

Yan-Ming WANG¹, Wen-Zheng WANG¹, Zhen-Lu SHAO², De-Ming WANG²
and Guo-Qing SHI^{3*}

TERAHERTZ MEASUREMENT OF INDICATOR GAS EMISSION FROM COAL SPONTANEOUS COMBUSTION AT LOW TEMPERATURE

TERAHERCOWE POMIARY EMISJI GAZU WSKAŹNIKOWEGO ZE SPONTANICZNYCH SAMOZAPŁONÓW WĘGLA W NISKIEJ TEMPERATURZE

Abstract: Coal spontaneous combustion is an extremely complicated physical and chemical changing process. In order to improve the indicator gases detection technology and coal spontaneous combustion monitoring, a novel forecast method for toxic gases emission from coal oxidation at low temperature is presented in this paper. The experiment system is setup combined with frequency-domain terahertz technology and coal temperature programming device. The concentration curves of carbon monoxide and sulphur dioxide gases from coal spontaneous combustion are estimated according to molecule terahertz spectra. The influences of coal rank and oxygen supply on coal spontaneous combustion characteristics are discussed. Both carbon monoxide and sulphur dioxide gases absorption spectra show the characteristic equi-spaced absorption peaks. Results demonstrate that under the condition of lean oxygen, there exists a critical oxygen concentration in the process of coal oxidation at low temperature. Comparing with Fourier infrared spectrum testing, the presented method is highly accurate and more sensitive, especially suitable for early-stage monitoring of the indicator gases produced by coal spontaneous combustion.

Keywords: coal spontaneous combustion, gas monitoring, carbon monoxide, sulphur dioxide, terahertz spectroscopy technique

Introduction

Carbon monoxide and sulphur dioxide are highly toxic gases in coalmine pollution gases. These products of the incomplete combustion of carbonaceous material are mainly formed by internal combustion engines, blasting and spontaneous combustion in coal mines. Oxidation of coal takes place after four stages [1]: 1) physical adsorption of oxygen, resulting in temperature increase; 2) chemical sorption (over 50°C), producing oxygenated hydrocarbons or peroxy-complexes; 3) decomposition of oxygenated hydrocarbons when self-heating

¹ School of Safety Engineering, China University of Mining and Technology, XU-ZHOU City, China

² State Key Laboratory of Coal Resources and Safe Mining, XU-ZHOU City, China

³ Key Laboratory of Gas and Fire Control for Coal Mines, XU-ZHOU City, China

*Corresponding author: shiguqing2011@163.com

temperature is reached (over 70°C), with concurrent oxidation of unaltered coal matter; and 4) spontaneous combustion may then occur if all the above processes result in temperatures higher than 150°C, typically referred to as the ignition threshold. This ignition threshold seems to depend on coal rank, with values around 130°C for the lowest rank, and probably even lower values for peat. In this respect, the 60-80°C range is regarded as critical [2].

Atmospheric emission of pollutants results from the coal combustion process and the volatilization of a number of coal and mineral matter elements during thermal alteration (pyrolysis). The compounds generated by volatilization mainly consist of CO₂, and CO, CH₄, NO, NO₂, SO₂, H₂S, HF, NH₃, HCl, n-alkanes, n-alkenes, sugars, alcohols, PAH, Hg, As, Pb, and Se, among others [3-7]. These reports provided a good overview of the organic gaseous pollutants emitted from spontaneous coal combustion (aliphatic and aromatic hydrocarbons). Some research [8-10] showed that the chemical composition of the waste material reflects the thermal influence of fire on thermal alteration halos. Less thermally stable compounds, such as lighter n-alkanes, cyclic isoprenoids, methyl and dimethylnaphthalenes and methylphenanthrenes are destroyed or evaporated in the most affected material. Examples are n-alkanes and n-alkenes formed by macromolecule cracking, acyclic isoprenoids, methylbiphenyls, and dimethylbiphenyls.

The emissions of aliphatic and aromatic hydrocarbons from coal fires are highly dependent on coal rank as well as on the degree of coal thermal alteration. Emission rates for gaseous emissions can be determined with an S-type Pitot tube, an instrument used extensively in volcanology [11] and apparently first used in the study of coal fires by [12], with further refinement in the studies by [13].

