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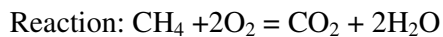
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APPENDICES

APPENDIX 1

GAS FLOW RATES FOR SIMULATED REHEATING ATMOSPHERE

In this section, the required gas flow rates in the reheating furnace was calculated with 3% and 4% excess oxygen to ensure complete combustion of methane in air. Calculations based on the combustion of methane are presented below.



Input: CH_4 , Air (21% O_2 , 79% N_2)

Output: CO_2 , O_2 , H_2O , N_2

Basis: 100g of CH_4

Table 1A and 1B below give the results of the mass balance calculation for respectively 4% and 3% O_2 in the off gas.

TABLE 1A: Methane combustion with oxygen excess in the off gas of 4%

INPUT	CH_4	Stoich. O_2	Stoich. N_2	Stoich. Air	Excess air	Total Air
n (mol)	6.25	12.5				
V (Ndm ³)		280	1053.33	1333.33	346.67	1680.00
OUTPUT	CO_2	O_2	N_2	H_2O	Off gas	Total gas
Mol (mol)	6.25			12.5		
V (Ndm ³)	140		1327.20	280	1473.33	1820
% offgas	7.70	4	72.92	15.39		100
% dry offgas	9.09	4.73	86.18	0		100

TABLE 2A: Methane combustion with oxygen excess in the off gas of 3%

INPUT	CH_4	Stoich. O_2	Stoich. N_2	Stoich. Air	Excess air	Total Air
n (mol)	6.25	12.5				
V (Ndm ³)		280	1053.33	1333.33	245.56	1578.89
OUTPUT	CO_2	O_2	N_2	H_2O	Off gas	Total gas
n (mol)	6.25			12.5		
V (Ndm ³)	140		1247.32	280	1473.33	1718.89
% offgas	8.1	3	72.60	16.30		100
% dry offgas	9.73	3.58	86.67	0		100

Based on these values, the total volume of gas fed to the furnace is calculated as follows:

Dimension of tube: OD = 9cm, ID = 7.6cm, Length = 150cm; speed of gas in the tube 0.1 m/s (1250°C, 1 atmosphere)

V_t , total volume of gas = area \times speed

$$V_{\text{tot}} = 8.13 \times 10^{-5} \text{ Nm}^3/\text{s}.$$

For oxygen excess of respectively 4% and 3%, the flow rates of the individual gases to the furnace should be:

TABLE 3A: Gas flow rates with 4% and 3% oxygen excess in the offgas

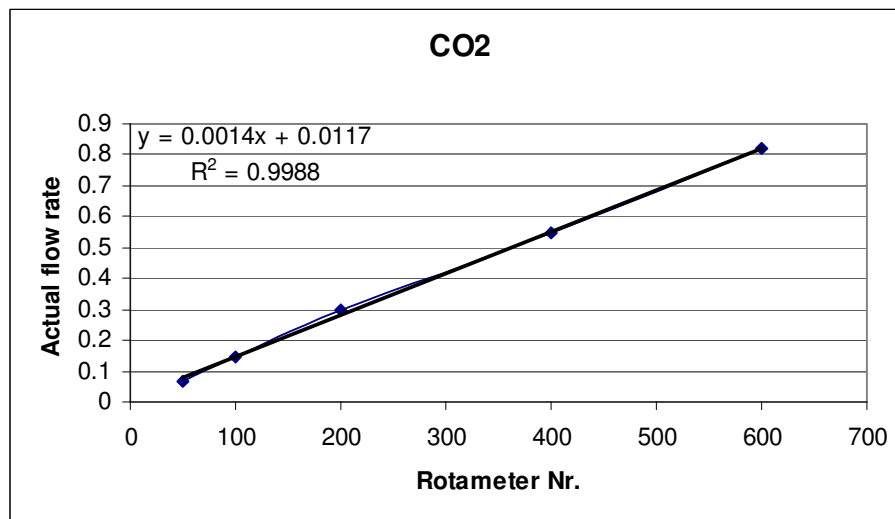
4% O ₂ Excess	Nm ³ /s	dm ³ /min
V _{N₂}	5.9×10 ⁻⁵	3.6
V _{CO₂}	6.3×10 ⁻⁶	0.38
V _{O₂}	3.3×10 ⁻⁶	0.20

3% O ₂ Excess	Nm ³ /s	dm ³ /min
V _{N₂}	5.9×10 ⁻⁵	3.6
V _{CO₂}	6.6×10 ⁻⁶	0.38
V _{O₂}	2.4×10 ⁻⁶	0.15

The following tables show the rotameter calibrations, as determined using a bubble tower:

CO₂ calibration

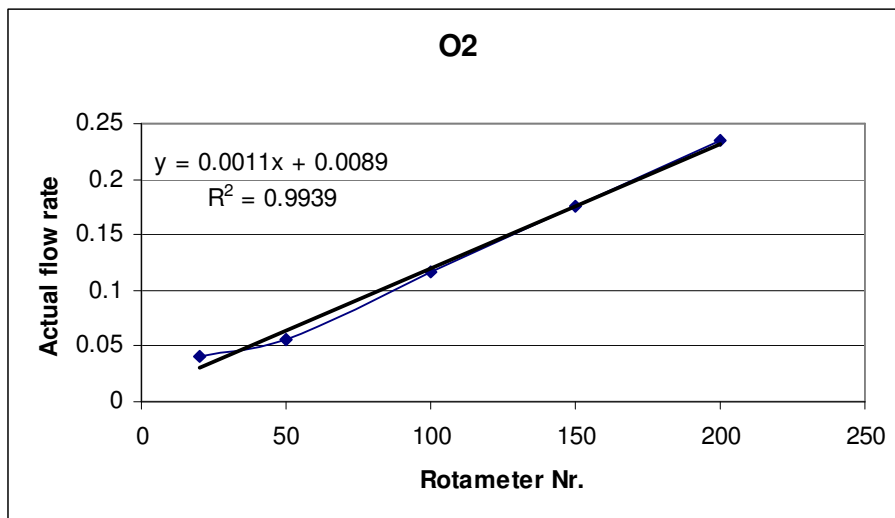
Pressure drop [mmHg]	Rotameter setting. [ml/min]	Bubble Meter [ml]	Average Time [second]	Measured rate [l/min]
51	50	50	43.584	0.06883
53	100	50	20.53	0.14613
60	200	50	10.0148	0.29956
66.5	400	50	5.4775	0.5477
73	600	50	3.655	0.82079





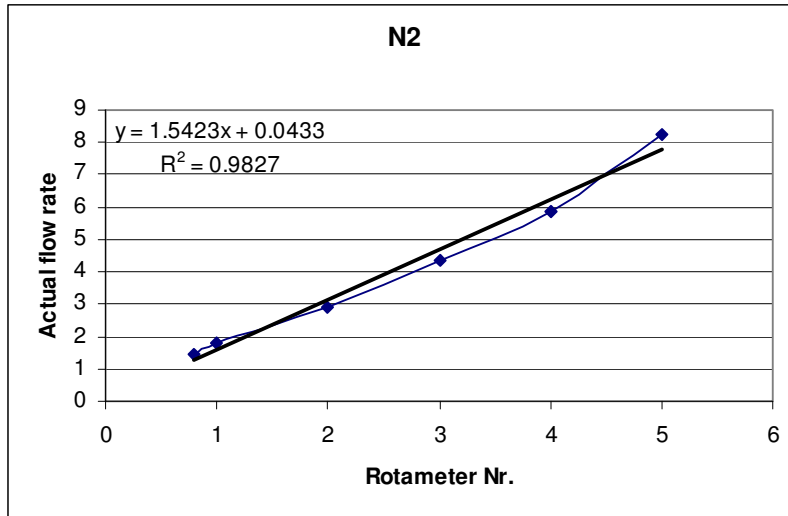
O₂ calibration

Pressure drop [mmHg]	Rotameter Nr. [ml/min]	Bubble meter [ml]	Average time [second]	Measured rate [l/min]
53	20	50	75.332	0.03982
55	50	50	53.2433	0.05635
57	100	50	25.6925	0.11677
60	150	50	17.1567	0.17486
61	200	50	12.8125	0.23415



N₂ calibration

Pressure drop [mmHg]	Rotameter Nr. [l/min]	bubble meter [ml]	Average time [second]	Measured rate [l/min]
57	0.8	300	12.202	1.47517
60	1	300	10.023	1.79587
70	2	300	6.21	2.89855
78	3	300	4.14	4.34783
87	4	300	3.065	5.87276
94	5	300	2.185	8.23799



APPENDIX 2

WATER CONTENT OF THE GAS MIXTURE

Preliminary high temperature reheating experiments were carried out by passing the exit gas (at the bottom of furnace) through a pre-weighed drierite column in order to check that the correct amount of vapour entered the furnace. The gas composition was chosen to obtain 3% O₂ excess in the furnace off-gas. The column was weighed again after the experiments were completed. The amount of water that was absorbed by the drierite column was given by the difference in the two masses.

Mass of drierite	257.01g
Mass of drierite + water	276.89g
Mass of water	19.88g

In this experiment, the value of 19.88g was compared with the calculated value of the mass of water that was expected in the gas mixture at the laboratory temperature and pressure.

