EFFECT OF INDUSTRIAL PROCESS PARAMETERS ON FISHSCALE: ELECTROLUX ITALIA EXPERIENCE.

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23 INTERNATIONAL ENAMELLERS CONGRESS FLORENCE

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AIM OF THIS WORK

The driving force for this activity was the need of having a user-friendly instrument, able to give in a short time (around 30 min) a **numerical evaluation** for the fish-scale defect probability in steels for enamelling. This method should overcome the limits of the currently available instruments and become a valid alternative to the "special test enamel", which results are visible only after 24 hours and after 5 days : in addition the evaluation is made on the steel alone, instead of the evaluation of the "special test enamel" that includes steel + process + enamel.

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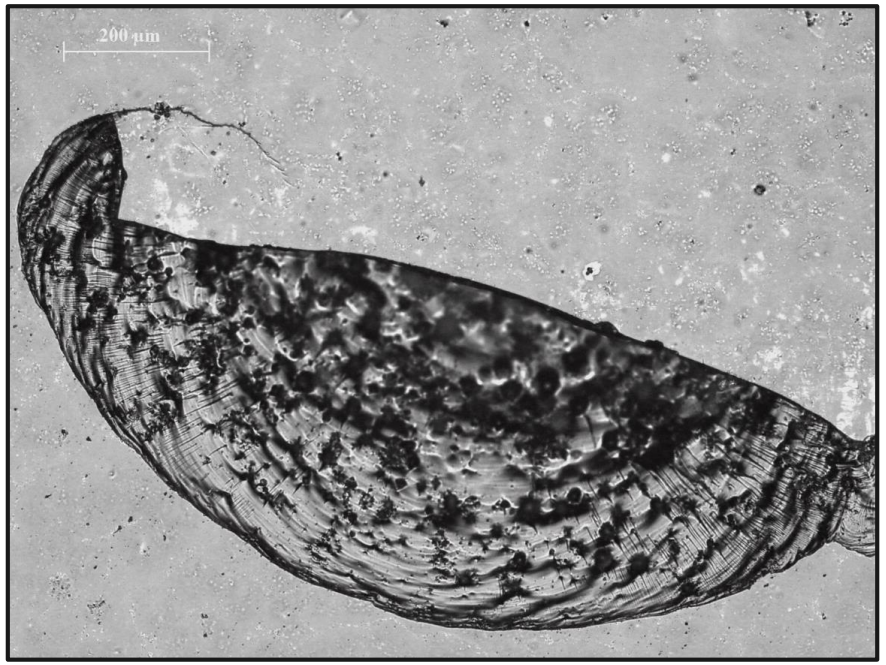
INTRODUCTION: THE FISH-SCALE PHENOMENON (1/2)

Fish-scales in enamel are small chips that pop loose from the layer after the enamel is cooled. It is caused by an **excess of hydrogen** which dissolves into steel, during **enamel firing**.



Fish-scales are the most dangerous damage in the production of enamelled steel products!!

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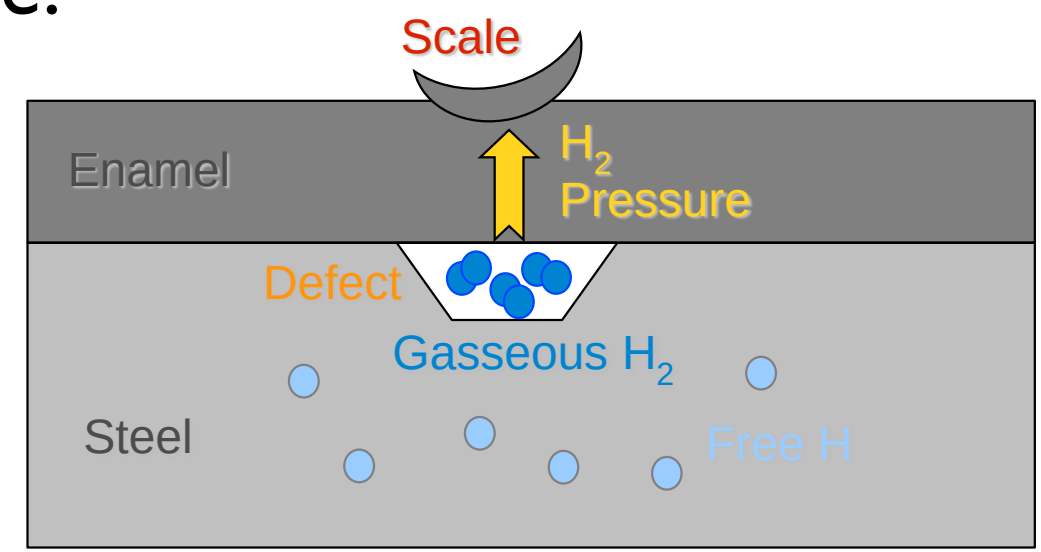
INTRODUCTION: THE FISH-SCALE PHENOMENON (2/2)

Since its solubility steeply decreases during subsequent cooling, **hydrogen moves towards the steel enamel interface** where, due to its high pressure, scales of enamel detach even after a lapse of time.



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CURRENT STATUS (1/3)

Steel susceptibility to fishscale depends on its microstructure in particular on the content, distribution and nature of site traps that are available for trapping the hydrogen thus preventing its diffusion toward the surface. Taking into account the influence of trapping on the diffusion process, fishscale resistance is evaluated by measuring the tendency of the steel to retain hydrogen under controlled electrochemical permeation.

Currently, the commonly used techniques for the evaluation of the fish-scale phenomenon on steel sheets for vitreous enamelling is defined by the **standard EN10209:2013**.

