中性子ラジオグラフィー法を用いた酸化物ナノ粒子水熱合成プロセスの可視化

1) 名大・工, 2) 東北大・工, 3) JAEA

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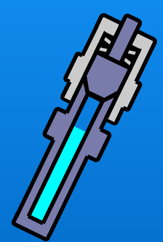
栗田 圭輔[3]、飯倉　寛[3]

Hydrothermal synthesis of metal oxide nanoparticles

Hydrothermal synthesis

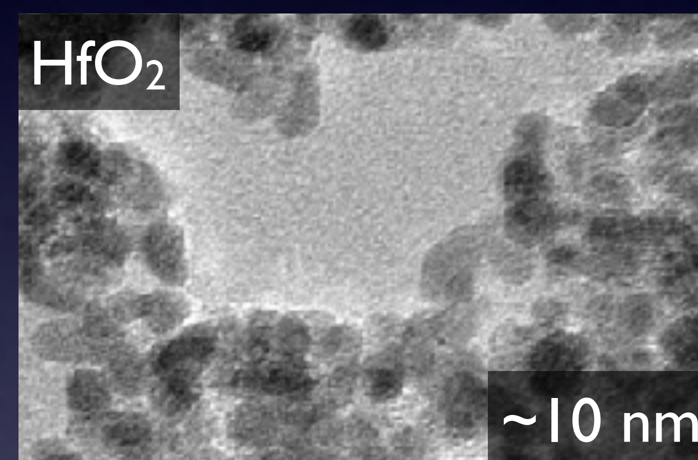


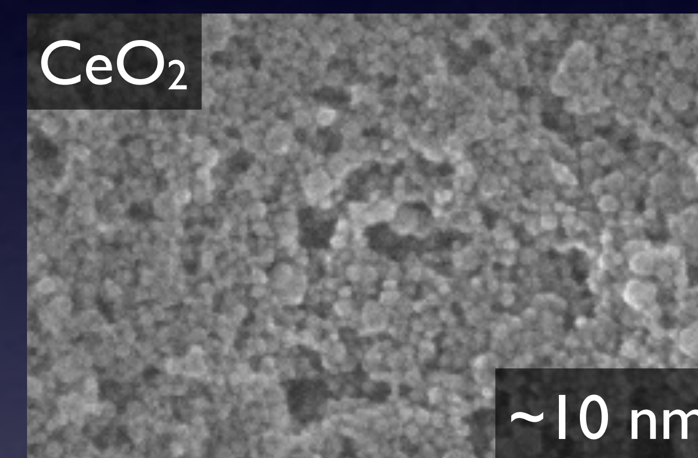
$M(NO_3)_n$

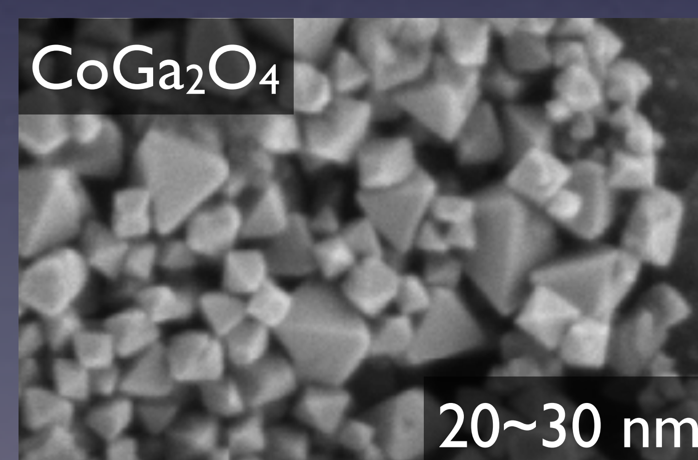
$$M^{n+} \xrightarrow{+\ n\ H_2O} M(OH)_n \xrightarrow{-\ n/2\ H_2O} MO_{n/2}$$

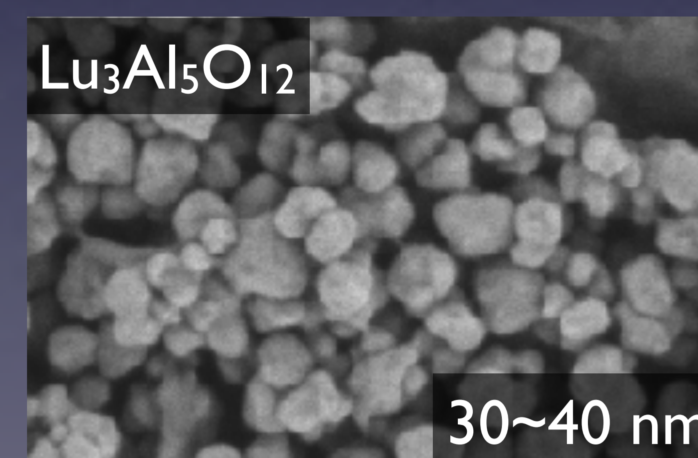
200~400°C
~30 MPa
in water

TiO_2	$MgFe_2O_4$
VO_2	$BaTiO_3$
MnO_2	$CoGa_2O_4$
Co_3O_4	ITO, IZTO
ZnO	YSZ
Ga_2O_3	$GdVO_4$
ZrO_2	LuAG:Ce, Eu
RuO_2	TiO_2:Nb-Co
HfO_2	CeO_2:Cr
CeO_2	$Gd(OH)_3$
Bi_2O_3	Pt, Ni, Bi



