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Oxidant stimulation for enhancing coal seam permeability: Swelling and solubilisation behaviour of unconfined coal particles in oxidants

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ABSTRACT

Low permeability renders a significant fraction of coal seam gas (CSG) resources sub-economic. An effective permeability enhancement strategy is thereby crucial in monetising a large proportion of low permeability CSG resources. This paper introduces the concept of using oxidants for permeability enhancement, describes a practical screening method to evaluate potential oxidants and provides knowledge about the coal behaviour in oxidants. A test based on time-lapse photography and image analysis of coal particles immersed in liquid oxidants was used to assess the extent and rate of change of coal particle size. Complementary leaching tests determined the extent of coal solubilisation by quantifying the change in coal mass and leachate organic content. The swelling profiles of coal particles hand-picked from a low permeability CSG coal core (Bowen Basin, Australia) were first examined in solutions of potassium chloride, and then pyridine for the purpose of method development and validation. Finally, the swelling ratio, S_R, and rate of swelling S_r (% area change per 6 h), of coal particles immersed in oxidising solutions of sodium hypochlorite (0.1%, 1% and 10% NaClO), potassium permanganate (0.015%, 0.03%, 0.1%, 1%, 3% and 5% $KMnO_4$), hydrogen peroxide (1%, 3%, 10% and 30% H_2O_2) and potassium persulfate (1% and 3% $K_2S_2O_8$) were examined.

Results provide evidence for coal solubilisation (maximum mass loss = 15%) and the propensity to swell (maximum particle size increase = 15%) in all the candidate oxidant stimulants as well as coal breakage in specific oxidants and at specific concentrations (1% NaClO and 3%, 5% $KMnO_4$). The swelling and solubilisation of the coals used in this study tends to increase with higher oxidant concentrations. Anisotropic swelling was also clearly observed in 1% NaClO. Coal reacted vigorously with NaClO and $KMnO_4$, but only slightly with $K_2S_2O_8$ and H_2O_2. Massive coal solubilisation occurs in NaClO and $KMnO_4$, but negligible in $K_2S_2O_8$ and H_2O_2. In terms of coal oxidation to enhance permeability, NaClO and $KMnO_4$ seem to be more promising than $K_2S_2O_8$ and H_2O_2.

For the situation of in situ application, it remains unclear if the net effect of coal swelling and coal solubilisation will increase or decrease permeability. In addition, coal breakage may lead to void space or new cracks in the coal matrix, which could have the potential to increase the coal permeability. Confined core-flooding tests that simulate in situ conditions are required to elucidate this behaviour.

1. Introduction

Commercial extraction of methane from coal seams is now well established in a number of countries throughout the world, including the USA, Australia, China, India and Canada [1]. Permeability of coal seams is a key controlling factor for gas migration in coal reservoirs and is often a critical technical barrier preventing economically viable gas production [2]. Therefore, permeability enhancement can be a crucial mitigation strategy to monetise CSG resources.

Coal permeability is primarily dictated by its cleat system, which is vastly different from conventional reservoirs [3]. Liu et al. (2013) summarised different characterisations such as reservoir properties of coal compared to those of conventional reservoirs. One of the most striking contrasts is that coal seam reservoirs tend to have much lower effective bulk permeability, and that this can hinder the commercial development of CSG plays [4]. Because of this, many CSG reservoirs require some form of stimulation to generate economic gas production. Low permeability stimulation treatments primarily consist of hydraulic fracturing and multi-lateral horizontal wells [5]. Though employed in a number of coal basins, these coal seam permeability enhancing methods have not been ubiquitously successful [6,7]. The associated damage to the coal formation, fines migration due to shear failure

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during hydraulic fracturing, and stress dependent permeability reduction including proppant embedment can significantly reduce the fracture connectivity and thus effective coal permeability [8,9].

The efficiency of horizontal wells is sometimes decreased by hole collapse, particularly when drilling underbalanced or drilling through depleted coal seams [7]. Some studies have been conducted with respect to the thermal enhancement of permeability [10] which is, however, only at the theoretical stage and currently remains sub-economic.

Chemical stimulation to dissolve parts of the coal have been proposed [11–13], chemicals could dissolve the minerals and/or the organic matrix. Oxidants could have potential to increase the coal cleat aperture by etching the coal cleat surface or dissolving a portion of the coal matrix. In addition, weakening the coal matrix by oxidant reactions may also prove applicable as a pre-hydraulic fracturing conditioning process. This study specifically aims to identify promising oxidants, those that can etch/dissolve the surface of a coal cleat while minimising matrix swelling. This is a critical step prior to the lengthy and relatively complex core flooding studies, such that insights gained from this work on coal behaviour in oxidising solutions will complement and improve the understanding of chemical and physical mechanisms that occur when coal comes into contact with oxidants.

Coal oxidation has been studied in coal structure investigations [14–16], desulfurization [17,18] as well as organic chemical extraction from coal [19,20]. Commonly used coal oxidation agents include sodium hypochlorite (NaClO), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2).

