流通式超臨界水熱合成反応器内の熱流動場の可視化

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Introduction

Hydrothermal synthesis of metal oxide nanoparticles

$$M^{n+} \xrightarrow{+\ n\ H_2O} M(OH)_n \xrightarrow{-\ n/2\ H_2O} MO_{n/2}$$

$M(SO_4)_{n/2}$
$M(NO_3)_n$

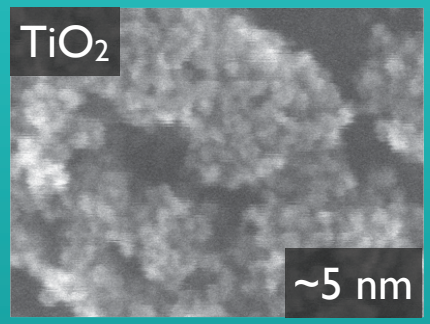
Cheap precursors can be used.

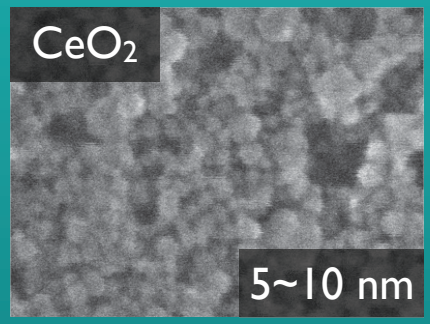
Water: solvent and reactant

200~400°C
25~30 MPa

Produced metal oxide nanoparticles

CeO_2	Cu_2O	$MgFe_2O_4$	TiO_2:Nb-Co
TiO_2	NiO	$BaTiO_3$	AlOOH
ZrO_2	CuO	$CoAl_2O_4$	$Gd(OH)_3$
ZnO	RuO_2	$LiCoO_2$	Cu
Fe_2O_3	MnO_2	$LiMn_2O_4$	Ni
Fe_3O_4		ITO, IZTO	





Synthesis with plug-flow reactors

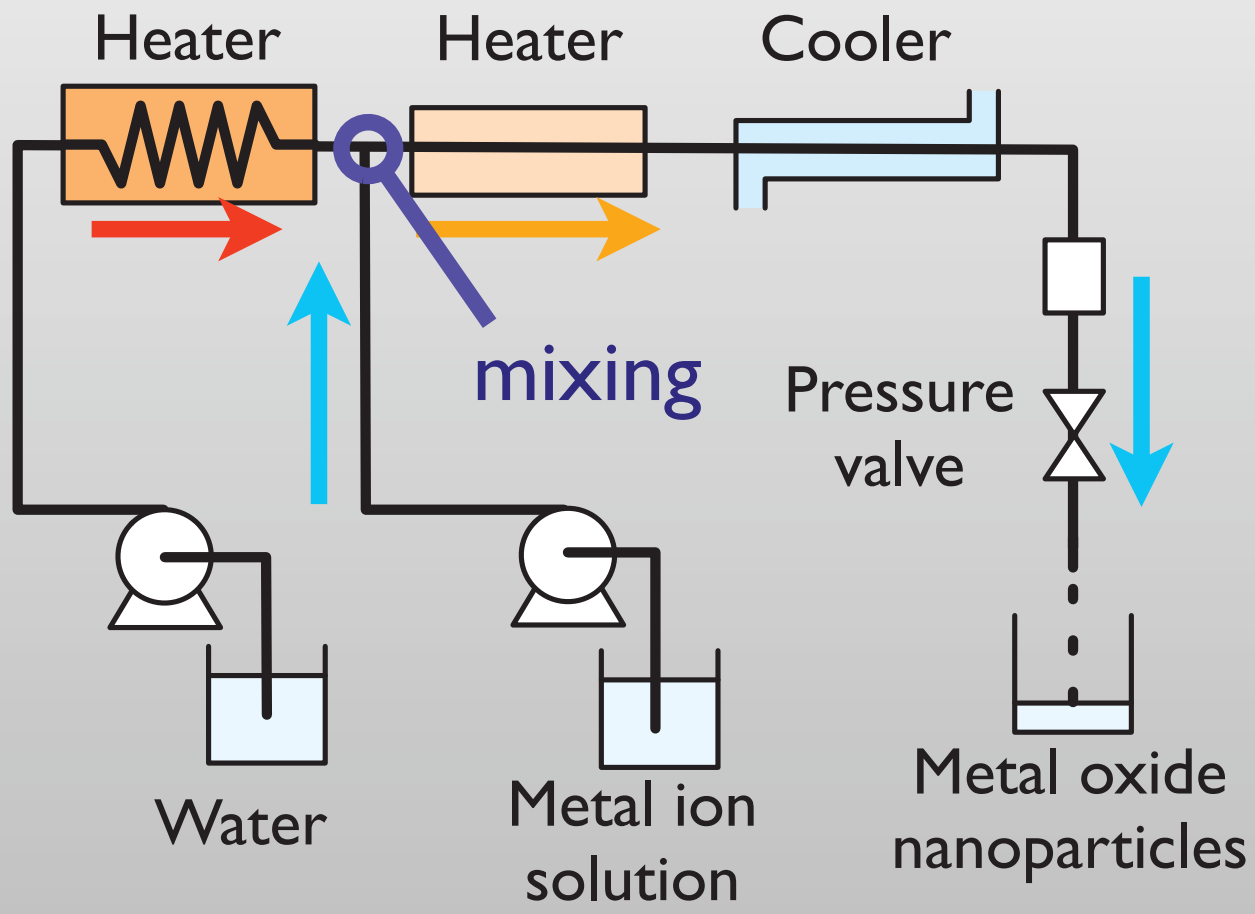
Batch reactor

~ 5 mL

Heater

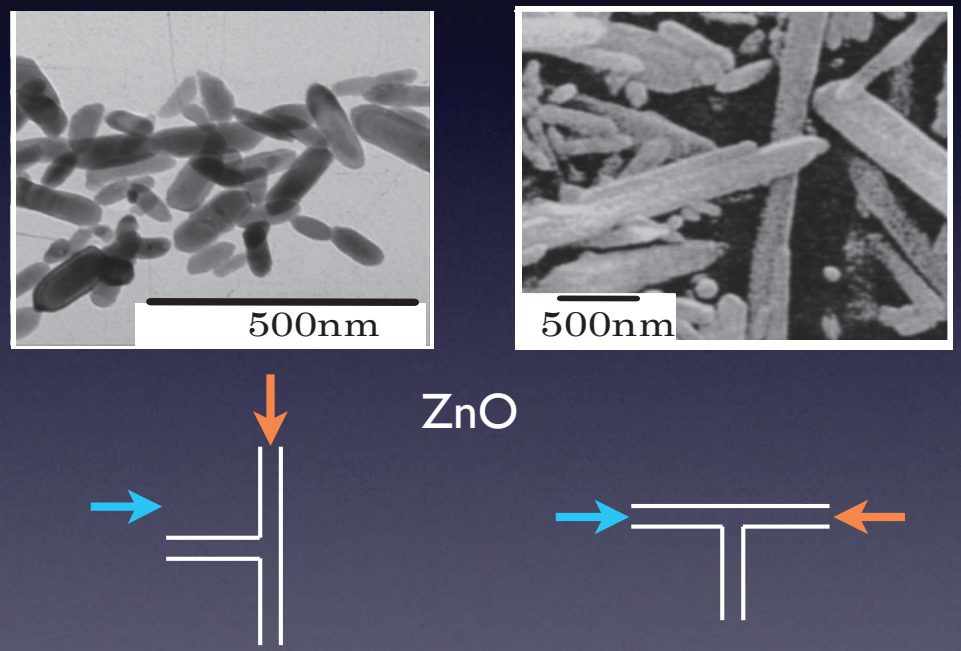
2~3 min

Plug-flow reactor



Synthesis with plug-flow reactors

Size of products



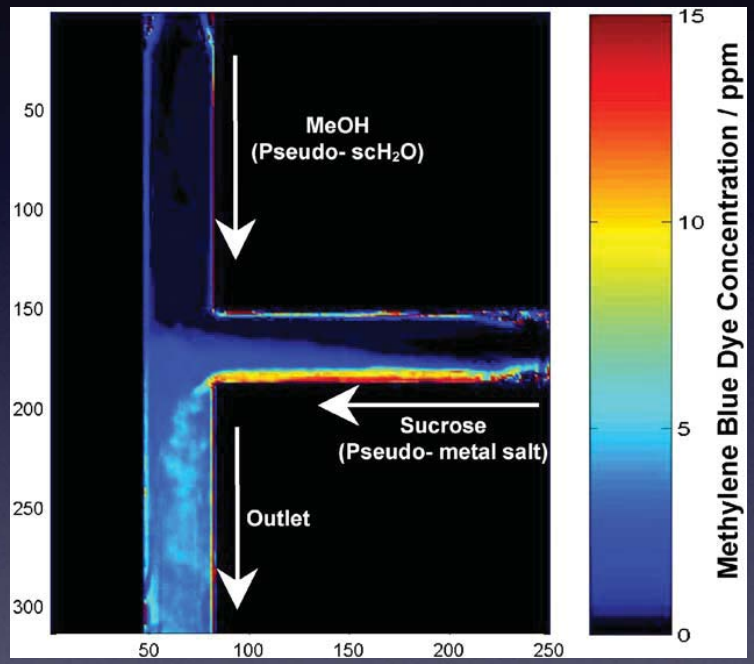
T. Adschiri, *et al.*, in Materials Chemistry in Supercritical Fluids, Research Signpost, 79–97 (2005)

