CATO-2 Deliverable WP 3.03-D09

Preliminary data on entry pressure, wetting behavior, and transport properties of coal/caprocks from the DSM site

(1st Year Progress Report)

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1 Executive Summary (restricted)

The wetting behaviour of the (cap-)rock-water-CO_2 system plays an important role in long-term behaviour of sequestrated CO_2 and thus storage safety. For accurate prediction of caprock sealing capacity, for example, the wetting behaviour needs to be determined in laboratory experiments. Previous results from the Delft University of Technology show that the capillary behaviour and contact angle of coal and sand can be measured at relevant pressure and temperature conditions using capillary pressure measurements and pendant drop cell measurements.

Sample material from specific sites, such as the DSM site, and detailed information on these materials is required, so that suitable replacement or analogue samples can be selected and acquired. The capillary pressure cell and the pendant drop cell have been refurbished and tested, using available coal samples, for application in the CATO-2 program and are now ready for use. Future experiments will investigate the wetting behaviour (capillary pressure curves and contact angle measurements) of site-specific seal materials, or a suitable replacement, at elevated pressure and temperature.

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Document Change Record

(this section shows the historical versions, with a short description of the updates)

Version	Nr of pages	Short description of change	Pages
2010.08.31	13	Original submitted 31 Aug 2010	
2010.09.05	13	Authors added by TU Delft	1

Table of Content

2 Applicable/Reference documents and Abbreviations

2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the “legal” basis to the work performed)

	Title	Doc nr	Version date
AD-01	Beschikking (Subsidieverlening CATO-2 programma verplichtingnummer 1-6843	ET/ED/90780 40	2009.07.09
AD-02	Consortium Agreement	CATO-2-CA	2009.09.07
AD-03	Program Plan	CATO2-WP0.A-D.03	2009.09.29

2.2 Reference Documents

(Reference Documents are referred to in the document)

	Title	Doc nr	Version/issue	Date

2.3 Abbreviations

(this refers to abbreviations used in this document)

3 General Text

3.1 Introduction

Two reservoir and caprock properties that are important for the storage of CO_2 are the wetting behaviour and the, related, capillary pressure of the caprock and sequestration geological formation. These properties determine, in part, the fluid displacement characteristics [*van lingen et al, 1996*] and the sealing capacity of the caprock. Indeed, the capillary sealing potential (threshold pressure) of the caprock plays an important role in storage safety [*Chiquet et al, 2005; Jimenez and Chalaturnyk, 2002*]. Capillary pressure is essential for safety analysis, especially when long-term behaviour needs to be considered for the containment of CO_2. In addition, contact angle measurements provide a simple method to characterize interfacial energies of a solid in contact with fluids and thus the wetting behaviour. The combination of the capillary pressure and the contact angle measurements allows a better description of the wetting behaviour of the caprock.

By convention, capillary pressure is defined as the pressure difference between the non-aqueous and the aqueous phase. The basic principles and transient effects of capillary pressure are discussed by Plug [*Ch 1.5 and appendix A, 2007*]. Experimental investigation of capillary pressure is generally limited to unsaturated flow. Indeed, literature data for capillary pressure for water-CO_2 in rocks is scarce, especially for systems at in situ conditions. Plug [2007] pioneered an experimental set-up for measuring capillary pressure behaviour at elevated temperature and pressure. This set-up has been refurbished for the CATO-2 program. Siemons [2007] modified a pendant drop cell for measuring

Contact angle measurements provide a simple method to characterize the interfacial energies of a solid in contact with fluids and thus the wetting behaviour (Adamson & Gast, 1990). In general, these measurements are performed by direct observations of drops deposited on the solid, and viewed from one side. Overview articles describe in detail various technical aspects of a set-up that measures droplet shapes (Spelt & Vargha-Butler, 1996).

3.2 Methods and materials

Figure 1 and Figure 2 provide details of the capillary pressure measuring set-up. The set-up [*Plug, 2007*] can measure the capillary pressure behaviour of the sample as a function of water saturation pressures up to 10.0 MPa and temperatures between 25 and 40℃.

