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► **To cite this version:**

J. Kittel, J.W. Martin, Thierry Cassagne, Christoph Bosch. Hydrogen induced cracking (HIC) - Laboratory testing assessment of low alloy steel linepipe. Corrosion 2008, Mar 2008, New-Orleans, United States. hal-02475529

HAL Id: hal-02475529

<https://hal-ifp.archives-ouvertes.fr/hal-02475529>

Submitted on 12 Feb 2020

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HYDROGEN INDUCED CRACKING (HIC) - LABORATORY TESTING ASSESSMENT OF LOW ALLOY STEEL LINEPIPE

J. Kittel
IFP-Lyon
Rond-point de l'échangeur de Solaize
BP3 – 69390 Vernaison, France.

J. W. Martin
BP Exploration Operating Co. Ltd
Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN.

T. Cassagne
Total
Avenue Larribau
64018 Pau Cedex, France.

C. Bosch
Salzgitter Mannesmann Forschung GmbH
Ehinger St. 200
47259 Duisburg, Germany.

Paper on behalf of the EPRG Corrosion Committee

ABSTRACT

As a first step, a literature survey was undertaken on Hydrogen Induced Cracking (HIC) phenomena. Material and metallurgical parameters were investigated; in addition the various testing methodologies, environments and pass/fail criteria used for HIC fit-for-purpose (FFP)⁽¹⁾ testing were assessed. The literature sources suggested a variety of methodologies that can be used for FFP HIC testing. However, a universally applicable FFP test method was not identified. Therefore, an experimental study was launched to establish a suitable methodology and better define the key parameters involved in HIC phenomena. The use of "sweet service

¹ The FFP terminology is used in accordance with the NACE MR0175/ISO 15156, where the following definition is given: "suitability for use under the expected service conditions".

grade" C-Mn linepipe in mild sour service could provide economic benefits, but would require an assessment of the HIC performance to be undertaken for the intended service conditions. Therefore, five different sweet service line-pipe steels were used for these studies. Experiments consisted of HIC exposure tests based on the NACE TM0284-2003 Standard Test Method. Parameters studied were pH (3.5 to 5.5), H₂S partial pressure (3 to 100mbar), and time of exposure (96 hours to 3 months). Characterisation included hydrogen content measurement for diffusible hydrogen (glycerol method). HIC cracking was evaluated by ultrasonic testing and by metallographic examination in accordance with the NACE TM0284-2003 Standard Test method.

From the HIC exposure tests, a good correlation was found between diffusible hydrogen and HIC. Above 1ppm diffusible hydrogen, all specimens exhibited severe HIC.

For specimens tested at a level of 10mbar H₂S no HIC was observed after 96 hours exposure. But tests with longer exposure (4 weeks) did result in HIC. This suggests that the low severity conditions require longer exposures to reach equilibrium levels of internal hydrogen. This must be taken into account for FFP HIC testing in mildly sour environment. Considering the impact of the environment, H₂S partial pressure seemed to have a much greater impact than pH on the extent of HIC.

These results suggest that a "regions of environmental severity" diagram, similar to that developed for sulphide stress cracking in the 1990s and later incorporated into NACE MR0175/ISO 15156, can be developed for the HIC resistance of suitable sweet service grade steels. This relates the HIC resistance to the two-dimensional environmental severity defined by the partial pressure of H₂S and the pH. This diagram will enable the mapping of HIC according to cracking susceptibility and help in defining the 'HIC sour service' limits for line-pipe steels.

Keywords: HIC, sour (H₂S containing) environment, linepipe steel

INTRODUCTION / BACKGROUND

In the presence of H₂S, hydrogen atoms originating from the cathodic reduction reaction (driving the anodic dissolution reaction) can diffuse into the steel, resulting in cracking mechanisms such as hydrogen-induced cracking (HIC), sulphide stress cracking (SSC) and stress-oriented hydrogen-induced cracking (SOHIC). The presence of liquid water necessary for the corrosion reactions can occur even if the gas temperature in the pipeline is above the water dew point, e.g. due to the lower temperature of the pipe wall compared to the gas temperature or where the reduction of gas temperature along the pipeline results in the water vapour in the gas condensing out. Due to the fact that such cracks can be very difficult to detect during routine inspection, this type of damage is often regarded as more dangerous than weight-loss corrosion.

The classification of carbon/low alloy steel materials within regions of environmental severity, as already defined for resistance to cracking in NACE MR-0175/ISO 15156 Part 2¹ (Figure 1), could provide a tool for the accurate assessment of HIC susceptibility of sweet service linepipe which may have adequate resistance to HIC in mild sour conditions thus providing significant economic benefits without impacting upon safety. However, it needs to be recognised that the

pH – p_{H2S} severity regions for SSC and HIC will not necessarily match. Thus, Figure 1 is suitable for SSC resistance only and a similar plot is required for HIC and related mechanisms. In addition, NACE MR0175/ISO 15156 Part 2 does not place any lower H₂S limit below which an assessment of HIC resistance is unnecessary. The definition of 'sour service' within NACE MR0175/ISO 15156 is not restricted to conditions above 3.5 mbar H₂S, as was the case in the previous editions of NACE MR0175 which considered only SSC resistance. Therefore, for the definition of the different region boundaries for HIC, environmental conditions with H₂S partial pressures at and below 3.5 mbar (i.e. region 0) have also to be taken into account. As the standard HIC test is performed under severe conditions, it is an overly conservative method to qualify materials for mildly sour conditions. In addition, it is not sufficient for establishing the region boundaries on a domain diagram of the type in Figure 1. Therefore, there is a strong need for new or modified test conditions/methods with respect to the different operating requirements for fit-for-purpose testing.

As the first step of this study by the European Pipeline Research Group (EPRG) Corrosion Committee, a literature survey was undertaken on HIC phenomena². Material and metallurgical parameters were investigated; in addition the various testing environments and criteria used for fit-for-purpose testing (FFP) were assessed. The literature sources suggested a variety of methodologies that could be used for FFP HIC testing. It was stated that hydrogen permeation measurements in general can provide a quantitative measure for differentiating HIC performance and that field measurements of the maximum concentration of dissolved hydrogen in steel could also be helpful for FFP classification. However, a universally applicable FFP test method was not identified.

From a consideration of the results from the literature survey a number of key conclusions were drawn, as follows:

- The clarification of the environmental boundary conditions was considered to be the key to FFP testing.
- To perform FFP laboratory testing, the test environment must represent the specific operating environment. This can be obtained by the variation of the test severity using modified test set-ups (e.g. the modification of number of exposed specimen sides, H₂S content, pH, specimen type).
- A HIC domain diagram similar to the ISO 15156-2 definition of SSC regions dependant on H₂S partial pressure and pH, might be obtained, in part, by hydrogen permeation measurements, if these could be correlated to HIC performance.
- For acceptable HIC testing, the transferability of the results to the actual field conditions must be achieved. It has been demonstrated that the surface concentration of diffusing hydrogen atoms on operating pipelines can reach a peak value within a short period (even a few days for sour service conditions²), such that in order to match the operating environment the test environment should reach the same peak value.
- It was finally stated that full-scale test results do not necessarily correlate with laboratory test results. In particular, tests involving six-sided hydrogen charging might not be correlated with the performance of the pipes under service conditions. During the laboratory test, the hydrogen activity remains constant over the specimen thickness, whereas under service conditions, there is a linear decrease from the inside to the outside of the pipe wall.

