中性子ラジオグラフィ法による流通式水熱合成装置における混合過程の可視化

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杉本 勝美[3]，大平 直也[4]，伊藤 大介[4]

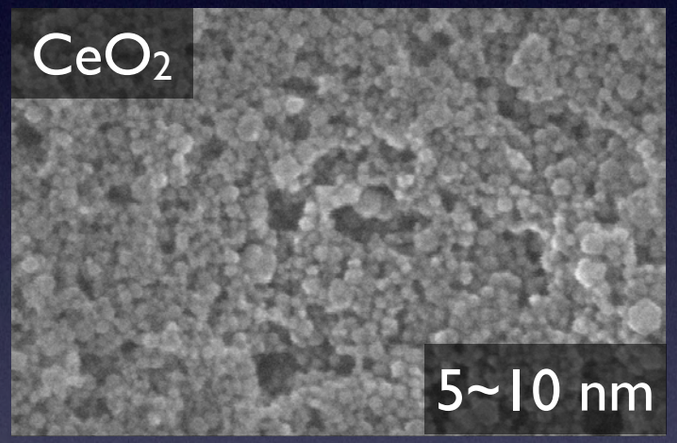
Hydrothermal synthesis of metal oxide nanoparticles

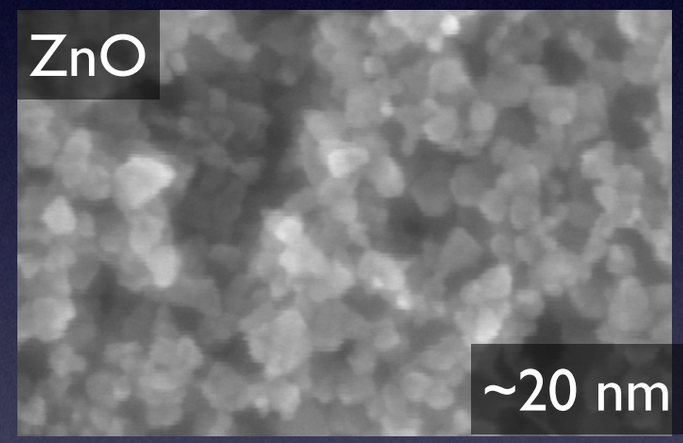
$$M^{n+} \xrightarrow{+\ n\ H_2O} M(OH)_n \xrightarrow{-\ n/2\ H_2O} MO_{n/2}$$

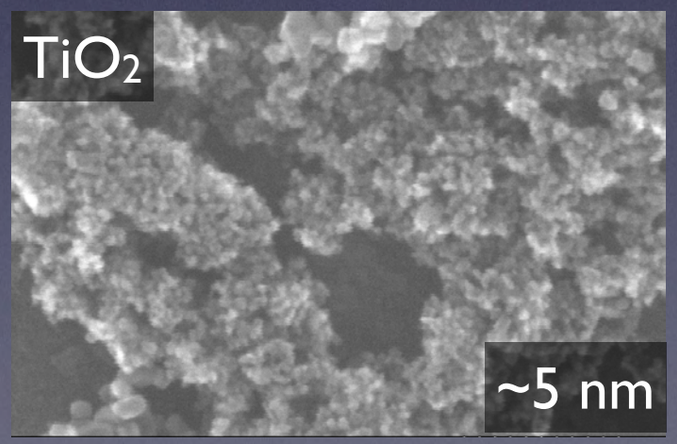
M^{n+}: $M(SO_4)_{n/2}$, $M(NO_3)_n$

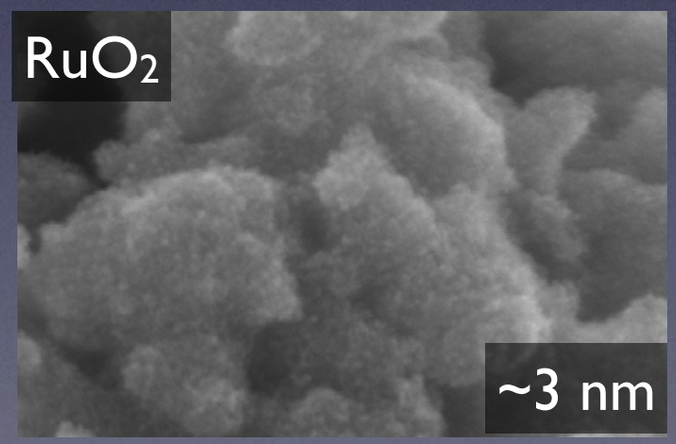
200~400°C
~30 MPa

TiO_2	$MgFe_2O_4$
VO_2	$BaTiO_3$
MnO_2	$CoAl_2O_4$
FeO_x	$LiCoO_2$
Co_3O_4	ITO, IZTO
NiO	YSZ
CuO_x	$GdVO_4$
ZnO	YAG:Ce
ZrO_2	LuAG:Ce
RuO_2	TiO_2:Nb-Co
HfO_2	$Gd(OH)_3$
CeO_2	Pt, Ni









