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The Interpretation of Carbon Oxides in the Gas-in-Oil Analysis

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Responsible for the material testing laboratory within Siemens transformers. Main topics of interest: testing of insulating fluids, insulating and conductive materials. Member of Cigre D1 „Materials for electrotechnical applications“ and IEC TC 10. Leader of 2 WG within Cigre D1 D1.30 „Oxidation stability of insulating fluids“, D1.52 „Capacitive sensors for moisture determination“.





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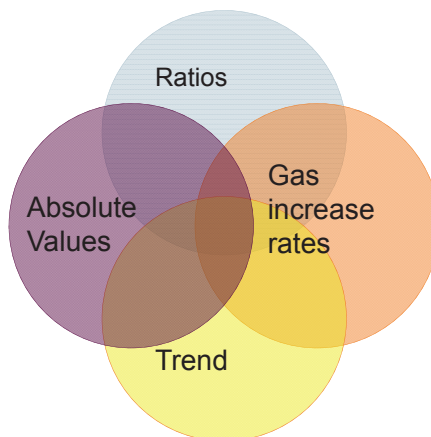
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Diagnostic Importance of Gas-in- Oil Analysis



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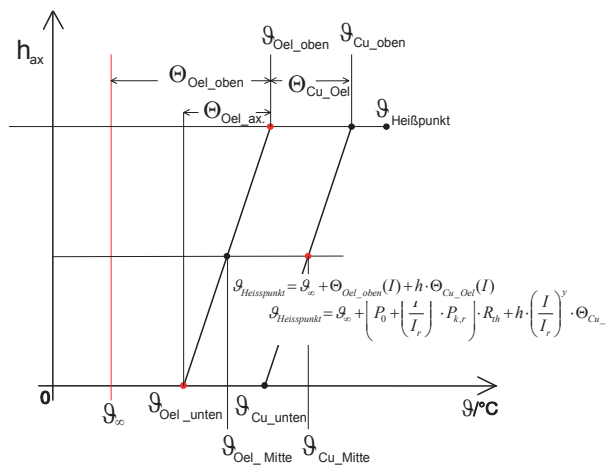
Different Specifications – Different Temperature Rise



IEEE C57.91 : 65° C Temp. Rise
110° C Hotspot



IEC 60076-2 : 55° Temp. Rise
98° C Hotspot

$$\theta_{\text{HeiBpunkt}} = \theta_{\infty} + \Theta_{\text{Oel_oben}}(I) + h \cdot \Theta_{\text{Cu_Oel}}(I)$$

$$\theta_{\text{HeiBpunkt}} = \theta_{\infty} + \left(P_0 + \left(\frac{I}{I_r} \right) \cdot P_{k,r} \right) \cdot R_{sh} + h \cdot \left(\frac{I}{I_r} \right)^2 \cdot \Theta_{\text{Cu_Oel}}$$

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Evaluation Scheme Acc. to IEEE 57.104

C. Dioxide	Ethylene	Acetylene	Ethane	Hydrogen	Methane	C. Monox.	TDCG	
CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	H ₂	CH ₄	CO	ppm	
2500	50	1	65	100	120	350	686	CONDITION 1
TDCG Below this level indicates the transformer is operating satisfactory.								
2501-4000	51 - 100	2 - 9	66 - 100	101 - 700	121 - 400	351 - 570	687 - 1879	CONDITION 2
TDCG within this range indicates greater than normal combustible gas level. Fault may be present								
4001-10000	101 - 200	10 - 35	101 - 150	701 - 1800	401 - 1000	571 - 1400	1880 - 4585	CONDITION 3
TDCG within this range indicates a high level of decomposition. Immediate action should be taken to establish a trend. Failure are probably present.								
>10000	>200	>35	>150	>1800	>1000	>1400	>4585	CONDITION 4
TDCG within this range indicates excessive decomposition. Continued operation could result in failure of the transformer.								

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Absolute Concentration Values

Ranges of 90% Typical Concentration Values in all transformer types IEC 60599

Values in microlitres per litre

Transformer sub-type	H ₂	CO	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
No OLTC	60-150	540-900	5 100-13 000	40-110	50-90	60-280	3-50
Communicating OLTC	75-150	400-850	5 300-12 000	35-130	50-70	110-250	80-270

NOTE 1 – The values listed in this table were obtained from individual networks. Values on other networks may differ.

