International
Cement review
January 2012

"First of its kind" Dual Process Grey & White Cement Plant Powered by *promac* & Taiheiyo, Japan

3000 TPD Grey & 1750 TPD White Cement Plant

for JK Cement WORKS (Fujairah), UAE

The ground breaking ceremony was performed under patronage of
H.H.SHEIKH HAMAD BIN MOHAMMED AL SHARQI
- Member of Supreme Council & Ruler of Fujairah.

By H.H.SHEIKH MOHAMMED BIN HAMAD AL SHARQI
- Crown Prince Of Fujairah

Mr. YADUPATI SINGHANIA
Managing Director & CEO, J. K. Cement Ltd

Cost-effective gas monitoring

by Kevin Ramazan Phd, California Analytical Instruments, USA

The importance of gas analysis during cement production has to be a top priority for cement producers around the world. The latest technology is now focusing on multiple gas sampling equipment to monitor real-time samples of various gases during the production process and fuel combustion. One of the successful developments in this area is California Analytical Instruments' 600 FTIR gas analyser.

The FTIR analyser from California Analytical Instruments (CAI) is an optimised sampling system that does not require liquid N_2 to measure multiple gases. It is designed to lower gas emissions by offering a variety of measurements from monitoring kiln operations.

CAI recently installed a 600 FTIR gas analyser at a major US cement plant. The instrument was configured for kiln sampling. The original purpose was to measure only hydrogen chloride (HCl) but later several other gases were added. HCl is typically a very difficult gas to measure; it is easily scrubbed from the sample and is also very corrosive. The 600 FTIR is able to measure HCl since the analyser is capable of measuring hot/wet corrosive samples, besides particulate filtration and heated lines. No other sample conditioning is required. The analyser measures the absorption of discrete segments of infrared (IR) light at high resolution. Since HCl is a strong absorber of Infra Red (IR) light and has a very unique absorbance structure, FTIR is an exceptional measurement technique for it. The analyser has been in operation 24/7 for the past month and has shown excellent resilience to the difficult environment seen at cement plants.

More stringent emissions control legislation

On 6 August 2010, the US Environmental Protection Agency (EPA) signed a final rule establishing and amending various air emission limits applicable to the Portland cement industry. The rule establishes National Emission Standards for Hazardous Air Pollutants for emissions of mercury, total hydrocarbons, and particulate matter (PM) from new and existing cement kilns located at major and area sources and for emissions of hydrogen chloride (HCl) from new and existing kilns located at major sources. The current floor that would be accepted as the standard for HCl would be 3ppm. However, based on resistance from the major cement manufacturers this is still under review.

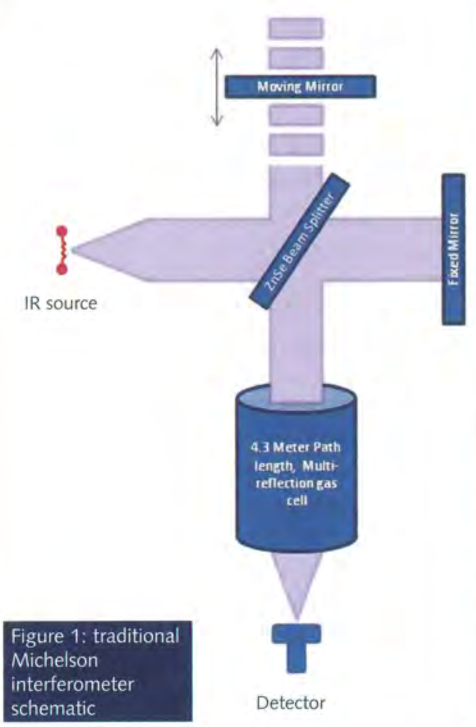

Figure 1: traditional Michelson interferometer schematic

Hydrogen chloride measurement

There are two accepted methods for measuring HCl at cement plants – the EPA method 26/26A and the EPA method 321 (also refer to EPA methods 301 and PS-15). Method 26/26A seeks to measure halides (HCl, HBr, HF), and halogens (Cl_2, Br_2, F_2). In method 26/26A the gaseous halides and halogens are collected in sulphuric acid and sodium hydroxide and a filter collects particulate matter including halide salts. The hydrogen halides are solubilised in the acidic solution and form chloride (Cl-), bromide (Br-), and fluoride (F-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolysed to form a proton (H+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulphate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that two halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). This method requires the use of dangerous chemicals and results can take several days to complete.

Methods 320 and 321 refer to the use of extractive FTIR. An FTIR operates by utilising a scanning Michelson interferometer. As illustrated in (Figure 1), an IR beam (from an incandescent source in the spectrometer) is split into two beams by a beam splitter. One beam travels to a fixed position mirror and one to a movable mirror. The reflected beams are recombined at the beam splitter after which they pass through a sample cell and continue to a detector. The CAI 600 FTIR takes a commercial FTIR and builds a gas analyser around it. A 4.3m multi-reflection, 316 stainless steel gas cell heated to 191°C is placed between the interferometer and the detector. Gas temperature and pressure are measured and compensated for fluctuation. The analyser is placed in a 48.3cm (19in) rack mounted case and the data is delivered to a laptop or rack mount computer. The computer software is fully automated to scan, quantify, auto range, report the data and compensate for pressure and temperature.