From the ideal gas law ($pV = nRT$), for an ambient pressure of 0.86 atm and temperature of 298 K, the number of moles of the dry gas mixture was calculated as follows:

Total dry gas flow rate (l/min)	Time (min)	Total dry gas volume (l)	Moles of dry gas
5	30	150	5.3

Based on the expected percentage of water in the gas mixture of 16.3% (based on the condenser temperature) the expected amount of water is then calculated as follows:

$$[5.3/(1-16.3/100)] \times (16.3/100) = 1.03 \text{ moles}$$

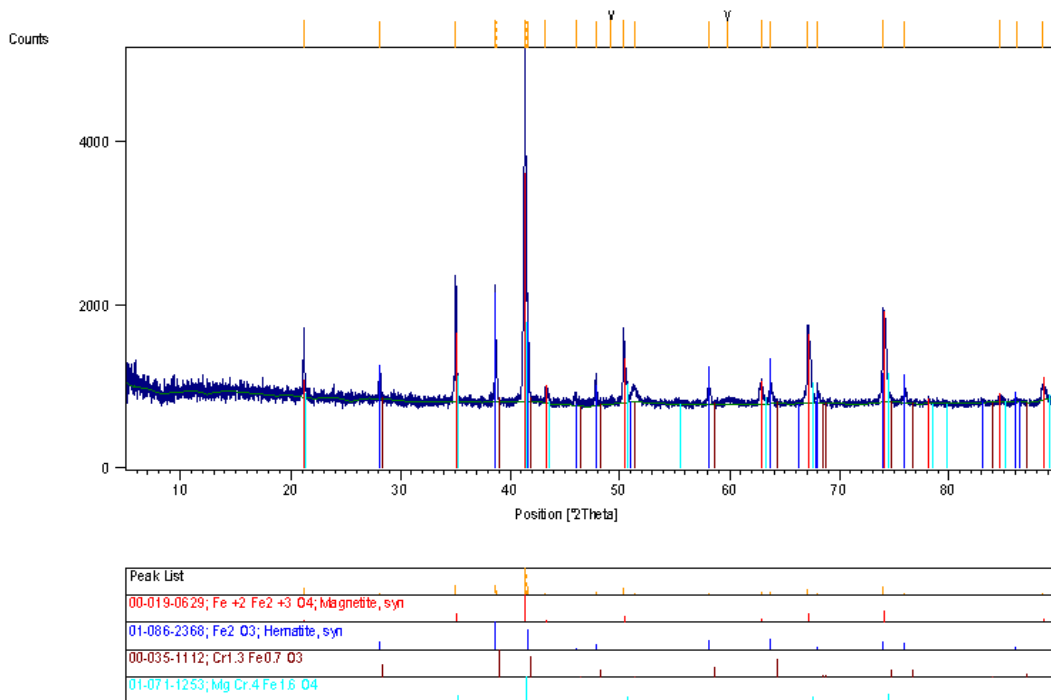
The expected mass of water calculated from the gas mixture is then:

$$1.03 \times 18 = 18.54\text{g}$$

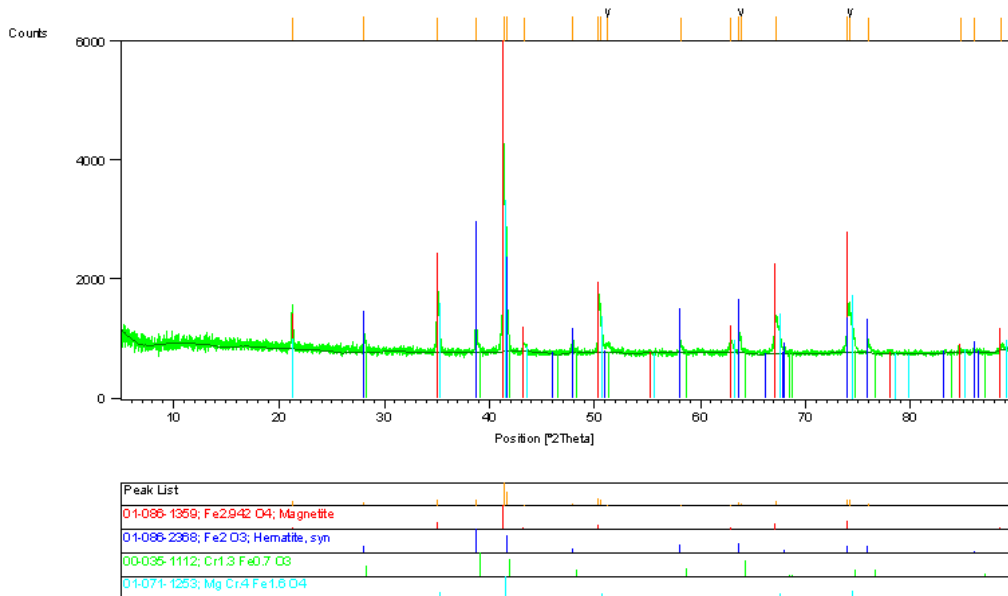
APPENDIX 3

XRD spectra of the scales

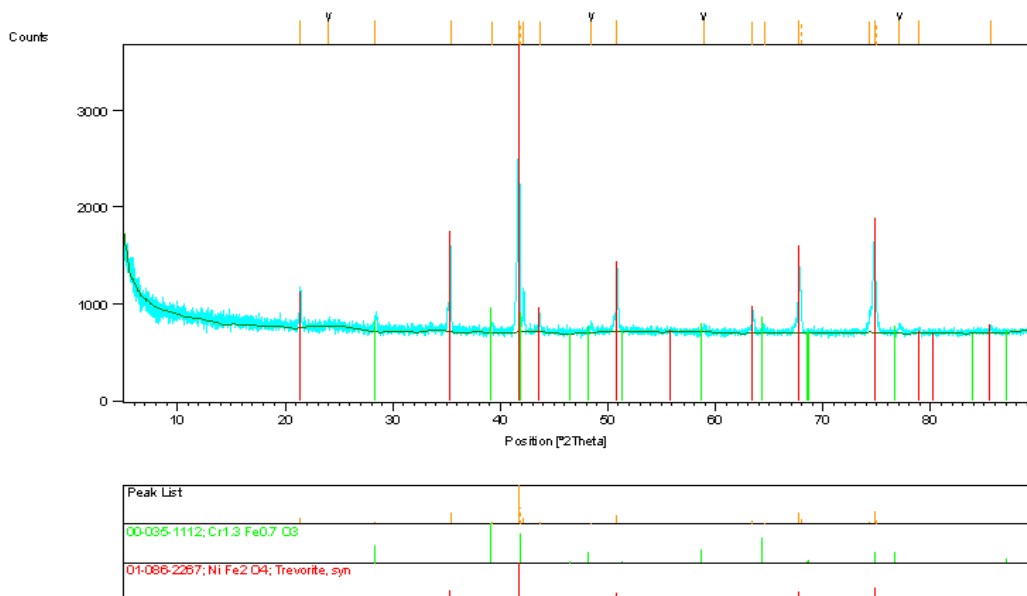
After reheating before hydraulic descaling, oxides scale were removed from contaminated and the uncontaminated samples for phase identification by means of X-ray diffraction analysis. The removed scale was pulverised before X-ray diffraction. The residual scale which remained on the sample surface after removing the outer scale was also analysed. Some pieces of removed scale were not pulverised, to allow the inner surfaces (closer to the steel) of the removed scale to be examined by X-ray diffraction.



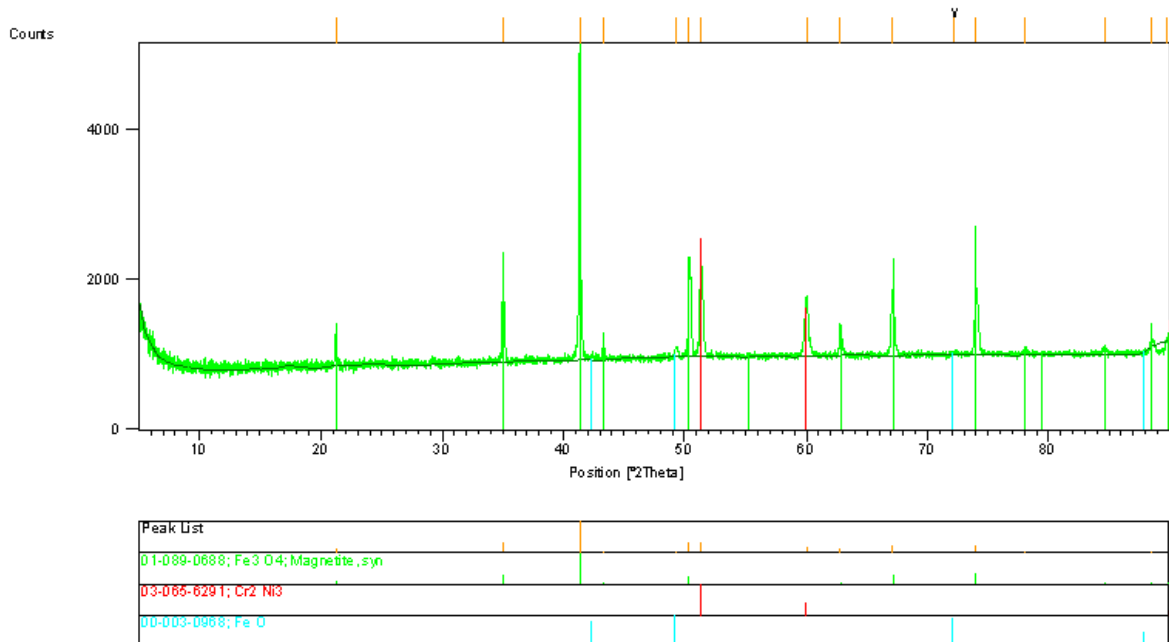
XRD pattern: scale removed from uncontaminated sample RP2. Main phases are magnetite, hematite, and Cr_2O_3 .



