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Calibrated dilatometer exercise to probe thermoplastic properties of coal in pressurized CO_2

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Abstract This research was aimed at testing a hypothesis, that at elevated CO_2 pressure coal can soften at temperatures well below those obtained in the presence of other gases. That could have serious negative implications for injection of CO_2 into deep coal seams. We have examined the experimental design issues and procedures used in the previously published studies, and experimentally investigated the physical behavior of a similar coal in the presence of CO_2 as a function of pressure and temperature, using the same high-pressure micro-dilatometer refurbished and carefully calibrated for this purpose. No notable reduction in coal softening temperature was observed in this study.

Keywords Dilatometry · Carbon dioxide · Coal · Plasticization

1 Introduction

The potential use of unmineable coal seams for carbon dioxide (CO_2) storage to mitigate global increase in greenhouse gas concentrations and the effectiveness of CO_2 in enhanced coalbed methane (ECBM) recovery had stimulated discussions on viability of the CO_2 injection technologies, due to reported observations of the CO_2-induced coal swelling (Larsen 2004). Traditional geological-scale reservoir simulators assume that compressibility of the solid matrix is limited to the viscoelastic response to macroscopic forces, and that any changes in the pore volume are mostly due to adsorption of the fluid on the coal surface. However, early large-scale field demonstrations of carbon dioxide storage in unmineable coal seams revealed large discrepancies between field results, simulation predictions, and laboratory data (Palmer 2004); particularly, dramatic changes in permeability—up to a complete loss of flow due to closed cleats upon initial CO_2 injection (Reeves

et al. 2004). That catastrophic failure resulted in a miniature 'clash of civilizations' which pitted the mechanical engineering approach that treats coal as a porous elastic medium with instantaneous deformation response, against the chemical engineering arguments in favor of a more specific nature of CO_2-coal interaction (Romanov et al. 2006b).

Coal can be viewed as a macromolecular network of cross-linked clusters of aromatic rings, in which is dissolved a mix of soluble and physically trapped "guest" molecules (Romanov 2007). Such embedded structure permits coal solubilizing and (anisotropic) swelling in appropriate solvents. Physical properties of coal that often vary systematically with coal rank (Figueiredo and Moulijn 1986) and changes in these properties upon heating are to a large extent a consequence of its physical structure as well.

Heating a packed bed of coal particles to high temperatures can result in surface softening and subsequent deformation. Quantitative appraisal of coal rheological properties requires measurement of several empirical parameters and the effect of experimental conditions on these parameters. The swelling index and dilatometry are important measurements of the swelling/contraction whereas plastometry measures the fluidity. Testing with a constant-torque plastometer (ASTM D-2639) gives a semi-

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quantitative measurement of apparent softening of coal when heated under the prescribed conditions. When bituminous coal is thus heated in the absence of air over the range of 300–550 °C, volatile materials are released and a powder of solid coal particles becomes a plastic-like, transiently softer mass that swells and eventually re-solidifies. Coal that produces 0–30 wt% volatile matter will have a softening point on the order of 340–445 °C (Maloney et al. 1980; Nandi and Montgomery 1971; Speight 2015). The plastic range spans between the softening and the re-solidification temperature.

Most of the measurements of these parameters are based on the experimental techniques which are very dependent on the experimental conditions. Therefore, an important aspect of the study of coal properties is the effect of changing process variables such as pressure, heating rate, gaseous atmosphere, and particle size. However, the swelling behavior of coals is normally measured at atmospheric pressure, and in comparison, very little work has been carried out at elevated pressures. Consideration of widely held views of the mechanism of swelling which involves the release of volatiles, suggests that the effect of pressure and heating rate should be significant. It is impossible to predict the shape of the dilatometry curves from measurements made under standard conditions or from the basic coal characterization data (Figueiredo and Moulijn 1986). A dilatometer which allows one to measure dilation/contraction is used to quantify the mechanical deformations, while the powder sample is heated at a certain rate and is simultaneously subjected to a compression force. ASTM D5515—97(2010)e1 "Standard Test Method for Determination of the Swelling Properties of Bituminous Coal Using a Dilatometer," ISO Standard 349 "Hard coal Audibert-Arnu dilatometer test" and DIN 51 739 "Ruhr Dilatometer and ISO 8264 "Hard coal—Determination of the swelling properties using a dilatometer" specify slightly different methods for such determination.

