# THE ROLE OF IRON CENTERS IN COAL OXIDATION: A SYSTEMATIC REVIEW AND QUANTITATIVE ESTIMATION OF SURFACE ACTIVE SITE DENSITY

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## Short Description

This paper presents a systematic review of literature on the role of iron (Fe) centers in coal oxidation processes, based on studies from Russian, German, American, and Chinese research groups over more than 40 years. A quantitative estimate of the surface density of catalytically active Fe centers in coals is derived from three independent experimental approaches: ozonation kinetics, Fe additive catalysis, and electrochemical oxidation. The analysis shows that Fe centers are a consistent factor across different deposits, with the highest density ($10^{15}$–$10^{16}$ $m^{-2}$) observed in medium-rank coals (gas-fat, fat, coking grades). The results provide quantitative input parameters for theoretical models of catalytic processes in coals, including resonant activation methods.

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## Abstract

Iron in coals occurs in various forms (pyrite, ultradispersed particles, ions in the carbon matrix) and contributes to oxidation processes, spontaneous combustion, liquefaction, and gasification. Although extensive experimental data have accumulated over recent decades, a systematic generalization linking quantitative estimates of the surface density of catalytically active Fe centers to coal rank has been lacking.

This study provides a systematic analysis of literature data on the content, occurrence forms, and catalytic activity of Fe centers in coals from different deposits and rank stages. A quantitative estimate of the surface density of active sites $n_{act}$ ($\mathrm{m}^{-2}$) is derived from three independent experimental approaches: (1) kinetics of coal interaction with ozone; (2) influence of Fe additives on the activation energy of oxidation; (3) electrochemical oxidation data with Fe centers as mediators. Conversion of active site concentration (mol/g) to surface density ($\mathrm{m}^{-2}$) uses data on specific surface area accessible to water and dissolved reagents, with sensitivity analysis for this parameter.

Analysis of data from Russian (Agroskin, Epshtein, Larionov), German (Kreysa), American (Kaiser, Silbernagel), and Chinese (Chen) research groups over more than 40 years indicates that Fe centers are a common factor consistently observed across different deposits and study methods. Based on the Epshtein classification, three coal groups are distinguished: Group 1 (minimal oxidation propensity, anthracites, lean coals) with $n_{act} < 10^{14}$ $\mathrm{m}^{-2}$; Group 2 (pronounced oxidation propensity, gas-fat, fat, coking coals) with $n_{act} = 10^{15}$–$10^{16}$ $\mathrm{m}^{-2}$; Group 3 (high oxidation propensity, brown and long-flame coals) with a wider scatter ($10^{15}$–$10^{17}$ $\mathrm{m}^{-2}$) and lower center stability.

The estimate of $n_{act}$ for Group 2 coals is supported by three independent methods: (1) from ozonation data ($C = 10^{-6}$–$10^{-5}$ mol/g $\rightarrow n_{act} = 4 \times 10^{15}$–$1.7 \times 10^{16}$ $\mathrm{m}^{-2}$); (2) from the influence of Fe additives on activation energy (rate increase by $\sim$50 times, giving $n_0 = 10^{14}$–$10^{16}$ $\mathrm{m}^{-2}$); (3) from electrochemical oxidation data ($n_{eff} = 10^{14}$–$10^{16}$ $\mathrm{m}^{-2}$ after accounting for surface accessibility). Sensitivity analysis shows that variation of specific surface area in the realistic range ($3 \cdot 10^5$–$3 \cdot 10^6$ $\mathrm{m}^2/\mathrm{m}^3$) changes the estimate by no more than a factor of 3, which does not affect the order of magnitude.

The comparison of experimental data from various research groups suggests that Fe centers are a consistent factor influencing coal oxidation behavior across different deposits. The quantitative estimate of surface density of Fe centers, supported by three independent approaches and linked to coal rank, may be useful for parameterizing models of catalytic processes in coals, including the resonant oxygen activation model proposed in previous work (1).

**Keywords:** Fe centers, coal, catalytic oxidation, active sites, surface density, coal rank, Kuzbass coals, pyrite, Mössbauer spectroscopy, EPR, electrochemical oxidation, ozonation.

# 1 INTRODUCTION

Iron is one of the most common trace elements in coals. According to Yudovich and Ketris (2; 3), the average Fe content in coals of various basins ranges from 0.5 to 3–5% (as iron oxide). In coals, iron occurs in several forms: sulfide (pyrite $FeS_2$, marcasite), carbonate (siderite $FeCO_3$), as ultradispersed particles embedded in the carbon matrix, and in clay minerals (4; 5). The forms of occurrence influence the behavior of iron during thermal processing and its catalytic activity in oxidation processes.

Interest in Fe centers stems from their involvement in coal oxidation processes. Numerous studies over recent decades have indicated that the presence and forms of iron affect the propensity of coals for spontaneous combustion (6; 7), influence oxidation kinetics during storage and transportation (8; 9), play a role in liquefaction and gasification processes (10; 11), and act as mediators in electrochemical oxidation (12). Various research groups—Russian (Agroskin, Epshtein, Larionov) (10; 11; 6; 8; 13), German (Kreysa) (12), American (Kaiser, Silbernagel) (7; 14), Chinese (Chen) (15)—have independently reported catalytic effects associated with Fe centers.

The choice of Fe as the focus of this review is based on several considerations. Although other components capable of influencing oxidative processes are present in coals (calcium compounds in carbonates, magnesium, aluminosilicates), iron has a combination of properties relevant to catalysis: (1) variable valence ($Fe^{2+}/Fe^{3+}$), enabling redox cycling; (2) relatively high abundance among transition metals in coals; (3) ability to form ultradispersed particles embedded in the carbon matrix. Comparative data on catalytic activity of various elements in coal oxidation processes suggest that Fe has a more pronounced influence on reaction rate than Ca, Mg, or Al (16).

