Hindered Transport and CO_2 Huff-n-Puff in Niobrara Samples

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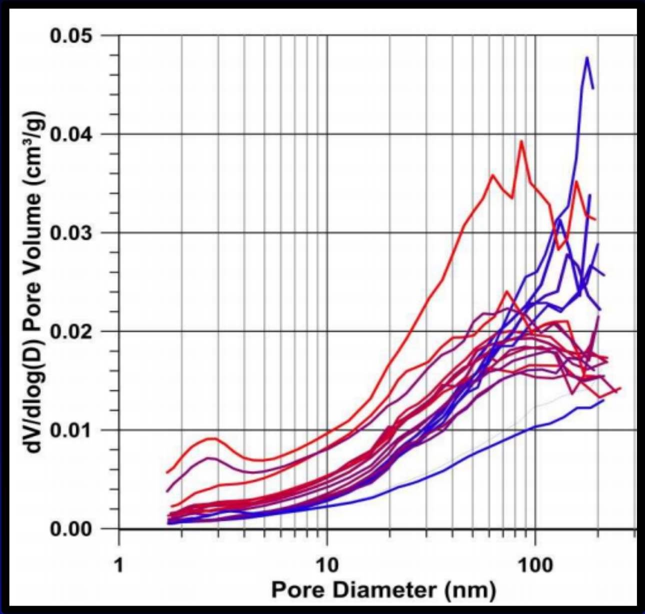
Outline

- Problem Statement
- Objective
- Results & Discussion
  - Filtration Test
  - CO_2 Huff Puff Test
- Conclusion
- Future Work

Problem Statement

- Pores and pore throats of Niobrara samples might have comparable sizes with hydrocarbon molecules.

—	size (diameter), nm
pore, Niobrara	1 -- >100
paraffins	0.4 -- 1
aromatics	1 -- 3



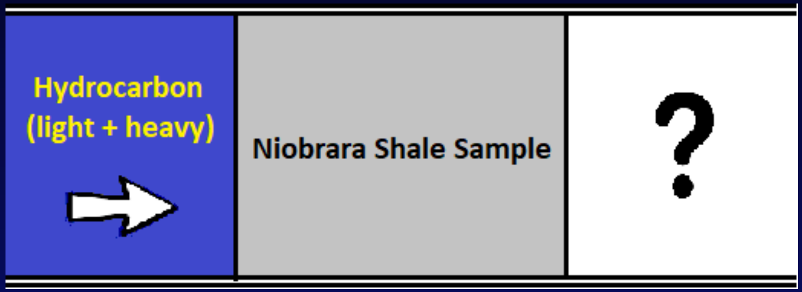
pore size distribution of Niobrara samples

- Field Observation

  Hunt and Jameson (1956), Brenneman and Smith (1958), and Hunt (1961) all noted that most of the source oils are composed of more heavy components when they are compared with their reservoir oils.

Problem Statement

- Niobrara sample might potentially behave as a semi-permeable membrane.
- When a hydrocarbon mixture flow through Niobrara samples, what will be produced?



Hypothesis:

light components are able to flow through.

heavy components might be restricted or hindered.

size exclusion, mobility difference, …, etc. ?

Possible result:

more light components, less heavy components will be produced.

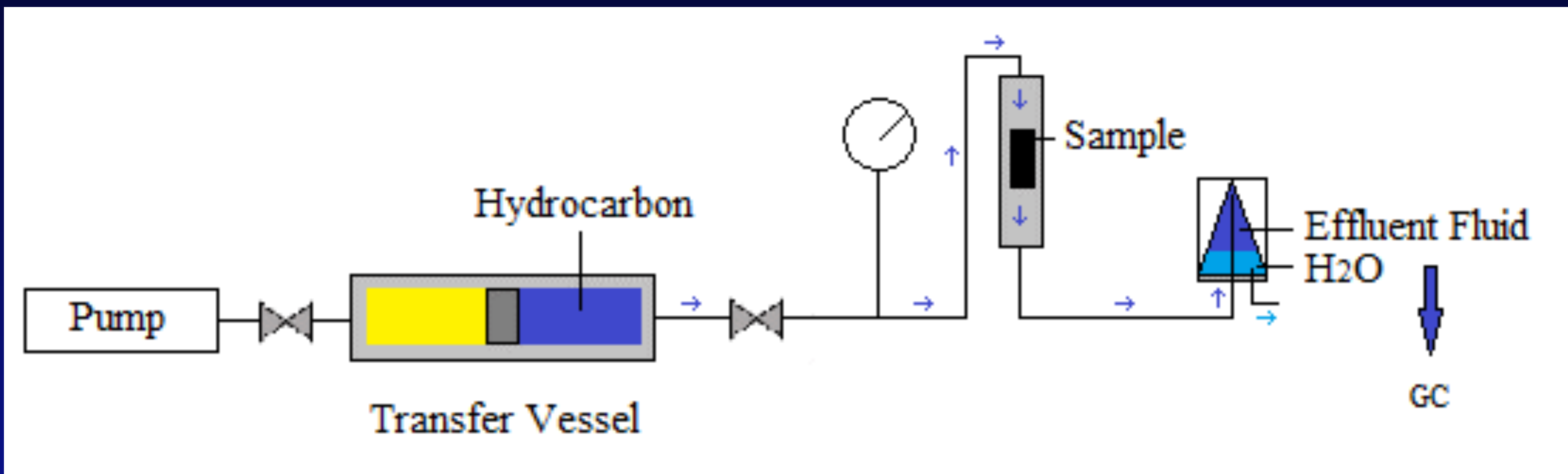
Objective

- Explore the membrane behavior or hindrance effect of Niobrara sample on hydrocarbon transport through experiments.

- Investigate factors might affect the compositional change of hydrocarbon mixtures flowing through Niobrara sample.
  - adsorption
  - hydrocarbon species
  - pressure gradient
  - temperature
  - …

