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Sulfur and Nitrogen Distributions during Coal Carbonization and the Influences of These Elements on Coal Fluidity and Coke Strength

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The present study focuses on examining the fate of coal-S and coal-N during carbonization in detail and making clear the effects of these elements on coal fluidity and coke strength. When eight kinds of caking coals with 80–88 mass%-daf C are carbonized in high-purity He at 3°C/min up to 1000°C with a quartz-made fixed bed reactor, 50–75% of coal-S remains as FeS and organic-S in the coke, and the rest is released as tar-S and H₂S. Most of coal-N is also retained in the coke, and the remainder is converted to tar-N, HCN, NH₃ and N₂. The eight coals give Gieseler maximum fluidity values between 435 and 480°C, and the value tends to be larger at a smaller sulfur content in coal or in the carbonaceous material recovered after carbonization at 450°C. It also seems that the value increases with increasing nitrogen content in coal or total amount of either HCN or NH₃ formed up to 450°C. Furthermore, the addition of S-containing compounds to an Australian bituminous coal lowers coal fluidity and coke strength considerably, whereas indole gives the reverse effect on them. On the basis of these results, it is suggested that coal-S or some coal-N has a negative or positive effect on the two properties, respectively.

KEY WORDS: caking coal; carbonization; fluidity; tensile strength; nitrogen distribution; sulfur distribution.

1. Introduction

When caking coal is fed into a coke oven, the softening and swelling occur around 400–500°C, and the resulting carbonaceous materials are subsequently resolidified to provide coke. It has been well-accepted that the degree of softening and swelling is one of the crucial factors determining the physicochemical properties (*e.g.*, strength and reactivity) of the coke formed. The thermoplastic behavior of coal particles during carbonization has thus been studied extensively with several types of analysis techniques and different kinds of coals.^{1–16)} Some researchers exhibit that coal thermoplasticity depends strongly on the amounts of chloroform solubles naturally-present in coal,^{1,4,6)} low-molecular-weight compounds (metaplasts)^{2,3)} and/or transferable hydrogen^{7,10)} formed upon carbonization. It has also been reported that the sulfur and nitrogen present in coal, denoted as coal-S and coal-N, respectively, affect coal fluidity,^{17–20)} and that the addition of denzo-[c]-acridine (C₁₇H₁₁N) to a coal blend, even at a small amount of 3 mass%, enhances the tensile strength of the coke after carbonization by a factor of about 1.2.²¹⁾ It is of interest to investigate the influences of S and

N elements on coal fluidity and coke strength in more detail. In the present paper, therefore, we first examine the fate of coal-S and coal-N during carbonization of several caking coals with different carbon contents, then investigate the effect of addition of some S- or N-containing compounds on coal fluidity and follow the change in the tensile strength of the coke produced.

2. Experimental

2.1. Coal Sample

Eight kinds of caking coals with size fraction of less than 215 μm were used in the present study. The as-received sample was stored in a N₂-filled plastic bag kept in a freezer to avoid air oxidation in coal storage. The ultimate and proximate analyses are given in **Table 1**, where Al, Si, Ca and Fe contents of all coals are also shown, and Na, Mg and K are excluded because of trace amounts. The C, S and N contents in the eight samples ranged 80–88, 0.55–1.8 and 1.2–2.3 mass% on a dry, ash-free basis (daf), respectively.

2.2. Mixture of Coal and S- or N-Containing Compound

To investigate the effects of sulfur and nitrogen on coal

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Table 1. Analyses of coal samples used.

Coal	Country ^a	Ultimate analysis (mass%-daf)					Proximate analysis (mass%-dry)			Metal content (mass%-dry)			
		C	H	S	N	O ^b	Ash	VM ^c	FC ^{b,d}	Al	Si	Ca	Fe
LL	AUS	79.9	5.7	0.57	2.1	11.7	9.2	35.2	55.6	0.63	3.0	0.14	0.25
RW	AUS	81.8	5.8	0.65	2.0	9.8	8.7	37.1	54.2	0.84	2.4	0.16	0.30
GY	AUS	82.8	5.6	0.70	2.3	8.6	7.6	31.8	60.6	0.97	2.3	0.04	0.17
NW	NZL	83.5	5.3	1.8	1.2	8.2	3.1	30.8	66.1	0.57	0.72	0.06	0.19
GA	AUS	85.6	5.3	0.62	2.0	6.5	8.5	25.4	66.1	1.1	2.4	0.01	0.30
TR	USA	86.4	5.2	1.4	1.6	5.4	8.5	23.8	67.7	0.96	2.2	0.03	0.52
SI	AUS	87.3	4.9	0.75	2.0	5.0	10.2	18.4	71.4	1.9	2.7	0.05	0.33
GC	AUS	87.5	4.9	0.55	2.1	4.9	9.4	19.0	71.6	1.1	2.3	0.08	0.61

^aAUS, Australia; NZL, New Zealand; USA, United States of America. ^bEstimated by difference.