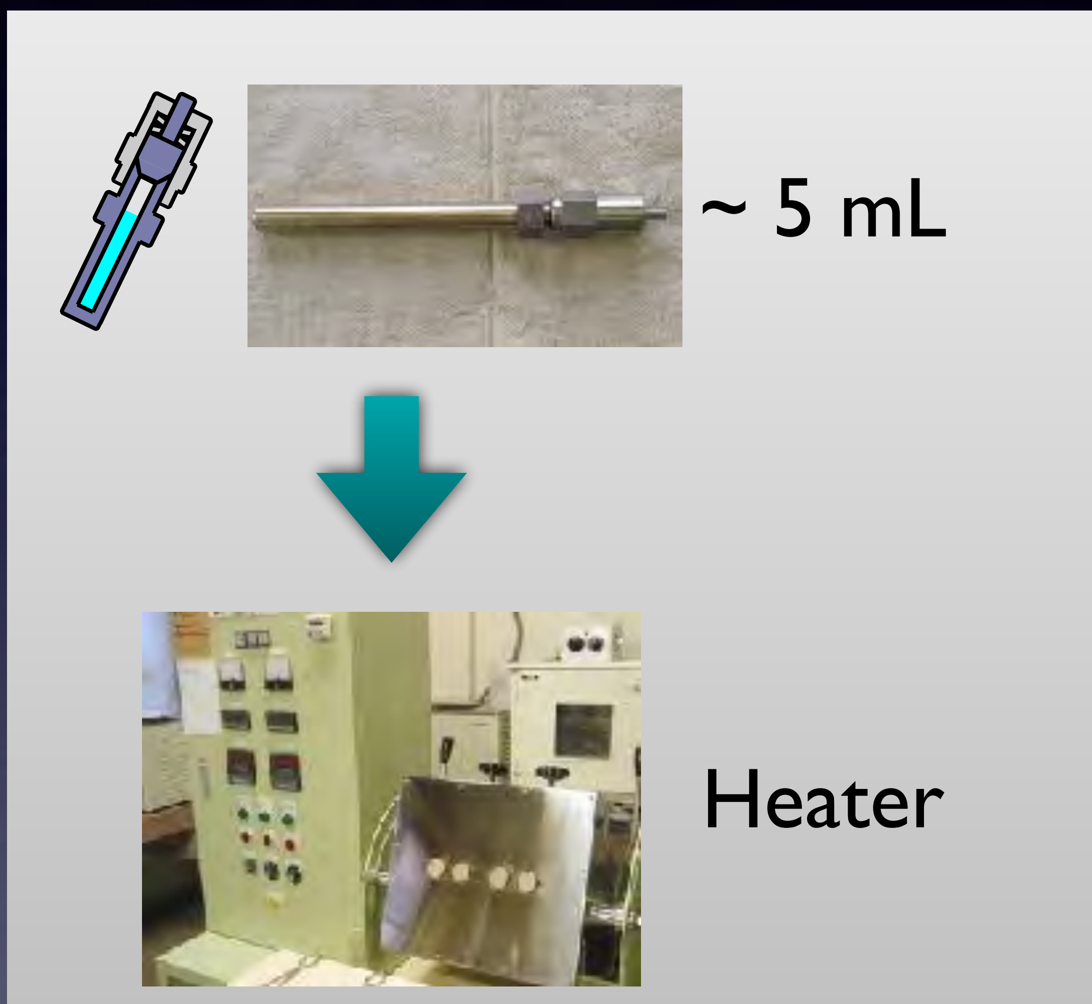




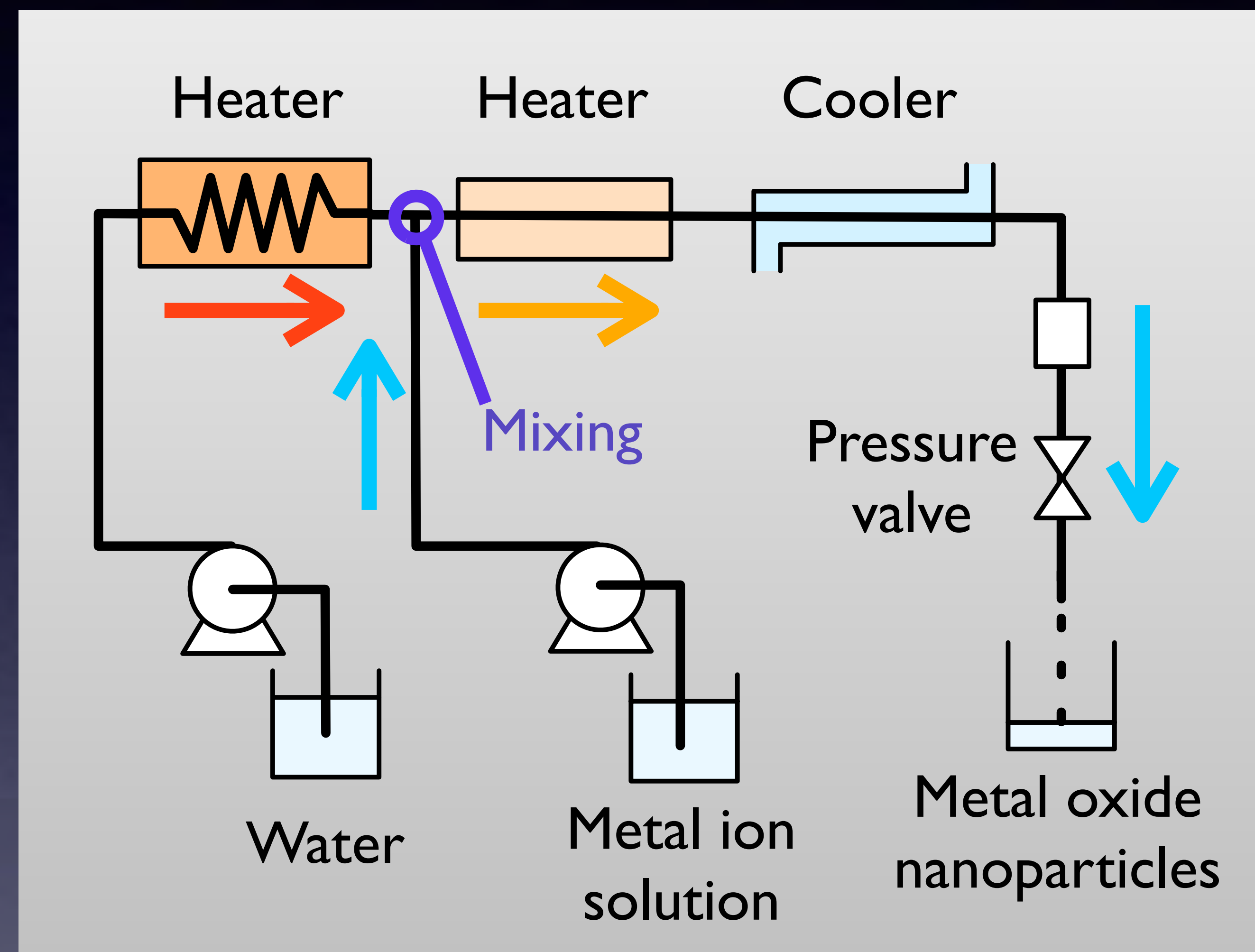


Reactors for hydrothermal synthesis

Batch reactor



Plug-flow reactor



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

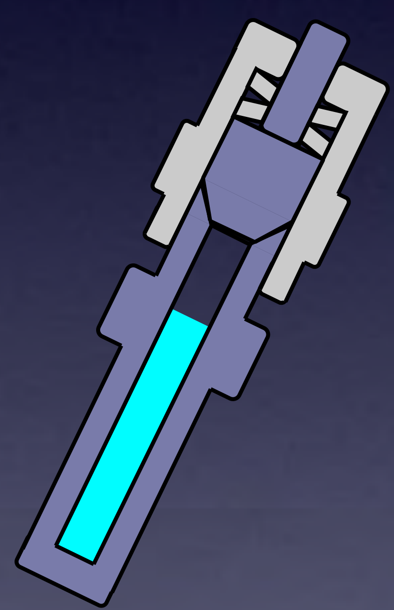
Heating time

~ 5 min

~ 0.5 s

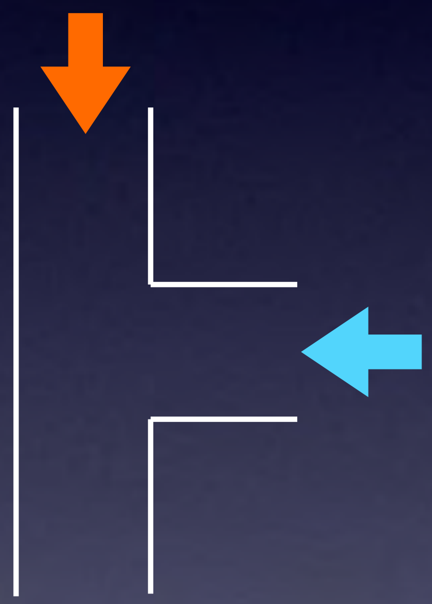
Topics

Batch-type reactor



Course of heating

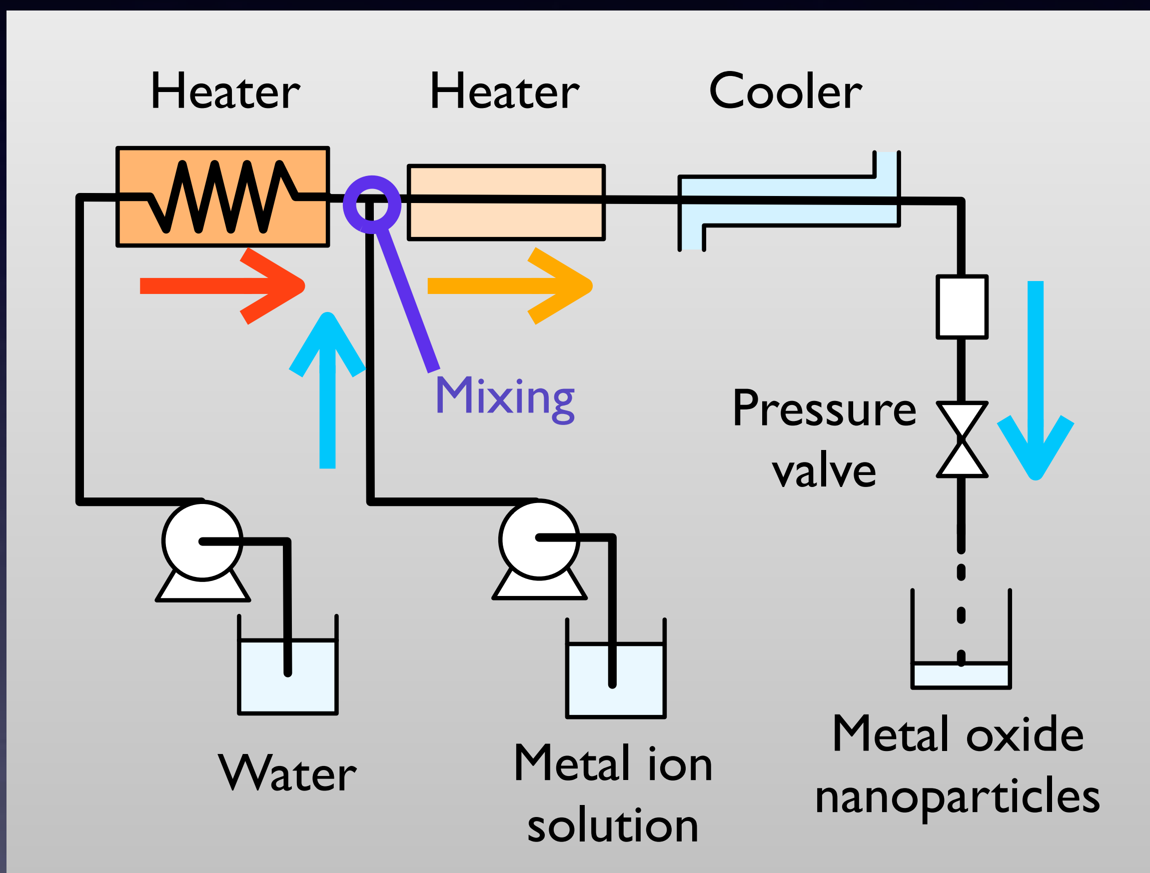
Flow-type reactor



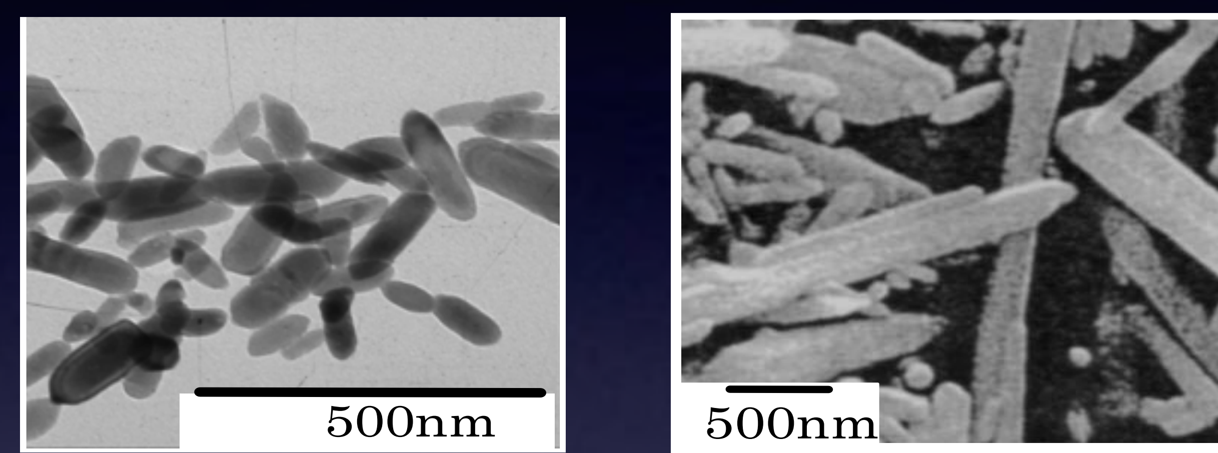
Dynamics of mixing

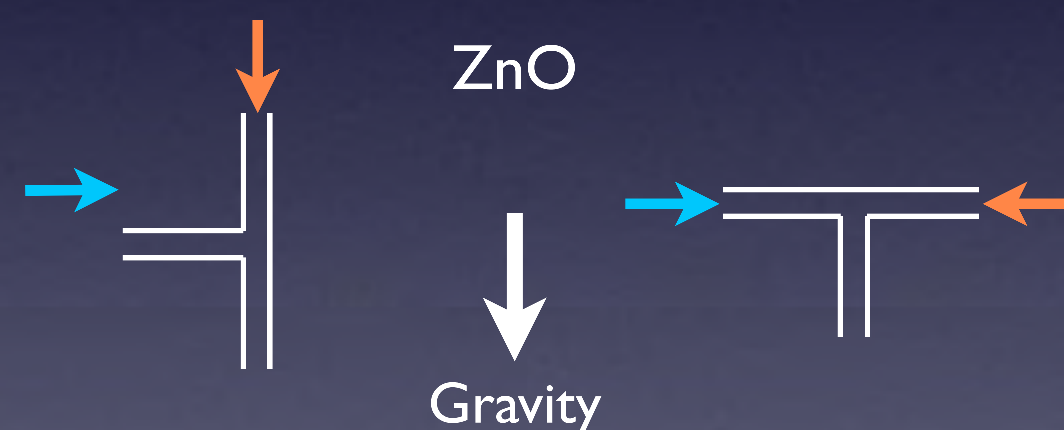
Synthesis with plug-flow reactor

Plug-flow reactor



Size of products



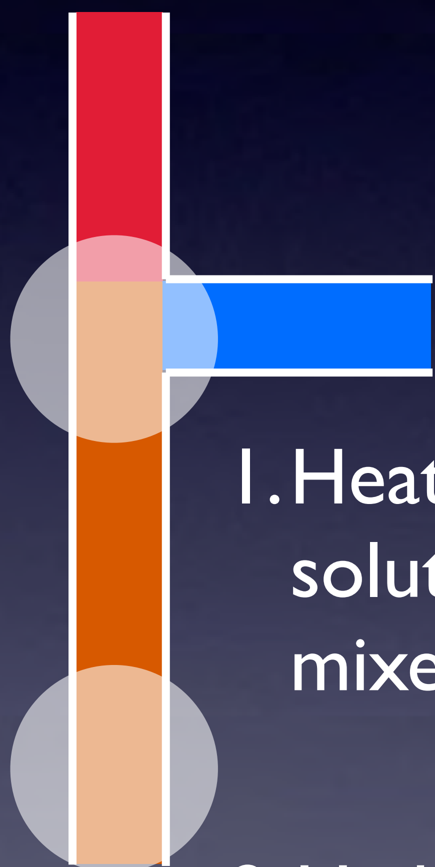


T. Adschiri, *et al.*, in Materials Chemistry in Supercritical Fluids, Research Signpost, 79–97 (2005)

Q: Why the mode of mixing affected the products ?

Answer : Reaction rate is very fast.

Reaction rate << Mixing rate



1. Heated water and reactant solution are completely mixed.
2. Hydrothermal reaction gradually proceeds.

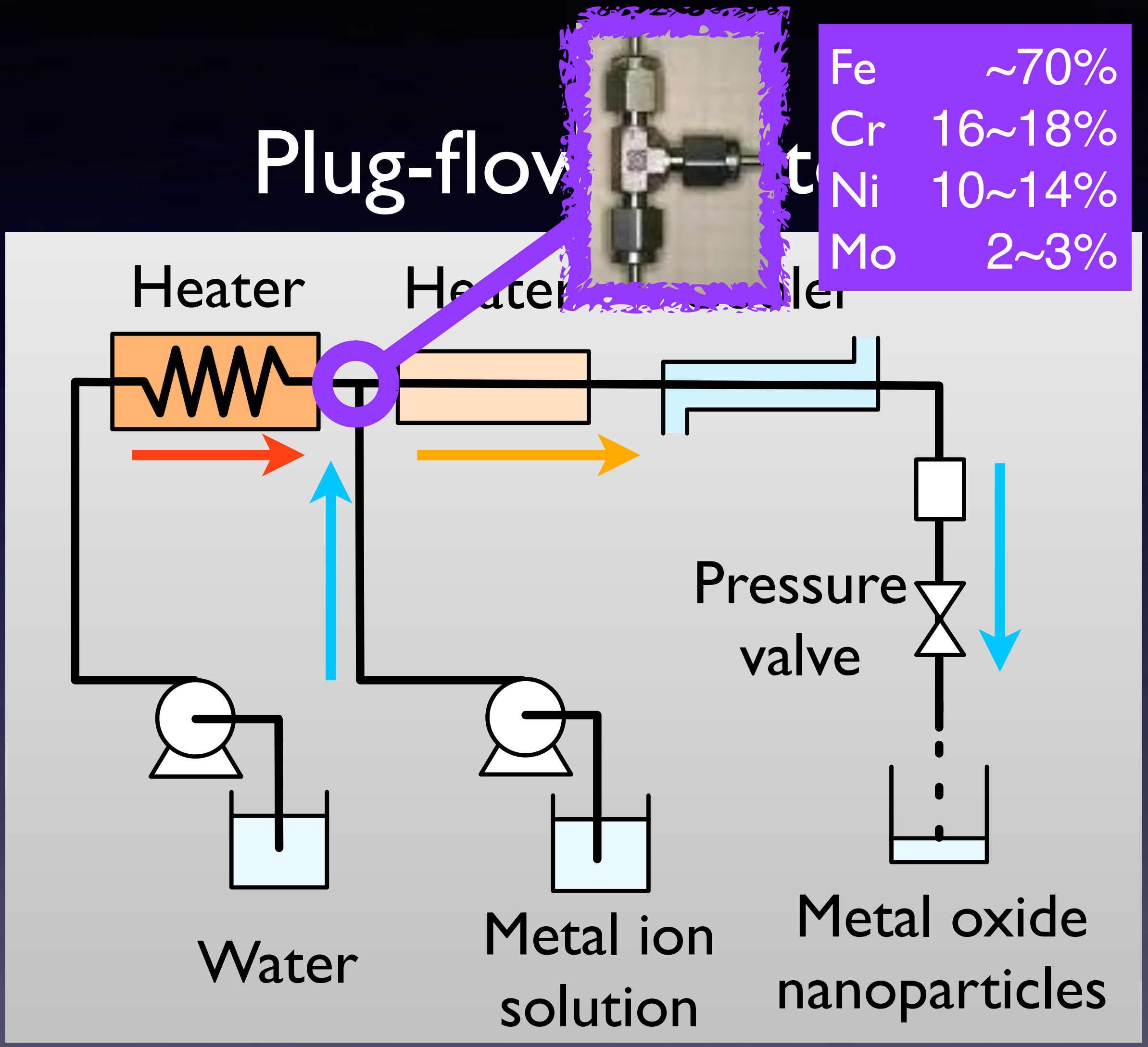
Reaction rate >> Mixing rate

Hydrothermal reaction proceeds with mixing.