XRD pattern: scale removed from contaminated sample RP3. Main phases are spinel ("magnetite"), hematite and Cr₂O₃

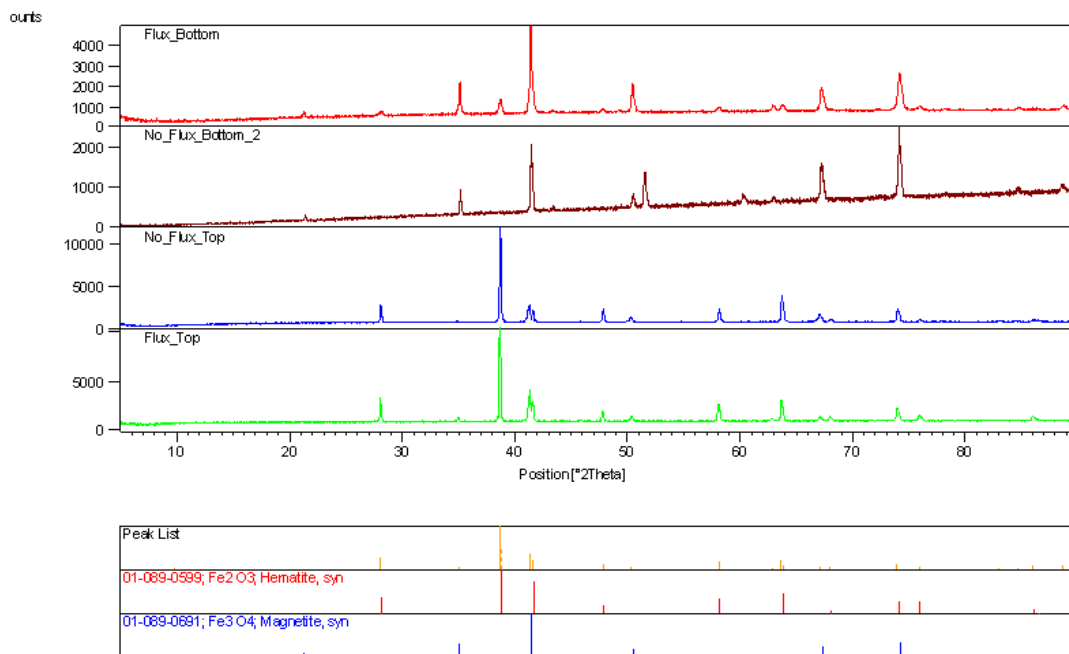


XRD pattern: inner surface of scale removed from contaminated sample D2. Main phases are Cr₂O₃ and spinel (here labelled "trevorite").