Refurbishments of the capillary pressure set-up

- Replacement of obsolete data acquisition system
- Replacement of most valves and tubing to curb leakage issues
- Improve thermal isolation for more constant temperature (planned)

Previous investigations of the wettability behaviour of coal usually contact angle measurements for the coal-water-air system at atmospheric pressure, while in situ conditions of interest are at elevated pressure. The contact angles appear to be largely in the range between 60°-90° (Keller, 1987); Gutierrez-Rodriguez *et al.* (1984) found that the contact angle depends on coal rank; Murata (1981) found that the contact angle depends on the hydrogen and oxygen content of the coal. It is expected that the wetting properties depend on the complex chemistry as a whole. Therefore, laboratory measurements are necessary in order to predict the wetting behaviour of coal caprock.

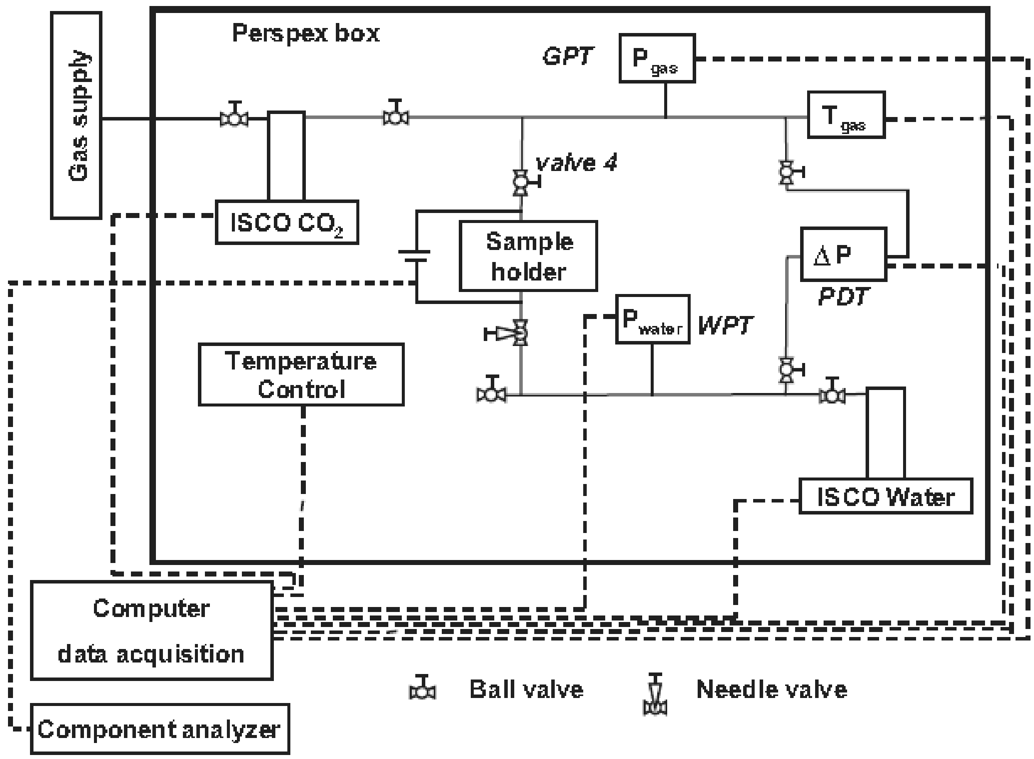

Figure 1: Schematic layout of the experimental set-up. PDT: pressure difference transducer; GPT: gas pressure transducer; WPT: water pressure transducer

The pendant drop cell, based on the work of Huygens (1990) and adapted to perform captive-bubble contact-angle measurements, allows the measurements of CO_2-water-coal contact angles. A digital camera records the image through an endoscope. The entire set-up is in an insulated air cabinet for temperature control. The cell is initially filled with water and a CO_2 bubble is injected through a capillary tube at the bottom of the set-up.

