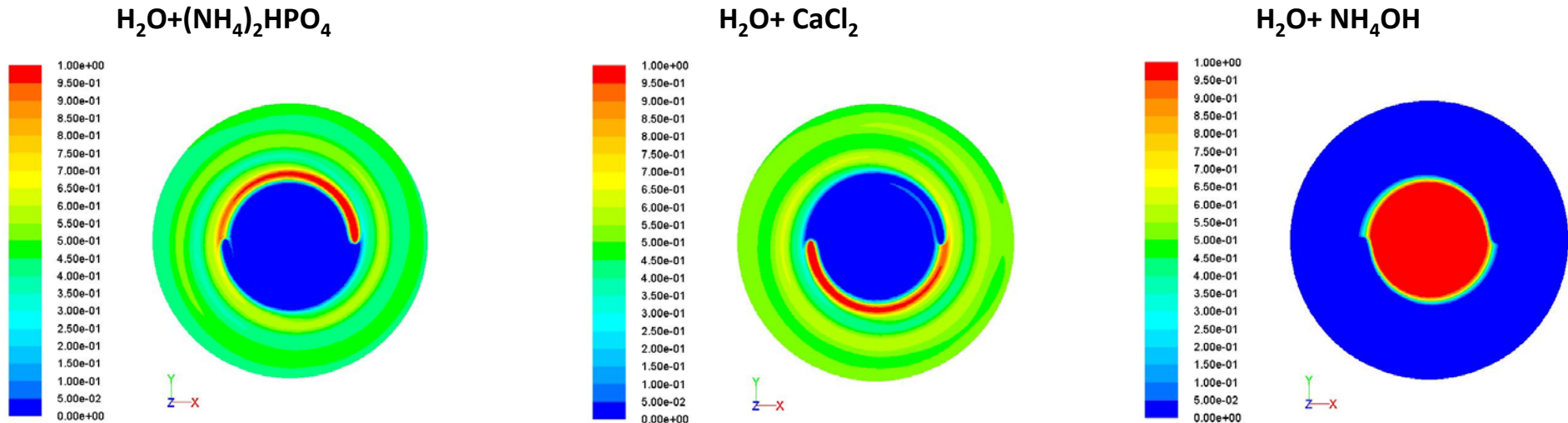
$$d \sim \varepsilon^{-0,5}$$

$$\tau_m = 12 \left(\frac{\nu}{\varepsilon} \right)^{0.5}$$

Dispersed energy and size of
particles appears to be
proportional

OUTPUT

$\omega=560$ rpm; looking at the surface $5\text{ }\mu\text{m}$ high from disk surface



Low RPM (<1000 rpm)

Less dispersed energy in the liquid

Low Mesomixing

Segregation of the streams

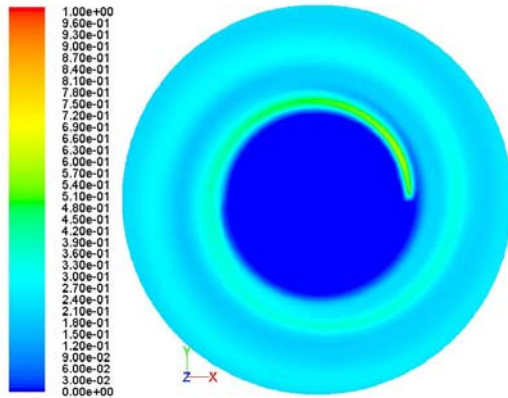
The side stream injections passes trough the liquid layer and adheres on the disk surface

The bulk is shifted to upper layers

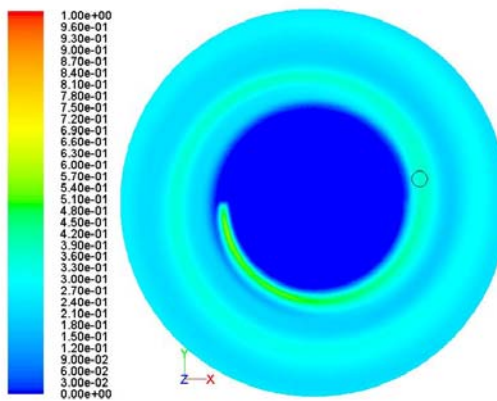
OUTPUT

$\omega=1400$ rpm; looking at the surface $5\text{ }\mu\text{m}$ high from disk surface

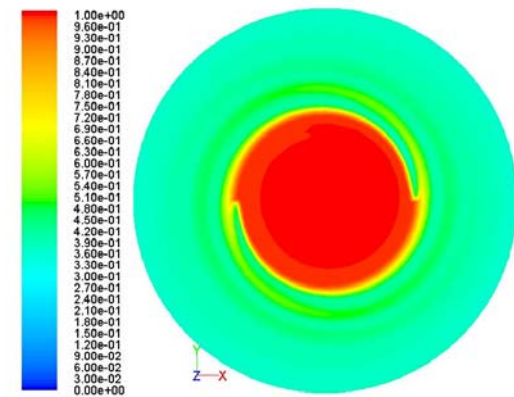
$\text{H}_2\text{O}+(\text{NH}_4)_2\text{HPO}_4$