NOTE 2 – “Communicating OLTC” means that some oil and/or gas communication is possible between the OLTC compartment and the main tank or between the respective conservators. These gases may contaminate the oil in the main tank and affect the normal values in these types of equipment. “No OLTC” refers to transformers not equipped with an OLTC, or equipped with an OLTC not communicating with or leaking to the main tank.

NOTE 3 – In some countries, typical values as low as 0,5 µl/l for C₂H₂ and 10 µl/l for C₂H₄ have been reported.

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WARNING

“Typical values” in the following application notes **are not limit values**. They are given for information only, as a maintenance tool. In a given transformer population, they indicate for example that 90 % of DGA values in service are below the 90 % typical values and 10 % are above. When typical values are exceeded, the only action recommended in this standard is to increase the frequency of DGA analyses.

Typical values depend on several parameters (age, type and manufacturer of equipment, operating and loading practices, climate, etc.), and are not exactly the same for all electrical networks. Ranges of typical values are therefore indicated in the following application notes, covering the different individual values observed worldwide and surveyed by IEC and CIGRE.

Individual networks are strongly encouraged to calculate the typical values corresponding to their own specific transformer population, using DGA data meeting IEC 60567 specifications for accuracy and following methods indicated in Clause 8 and in CIGRE Brochure # 296 (2006).

The ranges of typical values indicated in these application notes should be used only by default, when individual values are not available, and should not be used in a contract without a special agreement between the user and manufacturer of the equipment.

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This is the philosophy behind the use of 90% typical concentrations and 90% typical rates of increase, in order to concentrate maintenance efforts on the 10% of the population most at risk. A consensus has been reached at CIGRE on typical values observed in service worldwide (CIGRE Brochure # 296, 2006).

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Do really ratios $\text{CO}_2/\text{CO} < 3$ mean degraded cellulose?

IEC 60599

Mineral oil-impregnated electrical equipment in service – Guide to the interpretation of dissolved and free gases analysis

5.4 CO_2/CO ratio

The formation of CO_2 and CO from oil-impregnated paper insulation increases rapidly with temperature. Incremental (corrected) CO_2/CO ratios less than 3 are generally considered as an indication of probable paper involvement in a fault, with some degree of carbonization.

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Some examples

Carbon Oxides in Heavily Loaded Generator Transformers

Table I - Gas values, $\mu\text{L/L}$ (ppm) and ratio CO_2/CO for generator transformers

GAS, $\mu\text{L/L}$ (ppm)	Rate of transformer / Type of cooling / Year of service				
	1. 245 kV OFAF 2007.	2. 123 kV ONAF 2006.	3. 123 kV ONAF 2004.	4. 123 kV ONAF 2004.	5. 123 kV ONAF 2000.
Hydrogen, H_2	6	6	3	3	3
Methane, CH_4	15	11	10	10	10
Acetylene, C_2H_2	0	0	0	0	0
Ethylene, C_2H_4	1	0	0	0	0
Ethane, C_2H_6	2	0	0	0	0
CO	824	1307	716	1046	871
CO ₂	1637	2942	3462	3422	3878
Ratio CO_2/CO	2.0	2.2	4.8	3.2	4.4
Oxygen	9592	12581	5808	6497	5359
Nitrogen	45365	69544	28573	35817	25427

Ref: Anđela Hadži-Skerlev et al, Končar- Electrical Engineering Institute,
International Colloquium Transformer Research and Asset Management
Dubrovnik, Croatia, May 16 – 18, 2012

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Comparison of typical values in different standards

IEC 60599 "Table A.2"

Ranges of 90 % typical gas concentration values observed in power transformers

	CO	CO ₂
[ppm]	400-600	3800-14000

IEEE Std C57.104-2008 "Table 1"

Condition	CO	CO ₂
1	≤350	≤ 2500
2	... 570	... 4000
3	...1400	... 10000
4	> 1400	> 10000

