NON-EQUILIBRIUM MODELING OF HYDRATES IN POROUS MEDIUM

2nd World Congress on Petroleum and Refinery, Osaka, June 2, 2017

Bjørn Kvamme

Department of Physics and Technology
University of Bergen, Bergen, Allegaten 55
NORWAY

Bjorn.kvamme@ift.uib.no

MOTIVATION

HYDRATES IN SEDIMENTS CAN NOT REACH THERMODYNAMIC EQUILIBRIUM

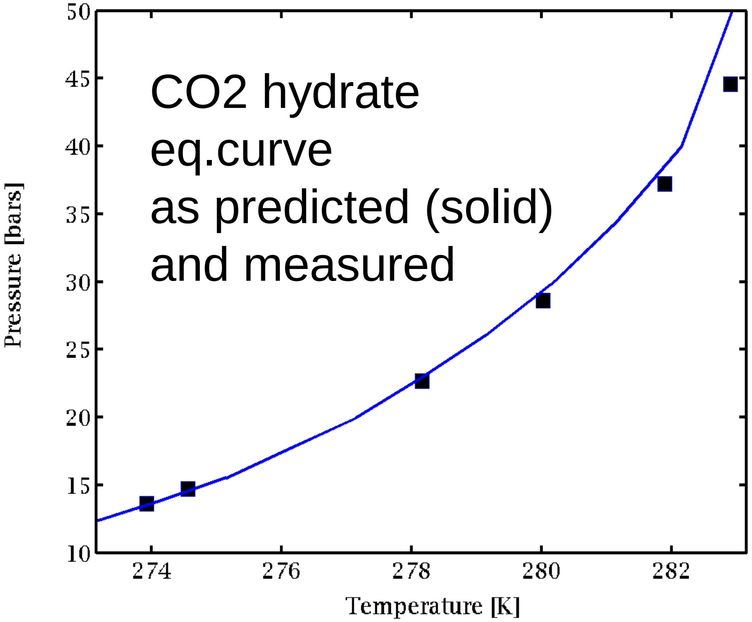
Numerous illustrations of solid surface impact on hydrate phase transition dynamics are available in open literature – the above is from Makogan

Even without free gas then hydrate, water and adsorbed phases (on minerals and on hydrate surfaces) will result in ***zero degrees of freedom*** (Gibbs phase rule) ***for*** a system of ***water and methane***.

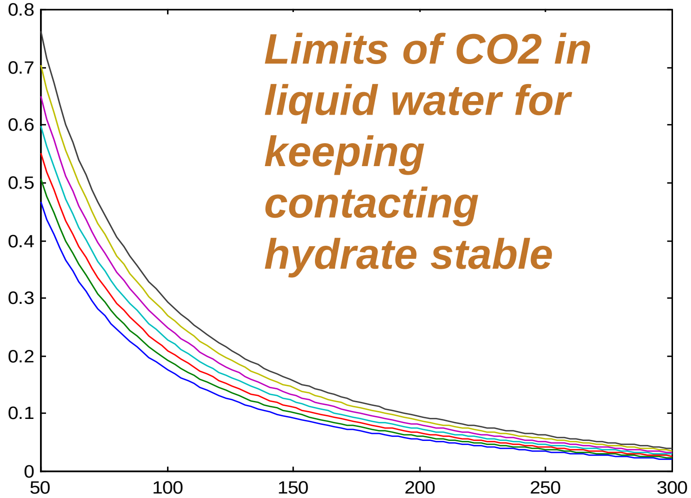
Solid mineral surfaces play a significant role due to ***efficient heterogeneous hydrate nucleation*** but mineral surfaces are incompatible with hydrate surface so more or less ***structured water separate mineral and hydrate***

More or less structured water between hydrate and mineral leads to a ***minimum of molecular diffusion flow***, but normally higher natural flow-rates which can lead to hydrate dissociation towards under saturated water

MOST HYDRATE RESERVOIR SIMULATORS ONLY FOCUS ON P AND T

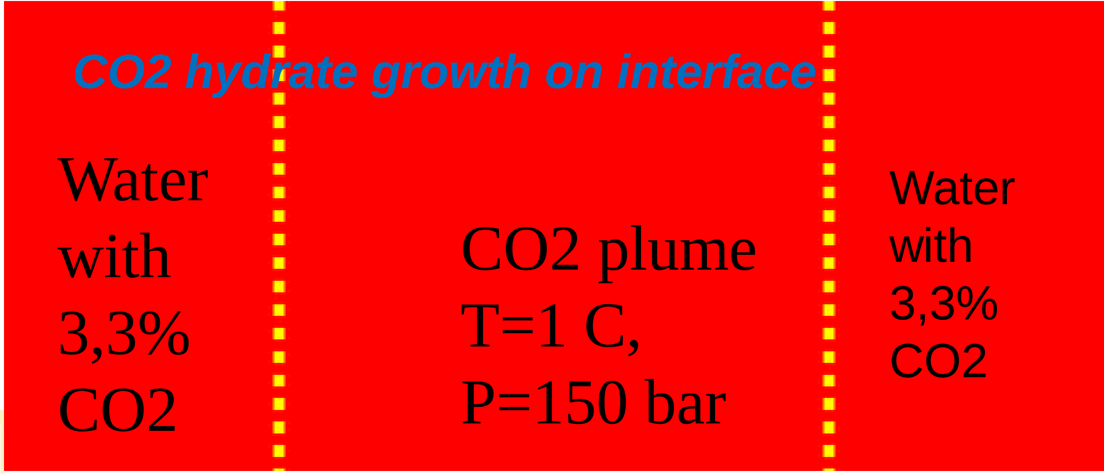


CO2 hydrate
eq.curve
as predicted (solid)
and measured



Limits of CO2 in liquid water for keeping contacting hydrate stable

Pressure and temperature dependency of hydrate stability is just a limited projection of the stability dependencies, in which concentrations of all components in all possible co-existing phases are other



CO2 hydrate growth on interface

Water with 3,3% CO2

CO2 plume
T=1 C,
P=150 bar

Water with 3,3% CO2

Above: ***When the hydrate layer closes in the most stable (lowest free energy) consumes smaller hydrate particles***

Left: ***Hydrate will dissociate towards under saturated liquid water as well as towards under saturated gas***

MOTIVATION CONTINUED

- The average salinity will not even be uniformely distributed since ions will adsorb on mineral surfaces
- Neglecting the non-equilibrium nature of hydrates inn porous media during production modelling implies that a number of mechanisms that can be important in the initial start of production

$$\Delta G_i = \delta\left[x_w^{H,j}\left(\mu_w^{H,j} - \mu_w^p\right) + x_{CH4}^{H,j}\left(\mu_{CH4}^{H,j} - \mu_{CH4}^p\right)\right]$$

FREE ENERGY CHANGES FOR *DIFFERENT* PHASE TRANSITIONS INVOLVING HYDRATE FROM CH4

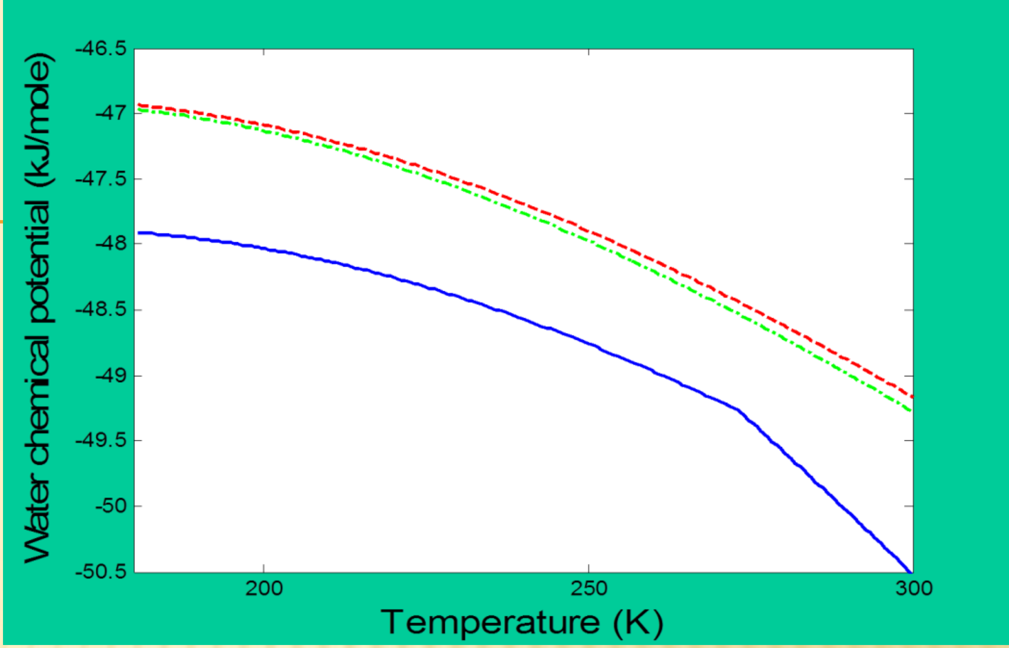
Table 1. Potential hydrate phase transition scenarios for a system of carbon dioxide with impurities as relevant for transportation pipeline. The change in the free energy for any of the processes mentioned in table 1 is calculated according to equation 1. Note that the different phase transitions may involve hydrate of different composition and as such the label hydrate for the phase does not distinguish between different free energy hydrates in this table.

i	δ	Initial phase(s)	Driving force	Final phase(s)
1	-1	Hydrate	Outside stability in terms of local P and/or T	Gas, Liquid water
2	-1	Hydrate	Sublimation (gas under saturated with water)	Gas
3	-1	Hydrate	Outside liquid water under saturated with respect to carbon dioxide and/or other enclathrated impurities originating from the carbon dioxide phase	Liquid water, (Gas)
4	-1	Hydrate	Hydrate gets in contact with solid walls at which adsorbed water have lower chemical potential than hydrate water	Liquid water, Gas
5	+1	Gas/fluid	Hydrate more stable than water and hydrate formers in the fluid phase	Hydrate
6	+1	Gas + Liquid water	Hydrate more stable than condensed water and hydrate formers from gas/fluid	Hydrate
7	+1	Surface reformation	Non-uniform hydrate rearranges due to mass limitations (lower free energy hydrate particles consumes mass from hydrates of higher free energy)	Hydrate
8	+1	Aqueous Phase	Liquid water super saturated with carbon dioxide and/or other hydrate formers, with reference to hydrate free energy	Hydrate
9	+1	Adsorbed	Adsorbed water on rust forms hydrate with adsorbed hydrate formers.	Hydrate
10	+1	Adsorbed +fluid	Water and hydrate formers from gas/fluid forms hydrate	Hydrate

Possible competing phase transitions involving hydrate with a basis from a system of CO2 containing water. More components in the CO2 phase will not change the picture as even more hydrate phases will occur (most stable hydrate form first)

THEORY

Right: Chemical potential for water. Solid line for ice or liquid water, dash line for SI empty hydrate and dash-dotted line for SII empty hydrate.

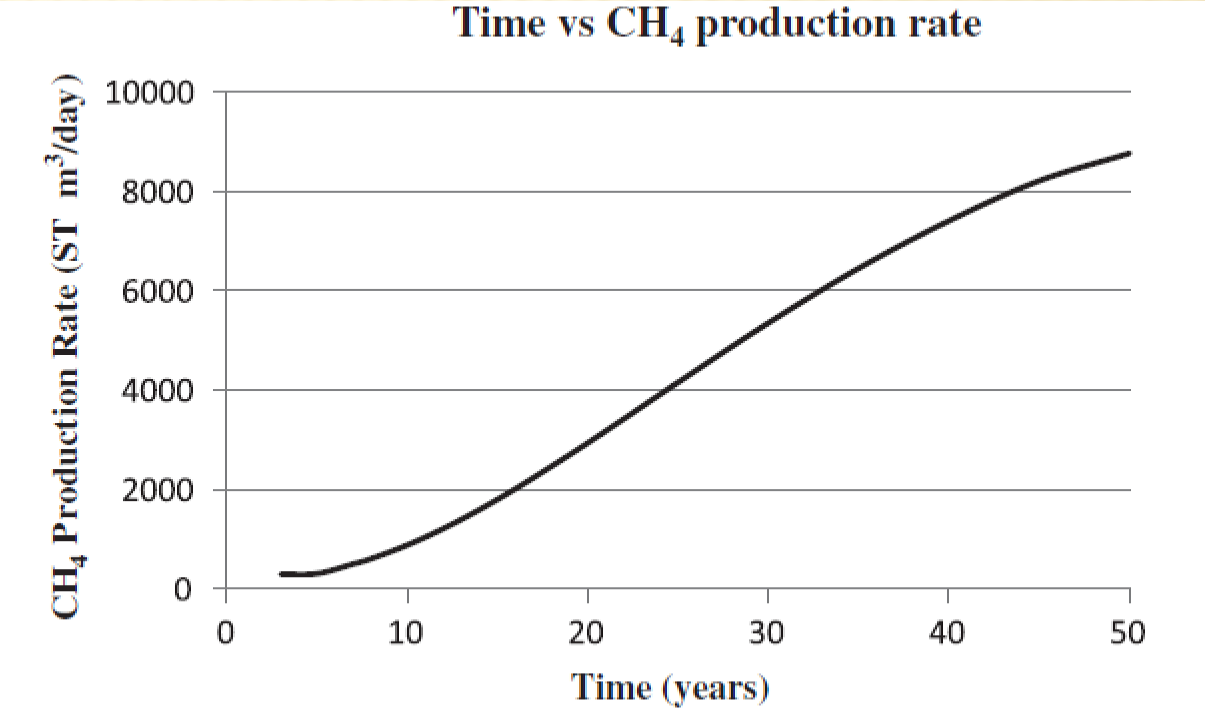


- All possible ***hydrate phase transitions*** (formation, dissociation and reformation) can be treated as ***pseudo reactions***.
- This is facilitated by ***absolute thermodynamic properties*** (ideal gas as reference state for all components in all phases), including hydrate and ice (Kvamme & Tanaka, 1995).
- And a ***reactive transport simulator*** to handle the logistics of mass exchanges due to all pseudo reactions involving hydrate, including couplings to real mineral reactions as well

NUMERICAL TOOL

RetrasoCodeBright (RCB) have been extended from an ideal gas hydrogeological reactive transport simulator into a reactive transport simulator for studies of aquifer storage of CO2 and during later years now into a simulator for hydrate production and impact of carbon dioxide formation on CO2 storage in cold reservoirs

Mount Elbert production case study using pressure reduction (Energy Conversion and Management, Volume 68, April 2013, Pages 313–323)

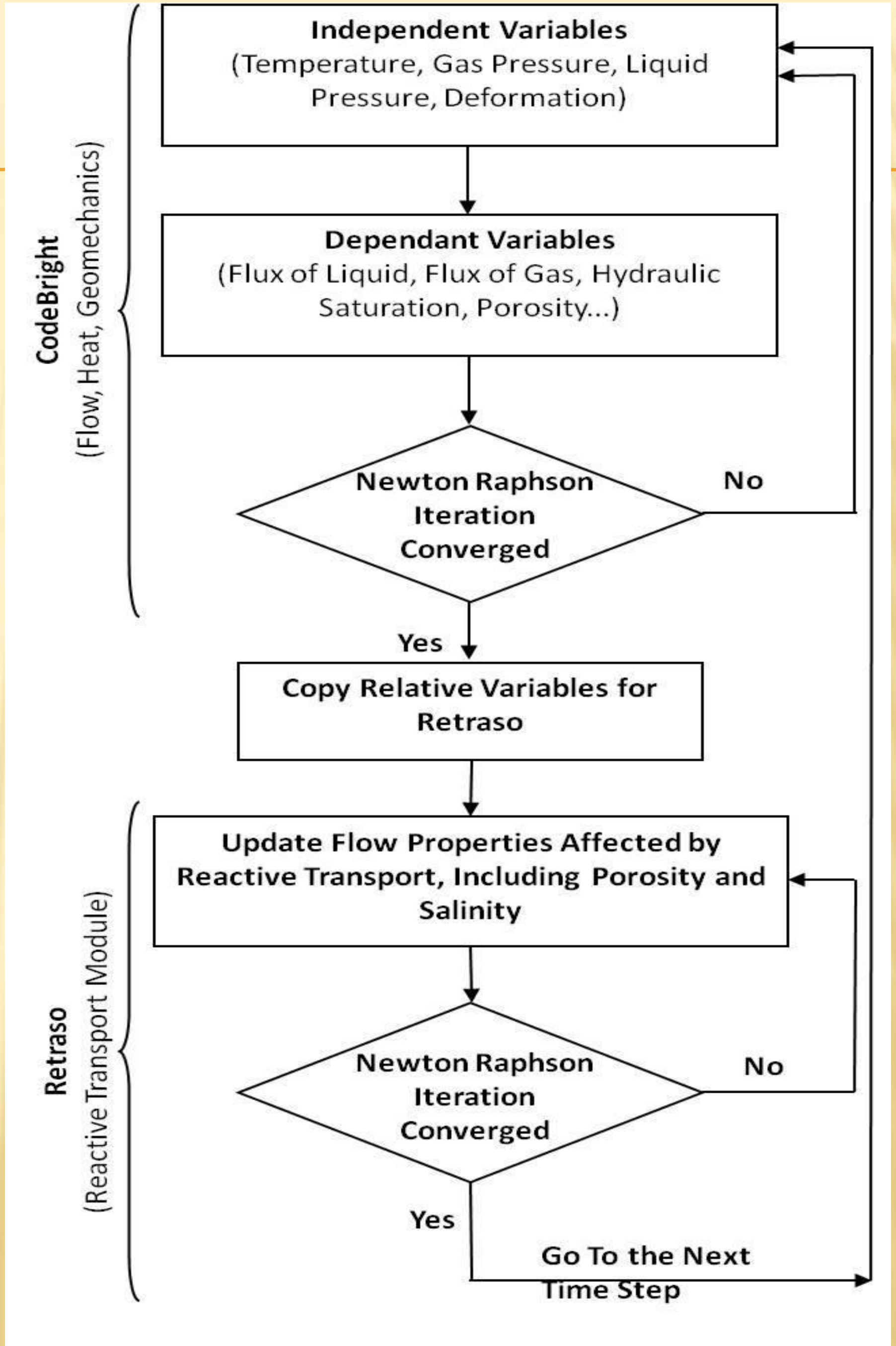


NUMERICAL TOOL

Spatial discretization:
Finite elements (1D, 2D and 3D)

Temporal discretization:
Finite differences

Non linear solver:
Newton-Raphson/Direct substitution Approach / Global Implicit



CodeBright
(Flow, Heat, Geomechanics)

Independent Variables
(Temperature, Gas Pressure, Liquid Pressure, Deformation)

Dependant Variables
(Flux of Liquid, Flux of Gas, Hydraulic Saturation, Porosity...)

Newton Raphson Iteration Converged

No

Yes

Copy Relative Variables for Retraso

Retraso
(Reactive Transport Module)

Update Flow Properties Affected by Reactive Transport, Including Porosity and Salinity

Newton Raphson Iteration Converged

No

Yes

Go To the Next Time Step

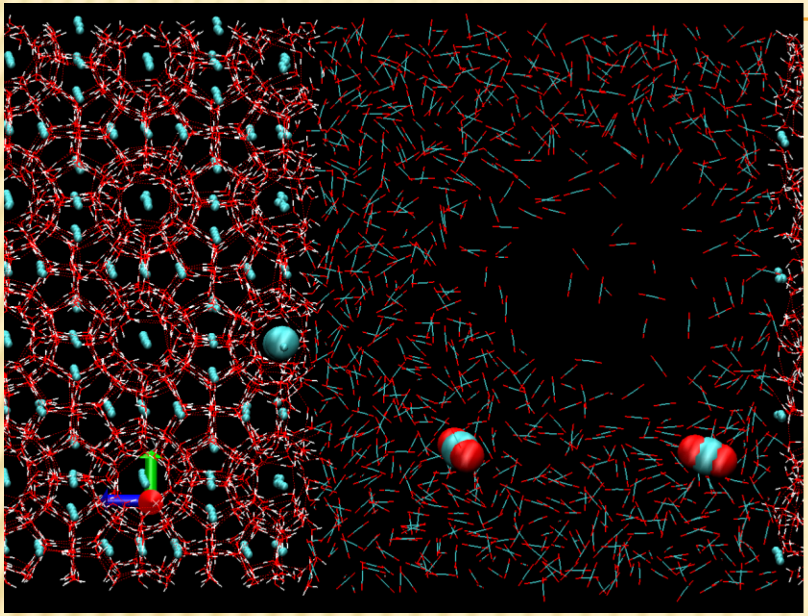
THERMODYNAMIC DATA

- Thermodynamic data for fluid phases and water is available outside of equilibrium, with variable accuracy depending on equation of state. Molecular Dynamics (MD) simulations are alternatives for liquid CO2 containing impurities. (Kvamme et.al., *Phys.Chem.Chem.Phys.,* 2014, 16, 8623)
- Liquid water based on MD (Above reference or Kvamme & Tanaka, *J. Phys. Chem.* 1995, *99,* 7114-7119, also for outside equilibrium
- Hydrate thermodynamics (Kvamme & Tanaka, 1995) is also based on absolute thermodynamics but linked to an equilibrium theory. Hydrate properties outside equilibrium from Taylor expansions in all independent variable (temperature, pressure and concentrations). (Kvamme et.al., *Phys.Chem. Chem. Phys.,* 2013, 15, 2063

KINETIC MODELS

- Our primary tool for development of kinetic models is ***Phase Field Theory (PFT)***, in which our latest models (Kvamme et.al., *Phys.Chem. Chem. Phys.*, 2013, 15, 2063) contain ***implicit hydrodynamics and heat transport.***
- In simplified language ***PFT*** theory implies ***minimization of free energy under constraints of mass- and heat transport.***
- ***Results*** from these rigirous models are extracted and transferred ***into simplified models***

PRODUCTION OF NATURAL GAS FROM HYDRATE USING CO2 INJECTION



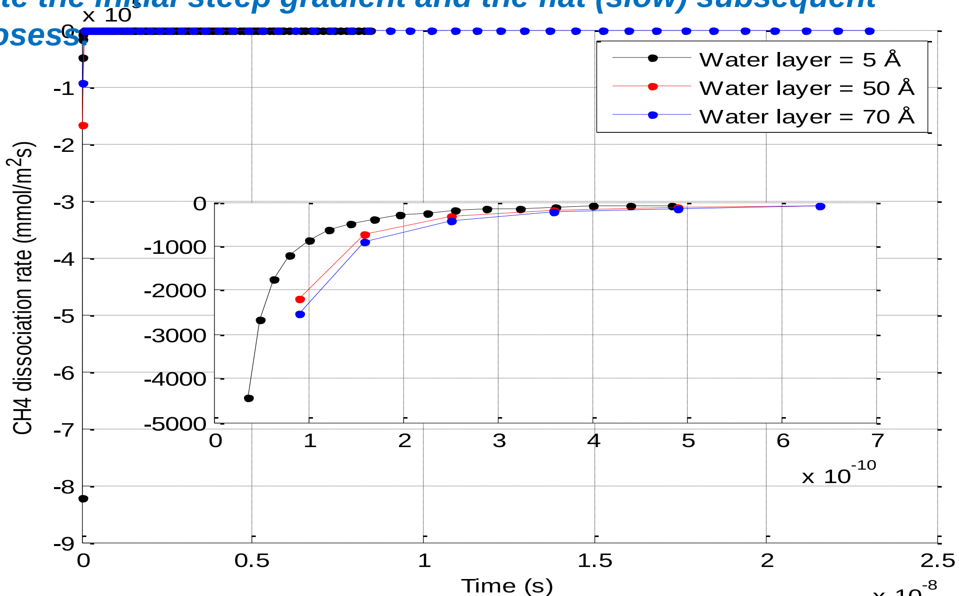
CH4 hydrate (left) exposed to CO2. Quadropole moment of CO2 loosens up outer water hydrogen bonds and CH4 escapes while CO2 enters the hydrate

Slow mechanism with diffusivities
In the order of 10^-16 m^2/s

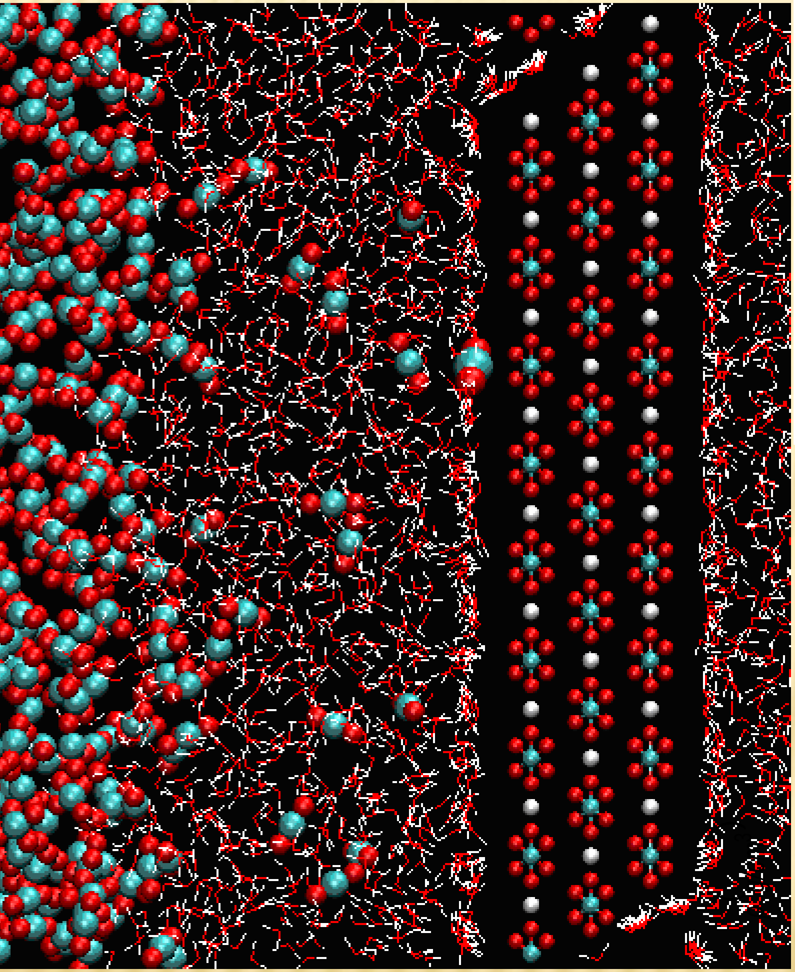
- The fastest mechanism is through formation of new hydrate from injected CO2 (eventually with N2)
- Corresponding released heat dissolves *in situ* CH4 hydrate

The more free water surrounding in situ CH4 hydrate (blue > red > black) the longer period of fast conversion (liquid mass transport diff.)

Note the initial steep gradient and the flat (slow) subsequent prosess

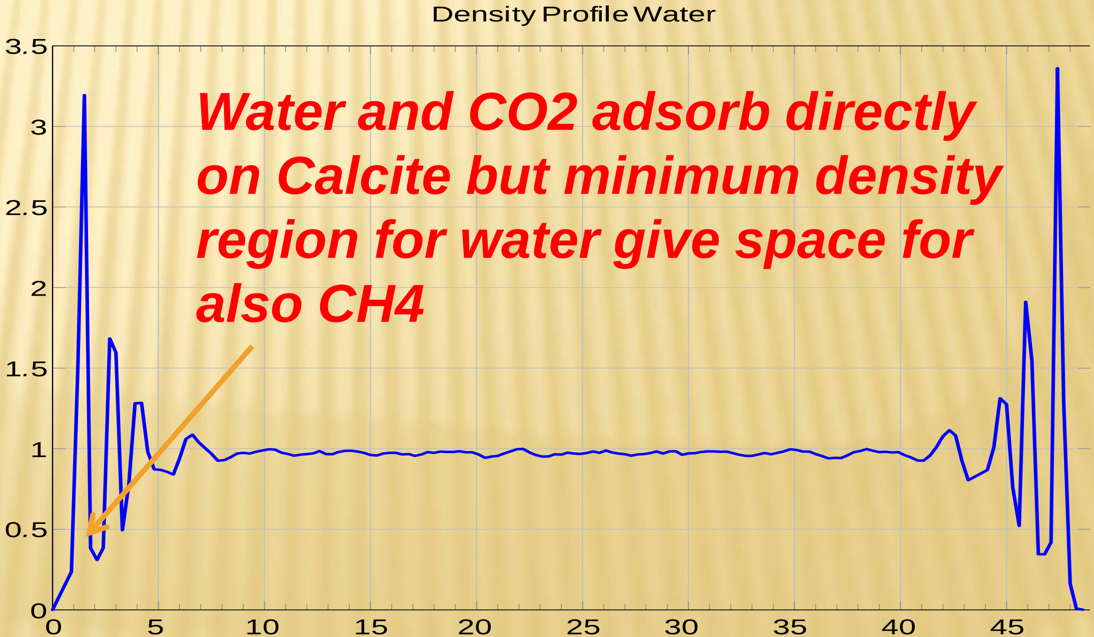


MINERAL SURFACES PROVIDE SITES FOR EFFICIENT HETEROGENEOUS HYDRATE NUCLEATION



Water adsorption onto Calcite results in a very structures packing (density to the right)

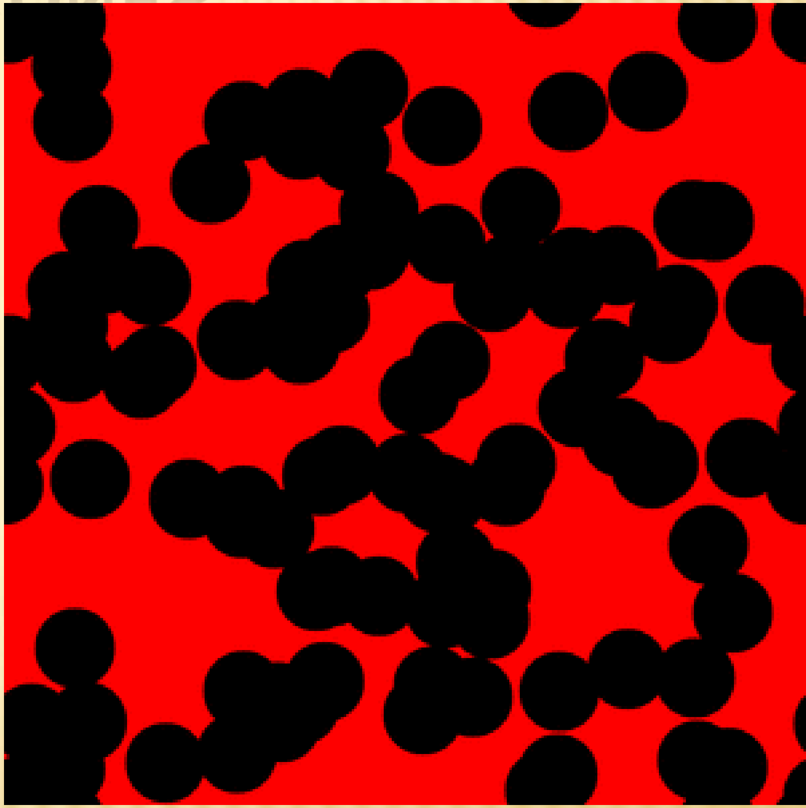
Carbon dioxe (left) diffuse efficiently through water and adsorb well directly on Calcite crystal (right) but water is very structured and secondary adsorption of other species around water density minimum can also be facilitated (see black void spaces)



Water and CO2 adsorb directly on Calcite but minimum density region for water give space for also CH4