$\text{H}_2\text{O}+\text{CaCl}_2$



$\text{H}_2\text{O}+\text{NH}_4\text{OH}$



HIGH RPM (>1000 rpm)

High dispersed power

Micromixing

Mixing appears to be rapid and complete

The bulk is mixed to the reactants

OUTPUT

CONSIDERING THE REACTION:

The population balance equation in terms of density function $n(V,t)$ is:

$$\frac{\partial}{\partial t}[n(V,t)] + \nabla[\vec{u}n(V,t)] + G = A_B + A_D + B_B + B_D$$

The boundary and initial conditions are given by:

BC: $n(V=0,t)=0$

IC: $n(V,t=0)=n_v$

Moments

m_0	$4.12 \cdot 10^7$
m_1	$9.04 \cdot 10^{-2}$
m_2	$1.63 \cdot 10^{-11}$
m_3	$7.82 \cdot 10^{-20}$

OUTPUT

ANALYSIS OF THE OPERATION AS A FUNCTION OF THE
INJECTION POINT POSITIONS

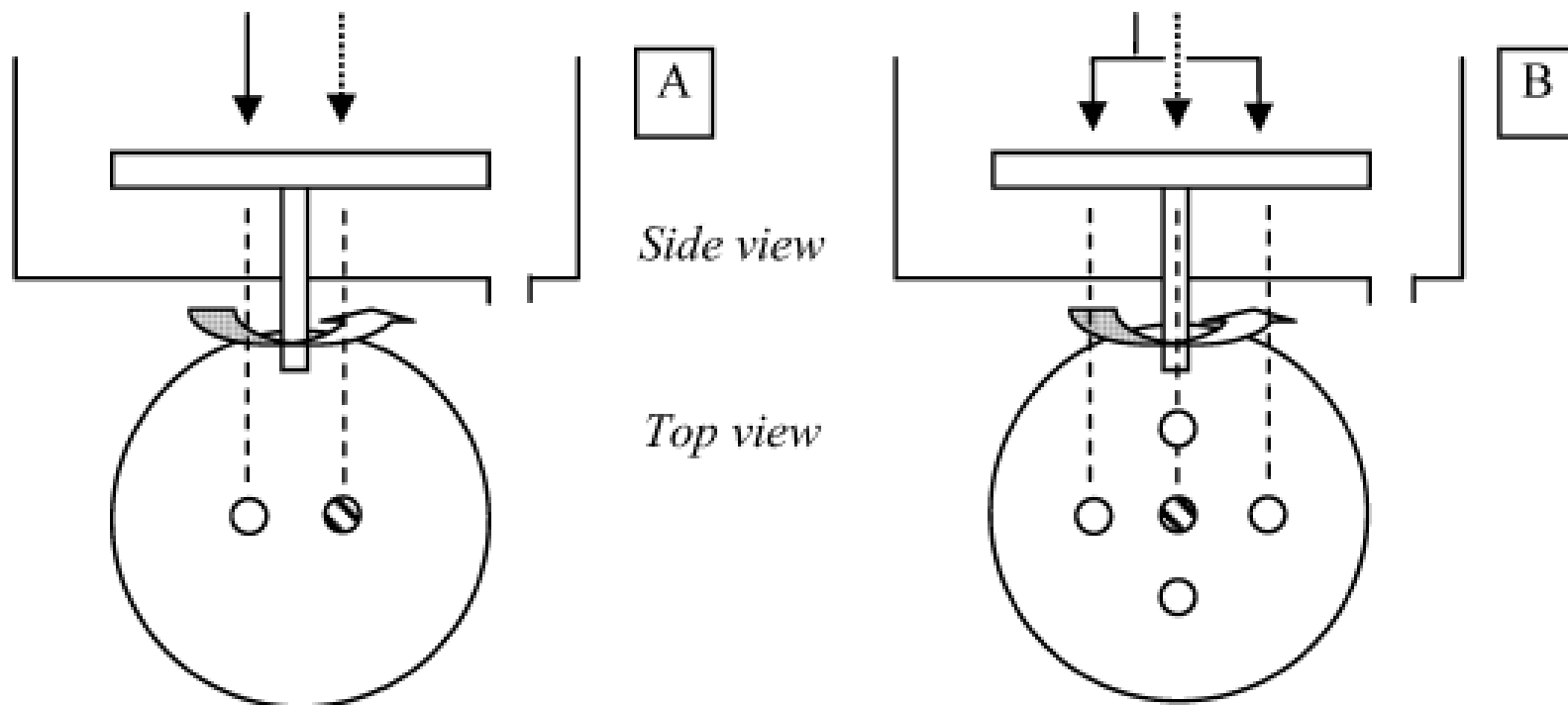
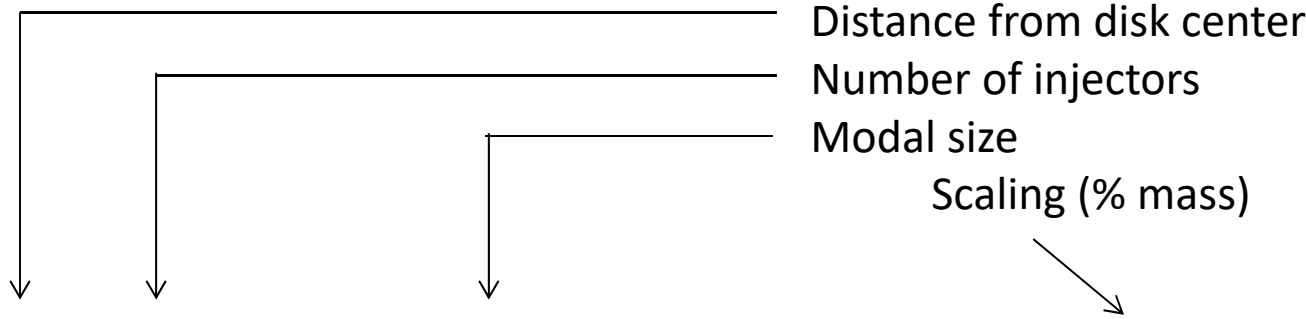


