CORROSION FATIGUE PROPERTIES OF AN OFFSHORE STRUCTURAL STEEL IN SEAWATER CONTAINING HYDROGEN SULPHIDE.

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The effect of hydrogen sulphide (H_2S) in concentrations up to 1000 ppm. in natural seawater on the corrosion-fatigue of a high-strength micro-alloy steel has been determined. The crack growth rate increased with increasing H_2S content but biologically generated H_2S was less potent than synthetic, added, H_2S. An upper "threshold" level of H_2S appears to exist in the range 200-500 ppm. above which H_2S levels are no longer limiting to crack growth.

INTRODUCTION

Cyclic stresses on offshore structures are mainly produced by the hydrodynamic loading of the structure by wave action, augmented by relatively high-frequency vibrations due to machinery and low-frequency transient stresses produced by wind and cargo movements. Sea waves have an average cyclic frequency of 0.167Hz. on the parts of the structure just below the tide marks (Heaf (1). Superimposed onto this cyclic loading is the effect of corrosion, which in open seawater is also greatest in and around the tidal area (LaQue, (2), where there is very high oxygen availability. The rate of crack growth under corrosion-fatigue conditions is controlled by the rate of dissolution of the metal at the crack tip and hydrogen embrittlement (Bristoll and Roeleveld (3). The pH of the crack tip remains in the range 3-4,

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irrespective of the pH of the bulk environment (Smith et al (4), Wilde (5) thus providing the necessary ionic hydrogen for embrittlement.

Any external supply of hydrogen to the metal is likely to increase hydrogen embrittlement and thus the crack growth rate. Increases in crack growth rate have been demonstrated in Hydrogen sulphide (H_2S) saturated environments for many steels ((3), Austen and Walker (6), Vosikovsky and Rivard (7)). This gas is particularly aggressive as the sulphide ions both stimulate anodic dissolution and poison the combination of hydrogen atoms to the gaseous molecule and thus make more hydrogen available for embrittlement.

Both the corrosion and stress components of corrosion-fatigue can be enhanced in a biologically active environment. Living organisms in the form of marine fouling can enhance the fatigue stresses imposed by wave action on an offshore structure by firstly, effectively increasing the diameter of the tubular members of the jacket and secondly, increasing the surface roughness and hence the drag factor (Wolfram and Theophanatos (8).

Any corrosion enhancement by living organisms on an offshore structure is likely to be in the region of their maximal growth ie. in the splash zone and the first thirty metres below it. This is also the greatest region of wave loading, the greatest region of seawater corrosion and the region of greatest increase in loading due to marine fouling (1).

The presence of marine fouling can cause physical damage to both protective coatings and the underlying metal while large differences in oxygen concentration can be created even under thin layers of bacteria (Costerton and Geesey (9). Differential aeration leads to crevice and pitting corrosion which, in turn, may initiate fatigue cracks. Pitting and crevice corrosion may also be initiated by bacterial metabolites (Cragnolino and Tuovinen (10). A wide range of potentially corrosive metabolites are produced by both macro- and microorganisms at the metal/fouling interface, ie. where the macrofouling organisms attach to the metal surface or beneath microbial "slimes", and both cathodic and anodic enhancement of the corrosion reaction have been reported as well as the production of H_2S by the sulphate- reducing bacteria.

Sulphate-reducing bacteria are anaerobic organisms found not only beneath marine fouling but also in marine muds, inside the legs and oil storage tanks of the platforms, in water injection systems and downwell; they are likely to be found in dynamic ecological associations with other species of bacteria and even higher organisms (Hamilton (11). Thus while inherent to

the fuel product of sour wells, H_2S can also be produced outside of the "supply line" by microbiological activity.

Although hydrogen embrittlement and the effects of sulphide on stress corrosion cracking in seawater have been studied for some time, the use of environments containing H_2S for corrosion-fatigue testing is comparatively recent. The initial studies were into the mechanisms of crack growth; the possibility of bacterially-generated H_2S being important in offshore applications was either overlooked or dismissed (3). However the safety hazard posed by biologically-produced H_2S in enclosed areas such as oil storage tanks led to a realisation that H_2S can reach significant levels in seawater in and around offshore structures. As a result, tests are now made in H_2S saturated seawater and may be compared with data collected in air, plain artificial seawater and dry H_2S gas environments.