^cVM, volatile matter. ^dFC, fixed carbon.

fluidity, a mixture of RW coal and a S- or N-containing compound was prepared by the impregnation method. The procedure has been reported in detail elsewhere¹⁹⁾ and is thus simply explained below. Two inorganic sulfur, three organic sulfur and six organic nitrogen compounds were selected according to earlier studies on S- and N-functional forms in coal.^{22–28)} Each compound was added to RW coal by mixing in benzene at room temperature, followed by dryness under vacuum at 38°C. As reported previously,¹⁹⁾ the influence of the impregnation in benzene on coal fluidity was negligibly small. The S or N loading in the dried sample was 1.0 mass%, unless otherwise stated.

2.3. Carbonization

All runs were performed with a quartz-made fixed bed reactor. The details of the apparatus have been described elsewhere.²⁹⁾ In a typical experiment, about 0.50 g of the as-received coal was first charged into a rectangular quartz cell on a quartz holder in the reactor. After prudent precautions against leakage, the reactor was then heated electrically at 3°C/min up to 350–1 000°C in a stream of high-purity He (> 99.99995%) and finally quenched to ambient temperature. The temperature was measured with a thermocouple (Ni/Cr:Ni/Al) inserted at the bottom of the cell.

2.4. Sulfur and Nitrogen Analysis

Carbonization products were separated into gas, tar and coke (or semicoke) in the same manner as reported previously.²⁹⁾ With the gas, H₂S was analyzed at intervals of 50°C by the Gastec standard detector tube. On the other hand, N₂ was determined online at 13°C intervals with a high-speed micro-gas chromatograph, and HCN and NH₃ were measured at 9°C intervals with a photoacoustic multi-gas monitor. The reproducibility was within ± 3% for H₂S, ± 2% for N₂ and ± 4% for HCN or NH₃. Although CS₂ and COS were also analyzed by the Gastec standard tube, no appreciable amounts of them were detectable in all cases. The S and N in the tar, denoted as tar-S and tar-N, respectively, were determined with separate combustion-type analyzers. These elements in the coke (coke-S and coke-N) were also measured with conventional elemental analyzers. The reproducibility of the tar-S, tar-N, coke-S or coke-N measurement was within ± 3, ± 5, ± 2 or ± 2%, respectively.

The modes of occurrence of coal- and coke-S were investigated by the ASTM D 2492 method and Gladfelter-Dickerhoof technique,³⁰⁾ whereas coal- and coke-N functionalities were determined by the N 1s X-ray photoelectron spectroscopy (XPS) method. The detailed procedure for each analysis has been described in the previous paper.^{31,32)}

2.5. Fluidity Measurement

The fluidity analyses of the as-received coal and mixture of RW coal and S- or N-containing compound were carried out according to the constant-torque Gieseler plastometer method (JIS M 8801).²⁰⁾ In the experiments, about 4.5 g of the sample charged into a stainless steel crucible was placed into a lead solder bath in a plastometer, then heated at 3°C/min from 270 to 500–550°C in laboratory air and finally quenched to ambient temperature. Every sample was stirred at a constant torque during heating, and the fluidity was recorded in dial divisions per minute (ddpm) against temperature.

2.6. Tensile Strength Analysis

The strength measurements of coke samples were conducted with a conventional automatic extensometer employing the indirect tensile method.^{33,34)} About 40 g of RW coal without and with benzothiophene or indole added was first carbonized in a flow of N₂ at 1 000°C for 30 min, and the resulting sample was cut into three cylindrically-shaped pellets (13 mm diameter, 9 mm thickness) and then supplied to the extensometer. Each strength data observed was subjected to the Weibull analysis, and the value at the Weibull failure probability of 63.2% was taken as the coke strength throughout the present paper.

3. Results and Discussion

3.1. Fate of the Sulfur in Coal during Carbonization

Figure 1 shows the temperature dependency of sulfur distribution during carbonization of all coals used. Since sulfate (SO₄²⁻) and sulfite (SO₃²⁻) minerals were approximately 1–2% of total sulfur in feed coal, such data were not shown. Sulfur mass balances for all runs fell within the reasonable range of 95–105%. At 200–350°C, as seen in Fig. 1, more than 90% of coal-S was retained as pyrite (FeS₂) and organic-