Figure 1: Scheme of the used feeding distribution systems (A. TIS; B. MIS)

OUTPUT



System	r^* [cm]	n^*	L_p [nm]	L_c [nm]	W_d^*	Z potential [mV]	ϵ [mW/g]	$m\%$ [%]
TIS	5	-	1	21	1,0	31	711,4	> 90,0
TIS	10	-	2	75	1,0	30	219,1	> 90,0
TIS	14	-	5	112	1,0	35	49,6	> 90,0
MIS-1	7	1	55	146	20,9	184	-	> 90,0
MIS-1	10	1	90	197	41,8	158	-	76,9
MIS-1	12	1	136	313	58,6	106	-	56,8
MIS-1	14	1	188	422	58,6	122	-	54,6
MIS-2	7	2	44	119	14,6	142	-	88,9
MIS-2	10	2	142	144	20,9	101	-	68,7
MIS-2	12	2	155	304	25,1	123	-	54,8
MIS-2	14	2	201	478	29,3	144	-	53,1
MIS-8	7	8	12	41	3,7	99	-	22,4
MIS-8	10	8	22	65	5,2	121	-	15,4
MIS-8	12	8	26	89	6,3	101	-	0
MIS-8	14	8	28	115	7,3	104	-	0

OUTPUT

ANALYSIS OF THE OPERATION AS A FUNCTION OF THE INJECTION POINT POSITIONS

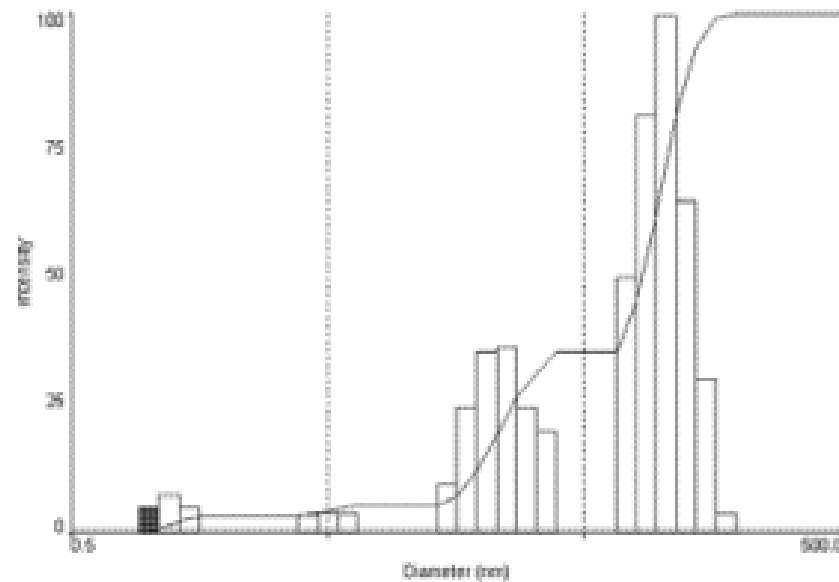


Fig. 2: PSD for TIS (feed point at 5 cm)