In recent years, with the development of terahertz Time-Domain Spectroscopy (THz-TDS) technique, researchers have begun to focus terahertz applications on the gas detection. Exter et al [14] measured the absorption spectrum of water vapor for the first time. Harde et al [15] measured the absorption and dispersion characteristics of ammonia vapor molecules by THz-TDS. Matron et al [16], who used two titanium sapphire laser beams incident to the LTG-GaAs mixer to generate a continuous terahertz radiation, measuring the absorption spectrum of OCS gas. Terahertz spectrum of carbon monoxide was measured by Hu et al [17]. The results show that the carbon monoxide has obvious characteristic absorption band between 0.2-2.5 THz. The far-infrared spectra of three organic vapors (methanol, ethanol and acetone) by THz-TDS and the gas absorption lines were also been calculated. Others measured the absorption coefficient in 0.3-0.9 THz by dispersive Fourier transform spectroscopy, and discussed the relationship between pressure and rotational transmission lines in detail [18].

In this study, a continuous monitoring system and forecast method for toxic gases emission from coal spontaneous combustion is presented. According to the molecule spectra on the range of terahertz wave, the frequency-domain terahertz spectroscopy technique is utilized to measure the carbon monoxide and sulphur dioxide concentrations produced by coal oxidation at low temperature. Considering different coal rank and oxygen supplying concentration, the characteristics of coal spontaneous combustion and gas emitting are analyzed. And also, the forecast method performances of accuracy and effectiveness are discussed compared with Fourier infrared technology.

Experiment setup

Monitoring system and operation

The monitoring system for carbon monoxide and sulphur dioxide concentration detection in mixed gas produced by coal spontaneous combustion is shown in Figure 1. As shown in the figure, the device includes a gas chamber (6). The gas chamber is a cylindrical barrel that made of quartz glass. The thickness of the wall, top and bottom of the gas chamber is 1-1.5 mm, and it's inside diameter ranges from 3-10 mm. There are respectively air inlet and outlet that distributed in the top and bottom of the gas chamber. One end of the gas chamber is combined with a cleaner (4) via pipelines (3). The internal of the cleaner (4) is covered with discolored 3A molecular sieves and activated carbon. The discolored 3A molecular sieves and activated carbon that installed in the cleaner account for 50% each. The other end of the cleaner (4) is combined with the coal pyrophoricity measuring instrument (1) fitted with coal sample via pipelines. The regulating valve (2) is set between the coal pyrophoricity measuring instrument (1) and the cleaner (4). The regulating valve (2) is used for adjusting the flow rate of gas that entering the device. The shut-off valve (5) is set between the cleaner (4) and the gas chamber (6). It is used to control the on and off of the gas entering the gas chamber (6). The other end of the gas chamber (6) is respectively connected to the intelligent vacuum pump (12) and the gas collection bag (13) via a three-way valve (10) and pipelines (3). The gas collection bag (13) is used for collecting the exhaust gas of the device and avoiding environmental pollution. There is a safety valve (11) between the three-way valve (10) and gas collection bag (13). A gate valve (14) is set between the three-way valve (10) and the intelligent vacuum pump (12). The gate valve (14) is used to open and cut off the connectivity between the gas chamber (6) intelligent vacuum pump (12). The frequency-domain terahertz-ray generator (7) and the terahertz signal receiver (8) are distributed in both sides of the gas chamber (6). The terahertz signal receiver (8) is connected with a computer (9). The frequency-domain terahertz-ray generator (7) includes QS1-260-1550-type BWO terahertz light source, terahertz lens, polarizing plate, attenuators and chopper. The model of the terahertz signal receiver (8) is Golay Cell II-type.

The frequency-domain terahertz technology-based method to realize the continuous monitoring of CO concentration during the coal spontaneous combustion by using the device described above.