Refurbishments of the pendant drop cell

- The camera has been improved
- Replacement of most valves and tubing.
- Addition of additional drainage outlet.

At this time, no samples for the DSM site have been provided. The selection of a suitable comparable sample is put on hold in concurrence with the DSM project. The capillary pressure behaviour of coal has been investigated by Plug (2007) using the capillary pressure apparatus and the wetting behaviour have been investigated by Siemons [2007]. These data are included to provide give a first estimate for modelling purposes.

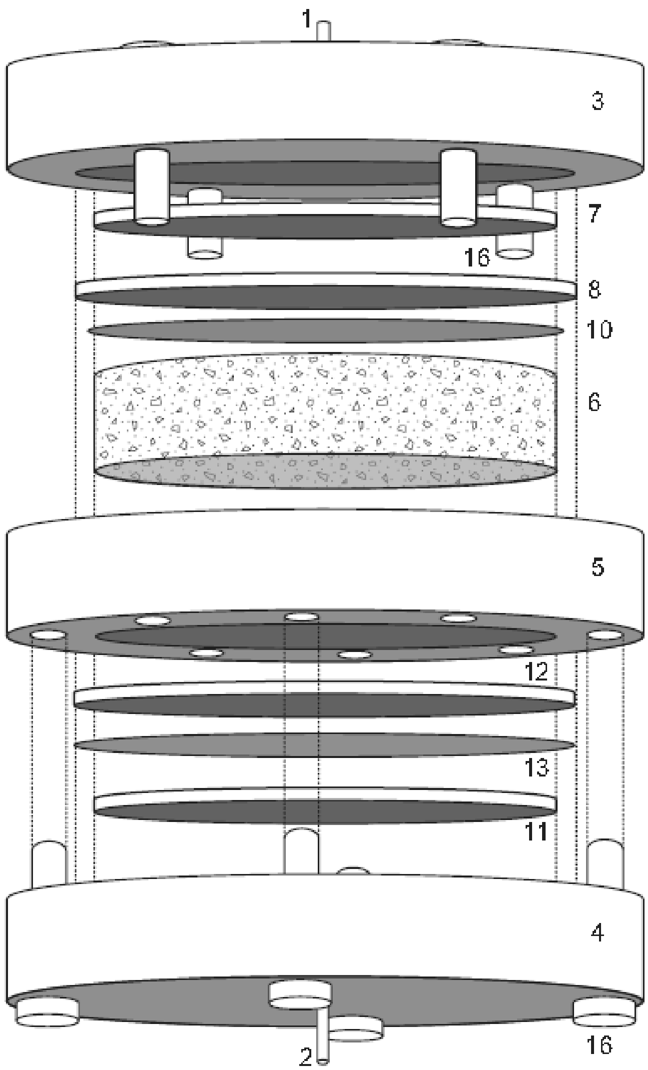

Figure 2: Three dimensional representation of the sample holder (not to scale). 1. Gas inlet; 2. Water inlet; 3. Stainless steel end piece 1; 4. Stainless steel end piece 2; 5. PEEK ring; 6. Porous medium; 7. Perforated plate; 8. Perforated plate; 9. Concentric grooves; 10. Nylon filter (pore size 210 μm); 11. SIPERM plate; 12. SIPERM plate; 13. Water-wet filter; 16. Stainless steel bolts. (Grooves and o-rings (15 and 15) are not shown to improve clarity.)

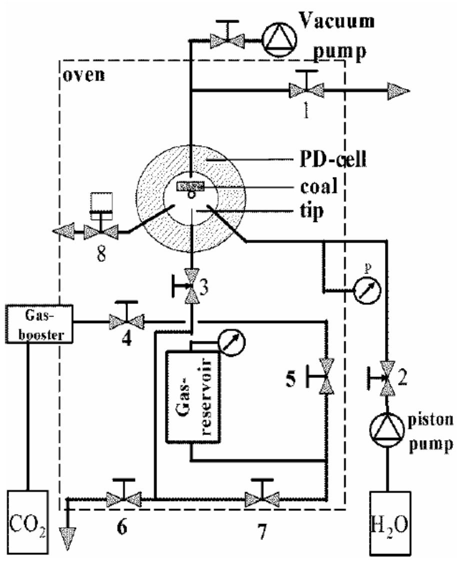

Figure 3: Schematic view of the pendant drop cell for measuring water-H2O-coal contact angles.