Hydrothermal synthesis reactors

Batch reactor

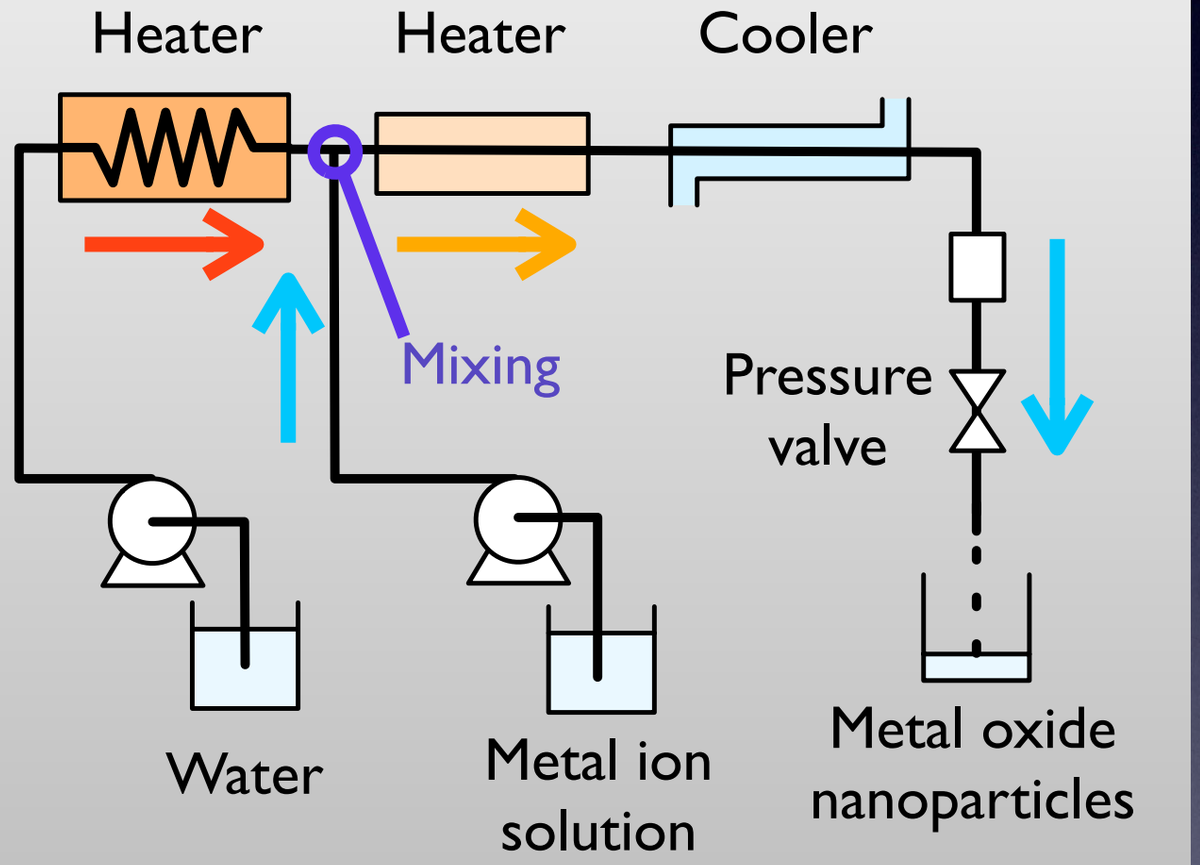
~ 5 mL

Heater

Reaction time

~ 5 min

Plug-flow reactor

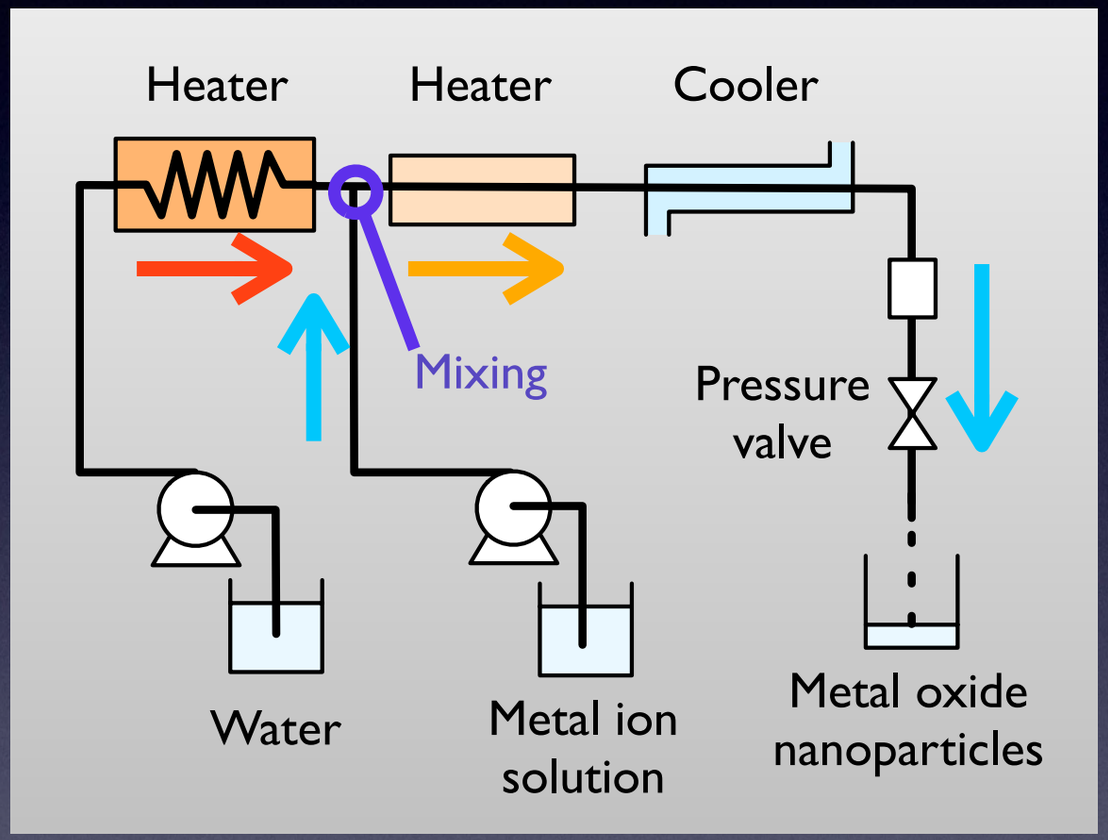


T. Adschiri, *et al.*, *J. Am. Ceram. Soc.* **75**, 1019 (1992)

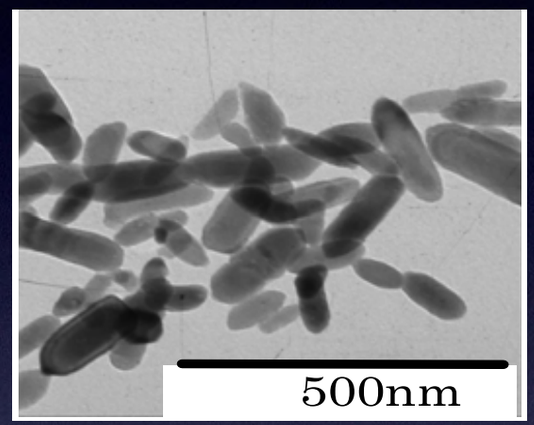
~ 10 s

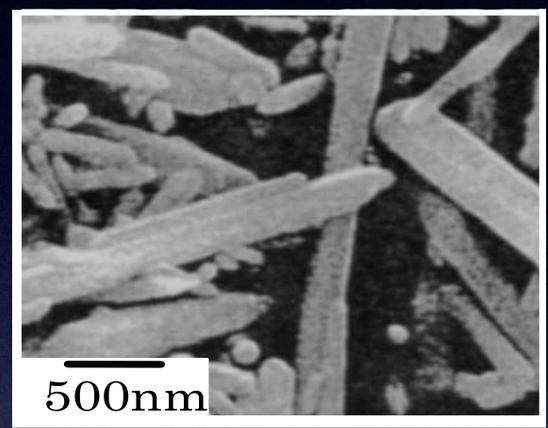
Synthesis with plug-flow reactor

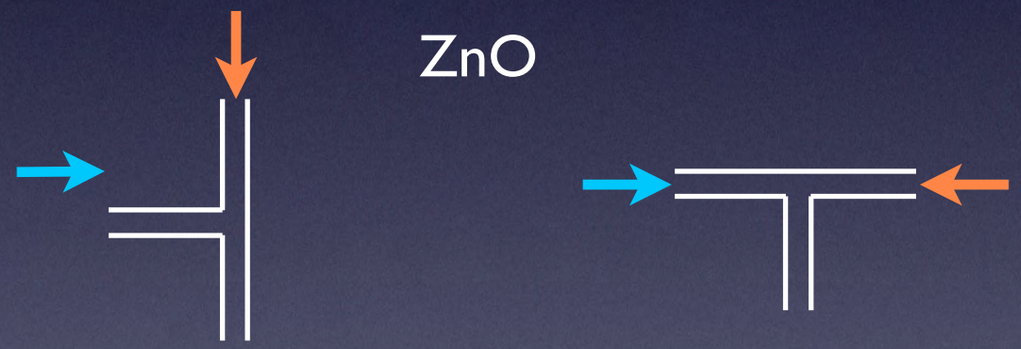
Plug-flow reactor



Size of products





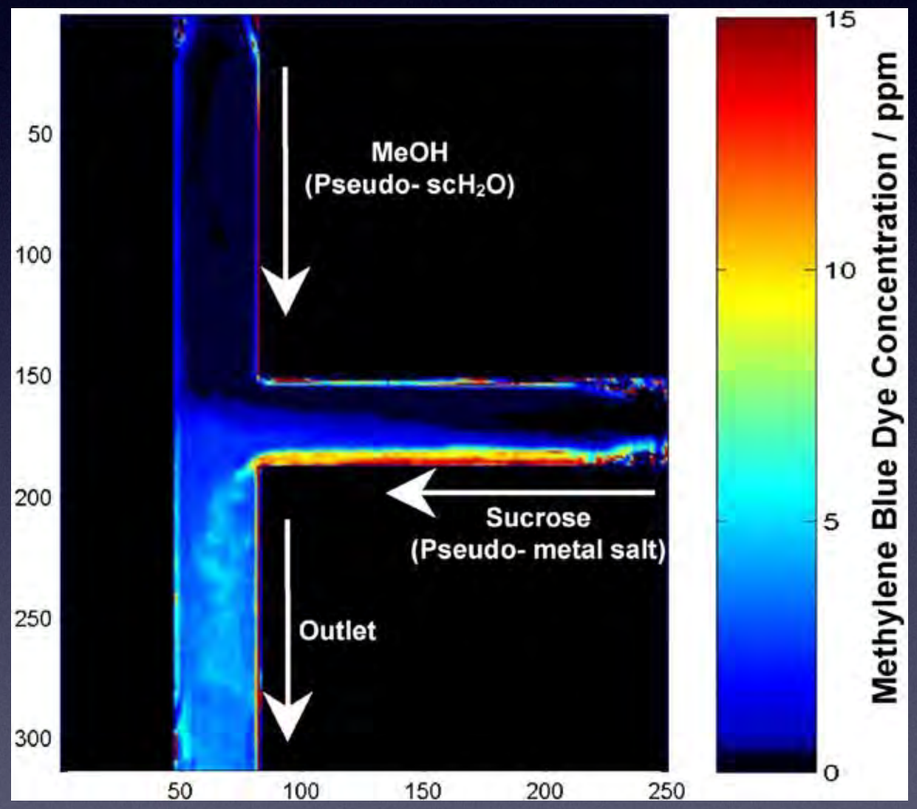


T. Adschiri, *et al.*, in Materials Chemistry in Supercritical Fluids, Research Signpost, 79–97 (2005)

Mixing of supercritical water and reactants affects the products

Experimental approaches

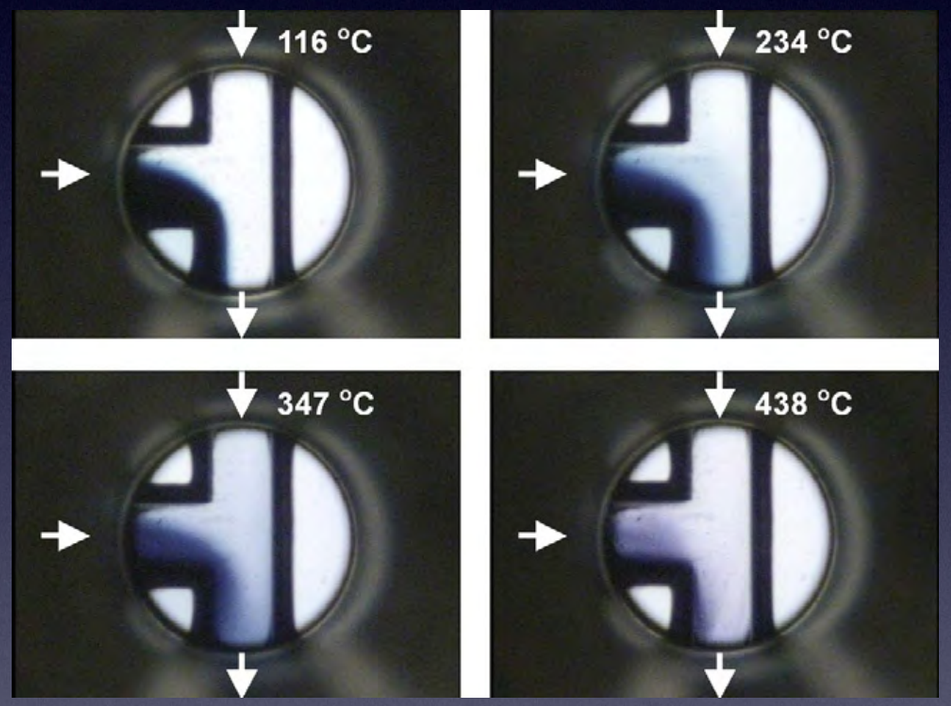
Model fluid



Buoyancy force

