D. Endurance tests for determining the susceptibility of prestressing steel to hydrogen embrittlement

DR. F. BERGSMA, DR. J. W. BOON AND IR. C. F. ETIENNE

Summary

By its high basicity concrete has a passivating character with respect to steel. Nevertheless, under the influence of free chloride ions that are present in the concrete, corrosion pits can be formed in the steel surface. The concrete medium in those pits has been proved to acidify slowly and finally steel attack is possible with simultaneous evolution of hydrogen. This (locally generated) hydrogen may enter the steel and lead to local embrittlements. In prestressed concrete (with prestressing wire in stressed condition) the embrittlement of the prestressing steel can become so serious, that (brittle) stress corrosion fractures result.

Similar fractures can be simulated in the laboratory in prestressing wire that is immersed in stressed condition in a non-passivating medium which attacks steel (quasi-) homogeneously with simultaneous evolution of hydrogen. In performing this in an aqueous solution of 20% NH_4NCS a high degree of reproducibility (of the exposition time-to-fracture) can be attained by a simple way of standardizing. This can be important for testing and improvement of the quality of the produced wire.

1 Introduction

Prestressing wire in concrete sometimes fractures without any evidence that it was stressed in excess of its tensile strength at the start of fracturing. In a number of cases it is subsequently found that distinct attack of the metal occurred at the fracture, but in others there is no macroscopically detectable sign of attack. Since tensile stress was acting in the steel prior to its fracturing and there has moreover been observable (or presumed) attack of the steel, such cases are often referred to as *stress corrosion fractures*. For the purpose of indicating the cause it is important to distinguish between two types of fracture.

If so high a degree of (generally local) attack has occurred that the remaining cross-section of the steel is stressed above the tensile strength, the wire will fracture in a completely ductile manner, i.e., with visible reduction of area (necking) and shearing and accompanied by observable elongation of the wire. Such fractures are almost invariably due to some trivial cause, such as a defect in the composition of the concrete or poor embedment of the steel by the concrete.

In many cases, however, there is no ductile fracture, but instead, after the occurrence of corrosive attack (local pitting) or even without any microscopically observable attack of the steel, brittle fracture suddenly ensues, i.e. fracture which is attended by practically no deformation of the wire and which occurs long before the stress in the wire exceeds its tensile strength. In such cases we have so-called *true stress corrosion fractures* which because of their premature and sudden occurrence, constitute a greater hazard than the above-mentioned completely ductile type of fracture. The brittle fractures are indeed usually attended by ductile residual fracturing, because towards the end of the fracturing phenomenon the conditions of a normal tensile fracture will arise.

It is known that the brittle fracture character is bound up with the presence of hydrogen in the steel. This hydrogen may have penetrated into the steel during the corrosion process, but may in principle have been wholly or partly present in the steel already from the very outset. The hydrogen which has made its way into the steel tends to collect at points where tensile stress concentrations occur. Such concentrations may be located at (possibly very minor) surface defects; they will in any case arise at those points where the steel is locally attacked. The collected hydrogen causes local embrittlement of the steel, which ultimately results in brittle fracture. The precise shape and behaviour of stress corrosion cracks induced by hydrogen in prestressing steel, are not known. Various mechanisms to account for the cracking characteristics have been proposed on theoretical and to some extent also on practical grounds. They will not be dealt with in this paper.

The present paper is concerned entirely with the *endurance tests* which have been performed on prestressing steel with a view to ascertaining its susceptibility to hydrogen embrittlement. The information given here is confined to research conducted on patented cold-drawn wire of 4 mm and 7 mm diameter, i.e., wire which is characterized metallographically in having a troostite structure.

To start with, it should be noted that the literature contains many references to the effect of certain steel properties (namely, chemical composition, structure and heat treatment, mechanical properties and surface condition) on the stress corrosion susceptibility of prestressing steel (both cold-drawn wire and quenched and tempered wire). A memorandum on these influencing factors reported in the literature is appended to this paper.

2 Research

In practice, stress corrosion fractures develop in a concrete environment under varying conditions without ascertainable reproducibility as to the working life attained by the wire. The endurance times up to fracture usually range from long to very long, but may be relatively short in exceptional cases. This is undoubtedly associated with the fact that in the concrete environment, where a pH of 12.6 can be presumed to exist as result of saturation with $Ca(OH)_2$, passivation of the surface of the steel occurs. If no carbonatation takes place, this passivation will continue to be present. Under such conditions, corrosive attack of the prestressing steel, which usually precedes the fracturing thereof, can occur only after rupturing of the passivating layer. This is something that may happen under the influence of admixtures in the concrete (mostly chloride) – usually only after a long incubation period and seldom in a reproducible manner. The stone-like solid constituents of the concrete exercise an influence which in relation to the process of corrosive attack cannot be clearly estimated and is therefore difficult to reproduce. In producing stress corrosion fractures in the laboratory, investigators therefore soon abandoned trying to employ the conditions encountered in actual practice and instead soon had recourse to judiciously simulated conditions. A well-known simulating solution is a solution saturated with $Ca(OH)_2$ and with 2% $CaCl_2$ added (this will further be referred to as solution "a"). Fractures which occur in this solution under simulated practical conditions in so far as the steel-solution potential *E* is concerned, could be regarded as equivalent to fractures occurring in actual practice.

Another simulating solution is provided by distilled water (further referred to as solution "b"). This is more particularly relevant to those parts of prestressing wires which are not, or only very incompletely, embedded in concrete (e.g., on the outside of concrete structures) or which are covered by a layer of pneumatically applied concrete (gunite) a long time after being tensioned. It has been found in practice that such uncovered prestressing wires may, after being corroded by condensation water, sometimes undergo brittle fracture.

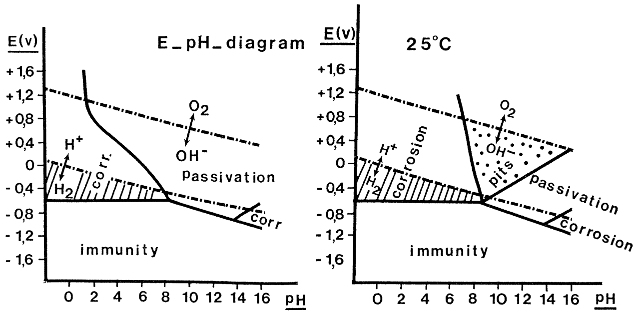
Particulars concerning tests performed in simulated practical solutions "a" and "b" are given in section 2.1.

Laboratory tests in solutions having a distinct hydrogen embrittling effect (more particularly tests with a 20% solution of NH_4NCS) are described in section 2.2.1.

2.1 *Stress corrosion fractures occurring in the simulated practical solutions "a" and "b"*

2.1.1 Tests in solution "a" (saturated $Ca(OH)_2$ with 2% $CaCl_2$)

In this solution one supposes to meet conditions that simulate those prevailing in chloride-containing concrete, thus passivating conditions, permitting local corrosion (see above).



A Fe/H_2O B Fe/H_2O with Cl^-ions

Fig. D1. *E*-pH diagram for iron/water at 25 °C without (A) and with (B) Cl-ions.

All the conditions of the system Fe/H_2O at 25 °C without and with the presence of chlorides are given in the diagrams E-pH (according to *Pourbaix*). See the Figs. D1A resp. D1B. The diagrams show the stability regions resulting from the deposition of the acidity (pH) on the X-axis and the metal-solution potential E (hydrogen scale) on the Y-axis. The corrosion region of Fe can be seen in Fig. D1A, the extension of this region and also the new corrosion region (with pitting corrosion) in Fig. D1B.

The pH of concrete (without and with chlorides) is 12.6. This indicates that the conditions in concrete are lying on the vertical line at pH $\sim$ 12.6 (not drawn). In Fig. D1B this line crosses the new corrosion region, indicating the posibility of pitting corrosion in chloride-containing concrete.

Corrosion of Fe with simultaneous evolution of hydrogen is only possible in the hatched regions of Figs. D1A and D1B. The diagrams show that this possibility is only present at a pH far lower than 12.6 (the pH in concrete) and at a suitable value of the potential E. We investigated the conditions prevailing in solution "*a*" at brittle fracture (see 2.1.1.1 and 2.1.1.2). We also performed endurance tests in solution "*a*" at conditions simulating the practice (i.e. at values of E, resembling those found in the preceeding investigations and described in 2.1.1.1) (see 2.1.1.3).