The materials responsible for the plastic properties of coal can be removed by solvent extraction, leaving a non-plastic residue (Speight 2015). Supercritical CO_2 is recognized as an important commercial and industrial solvent due to its role in chemical extraction, hence its potential role in changing physical properties of coal cannot be underestimated. The experimental work conducted over thirty years ago (Khan and Jenkins 1985; Khan 1985) remains the only indication of potentially extraordinary coal softening upon exposure to pressurized CO_2. Other studies have suggested that experimentally observed changes in "crack-damage" stress threshold for CO_2 exposed coal can be attributed to swelling induced by CO_2 adsorption (Mehic et al. 2006).

Dilatometry on coal cubes has shown coal swelling associated with CO_2 diffusion and sorption at room temperature and CO_2 pressure up to 3 MPa (Brzoska et al.

1991). The results have important implications for coal-seam sequestration of CO_2. More recent dilatometry studies have been conducted perpendicular and parallel to the bedding plane on 7 mm × 7 mm × 7 mm coal blocks, at CO_2 pressure below 2 MPa (Kelemen et al. 2006; Kelemen and Kwiatek 2007). These studies showed that there is a strong non-linear correlation between strain and the quantity of gas adsorbed, and the results for all gases and coals studied followed a common pattern: gas-induced strain for dry coal was significantly greater than that of the corresponding native coal; however, for Pocahontas coal the rates of CO_2 adsorption and gas-induced strain for dry and native coal were indistinguishable which may be related to its low native moisture and minimal amount of created porosity upon drying.

We have investigated the physical behavior of Pocahontas coal in the presence of CO_2 as a function of pressure and temperature using a High-Pressure Micro-Dilatometer (HPMD) refurbished for this purpose (as shown in Fig. 1). This research was initially aimed at validating earlier literature results obtained on a similar device, which showed that at elevated CO_2 pressure coal can soften at
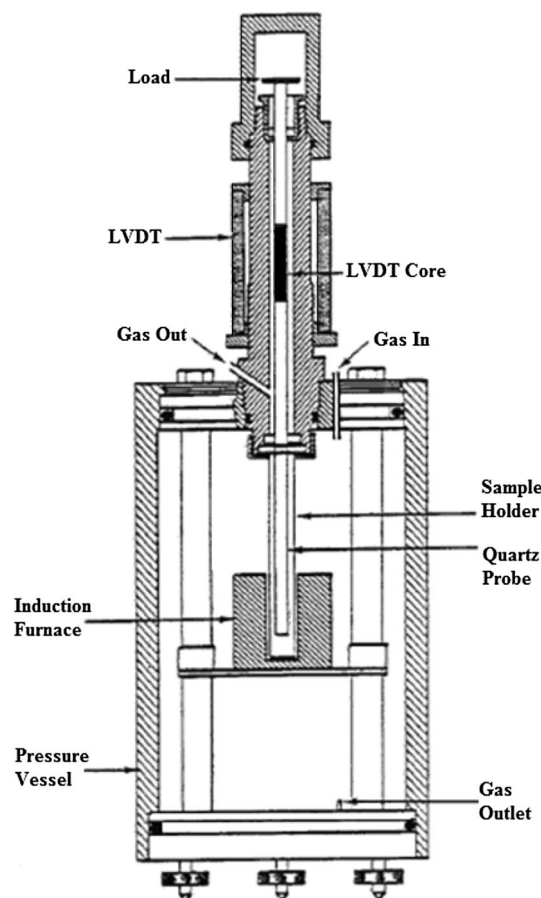

**Fig. 1** High-pressure micro-dilatometer (HPMD) design

temperatures well below those obtained in the presence of other gases (Khan and Jenkins 1985).

2 Experimental section

The HPMD (Fig. 1) used at the National Energy Technology Laboratory (NETL) to investigate the effect of CO_2 pressure on the thermoplastic properties of coal was a model HPD-1000 (Romanov et al. 2006a) manufactured by LECO (Bellefonte, Pennsylvania). It was the same model and was manufactured at the same time as the one used by Khan (1985). The replacement parts were also ordered from LECO, Tem-Pres Division (the original maker of the dilatometer).

A low volatile bituminous coal (Pocahontas No. 3, mesh size −100) as received from the Argonne Premium Coal set (Argonne National Laboratory, USA) was selected for this study. This coal has the rank and the chemical properties similar to the Lower Kittanning coal used in the referenced work (Table 1). Initially, we did plan to conduct similar experiments with coal sample from the Penn State Coal Sample Bank (PSOC 1197, mesh size −20, sealed in argon on December 3, 1990). However, upon inspection of the received container and based upon reports from Penn State (Maloney et al. 1980) it was presumed that the sample aged and would not be identical to the fresh coal that was allegedly softened by CO_2. Experiments were performed with 70 µg samples prepared as closely to the referenced procedure (Khan 1985) as possible.

