Demands for sour service requirements for pressure vessel steel plates
In the view of the steel producer

Steffen Martin[a], Luxenburger Günter[a], Thieme Andreas[a], Demmerath Anja[a]

[a]Dillinger Hütte GTS
PO-Box 1580
D-66748 Dillingen/Saar
name.prename@dillinger.biz

Abstract:

The first documented reports about sour service damaging are more than 50 years old. For that long period sour service has been an important issue of numerous engineers in different type of companies. In spite of this quite long tradition of this issue Oil-, gas- and engineering companies as well as many organisations like NACE or EFC are working still today on improved regulations. These general rules or recommended practices are aiming to prevent sour service induced damaging of the steel structures like hydrogen induced cracking (HIC) and sulphide stress corrosion cracking (SSC).

All well known requirements in the field of pressure vessel applications will be summarised especially focussing on the selection and treatment of the steel. It shall be shown in which way a steel producer with large experience in manufacturing plates for sour service adapts these demands on HIC, SSC and SOHIC from the specifications for the production of sour resistant steel plates with implying a risk assessment for the plate production.
Finally a reasonable specification practice in the view of a steel plate manufacturer is proposed.

Introduction

Although the problem of failure of pressure vessels operated in sour services is faced some 50 years there is nowadays still research going on to enable endusers to operate their installations safely. The phenomena of SSC (stress corrosion cracking) and HIC (hydrogen induced cracking) seem to be understood completely and there exist several standards e. g. NACE TM 0284, EFC 16, ... which enable the operators to order material that is safe in a sour environment. Others like SOHIC are still under discussion and test methods developed recently have to prove their reasonability. To catch up with the requirements of the material specifications for sour service the steel manufacturers had to do large efforts to create steel production routes enabling a economic safe and riskless production providing a warranty for the whole product to have these properties.

Basic requirements for hydrogen corrosion in wet sour service

Before hydrogen induced corrosion damages appear, the hydrogen must be absorbed by the steel. Basic requirement therefor is a corrosion reaction in a wet and sour environment. Furthermore the presence of H_2S as promoter is necessary. The result of the corrosion reaction is, that it will be created a source of atomic hydrogen moving free in the sour atmosphere. After the atomic hydrogen is taken up in the steel, it will migrate to areas such as imperfections or inclusions, where it can recombine to H_2. This recombination will create enormous pressures, which will cause cracks, depending to the general boundaries. The principle damaging reaction is shown schematically in Figure 1

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Cracking mechanism in the steel during H_2S corrosion process

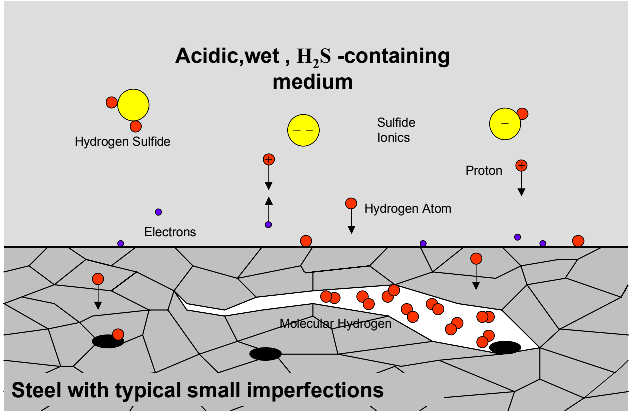

Figure 1: Sour service damage mechanism

Sour service corrosion mechanisms
When the above mentioned conditions are met, various types of damage mechanisms can be found in the presence of H_2S.
The main differentiating factor is the type of strain, the material is affected with. The simple and best understood case is with no applied strain. In this case, there is to be expected Hydrogen Induced cracking (HIC). Cracks of this type are more or less planar with some steps. Mostly, they are lying in the half thickness position of the plate. The second case is a corrosion attack in combination with strain in the material. It is the Sulphide Stress Corrosion (SSC) type, cracks, caused by hydrogen attack and strain. In service it is primary to be expected in the area of welds, correlated with hard zones. In the last years, a further corrosion mechanism, which is correlated as well to the presence of strain, was found. It is the Stress Orientated Hydrogen Induced Cracking (SOHIC). This mechanism is to be seen as a combination of above named corrosion types HIC and SSC. Whereas the first two mechanism are commonly defined, SOHIC is under recent discussion.

