



The effects of dissolved CO₂ on coal structure and properties

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Abstract

Carbon dioxide dissolves in coals and swells them slightly. The dissolved CO₂ seems to act as a plasticizer, enabling physical structure rearrangements and lowering the coal's softening temperature. Plasticized coals are known to rearrange to a more associated form in which fluids, including CO₂, will be less soluble. A comparison of the sorption of CO₂ and ethane, molecules of similar size, shows much greater CO₂ uptake probably because of much faster diffusion of CO₂ through the coal because CO₂ readily dissolves in coals and ethane does not. Only a little is known of the effects of confining coal and lithostatic pressure on CO₂ uptake and on the behavior of plasticized coals.

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1. Introduction

The central point of this brief and selective review is that CO₂ dissolves in coals and by so doing may change coals' physical structure, properties, and behavior. It is not possible to extrapolate from low-pressure studies of CO₂ adsorption on coals to high-pressure regimes. In contemplating sequestration of CO₂ in coal seams, attention must be paid to the possible effects of dissolved CO₂ on the structure and behavior of the coal.

The sequestration of CO₂ by pumping it into deep coal seams is being investigated. It is therefore worthwhile to gather the information available on the interactions of CO₂ with coals and the effects of CO₂ on coals' properties in order to attempt a prediction of the long-term effects of sequestration. Because

CO₂ has long been used to study coal surface areas by adsorption, there are many low pressure data available (Mahajan, 1982, 1991). Measuring coal surface areas using CO₂ adsorption in static (e.g. BET) experiments involves the assumption that CO₂ is only adsorbed and does not dissolve in coals. As will become clear, there are ample data demonstrating that CO₂ dissolves in coals and swells them. At the very low pressures used for surface area measurements, CO₂ dissolution does not seem to be a problem. The concern here is the behavior of CO₂ and coals at the higher pressures necessary for CO₂ sequestration. For this reason, surface area measurements using CO₂ will not be covered here. Reviews are available (Mahajan, 1982, 1991).

In a very important paper, Hsieh and Duda (1987) monitored the processes that occurred when a bituminous coal was exposed to toluene vapor at low pressures. Their results are summarized in Fig. 1 that shows toluene uptake as a function of time with the

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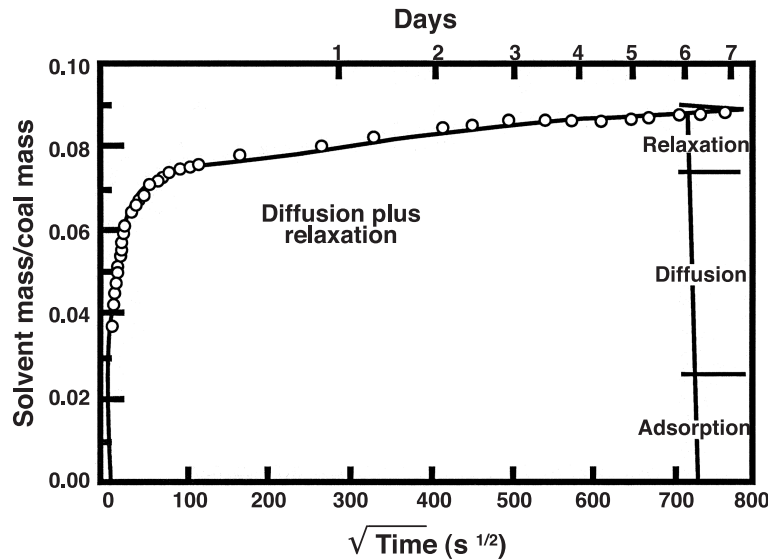


Fig. 1. Rate of toluene uptake by a pyridine extracted bituminous coal (71.0% C, daf) (from Hsieh and Duda, 1987).

accompanying processes denoted. Any fluid that is soluble in a coal is expected to behave similarly with both uptake amounts and uptake rates depending on the size of the molecule, the interactions between the molecule and the coal, and the identity of the coal. The behavior illustrated in Fig. 1 is general and not specific to toluene. Adsorption on the coal surface is almost instantaneous. This is immediately followed by a much slower diffusion of the molecules into the coal. In static experiments, it is very difficult to distinguish between adsorption and a mixture of adsorption and absorption because the latter immediately follows the former. The amount of a gas that dissolves in the coal will increase with increasing pressure.