Plugging

Mixing of supercritical water and reactants affects the products

Experimental approaches

Model fluid

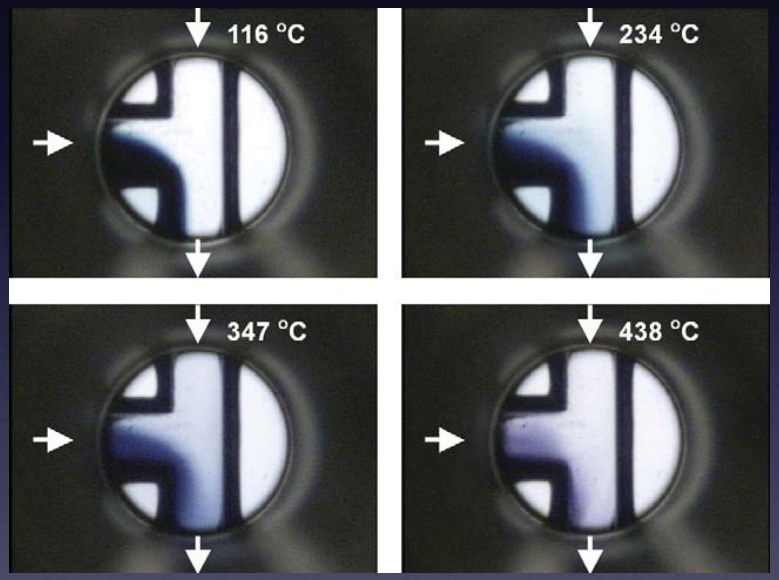


room temperature

Buoyancy force

Blood, *et al.*, *Chem. Eng. Sci.* **59**, 2853 (2004).

View cell



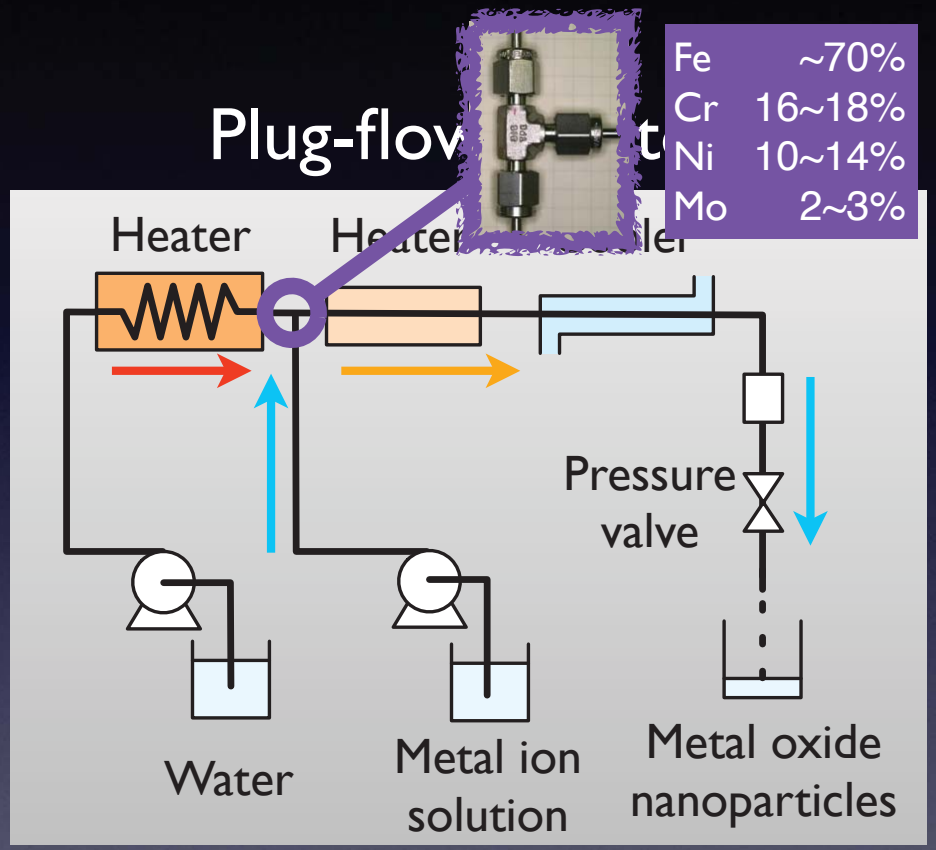
rectangular flow

Cascade down

Aizawa, *et al.*, *J. Supercrit. Fluids* **43**, 222 (2007).

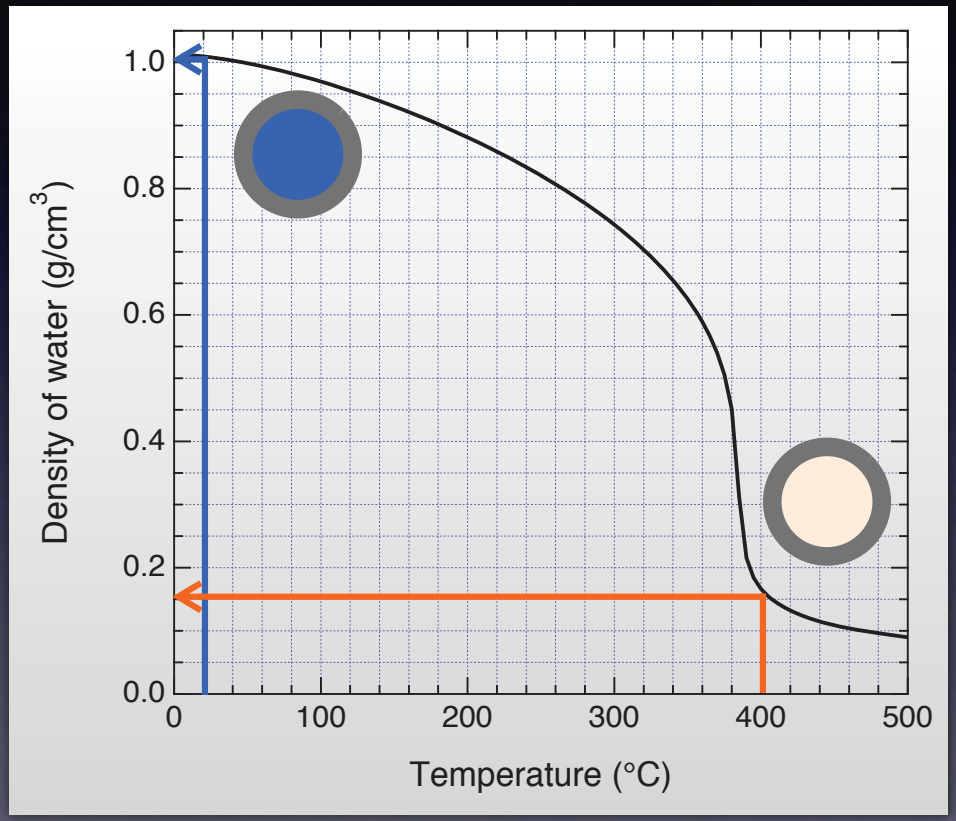
Mixing in real apparatus is difficult to visualize.

