With the increasing environmental concerns, sulfur recovery has become one of the leading issues in emissions reduction in industry. For gas processing and refining facilities, sulfur recovery requirements range from 97.5% to 99.8%. The well-known Claus Process with some form of tailgas cleanup or special processing capability can meet this requirement with the help of high performance process analytics.

Siemens Sensors and Communication, a leader in process analytics, has proven over decades its competence to plan, engineer, manufacture, implement and service analyzer systems for use in Claus plants. This Case Study provides details about the Claus process and related analyzer tasks.

Sulfur recovery

The relatively high sulfur content of the still available crude oil and natural gas reserves and the more stringent standards for sulfur emissions from oil, gas, and chemical processing facilities demand reliable and cost-effective technologies for sulfur recovery. Sulfur recovery refers to the conversion of hydrogen sulfide (H₂S) as byproduct of natural gas plants and crude oil refineries to elemental sulfur. The most common conversion method is the Claus Process. Approximately 90 to 95% of recovered sulfur is produced by the Claus process.

First invented over 100 years ago, the Claus Process has undergone a continuous evolution in attempts to increase the sulfur recovery efficiency of the process. In the 1930s, a thermal stage was added to the two catalytic stages, which increased the recovery efficiency from 95% to approximately 97%. In the 1970s, a hydrogenation/hydrolysis plus amine separation was added to treat the tail gas from the Claus process. In 1988, SuperClaus was introduced, which added a selective oxidation reactor to the end of the Claus process, increasing the efficiency to approximately 99%.

Sulfur recovered in Claus plants is used for manufacturing e.g. of medicines, cosmetics, fertilizers, and rubber products.

Chemical analysis of the process streams is required for controlling and monitoring the Claus process. Process gas chromatography together with continuous gas analyzers has proven to be a very reliable and cost-effective method. Siemens Sensors and Communication provides efficient solutions for this demanding analysis task.

Case Study - December 2007
The Claus Process

Claus Process for H₂S removal

Hydrogen sulfide (H₂S) is commonly found in natural gas and products from oil refineries, especially if the crude oil contains a lot of sulfur compounds. Typical sources are:
- Gas from natural gas fields
- Sour refinery gas
- Sour water stripper gas
- Sour gas from chemical plant
- Sour gas from salt production plant
- Sour gas from coal gasification

H₂S is a smelly, corrosive, highly toxic gas, which also deactivates industrial catalysts. Therefore it is converted to non-toxic and useful elemental sulfur at almost all locations where it is produced. The process of choice is the Claus Sulfur Recovery Process.

Most sulfur plants comprise two conversion stages: one non-catalytic, thermal conversion stage and two or more catalytic conversion stages in series (Fig.1). The Claus reaction is highly exothermic, releasing a great deal of heat energy that can be recovered by generating steam in heat exchangers following the conversion stages.

Thermal conversion stage

The H₂S containing gas (SWS acid gas, amine acid gas) is fed to the Thermic Converter where it is partially oxidized with air in a reaction furnace at high temperatures (1000 to 1400 °C). Combustion air is fed to the burner, with the amount of air controlled to combust only 1/3 of the H₂S to SO₂ (reaction 1). 2/3 of the H₂S remain unreacted due to lack of oxygen. Additionally air may be fed to combust also ammonia and hydrocarbons entering with the acid gas streams.

Combustion (reaction 1): 3 H₂S + 3/2 O₂ → 2 H₂S + SO₂ + H₂O

The furnace acts as a thermal conversion stage, as the high temperature in the furnace will cause part of the H₂S and SO₂ to combine via reaction (2). Thus sulfur is formed, but some H₂S and SO₂ remain unreacted.