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

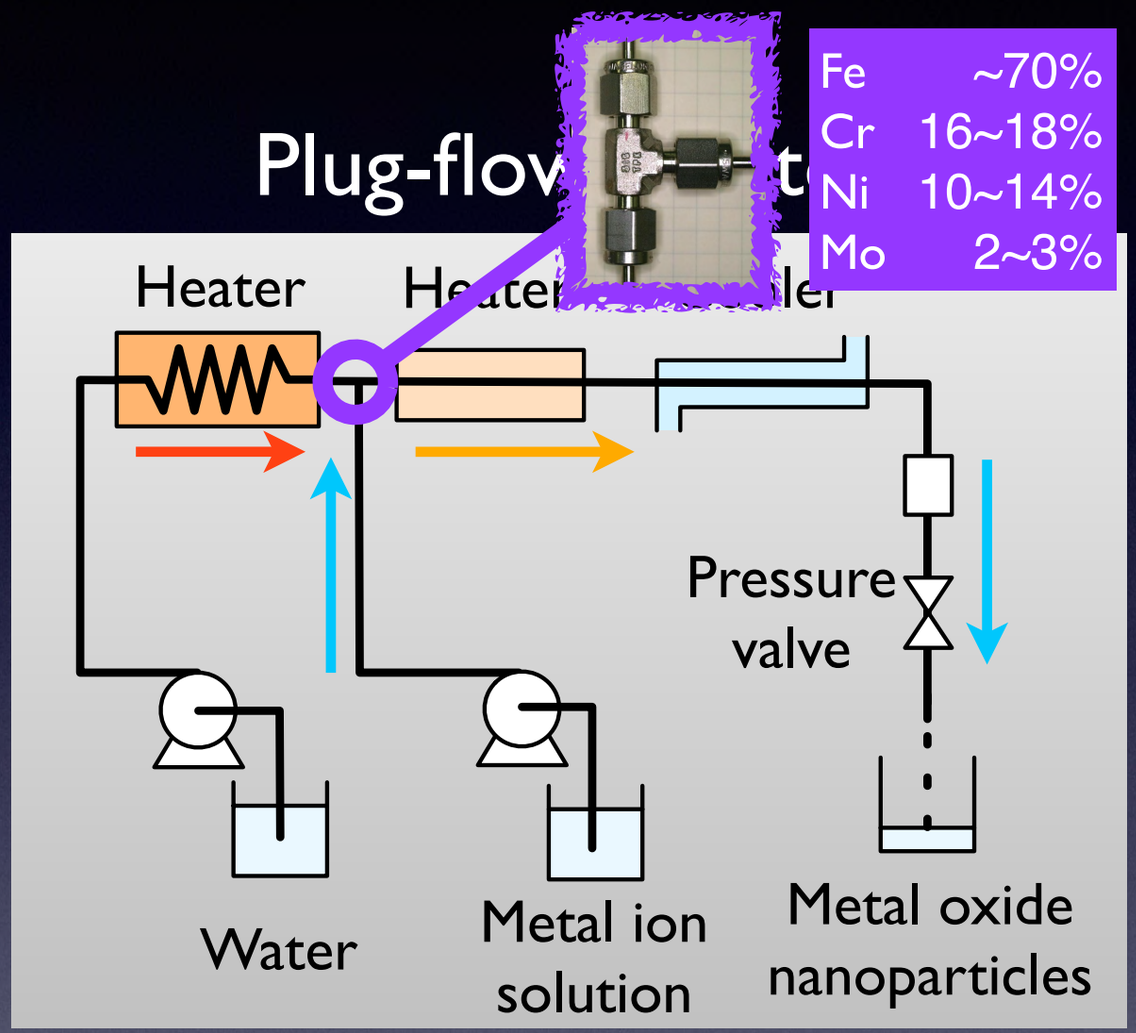
View cell



Cascade down

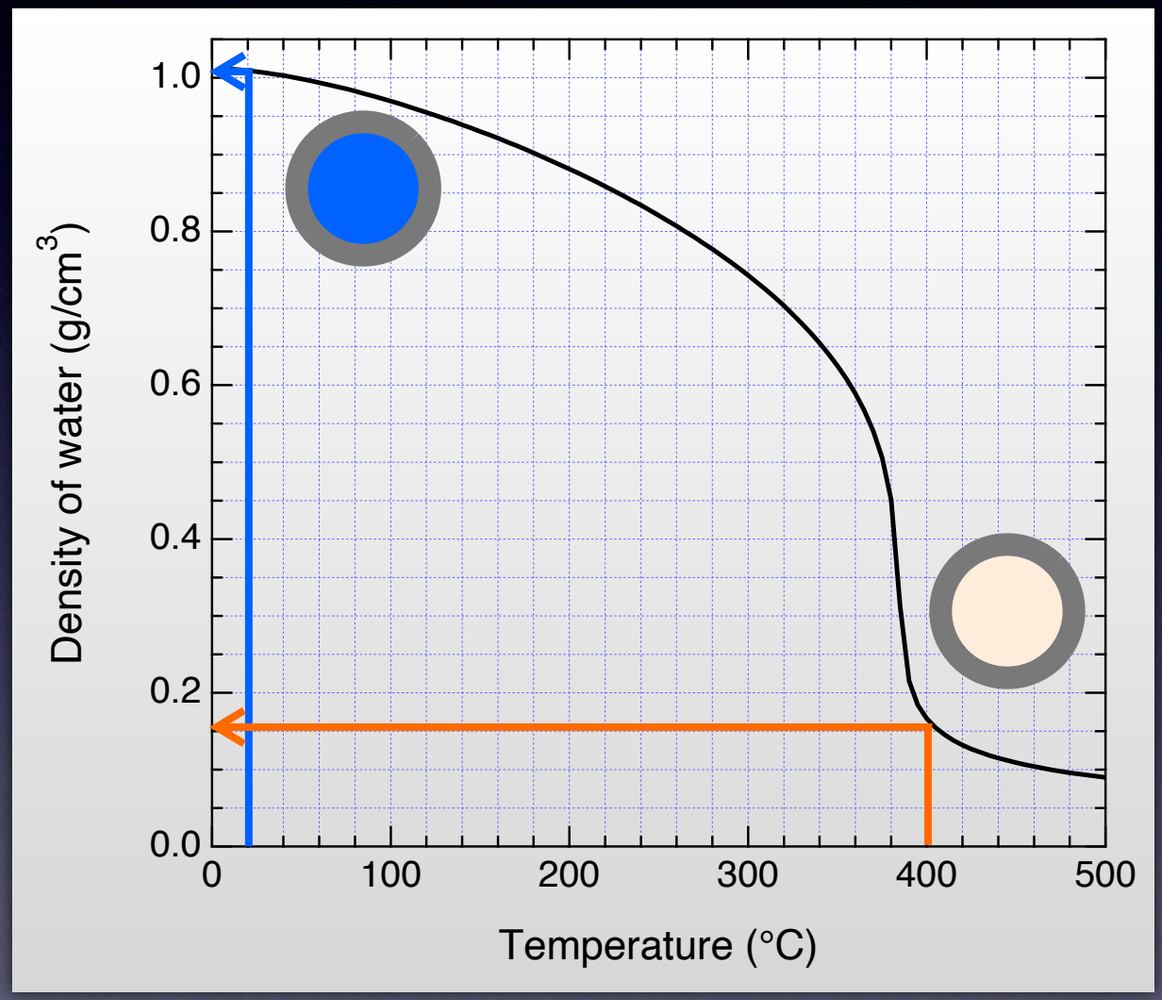
T. Aizawa, *et al.*, *J. Supercrit. Fluids* **43**, 222 (2007).

Mixing of two water streams



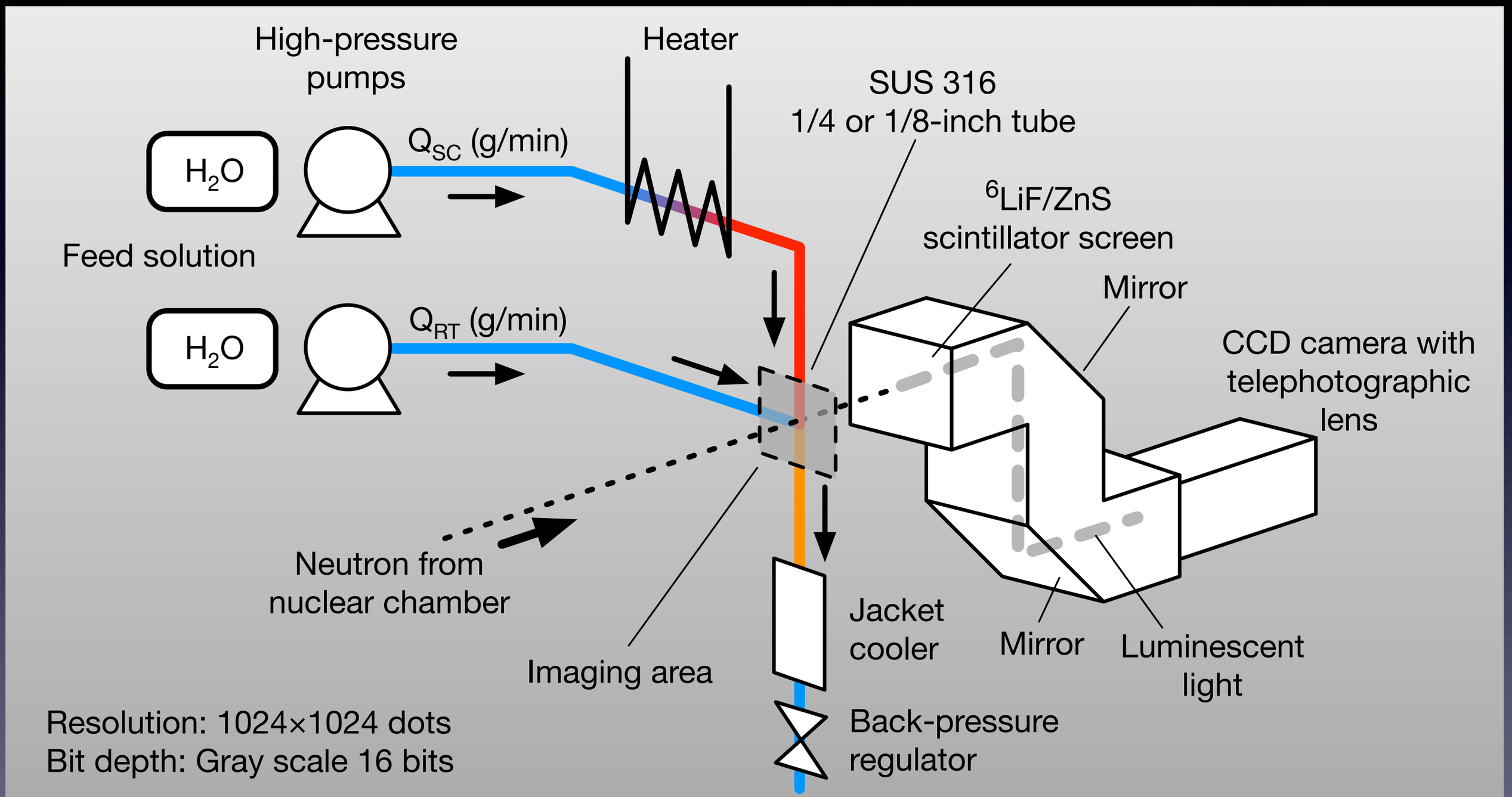
300~400°C, 25 MPa

Density of water @ 25 MPa



Difference in water density can be visualized.

Experimental setup



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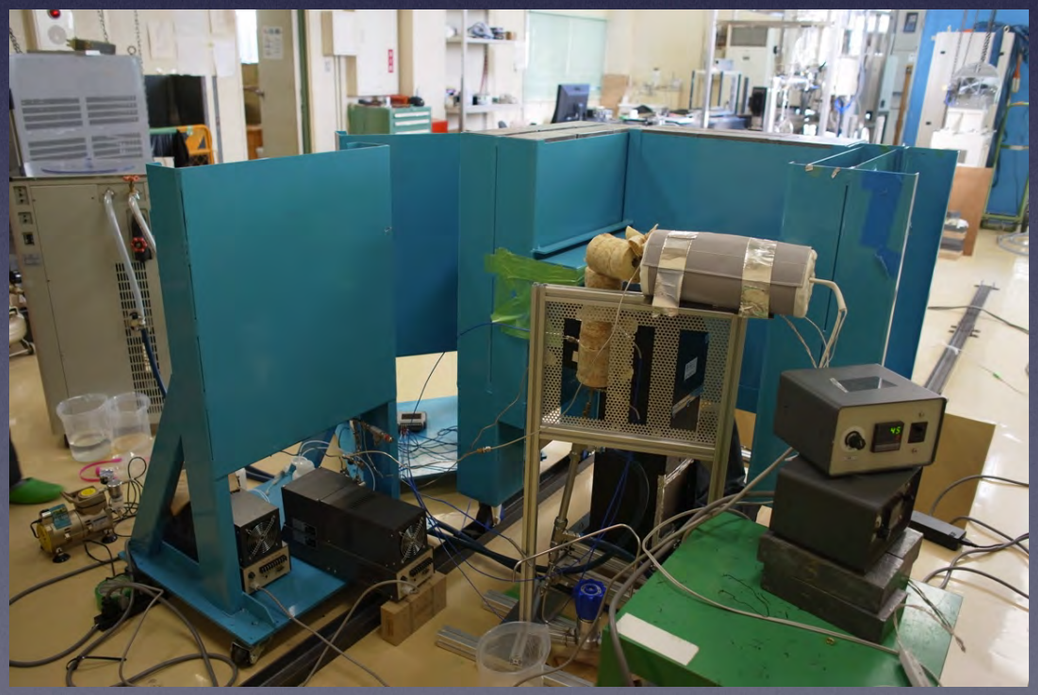
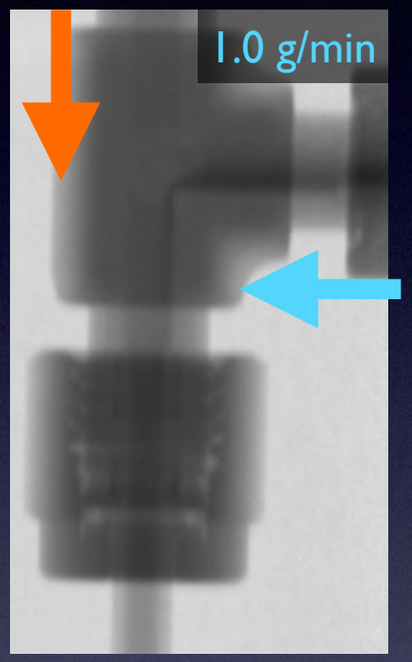
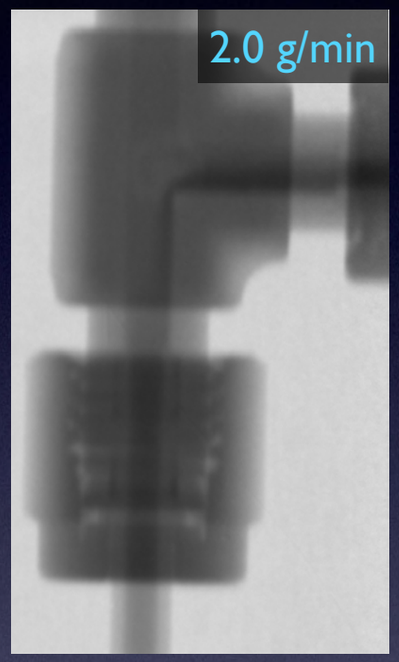
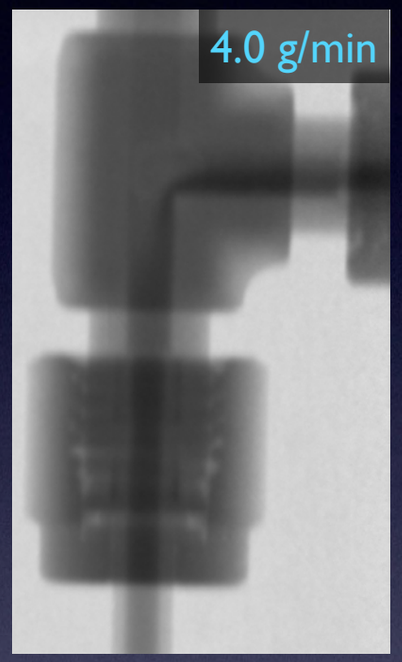
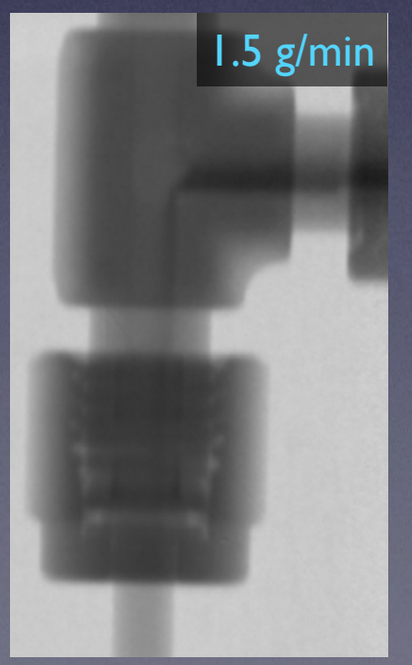
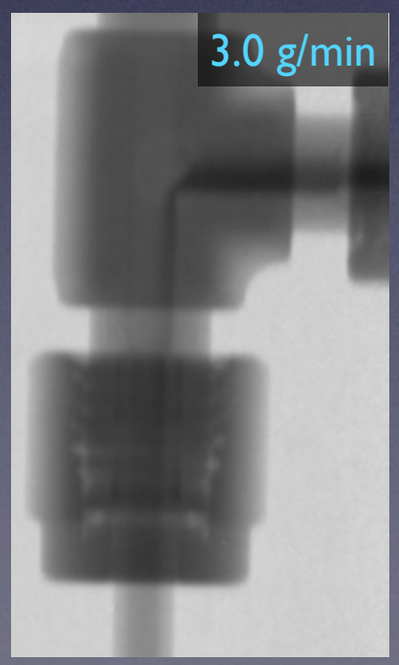
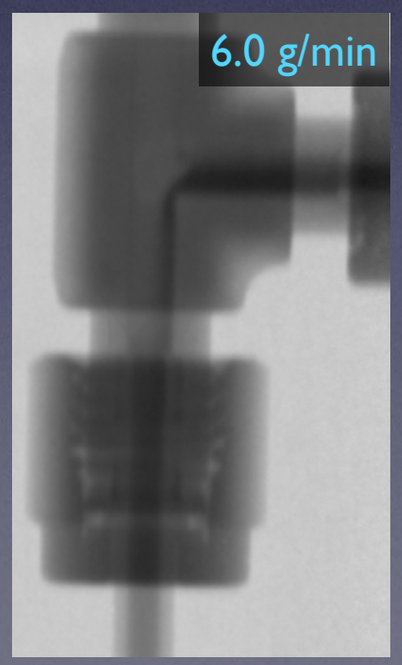
S. Takami *et al.*, *J. Supercrit. Fluids* **63**, 46 (2012).