Mixing of two water streams



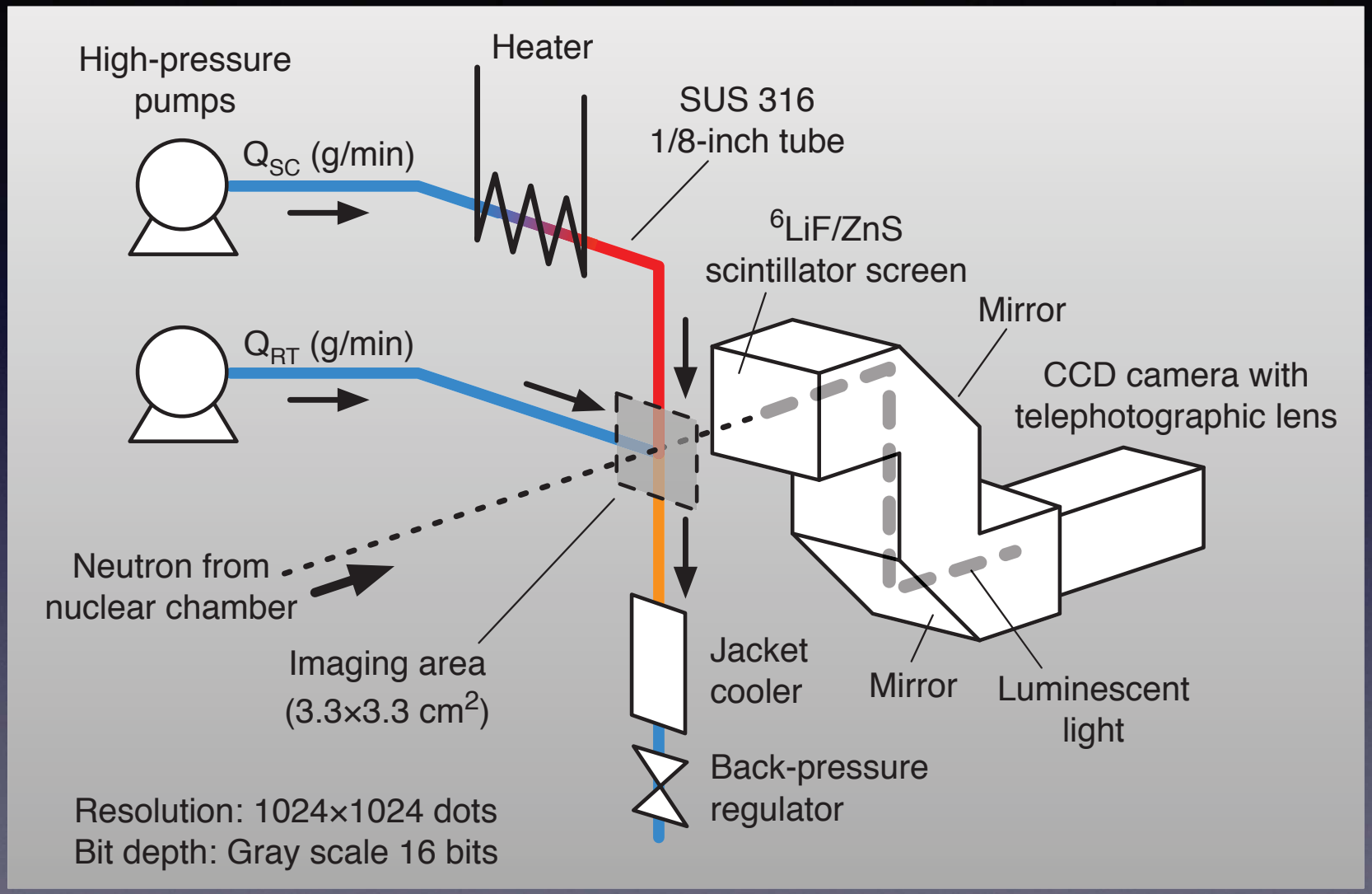
300~400°C, 25 MPa

Density of water @ 25 MPa



Difference in water density can be visualized.

Experimental setup



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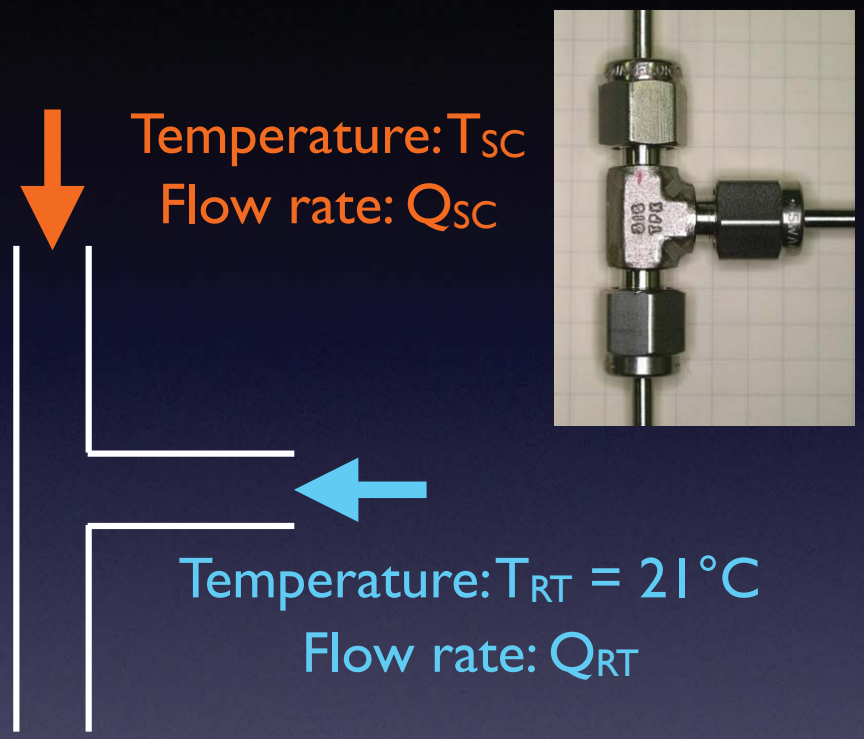
S. Takami *et al.*, *J. Supercrit. Fluids* **63**, 46 (2012).

Experimental condition for 2D



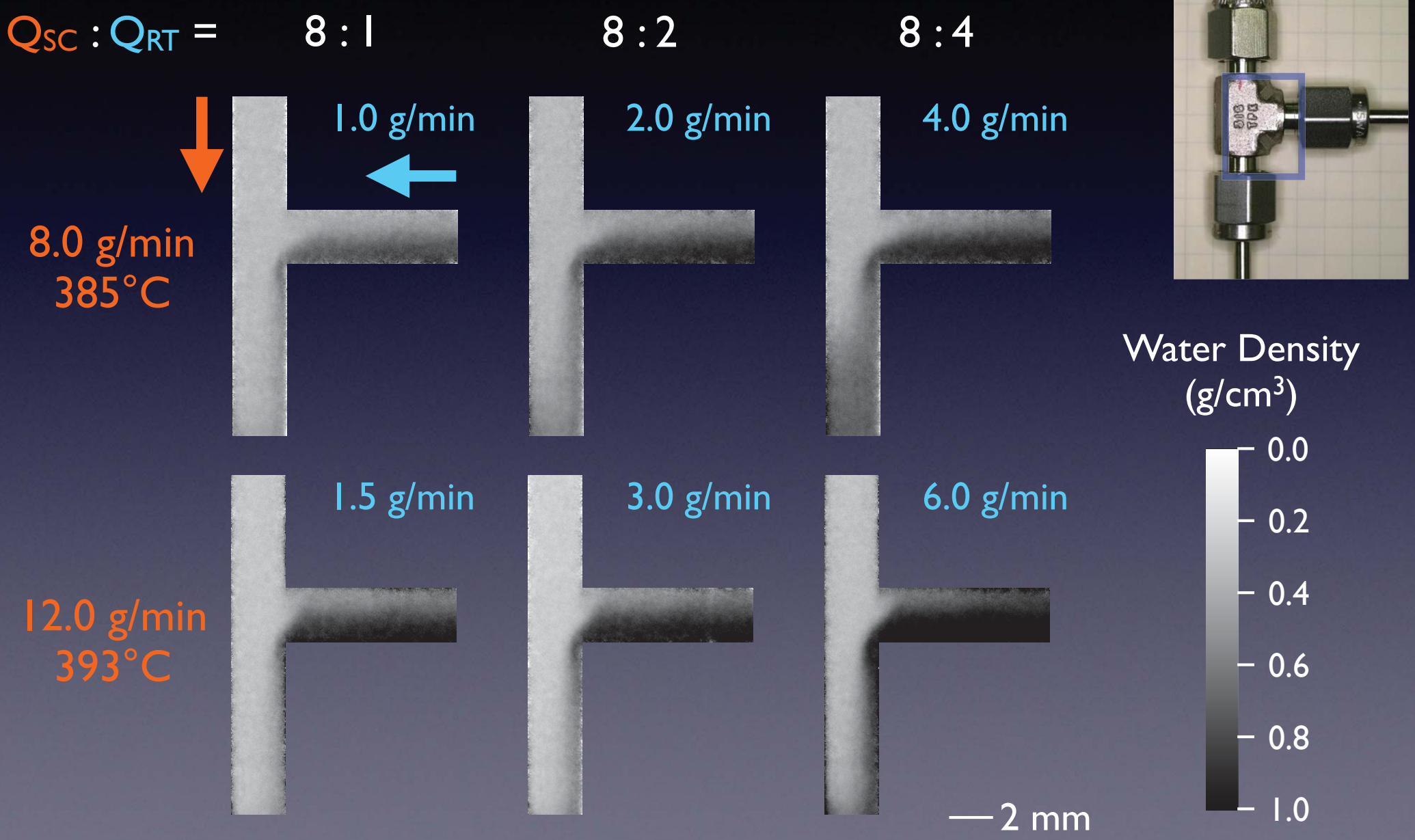
Q_{SC} (g/min)	Q_{RT} (g/min)	T_{SC} (°C)	Re_{Sc}	T_{mix} (°C)	Re_{mix}
8	1	385	2.5×10^3	360	1.2×10^3
8	2	385	2.5×10^3	341	1.2×10^3
8	4	385	2.5×10^3	303	1.1×10^3
12	1.5	393	4.8×10^3	380	2.4×10^3
12	3	393	4.8×10^3	377	2.3×10^3
12	6	393	4.8×10^3	338	2.0×10^3