The present interest in biologically active environments stems from the fact that, when saturated, seawater contains levels of H_2S (3150ppm.) that are extremely unlikely to be produced by any biological means and are thus unrepresentative of real conditions. The relative susceptibility to damage of constructional steels used offshore to more realistic H_2S contents is therefore a vital factor. Hydrogen sulphide levels of up to 2000ppm. have been found to be produced by biological organisms experimentally (Miller (12), but more realistic levels are of the order of 600ppm and below (Edyvean et al (13). There is also the possibility that a biologically active environment will have an influence on corrosion fatigue other than by H_2S production. This study compares the effect on crack growth by corrosion-fatigue of unsaturated solutions of H_2S added to seawater with those generated naturally. The alloy steel used in the tests is a candidate for the next generation of offshore structures.

MATERIALS AND METHODS

Corrosion fatigue crack growth measurements were made using 13 mm thick CTS specimens machined from a steel grade RQT 701 manufactured by the British Steel Corporation. (wt% C = 0.2, Si = 0.5, Mn = 1.5, V = 0.08, P = 0.035, S = 0.015, Mo = 0.2, B = 0.003, N = 0.06). The as-rolled plate was used in the YX orientation and tests were carried out at a stress ratio, R, of 0.7.

The specimens were precracked from a starter notch/specimen width ratio of 0.38 to an eventual crack length/width ratio of 0.5 using a reducing load technique to minimise the effects of local plasticity at

the crack tip. Tests to determine the fatigue crack growth rate were carried out under constant conditions of load range, waveform, cyclic frequency and stress ratio, in the required test environment. The progress of crack growth was monitored using a DC potential drop technique (6). Analysis of the results enables values of the crack growth rate, da/dN, and of the instantaneous stress intensity factor range, ΔK, to be calculated.

Tests in air were carried out at a cyclic frequency of 50Hz while those in seawater were carried out at 0.167Hz.

The following environments were used:-

1.Natural seawater at 5C.
2.Natural seawater saturated with H_2S at 20C.
3.Natural seawater (20C) containing various levels of H_2S (abiotic).
4.Natural seawater (20C) containing various levels of H_2S produced by the bacterial decomposition of algal material.

Tests in H_2S saturated seawater were carried out in perspex chambers (6)under conditions of free corrosion.

Biologically active H_2S environments were created by allowing the decomposition of marine algae to take place naturally in an enclosed seawater environment. Quantities of fresh marine algae (Enteromorpha spp. Porphyra sp. and Pelvetia sp.) were collected from the North-East coast of England. Natural seawater and 200 gms. (wet weight) of algal material were placed in 5L capacity glass containers and sealed. Access was provided for sampling and a water trap prevented any gas bulid up. The seawater containing the bacterially produced H_2S was transferred to the test chambers as required.

50 ml samples were removed at intervals for pH measurement and H_2S analysis by the iodometric method (Vogel (14). This method acidifies the solution and therefore measures total sulfide (H_2S, S= and HS-), though at the pH of seawater the primary constituent is HS-.

RESULTS AND DISCUSSION

Corrosion-fatigue test data obtained in various environments are shown in Figure 1. Crack growth rates for two levels of H_2S (130ppm and 500ppm.) produced by the action of naturally occurring sulphate reducing bacteria on Enteromorpha are shown and compared with rates in natural seawater and H_2S saturated natural seawater environments. The results show that, while a level of 130 ppm. H_2S gives an increase in crack growth