The last corrosion type of this group, which has to be named here is the Blistering corrosion. Cracks, caused by this type are lying beneath the surface. They are to be found as well at non stressed as on stressed material.

Dillinger Hütte as a steel producer has wide experience with testing steel plates according to the common testing procedures for HIC and SSC resistant material. The mechanisms, that case HIC cracks, are understood pretty good. Not the same understanding is collected in the field of SSC. For DH as a plate producer it is important, to get correlation of the laboratory results, collected in plate tests with the results, the end users found in service.
In the following paragraphs, the main testing procedures for HIC, SSC and partially SOHIC are described.

Hydrogen Induced Cracking HIC
HIC is appearing in specimens with no applied stress. To test the steels susceptibility towards HIC, prismatic specimens with defined machining of the surface are exposed in H_2S saturated solutions with certain pH levels.
After exposure, typically over 96 hours, three cross sections are taken equidistantly. These cross sections are investigated after polishing for the amount of cracks as shown in figure 2.

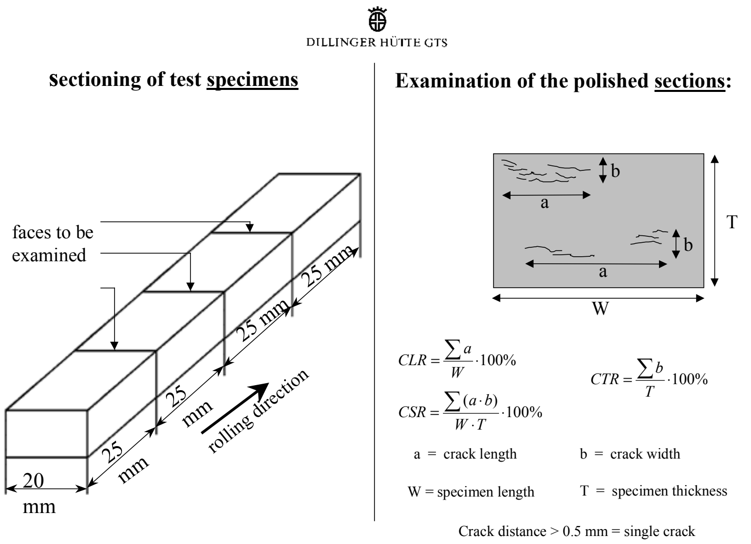

Figure 2: HIC test evaluation according to NACE TM 0284

In the following, the most common specification for evaluation of HIC susceptibility will be presented:
NACE TM 0284-2003:

"Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking"

origin:	1984, for evaluation and comparison of test results
test solution:	pH 3 (sol. A) and pH 5 (sol. B) saturated with H_2S
test specimens:	dimensions and position and preparation defined,
duration:	96 h
evaluation:	equidistant cutting, metallographic evaluation, no acceptance criterion defined, these are to be agreed between purchaser and supplier

Sulphide Stress Cracking SSC
The NACE TM 0177 („Laboratory Testing of Metals for Resistance to Specific Forms of Environmental Cracking in H_2S Environments ") was firstly published in 1977, revised 1986, 1990 and 1996. In this specification, four test methods are described to carry out the SSC testing:
- tensile test (sol.A); most common and preferred by DH-GTS
- Bent-Beam Test
- C-Ring test
- Double-Cantilever-Beam test (DCB,sol.A)

Further more two test solutions are defined:
A: pH: 2.7
B: pH: 3.5, both H_2S saturated

The test duration has to be 720 h. The test report will include besides the applied stress level the time to failure and / or the stress level of no failure after 720h.

Important remark for normalised material for pressure vessels. It is only possible, to reach sufficient SSC properties, if the material is produced for sour gas use (e.g. via the DICREST production route) and a sufficient PWHT is performed. Furthermore, normalised material must not contain any microalloying elements, which cause failures in the SSC test.
Apart from the tensile test, also a four point bend test acc. ASTM G39 in sol.A can be performed as well. This cheaper test is predominantly used to check the resistance of linepipe plates (type TMCP) against SSC.