Outer diameter: 1/8 inch
Inner diameter: 2.3 mm

P = 25 MPa

30 s for 1 image
6 images for one condition

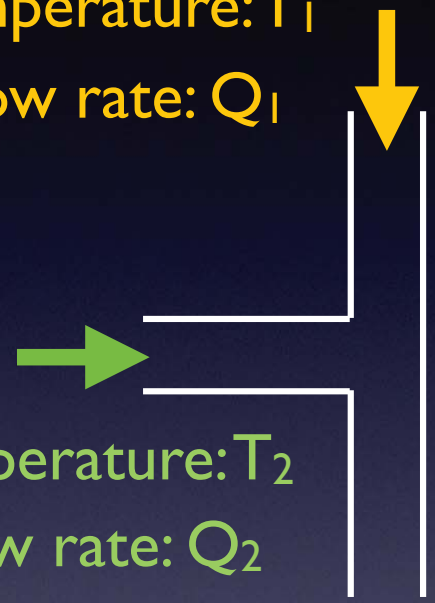
Averaged water density



Experimental condition for tomography

Temperature: T_1

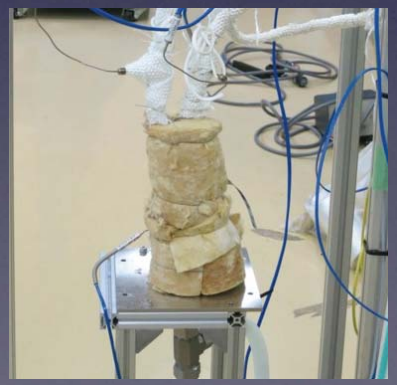
Flow rate: Q_1



Temperature: T_2

Flow rate: Q_2

Q_1 (g/min)	T_1 (°C)	Q_2 (g/min)	T_2 (°C)	T_{mix} (°C)	Re_{mix}
12	~385	6	30	335	2.0×10^3
6	30	12	~391	355	2.3×10^3



Outer diameter: 1/8 inch
Inner diameter: 2.3 mm

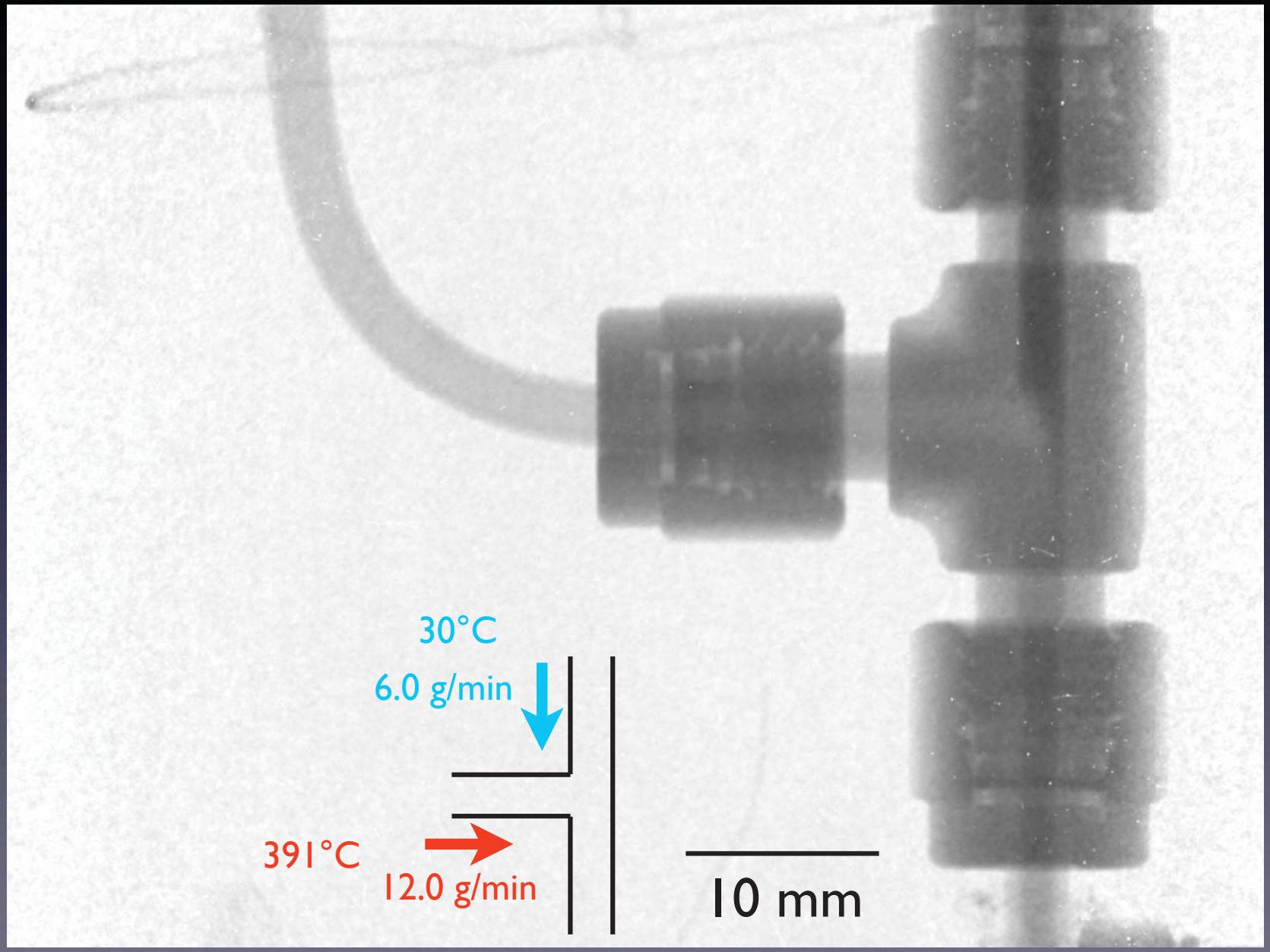
P = 25 MPa

Imaging area: 65×65 mm^2

60 s for 1 image
200 images for one condition

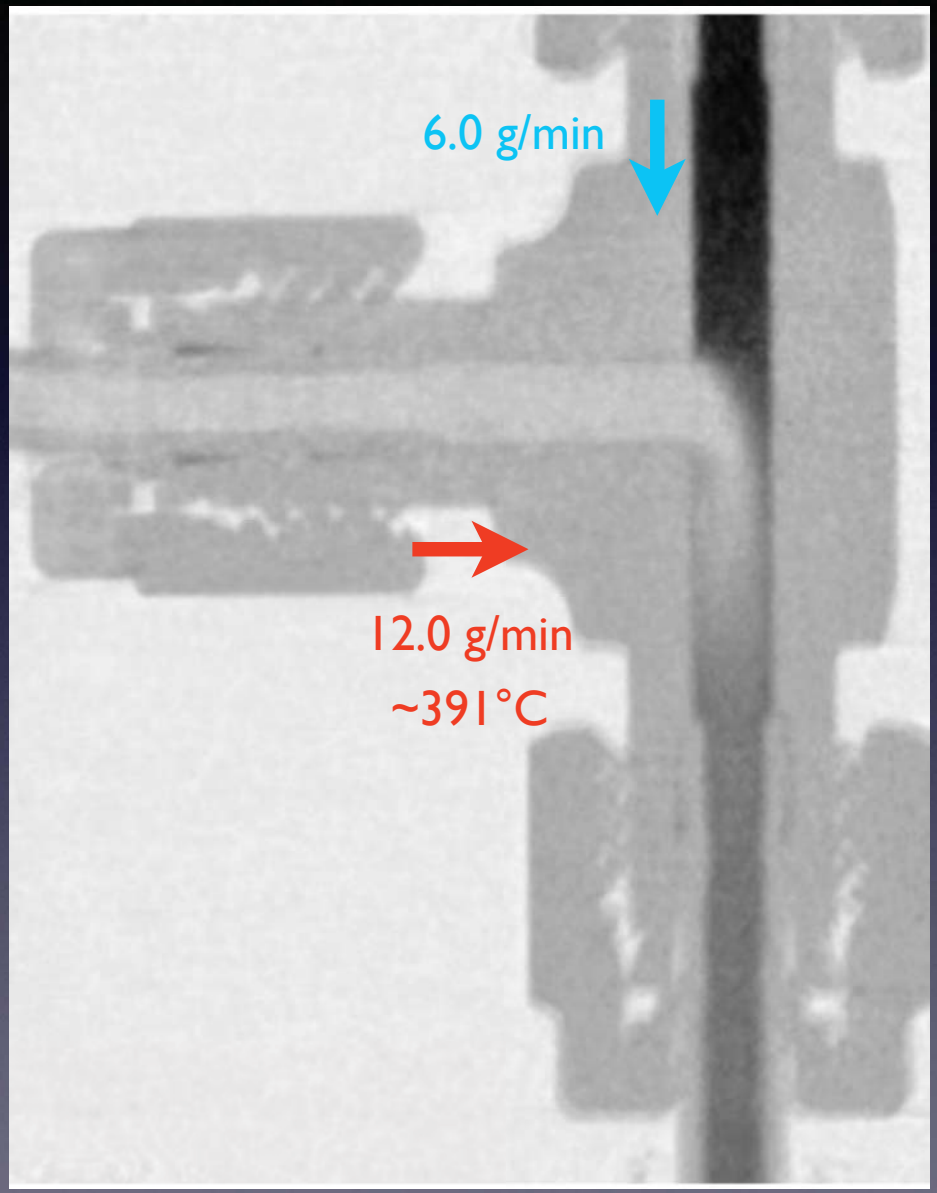
OCTOPUS software was used for CT reconstruction.