Starting from these insights, an experimental study was launched with the objective of establishing a suitable methodology for FFP HIC testing and to better define the key parameters involved in HIC phenomena. A 'reference steel' (type API 5L X65 non sour service steel) was first studied. Experiments consisted of HIC exposure tests based on the NACE TM0284-2003 Standard Test Method³. Parameters studied were pH (3.5 to 5.5), H₂S partial pressure (10 to 100mbar), and time of exposure (96 hours to 1 month). Comparisons between one-sided (more typical of field operating conditions) and six-sided exposure of HIC specimens were also undertaken. Characterisation of the material after test included measurements of the diffusible hydrogen content by the glycerol method. HIC cracking was evaluated both by ultrasonic testing and by metallographic examination in accordance with NACE TM0284-2003. The results of this preliminary study were reported in a previous Paper⁴. For the reference steel, cracking occurred mostly in the half thickness region. A good correlation was found between the crack length ratio (CLR) estimated from metallographic examinations, and the crack area ratio (CAR) from ultrasonic testing. A threshold diffusible hydrogen content of 1ppm was determined, above which 100% of the specimens exhibited HIC. It was also found that the low severity environments (down to 3 mbar H₂S) still could result in HIC, if the time of exposure was sufficiently long (up to 3 months).

The FFP test methodology established as a result of this preliminary study was generally in accordance with NACE TM0284-2003, but with the following deviations/additional features:

- Testing period of two weeks, although longer term tests are required to initiate cracking for lower severity conditions, e.g. 4 weeks at 10mbar H₂S and pH 3.5.
- Six-sided exposure, to ensure attainment of equilibrium levels of hydrogen within the testing period (with one-sided testing, equilibrium could not be ensured).
- Test solution parameters varied are pH (buffered values of 3.5, 4.5 and 5.5) and H₂S partial pressure (10mbar, 35mbar and 100mbar). It was found that the H₂S partial pressure had a far greater influence on the extent of HIC (and indeed the levels of diffusible hydrogen) than did the pH. Increasing the partial pressure of H₂S and, to a lesser extent, decreasing the pH resulted in an increased risk/extent of HIC.
- Measurements of the diffusible hydrogen made on samples at the end of the HIC test. A good correlation was found between diffusible hydrogen and the extent of HIC
- HIC cracking evaluated using both ultrasonic testing and metallographic examination in accordance with NACE TM0284-2003.

Following on from completion of the preliminary study, the present study to assess a total of five different sweet service steels was launched to evaluate the effects over a range of different steels.

MATERIAL TESTED DURING THE PRESENT STUDY

Five sweet service steel types were tested during the present study (Table 1). No welds were included in the tested specimens, only the base metal was tested.

The chemical compositions of all steels were analysed by optical emission spectrometry (OES), except for carbon and sulphur which were analysed by a chemical method (Table 2).

For all materials, the microstructure was observed using an optical microscope, after polishing with a 0.05µm finishing suspension and etching with a 2% Nital (nitric acid - ethanol) solution. The microstructures at the mid wall location are presented in Figure 2:

- Steel "P" presents a typical ferrite – pearlite microstructure. The grain size is between 10 and 30µm and the microstructure is highly orientated in the rolling direction.
- The microstructure of steel "R" is mainly composed of ferrite and pearlite, with traces of bainite. The pearlite content seems lower than in steel "P". The grain size is between 5 and 15µm. The microstructure is oriented in the rolling direction, with a segregation area in the mid-thickness.
- The phases observed in steel "S" are ferrite and pearlite. The grain size is between 5 and 20µm. The microstructure is highly orientated in the rolling direction, with a segregation zone in the mid-thickness.
- The major phases observed in steel "T" are ferrite and pearlite. The grain size is between 5 and 15µm. The microstructure is orientated in the rolling direction.
- The major phases observed in steel "U" are ferrite and a small proportion pearlite. The grain size is between 5 and 20µm. The microstructure is highly orientated in the rolling direction, with a segregation area in the mid-thickness.

Table 3 compares the tensile properties of all steels in the direction longitudinal to rolling, measured according to NF EN10002-1⁵.

The inclusion content was analysed according to ASTM E45 method A⁶. The results are presented in Table 4.

EXPERIMENTAL METHODS

Test solution and exposure conditions

The test solutions were prepared in accordance with EFC16⁷, using sodium acetate buffer, and the pH was monitored and adjusted, as required, during the experiments. The one exception to this was for tests where the standard NACE TM0284-2003 solution A was used (starting pH of 2.7).

All specimens were of 6-sided exposure type, 100mm long and 20mm wide and standard glass vessels were used. All HIC tests were performed following the general NACE TM0284-2003 standard, including three replicates for each condition and a volume / surface ratio greater than 3mL/cm².

The experimental parameters studied were pH (3.5, 4.5 and 5.5) and H₂S partial pressure (3, 10, 35 and 100mbar), with a CO₂ balance up to the 1bar total test pressure. The impact of the exposure time was also evaluated: longer exposures were performed for the "low severity" condition (i.e. 4 weeks at 10mbar H₂S and 3 months at 3mbar H₂S), while the higher pH₂S were tested for 96 hours and 2 weeks.

The corresponding pH-pH₂S regions of investigation are mapped onto the SSC regions map in Figure 3.

HIC specimen preparation

HIC specimens for 6-sided exposure were sampled following the NACE TM0284-2003 standard test method. The sample dimensions were 100mm in the longitudinal direction, 20mm

wide and the same thickness as the base material (0.5 to 1mm were removed from the inner and outer surfaces). All faces were machined to obtain a finish equivalent to that achieved using 320 grit SiC paper.

HIC evaluation by metallography and ultrasonic testing

Two methods were used for the determination of the extent of HIC.

The first consisted of the standard NACE TM0284-2003 practice, with three equidistant cuts along the length and metallographic examination of the cut faces.

For the other method, ultrasonic inspection was applied using a 15MHz transducer (1/4" diameter). The system was calibrated according to an in-house technique. For each specimen, the total area of the defects was calculated from the UT scans, and the crack area ratio (CAR) was determined as the ratio between the area of the defects and the total area of the specimen in the short transverse plan.

Hydrogen concentration

The determination of diffusible hydrogen concentration in the steel specimens was performed using an in-house procedure based on a Japanese standard⁸:

Immediately after removal of the specimen from the test solution, it was rinsed with tap water and wiped with paper to remove the non-adhering sulfur deposit, then immediately immersed in 45°C glycerol under a collector tube. The time gap between specimen sampling and immersion in glycerol was always less than 2 minutes. The diffusible hydrogen was then measured by the displacement of glycerol after one week immersion at 45°C. The experimental error associated with free hydrogen measurement is 0.1mL. The repeatability was evaluated by comparing three identical specimens. The standard deviation was always less than 20%. For the sake of comparison with literature data, the diffusible hydrogen content was expressed in ppm. The volume of hydrogen that was measured at 45°C was first corrected to standard temperature and pressure using the perfect gas law. The corresponding mass of hydrogen was then divided by the mass of the corresponding steel specimen to obtain the hydrogen content in mass ppm.

RESULTS AND DISCUSSION

Table 5 summarizes the diffusible hydrogen content measurements. CAR values from US tests and CLR values from metallographic cuts are reported in Table 6 and Table 7 respectively.

Comparisons between US method and metallographic examination

In order to further investigate the comparative results between both US examination and metallographic analysis, a correlation graph between CAR and CLR was generated covering all the experiments (Figure 4). Each point in the graph represents the CAR and CLR (average of three cross-sections) measured for one individual specimen.