Endurance tests were also performed in solution "*b*" (see 2.1.2) and in strongly embrittling solutions, especially in an aqueous solution with 20% NH_4NCS (see 2.2.1).

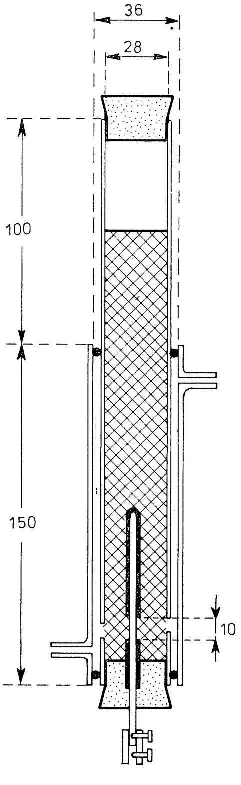


Fig. D2.
Apparatus for measuring the potential of prestressing wire in mortar (dimensions in mm).

2.1.1.1 *The potential E of prestressing steel*

The measurements of E were performed on specimens of prestressing wire placed in mortar (see Fig. D2). In the test arrangement the steel was entirely covered except for a small portion, and was inserted through a pierced plug into the inner glass tube. This tube, that was provided with openings (closed by small sealing plugs) at the level of the uncovered part of the steel, was filled with mortar which was allowed to harden. The small sealing plugs were then removed and the second (outer) glass tube was placed around the inner one. Gastight seals at top and bottom were formed with the aid of O-rings. The outer glass tube had a gas inlet and outlet through which gas could be passed through the space enclosed between the two tubes (named: space G). With the aid of a damp pad of cottonwool placed on top of the moist filling of mortar, it is, after removal of the upper plug, possible to measure with a calomel electrode the potential jump E at the boundary between the prestressing steel and the mortar liquid (and also the change of E with time).

The measurement can be performed with or without gas simultaneously being passed through space G. The measurements were performed on a number of test pieces, each of them separately placed in an apparatus according to Fig. D2. The results are summarized in the following table:

series of measurements	gas passed through space G	value of E in mV (hydrogen scale)
No. 1	none	-300 to -100
No. 2	moist air	no change from No. 1
No. 3	dry air	rising to maximal $+50$
No. 4	dry nitrogen	lowering to minimal -400

It is evident that the passing of moist air through the apparatus does not affect the moist mortar. Dry air causes a certain degree of drying of the mortar, resulting in more access of oxygen to the steel (which is attended by a rise in the value of E). On the other hand, dry nitrogen results in (partial) removal of the oxygen, attended by a lowering of E. Drying and subsequent wetting, with access or exclusion of air and oxygen, must be regarded as a natural set of conditions to which concrete is likely to be subjected and under which, according to the table, the value of E may fluctuate between -400 mV and $+50$ mV, measured on the hydrogen scale.* Galvanic cells can become active as a result of these shifts in potential. This will in the main occur locally and in this way cause local rupturing of the passivating layer on prestressing steel in concrete in the presence of chlorides.

To simulate practical conditions alternate polarisation between these limits is in any case permissible and must perhaps be recommended.

---

* Some investigators (a.o. Arup e.s.) mention higher potential values, viz. -400 to $+50\mathrm{m}\,V_{\mathrm{sat.cal.}}$ ($=-150$ to $+300$ $\mathrm{mV_h}$). Our values are in accordance with the potential range mentioned in literature (e.g. Arch. Eisenhüttenwesen 47 (1976) page 107 etc.).

2.1.1.2 The pH in a corrosion pit

As already stated in 2.1.1, the presence or the formation of more or less extensive areas with low pH is necessary for the occurrence of corrosive attack of steel with simultaneous evolution of hydrogen. A low pH was indeed measured in a very small artificially formed pit in a specimen of prestressing wire immersed in solution "a". The experimental set-up and conditions were as shown in Fig. D4. Before the measurement was performed, alternate anodic and cathodic polarization was applied. Measuring was first carried out with tungsten/bronze micro-electrodes, subsequently with iridium/iridum oxide electrodes. The first-mentioned electrodes were found to be unsuitable; the iridium/iridium oxide ones were better, but they too showed major deviations when contaminating deposits had formed on the surface. A lowering of potential from the original value of 12.5 to a value of 10.0 was observed, but afterwards the amount of contamination of the surface of the steel became too great for reliable continuation of testing. With the aid of indicator paper, however, it was shown that the pH of the liquid in the pit could go down to 5 or lower. Although not very satisfactory, this pH-lowering is, in conjunction with an unfavourable value from the steelpotential range mentioned in 2.1.1.1, sufficient to make it possible that steel is attacked with simultaneous evolution of the hydrogen gas (see Figs. D1A and D1B).

2.1.1.3 The endurance test

A prestressing wire, stressed to $0.8 T\sigma_B$, placed in solution "*a*" and exposed to alternate potentiostatic polarison: anodic to $+50$ mV$_h$ and cathodic to -400 mV$_h$, will show brittle fracture (for the test set-up: see Fig. D3).

In performing a number of experiments a strongly varying lifetime-to-fracture will be found. The Figs. D1A and D1B which are based on thermodynamical data, do not teach us anything about the velocity of the fracture process. Important differences in lifetime can be expected if a passivating layer must be perforated before corrosion can take place (with simultaneous cathodic reduction of oxygen in the solution or oxides on the steel surface). By subsequent hydrolysis of the dissolved iron salts in the pit and diffusion of chloride-ions into the pit, the acidity of the liquid in the pit (which can be considered as an occluded cell) increases and the pH decreases, ultimately leading to corrosion with simultaneous evolution of hydrogen and brittle fracture.

In connection with further research, the fractures CL3, CL6 and CL8 more particularly call for mention here; these developed after endurance test periods of 83, 23 and 167 days respectively. The investigation designated as Code CL4 should also be mentioned. In this latter case a prestressing wire not placed under tensile stress was subjected to polarization for 24 days. This so-called blank test did not result in fracturing of the wire but a certain amount of embrittlement thereof was nevertheless acertainable (see 2.3).

From the length and variation in the endurance times found in these tests it is evident that, even under the research conditions in solution "a" simulating those

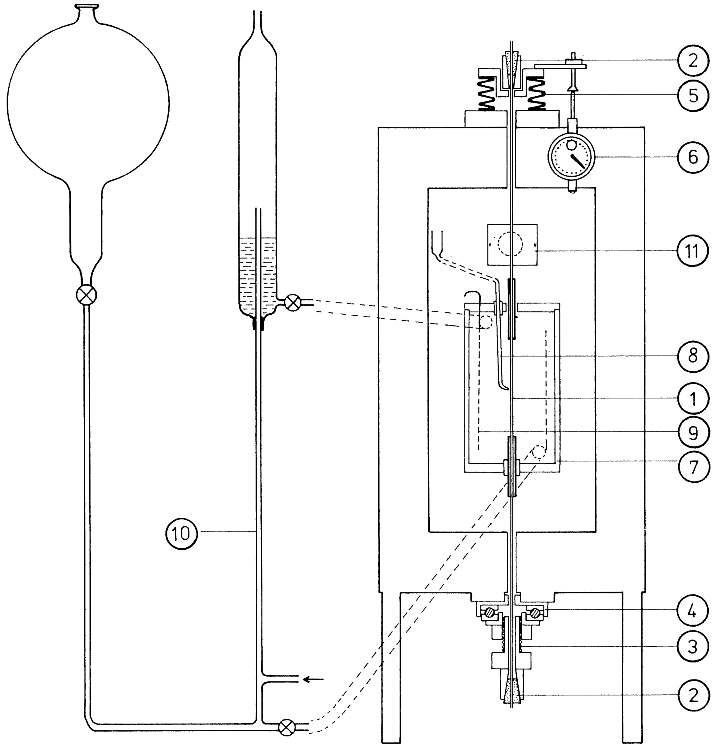


Fig. D3. Test set-up for producing stress corrosion fractures in prestressing steel.
1. prestressing wire (4 mm)
2. tensioning heads
3. screw jack for tensioning the wire
4. ball bearing associated with jack
6. dial gauge
7. vessel containing electrolyte
8. Luggin capillary tube
9. counter-electrode (platinum gauze)
10. gas lift system for recirculation of liquid
11. plate for attachment of AED equipment.

encountered in actual practice, fractures do not occur in a straightforward and direct manner, nor (in the investigations conducted up to the present) after reproducible lengths of endurance time. These results are in agreement with the fact that in practice, too, the fracturing of prestressing wires installed in concrete occurs in a sporadic manner. Incidentally, it should be noted that there were differences in the conditions of polarization in the various tests. These differences may have affected the endurance times to fracture that were observed and thus the reproducibility thereof. Besides, these endurance times are really too long for laboratory tests.