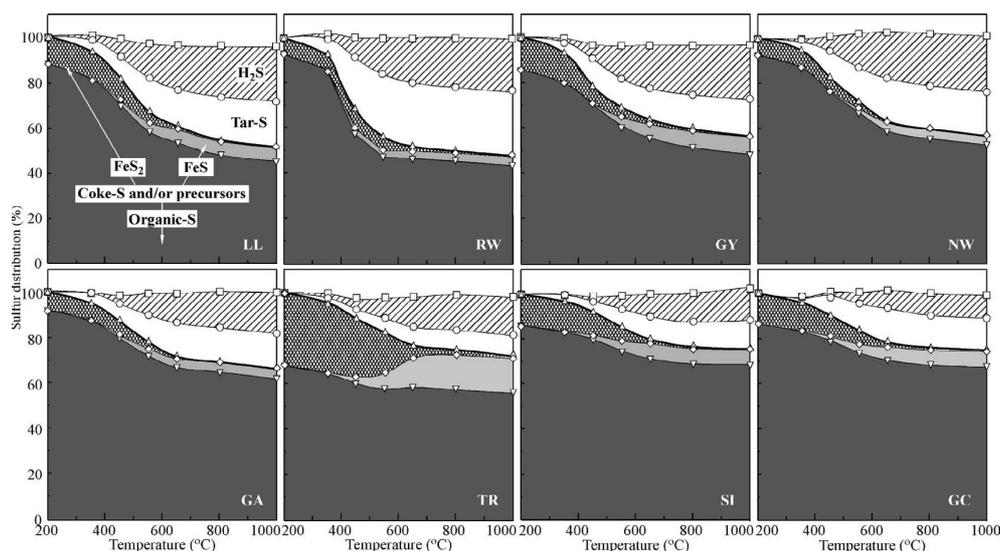


Fig. 1. Temperature change in sulfur distribution during carbonization of coals examined.

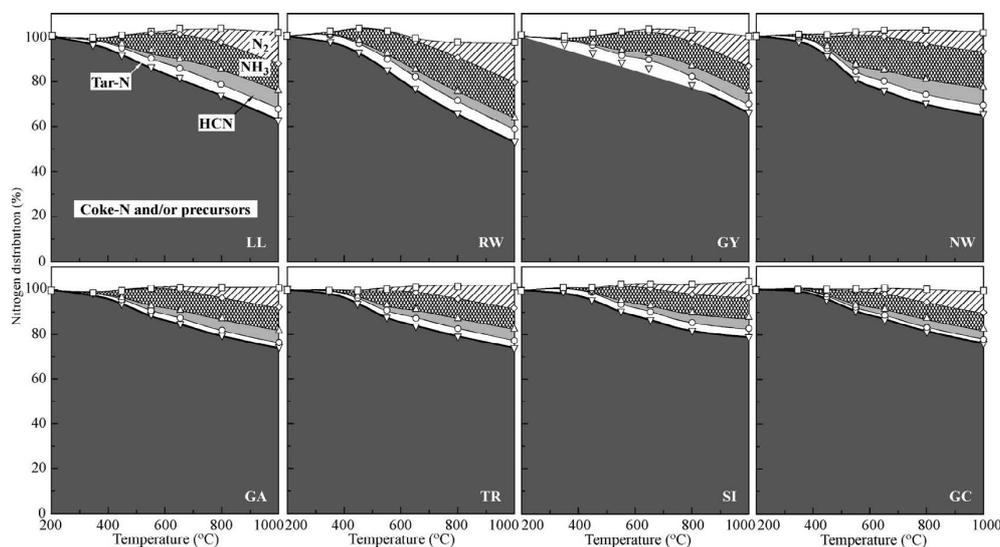
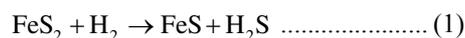


Fig. 2. Temperature change in nitrogen distribution during carbonization of coals examined.

S in solid phase, irrespective of the kind of coal, and most of the rest was released as tar-S. Small amounts of hydrogen sulfide (H_2S) were also observed with LL, RW, GY, NW and TR coals. When the temperature was increased from 350 to 650°C, the almost complete transformation of FeS_2 into pyrrhotite (FeS) and the significant decrease in organic-S took place with many coals, and the formation of H_2S and tar-S became more remarkable. Part of the H_2S observed may be formed via the reaction (Eq. (1)) of FeS_2 with H_2 evolved during carbonization.



According to thermodynamic calculations, the standard Gibbs free energy changes (ΔG) for this reaction at 350–650°C are -1.2 to -7.8 kcal/mol, indicating significant driving forces for H_2S formation. It has also been shown in slow heating rate pyrolysis with a TG-MS technique that aliphatic- and aromatic-S groups present in coal are transformed mainly into H_2S at ≤ 500 and 400–700°C, respectively.³⁵⁾ At 650–1000°C (Fig. 1), the increase in H_2S and the decrease in organic-S occurred slightly, and tar-S and FeS were almost

unchanged in many cases. The evolution of H_2S from thiophenic-S during coal pyrolysis at $\geq 600^\circ\text{C}$ under slow heating conditions has been reported.³⁵⁾ As shown in Fig. 1, about 50–75% of coal-S remained as FeS and organic-S in the cokes after carbonization at 1000°C. The latter S species retained might exist in the form that has strong interactions with condensed aromatic structures in the cokes.