Stress-Oriented Hydrogen Induced Cracking SOHIC
The SOHIC type cracking is a rather new phenomenon in the field of sour gas corrosion. Sporadic documentation is known from spiral welded pipes and from pressure vessels with no sufficient post weld heat treatment.
This type is appearing as a combination of rectangular (SSC type) and parallel cracks (HIC type) in the area of a multi-dimensional tension field. These fields are usually to be found in the area of welds, where the PWHT was not or improperly performed or beneath flaws.
This issue is still under large discussion and the mechanism is not fully understood yet.
A first specification for SOHIC testing is given in the new NACE TM0103 – 2003.
In this specification, a notched four point bent double beam test is defined as shown in figure 3.

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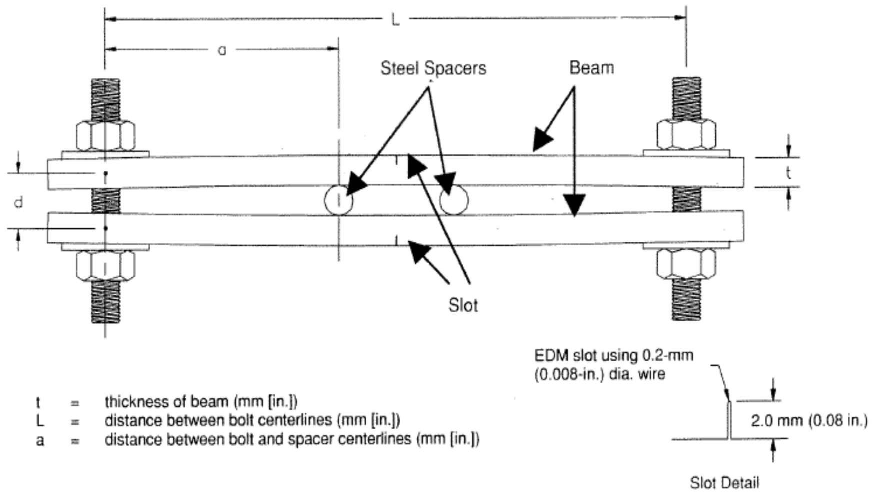
SOHIC test arrangement as per NACE TM0103 / 2003

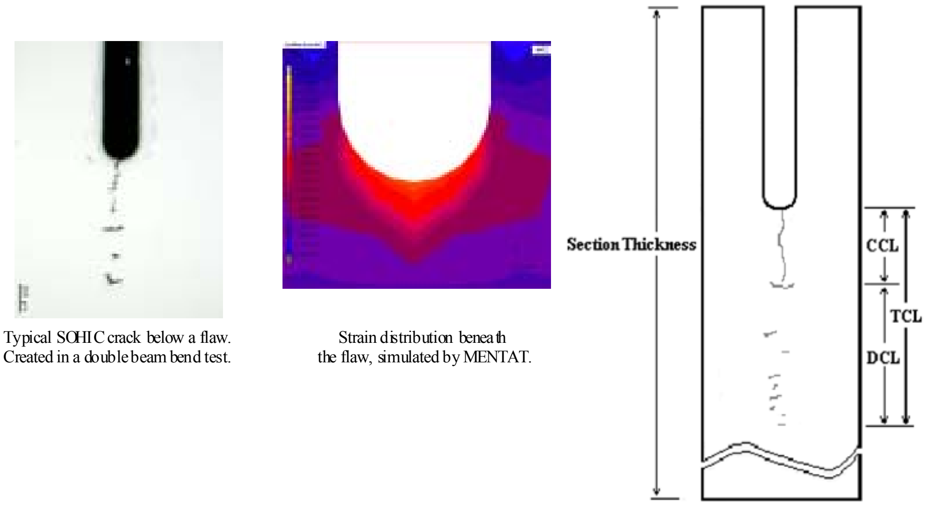


NACE TM0103 – Full Size Double-Beam Test Specimen Design

Figure 3: Four point bend double beam test as per NACE TM0103-2003

In this test, especially beneath the notch, a typical field of cracks can be produced. As shown in the right part of figure 4, the strain beneath the notch is much higher (up to 10 times) than at the surface of the specimen. Due to that, the type of cracks, which can be found, will change, depending on the load. Just beneath the flaw, continuos perpendicular cracks (CCL) from the SSC type will appear. When the load becomes lower, discontinuous parallel cracks (DCL) from the HIC type will appear. The complete field of cracks will be defined by the total length (TCL).

SOHIC testing: Evaluation and appearance of cracks



Typical SOHIC crack below a flaw. Created in a double beam bend test.

Strain distribution beneath the flaw, simulated by MENTAT.

