Passive detection of carbon dioxide in the high temperature cement-kiln by FTIR

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Abstract. Passive sensing by Fourier-transform infrared (FTIR) spectrometry allows detection and quantification of gas. In this work, the infrared radiation signal of the carbon dioxide in the cement-kiln was measured by FTIR. A new radiative transfer model was built to calculate transmittance from measured spectrum of the carbon dioxide in the cement-kiln. Based on the HITRAN database, the nonlinear least square fitting method was used to calculate the concentration of the carbon dioxide (CO\textsubscript{2}) from transmittance. The results show that this method of measuring the concentration of carbon dioxide and other gas in the high temperature cement-kiln is feasible and reliable. And this method is also applicable to the measurement of other gases, such as carbon monoxide (CO), sulfur dioxide (SO\textsubscript{2}), etc.

1. Introduction

Passive remote sensing by Fourier-transform infrared has the advantages of on-line telemetry, fast analysis, no sample preparation, etc \cite{1,2}. In industrial production it can analyze the component and content of gas in real time, and measure some physical parameters, such as temperature, spectral energy distribution and combustion efficiency, especially suitable for the industrial environment of high temperature and dust.

In this work, the CO\textsubscript{2} which produced in the cement rotary kiln calcination process of cement is the research object. We measure the concentration of CO\textsubscript{2} to determine whether the raw material is fully burnt. Firstly, the radiative transfer model of CO\textsubscript{2} is established according to the field situation. The theoretical expression of the CO\textsubscript{2} transmittance spectrum is obtained by analyzing the composition of the radiation received by detector. Then the calibration spectra were obtained according to the HITRAN database \cite{3} parameters combined with the reference spectrum model at high temperature. Finally, the calibration spectrum and the transmittance spectrum were fitted by the nonlinear least square fitting method to calculate the concentration of CO\textsubscript{2}.

2. Radiative transfer model

Passive remote sensing of CO\textsubscript{2} by FTIR is based on the analysis of infrared radiation emitted and absorbed by the molecules CO\textsubscript{2} \cite{4}. When the background radiation is projected onto the carbon dioxide, a part of the radiation is transmitted, and the rest is absorbed by the carbon dioxide (Because of the carbon dioxide gas, the reflection is not considered). According to Kirchhoff’s law of thermal
radiation [2], for an arbitrary body emitting and absorbing thermal radiation in thermodynamic equilibrium, the emissivity is equal to the absorptivity. Therefore, the radiation spectrum obtained by the detector includes not only the background radiation (such as the radiation of high temperature cement kiln wall) through the carbon dioxide, but also the radiation of the carbon dioxide in the high temperature cement-kiln.

\[ I_0 (\lambda) \] (radiant intensity) is the radiation of high temperature cement kiln wall. \( I_1 \) includes the background radiation through the carbon dioxide and the radiation of the carbon dioxide in the high temperature cement-kiln. \( I \) - the radiation measured by the spectrometer (through the carbon dioxide in the air).

The whole model is divided into two parts - inside and outside of the cement kiln, and then from the outside to the inside it is analyzed the composition of radiation to obtain the theoretical expression of the transmittance spectrum.

\section{The model outside the cement-kiln}

The model outside the cement-kiln is used to calculate \( I_1 \) by \( I_0 \) and transmittance spectrum \( \tau_1 \) of CO2 in the air. The temperature outside the cement kiln is much lower than inside, so the radiation of CO2 outside the cement kiln can be neglected (The radiation of the instrument is the same):

\[ \tau_1 (\lambda) = e^{-\alpha(\lambda)c} \] \hspace{1cm} (2)

\( \alpha(\lambda) \): the absorption coefficient of CO2, \( c \): the concentration of CO2 in the air, \( l \): the distance from the furnace to the detector.