Mode of mixing affects the products.

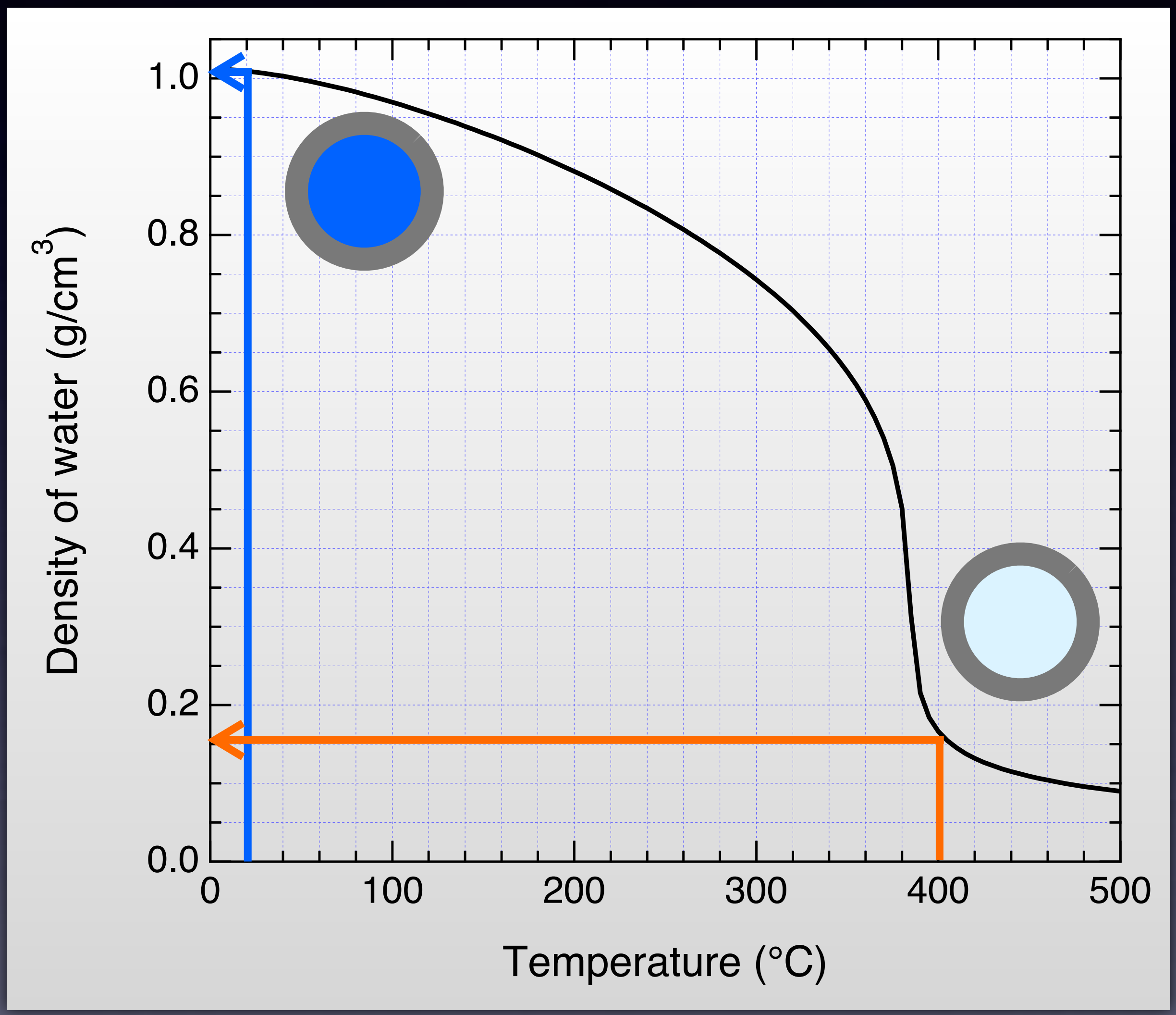
How two streams are mixed ?

Mixing of two water streams



300~400°C, 25 MPa

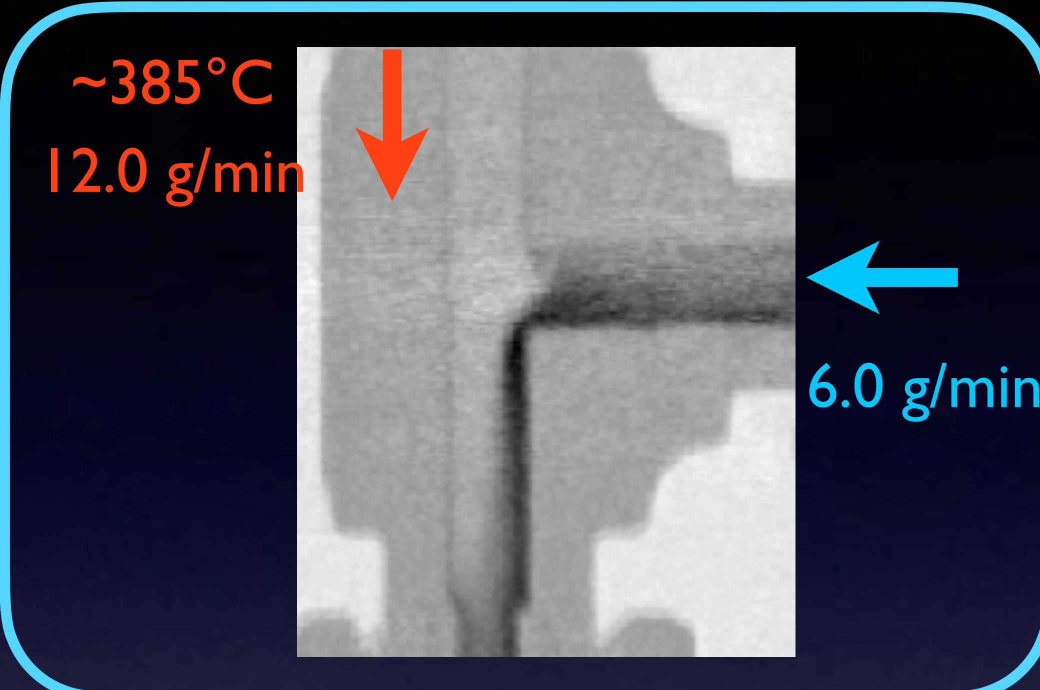
Density of water @ 25 MPa

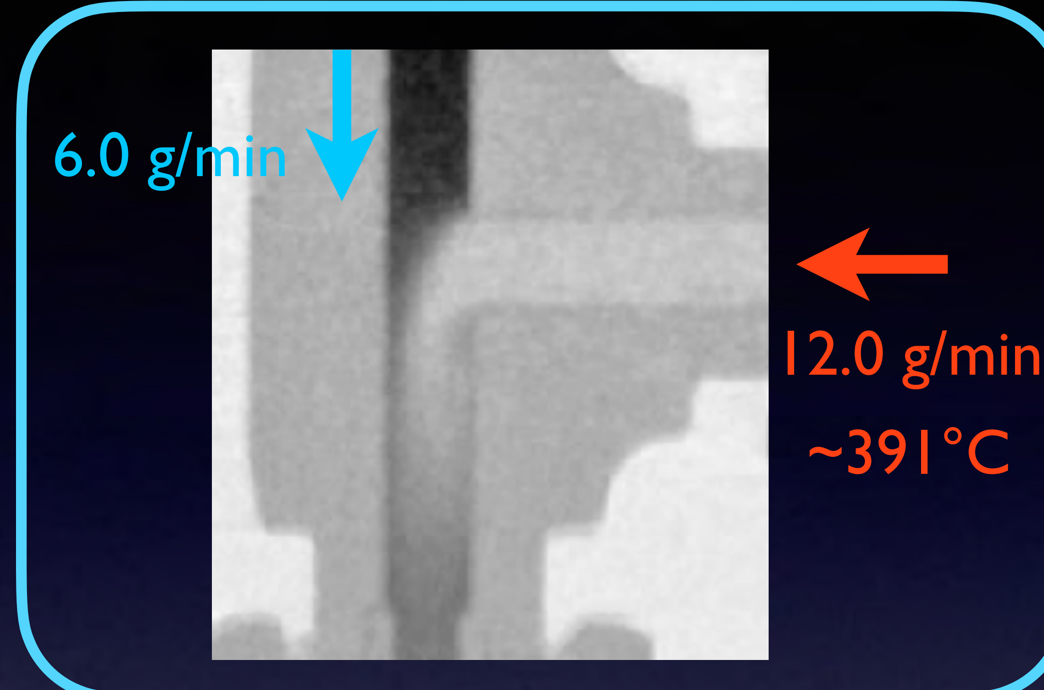


Difference in water density can be visualized.