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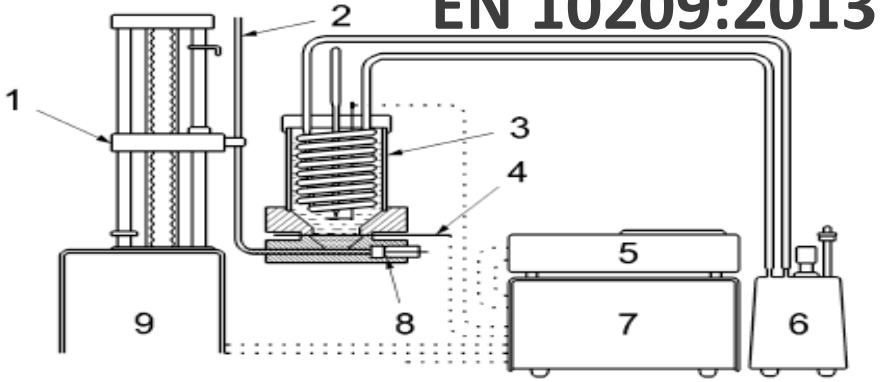
CURRENT STATUS (2/3)

Hydrogen permeation test – APPLICATION LIMITS:

- No reliable correlation between permeation time and the appearance of fish scaling for boron and titanium steels (e.g. IF steels)

EN 10209:2013



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CURRENT STATUS (2/3)

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- Use of MUTAGEN and CARCINOGENIC chemicals, e.g. Arsenic trioxide and Mercury (II) Chloride

MERCURY DICHLORIDE
CAS NUMBER: 7487-94-7

Classification:

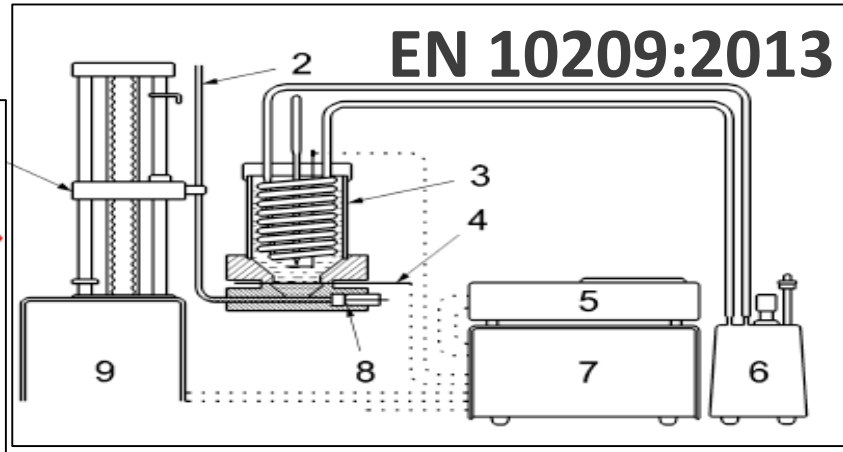
Acute Tox. 2	H300
Skin Corr. 1B	H314
Muta. 2	H341
Repr. 2	H361f
STOT RE 1	H372
Aquatic Acute 1	H400
Aquatic Chronic 1	H410

ARSENIC TRIOXIDE
CAS NUMBER: 1327-53-3

Classification:

Acute Tox. 2	H300
Skin Corr. 1B	H314
Carc. 1A	H350
Aquatic Acute 1	H400
Aquatic Chronic 1	H410

EN 10209:2013



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CURRENT STATUS (2/3)

Hydrogen permeation test – APPLICATION LIMITS:

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- Use of MUTAGEN and CARCINOGENIC chemicals, e.g. Arsenic trioxide and Mercury (II) Chloride
- Complex surface preparation and high hydrogenation condition set by the standard causes severe damage of the materials leading to the creation of new trapping sites and invalidating the correct valuation of fishscaling resistance.

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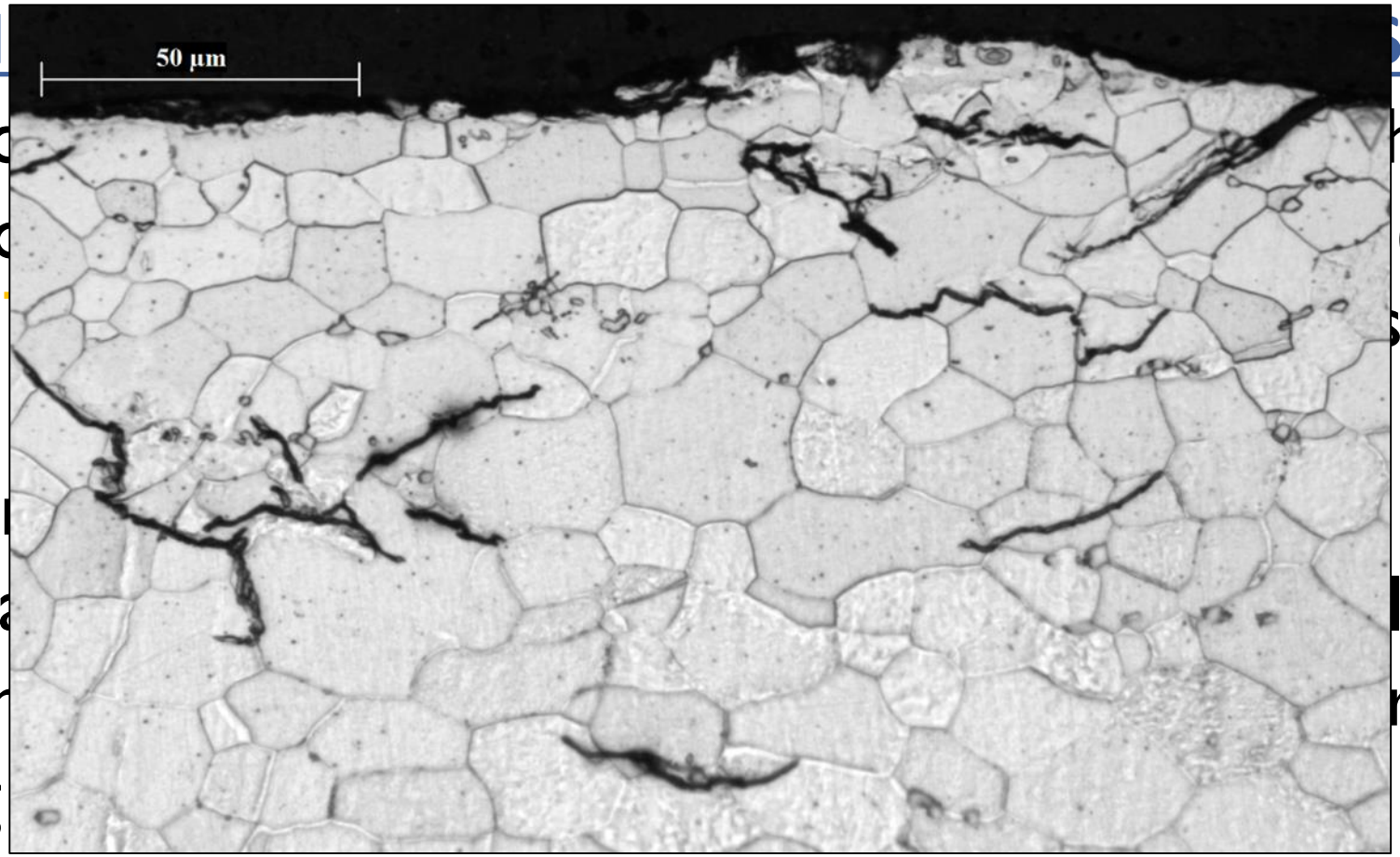
CURRENT STATUS (2/3)