Experimental Setup

- **Schematic Diagram**



Experimental Setup

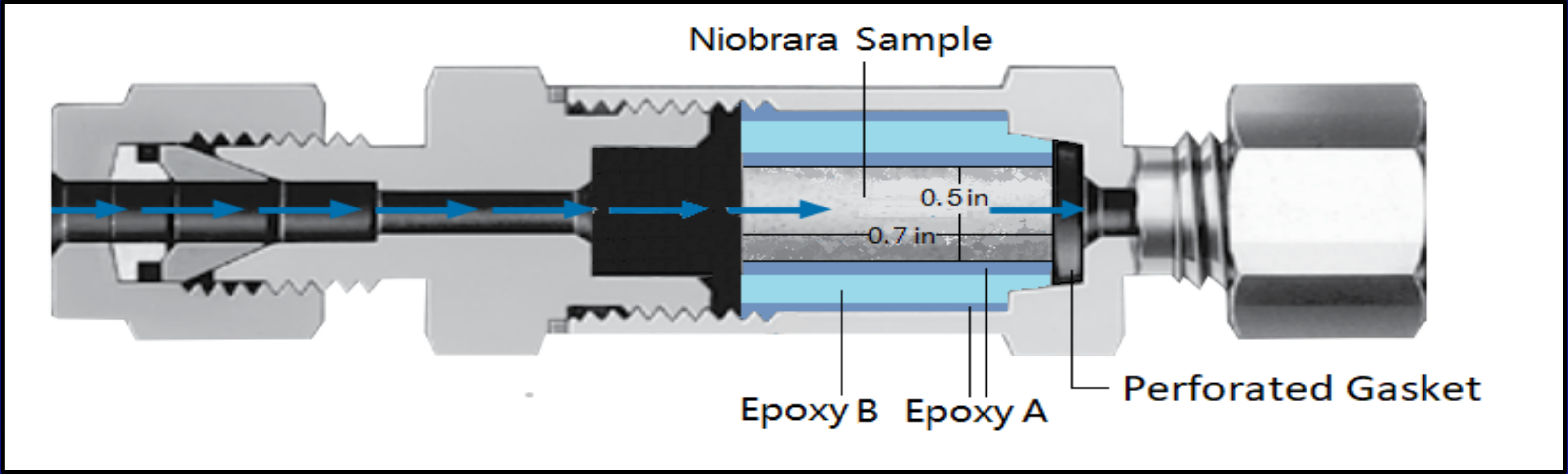
- **Gas Chromatograph**

  Agilent 7890B

- **Mini Core Holder**

  Modified from In-Line Filter

  Working Pressure: 0-2500 psi



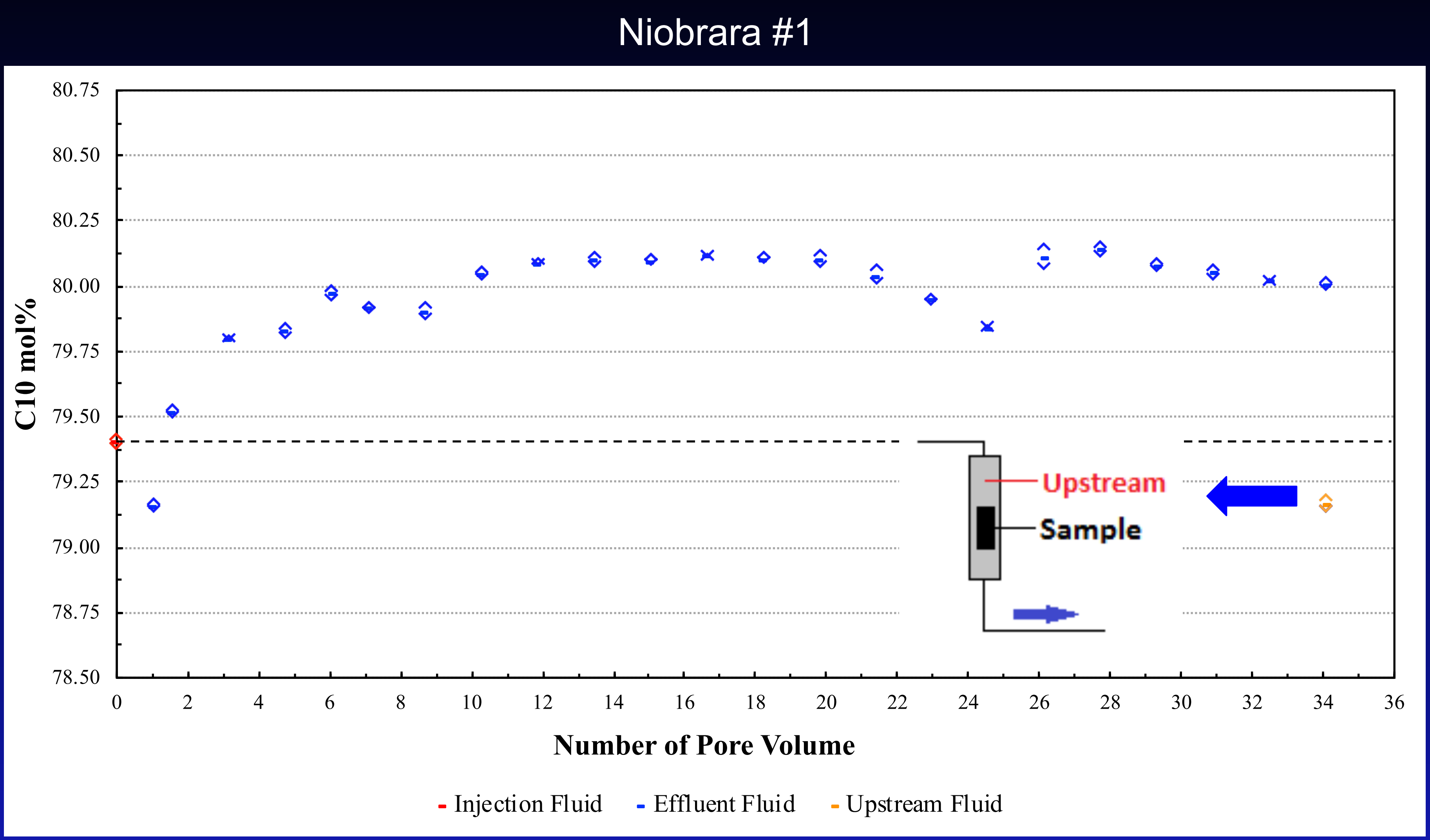
Filtration Test

- **Objective:** Does fluid composition change after flowing through Niobrara sample?
- **Injection Fluid:** mixture of C_{10} and C_{17}
- **Rock Samples:**

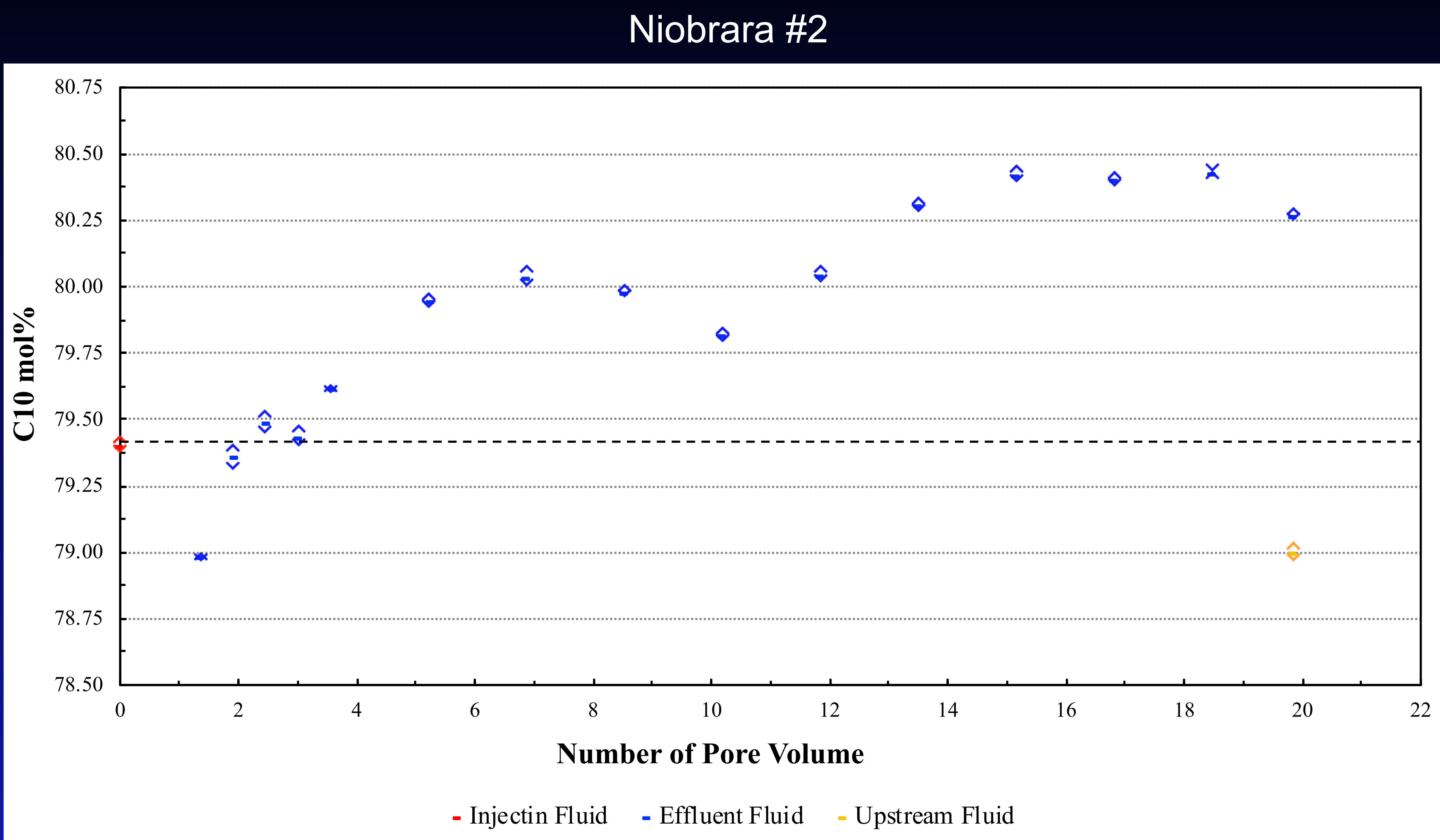
Sample #	Length (in)	Diameter (in)	Pore Volume* (cc)
Niobrara #1	0.735	0.5	0.189
Niobrara #2	0.704	0.5	0.181
Niobrara #3	0.741	0.5	0.191
Niobrara #4	0.688	0.5	0.177
Niobrara #5	0.716	0.5	0.184
Niobrara #6	0.731	0.5	0.188
Berea Sandstone #1	0.738	0.5	0.475
Berea Sandstone #2	0.733	0.5	0.472
Berea Sandstone #3	0.705	0.5	0.454

*Pore volumes are calculated based on an estimated porosity of 8% for Niobrara Shale and 20% for Berea Sandstone samples.

Result & Discussion



Result & Discussion



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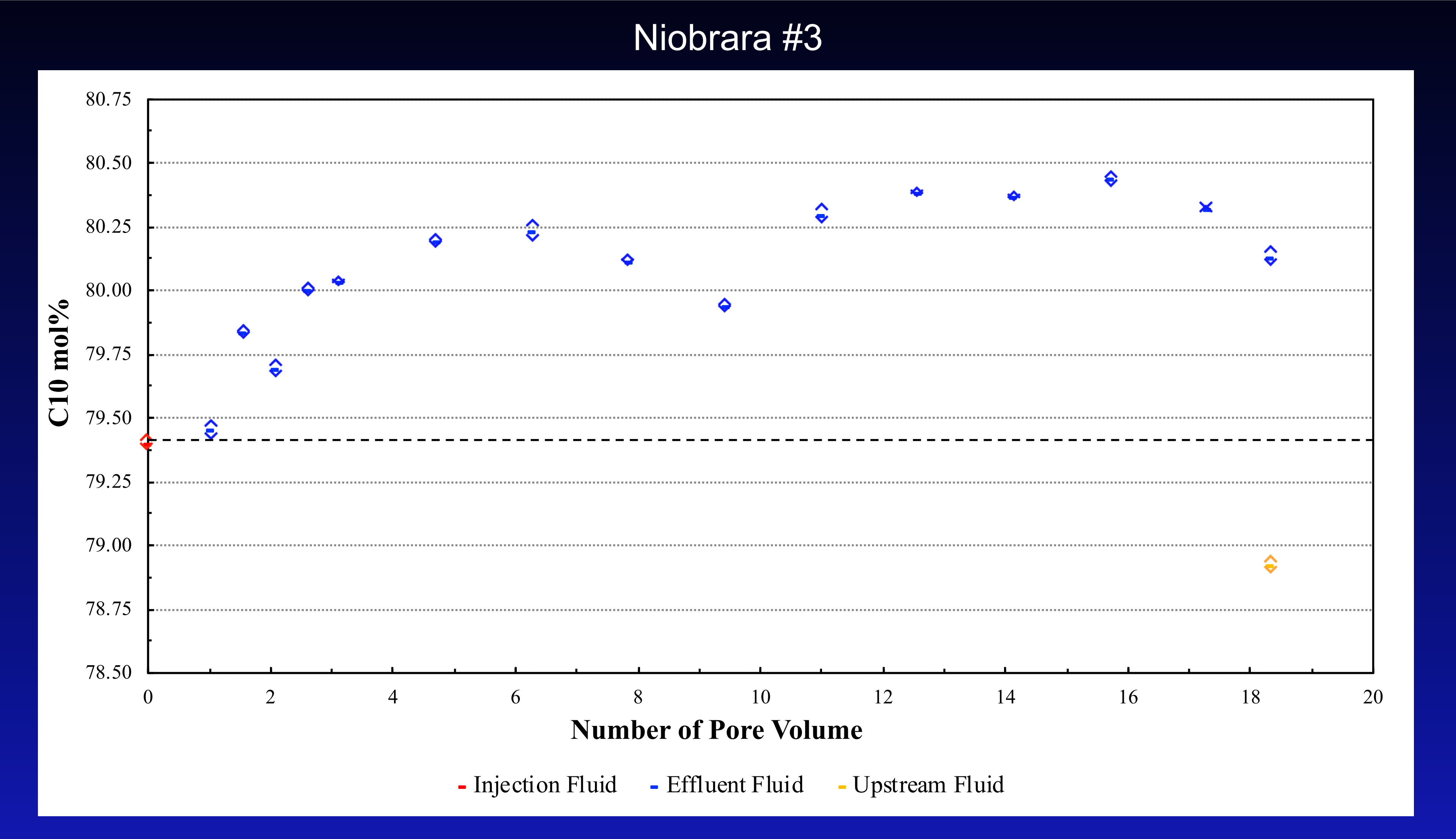