rate over air and natural seawater, a level of 500ppm. gives crack growth rates very similar to those found for natural seawater saturated with H_2S. While the reproducibility of some of these results require to be confirmed by further tests, the similarity between a biologically produced H_2S level of 500 ppm. and one of 3150 ppm. produced by saturating the seawater with H_2S gas suggests the presence of a "threshold" level of H_2S (13). ie. a value above which the availability of H_2S is no longer a limiting factor to crack growth, and which gives results similar to saturation levels. The existance of a threshold level and the ability of such a level to be produced naturally by the bacterial decomposition of marine fouling organisms raises two important points. Firstly it will mean that previous results from H_2S saturated seawater tests are valid, and secondly, providing no effects of biological activity other than those due to H_2S production, are found, then the easily controlled and reproducible environment of artificial seawater saturated with H_2S gas may be used as representative of worst case biological conditions. It may be significant that the test made using 130 ppm. H_2S showed highest $\Delta K_f H_2S$ (value at fracture) of the H_2S tests and showed a tendency towards stage II plateau behaviour. $\Delta K_f H_2S$ is less than ΔK_f seawater, a fact which could be due to the effect of crack blunting in H_2S-free seawater, as a result of corrosion processes.

Figure 2 shows results obtained in abiotic seawater containing additions of hydrogen sulphide. Two distinct trends are shown, dividing the data obtained in H_2S levels below 184 ppm. from that obtained in levels of 598 ppm. and above. While more rapid stage I crack growth is found in seawater containing 184 ppm. H_2S than that containing 50 ppm. H_2S, both these lower levels show stage II plateaus. Similar plateaus have been found by Vosikovsky and Rivard (7) for the corrosion-fatigue of a pipeline steel in oil environments at low H_2S levels. The data from our plateau regions indicates substantial local variations in crack growth rate with increasing ΔK. This suggests local variations in crack growth within the specimen as the crack extends, which may be due to varying degrees of blunting across the crack front. It is also significant that the ΔK_f H_2S of the 184 ppm. test is lower than the 50 ppm. test and the data at high ΔK levels for the lowest H_2S content suggests the beginning of a stage III regime in crack growth.

Crack growth rates in stage I are greater, overall, at the higher (598-976 ppm.) H_2S levels. In stage II, in contrast to the plateau behaviour shown at low H_2S levels, the data show a continued increase in da/dN with increasing ΔK but at a reduced rate. These results

reinforce the previous suggestion of "threshold" behaviour and put it between 184 and 598 ppm. H_2S. At low H_2S concentrations the crack growth could be influenced by local blunting, an effect overcome by higher H_2S concentrations which produce failure before the mass transport dependent plateau conditions are developed.

The data for seawater containing microbiologically generated H_2S (Figure 3) shows the same general pattern of behaviour between high and low H_2S levels as that shown for abiotic seawater in Figure 2, although an intermediate stage between the two trends is shown by the data from 200 ppm. of H_2S. Here crack growth rates at low ΔK levels are similar to those found from the higher H_2S environments, but a plateau region is found at high K levels. Comparing Figures 2 and 3, the data indicates that biologically generated H_2S is less damaging than similar levels of H_2S present under abiotic conditions. Figure 4 shows direct comparisons between two similar levels of H_2S, one produced biologically and one abiologically. The apparent reduction in effectiveness of microbiologically produced H_2S may be due to some of the H_2S released by the bacteria not being available to promote embrittlement. Bacteria are known to favour growth on surfaces rather than in suspension and to produce copious "slimes" (Maxwell and Hamilton (15). Such a slime layer could provide a barrier to H_2S dissociation or H+ transport to the metal. Other biological factors such as "interspecies transfer" (Mah et al (16) of ions between bacteria could render much of the measured H_2S unavailable to the steel. By contrast, all of the artificially added H_2S is able to contribute to the damage process.

Despite the results (Figures 1 and 2) showing similar effects of biologically producible levels of H_2S with saturation levels there is still the conclusion derived from practical experience of offshore structures that fatigue life predictions made from saturated H_2S tests are too severe a worst case simulation of marine fouling and sour oil. The implication of this is that maximal biological activity is rarely found offshore or that conditions in which maximum levels of H_2S production are found rarely coincide with areas of high stress. This could indeed be the case, maximal H_2S production will be limited by temperature, nutrient availability and suitable areas for growth of fouling. Previous results (13) indicate that temperature may not be a significant factor, only causing a variation in the time taken to reach maximum H_2S levels. Nutrient availability and suitable areas for growth are probably the most limiting parameters to H_2S production offshore. The most suitable

