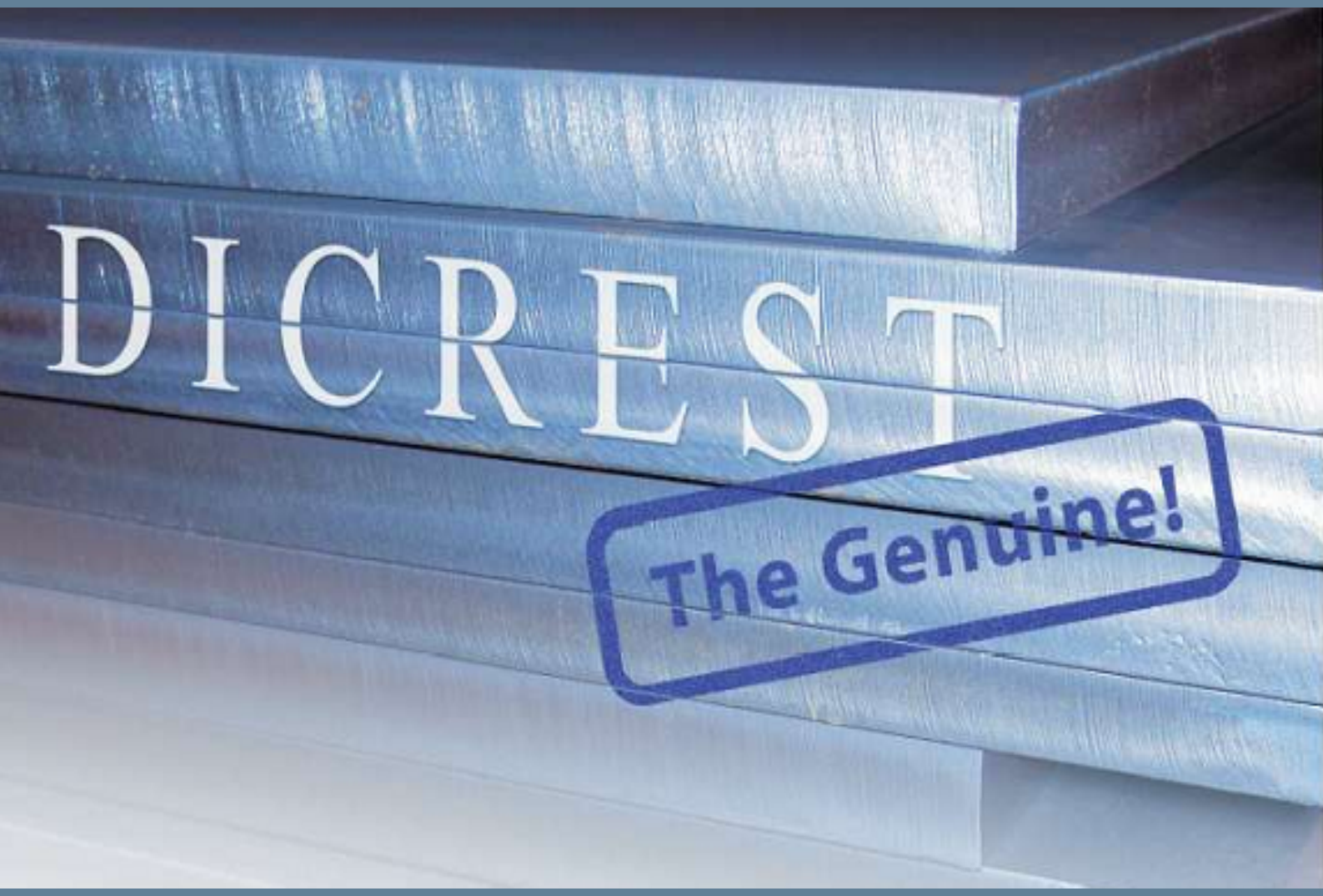
DILLINGER HÜTTE GTS

THE ANSWER TO SOUR GAS PROBLEMS



DICREST

EXPERIENCE - THE ROOT OF SAFETY

Processing of media containing hydrogen sulfide or amines in petrochemical plants can result in serious damage to vessels and piping. These problems are caused by corrosion phenomena due hydrogen set free. Since such damage occurs on the interior of components, or within the walls, it can be detected from outside only using complex inspection methods. Component failure as a result of this type of damage can thus occur very suddenly, without prior warning, and is capable, in extreme cases, of causing serious accidents, like the one at a refinery in Chicago in 1984.