To check for a possible effect of a particle size on the magnitude of coal softening, the work was also performed with a finer coal powder (−200 mesh) prepared by using the same procedure as the above. Prior to sieving, the samples were further ground with agate mortar and pestle and thoroughly homogenized; >95% of the finer powder was re-claimed. In the control measurements, we used a higher-precision pressure-relief valve, for better pressure stability during the heating. A reproducibility check was also performed using −20 +45-mesh (U.S. Sieve Series) samples of the same Argonne Premium Pocahontas No. 3 Coal.
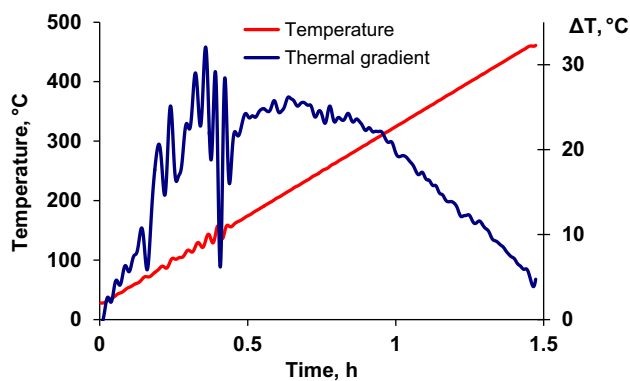
Fig. 2 Temperature (*red*); and temperature non-uniformity (*blue*: thermal gradient)—measured as the temperature differential, ∆T between the sample and control thermocouple—within HPMD filled with high-pressure CO_2

In all experiments, the samples were briefly exposed to air upon transfer to the HPMD and then purged by the filling gas/fluid (high-pressure helium or CO_2) flow-through and by cycling pressure more than five times. The Linear Variable Differential Transformer (LVDT) position sensor on the HPMD was zeroed each time after slow equilibration at 30 °C. Subsequently, the temperature was ramped up at a rate of 5 °C/min (Fig. 2) unless stated otherwise. A 10-g weight was placed on top of the probe rod. The experiment automation and data acquisition were done using NETL codes written with LabVIEW (National Instruments, USA).

A temperature calibration was performed at various pressures of helium and CO_2, with 70 µg of Pocahontas No. 3 coal powder (−100 mesh) into which a second thermocouple was inserted. It was ensured that there were no inner cold junctions with the control thermocouple and the calibration issues had been resolved in the current study, prior to starting the measurements. Following the calibration of the original setup, the control-thermocouple hot junction inside the device was repositioned to be closer to the sample and farther from the heater, and its re-calibration against the sample temperature was used to interpret the data. The increased power output of the replacement heater, which was needed to achieve the

Table 1 Comparison of proximate and ultimate analyses of the coals

Coal	ASTM rank	Vitrinite (reflect.)	V.M., dmmf	Ash, dry	C, dmmf	H, dmmf	O, dmmf	S, dry	Btu/lb, dmmf
PSOC 1197*	lvb	90% (1.73%)	17.3%– 18.6%	10.3%– 11.8%	90.4%– 91.0%	4.8%– 4.9%	2.2%	1.2%–1.4%	15841
Pocahontas No. 3	lvb	89% (1.68%)	18.6%– 18.7%	4.6%– 5.5%	90.6%– 91.8%	4.5%– 4.9%	1.7%	0.7%– 0.74%	15819

* Lower Kittanning (Somerset County, Pennsylvania) coal seam (Khan 1985)

anticipated maximum operating temperature of 500 °C, resulted in the increased local temperature gradient and made the temperature ramp more erratic (Fig. 2). However, the heating curves became more reproducible and no major modifications to the heater circuit and/or re-tuning of the controller were made at that time.

Control samples (A and B) of boric acid were tested in the refurbished HPMD. The tests were conducted at 500 psig (3.5 MPa) with a temperature ramp of 3 °C/minute. The samples softened as the temperature approached the well-established melting point, at around 170 °C, which was evidenced by a very distinct, rapid drop of the probe rod into sample as it melted.

3 Results and discussion

At the beginning of this work, we discovered that the HPMD design had a major flaw, which would result in a considerable reduction of the temperature readout when high-pressure CO_2 was used, but not when high-pressure helium was the filling gas. This was observed during the temperature calibration, when a second thermocouple was inserted into the coal sample. The calibration showed that the control thermocouple's temperature reading was very different from the actual sample temperature.