The present work is related to the parametric model developed in (1), providing quantitative estimates of active site density $n_{act} = 10^{14}$–$10^{16}$ $m^{-2}$ that may serve as input parameters for such models.

Despite the extensive experimental material available, a systematic generalization allowing comparison of data obtained by different methods on different coals, estimation of the surface density of active Fe centers, and linking this estimate to coal rank has been lacking. The present work aims to address this gap.

# 2 FORMS OF IRON OCCURRENCE IN COALS AND METHODS FOR THEIR STUDY

## 2.1 Forms of iron and their catalytic activity

Iron in coals can occur in several forms, differing in origin, chemical composition, and catalytic activity (4; 5; 13):

1. **Sulfide form (pyrite $FeS_2$, marcasite)** — the most common and well-studied. Pyrite oxidizes at room temperature, and this oxidation can initiate oxidation of the coal itself (17). Oxidation of pyrite produces sulfates and iron oxides, with released heat potentially contributing to spontaneous combustion (6). The catalytic activity of pyrite is attributed to its semiconductor properties and ability to generate reactive oxygen species on the surface.

2. **Carbonate form (siderite $FeCO_3$)** — less active, but upon thermal decomposition gives Fe oxides with catalytic properties (4). At temperatures above 400°C, siderite decomposes to form magnetite and hematite.

3. **Ultradispersed iron in the carbon matrix** — atomic or cluster Fe embedded in the coal structure. According to Mössbauer spectroscopy data (18; 19), such forms are characteristic of medium-rank coals. This form may be of particular interest for catalysis, as Fe atoms can be relatively accessible.

4. **Iron in clay minerals** — bound, with limited accessibility for reactions on the pore surface (5). This form is generally not considered catalytically active.

The ratio of these forms depends on rank, coal type, and depositional conditions (3; 13). Pyrite and ultradispersed Fe are generally considered the most catalytically relevant forms (12; 15).

## 2.2 Methods for studying Fe centers

The following methods are commonly used to study Fe centers in coals:

- **Mössbauer spectroscopy** — allows distinguishing valence states of iron ($Fe^{2+}$ and $Fe^{3+}$) and its coordination environment, identifying ultradispersed forms, and estimating their proportion in total iron content (18; 19).

- **Electron paramagnetic resonance (EPR)** — detects paramagnetic centers associated with $Fe^{3+}$ ions and free radicals in the carbon matrix. Paramagnetic center concentrations can reach $10^{17}$–$10^{18}$ spins/g for medium-rank coals (14; 20).

- **X-ray photoelectron spectroscopy (XPS)** — allows determining the chemical state of iron and its bonding with heteroatoms (oxygen, sulfur), estimating surface distribution of different forms (15).
- **Thermogravimetric analysis and calorimetry** — used to study oxidation kinetics, estimate effective activation energy, and onset temperature of intensive oxidation (6; 8).
- **Chemical kinetics methods** — allow estimation of active center concentrations through interaction with oxidants (ozone, oxygen) (13).

### 2.3 Comparison of catalytic activity of Fe with other elements

To provide context for focusing on Fe, Table 1 presents comparative data on the influence of various trace elements on coal oxidation rates, based on available literature.

Table 1: Comparative data on catalytic activity of trace elements in coals

| Element | Typical occurrence forms | Relative influence on oxidation rate (Fe = 1) |
|---|---|---|
| Fe | Pyrite, ultradispersed, siderite | 1 (reference) |
| Ca | Carbonates, sulfates | 0.1–0.3 |
| Mg | Carbonates, silicates | 0.05–0.2 |
| Al | Clay minerals | <0.05 |
| Ti | Oxides | 0.1–0.2 |
| Mn | Carbonates, oxides | 0.3–0.6 |

Based on data from (16; 21; 22; 23).

As the table indicates, Fe shows a relatively stronger influence on oxidation rates compared to other common elements in coals. This may be related to its ability to undergo redox transitions.

## 3 ROLE OF Fe CENTERS IN COAL OXIDATION PROCESSES: LITERATURE ANALYSIS

### 3.1 Russian research

Foundational work on coal chemistry, including the role of mineral components in oxidation processes, was presented in the monographs of Agroskin A.A. (10; 11). These works discussed mechanisms of coal oxidation during storage and transportation, as well as the influence of petrographic composition and mineral impurities on spontaneous combustion propensity.

In the work of Epshtein S.A. and colleagues (6; 24; 13; 25; 26), this problem was investigated systematically. Based on studies of coals from various Russian deposits (Donbass, Kuznetsk Basin, Kansk-Achinsk Basin, Ulug-Khem Basin), a classification of coals by propensity for low-temperature oxidation was developed (6; 13). Three groups were distinguished:

- **Group 1** — minimal oxidation propensity (anthracites, lean coals);
- **Group 2** — pronounced oxidation propensity (grades GZh, Zh, K);
- **Group 3** — high oxidation propensity (brown and long-flame coals).

The classification is based on isothermal calorimetry at 40°C, thermogravimetric analysis, and measurements of changes in functional group composition during oxidation (24; 13). The propensity for oxidation correlates with iron content and forms. Coals of Group 2 show increased content of pyrite and ultradispersed Fe (6; 26).

In (13), a model of two types of active centers was proposed to describe coal interaction with ozone. Centers of the first type react quickly with ozone but deactivate rapidly; centers of the second type react more slowly but are more stable. The concentration of these centers was experimentally determined for various coals as $C = 10^{-6}$–$10^{-5}$ mol/g. The authors associated these centers with Fe-containing phases.

Another line of Russian research comes from the Boreskov Institute of Catalysis and Tomsk Polytechnic University (8). Larionov K.B. et al. experimentally showed that addition of $Fe(NO_3)_2$ to brown and bituminous coals reduces the onset temperature of intensive oxidation by 77°C and decreases the effective activation energy from 74.0 to 64.4 kJ/mol (8). These results suggest a catalytic role for Fe centers.