Remark: Acoustic emission detection (AED)

For the various fractures produced in solution "a" and also for two cases of fracture in

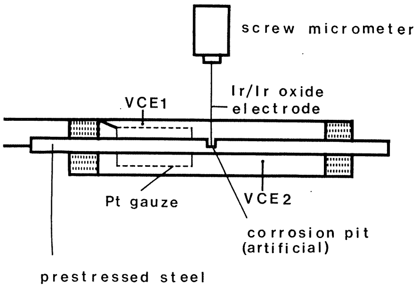


Fig. D4. pH measurement in a small artificial corrosion pit
Environment (test medium): saturated $Ca(OH)_2+2\%$ $CaCl_2$
VCE_1: saturated calomel electrode connected to the potentiostat (used for polarizing to the desired potential)
VCE_2: saturated calomel electrode (together with the Ir/Ir oxide electrode used for measuring the pH).

the 20% NH_4NCS solution, it was thoroughly investigated whether incipient cracking was detectable with the aid of AED and whether perhaps an early warning of impending fracture, long before its actual occurrence, might be obtained. Numerous signals were indeed observed, but were due to escaping bubbles of gas (hydrogen). Actual signals of fracturing were clearly observed only just before, during and long after its occurrence (these latter belated signals were probably associated with the escape of hydrogen taking place after fracture). This behaviour clearly indicates rapid growth of cracks and therefore short duration of the actual cracking process, as against a long duration of the incubation process (i.e., a long period of initiation of cracking). Hence the AED signals were found to have little or no predictive value as to the instant of fracture.

2.1.2 Test in solution "b" (distilled water)

In this endurance test to fracture, which was designated as fracture CL7, the vertically placed prestressing wire specimen was, after being stressed to $0.8\sigma_B$, immersed in distilled water along half its length. The apparatus employed was similar to that shown in Fig. D3, but without the airlift. Condensation and evaporation regularly occurred just above the surface level of the liquid. Corrosive attack of the wire was found to occur. In the liquid a voluminous light brown deposit of rust formed on the wire, where, at the end of the test the diameter of the wire was indeed found to have distinctly decreased. Above the surface of the liquid there was dark brown rust formation with black stains. After a test period of 15 months the wire fractured, in this last-mentioned rusted area, distinctly some distance above the surface of the liquid; there was no, or no clearly detectable, decrease in the diameter of the wire at the fracture, but demonstrable embrittlement of the wire occurred there (see 2.3).

2.2 *Determination of hydrogen embrittlement susceptibility of prestressing wire*

Brittle fractures of this wire, occurred in concrete or in solution "*a*", are preceded by perforations of the passivating layer and the formation of an occluded cell. The whole of the events is so inhomogeneous that it must be judged difficult and perhaps impossible to provoke in the laboratory and in a reasonable lapse of time brittle fractures in a reproducible way. For this reason comparative endurance tests were, from the outset, also performed in other solutions with a view to obtaining information on susceptibility to hydrogen embrittlement of the steel under investigation. These were more particularly solutions which were presumed to develop a homogeneous or quasi-homogeneous action upon the surface of the steel, resulting in hydrogen embrittlement.

From the historical point of view it should also be mentioned in this context that endurance tests in nitrate solutions used to be specified among the conditions for the issue of a certificate of approval of prestressing steel. It was erroneously supposed that such solutions developed a homogeneous action on the metal surface. When subsequent research cast doubt on the validity of the view that hydrogen embrittlement susceptibility could indeed be tested in nitrate solutions, this test was dropped from the approval requirements and not replaced by some other test criterion. Generally speaking, solutions which can rightly be assumed to act homogeneously on the steel surface and in which endurance tests can conceivably yield valid results, are acid solutions. More particularly, solutions of sulphuric acid and hydrosulphuric acid (H_2S) have already long been used for endurance tests. To these was subsequently added the endurance test in a solution of 20% ammonium rhodanide (NH_4NCS). It should of course be pointed out that, despite the seemingly homogeneous action of such solutions over the entire surface of the metal, fracture will as a rule occur only in one particular plane, namely, where there is stress concentration and where therefore the hydrogen penetrating into the steel can most intensively develop its harmful action, e.g., at a small external or internal fissure, notch or cavity.

Certain objections can indeed be made to the use of some solutions in endurance tests. In *acid solutions* such as sulphuric acid the steel surface is severely attacked, resulting in an intensification of the existing state of tensile stress and possibly to an ultimately ductile fracture. With *hydrosulphuric acid* the gaseous character of the reagent is an objectionable feature which necessitates special precautions on account of its toxicity and disagreeable smell. Furthermore, the requisite concentration must be maintained, while the early fracture (short endurance time to fracture) of prestressing steel tested in hydrosulphuric acid, is another drawback because it is liable to have a masking effect on differences in hydrogen embrittlement sensitivity. None of these drawbacks exists with regard to the 20% NH_4NCS *solution*: it produces a brittle fracture without macroscopically detectable corrosive attack of the surface of the metal. The solution is weakly acid, so weak that the corrosion reaction presumably has to be kept going by depolarization by oxygen.

It should be mentioned that the use of distilled water as an endurance testing medium has also been proposed. Having regard to what has been said in 2.1.2 concerning such a test, it cannot be expected to cause homogeneous corrosive attack, while the long endurance time (15 months) is moreover a major objection.

Finally, it should be noted that all the solutions in question can be used, and are indeed used, with or without cathodic polarization.

2.2.1 Endurance tests in embrittling solutions, especially an aqueous solution with 20% NH_4NCS

Endurance tests to fracture are carried out with the object of comparing the hydrogen embrittlement susceptibility of different grades and products of prestressing steel, the further aim being to arrive at a standardized procedure for the endurance test. With a view to selecting the most promising test, a comparative investigation into the reproducibility attainable with the various test solutions (sulphuric acid, hydrosulphuric acid, 20% NH_4NCS, distilled water, etc.) was undertaken under the auspices of the RILEM-FIP-CEB Joint Committee (Comité Mixte) in 1971. The specimens of prestressing wire, tensioned and immersed in the test solution, were investigated both with and without cathodic polarization. Netherlands participants in this research comprised Hoogovens, IBBC-TNO and MI-TNO. The test using 20% NH_4NCS

Table D1. Results of MI-TNO in the second RILEM-FIP-CEB research project
Solution: 20 weight% NH_4NCS in water
Type of wire: patented, cold-drawn prestressing steel, 7 mm diameter (RILEM)

series (of 6 tests)		I standard	II	III	IV	V	VI	VII	VIII
conditions of testing									
temperature	°C	35	25	45	35	35	35	35	35
tensile stress	F/F_B	0.80	0.80	0.80	0.70	0.80	0.80	0.80	0.80
purity of NH_4NCS	a.p./t.p.*	a.p.	a.p.	a.p.	a.p.	t.p.	a.p.	a.p.	a.p.
rate of pumped recirculation	Vo/min	0	0	0	0	0	4	1	0
N_2 passed through solution		no	no	no	no	no	no	no	yes
results									
grade 1									
average endurance time t_m	hours	52	153	15	74	55.5	>188	137	>125
coefficient of variation of t_m	%	10	9	15	16	16	(16?)	16.5	(10?)
to-and-fro bend value:									
original	N_m	72	49	57	59	65	70	69	59
near fracture	N'_m	18	11	10	11	10	7	9	10
grade 2									
average endurance time t_m	hours	7.1	24	4.7	11	7.5	35.5	15	5.0
coefficient of variation of t_m	%	12.5	9	17.5	6.5	14.5	4.0	42	38
to-and-fro bend value:									
original	N_m	50	58	57	63	55	50	49	48
near fracture	N'_m	13	10	10	10	10	12	9	10

* a.p. – analytically pure; t.p. – technically pure

was found to be superior to all the others as regards reproducibility. Since the high degree of reproducibility, moreover, was attainable with the simplest testing procedure (solution not circulated by pumping, no passing of nitrogen, no cathodic polarization, but careful control of temperature necessary, preferably raising it a little in order to reduce the length of endurance time) the test in 20% NH_4NCS was considered very suitable for further investigation. In order to achieve standardization it is necessary to have insight into the factors that determine the result of the test. An attempt was made to clarify the problem in a second international research project conducted under the auspices of the above-mentioned Joint Committee in 1973. On behalf of the Netherlands, MI-TNO and subsequently Hoogovens participated in this research.