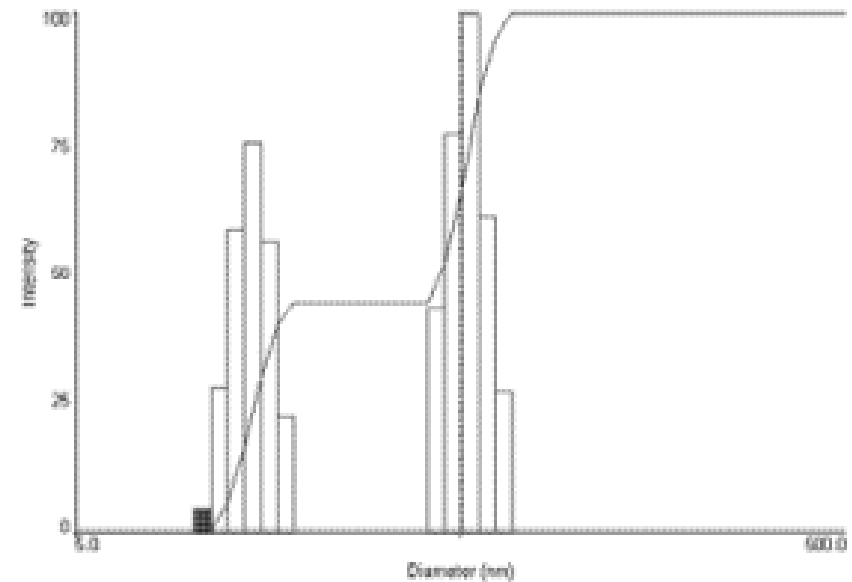


Fig. 3: PSD for MIS-8 (feed point at 7 cm)

OUTPUT

OPTIMIZATION OF THE OPERATION AS A FUNCTION OF THE NUMBER OF INJECTION POINT FOR THE MINIMUM REQUIREMENT FOR THEIR POSITION (DISTANCE FROM DISK CENTER)

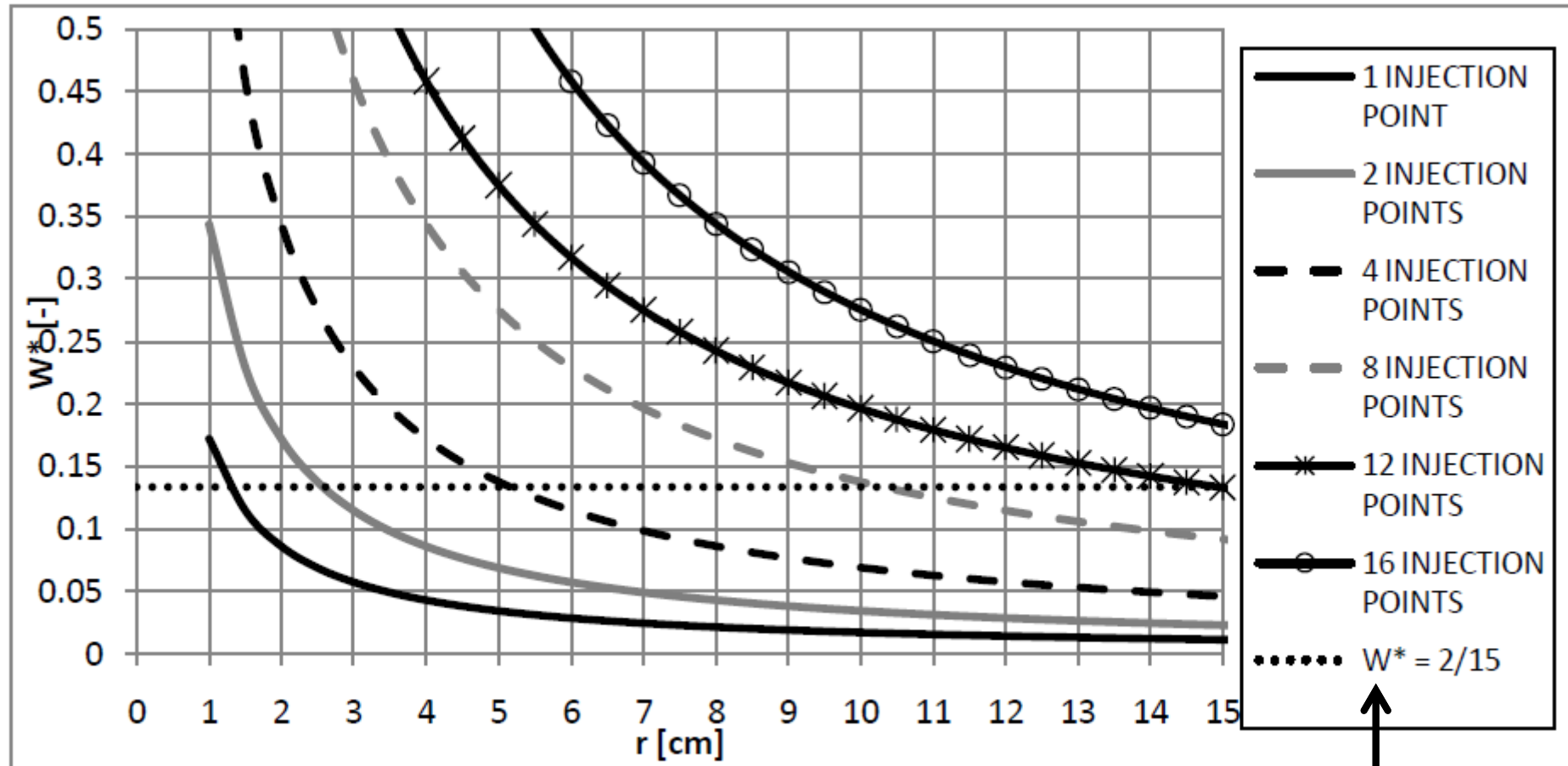
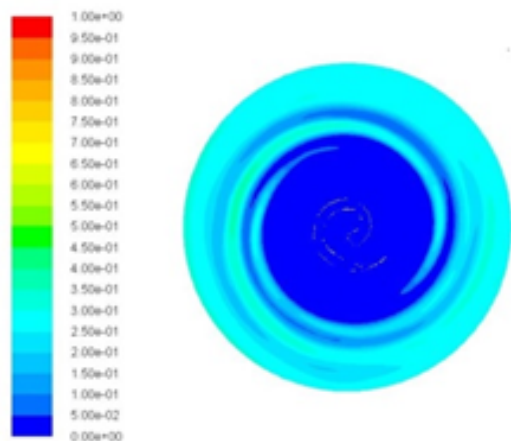