\section{The model inside the cement-kiln}

Since the temperature of CO2 inside of the cement-kiln is close to the temperature of background, the radiation of CO2 inside the cement kiln cannot be negligible. So \( I_1 \) includes the background radiation through the carbon dioxide and the radiation of the carbon dioxide in the high temperature cement-kiln:

\[ I_1 (\lambda) = \tau_2 (\lambda) * I_0 (\lambda) + (1 - \tau_2 (\lambda))I_{co2}(\lambda) \] \hspace{1cm} (3)

Conversion formula (3) to calculate the transmittance of CO2 \( \tau_2 (\lambda) \) in the cement-kiln:

\[ \tau_2 (\lambda) = \frac{I_1(\lambda) - I_{co2}(\lambda)}{I_0(\lambda) - I_{co2}(\lambda)} \] \hspace{1cm} (4)

The radiant intensity of CO2 \( I_{co2}(\lambda) \) is related to its radiance. In a range, the variation of the radiant intensity and the radiance can be approximated as a one-to-one correspondence with the wavelength:
\[
\frac{I_0(\lambda)}{I_{CO2}(\lambda)} = \frac{L_0(\lambda)}{L_{CO2}(\lambda)} \quad (5)
\]

\[I_0(\lambda): \text{the radiant intensity of the cement-kiln wall}, \quad L_0(\lambda): \text{the radiance of the cement-kiln wall}, \quad L_{CO2}(\lambda): \text{the radiance of CO2 in the cement-kiln}.\]

At the time of local thermodynamic equilibrium, the relative radiance is defined by the radiance of equivalent black body. According to the Planck equation, the radiance of equivalent black body can be obtained:

\[L(\nu) = B(\nu, T) = C_1 \nu^3 / \left[ \exp \left( \frac{C_2 \nu}{T} \right) - 1 \right] \quad (6)\]

\[\nu: \text{the wave number. } C_1 \text{ and } C_2 \text{ are the first and second radiation constants(in the form of wave number). } T: \text{the temperature of equivalent radiation blackbody}.\]

The emissivity of radiator is always less than 1, so the temperature of equivalent radiation blackbody is always smaller than the real temperature of radiator, which needs to be corrected by looking up the table (emissivities of surfaces) [6].

Equation (6) shows that the radiance is only related to the temperature of equivalent radiation blackbody. \(L_0(\lambda)\) and \(L_{CO2}(\lambda)\) are calculated by measuring the temperature of the cement-kiln wall and CO2, and then \(I_{CO2}(\lambda)\) and \(I_2(\lambda)\) can be calculated according to equation (5) and (4).

3. Quantification of CO2 with high temperature

The carbon dioxide absorption lines at different temperatures:

![Carbon dioxide absorption lines at different temperatures.](image)

The quantification of CO2 is performed by four steps [7,8]:

Correction of spectrum line strength \(S_{\eta\nu}(T)\) at high temperature - line strength is related to the temperature according to Maxwell-Boltzmann distribution and quantum theory:

\[S_{\eta\nu}(T) = S_{\eta\nu}(T_{ref}) \frac{Q(T)}{Q(T_{ref})} \left[ \exp \left( \frac{C_2 L}{T} \right) - 1 \right] \exp \left( \frac{C_2 L}{T_{ref}} \right) \left[ 1 - \exp \left( \frac{C_2 v_{\eta\nu}}{T_{ref}} \right) \right] \quad (7)\]

\[c_2: \text{the second radiation constant. } v_{\eta\nu}: \text{the frequency of absorption line. } L: \text{low energy of absorption line. } Q(T): \text{the reference temperature. } Q(T_{ref}): \text{the reference value of total partition function}.\]

Correction of spectrum lines broadening \(r_v\) at high temperature - the Voigt profile \(r_v\) is a line profile resulting from the convolution of two broadening mechanisms, one of which alone would produce a Gaussian profile \(r_G\) and the other would produce a Lorentzian profile \(r_L\):

\[r_v = 0.5(1.0692r_G + 0.86639r_L^2 + 4r_D^2) \quad (8)\]
Calibration spectrum $T(\gamma)$ - Based on the HITRAN database, we establish a high temperature mathematical model, including measurement conditions (temperature, optical path, pressure, gas species and environmental parameters) and the parameters of the instrument (resolution, the apodization function, etc.) \[9\]. Using this mathematical model to calculate the transmittance calibration spectrum $T(\gamma)$ by numerical integration method:

$$\mathcal{S}(\gamma) = \int_{\Delta \nu} \exp \left\{ - \sum_{i=1}^{N} \sigma_i(\nu) p(x) dx \right\} d\nu$$ \hspace{1cm} (9)

$[\sigma_i:]$ the molecular absorption coefficient of the spectral line in the wave number $\nu$. $p(x)$: The concentration of absorbed molecular at x. $N$: the number of all spectral lines in a wave number range; $\Delta \nu$: wave number range; $L$: optical path.