It is clear from this graph that the correlation between CAR and CLR was very good. For the specific range of conditions/materials as well as US equipment/calibration used in this study, the following equation can be proposed:

$$CLR = 0.64 \times CAR$$

This good correlation is explained by the location of cracks in a narrow zone at, and close to, the center line. This is often the case for sweet service steels, where the segregation of inclusions is often limited to the center line area. However, in the case of steels with a distribution of cracks throughout the thickness of the plate, the top view projection of the cracks, as used for the CAR determination from UT scans, might not be sufficient .

Using this ratio, the upper CLR limit value of 15% proposed in ISO 15156-2 after 96 hours exposure in the NACE TM0284 solution A would correspond to a CAR upper limit of 23%. The comparison between CAR and CLR as selection criteria is further illustrated in Figure 5. The CLR and CAR values of all specimens are reported in bar graphs, from the highest to the lowest CLR. Using 15% CLR or 23% CAR as pass or fail criteria gives the same ranking, i.e. specimen n°1 to specimen n° 15 failed.

It can thus be considered that, for the purposes of this study, there were no major differences between the two techniques. Therefore, the remaining discussion in the present report is based only on CAR results.

Correlations between diffusible hydrogen content and HIC sensitivity

In order to check if there is a correlation between HIC extent and the amount of diffusible hydrogen in the material, a correlation graph between CAR and diffusible hydrogen was generated for all the experiments (Figure 6). The CAR value used for this graph was determined on the same specimen which was subjected to diffusible hydrogen content determination.

Though there is no clear and direct correlation between the CAR value and diffusible hydrogen content, it is still possible to distinguish three distinct regions:

- Below 0.5ppm of diffusible hydrogen, where only one of the specimens suffered (slight) HIC,
- Between 0.5 and 1ppm of diffusible hydrogen, where most of the specimens of steels R, S and T and U had CAR values below 10%. Only 1 specimen of the other steel (steel P) suffered a higher CAR value (CAR 29%) and, even then, only after a very long duration test (i.e. 3 months under 3mbar H₂S),
- If the CAR upper allowable limit value of 23% indicated earlier was used, all specimens of steels R, S, T and U with less than 1ppm hydrogen would pass. For steel P, only one specimen had a high HIC ratio (CAR 29%) together with a moderate hydrogen concentration (0.9ppm) and, even then, only after a long duration test with low H₂S (3mbar / 3months),
- Above 1ppm diffusible hydrogen, most of the specimens exhibited a high level of HIC, with CAR values above 20%. However, 3 specimens exhibited lower CAR, respectively 11, 3 and 0%, the last two corresponding to 1.1ppm diffusible hydrogen (i.e. borderline).

These results are in good agreement with previous tests using the same diffusible hydrogen content methodology. Revie et al.⁹ studied the HIC resistance of eight steel grades exposed to buffered solutions from pH 1.1 to 5.9 saturated with H₂S. They determined a threshold hydrogen concentration above which HIC occurred. For 4 steel grades out of 5, this threshold

hydrogen concentration varied from 0.2 to 0.9mL/100g (standard pressure and temperature), which corresponds to 0.2 to 0.8ppm, in excellent agreement with the 1ppm limit proposed in this work.

Another study recently reported by Hara et Al.¹⁰ on HIC evaluation of X65 linepipe steels gave similar CAR / hydrogen concentration trends. For most of the studied steels (8 types of X65 linepipe) the critical hydrogen concentration was between 0.6 and 2ppm.

Therefore it is possible to consider that the diffusible hydrogen content could be a good indicator of the risks of HIC. For conventional ferrite pearlite steels, the critical concentration below which HIC risks are moderate could be 0.8 to 1ppm of diffusible hydrogen. Above 1ppm diffusible hydrogen, the situation requires a more detailed investigation, since some cases of low HIC were found for hydrogen content greater than 1ppm (albeit for two cases this was only marginally above the 1ppm limit). As suggested by the results from the literature, it may be necessary to determine a hydrogen limit on a case by case basis for different steels to provide more accuracy.

Impact of pH₂S and pH

The variation of H₂S partial pressure was found to significantly affect the severity of HIC for all the materials tested (Figure 7). Indeed, decreasing the partial pressure of H₂S from 100mbar to 10mbar drastically decreased the risks of HIC, even though the exposure time was increased from 2 weeks to 4 weeks at the same time. At 100mbar, all materials exhibited CAR values from 13% to 65% after 2 weeks exposure. At 10mbar H₂S and after 4 weeks exposure, two materials did not suffer HIC, and the highest CAR was only 14%. Intermediate values were found for the tests under 35mbar H₂S.

However, the exposure time also played a major role in the severity of HIC: for materials P and S, higher CAR values were found after 3 months at 3mbar H₂S than after 1 month at 10mbar. This result is potentially important since 3 mbar H₂S is an established limit below which the risk of SSC is often considered insignificant for all practical purposes (Region 0 in NACE MR0175/ISO 15156 part 2). For HIC, it seems that the situation is not straight-forward and this raises the question of what the optimum test duration is under 'mild' conditions for HIC laboratory tests, and their correlation to field exposure. The conclusion from the preliminary stages of the project that the hydrogen equilibrium concentration would be reached after 2 weeks exposure for all conditions⁴ might be misleading in that sense. Alternatively, diffusible hydrogen concentration alone might not be a good indicator, or the analysis method might not be appropriate. Full scale tests with representative 1-sided exposure are needed to further investigate this point. HIC laboratory tests aimed at studying specifically the impact of exposure time for different pH – pH₂S would also be helpful. At least two questions require evaluation:

- i/ is there a correlation between pH – pH₂S conditions and the incubation time for HIC start?
- ii/ Once HIC has started, how long does it take to progress and reach an "equilibrium level", and is this equilibrium level linked with pH, pH₂S, or both ?

The impact of test solution pH was also examined. Figure 8 presents the CAR value versus pH graph for all the experiments undertaken at 100mbar H₂S.

With the exception of steel P, which was the least resistant of the HIC tested materials and had high CAR values over the whole pH range, the steels had a tendency towards a decrease in

CAR when the pH increased. However, contrary to the case for H₂S partial pressure, there did not seem to be a clear pH threshold above which no HIC is expected in the pH range 2.7 to 5.5. Even though no tests were performed at pH levels above 5.5 during the present study, similar experiments were described in the literature¹¹, and CAR values above 5% were still observed after 4 days testing at pH 6.2 under 1bar H₂S, on a steel grade close to those used in the present work.

For the present tests the results for the NACE TM0284-2003 Solution A were always less severe than comparable results for EFC 16 solution at a constant pH of 3.5. This might be explained by the rapid pH increase when using the NACE TM0284-2003 solution A. As illustrated in Figure 9 for the tests under 100mbar, it took only 2 days to reach pH 3.5. Therefore, 2 weeks exposure in EFC 16 solution at a constant pH value of 3.5 was more severe than the corresponding 2 weeks test in NACE solution without pH adjustment.

pH – pH₂S severity diagram

From these results HIC severity diagrams were created for each steel grade, in a similar manner to the SSC region plot in NACE MR0175/ISO 15156 Part 2 (Figure 10). The following convention was adopted in order to classify CAR values into different categories:

- CAR < 5%: no or little HIC
- 5% ≤ CAR < 23% light HIC (corresponding to < 15% CLR)
- 23% ≤ CAR < 50% strong HIC
- CAR ≥ 50% very strong HIC

These values were chosen essentially to provide an average distribution of the results of the present study in the different categories. It is worth noting that with respect to the correlation between CAR and CLR that was indicated earlier, the 15% CLR acceptance criteria of ISO 15156 for the NACE TM0284-2003 Standard Test Method with Solution A would correspond to a 23% CAR. The SSC regions of ISO 15156-2 are also indicated on the graphs for comparison.