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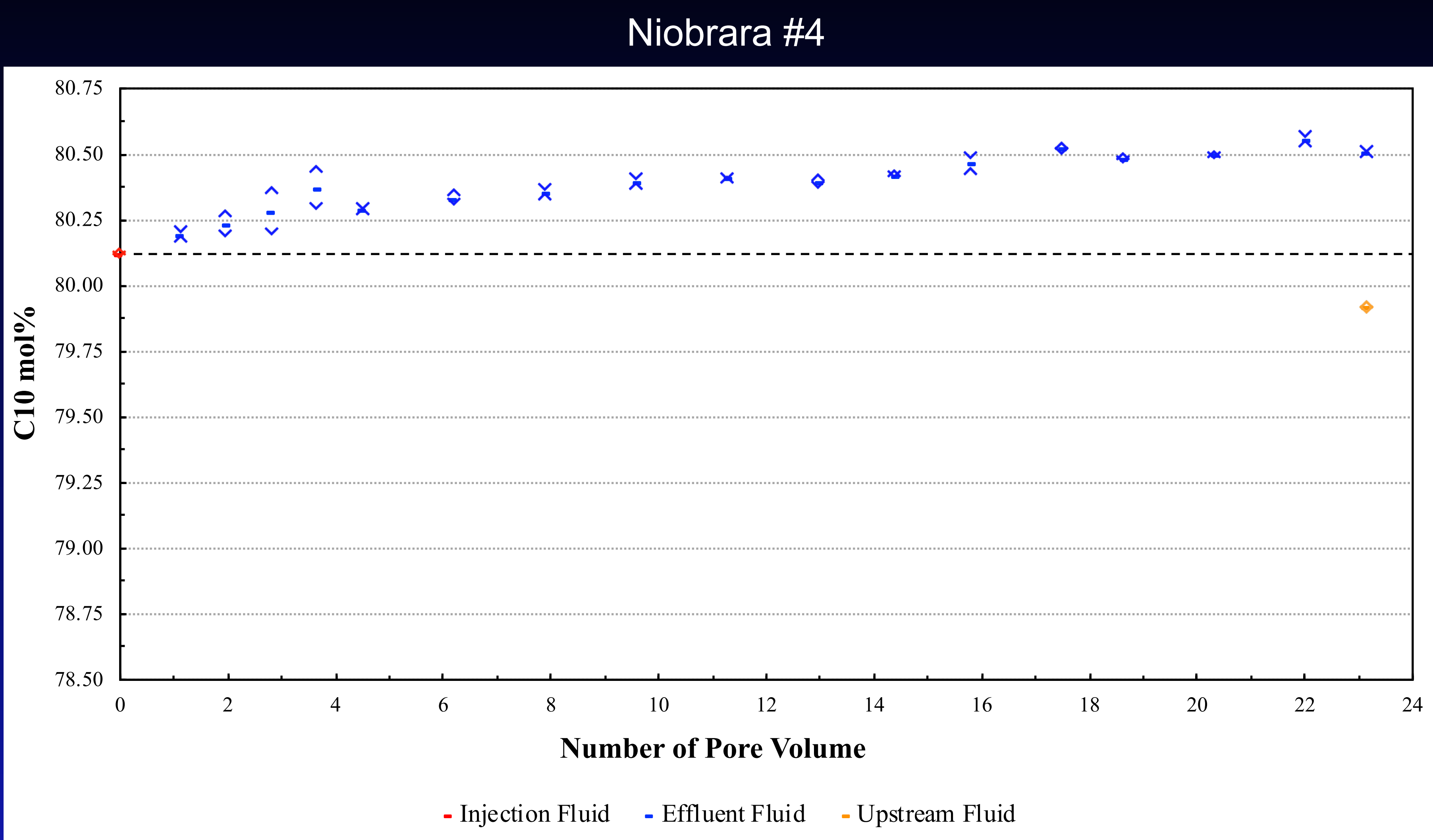

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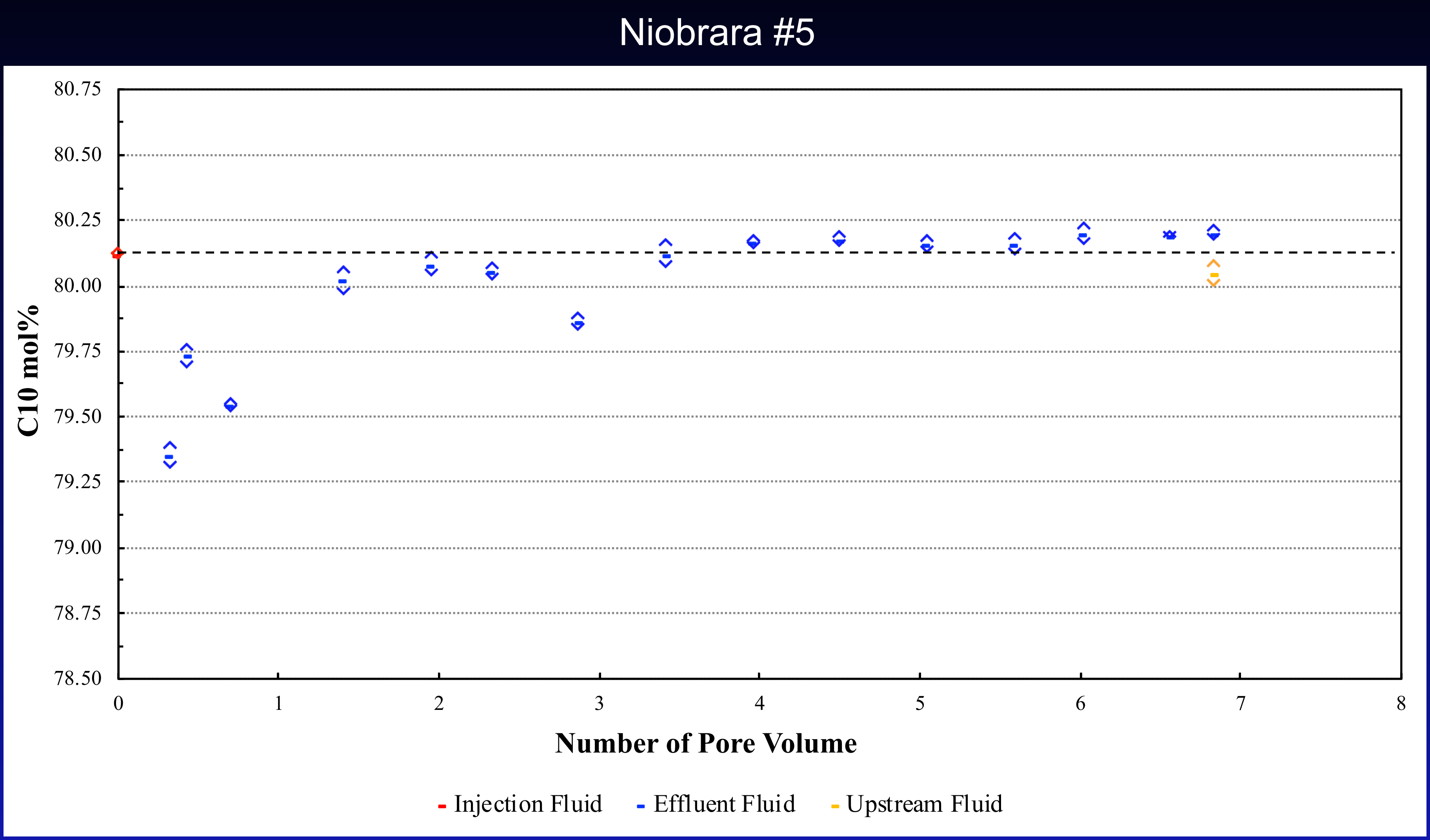