Catalytic conversion stage

The hot combustion products from the furnace enter the waste heat boiler and are partially cooled by generating steam. The gas is further cooled in the first sulfur condenser, to condense the sulfur formed in the furnace, which is then separated from the gas and drained to a collection pit. The gas leaving the sulfur condenser is heated again to avoid forming liquid sulfur in the downstream catalyst bed and enters the first catalytic converter. There, the remaining H₂S reacts with the SO₂ at lower temperatures over a conversion catalyst (mostly alumina-based) to make more sulfur. Unfortunately the reaction does not go to completion even with the best catalyst. Typically, about 70% of the H₂S and SO₂ in the gas will react via reaction (2) to form sulfur, which leaves the reactor with the gas as sulfur vapor. The hot gas is cooled in the second sulfur condenser, where more sulfur is formed, separated, and drained to the collection pit. This is usually followed by one or two more heating, reaction, and condensing stages to react most of the remaining H₂S and SO₂.

[Diagram: Generic flowsheet of the Claus Process, simplified]

Fig. 1: Generic flowsheet of the Claus Process, simplified
The Claus Process (ctd.)

Tailgas treatment stage
A small amount of H₂S and SO₂ remains in the tail gas. The tailgas is routed to either a Tailgas Cleanup Unit (Modified Claus Process with Tailgas Cleanup) for further processing, or to a Tailgas Thermal Oxidizer to incinerate all of the sulfur compounds in the tailgas to SO₂ before dispersing the effluent to the atmosphere.

Claus Process versions
Increasingly stringent standards for sulfur emissions have caused further developments of the Claus Process with the objective of higher recovery rates. Table 1 shows a selection.

Analysis Tasks
The continuous development of sulfur recovery processes has increased the demand in efficient process analytical techniques for process and emission control. Stringent requirements are placed on the process analyzers and especially on the tail gas analyzer to determine process parameter air demand.

Various measuring points with different tasks are located along the process route (Fig. 1 and table 2). The most important task is the determination of the concentrations of hydrogen sulphide (H₂S) and sulphur dioxide (SO₂) in the desulfurized gas (tail gas, MP 5 in Fig. 1) and following from this the calculation of the H₂S/SO₂ ratio.

Claus process versions (selection)

<table>
<thead>
<tr>
<th>Claus Process</th>
<th>This original Claus process uses only the catalytic reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Claus Process</td>
<td>This process uses the additional thermal conversion stage where 1/3 of the H₂S is converted to SO₂ and S. The modified Claus process is generally limited to a sulfur recovery efficiency of 94 ... 97%. Higher recovery rates are achieved by adding a tail gas treatment unit.</td>
</tr>
<tr>
<td>Oxygen Claus Process</td>
<td>This process uses an air/oxygen mixture to reduce the nitrogen content in the process flow for better plant efficiency.</td>
</tr>
<tr>
<td>Super Claus</td>
<td>This process uses a special catalyst material in the last catalytic reactor</td>
</tr>
</tbody>
</table>

This ratio is the only parameter for direct process control through the amount of combustion air fed to the furnace of the thermal stage. The ratio should be kept to 2:1 to run the process at optimum efficiency.

Challenges
There are two major analysis challenges that must be considered when choosing the measuring principle of the analyzer:
- Other gaseous components may be present in the sample gas such as CO₂, HC, COS and CS₂ with varying concentration levels. So the analyzer principle should be free from cross-interferences.
- The sample gas is saturated by sulfur vapor or even elementary sulfur may be produced that may amongst others block sample lines. So the entire sampling system must be heated to a temperature that prevents reliably from sulfur condensation.

Solution from one hand
Siemens Process Analytics is able to supply turnkey analyzer systems for Claus plants including CEM system, along with planning, engineering, start-up, commissioning and training services.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Measuring Components</th>
<th>Suitable Siemens Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling stream</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Process gas feed</td>
<td>H₂S, SO₂, CO₂</td>
</tr>
<tr>
<td>2</td>
<td>Inlet of first catalytic converter</td>
<td>H₂S, SO₂</td>
</tr>
<tr>
<td>3</td>
<td>Outlet of first catalytic converter</td>
<td>H₂S, SO₂</td>
</tr>
<tr>
<td>4</td>
<td>Outlet of last catalytic converter</td>
<td>H₂S, SO₂</td>
</tr>
<tr>
<td>5</td>
<td>Tail gas downstream the last condenser</td>
<td>H₂S, SO₂, COS, CS₂, N₂, H₂O, O₂</td>
</tr>
<tr>
<td>6</td>
<td>At the sulfur collection pit</td>
<td>H₂S, SO₂</td>
</tr>
<tr>
<td>7</td>
<td>Before / at the stack (CEM)</td>
<td>SO₂, CO, NOx, O₂</td>
</tr>
</tbody>
</table>

Measurements at MP 3, 4 and 5 can be performed with just one Analyzer using sample stream switching.

