PLASMA ASSISTED SPECTROSCOPIC MONITORING OF ALKALI METALS IN PRESSURISED COMBUSTION AND GASIFICATION

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ABSTRACT

The paper describes an instrument for on-line concentration measurement of vaporised alkali compounds in pressurised industrial combustion and gasification processes. The measurement is based on Plasma Excited Alkali Resonance Line Spectroscopy (PEARLS) at the elevated pressure (1-3 MPa) of the process. Results are presented from laboratory calibration measurements and test measurements of sodium and potassium vapours resulting from the combustion of coal powder in a pressurised entrained flow reactor.

INTRODUCTION

Pressurised combustion and gasification of solid fuels are used in advanced combined energy conversion cycles capable of producing electricity with high efficiency and low emissions. The presence of alkali metal vapours causes one of the complex technical problems encountered in pressurised processes based on coal or biomass fuels. Vaporised alkali compounds are liable to cause damage to gas turbine blades and to some of the materials used in hot gas cleaning devices. The current industrial gas turbine specification limit for alkali compounds in gas entering a turbine is of the order 0.1 ppm by weight [1]. To guarantee that the standard is met, an on-line technique for monitoring of the alkali concentration is required.

A few approaches for on-line alkali measurement have been reported in the litterature [2],[3],[4],[5]. The methodological approaches include, for example, flame emission spectroscopy, mass spectrometry and excimer laser induced fragmentation (ELIF). Commercial instruments specialised to the present purpose have not yet appeared on the market.

DESIGN PHILOSOPHY

In real industrial pressurised processes the large dimensions and the pressure containment impose serious practical contraints on diagnostic access. For example, these constraints make non-intrusive techniques, however attractive in principle, very complex to apply in engineering practice for on-line alkali monitoring. Techniques based on sampling have many problems, too. One of the most serious ones is the strong inclination of vaporised alkali salts to stick to solid surfaces, including sampling tube walls.

The philosophy behind the present approach is based on the use of a sampling tube of shortest possible length and simplest possible geometry combined with uniform electrical heating of the tube to above 1100 K, which is clearly above the dew point of alkali vapours, to avoid condensation of alkali vapours to the walls of the tube. To fulfill these criteria it is necessary to perform the measurement at the elevated pressure of the process, which is typically between 1 and 3 MPa. Otherwise the presence of a pressure reduction valve increases the risk of alkali capture. In a pressurised measurement the sampling tube length is only dictated by the dimensions of the lining and the connecting flange. A typical length is about 0.5 metre.

The use of thermal plasma atomisation of the alkali sample, as described below in more detail, is an essential feature in the design philosophy. The plasma is non-explosive, and therefore it can be safely used in pressurized systems. This is not the case with a flame, for example.

PHYSICAL PRINCIPLES AND INSTRUMENT DESIGN

The measurement is based on Plasma Excited Alkali Resonance Line Spectroscopy (PEARLS). At typical process conditions (T: 800-1400 K, P: 1-3 MPa), free alkali metal atoms are practically absent. Therefore, the gas sample is turbulently mixed with a DC nitrogen plasma jet to atomise the vapourised alkali salts present in the sample. This takes place in a mixing nozzle, which is integrally joined to the sampling tube as indicated in Fig. 1 and 2. The atomisation produces a gas jet of 2500 - 2800 K temperature. The degree of dissociation depends on the composition of the process gas and on the temperature after mixing. The

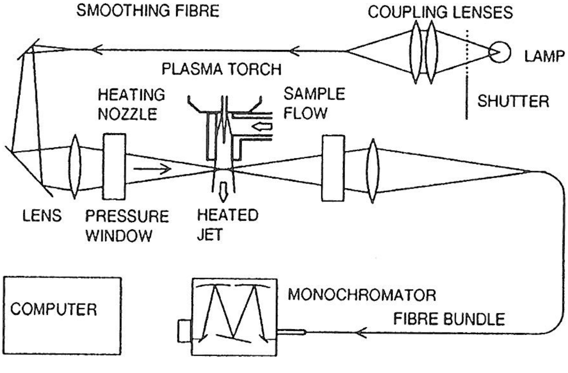

Fig. 1. The optical setup and the principle of plasma heating.

degree of dissociation is typically between 70 % and nearly 100% at the said temperature. The concentration of undissociated alkali is determined on the basis of a calculated equilibrium composition of the mixed gas jet. This is not always a very accurate procedure, but it contributes only little uncertainty to the final result due to the high degree of dissociation.

