

Removing Coal Radicals by Chemical Reduction

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The radical population of Wyodak coal was decreased by reaction with the reducing agents SmI_2 , YbI_2 , and CrCl_2 . The latter is the most effective, removing 67% of the radicals. It is also the easiest to prepare. The swelling of Wyodak coal in toluene, THF, and pyridine is independent of the coal's radical population demonstrating that radical sites are not responsible for intermolecular associative interactions.

The radicals in coal have been much studied.¹ Because they render carbons invisible in ^{13}C NMR experiments,^{1,2} Stock developed a procedure (reduction with $\text{Sm}(\text{II})$) that decreases their concentration in coals.³ We here report: (1) several other reagents useful for the reduction of radicals in coals, (2) a procedure for measuring the stability of radicals in coals, (3) a demonstration that in one coal the radicals are not involved in associative interactions.

We used a pulsed electron paramagnetic resonance (EPR) method to measure the numbers of spins in reduced and unreduced Argonne Premium Wyodak coal samples. The principal advantage of the method over conventional continuous wave (CW) EPR is the ease with which the difficult problem of microwave saturation can be avoided.⁴ The CW EPR technique requires measurements at multiple microwave powers⁵ in order to extrapolate accurately to sufficiently low power via Bloembergen-Purcell-Pound plots.⁶ This is often overlooked. The pulsed EPR method has been successfully applied to a set of Argonne Premium Coals.⁴ In this paper a two-dimensional (2D) version of the previous method⁴ is described. The present technique accounts for the possible magnetic field dependence of the echo shape and the spin coherence decay rate within the EPR line.

A typical gray scale plot time of the integrated two pulse (32 ns–64 ns) echo intensity versus magnetic field and echo delay is shown in Figure 1. Figure 2 shows the corresponding extrapolations of the two-pulse echo decays to zero delay time as a function of magnetic field

strength. The EPR intensities, such as in Figure 2, are integrated to give values proportional to the number of spins in the sample. The numbers of spins in Table 1 were obtained from triplicate EPR measurements on two different samples of the material. The absolute numbers of spins were determined by comparison with a DPPH (2,2-diphenyl-1-picrylhydrazyl) standard sample in frozen toluene solvent at 80 K.

As shown by the data in Table 1, the 1-electron reducing agents $\text{Sm}(\text{II})$ and $\text{Yb}(\text{II})$ destroy coal radicals by reducing them. Both SmI_2 and YbI_2 reductions were carried out following the procedure used by Muntean and Stock.³ The preparation of the iodides was as described by Girard et al.⁷ In our hands, purchased SmI_2 failed and SmI_2 made immediately before use did not always react, although it was the right color for $\text{Sm}(\text{II})$. We encountered no such problems with YbI_2 . CrCl_2 has been used to remove pyrite from geological samples and does this nicely.⁸ As the data in Table 1 reveal, it also removes radicals. It is readily prepared by reduction of $\text{Cr}(\text{III})$ using $\text{Zn}(\text{Hg})$. CrCl_2 is used in refluxing aqueous ethanol and the SmI_2 and YbI_2 reductions use tetrahydrofuran (THF) as solvent at room temperature. CrCl_2 is the easiest to prepare and the most effective at reducing the radicals in Wyodak coal and we are now working on its use in solvents that are better for higher rank coals.

It is expected that different fractions of the coal radicals will be reduced by metals having different reduction potentials. $\text{Sm}(\text{II})$, with a reduction potential of -1.55 V(THF) should reduce radicals that will be stable to $\text{Yb}(\text{II})$, whose reduction potential in THF is -1.05 V. Both of these reagents in our hands reduced about half the radicals in Wyodak coal. Stock reported a 46% reduction in radicals with $\text{Sm}(\text{II})$ and we achieved 55%. It is clear that the deciding factor in radical reduction is not radical stability. That the most stable reducing agent $\text{Cr}(\text{II})$ removes the most radicals demonstrates that thermodynamics is not controlling. The

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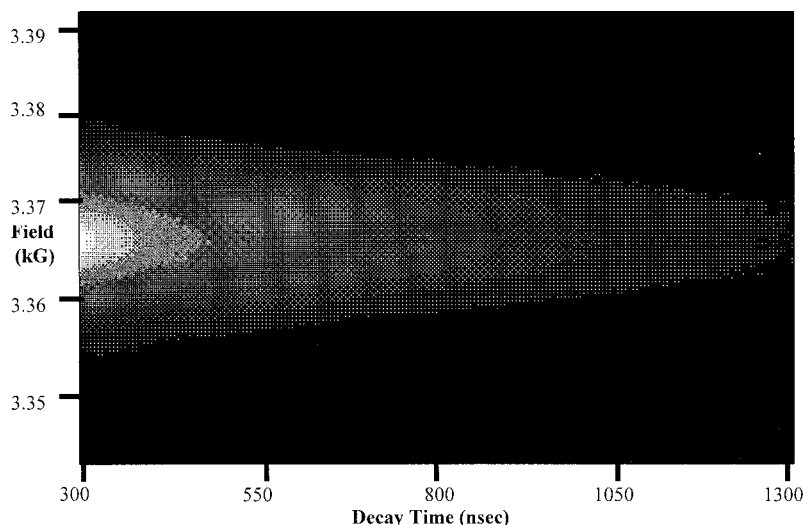


Figure 1. Example of the 2D linear gray scale plot of integrated electron spin-echo intensity versus magnetic field and decay time for a 22.6 mg sample of SmI_2 -treated Argonne Premium Wyodak coal at room temperature. The intensities run from highest in white to zero in black.