Figure 4.1.7. Plot of W^* as function of r^* and n^* .

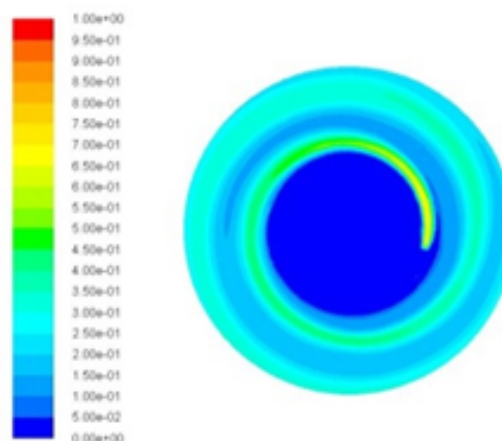
MINIMUM STOICHIOMETRIC REQUIREMENT

OUTPUT

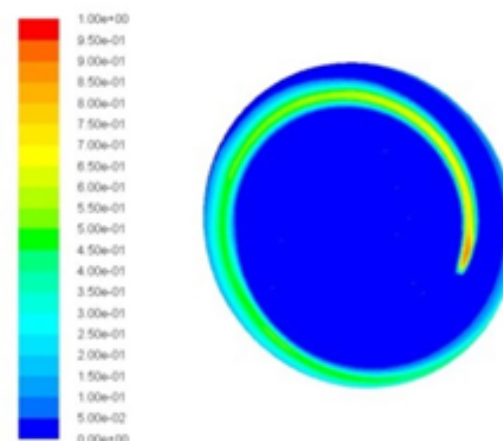
Configuration A



Configuration B

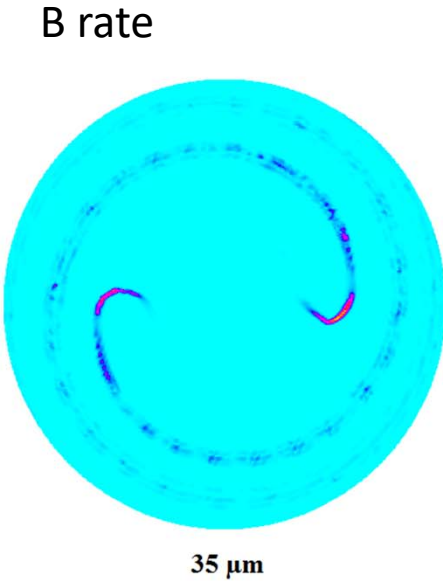
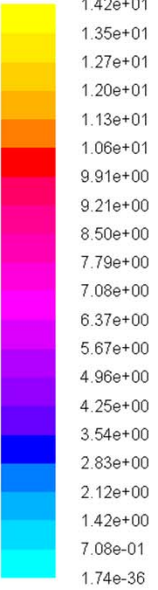
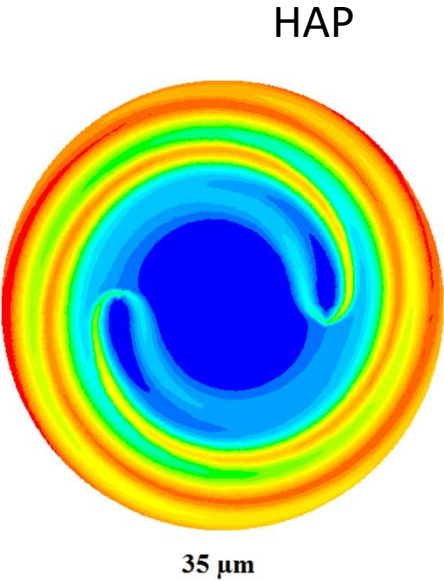
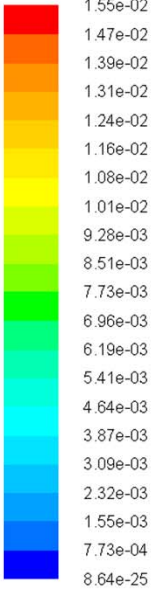