3.2. Fate of the Nitrogen in Coal during Carbonization

Figure 2 presents the temperature dependency of nitrogen distribution under the same experimental conditions as in Fig. 1. The nitrogen mass balance was in the reasonable range of 95–105% in every case. Tar-N was the only N species evolved below 350°C, regardless of the type of coal, indicating that tar-N is a primary volatile product under the present conditions. When the temperature was raised from 350 to 650°C, not only tar-N but also HCN, NH_3 and N_2 were formed, and the extent of the formation tended to be larger at a higher temperature in all cases. It has been reported that HCN come from secondary decomposition reactions of tar-N,^{27,36–38)} and that a larger degree of secondary reac-

tions between volatiles and char leads to higher conversion of HCN to NH_3 .^{37,38)} As seen in Fig. 2, NH_3 was the predominant product among N species evolved at 350–650°C for all coals, suggesting the significance of secondary reactions of volatile nitrogen (tar-N, HCN and NH_3) under the conditions applied. Some of the N_2 produced may arise from HCN (Eq. (2)) and/or NH_3 (Eq. (3)), because ΔG values for Eqs. (2) and (3) at 350–650°C are as small as –4.3 to –4.0 kcal/mol and –4.4 to –13 kcal/mol, respectively.



When the temperature was increased further to 800–1000°C, volatile-N distribution was almost unchanged, whereas N_2 increased more remarkably with a corresponding decrease in coke-N (Fig. 2). Since the increases in N_2 between 650 and 1000°C, 5.6–17%, were roughly the same as the decreases in coke-N, 7.4–20%, it is probable that the N_2 increased originates mostly from coke-N and/or precursors. It has been accepted that Fe cations naturally-present in low rank coals can catalyze N_2 formation from the devolatilized chars during pyrolysis at 600–1000°C.^{29,38–40)} It might thus be possible that Fe cations in the coals used, if present actually, promote conversion reactions of coke-N and/or precursors to N_2 .

As provided in Fig. 2, about 60–80% of coal-N was retained in the 1000°C-cokes. It is of interest to evaluate

coke-N functionality quantitatively. The N forms of the 1000°C-cokes estimated by the XPS method are summarized in Fig. 3, where those of the as-received raw coals are also given for comparison. Pyrrolic-N was the main N form, irrespective of the coal type, and the proportion was in the range of 50–60 mol%, followed by pyridinic-N in many cases. Quaternary-N also existed in all the coals in the range of 15–30 mol%. It has been proposed that the quaternary-N in coal can be assigned to pyridinic-N associated with the hydroxyl groups from phenols and/or carboxyl acids.²⁸⁾ When each coal was carbonized at 1000°C, as shown in Fig. 3, nitrogen functionality changed dramatically, and quaternary-N became the predominant form, the proportion being between 40 and 50 mol%. On the other hand, pyrrolic-N and pyridinic-N decreased considerably. Although oxidized-N was observed with all the cokes examined, this species might be formed during exposure to laboratory air for coke recovery from the reactor.⁴¹⁾ According to earlier work about the XPS analysis using char samples after pyrolysis at 500–800°C of Argonne premium coals,⁴²⁾ it has been reported that the quaternary-N present in the samples differs from that proposed for coals, and it can be assigned to nitrogen atoms incorporated in the interior of the char matrix. It is thus possible that the N in the cokes shown in Fig. 3 may exist mainly in the interior of condensed aromatic structures.

3.3. Fluidity Properties of As-Received Coals

Figure 4 illustrates Gieseler fluidity profiles for the as-received coals, and Table 2 summarizes the fluidity data for each sample. The coals started to soften at about 375–435°C, gave the maximum fluidity (MF) values between 435 and 480°C, and resolidified beyond 465–505°C. The MF value depended strongly on the kind of coal and ranged 13–13 000 ddpm [1.1–4.1 log(ddpm)]. It should be noted that GY and NW coals give the highest and lowest values, respectively, in spite of containing the similar C contents (Table 1). In other words, the degree of coal fluidization had no distinct relationship with C%.

Figure 5 illustrates the MF value (Table 2) as a function of S content (S%) or N content (N%) in coal (Table 1).