The last process identified in Fig. 1 is rearrangement of the coal. Here we turn to classical polymer chemistry to understand this phenomenon. Coals are glassy, strained, cross-linked macromolecular systems and are not in their lowest energy state (Larsen et al., 1997). A glassy solid is brittle because the intermolecular interactions are greater than the available thermal energy so the molecules and molecular segments are “frozen” in place. They do not have freedom to move except for small-scale rotations, vibrations, etc. When warmed to a temperature such that the thermal energy is greater than

the intramolecular interaction energy, the polymer becomes rubbery. Now large-scale molecular motion is possible and internal viscosities are liquid-like. The polymer has “melted” but retains its shape because it is cross-linked. The temperature required to cause the transition from a glass to a rubber is the glass transition temperature (T_g). The best evidence is that unplasticized coals remain glassy up to the temperatures at which they begin to thermally decompose (Opaprakasit and Painter, 2003). Materials dissolved in the polymer generally lower T_g . They are plasticizers. The toluene dissolved in the coal is allowing the coal molecules sufficient freedom of motion to rearrange and thereby to adopt a new lower energy physical structure. Because it involves the motion of very large molecules, this rearrangement will often be slow. It is caused by the energy difference between the beginning and ending coal structure. To a first approximation, the dissolved small molecule only enables the rearrangement. Any dissolved molecules will enhance the coal’s ability to rearrange to a new structure; the only question is: how does the rate of the rearrangement vary with the identity of the gas and the amount dissolved? Carbon dioxide is an effective plasticizer in many polymers (Wang et al., 1982, Smith and Moll, 1990).

While the rearrangement of coals that is caused by the presence of dissolved molecules has not been extensively studied, enough work has been done to provide a rough characterization. Nuclear magnetic resonance has been used to study coals containing large amounts of a dissolved molecule (Yang et al., 1994 and references therein). From this work it is clear that the coal T_g drops with increasing amount of dissolved molecule and is independent of the identity of the molecule as long as the interactions between the molecule and the coal remain constant. For example, pyridine and *N,N*-dimethylpyrrolidinone (NMP), both strong hydrogen bond acceptors, have similar effects that are quite different from non-hydrogen-bonding chlorobenzene.

The most thorough study involved four coals that were rearranged by warming in chlorobenzene. Chlorobenzene was chosen because its presence in the coal after rearrangement (undesirable) can easily be detected by analysis for chlorine, because it is not a very effective extracting solvent for coals, and because the rearrangement is complete in a reasonable time (a few days). Fig. 2 shows the changes in heat capacity of Pittsburgh No. 8 coal as a function of heating time in chlorobenzene. The heat capacity drops sharply demonstrating a structure change to a more rigid more highly associated structure. A lower heat capacity demonstrates that the structure is more rigid. It has fewer ways of “storing” energy. This is

Table 1

Pyridine extraction yields (wt.%) and solvent swelling ratios of coals heated at 115 °C for various times in chlorobenzene (from Larsen et al., 1997)

Heating time	Wandoan	Illinois No. 6	Pittsburgh No. 8	PSOC 1336	Pyridine swelling ratio, Pittsburgh No. 8
%C (daf)	77.3	79.9	83.8	84.1	
None	18	29	44	31	2.4
1 day	10	19	41	28	
2 days	10	19	38	23	2.0
4 days	11	20	32	24	1.9
7 days	11	21	32	28	
8 days					1.5
14 days	12	15	28	22	

consistent with a rearrangement to a more stable structure; one with more and stronger internal associative interactions. As the data in Table 1 show, extractability of coals decreases with increasing rearrangement, both because of more and stronger interactions in the coal and because of reduced diffusion. The swelling of Pittsburgh coal by pyridine is also reduced. Swelling is a measure of how much pyridine will dissolve in the coal. Pyridine dissolution is reduced by the rearrangement. This solubility reduction is expected to be general. Coals rearrange to structures in which fluids are less soluble than they are in the original coal.