3.3 Results

The secondary imbibition process for Warndt-Luisenthal (medium rank) coal is shown in Figure 4. The low pressure measurement (12) varies considerably from the high pressure measurement, because the interfacial tension between water-gaseous CO_2 is considerably different from the interfacial tension of water-supercritical CO_2. The drainage curves are lower than the associated imbibition curves, because displacement of the non-wetting phase by the wetting phase requires more pressure then vice versa. The negative imbibition curve for the high pressure experiments in Figure 4 are ascribed to a wettability alteration of the coal from water-wet to CO_2-wet. In addition, early water breakthrough is observed for pressures above 8.5 MPa.

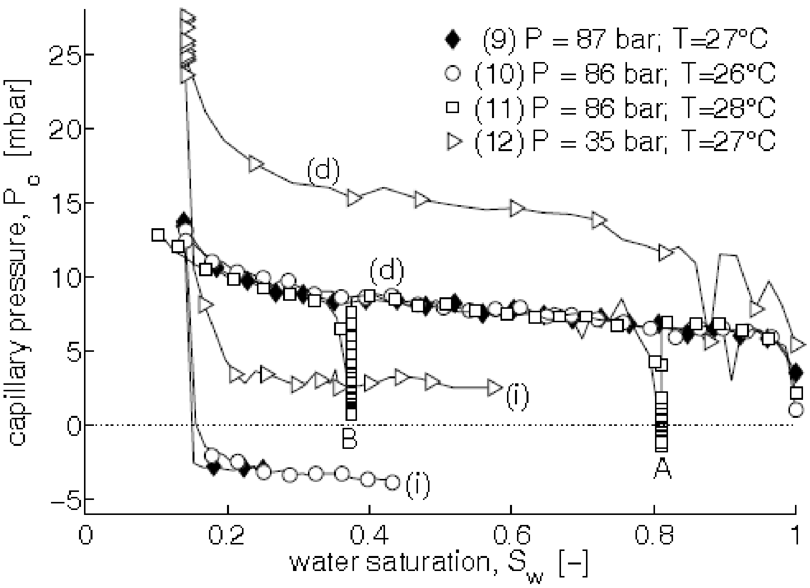

Figure 4: Measured primary drainage (d) and secondary imbibition curves (i) for Warndt-Luisenthal (medium rank) coal.

Figure 5 and Figure 6 show the primary drainage and imbibition capillary pressure curves of Selar Cornish coal, respectively. The sudden imbibition events in the drainage experiment (A, B and C in Figure 5) also occur during primary drainage in sand with supercritical CO_2. The primary imbibition curves exhibit irregular behaviour with sudden drainage events. The distinct character of experiment 17 and 18 has not yet been explained. The Selar Cornish coal shows CO_2 wet behaviour during imbibition.

Figure 7 and Figure 8 show the coarse sand capillary pressure curves various pressures, temperatures and injection conditions for primary drainage and secondary imbibition, respectively. The capillary pressure curves vary considerably, mainly due to the pressure and temperature dependence of the interfacial tension. The magnitude of variations in the capillary pressure curves due to variations in grain size and mineralogical composition are still to be investigated.

Figure 9 shows the measured contact angles of Warndt-Luisenthal coal for the 0 to 150 bar pressure range. The CO_2 bubble at the coal interface is slowly sorbed by the coal sample leading to a decrease in the bubble volume accompanied by a change in contact angle. Both the initial and final measurement of the contact angle is shown to provide the range of possible contact angles in the field. The relationship between pressure and contact angle is weak.