Tab. 1: List of Claus Process versions

Tab. 2: Analysis measuring tasks and suitable Siemens analyzers

Fig. 2: Claus plant
The MAXUM edition II Claus Analyzer
Solution provider for Tail Gas Analysis

MAXUM II Claus Analyzer

MAXUM II Gas Chromatograph
MAXUM Edition II represents the top technology in process gas chromatography with outstanding features resulting in a high versatility to solve any given application task with best possible analytical results at lowest costs:
• Multiple analytical tools such as ovens, detectors, valves etc.
• Single and independent dual oven concept for minimizing the number of analyzers
• Airbath and airless oven to reduce utility costs
• Valveless column switching to reduce maintenance
• Parallel chromatography for fast analysis, system simplification and increase of reliability
• Complete networking capabilities and powerful processing software.

MAXUM II Claus Analyzer
for tail gas analysis
Process gas chromatography has generally proven to be a reliable and cost effective method to solve the demanding task of Claus tail gas analysis. Especially MAXUM II, because of its double oven concept and outstanding modularized design, can be designed a very efficient Claus gas analyzer.
The two separately heatable ovens with airless mass heating (fig. 4) are used to clearly separate the functionalities required for the analysis task:
• The right oven contains the analysis system including the separating columns, circuit and detectors,
• The left oven contains sample conditioning, calibration media dosing and the dosing valve. To prevent from blockages by solid or plastic sulfur the sample line is purged with nitrogen or air.

Heated sampling and dosing
Sulfur becomes solid or semiliquid when the sample temperature drops below 135 °C or rises above 150 °C. Therefore the sample temperature must be kept at 145 °C continuously from the sampling point to the analyzer.
Steam heated sampling lines (tube-in-tube technology, Fig. 5) and sample conditioning components mounted in a high temperature environment (left oven) meet this requirement.

User Benefits
• Proven technology with high reliability, long term stability
• Reliable operation through backpurge to clean analyzer and sample lines in case of temperature drop or power failure and during maintenance
• Easy operation, remote operation
• Low maintenance efforts
• No UV-lamp, long-time stability, no expensive spare parts regularly needed
• High accuracy through use of chromatographic separation (no interferences by sulfur, COS, CS₂)
• High reliability because of comprehensive self diagnosis
• Extended analysis to other components possible such as N₂, CO₂, COS, H₂O
• Network with other GCs on plant
• Very cost efficient

Fig. 3: MAXUM ed. II Claus analyzer
Fig. 4: MAXUM ed. II Claus analyzer, open (covered by S film)
Fig. 5: Tube-in-Tube technology (left) and isolated sampling lines (right)
Siemens Process Analytics at a glance

Products

Siemens Process Analytics is a leading provider of process analyzers and process analysis systems. We offer our global customers the best solutions for their applications based on innovative analysis technologies, customized system engineering, sound knowledge of customer applications and professional support. And with Totally Integrated Automation (TIA). Siemens Process Analytics is your qualified partner for efficient solutions that integrate process analysers into automation systems in the process industry.

From demanding analysis tasks in the chemical, oil & gas and petrochemical industry to combustion control in power plants to emission monitoring at waste incineration plants, the highly accurate and reliable Siemens gas chromatographs and continuous analysers will always do the job.

Siemens process Analytics offers a wide and innovative portfolio designed to meet all user requirements for comprehensive products and solutions.

Our Products

The product line of Siemens Process Analytics comprises extractive and in-situ continuous gas analyzers (fig. 6 to 9), process gas chromatographs (fig. 10 to 13), sampling systems and auxiliary equipment. Analyzers and chromatographs are available in different versions for rack or field mounting, explosion protection, corrosion resistant etc.