- a. Close the regulating valve (2), open the coal pyrophoricity measuring instrument (1) in which the coal samples will burn and produce gas.
- b. Set the safety pressure of the safety valve (11) and the negative pressure of the intelligent vacuum pump (12), open the shut-off valve (5), gate valve (14), open the intelligent vacuum pump (12) to evacuate the gas chamber (6).
- c. When the pressure in the gas chamber (6) reaches the value of the negative pressure that set in the intelligent vacuum pump (12), the intelligent vacuum pump (12) will automatically shut down, then close the gate valve (14) manually.
- d. Open the regulating valve (2) slowly, so that the gas from the coal pyrophoricity measuring instrument (1) could enter the cleaner (4) with the speed of 30-50 cm³/min. The impurity substances in the gas such as moisture and carbon black will be absorbed by the discoloration 3A molecular sieve and activated carbon in the cleaner (4).

Therefore, this can avoid the influence of moisture and carbon black influencing the monitoring results.

- e. When the gas enter into the gas chamber (6) via the shut-off valve (5), the pressure of the gas is greater than the safety pressure of the safety valve (11), then the safety valve (11) will automatically open and release the gas into the gas collection bag (13). After the gas releasing reaching to 10 s, close the shut-off valve (5).
- f. Open the frequency-domain terahertz-ray generator (7) located in one side of the gas chamber (6) to transmit terahertz signal with the frequency of 1.5 THz. When the terahertz signal penetrate the gas chamber (6) full of gas along the diameter, it will be received by the terahertz signal receiver (8) that located in the other side of the gas chamber (6). Then the signal will be transmitted to the computer (9) and be processed according to the following formula:

$$n = -\frac{\ln \frac{I_{out}}{I_{in}}}{L \cdot K} a \quad (1)$$

Where n is the concentration of CO or SO₂ mixed in the gas sample; I_{out} is the terahertz signal intensity received by the terahertz signal receiver; I_{in} is the terahertz signal intensity transmitted by the frequency-domain terahertz-ray generator; L is the optical path of the terahertz-ray, *ie*, the diameter of the gas chamber; K is the absorption coefficient of pure gas at a certain terahertz spectra; a is correction coefficient of pressure. Thus, the concentration of CO in the gas under the moment can be calculated.

- g. Open the shut-off valve (5), and repeat steps e and f to realize continuous monitoring of CO concentration in the gas that produced by the spontaneous combustion of coal. When the coal pyrophoricity measuring instrument would not produce gas, stop the monitoring, and then we can get the relationship between the CO concentration and the process of spontaneous combustion of coal.

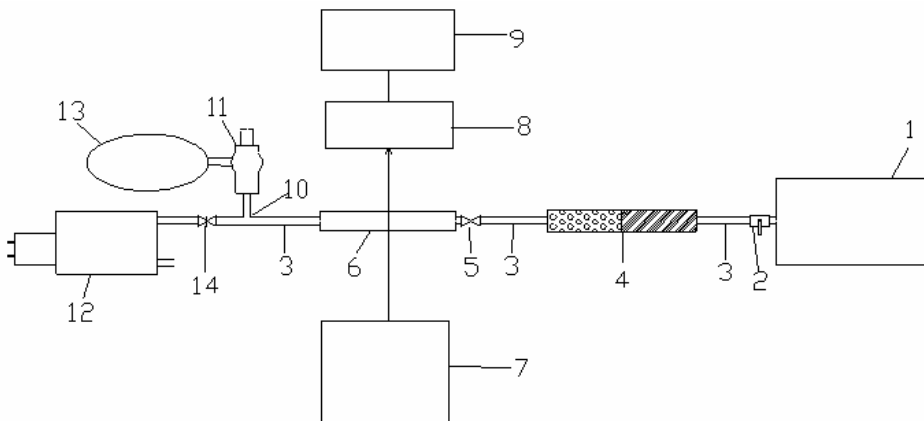


Fig. 1. The schematic drawing of the device structure: 1 - the coal pyrophoricity measuring instrument, 2 - regulating valve, 3 - pipelines, 4 - cleaner, 5 - shut-off valve, 6 - gas chamber, 7 - the frequency-domain terahertz-ray generator, 8 - the terahertz signal receiver, 9 - computer, 10 - three-way valve, 11 - safety valve, 12 - intelligent vacuum pump, 13 - gas collection bag, 14 - gate valve

Terahertz spectra of toxic gases and forecast principles

According to the principle of radiation transfer, the radiation emitted from the source and traveling through the gas cell can be absorbed by the carbon monoxide and sulphur dioxide molecule in the mixture gas emitted from coal oxidation. The absorption peaks of carbon monoxide and sulphur dioxide are summarized in Table 1. Data indicates that both carbon monoxide and sulphur dioxide have strong absorptions in THz band. And also, it is not difficult to find that the distribution of absorption peaks show regularity, thus both the spectrum of these gases almost have equivalent interval between adjacent absorption peaks.