Figure 10 shows the measured contact angles of Selar Cornish coal for the 0 to 150 bar pressure range. The contact angle clearly depends on the properties of the coal. The contact angle changes from 80°to 120°for pressure above 100 bar . It is expected that this is related to the change in density of CO_2 at 100 bar and 45℃.

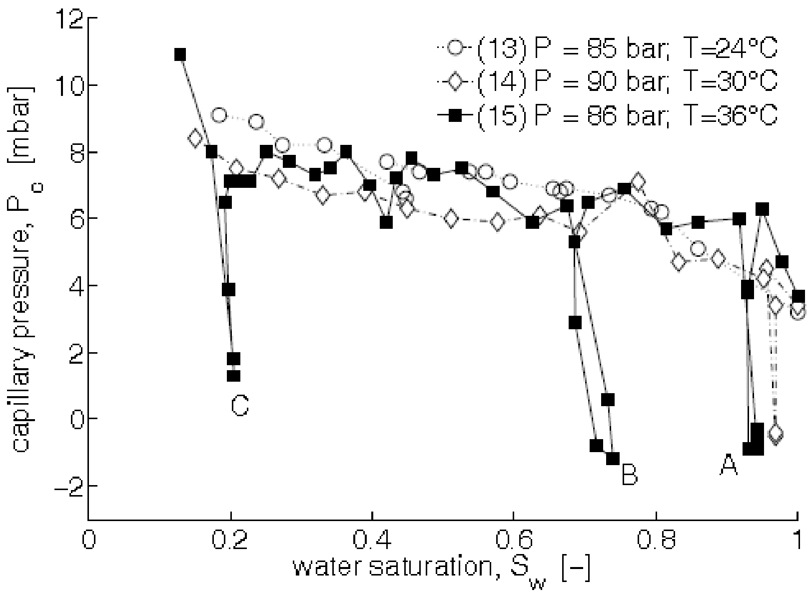

Figure 5: Primary drainage capillary pressure curves for CO_2 injection in Selar Cornish (high rank) coal. Points A, B and C indicate sudden imbibition events.

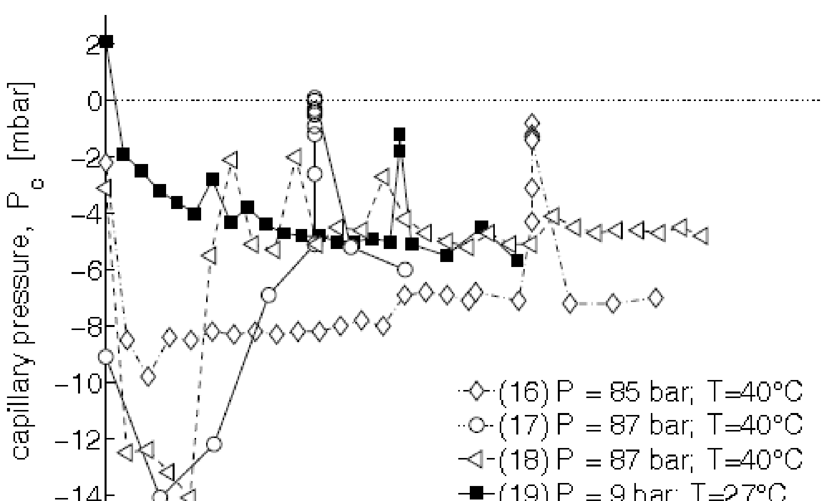

Figure 6: Primary imbibition capillary pressure curves in high rank Selar-Cornish coal when displacing CO_2. The cause of the behavior at water saturations below 0.1 is not known.

