1 Introduction

After around 10 years operation of the AKPC (Amir Kabir Petrochemical) duel feed cracker in Bander Imam, the transfer line exchangers of 6 from 7 furnaces have been replaced in 2016. The replaced TLEs were locally manufactured by two manufacturers where the original technical drawings, PQR and WSP were used as reference. After 14 month of operation, 4 of the replaced transfer line exchanger suffer leaks. During a site visit on 19th – 21st of April 2017, by Martin Opitz (Systems Engineering) and Shant Krekorian (Materials Engineering), the damaged TLE of furnace 4 (TL-1411C) was inspected. Samples from the damaged TLE were taken and investigated in LE headquarter, Materials Technology Department (ENQM). Water samples are analysed by Chemical Services at R&D department.

Target of this investigation is to find the root cause of this failure and to give recommendation for planned repair work on site.

2 Technical Data

Object:	Transfer line exchanger (TLE) tube sheet samples (TL-1411C)
Client:	Amir Kabir Petrochemical Plant (AKPC)
Time of failure:	01.04.2017
Sample:	TLE tube sheet samples
Dimensions:	Outer tube: Ø 73 x 5.6 mm; Inner tube: Ø 51 x 6.3 mm Oval header: 12 mm
Material:	Inner tube and Oval header: SA 209 Gr. T1a Outer tube: SA 106 Gr. B
Manufacturer:	Original Alstom; Copy: Pidemco
Type / Drawing No.:	101078-81-21-Z0-03
Code requirements:	ASME Sect. VIII Div. 1
Fluid:	Outer tube: BFW / Steam Inner tube: Cracked gas
Temp. / Pressure (Design):	Inner tube: 375 °C / 140 bar; Outer tube: 340 °C /4.5 bar

3 Abstract

The instable magnetite layer is the main cause of the failure. As a consequence, corrosion is taking place underneath the magnetite layer which leads to continuous layer flacking until leakage. Obviously, the process conditions during start-up and normal operation did not allow the formation of a stable magnetite layer. The source of Ca, P, Cl and S found underneath the magnetite layer is unclear. Following factors contributed to the damage: (1) No proper surface preparation i.e. chemical cleaning prior to start up. (2) High temperatures due to local flow restriction, deposit accumulation and insufficient cooling. (3) Manufacturing quality; (a) no full penetration of tube to tube sheet weld (b) Manufacturing leftovers in the oval header (c) improper storage (during inspection, new TLE found to have water in the oval head).
Provided that the design of the copy TLE used to be identical with the original, the following shall be considered in case of tube repair: (1) Mechanical cleaning after repair. (2) Chemical Cleaning. (3) welding with full penetration. (4) Potential repair welds shall be carried out as per original WPS and shall not affect the local flow conditions.

Distrib. to:	A. Mazraeh / AKPC	A. Nobakhto / AKPC	M. Opitz / PCDS	Dr. Schutze / PCDO	F. Penner / PCM	ENQM Original

01	09.06.17	Krekorian / ENQM	Dr. Grundwürmer / ENQM	Dr. Köpf / ENQ	
Issue	Date	prepared by	reviewed by	approved by	remarks

3.1 Failure Description (Attachment TRT 17 So 026.01)

The original double tube TLEs of Amir Kabir Petrochemical plant. 6 out of 7 TLEs were replaced by locally manufactured after 10 years of operation. AKPC uses 5 liquid feed furnaces (Naphtha) and 2 gaseous feed furnaces (see Fig. 1.1). The design of double tube TLE of liquid and gaseous feed differs slightly (refer to Fig. 1.2, Fig. 1.6 and Fig. 1.7) in which the TLEs of gaseous feed furnace have more tubes (Naphtha = 36 tubes, Gas = 60 tubes) and the water inlet for the liquid feed furnace is only on one side compared to two sides for gaseous. After 15 months of operation 4 leaks occurred in 4 different TLEs. The operational history of furnace No. 4 is shown in Fig. 1.3. Fig. 1.4 shows the damaged tube of furnace 4 (TL 1411C) in which the leak caused an immediate furnace shut down (BFW ingress into the cracked gas stream). During the site visit, TL 1511A (furnace 5) had a leak were almost the entire circumference of the tube was damaged as seen in Fig. 1.5.

The locations of failed tubes are seen in Fig. 1.6 and Fig. 1.7 for liquid and gas feed respectively.

The original technical drawings, and Welding Procedure Specifications (WPS) were used for re-manufacturing of the TLEs. As per AKPC an alkaline boiling out was done on the manufactured TLEs as per original manufacturer procedure before operation. This procedure specifies the use of trisodium phosphate Na_3PO_4 (with 20 % P_2O_5 content).

Samples were obtained from TLE 4C (TL 1411C) together with 4 water samples (from furnace 6 blow down, Demin Water make up, Turbine condensate and BFW) for analysis. The specified material of inner tube and tube sheet is SA 209 Gr. T1a where the composition is given in table 1 below.

Table 1: material composition of SA 209 Gr. T1a steel

Elements	C ≤	Mn	P ≤	S ≤	Si ≤	Mo
[%]	0.15–0.25	0.3–0.8	0.045	0.045	0.1–0.5	0.44–0.65

3.2 Visual Examination (Attachment TRT 17 So 026.02)

A borescope was used to inspect inside the TLE 4C (TL 1411C). The image helped to select the right samples. As seen in Fig. 2.1, the flaking /spalling of oxide layer visible starting from the tube to tube-sheet (oval header) interface point and extending roughly up to the height of 4−5 mm of the tube. Inside the oval header deposits and corrosion products were covering the tube-sheet/oval head surface. Tube-sheet front view (cracked gas inlet side) of TLE 4C is seen in Fig. 2.2 after removing of samples. For a better sample identification, the samples are re-numbered as per their position within tube sheet. The back side of oval header (internal surface) and outer tubes are seen in Fig. 2.3 and Fig. 2.4 representing the 2nd and 3rd row tube sheets respectively where the oval header is filled with corrosion product. In Fig. 2.5, the 5th tube of 6th row which was cut as investigation sample is shown (same tube as demonstrated in Fig. 2.1). The tube is located at the end of the oval header (last tube of the row). After cutting, great amount of loose scale fell off. The corroded parts are at the backside of the tube, with respect to the flow direction, as seen in Fig. 2.6. For further investigation, four samples were cut out of the tube from which sample 1 and 2 are from corroded surface and are located on back side of the pipe (opposite side of flow direction). Sample 3 and 4 are located on the front side of the tube/perpendicular to the flow direction. In the same manner, sample 1 and 3 are at the same height and opposite each other (located next to the tube sheet). The same applies for sample 2 and 4 (located further away from the tube sheet) as seen in Fig. 2.6. The circumference of inner tube is seen in Fig. 2.7 in which the material loss (tube wall thickness) of the tube with respect to flow direction is clearly documented.

The cut tube sheet samples of 2nd and 3rd rows (TS2 and TS3 as in Fig. 2.2) are seen in Fig. 2.8 and Fig. 2.9. The tube sheet lost 4 mm of the thickness and corrosion on tube is started at the groove (refer to Fig. 2.9).

Fig. 2.10 shows manufacturing residuals / leftovers found during borescope inspection within the oval header of TLE 4C.

3.3 Water Analysis (Attachment TRT 17 So 026.03)

Four water samples were brought from AKPC for analysis in chemistry labs of Linde Engineering Headquarters. Samples were taken from following locations:

- Blow down steam drum
- Demin make up water
- Turbine condensate
- Boiler feed water

The analysis showed no noticeable abnormality.

3.4 Metallography, SEM and EDX Investigation (Attachment TRT 17 So 026.04)

The cross sections of samples cut from TL 1411C as shown in Fig. 2.6 were metallographically investigated. Fig. 4.1 shows the cross section of sample 2, (refer to Fig. 2.6 for location) where the material loss on water side is clearly seen. The thickness of magnetite layer is not uniform on the cross section. The inhomogeneous/instable magnetite layer is cracked and deposits are concentrated between the base material and magnetite layer as seen by scanning electron microscopy (SEM) in Fig. 4.2. The layer formation is not as expected for a stable magnetite layer known in steam systems. Surface of sample 4 (located at same height to sample 2) is seen in Fig. 4.4 and Fig. 4.5 which shows a magnetite layer much thinner than that of sample 2. In addition the material loss is very low in this location. Furthermore, cross section of sample 1 which is located on the back side of the tube (with respect to flow direction) and next to the tube-sheet was inspected as in Fig. 4.7 and Fig. 4.8. The inhomogeneous magnetite layer consist mainly of porous layer.

An elemental mapping analysis technique is used to analyse the surface of cross sections of sample 2, sample 4 and sample 1 where the results are shown in Fig. 4.3, Fig. 4.6 and Fig. 4.9 respectively. Sample 2 showed the concentration of S and Cl underneath the magnetite layer (refer to Fig. 4.3). Sample 4, as in Fig. 4.6, shows Ca and P within the whole magnetite layer. Sample 1 as in Fig. 4.9, shows of Ca within the porous layer as well as S and P underneath the magnetite film.

The Energy Disperse X-Ray (EDX analysis), as in Fig. 4.10, shows that the composition of the base material of the tube is in the range of the specified material.

4 Discussion, Interpretation

The structure of the magnetite layer was identified to be inhomogeneous and does not appear like a stable magnetite layer typically known from adequate treated steam system, and hence the magnetite layer was providing no protection and the destroyed oxide layer was flacking/spalling continuously. The deposits (i.e. S, P, Ca and Cl) found underneath the magnetite layer promote corrosion when electrolyte (i.e. water) is available. The magnetite layer is created ideally after chemical cleaning of carbon steel surface followed by immediate operation. Misconducting or missing of this step could be the main reason of the instable / inhomogeneous magnetite layer.

Simple dimension check of oval header width (of tube-sheets cut as in Fig. 2.2) shows discrepancy. Nevertheless, tools used/measuring possibilities were not ideal and hence no conclusions can be made whether dimensions of the manufactured TLEs are matching the technical drawing. In this regard, it was noted that oval headers have different flow rates as per Schmidt'sche® design and hence, oval headers must have different dimensions. Since leaks occurred in tubes located at the end of oval header (among last tubes of a row with dead end), assumption is made that these locations are of highest water temperature. Material loss due to corrosion took place at the backside of the tubes (with respect to flow direction). These factors combined can lead to an accelerated corrosion.

