Process Analytics in Vinyl Chloride (VCM) Plants

Case Study • December 2007

Vinyl Chloride (VCM)

Vinyl chloride (CH_2=CHCl, M stands for Monomer, in contrast to Polymers, PVC) is a colorless, flammable gas, first obtained in 1912 through catalytic hydrochlorination of acetylene. VCM is heavier than air and may travel along the ground and can, under specific circumstances, form peroxides, initiating explosive polymerization. On burning, VCM decomposes producing toxic and corrosive fumes (hydrogen chloride and phosgene).

VCM is used as feedstock in the production of **PVC**, polyvinyl chloride) one of the world´s most versatile thermoplastics, which has a wider range of uses than any other plastic material. As a hard plastic, it is used as vinyl siding, magnetic stripe cards, window profiles, pipe, plumbing and conduit fixtures. It can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, and to make flexible hoses and tubing, flooring, roofing membranes, and electrical cable insulation. The material is often used for pipelines in the water and sewer industries because of its inexpensive nature and flexibility.

Beginning in 1940, acetylene as feedstock was replaced stepwise by the inexpensive ethylene. Complete changeover to almost exclusive use of ethylene became possible in 1955, when the large-scale oxychlorination of ethylene to 1,2-dichlorethane became possible. Today, more than 90% of the world wide VCM production is based on ethylene. Modern VCM plants use integrated processes combining the both highly exothermic reactions of ethylene chlorination and oxychlorination with the endothermic cracking process, which results in an almost energy balanced operation.

chemical INDUSTRY

Vinyl chloride (VCM), made from ethylene and chlorine by pyrolysis, is the feedstock for the production of the very common plastic material PVC. Modern VCM plants use integrated processes combining endothermic and exothermic reactions in an almost energy balanced operation. Plants are operated in view of product quality, plant safety and cost efficiency using advanced process control equipment including process analyzers.

Siemens, a leader in process analytical instrumentation, has proven over decades its capability to plan, engineer, manufacture, implement and service analyzer systems for VCM plants worldwide.

This *Case Study* provides an over-view of the typical processes and describes how Siemens with its analyzer and application know-how meets best the process requirements.

SIEMENS

Production of Vinyl Chloride

VCM process in brief

A modern VCM production can be considered as "balanced process" where ethylene, chlorine and oxygen are converted into VCM and water. The three process steps direct chlorination, oxychlorination and EDC cracking are summarized in the "VCM synthesis reaction". For details see text box below.

Based on the "VCM synthesis" principle different production technologies are in use. They differ, for instance, in details of the reactor design, kind of catalysts, and reaction temperatures applied.

Many hundreds of VCM plants are in use worldwide with capacities of 30000 up to 600000 t/year each. All plants are operated in view of a high and constant product quality as well as cost efficiency and safety (corrosive, poissoneous and explosive substances are handled). Considerable investments are required in instrumentation and control to meet these requirements.

Process analyzer contribute an important part to that.

VCM production process

Direct chlorination

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

EDC (1,2-dichlorethane, „DC-EDC") is formed by a highly exothermal direct chlorination reaction of ethylene and chlorine

Oxychlorination

$C_2H_4 + 2HCl + ½O_2 \rightarrow C_2H_4Cl_2 + H_2O$

EDC (1,2-dichlorethane, "Oxy-EDC") and water is formed by a highly exothermal calytic reaction of ethylene with hydrogen chloride and oxygen.

EDC cracking (pyrolysis)

$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$

The EDC is cracked at high temperatures in a fuel heated furnace in an endothermic and incomplete reaction. VCM and HCl are formed together with various by-products; some EDC remains unconverted.

VCM synthesis (Balanced Process)

$2C_2H_4 + Cl_2 + ½O_2 \rightarrow 2C_2H_3Cl + H_2O$

The three process sections as above can be combined into a one complete VCM synthesis process, in which only VCM and water is formed (balanced on hydrogene chloride).