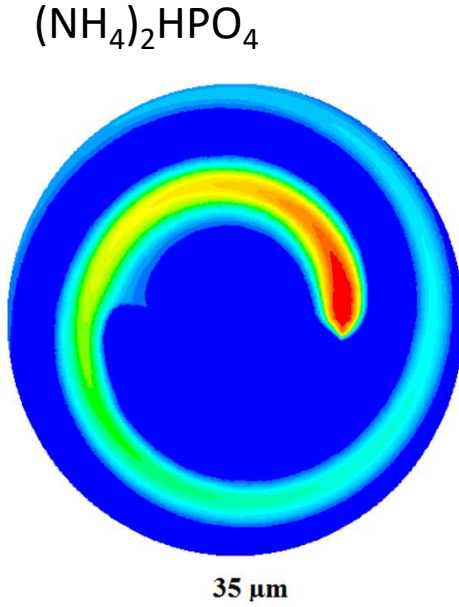
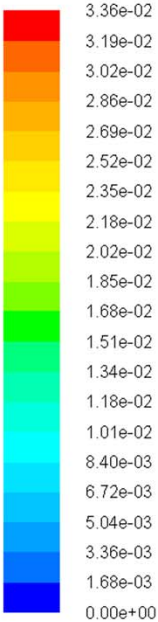
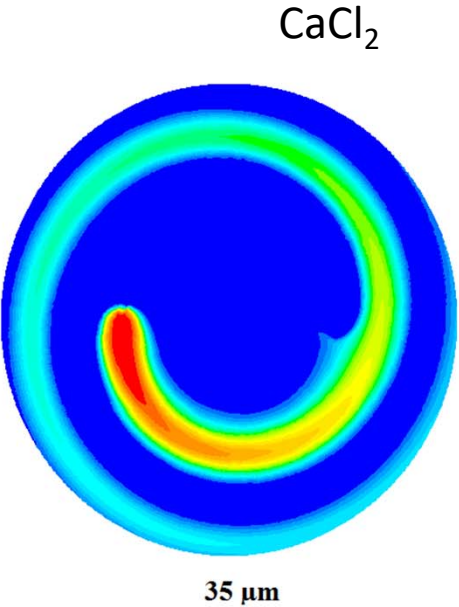
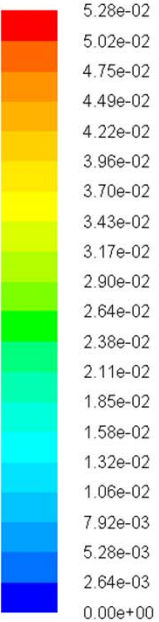


Configuration C



Configuration	Maximum Ca/P (CFD)	Minimum Ca/P (CFD)	Modal diameter (nm)	Minimum value (nm)	Maximum value (nm)
A	1.68	1.65	58	52	85
B	1.82	1.55	85	82	113
C	1.91	1.32	81	78	138
EXPERIMENTAL DATA				SIMULATION RESULTS	