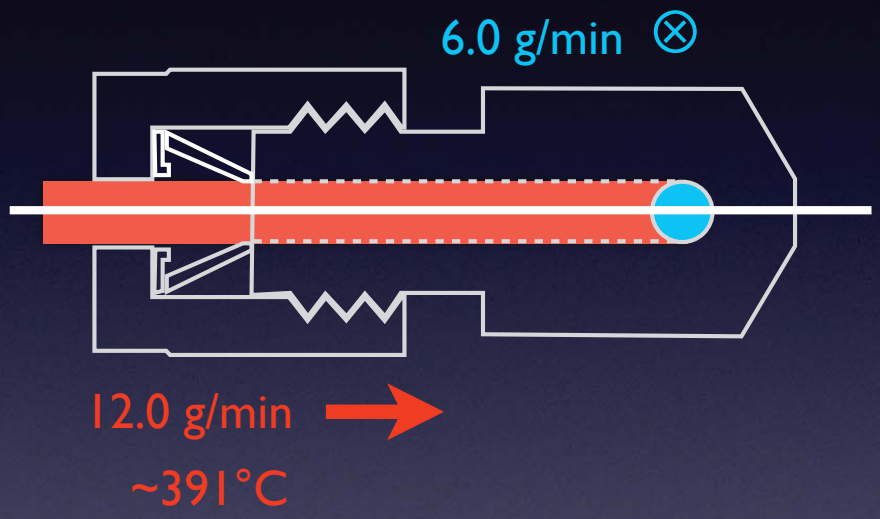
Heated water from side



200 images were obtained

Reconstructed image

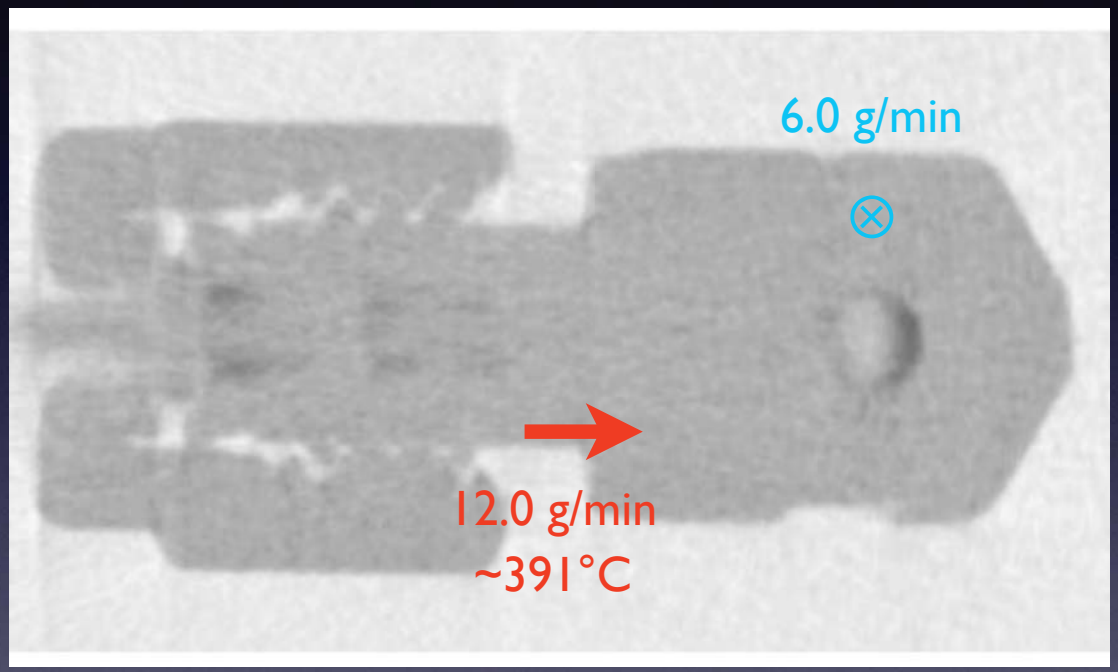




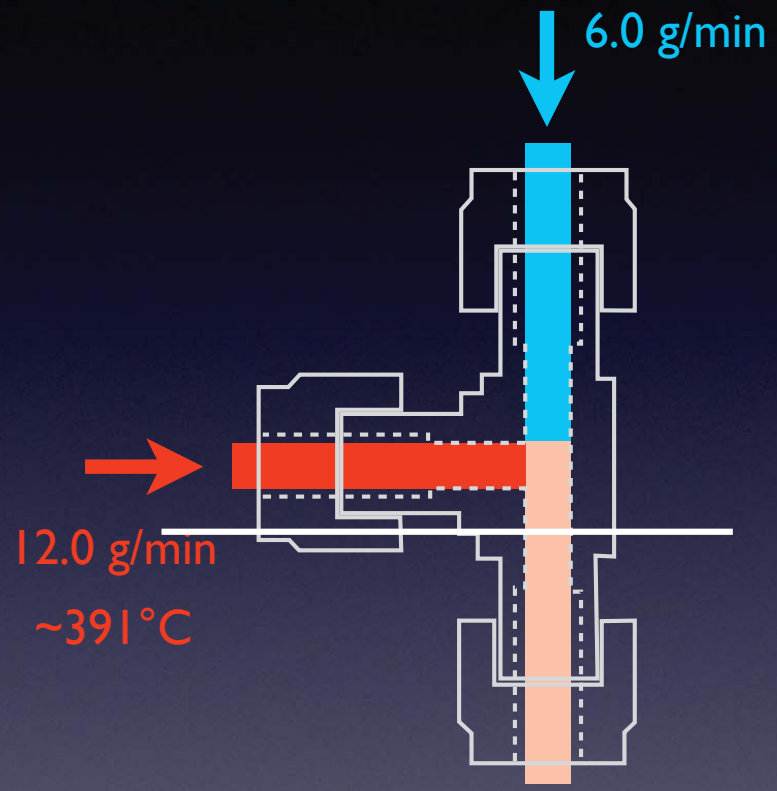
Vertical slicing

5 mm

Reconstructed image

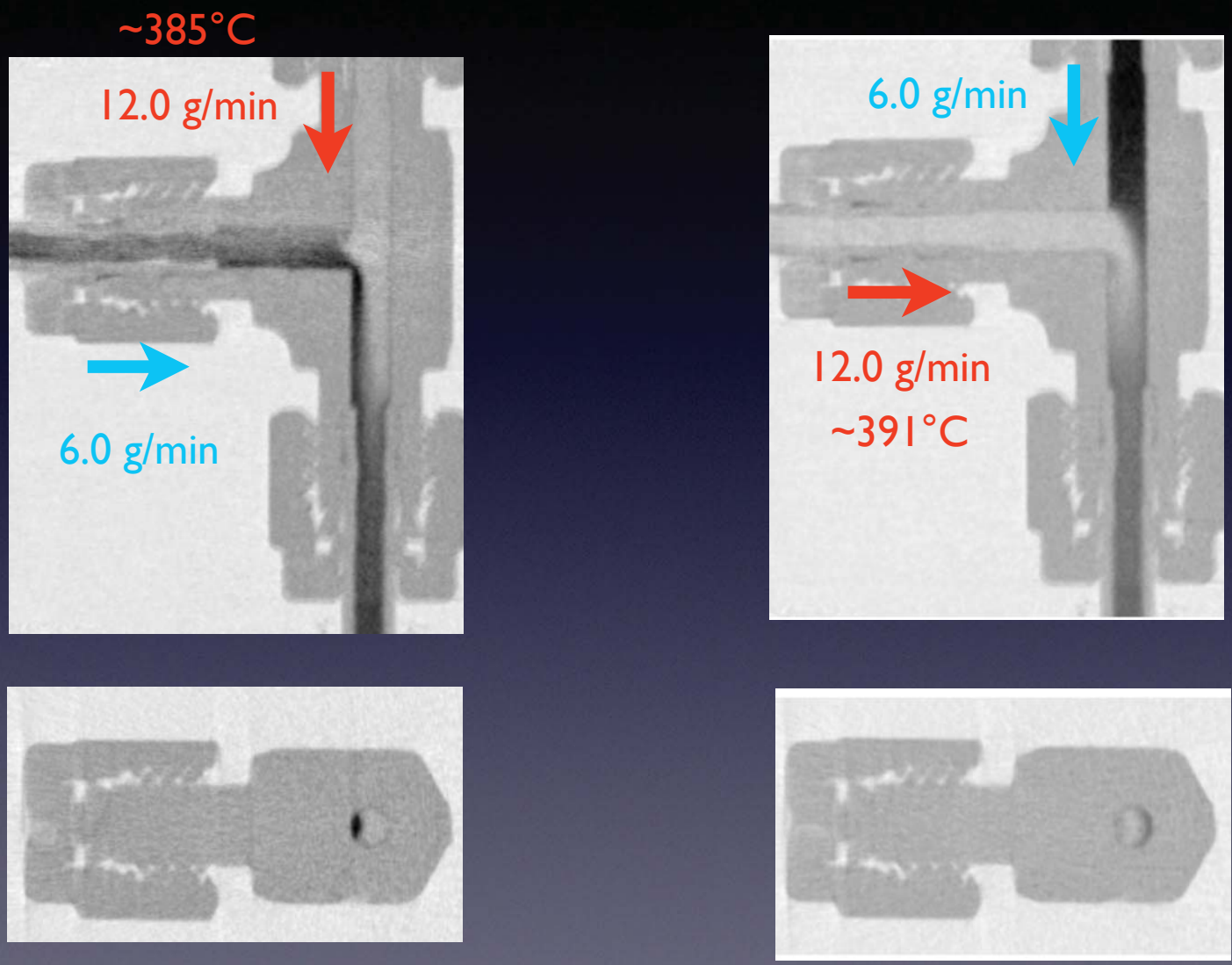


5 mm



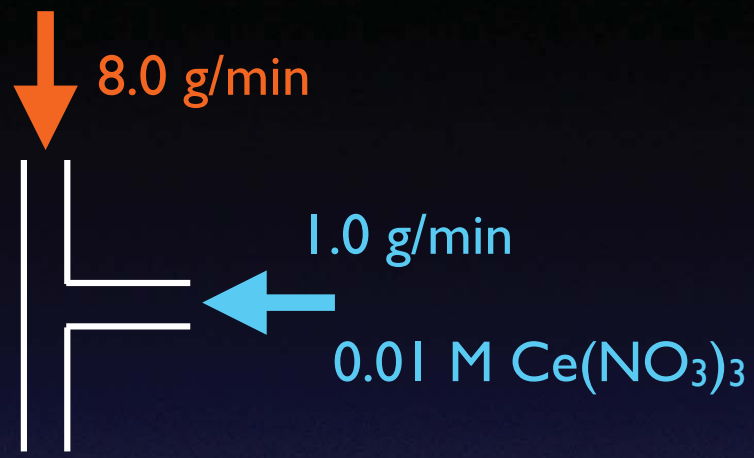
Horizontal slicing