Quantification by Nonlinear Modeling - The quantification is performed by minimization of the difference between the measured spectrum and calibration spectrum \[10\]. This is a process by which the objective function $x^2(A)$ is minimized to find the optimal concentration parameter $A$:

$$x^2(A) = \sum_{j=1}^{N} [\tau_j - \tau_{cal}(\nu_j, A)]^2$$ \hspace{1cm} (10)

$[N:]$ the number of spectral elements. $\tau_j$: the transmittance of measured spectrum. $\tau_{cal}(\nu_j, A)$: the transmittance of calibration spectrum. The concentration parameter A includes the position of each spectral line, the spectrum line strength and broadening.]

4. The infrared remote sensing system

The infrared remote sensing system is comprised of an spectrometer (resolution is $1 \text{cm}^{-1}$; average of 16 scans), a detector of thermoelectric refrigeration at $2000 \text{cm}^{-1} - 5000 \text{cm}^{-1}$, a Cassegrain telescope, a data processing and control system with a digital signal processor (FTIR DSP), and a personal computer (Figure 2 and Figure 3).

![Figure 3. The infrared remote sensing system.](image)

![Figure 4. The experimental field.](image)
The transmittance of CO2 (a) and the transmittance without radiation of CO2 in the cement-kiln (b).

5. Experimental

5.1. The model outside the cement-kiln
The optical path length is 1 meter. Considering the radiation of CO2 in the cement-kiln, according to equation (4) the transmittance of CO2 $\tau_2$ is calculated (Figure 4a). If CO2 radiation is ignored in the cement-kiln, the equation (4) is changed to $\tau_2 = I_2 / I_0$ (Figure 4b).

From Figure 4a to Figure 4b, we can see that the signal of CO2 in 2230-2390 cm$^{-1}$ is saturated in the case of considering the radiation of CO2 in the cement-kiln. In 3560-3800 cm$^{-1}$, but after deducting the water absorption, the signal of CO2 is not saturated according to the CO2 infrared absorption characteristic; If the radiation of the CO2 in the cement-kiln is ignored, the CO2 signal is not saturated in the two absorption bands. The concentration of calculation is different in two different cases.

5.2. The calculation of CO2 concentration
The absorption of CO2 is relatively strong and the signal is saturated at 2230-2390 cm$^{-1}$, so the transmittance of CO2 in 3560-3800 cm$^{-1}$ is selected to calculate concentration [2].

Figure 6. The calculation of transmittance CO2 by NLLS fitting method [7].
Table 1. The calculation of CO2 concentration in different situations and in different bands.

| Absorption band of CO2 | Concentration of CO2 % (fitting error) |
|------------------------|----------------------------------------|
|                        | With considering CO2 radiation | Without considering CO2 radiation |
| 2230-2390(2272)cm⁻¹ (Not saturated) | 1.7494%(0.6136%) | 0.5219%(0.1137%) |
| 3560-3800cm⁻¹          | 15.3972%(0.4412%) | 5.1332%(0.7443%) |

Figure 7. The concentration on-line monitoring results of gas in the cement kiln.

Table 2. The measurements in industrial field.

| Measurement time | SO2(ppm) | NO(ppm) | CO2(%) | CO(ppm) |
|------------------|----------|---------|--------|---------|
| 0:00             | 54.63    | 98.84   | 15.95  | 60.97   |
| 0:04             | 48.83    | 100.5   | 15.94  | 55.54   |
| 0:08             | 57.37    | 103.46  | 15.91  | 45.07   |
| 0:11             | 49.62    | 102.97  | 15.78  | 39.58   |
| 0:15             | 44.73    | 103.12  | 15.82  | 36.85   |
| 0:18             | 42.22    | 99.4    | 15.93  | 39.32   |
| 0:22             | 35.97    | 97.15   | 15.93  | 49.25   |
| 0:25             | 43.45    | 95.8    | 15.86  | 49.83   |
| 0:29             | 48.54    | 93.52   | 15.96  | 54.36   |
| 0:32             | 58.84    | 96.03   | 15.84  | 54.38   |
| 0:36             | 12.85    | 93.96   | 15.61  | 42.07   |
| 0:39             | 49.99    | 90.39   | 15.73  | 42.91   |
| 0:43             | 47.5     | 89.58   | 15.77  | 45.52   |
According to the absorption of H2O in this band, the corrected calibration spectrum and the transmittance spectrum (Figure 4a and Figure 4b) are fitted by the nonlinear least square fitting method to calculate the concentration of CO2 (Figure 5 and Table 1).