Comparison between mixing modes

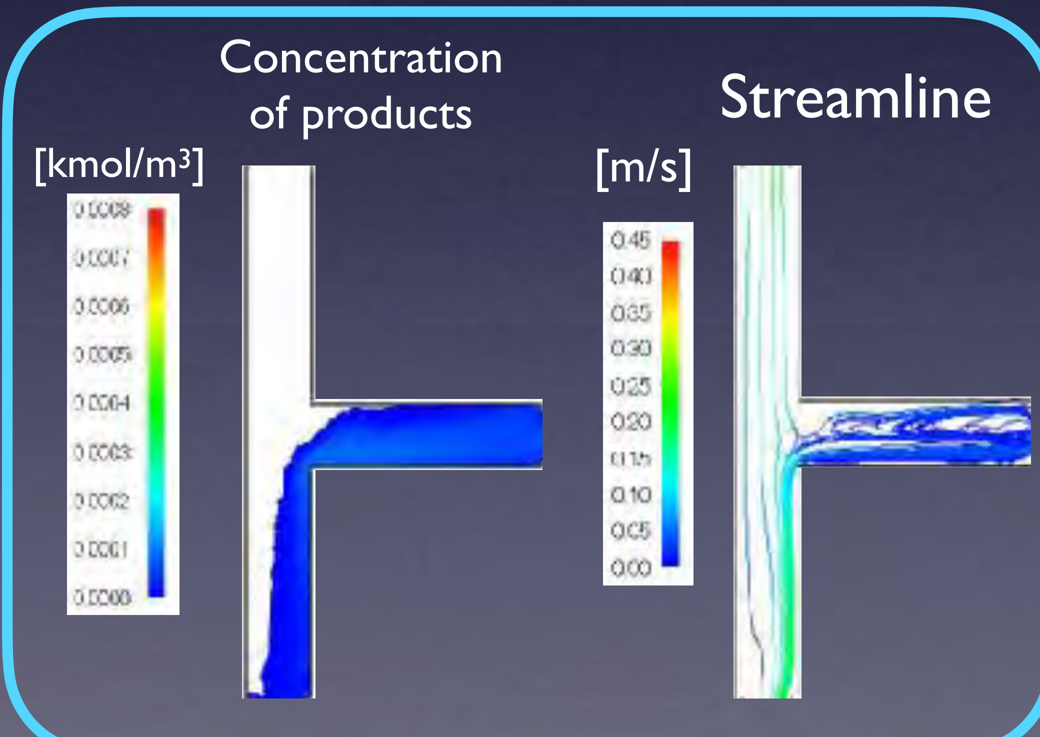
Measurement

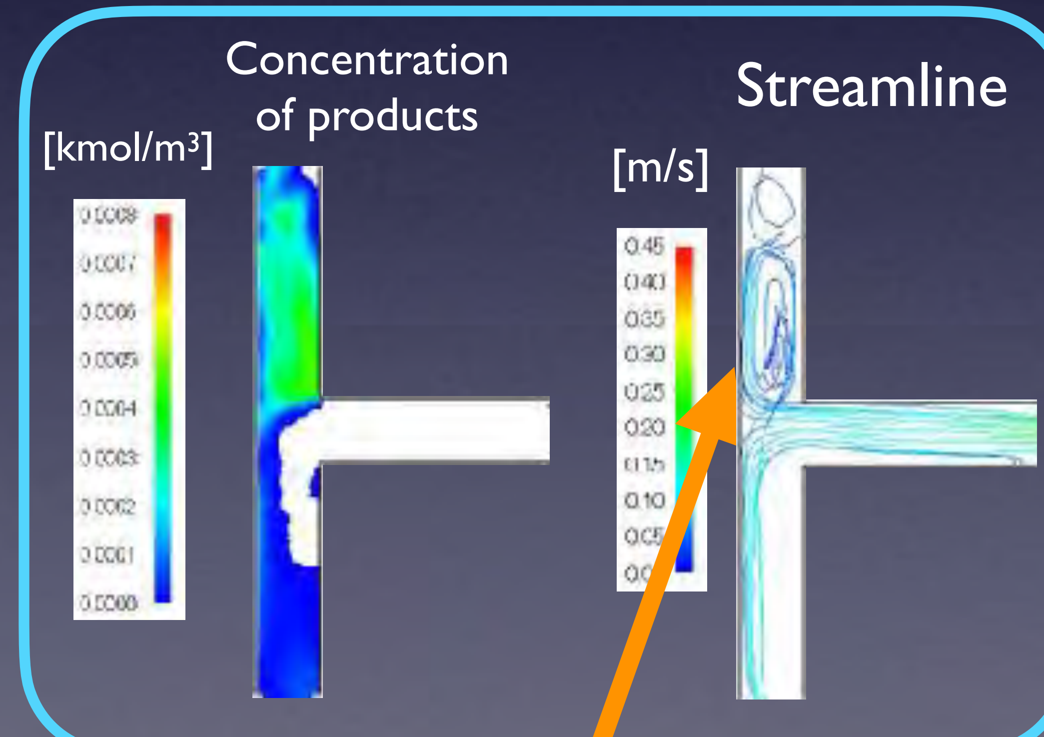




S. Takami, *et al.*, *Phys. Proc.* **69**, 564 (2015).

Simulation



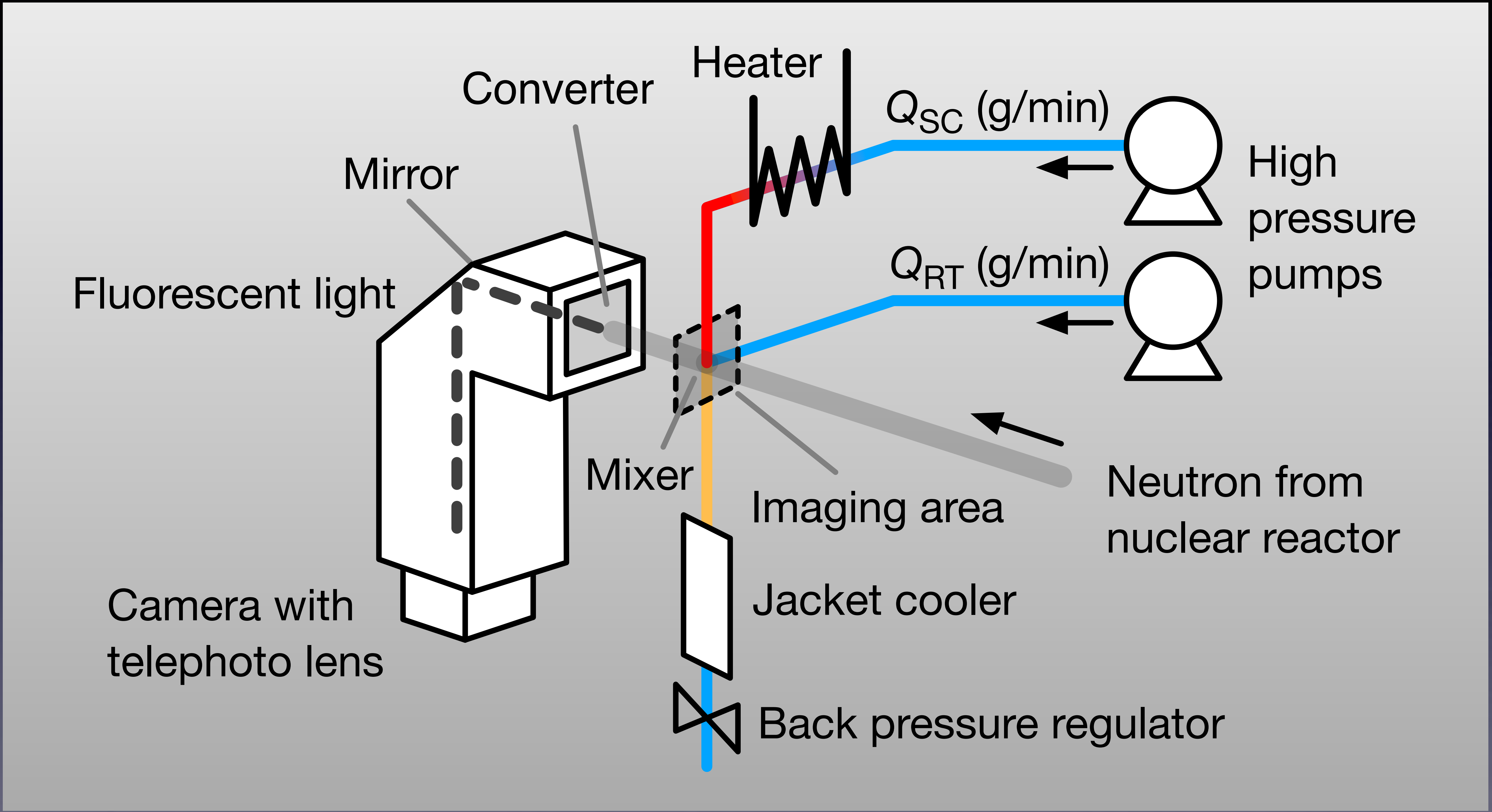


K. Sugioka, *et al.*, *J. Supercrit. Fluids* **109**, 43 (2016).

Unsteady-state vortex flow

Observation of dynamic behavior was tried.

Experimental setup

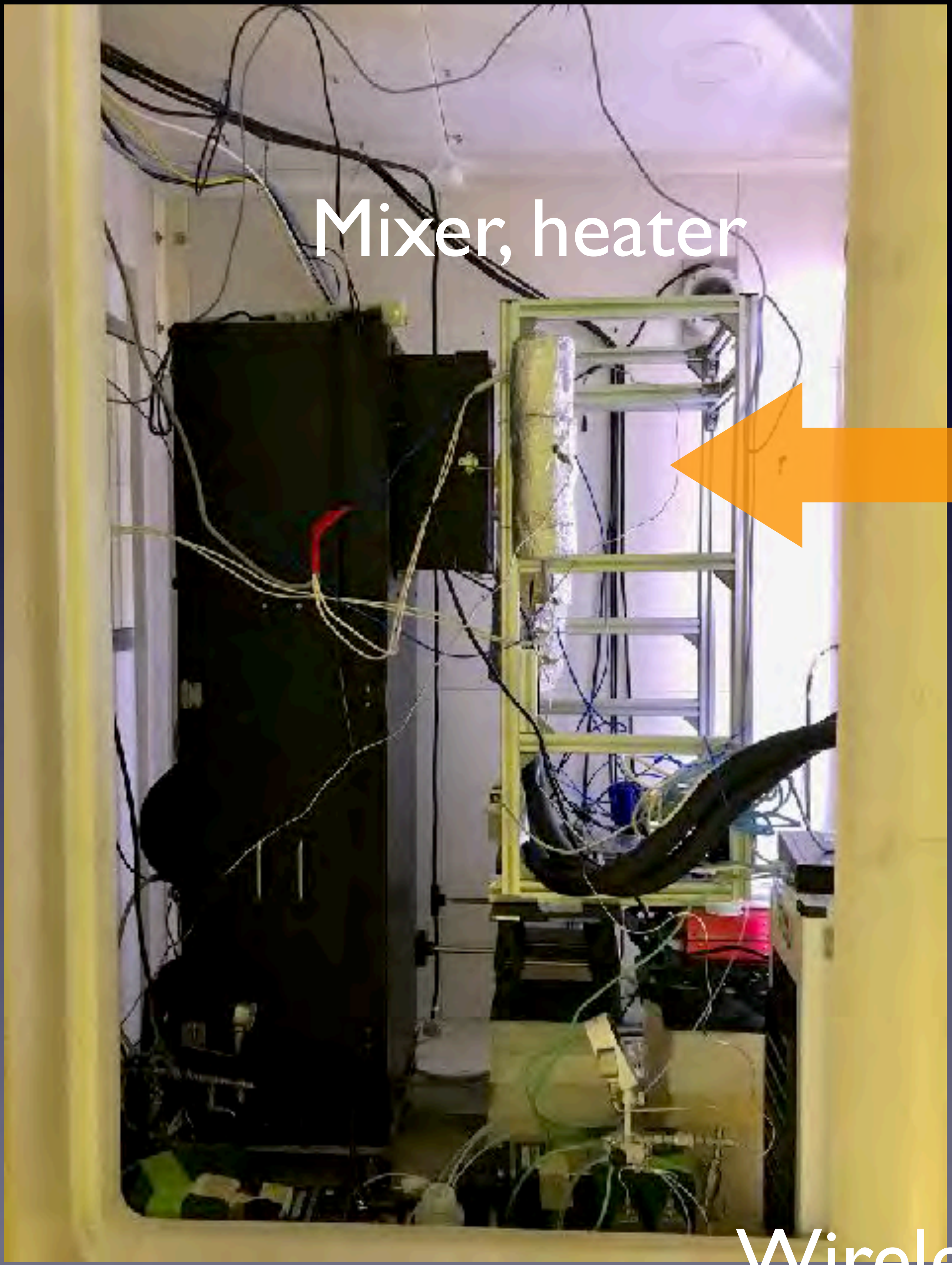


@ JAEA JRR-3 7R

Experimental setup

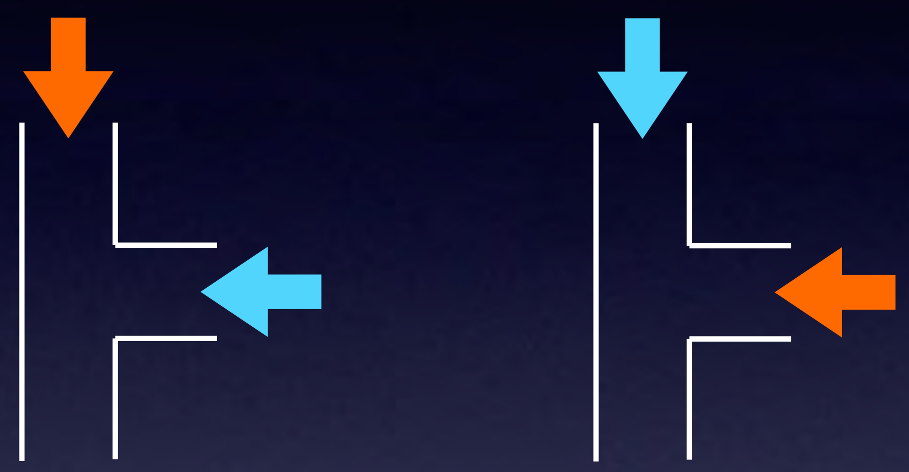
Outside of hatch

- Controllers of heater and pumps
- Temperature monitor



Experimental conditions

Inner diameter: 4.8 mm (1/4 inch)