Process steps

The major steps of a VCM production process (Fig. 1) include:

Direct chlorination

Ethylene and chlorine are fed to a reactor where a catalytic reaction (*direct chlorination)* takes place.
1,2-dichlorethan (EDC) is formed, together with heat, water and HCl-rich waste gas. The EDC is fed to a tank for temporarily storage. The waste gas is fed to the oxychlorination and re-used as reacting component.

Oxychlorination

Ethylene, oxygen and hydrogene chloride are fed into a fluidized-bed reactor for the oxychlorination process. Raw EDC is formed, removed by condensation and fed to the EDC distillation unit for purification, and heat. Waste gas and effluent are also formed and fed to the HCl recovery and water treatment units.

EDC distillation

To produce pure EDC both the EDC from the oxychlorination and the unconverted EDC from the cracking process (recycle EDC) are purified in the EDC distillation unit. The purified EDC is then fed to the EDC tank for temporarily storage.

EDC cracking (pyrolysis process)

Cracking of the EDC from the temporarily storage tank is performed in a fuel heated cracking furnace at temperatures of 500 °C and above. Vinyl chloride Monomer (VCM) and HCl are formed together with various by-products. Some EDC remains unconverted and is fed back to the EDC distillation unit. HCl is fed back into the oxychlorination unit and reused in the process as well. The VCM is either used as feedstock for direct manufacturing of PVC or stored as product for sale.

By-product recovery

The by-products formed during VCM production are further treated and recovered in an oxidation process at approx. 1250 °C and completely converted into CO_2, water and hydrogen chloride. The process heat is used to generate steam and the HCl is recovered as valuable feed stock and returned into the process.

Emission monitoring

In most countries VCM plants must comply with the statutory regulations and local specifications regarding the limit values of polltants that are released into the atmosphere. With an optimized operation of the by-product oxidation and recycle process only very low volume flow rates are emitted through the stack. Therefore, very often only discontinuous emisson control measurements of some compounds (see Fig. 1 and Table 1, MP 10) are requested by the authorities. Samples are taken at the stack daily or weekly, and measured in the laboratory.