NaClO has been used for fundamental research about coal structure [14,15] and obtaining organic substances from coal [20]. Because of its availability, NaClO is attractive as an industrial oxidant [16]. Coal oxidation with NaClO was used in Chakrabartty and co-workers' research to investigate coal's molecular structure [14] and then similar research was conducted by Mayo et al. [15,21,22]. Mayo et al. reported that during NaClO oxidation, the condensed aromatic rings in the coal structure could be attacked to generate primarily, a base-soluble "black acid", and secondarily, water-soluble light-colour acids and carbon dioxide [21].

The presence of oxidation products indicates the potency of NaClO to degrade coal. Recently, Wei and his team published a series of research articles about coal oxidation by NaClO to acquire an industrially useful organic substance and to investigate the coal oxidation mechanisms [16,19,20,23–25]. Employing GC–MS, they found that most of the coal, regardless of coal rank, could be oxidised by NaClO and the main oxidative products were short-chain alkanoic acids, benzene polycarboxylic acids and some carbon dioxide [23].

Of the few papers that report coal oxidation by $KMnO_4$ solutions, Norton et al. showed information about the coal desulfurisation with permanganate [26] and the limitations of this method, such as the necessity of multiple reactions and the deposition of manganese dioxide from the decomposition of $KMnO_4$ [18]. Moore et al. etched the coal surface using $KMnO_4$ with sulphuric acid to observe the fossil plant particles [27]. With $KMnO_4$ commonly used in soil and water remediation to remove excessive organic matter [28,29], it shows promise for our application.

Hydrogen peroxide is also a commonly used industrial oxidant. It has been used for coal desulfurisation [17,30], coal structure analysis [31] and obtaining organic acids from coals by oxidation [32]. Jones et al (2013) studied coal oxidation during dewatering procedures and found that the carbon in coal could be converted to CO_2 when exposed to 10% H_2O_2 [33]. Mae et al. (1997) used hydrogen peroxide as a pretreatment solution to increase coal extraction. They found that some of the covalent bonds in coal were cleaved by H_2O_2 and transformed into various oxygenated functional groups, such as –COOH, C–O–C and R–OH [34].

All the oxidants described above show various degrees of effectiveness in oxidising coal. However, very few investigations exist in the application of these oxidants for enhancing coal seam permeability.

Coal matrix swelling in solvents like pyridine has been widely studied [35–38]. A large body of research with regard to coal particle size change has been conducted using multiple methods [36,39], among which, camera observation is a simple and sufficient method as described in Van Niekerk's work [40,41]. Other researchers, such as Murata [38], Gao et al. [36,39,42] also utilised 2 or 3 cameras to study the anisotropic swelling of single coal particles with a size between 200 and 250 μm in solvents including pyridine and N-methylpyrrolidone (NMP). Therefore, this study employs the camera based swelling test in conjunction with leaching tests to screen potential oxidants that solubilise coal.

With knowledge of coal's behaviour in oxidising solutions, it is aimed to develop an appropriate technique to increase the coal permeability. Additionally, the oxidants with negligible environmental impact, would be considered further.

2. Experimental

2.1. Coal sample and candidate oxidants

Coal particles (~3–4 mm), hand-picked from a CSG bituminous coal core (depth > 1200 m) of the Bandanna Formation, Bowen Basin, Australia, were used for this study.

Particle selection ensured that obvious mineralisation in certain core sections where avoided, such that, mineral content of the matrix–dominated coal particles are at a minimum. The ultimate, proximate and petrographic analysis of this bituminous coal core sample is summarised in Table 1.

2.2. Swelling test

A time-lapse photographic method was developed to study the swelling behaviour of coal particles in various solutions and candidate oxidant stimulants. In the current method one camera was used with multiple coal particles (between 20 and 40 mg, 3–4 mm). This is to increase the representativeness of the test, because although all the coal particles are from one single coal core sample, they might have different maceral compositions and internal structures. The advantage of this method is that the extent and rate of swelling or shrinkage of larger individual coal particles can be studied. Each test was repeated to check the confidence of the results.

Table 1
Ultimate, proximate and petrographic analysis of CSG sample used in this study, shown in% composition.

Ultimate analysis (wt%, daf)					Proximate analysis (wt%, db)				Petrographic analysis (vol%, db)				Vitrinite reflectance
C	H	S	N	O (diff.)	Ash	VM	FC	MC	V	I	L	M	Ro ,%
85.54	5.06	0.33	1.97	7.10	6.6	28.7	62.2	2.5	62.8	32.4	2.2	2.6	0.84

Proximate analysis includes Ash, Volatile Matter (VM), Fixed Carbon (FC) and Moisture Content (MC). Maceral composition consists of vitrinite (V), inertinite (I), liptinite (L) and Minerals (M). daf: dry ash free base; db: dry base. The candidate oxidant stimulants used in this study include sodium hypochlorite (NaClO), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and potassium persulfate ($K_2S_2O_8$). All oxidants are of AR-grade quality sourced from Sigma Aldrich.