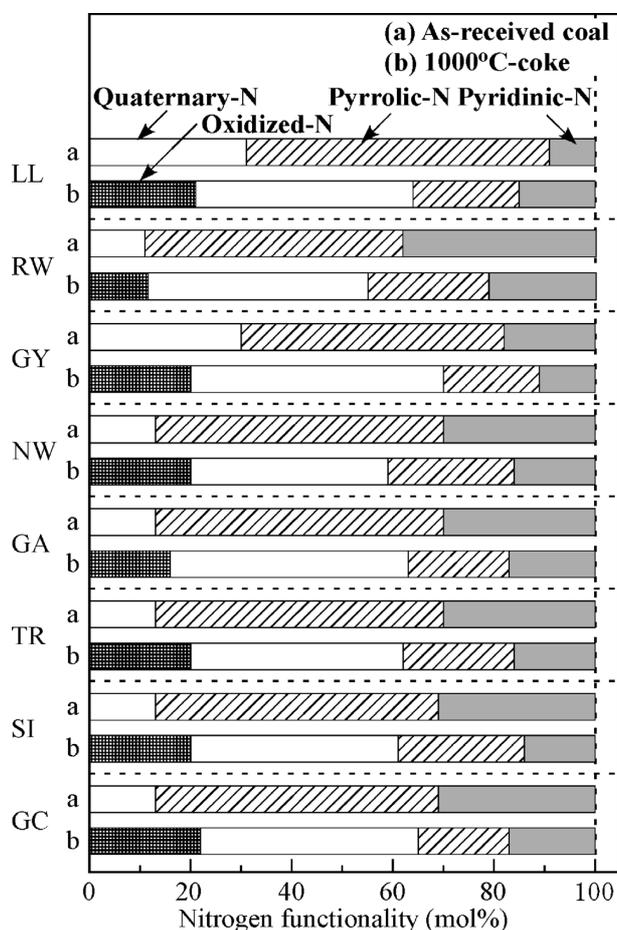


Fig. 3. Nitrogen functional forms of coal and 1000°C-coke samples estimated by XPS measurements.

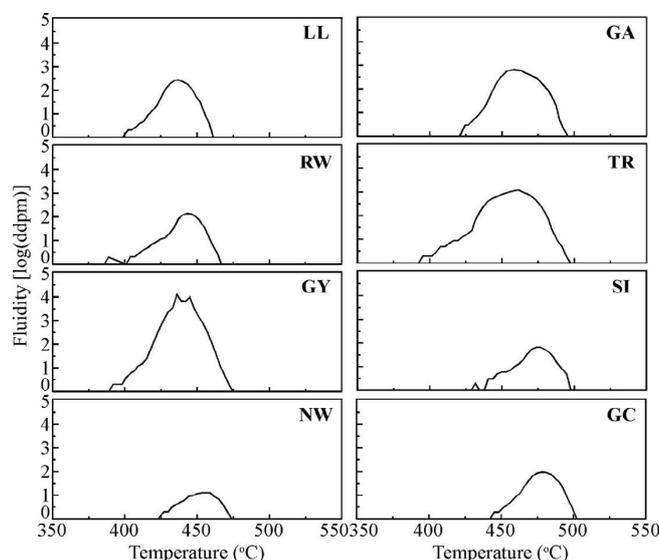
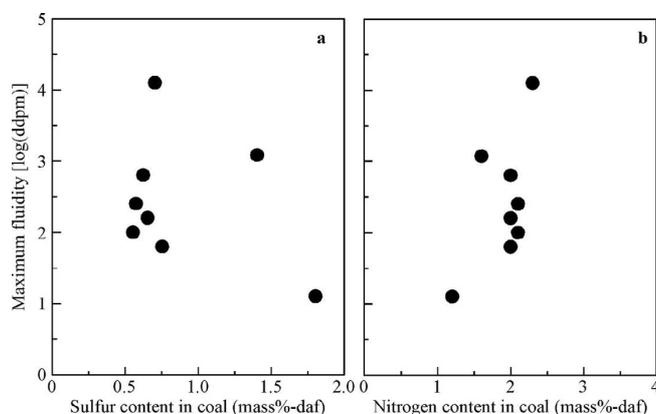


Fig. 4. Gieseler fluidity profiles for eight coals investigated.

Table 2. Fluidity properties of coal samples measured by the Gieseler plastometer method.

Coal	IST ^a (°C)	MFT ^b (°C)	RST ^c (°C)	MF ^d	
				(ddpm)	[log(ddpm)]
LL	395	437	467	280	2.4
RW	389	433	460	150	2.2
GY	377	445	475	13 000	4.1
NW	418	456	480	13	1.1
GA	413	460	502	670	2.8
TR	380	461	500	1 300	3.1
SI	432	477	504	67	1.8
GC	436	478	500	100	2.0

^aInitial softening temperature. ^bMaximum fluidity temperature.

^cResolidification temperature. ^dMaximum fluidity.

Fig. 5. Effect of sulfur (a) or nitrogen (b) content in coal on Gieseler maximum fluidity.

Although some data were scattered, the MF value tended to be larger at a lower S% (Fig. 5(a)) or at a higher N% (Fig. 5(b)). In addition, the value decreased with increasing content of the S remaining in the carbonaceous material recovered after carbonization at 450°C, whereas it tended to increase with increasing total amount of HCN or NH₃ evolved up to this temperature, as recently reported.^{19,20} These observations suggest that sulfur or nitrogen has a negative or positive effect on coal fluidity, respectively. The next section thus focuses mainly on examining the effect of addition of S- or N-containing compounds on the fluidity.

3.4. Changes in Coal Fluidity and Coke Strength by Addition of S- or N-Containing Compounds

3.4.1. Effect of Addition of S-Containing Compounds on Coal Fluidity

The results for the Gieseler fluidity analyses of RW samples with several types of S-containing compounds added are given in **Table 3**, where the choices of four S compounds, such as pyrite (FeS₂), diphenyl disulfide (C₁₂H₁₀S₂), benzothiophene (C₈H₆S) and dibenzothiophene (C₁₂H₈S), are made according to previous studies,^{22–25} and elemental sulfur is also used. The comparison of Tables 2 and 3 exhibited that the five S species impregnated with RW coal did not affect the initial softening, maximum fluidity and resolidification temperatures significantly, but they lowered the MF

Table 3. Effect of addition of S-containing compounds on fluidity property of RW coal.