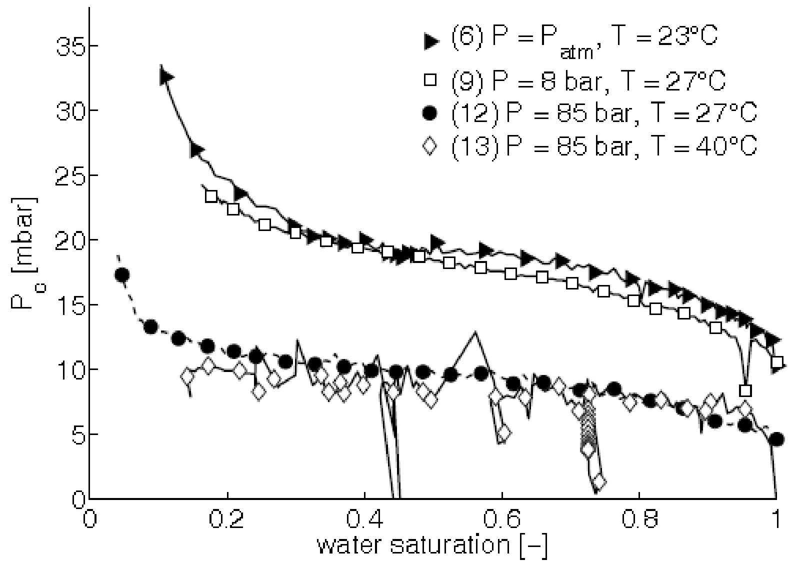

Figure 7: Primary drainage capillary pressure curves for CO_2 injection in coarse sand at various pressure and temperature conditions. Experiment 6 is performed with a varying CO_2 injection rate (below or equal to 1 ml/h). Experiment 12 and 13 have a CO_2 injection rate of 0.5 ml/h; experiment 9 has a water extraction rate of 0.5 ml/h. The differences between the low (6 &9) and high pressure (12 & 13) curves are explained by a decrease in interfacial tension.

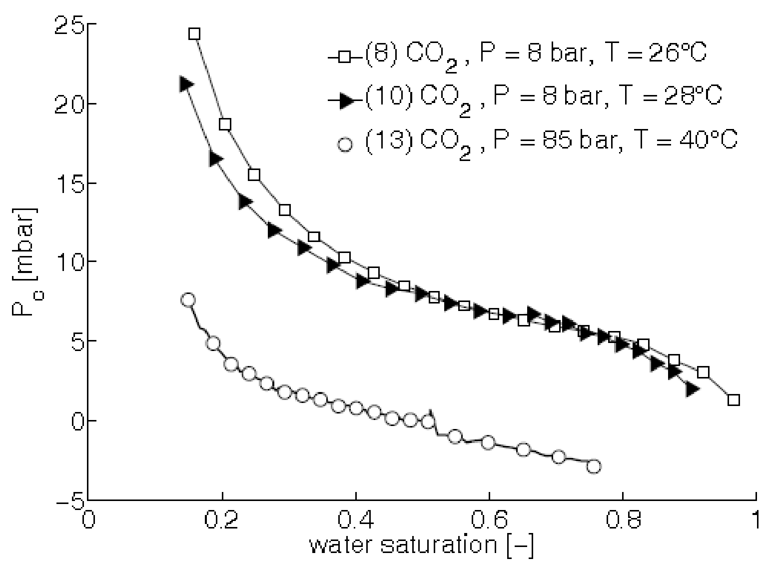

Figure 8: Secondary imbibition capillary pressure curves for the CO_2-water system in coarse sand. Water injection rate is 0.5 ml/h fir all experiments. The differences between the low and high pressure curves are explained by wetting alteration.