Monitoring plant operators' needs, Dillinger Hütte GTS has developed a series of pressure-vessel steels that incorporate a high degree of resistance to hydrogen-induced cracking (HIC). The result, developed on the basis of experience with sour gas resistant linepipe steels, are grades which assure a high level of safety: DICREST, an acronym for Dillinger Crack Resistant Steel. Their special feature: Product design is tailored in such a way that homogeneous resistance to HIC is assured throughout the plate material.

DICREST steels have been busy proving their capabilities in a large range of petrochemical plants around the world since the early nineties.

Distilling column Bayernoil Raffineriegesellschaft mbH

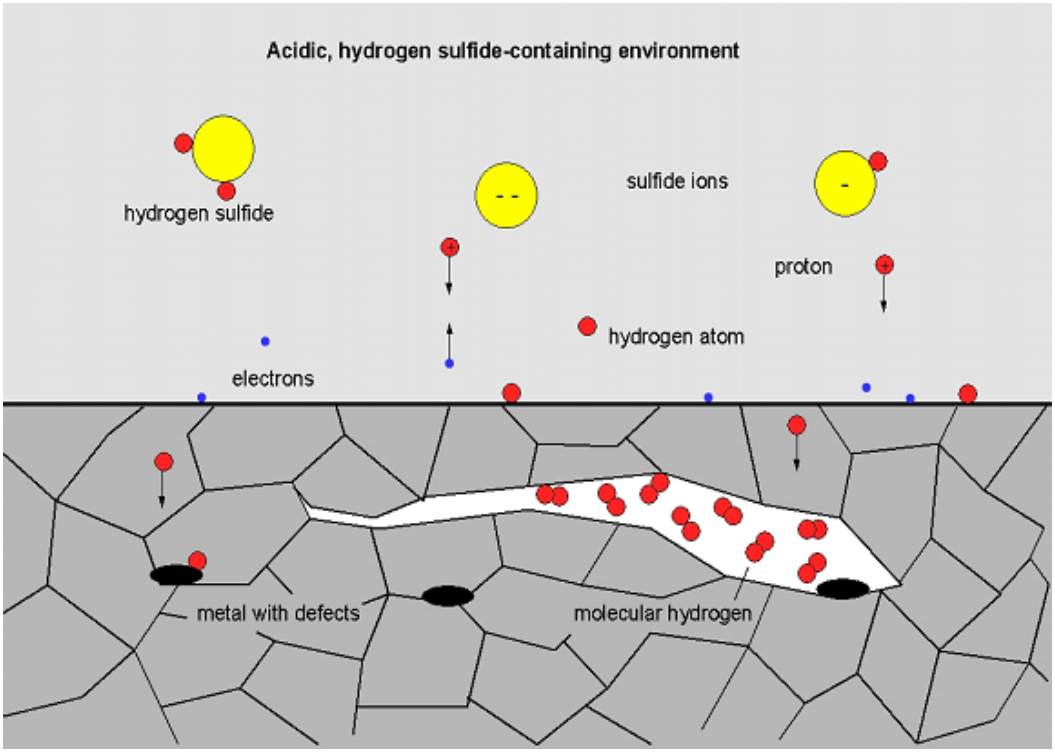
THE PROBLEM

Hydrogen-induced damage is the result of electrochemical corrosion reactions between the surface of the material and the sour gas environments. This leads to atomic hydrogen which diffuses into the metal.

The dissolved hydrogen reduces the bond energy in the crystal lattice, thus lowering cleavage stress and decreasing fracture toughness. Where, in addition, it is possible for the atomic hydrogen to accumulate on non-metallic inclusions or in micropores, it will recombine to form molecular hydrogen, H2. This reduces greatly the ability to diffuse in the crystal lattice. The results may then be the occurrence of enormous pressures at the accumulation points, generating stresses that exceed the steel's deformability limit. Microcracking parallel to the surface can occur in this way, particularly on rolled out sulfides and at segregations.

This form of hydrogen damage is referred to as "Hydrogen-Induced Cracking". During plant operating, such cracks propagate and may, after a prolonged period, reach a critical magnitude.

Deterioration mechanism



THE DICREST CONCEPT

The failure pattern described above results in very special demands on the material used. The DICREST steel and plate production process is tailored to meet these requirements. The first step is hot-metal desulfurization in the steel works. Phosphorus contents of maximum 0.01 percent are then adjusted in the steelplant's 185 t converters.

DICREST heats are subjected to vacuum treatment after the converter process; simultaneous removal of nitrogen and hydrogen is accompanied by low-level desulfurization. The subsequent cleanness stirring operation produces extremely clean steel with sulfur contents of maximum 0.001 percent. The few globular inclusions remaining have a low "notching" effect and are therefore not harmful for the material. Thus, the risk of hydrogen induced cracking is reduced.