areas for sulphate reducing bacterial growth are the interiors of flooded jacket legs and oil and seawater storage tanks. These areas can become rapidly anaerobic but tend to have low levels of nutrients, producing between 5 and 100 ppm of H_2S depending on the presence of residual oil in the seawater (Wilkinson (17). Nutrient availibility will be much higher on the external surfaces of the jacket, due to the presence of marine fouling organisms and their products, but anaerobic environments will be limited to sites underneath this fouling. These sites are likely to be small in area, transitory and, again, nutrient limited. Such a site, for example decaying organic material under the holdfast of a large kelp may coincide with a pre-existing crack (or even initiate a crack) at an area of high stress. The levels of H_2S produced could then significantly increase crack growth rate and lead to rapid failure.

Much of the time taken by a component to fail in service by corrosion-fatigue is taken up in the initiation of crack growth at very low ΔK values. Alternatively, if no pre-existing cracks are present, it involves the time taken for localised corrosion to proceed to a point at which surface cracks form and develop to a stage at which stress can exert an appreciable influence. With the exception of H_2S production, biologically influenced corrosion may be expected to influence crack initiation more than crack growth. It is difficult to estimate the effects of both macro- and microbiological marine fouling on the corrosion of offshore structures. Few direct measurements have been made and very little account taken of interactions between species. The initial deterioration at a site of microbial activity may be due to differential aeration. However, the presence of H_2S and other metabolic products will tend to encourage crack initiation. Thus a study of crack initiation and crack growth at very low ΔK values in biologically active environments would be worthwile. However such investigations are both lengthy and complex due to the time scale of the events involved and the variability inherent in biological systems.

CONCLUSIONS

In a high strength micro-alloy steel:

(1) The presence of H_2S considerably enhances crack growth rates due to corrosion-fatigue in seawater environments.

(2) A "threshold" level of H_2S is apparent, below which crack growth rates are determined by the level of hydrogen sulphide and above which crack growth rates are

similar to those found at saturation levels of H_2S.
(3) Biologically-produced H2S is a less potent embrittling agent in seawater than when added to an abiotic solution. The mechanism responsible needs to be elucidated.
(4)Experiments are required to determine realistic levels of H_2S produced by microorganisms offshore and to test in these environments.
(5) Experiments are required to investigate the role of biologically enhanced corrosion on crack initiation.

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SYMBOLS USED

ΔK = Stress intensity factor range
$\Delta K_f H_2S$ = Stress intensity factor range at failure in hydrogen sulphide
H_2S = Hydrogen sulphide
da/dN = Crack growth rate (m cycle^{-1})