OUTPUT

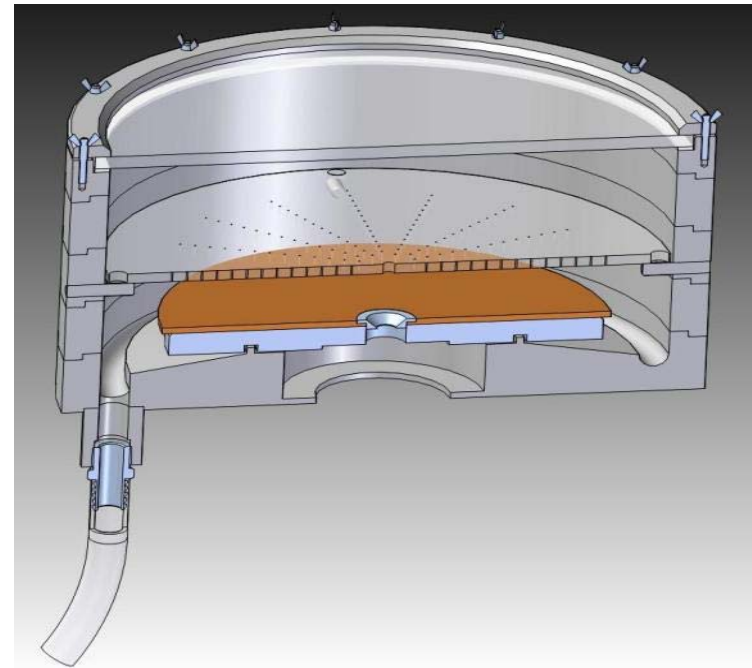


SDR



Diameter 30 mm

RPM 500 -1500 rpm



SDR

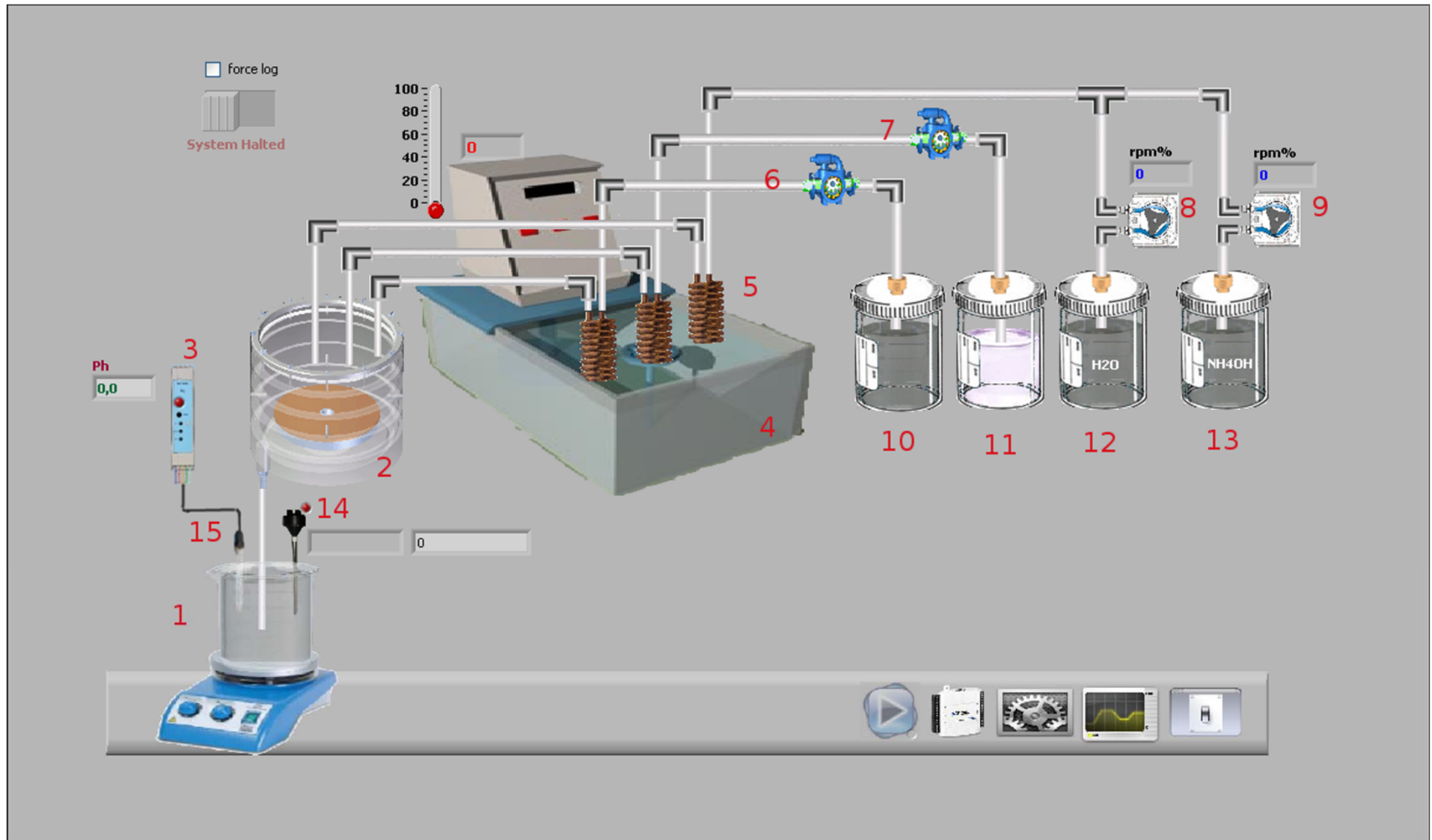


Feed injectors

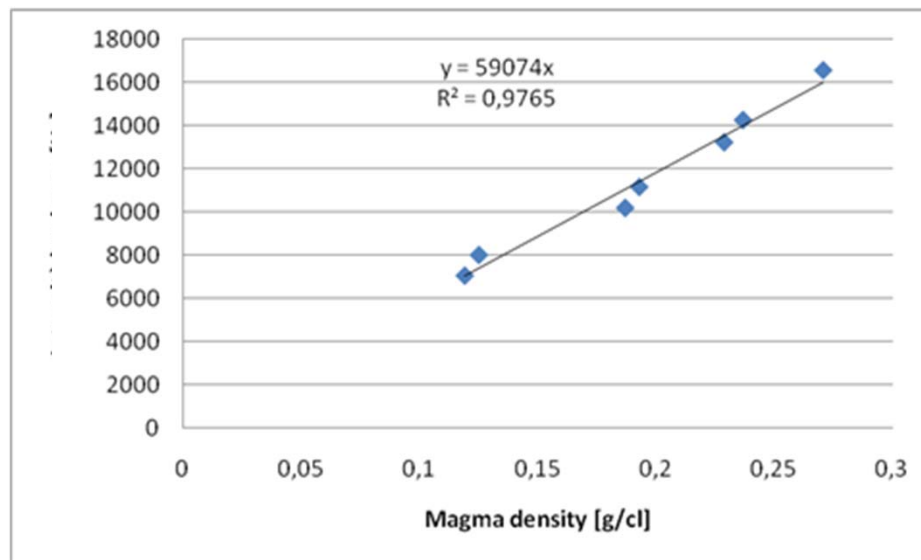
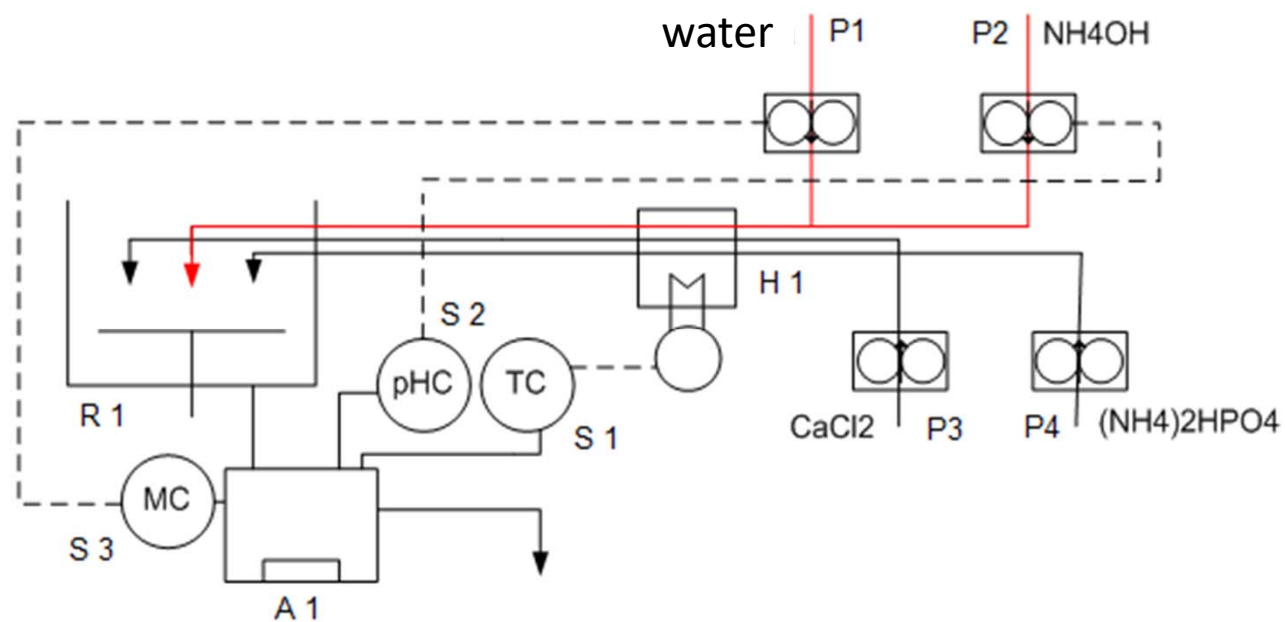


Nephelometer for suspension monitoring and control

SDR CONTROL SYSTEM



SDR CONTROL SYSTEM



The measurement (LUXSCAN) and the magma density are proportional

t [min]	T [°C]	pH [-]	Flow rate bulk [ml/min]	Intensity Hz	Modal size [nm]	Magma density [g HAP / cl solution]
0	40	10.0	83	13416	102	0.231
10	40	10.0	78	14016	122	0.221
20	40	10.0	75	11934	100	0.189
35	40	10.1	71	10278	92	0.200
50	40	10.3	73	11722	92	0.193
65	40	10.0	84	14124	104	0.207