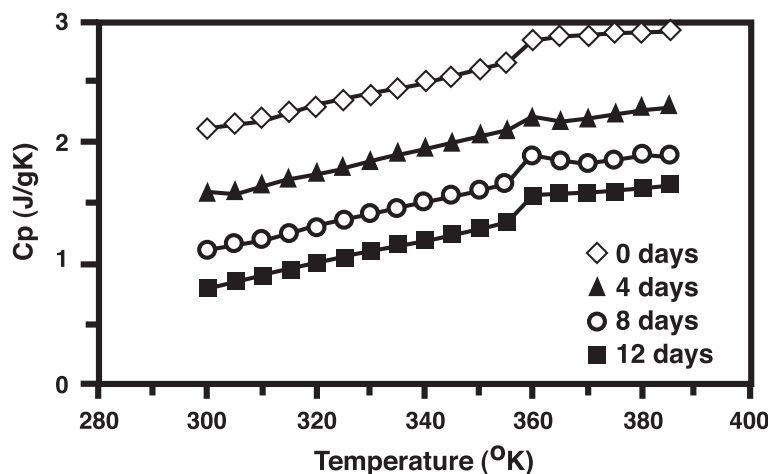


Fig. 2. Changes in the heat capacity of Pittsburgh No. 8 coal caused by heating (115 °C) in chlorobenzene for the indicated time (from Larsen et al., 1997).

2. Results and discussion

2.1. Swelling by CO₂

In 1983, Reucroft and Patel (1983, 1986) reported that CO₂ dissolved in coals and swelled them in addition to adsorbing on the coal surface. The data most relevant for this work are contained in the second paper and may be found in Table 2 (Reucroft and Sethuraman, 1987). The total CO₂ uptake consists of adsorbed CO₂ and CO₂ dissolved in the coal. As expected, the total uptake increases with gas pressure. At all pressures, small coal swelling was observed, the largest amount being about 4%. This small volume increase is due to dissolution of the CO₂ in the coal. Often, half of the total uptake is due to dissolved CO₂. More CO₂ is dissolved as the coal rank decreases. Swelling rates were measured and increase with increasing pressure. The time to reach half of maximum swelling of the 84% C coal decreases from about 40 h at 1 atm to about 10 h at 15 atm. With only three samples, the dependence of swelling rate on coal rank cannot be discerned. These data make it clear not only that CO₂ dissolves in coals, but also that at higher pressures dissolution will exceed adsorption. Coal swelling accompanying CO₂ dissolution should decrease the permeability of the coal as cleats and pores are squeezed. This has been observed and is shown in Fig. 3 (Skawinski 1999).

The swelling of coals by CO₂ is anisotropic, just as is coal swelling by organic liquids (Ceglarska-Stefanska and Czaplinski, 1993, Larsen et al., 1997).

Table 2
Carbon dioxide adsorption and dissolution (from Reucroft and Sethuraman, 1987)

Coal (%C, daf)	CO ₂ pressure (atm)	Coal swelling (vol.%)	CO ₂ dissolved (%) ^a
KCER 7259 (84)	5	0.75	14
	10	0.85	16
	15	1.33	24
KCER 7122 (78)	5	1.24	23
	10	2.23	41
	15	3.11	58
KCER 7463 (66)	5	2.16	24
	10	3.00	33
	15	4.18	47

^a Percent of the total CO₂ uptake that is dissolved in the coal. The rest is adsorbed.