The temperature difference (between the sample and control thermocouple) tends to decrease as the heater on the HPMD gradually deteriorates with use and the heating rate decreases, thus giving more time for the gas and sample temperatures to equilibrate; without a sample, the temperature differential decreases as well, approximately by a factor of two to three. It appears to vary significantly depending on the choice of the heater, gas, and pressure, which is related to a competition between the irradiative and convective heating rates. For example, the lower-molecular-mass helium equilibration times are much shorter than they are for CO_2, and the resulting gas temperature increase can be faster than direct irradiative heating of the sample; on the other hand, the CO_2 density increases with pressure much faster than that of helium, which results in increasing role of the convective heat exchange between the high-pressure gas/fluid and sample. Combined with another potential error due to a "cold" junction on the inner side of the instrument—that we had found in the original control thermocouple—this could possibly account for the entire "softening effect" previously observed in the presence of pressurized CO_2 (Khan 1985). Both the magnitude ($\sim$ 100 °C) and the sign of the total plausible error in the temperature are in line with the reported effect. The problem with having the thermocouple's reference, "cold" junction on the inner side of the HPMD is that its temperature may increase significantly;

without proper cooling of the instrument's base, especially at a higher density of the filling gas, which requires higher thermal power inflow to keep up with the preset, fixed temperature ramp. Therefore, the unintended increase in the reference junction temperature could result in observation of an apparent decrease (relative to the designated-hot-junction temperature) in the thermocouple readout as caused by reduction in electromotive force. All these issues have been addressed in this study per improved experimental design and procedures as outlined in the Experimental Section.

Having resolved the above problems, experiments to study softening and re-solidification of the Pocahontas No. 3 coal were conducted with the refurbished and properly calibrated instrumentation. Coals have been shown to undergo such thermoplastic changes concurrently with thermal decomposition, and gas evolution as the temperature increases further (Pierron et al. 1959). To de-convolute the measurement artefacts such as reproducible temperature effects on LVDT coils, we used the cooling-leg post-resolidification as a baseline (Fig. 3). Attempts at using quartz-on-quartz (i.e., the measuring rod against the vial, without a sample) experimental data to establish a baseline, resulted in completely different LVDT plots that were not suitable for the baseline subtraction; because a sample's heat capacity and the ability to absorb irradiative power change thermodynamics of the process. Hence, it is more appropriate to use the data from re-solidified sample experiments during experimental data workup and analysis. The experimental error was estimated from successive measurements of these baselines.

Since the contraction (Tc) and re-solidification (Tr) temperatures observed by Khan (1985) did not change, while the reported softening temperature (Ts) plummeted with the increase of CO_2 pressure; we may conclude that
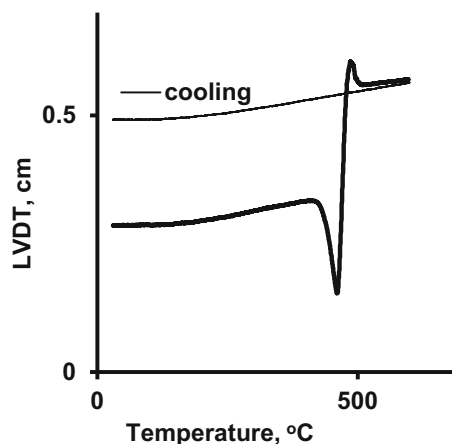

Fig. 3 Coal dilation phases: softening/plasticization, thermal decomposition and gas evolution, re-solidification and cooling (Pocahontas No. 3)

the "softening effect" was subtle and had to be determined by either elimination of the baseline drift or its stabilization and baseline subtraction. These details were not provided in the published reports. Based upon discussions with Dr. Khan (Khan 2006), it was surmised that either one of the above baseline approaches was used in his study. Specifically, Khan (1985) presumably used a part of the test run (with a fresh sample) up to the temperature of 350 °C, and its extrapolation to higher temperatures as a baseline. This leaves the question of what alternative detection method was used for the lower softening temperatures (either around 60 °C or even if it were just under 350 °C) unanswered.