Figure 4: SOHIC type cracks in the area of a stressed notch, strain distribution at the bottom of a notch and evaluation criteria for SOHIC cracking.

Unfortunately reasonable acceptance criteria for CCL (Continuous Crack Length), DCL (Discontinuous Crack Length) and TCL (Total Crack Length) are not yet reported. As well as reasonable loads are not yet defined. Due to that the practical use of the test method is still limited as acceptance criteria are missing so far.
The following general findings from internal tests in DH laboratories can be published:
Although the tests were performed with HIC resistant DICREST material, SOHIC cracks appeared in pH3 solution at loads apparently lower than those, used for SSC tests.
Rising the load increased the appearance of these cracks.
Testing in pH5 solution produced no SOHIC cracks.
For a further discussion of the corrosion phenomenon the following aspects should be taken into consideration: The notch in the specimens generates a very harmful stressed area. It should be taken into consideration, whether a notch like this is permitted generally at pressure vessels.
SOHIC resistant material (according to this test method) can not be produced with normalised steels with sufficient results. It seems to be that Q+T or TMCP material will reach this aim. Investigations are in progress.

Production of HIC-resistant plates
All HIC-resistant plates both for pressure vessels and for linepipe are produced following a special route which ensures good properties in regard to sour service operation. The production route is applied to obtain a homogenous HIC-resistance level over the whole plate and consists both of special technical treatments and improved quality assurance measures.
Steel making and casting: The various different processes applied in the steel plant are shown in figure 5. After the pig iron is delivered from the blast furnaces it undergoes a first desulphurising process before it enters the converter. In the converter the decarburisation, denitrogenisation and dephosphorisation takes place. Afterwards, in the ladle, the analysis

adjustment is done. In a first step, together with the controlled overheating of the melt for later casting, a rough adjustment of the chemical analysis is carried out.

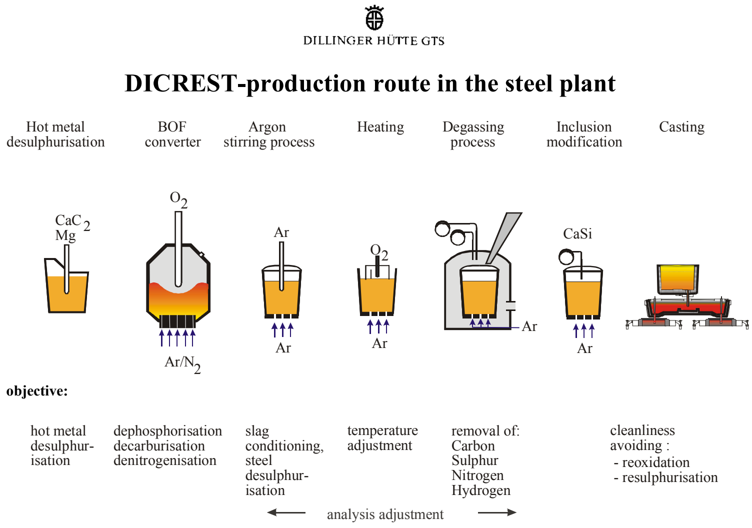


Figure 5: Production route in the steel plant

Subsequently the fine adjustment of the chemical analysis under vacuum is done. In the degassing process Nitrogen, Hydrogen and Sulphur evaporate from the melt, which is stirred by Argon to speed up the process. After this process the heat is so-called deep desulphurised with the result of Sulphur contents of less than 10ppm. With this clean degassed heat now a Calcium treatment is done for inclusion forming of the remaining impurities. The target for the Ca/S ratio after the completion of the metallurgical treatments is a window between 1,5 and 5 as shown in figure 6.