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Further examples

Carbon Oxides in Closed Type Transmission Transformers (21, Operation 1 – 10 years)

Table II - Range of gas values, $\mu\text{L/L}$ (ppm) and ratio CO_2/CO for transmission power transformers

GAS, $\mu\text{L/L}$ (ppm)	Rate of transformer/ Type of cooling / number of units				
	20 MVA 110 kV ONAN/ONAF 7 units	40 MVA 110 kV ONAF, ONAN 6 units	63 MVA 110 kV ONAF 2 units	100 MVA 110 kV ONAF 1 unit	≥ 300 MVA 420 kV OFAF 5 units
Hydrogen, H_2	5-20	11-18	12-17	16	2-31
Methane, CH_4	2-8	7-12	11-14	22	10-18
Acetylene, C_2H_2	0	0	0	0	0
Ethylene, C_2H_4	0	0	0	1	0-1
Ethane, C_2H_6	0	0	0	3	0-3
CO	148-1197	761-1457	1135-1157	1208	468-825
CO_2	337-2853	1274-4652	2270-2521	2817	1945-2892
Ratio CO_2/CO	1,0-11,2	1,7-3,6	2,0-2,2	2,3	2,5-4,9
Oxygen	7117-19444	5532-10794	9706-10582	7857	5642-11384
Nitrogen	31850-63613	27110-55101	52276-60703	50629	24404-58148

Ref: Anđela Hadži-Skerlev et al, Končar- Electrical Engineering Institute,
International Colloquium Transformer Research and Asset Management
Dubrovnik, Croatia, May 16 – 18, 2012

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Is this a faulty condition?

**No, since there are no further fault gases
IEC 60599 is being revised in this respect!**

The formation of CO_2 and CO from oil-impregnated paper insulation increases rapidly with temperature. High values of CO (e.g., 1000 ppm) and CO_2/CO ratios less than 3 are generally considered as an indication of probable paper involvement in a fault, with possible carbonization, **in the presence of other fault gases.**

However, in closed-type transformers or in open transformers operating at constant load (i.e., with low breathing), CO accumulates in the oil, leading to ratios $\text{CO}/\text{CO}_2 < 3$, without any irregularities or faults if no other gases such as H_2 or hydrocarbons are formed.

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Looking for a sign of cellulosic degradation

IEC 60599

Mineral oil-impregnated electrical equipment
in service –
Guide to the interpretation of dissolved
and free gases analysis

5.4 CO₂/CO ratio

The formation of CO₂ and CO from oil-impregnated paper insulation increases rapidly with temperature. Incremental (corrected) CO₂/CO ratios less than 3 are generally considered as an indication of probable paper involvement in a fault, with some degree of carbonization.

When excessive paper degradation is suspected (CO₂/CO < 3), it is advisable to ask for a furanic compounds analysis or a measurement of the degree of polymerization of paper samples, when this is possible.

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**IN ALL CASES 2-FURFURAL WAS VERY
LOW OR NOT DETECTABLE**

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THEREFORE:

RATIO $\text{CO}_2/\text{CO} < 3$ IS NOT INDICATIVE FOR CELLULOSIC DEGRADATION

QUESTIONS STILL PENDING:

- WHAT IS THE REASON FOR HIGH CO CONTENT?
- WHAT IS INDICATIVE FOR CELLULOSIC DEGRADATION?

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REASONS FOR HIGH CO CONTENT:

- SOLUBILITY
- RATE OF GENERATION OF CO AND CO_2 WITH TEMPERATURE
- OXIDATION PRODUCTS AS A RESULT OF OIL AGEING

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Solubility of carbon oxides

SOLUBILITY

$K = C_{iOil}/C_{iGas}$

At 20° C

<div style="display: flex; align-items: center; justify-content: center;"> <div style="background-color: #cccccc; padding: 5px; margin-right: 5px;">1</div> <div style="background-color: #ffff00; padding: 5px; margin-right: 5px;">0,1</div> </div> <p>solubility coefficient CO (carbon monoxide) – 0,1</p>	<div style="display: flex; align-items: center; justify-content: center;"> <div style="background-color: #cccccc; padding: 5px; margin-right: 5px;">1</div> <div style="background-color: #ffff00; padding: 5px; margin-right: 5px;">0,93</div> </div> <p>solubility coefficient CO₂ (carbon dioxide) – 0,930</p>
CO	CO ₂