The moving average of the baseline-subtracted coal dilation's second derivative (Newton–Raphson's approximation, with respect to sample temperature) at its peak value was used to detect the onset of the sample softening in this work. Predictably, in the helium environment, the softening temperature of the sample (Fig. 4) was about the same as the previously reported softening temperature of the Lower Kittanning coal. However, the current results, in contrast, indicated that the softening temperature did not change at CO_2 pressure as high as 5–6 MPa, as shown in Fig. 4. Prior to the improvements described in Experimental Section, some minor (within the experimental error) features could be observed around 100–200 °C, on the baseline-subtracted plots (Fig. 5) but such features were not reproducible and were most likely related to instability of the CO_2 pressure or other unknown factors. Yet experiments using a higher-precision pressure-control valve showed only minor correlation between pressure fluctuations and displacement readings—the irregular undulation persisted but with greatly reduced magnitude. No low-
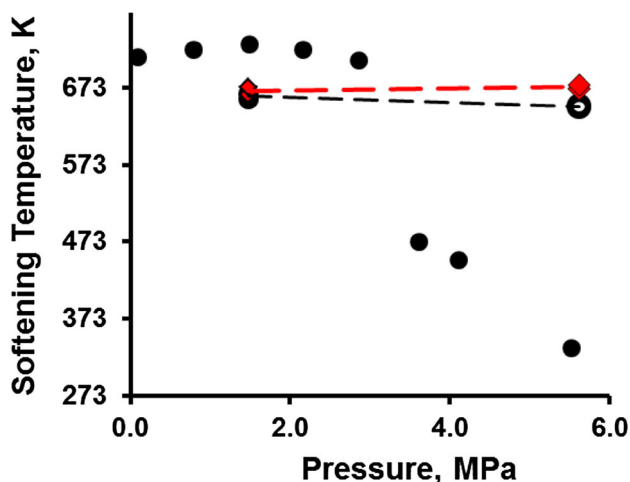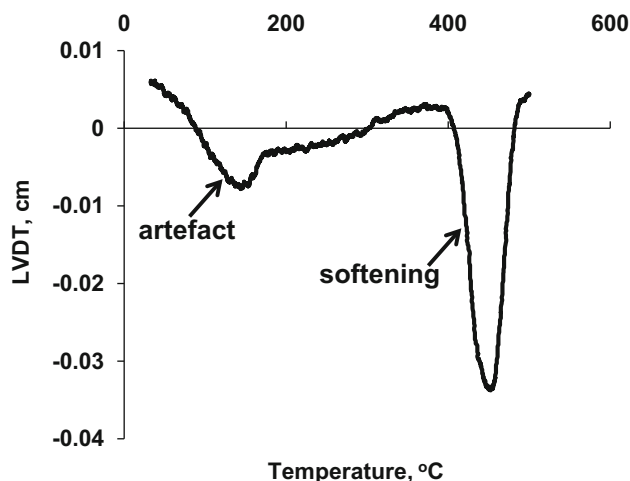
Fig. 5 Baseline-subtracted dilatometry plots for a Pocahontas No. 3 coal in high-pressure CO_2 (without higher-precision pressure-control valve)

temperature "softening" artefacts were observed with the improved setup, as shown in Fig. 3.

Since the results for "as received" (−100 mesh powder) Argonne Premium Pocahontas No. 3 powder samples did not show any significant lowering of the softening temperature, the measurements were also made using a finer coal powder (−200 mesh). With the fine powder samples, the magnitude of the rod displacement (at high pressures) due to coal softening ranged between 7% and 15% of the original sample height. The finest (−200 mesh) powder pre-soaked in liquid (5 MPa, at room temperature) CO_2 did show an apparent, about 35 °C reduction in the onset of the coal softening (sample H as compared to sample G, see Table 2); but the long-term dilatometry was convoluted by slow drift in the baseline LVDT readout that was not reproducible. Some portion of that drift can be attributed to the actual sample contraction—e.g., due to compaction caused by slippage along the particle surfaces, lubricated or frictionally weakened (Pluymakers et al. 2014) by high-pressure CO_2—as the apparent contraction within the plasticity range was the smallest among all the tested samples. A very slow, negative drift of unidentified origin was also observed with a fresh (−20 +45 mesh) Pocahontas No. 3 sample within the first 24 h of exposure to 800 psig (5.5 MPa) CO_2. Poor reproducibility of the slow LVDT drift was likely associated with small variations in the room temperature—water was not circulated in the pressure shell of the HPMD as it would have caused unfavorable displacement profiles during the heating. For these reasons, results of the long-term studies are inconclusive.