Hyd **S:**



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- Complex su condition set by the standa leading to the creation of r rect valuation of fishscaling

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CURRENT STATUS (3/3)

Fish scaling test using "special test enamel" – APPLICATION LIMITS:

- Enamelling of steel required
- No numerical evaluation, attribute only
- 24 hours time to first visual evaluation and 5 days for complete evaluation
- No distinction between the contribution of the steel or the enamel process or the "special test enamel" to the fish-scale issue.

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HELIOS II (1/3)

A series of experiments were conducted on steel samples representative of the materials employed in Electrolux products.

HELIOS II is a new technology, results of a collaboration between Electrolux Italia SpA Forlì and Letomec Srl (spin off acknowledgement of University of Pisa), it is an electrochemical permeation test for materials, based on a solid-state sensor for hydrogen measurements.

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HELIOS II (1/3)

A series of experi mples representative of t ux products.

HELIOS II is a new tion between Electrolux Italia Sp lectrochemical permeation test fc sensor for hydrogen measure

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HELIOS II (2/3)

Advantages of the instrument:

- **ANALYSIS ARE SAFE,** the test solution doesn't contain Arsenic or Mercury compunds which are indicated by EN10209 but restricted by the current REACH norm. On the contrary the test solution in HELIOS II is not classified as HAZARDOUS!

SAFETY FIRST

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- **QUICK RESULTS,** significantly reduces the analysis time, by using a solid sensor, which immediately captures the hydrogen flux and thanks to easy samples preparation

TIME SAVING

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- EVALUATION OF BORON AND TITANIUM STEELS

NO SAMPLES LIMITS

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LOW COSTS

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- **INEXPENSIVE ANALYSIS, LOW MAINTENANCE COSTS**
- **EASY CALIBRATION,** using a certified kit calibration (ISO DIS 6145-11)

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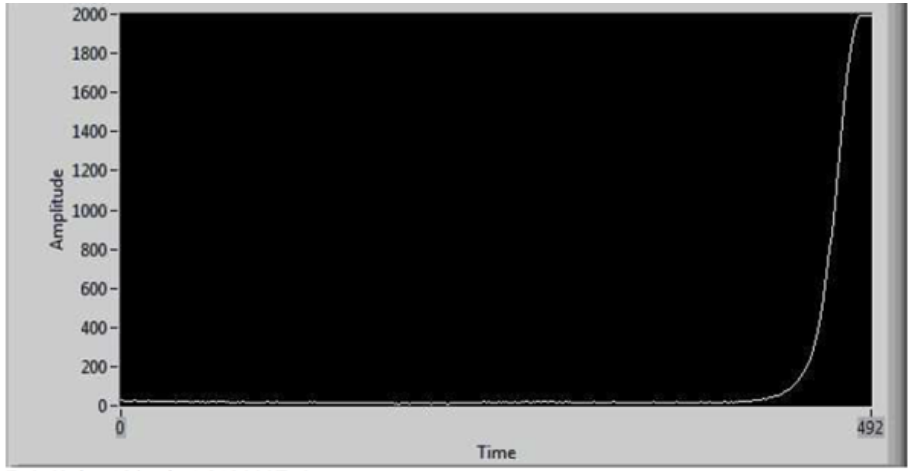
- INEXPENSIVE ANALYSIS, LOW MAINTENANCE COSTS
- EASY CALIBRATION, using a certified kit calibration (ISO DIS 6145-11)
- EASY-TO-USE, thanks to management automatic software
- SERVICE-FRIENDLY: all parts are easily accessible

HELIOS II (3/3)

Examples of hydrogen permeation test for fishscale risk assessment:

------- DATI PROVA -------
DATA E ORA
OPERATORE:
FORNITORE:
SIGLA COIL:
QUALITA' ACCIAIO:
SPESSORE (0.01 mm): 70
NOTE:



D 0.63 (cm^2/sec): 1.212000E-6
D TL (cm^2/sec): 1.241200E-6
D Fourier (cm^2/sec): 6.176000E-7
D BT (cm^2/sec): 4.715900E-7
TH: 3.450000E+2