Q_{SC} (g/min)	Q_{RT} (g/min)	T_{SC} (°C)	Re_{Sc}	T_{mix} (°C)	Re_{mix}
8	2	390	1.1×10^{3}	~379	8.7×10^{2}
12	3	390	1.6×10^{3}	~379	1.3×10^{3}

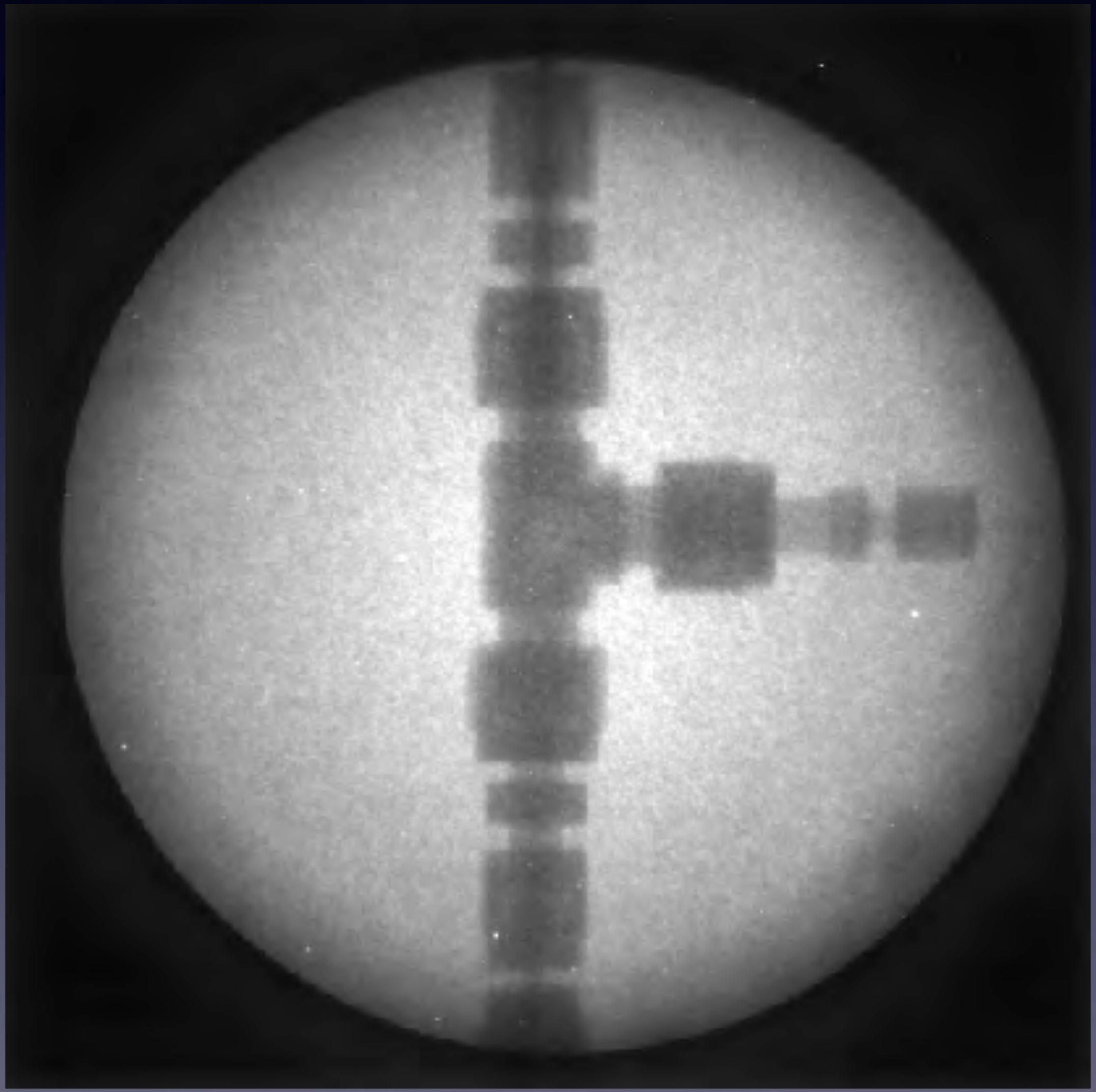
Camera

FASTCAM SA5 (Photron)
Nikon 105 mm F2.8

1024×1024 pixel
12 bits/pixel
60 fps

Image processing

as observed (I)



$$\mathrm{Abs} = -\log \frac{I - I_{\mathrm{dark}}}{I_{\mathrm{flat}} - I_{\mathrm{dark}}}$$

$$\mathrm{Abs}_{\mathrm{filled}} = -\log \frac{I_{\mathrm{filled}} - I_{\mathrm{dark}}}{I_{\mathrm{flat}} - I_{\mathrm{dark}}}$$

$$\mathrm{Abs}_{\mathrm{empty}} = -\log \frac{I_{\mathrm{empty}} - I_{\mathrm{dark}}}{I_{\mathrm{flat}} - I_{\mathrm{dark}}}$$

$$D = \frac{\mathrm{Abs} - \mathrm{Abs}_{\mathrm{empty}}}{\mathrm{Abs}_{\mathrm{filled}} - \mathrm{Abs}_{\mathrm{empty}}}$$

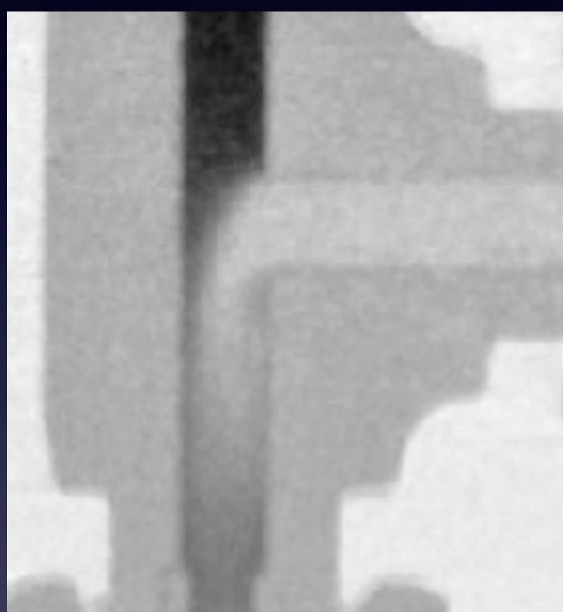
Calculation of moving averaged images

SCW from side

Moving averaged images of absorbance

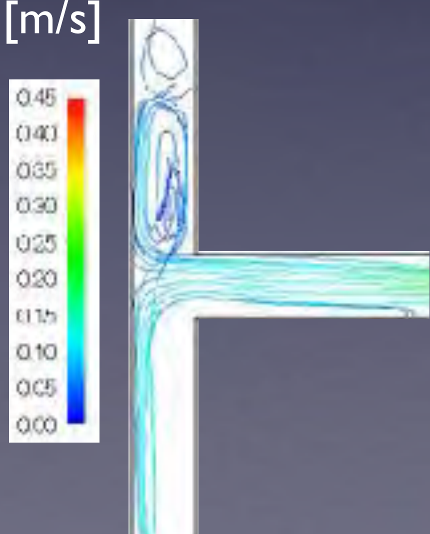
Previous results

Neutron CT image

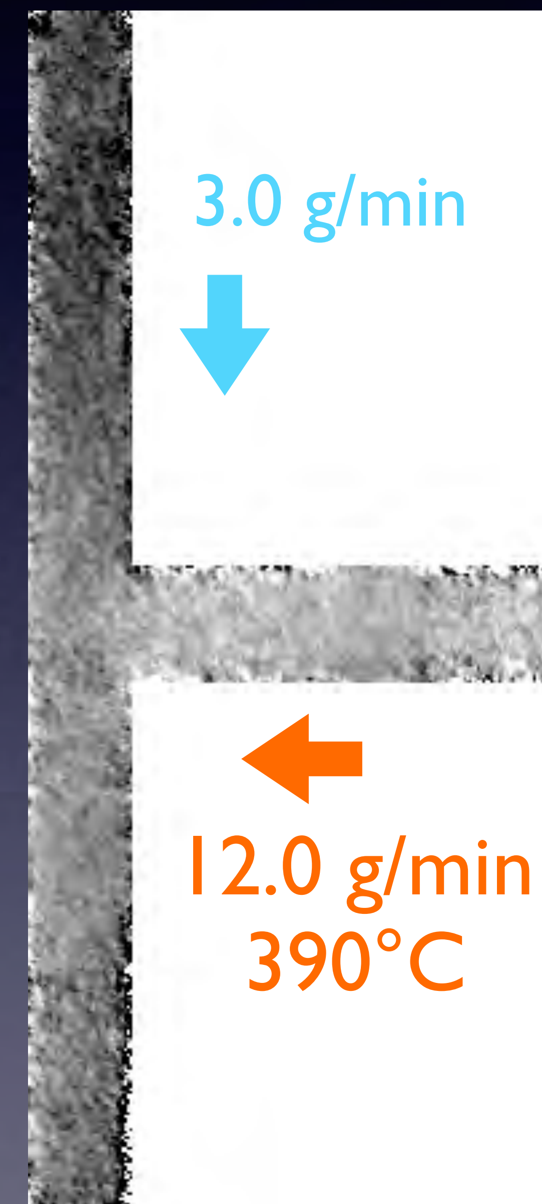


Streamline

[m/s]