Kyoto University Research Reactor Institute



I/I_0 images

$Q_{SC} : Q_{RT}$ =

	8 : 1	8 : 2	8 : 4
8.0 g/min 385°C	 1.0 g/min	 2.0 g/min	 4.0 g/min
12.0 g/min 393°C	 1.5 g/min	 3.0 g/min	 6.0 g/min

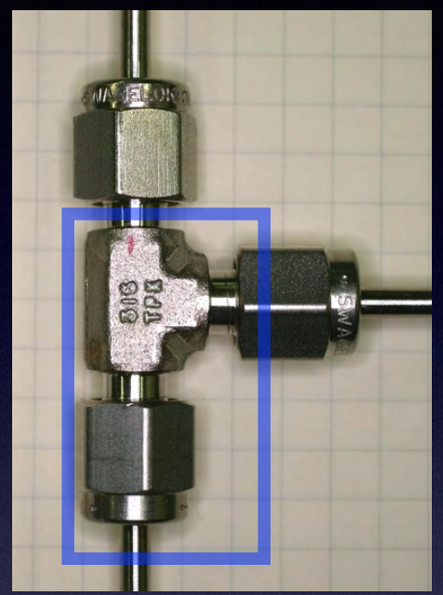


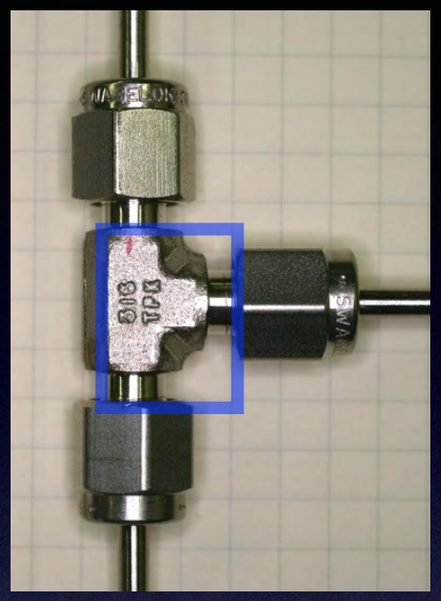
image	scattering
light	small
dark	large

Averaged water density

$Q_{SC} : Q_{RT}$ = 8 : 1 | 8 : 2 | 8 : 4

1.0 g/min | 2.0 g/min | 4.0 g/min

8.0 g/min
385°C



1.5 g/min | 3.0 g/min | 6.0 g/min

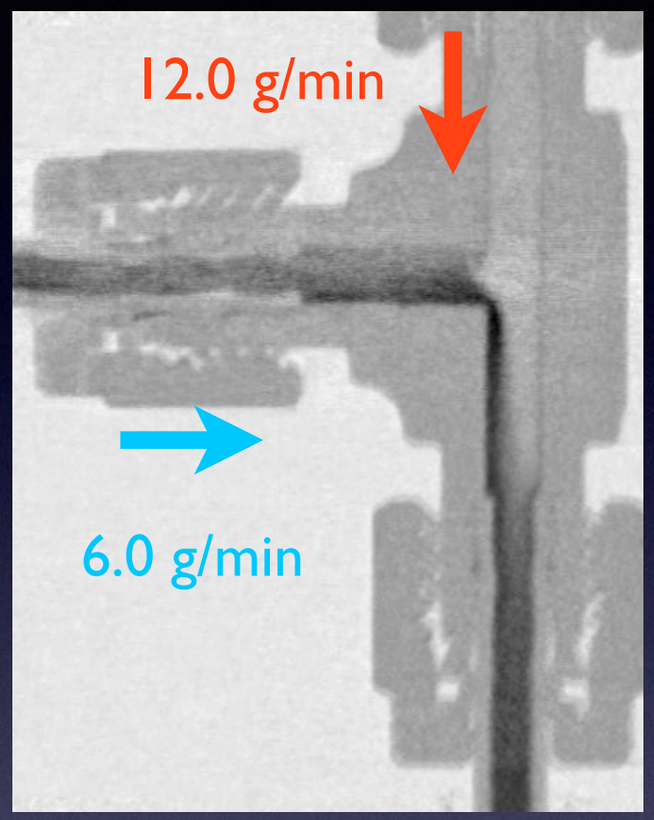
12.0 g/min
393°C

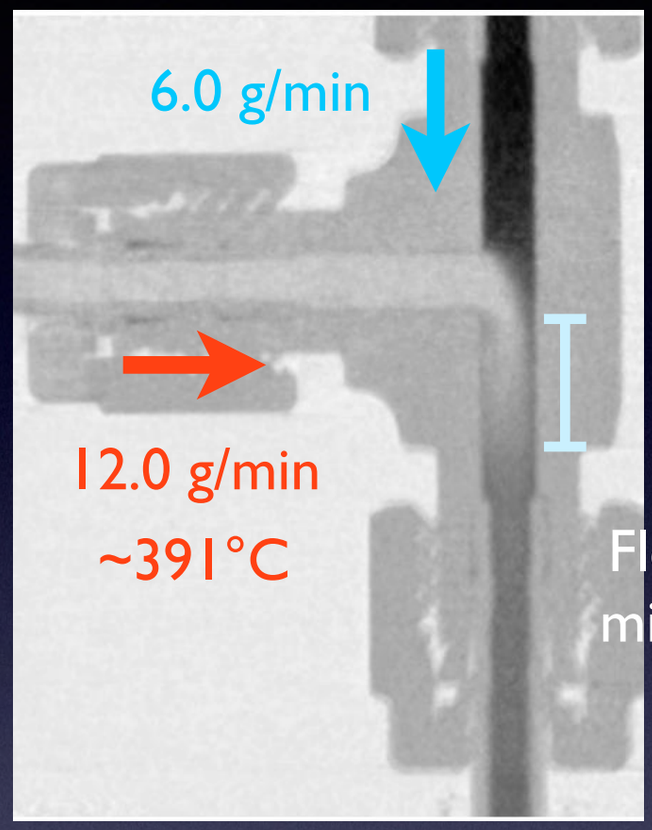
Water Density
(g/cm^3)