Sulfur compound	IST ^a (°C)	MFT ^b (°C)	RST ^c (°C)	MF ^d	
				(ddpm)	[log(ddpm)]
Elemental sulfur	405	440	458	25	1.4
Pyrite (FeS ₂)	405	440	461	25	1.4
Diphenyl disulfide (C ₁₂ H ₁₀ S ₂)	395	436	457	70	1.8
Benzothiophene (C ₈ H ₆ S)	397	439	466	90	2.0
Dibenzothiophene (C ₁₂ H ₈ S)	397	436	463	90	2.0

^aInitial softening temperature. ^bMaximum fluidity temperature.

^cResolidification temperature. ^dMaximum fluidity.

value considerably: the value decreased from the original 150 to 25–90 ddpm (Table 3). On the other hand, the S content in the carbonaceous material recovered after carbonization at 390°C increased from 0.69 mass%-daf without any S species added to 0.72–1.5 mass%-daf. It has been reported that the amount of transferable hydrogen formed during coal carbonization is one of the important factors determining MF value, and there is an almost linear correlation between the two.^{7,10} On the basis of this information, the decrease in the MF observed in Table 3 may be caused by the reaction of transferable hydrogen produced with each S compound added. If transferable hydrogen can be regarded as atomic hydrogen (H*) according to earlier work,⁷ the reactions with the five S species may be expressed as follows (Eqs. (4)–(8)):



Thermodynamic calculations show that ΔG values for Eqs. (4)–(8) at 350–500°C are less than 0 kcal/mol in all cases. These reactions are thus favorable thermodynamically in the temperature region where coal fluidization takes place remarkably (Fig. 4, Tables 2 and 3).

3.4.2. Effect of Addition of N-Containing Compounds on Coal Fluidity

Figure 6 presents the profiles for the fluidity of RW samples with N-containing compounds added. As seen in Fig. 6(a), pyrrole (C₄H₅N) or pyridine (C₅H₅N) mixed with RW coal did not affect the profile significantly. Such a trend were also observed with the mixture of RW and isoquinoline (C₉H₇N) (Fig. 6(b)), carbazole (C₁₂H₉N) (Fig. 6(c)) or phenanthroline (C₁₂H₈N₂) (Fig. 6(c)). On the other hand, the addition of indole (C₈H₇N) to the coal enhanced the fluidity remarkably, and the MF value increased from 150 ddpm without any additives to 400 ddpm (Fig. 6(b)). When indene (C₉H₈) was mixed with the coal, the value was approximately 250 ddpm, which was much smaller than that for the indole-added coal. As is well-known, five-membered N-containing heterocycles, such as pyrrole, indole and carbazole, are π-

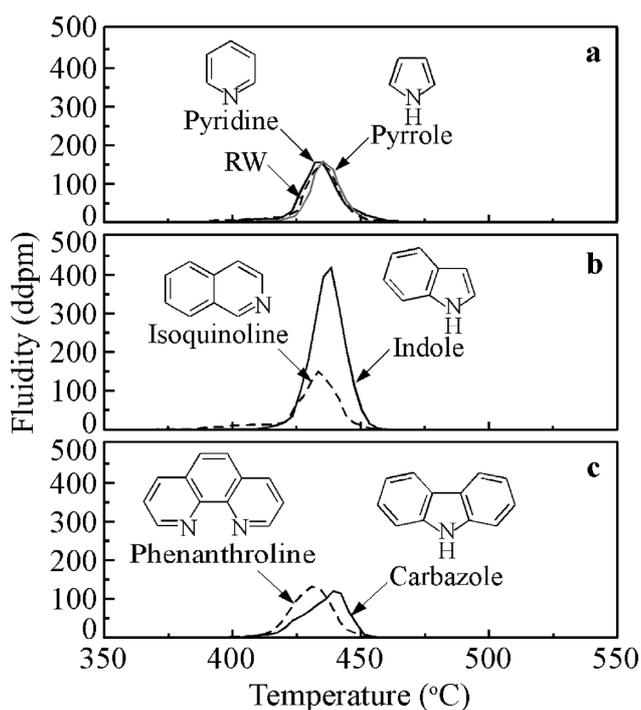


Fig. 6. Gieseler fluidity profiles for RW samples with N-containing compounds added: (a) monocyclic, (b) bicyclic and (c) tricyclic aromatic compounds.

electron rich aromatics, which have higher reactivity than π -electron deficient aromatics (*e.g.*, pyridine, isoquinoline and phenanthroline) toward electrophilic substitution reactions. It has also been shown by the *in situ* ^1H nuclear magnetic resonance (NMR) imaging analyses during heating that the proportion of mobile component present in coal increases gradually beyond 220–230°C, but it decreases steeply after the maximal value at about 450°C.⁴³ It may be noteworthy that the former temperature is close to the boiling point (253°C) of indole. This similarity suggests that the externally added indole might play an important role in the formation of mobile component at the initial stage of coal carbonization. Further, the H atom attached to the N in indole as well as coal-derived transferable hydrogen might affect the transformation of immobile component into mobile component. A detailed mechanism for the indole-enhanced coal fluidity should be clarified in future work.