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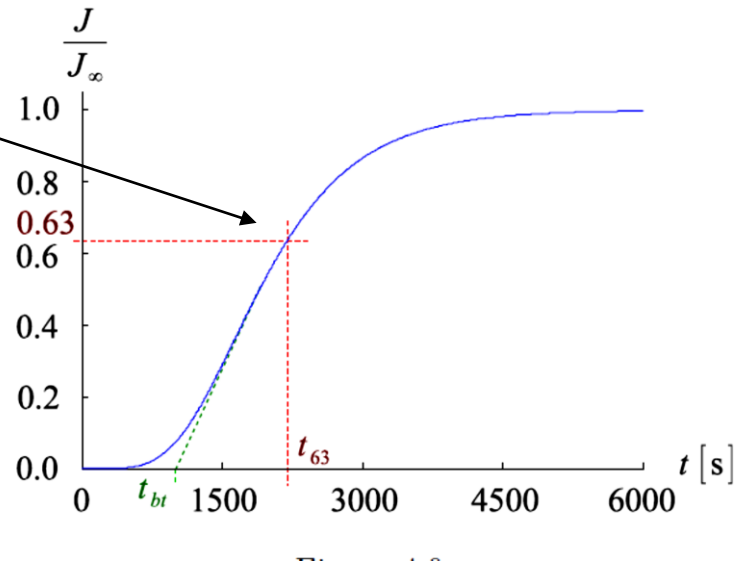
EVALUATION OF HYDROGEN DIFFUSION COEFFICIENT (1/2)

HELIOS II calculates hydrogen diffusion coefficient using the following method:

- 63%, according to ASTM G148-97 (2011)



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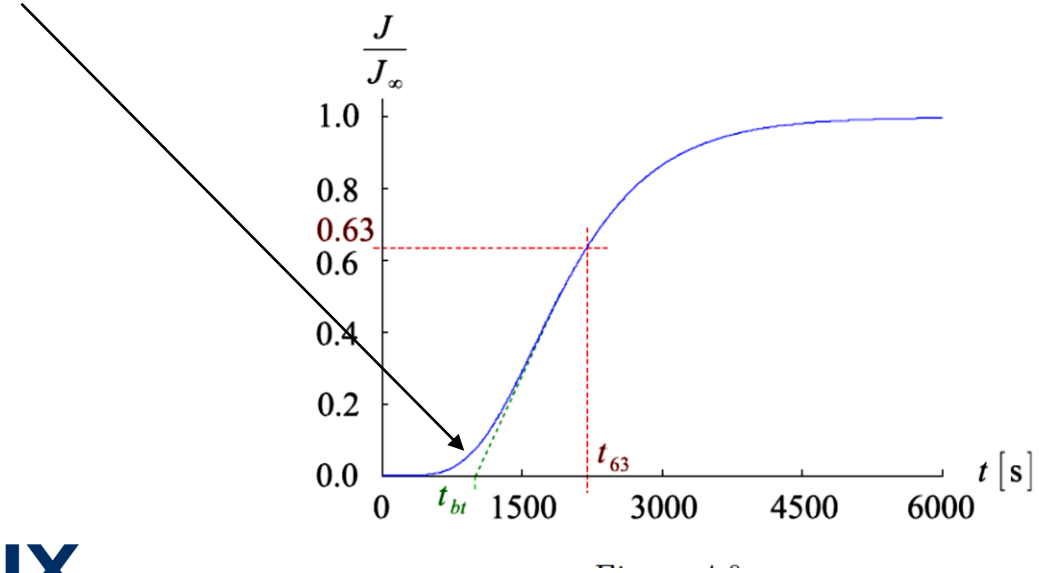

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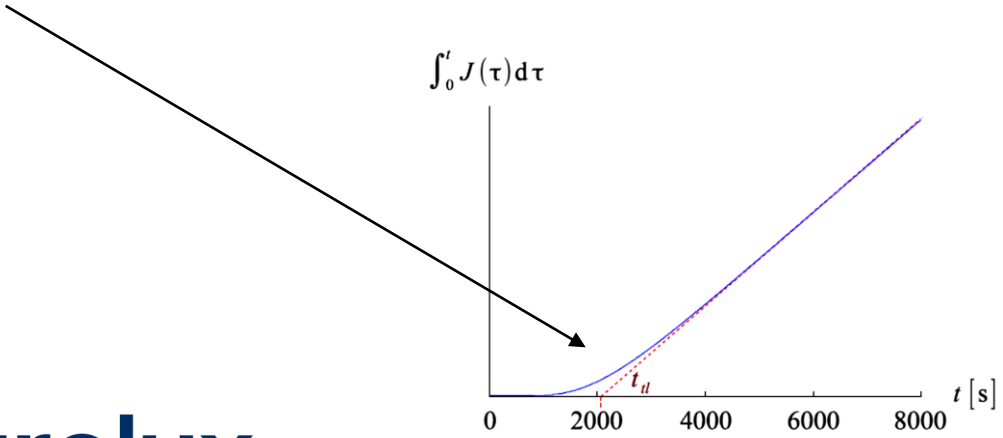

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- Fourier according to BS 7886:1997 (or EN ISO 17081:2014)

$$\frac{J(t)}{J_\infty} = 1 + 2\sum_{n=1}^{\infty} \cos(n\pi)\, e^{-D_F \frac{n^2\pi^2 t}{a^2}}$$