Manufacturing residues/leftovers found inside oval header and large grooves between tube-sheet and tubes are signs of improper manufacturing.

Water found during inspection of new standby TLE reviled high amount of water at the oval header which indicates improper preservation after manufacturing.

Water analysis of four samples obtained from site showed no noticeable abnormalities. The source of the detected deposit inside and underneath the magnetite layer is unknown and may go back to earlier up-set conditions. It is possible that P element originates from trisodium phosphate which was used during alkaline boiling out after manufacturing of TLEs.

5 Recommendations

The investigation shows that the leaked tubes were not a single case incidents and that continuing of operation will yield in other leaks on the shorter run. For this reason a major repair (or replacement of TLE) shall be done on all TLE tubes at the lower oval header part where the following shall be considered (assuming original design) :

- Mechanical cleaning of oval header from residuals.
- Chemical cleaning just prior to start up.
- Exclusion of process up-sets in BFW treatment (also short-term) causing S, P, Ca, and Cl deposits.
- Welding with full penetration.
- Welding as per the original WPS and potential repair welds shall not affect flow conditions.

6 Attachments, Documentation

Attachment TRT 17 So 026.01	Failure Description
Attachment TRT 17 So 026.02	Visual Inspection
Attachment TRT 17 So 026.03	Water Analysis
Attachment TRT 17 So 026.04	Metallography, SEM and EDX Investigation

7 Storage of Samples/Specimens

The investigated samples / tested specimens will be stored at Linde LE for minimum 1 year. Unless other instructions received from client, the samples will be scrapped after that period.

Failure Description **Attachment TRT 17 So 026.01, page 1 of 5**

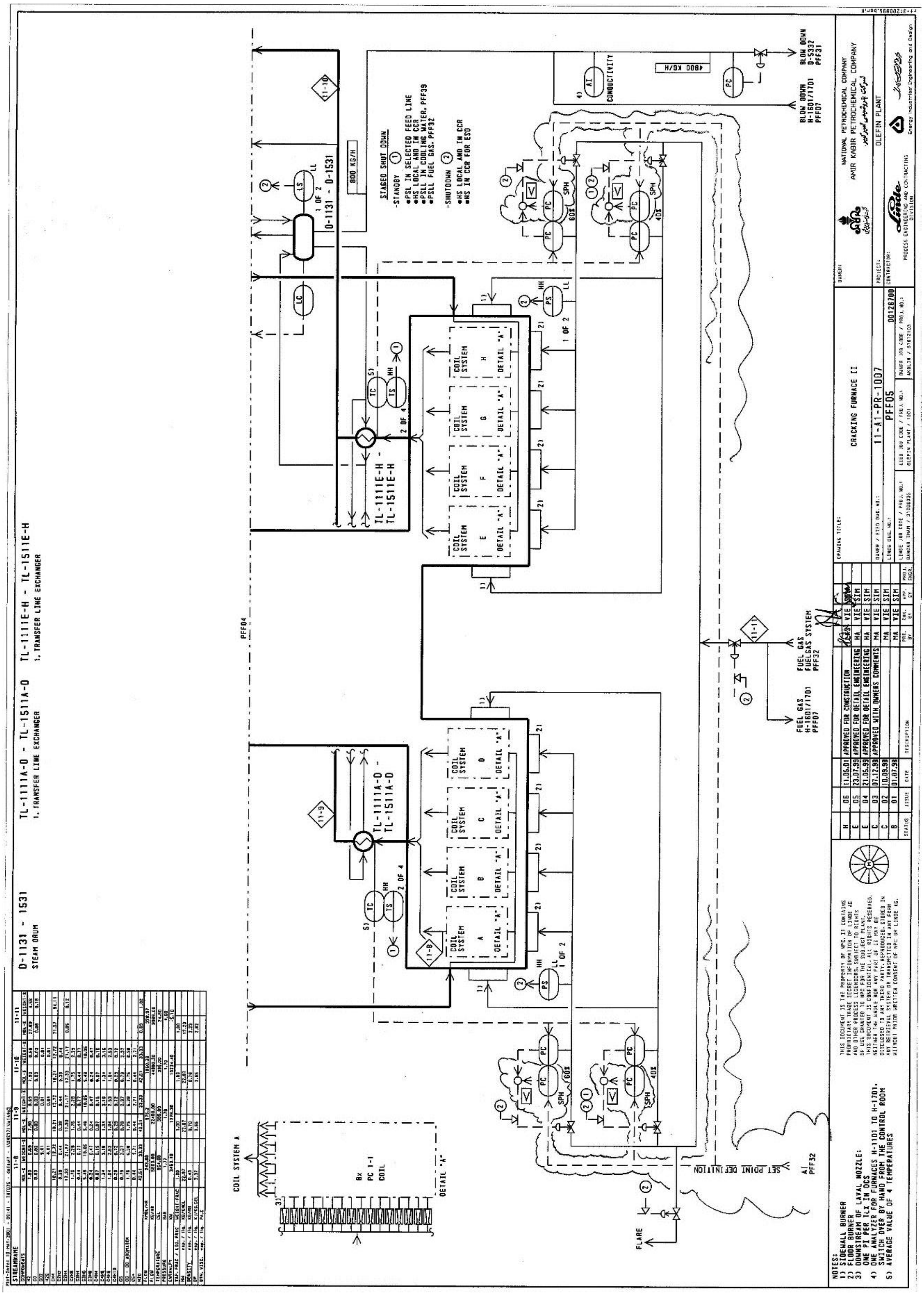


Fig. 1.1: Original process flow diagram showing the position of TLE within the system.

Failure Description **Attachment TRT 17 So 026.01, page 2 of 5**

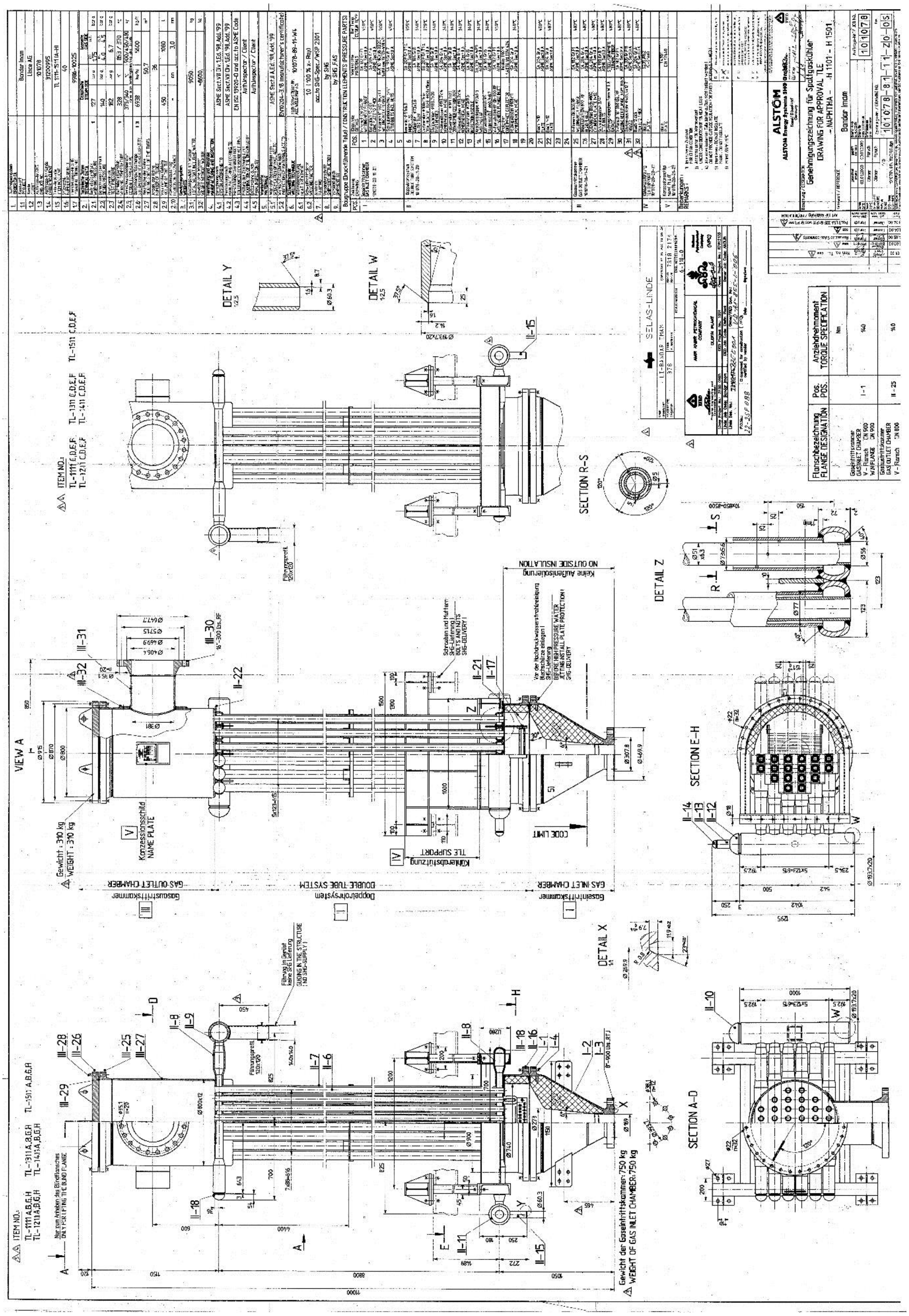


Fig. 1.2: Technical drawing of the TLE Furnace H1101−H1501 (Naphtha), issued on Sep. 2009, Drawing No. 101078-81-11-Z0 Rev. 5.

