Sour Service Pressure Vessel Steel Plates with Homogeneous HIC-Properties

Corrosion Mechanisms, Production Routes and Corrosion Test Procedures

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1. Sour gas corrosion

First question:

What is Sour Gas Corrosion?
Cracking mechanism in the steel during H$_2$S corrosion process

Acidic, H$_2$S-containing medium

Hydrogen Sulfide

Sulfide Ionics

Proton

Electrons

Hydrogen Atom

Molecular Hydrogen

Steel with typical small imperfections
Corrosion reaction

- $H_2S \rightarrow 2H^+ + S^{2-}$
- $Fe + 2H^+ \rightarrow Fe^{2+} + 2H_{ad}$
- $Fe^{2+} + S^{2-} \rightarrow FeS$
- $H_2S + Fe \rightarrow FeS + 2H_{ab}$
- $2H_{ab} \rightarrow H_2$
Schematical appearance of damage mechanisms in sour service

- HIC / SWC
- Blistering
- SSC
- SOHIC
HIC or SWC damage

HIC-crack on PV-plate
Basis:

Well developed know how (Dillinger Hütte GTS has been engaged in this field for more than 20 years)

Adequate production installations

Permanent exchange with the end-users

Follow up in international research projects
Practice:

Quality assurance systems for the production of HIC-resistant steel in all the following production steps:

• steel shop
• casting
• rolling mill

Reliable certified test house
Requirements for homogeneous Dillinger Crack Resistant Steel plates: DICREST-route

- Hot metal desulphurisation
- deep vacuum degassing
- cleanliness stirring by Argon
- Calcium treatment
- special chemical composition (C, Mn, S, P)
- special casting parameter (no bulging, adapted superheating)
- intensified QA-process
- special care to avoid unacceptable segregations
- high shape factor rolling (strong reduction in thickness per rolling pass)
Steelmaking
DICREST-production route in the steel plant

- **Hot metal desulphurisation**
- **BOF converter**
- **Argon stirring process**
- **Heating**
- **Degassing process**
- **Inclusion modification**
- **Casting**

**Objective:**
- hot metal desulphurisation
- dephosphorisation
decarburisation
denitrogenisation
- slag conditioning,
steel desulphurisation
- temperature adjustment
- removal of:
Carbon
Sulphur
Nitrogen
Hydrogen
- cleanliness
avoiding:
- reoxidation
- resulphurisation

CaC$_2$, Mg, O$_2$, Ar/N$_2$, Ar, CaSi

Analysis adjustment
Casting
Strand
Inclusion distribution for different caster types

Vertical caster

Curved caster

Distance from the fixed side in %

Total oxygen in ppm

- Curved caster
  \( r = 5.0 \text{ m}; \, v_c = 1.0 \text{ m/min} \)

- Vertical caster
  \( v_c = 0.5 \text{ m/min} \)
Results from HIC test, according to NACE TM 0284-96 test solution A (pH3).

The HIC-results of the red coloured areas will not be satisfying.
Aspects of quality assurance: casting incidents

Example of deviation in casting parameter combination
The HIC-results of the red coloured areas will not be satisfying.
Rolling Mill
Rolling schedule

Optimized production steps for DICREST plates in the heavy plate mill
Influence of High Shape Factor Rolling

Rolling Shape Factor = \frac{2 \sqrt{R(t_0 - t_i)}}{t_0 + t_i} = m

Reduction = \frac{t_0 - t_i}{t_0} \times 100\%

a) \epsilon_t = 1.71 (250\rightarrow146mm) / 12 passes  
b) \epsilon_t = 1.71 (250\rightarrow146mm) / 3 passes

1st stand (5.5m-4-high stand)  
Work roll Ø: 1180mm  
Max. torque: 2 \times 4500kNm  
AC synchr. motor  
(2 \times 10900kW)  
Max. force 108000kN
3. Dillinger test house - specimen preparation
Tensile and toughness testing
Dillinger HIC-test lab
Equipment:

- 8 laboratory fume hoods (7 for tests, 1 for cleaning)
- Overall 39 connections for tests vessels
- 12 connections for SSC tensile tests (CorTest rings) equipped with computer aided monitoring of specimen failure
- 3 independent gas supply systems for parallel use of 3 different types of test gases
- Temperature adjustment and control system

Additionally health and safety-installations: gas detection systems, flame guard system to maintain H₂S combustion, activated carbon filters in the exhaust air conduit, collecting tanks for all waste waters from the process
Fume hood with gas supply system and test vessels
Gas supply
HIC test vessel

Test specimens during HIC-test
Test specimens, cuts for sectioning are marked
Certificate as per DIN EN ISO 17025 by GAZ for Dillinger Hütte Abnahme
Sectioning of test specimens

Examination of the polished sections

faces to be examined

20 mm

25 mm

25 mm

25 mm

rolling direction

a = crack length

b = crack width

W = specimen length

T = specimen thickness

CLR = \( \frac{\sum a}{W} \cdot 100\% \)

CTR = \( \frac{\sum b}{T} \cdot 100\% \)

CSR = \( \frac{\sum (a \cdot b)}{W \cdot T} \cdot 100\% \)

Crack distance > 0.5 mm = single crack
### 4. DH standardised offer for HIC resistant plates: DICREST HIC test as per NACE TM 0284-2003

<table>
<thead>
<tr>
<th>grade</th>
<th>max. plate thickness</th>
<th>test solution acc. TM 0284-96</th>
<th>acceptance criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>DICREST 5</td>
<td>80 mm</td>
<td>A (pH 3)</td>
<td>CLR ≤ 5, CTR ≤ 1,5, CSR ≤ 0,5</td>
</tr>
<tr>
<td>DICREST 10</td>
<td>80 mm</td>
<td>A (pH 3)</td>
<td>CLR ≤ 10, CTR ≤ 3, CSR ≤ 1</td>
</tr>
<tr>
<td>DICREST 15 1)</td>
<td>150 mm</td>
<td>A (pH 3) B (pH 5)</td>
<td>CLR ≤ 15, CTR ≤ 5, CSR ≤ 2</td>
</tr>
</tbody>
</table>

1) The requested test solution must be stated in the order in case of DICREST 15

- The HIC-resistance even of intentionally for HIC-service produced normalised plates can only be assured in the condition normalised + stress relieved
- Acceptance criteria are defined as the average of all sections of all specimens per plate
Possible acceptance levels for CLR values in ph3 solution averaging the values for a certain no. of sections:

<table>
<thead>
<tr>
<th>No. of sections</th>
<th>CLR ≤ 15 %</th>
<th>CLR ≤ 10 %</th>
<th>CLR ≤ 5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/15 &gt; 88mm / 21 &gt; 144mm</td>
<td>ok*</td>
<td>ok*</td>
<td>ok*</td>
</tr>
<tr>
<td>3</td>
<td>ok*</td>
<td>ok*</td>
<td>***</td>
</tr>
<tr>
<td>1</td>
<td>ok**</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- t ≤ 120 mm
- t ≤ 88 mm

* for higher thickness possible offer in case of inquiry
** good chance to be offered in case of inquiry
*** some chance to be offered in case of inquiry
Actual DH offers for thick pressure vessel steels

- As far as to be produced by CC-material DH is able to offer up to acceptance criteria of DICREST 5 and equivalent specifications. Same will be offered for most of plates to be produced from ingots.

- For from ingots with other specifications especially with more severe demands on acceptance criteria, variation of the acceptance criteria will be necessary:
  - Average of three sections: as function of the position over the thickness staggered specimens either CLR <= 15 % or <= 30 % will be offered.
  - Delivery condition will be Normalised or N+ACC+T, depending on toughness requirements.

- For all other cases of doubt, please give us an inquiry.
Thank you for your attention!