0.0
0.2
0.4
0.6
0.8
1.0

— 2 mm

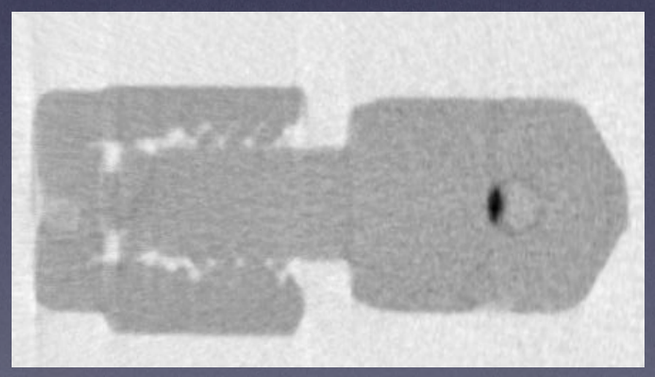
Comparison between mixing modes

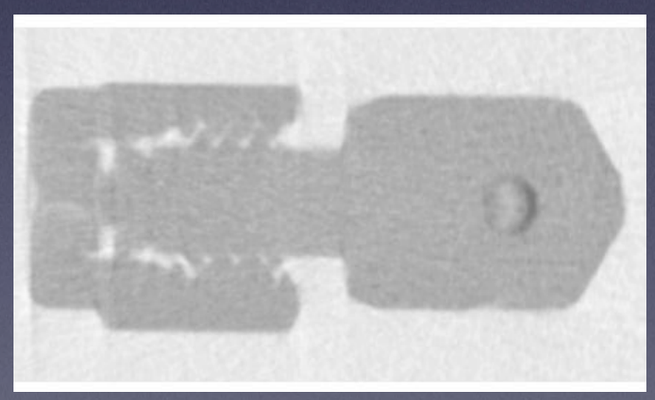




50 ms

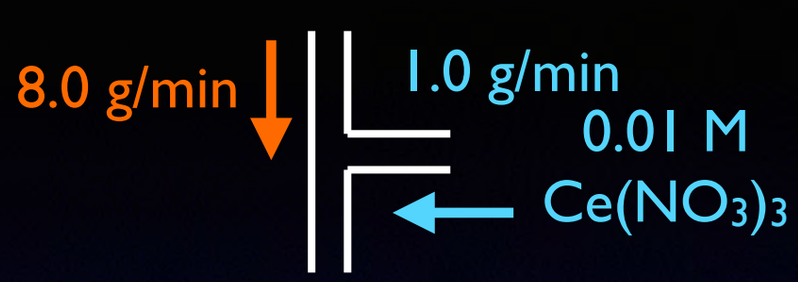
Flow velocity after mixing = 119 mm/s



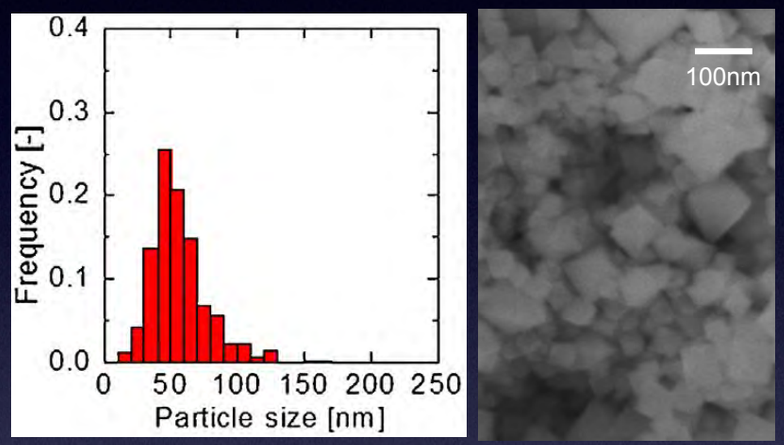


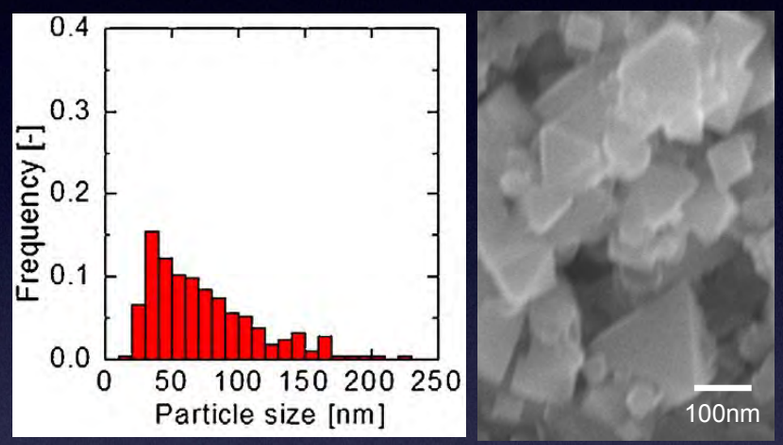
Nanoparticles were produced using these mixer.

Simulation by Prof. Tsukada

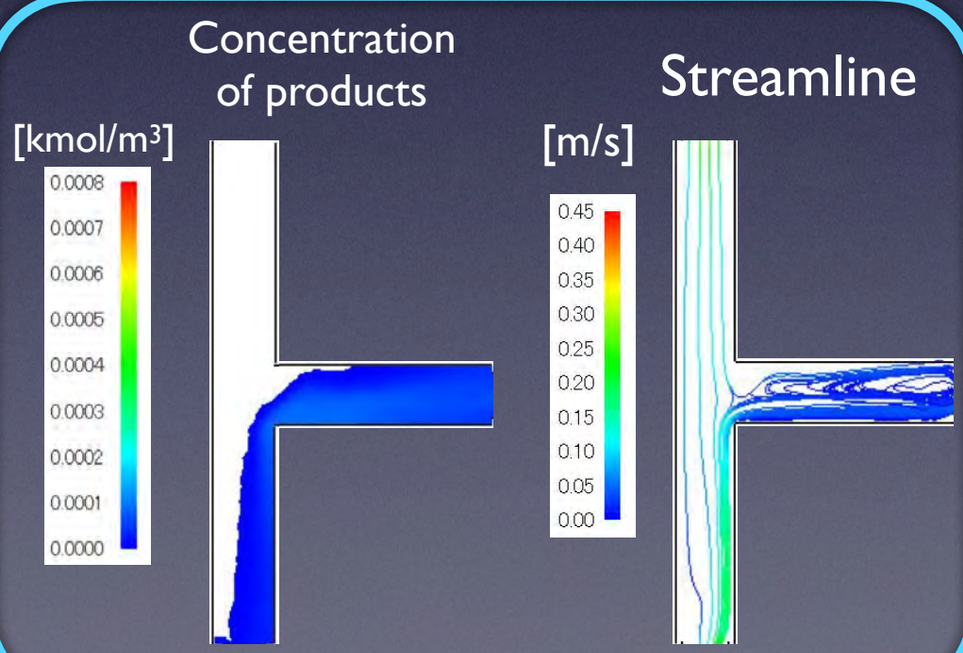


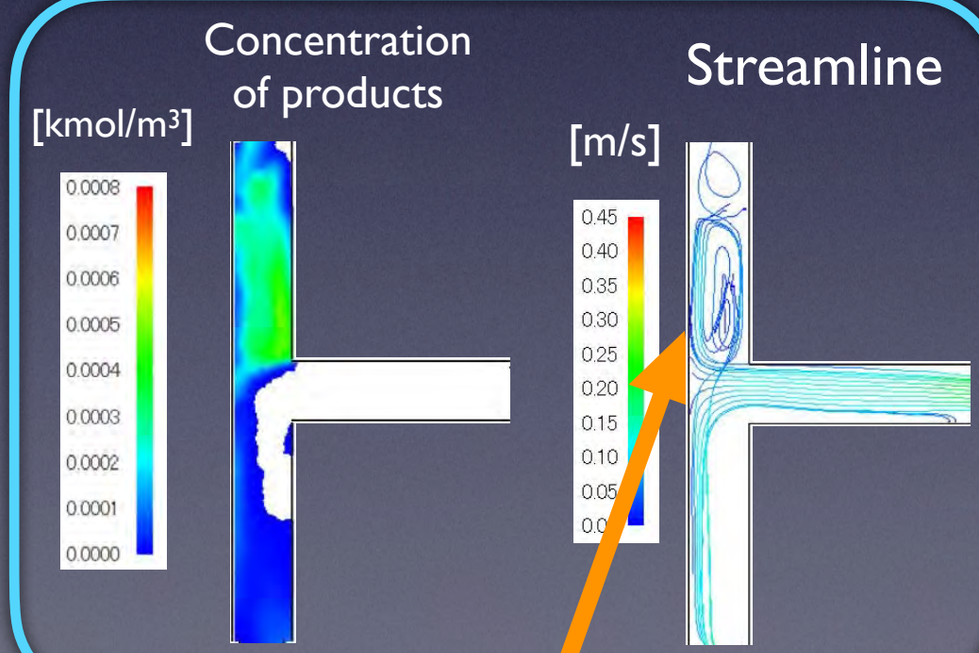
Experiment





Simulation

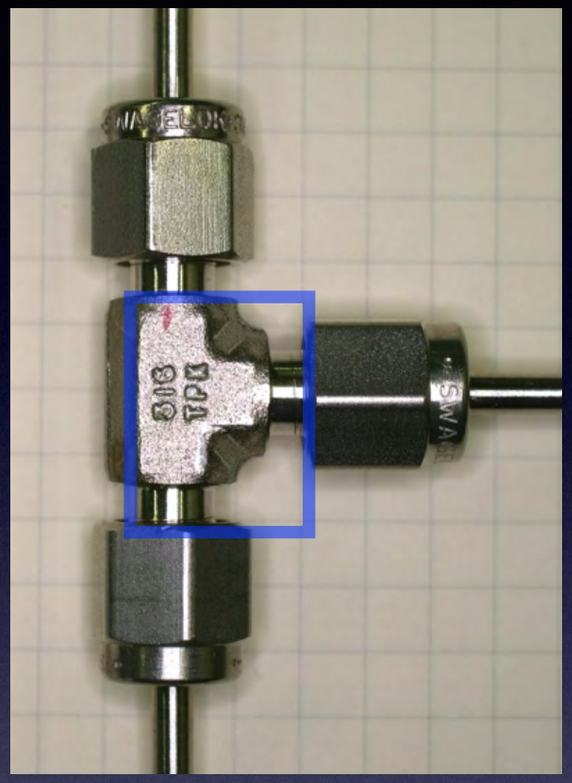


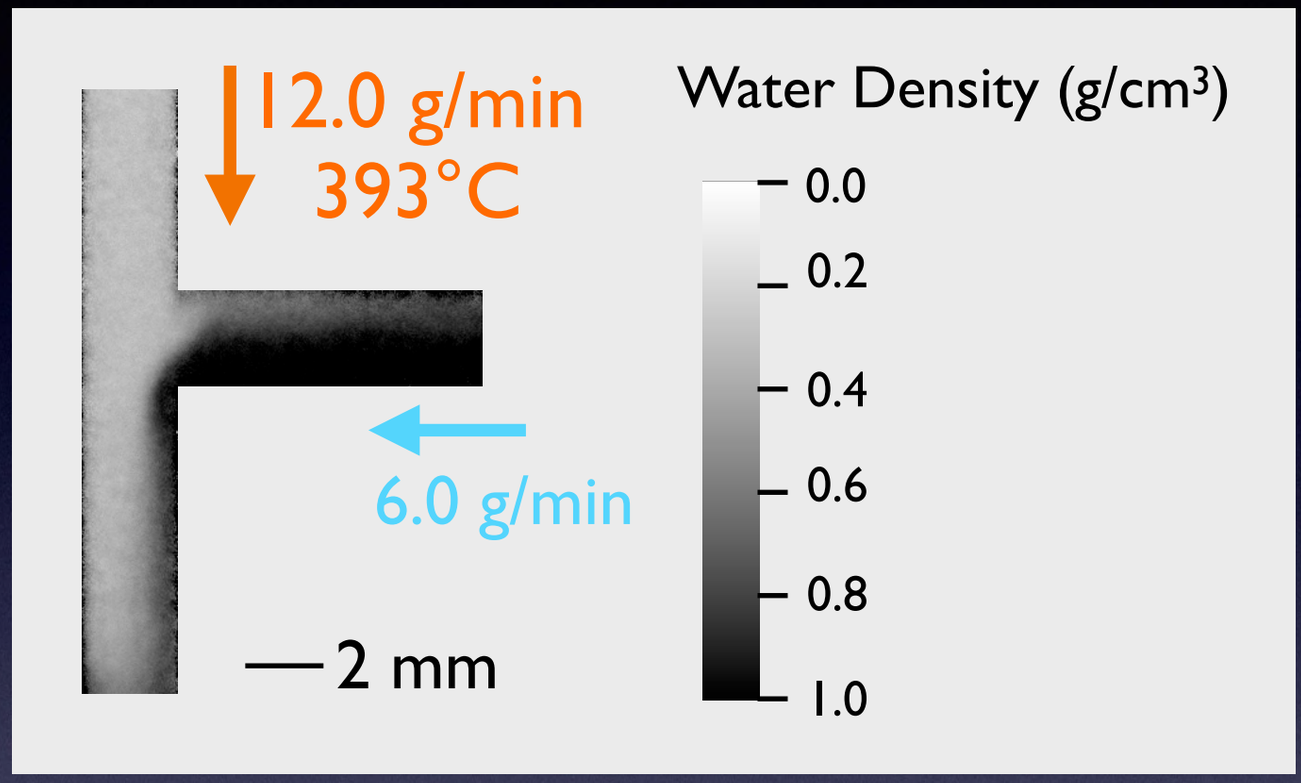


K. Sugioka, *et al.*, *J. Supercrit. Fluids* **109**, 43 (2016).

Further questions

Density (temperature at constant pressure) was visualized by radiography.