TLE replacement done on 02/01/16 and failure happen on 01/04/17 or 15 month working time.		
Date(dd/mm/y)	**Duratation**	**Comments**
20/01/16 til 19/02/16	30 days liquid feed	21 to 26 ton/hr
20/02/16 til 22/02/16	3 days ethane feed	23 ton/hr
23/02/16 til 26/02/16	4 days HSS	
27/02/16	Deckoking	
28/02/16	HSS	
29/02/16 til 30/04/16	61 days liquid feed	30 ton/hr
01/05/16 til 24/5/16	24 days ethane feed	10,18,26 ton/hr
25/05/16 til 28/05/16	4 days decoke	
29/05/16 til 17/06/16	20 days repair work	Furnace is stoped because of Damages on its roof.TLX were cleaned by air.
18/06/16 til 21/06/16	4 days Dry out	
22/06/16 til 25/06/16	4 days Warming up and HSS	
26/06/16 til 29/06/16	4 days decoke	Due to uncomplete decoking and high coil pressure.
30/06/16 til 02/07/16	3 days HSS	
03/07/16 til 31/07/16	29 days liquid feed	21 to 30 ton/hr
31/07/16 til 16/08/16	16 ethane feed	
17/08/16	HSS	
18/08/16 til 21/08/16	4 days decoke	
22/08/16 til 02/09/16	12 days HSS	
03/09/16 til 08/11/08	67 liquid feed	
11.09.2016	HSS	
10/11/16 til 14/11/16	5 days decoke	
15/11/16	HSS	
16/11/16 til 28/12/16	43 days liquid feed	
29/11/16 til 02/01/17	5 days decoke	
03/01/17 til 04/01/17	2 days HSS	
05/01/17 til 23/01/17	19 days liquid feed	
24/01/17	HSS	
25/01/17 til 27/01/17	3 days ethane feed	3 to 8 ton/hr
28/01/17 til 30/01/17	HSS	
31/01/17 til 01/02/17	2 days ethane feed	
02/02/17 til 06/02/17	HSS	Plant shutdown
07/02/17 til 24/02/17	17 days ethane feed	on 09/02/17 furnace tripped because of failure in PV-14804B in fuel gas to furnace
25/02/17	HSS	
26/02/17 til 01/04/17	35 days liquid feed	

Fig. 1.3: Operation date of furnace No. 4 starting after the replacement of transfer line exchangers till ending with the failure C.

(a) (b)

Fig. 1.4: View of the damaged tube of the TLE (furnace 4, TLE C); (a) In position inside the TLE (crack gas side); (b) After removing from TLE (view from water side). The edges were grinded while removing the welding seam to tube sheet.

Fig. 1.5: View of the damaged TLE tube of furnace 5, TLE A. Almost the entire circumference of the tube was almost damaged (location is 3-4 cm away from tube-sheet).

Failure Description **Attachment TRT 17 So 026.01, page 5 of 5**

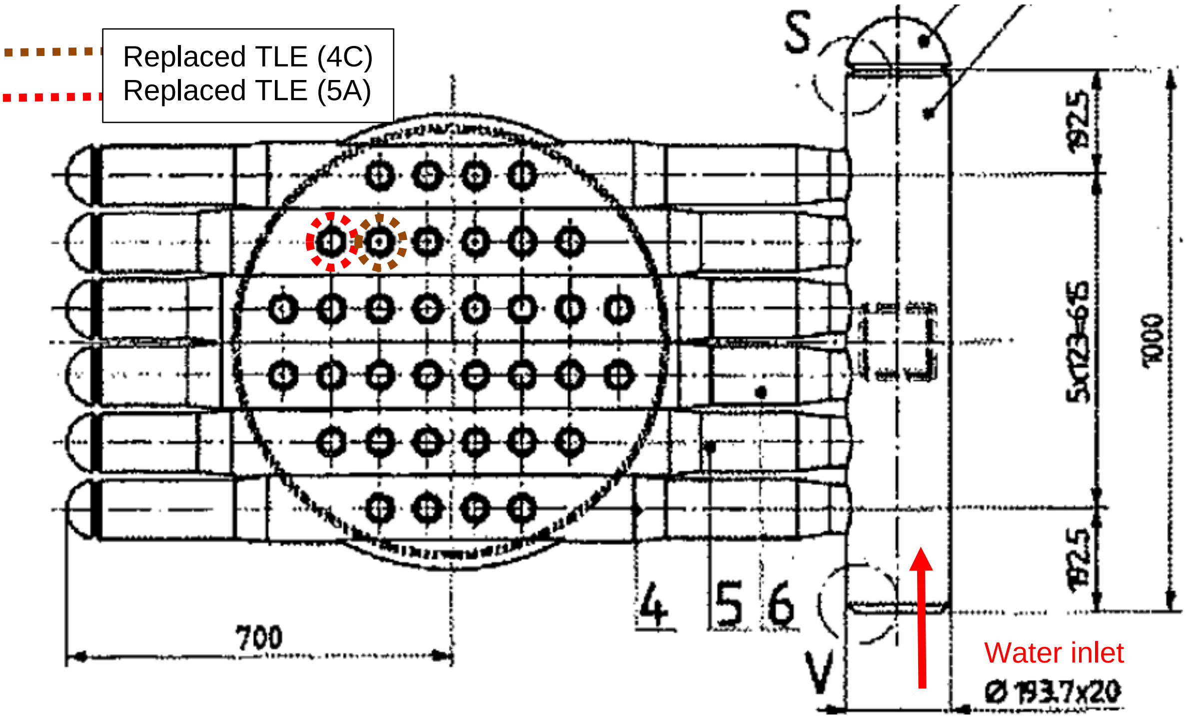


Fig. 1.6: Overview of tube sheet drawing of Naphtha cracking furnace with position marking of the damaged tubes. In total 3 damages took place till date on this TLE type (the position of the 3rd damage is unknown)

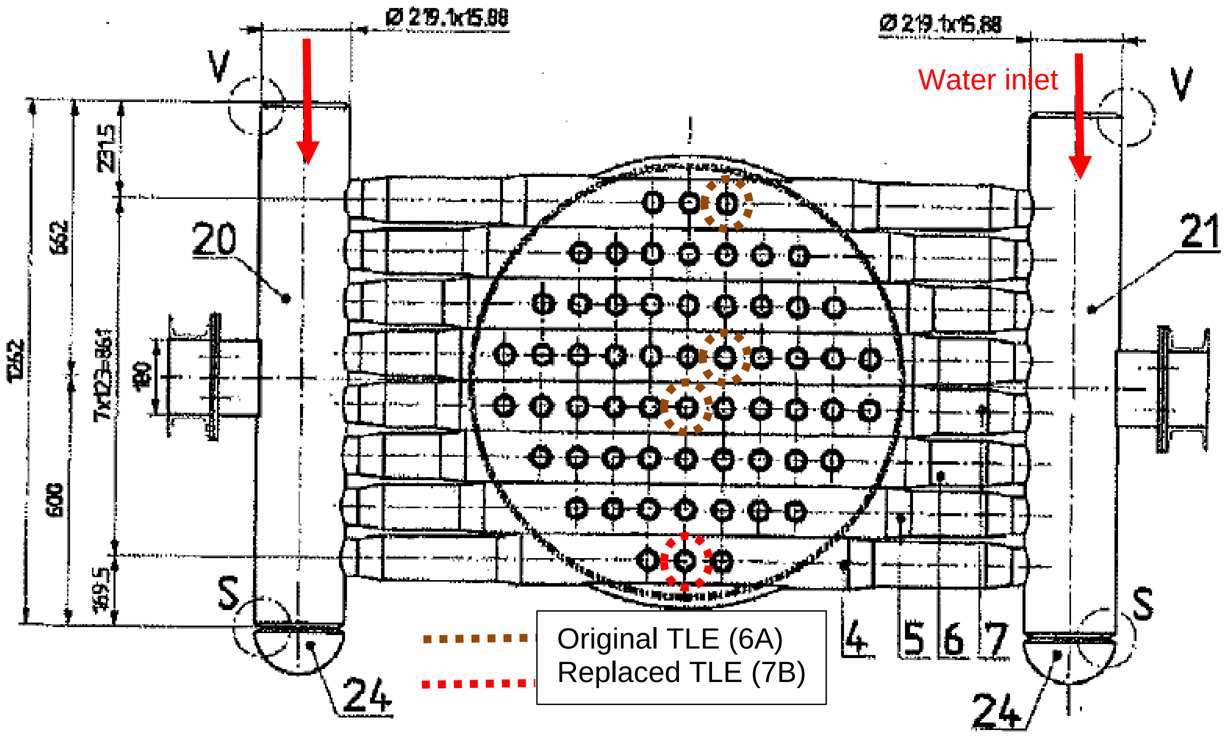


Fig. 1.7: Overview of tube sheet drawing of gas cracking furnace with position marking of the damaged tubes. The red marked tube represents the damaged of the replaced TLE. The brawn circle represents the damaged tubes of an original TLE of furnace 6 still available on site.

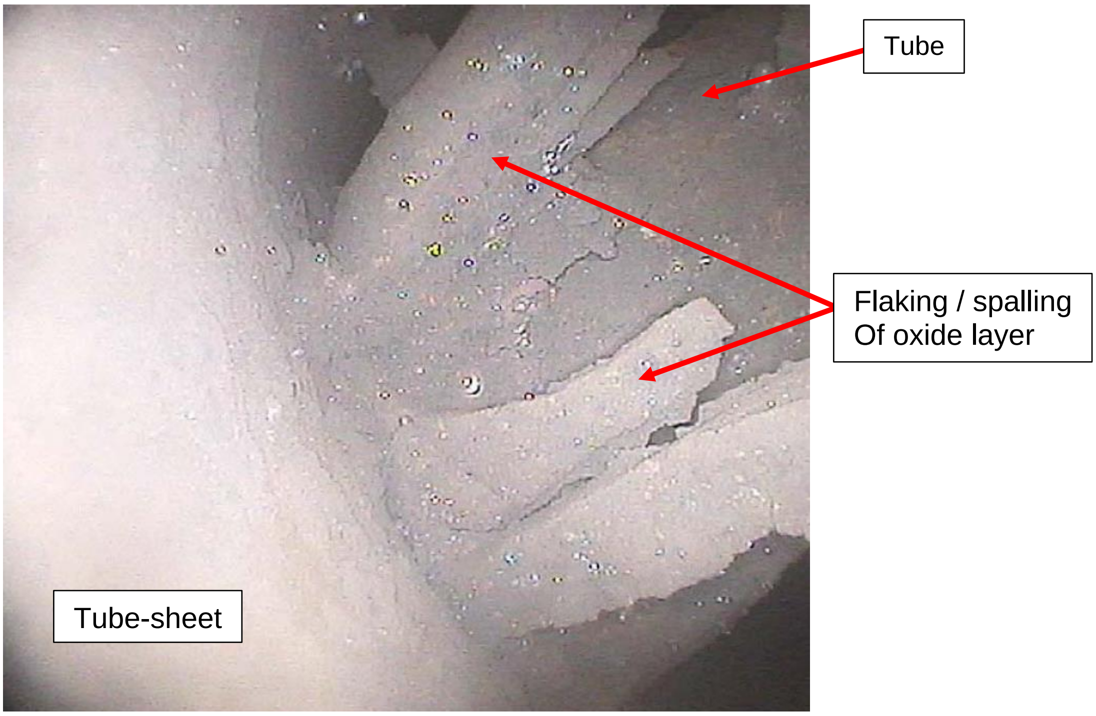


Fig. 2.1: Borescope image of TLE tube (row 6, position 4) of furnace 4, TLE C. The flaking /spalling of oxide layers is seen. Based on this image, this tube was selected as a sample for this investigation (see Fig. 2.5).