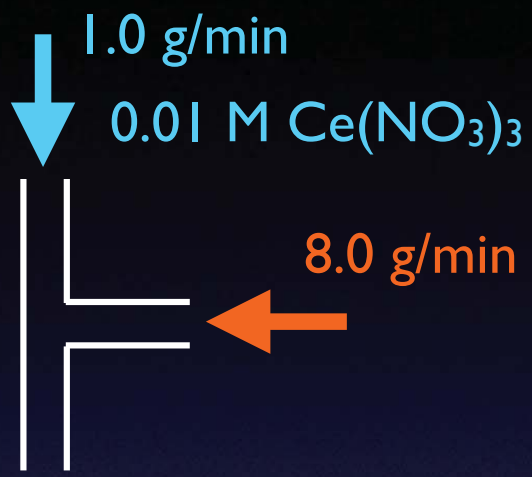
Comparison between mixing modes

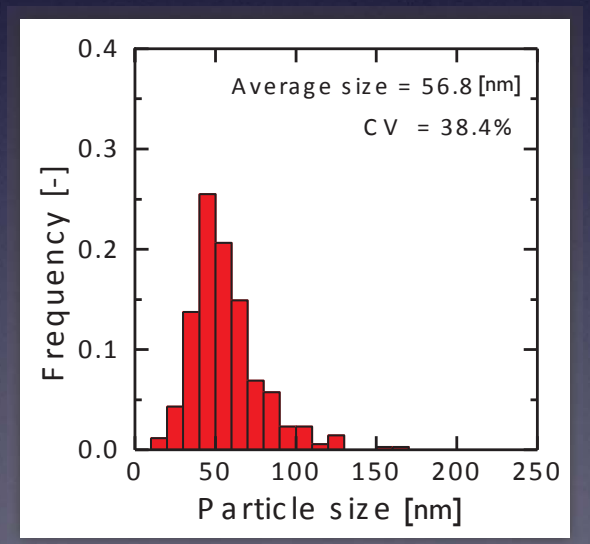


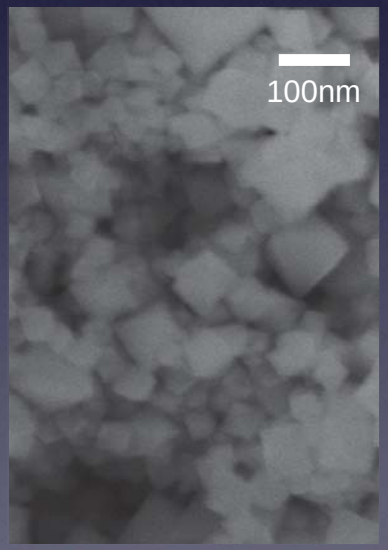
Nanoparticles were produced using these mixer.

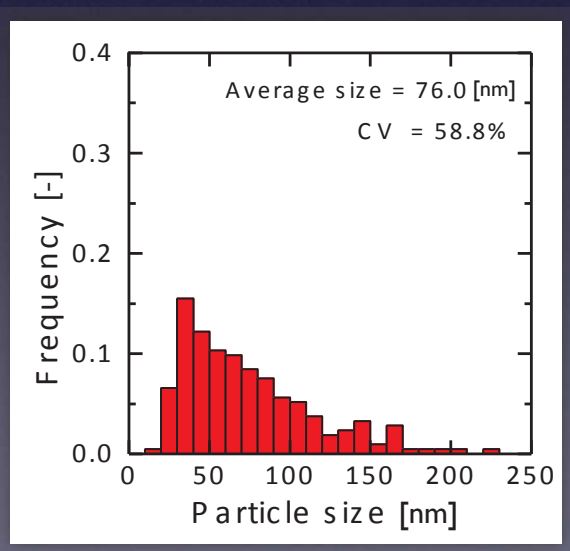
Experimental results

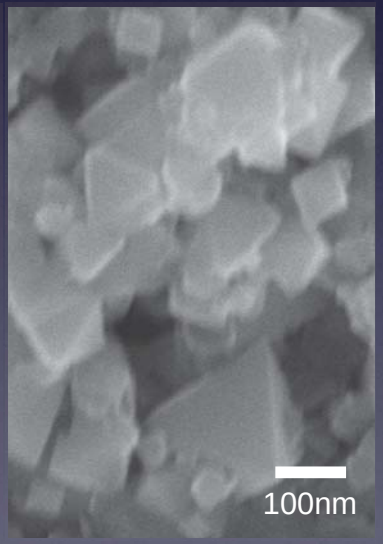








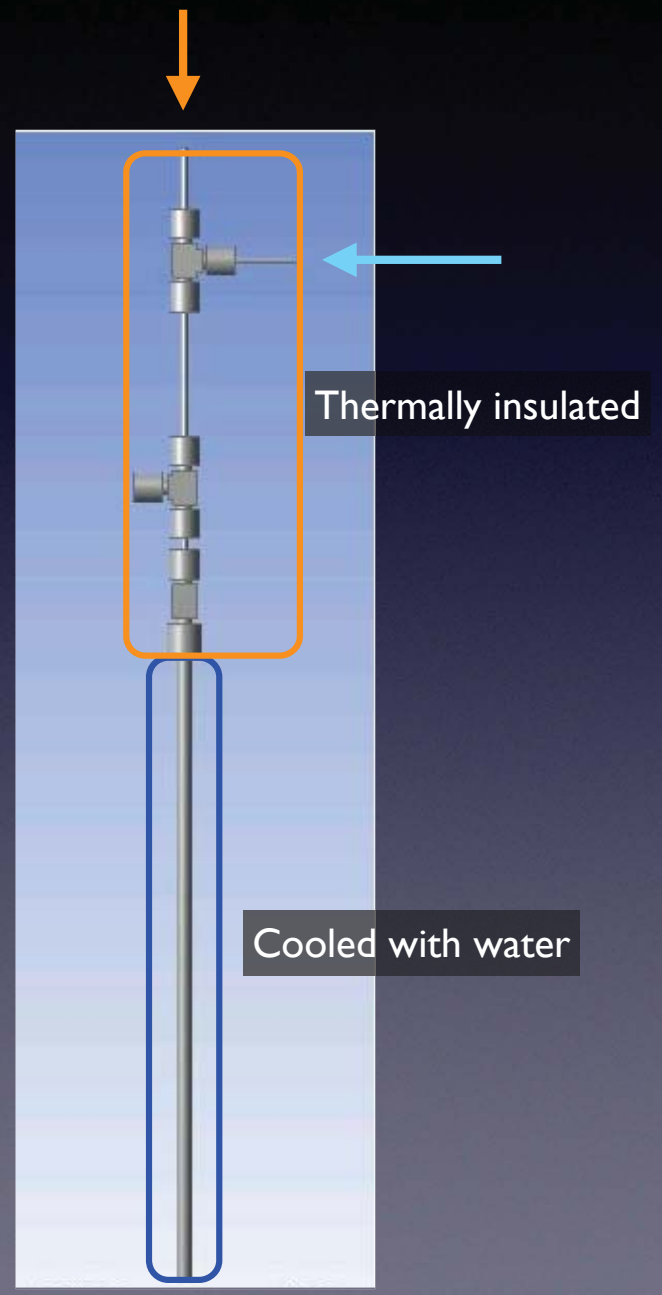




How these products were formed ?