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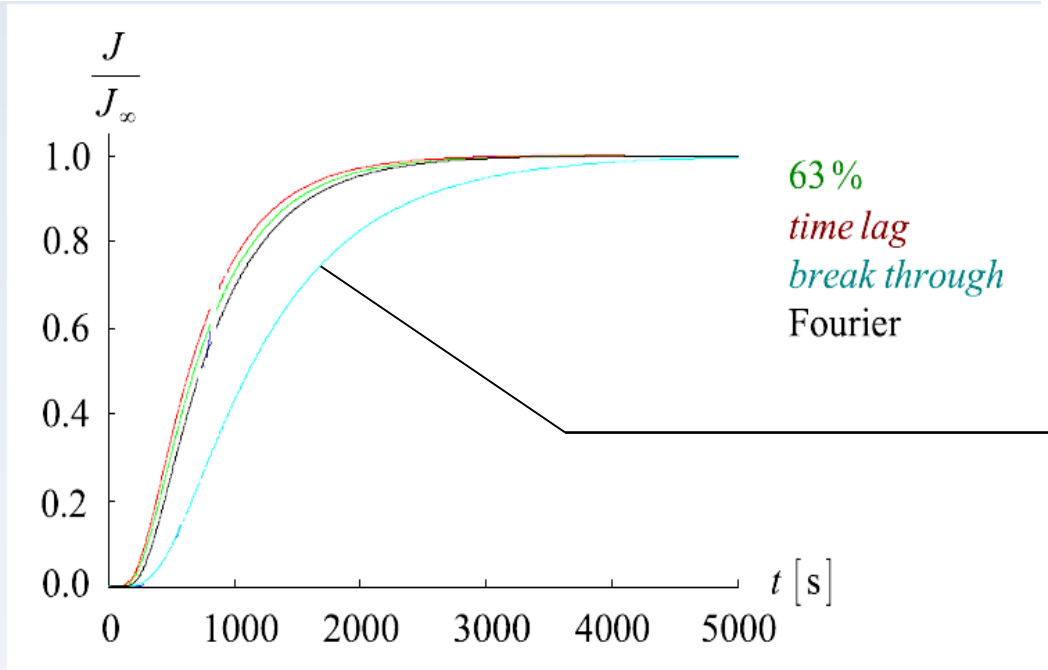
EVALUATION OF HYDROGEN DIFFUSION COEFFICIENT (2/2)

Comparison of the 4 methods for determination Hydrogen coefficient diffusion:



EN10209: 2013 considers the first time of appearance and it is the same to use break through time

Hydrogen diffusion correlation represented by break through correlation is considered as the «worst method»

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RESULTS EVALUATION AND THRESHOLD LIMITS (1/2)

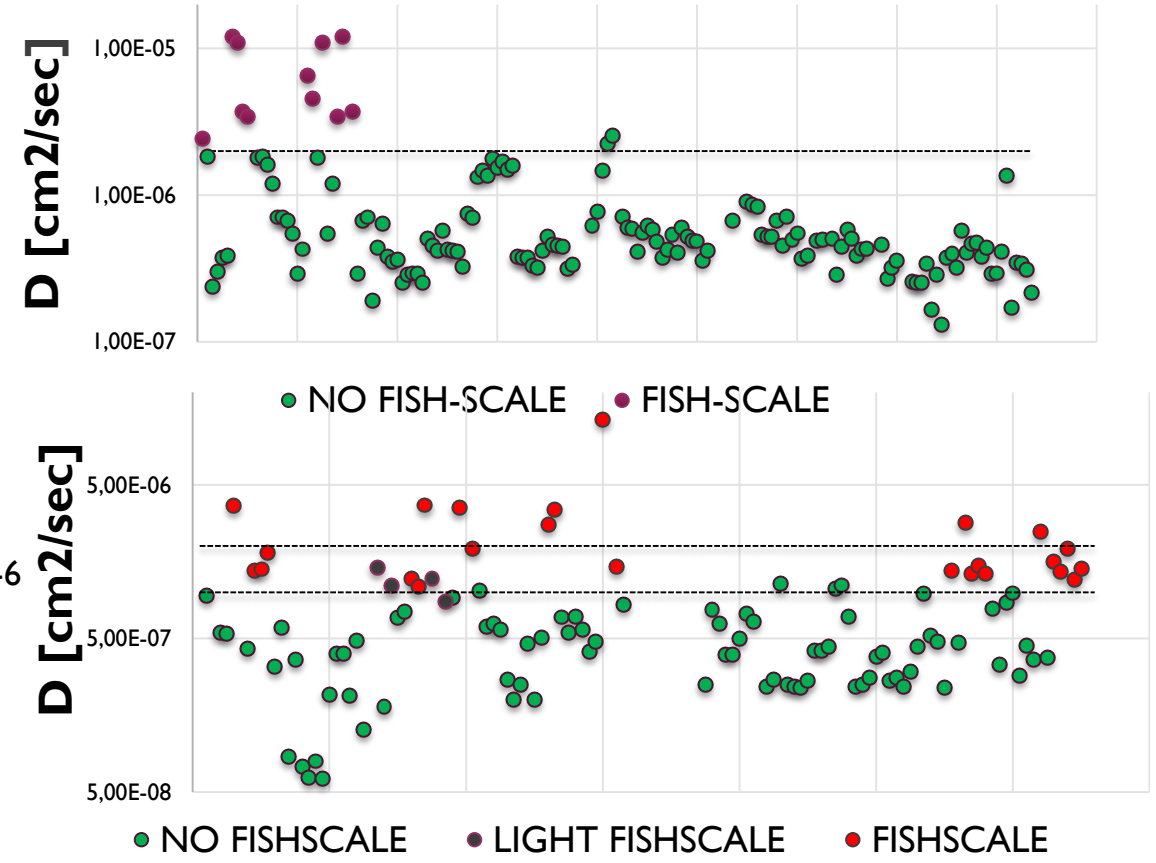
From literature data and 18 months of collaboration between Letomec srl and Food Preparation Quality team of Electrolux, the following limits for the diffusion coefficient «D» (cm^2/sec) were defined:

DECARBURATED STEEL OPEN COIL:

- Low probability of fish-scale $D < 2 \cdot 10^{-6}$
- High probability of fish-scale $D > 2 \cdot 10^{-6}$

INTERSTITIAL FREE STEEL:

- Low probability of fish-scale $D < 1 \cdot 10^{-6}$
- Medium probability of fish-scale $2 \cdot 10^{-6} < D < 1 \cdot 10^{-6}$
- High probability of fish-scale $D > 2 \cdot 10^{-6}$