YET ANOTHER MOTIVATION – HYDRATE FORMATION DURING AQUIFER STORAGE OF CO2 IN RESERVOIRS WITH COLD ZONES

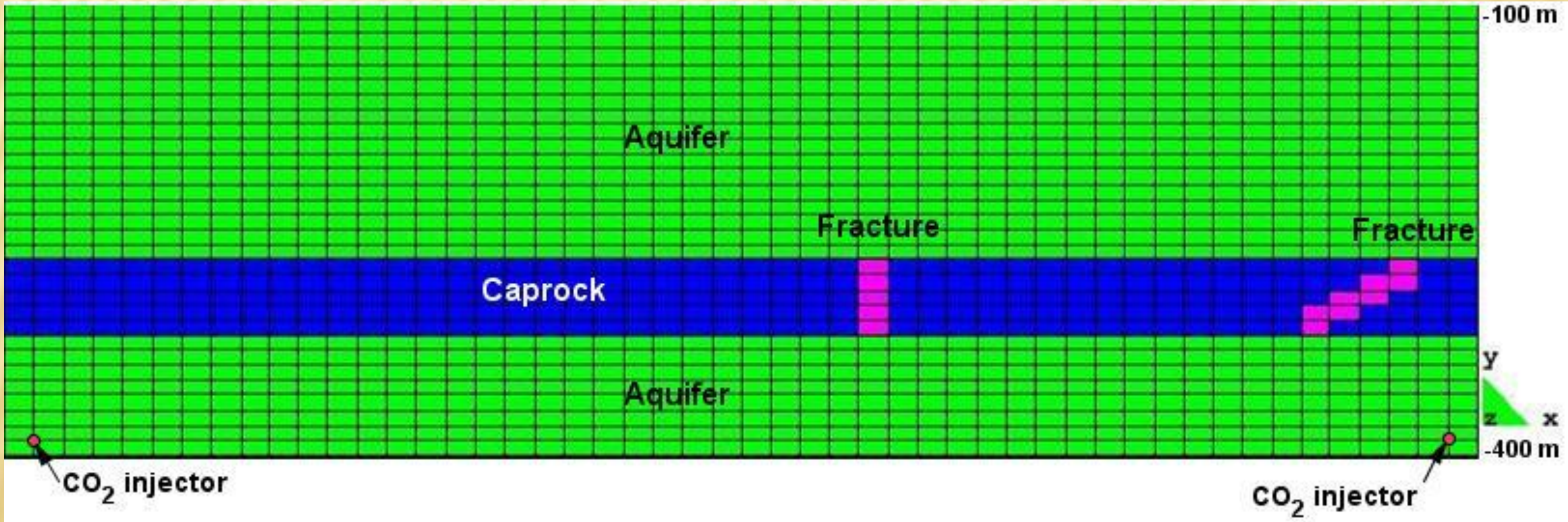
- Many promising reservoirs for aquifer storage of CO2 are in regions where ***zones of low temperatures and high enough pressures leads to hydrate formation***
- What will the impact be for ***storage stability*** and possible ***reductions in distribution flow pathways ?***



Hydrate formation (yellow) is facilitated in inclinements between solid particles (black)

MODEL DESCRIPTION

- 1000 m x 300 m rectangle model.
- 2 aquifers, 1 cap-rock and 2 fractures.
- Top aquifer is 1000 m x 170 m.
- Bottom aquifer is 1000 m x 80 m.
- Cap-rock is 1000m x 50 m.
- The first fracture has the dimensions of 20m x 50m, while the second one has a zigzag path throughout the cap rock from 900m to 960m along the -axis and from 270m down to 320m along the -axis
- CO2 is injected at 10 meter from the bottom in the right and left corners of the bottom aquifer with 4 MPa constant pressure
- Pressure gradient in reservoir is 1.0 MPa/100m and temperature gradient is 3.6 °C/100m



MODEL DESCRIPTION

Property	Aquifers	Cap rocks	Fractures
Young's modulus, E [GPa]	0.5	0.5	0.5
Poisson's ratio	0.25	0.25	0.25
Zero stress porosity, Φ_0	0.1	0.01	0.05
Zero stress permeability, k_0 [m^2]	1.0e-13	1.0e-17	1.0e-10
Irreducible gas and liquid saturation, S_{rg}	0	0	0
Van Genuchten's gas-entry pressure, P_0 [MPa], (at zero stress)	0.0196	0.196	0.196
Van Genuchten's exponent [m]	0.457	0.457	0.457

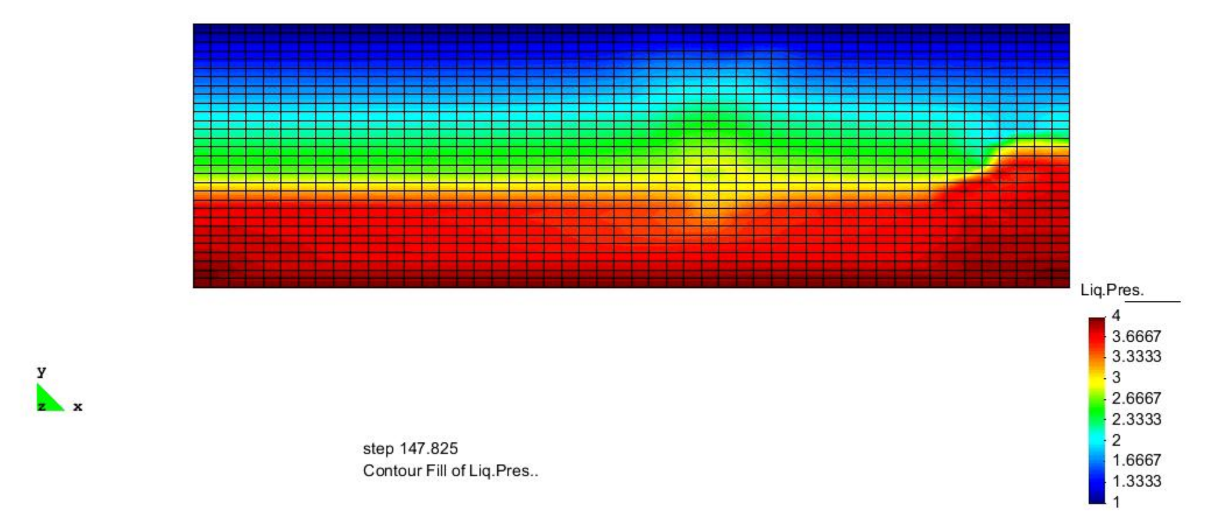
MODEL DESCRIPTION (CONTINUED)

Parameter	Bottom Boundary	Top Boundary
Pressure, (MPa)	4	1
Mean Stress, (MPa)	8.76	2.33
CO2 injection pressure, (MPa)	4	-
Gas and liquid outgoing pressure (MPa)	12	7
Temperature	284.15	273.35

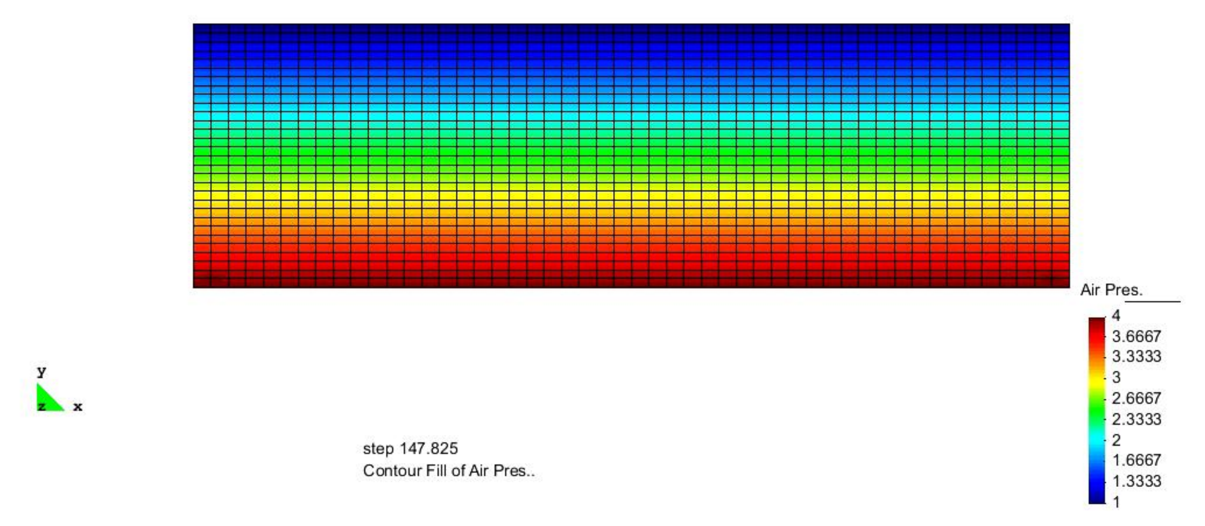
Zone	Aquifers	Cap rocks	Fractures
Permeability (m^2)	1e-13	1e-15	1e-11
Longitude dispersion factor (*m*)	11	11	11
Molecular diffusion (*m*)	1e-10	1e-10	1e-10

Phase	Species
Aqueous	H2O , HCO3- , OH- , H+, CO2(aq), CO32-,O2, SiO2(aq), H2SiO42-, HSiO3-
Gas	CO2(g)
Rock Mineral	Quartz

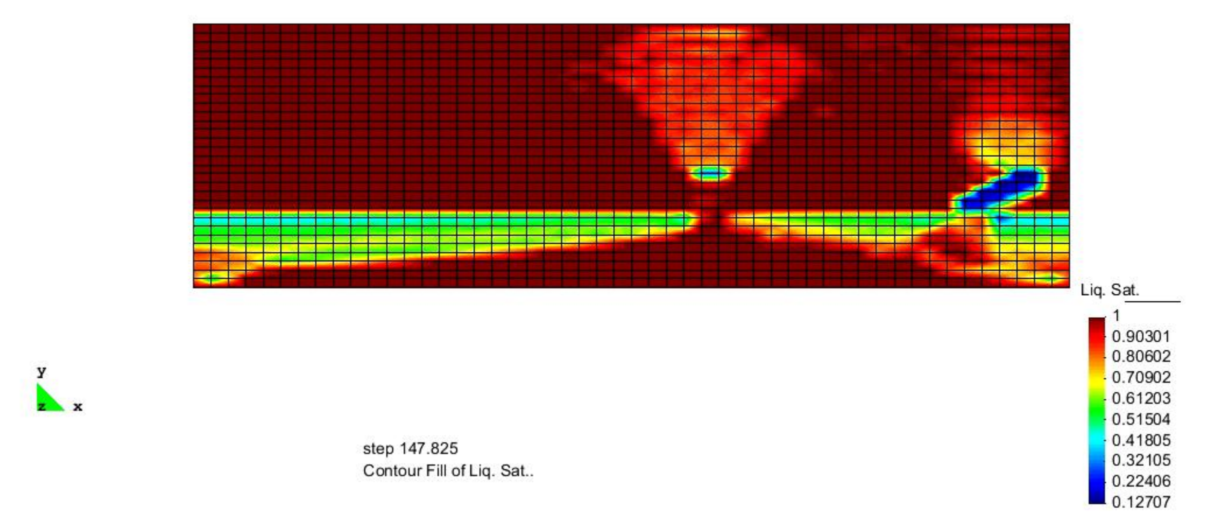
RESULTS (LIQUID PRESSURE)



RESULTS (GAS PRESSURE)



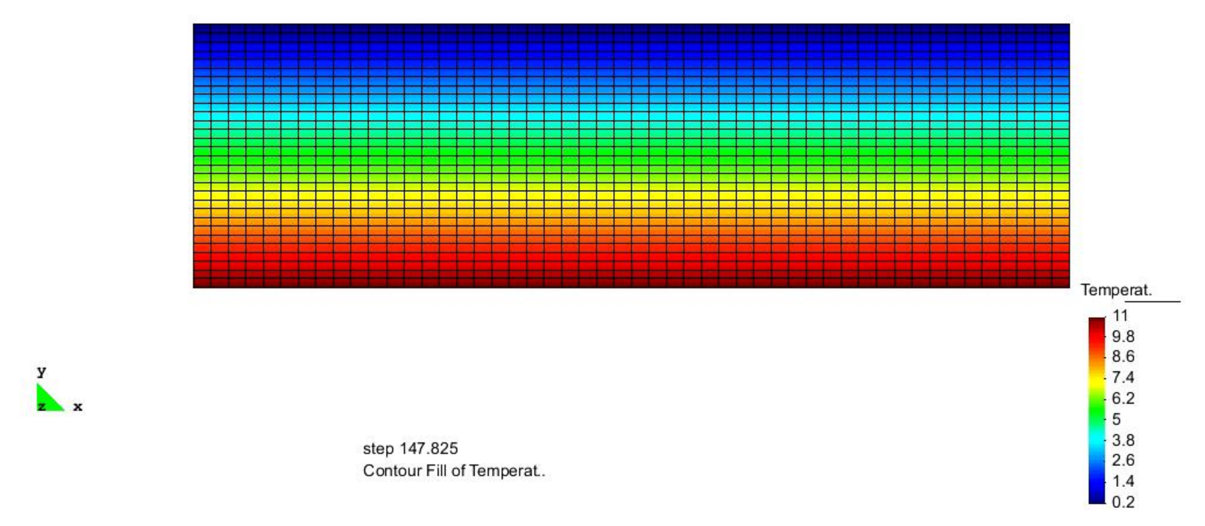
RESULTS (LIQUID SATURATION)



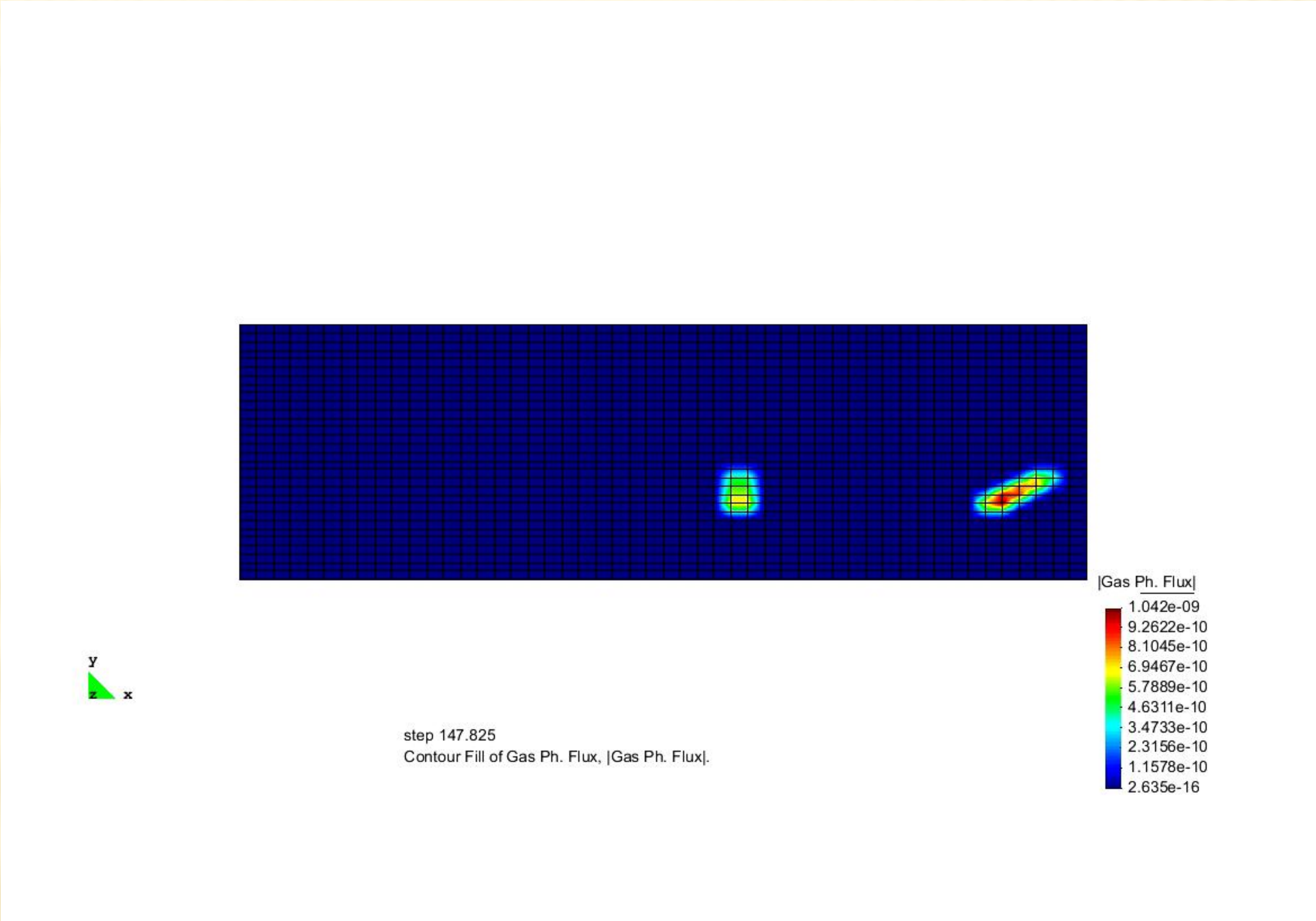
RESULTS (HEAT FLUX)

step 147.825
Contour Fill of Heat C. Flux, |Heat C. Flux|.

RESULTS (TEMPERATURE)



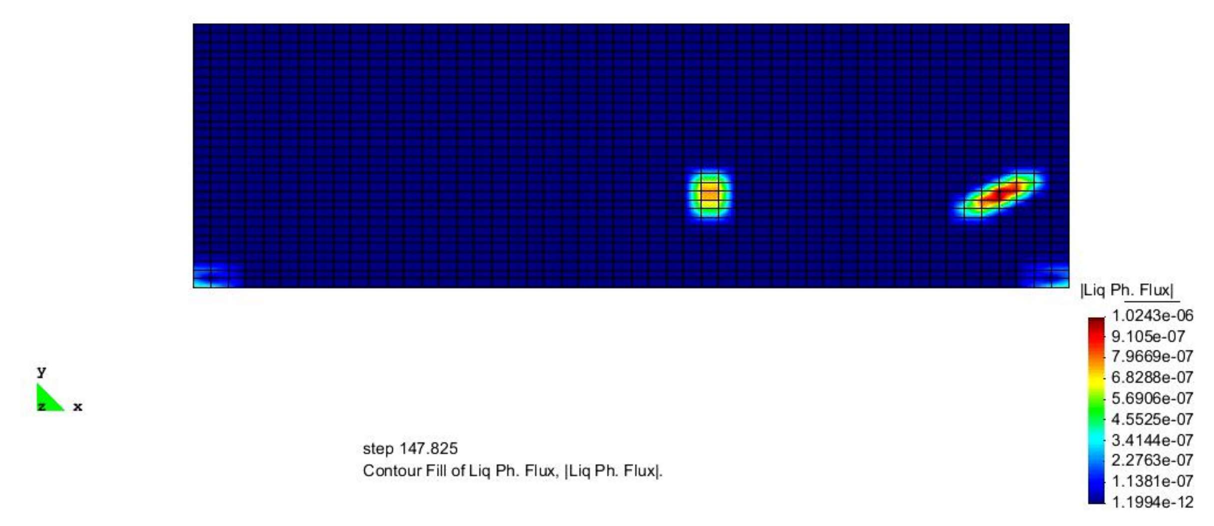
RESULTS (GAS FLUX)



step 147.825

Contour Fill of Gas Ph. Flux, |Gas Ph. Flux|.

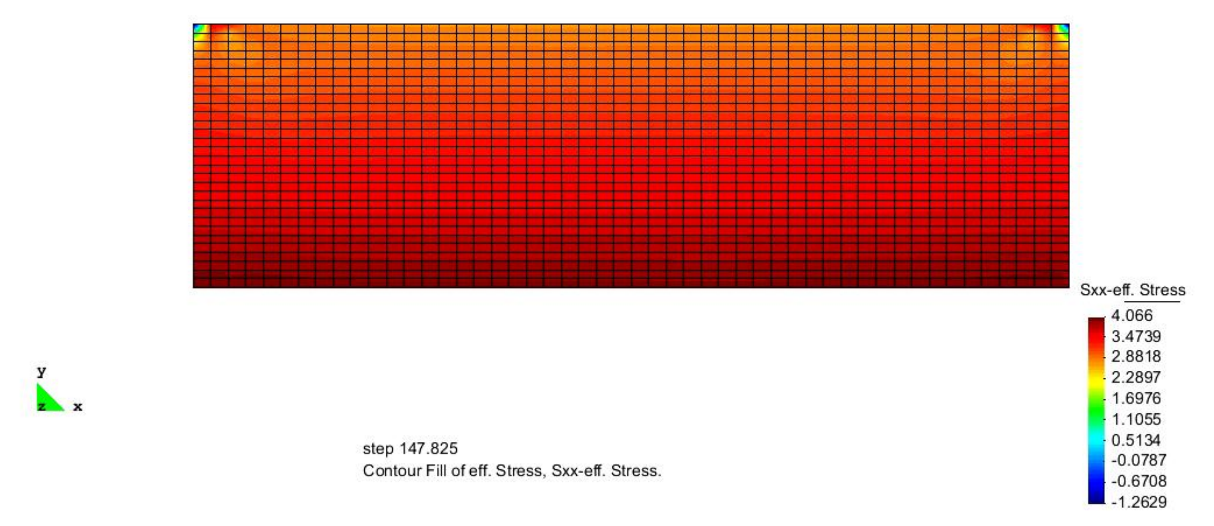
RESULTS (LIQUID FLUX)



step 147.825

Contour Fill of Liq Ph. Flux, |Liq Ph. Flux|.

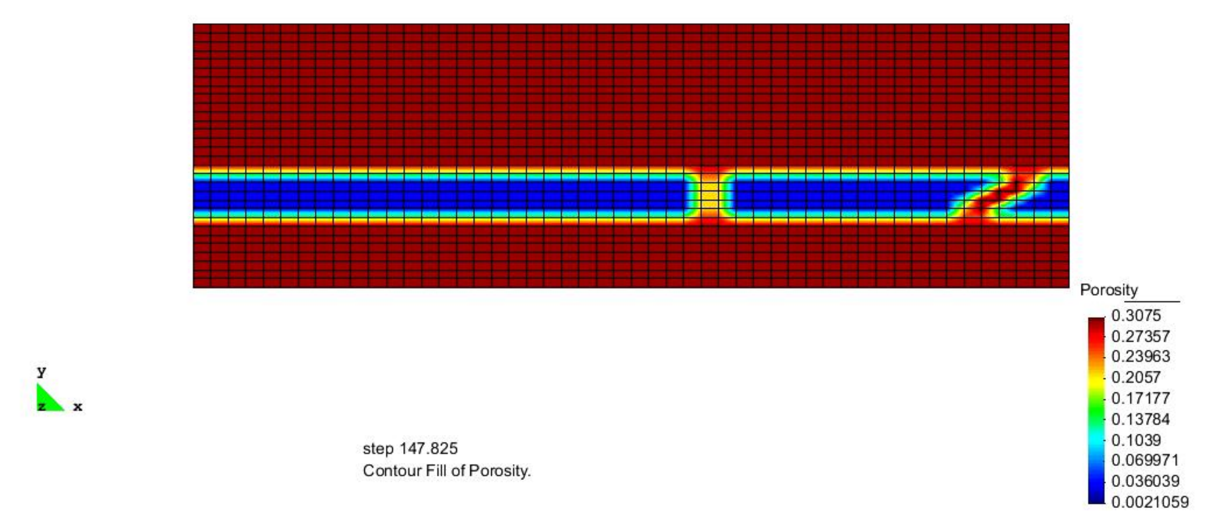
RESULTS (EFFECTIVE STRESS Sxx)



step 147.825
Contour Fill of eff. Stress, Sxx-eff. Stress.

RESULTS (EFFECTIVE STRESS Syy)

RESULTS (POROSITY; IN THE MEANING OF VOLUME FRACTION AVAILABLE TO WATER AND FLUID)



CONCLUSIONS

- Hydrates in porous media can never establish equilibrium and only reason that ***natural gas hydrate reserves*** are found is because they ***are trapped*** in similar fashion as oil and gas by shale, clay or ice
- Hydrate production by pressure reduction has been proven feasible in Messoyakha, as well as in pilot projects
- Messoyakha is a gas field which has gradually released natural gas by production generated pressure drop
- Mallik I and II are fields of high hydrate saturation and no free gas. It is not given that pressure reduction is the best choice for this type of reservoirs given potential problems of sand production and costs of associated water

CONCLUSIONS CONTINUED

Replacement of natural gas by CO2 is feasible and proceed according to two primary mechanisms. The fastest route involves creation of a new hydrate from injected CO2 and dissociation of the in situ natural gas hydrate from the released heat.

Mixing in N2 with CO2 increases permeability but the amount of CO2 that will be stored as hydrate is uncertain and depends very much on well configurations and flow rates compared to hydrate phase transition kinetics, as well as CO2/N2 ratio

CONCLUSIONS CONTINUED

We have presented an alternative platform for hydrate production simulator in which each ***hydrate phase transition*** is treated as a ***"pseudo" reaction***

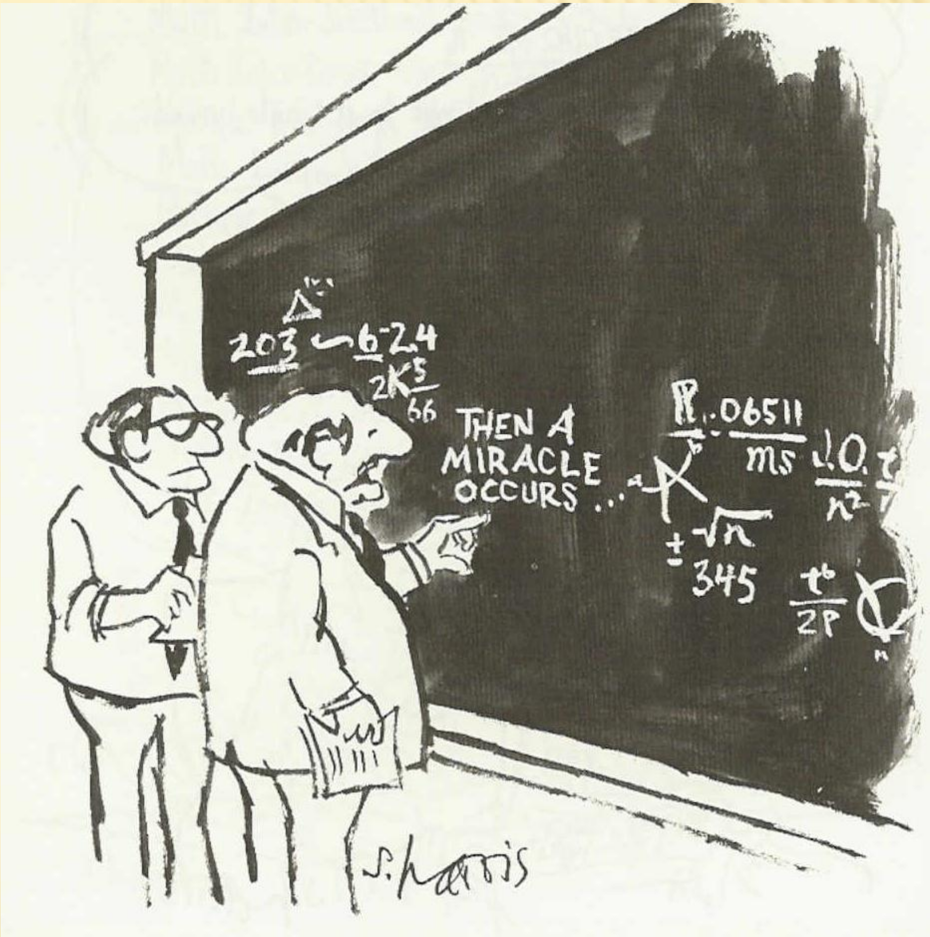
This facilitates incorporation of ***non-equilibrium thermodynamics*** which enable convenient evaluation of ***simultaneous phase transitions that can lead to hydrate dissociation***

Hydrate ***reformation*** after pressure reduction generated cooling can happen in ***a number of ways simultaneously (for instance gas/water contact, mineral/water/gas contact)***

CONCLUSIONS CONTINUED

Current extensions include CH4/CO2 conversions based on the two primary mechanisms for conversion and kinetic rates derived from Phase Field Theory (PFT)

Other current extensions involve heterogeneous nucleation from adsorbed water and hydrate formers on mineral surfaces.



"I think you should be more explicit here in step two."

I think you should be more explicit here in step two.

ACKNOWLEDGEMENT

- We acknowledge the grant and support from Research Council of Norway and Industrial partners through the following projects:
- SSC-Ramore, “Subsurface storage of CO2 - Risk assessment, monitoring and remediation”, project number: 178008/I30.
- FME-SUCCESS, project number: 804831.
- PETROMAKS, “CO2 injection for extra production”, Research Council of Norway, project number: 801445.
- CLIMIT “Safe long term sealing of CO2 in hydrate”, Research Council of Norway, project number: 224857.
- PETROMAKS “CO2 Injection for Stimulated Production of Natural Gas”, Research Council of Norway, project number: 175968 and 230083.
- STATOIL, under contract 4502354080.