Three high-rank Polish coals were treated with CO₂ at pressures up to 4.0 MPa (atm). They expanded more perpendicular to the bedding plane than they did parallel to it. Furthermore, the kinetics of the initial sorption were different from those obtained subsequently, when the coal was degassed and the sorption process repeated. This is the same behavior observed by Hsieh and Duda (1987) and demonstrates that CO₂ absorption resulted in a change in the coal structure. Fig. 1 contains one example of this behavior. Both of these behaviors, anisotropic swelling and changes in sorption kinetics have been observed during the uptake of organic liquids by coals. The CO₂ dissolves in the coal and serves as a plasticizer enabling a structure rearrangement so that the second absorption of CO₂ is into a different material, the same coal with a different structure. The kinetics are therefore different. The swelling anisotropy is due to mechanical stress having deformed the coal and the release of the deformation when the coal is plasticized by the dissolved CO₂. The behavior of CO₂ is parallel to that of organic liquids that swell (i.e. dissolve in). The anisotropic swelling of coals was reported by Cody et al. (1988) and explained later when it was realized that only the first swelling was anisotropic, greater perpendicular to the bedding plane than parallel to it (Larsen et al., 1997). If the swelling liquid is removed and the swelling process repeated, the swelling is isotropic and remains isotropic throughout further trials. The origin of the anisotropy must lie in the original state of the coal. It is strained, compressed and this strain is released when the swollen coal becomes rubbery and facile molecular motion becomes possible. Recent measurements of coal porosity using CO₂ at pressures below 0.2 MPa show that the swelling and shrinking of the coal structure caused by CO₂ dissolution in the coal are reversible (Rodrigues and Lemos de Sousa, 2002). High-pressure isotherms for CO₂ on coals have recently become available (Krooss et al., 2002, Busch et al., 2003).

Carbon dioxide has the same effect on coals' behavior as do liquids known to dissolve in and to swell coals. The most reasonable conclusion is that CO₂ also dissolves in coals and acts as a plasticizer enabling rearrangements in the coal physical structure.

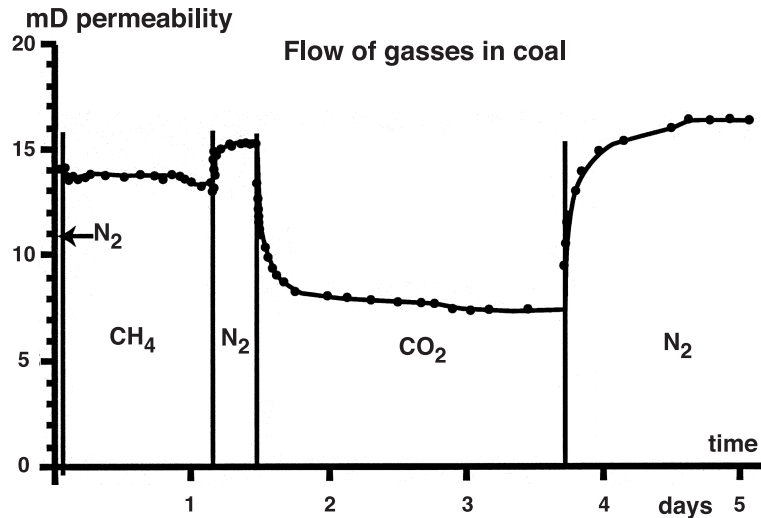


Fig. 3. Effect of CO₂ on coal permeability (from Skawinski 1999).

2.2. Effect of dissolved CO₂ on coal properties

Given that very long term storage of CO₂ in coals has been proposed, one might expect to find a large and growing body of information about the effect of CO₂ on coal properties. In fact, there is very little information. For many years, it was generally assumed that CO₂ only adsorbed on coals. If one assumes that, there is little reason to investigate its effects on coal properties. That CO₂ is a plasticizer and facilitates rearrangements of coal structure has already been documented. The question facing us now is: how effective a coal plasticizer is CO₂. That it is a sufficiently good plasticizer to change the absorption properties of coals and to effect coals' permeability has already been documented here.