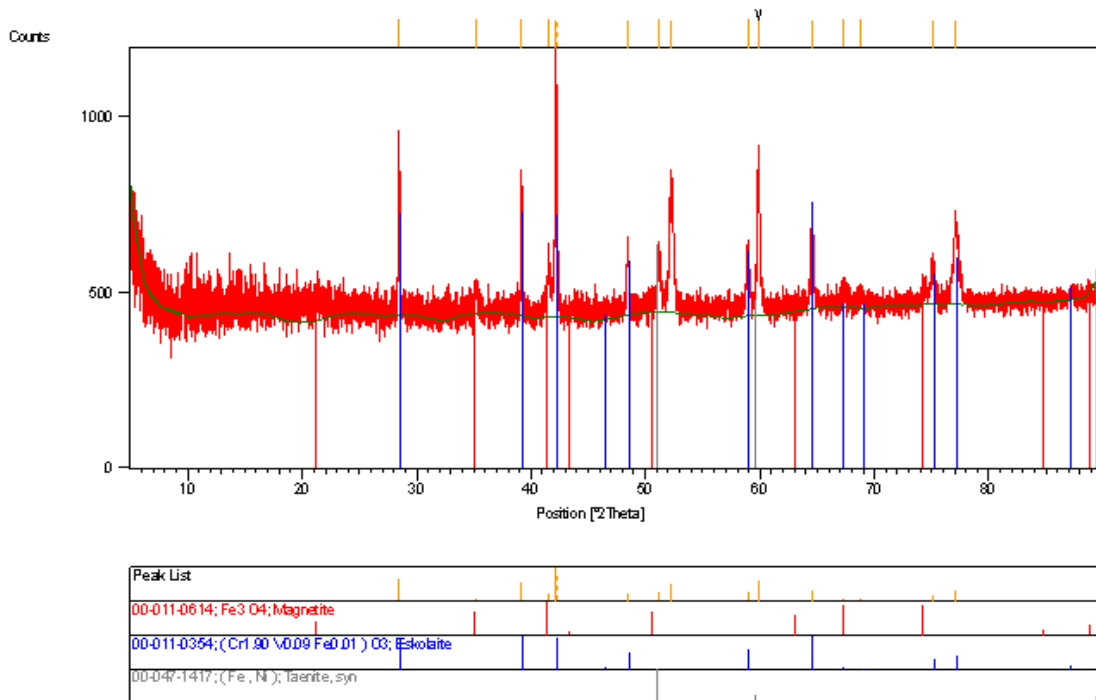


XRD pattern: inner surface of scale removed from the uncontaminated sample D1.

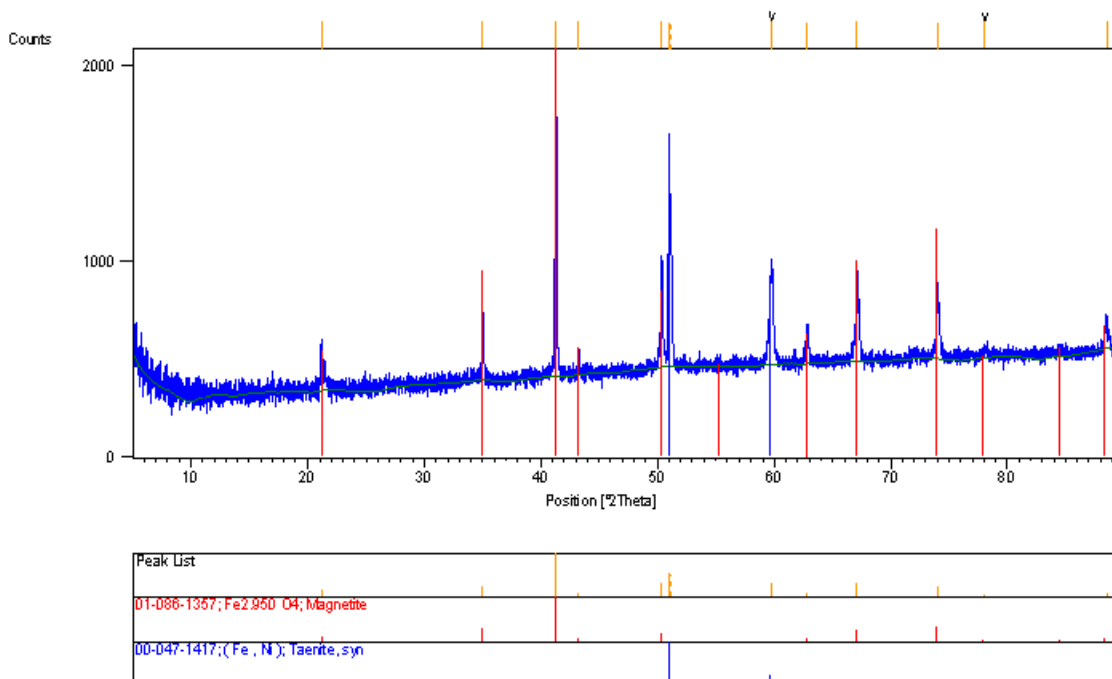
Main phases are spinel (magnetite) and austenite (here labelled "Cr₂Ni₃")



Comparison of XRD patterns of scales removed from contaminated samples (bottom and top side) and uncontaminated samples (bottom and top side)



XRD pattern: residual scale after descaling top side of the contaminated sample D1. Main phases are spinel ("magnetite"), Cr₂O₃ ("eskoilitite") and austenite ("taenite")