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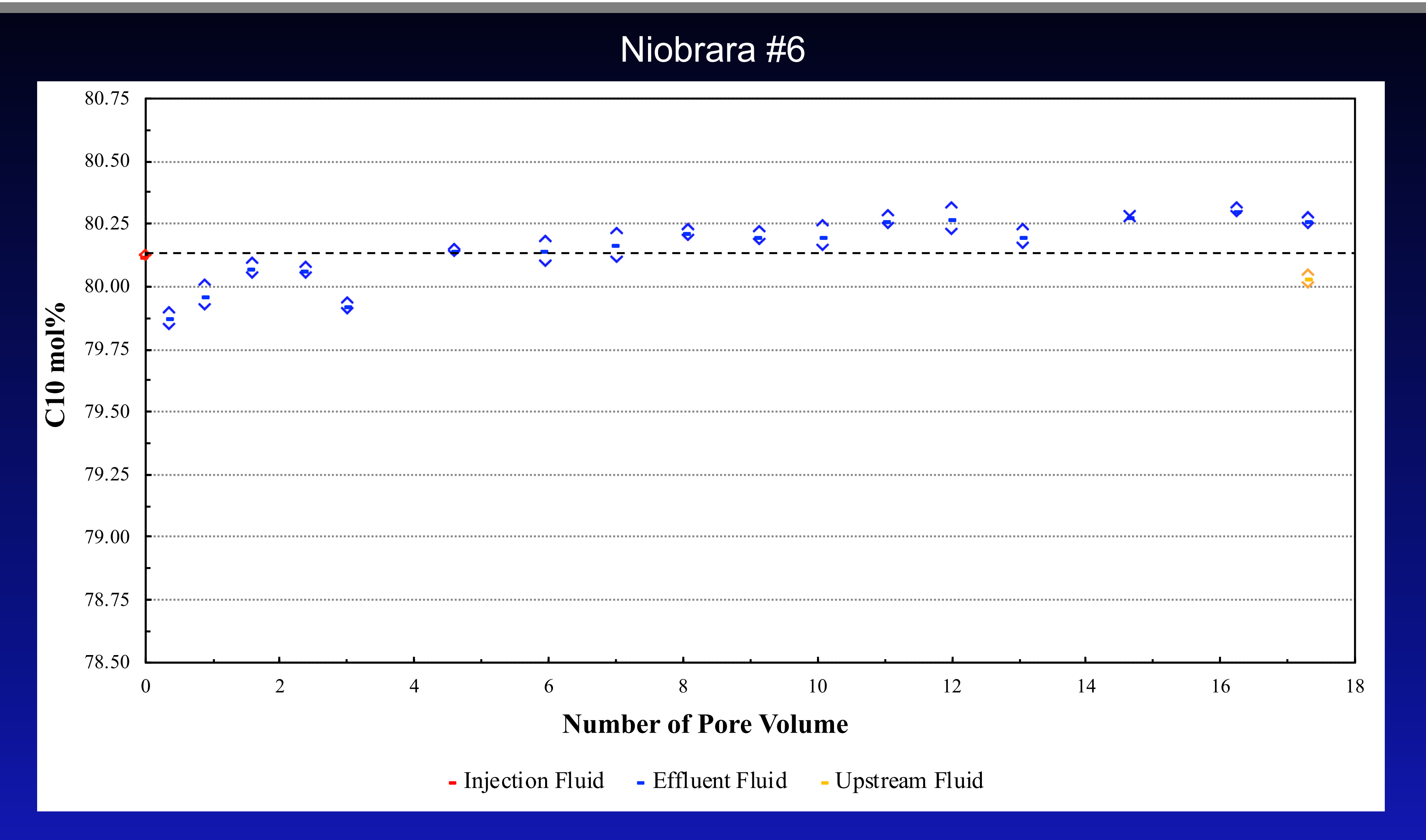

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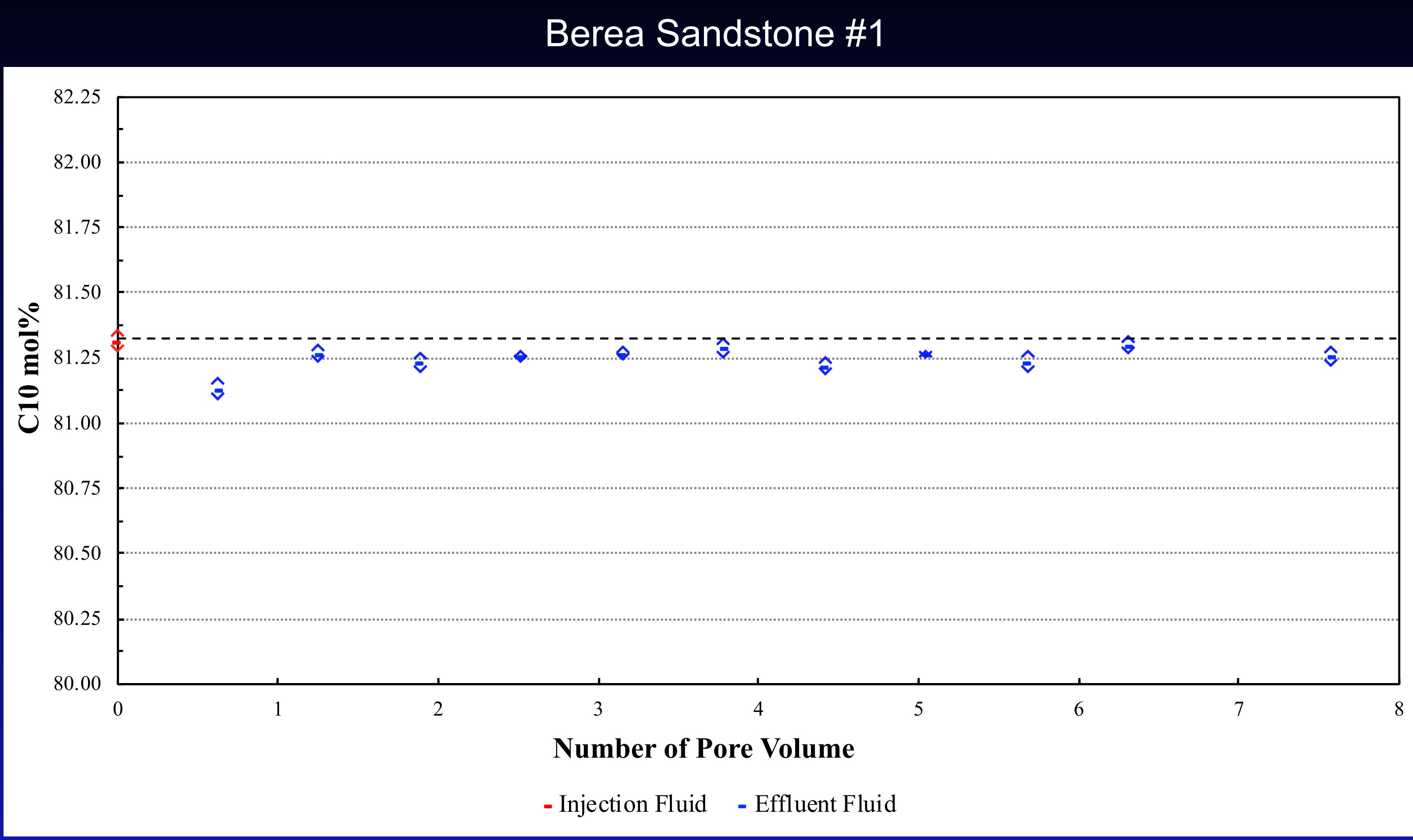