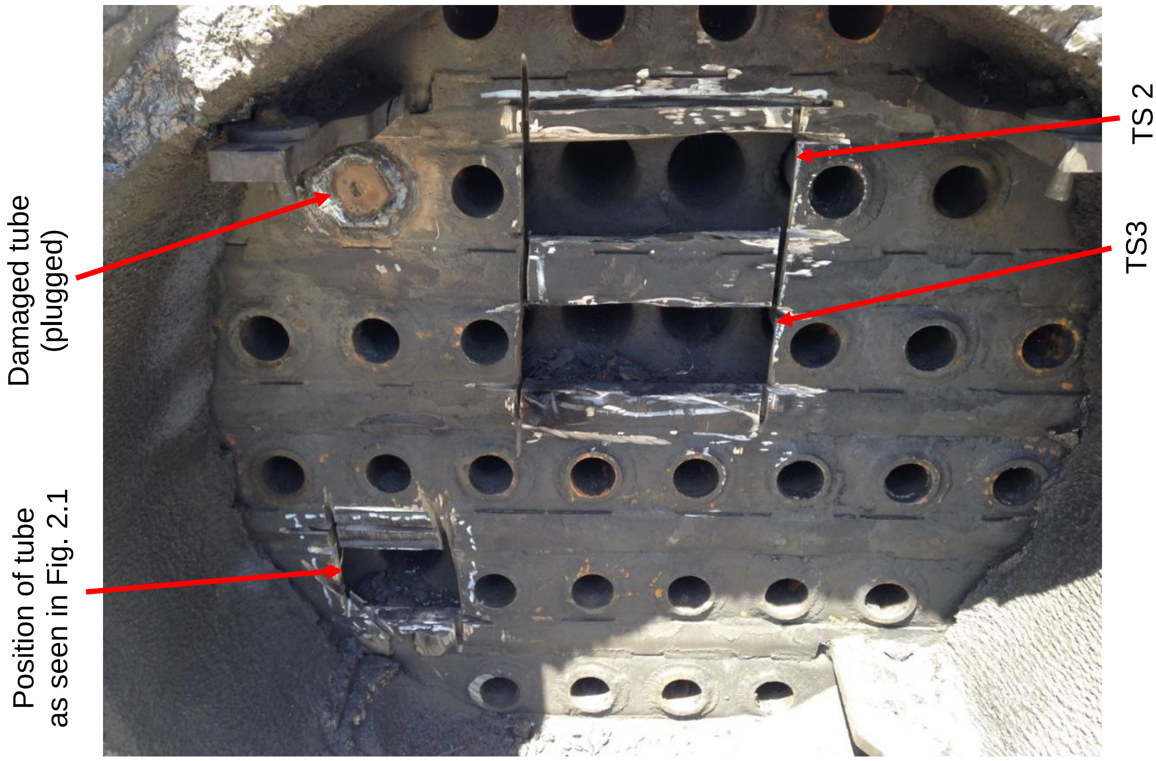


Fig. 2.2: Tube sheet view of TLE C of furnace 4 after removing of selected samples. TS 2 and TS 3 represent the samples of 2nd and 3rd row respectively which was cut out of the tube sheet.

Fig. 2.3: View of the cut tube sheet marked as TS 2 in Fig. 2.2. Position: 2nd row, tube No. 3 and 4. No abnormality is seen.

Fig. 2.4: View of the cut tube sheet marked as TS 3 in Fig. 2.2. Position 3rd row, tube 4 and 5. No abnormality is seen.

Fig. 2.5: Overview of the cut tube as seen in Fig. 2.2. Tube from 6th row, tube No. 5 from furnace 4 C (TL 1411C). The flow direction is shown. Cross section samples were obtained from the red dotted area as seen in Fig. 2.6.

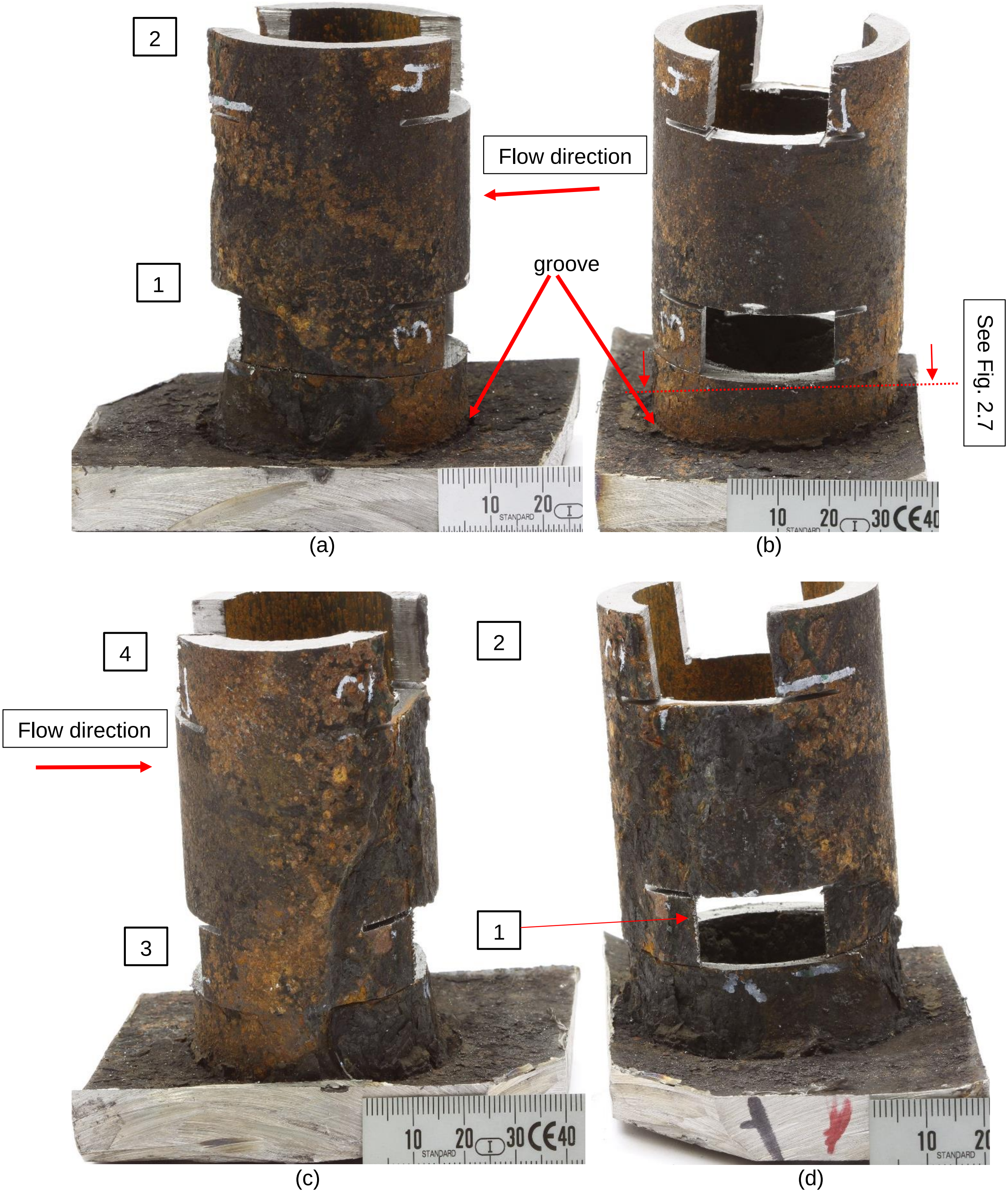


Fig. 2.6: View of samples cut out of tube No. 5 of 6th row, furnace 4 TLE C (refer to Fig. 2.3). In total 4 samples were cut out for further investigation as seen above. The flow direction is given; hence sample 1 & 2 are at the back of the tube with respect to the flow direction.

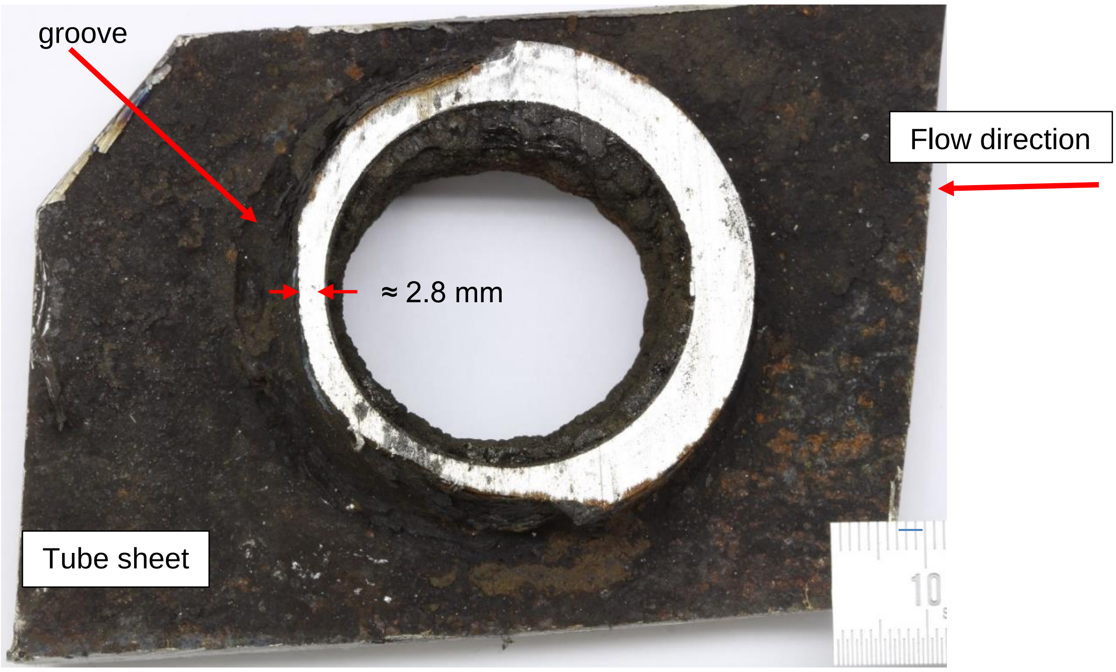


Fig. 2.7: Top view of the cut pipe of the as seen in Fig. 2.5 and Fig. 2.6 b. The tube is partially covered with coke from inside. The corrosion of the tube is clearly seen on the back side of the flow in form of material loss.

