SAFE OPERATION OF ANODE BAKING FURNACES

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Abstract

The baking of anodes is a process in which combustible substances are released. Ring main fires do occur and even explosions in the fire zones, ring main or fume treatment plant have happened in carbon plants. The risks associated with different process deviations and the possible consequences of these, can be evaluated for both existing and new furnaces to be built.

European and IEC safety standards give useful guidelines for the design of process control and safety systems applicable to the baking process.

This paper will present and discuss methods for evaluating the risks and consequences, and give examples for how operational procedures and the design of safety systems can reduce the occurrence of unwanted events for open as well as closed top furnaces.

Introduction

The total energy consumption in modern baking furnaces amounts to typically 4.8 – 5.2 GJ/t baked anodes, which is a combination of the following fuel sources:

- Oil or gas: 40 – 50 %
- Pitch volatiles: 40 %
- Packing coke: 10 – 20 %

The pitch volatiles may be classified in two main groups of hydrocarbons:

- Condensable hydrocarbons (tar), which are mainly poly-cyclic aromatic hydrocarbons (PAH).
- Non-condensable substances, which are mainly hydrogen and methane.

The condensable hydrocarbons appear during distillation of the lightest fractions in the pitch. The non–condensable substances appear in complex chemical reactions, polymerization and cracking at temperatures above 400 °C. In total, the volatilized components of the pitch coking are:

- Tar: Released at temperatures of 200 – 500 °C.
- Methane: Released at temperatures of 400 – 800 °C.
- Hydrogen: Released at temperatures of 400 – 1000 °C.

Particular safety aspects of baking furnace operations are related to the following specific features:

- Only 40 - 50 % of the total energy input is controllable by immediate actions.

- Strict control of the air to fuel ratio is practically hampered by false air ingress into the furnace atmosphere.

International safety recommendations, i.e. European and IEC safety standards, prescribe essential design and operational characteristics to be fulfilled for safe operation of similar furnaces.

A risk assessment of the anode baking furnace has been completed based on hazard analysis by explosion simulation. Explosion simulations are particularly useful to evaluate hazardous consequences caused by process disturbances, and to reduce the risks by design measures. This paper describes the furnace operation conditions used in simulations, the results of simulations and aspects of the safety systems required to safeguard against explosions and fires.

Principal Risk Assessment

Flammability of Flue Gas Compositions of Baking Furnaces

The vaporization and pyrolysis of pitch generates a large number of components throughout the ordinary heat treatment range of anodes. The resulting fuel composition may vary [1,2]. For this study the following, typical average composition was chosen:

- Tar: 91.3 weight %
- Hydrogen: 6.5 weight %
- Methane: 2.2 weight %

Homogeneous, combustible gas-air mixtures are flammable within a limited range of compositions. In the flammable range a flame can propagate freely upon ignition. The flammable range is defined by the following limits:

- The Lower Explosion Limit (LEL).
- The Upper Explosion Limit (UEL).
- The Limiting Oxidant Concentration (LOC).

The relationship between combustible gas, air and inert gas and the location of the flammable range can be visualised by a ternary diagram as shown in Fig. 1 and Fig. 2. The stoichiometric air to fuel ratio $\lambda = 1$ is also shown.

Tars are known to include a large number of components (3000-4000). Analysis carried out by Charette et al. [3] found that the poly-cyclic aromatic hydrocarbon (PAH) components constitute approximate 70% of the total hydrocarbon loss. For this study, an average formula weight of approximately 200 g/mol with a C/H – ratio of 1.6, as for fluoranthene and pyrene ($C_{16}H_{10}$), was chosen

as the average, representative characteristics of tar and is referred to as "Tar" in this paper.

Zabetakis [4] gives LEL of aromatic hydrocarbons as $(50\pm2)*10^{-3}$ g/l, giving the LEL of Tar as approximately 0.6 vol%, while the value of UEL of Tar can be derived as approximately 6,0 vol%. All values are normalised to 25 $^{\circ}$C and atmospheric pressure.