Patented cold-drawn prestressing wire of 7 mm diameter was made available in two grades. Grade 1 was the normal heat-treated quality for which susceptibility to ageing was not to be expected; in the case of grade 2 the heat-treatment had not, or only imperfectly, been applied, so that residual stresses were present in the wire, as well as susceptibility to ageing and greatly increased hydrogen embrittlement sus-

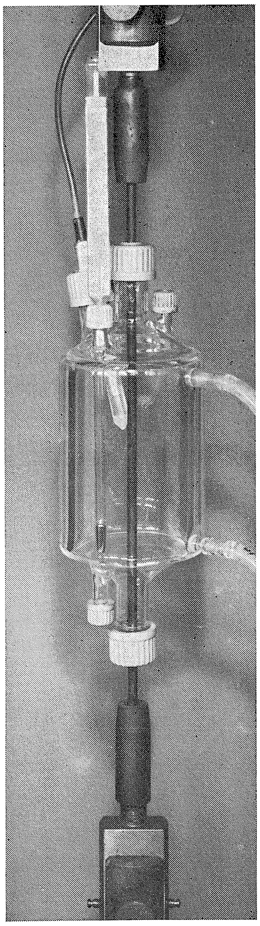
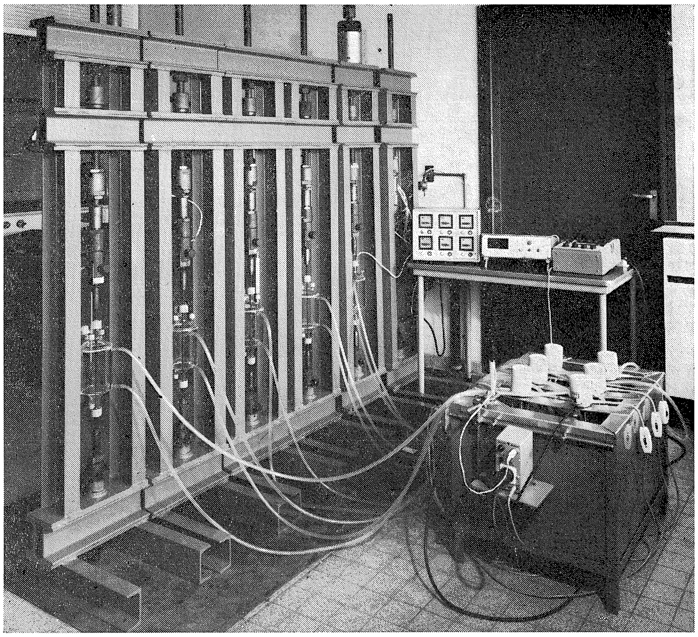


Fig. D5. Double-walled corrosion cell, used in the standardized endurance tests in 20% NH_4NCS. The thermometer and calomel cell are visible.

Fig. D6. Test set-up for the endurance tests in 20% NH_4NCS.



ceptibility. The tests were performed in solutions of unvarying composition (200 g NH_4NCS in 800 g of distilled water). The following influences were varied: the tensile stress in the tested wire, the temperature of the solution, the amount of oxygen access to the surface of the steel (by varying the rate of pumped recirculation of the test solution from zero to a certain upper value), the passing of nitrogen (or the omission thereof) through the solution, and the purity of the NH_4NCS employed (namely, analytically pure or chemically pure). Electrical polarization was not applied in any of the tests. In general, there was little scatter in the results of the various series of tests, as appears from Table D1, in which the results obtained by MI-TNO are summarized.

The to-and-fro bend values indicated in Table D1 will be discussed later on (see 2.3.1).

Fig. D5 shows the corrosion cell used in the tests, while Fig. D6 is a view of the test set-up, showing the six tensile test stands which originally were combined in one frame but were subsequently separated.

Among the several factors that were varied, as mentioned above, the degree of purity of the NH_4NCS was, as expected, found to have little effect on the results. This is because the chemically pure salt contains only a small additional amount of impurities as compared with the analytically pure salt. The other variations did have a significant effect, however. As was to be expected, the endurance time was shortened as a result of raising the temperature of or increasing the tensile stress in the wire.

Increased access of oxygen to the surface of the steel (due to a higher recirculation rate of the solution) lengthened the endurance time. This was likewise to be expected, since the increased amount of oxygen reaching the steel can combine with more hydrogen. As a result, less hydrogen remains available for penetration into the steel, so that it takes a longer time for fracture to develop. Passing nitrogen through the solution gives rise to two antagonistically acting effects, namely, removal of (hydrogen-binding) oxygen and weakening of the (hydrogen-producing) corrosion reaction. Which of these two effects predominates, will depend on circumstances: thus, nitrogen may either cause a shortening of the endurance time due to removal of oxygen or a lengthening thereof due to diminished corrosion reaction. The final condition is to some extent dependent on chance, and for this reason the reproducibility of the results of tests in which nitrogen is passed through the solution, is generally much diminished.

From Table D1 it furthermore appears that steel grade 2, with its ageing susceptibility, is more highly susceptible to hydrogen embrittlement than the non-ageing grade 1. Thus, the endurance times obtained for grade 2 under equivalent conditions were always shorter than those for grade 1.

Statistical comparison of the results obtained by the various participants in the second international research project showed those of MI-TNO to have the least scatter (usually 15% or less). This low scatter was also achieved under simple experimental conditions (no electrical polarization; no nitrogen through the solution; no recirculatory pumping). Besides, the scatter which was later found in the tests performed by Hoogovens, proved to be almost as low as that found in the MI-TNO tests.

Another conclusion to be drawn from the table is that accuracy in maintaining the standard test temperature is essential. The precise value to be adopted for this temperature is certainly discussable; 35 °C is by no means to be regarded as final.

It is important to note that the low scatter obtained in the MT-TNO results was maintained in course of time, as was evident when the tests were repeated in 1974 and 1975.

Finally, it should be pointed out that the said low scatter in the results has hitherto been obtained only with patented cold-drawn 7 mm prestressing wire. The low scatter proves the homogeneous character of the procured 7 mm wire (concerning its sensibility to hydrogen embrittlement). In similar tests which MI-TNO performed with cold-drawn 4 mm wire the results were found to show considerable scatter, though admittedly only a relatively small number of tests on this wire have so far been carried out by us. Further investigation will have to show why there is such large scatter: inhomogeneity of the material, inhomogeneity of the surface condition, or some other cause.

As a final conclusion it can be said that the endurance test to fracture as performed in the occluded corrosion cells of MI-TNO with the simplest experimental conditions (i.e., without cathodic polarization, without recirculation of the solution by pumping, and without passing nitrogen through it, but with careful maintenance of the specified temperature and tensile stress condition) can certainly be considered interesting for standardization.

The adverse effect that hydrogen present in steel is liable to produce, is clearly demonstrated in the two following tests carried out by TNO. Prestressing wires which, in a 20% NH_4NCS-solution, were first subjected to cathodic polarization (of *varying* duration for the different wires tested) and were then, immediately after polarization, tensioned to a stress equal to $0.8\sigma_B$ ($= 80\%$ of ultimate stress) in the same solution, were found generally to have shorter endurance time to fracture according as polarization has lasted longer and therefore more hydrogen had been able to penetrate into the steel during polarization.

Prestressing wires which, in a 20% NH_4NCS solution, were first subjected to cathodic polarization for an *identical* length of time, then cleaned and exposed to air for *varying* periods, and finally tensioned to $0.8\sigma_B$ in air, have in principle a shorter endurance time to fracture (in the tensioned condition) according as the period of exposure to air was shorter and therefore less hydrogen had had time to escape from the wire during that period.