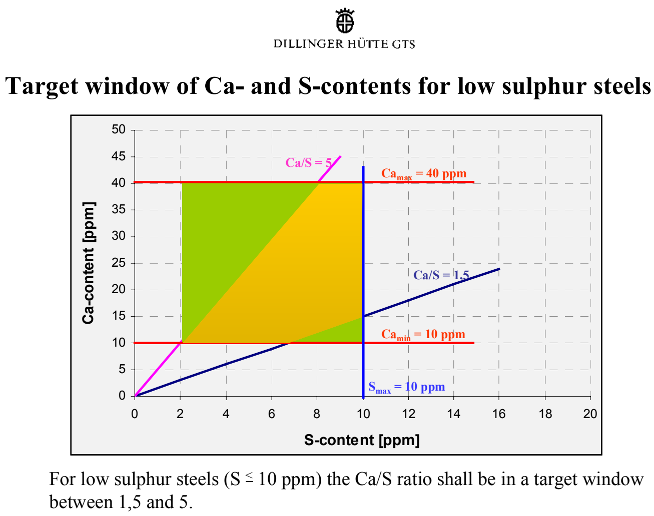


Figure 6: Target window of Ca/S ratio after Ca treatment

During casting there must be applied measures to avoid an Oxygen and Sulphur uptake in the liquid steel. This is mainly done by using casting powder which prevents the contact between steel and air. In the casting process optimised slabs for later plate rolling are produced and besides continuous casting also ingot casting is used up to a certain extend. One of the main targets in casting besides getting the initial geometry for rolling is the avoidance of segregations in the steel. In continuous casting vertical caster types show best results in regard to homogeneous low level distribution of non-metallic inclusions and segregations, which is required for HIC-resistant steels. The reason can be seen in figure 7. In vertical casting the cast strand will only be bend after complete solidification which allows for ascension of non-metallic inclusions in the liquid steel whereas in the curved caster type the inclusions get caught at the solidus line in roughly quarter thickness of the slab. The centre line segregation and shrinkage cavities can be minimised due to exact alignment of the rolls of the caster. Ingot casting is also used to produce HIC-resistant plates, but the concast method creates more homogeneous slabs and is therefor preferred in production. With the increased production risk using ingots for HIC resistant plates the application of additional measures in regard to quality assurance have to be taken.

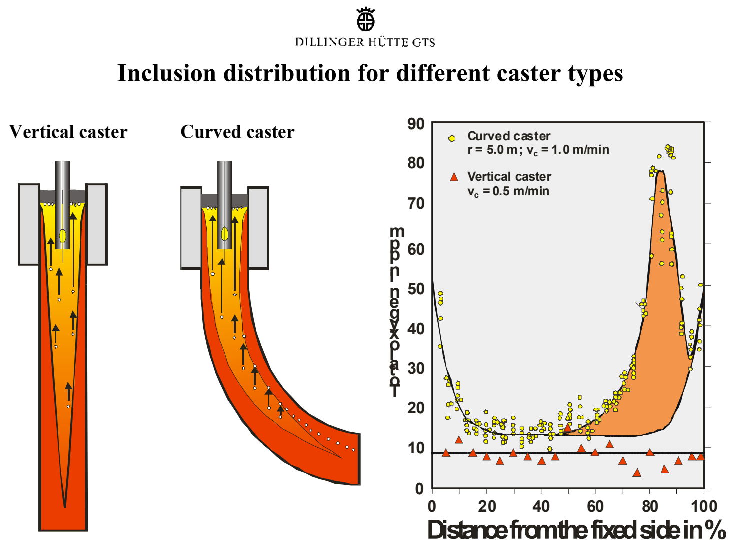


Figure 7: Differences between different continuous casting types

Plate making process

After casting the slabs will be prepared for the following rolling process as e.g. not the whole length of the cast strand length can be taken for plate production. Also other zones of the initial cast strand length cannot be taken for production if e.g. so called casting incidents influenced the homogeneity of the slab. Additional quality assurance measures are taken at the beginning and the end of the incident risk range.

The general processing of the slabs in the plate mill is shown in figure 8. After reheating of the slabs in the pusher furnaces to al level of 1100 to 1250°C the slabs get rolled to plates. To ensure the complete deformation over the whole thickness of the final plate the "high shape factor rolling" is applied. This means that very high deformation rates per rolling pass are obtained by using very strong forming forces. The effects of the high shape factor rolling on the plate are shown in figure 9, which shows the result of a rolling experiment. 7 stainless steel bars were embedded in to two 250mm thick slabs and afterwards the slabs were rolled into plates of 146mm thickness. One was rolled using 12 rolling passes whereas the other was shaped using 3 rolling passes. Afterwards the results were examined.

As you can see the plate rolled by 3 passes shows good deformation even in the core whereas the plate rolled using 12 passes shows deformation near plate surface, but almost no deformation in the plate core. The aim of the rolling process using forming forces up to 108.000 kN again is the creation of a very homogenous plate which of course enhances the mid thickness properties.