In typical combustion regions, where the temperatures of the flue gas and the brickwork are higher than the Auto Ignition Temperature (AIT) of the combustible gases, the flammable region of the gas mixture is irrelevant and available oxygen will be consumed by oxidation. Process deviations may, however, increase the risk of forming gas-air mixtures within the flammable range downstream the combustion region of the fire zones:

1. Loss of draft situations followed by re-establishment of draft.
2. Sub-stoichiometric combustion. Too high fuel supply or too low draft, or a combination of the two conditions.

Oxygen deficit situations as described above may also be the root cause of formation of ignition sources. Cracking of heavier hydrocarbons forms soot/carbon particles. Light, glowing particles transported into the preheating sections facilitates ignition in pockets of flammable gas-air mixtures, or deposit in low velocity areas of the ring main system. High flue gas temperatures may also serve as ignition sources of soot/tar deposits in the ring main.

If the furnace is operated at oxygen deficit conditions caused by too low draft or excessive fuel, the resulting sub-stoichiometric concentration will be as shown in Fig. 1.
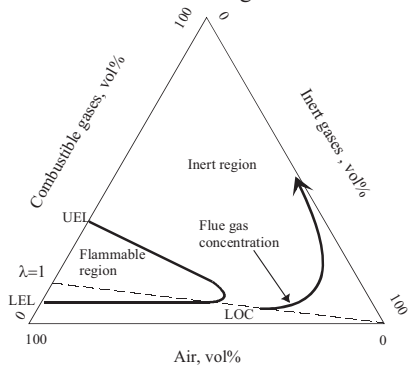

Figure 1. Idealized flue gas concentration in the combustion region by sub-stoichiometric combustion or lost draft.

Downstream of the flammable temperature range, dilution take place by air ingress through brickwork or access hatches, and the flue gas can enter the flammable composition range as principally shown in Fig. 2. The presence of an ignition source along the

exhaust system will in that case initiate a hazardous fire or explosion, depending on the amount of fuel and the fuel/air mixture.
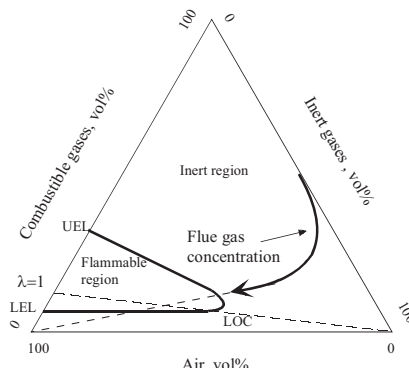

Figure 2. Idealized flue gas concentration in - and downstream the combustion region following a sub-stoichiometric combustion or lost draft situation.

Equation of Tar Combustion

The average values of reactants and products of combustion at normal operation measured in a closed top baking furnace are provided in Table 1.

The total of the combustion products is approximately 1300 Nm^3/t, while the total flue gas rate at the outlet of the combustion region is 1600 – 1900 Nm^3/t, since the furnace is operated at an oxygen surplus.

The flue gas entering the Tar combustion region contains the combustion products of the preceding fuel sources, e.g. propane, coke and the non-condensable substances from pitch pyrolysis. The principal equation of the stoichiometric Tar combustion ($\lambda=1$) in the fire can thus be described by:

$$C_{16}H_{10} + 18.5(O_2 + 3.76N_2) + \Sigma Inert \rightarrow \qquad (1)$$
$$16CO_2 + 5H_2O + 69.6N_2 + \Sigma Inert$$
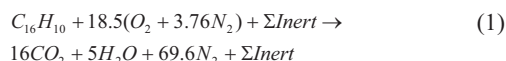
The average total of combustion products from energy sources other than Tar ($\Sigma Inert$) at normal operation is approximately 193 [mol/mol Tar], as shown in Table 1.

Explosion simulations are carried out at stoichiometric air to fuel ratios. The stoichiometric air to fuel ratio of Tar combustion is 88:1 [Nm^3/Nm^3], as seen from Eq. 1, and is one of the essential factors considered by explosion simulation.