Inner diameter: 4.8 mm



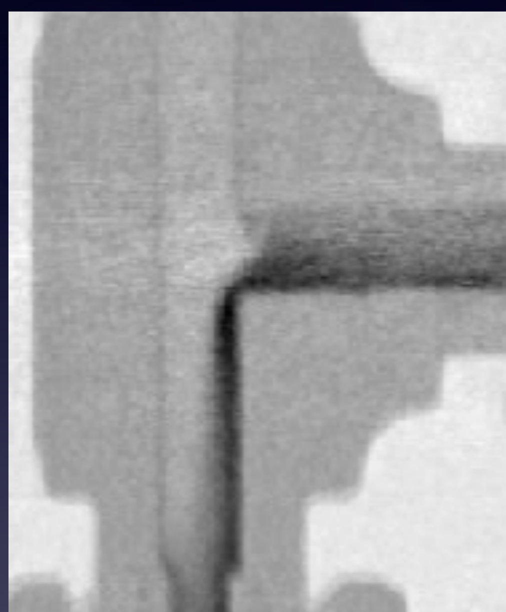
Recorded at 60fps, playback at 30 fps

SCW from top

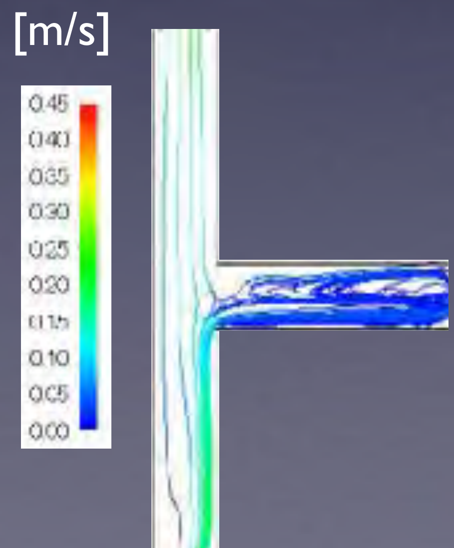
Moving averaged images of absorbance

Previous results

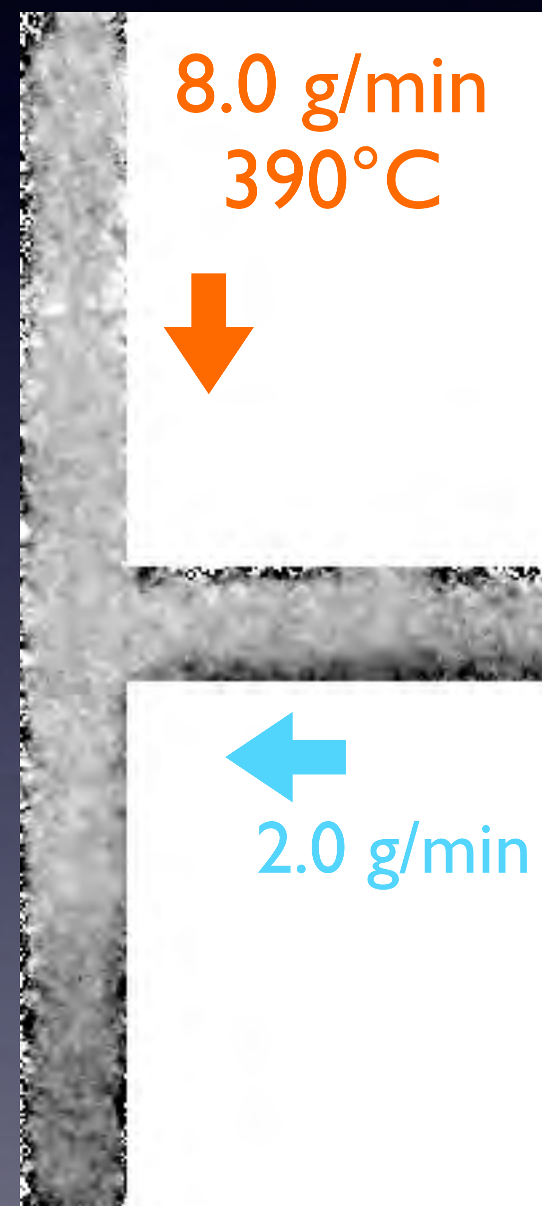
Neutron CT image



Streamline



Inner diameter: 4.8 mm



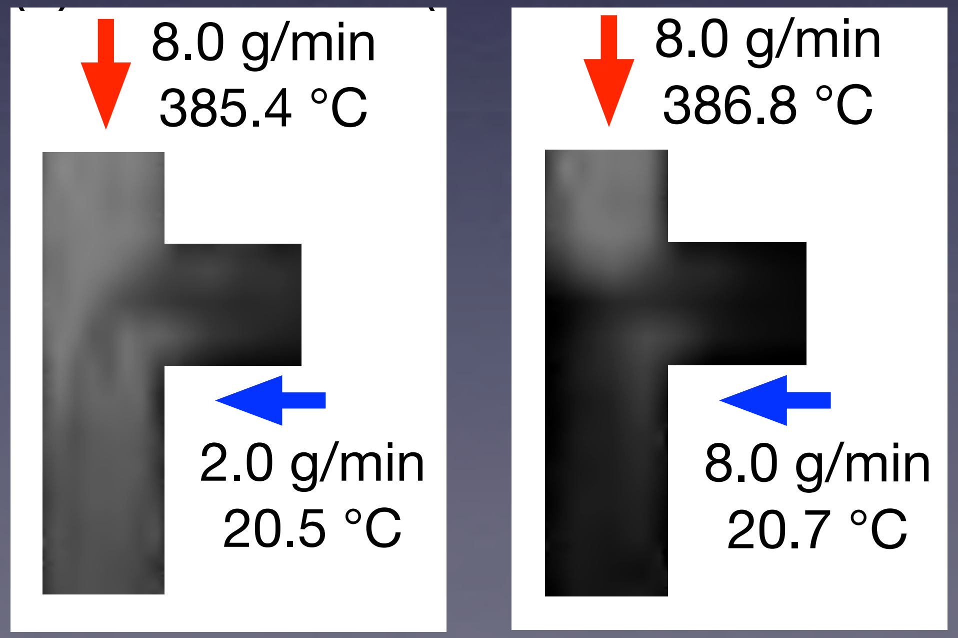
Recorded at 60fps, playback at 30 fps

Tentative summary

Dynamic behavior of mixing in a supercritical flow reactor was observed at 60 fps.

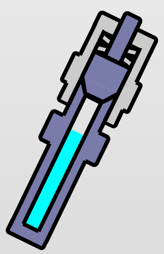
Next plans

- 1/8 inch mixer
- Higher frame rates
- Mixer with an inserted tube
- Different shape of mixer



Batch-type reactor

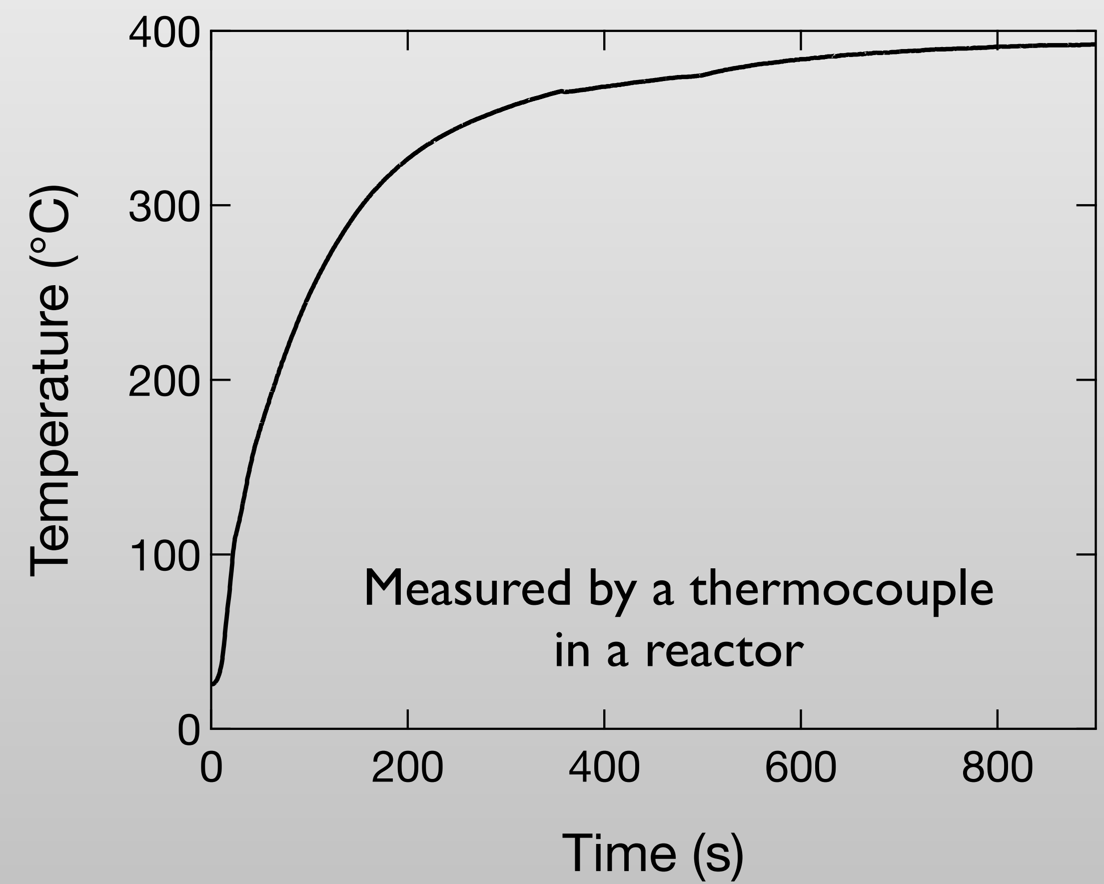
Batch reactor



~ 5 mL

Heater

Course of heating

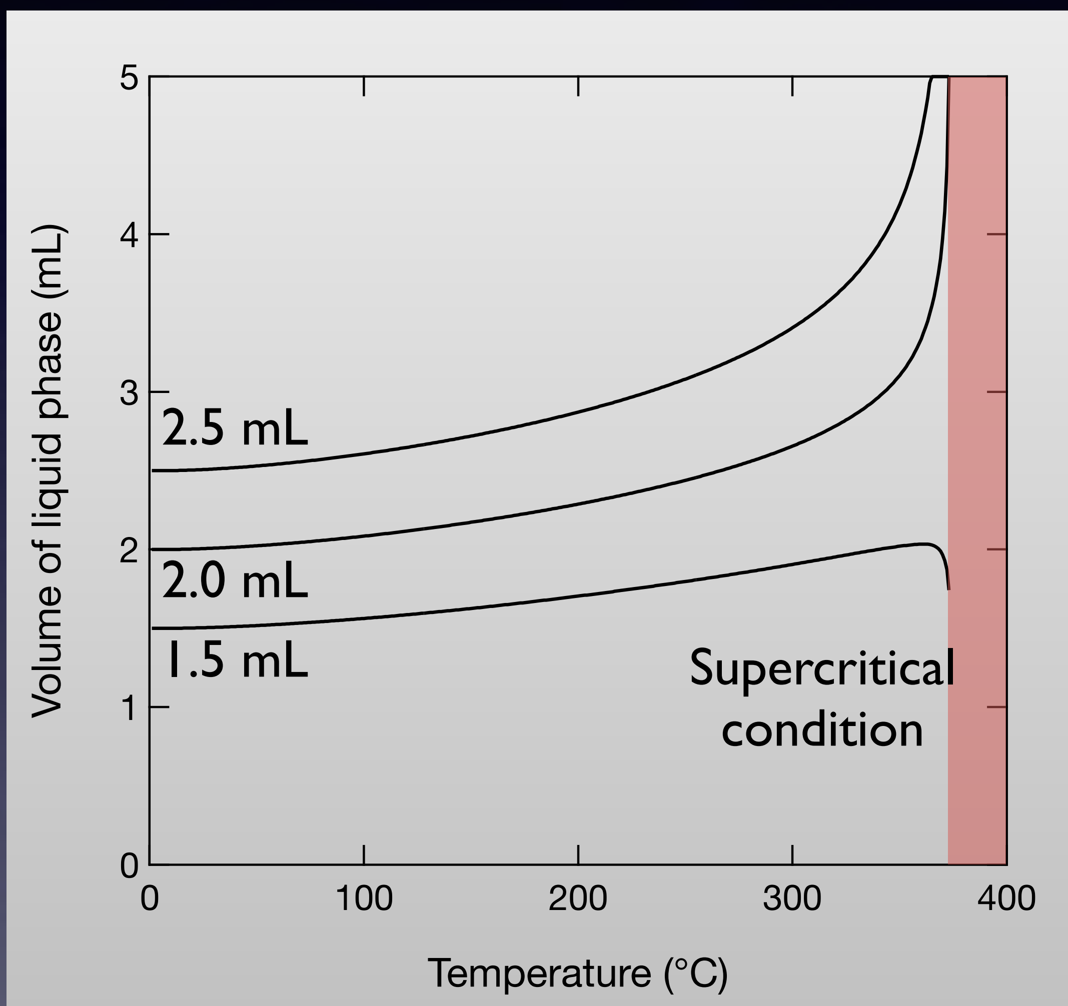


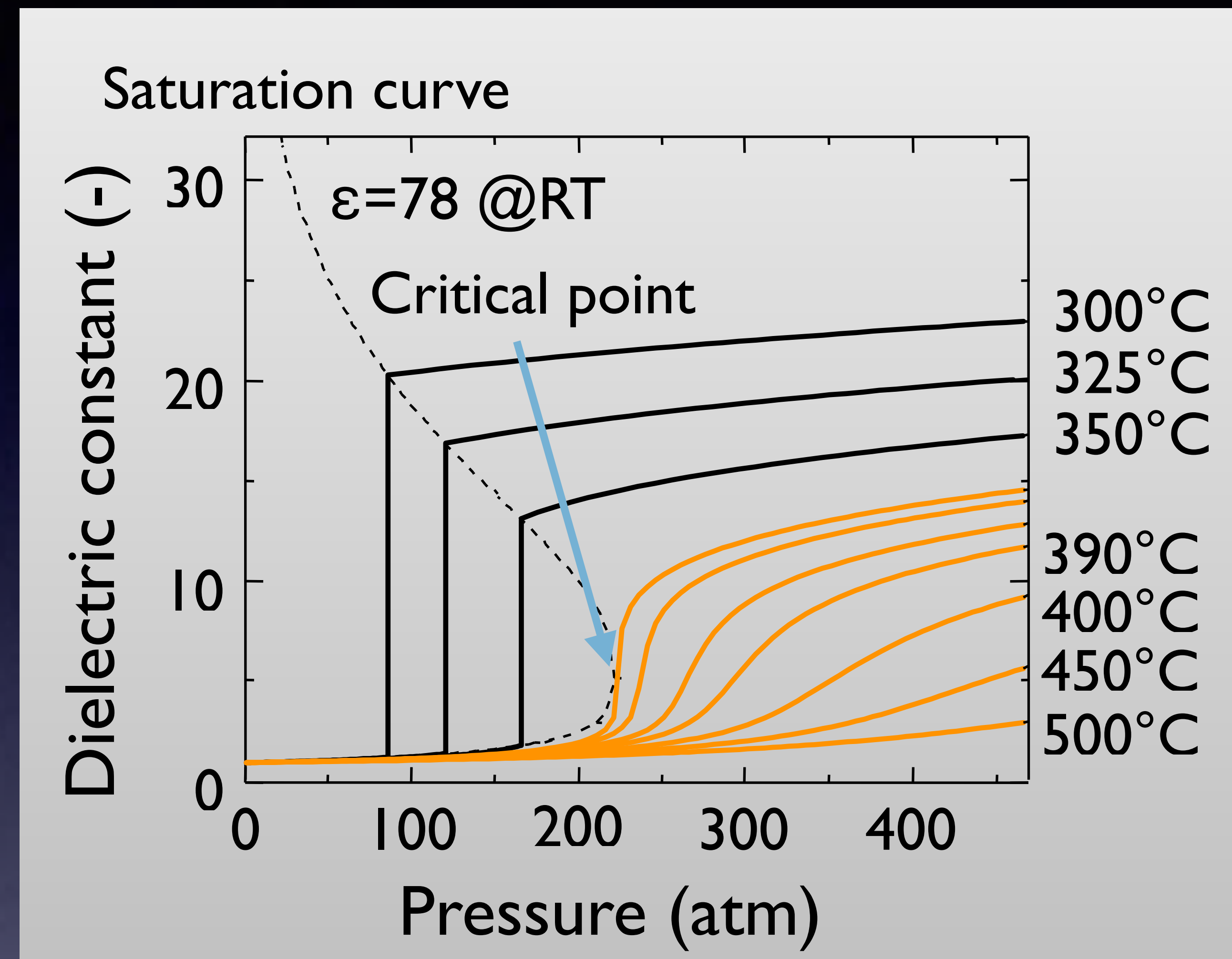
Metal ion solution was gradually heated to ~400°C.

ex. $M(NO_3)_n$

What happens during heating ?