EXTRA: THE PHASE FIELD THEORY MODEL

PHASE FIELD THEORY MODEL

$$F = \int d\underline{r}\left(\boxed{\frac{\varepsilon_{\phi}^{2}}{2}T(\nabla\phi)^{2} + \sum_{i,j=1}^{3}\frac{\varepsilon_{xi,j}^{2}}{4}T\rho\left(x_i\nabla x_j - x_j\nabla x_i\right)^{2}} + f_{bulk}(\phi, x_1, x_2, x_3, T)\right)$$

Free energy changes due to phase transition (ϕ is 0 for solid and 1 for fluid)

Free energy changes due to concentration gradients across the interface

Ɛ is unique for each component according to distribution profile across the interface but as an average value it may not be very different from the similar parameter for the phase transition so setting them equal is a first approximation which makes at least numerical solutions feasible

- Free energy due to thermal fluctuation across the interface
- Function of interface
  - Thickness
  - Free energy of interface
  - Interface structure(available from interface density profile for all components)

MODEL PARAMETERS

Estimated to 8.5 Å for hydrate/liquid water (Kvamme et.al. (2007))

$$d = \left(\frac{\varepsilon^2 T}{2}\right)^{1/2} \int_{0.05}^{0.95} d\xi \left\{\Delta f[\xi, \vec{x}(\xi)]\right\}^{-1/2}$$

Phase Field Theory parameter ***w*** is in the free energy *f* (previous slide) as the barrier for transition over to the new phase

where $\Delta f = f - f_0$, and

$$\gamma_\infty = (\varepsilon^2 T)^{1/2} \int_0^1 d\xi \left\{\Delta f[\xi, \vec{x}(\xi)]\right\}^{1/2}$$

ξ is the interface profile

$$f_0 = G_L(\vec{x}_L^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,L}}{\partial x_{i,L}}\bigg|_{\vec{x}_L^{eq}} (x_{i,L} - x_{i,L}^{eq})$$

$$f_S = G_S(\vec{x}_S^{eq}) + \sum_{i=1}^{n} \frac{\partial \mu_{i,S}}{\partial x_{i,S}}\bigg|_{\vec{x}_S^{eq}} (x_{i,S} - x_{i,S}^{eq})$$

Phase Field Theory parameter ε

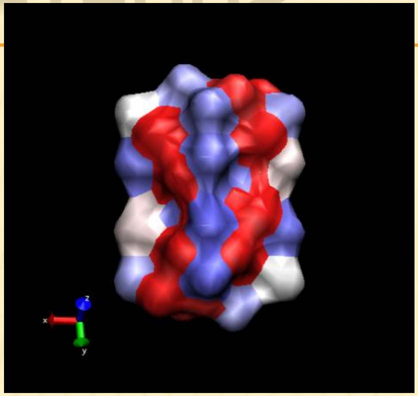
Interface free energy ≈ liquid water/ice 29 mJ/m² – (S.C.Hardy, Philos. Mag. 35 (1977)471)

(Different methods for estimation of hydrate/water interrface free energy is currently being investigated, including cleaving and capillary wave theory)

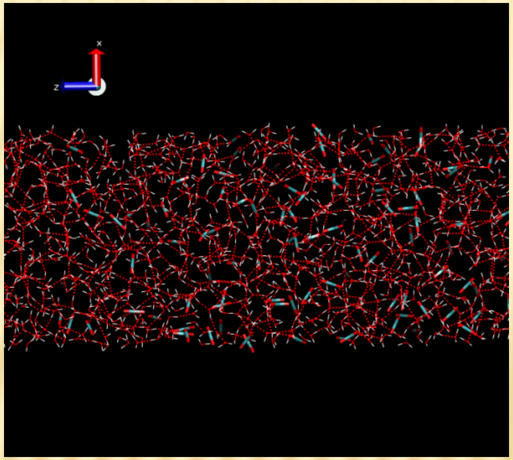
Interface thickness d and interface free energy fixes the two model parameters *w* and ε. The extension over to the multi-components case in current use

SCIENTIFIC METHODS

Charge distribution for hematite by Gaussian03



MD for Studies of mechanisms, thermodyn, interface properties and parametrisati



- Multiscale modelling

from

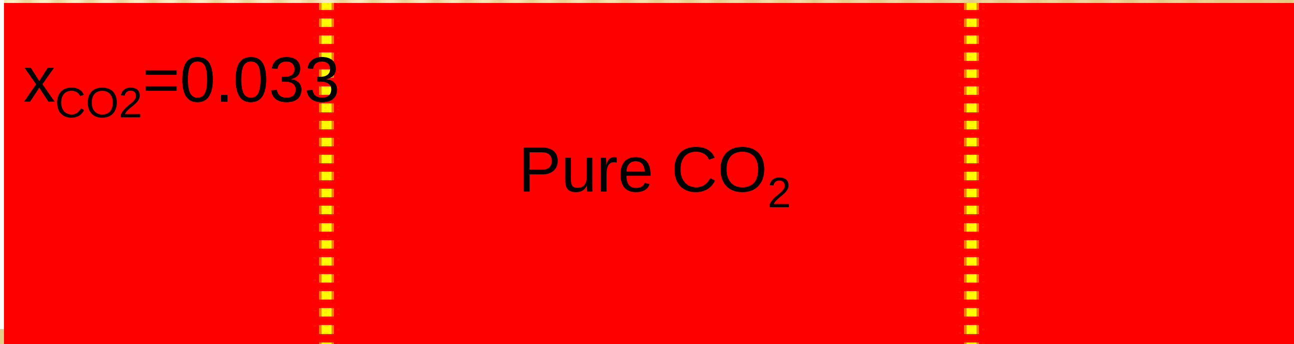
quantum (characterisation of charge distribution in model molecules, from below nano in scale)

to

nano (Molecular Dynamics simulations, MD)

and

Simulation of hydrate growth dynamics on interface of a CO2 plume



PHASE FIELD THEORY MODEL

$$F = \int d\underline{r}\left(\frac{\varepsilon_\phi^2}{2}T(\nabla\phi)^2 + \sum_{i,j=1}^{3}\frac{\varepsilon_{xi,j}^2}{4}T\rho\left(x_i\nabla x_j - x_j\nabla x_i\right)^2 + f_{bulk}(\phi, x_1, x_2, x_3, T)\right)$$

$$f_{bulk} = WTg(\phi) + \left(1 - p(\phi)\right)f_S(x_1, x_2, x_3, T) + p(\phi)f_L(x_1, x_2, x_3, T)$$

g(Φ) is assumed symmetric quadratic p(Φ) is the propablity distribution of phases across the interface as sampled from MD

$$f_s = G_H\rho_m^H \quad , \quad f_L = G_L\rho_m^L$$

$$\frac{\partial\phi}{\partial t} + (\vec{v}.\nabla)\phi = -M_\phi(\phi, x_1, x_2, x_3)\frac{\delta F}{\delta\phi}$$

$$\frac{\partial x_i}{\partial t} + (\vec{v}.\nabla)x_i = \nabla.\left(M_{xi}(\phi, x_1, x_2, x_3)\nabla\frac{\delta F}{\delta xi}\right)$$

Mobilities across the interface are complex but in the simplest approximation diffusivity constants are applied

Hydrodynamics

$$\frac{\partial\rho}{\partial t} = -\rho_m\nabla.\vec{v}$$

$$\rho\frac{\partial\vec{v}}{\partial t} + \rho(\vec{v}.\nabla)\vec{v} = \rho\vec{g} + \nabla.P$$

Total stress tensor

$$P = \mathfrak{z} + \Pi$$

PFT with Hydrodynamics

Heat transport Model

Primary contributions to heat transport is conduction and convection are lumped into an “efficient” conductivity

$$\longrightarrow \quad \left(\frac{\Delta H}{\Delta t}\right)_i = k_i A_i \Delta T_i$$

These enthalpies are evaluated directly from the ***free energy of each grid*** block

$$H_i = -RT^2\left(\frac{\left(\frac{G_i}{RT}\right)_{T+\Delta T} - \left(\frac{G_i}{RT}\right)_T}{\Delta T}\right)$$

$$k_i = (1-p(\phi))k_{S,i}(T,P,\vec{x}_{S,i}) + p(\phi)k_{L,i}(T,P,\vec{x}_{L,i})$$

Rearrangements of water involves significant enthalpy and entropy changes which affects structuring and rearrangements into new phases like for instance ice and/or hydrate.

Substantial room for improvements on this part but at least a convenient starting point for illustration purposes

DENSITY CALCULATIONS

$$\rho_m^{L,Fluid} = \frac{1}{\bar{V}_L^{\,Fluid}}$$

$$\rho_m^{L,aqueous} = \frac{1}{\bar{V}_L^{\,aqueous}}$$

$$\bar{V}_L^{\,Fluid} = \sum_{i=1}^{3} x_i \bar{V}_i$$

$$\bar{V}_L^{\,aqueous} = \sum_{i=1}^{3} x_i \bar{V}_i + x_3 \bar{V}_3^{\,0}$$

Approximated to average molar volume of pure water

Estimated from MD using first shell approximation in integration over pair correlation functions

$$\bar{V}_i = \frac{ZRT}{p} + \frac{nRT}{p}\left(\frac{\partial Z}{\partial n_i}\right)_{p,T,n_{i \neq j}}$$

Partial molar volume for ***water in hydrate*** is trivially calculated from the ***unit cell dimensions and compositions***, see for instance Sloan et al. (2008), 3rd edition, CRC Press for examples. ***Guest molecule partial molar volumes*** evaluated by ***Monte Carlo*** (Kvamme & Lund, 1993).

$$\rho_m^{Hyd}$$

SUMMARY - PFT

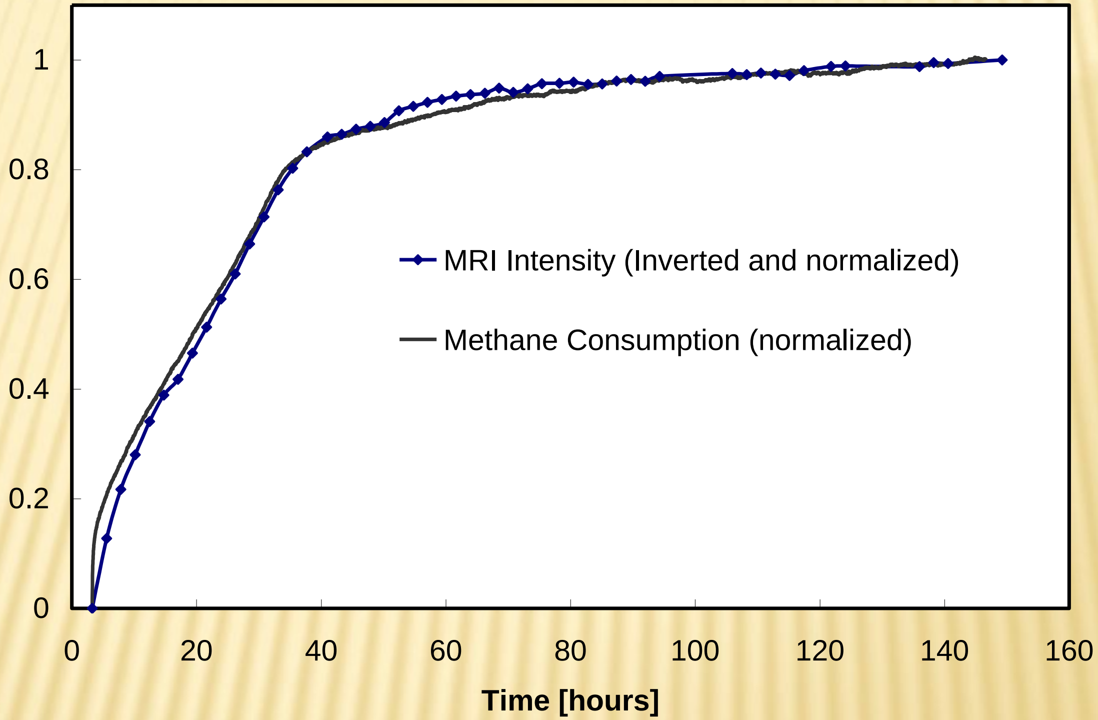
- PFT can, in simplified terms, be considered as free energy minimation under the constraints of mass- and heat-transport.
- Application of phase field theory to emulsions requires consistent thermodynamic properties for the phases involved.
- In addition interface thickness, interface concentration profiles and interface free energy is needed.
- All of the above properties can readily be estimated by careful molecular modeling in which relevant experimental data is used for verification of model systems.

Spontaneous crystallisation from binary alloy by supercooling

Different models for droplet merging are available and have been examined for different systems, depending on droplet elasticity

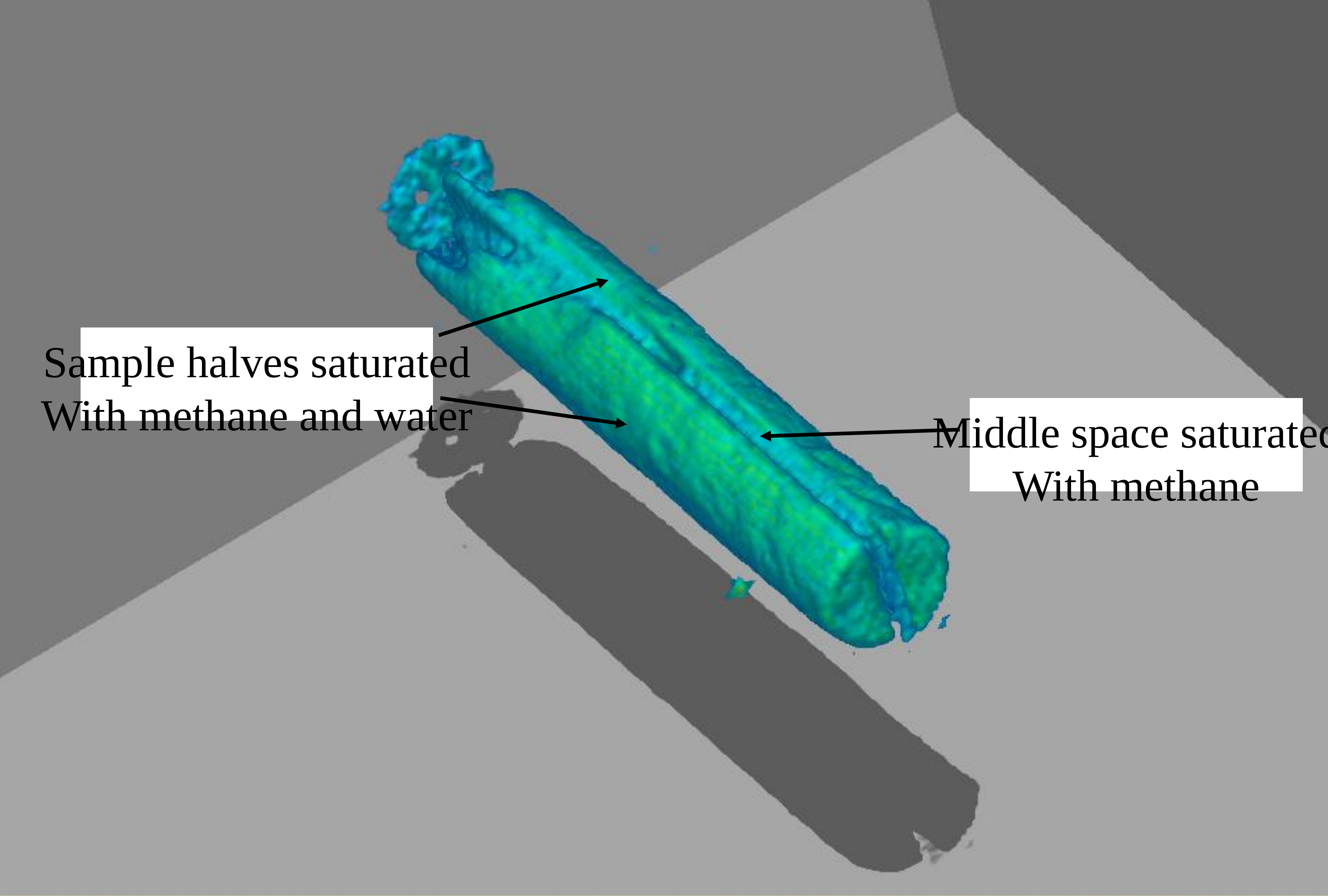
Extra: The MRI experiments

VOLUMETRICS AND MRI RESULTS



MRI Intensity in Core and CH_4 Volume Consumption

Sample – BH-01



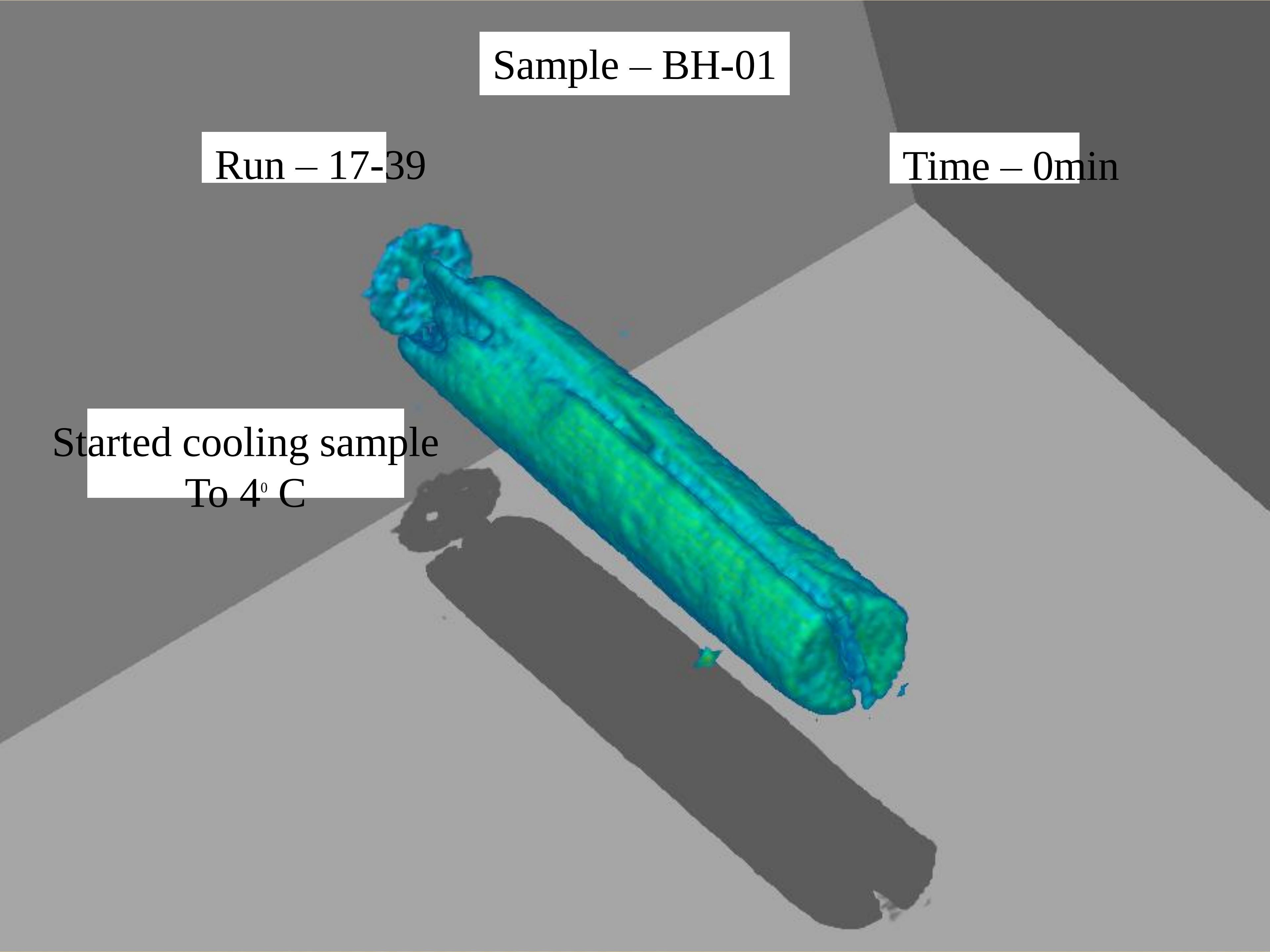
Sample halves saturated
With methane and water