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Optimized production steps for DICREST plates in the heavy plate mill

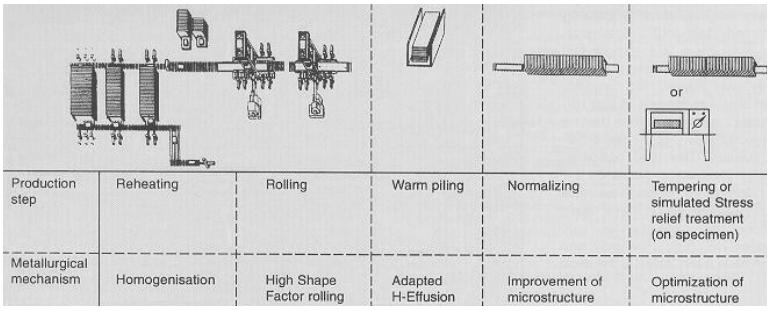

Figure 8: Production steps in the plate mill

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Influence of High Shape Factor Rolling

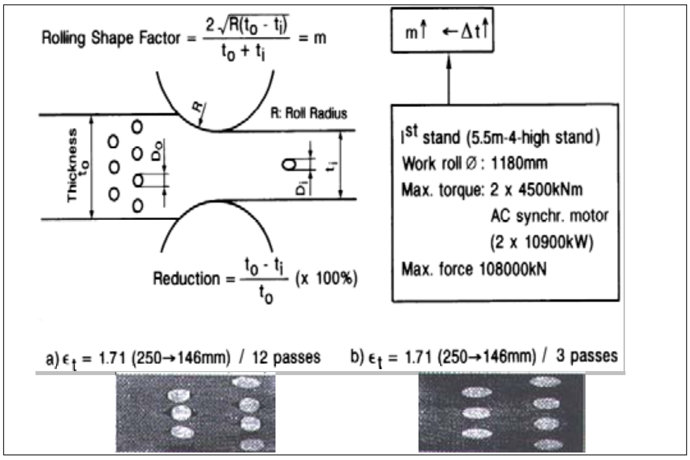

Figure 9: Influence of high shape factor rolling on plate core deformation

After levelling of the plate a warm piling at 200 to 500°C takes place to allow for Hydrogen effusion off the plate. The final step in the plate mill is the normalising of the plate. However the full HIC resistance of the plate can only be obtained after stress relieving treatment. As normally the plates get a stress relieving after welding at customer's work shop this is usually not done in the mill.

The effect the production following the special route has on product properties is shown in figure 10. In this picture the HIC values obtained in the HIC test acc. to NACE TM 0284 between intentionally produced HIC resistant plates and plates specified with some (e.g. low Sulphur, Ca-treatment, ...) elements of the special production route are compared. These so called Pseudo-HIC plates show a probability of roundabout 37% for obtaining values of less than 2% CLR whereas plates produced following the whole route are likely to obtain CLR values below 2% in ca. 88%. This means that the special route provides not only far better results in regard to the HIC properties but also the delivery times will be kept more likely as the risk in failing the HIC test is very small.

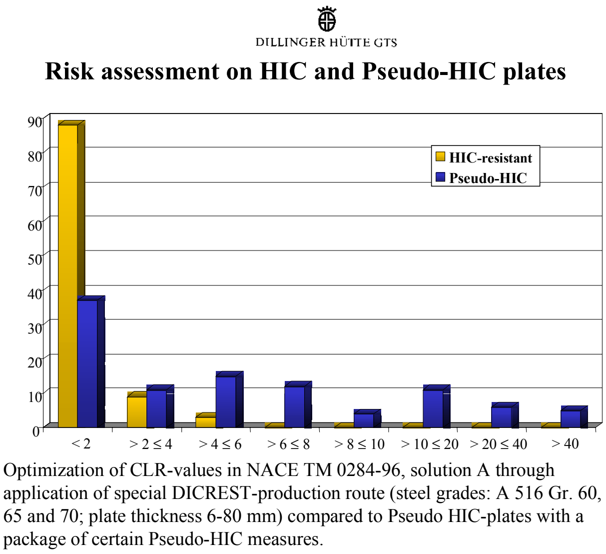

Figure 10: Risk assessment between HIC resistant plates and Pseudo-HIC

Market overview

The market in HIC-resistant plates is very complicated as almost every single oil- and gas company as well as major engineering companies issue their own specification for HIC resistant plates. Normally single orders are with an average of roundabout 230 tons rather small tonnagewise if you take into consideration that economic steel production starts at casting sequences of some 400 tons. To be able to produce economically as a plate mill it is necessary to define a certain standard in production which allows to offer at reasonable prices and at least not to lose money. Figure 11 gives an overview what grades are requested and what acceptance level in HIC test usually are needed.