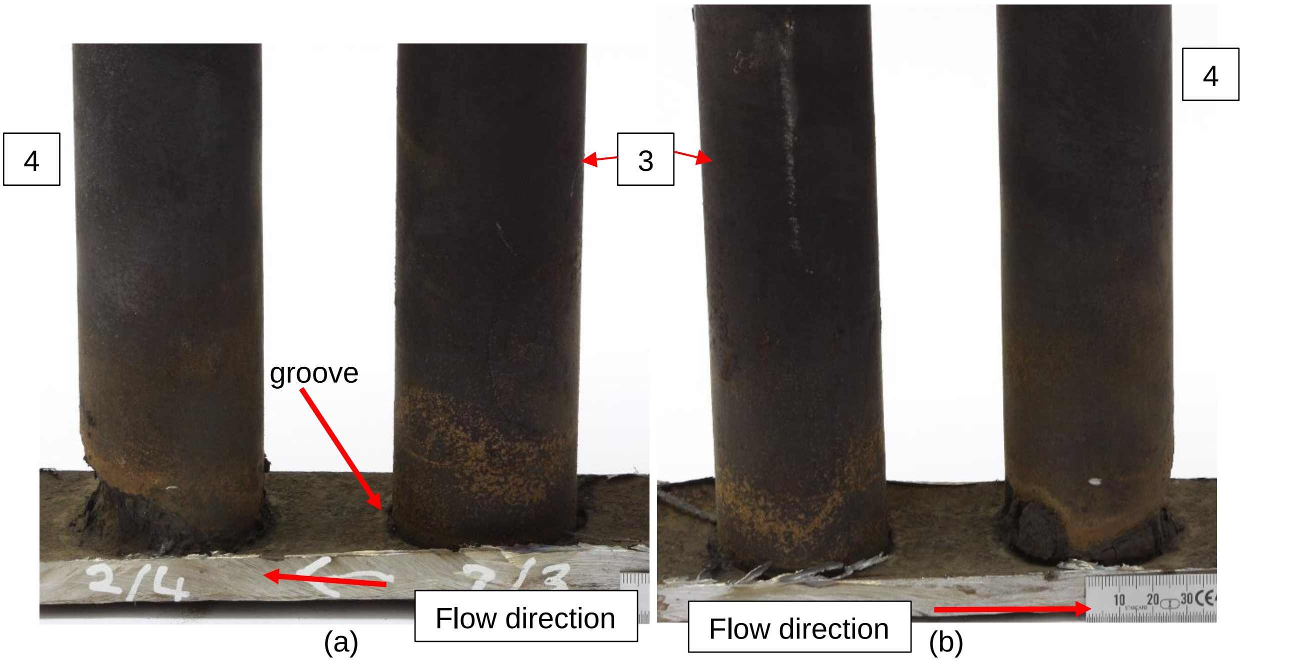
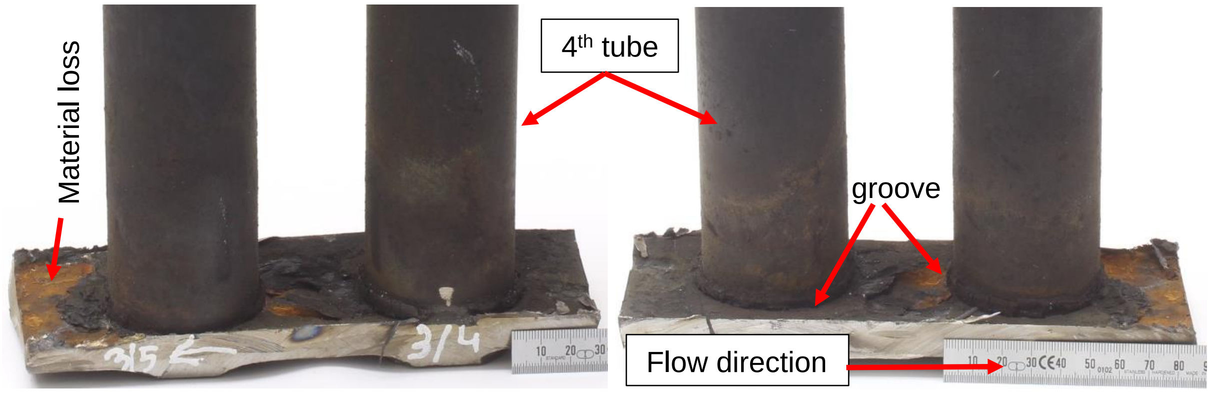


Fig. 2.8: Front and back side view of sample TS2 (with respect to flow direction) as seen in Fig. 2.2. Flow direction is given in both figures. The tube sheet represents the 2nd row of TLE C of furnace 4. Tubes are the 3rd and 4th in row with respect to flow direction. The 4th tube is totally highly corroded in a position on the back side of the flow at a position next to welding groove. Tube No. 3 shows some surface corrosion traces but no flaking is seen.



(a) (b)

Fig. 2.9: Front and back side view of sample TS3, 3rd row of TLE C of furnace 4, (with respect to flow direction) as seen in Fig. 2.2 with flow direction given. Tubes are the 4th and 5th in row with respect to flow direction. The tube sheet lost 4 mm of the thickness. Corrosion on tube is started at the groove as seen above.

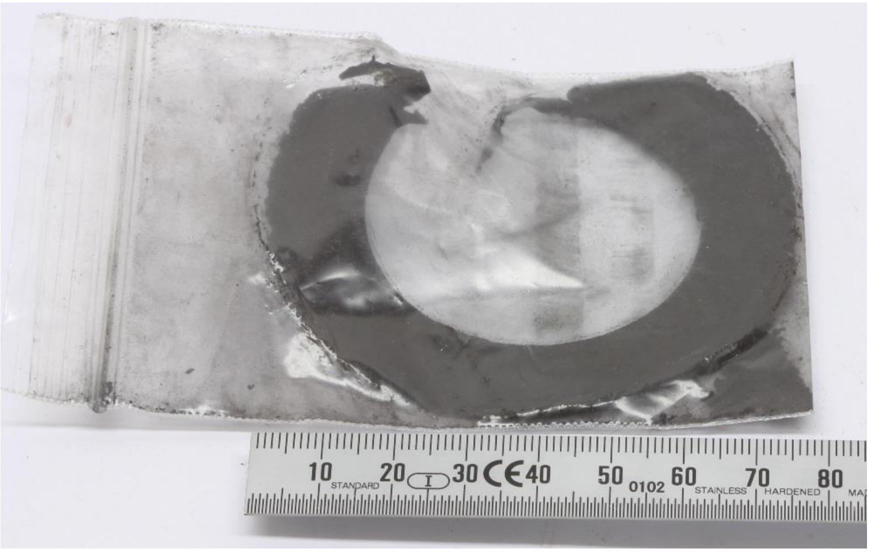


Fig. 2.10: View of leftover /manufacturing residuals within the oval head of TLE C of furnace 4. During the borescope inspection of TLE 4C, this piece was found within the oval head.

Water Analysis

Attachment TRT 17 So 026.03, page 1 of 1

Customer (Name / Dept. / Tel.)	Hr. Martin Opitz / PCDS			Sample received by		Mr. Taube	
Project-No.	3130 BPCE - 9988			Date of Receipt		24.04.2017	
Plant	Bandar Imam JS 10			Analyses finalized		05.05.2017	
Sample ID	RDC-2017-133			Sample Lead		Mrs. Eitzenberger	
Final Report prepared by	Katrin Eitzenberger			Lab. Team		Mrs. Eitzenberger	
		Blow Down Steam Drum Furnance 6; AP.16556 (Hlbo/Bl.down)	Demin Water Make Up; AP.55255 (TK 5502)	Turbine Condensate; AP.55365 (Tur. Cond.)	BFW; AP (54160)(DE5431)		
Parameter	**Unit**	**RDC-2017-133**	**RDC-2017-134**	**RDC-2017-135**	**RDC-2017-136**	**Method**	**Notes**
Physical Parameters							
Sample Volume	ml	1000	1000	1000	1000		
Appearance		clear, colorless	clear, colorless	clear, colorless	clear, colorless	DIN EN ISO 7887	
Conductivity	µs/cm	20	23	5	23	DIN EN 27888	
Chemical Parameters							
pH (measured)		9,1	9,9	9	9,9	DIN 38404-5	
Cations							
Calcium (Ca)	mg/l	<0,02	<0,02	<0,02	<0,2	DIN EN ISO 11885	
Copper (Cu)	mg/l	<0,003	<0,003	<0,003	<0,003	DIN EN ISO 11885	
Dissolved Iron (Fe)	mg/l	0,023	<0,01	<0,01	<0,01	DIN EN ISO 11885	filtered (0,45 µm)
Potassium (K)	mg/l	<0,02	<0,02	<0,02	<0,02	DIN EN ISO 11885	
Magnesium (Mg)	mg/l	<0,02	<0,02	<0,02	<0,02	DIN EN ISO 11885	
Sodium (Na)	mg/l	<0,02	<0,02	<0,02	<0,02	DIN EN ISO 11885	
Silicon (Si)	mg/l	<0,01	<0,01	<0,01	<0,01	DIN EN ISO 11885	
Total - silica (SiO_2)	mg/l as SiO_2	<0,02	<0,02	<0,02	<0,02	calculated	
Total hardness	°dH	<0,03	<0,03	<0,03	<0,03	calculated	
Anions							
Chloride (Cl^-)	mg/l	<0,1	<0,1	<0,1	<0,1	DIN EN ISO 10304-1	
Sum parameters							
Total organic carbon (TOC)	mg C /l	14	24	3,2	24	DIN EN 1484	
Total nitrogen (TNb)	mg N /l	3,5	5,2	0,8	5,2	DIN EN 1484	
n.a. = not analysed Disposal Information: Sample discarded two weeks after reporting.							
Comments							

Fig. 3.1: Chemical analysis of the 4 water samples collected on site. The water analysis is considered to fulfilling the requirements.