Middle space saturate
With methane

Sample – BH-01

Run – 17-39

Time – 0min

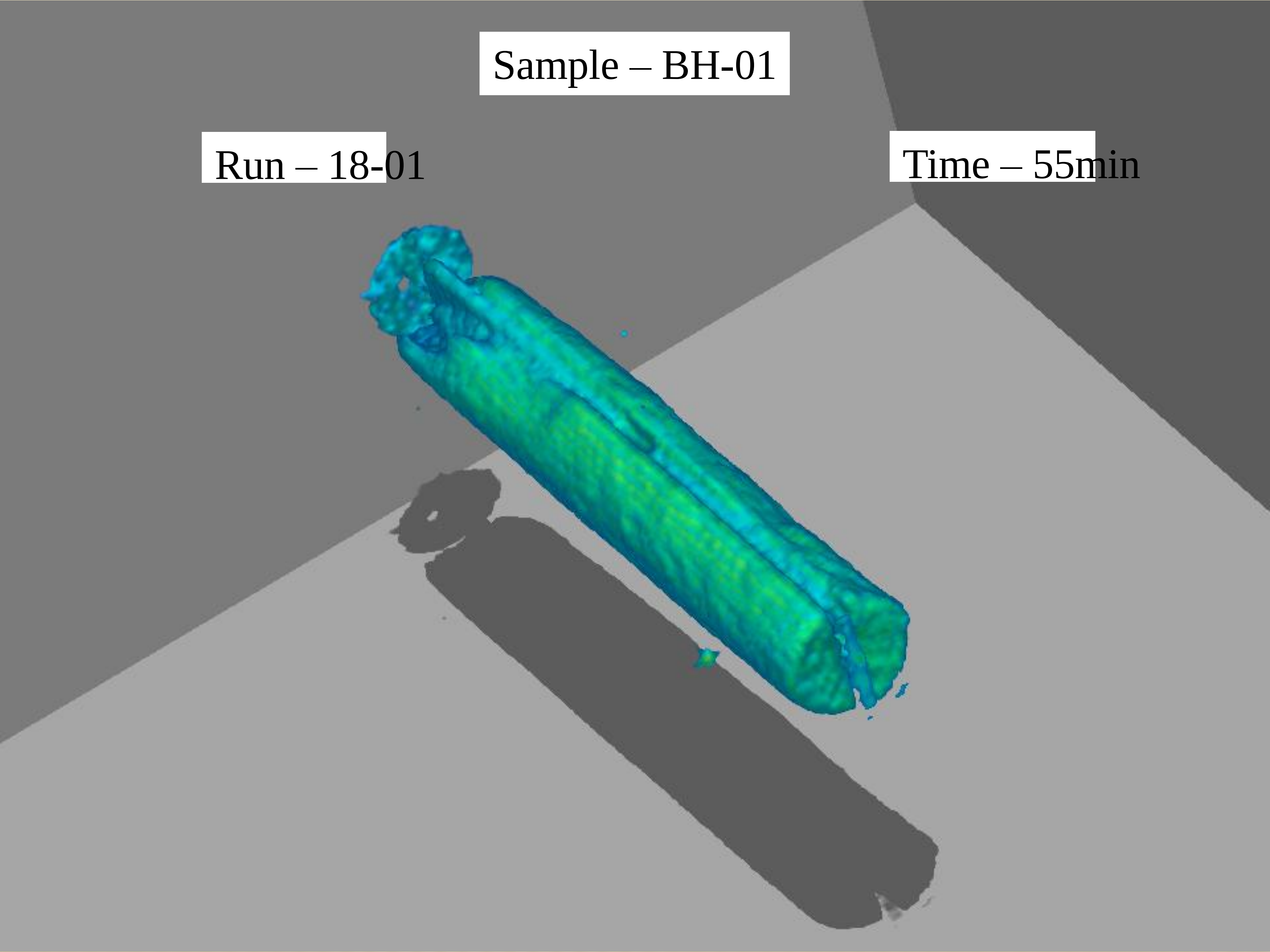


Started cooling sample
To 4^0 C

Sample – BH-01

Run – 18-01

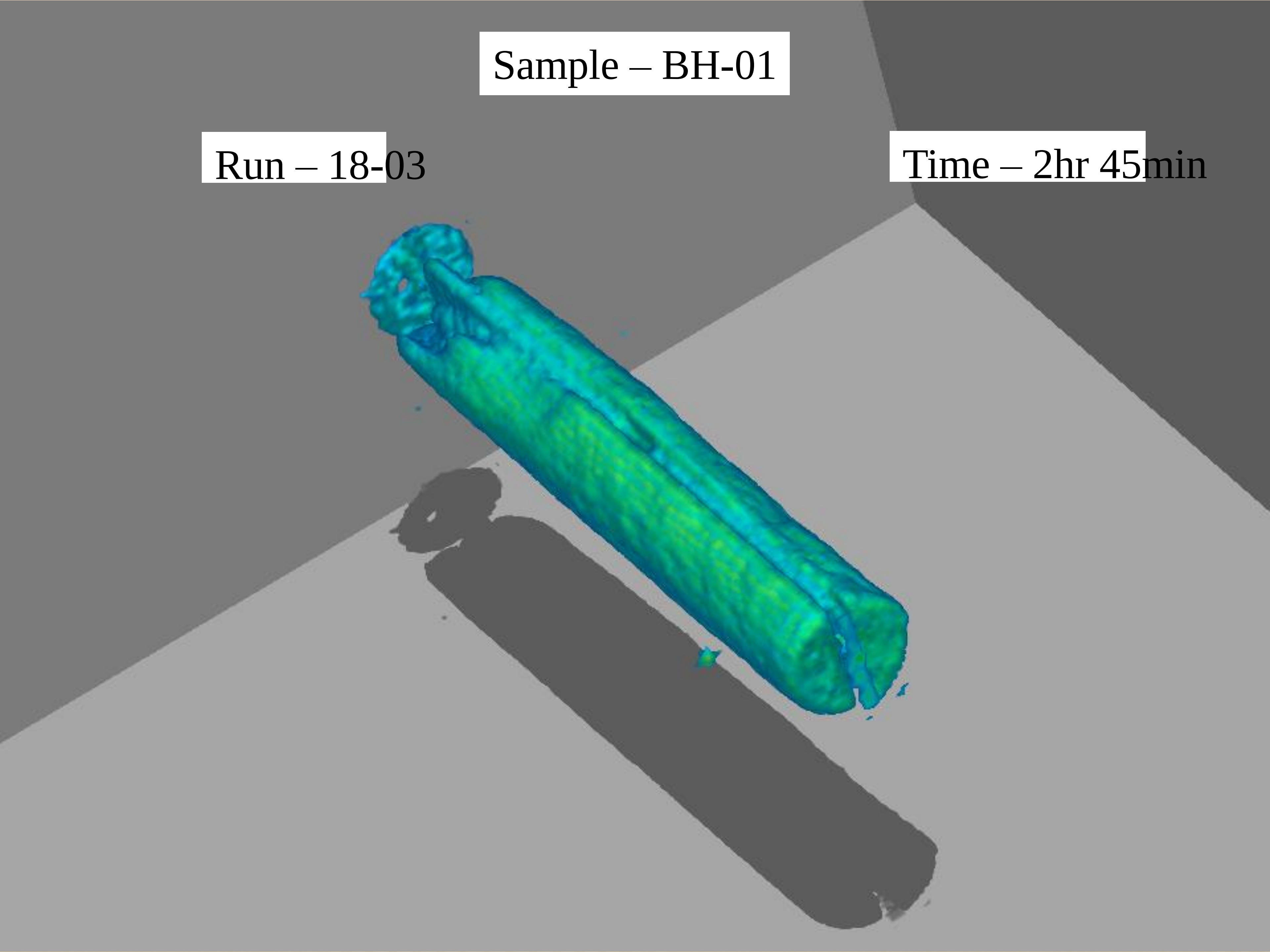
Time – 55min



Sample – BH-01

Run – 18-03

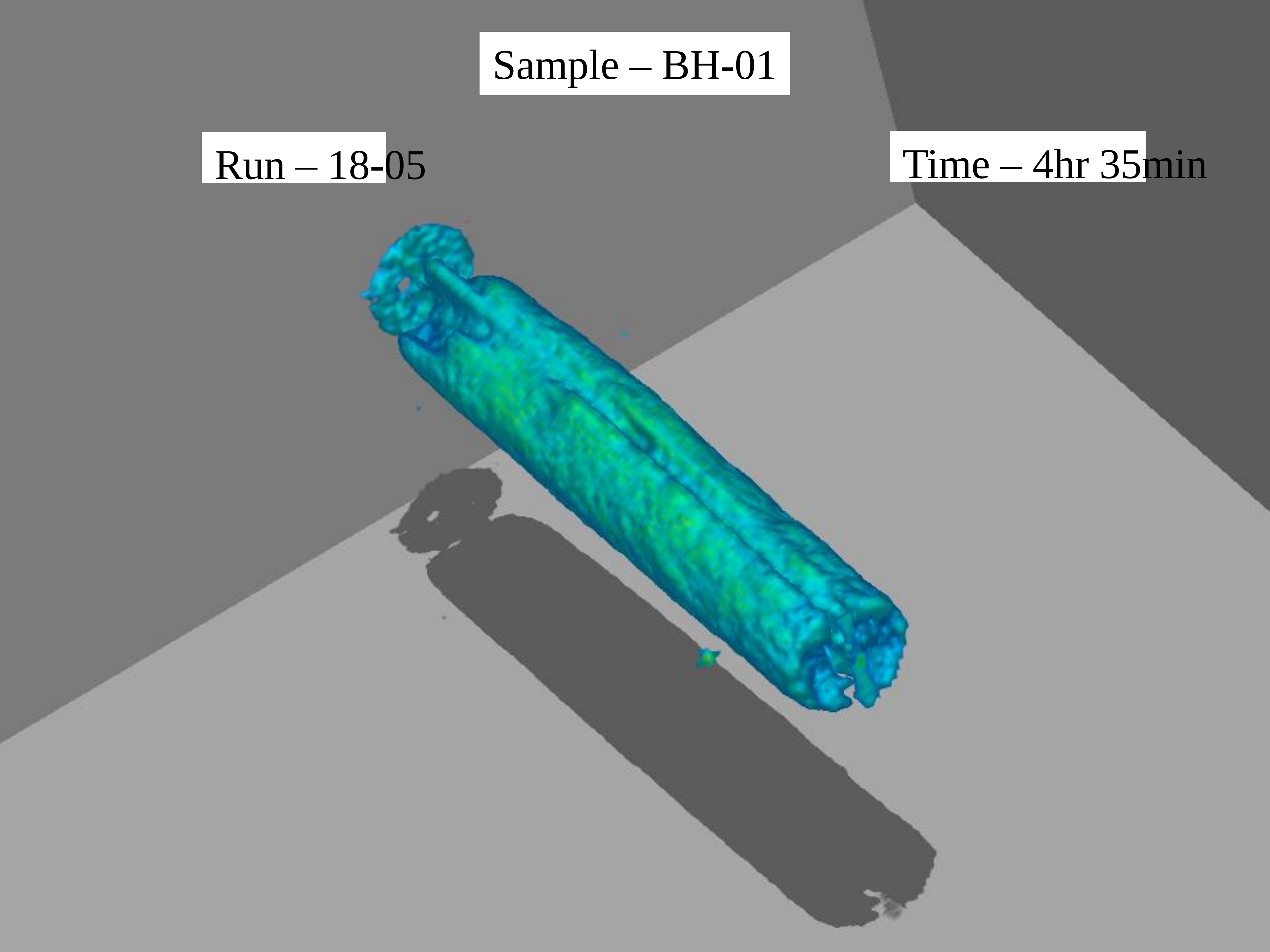
Time – 2hr 45min

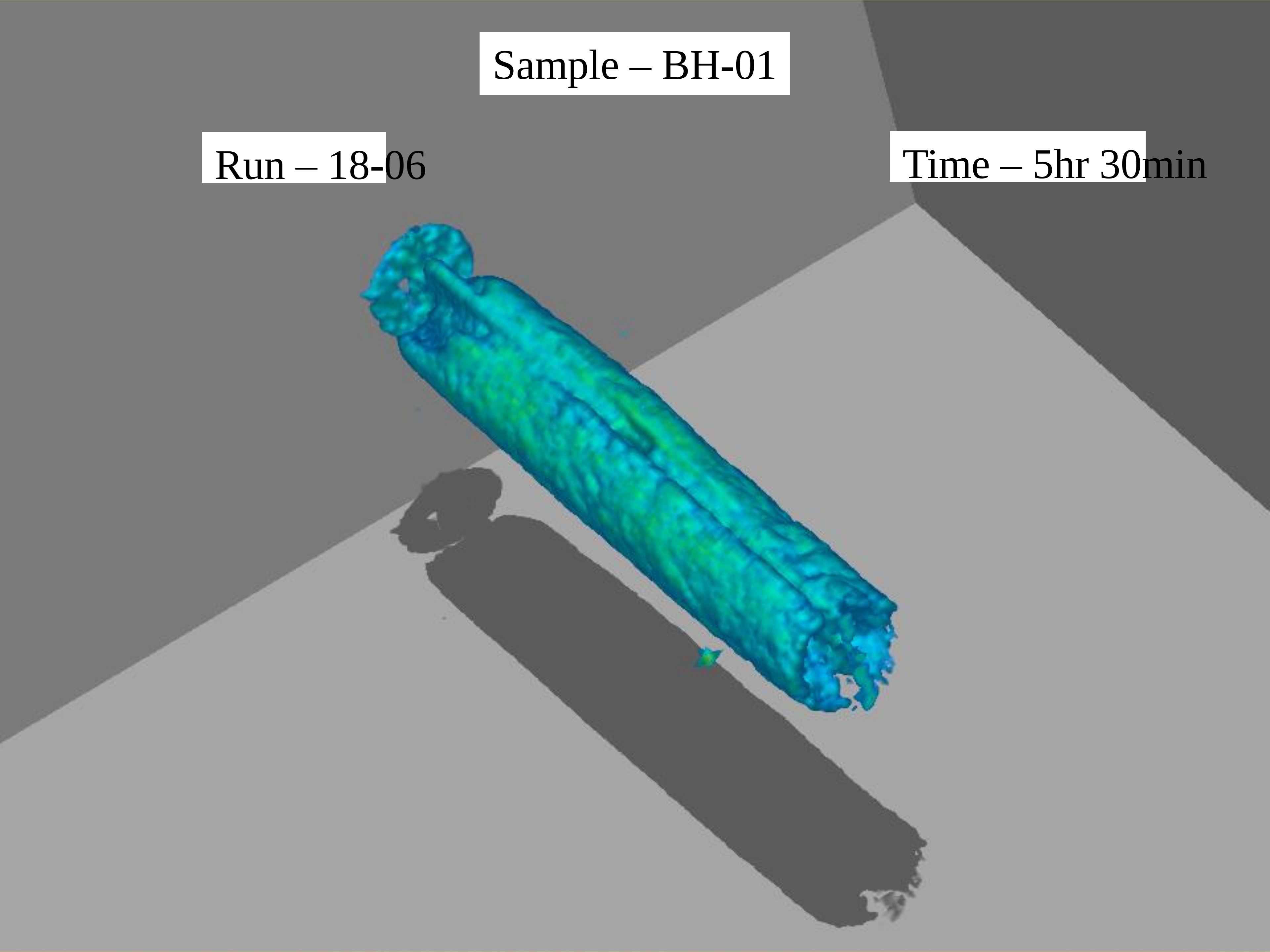


Sample – BH-01

Run – 18-05

Time – 4hr 35min

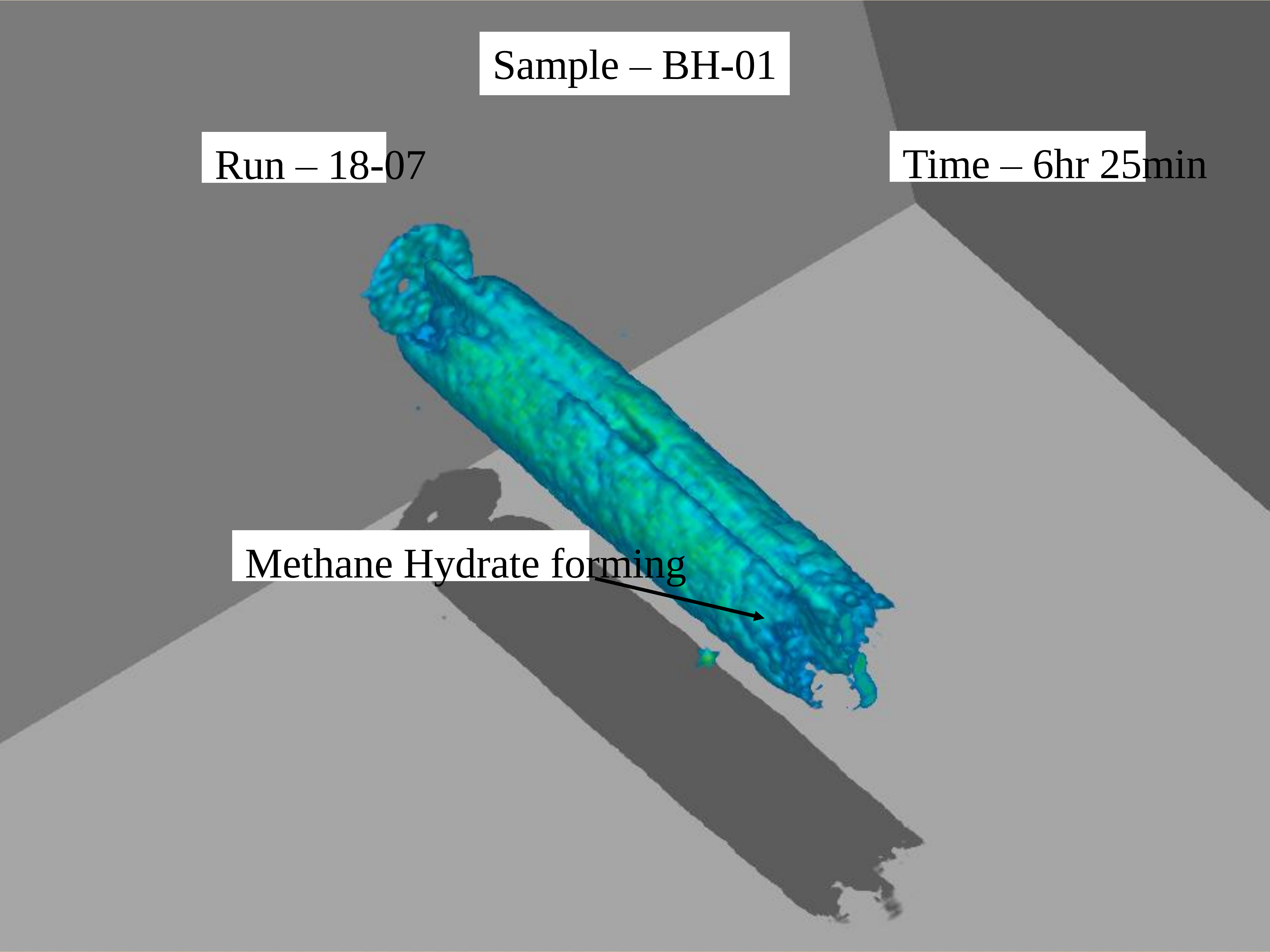




Sample – BH-01

Run – 18-06

Time – 5hr 30min



Sample – BH-01

Run – 18-07

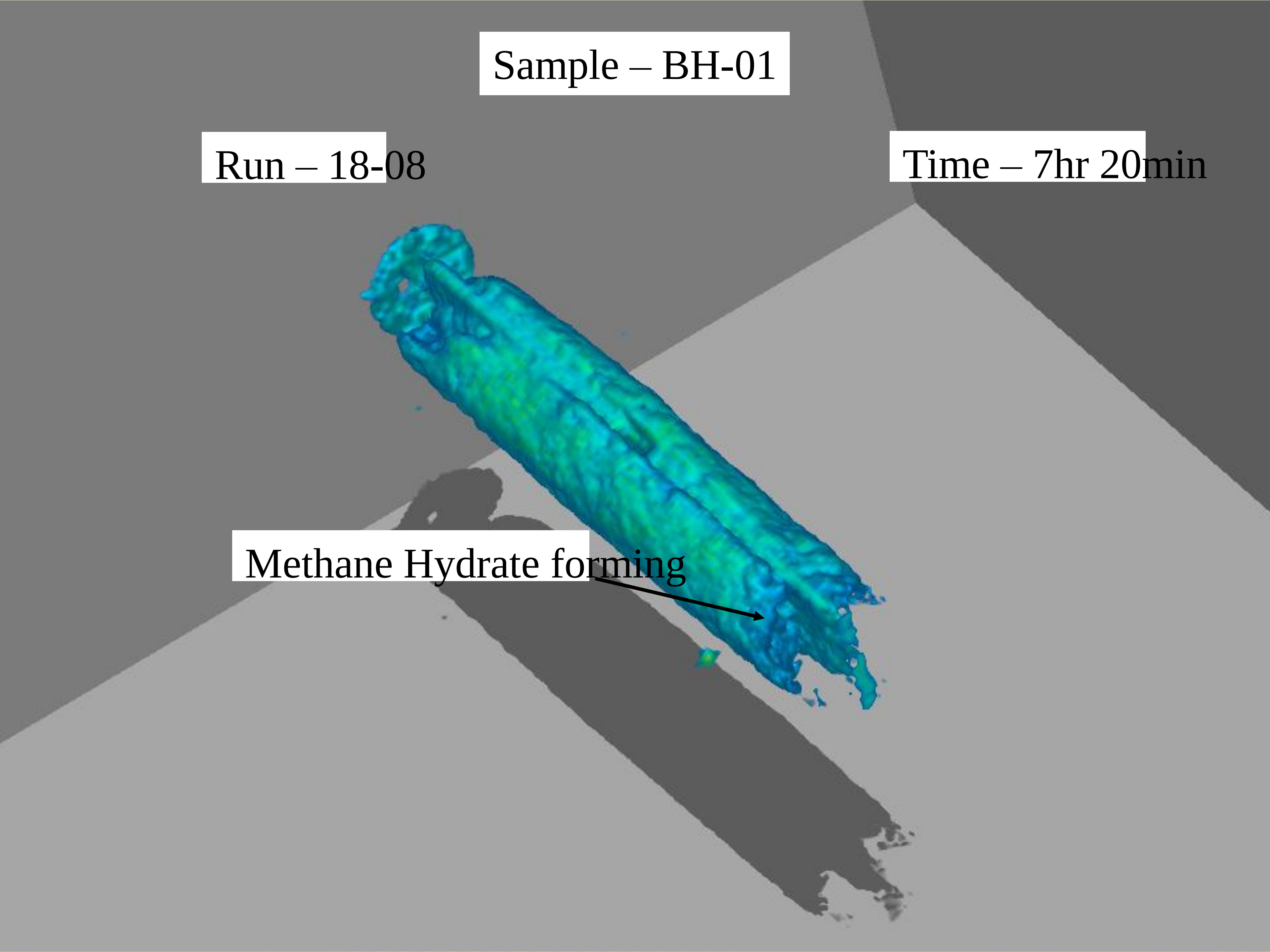
Time – 6hr 25min

Methane Hydrate forming

Sample – BH-01

Run – 18-08

Time – 7hr 20min

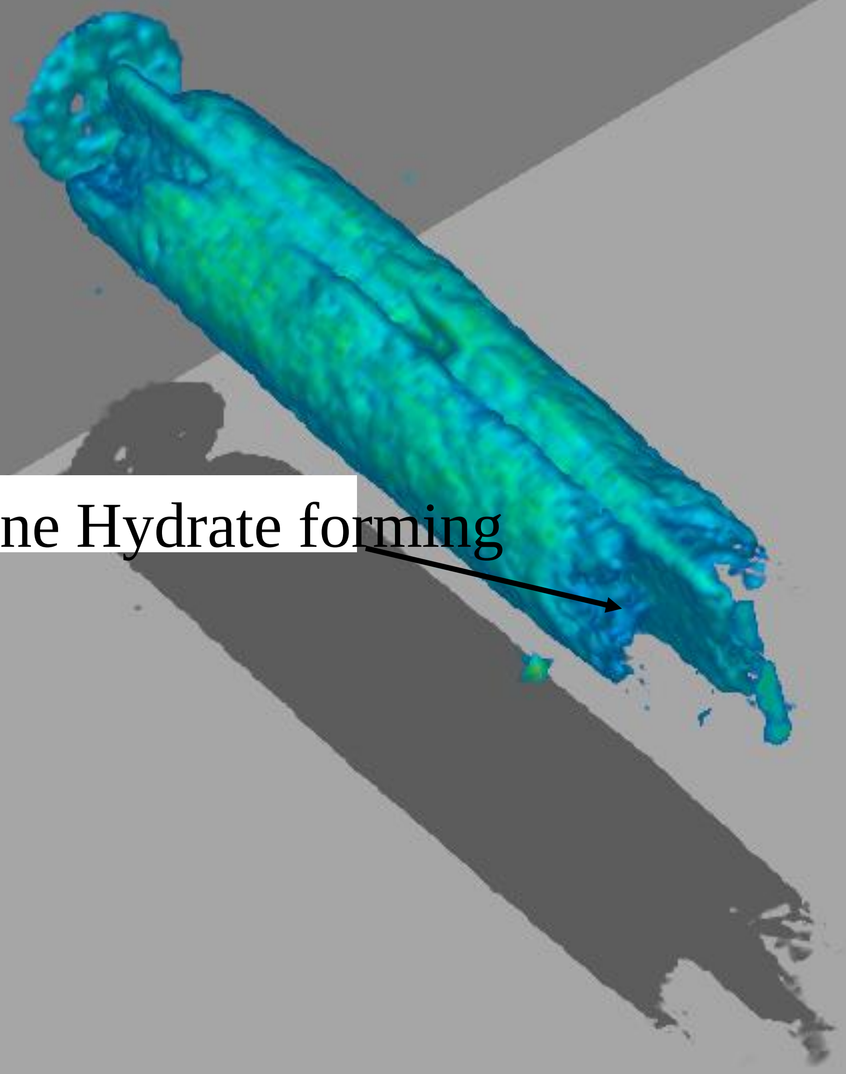


Methane Hydrate forming

Sample – BH-01

Run – 18-09

Time – 8hr 15min

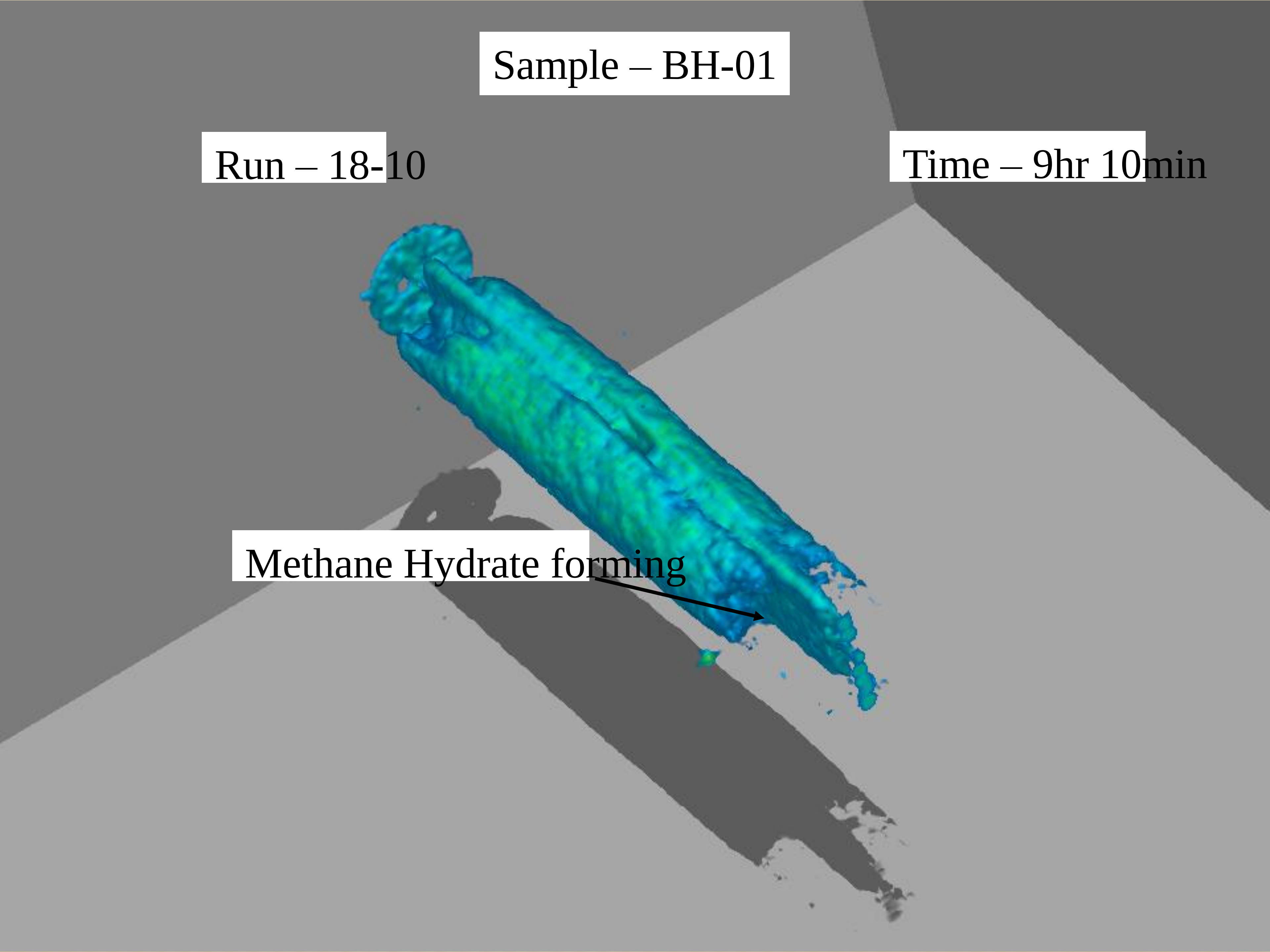


Methane Hydrate forming

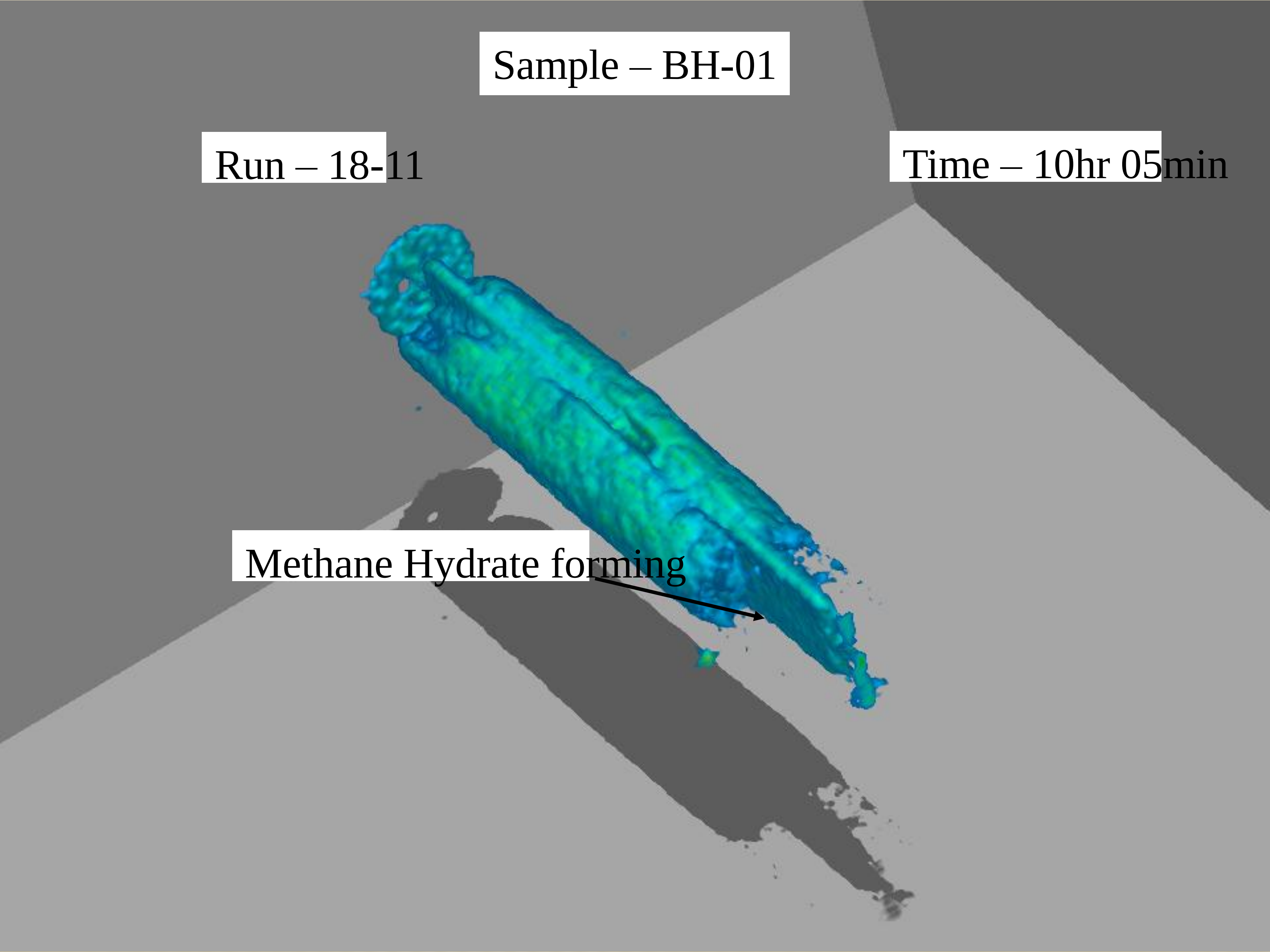
Sample – BH-01

Run – 18-10

Time – 9hr 10min



Methane Hydrate forming



Sample – BH-01

Run – 18-11

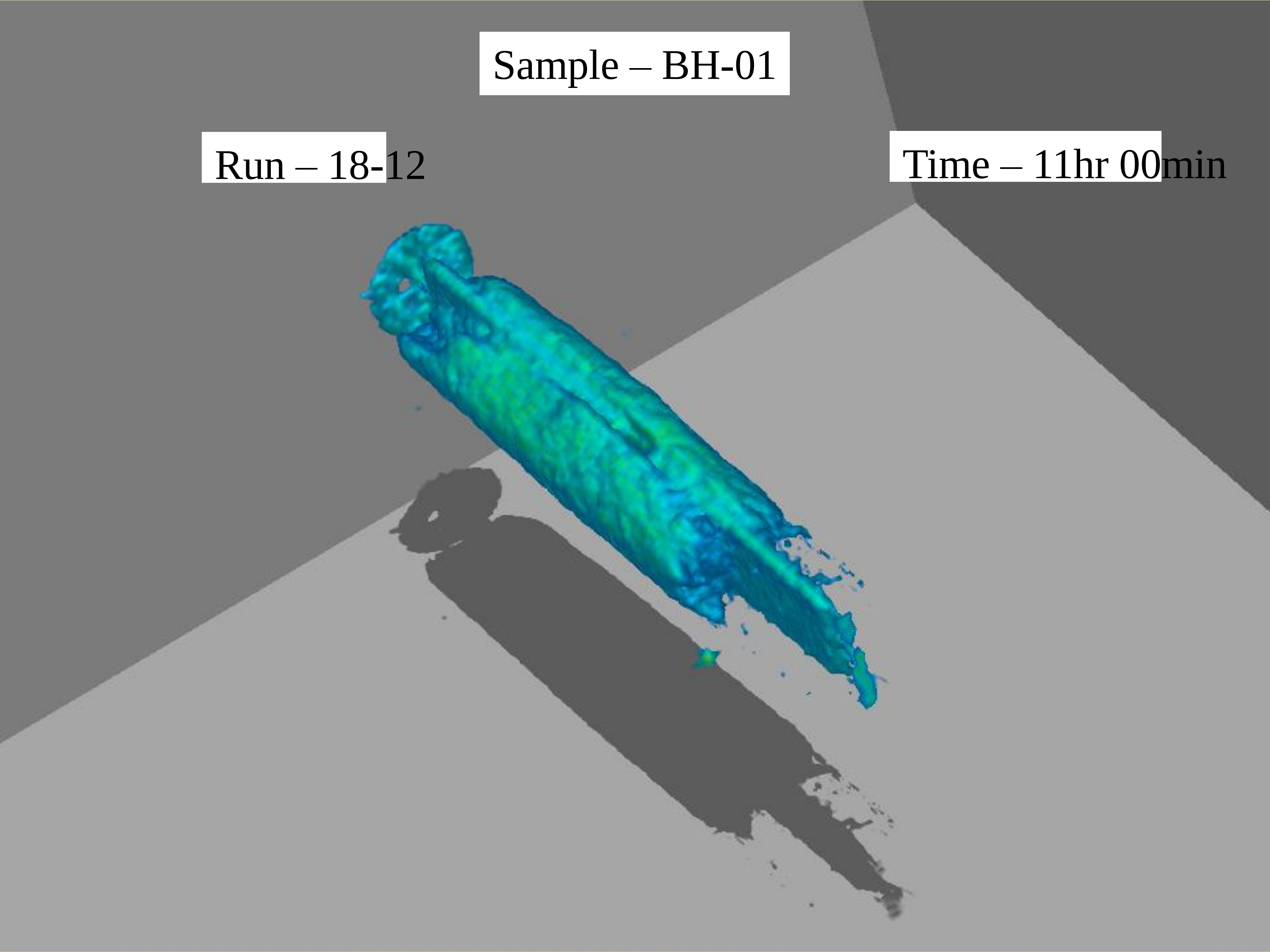
Time – 10hr 05min

Methane Hydrate forming

Sample – BH-01

Run – 18-12

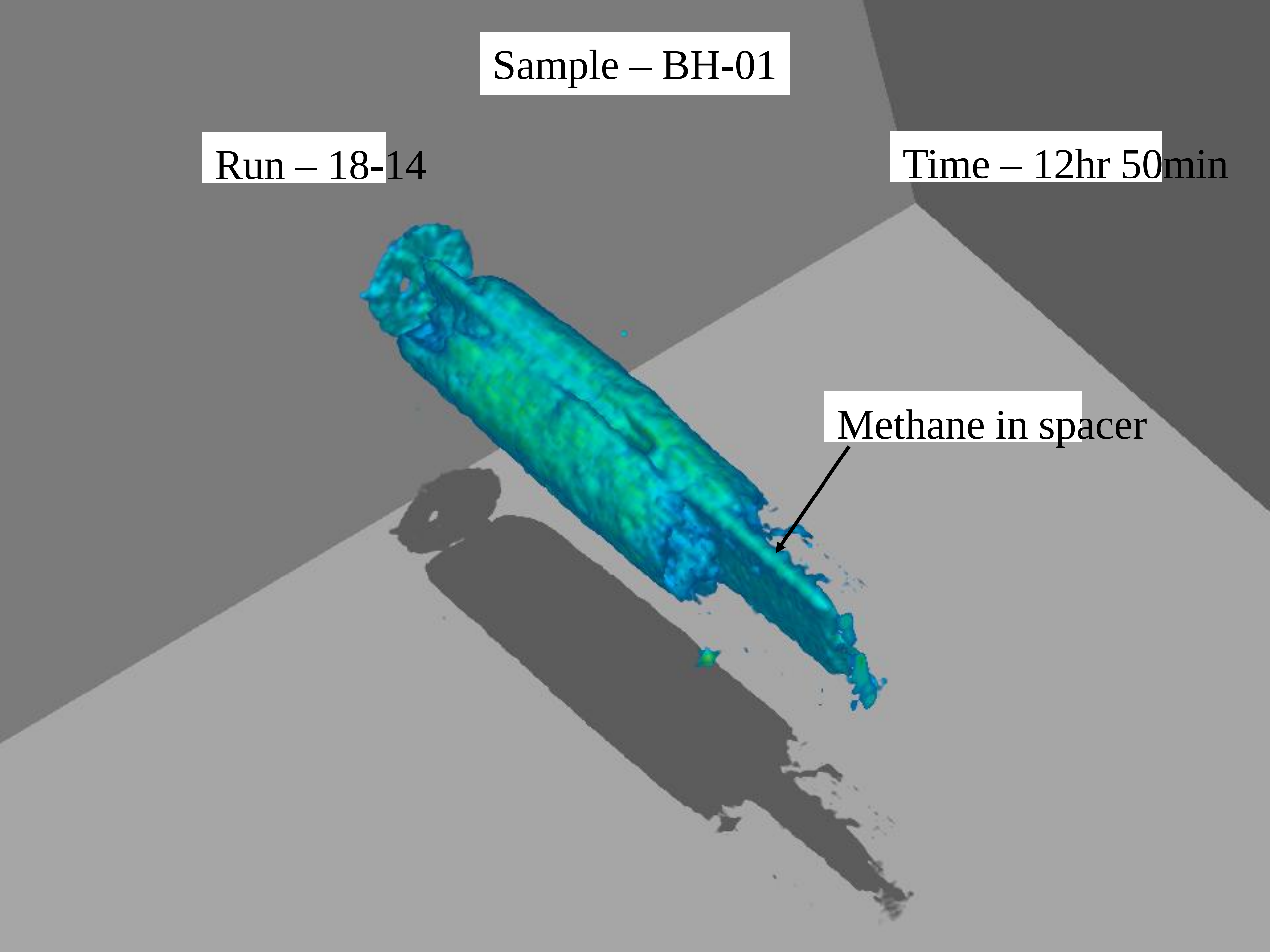
Time – 11hr 00min



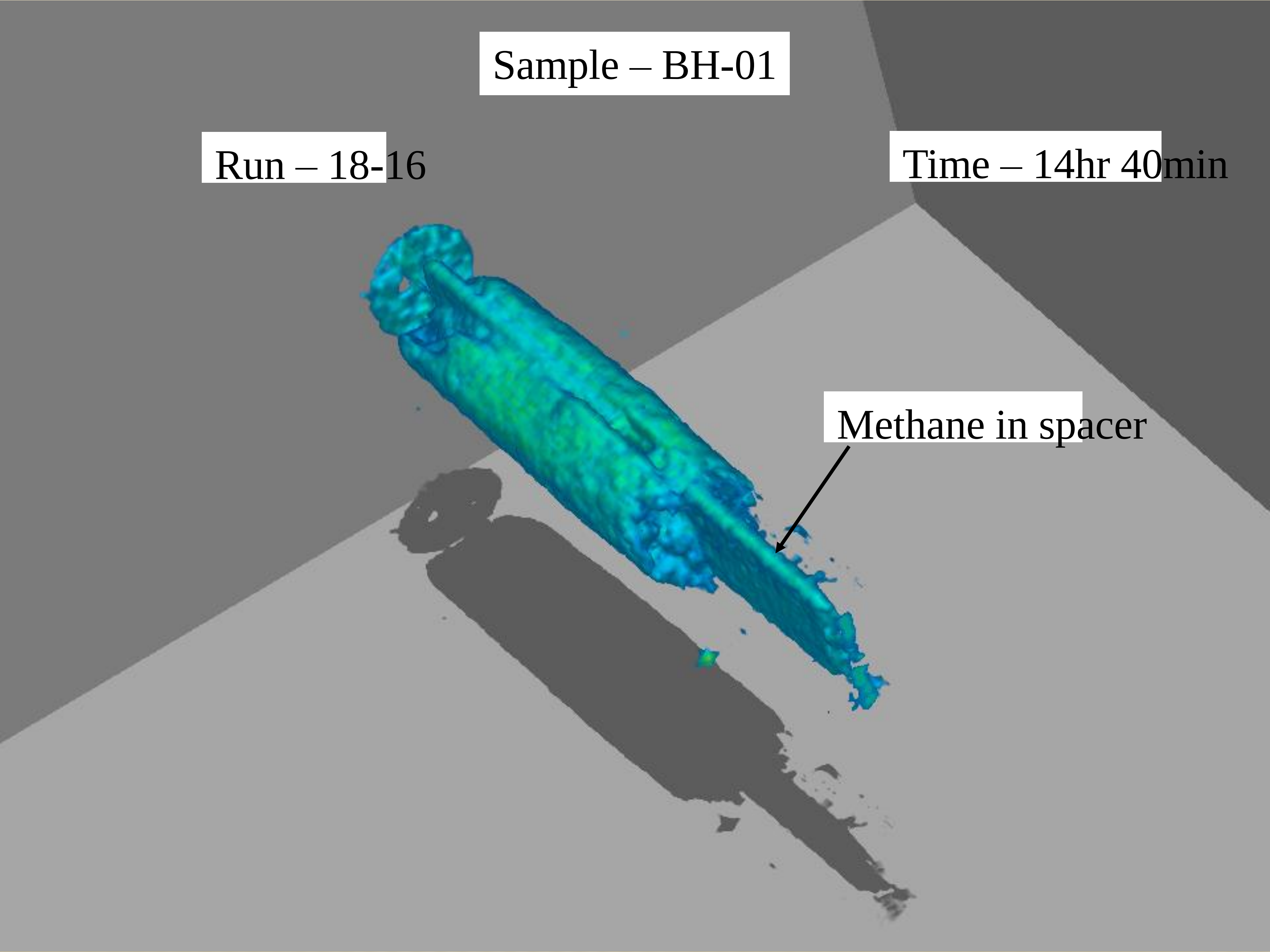
Sample – BH-01

Run – 18-14

Time – 12hr 50min



Methane in spacer