The most impressive and worrisome data shows (Fig. 4) the effect of CO₂ and He at elevated pressures on the softening temperature of a high-rank Lower Kittanning coal (PSOC 1197, 91% C, dmmf) (Khan and Jenkins, 1985, Khan, 1985). The measurements were made using a high-pressure dilatometer. The results are stunning and raise concern over the practicality of storing CO₂ in coals should this behavior be general. While He has no effect on the softening temperature of this coal, the dilatometer reading begins to decrease sharply at a CO₂ pressure of 30 atm and drops from 673 to about 300 K at 55 atm. Presumably, this is due to softening of the coal. It is

shown in Fig. 4 (copied without change from Khan, 1985). Coals of this high rank are not normally significantly soluble so extraction by the gas phase CO₂ is an unlikely explanation for this observation. Similar effects of high-pressure CO₂ on confined coals have recently been observed (vide supra).

While the coal rearrangements that occur using CO₂ as a plasticizer have not been systematically studied, there is no reason to suppose that the rear-

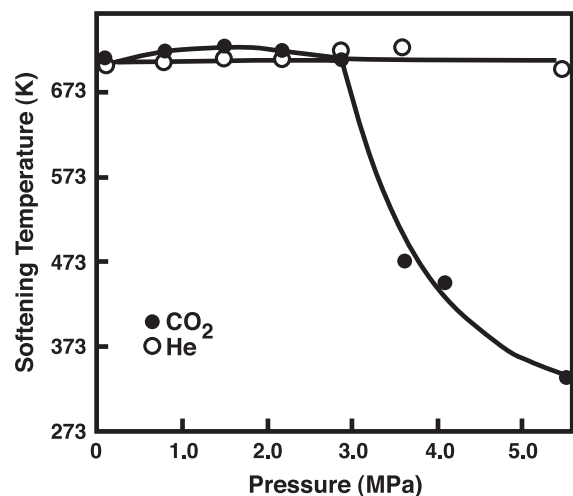


Fig. 4. Effect of CO₂ and He on the softening temperature of a Lower Kittanning (89.6% C, daf) (from Khan and Jenkins, 1985).

rangements will be any different than those that occur with other plasticizers. The rearrangement is largely controlled by the coal. The plasticizer increases free volume thus lowering T_g and enabling the rearrangement. For coals having less than about 86% C (dmmf), the rearrangement is to a more highly associated structure in which the solubility of liquids is reduced, sometimes cut in half. The data for Pittsburgh No. 8 coal shown in Fig. 2 and Table 1 show this nicely. The DSC data in Fig. 2 show a decrease of about 50% in heat capacity when the coal has been fully rearranged by heating in chlorobenzene which serves as a plasticizer. The same treatment reduces the solubility of pyridine in the coal by almost 50%. Under long-term storage conditions with CO₂ dissolved in a coal, that coal is expected to undergo a slow rearrangement that will decrease the solubility of CO₂ in the coals and some CO₂ will be expelled. The rate and extent of these processes are unknown, but recent data indicates that some structure rearrangements and CO₂ expulsion in confined coals occurs on a time scale of 4–5 days (Karacan and Mitchell, 2003, Karacan, in press).

The situation is more complicated for coals having more than 86% C (dmmf). Only two, Upper Freeport and Pocahontas, have been studied (Yun and Suuberg, 1992, 1993). Their behavior is complex and they may rearrange to a more or to a less highly associated structure. It is worth noting that the Lower Kittanning coal that showed such a dramatic lowering in softening temperature has 91% C (dmmf) and is similar in rank to Upper Freeport and Pocahontas coals.

2.3. CO₂ Diffusion and interaction energy

The interaction thermodynamics of CO₂ with the surface of Illinois No. 6 coal have been measured using inverse gas chromatography (coal packed gas chromatography columns) that allows the surface interactions to be isolated and avoids complications from dissolution of the CO₂ in the coal (Glass and Larsen, 1994 and references therein). Hydrocarbons and inert gasses can only interact with the coal by polarizability (London) interactions and constitute the base case. The isosteric enthalpies of adsorption of a set of nonpolar molecules and CO₂ on Illinois No. 6 coal are shown in Fig. 5. As expected, the adsorption enthalpy of the nonpolar molecules shows a straight line dependence on their polarizability. The more favorable interaction enthalpy of CO₂ is revealed by its exothermic deviation from the line. This favorable interaction will increase CO₂ solubility in coals compared to hydrocarbons and may enable it to diffuse more rapidly into coals.