Table 1. Average composition of reactants and products of combustion

| | Unit | Coke | Propane | Pitch volatiles | | | Total | Total excl. Tar combustion |
				Tar	H₂	CH₄		
Reactants of combustion								
Fuel consumption	kg/t	30,6	38,8	41,6	3,0	1,0		
Fuel consumption	Nm³/t		19,8	4,62	33,2	1,40		
Air for combustion	Nm³/t	272	470	407	79	10	1238	831
Products of combustion								
CO₂	Nm³/t	57	59	74	0	1		
H₂O	Nm³/t	0	79	23	33	3		
N₂	Nm³/t	215	371	321	62	8		
Total products	Nm³/t	272	510	418	96	12	1307	889
Total products	Nm³/Nm³ Tar	58,9	110,4	90,6	20,7	2,6	283	193
Total products	mol/mol Tar	58,9	110,4	90,6	20,7	2,6	283	193

      * Nm³/t = Nm³/(tonne baked anode)

Loss of Draft Situations

Following a loss of draft, a rapid increase in the concentration of combustible gases will take place as discussed above (see also Fig.1). For the actual Tar gas mixtures, the air access in the off-gas system (preheating sections, ring main, fume treatment plant) define the fuel compositions adequate for explosion simulations, see Case 1 - 3 in Table 2.
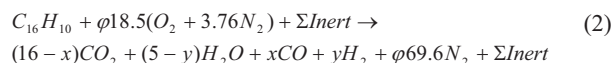
Methane and hydrogen are substantial parts of the pitch pyrolysis, and released at higher anode baking temperatures than Tar. False air ingress above the Auto Ignition Temperature will contribute to the combustion of methane and hydrogen, and thus limit the maximum concentration level at the outlet of the combustion region. An explosion simulation of a gas mixture with high hydrogen concentration is shown as in Table 2.

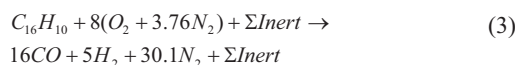Table 2. Cases for explosion simulation, loss of draft situations

	Oxygen concentration, [vol%]	Gas concentration at the outlet of the combustion region, [vol%]	
Case 1	12.5	Tar:	1.7
		Inert:	98.3
Case 2	16.0	Tar:	3.7
		Inert:	96.3
Case 3	18.8	Tar:	10.3
		Inert:	89.7
Case 4	12.9	H₂:	68.0
		Inert:	32.0

Sub-Stoichiometric Combustion

Maximum CO + H₂ Concentrations. The primary effect of air deficit is sub-stoichiometric combustion of Tar. The principal equation of sub-stoichiometric Tar combustion is attributed to the ratio factor range of $0.432 < \varphi < 1$ in Eq. 2:

$$C_{16}H_{10} + \varphi 18.5(O_2 + 3.76N_2) + \Sigma Inert \rightarrow \qquad (2)$$
$$(16 - x)CO_2 + (5 - y)H_2O + xCO + yH_2 + \varphi 69.6N_2 + \Sigma Inert$$

A sub-stoichiometric air ratio of $\varphi = 0.432$ gives the theoretical maximum of CO + H₂:

$$C_{16}H_{10} + 8(O_2 + 3.76N_2) + \Sigma Inert \rightarrow \qquad (3)$$
$$16CO + 5H_2 + 30.1N_2 + \Sigma Inert$$

$$Vol\%(CO + H_2)_{max} = \frac{16 + 5}{16 + 5 + 30.1 + \Sigma Inert} *100\% \qquad (4)$$

The total products from the other energy sources (*ΣInert*) will vary depending on the propane consumption and the flue gas rate.

Cases 5 - 8 in Table 3 refer to operational conditions, where air deficits provide conditions of maximum CO + H₂ concentration. Case 5 is sub-stoichiometric combustion of Tar. Case 6 – 8 refer to sub-stoichiometric combustion of Tar and propane. For all basic conditions included in Cases 5 – 9, maximum values of Tar release rates were assumed and estimated to be 25% above the average value.