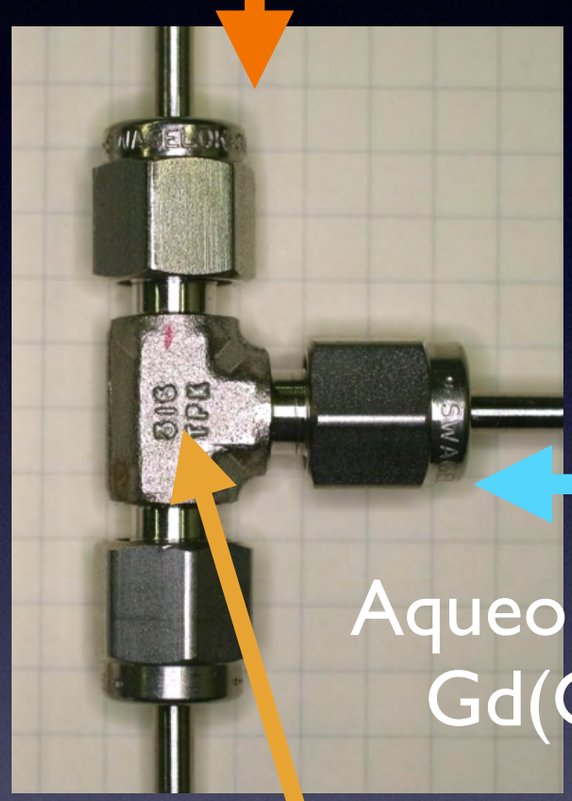


However, temperature is affected by heat transfer from tube wall, in addition to mixing.

➡ Questions

- Distribution of reactant solution (flow from side)
- Chemical reaction of metal ion
- Nucleation and growth of particles

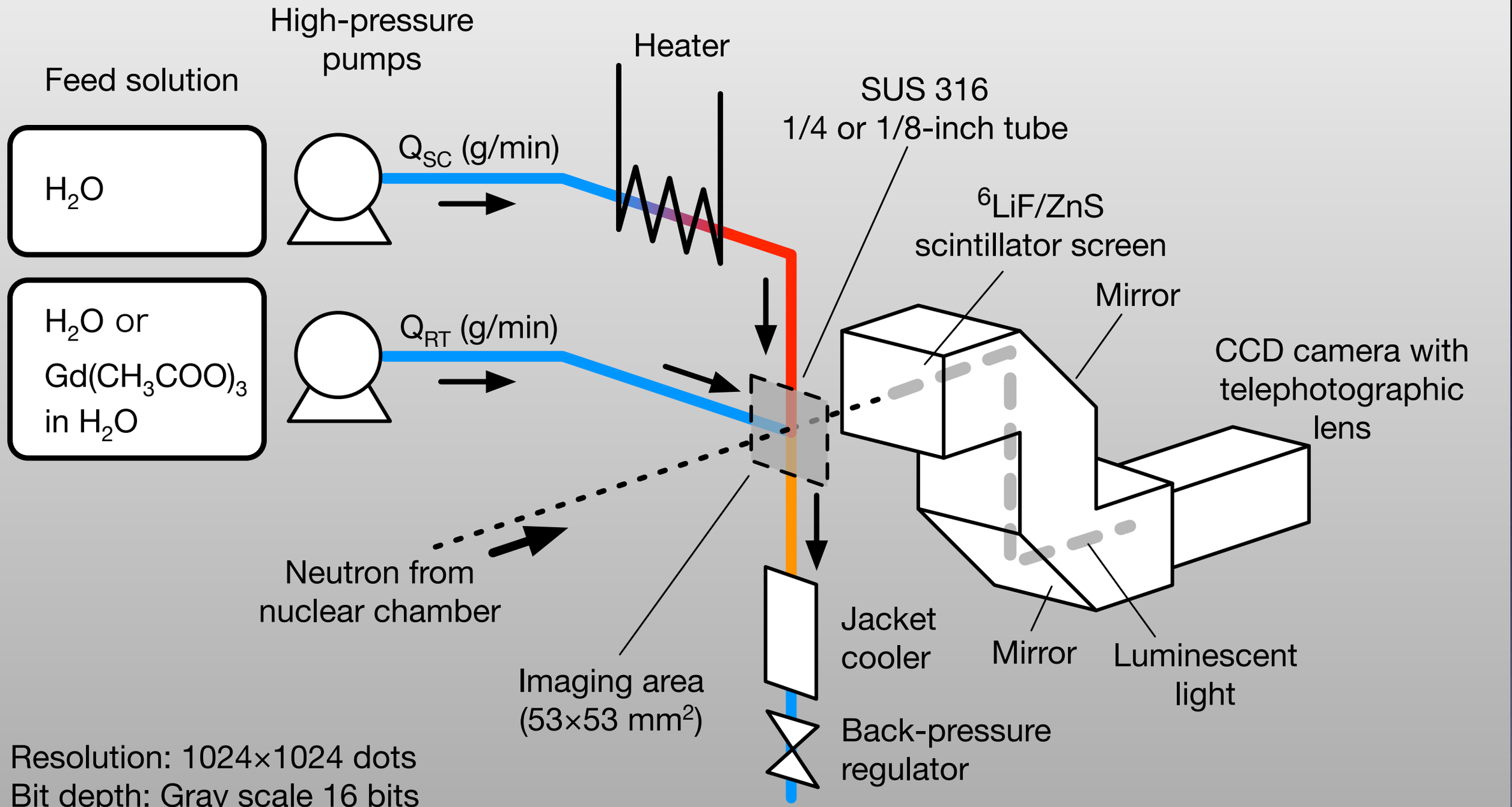
Visualization of reactant solution



Linear attenuation coefficient of solutions at 25°C, 1 atm (cm^{-1})

H_2O	3.83
0.1 M Gd^{3+} solution	6.79
0.1 M B^{3+} solution	3.88

Experimental setup



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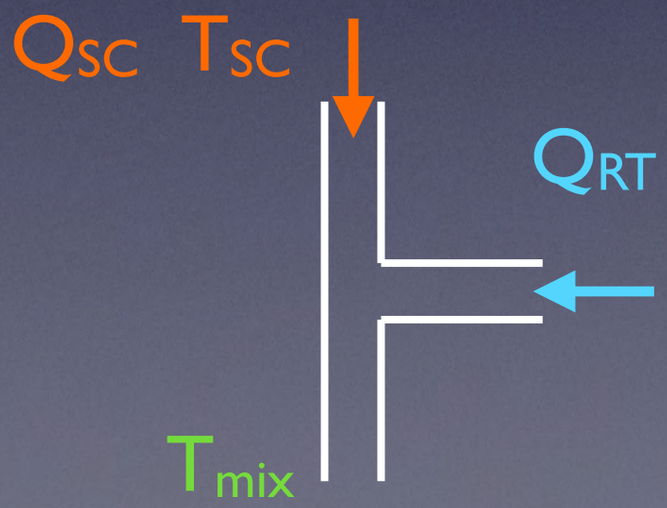
Experimental condition

Tube diameter	Q_{SC} (g/min)	Q_{RT} (g/min)	T_{SC} (°C)	T_{mix} (°C)	$C_{Gd^{3+}}$ (mol/L)	
1/4 in. (4.8 mm)	16	8	23	23	0.1, 0.2	
			219	113	0.1	5 MW
			285	181	0.1	
			388	331	0.025	1 MW
1/8 in. (2.3 mm)	20	4	384	279	0.1	1 MW



60 s for 1 image (1 MW)

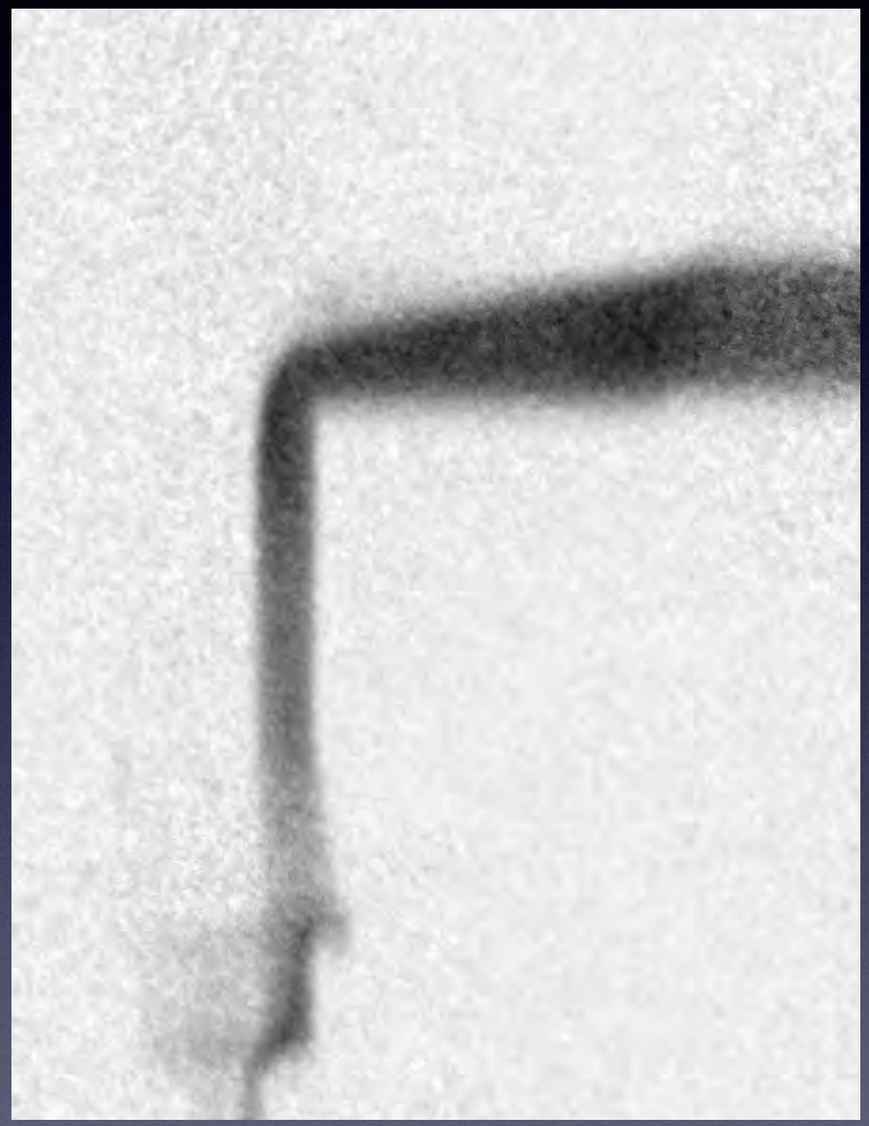
30 s for 1 image (5 MW)

5 images for 1 condition

Mixing at room temp.