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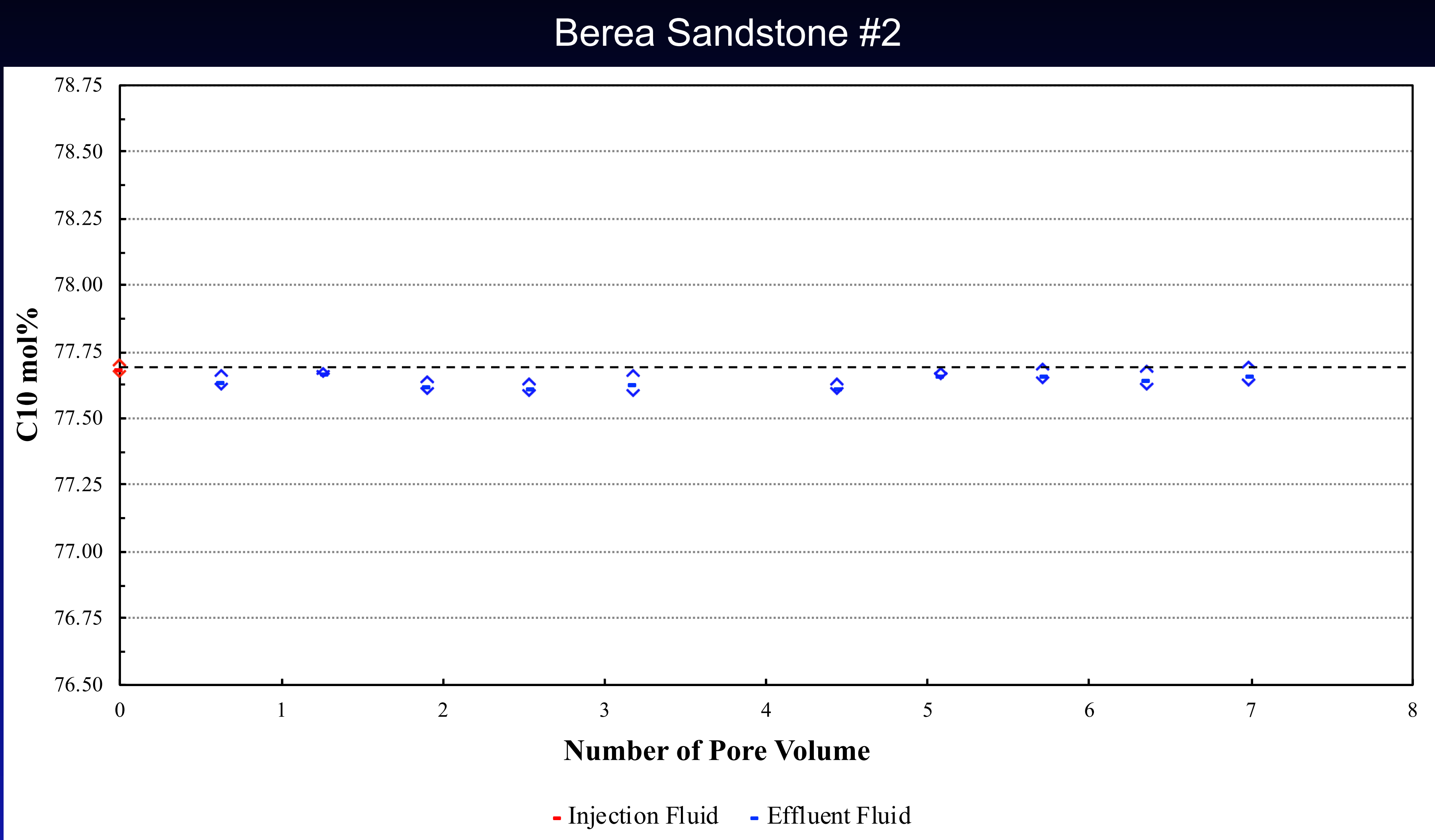
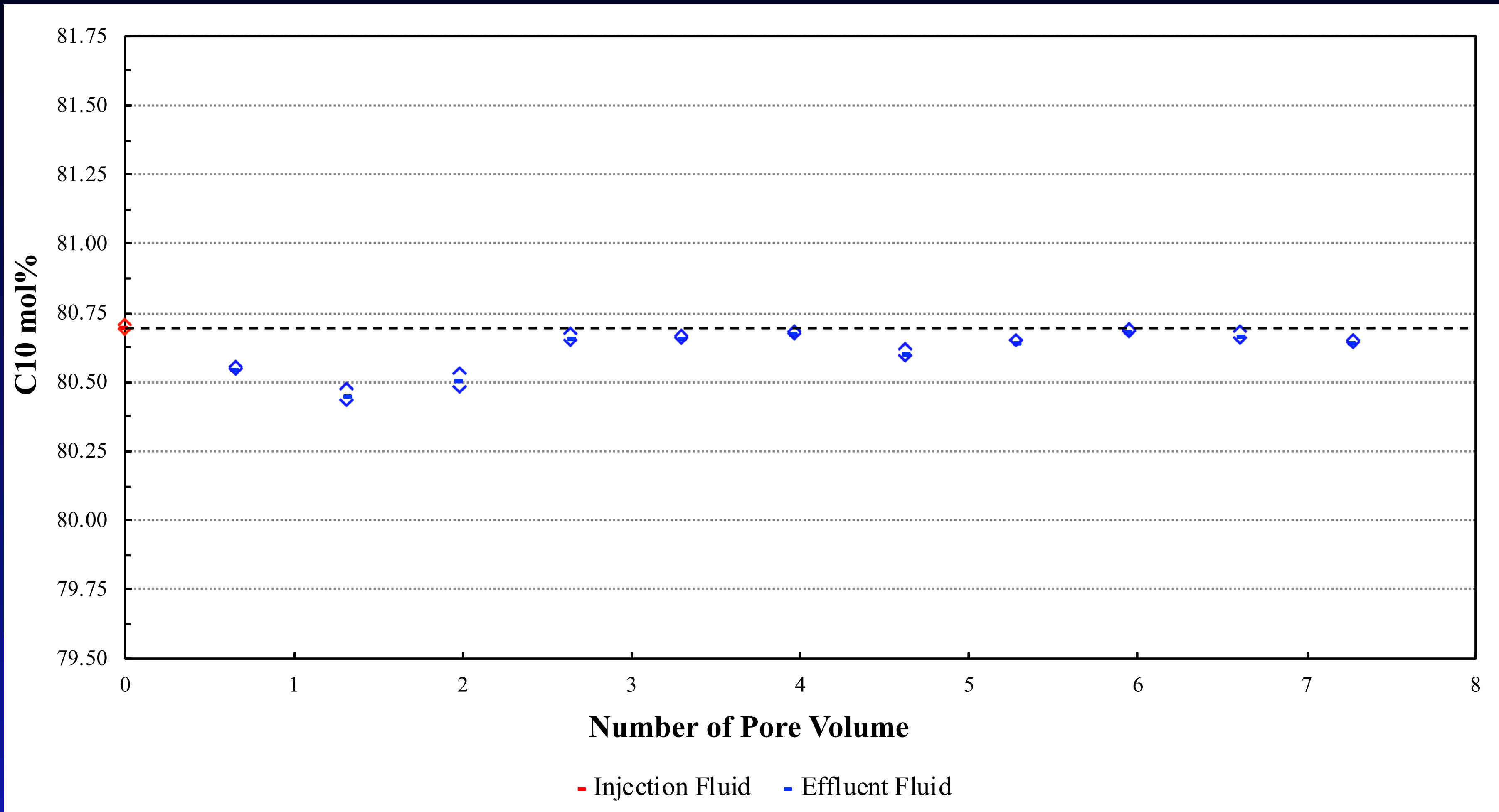


Result & Discussion

Berea Sandstone #3



Result & Discussion

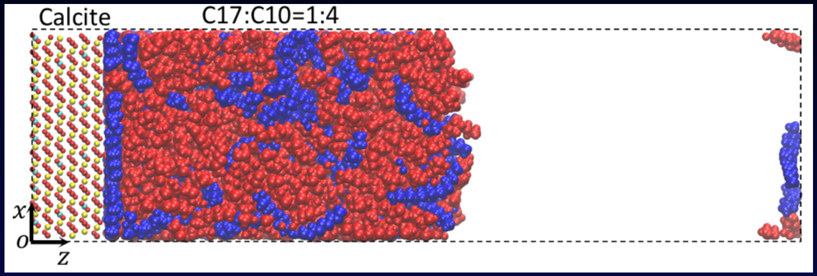
- Compare the composition of injected, produced and upstream fluid for each sample

Sample #	Injection	Production		Upstream	
	C_{10}%	Max C_{10}%	Change % (vs. injection)	C_{10}%	Change % (vs. injection)
Niobrara #1	79.41	80.14	0.73 ↑	79.17	0.24 ↓
Niobrara #2	79.41	80.43	1.02 ↑	79.00	0.41 ↓
Niobrara #3	79.41	80.44	1.03 ↑	78.92	0.49 ↓
Niobrara #4	80.12	80.56	0.44 ↑	79.92	0.20 ↓
Niobrara #5	80.12	80.20	0.08 ↑	80.05	0.07 ↓
Niobrara #6	80.12	80.31	0.19 ↑	80.03	0.09 ↓
Berea Sandstone #1	81.32	81.31	0.01 ↓	--	--
Berea Sandstone #2	77.69	77.67	0.02 ↓	--	--
Berea Sandstone #3	80.70	80.69	0.01 ↓	--	--

Niobrara Shale	C_{10} ↑ C_{17} ↓ in produced fluid C_{10} ↓ C_{17} ↑ in upstream fluid amount of composition change varies between each sample
Berea Sandstone	no obvious compositional change in produced fluid

Result & Discussion

- From molecular simulation results, Niobrara sample adsorbs more C_{17} than C_{10}. (collaboration with Dr. Rui Qiao, Virginia Tech)



- **Question:**

  If more C_{17} is adsorbed, what's the main reason for the compositional change observed?

  size exclusion or preferential adsorption

- **Solution 1:**

$$N\_C_{17\,\text{adsorbed}} \text{ vs } N\_C_{17\,\text{missing}}$$

Compare the extra amount of C_{17} adsorbed in Niobrara sample relative to C_{10} with the amount of C_{17} missing in the produced fluid relative to the injected fluid

Possible result: $N\_C_{17\,\text{adsorbed}} \ll N\_C_{17\,\text{missing}} \rightarrow$ size exclusion

$N\_C_{17\,\text{adsorbed}} \geq N\_C_{17\,\text{missing}} \rightarrow$ preferential adsorption

Result & Discussion

- **Calculations:**

$$N_{C_{17}\,adsorbed}(mol) = \frac{specific\ surface\ area \times mass}{avogadro\ constant} \times excess\ adsorption\ capacity \qquad (1)$$

$$N_{C_{17}\,missing}(mol) = \sum_{effluent\ points} \left\{ \left[\left(\frac{X_{C_{17}}}{V_m} \right)_{injected} - \left(\frac{X_{C_{17}}}{V_m} \right)_{produced} \right] \times Volume \right\} \qquad (2)$$

Note:

$$specific\ surface\ area = \ 3.88 \sim 14.31\ m^2/g$$

$$excess\ adsorption\ capacity\ (nm^{-2}) = \ surface\ excess_{C_{17}} - surface\ excess_{C_{10}} \times \left(\frac{X_{C_{17}}}{X_{C_{10}}} \right)_{injected}$$

$$surface\ excess_{C_{17}} = \ 1.8 \times 10^{-1} \mathrm{nm}^{-2} \quad surface\ excess_{C_{10}} = 5.56 \times 10^{-2} \mathrm{nm}^{-2}$$

$$V_m(cm^3/mol) = \ X_{C_{10}} \times \frac{M_{C_{10}}}{\rho_{C_{10}}} + \ X_{C_{17}} \times \frac{M_{C_{17}}}{\rho_{C_{17}}}$$

Volume and composition of each effluent point are measured in the experiment.

Result & Discussion

Sample	$N\_C_{17\ adsorbed}$ $(10^{-5}$ mol)	$N\_C_{17\ missing}$ $(10^{-5}$ mol)	$\frac{N\_C_{17\ missing}}{N\_C_{17\ adsorbed}}$
Niobrara #1	0.59 – 2.17	15.33	7.06 – 25.98
Niobrara #2	0.56 – 2.08	8.89	4.27 – 15.88
Niobrara #3	0.59 – 2.17	10.88	5.01 – 18.44
Niobrara #4	0.55 – 2.04	4.84	2.37 – 8.80
Niobrara #5	0.58 – 2.12	-0.40	-
Niobrara #6	0.59 – 2.17	-0.81	-

- Based on experimental and calculation results, size exclusion should exist, because preferential adsorption alone cannot explain the fate of all missing heavy component (C_{17}).