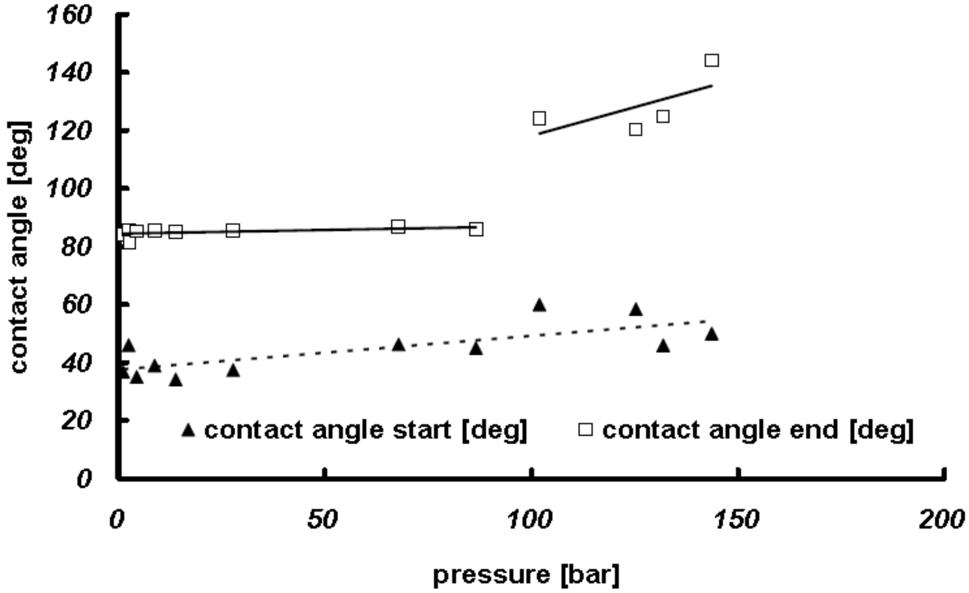

Figure 9: Contact angles at start and end of the experiments for Warndt-Luisenthal as a function of pressure at 45℃. Contact angles at the start are all below 60°. Contact angles at the end of the experiment exceed 90° at pressure s above 100 bar.

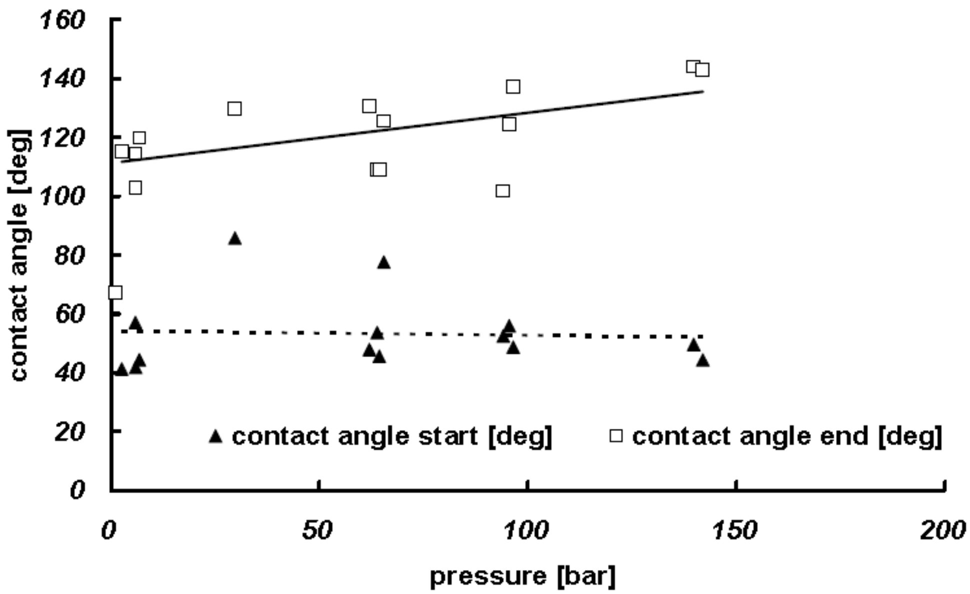

Figure 10: Contact angles at the start and end of the experiments for Selar Cornish coal as a function of pressure at 45℃. Contact angles at t he start are all below 90°. Contact angles at the end of the experiment exceed 90°, except at atmospheric pressure.

3.4 Discussion & conclusions

The wetting behaviour of the (cap-)rock-water-CO_2 system plays an important role in long-term behaviour of sequestrated CO_2 and thus storage safety. For accurate prediction of caprock sealing capacity, for example, the wetting behaviour needs to be determined in laboratory experiments. Previous results from the Delft University of Technology show that the capillary behaviour and contact angle of coal and sand can be measured at relevant pressure and temperature conditions using capillary pressure measurements and pendant drop cell measurements.

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