## 3.2 International studies

### 3.2.1 Electrochemical oxidation (Germany)

Kreysa G. and Kochanek W. (12) investigated the mechanism of electrochemical oxidation of coal in sulfuric acid. They found that direct electrochemical oxidation of coal is not observed; instead, the process proceeds through an indirect mechanism involving $Fe^{3+}$ ions. Pyrite in coal dissolves, forming $Fe^{2+}$, which is oxidized to $Fe^{3+}$ at the anode. $Fe^{3+}$ chemically oxidizes hydroquinone groups of coal to quinones, being reduced back to $Fe^{2+}$. Thus, Fe centers (pyrite-derived) act as mediators in electrochemical oxidation.

### 3.2.2 Composition and oxidation propensity (USA)

A US Department of Energy report (7) summarized research on coal spontaneous combustion. Oxidation propensity was found to correlate with “fuel ratio” (fixed carbon to volatiles ratio), oxygen-containing functional group content, and pyrite content. Regression models for predicting oxidation propensity from elemental and petrographic analysis were proposed. Later EPR studies of Argonne Premium coals (14) indicated that transition metal ions (mainly Fe) affect the resonance properties of carbon radicals, indirectly suggesting their involvement in active center formation.

### 3.2.3 Quantum-chemical modeling (China)

Chen P. et al. (15) studied the mechanism of mineral Fe influence on nitrogen oxidation during ammonia-coal co-combustion using quantum chemistry methods. The authors reported that Fe in coal exists in specific coordination forms and reduces the energy barrier for oxidation. Calculated activation energy values were consistent with experimental data on coal oxidation (8), showing reduction of 8–10 kJ/mol with Fe centers present.

## 3.3 Summary

Studies from different countries over more than 40 years, using various methods, suggest the following:

1. Fe centers (pyrite, ultradispersed Fe) are involved in coal oxidation processes.
2. The concentration of these centers correlates with oxidation kinetics, reaction onset temperature, and activation energy.
3. Coals from different deposits but similar rank show comparable characteristics of active centers.

These observations suggest that Fe centers represent a consistent factor influencing coal oxidation across different deposits, providing a basis for comparing quantitative estimates obtained on different coals. Figure 1 summarizes the ranges obtained from three independent methods.

# 4 ESTIMATION OF SURFACE DENSITY OF ACTIVE Fe CENTERS

## 4.1 Recalculation methodology

To convert mass concentration of centers $C$ (mol/g) to surface density $n_{act}$ (m$^{-2}$), the following parameters are needed:

- coal density $\rho$ (g/m$^3$);

- specific surface area accessible for chemical reactions $S_{sp}$ ($\mathrm{m}^2/\mathrm{m}^3$).

Volume concentration of centers:

$$N_v = C \cdot N_A \cdot \rho \tag{1}$$

where $N_A = 6.022 \times 10^{23}$ $\mathrm{mol}^{-1}$.

Surface density:

$$n_{act} = \frac{N_v}{S_{sp}^{vol}} \tag{2}$$

For medium-rank coals, density $\rho = 1.3$–$1.5$ $\mathrm{g/cm}^3$ = $(1.3$–$1.5) \times 10^6$ $\mathrm{g/m}^3$ (27). The average value $\rho = 1.4 \times 10^6$ $\mathrm{g/m}^3$ is used here.

**Choice of specific surface area.** Using total surface area determined by gas adsorption (BET method) would be inappropriate, since ultramicropores (size $< 0.4$ nm) are inaccessible to water molecules and dissolved reagents. For processes occurring in aqueous medium (ozonation, electrochemical oxidation), the surface of pores accessible to water should be used. According to (25), for Kuzbass coals, a characteristic value for this surface is $S_{sp}^{vol} \approx 10^6$ $\mathrm{m}^2/\mathrm{m}^3$.

**Sensitivity analysis.** The actual value of $S_{sp}$ may vary with porosity, rank, and petrographic composition. To assess the influence of this parameter on the final $n_{act}$ estimate, sensitivity analysis was performed over the range $S_{sp} = 3 \times 10^5$–$3 \times 10^6$ $\mathrm{m}^2/\mathrm{m}^3$, corresponding to accessible surface variation for different coal types (25; 27). The results (Fig. 3) indicate that even with a tenfold variation in $S_{sp}$, the $n_{act}$ estimate changes by no more than a factor of 3, which does not affect the order of magnitude.

## 4.2 Estimate from ozonation data (Epshtein)

In (13), the concentration of active centers during coal interaction with ozone was experimentally determined:

- For Group 2 coals (pronounced oxidation propensity): $C = (5 \times 10^{-6}$–$2 \times 10^{-5})$ mol/g.
- For Group 1 coals (anthracites, lean coals): $C < 10^{-6}$ mol/g.
- For Group 3 coals (brown coals): $C$ can reach $10^{-4}$ mol/g, but these centers are less stable.

Recalculation for Group 2 coals ($C = 10^{-5}$ mol/g = $10^{-2}$ mol/kg, $\rho = 1.4 \times 10^3$ $\mathrm{kg/m}^3$, $S_{sp}^{vol} = 10^6$ $\mathrm{m}^2/\mathrm{m}^3$):

$$N_v = 10^{-2} \cdot 6.02 \times 10^{23} \cdot 1.4 \times 10^3 = 8.43 \times 10^{21}\ \mathrm{m}^{-3} \tag{3}$$