Density of liquid phase decreases at high temperature.

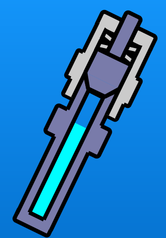




Dielectric constant decreases to ~20 at 300°C.

Metal ions can be soluble at around reaction temperature ?

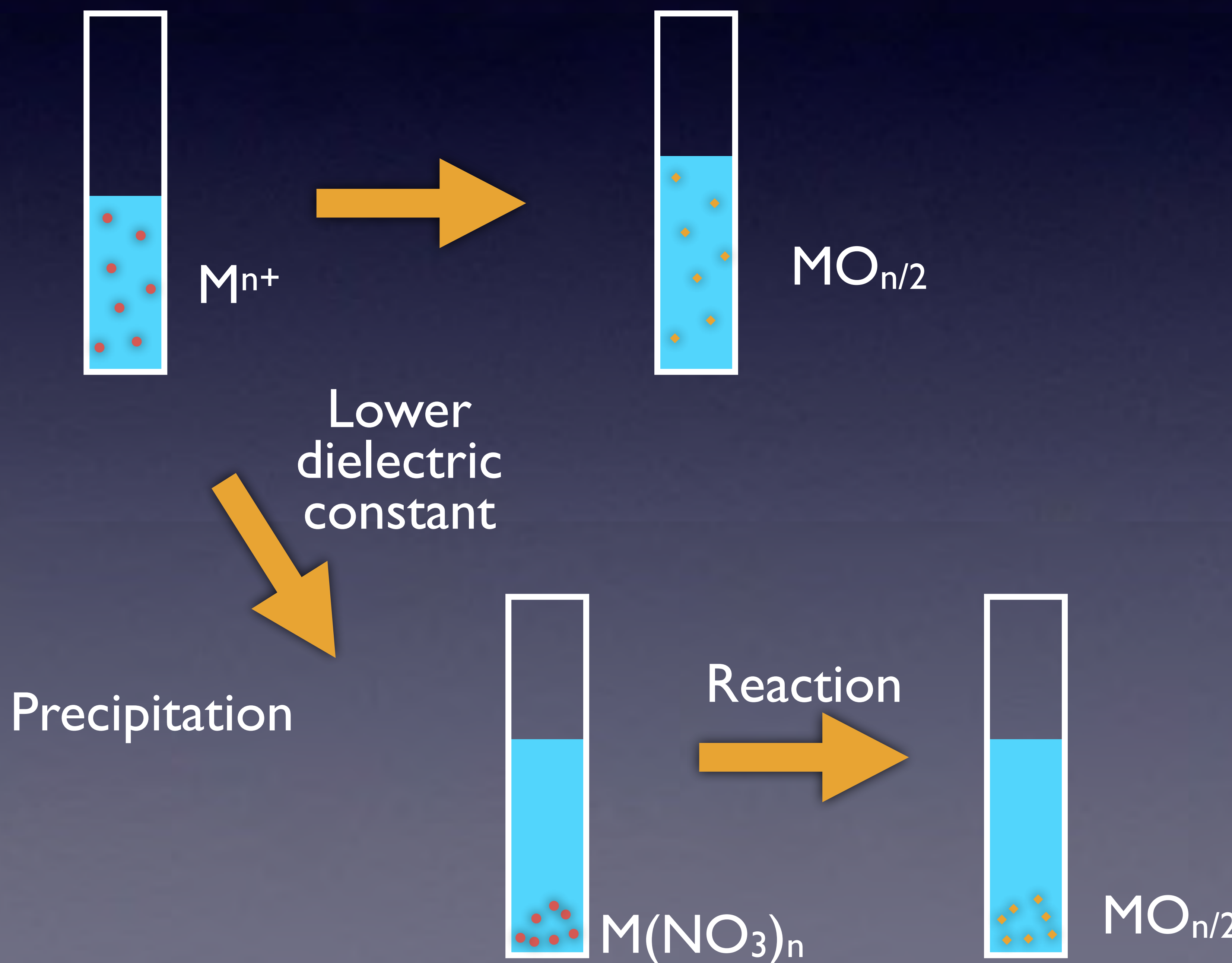
Course of reaction


$M(NO_3)_n$

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

in water

200~400°C
~30 MPa



Neutron radiography of batch type reactor

Batch type reactor was heated using cartridge heater.

Experimental conditions

- 1.25 mL of water
- 2.0 mL of $Gd(NO_3)_3$ solution

Course of heating was measured for ~25 min.

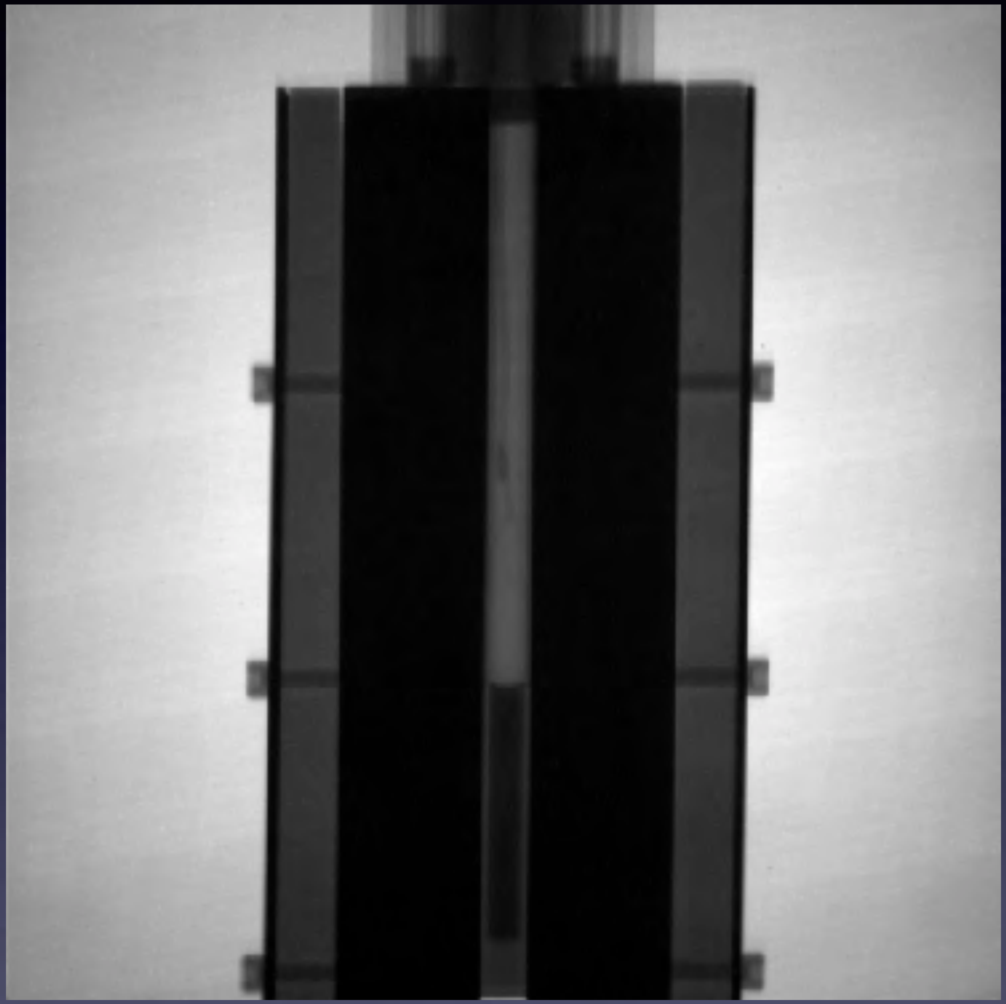
Radiography condition

Camera

iKon-L 936 (ANDOR)
Nikon 105 mm F2.8

- 2048×2048 pixels
- 16 bits/pixel
- 0.2 fps (3.5 s/pixel)

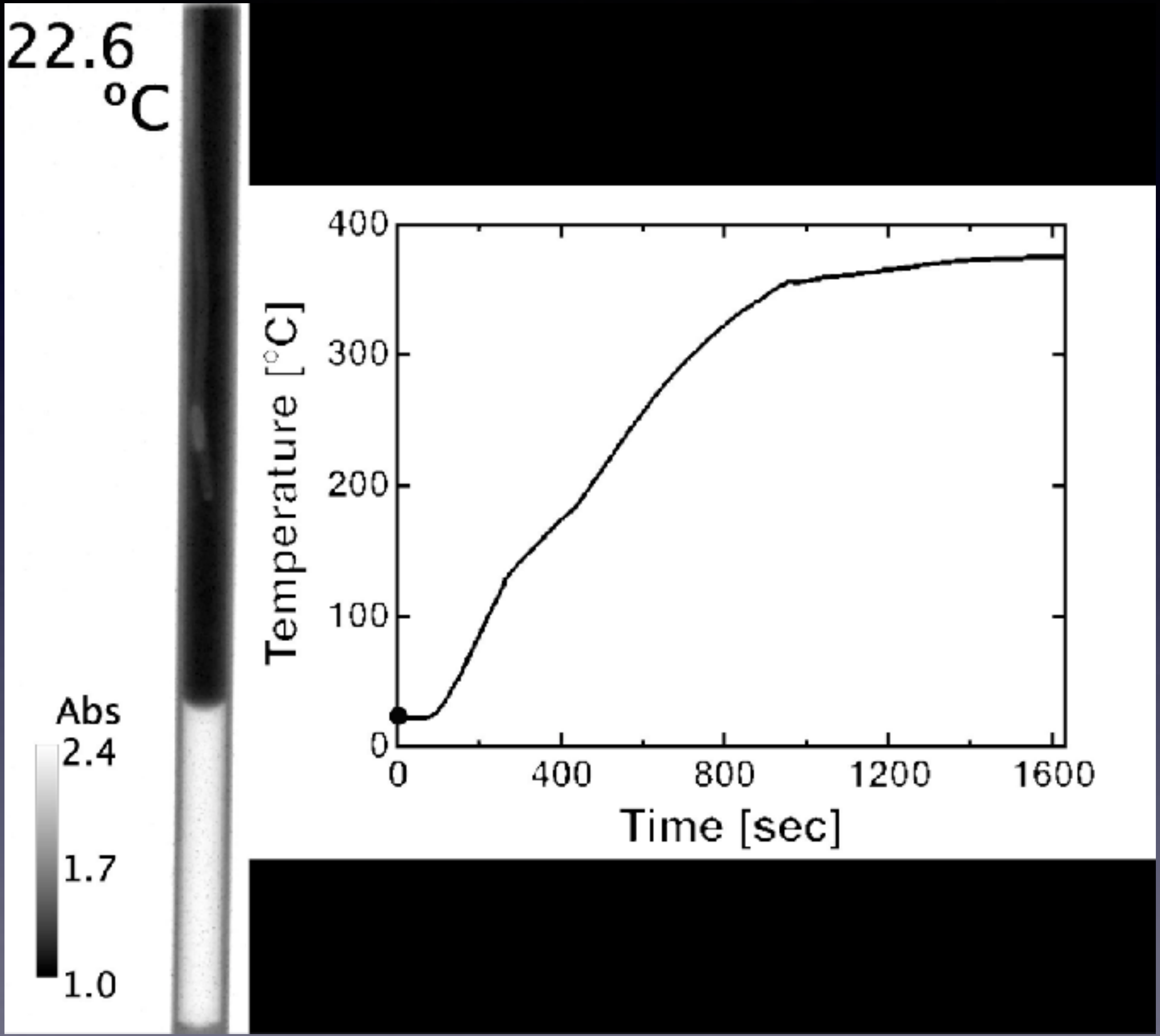
as observed (I)