Maximum Tar Concentration. At stoichiometric air to fuel ratios, the oxygen concentration in the off-gas system is the limiting factor in defining the maximum Tar concentration at low flue gas rates. The operating conditions for the explosion simulation are shown as Case 9, Table 3 with an oxygen content of 14.0 vol%.

Table 3. Cases for explosion simulations, sub-stoichiometric combustion

	Process data of combustion region	Gas concentration at the outlet of the combustion region	
Case 5	Flue gas rate: 695 Nm³/t	H₂:	4.5 vol%
	Propane supply: 0	CO:	14.3 vol%
		Inert:	81.2 vol%
Case 6	Flue gas rate: 1750 Nm³/t	H₂:	7.7 vol%
	Propane supply: 108 kg/t	CO:	10.0 vol%
		Inert:	82.3 vol%
Case 7	Flue gas rate: 1320 Nm³/t	H₂:	17.5 vol%
	Propane supply: 108 kg/t	CO:	18.8 vol%
		Inert:	63.6 vol%
Case 8	Flue gas rate: 1320 Nm³/t	H₂:	7.6 vol%
	Propane supply: 66.5 kg/t	CO:	11.4 vol%
		Inert:	81.0 vol%
Case 9	Flue gas rate: 260 Nm³/t	Tar:	2.3 vol%
	Propane supply: 0	Inert:	97.7 vol%

Explosion Simulations

Explosion simulations were carried out by use of the FLame ACcelleration Simulator (FLACS) Code [5]. All explosion simulations are performed at stoichiometric air to fuel ratios and at a flue gas temperature of 200 °C, assuming dilution of all mixtures to stoichiometric composition by air ingress

The explosion characteristics of Tar are not known. For the simulation, the explosion characteristics of propane were chosen. The Tar concentrations considered in Table 2 were scaled to the flammability limits of propane by maintaining the stoichiometric

air to fuel ratio. Characteristics of propane adapted to Tar mixtures by explosion simulations are considered to be a conservative assumption.

The laminar flame velocity is an important characteristic for explosion simulations. Values for the reference cases in Tables 2 and 3 are shown in Fig. 3. Results derived by explosion simulations in the ring main are shown in Fig. 4 at compositions referred in Table 2 and 3 (Case 1-8).

As seen from Fig. 3 and 4, the highets safety risk is related to total loss of draft or very low flue gas rate (Case 1 - 4, 9). The main differences are attributed to the level of fuel enrichment reached prior to air access, i.e. to the period of lost draft. An extended duration of lost draft represents an additional risk by enrichment of non-condensable gases - H_2, CH_4 and CO at reduced inert gas concentration. Although Case 3 represents the highest explosion pressure, cases with high concentrations of CO and/or H_2 (as Case 4) represent a higher probability of occurrence due to a wider flammable region combined with a lower oxygen demand (lower LOC).

Sub-stoichiometric combustion of Tar and propane rendering high concentrations of CO + H_2 (Case 5 – 8, explosion pressure all below 0.05 bar) do not cause gas pressures damaging the ring main (Fig. 4). The reason is probably the high concentration of inert gases from the other energy sources, in combination with low volumetric energy content. However, the flame continuation and gas pressure breakthrough at weaker parts of the ring main design may still represent a high risk to the working environment.
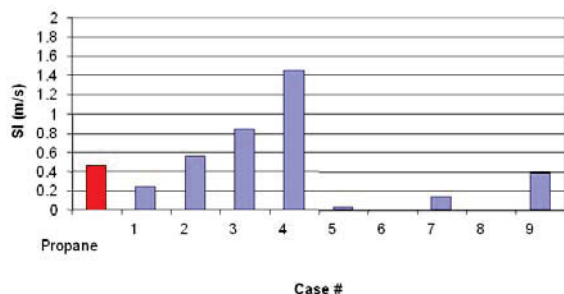