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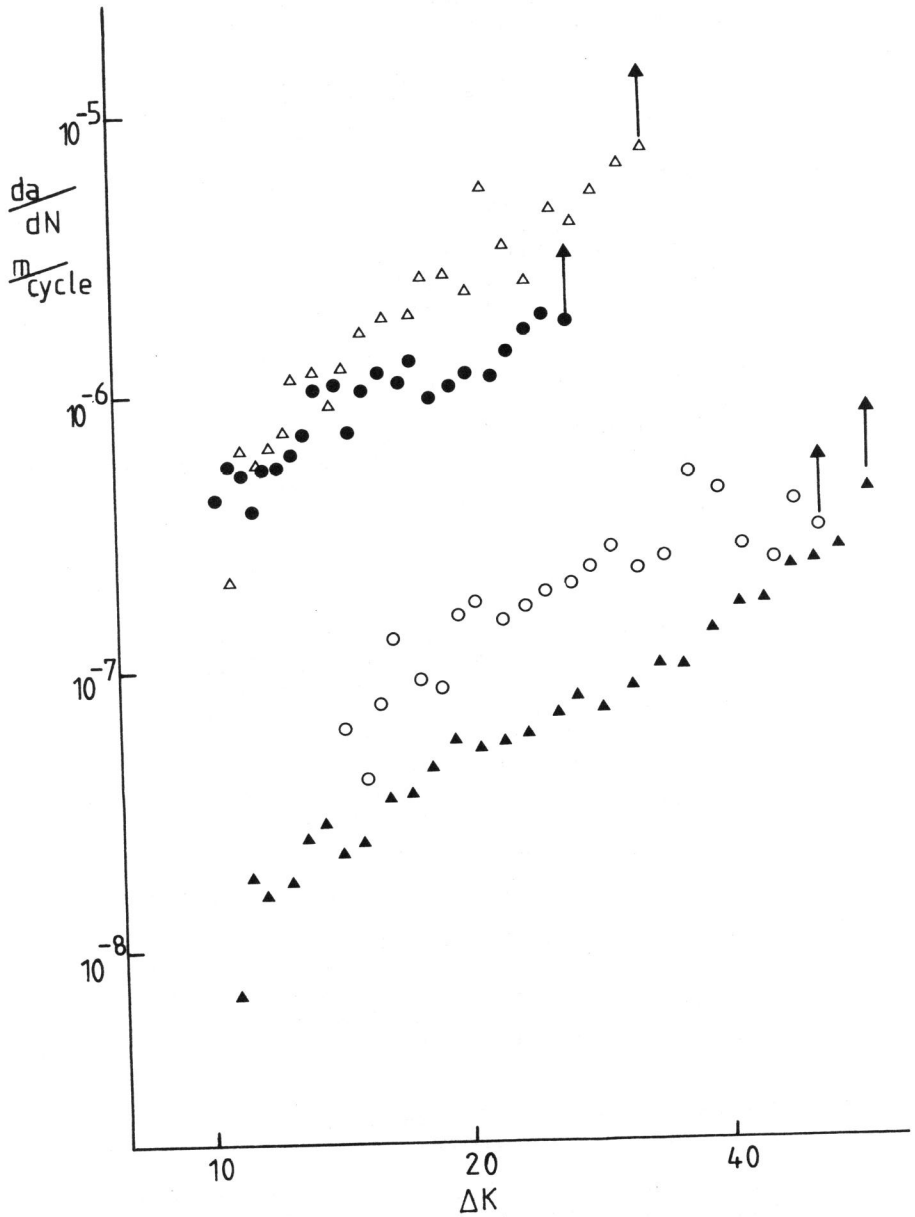

Figure 1. Fatigue crack growth rates. ▲ Natural seawater △ Seawater saturated with H_2S gas. ○ Seawater + 130ppm biological H_2S. ● Seawater + 500 ppm biological H_2S.

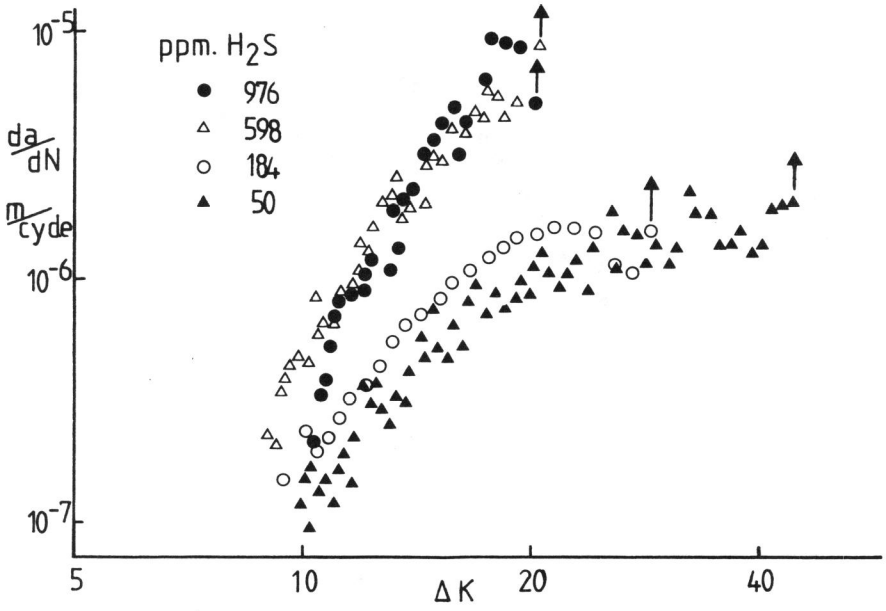

Figure 2. Fatigue crack growth rates in abiotic seawater containing various levels of hydrogen sulphide.