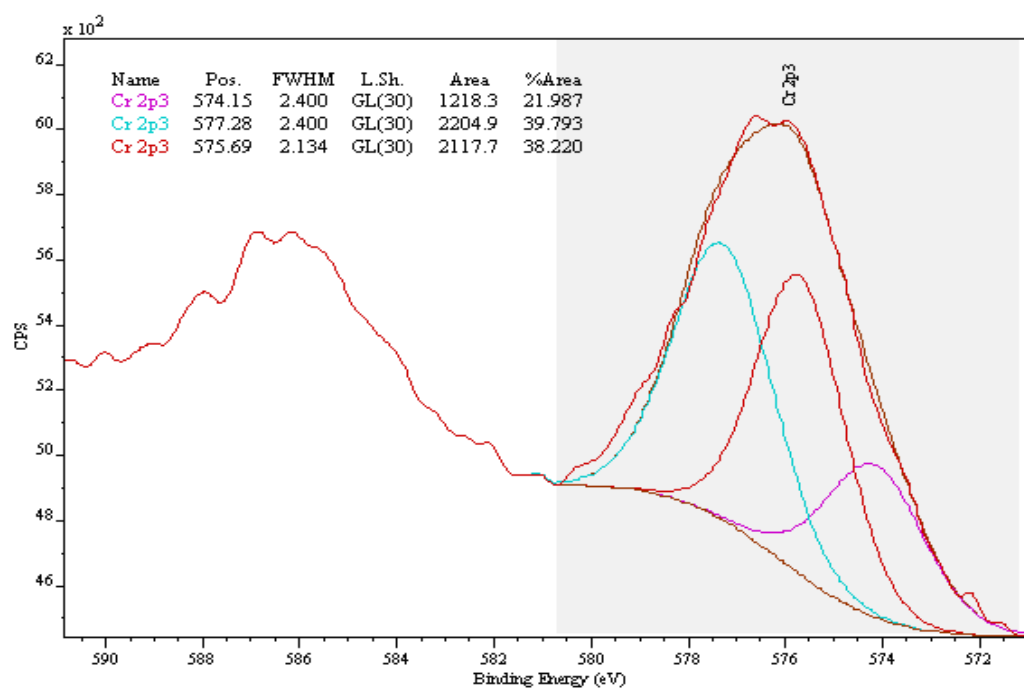


XRD pattern: residual scale after descaling top side of the uncontaminated sample D1. Main phases are spinel ("magnetite") and austenite ("taenite").