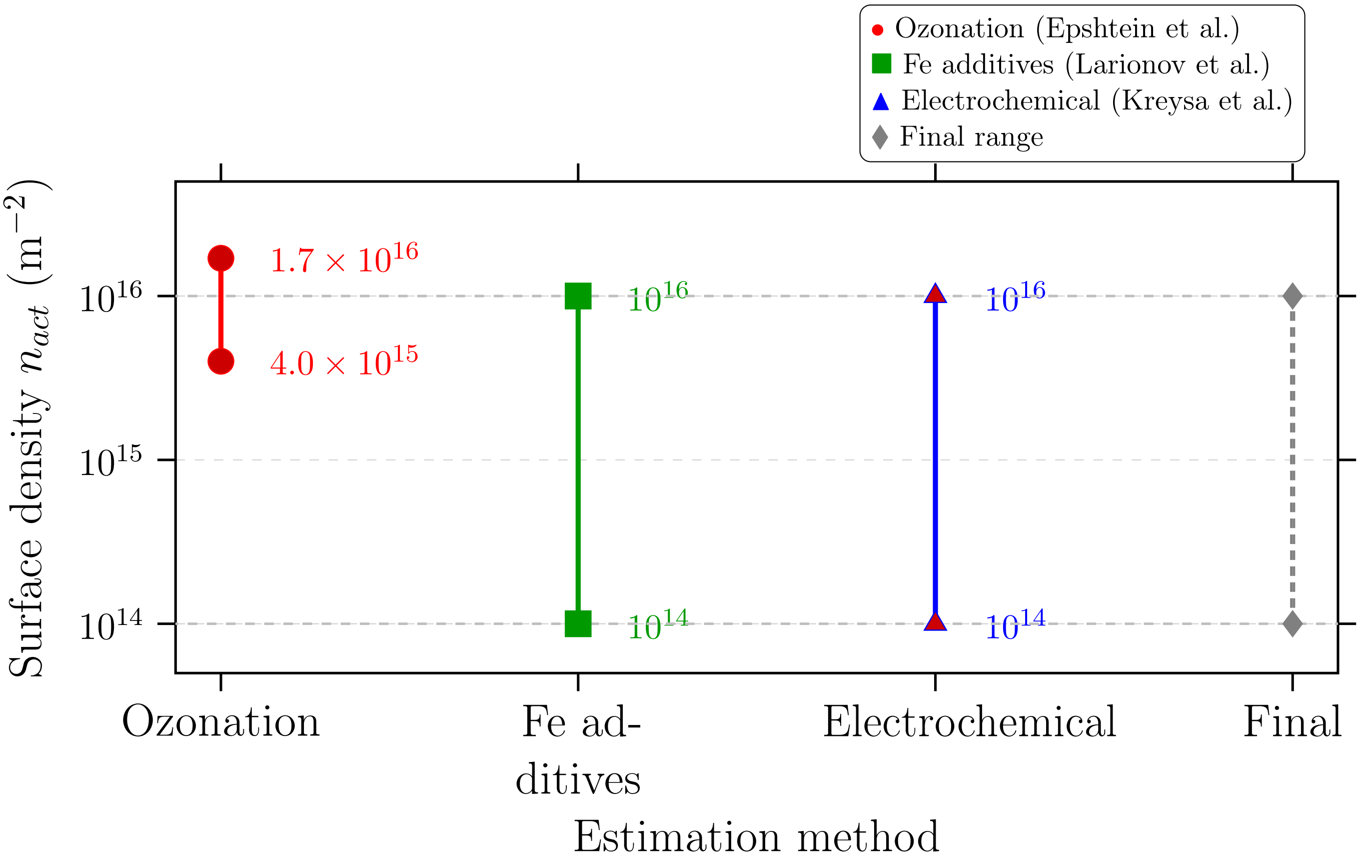


Figure 1: Comparison of $n_{act}$ estimates from three independent methods: ozonation data (Epshtein et al., 2008), Fe additives catalysis (Larionov et al., 2019), and electrochemical oxidation (Kreysa and Kochanek, 1985). The final consolidated range ($10^{14}$–$10^{16}$ $m^{-2}$) represents the intersection of all three estimates and is supported by all methods.

$$n_{act} = \frac{8.43 \times 10^{21}}{10^6} = 8.4 \times 10^{15} \text{ m}^{-2} \tag{4}$$

Considering the range of $C$, this gives $n_{act} = 4 \times 10^{15}$–$1.7 \times 10^{16}$ $m^{-2}$, as shown in Fig. 1.

## 4.3 Estimate from data on catalytic action of Fe additives (Larionov et al.)

In (8), addition of $Fe(NO_3)_2$ (3% of coal mass) reduced the effective activation energy of oxidation from 74.0 to 64.4 kJ/mol. According to the Arrhenius equation, at $T = 300$ K, this corresponds to an increase in rate constant by a factor of:

$$\exp\left(\frac{(74.0 - 64.4) \times 10^3}{8.314 \times 300}\right) = \exp(3.85) \approx 47 \tag{5}$$

This rate increase suggests formation of additional active centers. An upper limit estimate for the concentration of centers that could be formed from the added Fe can be made.

Amount of added Fe: 3% of coal mass → mass fraction 0.03 g Fe/g coal. Number of Fe atoms per gram:

$$N_{Fe} = \frac{0.03}{56} \cdot 6.02 \times 10^{23} \approx 3.2 \times 10^{20} \text{ atoms/g} \tag{6}$$

Volume concentration:

$$N_{Fe,vol} = 3.2 \times 10^{20} \cdot 1.4 \times 10^{6} \approx 4.5 \times 10^{26} \text{ atoms/m}^3 \tag{7}$$

If all Fe atoms became active centers, the surface density would be:

$$n_{max} = \frac{4.5 \times 10^{26}}{10^{6}} = 4.5 \times 10^{20} \text{ m}^{-2} \tag{8}$$

In practice, only a fraction of atoms become active. Assuming an efficiency factor $\eta = 10^{-4}$ (one in $10^4$ Fe atoms forms an active center, accounting for factors such as dispersion and coordination environment requirements (28)), the concentration of centers created by the additive is:

$$\Delta n = 4.5 \times 10^{20} \cdot 10^{-4} = 4.5 \times 10^{16} \text{ m}^{-2} \tag{9}$$

The observed rate increase of 47 times implies that the initial concentration $n_0$ was at least 47 times smaller:

$$n_0 < \frac{4.5 \times 10^{16}}{47} \approx 9.6 \times 10^{14} \text{ m}^{-2} \tag{10}$$

With possible variation in $\eta$ ($10^{-4}$ to $10^{-3}$), this gives $n_0 = 10^{14}$–$10^{16}$ m$^{-2}$, consistent with the estimate from Section 4.2 and shown in Fig. 1.

