Air pollution control using laser analysis

An LDS 6 analyzer monitors HF emissions during the production of hydrofluoric acid in accordance with the German Technical Instructions on Air Quality Control (TA Luft)

Case Study · September 2011

The customer

Fine chemicals and inorganic basic chemicals have been developed and produced at the Seelze chemical site in northern Germany for more than 100 years.

Such a basic chemical is hydrofluoric acid (HF), an extremely corrosive, colorless, and pungent smelling liquid. It even attacks glass and has a strong caustic effect on skin, mucous membranes, and the corneas of the eyes. The production of hydrofluoric acid causes emissions which must be monitored. The use of analyzing equipment approved for this purpose is mandatory. The limit values for production equipment in Germany are defined by the factory inspectorate in accordance with TA Luft.

In view of its high maintenance requirement and the related costs, the existing extractive measuring equipment should be replaced by a more state-of-the-art solution. In-situ measurement with the LDS 6 is largely maintenance-free. The LDS 6 reliably measures trace concentrations of HF. Unfortunately this system is not officially certified, yet.

Nonetheless, an approach using a so-called "extended calibration" was specified to enable the LDS 6 to be used for the sake of compliance with the regulatory requirements. This is a case of an individual approval, for which the proof of correct measurement must be provided by a weekly calibration check. Acceptance and approval are coordinated with the official authority and carried out by an approved institute. It is limited to the local source of emission.
The challenge

HF emissions occur at various points during the production of hydrofluoric acid (HF) from fluorite (CaF$_2$) and sulfuric acid (H$_2$SO$_4$):

During the drying of fluorite
The moist fluorite (moisture content approx. 10%) is dried in a continuous flow drum at 800 °C. This drum is heated indirectly. The drum exhaust gases are collected, purified and discharged via a stack. The end product is dry CaF$_2$ (moisture content < 0.1%).

During the production of HF
Fluorite and sulfuric acid are premixed and transferred to a heated rotary kiln. The conversion to hydrogen fluoride (HF) and anhydride (CaSO$_4$) takes place here. The kiln exhaust gases are passed through a heat exchanger and then discharged via the stack. The end products are hydrogen fluoride (HF) and calcium sulfate (CaSO$_4$).

During the milling of anhydride
The anhydride produced along with the hydrofluoric acid is neutralized using calcium hydrate and subsequently milled. The resulting emissions are collected, purified and likewise discharged through the exhaust stack. The end product is calcium sulfate (CaSO$_4$).

In the bunker exhaust
The CaF$_2$ produced during the fluorite drying process is transferred by a chain conveyor to the fluorite bunker. The displaced air is collected, purified and discharged via the stack.

The HF limit value to be monitored in the plant is 3 mg/m$^3$.

To reduce the emissions, the collected exhaust gas is routed through and purified in a six-stage wet scrubber.

The exhaust gas following the wet scrubber is routed into the environment via a GRP stack (30 m; diam. = 0.49 m). Two ventilators support the natural draft effect of the stack. The volumetric flow is 6 000 m$^3$/h.

The solution

The plant operator installed the innovative laser-based in-situ measuring system in addition to the officially approved extractive HF measurement.

In view of the positive experiences made during practical testing, the old and maintenance-intensive measuring equipment should be replaced by the LDS 6.

The concept was prepared and approved together with the local supervisory authority. An approved test institute was commissioned with the required investigations.

The concept covered the following procedures:

- Presentation of the data previously measured in the plant compared to the existing, approved measuring equipment
- Preparation of a maintenance concept complying with EN 14181 with proof of functionality
- Preparation of an installation certificate in accordance with VDI 3950 and EN 14181
- Implementation of function test (AST) in accordance with VDI 3950 or EN 14181
- Calibration with consideration of the marginal conditions of EN 14181 or VDI 3950 for a period of four weeks following the function test
- In order to prove the stability (drift response) of the LDS 6, the QAL3 test will be repeated by the plant operator at short intervals in the first year and, in addition, a function test with consideration of the requirements of EN 14181 (i.e., including five comparison measurements) will be repeated by a test institute approved in accordance with §26 BImSchG (German Federal Immission Protection Ordinance) three months following the calibration
- And, finally, the produced reports will be submitted to the responsible supervisory authority for approval

The results

The previously used extractive emission measurement could be replaced by an LDS 6 following successful testing.

The test institute established that the LDS 6 fulfilled the requirements in accordance with DIN 3950 in conjunction with DIN EN 14181 as regards installation.

The QAL3 tests will be carried out on a weekly basis using calibration verification cells. The requirement approves a drift in the zero and reference points of ≤ 3% of the full-scale value of the measuring range.

In addition, the functional test will be carried out annually in accordance with DIN EN 14181 in conjunction with VDI 3950, with the stipulated calibration taking place every three years.

The benefits

The operator’s decision in favor of the in-situ system and the determination to work together with Siemens in obtaining approval from the authorities were driven mainly by cost considerations.

The maintenance-intensive sample preparation could be completely omitted while, at the same time, the LDS 6 device concept allows parallel measurement at three positions with observation of the T90 time.
Further user advantages include:

- The officially stipulated check in accordance with QAL3 now takes place using closed calibration verification cells and fiber-optic cables instead of the previously used HF calibration gases. Direct access to the installed position within the plant is no longer necessary, thus providing increased protection for personnel.
- The limit values according to the 17th Federal Immission Control Act also are monitored.
  TMW: 1 mg/m³
  HMW: 4 mg/m³
- The costs for the “extended calibration” amortize already after a few months.

Since its successful optimization in 2004, the measuring equipment has been running fault-free and to the complete satisfaction of the customer. This again confirms the suitability of in-situ laser spectroscopy even for highly sensitive measuring tasks associated with the monitoring of emissions.

### Measurement of HF for limit monitoring in accordance with the German Air Pollution Control Code

<table>
<thead>
<tr>
<th>Measured component</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF measuring range</td>
<td>0 ... 5 ppmv</td>
</tr>
<tr>
<td>HF resolution</td>
<td>0.1 ppmv/m</td>
</tr>
<tr>
<td>Dust load</td>
<td>No dust load</td>
</tr>
<tr>
<td>Temperature</td>
<td>0 ... 150 °C</td>
</tr>
<tr>
<td>Optical path length</td>
<td>1.5 m</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>Required response time</td>
<td>10 seconds</td>
</tr>
<tr>
<td>Recommended type of purging</td>
<td>On process and sensor sides, due to the corrosive environmental conditions. Moderate flow rate</td>
</tr>
<tr>
<td>Purging medium</td>
<td>Instrument air</td>
</tr>
<tr>
<td>MLFB user code</td>
<td>GA</td>
</tr>
</tbody>
</table>

Further information:

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