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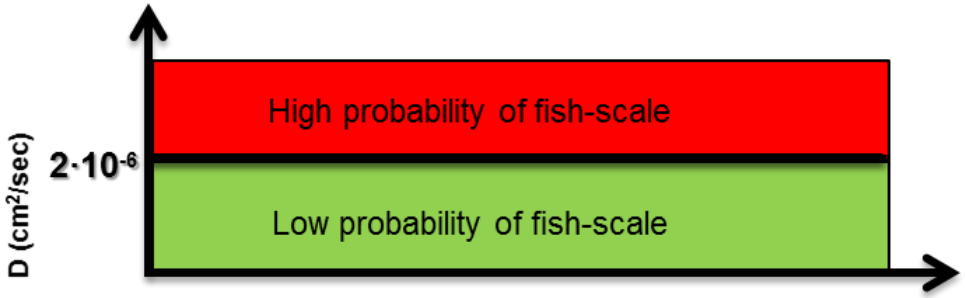

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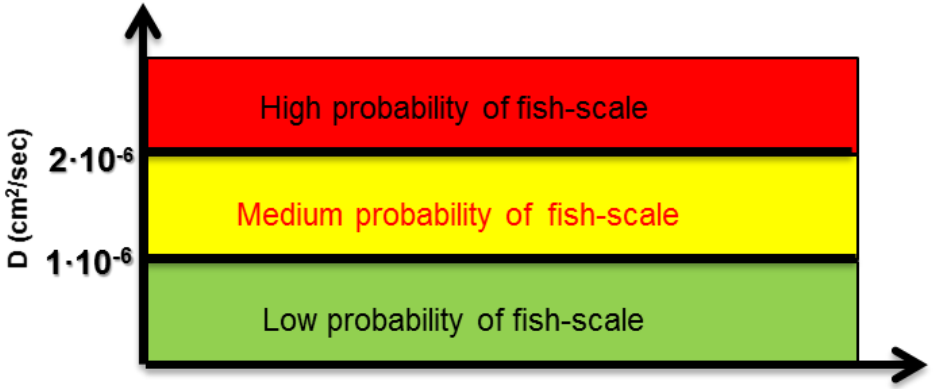

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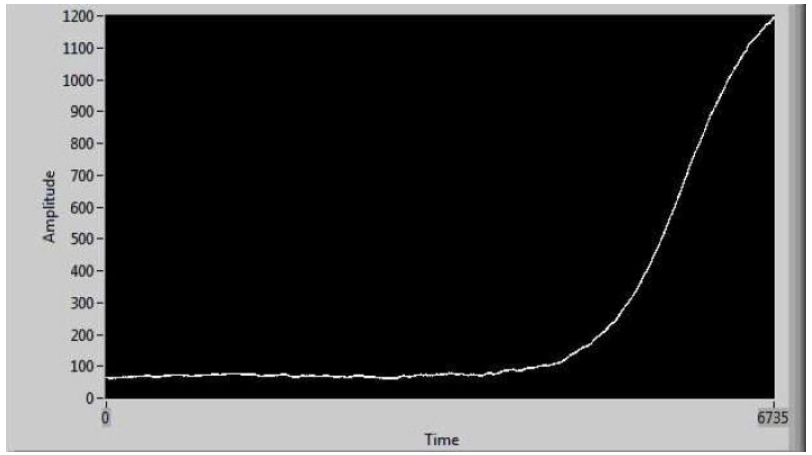
RESULTS EVALUATION AND THRESHOLD LIMITS (2/2)

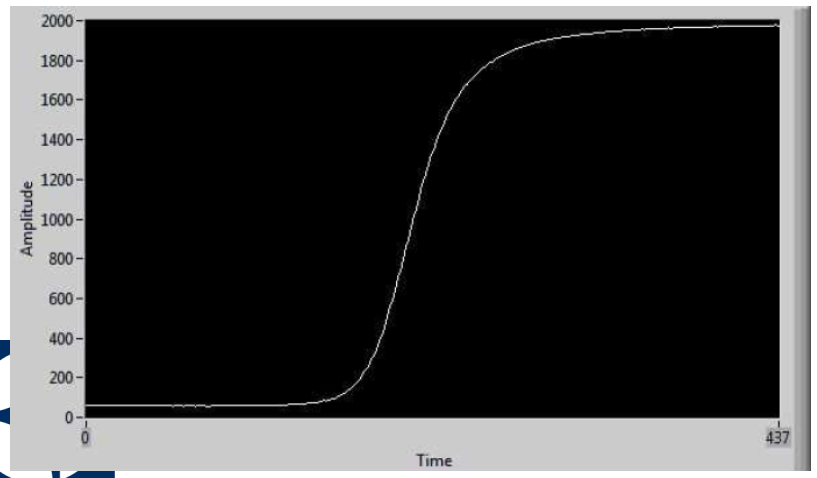
Examples of hydrogen permeation test for fishscale risk assessment:



➢ GOOD MATERIAL

Hydrogen permeation occurs after 112 minutes

The diffusion coefficient D is $0{,}2 \cdot 10^{-6}$ cm^2/sec



➢ DEFECTIVE MATERIAL

Hydrogen permeation occurs after 7,3 minutes

The diffusion coefficient D is $2{,}8 \cdot 10^{-6}$ cm^2/sec

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THE INSTRUMENT CAN BE USED TO …

- guarantee a better quality control. The acceptance of the products is important to both retailers and suppliers.

Sharing the appropriate information helps both retailers and manufacturers

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THE INSTRUMENT CAN BE USED TO …

- guarantee a better quality control. The acceptance of the products is important to both retailers and suppliers.
- identify the possible cause which caused the fish-scale defect.

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THE INSTRUMENT CAN BE USED TO …

- guarantee a better quality control. The acceptance of the products is important to both retailers and suppliers.
- identify the possible cause which caused the fish-scale defect.
- give a quantitative evaluation for the fish-scale defect probability in steels for enamelling¥.