Absorption by solution

Absorption by solute

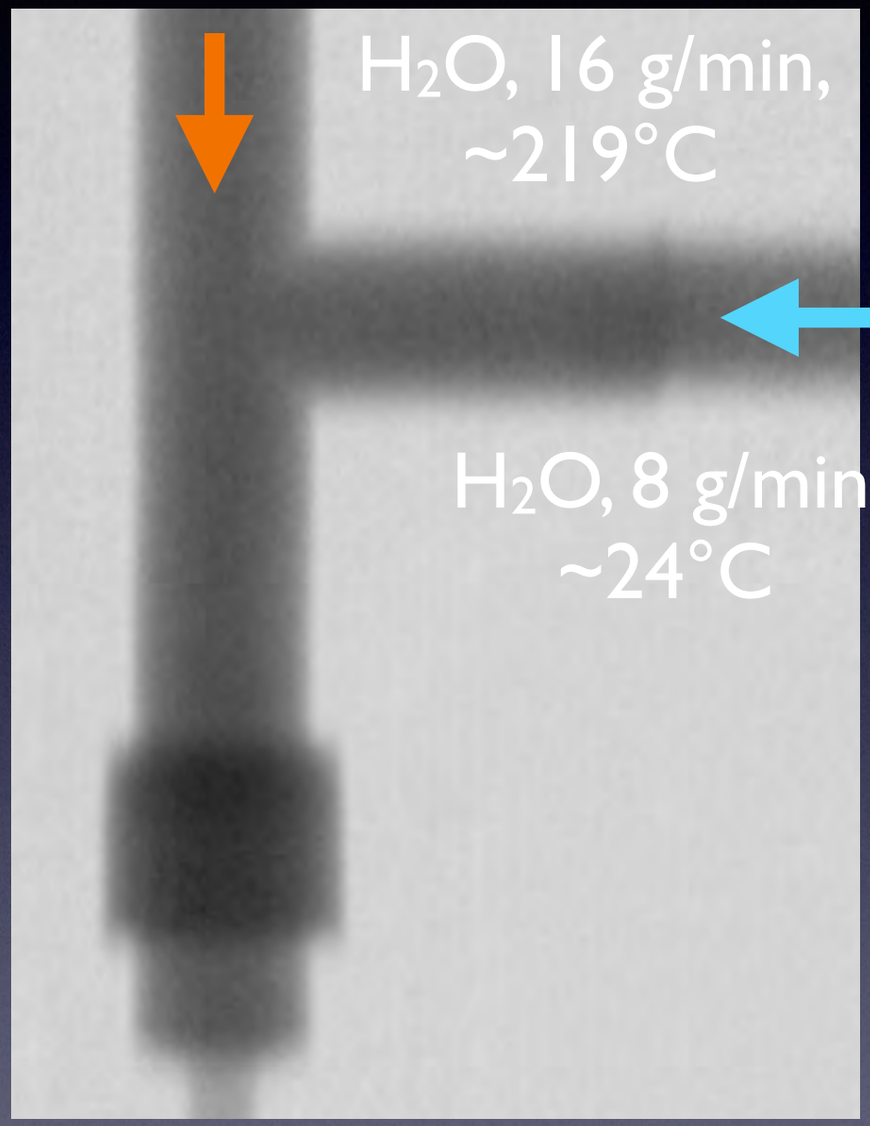


5 mm

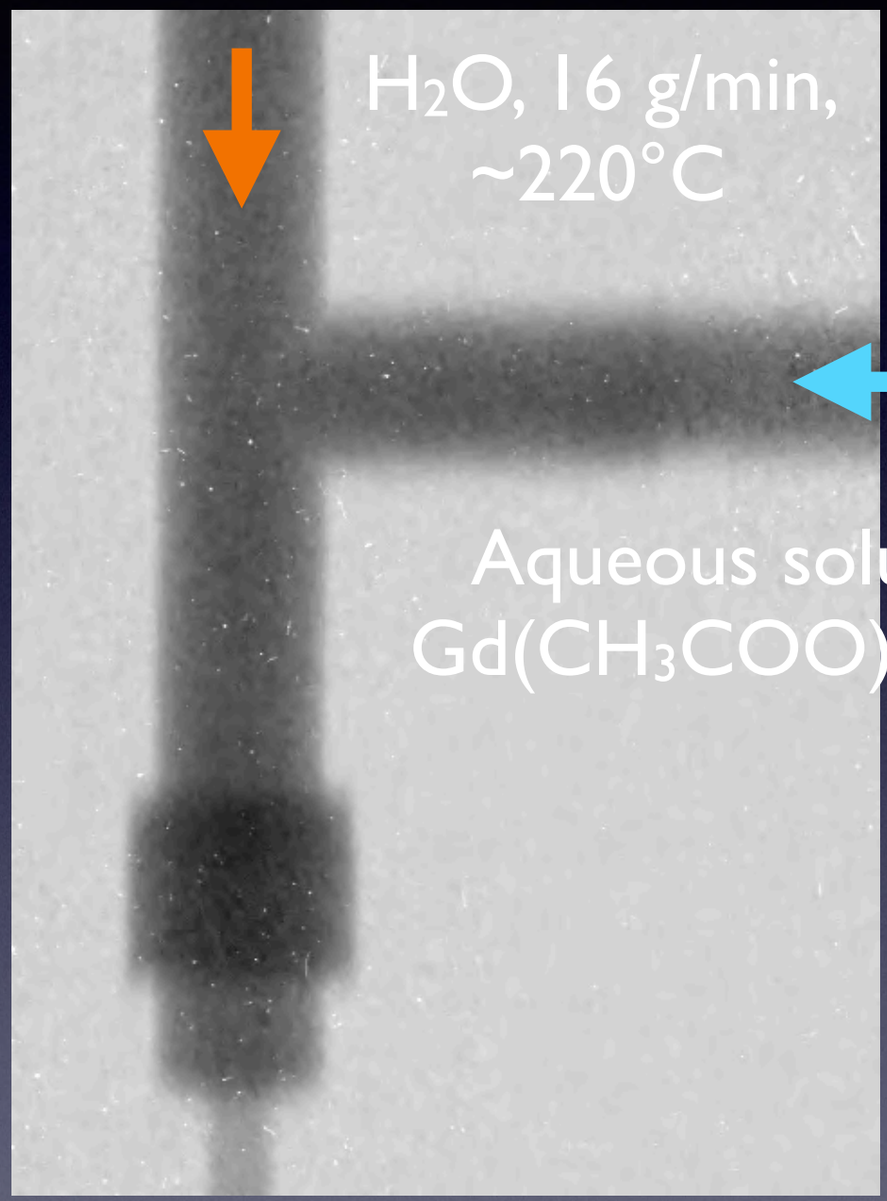
Distribution of metal ion solution was visualized.