The spectroscopic setup is shown in Fig. 1.The 3s-3p resonance transition of sodium at 589 nm and the corresponding 4s-4p transition of potassium at 767 nm are used in the detection of these elements. At the temperature of the sample jet these lines appear strongly both in emission and absorption, which must be taken into account in the measurement. This is done by measuring three light fluxes at the respective resonance line wavelengths: Φ_G is the flux emitted by the hot gas with no reference light source, Φ_L is the flux from the reference source only and Φ_{GL} is the flux emitted by the gas and the reference source together. The fluxes are transferred to a remote monochromator unit using an optical fibre bundle. The light source is a tungsten halogen lamp. An optical fibre is used to smooth the coil structure of the lamp and provide a uniform illuminating surface [6]. Φ_G and Φ_{GL} are measured by positioning the monochromator grating at the center of the line and operating the shutter. The reference lamp signal Φ_L is measured by positioning the grating to the side of the line.

The spectral absorption coeffient $\varkappa(\lambda)$ of the gas is linearly proportional to the concentration of alkali atoms. The relationship between $\varkappa(\lambda)$ and the measured fluxes can be expressed in the form:

$$\frac{\Phi_{GL}-\Phi_G}{\Phi_L} = \int_0^\infty h(\lambda)\exp(-\kappa(\lambda)L)d\lambda \tag{1}$$

h(λ) is the normalised spectral transmittance of the optical filter (monochromator) used to set the desired spectral band. L is the length of the absorption path which is equal to the diameter of the gas jet.

Quantities required to calculate $\varkappa(\lambda)$ are the temperature of the heated gas jet and the FWHM of the spectral line. The temperature of the gas jet can be determined from the measured light fluxes using the generalised line reversal method [7]. This method has earlier been used succesfully in difficult hot gas flow conditions like, for example combustion MHD generator channels [6],[8],[9].

The profiles of the resonance lines were experimentally verified to be Lorentzian. This is explained by the high pressure, at which pressure broadening is the dominating mechanism. The FWHM of the Lorentz profile can be written [10]:

$$\Delta\lambda_L = \frac{6.6\cdot10^5 Qp\lambda_{ki}^2}{\sqrt{M_a T}} \tag{2}$$

P is the pressure in Torr, M_a is the atomic weight and Q is the optical cross section in cm^2. The values for Q are [11]: Na: 85 $\cdot 10^{-16}$ cm^2, K: 125 $\cdot 10^{-16}$ cm^2.

The molar fraction x of atomic alkali metal in the gas jet can now be solved from eq.(1) using basic spectral data. The desired quantity, the molar fraction C of alkali atoms in the sample gas is calculated from

$$C = \frac{x}{k_{diss}\, k_{mix}} \tag{3}$$

k_{diss} is the degree of dissociation and k_{mix} is the molar fraction of sample gas in the jet from

$$k_{mix} = \frac{V_{sample}}{V_{sample} + V_{plasma}} \tag{4}$$

The calculations above are based on uniform conditions in the heated gas jet. Deviations arising from the nonuniformity of the jet are corrected using an empirical factor which is determined by calibration measurements, as will be described below.

The mechanical setup of the instrument is shown in fig. 2. The measuring device is connected via the flange to the process flow duct and forms an integrated part of the pressure containment. The sampling tube is electrically heated to keep the temperature above the dew point of the alkali compounds. The mixing nozzle is made of stainless steel. The sample gas flow is controlled by adjusting the exhaust gas, plasma gas and window purge gas flows

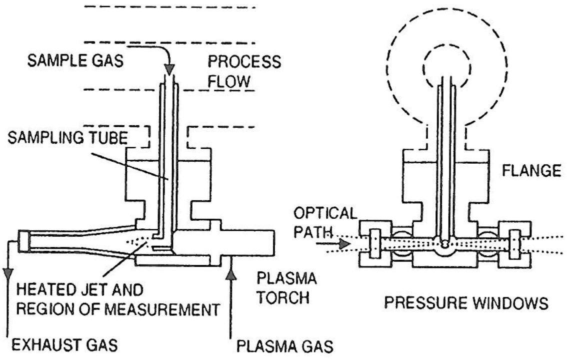

Fig. 2. The mechanical setup of the instrument.