First, Table 1 shows that the calculation result of concentration is not satisfactory in the 2230-2390 cm⁻¹ (compared with the concentration, the fitting error is too high). The reason may be CO2 in the air. Although the CO2 concentration in the air (400-500ppm) is lower than that in the cement kiln, the absorption of CO2 is too strong in the 2230-2390 cm⁻¹ (Figure 6). So the concentration calculation of the CO2 in the cement kiln is affected. Secondly, from the comparison of whether or not to ignore the CO2 radiation, it shows that the radiation of the target gas with high temperature in the passive remote sensing model has a significant impact on the calculation of the concentration. According to equation 4, 5 and 6, the smaller the difference between the temperature of background and target gas is, the greater the impact of self radiation on the calculation of concentration.

When we measure the concentration of CO2 in the cement kiln, the CO2 outside the cement kiln cannot be neglected. But for other gases in the cement kiln, we just have to think about the model inside the cement-kiln. According to the absorption spectrum of gas in the HITRAN database (SO2: 2440-2532 cm⁻¹, NO: 1835-1920 cm⁻¹, NO2: 2790-2962 cm⁻¹, CO2: 3560-3800 cm⁻¹, CO: 2008-2248 cm⁻¹), the calculation of the gas concentration of the two cement plants in different time periods are shown in Figure 7 and Table 2.

6. Summary and conclusions

Passive sensing by infrared spectroscopy is one of the methods used for detection of gases. Many situations need the measurement of pollutants prior to the measurement of background in order to perform background removal. The spectral radiance of the gases can be measured after a radiometric calibration of the FTIR spectrometer. But sometimes, due to the harsh conditions of the industrial field measurement, the instrument parameters are easy to change and cannot be calibrated. In this paper, the background spectrum can be fitted by removing gas absorption of measured spectrum, and then the gas transmittance can be calculated.

The measurement results of carbon dioxide and other gas concentrations in industrial cement kilns show that the concentration detection method in this paper is feasible for passive detection of gases in high-temperature cement kilns.

References

[1] MGGao, WQLiu, TSZhang, JG Liu, YHLu, JZhu, YLian, FLu2005Passive remote sensing of VOC in atmosphere by FTIR spectrometry, Spectroscopy and Spectral Analysis 25(7) 1042-1044 (in Chinese)
[2] J G Wu 1994 Modern Fourier Transform Infrared Spectroscopy And Its Application1 (Beijing: Scientifical and Technical Documents Press) (in Chinese)
[3] L S Rothman, DJacquemart and A. Barbe 2004 The HITRAN 2004 molecular spectroscopic database. Journal of Quantitative Spectroscopy & Radiative Transfer 96 139
[4] Harig R, Matz G, Rusch 2002 Scanning infrared remote sensing system for identification, visualization, and quantification of airborne pollutants. Environmental & Industrial Sensing 4574(2) 116-121
[5] Liu ZM, Gao MG, Liu WQ, Lu YH, Zhang TS, Xu L and Wei X.L 2008 The Study of Instrument Response Function of FTIR Detectors. Chin. Phys. B 28(8) 1786-1789
[6] Roland H, Peter R, Chris D, Anita J, Richard M, Benjamin 2005 Remote Measurement of Highly Toxic Vapours by Scanning Imaging Fourier-Transform Spectrometry. International Society for Optical Engineering doi10.1117/12.631730
[7] J Fang, WQ Liu, TS Zhang 2007 A line-by-line trace gas absorption model and its application in FTIR gas detection[J]. Infrared 28(8) 27-32 (in Chinese)
[8] Cheng SY, Zhang TS, Gao MG, Liu ZM, Tong JJ, Jin L 2011 Concentration inversion of high temperature air from FTIR spectra and analyzing residual error structure Spectroscopy and
Spectral Analysis 31(1) 82-85 (in Chinese)

[9] Lin JL, Huang YQ, Lu H 2005 Determination of relative error of pressure-broadening linewidth for the experimentally indistinguishable overlapped spectral lines with Voigt profile, Spectroscopy and Spectral Analysis 25(1) 128-132

[10] Zhang H., Shi GY 2000 A fast and efficient line-by-line calculation method for atmospheric absorption, Chinese Journal of Atmospheric Sciences 24(1) 111-121