A preliminary attempt at defining HIC severity domains has been made using the results from this study. It is emphasised that the impact of exposure time is not well understood at this stage of the investigation such the severity domains should be treated as preliminary. The HIC severity domains that have been proposed are therefore based mainly on the results with comparable exposure times, i.e. 2 weeks and up to 1 month. The results obtained under 3 mbar and after 3 months immersion have not been included for the purpose of this discussion.

One of the more important conclusions concerns the impact of pH₂S, which always had a greater influence on HIC than pH. This confirms previous findings¹¹, but is also in contradiction with the well established theory that HIC is only linked with the hydrogen activity in the system, and therefore more closely linked with the test solution pH. Nevertheless, it seems reasonable to propose to incorporate a lower threshold for H₂S partial pressure in a HIC severity diagram. From the results of this work, a lower H₂S partial pressure threshold could be chosen between 1mbar and 10mbar, but further work is required to establish whether such a threshold exists.

The proposal to incorporate a diagonal threshold line in a HIC diagram is also open to question. The SSC diagonal limit with a slope of 1 between (1mbar H₂S; pH 3.5) and (1bar H₂S; pH 6.5) does not seem to be well adapted to HIC. Indeed, for 3 out of 5 materials tested

CAR values were greater than 20% when tested under 100mbar H₂S and pH 5.5. However, if no diagonal threshold was used, the impact of pH would be completely disregarded. This option is considered excessive; though limited, it was observed that pH did have an impact on the severity of HIC. It is proposed that the diagonal threshold for HIC could link (3mbar H₂S; pH 3.5) and (100mbar H₂S; pH 6.5). However, during the present work no experiments above this diagonal line were performed such that more testing will be required, including an investigation of the impact of test duration, to better define this diagonal limit. Concerning the test duration, it should be remembered that steel "P" did not suffer HIC after 4 days exposure at pH 3.5 and 10mbar H₂S whereas 4 weeks exposure in the same conditions resulted in 14% CAR. HIC in low severity conditions is therefore not "instantaneous", and several days or weeks might be necessary to initiate cracking. This could be related to the low hydrogen permeation rates observed at low pH₂S¹²⁻¹³, such it takes more time to reach the critical hydrogen content for HIC.

As has already been indicated, further investigations are required to establish the principle and limits of the domains. For example:

- Within this work, only few experiments were performed in region 1, as defined below (Figure 10).
- A still wider range of steels will also have to be tested.
- Additionally, full scale experiments will be necessary for a definition of acceptance criteria, especially in the case of US testing, and also to re-define the necessary exposure times of HIC tests. This is particularly true for the low H₂S conditions.

Notwithstanding the need for further work, at this stage a preliminary HIC severity diagram could be proposed, with four distinct regions (Figure 11):

- Region 0: non sour. No specific steels are required. The existence and value of the threshold H₂S level still needs to be established but it is proposed that this could be somewhere between 1 and 10 mbar.
- Region 1: mildly sour region. At the present stage of investigations, it might become necessary that longer term (e.g. 4 weeks) tests are required to demonstrate suitability of specific 'sweet service steels' in terms of HIC resistance in this region.
- Region 2: transition region. It is recommended to perform HIC exposure tests for the qualification of 'sweet service' steels for use in these conditions.
- Region 3: sour region. It is mandatory to use sour service materials.

CONCLUSIONS

Use of sweet service grade linepipe in mild sour service could provide potential economic benefits, but would require an assessment of the HIC performance under the intended service conditions. For this purpose, a test methodology developed for the assessment of the HIC resistance of linepipe steels for 'mild sour environments'⁴ has been applied to five commercially available sweet service linepipe steels. Experiments consisted of exposure tests based on the NACE TM0284-2003 standard test method, but with different pH and H₂S partial pressure levels. The impact of the 'time of exposure' was also examined. Characterisation methods comprised diffusible hydrogen content measurements and cracking evaluations, by both metallographic examination and ultrasonic testing.

These tests showed that:

- A good correlation was found between diffusible hydrogen and the extent of HIC:
 - For a diffusible hydrogen level of below 0.5 ppm no HIC was observed.
 - For a diffusible hydrogen level above 1ppm all samples exhibited high extents of HIC, with CAR values of between 21% and 75%.

These values are in good agreement with previously published values and indicate that diffusible hydrogen may be a good indicator of HIC resistance. However, the threshold hydrogen content might be specific to each material.

- For the five steels used in this study, a good correlation was found between the CLR determined by metallographic examination and the CAR calculated from the ultrasonic scans. This good correlation is probably a consequence of the localisation of the cracks in the half thickness area for all tested steels. CSR and CTR correlations might be required for other types of steels.
- All steels exhibited moderate to high HIC after 2 weeks exposure tests to 35mbar or 100mbar partial pressure of H₂S. For the tests at pH 3.5 and low H₂S partial pressure, HIC was found for three steel grades after 1 month exposure under 10mbar H₂S, and for three steel grades after 3 months exposure under 3mbar H₂S.
- When comparing the results of two week exposure tests, H₂S partial pressure had a far greater influence on the extent of HIC (and indeed the levels of diffusible hydrogen) than did the pH. Increasing the partial pressure of H₂S and, to a lesser extent, decreasing the pH resulted in an increased risk/extent of HIC.

From these results a preliminary HIC severity diagram, synonymous to the SSC severity diagram in ISO 15156-2, has been proposed (Figure 11) with the following Regions:

- Region 0, non sour, where no special precautions are required.
- Region 1, mildly sour, where longer term (e.g. 4 weeks) tests might be necessary to demonstrate suitability of 'sweet service' linepipe materials in terms of HIC resistance.
- Region 2, transition, where HIC testing with a test period of two weeks might be sufficient to qualify 'sweet service' linepipe materials.
- Region 3, sour, where sour service materials must be used.

It should be recognised that this HIC severity diagram has been generated by testing a limited number of steels (five to date) such that further testing is required on a range of 'sweet' materials to confirm the limits of the regions, and especially the boundary between regions 0/1 and 2/3.

A problem that has been identified during this study is that the requirement in NACE MR0175/ISO 15156 Part 2 for acceptance criteria of 'no cracking' for HIC testing under application specific environmental conditions would be extremely difficult to conform to, even under the most mild sour conditions, and hence requires further study. One possibility is to investigate this in a further Phase of the EPRG programme, with a view to generating acceptance criteria that could be applied to milder sour conditions frequently associated with

'application specific' test conditions. This would also enable further refinement of the HIC severity diagram.

The second problem that requires additional investigation is the impact of exposure time, which is not well understood at this stage.

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Table 1: Origins of steels used for the study.

Steel designation	Strength level / Process	Coming from	Thickness	Made for type of pipe
P	X65 TMCP*	LSAW pipe	25	LSAW
R	X70 HSM**	Sheet (coil)	14.2	HSAW
S	X60 HSM	HSAW pipe	14.2	HSAW
T	X60 HSM	Sheet (coil)	8.7	HFI
U	X70 HSM	Sheet (coil)	14.2	HFI

*TMCP: thermo mechanical controlled heavy plate

** HSM: thermo mechanical rolled hot strip

Table 2: Comparison of chemical composition (wt %) for tested materials.