The steel is then either continuous or ingot cast, under quality assurance measures specially adapted to sour gas resistant steels. The vertical continuous casters operated by Dillinger Hütte GTS offer decisive metallurgical advantages over normal circular-arc and oval-bow machines. The strand is only bent after it has solidified completely, i.e., the oxides still present in the heat are able to ascend and separate from the metal at the meniscus, since they are not trapped on the solidification front. In addition, the continuous caster's so-called Soft Reduction facility largely eliminates the macro- and center segregation phenomena typical of continuous-cast strand. Only the strict adherence to the scheduled casting parameters assures excellent HIC properties, as e.g. changes in casting speed can lead to reduction in quality. For DICREST production only heats which fulfill highest requirements are applied.
Rolling is performed on the world's most powerful rolling stands, with rolling forces of as much as 108 MN, and drives developing torques of up to 2x4500 kNm. These extraordinary rolling forces make it possible to roll even exceptionally wide (and thick) plates using so-called "high shape factor rolling". This rolling process utilizes extremely large per pass reduction rates, with the result that structure deformation is extremely high, even in the center zone of thick plates. Any cavities are "forged" compact. Plate production concludes with normalizing of the plates in an annealing furnace. This heat treatment produces a homogeneous, fine-grained structure.

The homogeneous HIC resistance is assured for every individual DICREST plate in the component if either the complete vessel is stress relieved or if the plates are stress relieved after normalization prior to fabrication of the vessel. In the latter case a local stress relieving of the weld seam after fabrication is necessary.

Specimen with huge hydrogen induced crack

NO COMPROMISES

HIC resistance is verified to the NACE TM 0284 standard in Dillinger Hütte GTS's own laboratories, which are accredited in accordance with DIN EN ISO 17025. Specimens with defined dimensions are taken from a specified location on a plate which is representative of all the plates produced from the same heat for the particular order. These specimens are then stress relieved, which is strictly necessary for achievement of the specified HIC resistance in normalized plates. The specimens are then exposed to a test solution saturated with hydrogen sulfide for a period of 96 hours. Two different test solutions conforming with NACE TM 0284 are optionally available for this purpose: Solution A, with a pH of 3, and Solution B, of pH 5.

In the next step, the specimens are cut at three defined positions, ground and polished, and then subjected to metallographic examination. The degree of cracking is then determined using the assessment criteria of CLR (crack length ratio), CTR (crack thickness ratio) and CSR (crack sensitivity ratio). The test results refer in all cases to the mean of all specimens and microsections from a test. Three specimens with a maximum thickness of 30 mm are taken, at graduated intervals across plate thickness, for plate thicknesses up to 88 mm. Five graduated specimens are taken from 88 mm onward, and seven from a plate thickness of 144 mm or more. This ensures that the entire cross section of plate is always subjected to the HIC test.

Since all DICREST production is aimed at achieving homogeneous HIC resistance, the HIC test is representative of the entire test batch. The HIC test results are normally confirmed with the test certificate for your specific order. HIC resistance can also be warranteed without verification by the HIC test.

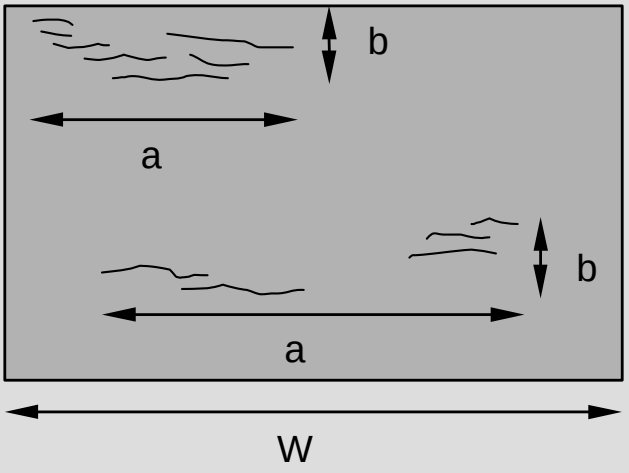
As far as is technically possible, inspection and acceptance criteria can, of course, also be tailored to your own requirements.