Table 1

Peak positions of carbon monoxide and sulphur dioxide in THz range

| Carbon monoxide | | Sulphur dioxide |
|---------------------|---------------------|---------------------|
| Peak position [THz] | Peak position [THz] | Peak position [THz] |
| 0.11 | 2.41 | 0.32 |
| 0.23 | 2.53 | 0.43 |
| 0.35 | 2.64 | 0.56 |
| 0.46 | 2.76 | 0.64 |
| 0.58 | 2.87 | 0.76 |
| 0.69 | 2.98 | 0.86 |
| 0.81 | 3.10 | 0.98 |
| 0.92 | 3.21 | 1.08 |
| 1.04 | 3.33 | 1.20 |
| 1.15 | 3.44 | 1.30 |
| 1.27 | 3.55 | 1.41 |
| 1.38 | 3.66 | 1.52 |
| 1.50 | 3.78 | 1.64 |
| 1.61 | 3.89 | 1.71 |
| 1.73 | 4.00 | 1.83 |
| 1.84 | 4.12 | 1.95 |
| 1.96 | 4.23 | 2.05 |
| 2.07 | 4.34 | 2.17 |
| 2.19 | 4.45 | 2.26 |
| 2.30 | 4.56 | |

The pioneer work showed that the frequency positions of the spectral lines did not change for the different concentration conditions; however, there was a significant change in the intensity of the lines from one concentration level to another. As concentration increases, so does the intensity of the rotational transition lines. There is evidently a near linear relationship between the pressure and the change in intensity of the absorption peaks. This is also true for all rotational lines in CO and SO₂ gas. In another word, varying the concentration of the gas affects only the amplitude of the absorption lines and not their exact position. This is critical in air pollution studies when trying to single out a specific gas (such as CO and SO₂) from a field sample with unknown constituents.

Results and analysis

Observed results

Here, three kinds of coal samples with different rank are involved in this work. Results of proximate and elemental analysis of coal samples are listed in Table 2. Coal sample A, B and

C are long flame coal, gas coal and fat coal respectively that means sample A has the lowest rank. Especially, the coal sample C is one kind of high-sulphur coal.

Table 2

Proximate and elemental analysis of coal samples

| Sample | Mad /% | Aad/% | Vad/% | FCad/% | Had/% | Std/% |
|--------------------|--------|-------|-------|--------|-------|-------|
| A(long flame coal) | 12.15 | 6.82 | 33.67 | 47.36 | 4.79 | 0.14 |
| B(gas coal) | 2.82 | 7.85 | 34.82 | 54.51 | 3.21 | 0.21 |
| C(fat coal) | 1.94 | 14.48 | 26.71 | 56.87 | 4.59 | 3.01 |

Employing the experimental system discussed above, the gas emissions of CO and SO₂ in the process of coal spontaneous combustion are measured. The volume fraction curves of carbon monoxide release of different samples are drawn in Figure 2. When discussing very small concentrations, it is convenient to refer to parts per million (ppm) rather than percentages; the conversion between the two is accomplished simply by moving the decimal point four places in the appropriate direction. It can be seen that CO emission is increasing when the oxidizing temperature raise for any samples. Meanwhile, the critical temperature at which gas begins to release of low rank coal is similarly lower.