Steel	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Nb	V
P	0.09	1.56	0.28	0.014	0.001	0.05	0.03	0.01	0.02	0,040	0,050
R	0.093	1.8	0.393	0.014	0.005	0.038	0.035	0.007	0.026	0.036	0.083
S	0.098	1.4	0.238	0.017	0.006	0.046	0.046	0.009	0.077	0.025	0.055
T	0.12	1.26	0.274	0.01	0.003	0.042	0.044	0.01	0.055	0.035	<0.005
U	0.06	1.25	0.227	0.007	0.003	0.092	0.194	0.017	0.028	0.038	0.074

Table 3: Comparison of mechanical and microstructural properties of tested materials.

Steel	Rp _{0.2} (MPa)	Rm (MPa)	A (%)	grain size (µm)
P	523	649	24.1	10-30
R	590	671	25.5	5-15
S	480	597	31	5-20
T	510	625	25	5-15
U	548	616	28	5-20

Table 4: Comparison of inclusion content of tested steels, according to ASTM E45 method A.

Steel	Type A (sulfides)		Type B (aluminates)		Type C (silicates)		Type D (oxides)	
	Thin	Heavy	Thin	Heavy	Thin	Heavy	Thin	Heavy
P	0	0	0	0	0	0	0.5	0.5
R	0	0	0	0	0	0	1.5	0.5
S	1	0.5	0.5	0	0	0	1	0.5
T	1.5	0	0	0	0	0	1	0.5
U	0	0	1.5	0	0	0	0.5	0

Table 5: Diffusible hydrogen content measured by the glycerol method after each experiment and for each steel grade (mass ppm).

pH ₂ S	3mbar	10mbar		35mbar		100mbar			
pH	3.5**	3.5*	2.7	4.5	3.5	5.5	4.5	3.5	2.7
P	0.9	1.0	0.9	1.1	1.5	2.1	1.2	1.7	1.3
R	0.5	0.4	0.4	0.6	1.5	0.4	2.8	1.1	1.1
S	1.3	0.9	0.8	1.1	1.3	1.9	4.1	3.4	1.7
T	0.2	0.6	0.2	0.2	0.3	0.5	0.5	1.5	0.6
U	0.4	0.6	0.5	0.9	0.9	0.8	0.7	0.8	2.2

* 1 month test; ** 3 months test

Table 6: CAR values determined from the US scans on all specimens after each experiment.

pH ₂ S pH duration	3mbar		10mbar			35mbar		100mbar						
	3.5 3m	4.5 2w	3.5 4d	2.7 1m	2.7 2w	4.5 2w	3.5 2w	5.5 4d	5.5 2w	4.5 4d	4.5 2w	3.5 4d	3.5 2w	2.7 2w
P	25	0	0	14	0	32	75	21	66	49	56	52	63	48
R	0			5	0	6	39		23		38		65	35
S	18			1	0	3	23		38		43		48	39
T	0			0	0	0	4		0		3		13	2
U	1			0	0	10	7		3		21		15	15

Duration: d=days; w=weeks; m=months

Table 7: CLR values determined from three metallographic cuts (25-50-75mm) on all specimens after each experiment

pH ₂ S pH duration	3mbar		10mbar			35mbar		100mbar						
	3.5 3m	4.5 2w	3.5 4d	2.7 1m	2.7 2w	4.5 2w	3.5 2w	5.5 4d	5.5 2w	4.5 4d	4.5 2w	3.5 4d	3.5 2w	2.7 2w
P	12	0	0	11	0	21	46	6	38	13	33	44	38	21
R	0			1	0	2	33		11		22		35	26
S	7			0	0	3	12		23		33		44	24
T	0			0	0	0	0		0		0		9	1
U	0			0	0	6	1		1		13		7	7

Duration: d=days; w=weeks; m=months

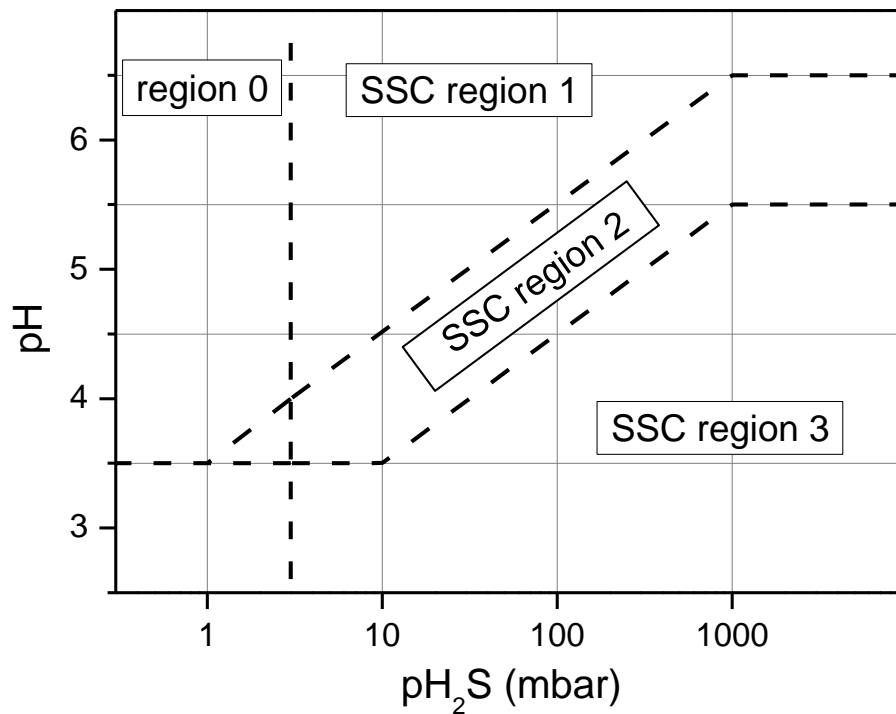


Figure 1: SSC regions of environmental severity according to ISO 15156-2.

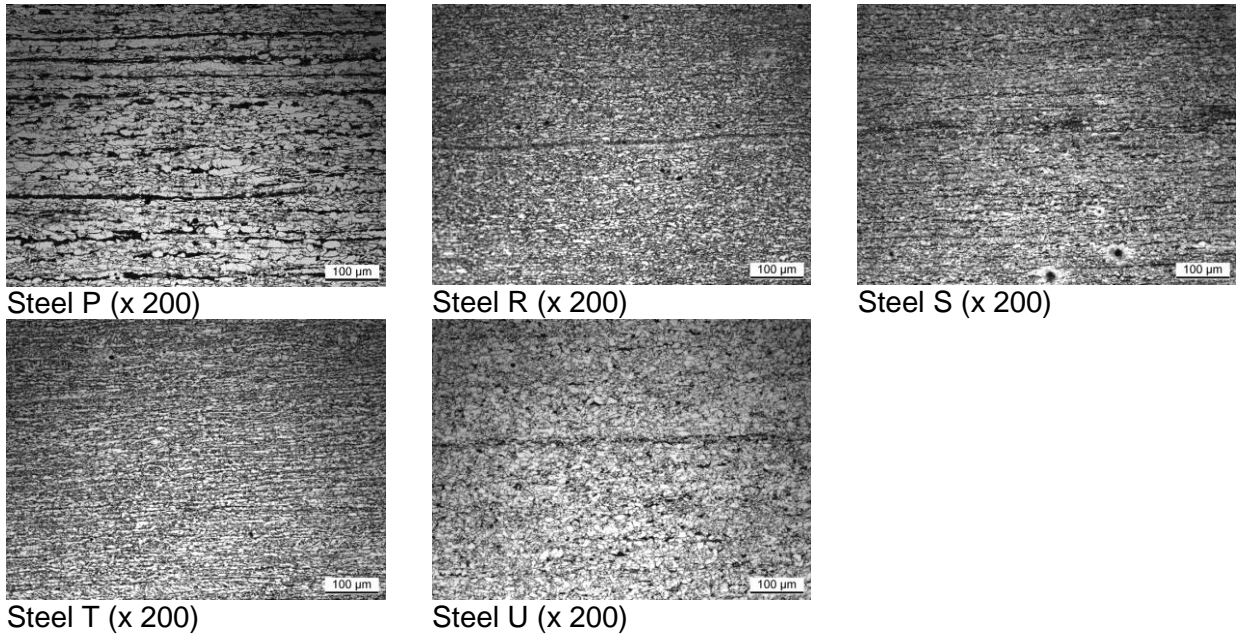


Figure 2: Microstructure of tested steels.