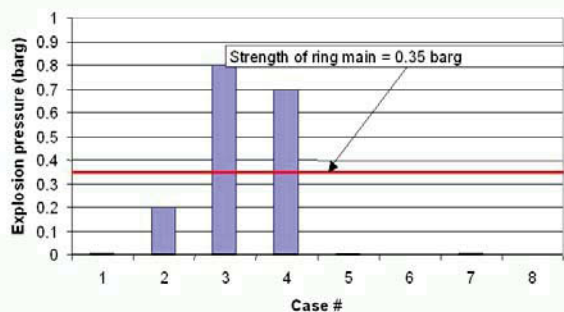Figure 3. Laminar flame velocity of different gas mixtures.

Figure 4. Explosion simulations of ring main pressures.

Technical Solutions and Procedures for Risk Reduction

European and International Electro-technical Commission (IEC) safety standards give useful guidelines for requirements and solutions for risk reduction. By definition, the Directive of Machinery (law in the European Union) applies to the Anode Baking System. The complete Machine includes the burner system, the baking furnace and the fume treatment plant/ emergency ventilation system. The Directive of Machinery outlines basic requirements, guidelines and standards related to safety, health and environmental requirements of baking furnace design and operation.

Safe Limits of Operation

Since no standards are specific to the anode baking process, the standard EN 1539 "Dryers and ovens, in which flammable substances are released – Safety requirements" gives useful guidelines for evaluation of the process.

Two main process requirements give guidelines to safeguard against fires or explosions in the ring main or fume treatment plant:

- An upper concentration of combustible substances as a percent of the LEL downstream of the combustion region (e.g. 25 %), dependent on to which level safety requirements are implemented.
- A Limiting Temperature for the flue gas, in practical terms defined to be the temperature at the exhaust manifold.

Basic process inputs and safety systems required to assure corrective action to unsafe conditions by Process Safety Supervision include the following functions:

Process Safety Function
The following are essential safety functions:

- The flue gas rate of from each combustion system.
- The fuel supply into each combustion system.
- The flue gas temperature in the exhaust manifold.
- Refractory temperature, interlocked to each burner group.

Safe limits of operation and corrective actions for each of the safety related functions must be defined for each furnace separately.

Safety Integrity Level
Operational safety levels are by international standards graded in terms of Safety Integrity Level (SIL) Figures, which are linked to the severity of hazardous consequences and the probability of occurrence.

Ring main fires do occasionally happen – and rare incidents of explosions as well. Hence the history provides strong arguments in favor of SIL 2 risk reduction measures.

The IEC standards of Safety Instrumented Systems [6, 7] cover aspects to be considered when electrical/electronic/programmable electronic systems are used to carry out safety functions. The requirements of SIL 2 risk reduction measures incorporates the following specific features:

The Process Shut Down Logic Solver must have redundant CPU and I/O on line fault diagnosis, and allow for online replacement of CPU and I/O cards. In case of failure of one CPU, the systems are allowed to operate as a single system for a limited period of time.

Safety Related Protective Systems
The protective systems are intended to take over when the control system fails, and bring the process to a safe condition. To achieve adequate safety, the protective systems must be separated from the control systems. The following functions can be defined as parts of the safety related protective system:

- Instrumentation necessary to supervise the process safety functions.
- Safety shut-off valves at the burner bridges.
- Safety shut-off valves at the main fuel circuit.
- Flue gas dampers necessary to bring the process to a safe position.
- An emergency alternative for the flue gas draft system.

The systems must be designed according to the fail-to-safe principle. For all functions a maximum reaction time needs to be defined.

Safety Related Utility Systems
The following function can be defined as a safety related utility system:

- Uninterrupted power supply to the safety related systems, including an emergency power system.

A maximum reaction time needs to be defined.

Procedures of Furnace Shut Down
Since only 40 – 50 % of the total fuel consumption can be controlled by immediate actions, the first priority during furnace operation is to maintain sufficient flue gas rate to provide oxygen surplus in each combustion system within acceptable time limits.