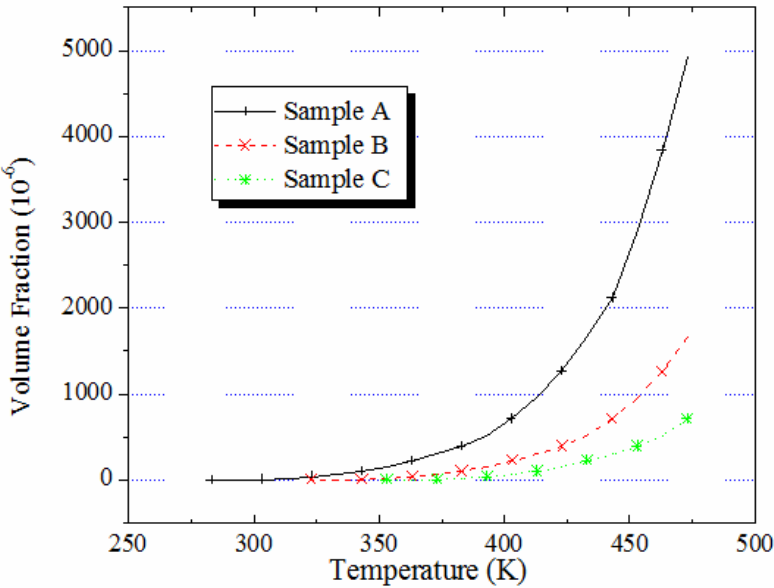


Fig. 2. CO volume fraction of 3 coal samples at different temperature

For the second part, carbon monoxide and sulphur dioxide gases are synchronously estimated for coal sample C. As demonstrated in Figure 3, the occurring temperature of sulphur dioxide is less than that of carbon monoxide for high-sulphur coal, but the volume of carbon monoxide emitting is more at same temperature.

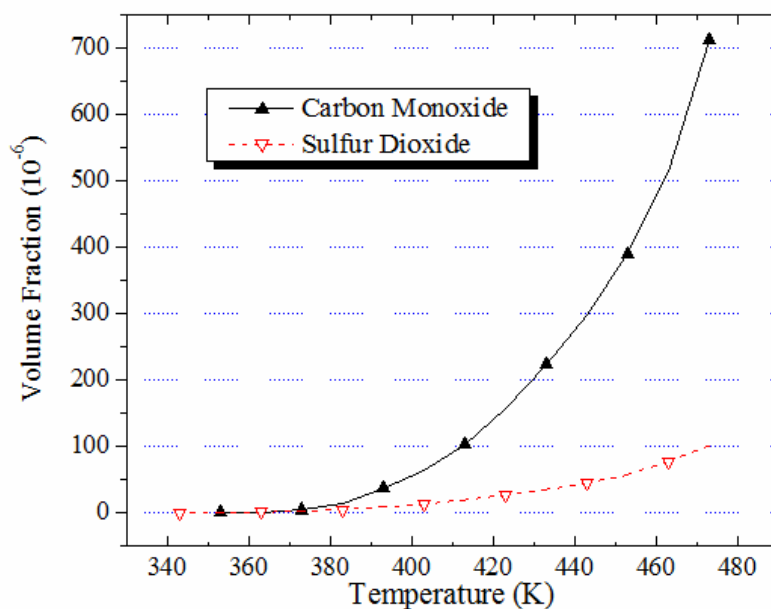


Fig. 3. CO and SO₂ volume fractions of high-sulphur coal sample at different temperature

Influence of oxygen supply

There are many inner and outer factors affecting the development process of coal spontaneous combustion, among them, the oxygen condition is also one of the important influencing factors. Taken coal sample C as the experimental object, CO volume fractions in process of coal spontaneous combustion under different oxygen concentration are investigated at low temperature oxidation stage.