Result & Discussion

- **Solution 2**:

  Assumption: size exclusion does not exist.

  compositional difference is entirely caused by preferential adsorption.

  Expectation: after Niobrara samples reach adsorption saturation, there should be no more compositional changes in the produced fluid.

  Observation: sustaining compositional difference between the injected and produced fluid.

- **Solution 3**:

  Observation: increase of heavy component (C_{17}) in the upstream fluid of Niobrara samples.

- These two observations point to the presence of size exclusion (exclusion of access of C_{17} into certain pores of the sample), because they could not be explained solely by preferential adsorption.

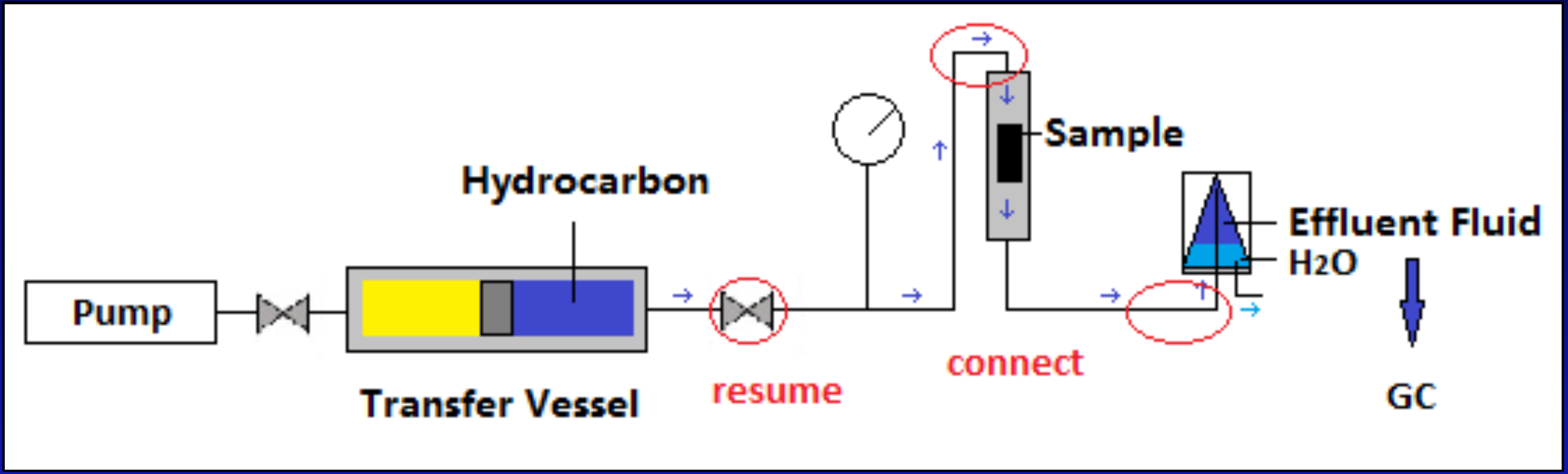
Conclusions

- Filtration test results show that more light component (C_{10}) are produced than heavy component (C_{17}), demonstrating the existence of hindrance effect in Niobrara samples.
- Calculation results based on MD Simulation, observed sustaining compositional changes in the produced fluid and observed increases of heavy component (C_{17}) in the upstream fluid all support the presence of size exclusion in Niobrara samples.

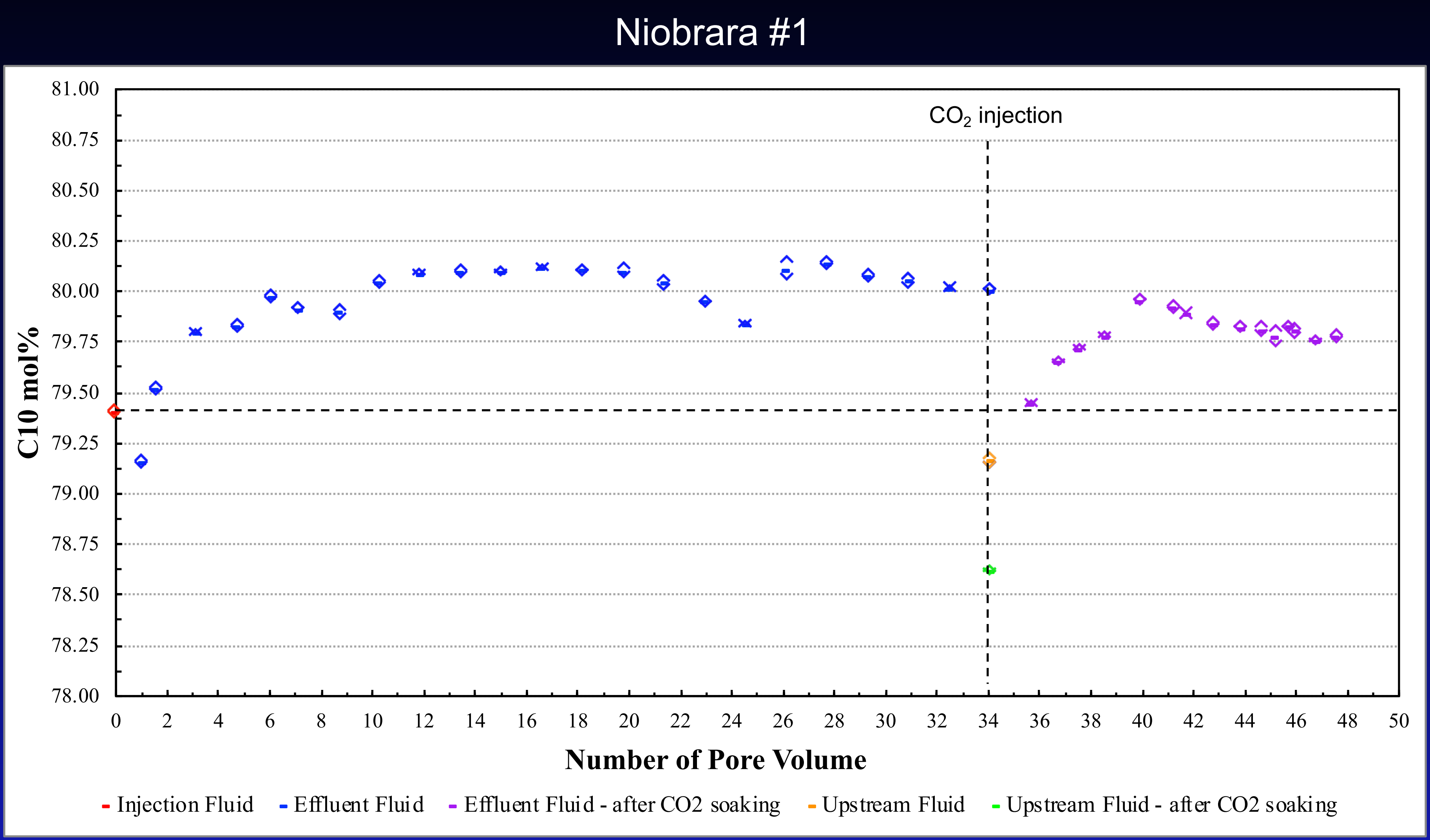
CO2 Huff & Puff

- Objective: Can CO_2 mitigate hinderance effect?
- Procedure:

Shut down hydrocarbon injection → Disconnect core holder → Inject CO_2 from producing side → Soak core sample 600 psi 8~10 days → Connect core holder → Resume hydrocarbon injection