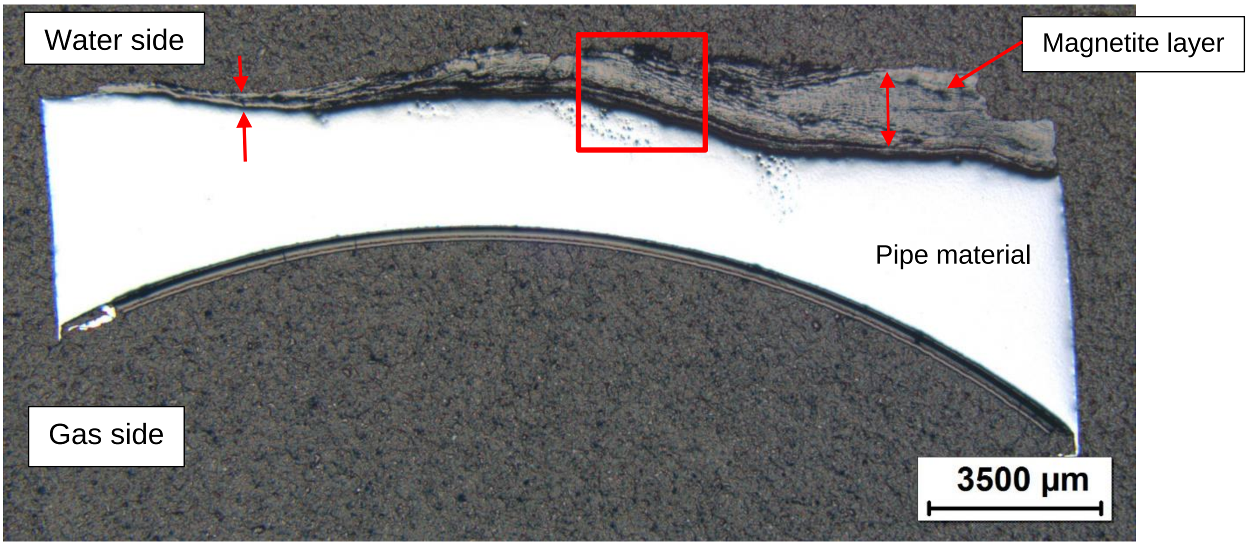


Fig. 4.1: Metallographic image of sample 2 cross section (see Fig. 2.6). The material loss is seen on the cross section as well as the magnetite layer thickness difference throughout the cross section. The red marked area is seen in Fig. 4.2.

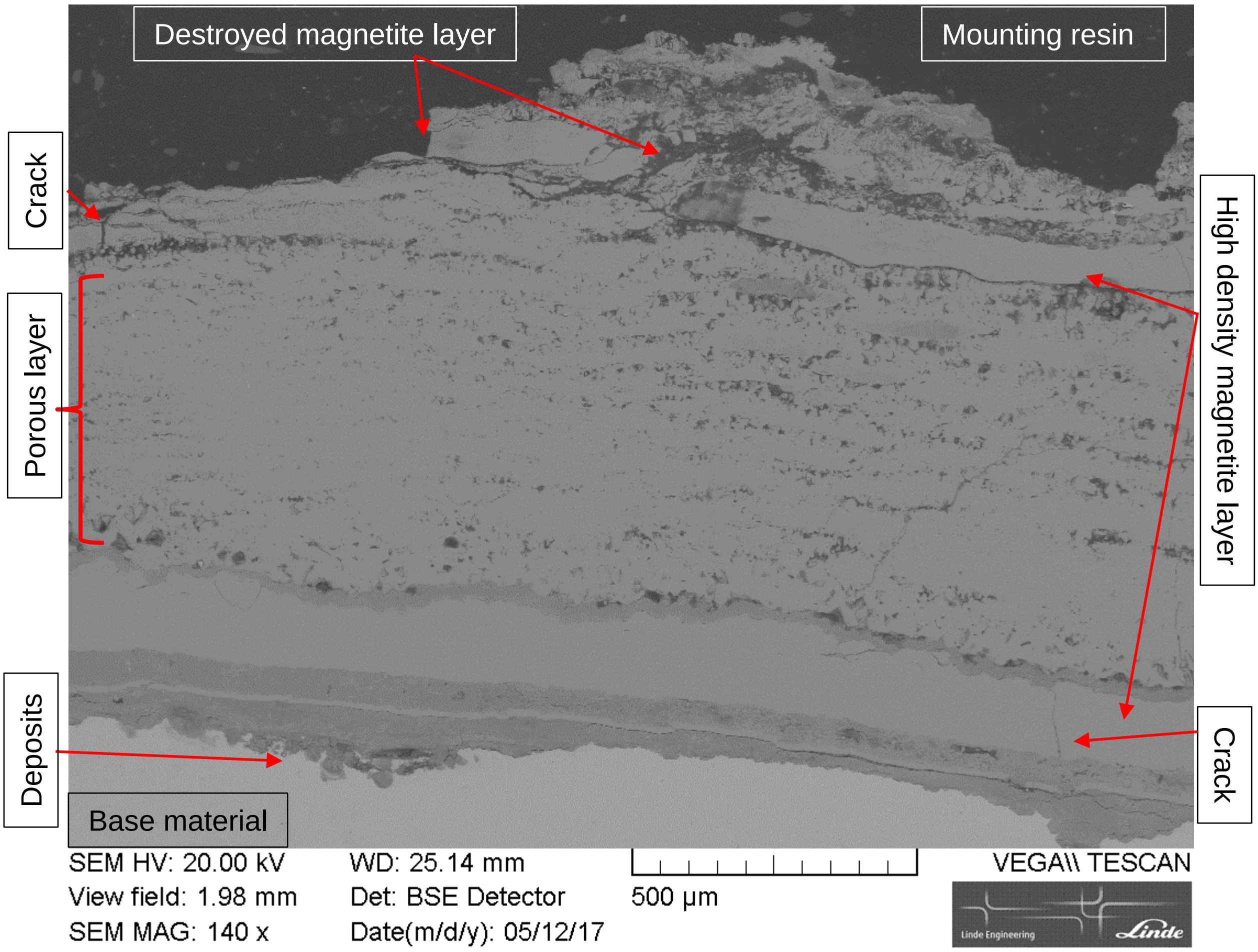


Fig. 4.2: SEM (Scanning Electron Microscopy) image of sample 2 for the area seen in Fig. 4.1 (for location of S2 refer to Fig. 2.6). The inhomogeneous multi-layer magnetite is seen covering the base material. The high-density magnetite layer is available twice, which is partly destroyed and cracked. A layer of deposit is available underneath the hard magnetite layer.

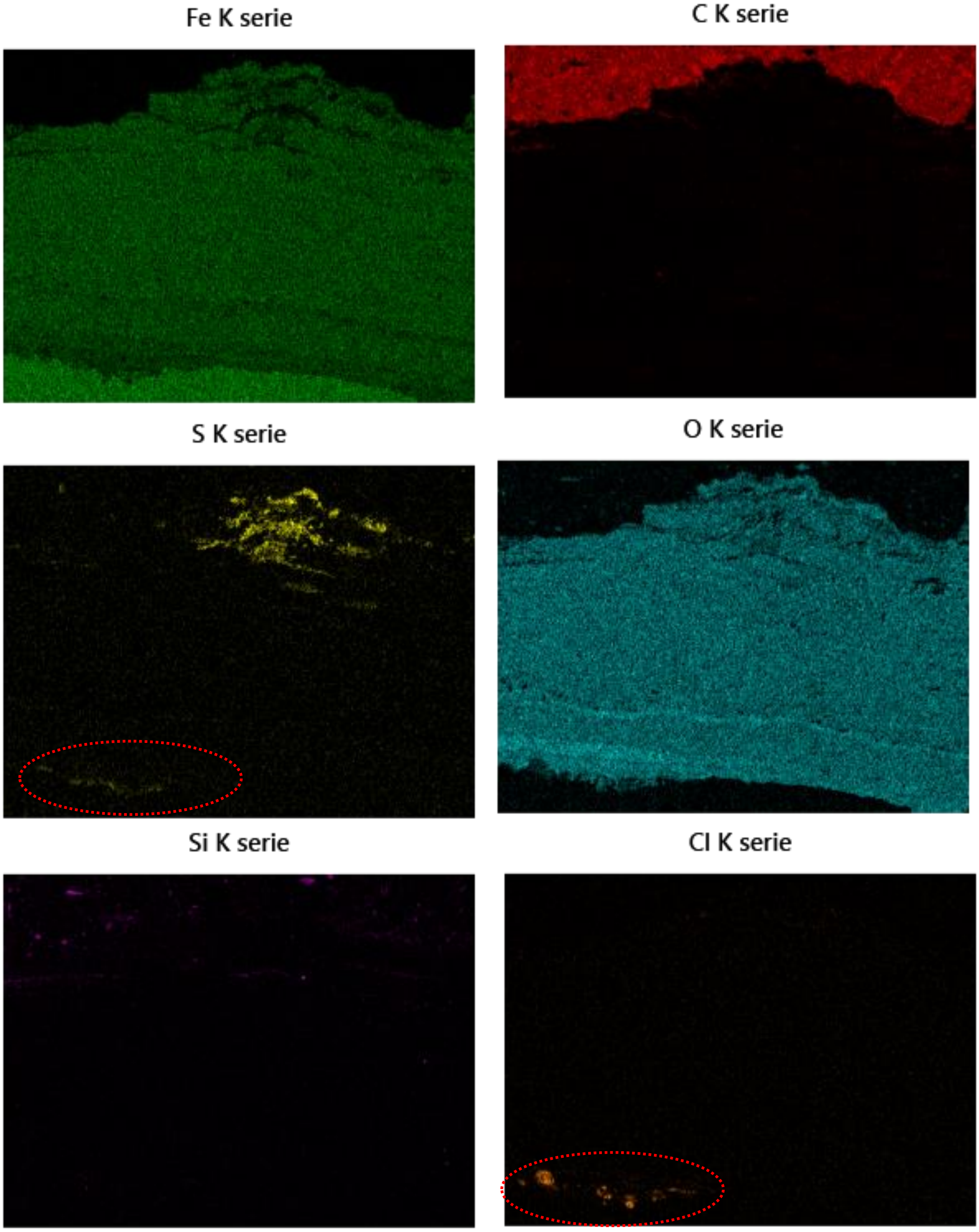


Fig. 4.3: Mapping of sample 2 of the surface shown in Fig. 4.2. The mapping showed the availability of S and Cl underneath the magnetite layer.