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Rate of generation of carbon monoxide with temperature out of the oil

20° C cause a 4x acceleration in the CO production rate

Development of CO in different oil types without cellulose or other transformer materials

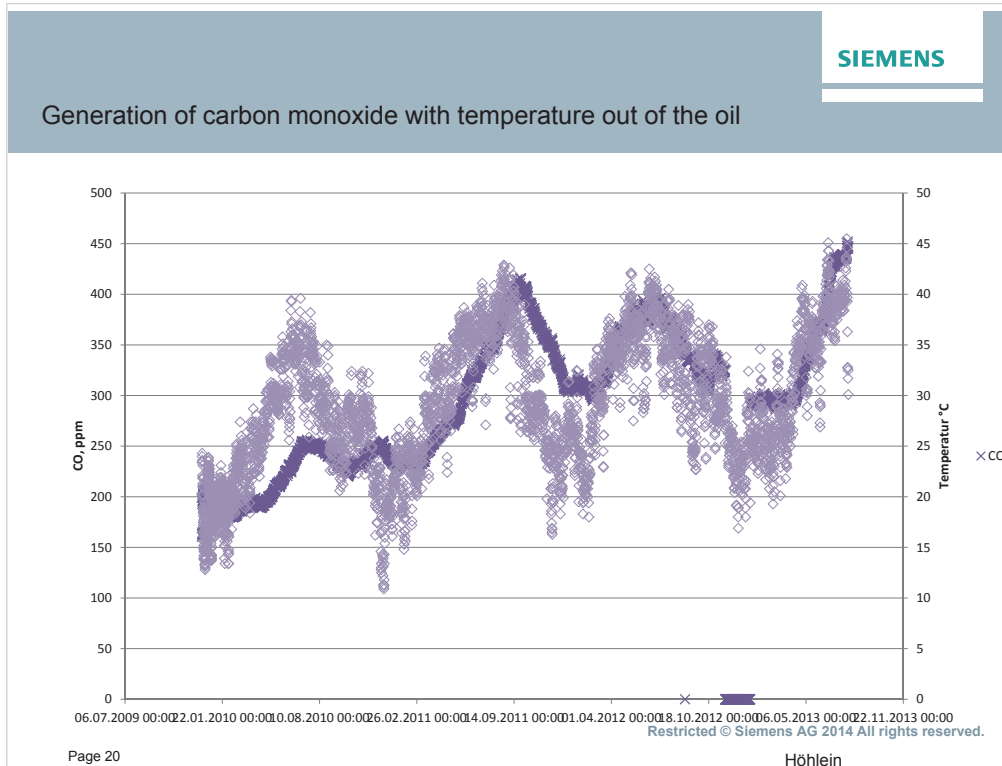
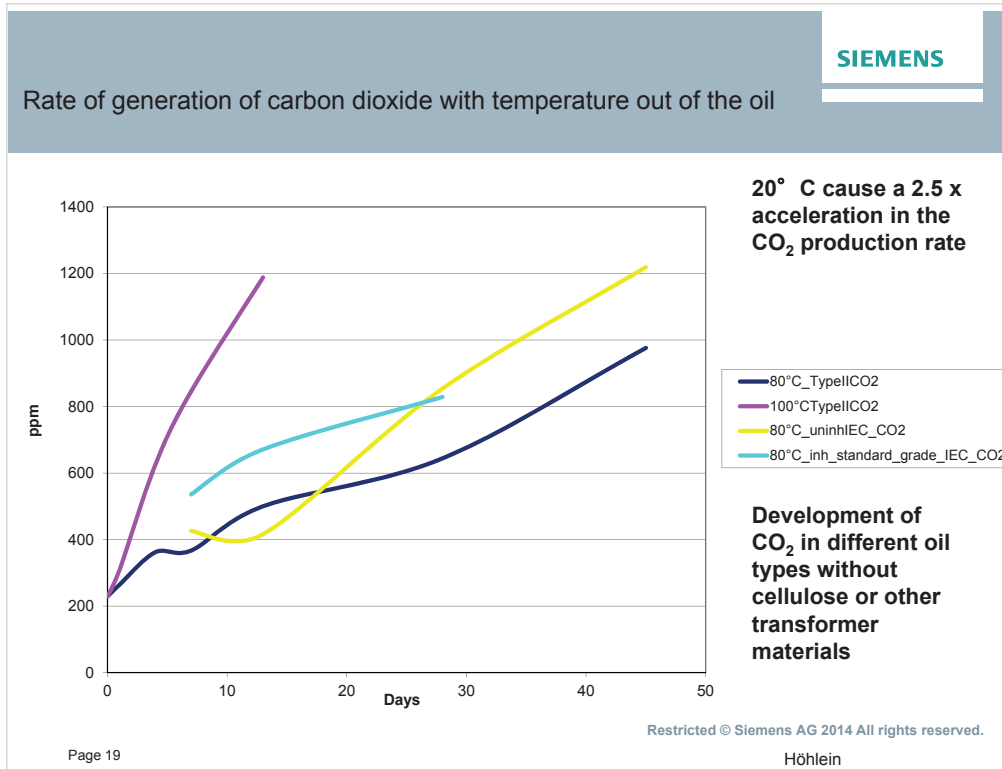
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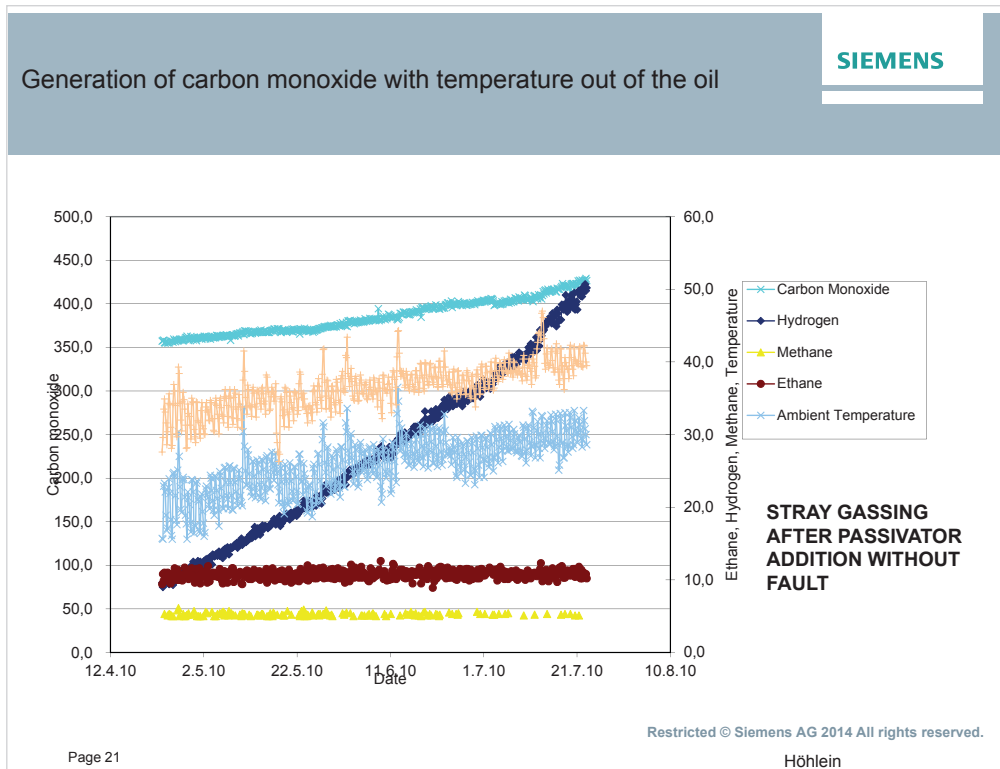
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Seeking for cellulosic degradation markers