HIC test vessel

EVALUATION ACCORDING TO NACE

Evaluation and assessment of the HIC test according to NACE TM 0284

Grade	Plate thickness [mm]	Test solution acc. TM 0284	Acceptance criteria		
			CLR	CTR	CSR
DICREST 5	≥ 10 ≤ 80	A (pH3)	≤ 5	≤ 1.5	≤ 0.5
DICREST 10	≥ 10 ≤ 120	A (pH3)	≤ 10	≤ 3	≤ 1
DICREST 15 [1)]	≥ 10 ≤ 150	A (pH3)	≤ 15	≤ 5	≤ 2
		B (pH5)	≤ 0.5	≤ 0.1	≤ 0.05



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

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

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

a = crack length b = crack width

W = section width T = section thickness

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

The CLR, CTR and CSR values (please refer to page 5) are calculated as mean values of all individual sections of one HIC test. Mean values per specimen (3 sections) or individual values per section can be offered upon agreement.

Other plate thicknesses are possible upon agreement.

AND THAT'S NOT ALL!

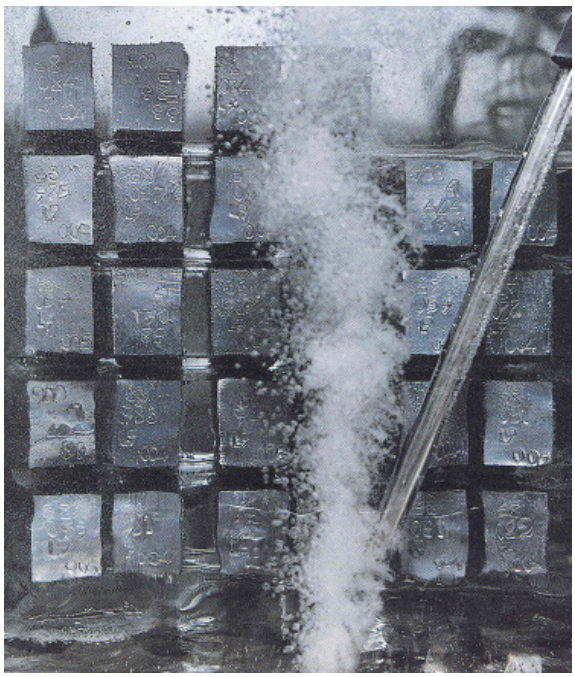
The most frequently used DICREST grades, A/SA 516 Grades 60, 65 and 70 as per ASTM/ASME and P275 and P355 as per EN 10028, Part 3, can be supplied as standard grades. It goes without saying that we can also supply DICREST to other standards and to your individual specifications.

DICREST is available in formats which go well beyond the normal heavy plate framework. Our limits can be found at lengths of 25000 mm, widths of 5200 mm and piece weights of 40 t. The maximum plate thickness depends on many parameters as HIC test level and steel grade. Please see the DICREST-specifications for further details.

In addition to the HIC test, Dillinger Hütte GTS can also offer for DICREST the SSC test in accordance with NACE TM 0177, Test Method A. "Sulfide stress cracking" (SSC) is a cracking type caused by simultaneous impact of hydrogen and stress applied from outside which can occur in high-tensile strength steels and in the heat affected zone (HAZ) of welds. Since this form of failure is associated primarily with the hardness of the material, the parent material's hardness is restricted in accordance with NACE MR 0175 to 22 HRC. The test solution, test duration and the magnitude of the tensile stress, must be agreed for the performance of the SSC test.

For the sake of completeness we want to mention "Stress Oriented Hydrogen Induced Cracking" (SOHIC), another hydrogen-induced cracking phenomenon which, for plate applications, is of minor importance. Unlike the types of cracking described before, in this defect type, a different pattern of cracking is found at defective sites in the component where multi-dimensional stress states occur. The cracks initiate from notches, the tips of cracks or the stress-loaded heat-affected zones of welds. A combination of through cracking perpendicular to the direction of principal stress of the most heavily loaded area and horizontal cracks at a larger distance from it are typical of this type of cracking. On an international level, work is being performed on the clarification of this failure mechanism and its influencing factors. No standardized test supplying repeatable data for use as test criteria is as yet available.

Test specimens during HIC-Test



High Pressure Production Trap made of DICREST for the Haradh GOSP III project (courtesy of Gulf Engineering)

Please contact the Dillinger Hütte GTS sales organizations for information on and orders for the DICREST range of steels. Our marketing department will be happy to supply more detailed information: Tel.: +49 6831 47 3461

To assure the availability of DICREST plates even for short delivery times or small order tonnages Dillinger Hütte GTS offers DICREST plates also ex stock at AncoferWaldram Steelplates in the Netherlands and Dillinger MiddleEast in the United Arab Emirates. For any inquiry please contact your sales partner.

DILLINGER HÜTTE GTS

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