Mixing at ~113°C

Mixing with water



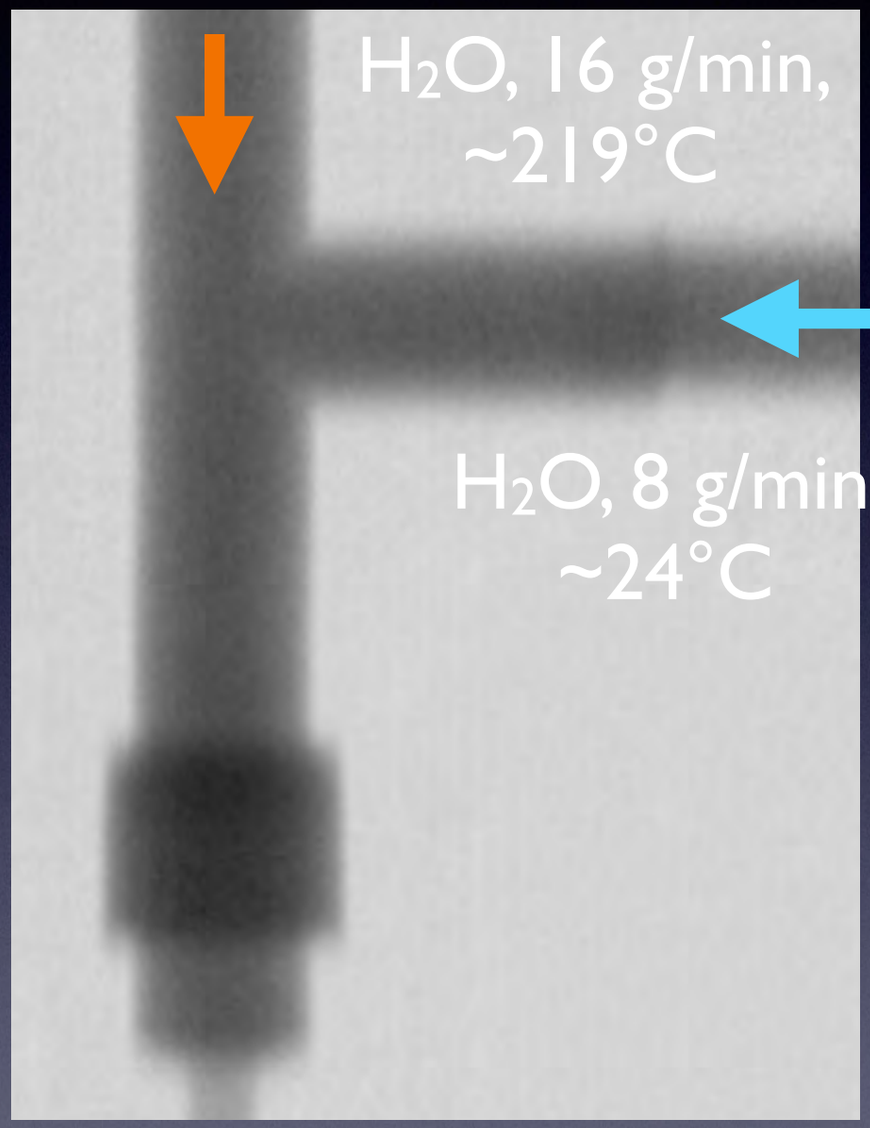
Mixing with Gd^{3+} solution



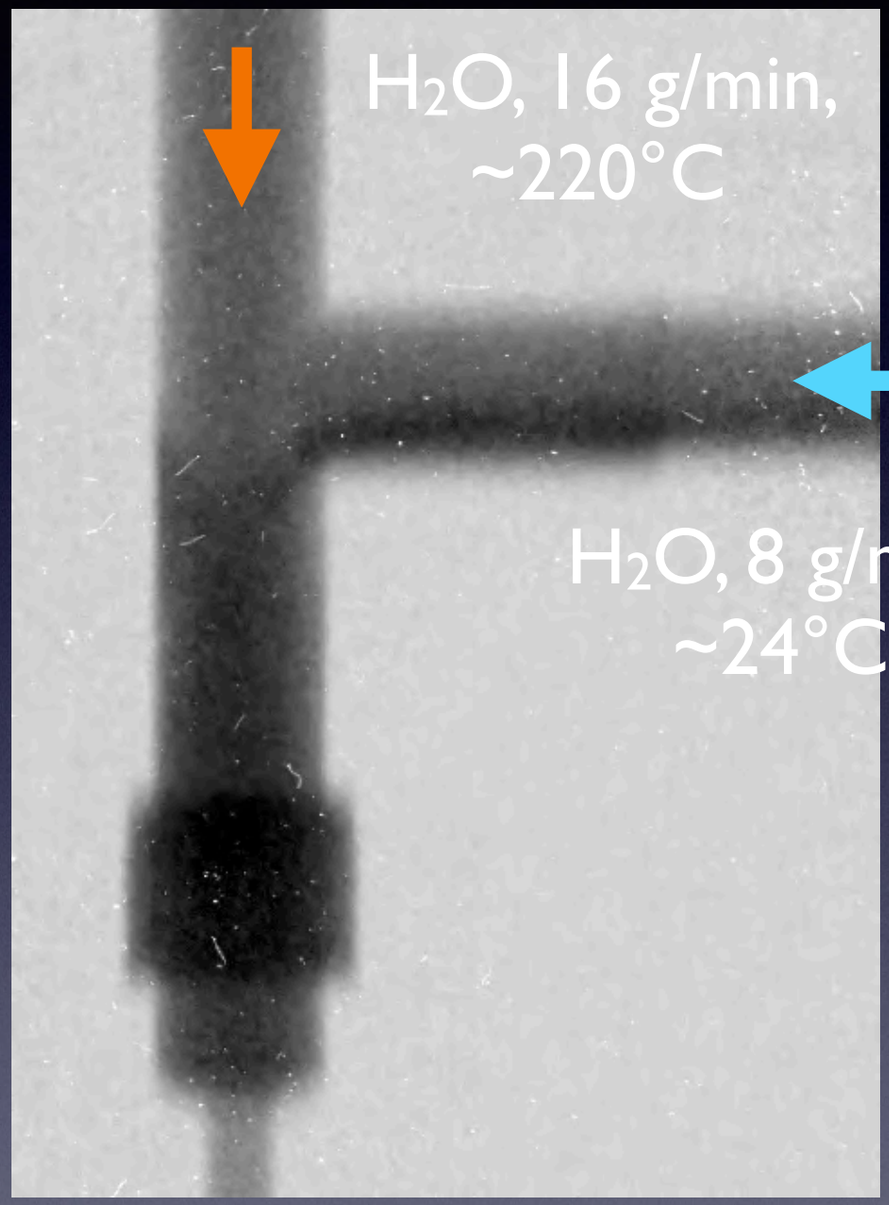
15 s for 1 image
40 images

Mixing at ~113°C

Mixing with water



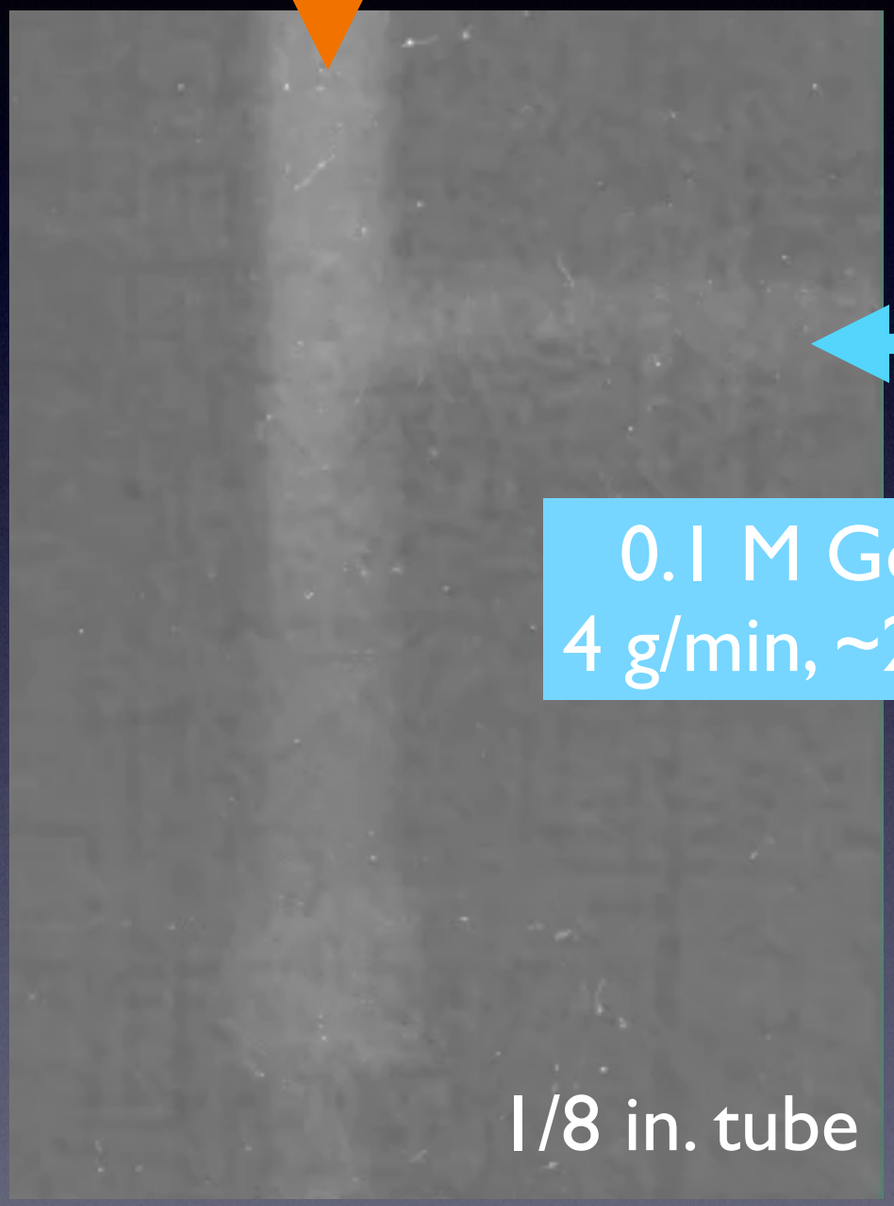
Mixing with Gd^{3+} solution



Deposition of $Gd(OH)_3$ on the inner wall of tube occurred.

Other conditions

H_2O, 20 g/min,
~384°C

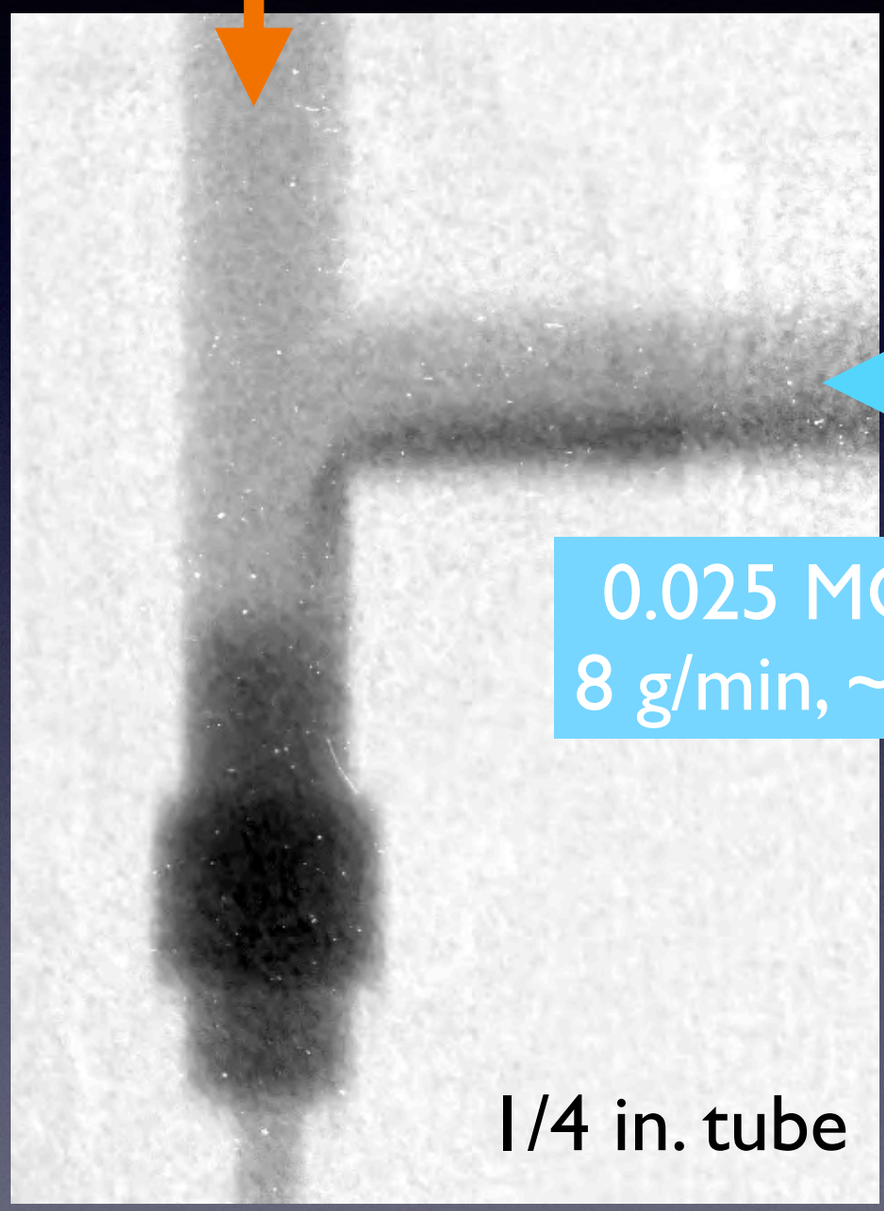


0.1 M Gd^{3+},
4 g/min, ~24°C

1/8 in. tube

60 s for 1 image
10 images

H_2O, 16 g/min,
~388°C



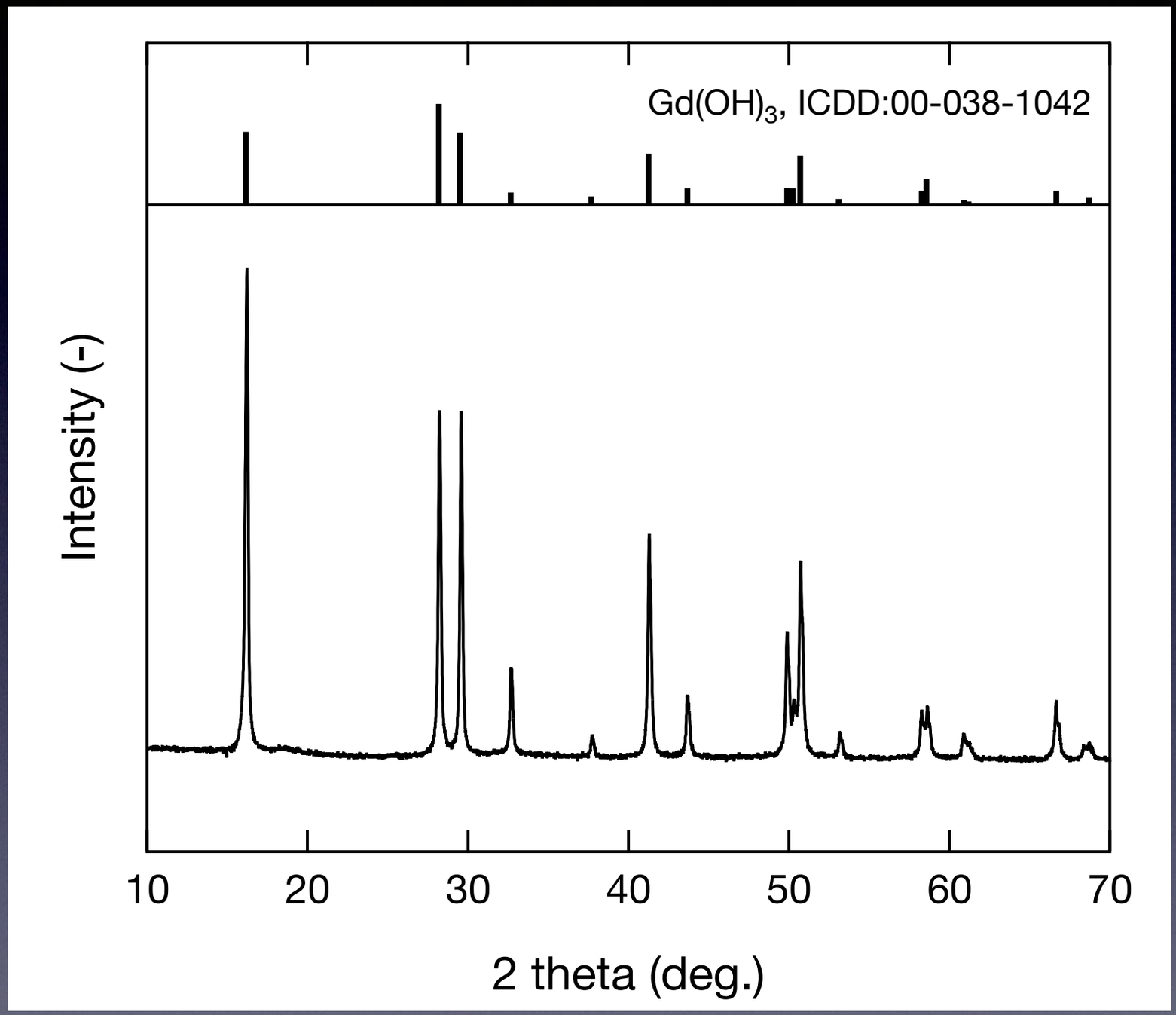
0.025 M Gd^{3+},
8 g/min, ~26°C

1/4 in. tube

60 s for 1 image
40 images

Plugging occurred in both cases.

Product from $Gd(CH_3COO)_3$



$Gd(OH)_3$ was produced by hydrothermal reaction.

Summary

Neutron radiography was performed to visualize the mixing of reactant solution with water in plug-flow reactor.

- Distribution of reactant solution around mixing point was visualized using $Gd(CH_3COO)_3$.
- $Gd(OH)_3$ was produced during imaging.
- Deposition of $Gd(OH)_3$ on the inner wall of reactor occurred at high temperature.

To visualize the distribution of reactant solution, we will try

- Diluted Gd^{3+} solution / Inactive Gd species
- Synthesis of Gd-containing compound nanoparticles
- Use of Gd_2O_3 nanoparticles as a tracer
- Use of B^{3+} or other metal ions in heavy water