2.3 *Investigation into differences and similarities in the fractures discussed in 2.1 and 2.2*

It was of course evident from the outset that a solution of NH_4NCS is something entirely different from a practical or a simulated concrete environment. It is therefore very important to investigate to what extent there exist distinct similarities or differences between the fractures which develop in NH_4NCS solutions and in simulated practical solutions respectively. On the answer to this question will largely depend the value that can be attached to the excellently reproducible results obtained in a 20% NH_4NCS solution. True "practical" fractures, i.e., in actual structures, are fortunately of too rare an occurrence and are moreover usually not available for thorough examination. We must therefore confine ourselves to the fractures occurring in the simulated practical solution "a" (namely, the fractures CL3, CL6 and CL8, as well as the blank test Code CL4) and the fracture CL7 in the simulated practical solution "*b*". All these fractures have already been mentioned in 2.1.1.3 and 2.1.2. They should therefore be compared with the fractures obtained in the 20% NH_4NCS solution referred to in 2.2.1. The comparison relates to two phenomena: the to-and-fro band values (see under 2.3.1) and the appearance of the fracture (see under 2.3.2).

2.3.1 To-and-fro bend values (also called: Alternate bending numbers) N and N'

The to-and-fro bend value of the original unused wire or, in some instances, of a part of the fractured wire not affected by the test solution is designated as N.
The to-and-fro bend value of the fractured wire near the fracture or of the part of the wire affected by the test solution in the case of non-fractured wires i.e., the number of to-and-fro bending operations that the wire can sustain, is designated as N'. The change that N' undergoes during the test, can be added to the comparison.

The values N and N' were determined for Code CL4 and for the fractures CL3, CL6, CL8 and CL7 produced in the solutions "*a*" and "b" respectively. This was also done for most of the fractures produced in the 20% NH_4NCS solution. The to-and-fro bend values were determined by the standard testing procedure i.e., by slowly bending the specimen to and fro through an angle of 180° around a round former or mandrel with a diameter equal to 7 times the diameter of the wire, in a special apparatus constructed for the purpose (see Fig. D7). The average to-and-fro bend values N' and N of the fractures listed in Table D1 (see 2.2.1) are indicated there. For grade 1 and grade 2 of the prestressing wire envisaged in Table D1 the values of N' and N in the various series of tests do not vary greatly. For this reason the values of N and N' for grade 1 and grade 2 have been separately averaged for all the fractures listed in the table. These averages are given in Table D2, which also includes N and N' for the fractures which were obtained in the solutions "a" and "b".

From Table D2 it clearly emerges that the value N' in all case is significantly lower than the value N. This lowering of the to-and-fro bend value is most pronounced in the NH_4NCS solution and usually greater than in the solutions "a" and "b"; it indicates the embrittlement of the steel in consequence of penetration of hydrogen into it. In terms of the to-and-fro bend value this embrittlement is therefore more distinctly manifested by the fractures in the NH_4NCS solution than by those occurring in the solutions "a" and "b". This could denote that in the NH_4NCS solution more hydrogen penetrates into the steel and that this moreover occurs more evenly distributed over the entire surface of the wire, for after fracture in the NH_4NCS solution there is hardly any macroscopically observable attack of the surface. In the solutions "a" and "b" the occurrence of fracture is usually preceded by distinct local pitting of the steel: the hydrogen that penetrates into the steel develops a very local action

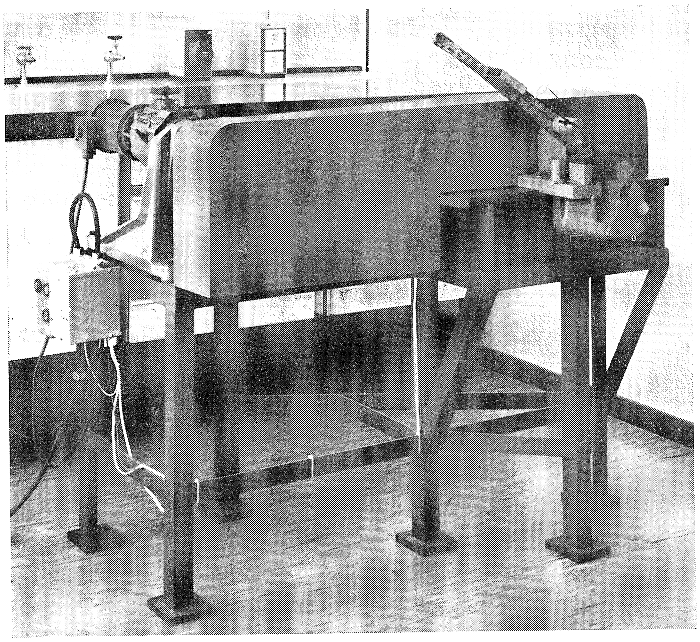


Fig. D7. Apparatus for determining to-and-fro bend values.

Table D2. Fractures in cold-drawn prestressing steel; to-and-fro band values

description*	wire diameter mm	endurance time to fracture: days	to-and-fro bend value	
			N′	*N*
occurred in solution "a"				
code CL4	4	24***	50	75
CL3	4	83	44	73
CL6	4	23	32	82
CL8	4	167	7	82
occurred in solution "b"				
CL7	4	460	34	80
occurred in 20 weight% NH_4NCS in water				
grade 1 steel	7	15 to 188 hours*	9	62
grade 2 steel	7	4.7 to 35 hours**	10	54

* Solution "a": a saturated solution of $Ca(OH)_2$ with 2% $CaCl_2$ (Cf.2.1.1.3)
Solution "b": distilled water (Cf.2.1.2)
Grade 1 steel: from normal production
Grade 2 steel: intentionally given incomplete heat treatment

** The extreme values of the average endurance time for the series indicated in table 1 are given here (Cf.2.2.1 and table D1).

*** No fracture

– so local that in the determination of N' the section where the to-and-fro bend fracture occurs, though close to the endurance test fracture, is nevertheless at such a distance from it that there is already a lower concentration of hydrogen there than at the endurance test fracture. This could account for the differences that were observed.

Furthermore, the endurance time to fracture varies greatly for the fractures that occurred in the solution "*a*". If cathodic polarization is applied during an endurance test, it can give rise to a difference in the amount of hydrogen that penetrates into the steel. The longest endurance time to fracture of all the fractures reported for solution "*a*" occurred in the case of CL8, where the wire test specimen had been cathodically polarized. In this case we find the lowest value for N' of all the fractures in solution "*a*", this being possibly attributable to the penetration of an extra large amount of hydrogen into the steel. On comparing with the fractures CL3 and CL6 we see that Table D2 also shows that a longer endurance time is not just simply correlated to a lower value of N'. Hence it can be inferred that the results of the investigations do not furnish evidence of any simple correlation between polarization time or endurance time to fracture and the value N'.

It might be supposed that fracture (in the enduranc tests) occurs at the instant when the to-and-fro bend value has gone down to the value found for N'. This is not so, however. Long before fracture takes place, N' has already reached its final value. This is evident from the data in Table D3 (series A and B), which is concerned with the determination

Table D3. The value of N′ during the exposition to the embrittling NH_4NCS-solution

A series of 6 test wires of steel QP-170, 4 mm diameter (NDI), is exposed to the NH_4NCS-solution under standard conditions (t_m approx. 75 hours). After periods of 2, 5, 8^5, 15, 20 and 25 hours, respectively, a wire is removed from the test solution (no fracture) and the to-and-fro bend values N and N' are determined (on the parts of the wire which were not and which were immersed in the solution respectively).In all, four series of tests were performed, namely:

series A: in accordance with the procedure described above;
series B: series A repeated;
series C: same as series A, except that N and N' are not determined until the wires have, after removal from the test solution, been heated at 100 °C for 2 hours;
series D: same as series C, except that now the 100 °C heating period is 100 hours.

Results: see table; *Results in graph form:* see fig. 8

test period in NH_4NCS (hours)	series A		series B		series C		series D	
	N	N'	N	N'	N	N'	N	N'
2	82	43^5	70	48	75	65	79	76
5	74	19	82	23	69	42	76	75
8^5	79	15	80	13	69	43	77	78
15	69	14^5	74	13^5	79	45	82	76
20	68	14	81	12	74	48	76	80
25	75	13	72	13	82	45	73	80
N_m	75	–	77	–	75	–	77	75
coefficient of variation (%)	7.3	–	6.6	–	6.9	–	4.0	4.5

of the values N and N' of colddrawn 4 mm diameter prestressing wire in a 20% NH_4NCS solution under standard condition (see column I of Table D1). Under these conditions an average fracturing time t_m of 74 hours was found and, after fracture, an average value of 75 for N and 14 for N'. When the endurance tests were then repeated and prematurely terminated (e.g., after 2, 5, 8.5, 20 and 25 hours respectively), so that fracture had not yet occurred, and when N' was now determined for the part of the (nonfractured) wire which had been in the solution, the results stated in Table D3 were obtained (series A and B) (see also Fig. D8, where the same results have been presented in graph form). It emerges that already after a little more than 8.5 hours the final value of N' has practically been attained i.e., after about 15% of the total endurance time to fracture.