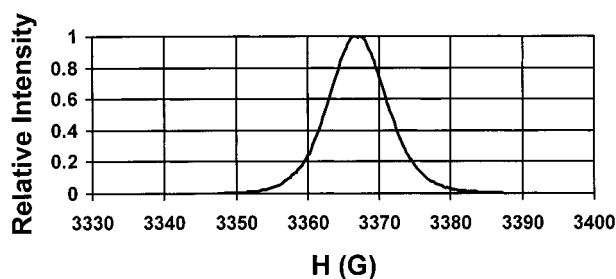


Figure 2. Example of the EPR intensity extrapolated to zero pulse interval from the two-dimensional plot of integrated echo intensity versus magnetic field and pulse interval shown in Figure 1. The data were obtained from a 22.6 mg sample of SmI_2 treated Argonne Premium Wyodak coal at room temperature.

Table 1. Relative Spin Concentrations in Wyodak Coal

sample	reduction potential (V) ^a	radicals remaining ^b (%)	spins/unit mass $\times 10^{-19}$ (g^{-1})
Whole Coal		100	1.12 ^c
YbI_2 -reduced	-1.095	48(2.8)	0.54
SmI_2 -reduced	-1.55	45(2.5)	0.51
SmI_2 -reduced ^d		54	
CrCl_2 -reduced	-0.42 ^e	33(2.1)	0.37

^a In THF. Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; W. H. Freeman and Co.: New York, 1994. ^b Standard deviations in parentheses next to values. ^c The literature value³ is 1.00×10^{19} . ^d From ref 3. ^e In water.

Cr^{2+} reagent has a significantly smaller ionic radius than Sm^{2+} and Yb^{2+} and is therefore expected to be the most nearly under thermodynamic control. Figure 3 shows two calculated curves for coal radical potentials that give the observed $\text{Cr}(\text{II})$ result, with (a) a negligible spread in coal radical reduction potential, (b) a 1.00 V Gaussian spread (1/e width) in coal radical reduction potential. The curves illustrate the degree to which at least the $\text{Sm}(\text{II})$ and $\text{Yb}(\text{II})$ reagents fail to achieve thermodynamically controlled reduction of the coal radicals. We are attempting to develop a range of systems in which the reduction of radicals in coals will be under thermodynamic control. If this can be achieved, the spread of radical stabilities in coals can be determined by using 1-electron reducing agents having differing reduction potentials.

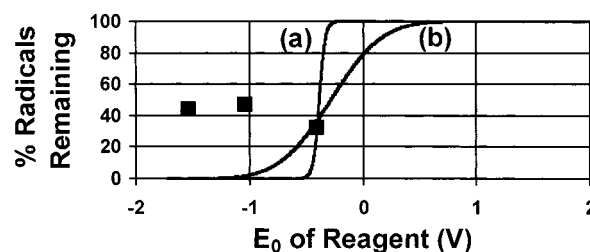


Figure 3. Predicted percentages of coal radicals remaining after treatment with reagents of the given reduction potentials (E_0) at room temperature. The curves are based on coal radical reduction potentials that give the observed $\text{Cr}(\text{II})$ percentage, with (a) a negligible spread in coal radical reduction potential, (b) a 1.00 V Gaussian spread (1/e width) in E_0^{coal} about a mean value of -0.283 V.

Table 2. Volume Increase (final volume/original volume) of Wyodak Coal on Swelling in the Listed Solvent

sample/solvent	toluene	THF	pyridine
unreacted	1.3	2.4	2.6
EtOH -treated	1.2	2.0	2.8
$\text{CrCl}_2/\text{EtOH}$	1.2	2.3	2.8
THF -treated	1.2	1.9	2.7
SmI_2/THF	1.2	1.8	2.9
YbI_2/THF	1.2	2.1	2.4

It has been suggested that radicals may be the loci of strong intermolecular interactions in coals by 3-electron 2-orbital or 1-electron 2-orbital interactions.⁹ We now have a sample of a single coal with several different radical populations so this suggestion can be tested by solvent swelling the coal. If radicals are participating in intermolecular associative interactions, as the radical population decreases, swelling should increase. The data in Table 2 demonstrates that swelling is independent of radical concentrations. In this coal, radicals are not responsible for associative interaction.

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