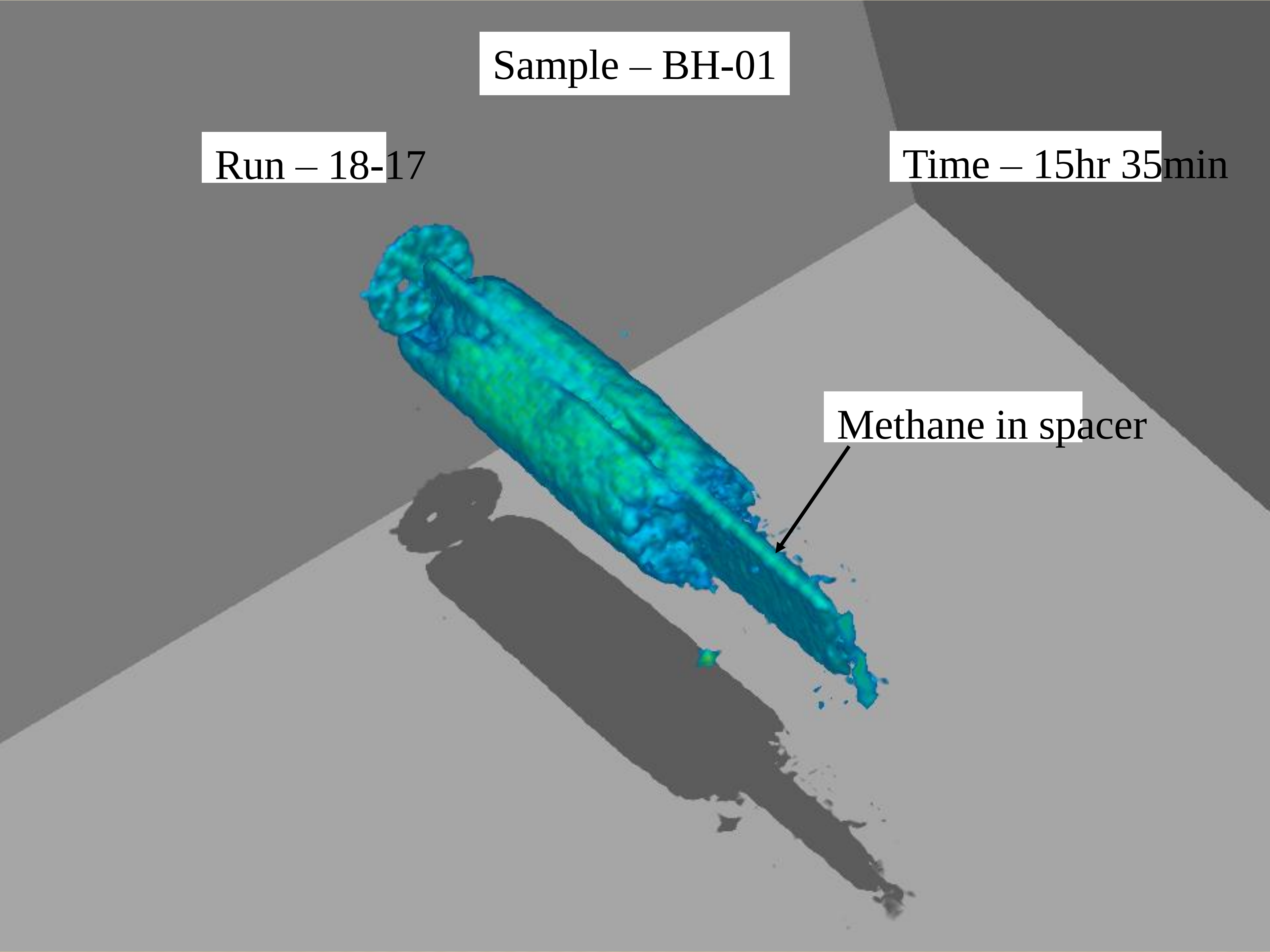


Sample – BH-01

Run – 18-16

Time – 14hr 40min

Methane in spacer



Sample – BH-01

Run – 18-17

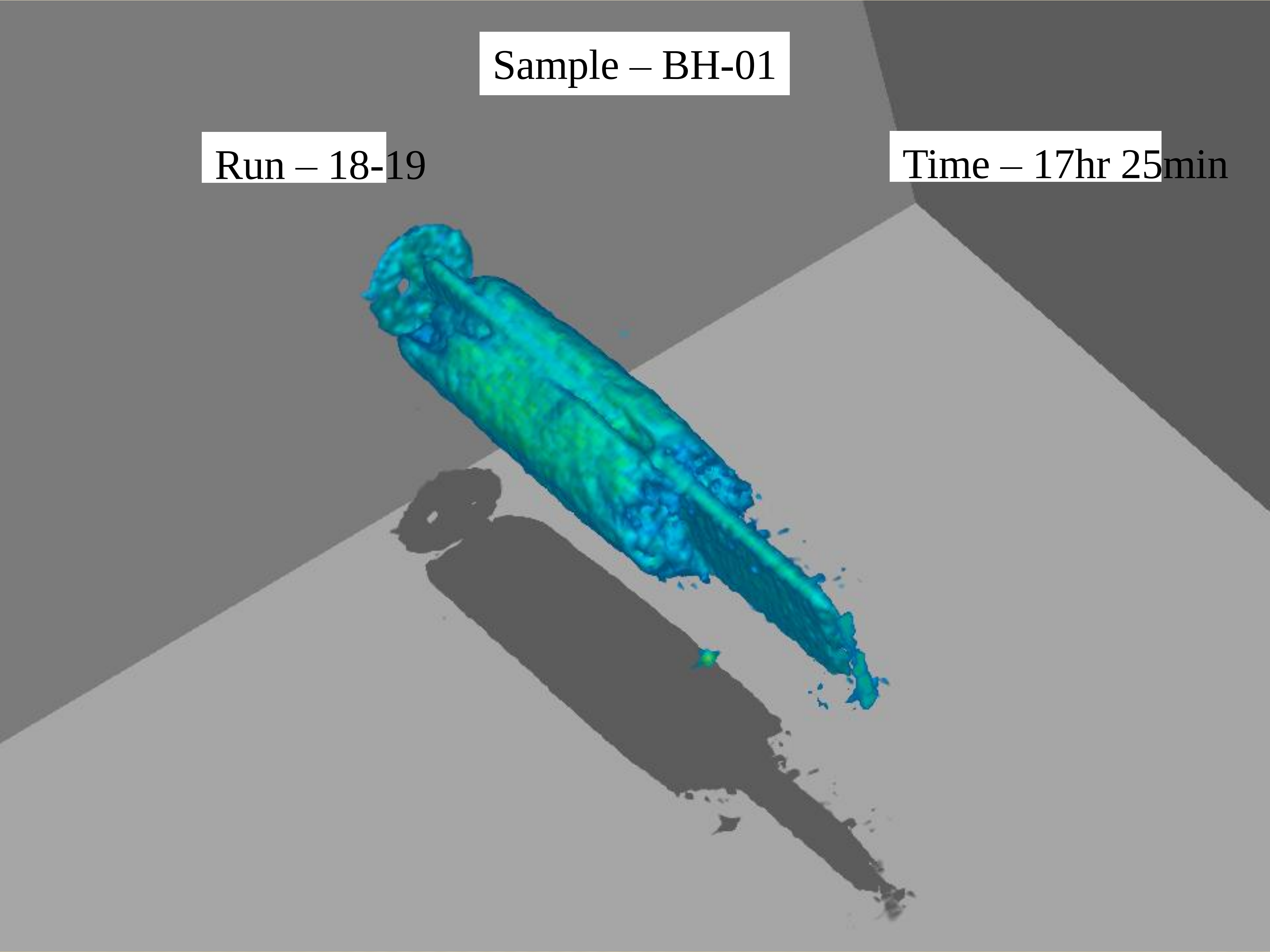
Time – 15hr 35min

Methane in spacer

Sample – BH-01

Run – 18-19

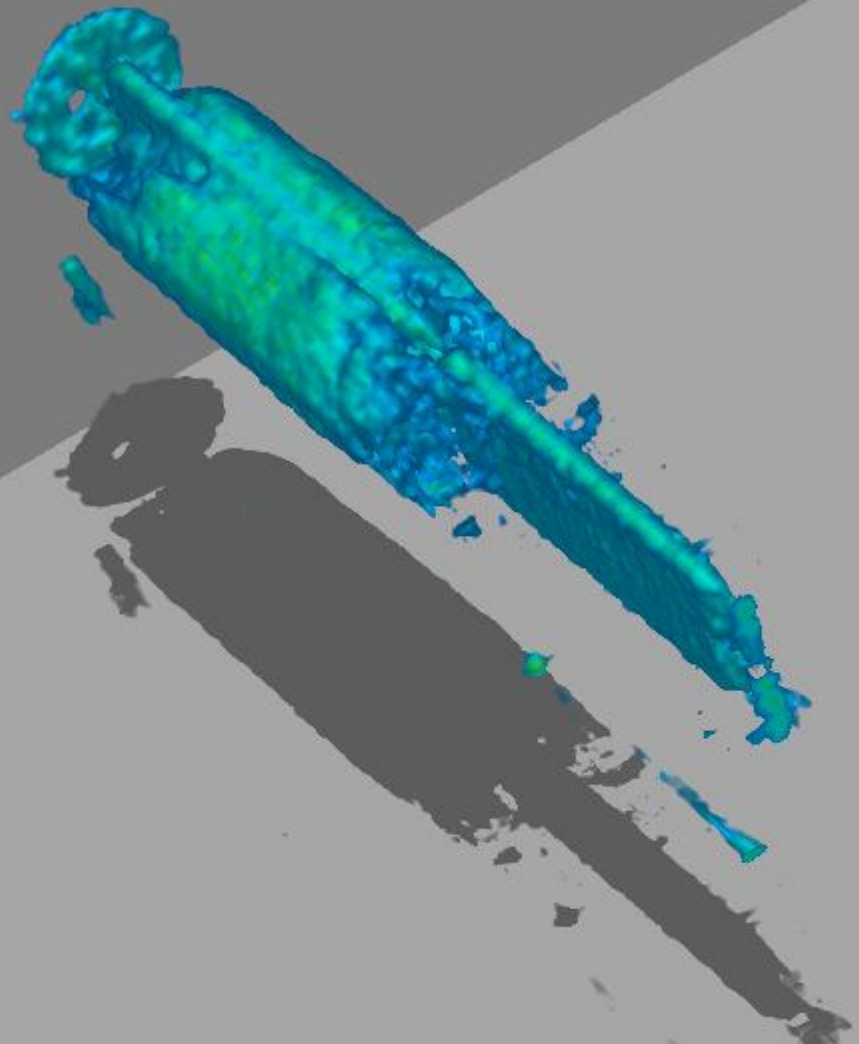
Time – 17hr 25min



Sample – BH-01

Run – 18-37

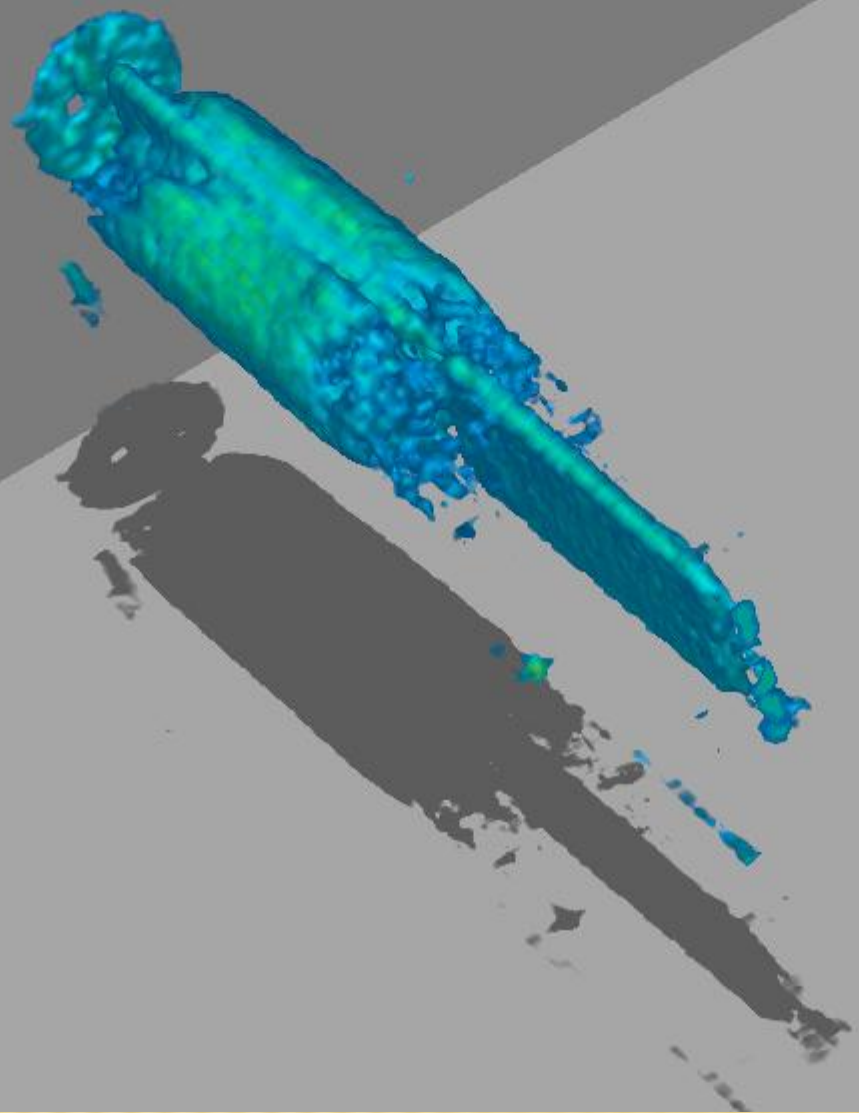
Time – 31hr 05min



Sample – BH-01

Run – 18-42

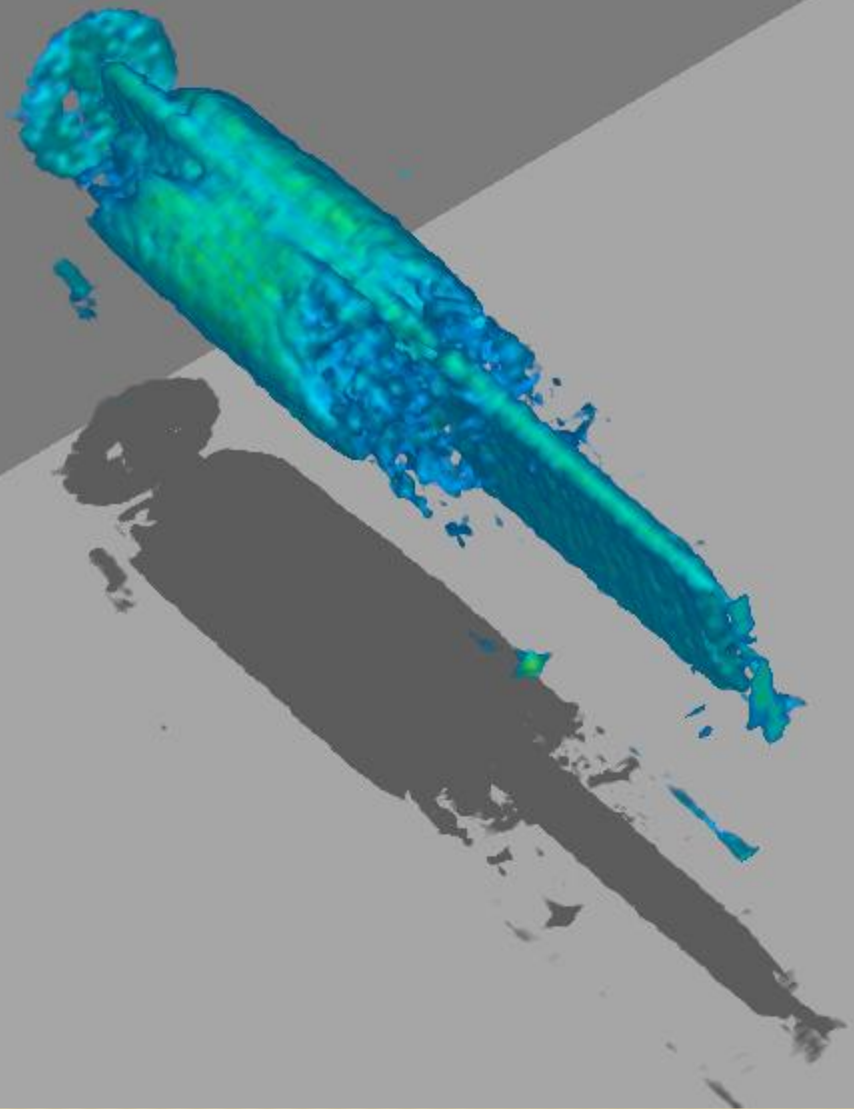
Time – 36hr 20min



Sample – BH-01

Run – 18-43

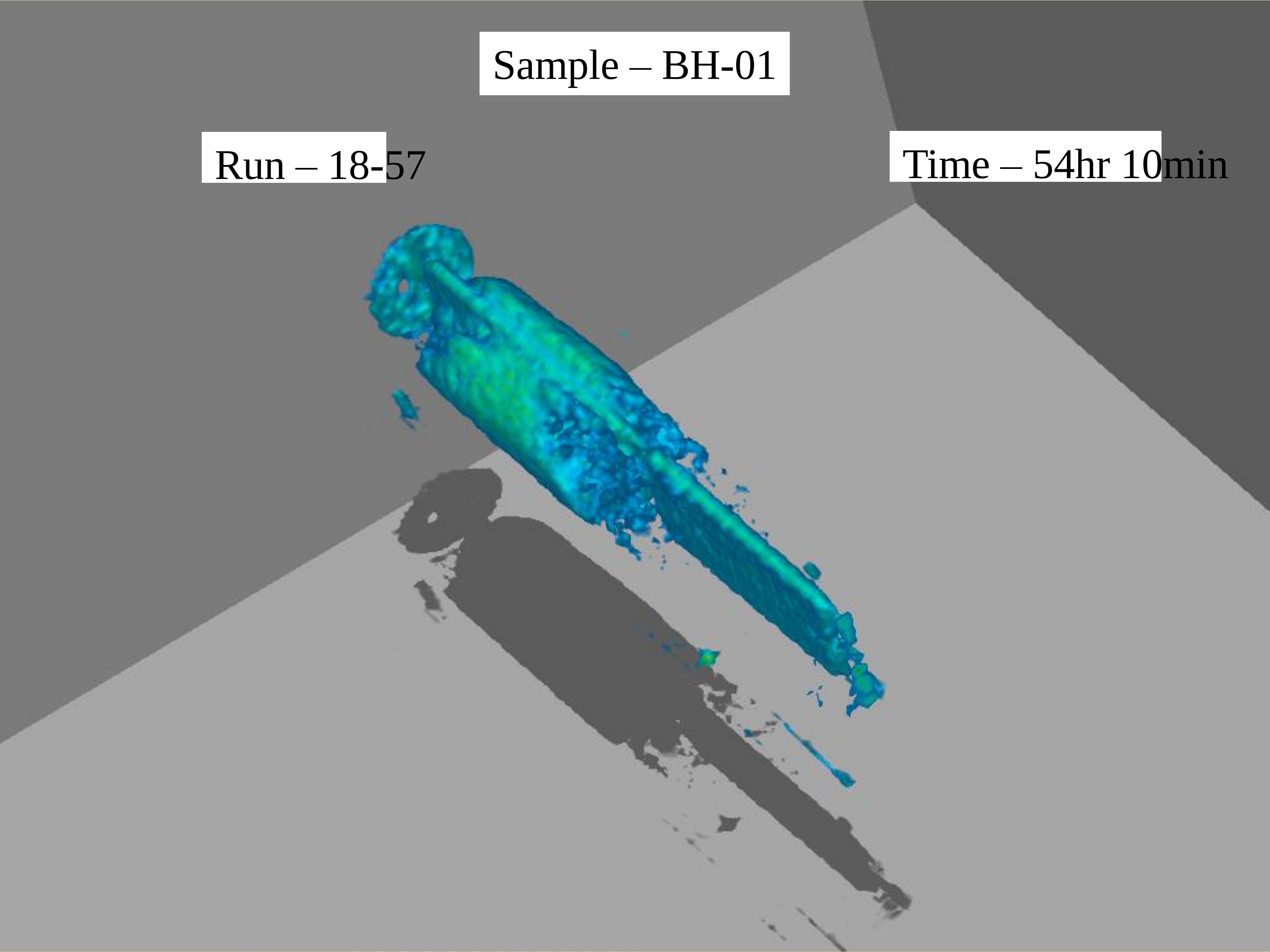
Time – 37hr 15min



Sample – BH-01

Run – 18-57

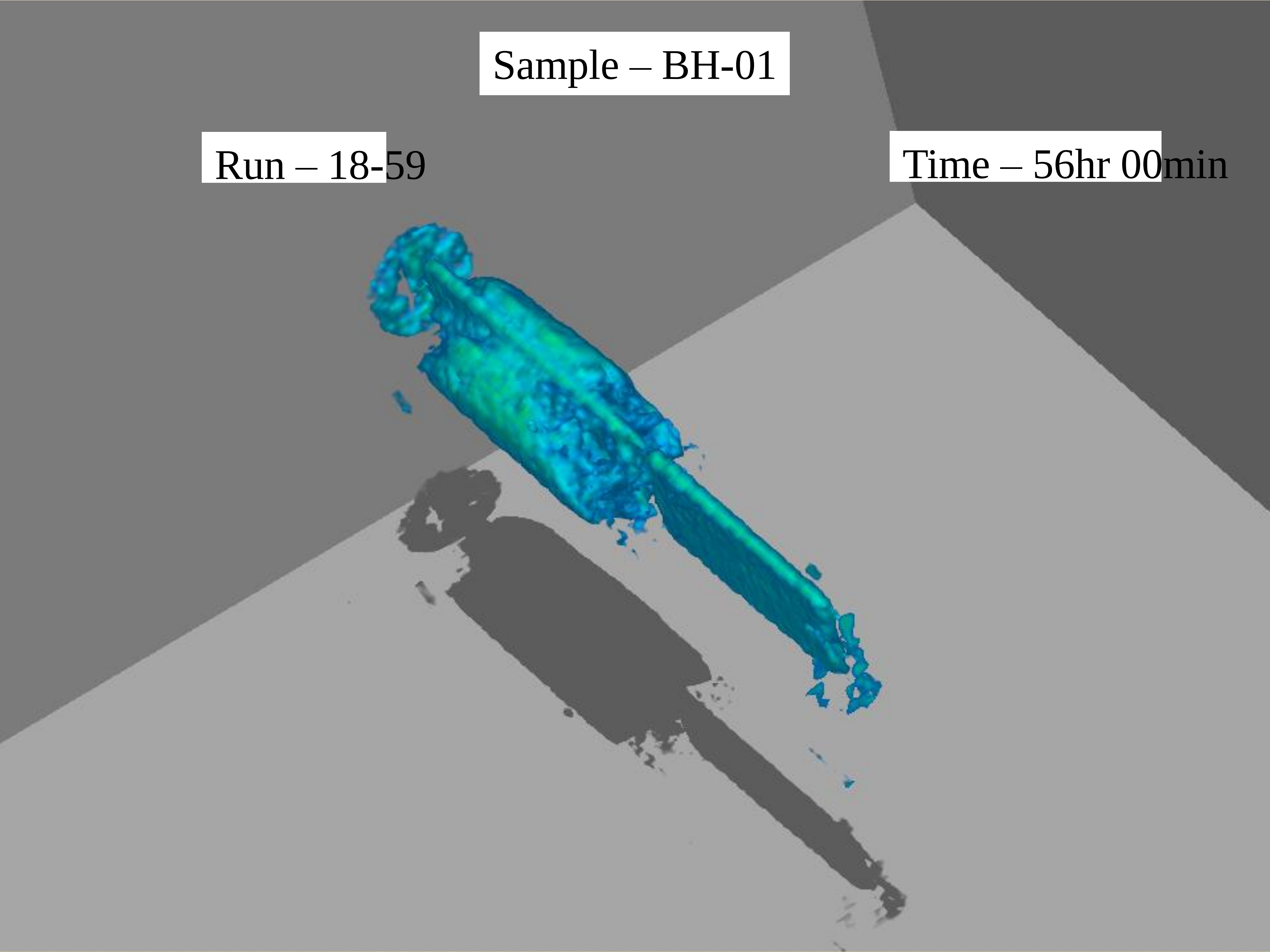
Time – 54hr 10min

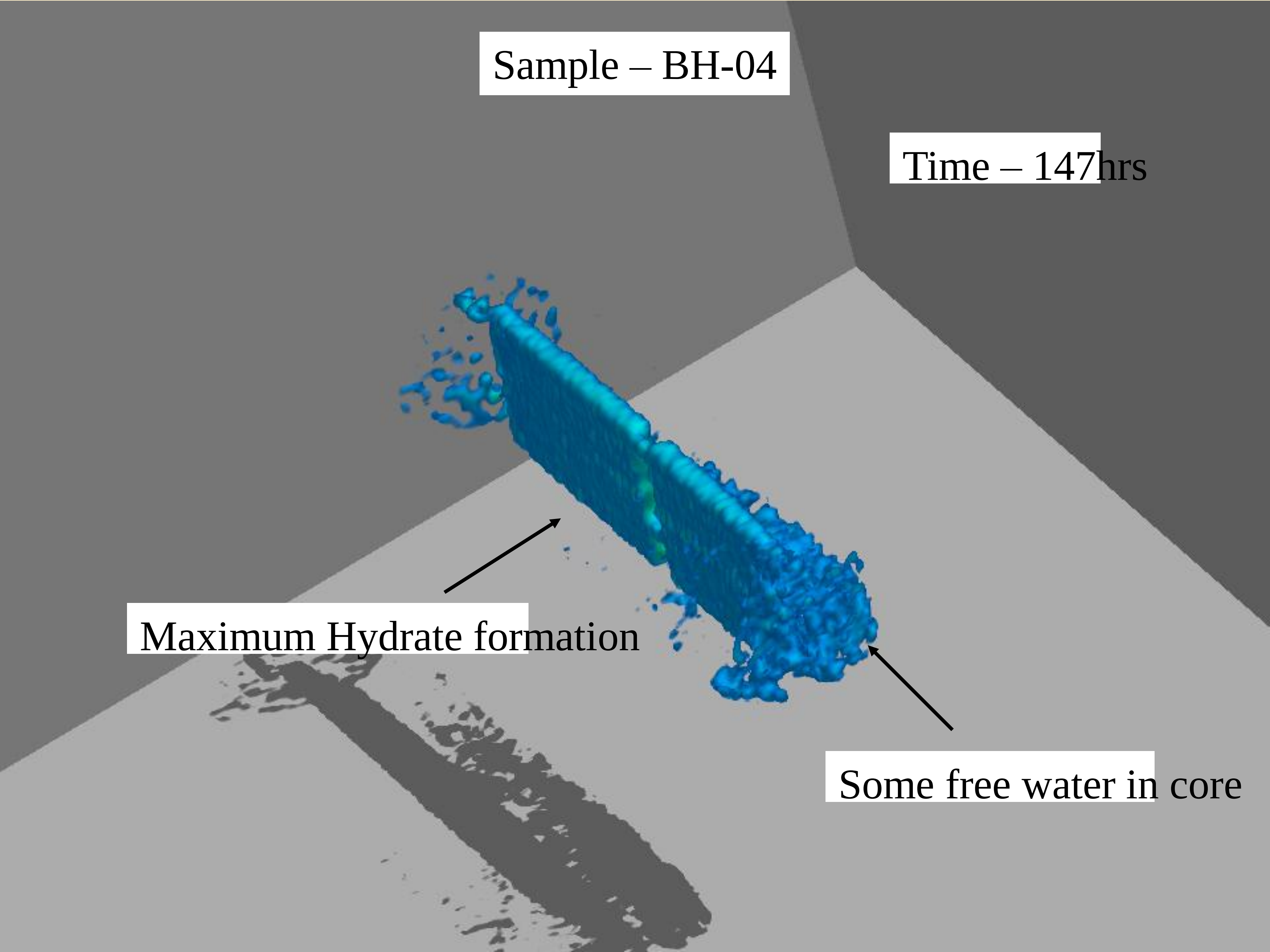


Sample – BH-01

Run – 18-59

Time – 56hr 00min



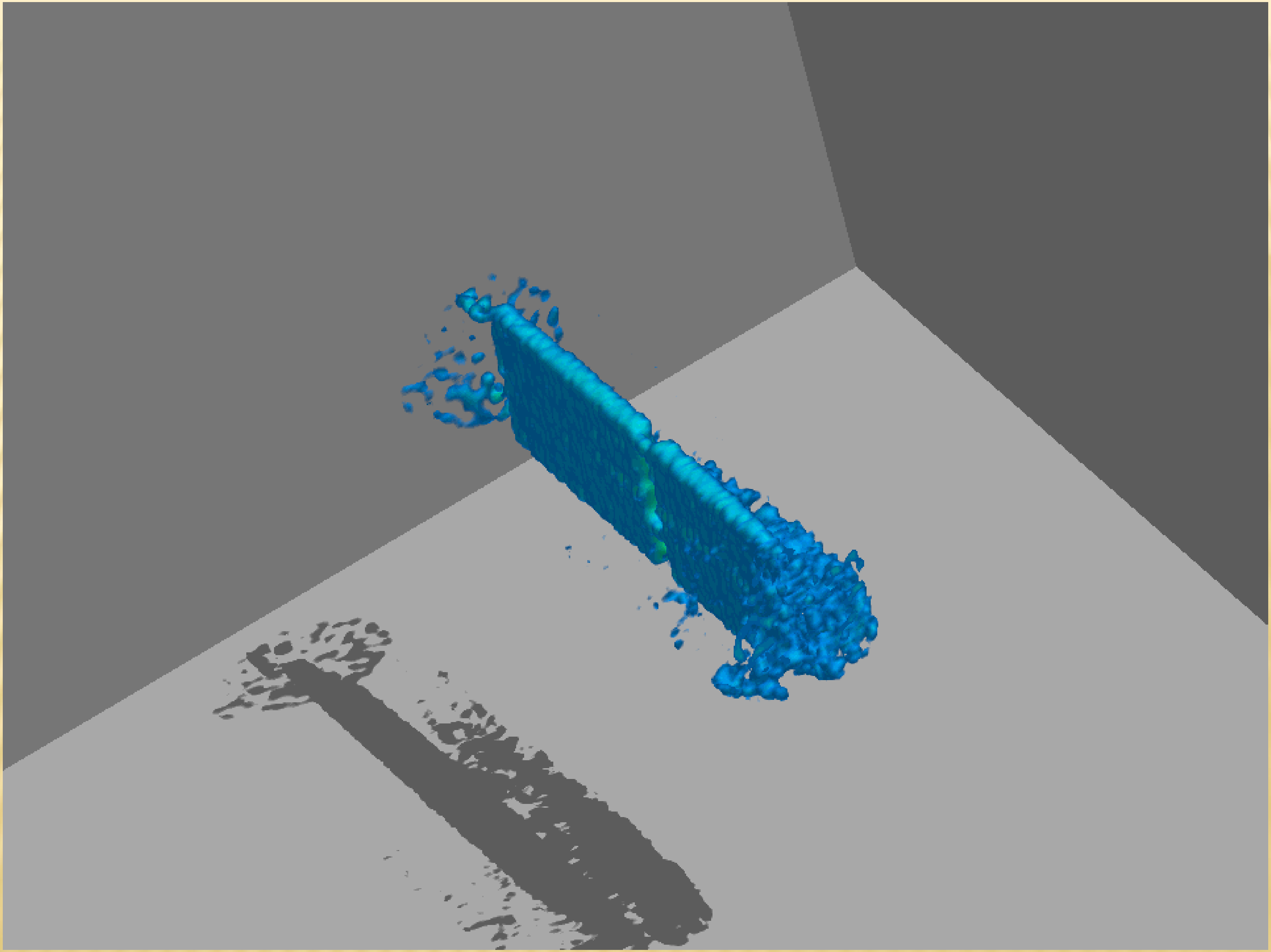


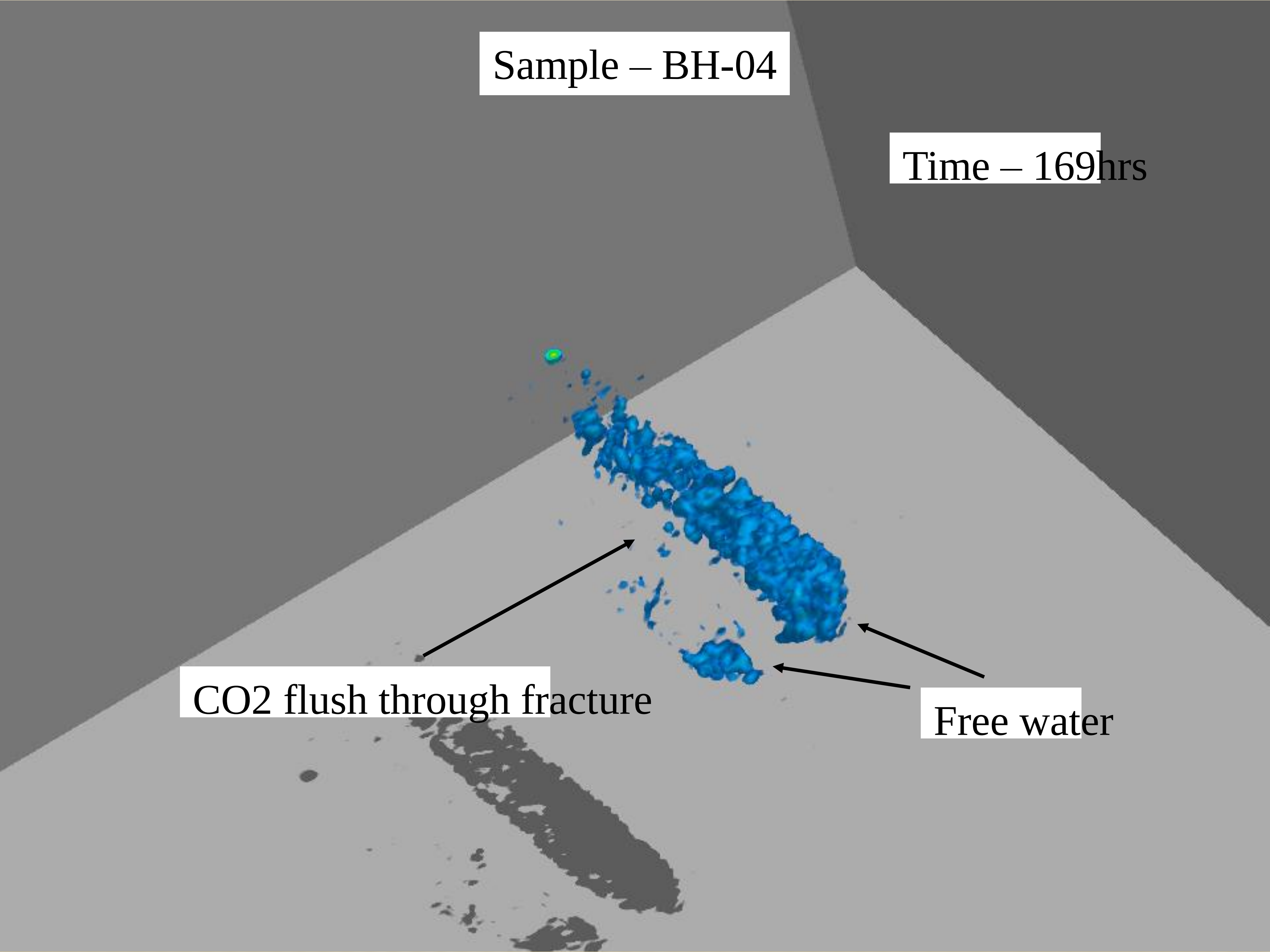
Sample – BH-04

Time – 147hrs

Maximum Hydrate formation

Some free water in core





Sample – BH-04

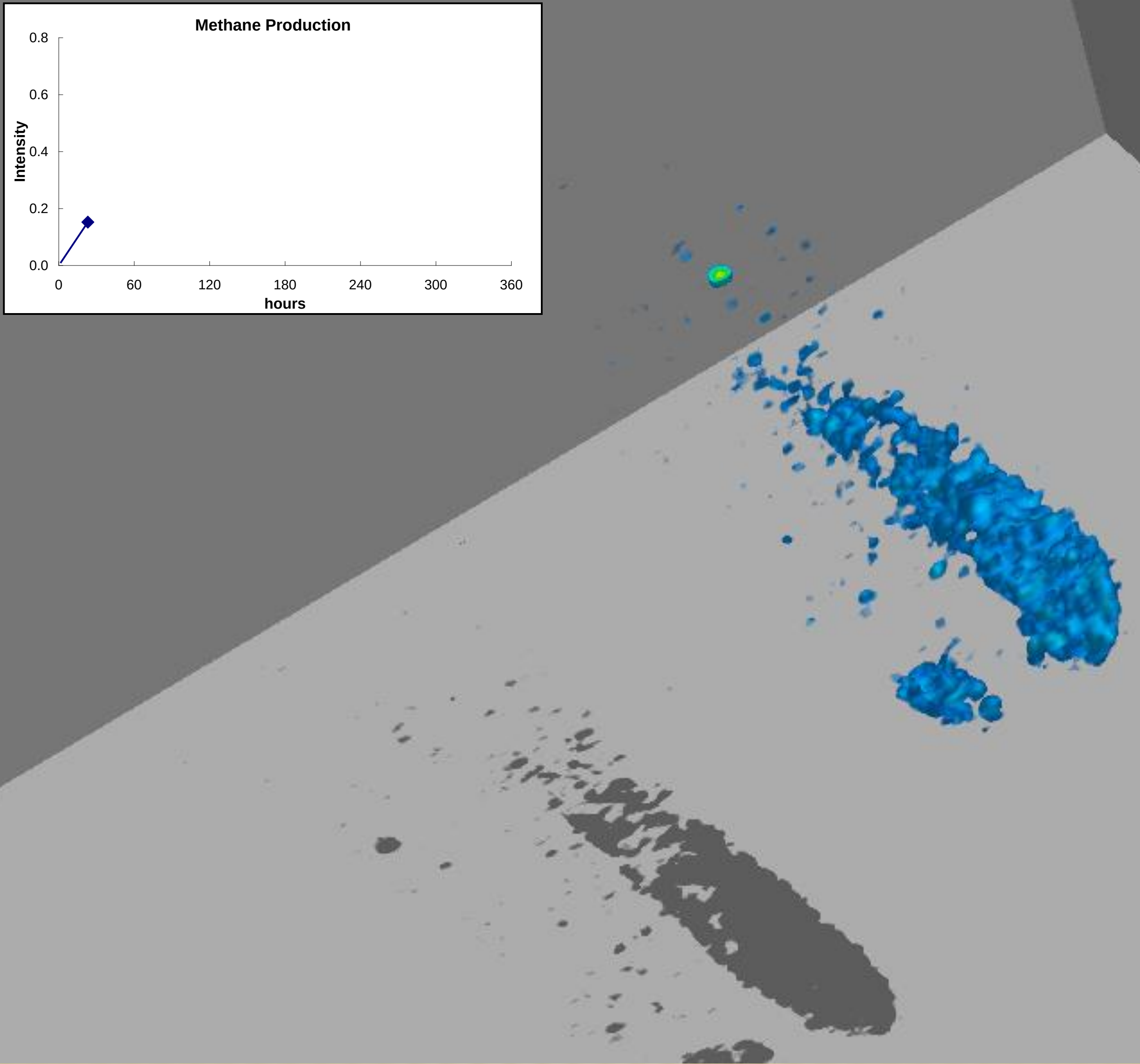
Time – 169hrs

CO2 flush through fracture

Free water

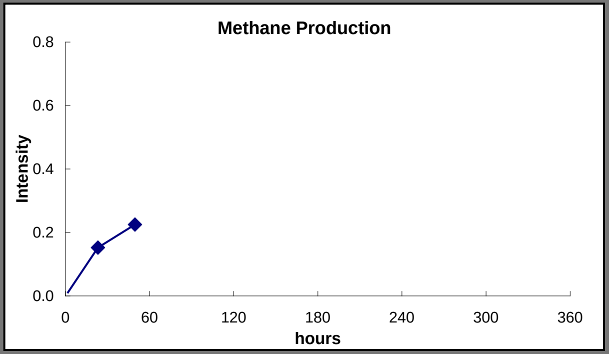
Sample – BH-04

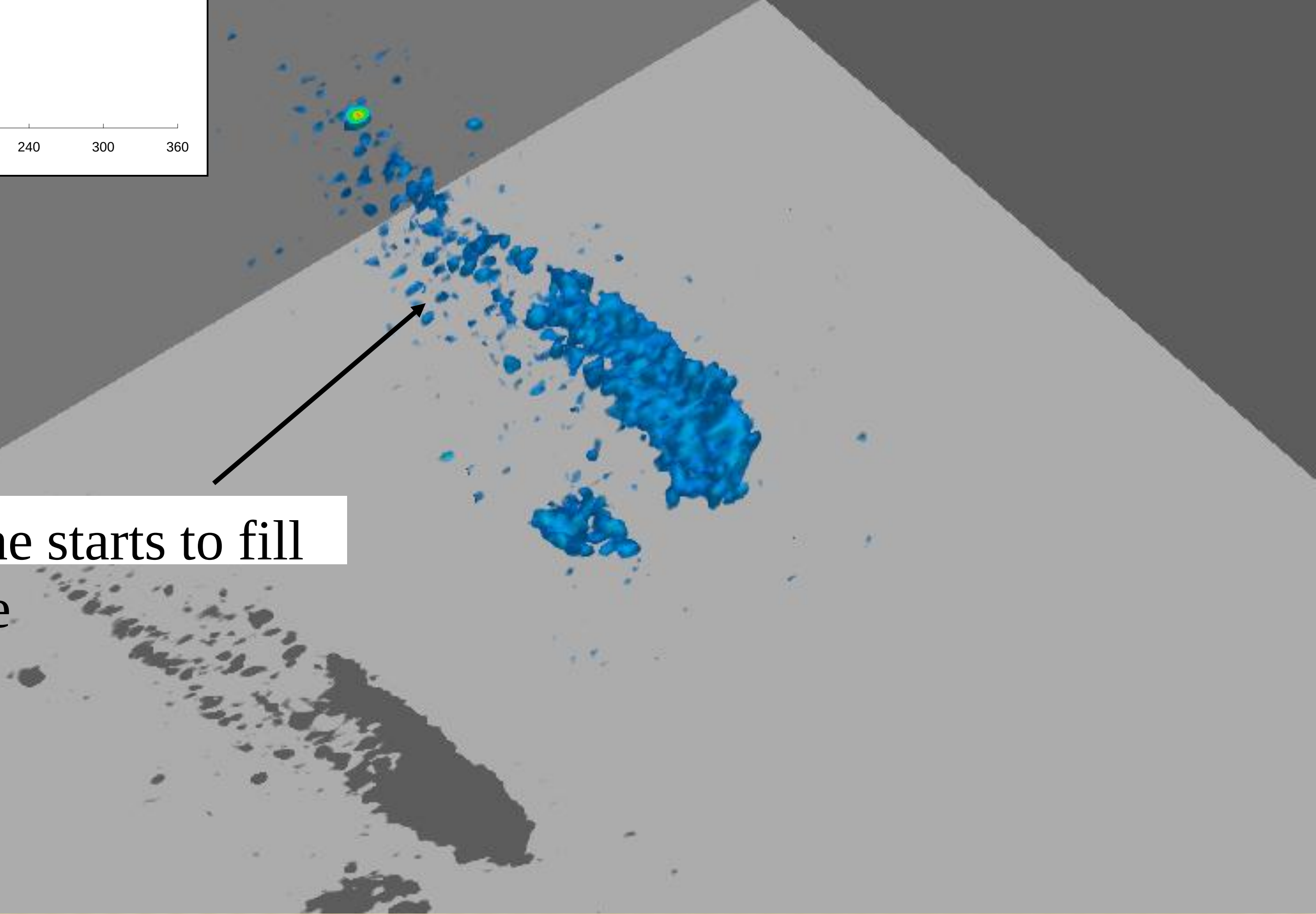
Time – 190hrs



Sample – BH-04

Time – 214hrs

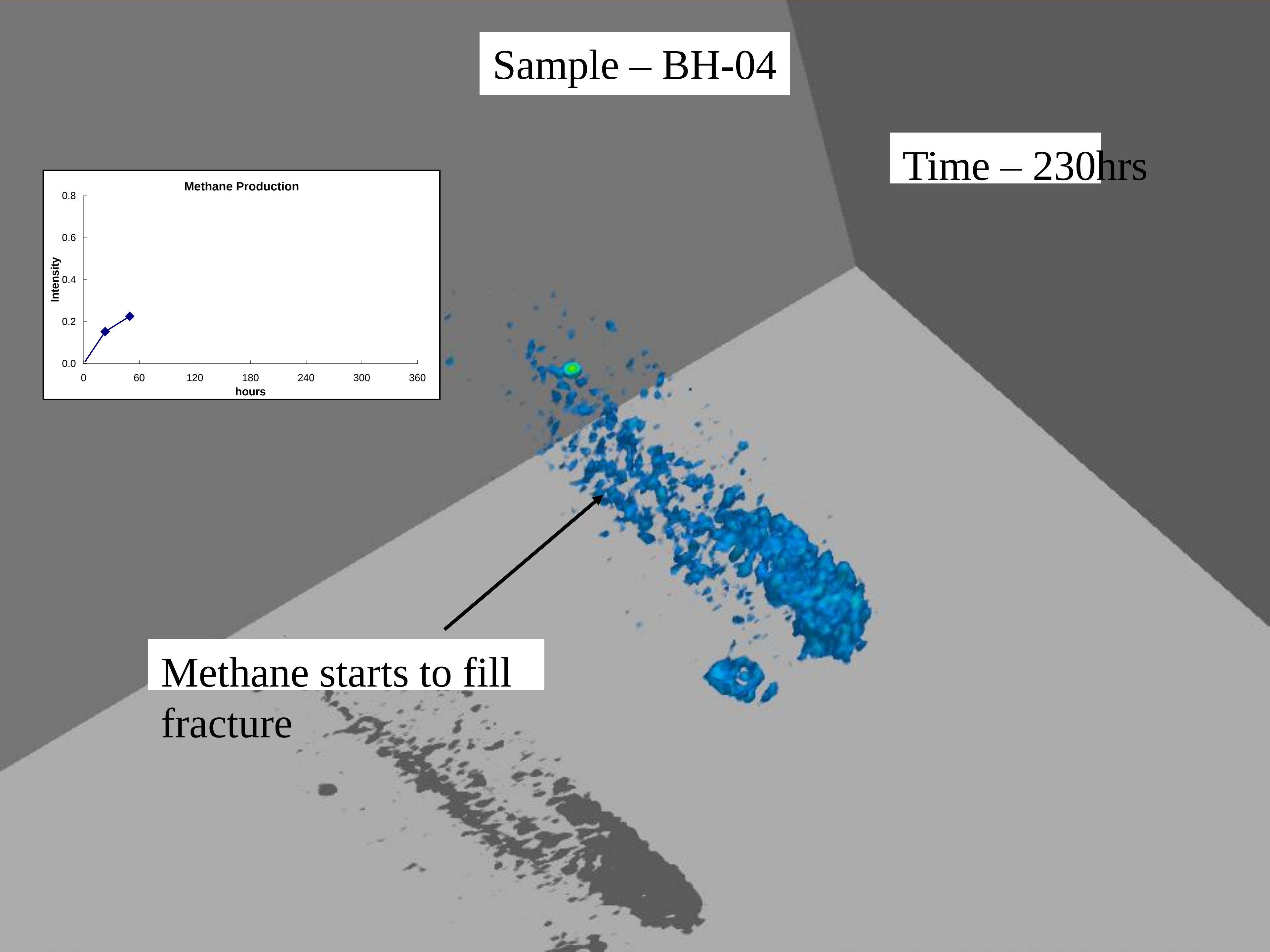




Methane starts to fill fracture

Sample – BH-04