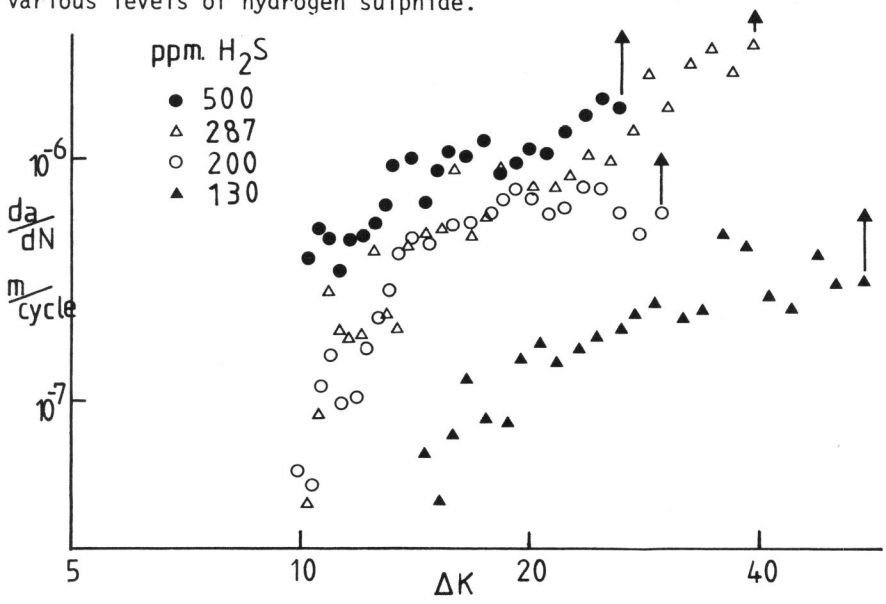

Figure 3. Fatigue crack growth rates in seawater containing biologically produced hydrogen sulphide.

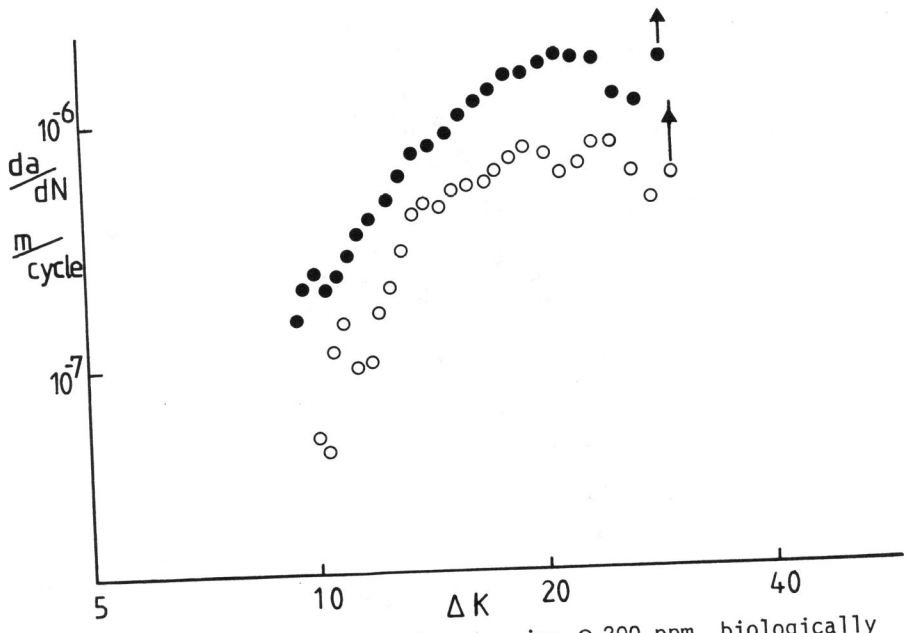

Figure 4. Fatigue crack growth rates in: ○ 200 ppm. biologically produced H_2S. ● 184 ppm. abiological H_2S.