Table 3
CO volume fractions with different lean oxygen condition at low temperature oxidation stage (sample C)

| Temperature [°C] | CO volume fraction (10 ⁻⁶) | | | |
|------------------|--|--------------------|--------------------|--------------------|
| | 5% O ₂ | 10% O ₂ | 15% O ₂ | 20% O ₂ |
| 0 | — | — | — | — |
| 10 | — | — | 0.04574 | — |
| 20 | — | 0.44 | 0.484 | 0.46095 |
| 30 | 2.4583 | 3.35223 | 3.68745 | 3.51186 |
| 40 | 8.40627 | 11.46309 | 12.6094 | 12.00895 |
| 50 | 24.63912 | 33.5988 | 36.95868 | 35.19875 |
| 60 | 42.70643 | 58.23604 | 64.05964 | 61.00918 |
| 70 | 68.68815 | 93.66566 | 103.03222 | 98.12592 |
| 80 | 103.9308 | 141.72381 | 155.89619 | 148.47256 |
| 90 | 148.35366 | 202.30045 | 222.5305 | 211.93381 |
| 100 | 199.19432 | 271.62862 | 298.79148 | 284.56331 |
| 110 | 260.297 | 354.95046 | 390.4455 | 371.85286 |
| 120 | 343.35894 | 468.21674 | 515.03841 | 490.51277 |
| 130 | 475.0566 | 647.80446 | 712.5849 | 678.65229 |

| | | | | |
|-----|------------|------------|------------|------------|
| 140 | 634.45506 | 865.16599 | 951.68259 | 906.36437 |
| 150 | 844.56523 | 1151.67986 | 1266.84784 | 1206.52176 |
| 160 | 1106.83711 | 1509.32333 | 1660.25567 | 1581.19587 |
| 170 | 1414.15327 | 1928.39082 | 2121.2299 | 2020.21896 |
| 180 | 1941.54476 | 2647.56103 | 2912.31714 | 2773.63537 |
| 190 | 2563.98755 | 3496.34666 | 3845.98133 | 3662.83936 |
| 200 | 3284.93176 | 4479.4524 | 4927.39764 | 4692.75966 |

Data are collected in Table 3, it can be found that the change rules of CO products with the temperature rising are roughly same. Generally speaking, lower oxygen concentrations can inhibit oxidation of coal combustion reaction and gas release. There are two oxygen supply conditions in the process of coal combustion named low lean oxygen condition and micro oxygen-rich condition. That means there exists a critical oxygen concentration which is around 10% to 15%. When oxygen concentration less than the critical value, belongs to the low state of lean oxygen reaction, coal oxidation and burning is not full, gas emission is changing significantly along with the change of oxygen concentration. When oxygen concentration is higher than that value, belongs to the micro oxygen enrichment reaction, coal oxidation and burning completely, and change range of gas emission is relatively small.

Discussions

To determine the effectiveness of presented forecast method, Fourier infrared technology is applied in this section to repeat the measurement since it is a general method in gas component analysis. The observed data of CO and SO₂ emissions by using two measurement methods are listed in Table 4.

Table 4
Gas emissions observed by terahertz and Fourier infrared analysis for high-sulphur coal oxidation

| Temperature [°C] | CO volume fraction (10 ⁻⁶) | | SO ₂ volume fraction (10 ⁻⁶) | |
|------------------|--|---------------------------|---|---------------------------|
| | Terahertz analysis | Fourier infrared analysis | Terahertz analysis | Fourier infrared analysis |
| 40 | — | — | — | — |
| 50 | — | — | — | — |
| 60 | — | — | — | — |
| 70 | 0.003 | — | 0.006 | — |
| 80 | 0.045 | — | 0.068 | 0.32 |
| 90 | 0.484 | 1.02 | 0.507 | 0.69 |
| 100 | 3.687 | 1.72 | 1.69 | 0.59 |
| 110 | 12.6 | 5.87 | 4.824 | 3.72 |
| 120 | 36.95 | 35.4 | 8.15 | 6.95 |
| 130 | 64.05 | 67.3 | 12.78 | 11.48 |
| 140 | 103.1 | 100.2 | 18.87 | 17.47 |
| 150 | 155.8 | 165.9 | 26.3 | 24.8 |
| 160 | 222.5 | 230.3 | 34.5 | 32.9 |
| 170 | 298.7 | 295.2 | 44.06 | 42.36 |
| 180 | 390.4 | 399.5 | 56.84 | 55.04 |
| 190 | 515.1 | 520.6 | 76.95 | 75.05 |
| 200 | 712.5 | 732.7 | 100.6 | 98.6 |

Both CO and SO₂ emissions could be identified earlier from terahertz observation than that from Fourier infrared observation. The positive effect of terahertz forecast method of coal oxidation is more sensible. The frequency-domain terahertz spectroscopy is characteristic by large peak power, high resolution and can go through the gas-phase material. And it achieves continuous monitoring of the gas concentration without repeating experiment, meanwhile, significantly reduce the injection interval. The monitoring results obtain the amplitude and phase information at the same time, and the absorption peak is very sharp without the phenomenon of spectral overlap. Consequently the detection accuracy of the gas concentration is very high.