¥We expect you to our stand for further technical information

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ENAMEL PROCESS EVALUATION (1/3)

The Hydrogen formation during the enamelling process is related to the humidity level (dew point) into the vitrification furnaces. The dew point inside the 3 Forlì enamelling lines was measured by means of Dräger tubes every 2 hours during the working time.

	06:00	08:00	10:00	12:00	14:00	16:00	18:00	20:00	22:00	max
1	9	11	10	10	10	9	8	15	14	15
2	12,5	16	15	17,5	12,5	11	10	10	15	17,5
3	11	10	10	11	10					11

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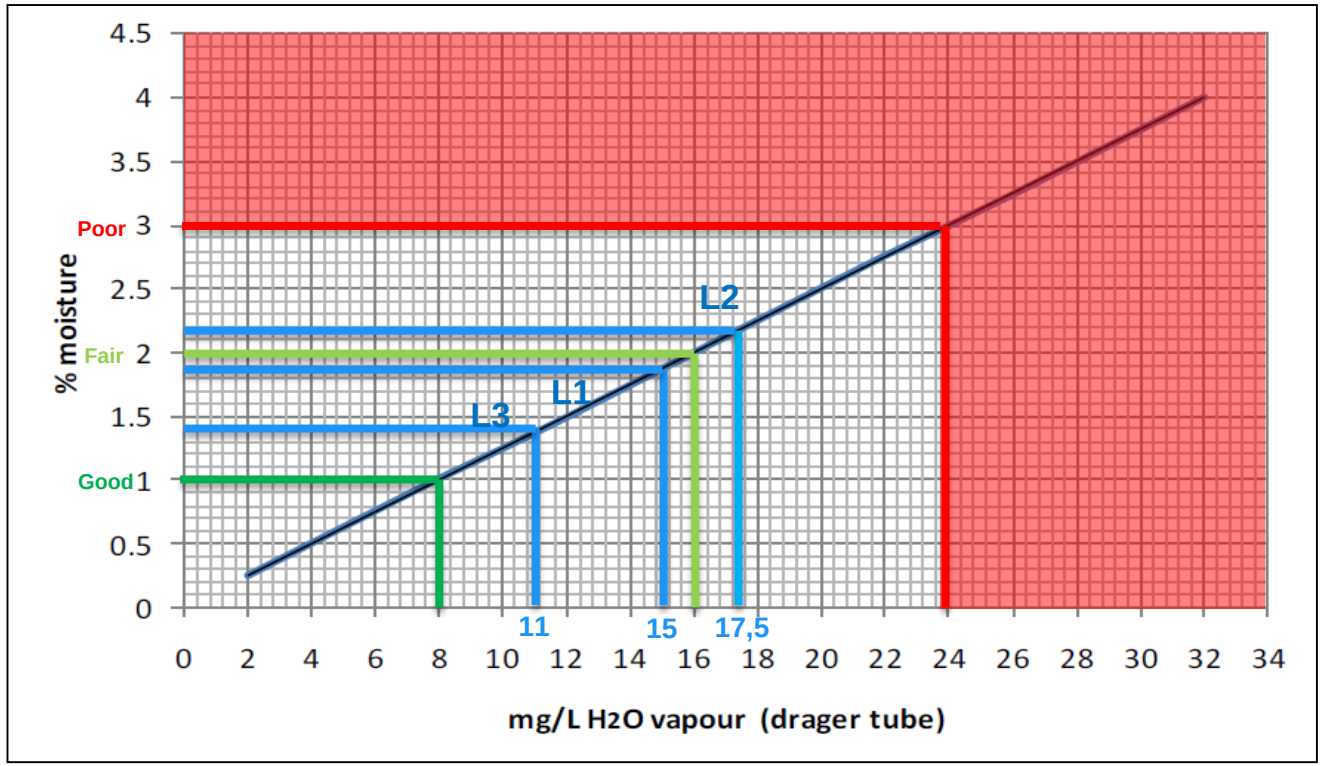
ENAMEL PROCESS EVALUATION (2/3)

Max Dew point in enamelling lines:



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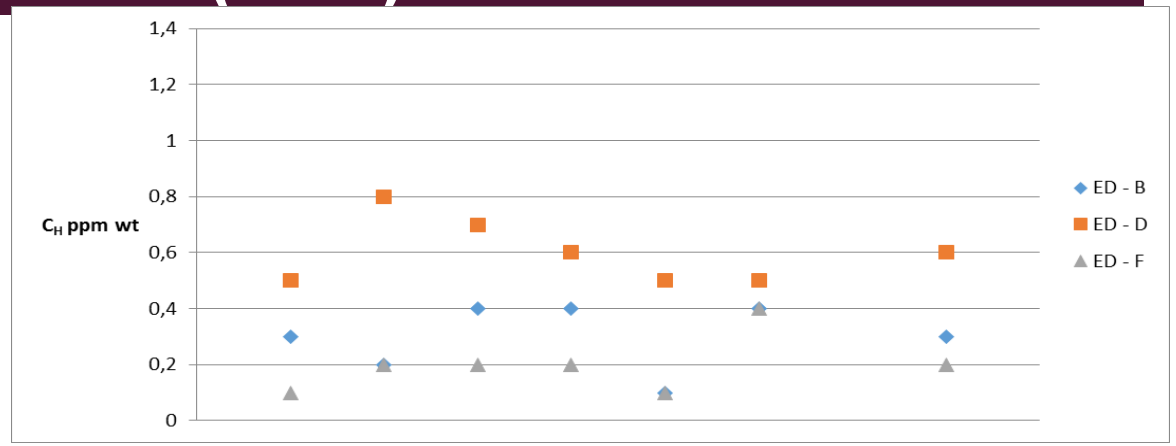
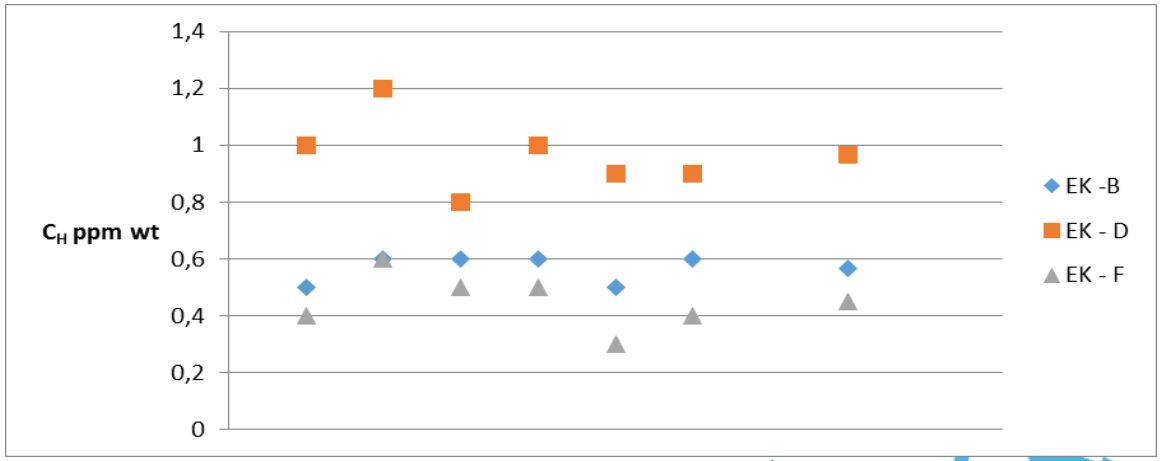
RESULTS EVALUATION AND THRESHOLD LIMITS (3/3)

Diffusible hydrogen content was measured by HELIOS III in specimens with enamel on both side, to quantify the hydrogen content that dissolves into the metal during enamel firing.





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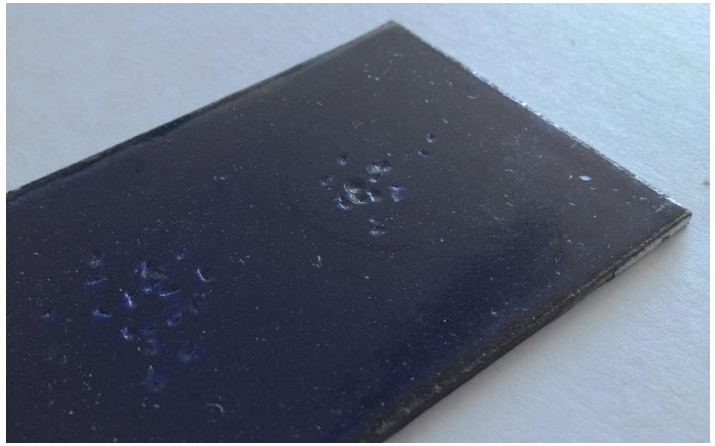
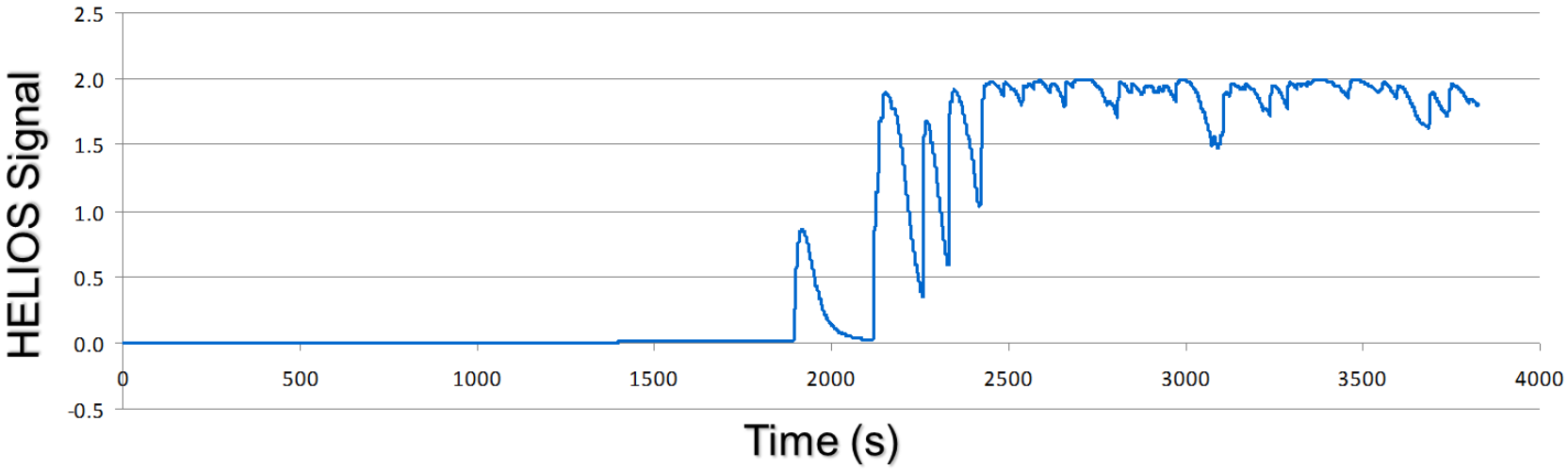
FUTURE WORKS (1/2)

IN DEVELOPMENT :

Forced Fishscale by electrochemical test to assess the enamel performance





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FUTURE WORKS (2/2)

It is possible to evaluate steel resistance to fishscale, using an innovative measuring procedure based on a recently developed device, that is easier than the procedure indicated by EN10209:2013.

The presented results can be considered a base for the renewal of the standard EN 10209:2013.

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THANK YOU FOR YOUR ATTENTION

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