The coal samples with relatively uniform (−20 +45 mesh) particle size were also used to assess repeatability and reproducibility of the data. With proper calibration,

Fig. 4 Effect of CO_2 (*red square*) and helium (*open circle*) on the softening temperature of a Pocahontas coal, compared to Khan's (Khan and Jenkins 1985) data (*filled circle*)

Table 2 Summary of the softening temperature (Ts) measurements on Pocahontas No. 3 coal

ID	Coal particles	Gas	Pressure (MPa)	Contraction (LVDT, in)	LVDT noise (10^{-3} inch)	Ts, °C (est.)	Ts, °C (raw)
A	Test: BH$_3$O$_3$	He	2.89	Melted			168
B	Test: BH$_3$O$_3$	CO$_2$	3.71	Melted			167
C	−100 mesh	He	∼1.5			∼385	>400
D	−100 mesh	CO$_2$	∼1.5			∼390	>400
N	−20 +45 mesh	He	1.35	0.053	3	390	405
O	−20 +45 mesh	He	1.49	0.075	10	395	415
R	−20 +45 mesh	He	1.48	0.08	4	395	415
I	−20 +45 mesh	CO$_2$	1.48	0.07	10		435
K	−20 +45 mesh	CO$_2$	1.48	≥0.045	2		440
L	−20 +45 mesh	CO$_2$	1.54	0.07	3	330–400	360**
M	−20 +45 mesh	CO$_2$	1.48	0.065	5	400	435
S	−20 +45 mesh	CO$_2$	1.49	0.047	3	395	430
E	−100 mesh	He	5.1			∼375	425
F	−100 mesh	CO$_2$	6.17			∼405	430
G	−200 mesh	CO$_2$	5.96	0.028	3		390
H	−200 mesh	CO$_2$	5.34	0.02	4		355*
P	−20 +45 mesh	He	5.62	0.04	2	380	450
Q	−20 +45 mesh	He	5.63	0.05	2	375	450
J	−20 +45 mesh	CO$_2$	5.7	0.035	2	395	415
T	−20 +45 mesh	CO$_2$	5.62	0.045	6	390	400

* Pre-soaked in CO$_2$ for 5 days at room temperature; ** partial thermocouple failure

standard deviation of the derived softening temperature (Ts) was about 10 °C. The overall reproducibility is summarized in Table 2. Characters in the sample ID column represent the overall test sequence, in alphabetic (ISO basic Latin) order. On a side note, it was estimated that the temperature corresponding to maximum contraction (Tc) was (440 ± 10) °C in all the calibrated tests; on the other hand, the re-solidification temperature appears to depend on filling-gas density and on heater performance.

4 Summary

Thermoplastic properties of the Argonne Premium Pocahontas No. 3 Coal were investigated by high-pressure micro-dilatometry. In the helium environment, the observed softening temperature (Ts) of the samples was about the same as the previously reported softening temperature of the Lower Kittanning coal; no discernable high-pressure effect was observed in either case.

More importantly, no notable reduction in coal softening temperature (Ts) was observed under high-pressure CO$_2$ that would corroborate the prior work (Khan and Jenkins 1985; Khan 1985). One may conservatively say that the phenomenon of extraordinary coal softening and plasticization induced by supercritical CO$_2$ is not common, even

for the coals similar to those used in the referenced study. The authors acknowledge that it is plausible that high-pressure CO$_2$ may facilitate some minor compaction of coal powder under applied load; however, the long-held belief in commonality of the appreciable CO$_2$-induced softening of the coal matrix was evidently based on erroneous interpretation of the observed experimental artefacts.

Specifically, the findings of this research indicate that the previously reported observations of the "CO$_2$-induced coal softening" were, plausibly, artefacts of the instrument design, data analysis procedures, and heat transfer variations between the reference gas and the CO$_2$ which has a much higher density at the experimental conditions than either helium or nitrogen. Our experience with the HPMD at NETL has shown it to be a difficult device to maintain and operate, and that many factors must be considered to ensure that reliable data are being obtained. The issues were carefully resolved prior to starting the measurements on Pocahontas coal. The used dilatometer model is no longer manufactured, nor are there any other commercial high-pressure dilatometers that are configured to permit continued validation work. Ideally, in any future work, an HPMD or similar device should be constructed to directly measure the sample's temperature and/or change the heat transfer method to eliminate the temperature uncertainty due to radiant heating effects.

The main conclusion is that the highly-reproducible, cross-validated and high-fidelity evidence produced in this study supports the mechanical engineering view of high-rank coal (like the Argonne Premium Pocahontas No. 3 Coal) in high-pressure CO_2 environment, while there is no high-fidelity, corroborated evidence to the contrary.

Compliance with ethical standards

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