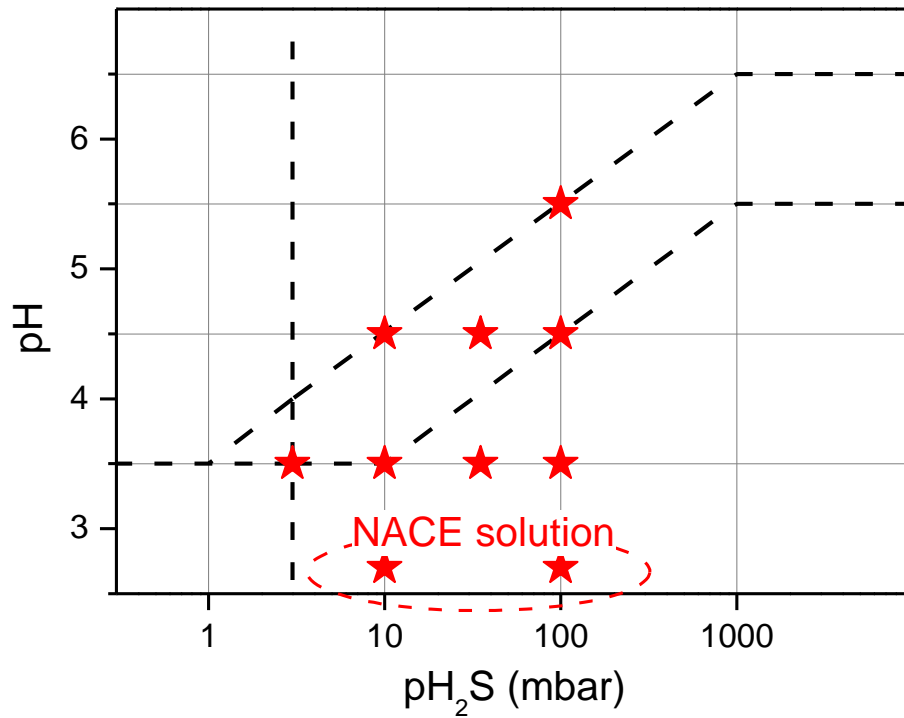


Figure 3: Experimental matrix.

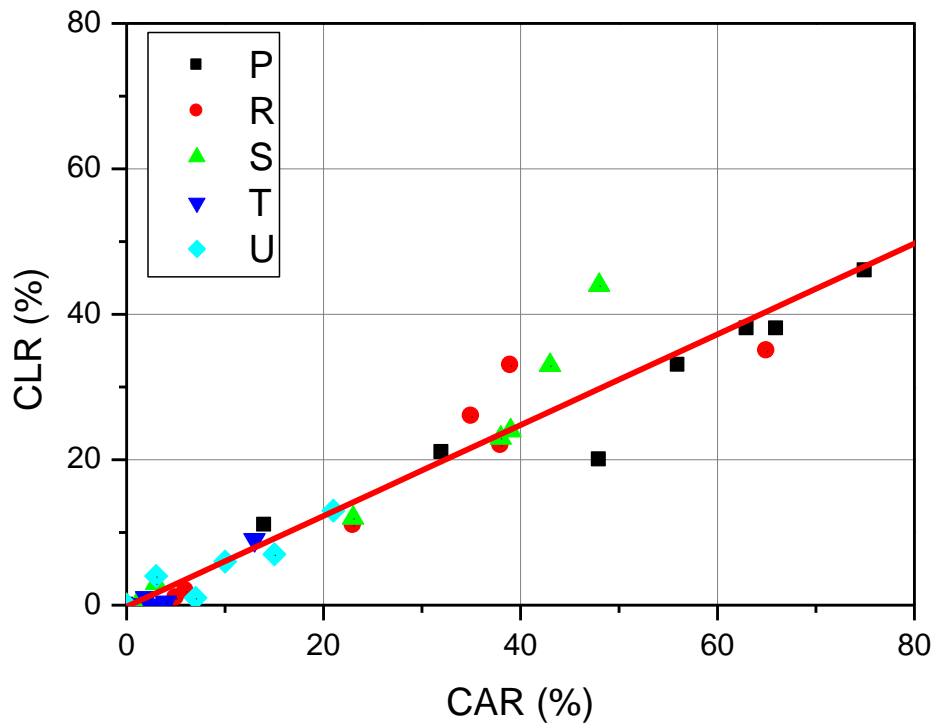


Figure 4: Correlation graph between CAR and CLR for all specimens after HIC experiments.

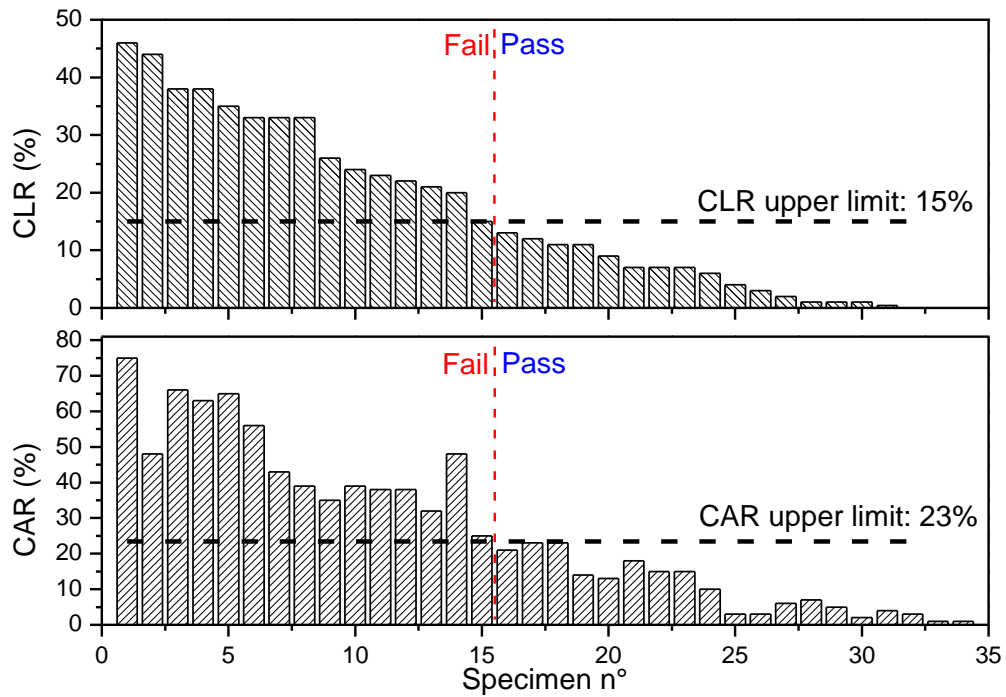


Figure 5: CLR and CAR values of all specimens.