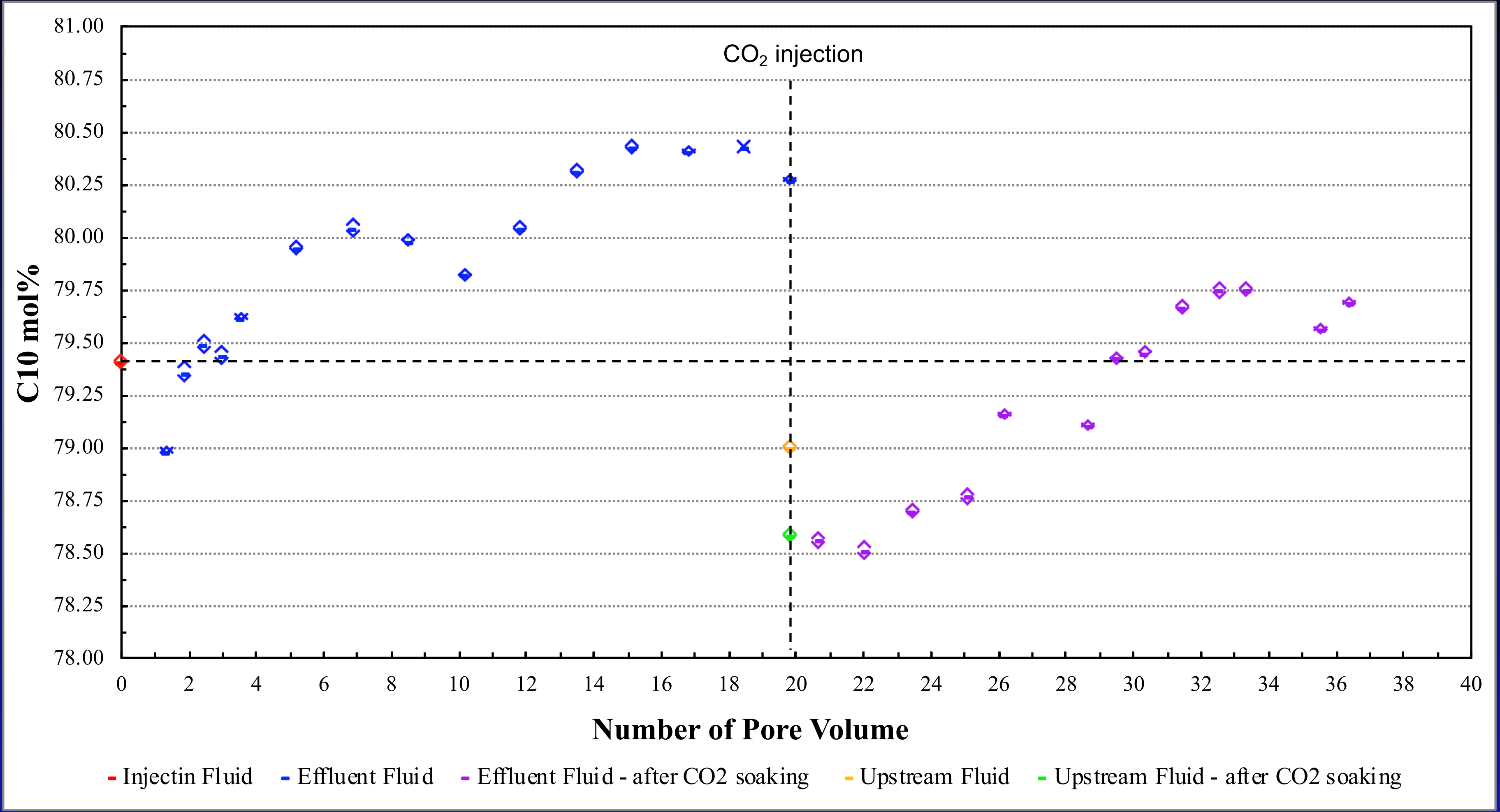


Result & Discussion

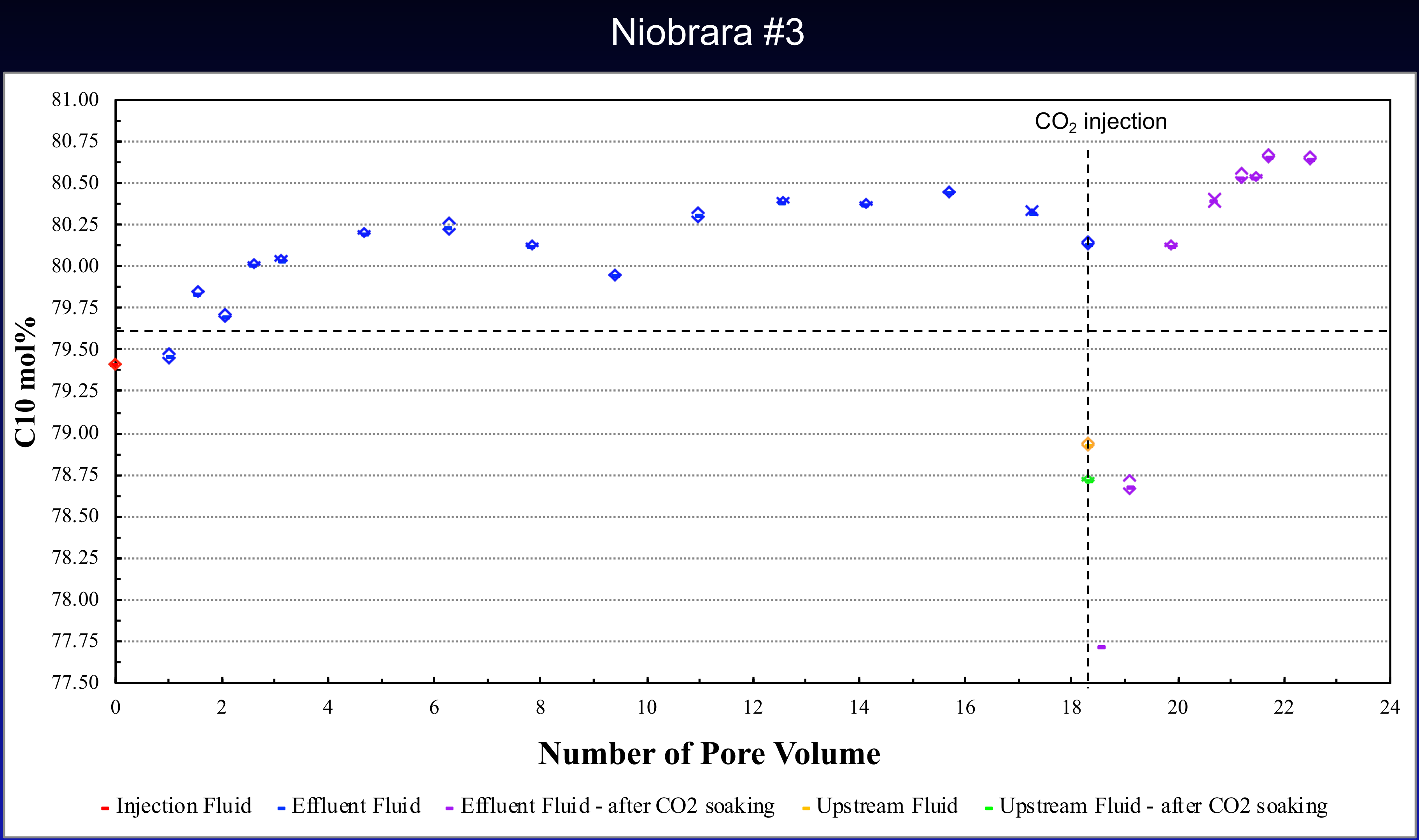


Result & Discussion

Niobrara #2



Result & Discussion



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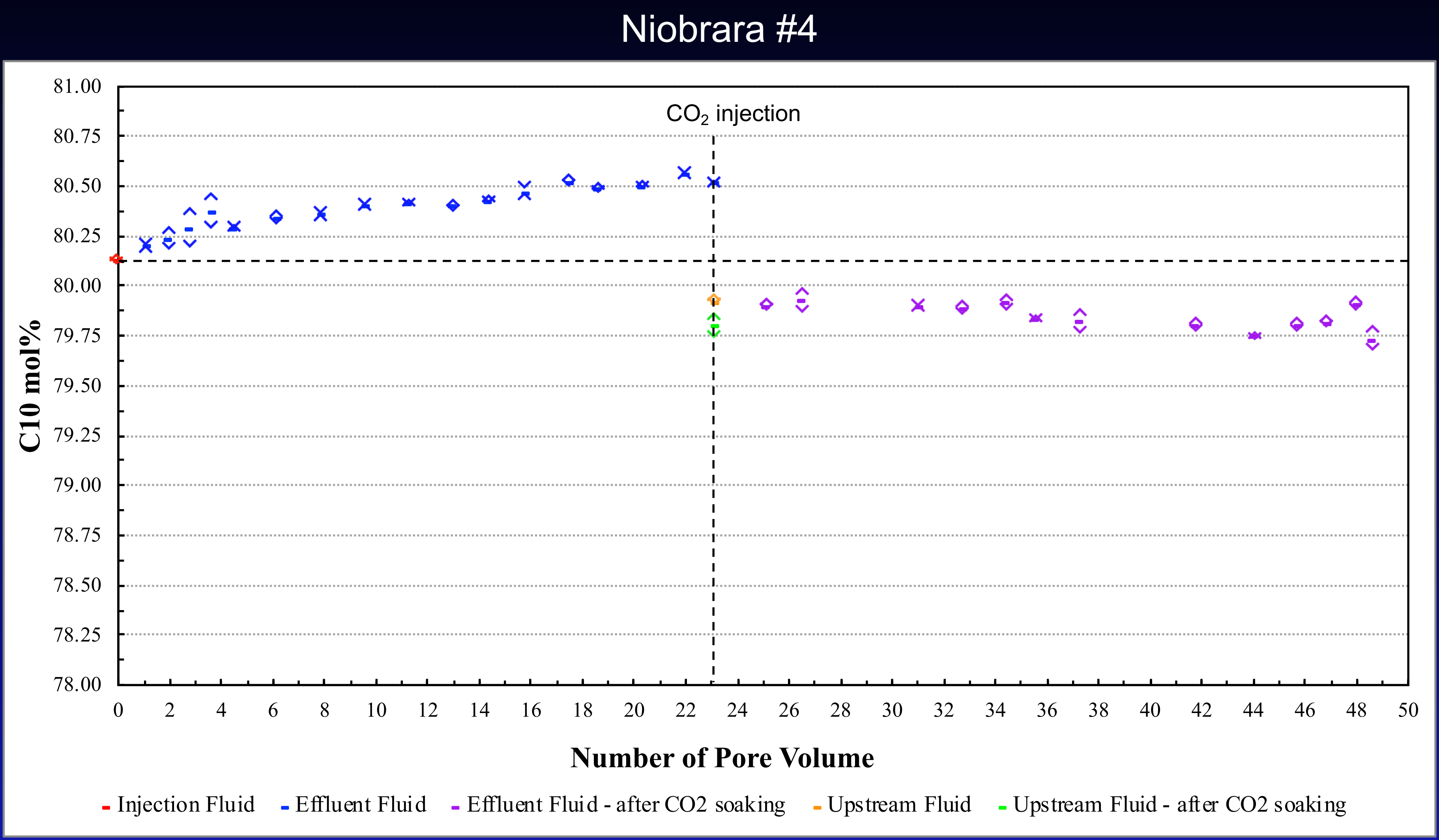
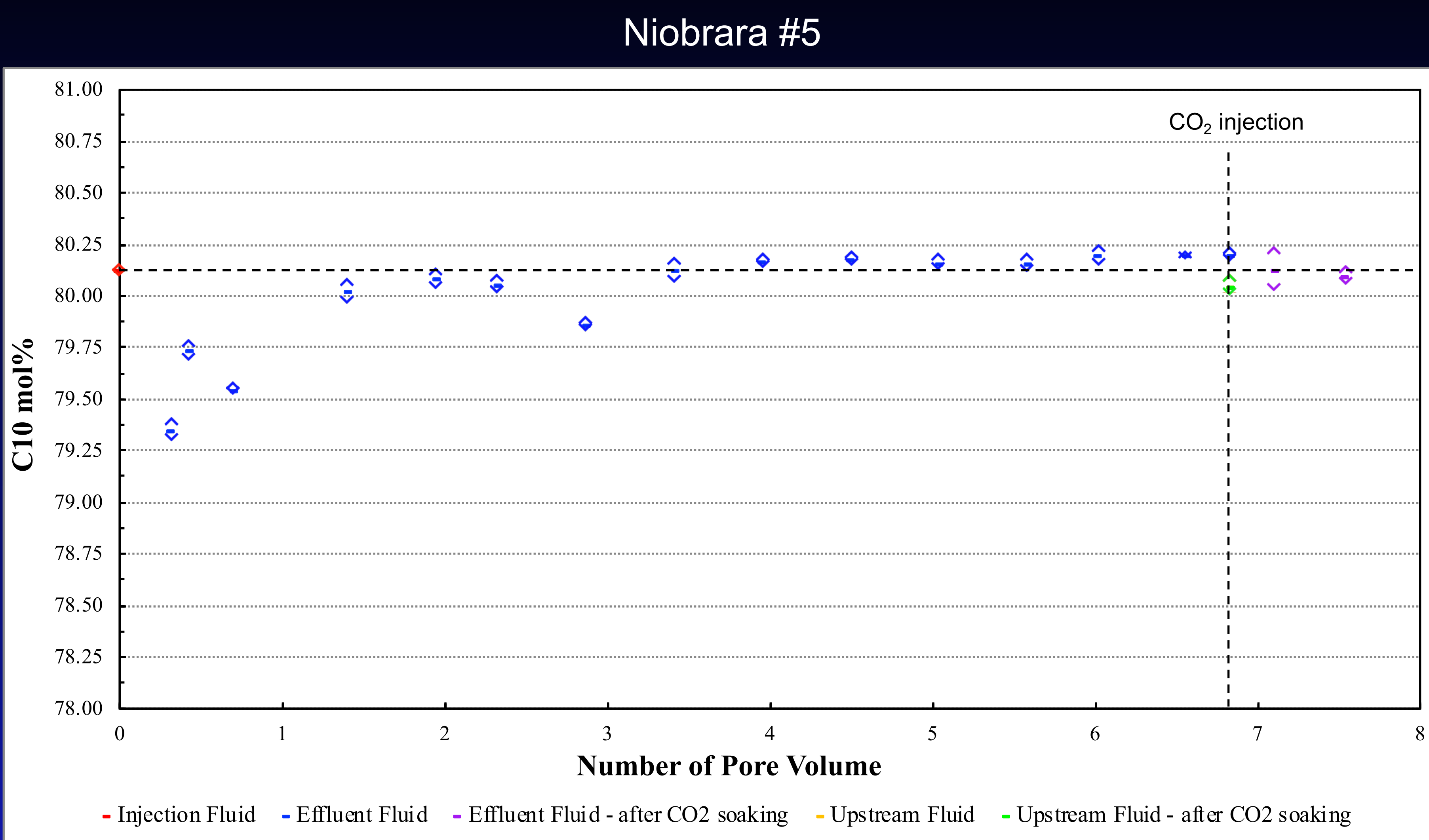
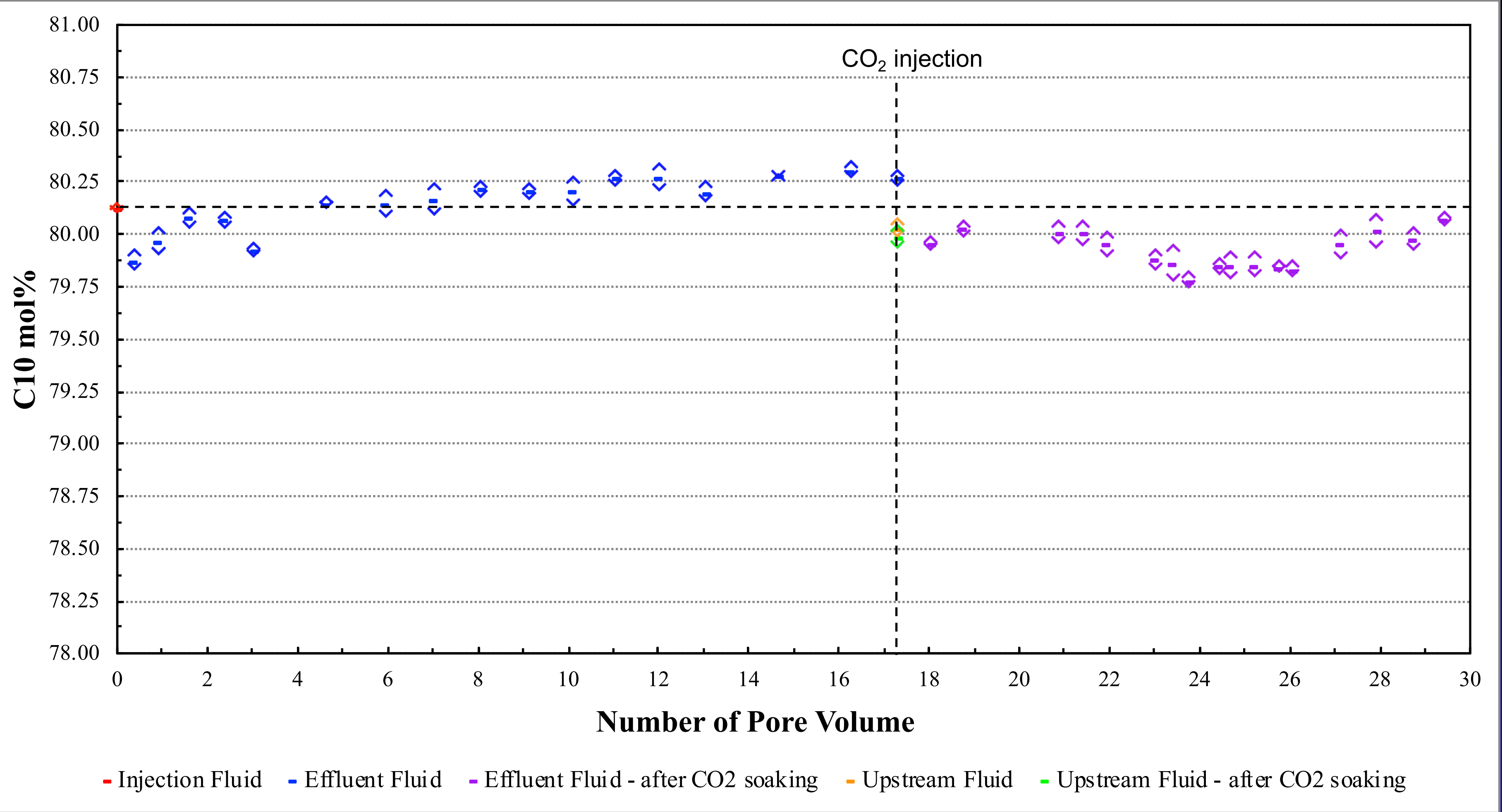


Result & Discussion



Result & Discussion

Niobrara #6



Result & Discussion

Sample #	Average Flow Rate (PV/day)		
	Before CO_2 Huff Puff	After CO_2 Huff Puff	After/Before
Niobrara #1	0.44	0.55	1.25
Niobrara #2	0.28	1.21	4.32
Niobrara #3	0.26	0.38	1.46
Niobrara #4	0.79	10.88	13.77
Niobrara #5	0.25	0.18	0.72 ↓
Niobrara #6	0.61	1.41	2.31

Note: PV stands for pore volume

Summary

- Observed effects before and after CO_2 Huff Puff:

Sample #	Before CO_2 Huff Puff	After CO_2 Huff Puff		
	Hindrance (C_{10}% ↑)	Mitigation of Hindrance (C_{10}% ↓)	Recurrence of Hindrance (C_{10}% ↑)	Flow Rate ↑
Niobrara #1	✓	✓	✓	✓
Niobrara #2	✓	✓	✓	✓
Niobrara #3	✓	✓	✓	✓
Niobrara #4	✓	✓	✗	✓
Niobrara #5	✓	✗	--	✗
Niobrara #6	✓	✓	✗	✓

Note: ↑ or ↓ of C_{10}% is compared with the initial injection fluid.

- Experimental results demonstrate CO_2 might be able to mitigate the hindrance effect and also stimulate the production rate, while the mechanism is not clear.

Conclusion

- The existence of hindrance effect of Niobrara shale on the transport of hydrocarbon mixture has been demonstrated through experiment.
- Size exclusion, as a factor leading to hindrance effect, has been demonstrated through molecular dynamics results and experimental observations.
- Niobrara sample behaves as a semi-permeable membrane, allowing the transport of light component (C_{10}) and restricting the heavy component (C_{17}).
- CO_2 might be able to mitigate the hindrance effect and stimulate the production rate in Niobrara sample.

Future Work

- Repeat experiments using Niobrara oil.
- Investigate the mechanism of CO_2 mitigating hindrance effect.
- Investigate other factors that might affect the compositional change of hydrocarbon mixtures flowing through Niobrara sample.

Thank You

Questions?