At that instant the amount of hydrogen present in the steel was sufficient to enable fracture to develop with minimum to-and-fro bend value, but not sufficient for fracture in the endurance test. Of course, a to-and-fro bend test is much more severe: the wire is repeatedly stressed above its proof stress, i.e., it is subjected to plastic deformation. It is therefore possible that hydrogen has a more strongly adverse effect in the to-and-fro bend fracturing of the wire than in bringing about fracture in the corresponding endurance test.

Finally, it should be noted that in the series C and D of Table D3 the values N' were determined after a stress relieving treatment at 100 °C of 2 hours' (series C) and 100 hours' duration (series D) had been applied. In the latter case the embrittlement disappeared completely (the steel was restored to the original value N), because this treatment lasting 100 hours drove out all the hydrogen. This provides additional evidence of the effect of the hydrogen in the steel upon the to-and-fro bend value.

2.3.2 Appearance of the fracture (fractography)

The appearances presented by the various fractures, are compared; the data for comparison are obtained from examination with the optical microscope and the scanning electron microscope. Three types of fracture produced in cold-drawn prestressing steel, were investigated:

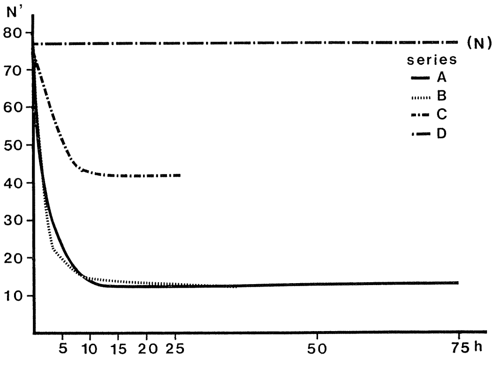


Fig. D8. Results of Table D3.

2.3.2.1 – tensile fractures;
2.3.2.2 – fractures in endurance tests in 20% NH_4NCS solution;
2.3.2.3 – fractures in endurance tests in solutions "a" and "b".

Re 2.3.2.1 Tensile fractures

These fractures are purely ductile. They have a so-called cup-cone character. Necking is discernible under the microscope and often also on macro-examination. Etching of the steel reveals shearing. In Fig. D9 the left-hand microscopic photograph (magnification 11 ×) clearly shows the necking of the specimen. The right-hand photograph shows the microscopic appearance presented by a fractured wire after etching and more particularly reveals the shearing which has occurred in a ductile residual fracture (magnification 200 ×).

Under the scanning electron microscope at low magnification (see composite Fig. D10, magn. 45 ×) we see what seems to be a brittle central region and a smooth peripheral region. Under higher powers of the microscope there are seen to be so-called dimples (small round depressions) in both these regions, i.e., occurring over the entire fracture surface. These features are typical of ductile fracture surfaces. The dimples

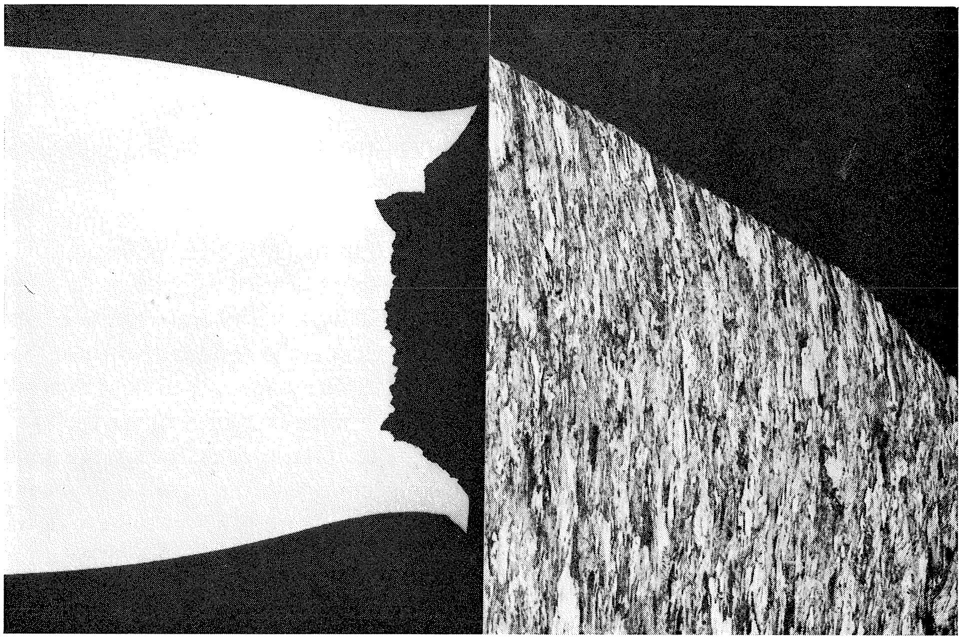


Fig. D9. Ductile fracture (micrographs).
Left (magn. 11 ×): necking caused by tensile test of wire to fracture (cup-cone character).
Right (magn. 200 ×): etched specimen of fractured wire; the ductile *residual* fracture, and the shearing which occurred there, are distinctly visible (fracture occurred in solution "*b*" = distilled water).
See also Fig. D13, upper micrograph.

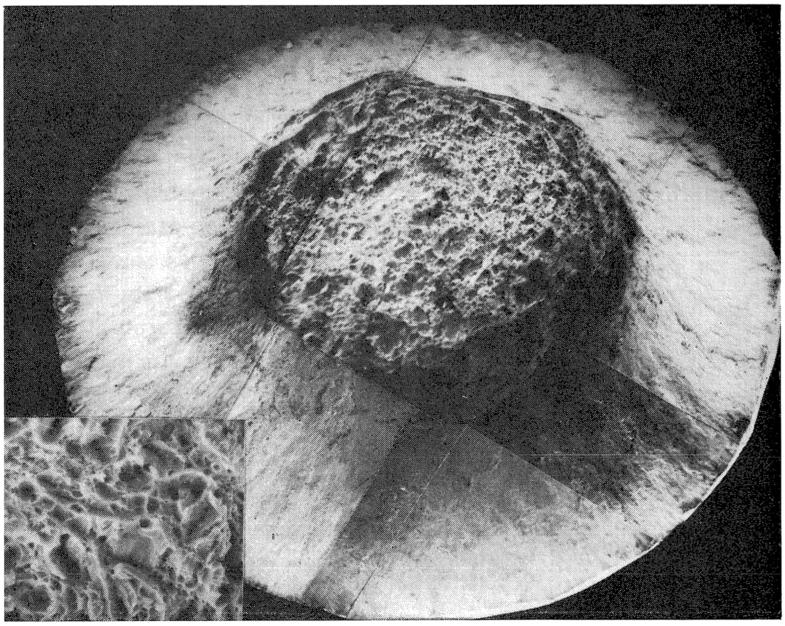
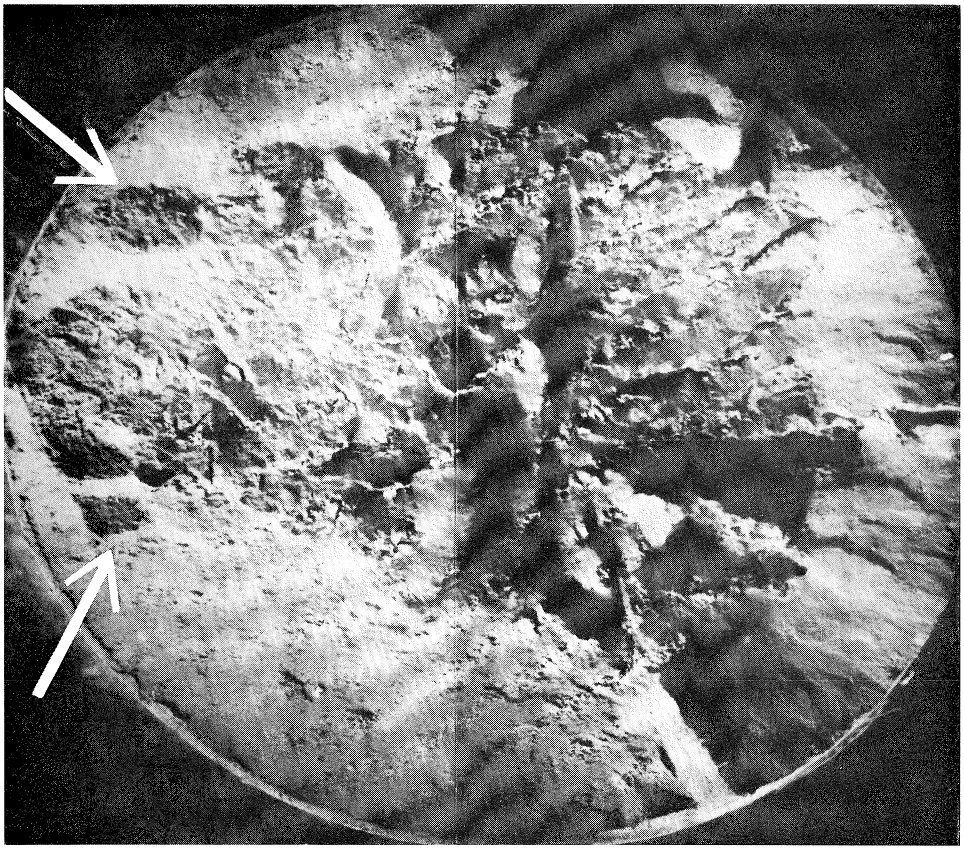