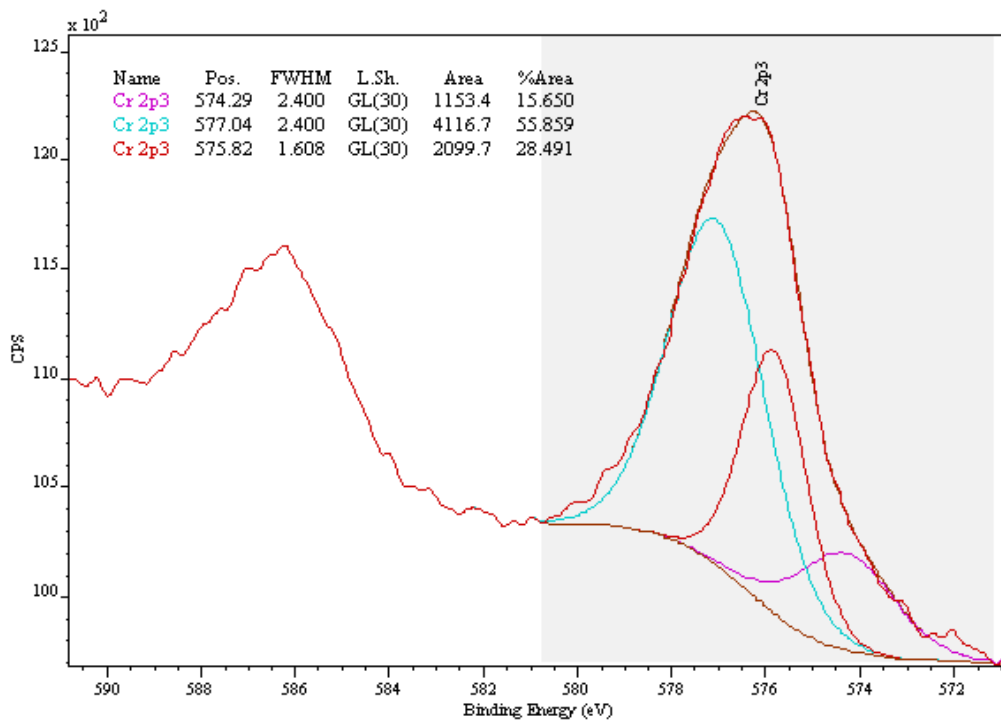
APPENDIX 4

XPS ANALYSIS OF THE SCALE FOR CHROMIUM QUANTIFICATION

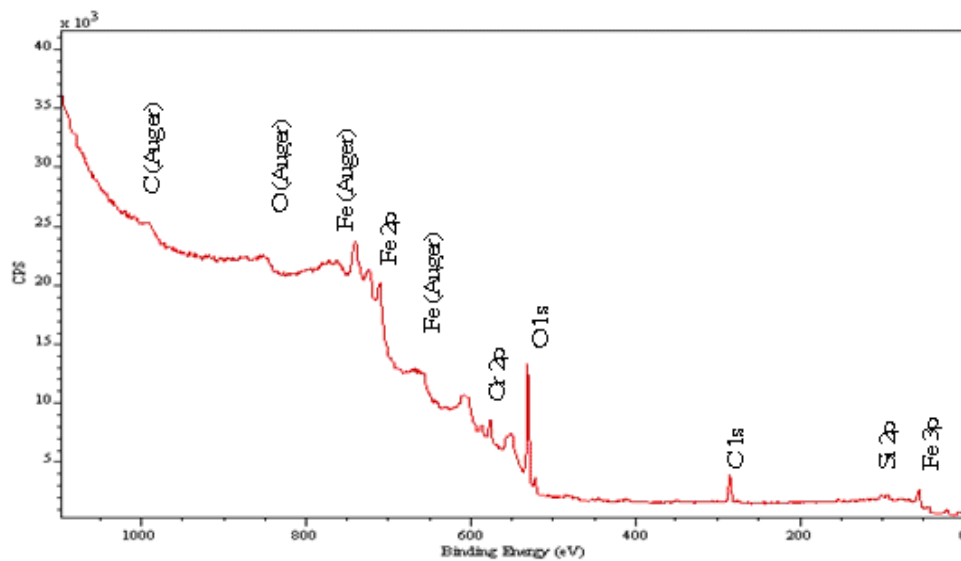
XPS survey, multiplex and deconvolution analyses were performed on samples RP2, RP3, RP5 and RP8 for the determination of chromium oxidation state. Samples RP2 and RP3 were reheated at 1250°C, for 3h, 4% O₂ in gas (RP3 covered with flux type 832; C_f = 0.015 g/cm²). Samples RP5 and RP8 (RP8 also covered with flux type 832; C_f = 0.015 g/cm²) were reheated at 1280°C, for 6h, 4% O₂ in gas. The following XPS spectra give the results of the analyses performed on samples RP5 and RP8.



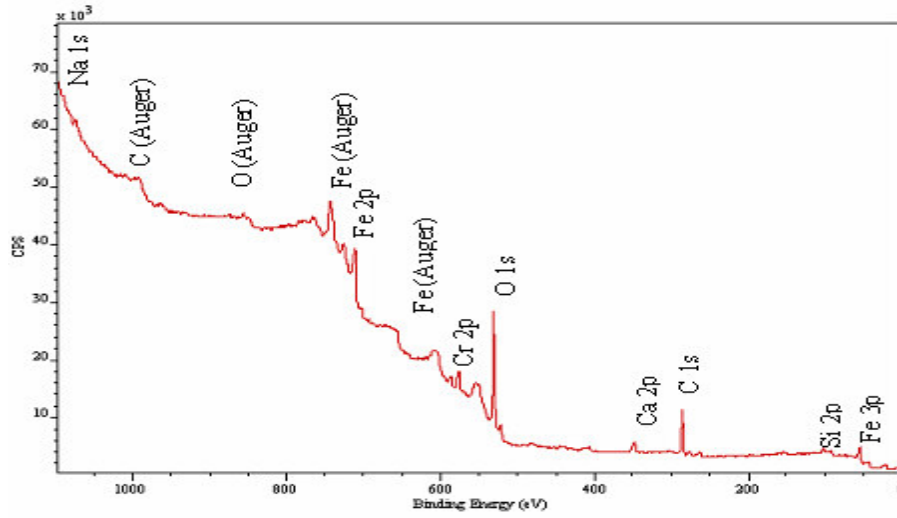
XPS deconvolution for chromium quantification of the uncontaminated sample RP5 reheated at 1280°C, 4%O₂, for 6 hours



XPS deconvolution for chromium quantification of the contaminated sample RP8 reheated at 1280°C, 4%O₂, for 6 hours



XPS Survey of the scale removed from the uncontaminated sample RP5 reheated at 1280°C, 4%O₂, for 6 hours.



XPS Survey of the scale removed from the contaminated sample RP8 reheated at 1280°C, 4%O₂, for 6 hours