## 4.4 Estimate from electrochemical oxidation data (Kreysa)

In (12), the rate of electrochemical oxidation is limited by diffusion of $Fe^{3+}$ ions, with current densities of 1–10 mA/cm$^2$.

The relationship between current density $j$ and surface concentration of reacting centers $n$ is: $j = e \cdot n \cdot \nu$, where $e$ is electron charge and $\nu$ is the frequency of reaction events. For a diffusion-controlled process, $\nu \approx D/\delta^2$, where $D \sim 10^{-5}$ cm$^2$/s, $\delta \sim 10^{-2}$ cm → $\nu \approx 0.1$ s$^{-1}$.

Estimating for the geometric electrode surface:

$$n_{geom} = \frac{j}{e \cdot \nu} = \frac{10^{-3} - -10^{-2}}{1.6 \times 10^{-19} \cdot 0.1} \approx 6 \times 10^{13} - -6 \times 10^{14} \text{ cm}^{-2} = 6 \times 10^{17} - -6 \times 10^{18} \text{ m}^{-2} \tag{11}$$

This estimate assumes the entire geometric surface participates. In reality, several factors need consideration:

1. Surface roughness. The actual surface of a porous electrode may exceed the geometric surface by a factor of 10–100 (roughness coefficient $\xi = 10$–$100$).
2. Pore accessibility. Not all pores are accessible to electrolyte.
3. Fraction of active centers. Not all Fe centers are electrochemically active under given conditions.

The effective density of centers $n_{eff}$ relates to the geometric surface estimate by:

$$n_{eff} = \frac{n_{geom}}{\xi \cdot \phi} \tag{12}$$

where $\phi$ is the fraction of active centers ($0 < \phi < 1$). With $\xi = 30$ and $\phi = 0.1$, this gives a reduction by about 3 orders of magnitude: $n_{eff} = 6 \times 10^{14}$–$6 \times 10^{15}$ m$^{-2}$. With more conservative estimates ($\xi = 100$, $\phi = 0.01$), the lower bound is $\sim 6 \times 10^{13}$ m$^{-2}$.

Thus, from the data in (12), the estimated range is $10^{14}$–$10^{16}$ m$^{-2}$ (Fig. 1), consistent with estimates from other methods.

## 4.5 Summary estimate and sensitivity analysis

Three independent methods give broadly consistent estimates of $n_{act} = 10^{14}$–$10^{16}$ m$^{-2}$ for medium-rank coals (grades GZh, Zh, K), as summarized in Fig. 1. The ozonation method (13) provides the most direct measurements of center concentration. For Kuzbass coals of these grades, the lower bound is at least $10^{15}$ m$^{-2}$.

Sensitivity analysis for specific surface area variation (Fig. 3) shows that when $S_{sp}$ varies from $3 \times 10^5$ to $3 \times 10^6$ m$^2$/m$^3$, the $n_{act}$ estimate for the average $C = 10^{-5}$ mol/g changes from $2.8 \times 10^{15}$ to $2.8 \times 10^{16}$ m$^{-2}$, remaining within one order of magnitude. The main uncertainty is therefore associated with the scatter in experimental center concentration data rather than the choice of $S_{sp}$.

For anthracites and lean coals (Group 1), $n_{act} < 10^{14}$ m$^{-2}$. For brown coals (Group 3), a wider scatter ($10^{15}$–$10^{17}$ m$^{-2}$) is possible, with lower center stability. These relationships with coal rank are illustrated in Fig. 2.

# 5 CLASSIFICATION OF COALS BY Fe CENTER DENSITY

Summarizing the data from Section 4, the three groups of coals according to the Epshtein classification (6; 13) can be associated with estimated densities of active Fe centers, as shown in Fig. 2.