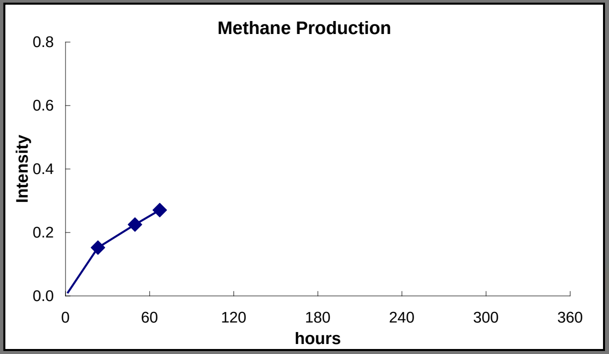
Time – 230hrs

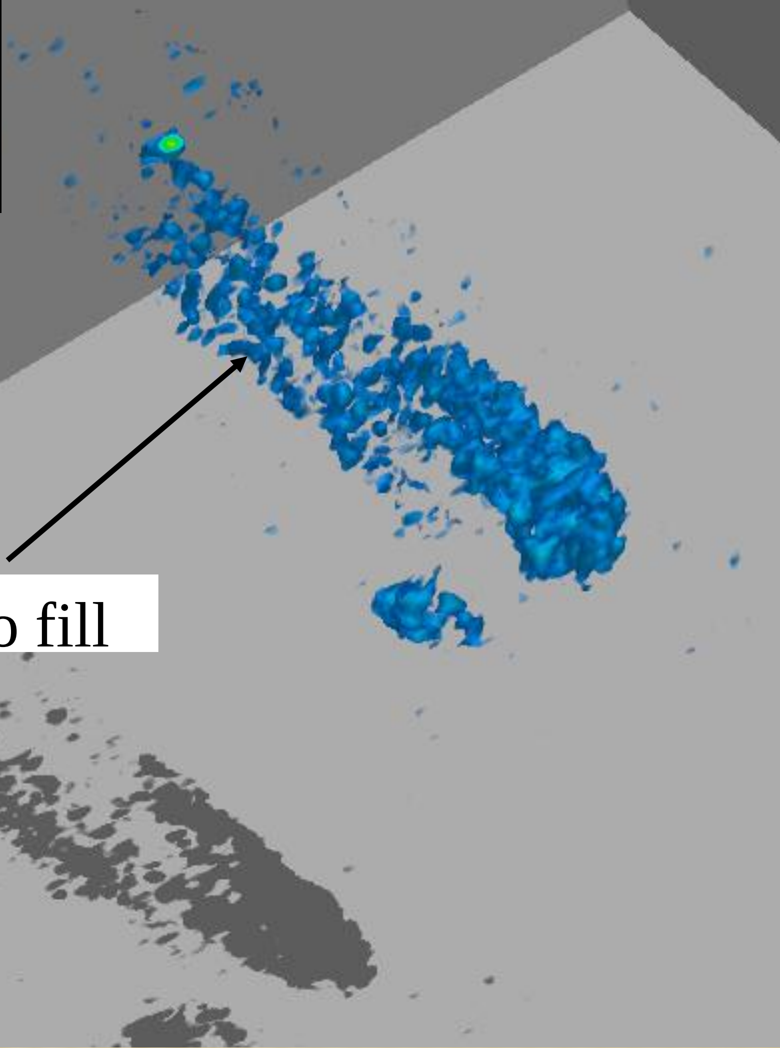


Methane starts to fill fracture

Sample – BH-04

Time – 238hrs

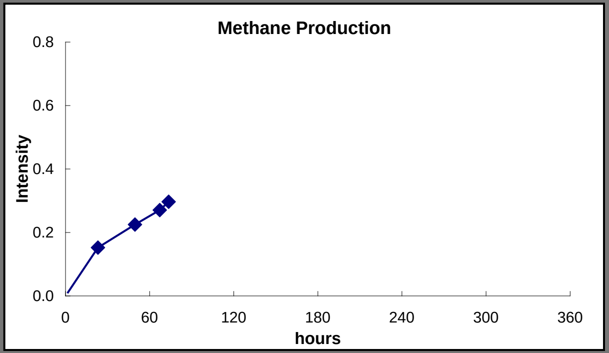


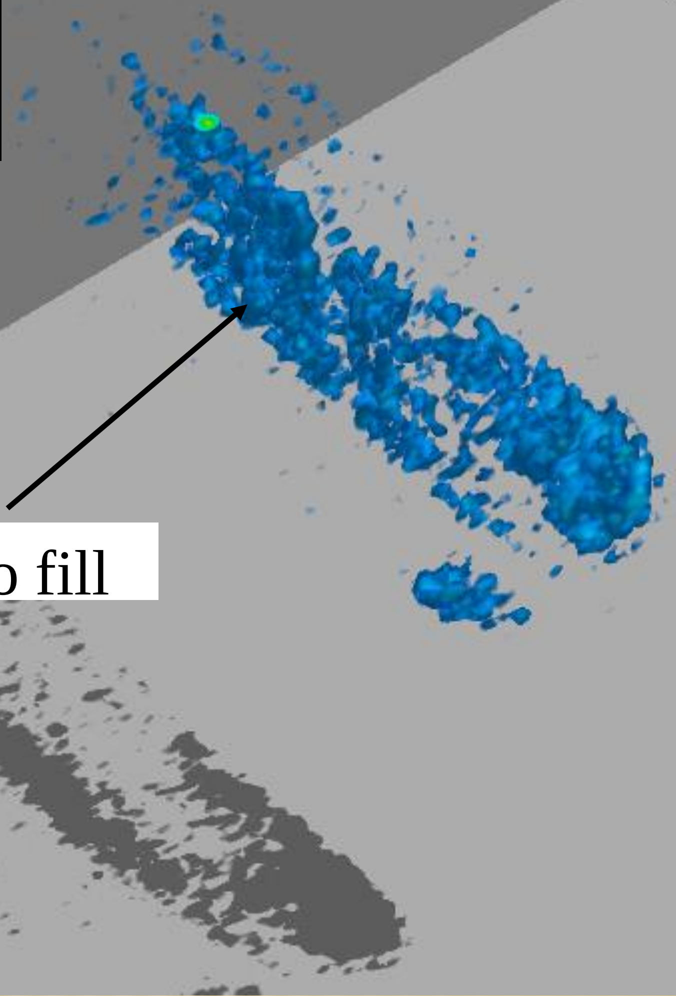


Methane starts to fill fracture

Sample – BH-04

Time – 253hrs

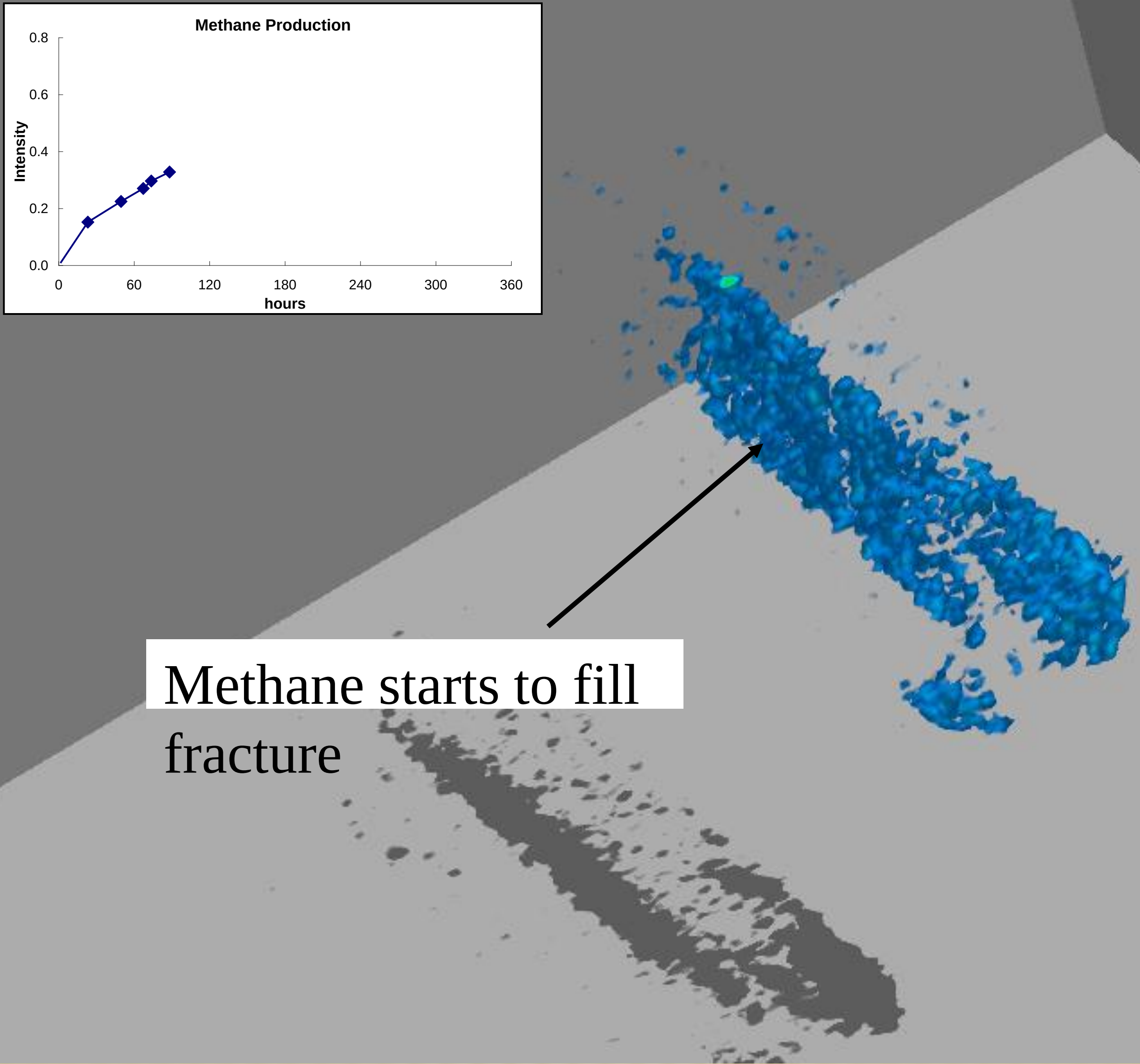




Methane starts to fill fracture

Sample – BH-04

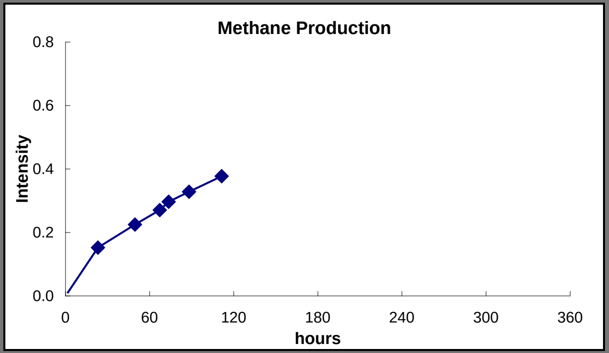
Time – 264hrs

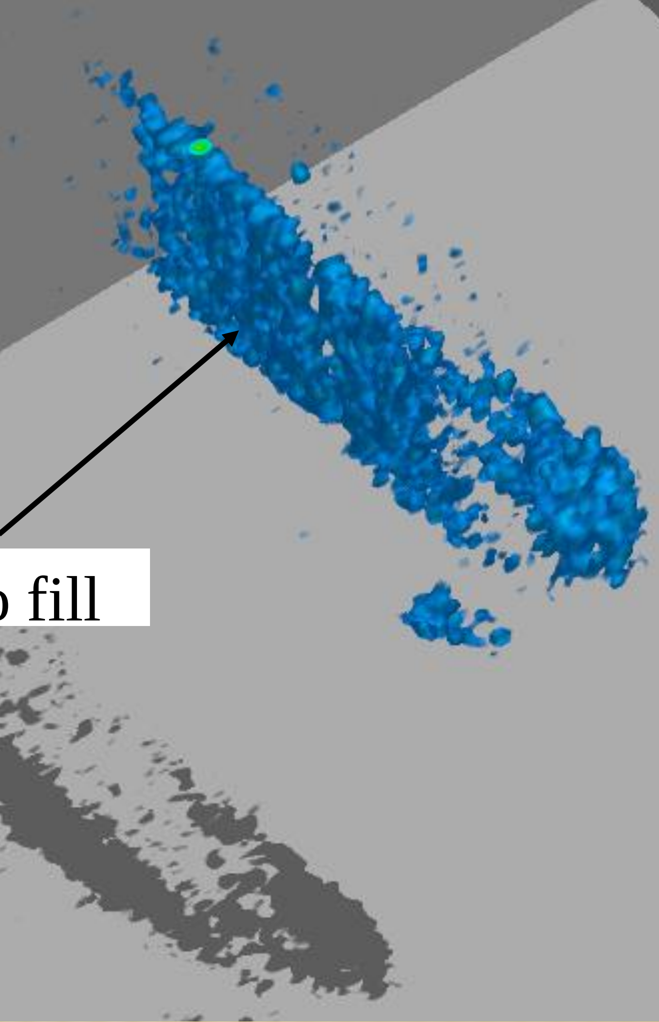


Methane starts to fill fracture

Sample – BH-04

Time – 278hrs

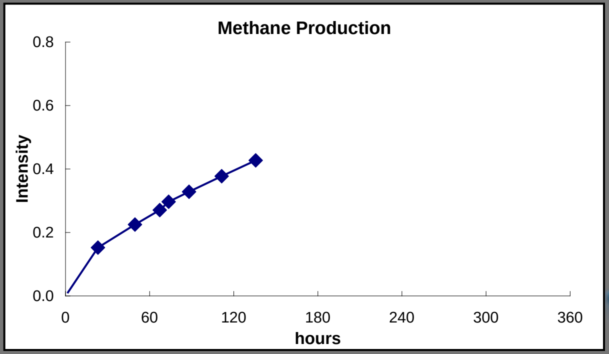


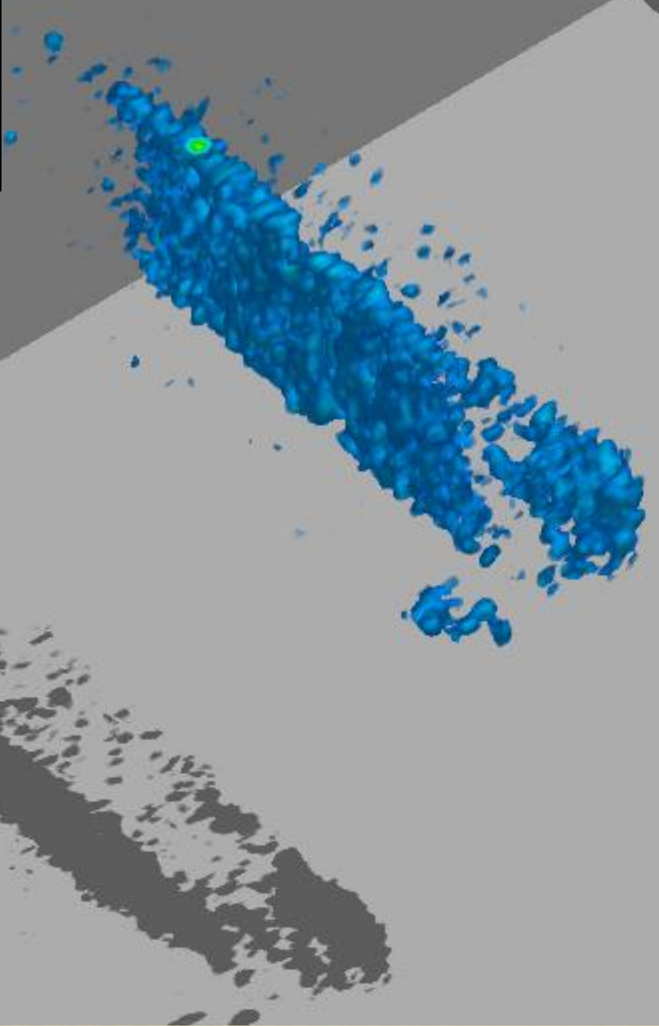


Methane starts to fill fracture

Sample – BH-04

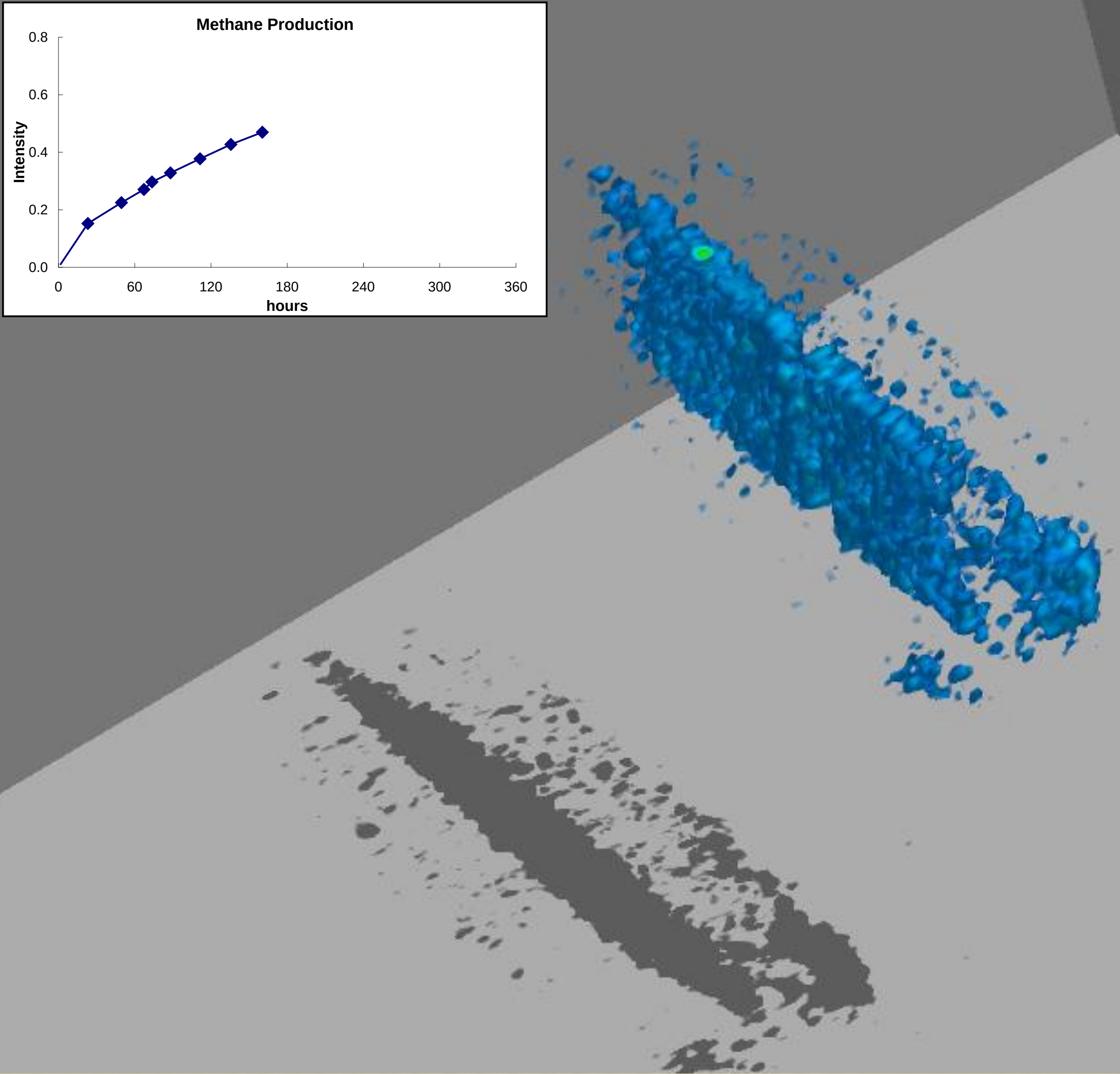
Time – 302hrs





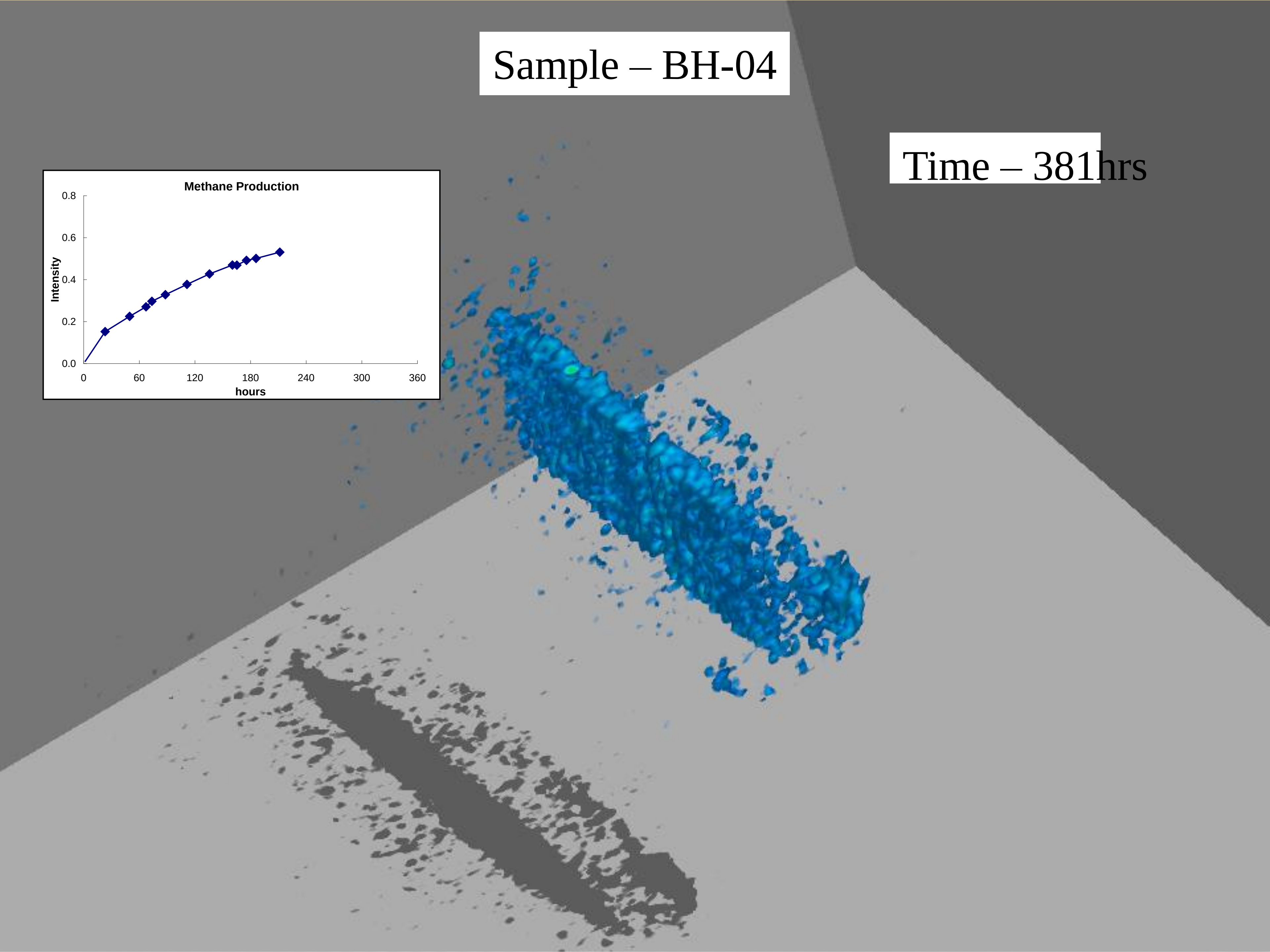
Sample – BH-04

Time – 327hrs



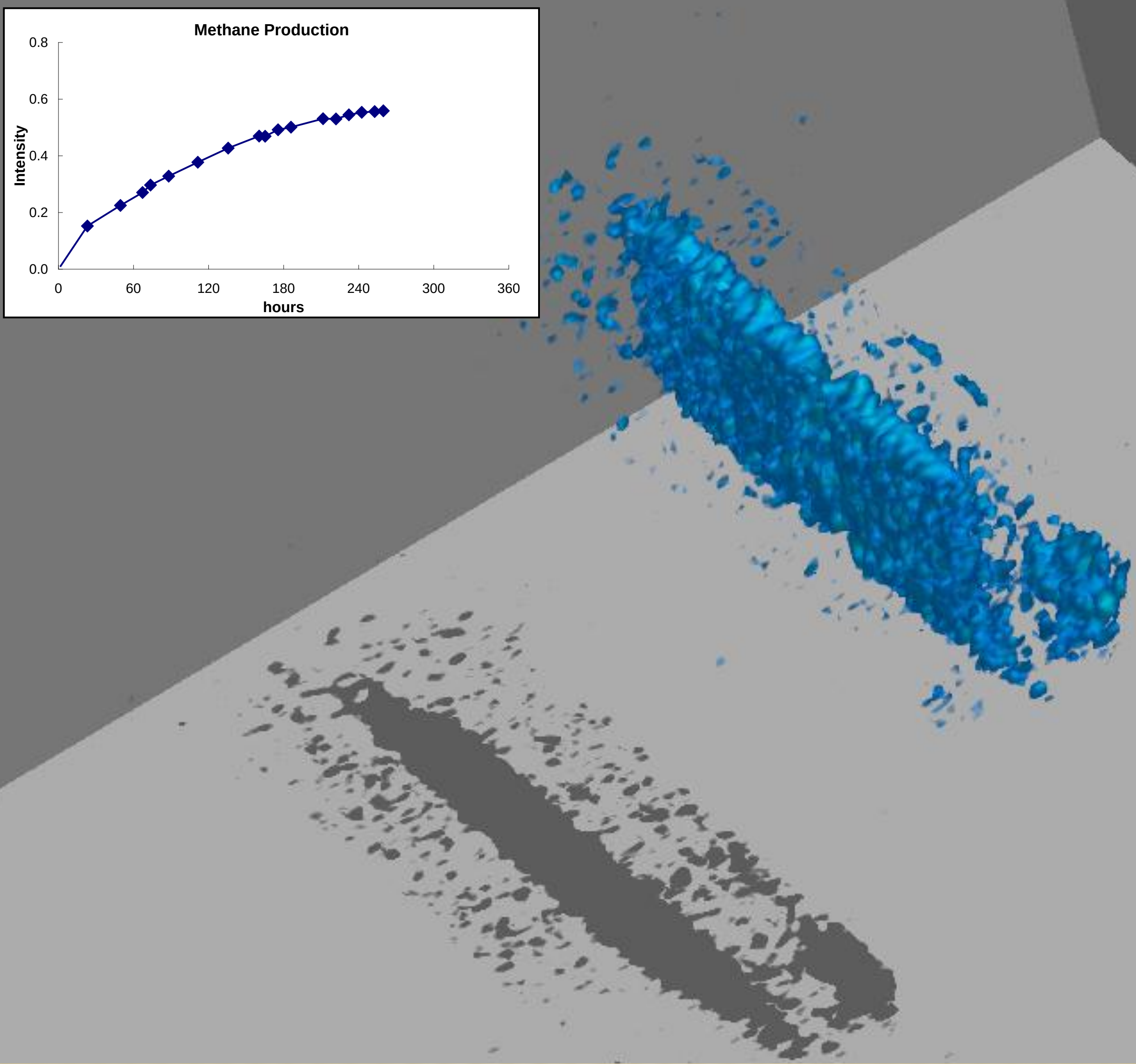
Sample – BH-04

Time – 381hrs



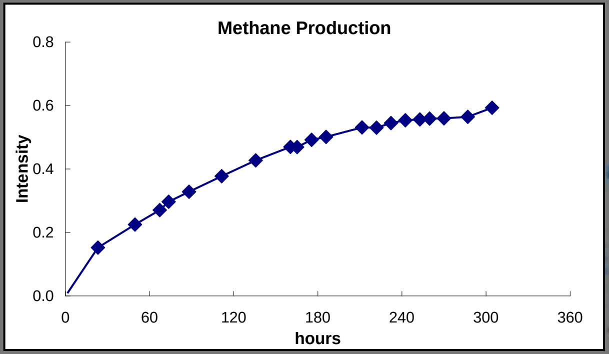
Sample – BH-04

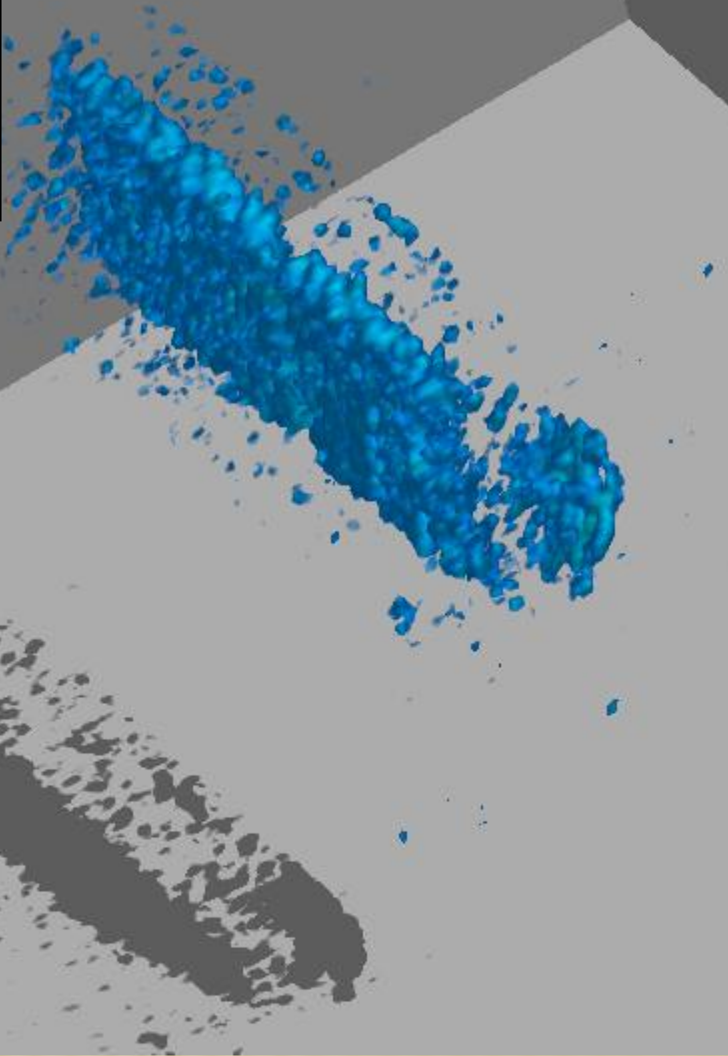
Time – 429hrs



Sample – BH-04

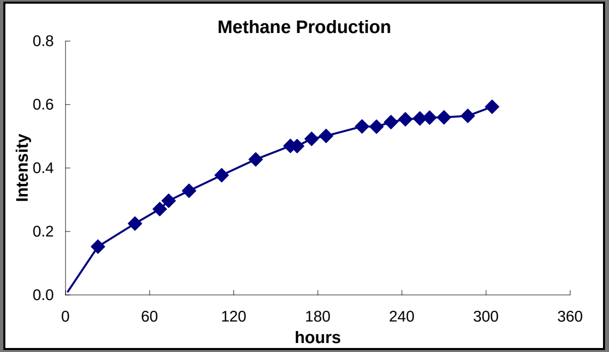
Time – 483hrs

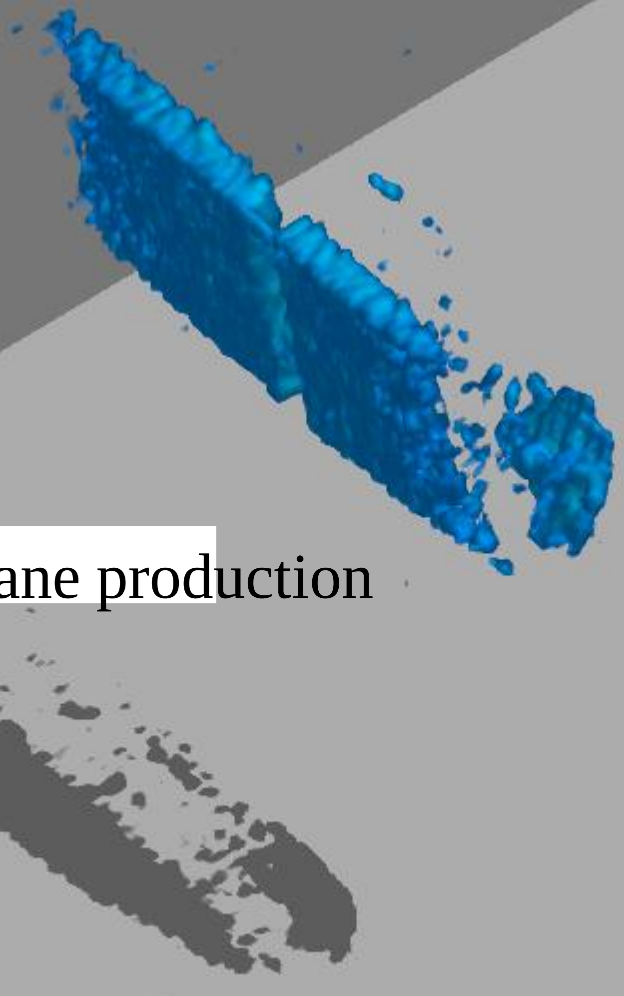




Sample – BH-04

Time – 484hrs

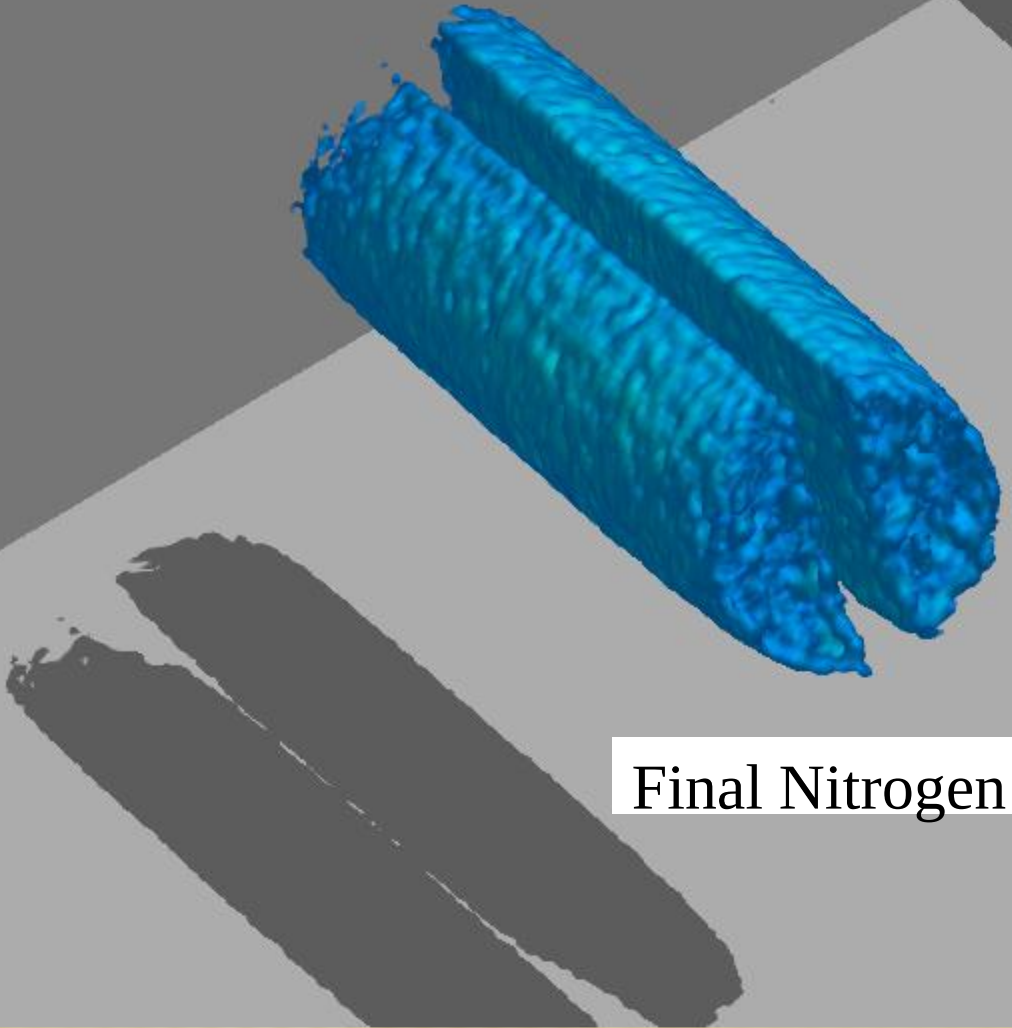




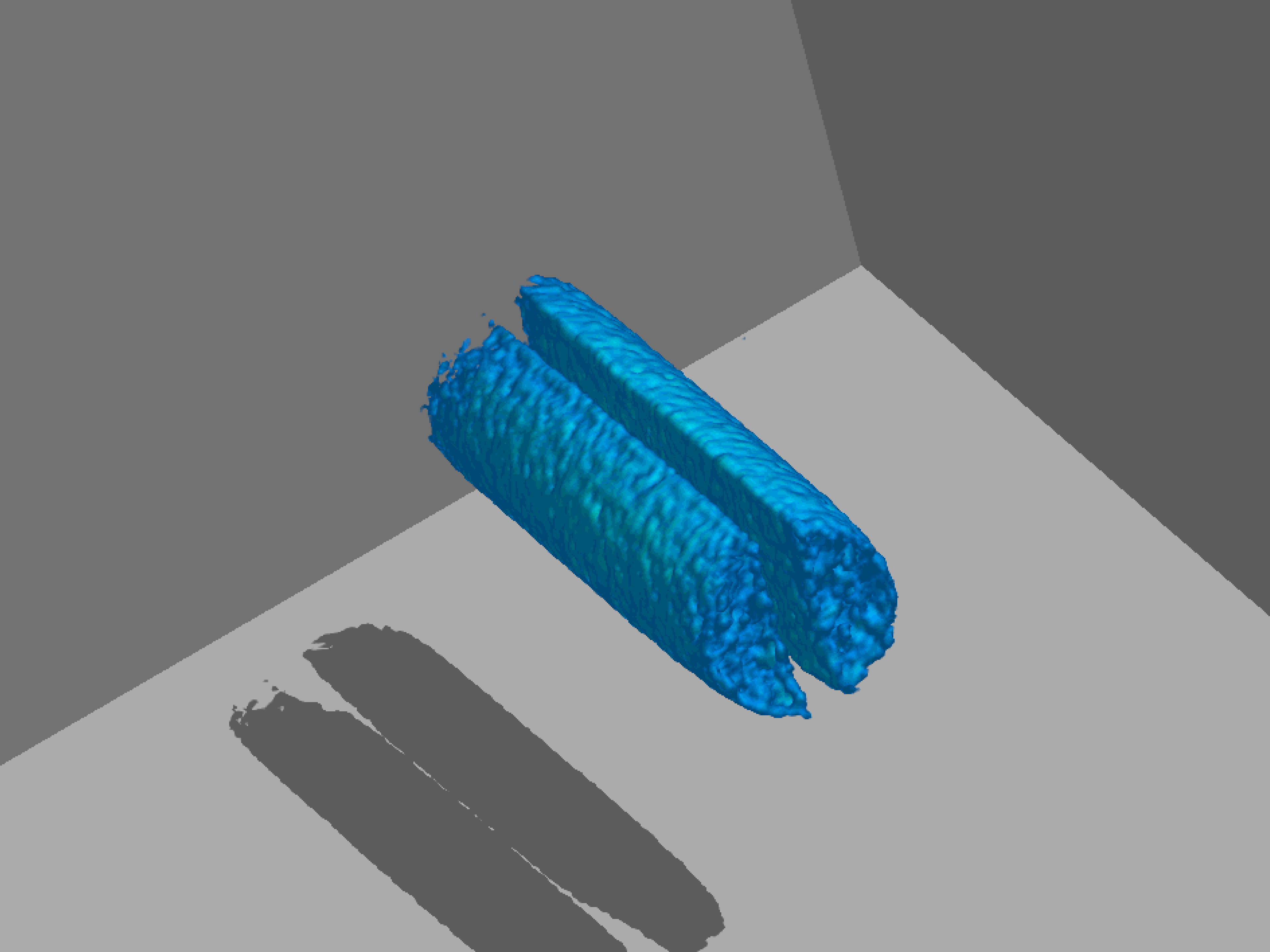
315hrs Methane production