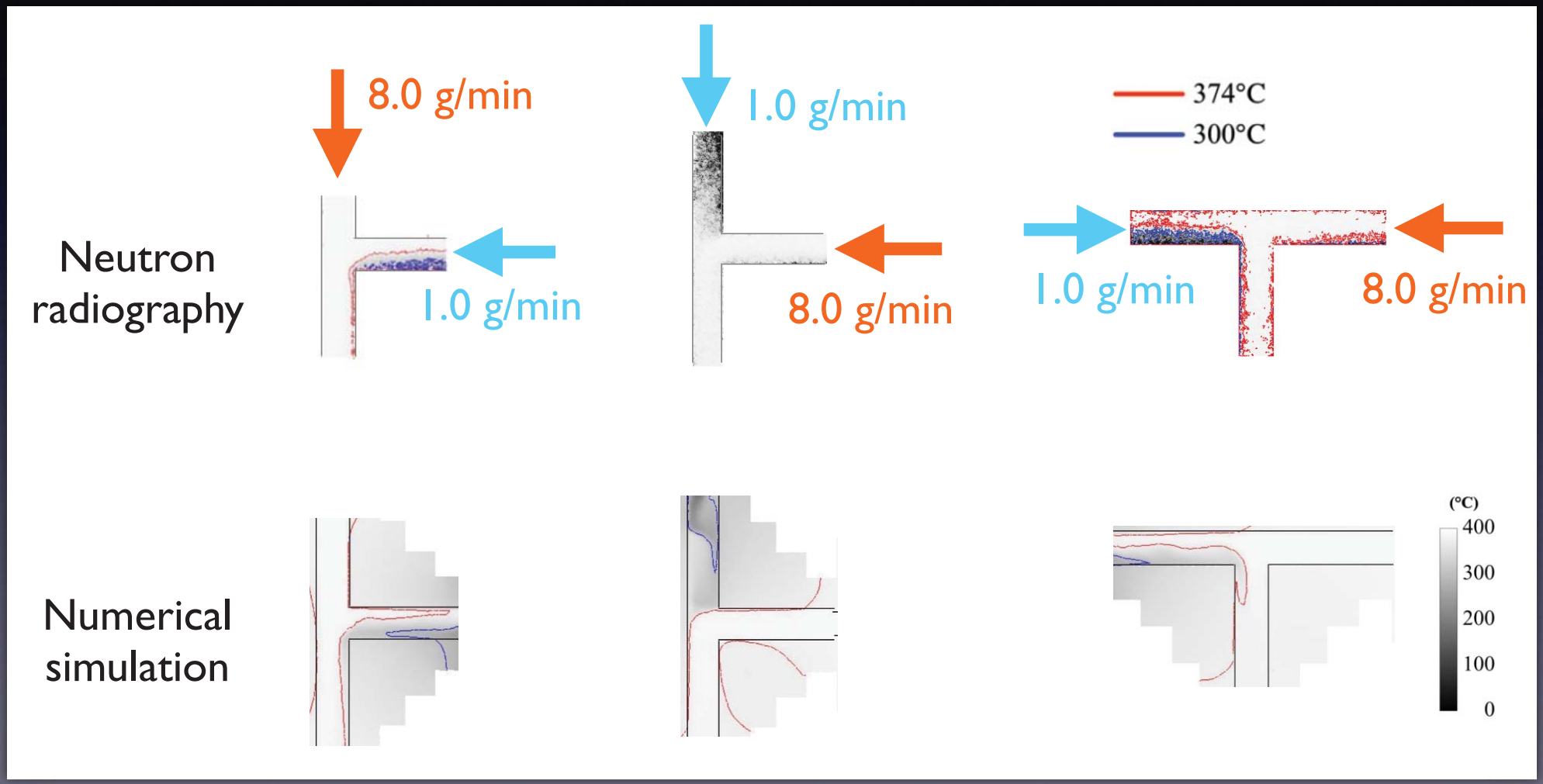
Flow dynamics simulation

- Navier-Stokes equations were solved considering buoyant force
- Temperature-dependent properties of water were given as fit curves of NIST database
- Temperature and flow rate of inlet streams were given
- Parabolic flow velocity profile at the inlet was supposed
- No control at outlet stream
- FLUENT code was used to solve the equations
- Non steady-state calculation was performed



Validation of simulation

Temperature of streams



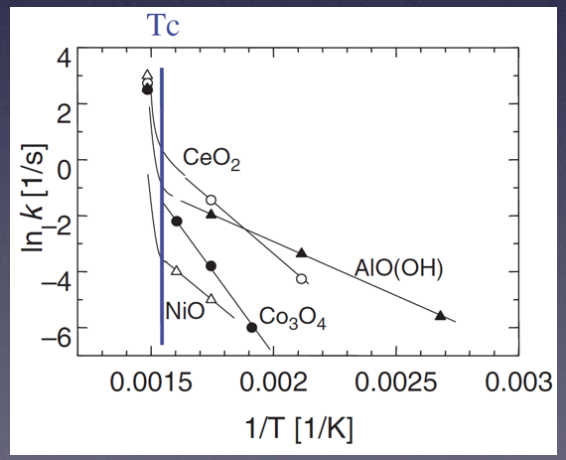
Numerical simulation reproduced experimental results.

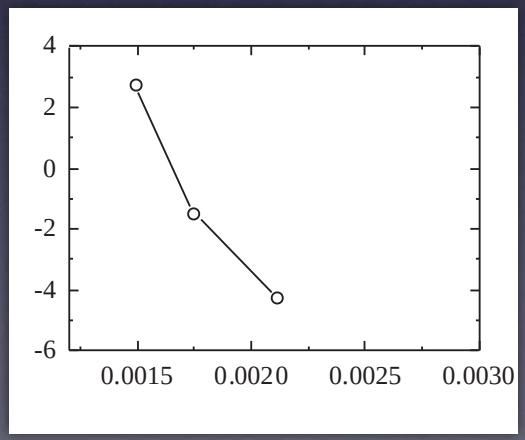
Chemical reaction

$$Ce(NO_3)_3 \rightarrow CeO_2$$

Reaction rate $$r = k\,[\mathrm{Ce(NO_3)_3}] = \frac{d\,[\mathrm{CeO_2}]}{dt}$$

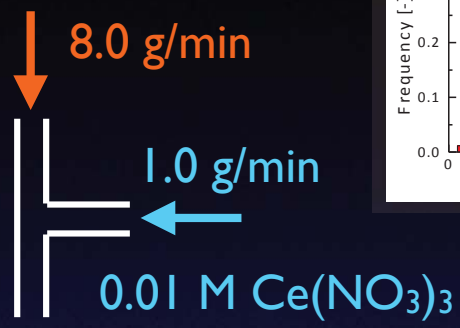
Reaction rate constant

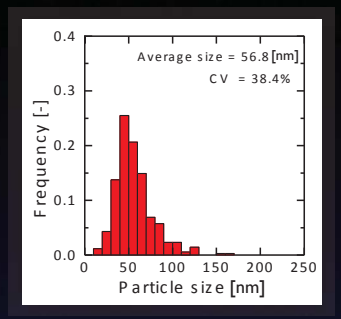


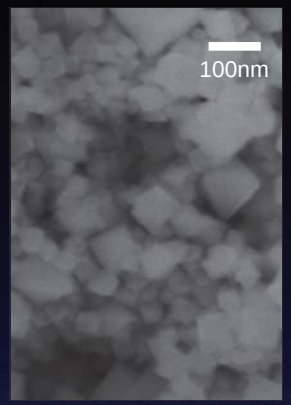


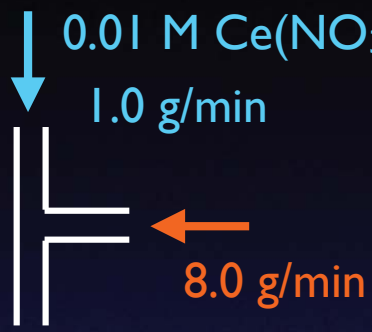
Adschiri T. Chem. Lett., 2007, 36, 1188-1193