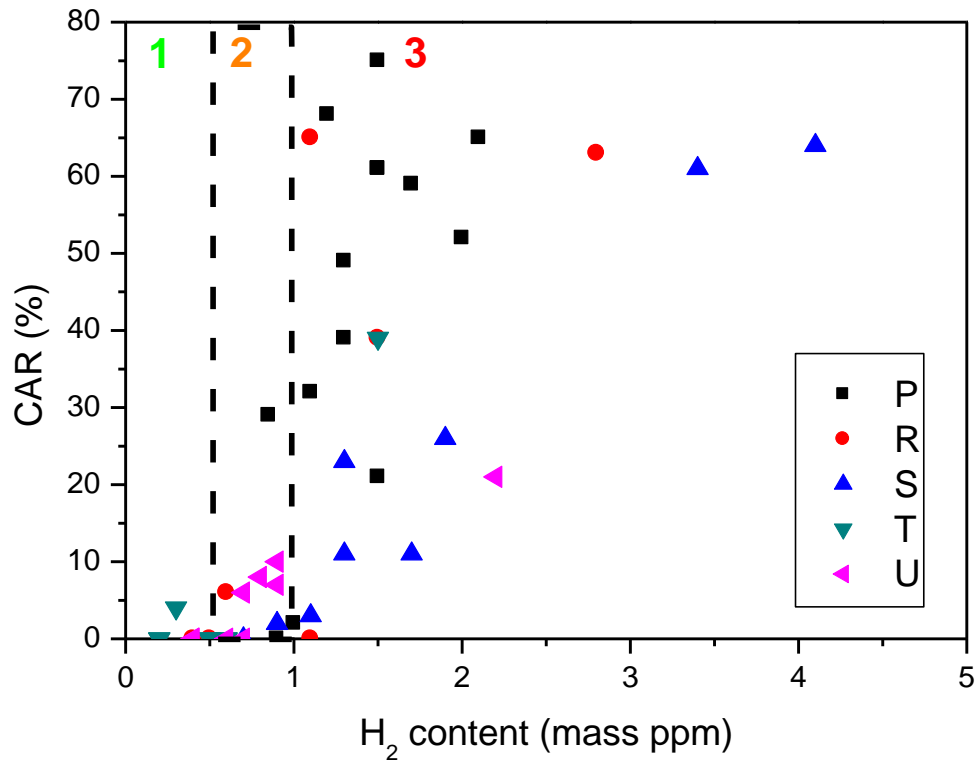


Figure 6: Correlation graph between CAR (%) and diffusible hydrogen content (mass ppm) for all HIC experiments.

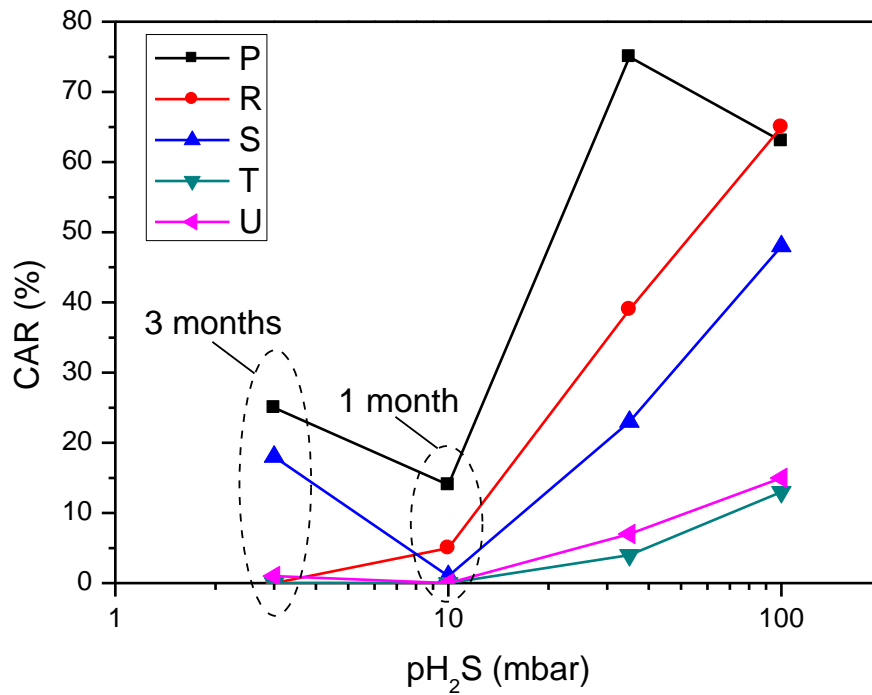


Figure 7: Impact of H₂S partial pressure on CAR for the experiments at pH 3.5.

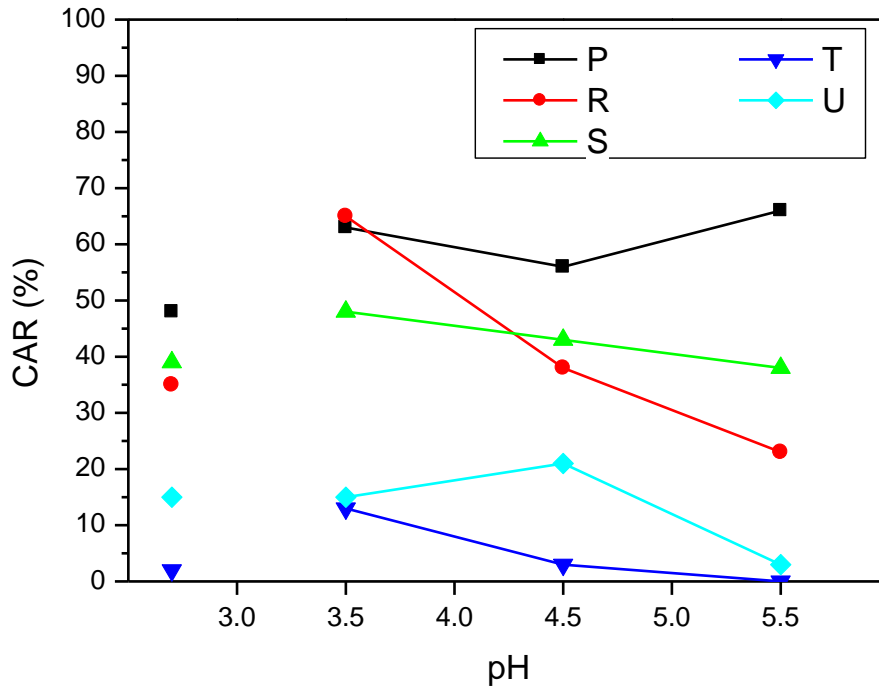


Figure 8: Impact of pH on CAR values for the 2 week exposure under 100mbar H₂S (points at pH 2.7 corresponds to test in NACE solution, without pH adjustment).