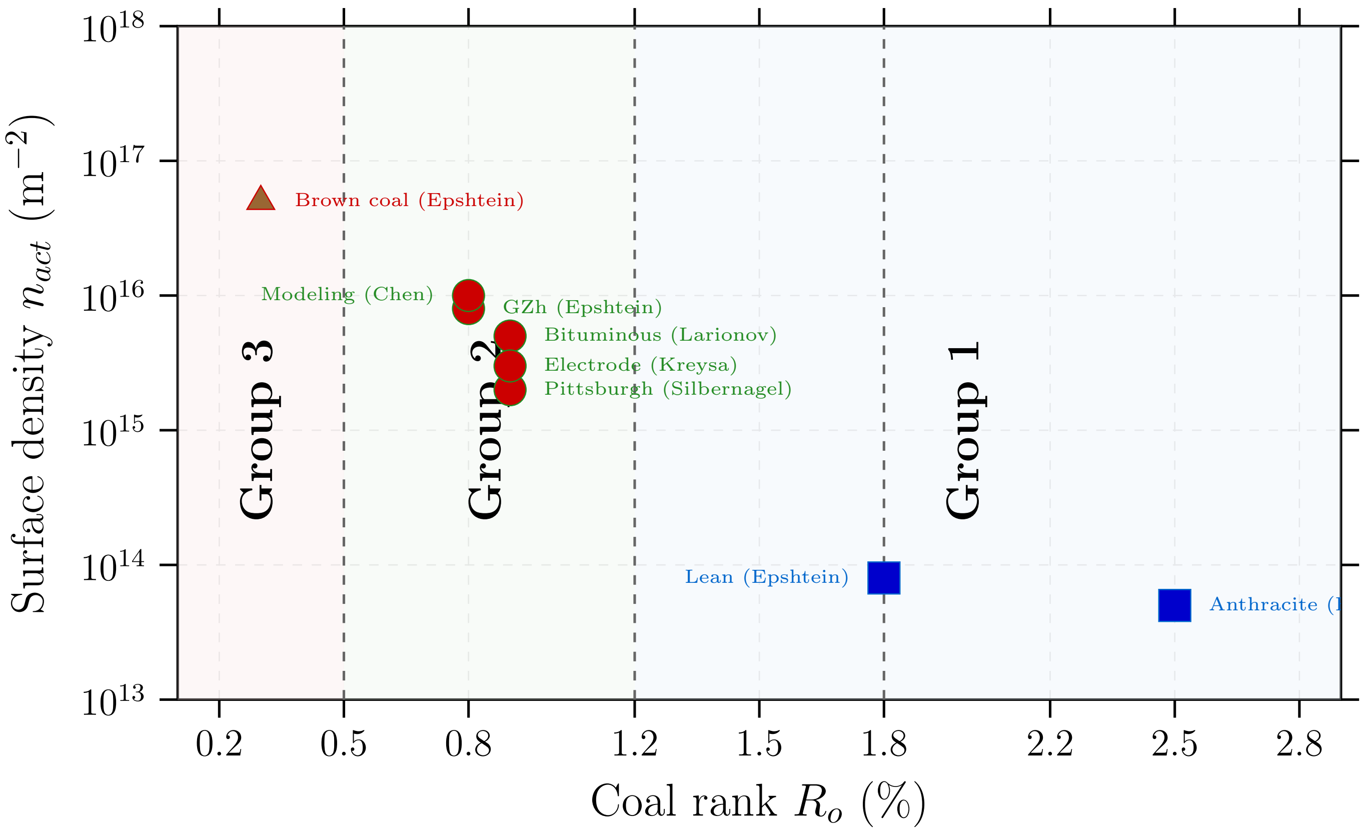


Figure 2: Dependence of Fe center surface density on coal rank (vitrinite reflectance $R_o$). Data compiled from multiple sources: Epshtein et al. (2007, 2008, 2019) for Russian coals; Silbernagel et al. (1993) for Argonne Premium coals (USA); Larionov et al. (2019) for bituminous coals; Kreysa and Kochanek (1985) from electrochemical data; Chen et al. (2024) from quantum-chemical modeling. Vertical dashed lines indicate approximate boundaries between coal groups according to the Epshtein classification. Group 2 coals (gas-fat, fat, coking) show the most consistent densities in the range $10^{15}$–$10^{16}$ $\mathrm{m}^{-2}$.

Table 2: Characteristics of different coal groups by oxidation propensity and estimated Fe center density

| Group | Oxidation propensity | Coal grades | Estimated $n_{act}$ ($\mathrm{m}^{-2}$) | Center stability |
|---|---|---|---|---|
| 1 | Minimal | A, T | $< 10^{14}$ | High |
| 2 | Pronounced | GZh, Zh, K | $10^{15}$–$10^{16}$ | High |
| 3 | High | B, D | $10^{15}$–$10^{17}$ | Low, rapid deactivation |

Based on data from (6; 13). Notes: Group 1 — Fe mainly in bound forms (clays), little pyrite or ultradispersed Fe; Group 2 — combination of pyrite and ultradispersed Fe, accessible surface; Group 3 — high Fe content, but centers unstable, high moisture content.

Group 2 coals represent a combination of relatively high Fe center density and moderate spontaneous combustion propensity (lower than Group 3). These coals have been the focus of many cited studies.