Sample – BH-04

Time – 703hrs

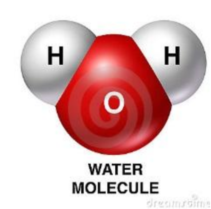


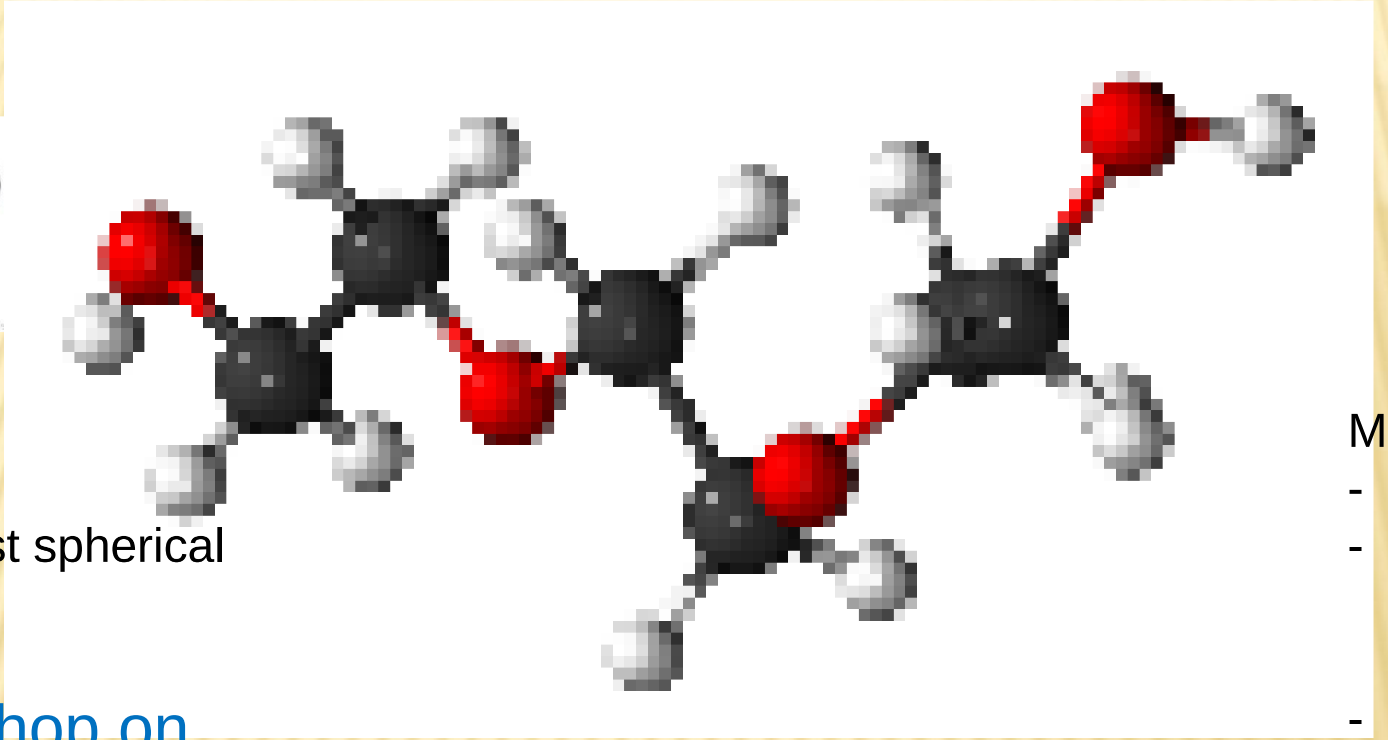
Final Nitrogen flush, core at room te

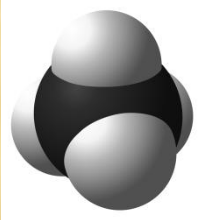


EXTRA: ADSORPTION

MAIN PARAMETERS IN MODELLING







Water:
- Polar
- Almost spherical
- Rigid

TEG:
- Polar
- Large
- Non-spherical
- MW more than 9 times that of water
- Flexible

Methane:
- non-polar
- Slightly larger than water
- Almost same mass as water
- Rigid

Workshop on adsorption for capture of water from methane
March 16th, 2016

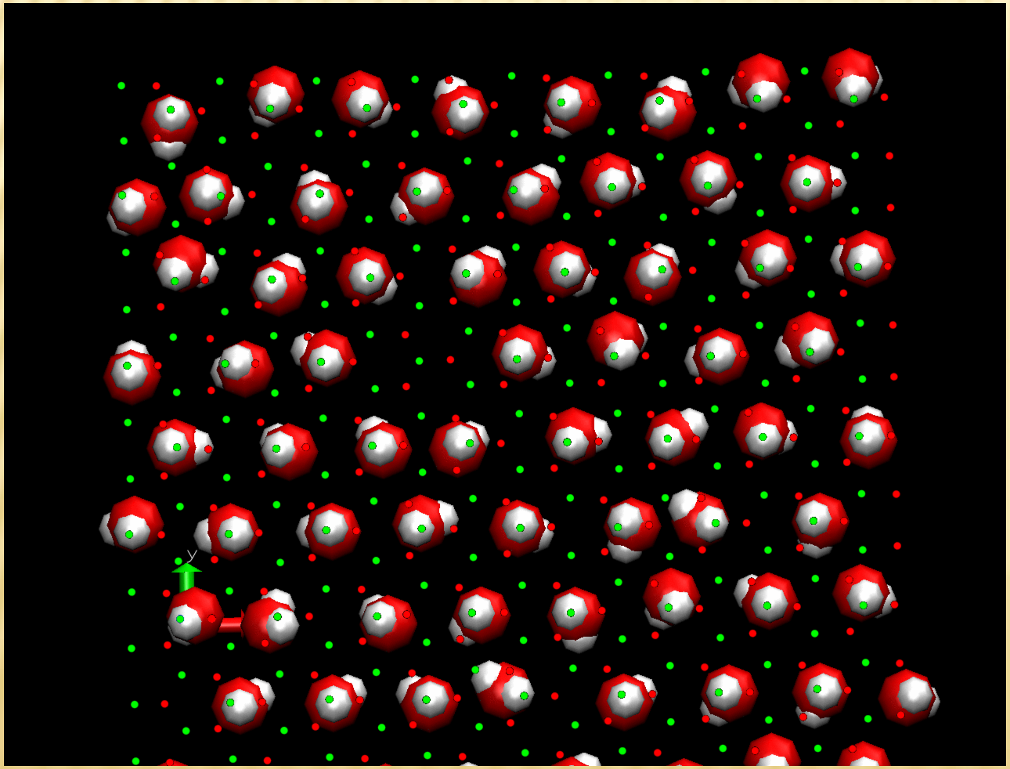
Professor Bjørn Kvamme
Department of Physics and Technology
University of Bergen
Bjorn.kvamme@uib.no

OUTLINE

- First a few general things related to clay based binding materials for Zeolite which has been the basis for our work so far in this project
- Some reflections and questions on papers from Prof. Wander L. Vasconcelos group
- Why are Zeolite based systems good and what characteristics do we need play on if we go for other materials ?
- Which types of experiments can support modelling ?

WHAT IS ADSORPTION AND ADSORBED PHASE?

- Accumulation of molecules ***on a solid surface*** with a ***unique concentration*** and a ***unique density*** and ***density profile*** is an ***adsorbed phase***.