3.4.3. Change in Coke Strength by Addition of S- and N-Containing Compounds

Figure 7 illustrates Weibull failure probability plots for the tensile strength of 1000°C-cokes from RW samples without and with benzothiophene or indole added. Although the data points are insufficient, it seems that the strength data of each sample investigated can fall on or around a straight line on the Weibull plot. In the absence of any additives, as provided in Fig. 7, the strength (η) value at the failure probability of 63.2% was estimated to be 3.9 MPa. As expected from the results in Table 3 and Fig. 6, the addition of benzothiophene and indole to RW coal changed the strength significantly: the former compound drastically decreased the η value from 3.9 to 1.6 MPa, whereas the latter one exhibited the reverse effect on the strength, and the η value reached about 6.0 MPa (Fig. 7). It is thus evident

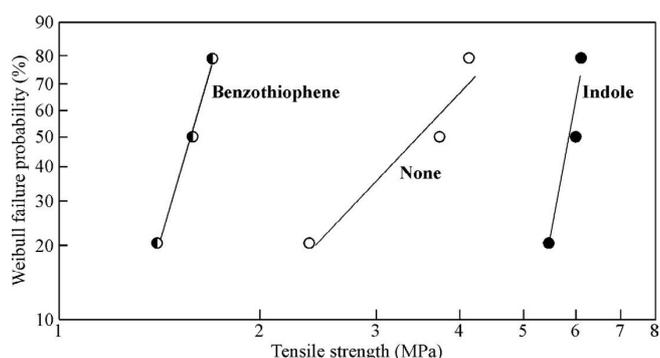


Fig. 7. Weibull failure probability plots for the tensile strength of 1000°C-cokes derived from RW coal without and with benzothiophene or indole added.

that the added benzothiophene or indole has a negative or positive effect on coke strength, respectively. The η value of the indene-added coal was ≤ 5.5 MPa.

On the basis of the results described in section 3.4, it is suggested that most of coal-S lowers coal fluidity and coke strength, but contrarily part of coal-N can enhance the two properties. The results obtained in the present study may elucidate the fate of these elements in coke ovens, help us to understand the chemistry of coal fluidization, and contribute to the development of a novel technique of producing high-strength coke from low-rank coals and/or unused carbon resources.

4. Conclusions

Carbonization of eight caking coals with carbon contents of 80–88 mass%-daf has been studied with a quartz-made fixed bed reactor to make the fate of coal-S and coal-N clear and to investigate the influences of these elements on coal fluidity and coke strength. The principal conclusions are summarized as follows:

- (1) When the coals are heated in high-purity He at 3°C/min up to 1000°C, more than half of coal-S and coal-N are retained in the coke, the remainder being released as tar, H_2S , HCN, NH_3 and N_2 .
- (2) The coals provide 1.1–4.1 log(ddpm) of Gieseler maximum fluidity, and the value tends to be larger at a lower sulfur or higher nitrogen content in coal.
- (3) The addition of S-containing compounds to an Australian bituminous coal lowers the maximum fluidity considerably, whereas indole shows the reverse effect on it.
- (4) The tensile strength of the coke formed decreases significantly by benzothiophene addition, but contrarily it increases by indole addition, the increment factor at the Weibull failure probability of 63.2% being approximately 1.5.
- (5) On the basis of the above results, it is suggested that coal-S and some coal-N have the reverse effects on the changes in coal fluidity and coke strength.