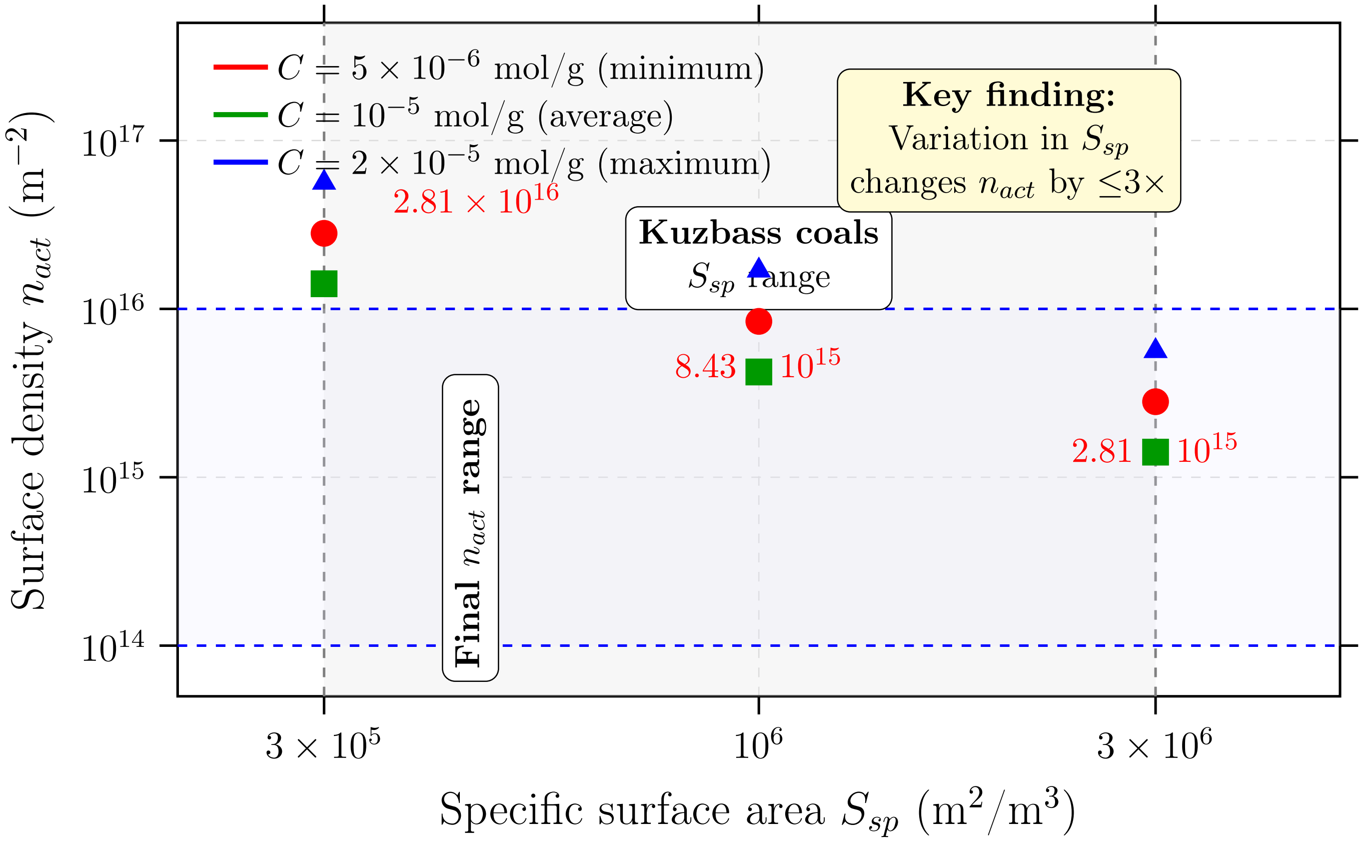


Figure 3: Sensitivity analysis of $n_{act}$ to specific surface area $S_{sp}$. Calculations use $n_{act} = C \cdot N_A \cdot \rho / S_{sp}$ with $\rho = 1.4 \times 10^6$ g/m$^3$ and three concentrations $C$ covering the experimental range for Group 2 coals ($5 \times 10^{-6}$–$2 \times 10^{-5}$ mol/g) from Epshtein et al. (2008). Vertical gray band shows $S_{sp}$ range for Kuzbass coals ($3 \times 10^5$–$3 \times 10^6$ m$^2$/m$^3$) from Epshtein et al. (2017). Horizontal blue band shows final estimate $n_{act} = 10^{14}$–$10^{16}$ m$^{-2}$. Even with tenfold variation in $S_{sp}$, $n_{act}$ changes by no more than a factor of 3, preserving the order of magnitude.

# 6 DISCUSSION

## 6.1 Fe centers as a consistent factor across studies

The analysis presented here indicates that Fe centers appear as a common factor in coal oxidation processes studied by different research groups over several decades. This suggests that Fe centers are a characteristic feature of coals not specific to particular deposits. Coals of similar rank from different basins (Donbass, Kuzbass, Appalachians, Chinese deposits) show comparable active center characteristics, as demonstrated in Fig. 2.

## 6.2 Reliability of the $n_{act}$ estimate

The agreement of results from three independent methods within one to two orders of magnitude supports the reliability of the estimate (Fig. 1). The ozonation data (13) provide the most direct measurements of center concentration. The estimate from Fe additives (8) gives consistent results under reasonable assumptions about the fraction of Fe atoms that become active. Electrochemical data (12), after accounting for accessibility factors, fall within the same range.

Sensitivity analysis (Fig. 3) indicates that even with tenfold variation in $S_{sp}$, the $n_{act}$ estimate changes by no more than a factor of 3, preserving the order of magnitude. The range $10^{14}$–$10^{16}$ $\mathrm{m}^{-2}$ thus appears robust.

## 6.3 Factors affecting center accessibility in situ

The estimates presented are based on laboratory measurements, typically on dry or specially prepared samples. Under in situ conditions, several factors may reduce the effective concentration of accessible Fe centers, as schematically shown in Fig. 4:

1. **Pore blocking by water.** Under in situ moisture conditions, part of the pore surface may be covered by a water film. At full water saturation, the effective surface for gas transport may be reduced by a factor of 2–5 (25). For processes requiring aqueous conditions, however, sufficient moisture is necessary.

2. **Poisoning by sulfur and other components.** Pyrite and other Fe-containing minerals can form surface sulfates and oxides during oxidation, potentially passivating centers (17). In sulfur-rich conditions, some Fe centers may be blocked.

3. **Competition for active sites.** In gas-saturated coal seams, methane can compete with water for adsorption sites. Methane sorption on coals reaches 20–30 $\mathrm{m}^3/\mathrm{t}$ (29), corresponding to significant surface coverage, which may reduce center accessibility.