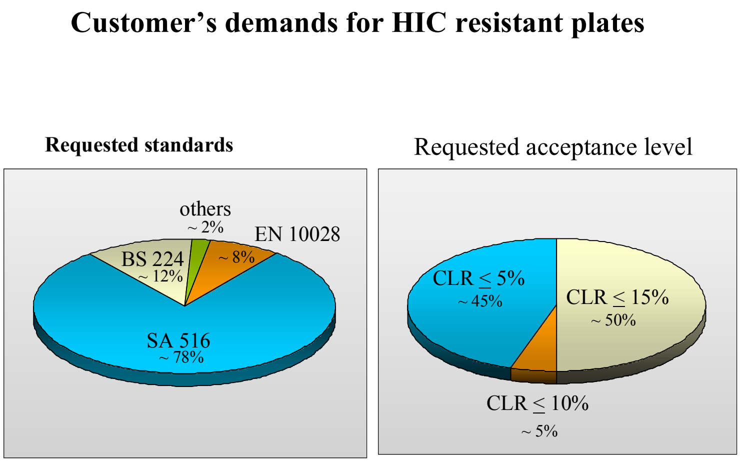

Figure 11: Statistical data in regard to customer's needs for HIC plates

With all the additional requested properties like PWHT or Charpy values it is imaginable that it is sometimes very difficult to satisfy customers demands as the needed tonnage is too small for special steel design.

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Dillinger Hütte´s standardised offer for HIC resistant plates: DICREST

grade	max. plate thickness	test solution acc. TM 0284-96	acceptance criteria		
			CLR	CTR	CSR
DICREST 5	80 mm	A (pH 3)	= 5	= 1,5	= 0,5
DICREST 10	80 mm	A (pH 3)	= 10	= 3	= 1
DICREST 15 [1]	150 mm	A (pH 3)	= 15	= 5	= 2
		B (pH 5)	= 0,5	= 0,1	= 0,05

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

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

Note: Acceptance criteria are defined as the average of all sections of all specimens per plate
ETC = Extent of transverse cracking = b_{max}
ELC = Extent of longitudinal cracking = a_{max}

Figure 12: Standardised product offer for HIC resistant plates

In the past it was tried to define certain levels (like shown in figure 12) to be able to produce the plates in a economic way and offer with some deviations. As long as there are so much different specifications in the market the customers will have trouble to find a supplier offering plates fulfilling the whole specification together with an acceptable delivery time and price. To overcome this there are plates produced fulfilling as much specifications as possible at the same time and to offer these from stock with the result that requirements which would have been declined beforehand due to certain production risk can be fulfilled now by having test results already available. A positive effect on deliveries with plates in stock up to 80mm thickness will also help customers to satisfy their needs.

Conclusion

Years ago when research activities were implemented to understand the mechanisms of SSC and HIC it was very unlikely to get material which could be used in sour service. Nowadays after strong efforts in research producing sour service resistant material is still a challenge and needs a lot of know how. However market demand can be satisfied and production is controlled in a way that allows very low production risk ensuring secure deliveries within the anticipated time frame. The more severe production limits steel manufacturer are facing are the many different specifications in the market making it nearly impossible to build a economic production of sour service products, because single order lots are still rather small. From customer's point of view a individual specification for the material certainly makes sense, because, especially in the early years, some bad experiences were made with suppliers not being aware of their responsibility in regard to this. Today sticking to individual specifications is hindering the urgently needed "liberation" from these as leading manufacturers offer their products with a warranty for the material to have certain sour service resistance. The liberation from the specifications is needed as very often the limits set in the requests lead to the situation that it is simply technically impossible to produce material with those properties. In other cases cost are driven that much that the material is way too expensive to sell. This particular situation leads to dubious behaviour in some markets as time and price pressure urges to take any material available declaring it suitably by randomly carried out tests. The effect is that the risk rises that installations have the same safety standard as 20 years ago, because finally the same materials are used due to shortness of availability of the sour service resistant material.