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REFERENCES

- 1) T. Shimmura: *Fuel*, **12** (1933), 204.
- 2) D. W. van Krevelen, C. van Heerden and F. J. Huntjens: *Fuel*, **30** (1951), 253.
- 3) H. A. G. Chermin and D. W. van Krevelen: *Fuel*, **36** (1957), 85.
- 4) H. R. Brown and P. L. Waters: *Fuel*, **45** (1966), 17.
- 5) R. C. Neavel: *Coal Science*, ed. by M. L. Gorbaty, J. W. Larsen and I. Wender, Academic Press, New York, USA, (1982), 1.
- 6) K. Ouchi, K. Tanimoto, M. Makabe and H. Itoh: *Fuel*, **62** (1983), 1227.
- 7) T. Yokono, T. Obara, S. Iyama, J. Yamada and Y. Sanada: *J. Fuel Soc. Jpn.*, **63** (1984), 239.
- 8) M. L. Chan, N. D. Parkyn and K. M. Thomas: *Fuel*, **70** (1991), 447.
- 9) I. M. Butterfield and K. M. Thomas: *Fuel*, **74** (1995), 1780.
- 10) K. Kidena, S. Murata and M. Nomura: *Energ. Fuel.*, **10** (1996), 672.
- 11) Y. Ohtsuka, Z. Wu, A. Tomita and S. Itagaki: *Tetsu-to-Hagané*, **82** (1996), 372.
- 12) M. M. Maroto-Valer, J. M. Andrésen and C. E. Snape: *Energ. Fuel.*, **11** (1997), 236.
- 13) H. Gao, S. Murata, M. Nomura, M. Ishigaki, M. Qu and M. Tokuda: *Energ. Fuel.*, **11** (1997), 730.
- 14) S. Nomura and K. M. Thomas: *Fuel*, **77** (1998), 829.
- 15) T. Yoshida, M. Iino, T. Takanohashi and K. Katoh: *Fuel*, **79** (2000), 399.
- 16) T. Yoshida, T. Takanohashi, M. Iino, H. Kumagai and K. Kato: *Energ. Fuel.*, **18** (2004), 349.
- 17) C. P. Clark, G. B. Freeman and J. C. Hower: *Scan. Electron Microsc.*, **11** (1984), 537.
- 18) K. Fukada, I. Shimoyama, T. Anyashiki, H. Fujimoto and H. Sumi: JP Patent 74048 A, (2009).
- 19) Y. Mochizuki, Y. Ono, K. Uebo and N. Tsubouchi: *Int. J. Coal Geol.*, **120** (2013), 50.
- 20) N. Tsubouchi, Y. Mochizuki, Y. Ono, K. Uebo, N. Sakimoto and T. Takanohashi: *Energ. Fuel.*, **27** (2013), 7330.
- 21) N. Sakimoto, T. Takanohashi, Y. Harada and H. Fujimoto: Proc. 48th Conf. of the Japan Institute of Energy for Coal Science, the Japan Institute of Energy, Tokyo, Japan, (2011), 18.
- 22) S. R. Kelemen, G. N. George and M. L. Gorbaty: *Fuel*, **69** (1990), 939.
- 23) G. P. Huffman, S. Mitra, F. E. Huggins, N. Shah, S. Vaidya and F. Lu: *Energ. Fuel.*, **5** (1991), 574.
- 24) J. L. Vernon and T. Jones: *Sulfur and Coal*, IEA Coal Research, London, UK, (1993), IEACR/57.
- 25) R. M. Davidson: *Organic Sulfur in Coal*, IEA Coal Research, London, UK, (1993), IEACR/60.
- 26) O. C. Mullins, S. Mitra-Kirtley, J. van Elp and S. P. Cramer: *Appl. Spectrosc.*, **47** (1993), 1268.
- 27) R. M. Davidson: *Nitrogen in Coal*, IEA Coal Research, London, UK, (1994), IEAPER/08.
- 28) S. R. Kelemen, M. L. Gorbaty and P. J. Kwiatek: *Energ. Fuel.*, **8** (1994), 896.
- 29) Z. Wu and Y. Ohtsuka: *Energ. Fuel.*, **11** (1997), 477.
- 30) W. L. Gladfelter and D. W. Dickerhoof: *Fuel*, **55** (1976), 355.
- 31) T. Sugawara, K. Sugawara and H. Ohashi: *Fuel*, **67** (1988), 1263.
- 32) Y. Ohtsuka, T. Watanabe, K. Asami and H. Mori: *Energ. Fuel.*, **12** (1998), 1356.
- 33) T. Miyagawa and I. Fujishima: *J. Fuel Soc. Jpn.*, **54** (1975), 983.
- 34) T. Takanohashi, T. Shishido and I. Saito: *Energ. Fuel.*, **22** (2008), 1779.
- 35) K. Miura, K. Mae, M. Shimada and H. Minami: *Energ. Fuel.*, **15** (2001), 629.
- 36) J. E. Johnsson: *Fuel*, **73** (1994), 1398.
- 37) J. Leppälähti and T. Koljonen: *Fuel Process. Technol.*, **43** (1995), 1.
- 38) N. Tsubouchi and Y. Ohtsuka: *Fuel Process. Technol.*, **89** (2008), 379.
- 39) Z. Wu and Y. Ohtsuka: *Energ. Fuel.*, **11** (1997), 902.
- 40) Y. Ohshima, N. Tsubouchi and Y. Ohtsuka: *Appl. Catal. B-Environ.*, **111–112** (2012), 614.
- 41) J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu and K. M. Thomas: *Carbon*, **33** (1995), 1641.
- 42) S. R. Kelemen, M. L. Gorbaty, P. J. Kwiatek, T. H. Fletcher, M. Watt, M. S. Solum and R. J. Pugmire: *Energ. Fuel.*, **12** (1998), 159.
- 43) K. Saito, I. Komaki, K.-I. Hasegawa and H. Tsuno: *Fuel*, **79** (2000), 405.