- CO and CO₂ are the main criteria
- Furanics
- Methanol

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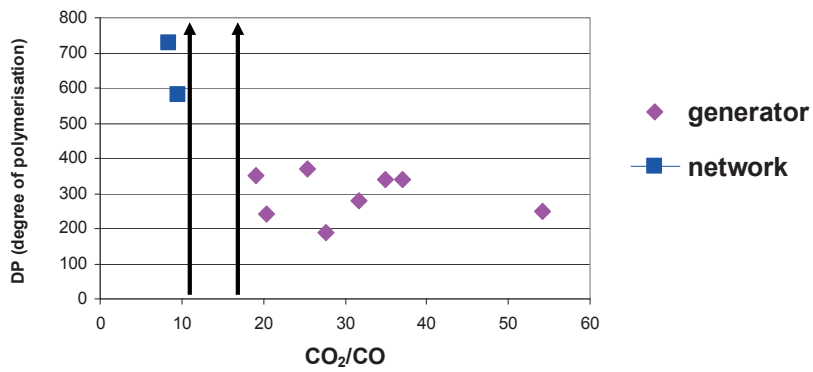
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High ratio carbon dioxide/carbon monoxide may be indicative for cellulosic dehydration

Transformer Age: 25 - 30



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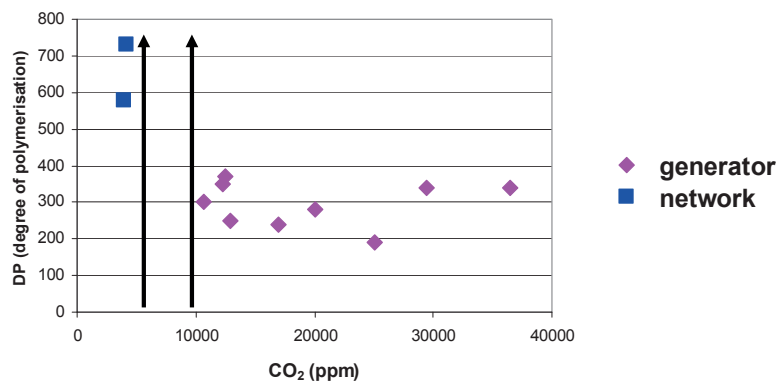
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High absolute values of carbon dioxide may be indicative for cellulosic dehydration