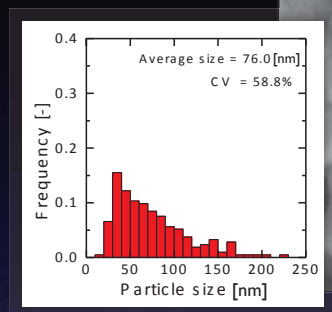
Simulation results

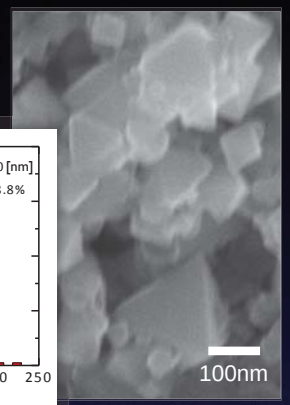


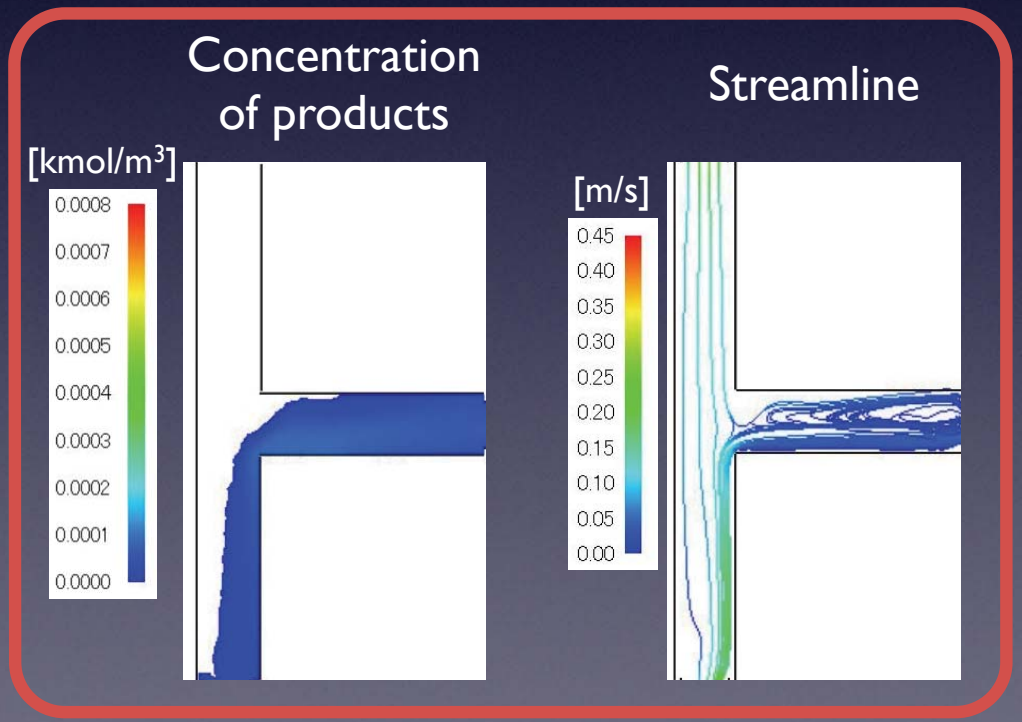


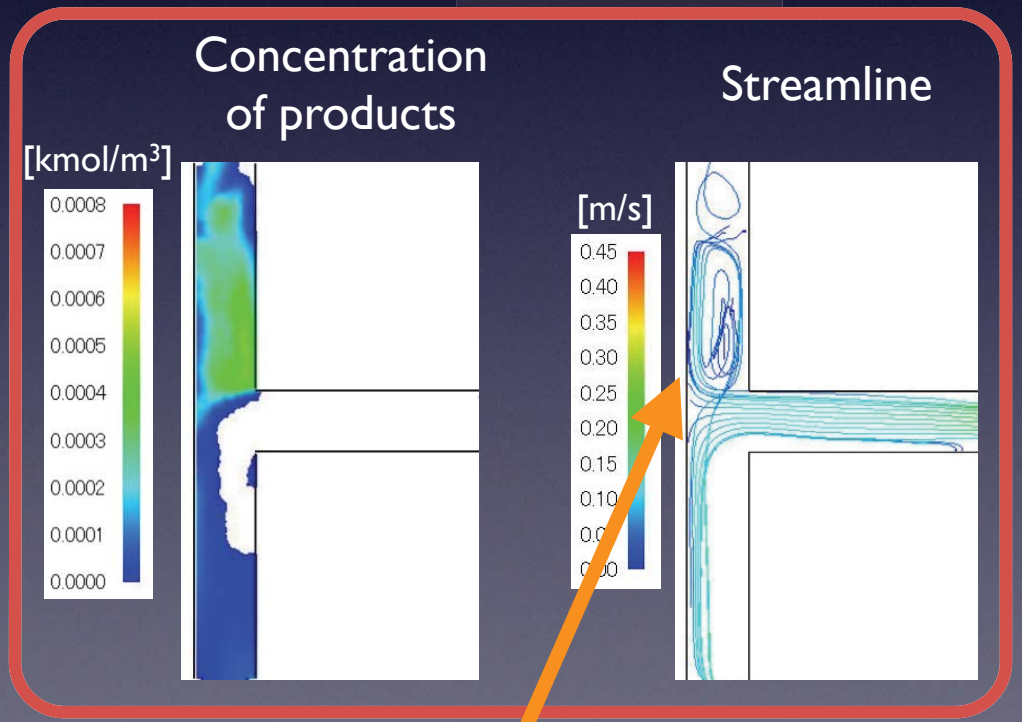










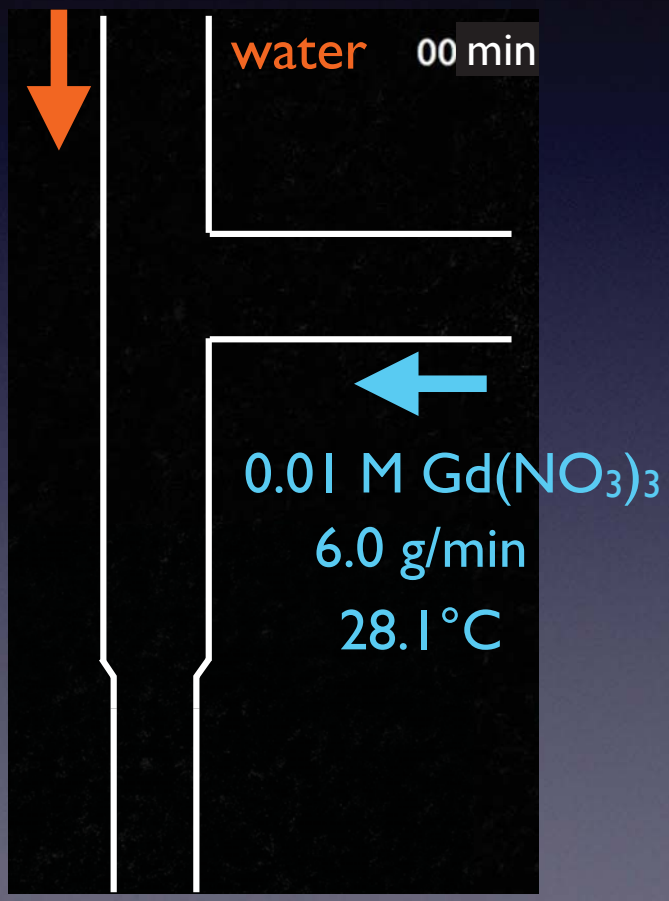


Unsteady-state vortex flow

Visualization of plugging

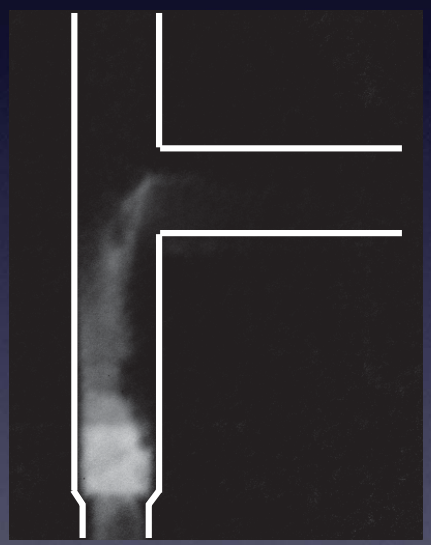
Radiography measurements with supplying metal ion solution

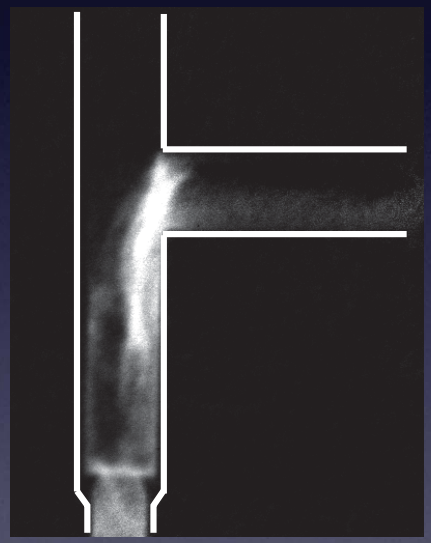
395.3°C 24.0 g/min



Products: $Gd(OH)_3$

Other plugging behaviors





Summary

- Mixing behavior of water streams in a flow-type chemical reactor was visualized by neutron radiography.
- Mode of mixing affected the produced nanoparticles.
- Numerical simulation was checked by neutron radiography.
- In future, the combined use of radiography and simulation can design new mixer to produce better nanoparticles.

Acknowledgment

This work has been performed under the Visiting Researchers Program of Kyoto University Research Reactor Institute.