An example of this is shown in the data in Table 3 that contains the BET surface areas of the Argonne premium coals measured at $-78\text{ }^\circ\text{C}$ with both CO₂ and ethane (Larsen et al., 1995). Both molecules have the same shape and ethane is 16% larger than CO₂. In all cases, CO₂ uptake is greater, often much greater, than ethane uptake. Because CO₂ measured coal surface areas are similar to those measured by X-ray scattering, the difference between the surface areas was ascribed to a very slow diffusion of the relatively insoluble ethane through the coal and a rapid diffusion of CO₂ through the coal. No matter what the expla-

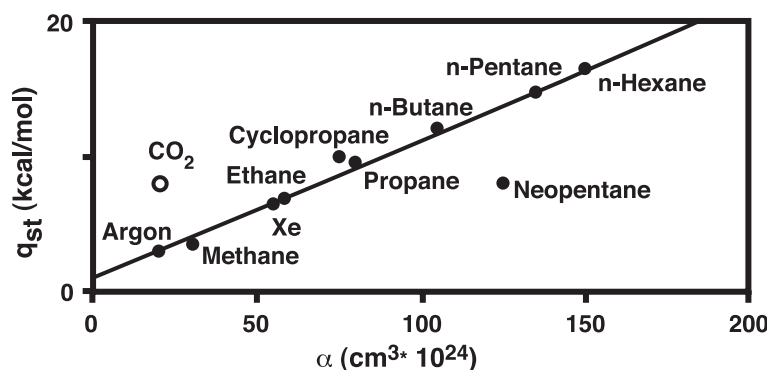


Fig. 5. Isosteric enthalpies of adsorption of nonpolar gasses and CO₂ on Illinois No. 6 coal (from Larsen et al. 1995).

Table 3

Surface areas (m^2/g) of coals measured by gas adsorption at $-78^\circ\text{C}^{\text{a}}$ (from Larsen et al., 1995)

Coal (%C, dmmf)	CO_2	Ethane
Pocahontas (91.8)	202	69
Upper Freeport (88.1)	166	72
Stockton (75.5)	175	34
Pittsburgh No. 8 (85.0)	177	37
Blind Canyon (81.3)	239	122
Illinois No. 6 (80.7)	132	38
Wyodak (76.0)	330	106
Beulah Zap (74.1)	274	11

^a BET equation $\pm 3 \text{ m}^2/\text{g}$.

nation, the data demonstrate that CO_2 and hydrocarbons behave very differently in their interactions with coals.

2.4. Confined coal

A central question is the effect of confining the coal on CO_2 uptake and the effect of dissolved CO_2 on coal properties. There are not many data. There is one report that confining a sample of coal resulted in an increase in CO_2 uptake (Ceglarska-Stefanska and Czaplinski, 1991). Pressure is known to increase polymer T_g by decreasing free volume. However, if the rearranged coal has a smaller volume than original coal, pressure will exert a driving force for rearrangement.

The effect of CO_2 at pressures up to 4.42 MPa on Pittsburgh No. 8 coal confined at pressures up to 5.78 MPa have been studied by using X-ray tomography (Karacan, in press; Karacan and Mitchell, 2003). The second of these papers provides the most information because, by using X-rays of two different energies, changes in the coal bulk density and the position of the CO_2 in the coal could be simultaneously determined. Even when the coal is physically confined, CO_2 dissolves in vitrinite and swells it significantly compressing other lithotypes, especially clay and inertinite. The plasticized vitrinite rearranges and expels some CO_2 within 4–5 days. In this coal, most of the sorbed CO_2 is found in the clays and interinites with vitrites absorbing smaller amounts. This seminal paper demonstrates that significant changes in the structure of confined coals rapidly occur upon CO_2 uptake. Characterization of these changes is crucial for evaluating the practical-

ity of CO_2 sequestration in coals. While an adequate theoretical framework for understanding coal– CO_2 interactions exists, much more data are needed, especially data on the changes in coal structure caused by CO_2 absorption.

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