Process scheme and analyzer measuring points

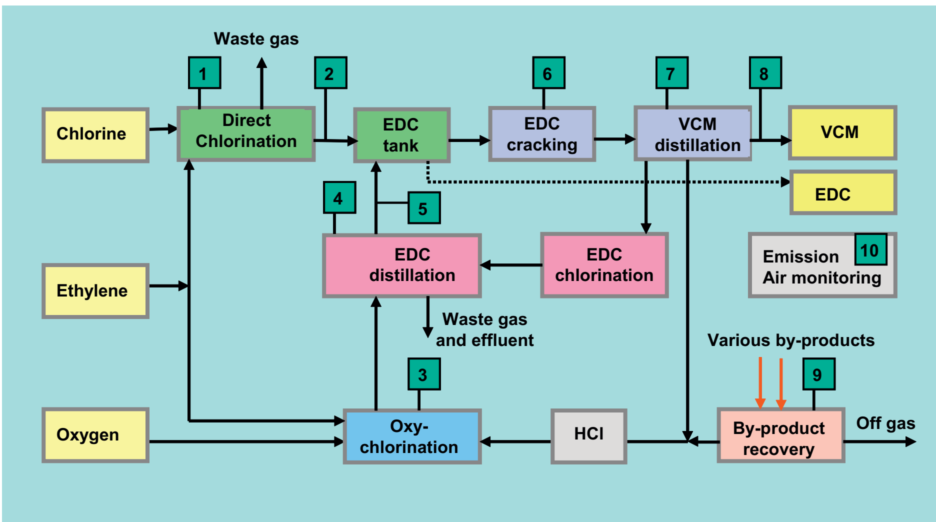

Fig. 1: Generic VCM production process, simplified, with measuring locations

Sampling point Sampling stream		Component	Measuring Range	Measuring Task	Suitable Analyzer
1	Direct chlorination	C_2H_4 O_2	0 … 3% 0 … 10%	Process control, Safety monitoring	ULTRAMAT OXYMAT
2 5	From Direct chlorin. and EDC distillation	HCl H_2O Impurities	0 … 10 ppm 0 … 20 ppm ppm range	EDC quality	LDS 6 TPA MAXUM
3	Oxychlorination	O_2 CO CO_2 C_2H_4 pH, Conduct..	0 … 10% 0 … 10% 0 … 100% 0 … 3%	Process control, Safety monitoring	OXYMAT ULTRAMAT ULTRAMAT ULTRAMAT TPA
4	EDC distillation	H_2O	0 … 20 ppm	Process control	TPA
5	See line 2				
6	EDC cracking	O_2 H_2O	0 … 10% 0 … 20 ppm	Process control	TPA (ZrO_2 probe) TPA
7	VCM distillation	H_2O	0 .. 100 ppm	Process control	TPA
8	From VCM distillation	Impurities*	ppm range	VCM quality	MAXUM
9	By-product recovery	O_2 pH O_2	0 … 10% 0 … 10%	Process and emission control Safety monitoring	OXYMAT (Tantalum) TPA LDS 6
10	Plant ambient air and stack	EDC / VCM various	ppm range various	Environmental compliance	MAXUM II FIDAMAT CEM system (or laboratory devices)
TPA: Third party analyzer					

Table 1: Sampling points and measuring details of a VCM production plant, according to Fig. 1

* e.g. methyl chloride, ethyl chloride, vinyl acetylene, butadiene, dichloroethanes, dichloroethines

Use of process analyzers

Analyzer Tasks

Process analytical equipment is an indispensable part of any VCM plant because it provides the control system and the operator with key data about the process and its environment.

Four major applications
Analyzer applications can be classified in four groups depending on how the analyzer data are used:

- **Closed-loop control for process and product optimization**
  This application helps to increase yield, reduce energy consumption, achieve smooth operation, and keep product quality accoding to the specification
- **Quality control and documentation**
  e.g. for ISO compliance
- **Plant monitoring and alarms**
  This application protects personnel and plant from possible hazard from toxic or explosive substances
- **Emission monitoring**
  This application helps to keep emission levels in compliance with local environmental regulations.

Analyzers and sampling points
Different analyzers are used in VCM plants ranging from simple sensor type monitors to high technology process gas chromatographs. The list typically includes

- Process gas chromatographs
- Continuous gas analyzers (paramagnetic oxygen analyzers, NDIR analyzers, total hydrocarbon content analyzers)
- Analyzers for moisture and O_2 traces
- Low Explosion Level (LEL) analyzers

Fig. 1 and Table 1 show typical sampling points of a VCM plant along with the respective measuring components and suitable analyzers.

Analyzer installation
Analyzers are installed partially in the field close to the sampling location and/or in analyzer houses (shelter). In modern plants the analyzers are interfaced to a plant wide data communication system for direct data transfer from and to the analyzers.

The **number of analyzers** in a VCM plant varies from plant to plant depending on the type of process, specific plant conditions and user requirements.

Special Solutions

Oxygen measurements
Continuous monitoring of oxygen in the process gas in both the direct chlorination and oxychlorination plant units (MP 1 and 3 of Fig. 1 and table 1) is of exceptional importance. To protect from the danger of heavy explosions, the process must be ensured to run outside the critical ignition levels of the process gas at any time. Therefore, the use of the most reliable and accurate oxygen measuring technology is appropriate, as provided by the Siemens OXYMAT 6 gas analyzer, see text box. Because of the high importance, this oxygen measurement is often engineered redundantly with two analyzers at the same sampling point and fail-safe data processing.

The oxygen measurement at sampling point 9 (by-product recovery) has a different meaning. Here, the oxygen content reading is used to optimize the incineration conditions in order to minimize the remaining emission rate of pollutants. High measuring accuracy is required here as well, but along with corrosion resistance because of the aggressive gas composition. Again, the OXYMAT 6, in its tantalum version, is most suitable for this task.

Measurement of impurities
Gas chromatographs are standard equipment in VCM plants to measure impurities in trace concentrations. They are used to analyze the product stream at MP 2 and 5 (Fig. 1) and help very much to ensure compliance with product specification and quality.
The Siemens Process Gas Chromatograph MAXUM edition II is very much suited for this task, see also pages 5 and 6.