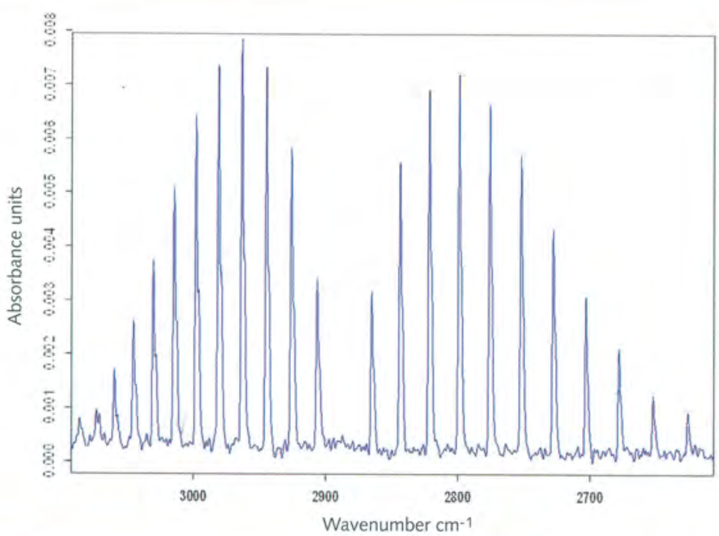

Figure 2: FTIR spectrum of 15 ppm HCl obtained on a CAI 600 FTIR

Characteristics of HCl

Hydrogen chloride is not a major byproduct of the reactions that form cement, rather it is formed during the burning of various fuels. Kilns often use a variety of sources of fuel ranging from coal to waste materials, which often include tyres. From a measurement perspective, once HCl is formed it is difficult to keep it in the gaseous state. It is highly reactive with other components in the stream, and will condense if temperature is low enough. This requires the sampling system to be well designed. The key parameters for HCl measurement include keeping all sample lines hot (>180°C) and having adequate particulate filtration without allowing the filters to be plugged with dust and other components. Dust that forms on filters can be efficient HCl scrubbers. Filters can be effectively unplugged using an appropriate blow back procedure.

Since HCl is a linear molecule with a hydrogen atom connected to a chlorine atom, it will absorb infrared light and cause both vibration and rotational motions to the molecule. Using an FTIR to measure this IR absorption produces a spectrum (see Figure 2).

HCl has several strong absorbance bands with a unique pattern that enables it to be quantified even in difficult sample streams. In a typical cement sample stream there are several other components that need to be taken account of as interferences. HCl does have several interferences. Utilising a partial least squares quantification algorithm CAI accounted for water, several hydrocarbons, aldehydes, and nitrogen dioxide.

...about California Analytical Instruments

California Analytical Instruments (CAI) based in Orange, California, USA, has been a premier supplier of quality gas analysers and systems for use in industrial, environmental, process, health and safety, and automotive emissions measurement applications for over 25 years. CAI's goal is to provide innovative, cost-effective and reliable solutions.

CAI utilises technologies such as: chemiluminescence, non-dispersive infrared (NDIR), flame ionisation detection (FID), paramagnetic, FTIR, and photoacoustic infrared spectroscopy (PAS) for measurement of CO, CO_2, NO, NO_2, N_2O, NH_3, O_2, CH_4, SO_2, SF_6 and HCl gases. CAI's computer controlled analysers are currently installed in over 10,000 facilities, in over one hundred countries.

Beyond the cement plant, the CAI 600 FTIR is a proven analyser and has already been applied to several applications including, agriculture emissions, gas purity, jet turbine emissions, power plant emissions, FAA testing, biomass burning, auto/ diesel emissions, aerospace air quality, catalyst efficiency testing and more.

CAI 600 FTIR performance

The CAI 600 FTIR dynamic qualities allow for the measurement of practically any gas (as long as it an asymmetrical molecule). Its heated gas cell (191°C) enables the measurement of hot/wet samples to minimise sample conditioning and sample degradation (by condensation). All the optics, including windows and the beam splitter are constructed of zinc selenide (ZnSe) optics for enhanced moisture stability. It does not require liquid nitrogen to cool its detector like most FTIR analysers available today. It has high-resolution measurement capabilities (0.8 cm^{-1}) and will provide real time data analysis. It is a 48.3cm (19in) rack mountable unit that can continuously samples and reports real time data. This analyser is compact and considered a portable unit, so it can be easily transported and utilised for several applications.

The CAI 600FTIR was installed in the instrument room roughly 15.24m (50ft) away from the kiln. A heated sample probe with a sintered stainless steel 316 filter was directly connected to a sample port on the kiln. Following the sample probe was a heated sample line leading to another heated filter prior to the analyser. All wetted parts were kept at greater than 180°C. The sample cell of the analyser was maintained at 191°C.

At the time this article was submitted, the analyser had been running 24/7 for more than a month. Recently additional gases were added from the reference FTIR library. The gases added were common CEMS gases, NO, NO_2, SO_2, CO, CO_2 and NH_3. With this capability a single FTIR can replace a chemiluminescence NO_x analyser, two non-dispersive infrared analysers (NDIR) for CO and CO_2, and a UV fluorescence analyser for SO_2. Since it is a single analyser that only requires a single line from the kiln, which previously required multiple analysers and possibly multiple lines and sampling equipment, the cost savings can be extreme.

Additionally, the FTIR can also report moisture content, acidified gases, speciated hydrocarbons, and ammonia. The real-time ammonia results allow for SCR tuning as well. It has proven to be a very robust unit and the data has been stable and tracked very well with the available CEMS equipment. In the near future a RATA is scheduled to be performed on the unit.