Fig. D10. Ductile tensile fracture: observations under the scanning electron microscope. The large photograph (magn. 45 ×) is a composite micrograph of the tensile fracture. An apparently brittle central region and a smooth peripheral region are seen. Under powerful magnification so-called dimples (small round depressions) are found to be present in both regions (see detail at bottom left: magn. 2000 ×).

are clearly visible in the much enlarged detail in the bottom left-hand corner of Fig. D10 (magn. 2000 ×).

Re 2.3.2.2 Fractures in endurance tests performed in the 20% NH_4NCS solution

In the central region these fractures show signs of great brittleness, with terrace-like differences in level, ridges and fissures, surrounded by a peripheral region wholly or in part characterized by purely ductile features (ductile residual fracture). See Figs. D11 and D12, which are composite micrographs (magn. 40 to 45 ×) of two endurance fractures in the NH_4NCS solution which were examined under the scanning electron microscope. The smooth zone in Fig. D11 is seen to contain some brittle areas (arrowed) which have no visible connection with the external surface of the wire. It is suspected that these are fracture nuclei; they are believed to have developed without any visible effect of the external environment, under the influence of hydrogen which penetrated into the steel. Under powerful magnification the scanning electron microscope reveals the brittle central region as containing large and small cleavage surfaces (partly in the form of rosettes), as well as areas with cleavage surfaces and dimples interspersed: these are called quasi-cleavage areas. These features are clearly visible in the two much enlarged details in Fig. D12 (magn. 1000 × and 3000 × respectively. Such quasi-cleavage areas are always found in fractures due to hydrogen embrittlement.



Figs. D11 and D12 (page 66). Brittle stress corrosion fracture in 20% NH_4NCS: observations under the scanning electron microscope, mag. 40–45 ×. Here we see the very brittle central region with terrace-like differences in level, ridges and fissures, and furthermore a peripheral region with wholly or partly ductile features (ductile residual fracture). Two enlarged details are included in Fig. 12 (1000× and 3000× respectively). These reveal the so-called quasi-cleavage character of the fracture (true cleavage surfaces and cleavage surfaces in rosette form, interspersed with dimples).

Re 2.3.2.3 Fractures in endurance tests performed in the simulated practical solutions "a" and "b"

Fractures which developed in solution "a" (saturated $Ca(OH)_2$ solution with 2% $CaCl_2$) as well as the fracture which developed in solution "b" (distilled water) were investigated. Optical microscopic examination revealed that, in general, only the residual fracture is ductile with shearing and possibly some slight necking. The residual fracture of the endurance fracture produced in solution "b", is shown in the right-hand part of Fig. D9.

Examination with the aid of the scanning electron microscope of the brittle parts of the fracture surface (i.e. those parts which do not belong to the residual fracture) clearly reveals the presence of dimples besides cleavage rosettes or sharp cleavage

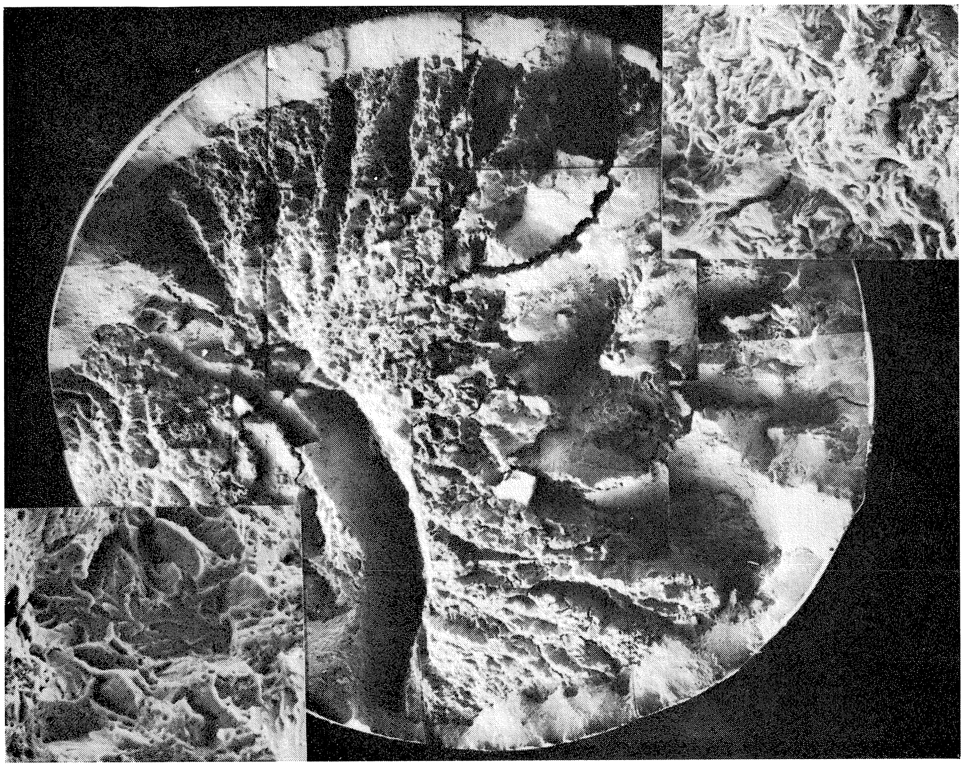


Fig. D12 Details in text under fig. D11

fractures: in other words, the brittle parts have a quasi-cleavage character, as do also the brittle parts of the fractures caused by hydrogen in the NH_4NCS solution. This is seen in the scanning electron micrographs reproduced in Fig. D13 (mag. 1000 ×). The lower illustration shows a brittle area of a fracture produced in solution "a"; the upper one shows a brittle area of the fracture produced in solution "b". In both cases the effect of hydrogen is thus distinctly detectable in the appearance presented by the fracture.

3 Summary and conclusions

The conclusions given here relate in the first place to the premises stated in the Introduction 1 and furthermore to the research reported in 2. The subdivision adopted here corresponds as closely as possible to the one, given in 1 and 2. Where prestressing steel is mentioned in the conclusions, the material envisaged is patented cold-drawn prestressing wire.