A total loss of furnace draft may occur with the ultimate risk previously discussed (Case 1 - 4). Hence, alternative ways of maintaining the flue gas in the non-flammable composition range below the flammability temperature must be considered, e.g. by flaring procedures. In the closed top furnace design, the temperature gradients along the fire zone have been proven to support transportation of flue gases towards high temperature sections in the fire zone. By reversing the flue gas direction in the sections with pitch pyrolysis, pitch volatiles are partly oxidized in the fire zone, and partly burned off by diffusion flames through hatches opened in the high temperature sections (T > 1000 °C).

When surplus air is established in all fires (visual observation of a clear transparent furnace atmosphere and no flame front inside or externally through openings on the furnace), normal operation can be re-established without any risk of forming flammable gas mixtures by restart of the draft. The risks involved with Case 1 – 4 are thus eliminated. The flaring procedure may take 3 – 12 hours for a closed top furnace.

Consequence Reduction Measures
The false air ingress along the fire zone makes a continuous, accurate, measurement of the air to fuel ratio challenging. Situations of sub-stoichiometric combustion can occur undetected by a safety supervision system and fire/explosions could occur in the ring main with minimal warning. By elimination of risks involved with loss of draft (Case 1 - 4), sub-stoichiometric combustion represents the highest remaining risk of furnace operation. Case 9, representing the highest explosion pressure, was used as the flue gas input concentration in the evaluation of pressure relief panels.

Pressure relief panels should be mounted at the ring main to direct any gas pressure away from working areas at a safe pressure level below the level of breakthrough for any other outlet hatches. The number of panels depends on the size of each panel. Fig. 5 shows the results from a FLACS simulation with different numbers of ø500 mm panels at each side of a 30 sections furnace. Eight panels where finally concluded to be sufficient. All hatches of the ring main shall include mechanical locking which is designed to withstand the explosion pressure.

Probability Reduction Measures
Steps can also be taken to reduce the probability of ignition sources in the ring main and ducting system. Ignition sources due to glowing of flammable substances can hibernate in the ring main and ducting system for long periods, e.g. due to embedded glowing particles in pitch/soot deposits with access to air through flanges/expansion joints.
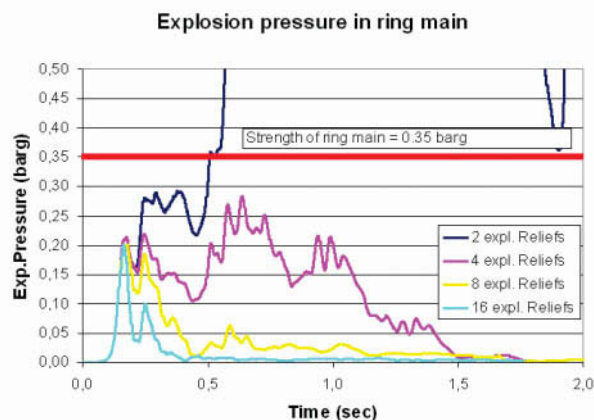

Figure 5. Explosion pressure in a ring main, Case 9.

The following counteractive measures reduce the existence of ignition sources:

- The intervals of cleaning of ring main and ducting system are chosen to reduce hibernation of ignition sources.
- The ring main and scrubber system is equipped with straps to provide effective earth potential along the whole flue gas system.

Another probability reduction measure is to ensure that air surplus for combustion of pitch volatiles are maintained by the procedures of energy and draft control at delayed fire step.

Flue Gas Measurements

Flue gas analyses have been carried out to verify the concentration of combustible gases under normal operation and at enforced process deviations. The concentration measurements versus time at the outlet of the exhaust manifold required, include as a minimum: Tar, H_2, CO, CH_4, O_2 and CO_2, while some supplementary checks on C_2H_6 and C_3H_8 are recommended. Flue gas rate and temperature measurements were also measured.