A flexible networking concept allows interfacing to DCS and maintenance stations via 4 to 20 mA, PROFIBUS, Modbus, OPC or industrial ethernet.

Extractive Continuous Gas Analyzers (CGA)

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTRAMAT 23</td>
<td>The ULTRAMAT 23 is a cost-effective multicomponent analyser for the measurement of up to 3 infrared sensitive gases (NDIR principle) plus oxygen (electrochemical cell). The ULTRAMAT 23 is suitable for a wide range of standard applications. Calibration using ambient air eliminates the need of expensive calibration gases.</td>
</tr>
<tr>
<td>CALOMAT 6/62</td>
<td>The CALOMAT 6 uses the thermal conductivity detection (TCD) method to measure the concentration of certain process gases, preferably hydrogen. The CALOMAT 62 applies the TCD method as well and is specially designed for use in application with corrosive gases such as chlorine.</td>
</tr>
<tr>
<td>OXYMAT 6/61/64</td>
<td>The OXYMAT 6 uses the paramagnetic measuring method and can be used in applications for process control, emission monitoring and quality assurance. Due to its ultrafast response, the OXYMAT 6 is perfect for monitoring safety-relevant plants. The corrosion-proof design allows analysis in the presence of highly corrosive gases. The OXYMAT 61 is a low-cost oxygen analyser for standard applications. The OXYMAT 64 is a gas analyzer based on ZrO2 technology to measure smallest oxygen concentrations in pure gas applications.</td>
</tr>
<tr>
<td>ULTRAMAT 6</td>
<td>The ULTRAMAT 6 uses the NDIR measuring principle and can be used in all applications from emission monitoring to process control even in the presence of highly corrosive gases. ULTRAMAT 6 is able to measure up to 4 infrared sensitive components in a single unit.</td>
</tr>
<tr>
<td>ULTRAMAT 6 / OXYMAT 6</td>
<td>Both analyzer benches can be combined in one housing to form a multi-component device for measuring up to two IR components and oxygen.</td>
</tr>
<tr>
<td>FIDAMAT 6</td>
<td>The FIDAMAT 6 measures the total hydrocarbon content in air or even in high-boiling gas mixtures. It covers nearly all requirements, from trace hydrocarbon detection in pure gases to measurement of high hydrocarbon concentrations, even in the presence of corrosive gases.</td>
</tr>
</tbody>
</table>

In-situ Continuous Gas Analyzer (CGA)

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDS 6</td>
<td>LDS 6 is a high-performance in-situ process gas analyser. The measurement (through the sensor) occurs directly in the process stream, no extractive sample line is required. The central unit is separated from the sensor by using fiber optics. Measurements are carried out in real-time. This enables a pro-active control of dynamic processes and allows fast, cost-saving corrections.</td>
</tr>
</tbody>
</table>

Fig. 7: Product scope „Siemens Continuous Gas Analyzers“

Fig. 6: Series 6 gas analyzer (rack design)
Fig. 8: Series 6 gas analyzer (field design)
Fig. 9: LDS 6 in-situ laser gas analyzer
Process Gas Chromatographs (Process GC)

MAXUM edition II

MAXUM edition II is very well suited to be used in rough industrial environments and performs a wide range of duties in the chemical and petrochemical industries and refineries. MAXUM II features e.g. a flexible, energy saving single or dual oven concept, valveless sampling and column switching, and parallel chromatography using multiple single trains as well as a wide range of detectors such as TCD, FID, FPD, PDHID, PDECD and PID.

MicroSAM

MicroSAM is a very compact explosion-proof micro process chromatograph. Using silicon-based micromechanical components it combines miniaturization with increased performance at the same time. MicroSAM is easy to use and its rugged and small design allows mounting right at the sampling point. MicroSAM features drastically reduced cycle times, provides valveless sample injection and column switching and saves installation, maintenance, and service costs.

SITRANS CV

SITRANS CV is a micro process gas chromatograph especially designed for reliable, exact and fast analysis of natural gas. The rugged and compact design makes SITRANS CV suitable for extreme areas of use, e.g. offshore exploration or direct mounting on a pipeline. The special software "CV Control" meets the requirements of the natural gas market, e.g. custody transfer.