The nitrogen plasma jet is produced by a swirl stabilised DC plasma torch with water cooled copper anode and tungsten cathode. The nozzle diameter is 0.8 mm. The torch has been specially designed to withstand the rated pressure 3.2 MPa. The nitrogen flow rate is 5 Nl/min. The plasma current is 6 A and the electrical power 1.2 kW.

RESULTS AND DISCUSSION

The instrument was calibrated by evaporating a known quantity of alkali salt in the sampling tube. The calibration factor k_{cal} is defined in the following way:

$$C_{true} = C_{meas} k_{cal} \tag{5}$$

Calibrations were performed at C_{true} = 0.4 - 2.5 ppm and 1.0 MPa pressure using nitrogen as the carrier gas. k_{cal} was found to be independent on C_{true} and its value was

1.4±0.15. The most likely reason for its deviation from unity is fluctuation and nonuniformity of the gas jet. Other possible reasons associated with loss of alkali in the sampling train are being studied, too.

A desired capability of the method is to measure vapour phase alkali compounds separately from alkali bound in ash aerosol particles. This question is being studied at present. Preliminary experiments indicate that very small particles in the submicron range with alkali vapours condensed on their surface may revaporise in the mixing nozzle and contribute to the measured alkali concentration, whereas larger particles are likely not to vaporise due to their short residence time in the mixing nozzle, which is, on the average, 0.7 ms at 1 MPa pressure. In an experiment where ash laden gas was fed to the instrument, only 1 % of the total alkali content of the ash was detected by the instrument, which indicates that the method is to a reasonable degree capable of ignoring alkalis bound in larger aerosol particles. The ash used in the experiment had a polydisperse size distribution. The size distribution was 4 - 78μm with a number of smaller particles agglomerated on the surface of the larger particles.

Operation of the instrument has been tested to 2.5MPa pressure. The threshold sensitivity estimated on the basis of the signal to noise ratio was found to be 5 ppb.

The instrument was used to measure vapourised alkali concentrations in a number of experiments concerning pressurised combustion of pulverised coal. The experiments were carried out in a pressurised entrained flow reactor operating at 1173 K temperature and 1 MPa pressure. The instrument operated reliably and the results exhibited high reproducibility. New results were obtained concerning the dependence of alkali release on the fuel particle temperature [12]. Typical raw data produced by the instrument is shown in Fig. 3. The fluctuations are due to variations in the coal feed rate and variations in the composition of individual coal particles. The instrument proved to be able to respond rapidly to variations in the alkali concentration. This is indicated by the last sharp drop in the curve, which is the instrument's response to shutdown of the coal feed.

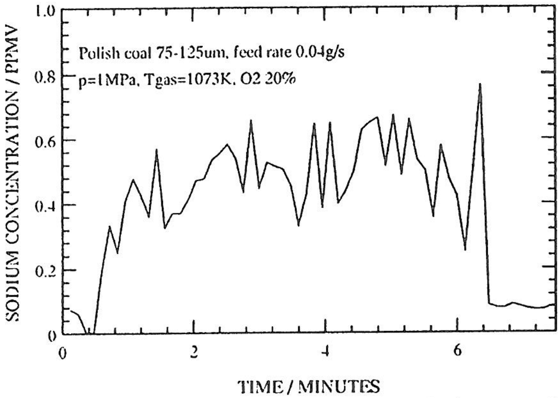

Fig. 3. Measured sodium concentration during a coal combustion experiment.

At present erosion of the plasma torch anode limits the accumulated torch operational time to approximately 5 hours. However, the torch is shut off between measurements, and the available total 5 hours can be distributed over practically any desired length of time.

CONCLUSIONS

The application of a thermal plasma jet as the exciting agent for online spectroscopic monitoring of alkali vapour concentrations in pressurised energy conversion processes has been demonstrated and shown to operate efficiently and reliably. An instrument prototype has been developed, calibrated and tested on a pressurised entrained flow reactor. Application of the instrument to several pilot plants in Europe are scheduled for the present and next year.

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