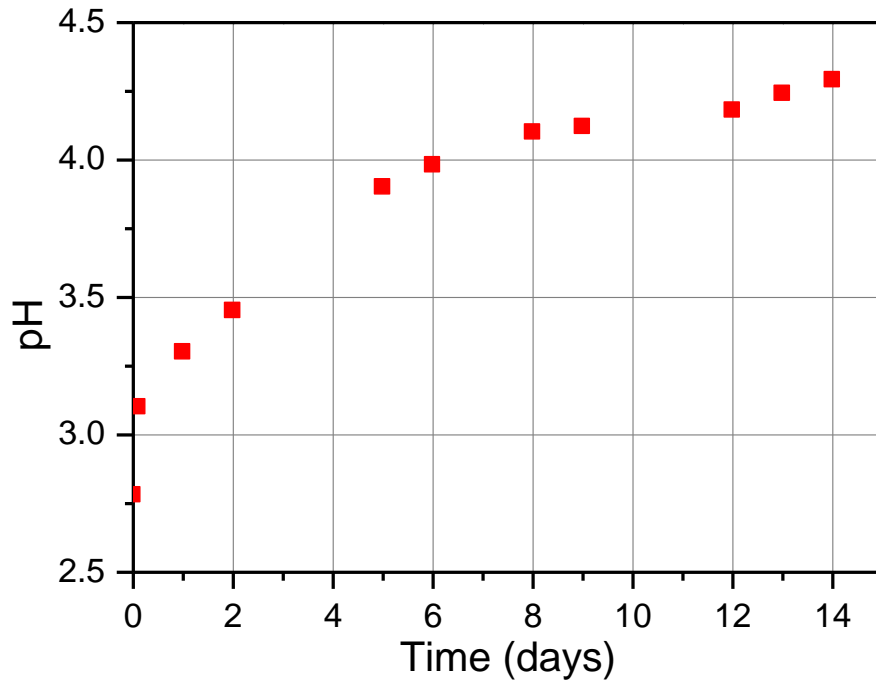


Figure 9: pH evolution during 2 weeks test in NACE TM0284-2003 Solution A under 100mbar H₂S.

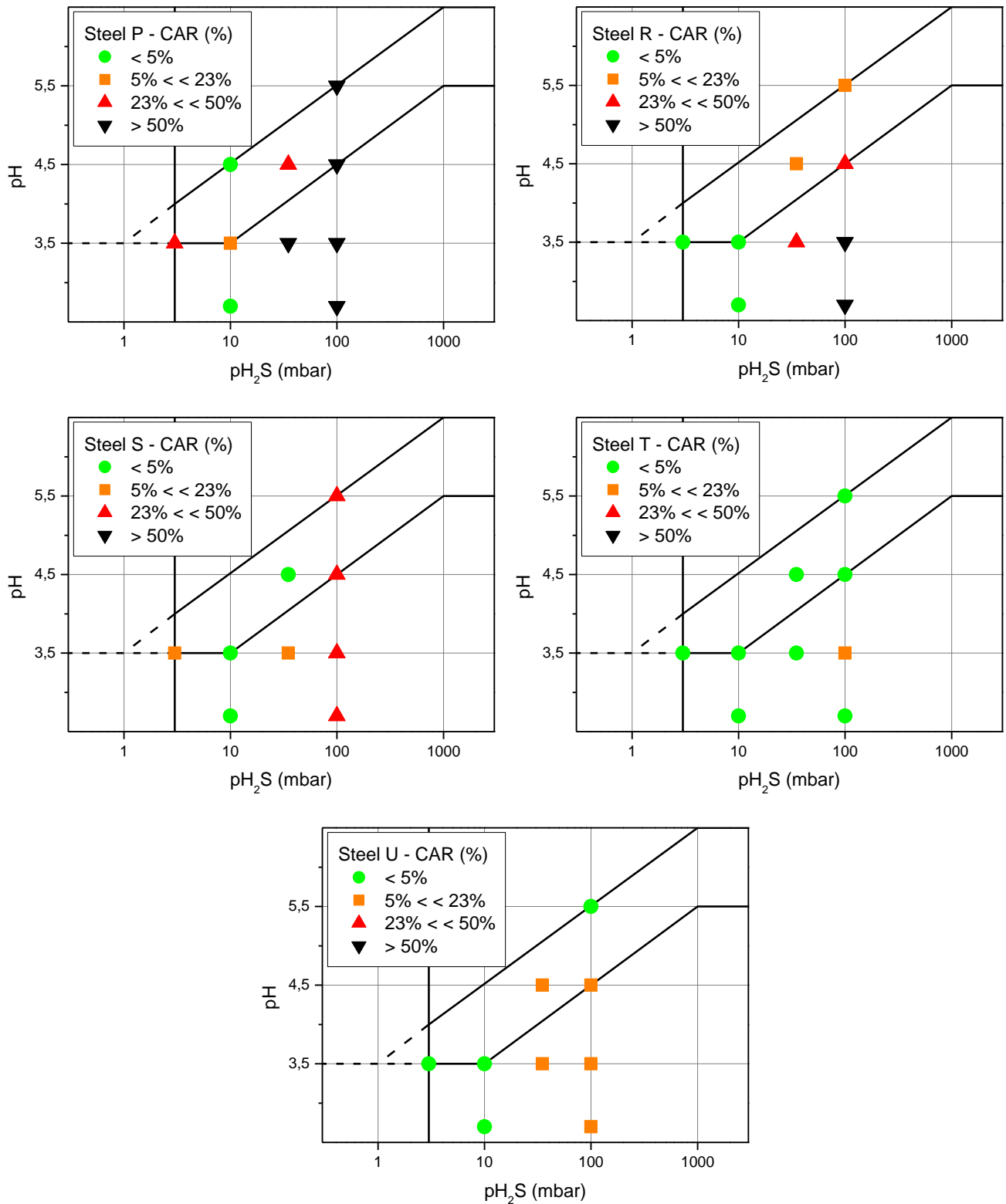


Figure 10: Representation of CAR results in the pH- pH_2S diagram. Exposure time was 2 weeks for all experiments, except at pH 3.5 – 10mbar (4 weeks) and at pH 3.5 – 3mbar (3 months). EFC 16 solution A was used for all tests, except for tests at pH 2.7, where NACE TM0284-2003 solution A was used.

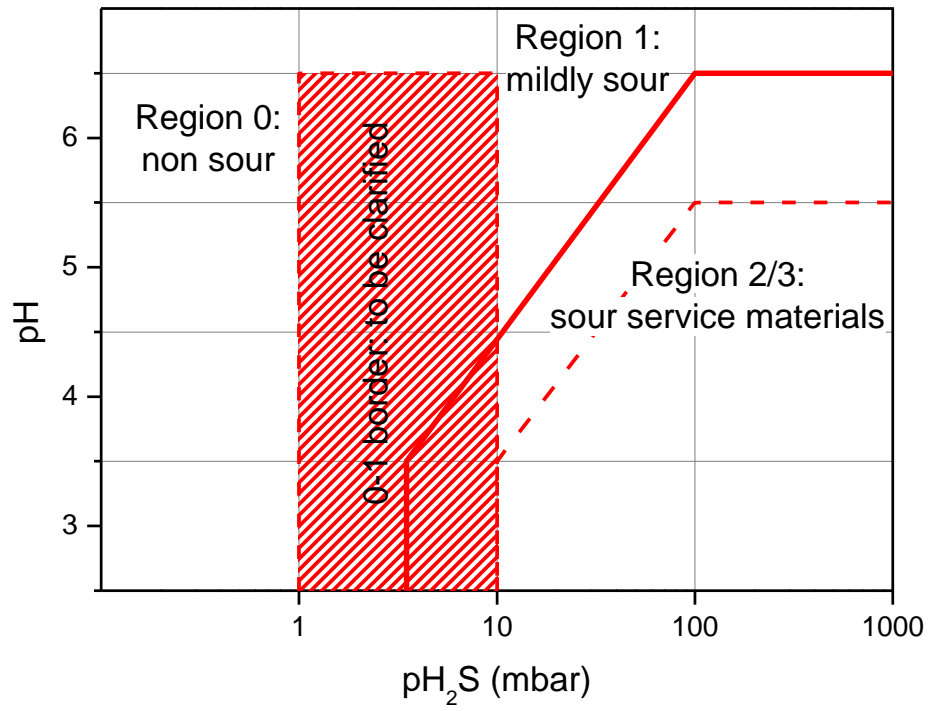


Figure 11: Proposal of HIC severity regions.