Our solutions

Analytical solutions are always driven by the customer’s requirements. We offer an integrated design covering all steps from sampling point and sample preparation up to complete analyser cabinets or for installation in analyser shelters (fig. 14). This includes also signal processing and communications to the control room and process control system.

We rely on many years of world-wide experience in process automation and engineering and a collection of specialized knowledge in key industries and industrial sectors. We provide Siemens quality from a single source with a function warranty for the entire system. Read more in "Our Services".
Siemens Process Analytics at a glance
Solutions (continued) and Services

Our solutions ...
Analyzer networking for data communication
Engineering and manufacturing of process analytical solutions increasingly comprises “networking”. It is getting a standard requirement in the process industry to connect analyzers and analyzer systems to a communication network to provide for continuous and direct data transfer from and to the analysers.
The two objectives are (fig. 16):
· To integrate the analyzer and analyzer systems seamless into the PCS / DCS system of the plant and
· To allow direct access to the analyzers or systems from a maintenance station to ensure correct and reliable operation including preventive or predictive maintenance (fig.15).

Siemens Process Analytics provides networking solutions to meet the demands of both objectives.

Our Services
Siemens Process Analytics is your competent and reliable partner worldwide for Service, Support and Consulting.

Our resources for that are
· Expertise
As a manufacturer of a broad variety of analyzers, we are very much experienced in engineering and manufacturing of analytical systems and analyzer houses.
We are familiar with communication networks, well trained in service and maintenance and familiar with many industrial processes and industries. Thus, Siemens Process Analytics owns a unique blend of overall analytical expertise and experience.

· Global presence
With our strategically located centers of competence in Germany, USA, Singapore, Dubai and Shanghai, we are globally present and acquainted with all respective local and regional requirements, codes and standards. All centers are networked together.
Siemens Process Analytics at a glance
Services, continued

Our Services ...

Service portfolio
Our wide portfolio of services is segmented into Consulting, Support and Service (fig. 17 to 18). It comprises really all measures, actions and advises that may be required by our clients throughout the entire lifecycle of their plant. It ranges from site survey to installation check, from instruction of plant personnel to spare part stock management and from FEED for Process Analytics (see below) to internet-based service Hotline.

Our service and support portfolio (including third-party equipment) comprises for example:
- Installation check
- Functionality tests
- Site acceptance test
- Instruction of plant personnel on site
- Preventive maintenance
- On site repair
- Remote fault clearance
- Spare part stock evaluation
- Spare part management
- Professional training center
- Process optimisation
- Internet-based hotline
- FEED for Process Analytics
- Technical consulting

FEED for Process Analytics
Front End Engineering and Design (FEED) is part of the planning and engineering phase of a plant construction or modification project and is done after conceptual business planning and prior to detail design. During the FEED phase, best opportunities exist for costs and time savings for the project, as during this phase most of the entire costs are defined and changes have least impact to the project. Siemens Process Analytics holds a unique blend of expertise in analytical technologies, applications and in providing complete analytical solutions to many industries.

Based on its expertise in analytical technology, application and engineering, Siemens Process Analytics offer a wide scope of FEED services focused on analysing principles, sampling technologies, application solutions as well as communication system and given standards (all related to analytics) to support our clients in maximizing performance and efficiency of their projects.

Whether you are plant operators or belong to an EPC Contractor you will benefit in various ways from FEED for Process Analytics by Siemens:
- Analytics and industry know how available, right from the beginning of the project
- Superior analyzer system performance with high availability
- Established studies, that lead to realistic investment decisions
- Fast and clear design of the analyzer system specifications, drawings and documentation
- Little project management and coordination effort, due to one responsible contact person and less time involvement
- Additional expertise on demand, without having the costs, the effort and the risks of building up the capacities
- Lowest possible Total Costs of Ownership (TCO) along the lifecycle regarding investment costs, consumptions, utilities supply and maintenance.

Fig. 18: Portfolio of services provided by Siemens Process Analytics
Case Study

Siemens Process Analytics - Answers for industry

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