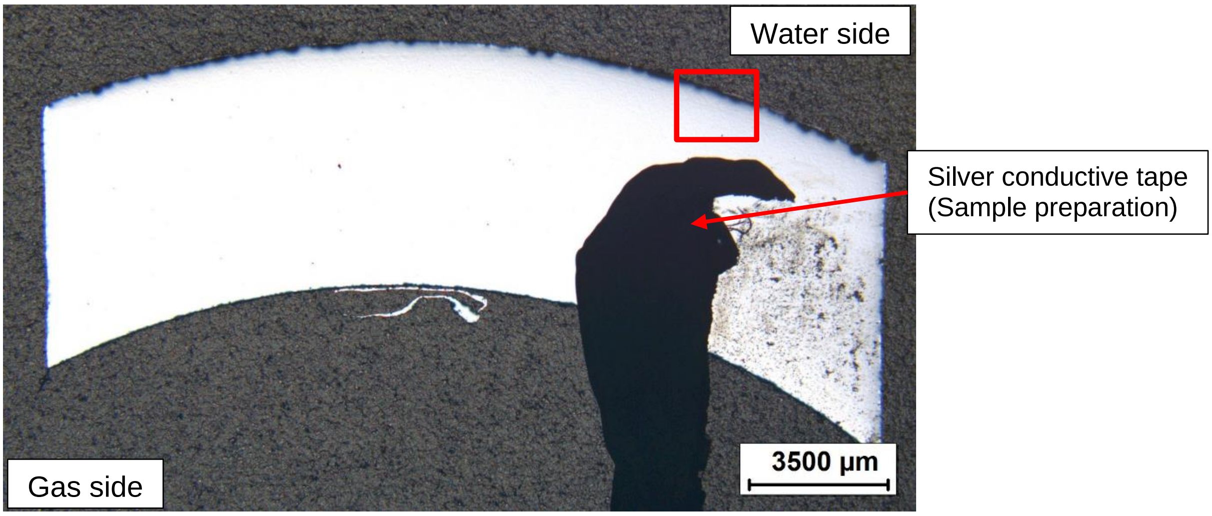


Fig. 4.4: Metallographic image of sample 4 cross section (see Fig. 2.6). Sample 4 is located on the opposite side of sample 2 (refer to Fig. 4.1). The surface is less corroded compared to sample 2. The red marked zone is seen in Fig. 4.5. The

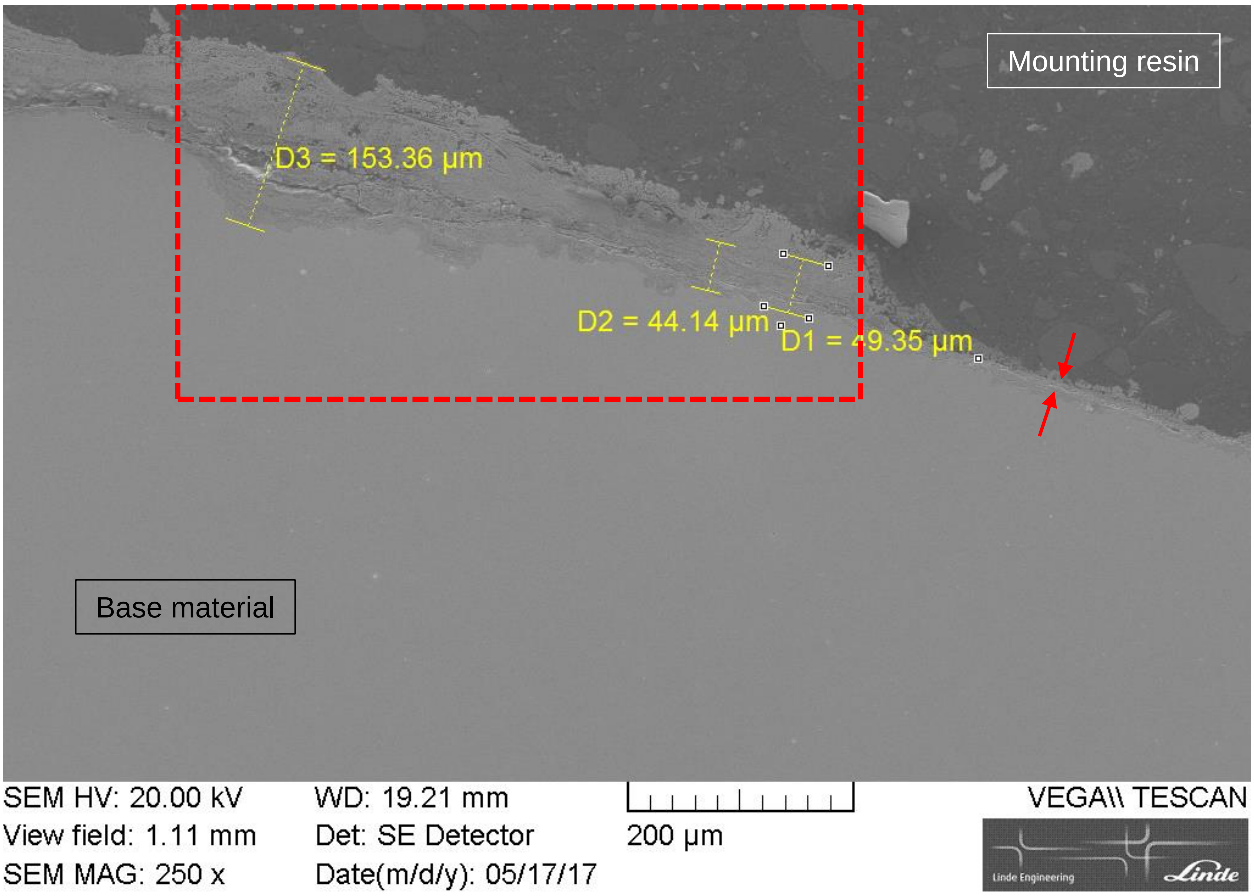


Fig. 4.5: SEM (Scanning Electron Microscopy) image of sample 4 for the area as seen in Fig. 4.4. The magnetite layer is much thinner compared to sample 2. The layer is inhomogeneous and deposits are seen underneath the magnetite layer. The red marked area is the reference for mapping as seen in Fig. 4.6.

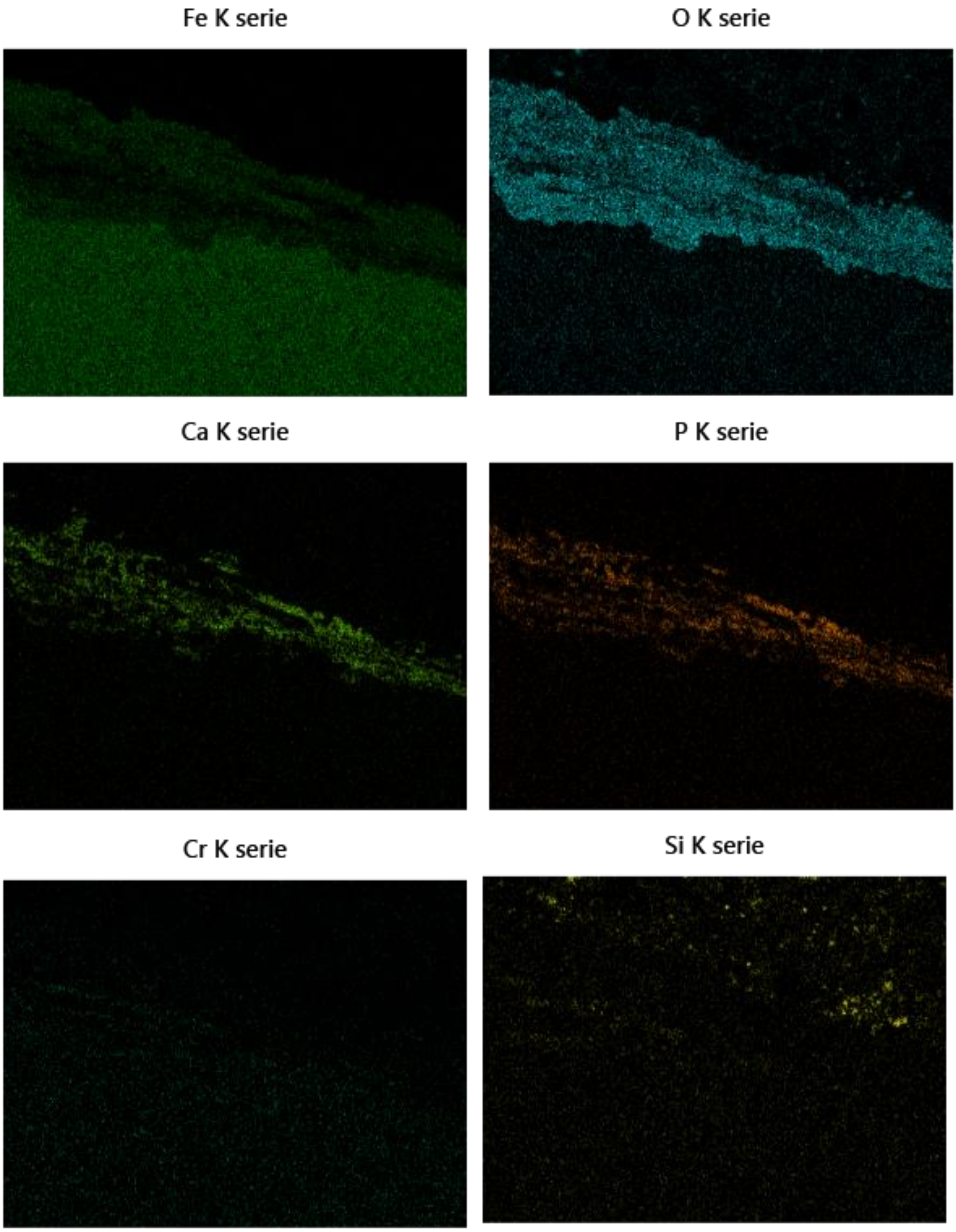


Fig. 4.6: Mapping of sample 4 of the surface shown in Fig. 4.5. Elements of P and Ca are found inside the porous layer.