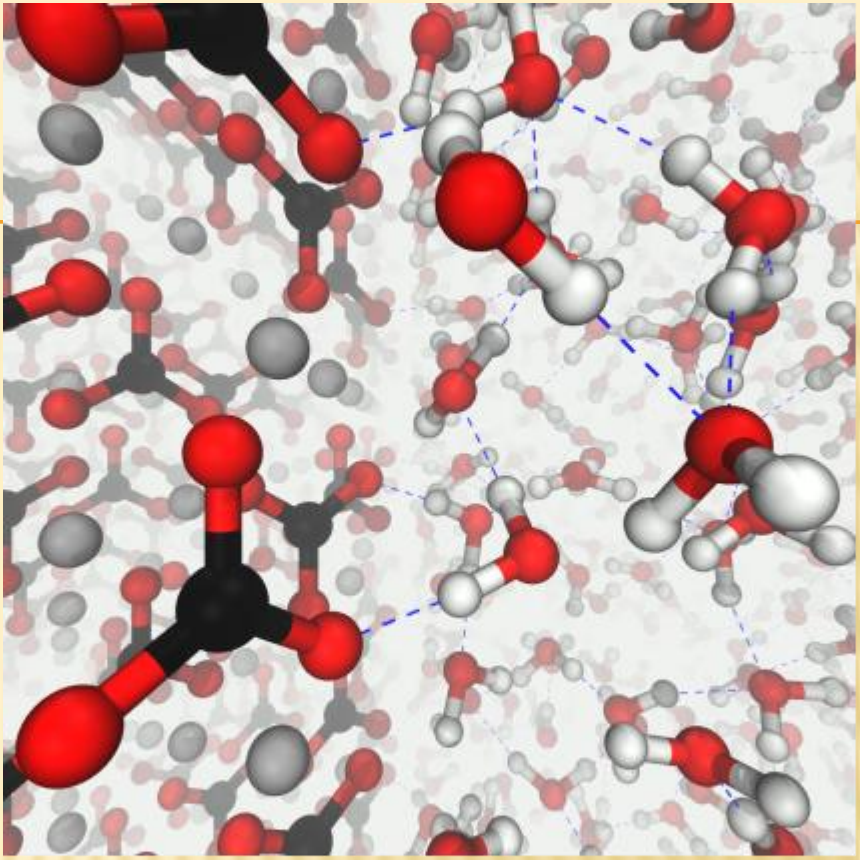


Water adsorbs onto Hematite due to favorable coulumbic interactions between partial charges on Hematite atoms (Fe2O3) and partial charges on water (due to dipole moment).

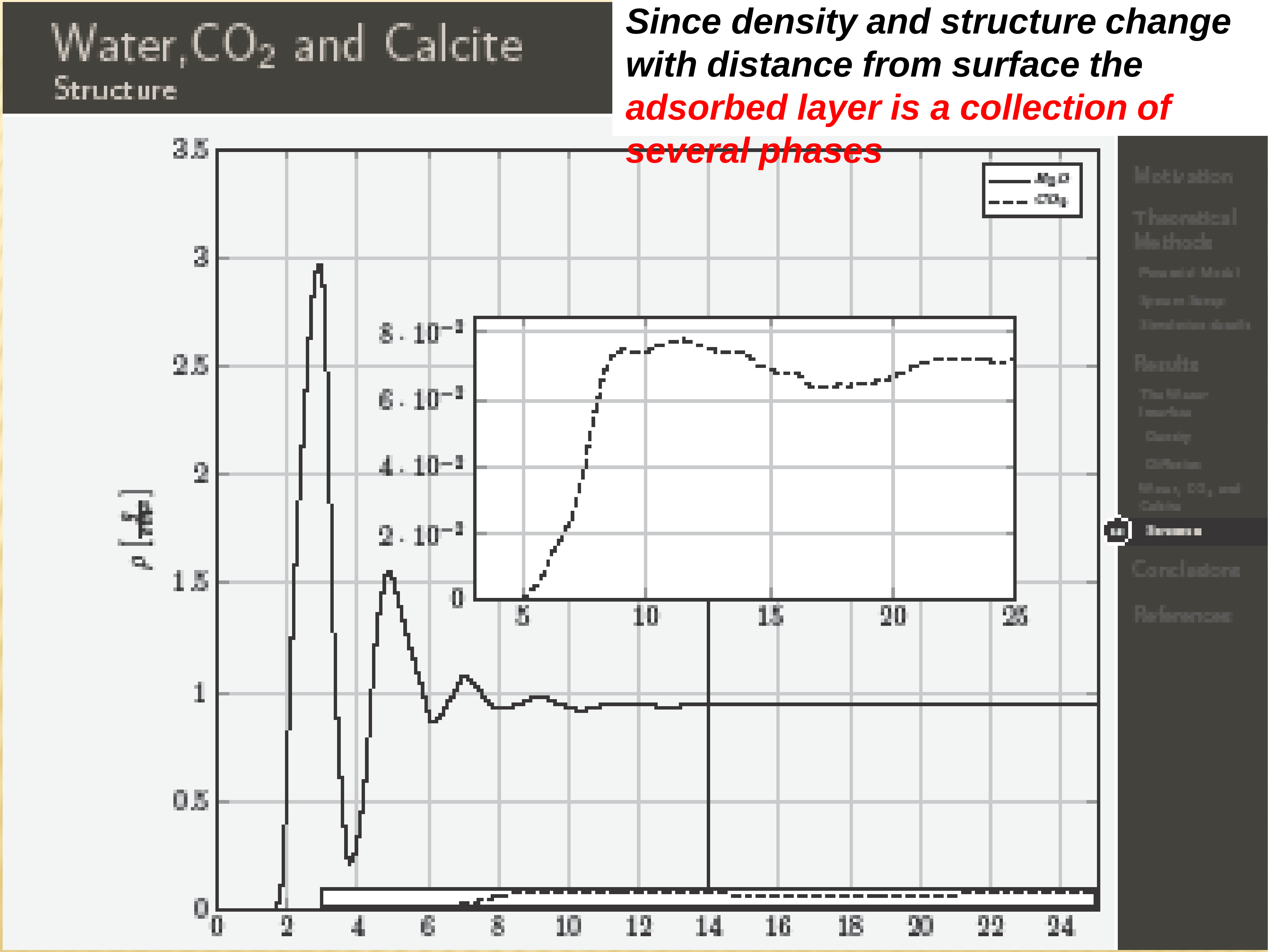
But at the same time water tries to retain as much water-water hydrogen bonds as possible. For this reason this is a 3D adsorption problem, The structuring of water perpendicular to the surface is

WHY IS THIS IMPORTANT TO KNOW?

- 3 D adsorption results in ***non-uniform adsorption***.
- In the deepest consequence of that it means that the ***adsorbed layer is not one phase*** but rather a ***continuous collection of phases*** with varying structure
- And put into practical words:
- 1) The ***chemical potential*** of adsorbed molecules ***vary*** with distance from the solid surface
- 2) And from the above: ***equilibrium cannot be achieved*** since there are many adsorbed phases



Water adsorption on Calcite, and several other mineral surfaces, is highly non uniform. Corresponding chemical potential as function of distance from the surface is very complex, with two pronounced minima and a maximum in between



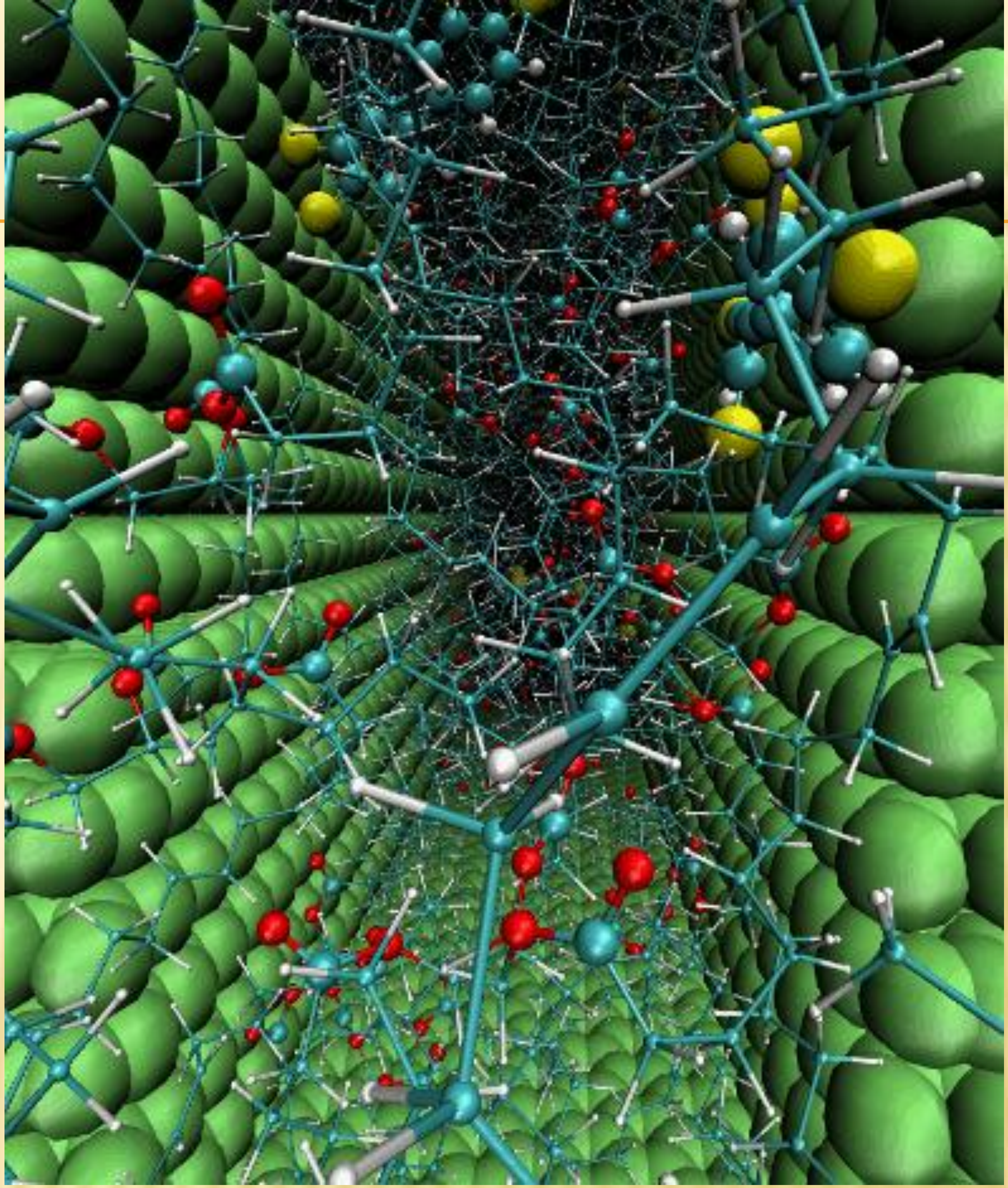
Water, CO_2 and Calcite

Structure

Since density and structure change with distance from surface the adsorbed layer is a collection of several phases

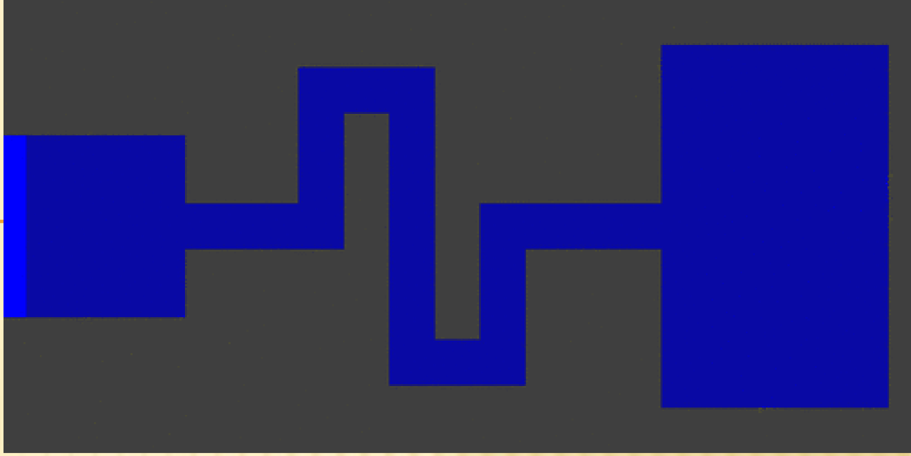
CONSEQUENCES FOR MODELING

- Adsorption of water from a dilute gas requires strong interactions and long range impact (water structuring that facilitates more than mono layer)
- Cavity trapping of water as in Zeolite structures facilitate high capacity
- Binding material for Zeolite structures also adsorbs water



In active coal as utilized for adsorption of PCB and dioxines both geometry (slit pores of 2 – 5 nm) and atomistic interactions play a role. Jensen, B., Kvamme, B., Kuznetsova, T. & Oterhals, Å***. 2011, "Molecular dynamics study of selective adsorption of PCB on activated carbon.", Fluid Phase Equilibria, 2011, 307, 58 - 65***

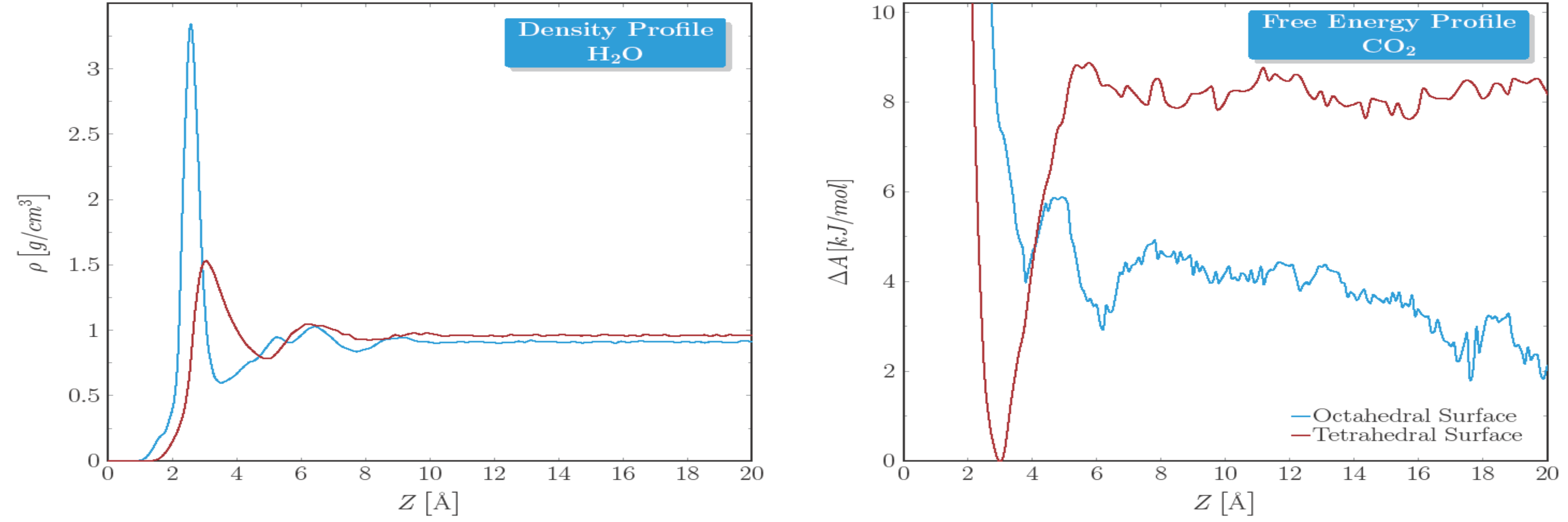
THE EXAMPLE IS NOT TOTALLY RANDOM



- As we all know ***pore sizes and shapes*** (average diameter and depth) are some of the features that ***can be used*** in design of adsorption structures
- ***Mass transport*** in and out from these pores, as well as ***molecular motions*** inside the pores can be modelled using molecular dynamics and Phase Field Theory (PFT)
- Knudsen diffusion in pores is a classical simplified relationship for large pores but ***using pore size/geometry can involve substantially smaller pores***.

Examples are from PFT modeling of crystallization in confined structures (neutral surfaces). Note that nucleation takes place in corners and geometric features that involve molecule trappings

KAOLINITE IS A TYPICAL NORWEGIAN CLAY MINERAL WHICH MIGHT BE USED FOR BINDING ZEOLITE



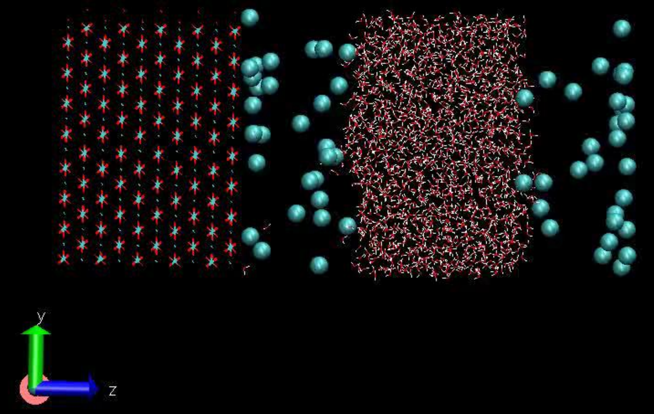
For the tetrahedral cutting ***direct adsorption of CO2*** is feasible (see free energy change for CO2 on right figure) before first maximum for water while ***secondary adsorption*** in water density minimums might occur in both cases. Figures from Leirvik, Kvamme & Kuznetsova [1]. Methane is smaller but practically non-polar so it remains to be seen if methane would adsorb directly onto the binding material directly.

Another important aspect of these results is the potentially ***strong adsorption of water on the binding material***, which needs quantification in order to evaluate whether this water adsorption is too strong compared to a ***desired superior adsorption of water in the Zeolite cavities***.

EXPERIMENTAL NEEDS AS SUPPORT FOR MODELING

- Adsorption of water from a gas phase dominated by methane is another story

Methane on Calcite and a water slabe at 264 K



Critical questions:

- 2 D adsorption ?
- Monolayer ?

If yes on both then it is reasonable to assume ***equilibrium*** model and the following steps:

- Identify ***adsorption sites***
- ***Quantify*** adsorption sites per unit area
- Estimate ***chemical potential*** for ***water*** and ***possible pollutant (TEG)***

ADSORPTION ON BINDING MATERIAL IS LIKELY A 2D PROBLEM

THERE ARE MANY ALTERNATIVES. I UTILIZED THIS APPROACH TO EVALUATE RELATIVE ADSORPTION OF CO2 FROM FLUE GAS ON LIQUID WATER 16 YEARS AGO

- The reason that this approach also might be an adequate choice is the dominance of non-polar methane in the gas above which has three implications

- the 2D correlations in the canonical partitition function perpendicular to the adsorption plane is approximately orthonormal to the canonical partition function in the adsorption direction

- The 2D equation of state needed for the perpendicular part of the chemical potential can be well represented by a non-polar equation of state

- Evaluation of the 1D integral over the Boltzmann function of the various adsorption molecules and the adsorption surface is simple

DETAILS ARE NOT VERY IMPORTANT IN THIS CONTEXT BUT AVAILABLE IN KVAMME [1, 2]

$$\mu_i^{gas} = \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_i N) - \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

$$= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_i N) - \frac{1}{\beta}\left(\frac{\partial \ln Q^{2D}}{\partial N_i}\right)_{T,V,N_{j\neq i}} - \frac{1}{\beta}\ln Q_i^{1D}$$

$$= \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(x_i N) - \frac{1}{\beta}(\beta\mu_i^{2D}) - \frac{1}{\beta}\ln Q_i^{1D}$$

$$\mu_i^{gas} = \frac{1}{\beta}\ln(\beta\Lambda_i^3) + \frac{1}{\beta}\ln(y_i \varphi_i^{gas} P)$$

1) Bjørn Kvamme, *“Feasibility of simultaneous CO2 storage and CH4 production from natural gas hydrate using mixtures of CO2 and N2”, 2015, Canadian Journal of Chemistry*, 2015, 93(8): 897-905

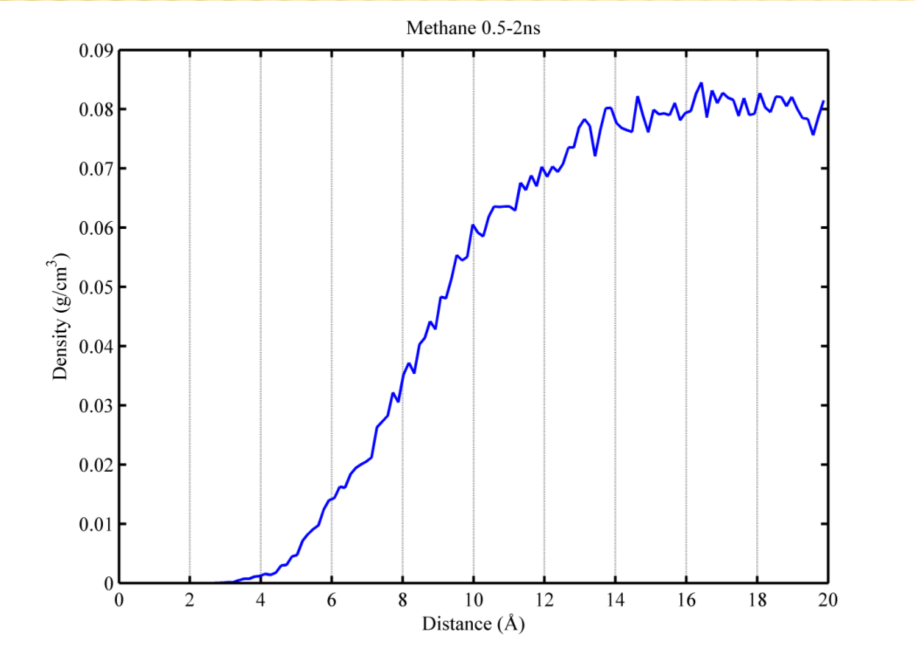
2) Bjørn Kvamme,” Thermodynamic limitations of the CO2/N2 mixture injected into CH4 hydrate in the Ignik Sikumi field trial, 2016, J. Chem. Eng. Data, in press

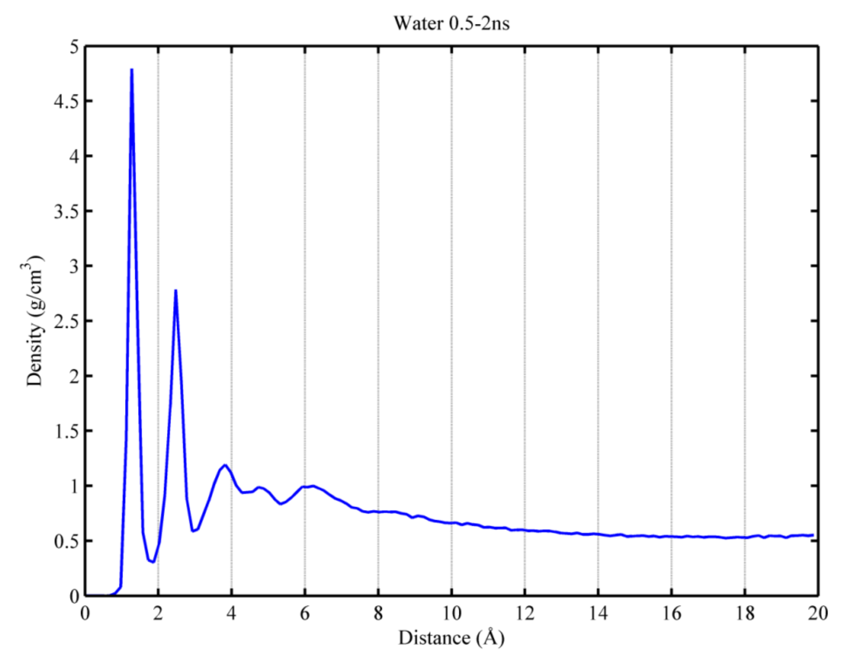
FOR BINDING MATERIAL

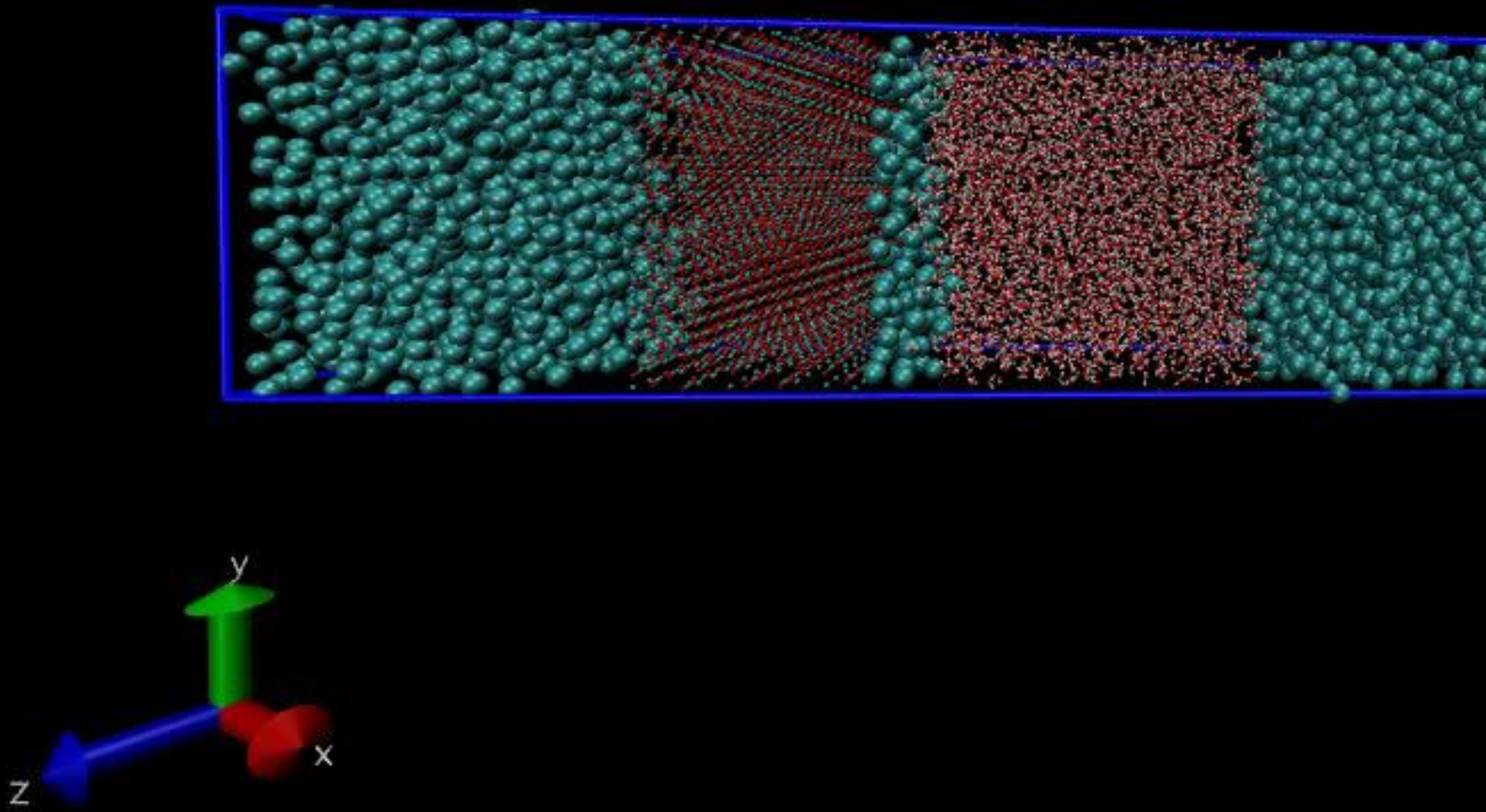
NPT_liquid_methane_1.mpg

The results below are densities of methane and water at 150 bar but starting with methane liquid density. Movie at next slide

- May not be worthwhile to spend experimental efforts before more detailed Molecular modeling studies of methane containing water as well as TEG has been conducted.
- As with Calcite ***water at liquid densities*** will displace original methane at surface
- But despite the non-polar nature of methane the high CH4 concentration might reduce losses of H2O to outside binding material






y
x
z

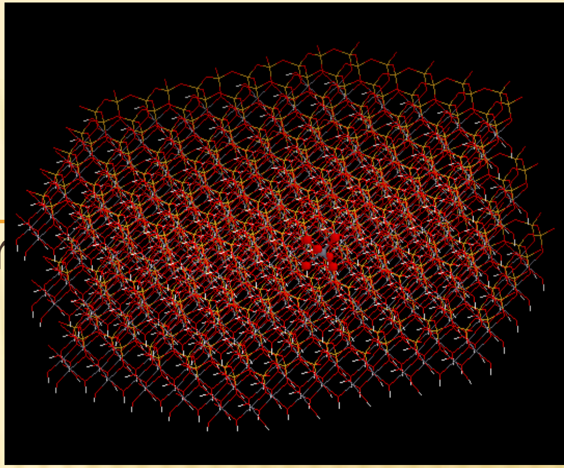
SUMMARY – BINDING MATERIAL

- If Zeolite is still the focus for adsorption then the binding material should be exposed to some further theoretical studies with focus on:

  - selective adsorption for realistic concentrations of water and TEG in CH_4. Molefractions of H_2O of 0,00001 is feasible with our graphical computers

  - if selective water adsorption is still feasible for low concentrations – how will this be affected by fluid mechanics ?

  - if selective adsorption will also «survive» hydrodynamics impact of a large amount of gas solvent then there is a need for re-evaluation of a 2 D adsorption assumption



Top: Kaolinite (a clay) reacts over to Dawsonite (below) when exposed to CO2

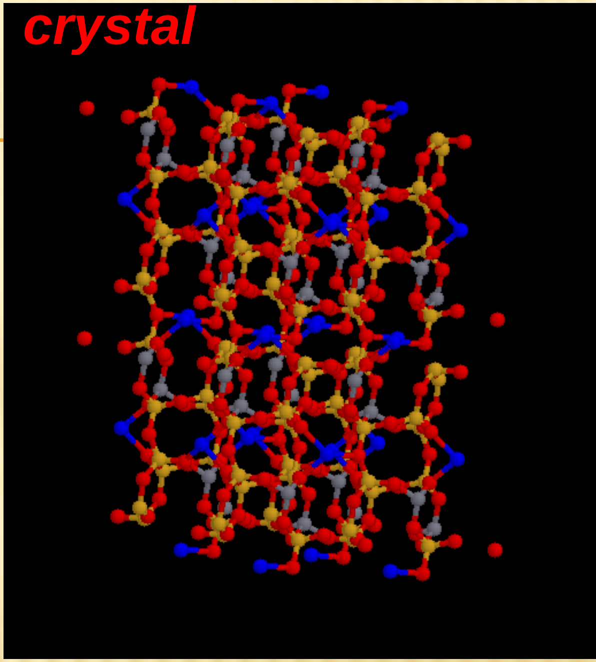
We purchased most available Dawsonite on e-bay from collectors to investigate if Dawsonte could be formed during long

Hellevang, H , Declercq, J , Kvamme, B , Aagaard, P., 2010. Applied Geochemistry 25: 1575-1586

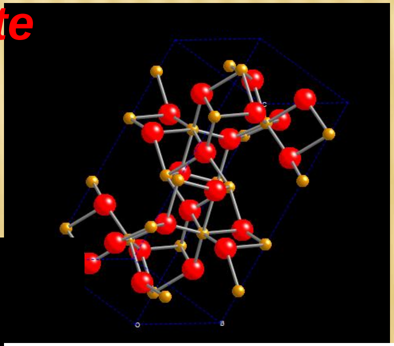
BINDING MATERIAL CONTINUED

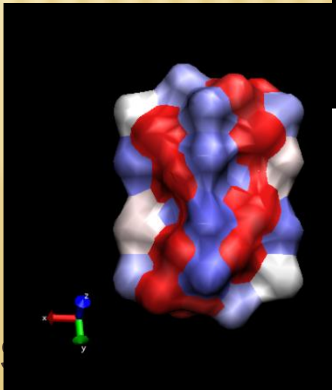
- What might ne even more important to investigate first is binding material adsorption of pollutants from a dilute methane solution.
- It will be desirable that the binding materal adsorbs TEG and other glycols better than adsorption of the same on Zeolite openings.
- It is also desirable that the adsorption energy is weak enough compared to flow induced stress so that adsorbed glycols releeease again. Algorithms for calculating this competition is yet being implemented in other projects.
- But again – theoretical investigations are less expensive at first – and can assist in directing possible experiment

Albite crystal



A small piece of Hematite





And the Corresponding surface charge distribution

(from DFT in

10 waters in 2038 methane is a very high water concentration compard to water saturated methane at 100 bar. Water diluted in the gas struggle to totally outcompete methane in adsorption. Buy still manages after 2 ns