Another gas chromatograph application in VCM plants is to monitor ambient air for chemical compounds that may emerge from certain plant units in case of sudden leakages (MP 10, combined with sample point switching).

Measurement of HCl

- HCl in the ppm range (MP 2, 5 and 8) usually is determined by conductivity measurements. However, at MP 3 with a concentration range of 0 to 3%, photomertric measurements are preferred. With the in-situ Laser Spectrometer LDS 6, Siemens offers a very effective solution for this tasks. **LDS 6** (Fig. 7) is a diode laser-based in-situ gas analyzer for measuring specific gas components directly in a process gas stream. Measurements are carried out free of spectral interferences and in real-time enabling pro-activ control of dynamic processes.

The **OXYMAT 6** operates according to the paramagnetic principle and is designed for high-precision measurements of oxygen concentrations in gases. The pulsating magnetic field creates minute flow pulses detected by the Siemens micro-flow sensor and converted into the measuring signal. Thus, the
OXYMAT 6 does not comprise any moving parts and the sample gas does not come into contact with the microflow sensor, which ensures an extremely long life time and high operating stability. A good example for that is the independence from humidty which may be present in the sample gas and could cover the surface of mirrors (with negative impact to the measuring accuracy) that are used with other oxygen measuring principles.

Siemens Process Analytics at a glance
Products

Siemens Process Analytics

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 automations 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. 2 to 5), process gas chromatographs (fig. 6 to 9), 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.

Fig. 2: Series 6 gas analyzer (rack design)

Extractive Continuous Gas Analyzers (CGA)	
ULTRAMAT 23	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.
CALOMAT 6/62	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.
OXYMAT 6/61/64	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 ZrO_2 technology to measure smallest oxygen concentrations in pure gas applications.
ULTRAMAT 6	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.
ULTRAMAT 6 / OXYMAT 6	Both analyzer benches can be combined in one housing to form a multi-component device for measuring up to two IR components and oxygen.
FIDAMAT 6	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.
In-situ Continuous Gas Analyzer (CGA)	
LDS 6	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.

Fig. 3: Product scope „Siemens Continuous Gas Analyzers“

Fig. 4: Series 6 gas analyzer (field design)

Fig. 5: LDS 6 in-situ laser gas analyzer

Siemens Process Analytics at a glance
Products (continued) and Solutions

Fig. 6: MAXUM edition II Process GC

Fig. 7: MicroSAM Process GC

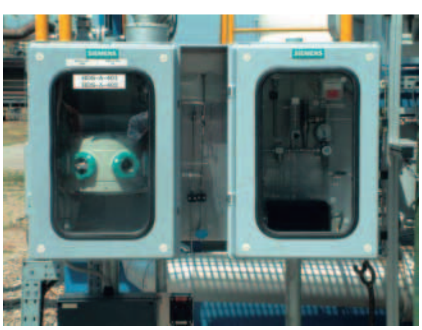

Fig. 8: SITRANS CV Natural Gas Analyzer

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 PDPID.
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.

Fig. 9: Product scope „Siemens Process Gas Chromatographs“

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. 10). 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“.

Fig. 10: Analyzer house (shelter)

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. 12):

- 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.11).