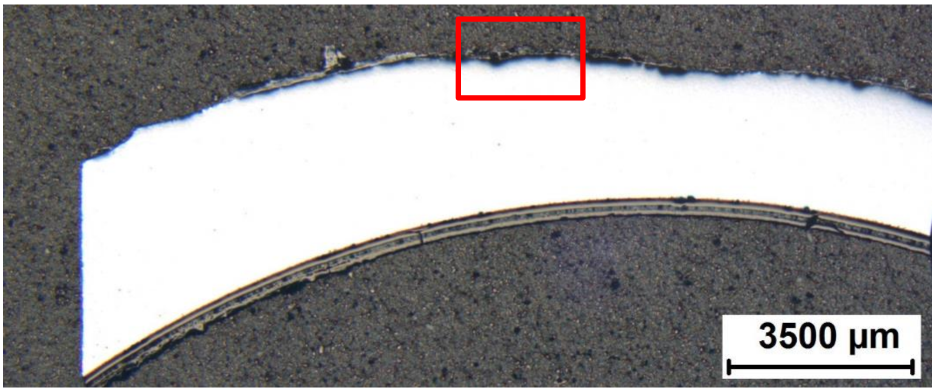


Fig. 4.7: Metallographic image of sample 1 cross section (refer to Fig. 2.6 for location). Sample 1 is located next to the tube sheet on the back of the tube (with respect to flow direction). The red marked area is seen in Fig. 4.8.

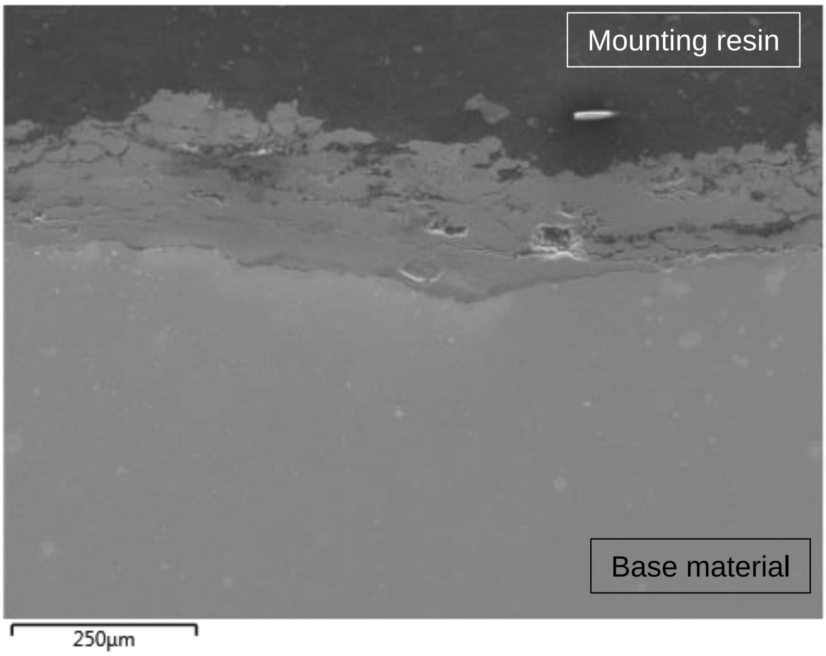


Fig. 4.8: SEM (Scanning Electron Microscopy) image of sample 1 for the area as seen in Fig. 4.7. An inhomogeneous magnetite layer is seen. The image will be the reference image of a mapping scan as seen in Fig. 4.9.

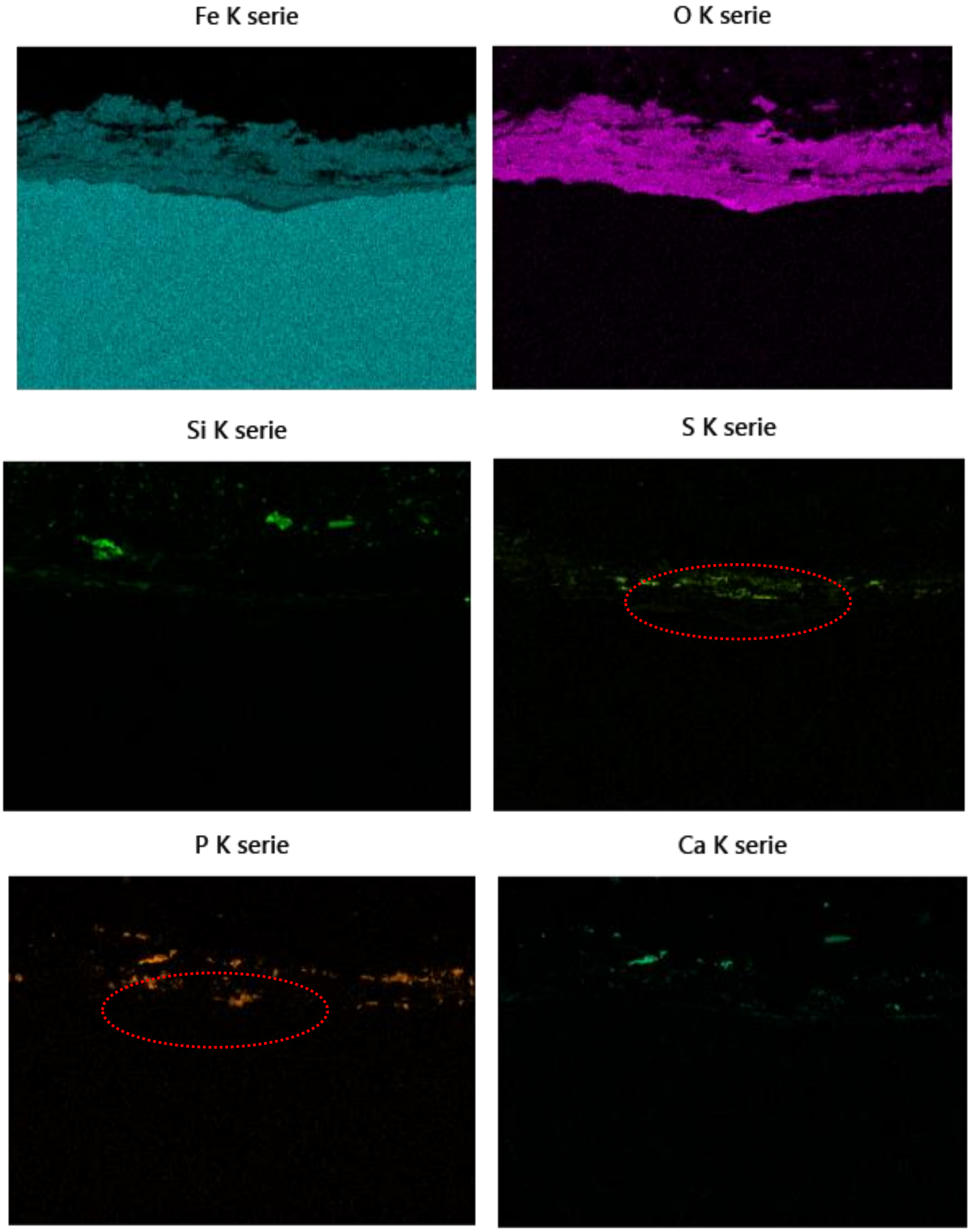


Fig. 4.9: Mapping of sample 1 of the surface shown in Fig. 4.8. The mapping revealed the S, Ca and P elements within and underneath the magnetite layer.

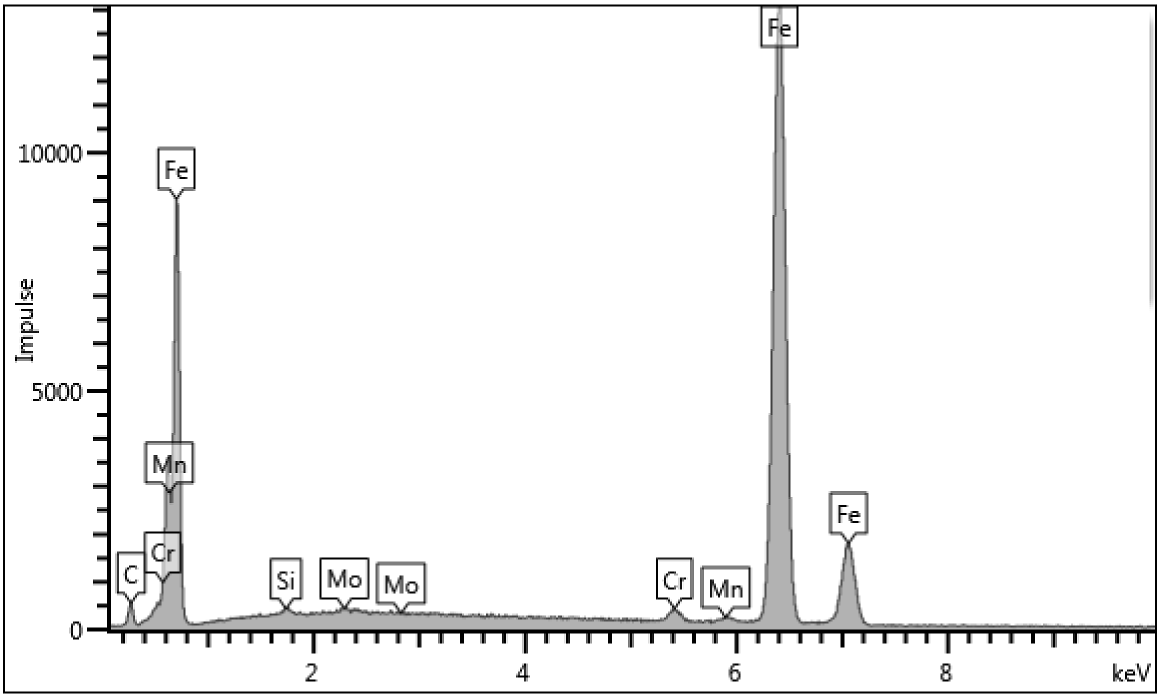


Fig. 4.10: EDX (Energy Dispersive X-ray) analysis of pipe base material analysis. The base tube material is matching with the specified material.