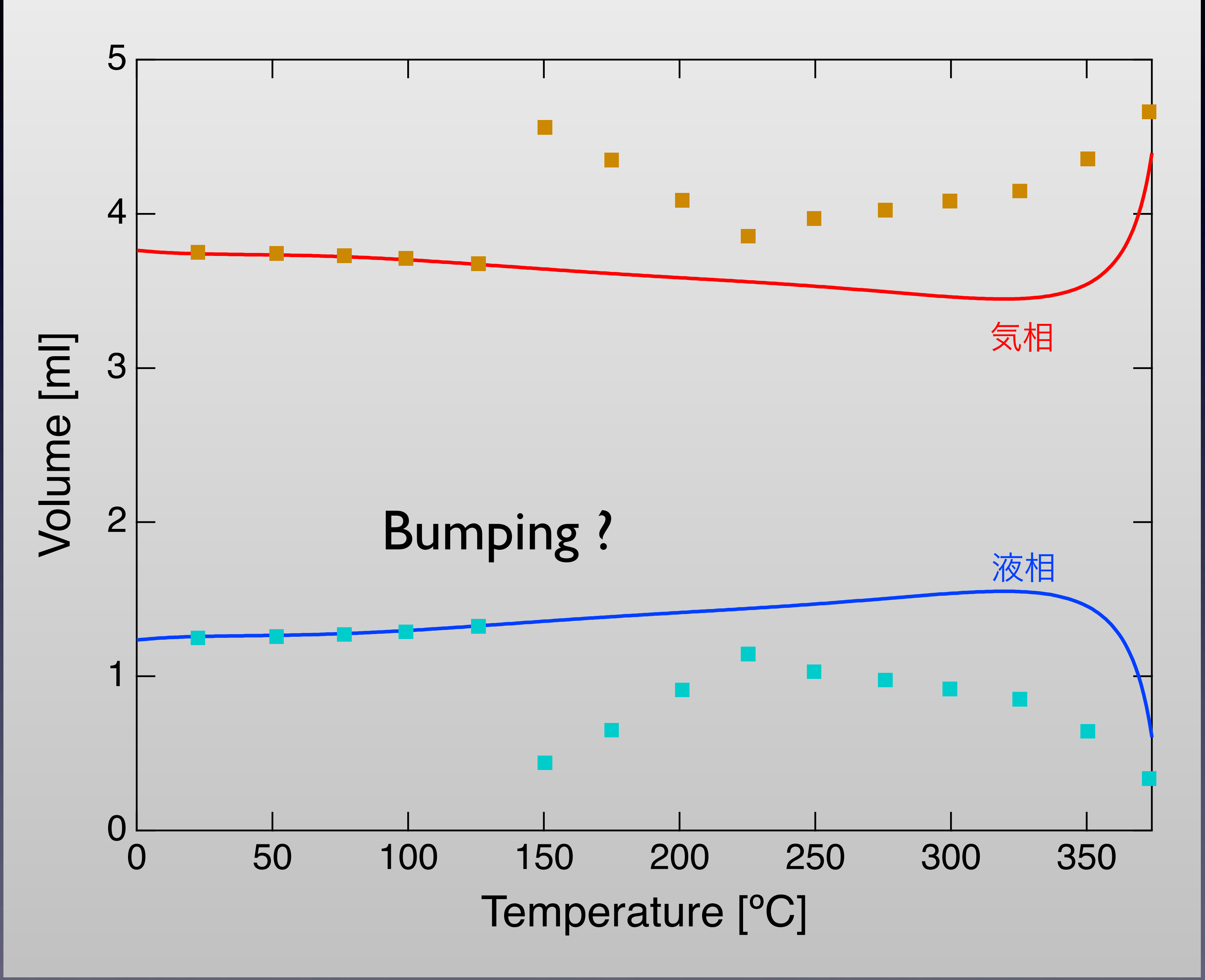
Inner diameter: 5 mm

$$\mathrm{Abs} = -\log \frac{I - I_{\mathrm{dark}}}{I_{\mathrm{flat}} - I_{\mathrm{dark}}}$$

Heating of water (1.25 mL)

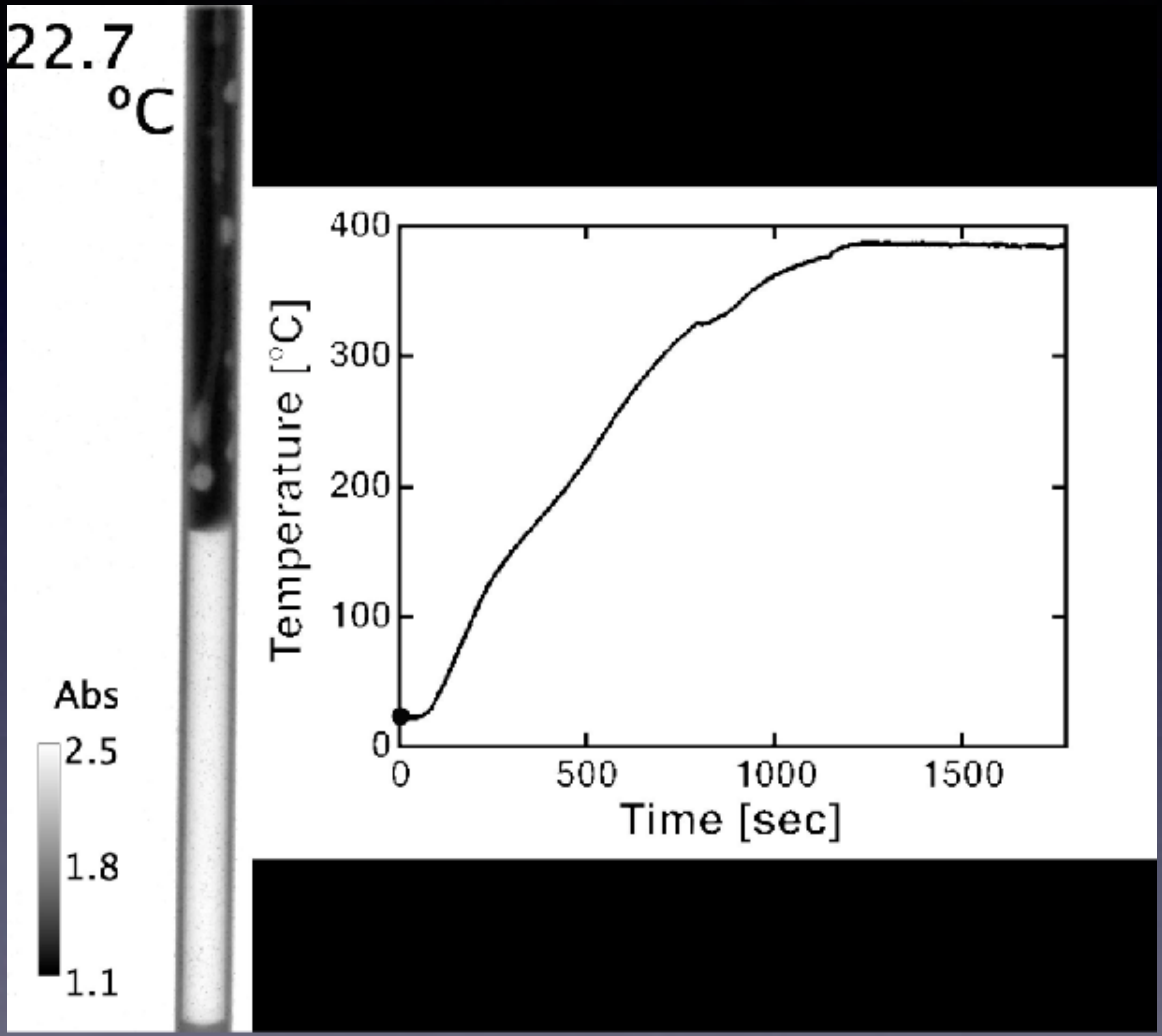


Volume of liquid and gas phases



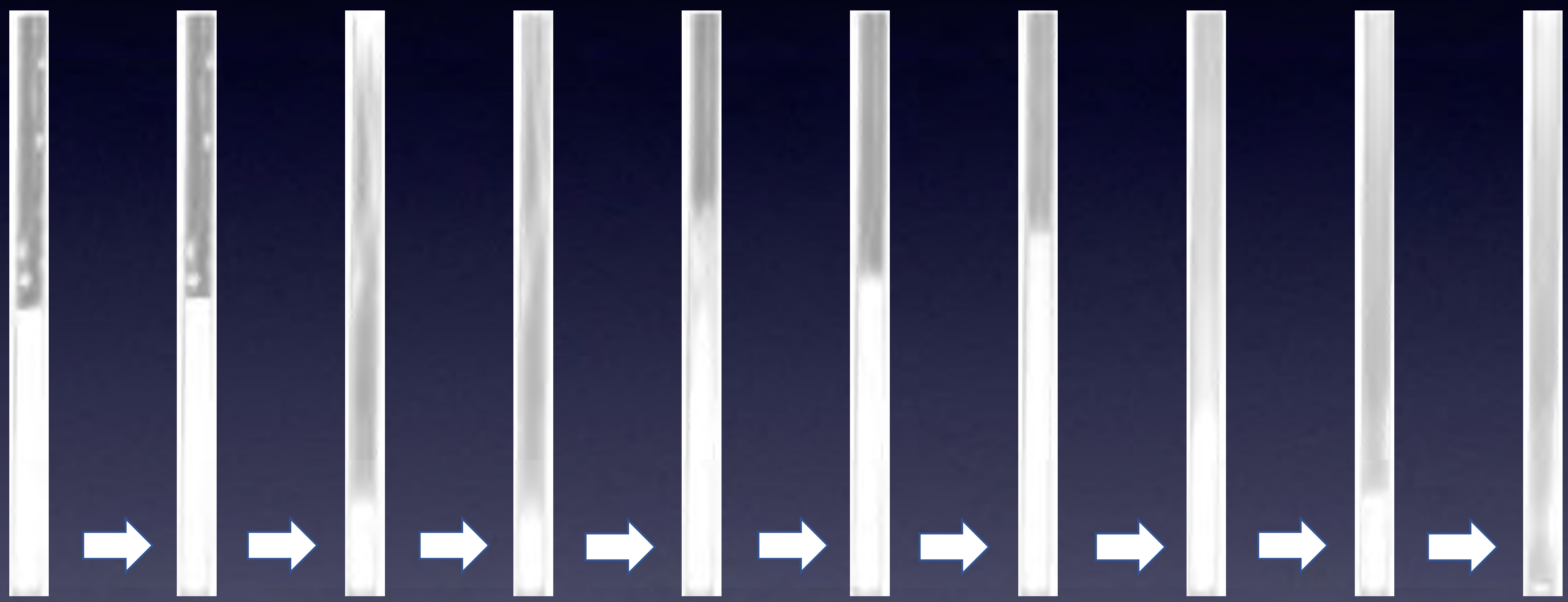
Trapping of water at head ?

Heating of $Gd(NO_3)_3$ solution (2.0 mL)



Course of heating

23°C 100°C 150°C 200°C 250°C 300°C 350°C 375°C 385°C 385°C after 7.5 min



Bumping ?

Decrease in the density

Gd^{3+} ion and/or $Gd(OH)_3$

$Gd(OH)_3$ was precipitated at bottom.

Tentative summary

Phase behavior of water in hydrothermal batch-type reactors was visualized.

Next plans

- Heating whole reactor
- Reactor exchanger
- Use of B^{3+} ions