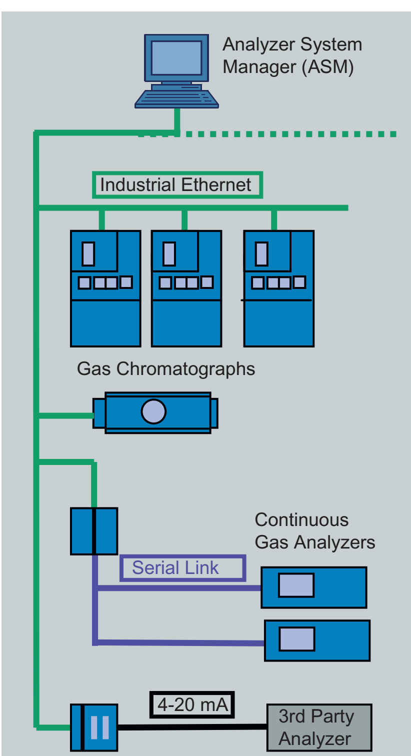

Fig. 11: Communication technologies

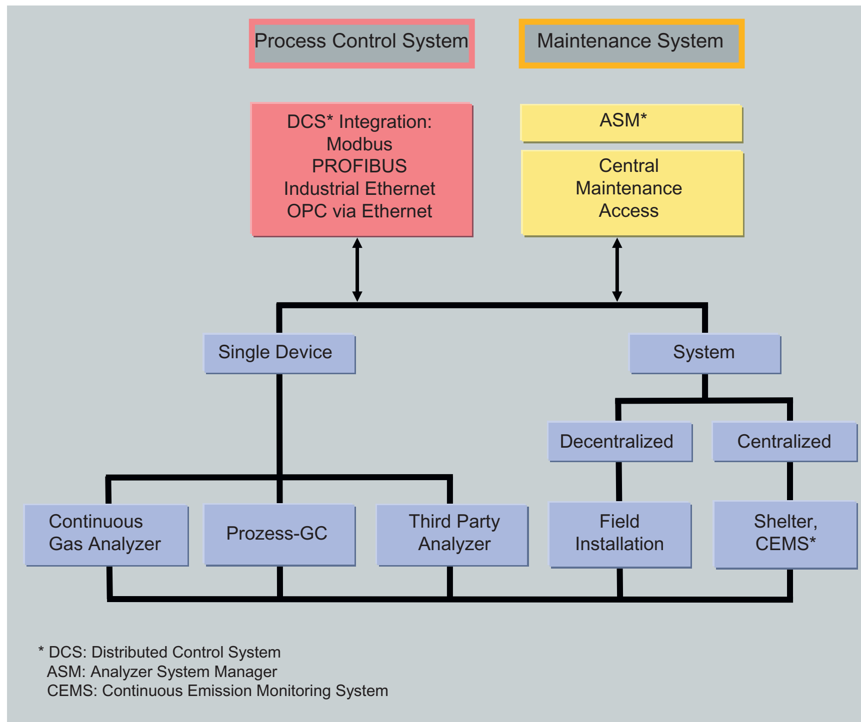

Fig. 12: Networking for DCS integration and maintenance support

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

Our Services

Siemens Process Analytics is your competent and reliable partner world wide for Service, Support and Consulting.

Our rescources 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 pro cesses 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.

Fig. 13: Portfolio of services

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. 13 to 14). 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 consullting

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.

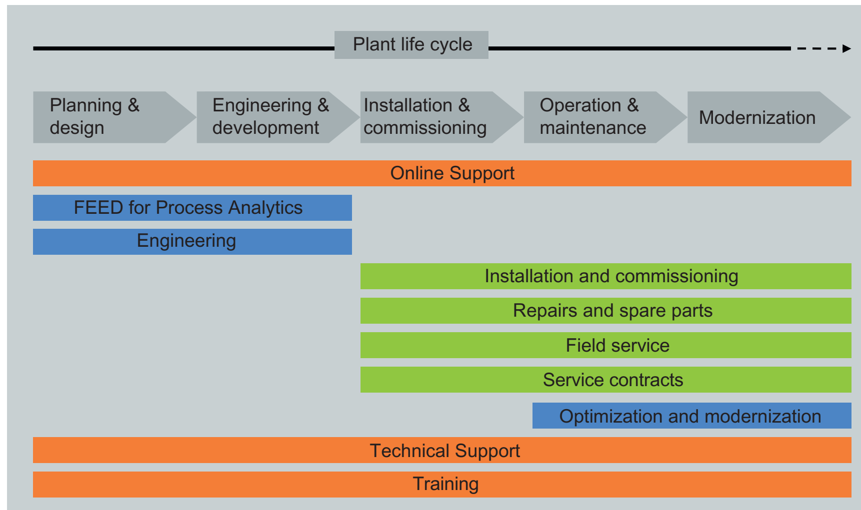

Fig. 14: Portfolio of services provided by Siemens Process Analytics

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.

Case Study

Siemens Process Analytics - Answers for industry

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