The concentration of combustible substances [X] in volume% or [ppm] is determined by entries measured in the following equation:

$$X_{Mixture}[ppm] = X_{Tar}[ppm] + X_{CO}[ppm] + X_{H_2}[ppm] + X_{CH_4}[ppm] \quad (5)$$

The Lower Explosion Limit (LEL) of a gas mixture is found by the Lé Chatelier's principle [8].

$$LEL_{Mixture} = \frac{100\%}{\frac{Vol\%Tar}{LEL_{Tar}} + \frac{Vol\%CO}{LEL_{CO}} + \frac{Vol\%H_2}{LEL_{H_2}} + \frac{Vol\%CH_4}{LEL_{CH_4}}} \quad (6)$$

Where: Vol% Tar + Vol% CO + Vol% H_2 + Vol% CH_4 = 100%

The total combustible substances as % of LEL is calculated by:

$$\frac{X_{Mixture}}{LEL_{Mixture}} * 100\% \quad (7)$$

The Lower Explosion Limit decreases with increased temperatures [9] (t = temperature, ^oC):

$$LEL_t = LEL_{25^oC} * [1 - 0.000784(t - 25)] \quad (8)$$

Flue gas analyses were carried out on three closed top furnaces as part of the approach to establish safe limits of operation. Furnace A operates at a 26 hours fire step, Furnace B at a 36 h fire step and Furnace C at a 28 hour fire step. Measurements were carried out in the ordinary operation range (3000 – 4500 Nm^3/ton) and at stepwise, reduced flue gas rates. The results (Fig. 6) confirm the increased risk of fire or explosion under low draft conditions.
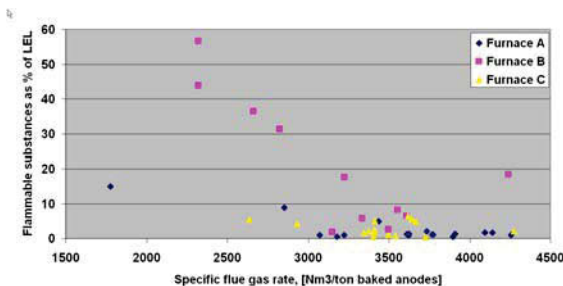

Figure 6. Calculated margins to LEL at normal operation and at enforced low flue gas rates. Measured at the exhaust manifold.

Summary

European and IEC safety standards give useful guidelines in design of safety systems applicable to the baking process.

Two major process requirements are critical to safeguard against fires or explosions in the ring main or fume treatment plant:

- Maximum concentration of flammable substances as percent of LEL at the outlet of the combustion region.
- A limiting maximum flue gas temperature at the outlet of the fire zone.

A process safety supervision system, independent of the process control system, is considered to be essential to maintain a safe process condition.

In order to design a safety supervision system, the inherent safety functions need to be defined:

- Process safety functions to be supervised, e.g. flue gas rate, flue gas temperature and fuel supply.
- Safe limits of operation for each of the safety functions.
- Actions and equipment necessary to re-establish safe operation.
- Procedures to cater for loss of draft situations.

A process safety supervision system, which is designed to provide adequate corrective actions to safety offsets, basically needs to include:

- PLC according to IEC 61508-1. SIL 2.
- Safety related protective systems, intended to supervise the process and provide backup by any control system failure.
- Safety related utility systems.

Explosion simulations are useful to classify different kinds of process deviations and assign priorities to minimize the remaining risk level.

By flaring procedures, as proven for closed top furnaces, the risk involved with restart after loss of draft situations can be eliminated. Situations of sub-stoichiometric combustion are challenging to detect due to the false air ingress into the furnace, and represents the highest remaining risk of furnace operation. Corresponding flue gas concentrations are used for design of explosion relief panels.

Typical preventive measures to cater for the remaining risk level include:

- Routine schedule for cleaning of the ring main.
- Effective earth potential along the flue gas system.
- Pressure relief panels to direct any gas pressure away from working areas.

Some safety limits can be verified by direct measurement of combustible substances in the flue gas while others need to be estimated on the basis of measurements and calculations.

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