Conclusions

A novel forecast method for toxic gas emission monitoring which provided with frequency-domain terahertz spectroscopy technique and coal temperature programming system is presented in this paper. Carbon monoxide and sulphur dioxide emissions from coal spontaneous combustion are measured according to terahertz spectra characteristics of molecules. It can be concluded that the THz spectra peaks of CO and SO₂ gases are known to have a number of equi-spaced signature spectral lines that are at very precise frequency locations. Observed results show that CO and SO₂ emissions are increasing when the oxidizing temperature raises, and CO occurring temperature of low rank coal is similarly lower. Investigating results of influence of oxygen supply on coal oxidation at low temperature indicate that there exists a critical oxygen concentration between two oxygen supply conditions in the process of coal spontaneous combustion. Compared with Fourier infrared analysis, terahertz measurement can identify the toxic gases earlier and more accurately. In summary, the presented method is especially suitable for continuous monitoring the toxic gas emission during coal spontaneous combustion process. This study provides certain theoretical guidance to effectively governing existing mine fire area and restraining the formation of new fire area.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (Grant no. 51134020, 51106175 and 51104154), and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

- [1] Pone JDN, Hein KAA, Stracher GB, Annegarn HJ, Finkelman RB, Blake DR, et al. The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. *Int J Coal Geol.* 2007;72:124-140. DOI: 10.1016/j.coal.2007.01.001.
- [2] Misz M, Fabiańska M, Ćmiel S. Organic components in thermally altered coal waste: preliminary petrographic and geochemical investigations. *Int J Coal Geol.* 2007;71:405-424. DOI: 10.1016/j.coal.2006.08.009.
- [3] Misz M, Fabiańska M. Thermal transformation of organic matter in coal waste from Rymer Cones (Upper Silesian Coal Basin, Poland). *Int J Coal Geol.* 2010;81(4):343-358. DOI: 10.1016/j.coal.2009.08.009.
- [4] Finkelman RB. Potential health impacts of burning coal beds and waste banks. *Int J Coal Geol.* 2004;51:19-24. DOI: 10.1016/j.coal.2003.11.002.
- [5] Simoneit BRD, Bi X, Orors DR, Medeiros PM, Sheng G, Fu J. Phenols and hydroxy-PAHs (arylphenols) as tracer for coal smoke particulate matter: source tests and ambient aerosol assessment. *Environ Sci Technol.* 2007;41:7294-7302. DOI: 10.1021/es071072u.