Transformer Age: 25 - 30



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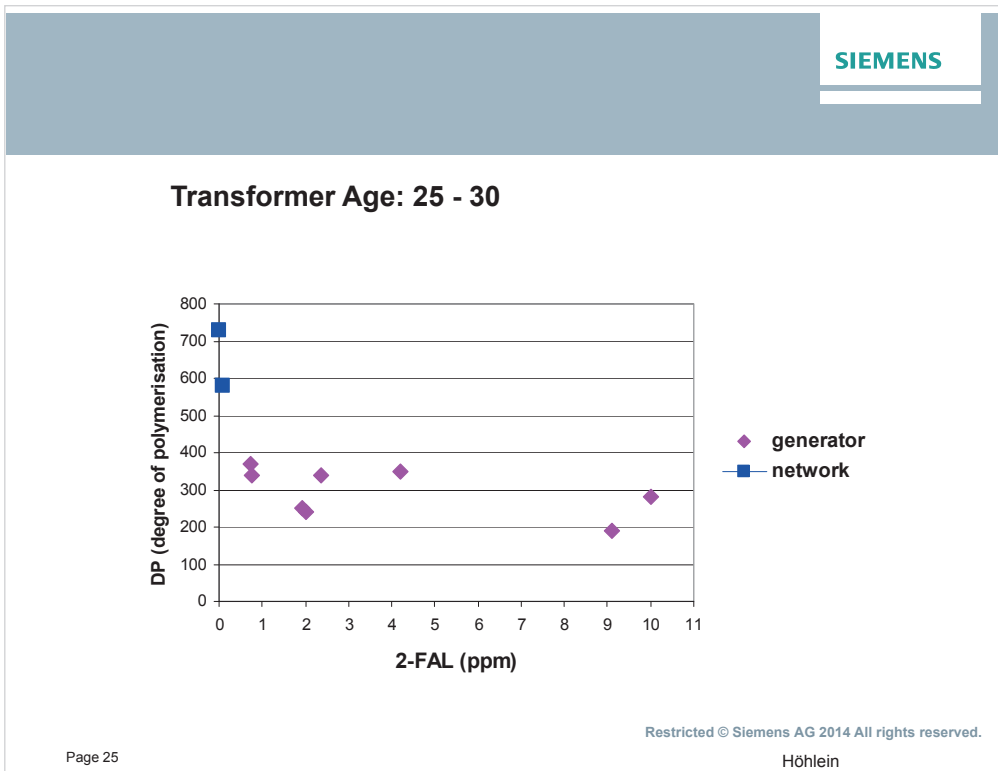
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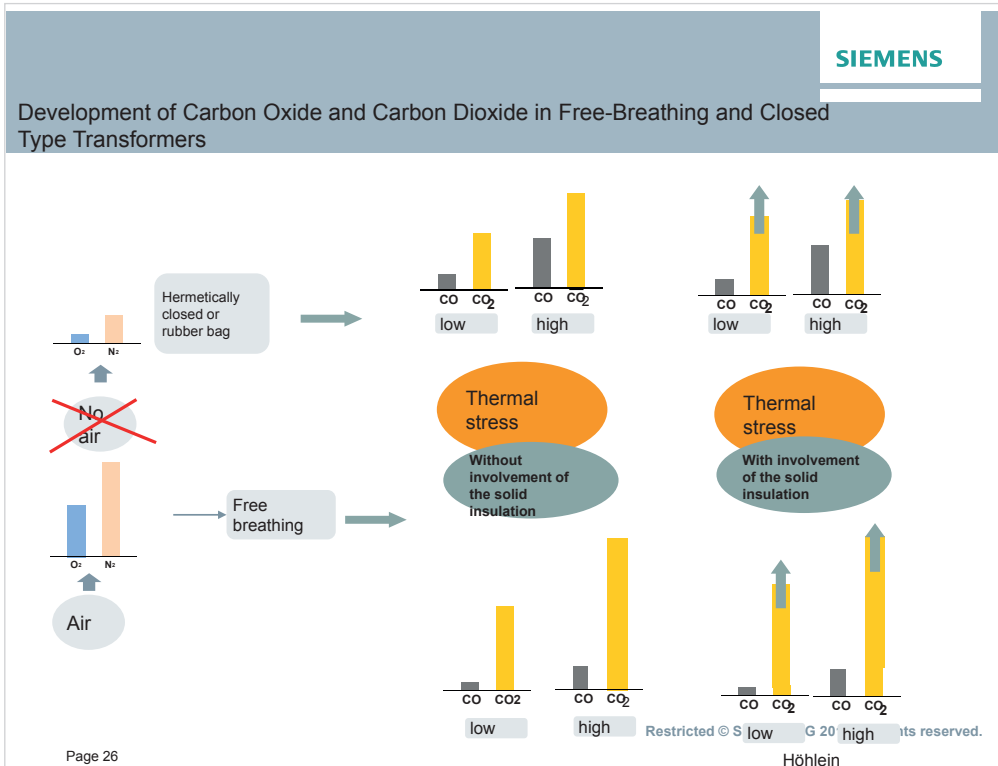


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Conclusions

- Until recently, CO and CO₂ were considered as good indicators of paper involvement in faults. Recent investigations at CIGRE, however, have shown that this is not always the case.

High concentrations of CO (>1000 ppm) and/or low CO₂/CO ratios (<3), WITHOUT the formation of significant amounts of hydrocarbon gases, are NOT an indication of a fault in paper, particularly in closed transformer, but are rather due to oil oxidation under conditions of limited supply of O₂.

- High concentrations of CO (>1000 ppm) and low CO₂/CO ratios (<3), TOGETHER WITH the formation of significant amounts of hydrocarbon gases, may be an indication of a fault in paper (to be confirmed with Triangles 4 or 5 and furans).

High concentrations of CO₂(>10,000 ppm), high CO₂/CO ratios (>20) and high values of furans (>5 ppm) are an indication of the slow degradation of paper at relatively low temperatures (<140° C), down to low degrees of polymerisation (DP) of paper.

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