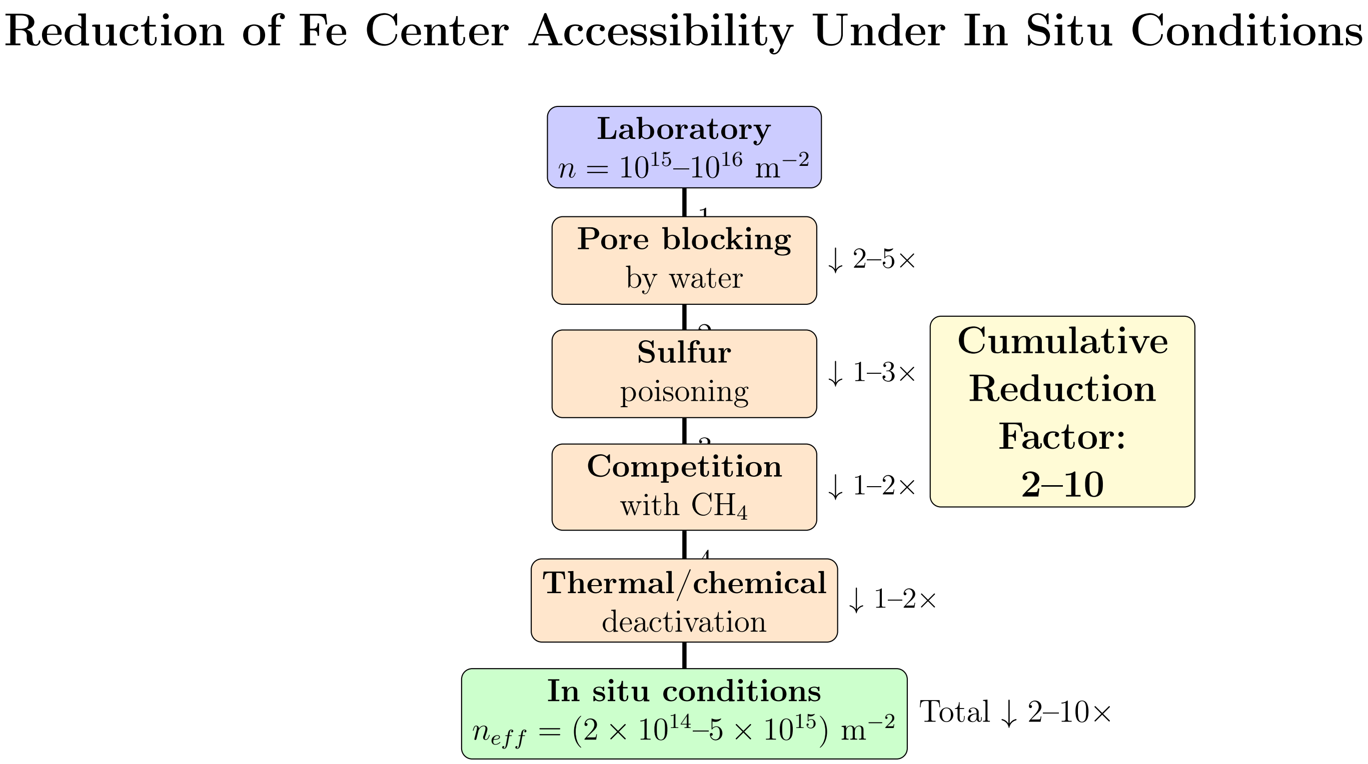
4. **Thermal and chemical deactivation.** During low-temperature oxidation, gradual deactivation of centers may occur due to formation of stable oxide phases or structural changes. EPR signal intensity from $\mathrm{Fe}^{3+}$ changes upon heating, indicating structural transformations (14).

## 6.4 Limitations of the present analysis

1. **Indirectness of some estimates.** In several cited works, Fe centers were studied under conditions different from in situ conditions.

2. **Specific surface area variation.** The $n_{act}$ estimate depends on $S_{sp}$, which can vary by a factor of 2–3 for different coals of the same rank.

3. **Coal heterogeneity.** Within a single seam or sample, Fe center distribution may be uneven. Estimates from bulk samples give average values.



Based on data from: Epshtein et al. (2017) for water blockage, Rimstidt and Vaughan (2003) for sulfur poisoning, Ruban et al. (2020) for methane sorption, and Silbernagel et al. (1993) for thermal deactivation.

Figure 4: Schematic representation of factors reducing the accessibility of Fe centers under in situ conditions compared to laboratory measurements. Laboratory estimates of $n_{act} = 10^{15}$–$10^{16}$ m$^{-2}$ are sequentially reduced by four factors: (1) pore blocking by water (factor 2–5) from Epshtein et al. (2017); (2) poisoning by sulfur compounds (factor 1–3) from Rimstidt and Vaughan (2003); (3) competition with methane adsorption (factor 1–2) from Ruban et al. (2020); and (4) thermal/chemical deactivation (factor 1–2) from Silbernagel et al. (1993). The cumulative reduction factor of 2–10 leads to effective in situ densities of $n_{eff} = 2 \times 10^{14}$–$5 \times 10^{15}$ m$^{-2}$.

4. **Limited data on deactivation kinetics.** More accurate estimation of effective center density in long-term processes would require additional studies of Fe center stability.

## 6.5 Potential applications of the results

The quantitative estimates obtained in this study may be useful for parameterizing theoretical models of catalytic processes in coals. For example, the resonant oxygen activation model proposed in (1) uses active Fe center density as an input parameter. The present analysis provides a range ($10^{14}$–$10^{16}$ m$^{-2}$) and a lower bound ($> 10^{15}$ m$^{-2}$ for Kuzbass GZh, Zh, K coals) that may help constrain such models.

Further research could usefully focus on direct experimental determination of $n_{act}$

for specific samples and on studying center stability under conditions approximating in situ environments.

# 7 CONCLUSION

1. A systematic analysis of literature on the role of Fe centers in coal oxidation processes has been performed. Studies by Russian (Agroskin, Epshtein, Larionov et al.), German (Kreysa), American (Kaiser, Silbernagel), and Chinese (Chen) research groups give a consistent picture: Fe centers (pyrite, ultradispersed Fe) are involved in coal oxidation, influencing kinetics, reaction onset temperature, and activation energy.

2. Based on the Epshtein classification, three groups of coals by oxidation propensity can be distinguished. The highest density of Fe centers is observed in Group 2 coals (grades GZh, Zh, K).

3. Using three independent methods (ozonation, catalysis by Fe additives, electrochemical oxidation), the surface density of active Fe centers is estimated as $n_{act} = 10^{14}$–$10^{16}$ $m^{-2}$ (Fig. 1). For Kuzbass coals of grades GZh, Zh, K, the lower bound is at least $10^{15}$ $m^{-2}$. The dependence on coal rank is shown in Fig. 2.

4. Sensitivity analysis (Fig. 3) indicates this estimate is robust to variation in input parameters: even with tenfold variation in specific surface area, the estimate changes by no more than a factor of 3.

5. Factors that may reduce the accessibility of Fe centers under in situ conditions (pore blocking by water, poisoning by sulfur, competition with methane, deactivation) have been considered (Fig. 4). A conservative estimate for effective center density in situ is $n_{act\_eff} \approx (2 \times 10^{14}$–$5 \times 10^{15})$ $m^{-2}$.

6. Group 2 coals may be of particular interest for processes involving catalytic activation on Fe centers, including oxidation, liquefaction, and gasification.

7. The quantitative estimates obtained may be useful for parameterizing theoretical models of catalytic processes in coals, including the resonant oxygen activation model (1).

8. Further research could usefully include direct experimental determination of $n_{act}$ for specific coal seams and studies of center stability under conditions approximating in situ environments.

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