- [6] Stracher GB, Taylor TP. Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe. *Int J Coal Geol.* 2004;59:7-17. DOI:10.1016/j.coal.2003.03.002.
- [7] Stracher GB, Hower JC, Schroeder PA, Fleisher C, Kitson J, Barwick LH, et al. Environmental dangers of coal fires in Kentucky and Alabama. *Geological Society of America Abstracts with Program*, 2008;310-7.
- [8] Hower JC, Henke K, O'Keefe JMK, Engle MA, Blake DR, Stracher GB. The Tiptop coal mine fire, Kentucky: preliminary investigation of the measurement of mercury, carbon dioxide and carbon monoxide from coal-fire gas vents. *Int J Coal Geol.* 2009;80: 63-67. DOI: 10.1016/j.coal.2009.08.005.
- [9] Hower JC, Rangwala AS, O'Keefe JMK, Henke K, Engle MA. Time series analysis of CO emissions from a coal fire, Eastern Kentucky. *Geochim Cosmochim Acta.* 2010;74:A422.
- [10] Ribeiro J, Ferreira da Silva E, Flores D. Burning of coal waste piles from Douro Coalfield (Portugal): petrological, geochemical and mineralogical characterization. *Int J Coal Geol.* 2009;81(4):359-372. DOI: 10.1016/j.coal.2009.10.005.
- [11] Zhao Y, Zhang J, Chou CL, Li Y, Wang Z, Ge Y, et al. Trace element emissions from spontaneous combustion of gob piles in coal mines, Shanxi, China. *Int J Coal Geol.* 2008;73:52-62. DOI: 10.1016/j.coal.2007.07.007.
- [12] O'Keefe JMK, Henke K, Hower JC, Engle MA, Stracher GB, Stucker JD, et al. CO, CO₂, and Hg emission rates from the Truman Shepherd and Ruth Mullins coal fires, Eastern Kentucky. *Sci Total Environ.* 2010;408:1628-1633. DOI: 10.1016/j.scitotenv.2009.12.005.
- [13] Matsushima N, Kazahaya K, Saito G, Shinohara H. Mass and heat flux of volcanic gas discharging from the summit crater of Iwodake volcano, Satsuma-Iwojima, Japan, during 1996-1999. *J Volcanol Geotherm Res.* 2003;126:285-301. DOI: 10.1016/S0377-0273(03)00152-5.
- [14] Exter van M, Fattinger C, Grischkowsky D. Terahertz time-domain spectroscopy of water vapor. *Opt Lett.* 1989;14:1128-1130. DOI: 10.1364/OL.14.001128.
- [15] Harde H, Zhao J. THz time-domain spectroscopy on ammonia. *J Phys Chem A.* 2001;105:6038-6047. DOI: 10.1021/jp0101099
- [16] Matron S, Rohart F, Bocquet R. Terahertz spectroscopy applied to the measurement of strengths and self-broadening coefficients for high-J lines of OCS. *J Mol Spectrosc.* 2006;239:182-189. DOI: 10.1016/j.jms.2006.07.004.
- [17] Hu Y, Wang XH, Guo LT, Zhang CL. Terahertz time domain spectroscopic study of carbon monoxide. *Spectrosc Anal.* 2006;26(6):1008-1011.
- [18] Almoayed NN, Piyade BC, Afsar MN. High-resolution absorption coefficient and refractive index spectra of common pollutant gases at millimeter and THz wavelengths. *Proc SPIE*, 2007;6772: 67720G. DOI: 10.1117/12.737143.

TERAHERCOWE POMIARY EMISJI GAZU WSKAŹNIKOWEGO ZE SPONTANICZNYCH SAMOZAPŁONÓW WĘGLA W NISKIEJ TEMPERATURZE

Abstrakt: Spontaniczny zapłon węgla jest bardzo skomplikowanym procesem fizycznym i chemicznym. W artykule opisano usprawnienia technologii wykrywania gazów i monitorowania wskaźników spontanicznego zapłonu węgla, wynikające z opracowania nowatorskiej metody przewidywania emisji gazów toksycznych z utleniania węgla w niskiej temperaturze. Układu doświadczalnego był zbudowany z systemu technologii częstotliwości terahercowych w połączeniu z technologią programowania temperatury węgla. Przebiegi krzywych stężenia tlenu węgla i ditlenku siarki z gazów samozapłonu węgla szacowane są na podstawie widma terahercowego. Przedstawiono wpływ rodzaju węgla i zaopatrzenia w tlen na cechy charakterystyczne samoistnego zapłonu węgla. Widma absorpcji obu gazów, tj. tlenu węgla i ditlenku siarki, wykazują charakterystyczne, tak samo odległe, piki absorpcji. Wyniki pokazują, że w warunkach niskiej zawartości tlenu istnieje pewne krytyczne stężenie tego gazu w procesie utleniania węgla w niskiej temperaturze. Porównując wyniki badań z widmem Fouriera w podczerwieni, można uznać, że przedstawiona metoda jest dokładniejsza i czulsza, nadając się szczególnie do monitorowania wczesnej fazy wytwarzania gazów wskaźnikowych, produkowanych przy samozapłonie węgla.

Słowa kluczowe: samozapłon węgla, monitorowania gazów, tlenek węgla, ditlenek siarki, technika spektroskopii terahercowej