3.1 *Conclusions concerning the premises stated in the Introduction*

A. Research on stress corrosion fractures of prestressing steel should more particu-

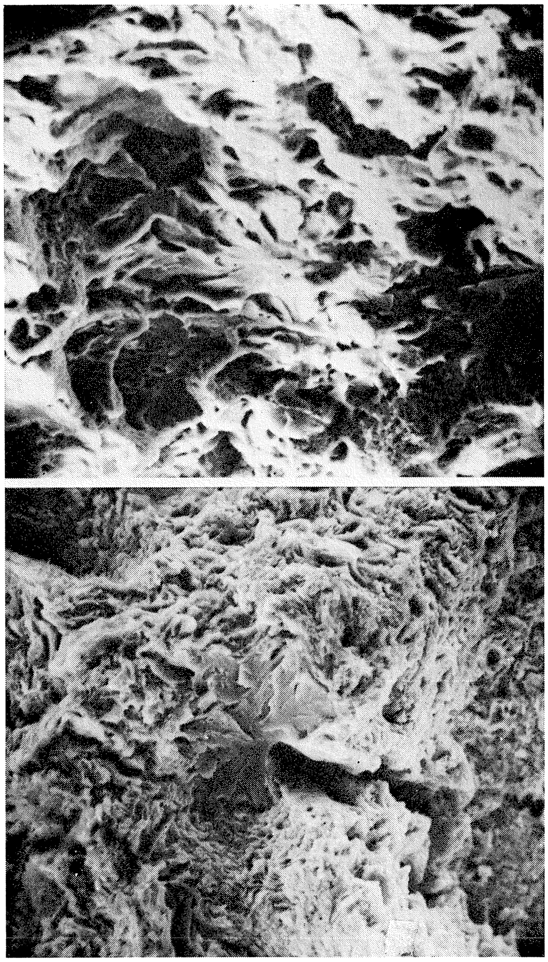


Fig. D13. Scanning electron micrographs of brittle fractures which occurred in the simulated practical solutions "a" and "b" (magn. 1000 ×).
lower part: fracture in solution "a" (saturated $Ca(OH)_2 + 2\% \; CaCl_2$)
upper part: fracture in solution "b" (distilled water).
The ductile residual fracture of the specimen tested in solution "b" is shown in the micrograph on the right in Fig. 9.

larly concern itself with so-called *true* stress corrosion fractures, i.e., fractures with a brittle character (and therefore hardly any deformation) which occur long before a state of stress exceeding the tensile strength has been attained. The general opinion is that such fractures occur under the influence of hydrogen which penetrates into the steel during the process of corrosive attack or which was present in the steel already from the outset.

B. Corrosive attack of steel in concrete usually occurs in consequence of local rupturing of the passivating layer under the influence of foreign ions, frequently chlorine ions. The hydrogen which is formed in this process of attack penetrates to a greater or less extent into the steel, accumulates at tensile stress concentrations locally present in the steel and can thus result in the occurrence of a brittle fracture at such a section.

3.2 *Conclusions concerning the results obtained from endurance tests*

3.2.1 Stress corrosion fractures in simulated practical solutions

3.2.1.1 Solution "a" (saturated $Ca(OH)_2$ with 2% $CaCl_2$)

A. From the *E*-pH diagram of iron at 25 °C according to *Pourbaix* it follows that attack of prestressing steel in concrete with simultaneous evolution of hydrogen can take place only if lowering of the pH occurs. Such lowering may be due to local rupturing of the passivating layer which forms on steel in concrete. This rupturing is caused more particularly under the influence of chlorine ions present in the concrete. Pitting occurs in consequence, and in a pit thus formed in the steel the liquid can acquire such an acid character that the steel is attacked with simultaneous evolution of hydrogen.

B. In the research conducted by TNO it was shown that a pH of 5 could develop in a small artificially formed pit in a specimen immersed in solution "a". It was furthermore shown that prestressing steel in concrete could acquire a potential between about -400 mV and $+50$ mV (hydrogen scale) in relation to the liquid in the concrete, these extreme potential values corresponding respectively to the complete (or almost complete) absence and the definite presence of oxygen – the latter condition being due to partial drying of the concrete.

From these facts it is evident that in concrete containing chloride it is, in principle, possible, that conditions arise under which prestressing steel undergoes corrosive attack with simultaneous evolution of hydrogen. In solution "a" the practical conditions can be simulated for tensioned prestressing steel by means of electrolytic polarization: the fractures that develop in such circumstances can be expected to correspond to the brittle fractures observed in actual practice.

3.2.1.2 Solution "b" (distilled water)

Prestressing steel under tension may, in the long run, develop brittle fracture under the influence of condensing water vapour.

3.2.2 Stress corrosion fractures in solutions causing hydrogen embrittlement (especially the 20% NH_4NCS solution)

A. From research carried out under an international project initiated by the RILEM-FIP-CEB Joint Committee (Comité Mixte) it appears that standardized endurance tests can be performed on prestressing wire under tension in a 20% solution of NH_4NCS in such a manner that satisfactorily reproducible fracture times are obtained which can be regarded as a measure of the hydrogen embrittlement susceptibility of the prestressing steel investigated.

B. Comparative statistical analysis has shown that the method of investigation applied by TNO has hitherto given the best results in that a scatter of 15% or less was obtained in the fracture times found in six tests performed under identical conditions.

C. Investigation has shown that in carrying out the tests it is necessary accurately to maintain agreed values of temperature and tension (which values have yet to be finalized) and furthermore that electrolytic polarization of the wire specimen, pumped recirculation of the test solution and the passing of nitrogen through the latter should not be applied. As for the purity of the NH_4NCS employed, there appears to be no significant difference between analytical grade and technical grade purity.

3.2.3 Similarity of the stress corrosion fractures envisaged in 3.2.1 and 3.2.2
The practical usefulness of determining the hydrogen embrittlement susceptibility of prestressing wire by the method indicated in 3.2.2 is demonstrated by the following similarities which have been found in the fractures envisaged in 3.2.1 and 3.2.2.

3.2.3.1 In simulated practical solutions as well as in 20% NH_4NCS solution the fractured wires are found to have a greatly reduced to-and-fro bend value N' in the vicinity of the endurance fracture that developes in such solutions (in relation to the original value N).

Thus $N' < N$ or $N' \ll N$.

In the tests performed in the 20% NH_4NCS solution this decrease in the to-and-fro bend value is usually more pronounced than in those performed in the simulated practical solutions. The decrease of the to-and-fro bend value, developed at any moment of a not yet ended NH_4NCS-test, is not proportional to the length of the elapsed exposition period, but its maximal value is instead fully attained already at about 15% of the endurance time to fracture.

3.2.3.2 Examination of fractures by means of the optical microscope and the scanning electron microscope reveal a marked similarity between the fractures which occur in simulated practical solutions and those in a 20% NH_4NCS solution. In both cases there is a quasi-cleavage character with ductile residual fracture.

4 Concluding remarks

It is evident that the endurance test performed in NH_4NCS solution in accordance with the standard conditions described here provides a dependable measure of the hydrogen embrittlement susceptibility of the prestressing wire investigated. The testing procedure ensures always equal chance of hydrogen penetration into the steel. The resulting embrittlement differs from one type of steel to another, this being bound up with intrinsic differences in the embrittlement properties of these steels. This is most conclusively proved by the results given in Table 1, from which it clearly emerges that the above-mentioned standardized test distinctly reveals such differences between steels which, though having identical properties as determined by the usual technological tests, differ greatly in their hydrogen embrittlement susceptibility because of a difference in the heat treatment applied. Hence it follows that by means of this test any such differences can be clearly recognized and also that the test can render very useful services in connection with any attempt to improve the behaviour of steel in this respect.

It is also evident from the foregoing that the test cannot yield any absolute figures as to the service life or hydrogen embrittlement properties of prestressing steel; the test results permit only a *relative* comparison of susceptibility to embrittlement. This can be of considerable importance in many cases, however. For arriving at service life predictions it will be necessary to evaluate a good deal of additional data, including more particularly data concerning the manner in which, and the extent to which, hydrogen becomes available for penetration into the prestressing wire. Endurance tests in NH_4NCS solution do not give relevant information on this; the results of current-voltage curve (*E–i* curve) determinations are of more importance with regard to this aspect. The tests in NH_4NCS give (*relative*) information as to the deleterious effects of hydrogen that has penetrated into the steel during the test or that has been present in the steel all along, and Table 1 shows that important differences are possible for technologically identical steels. *E–i* curves procure data about the intensity with which hydrogen is introduced into the steel from the environment. For technologically identical steels strongly different *E–i* curves are improbable in the concrete medium, as for the quality of the passivation layer in concrete it is more the nature of the concrete medium that is important than the quality or grade of the prestressing steel.

Besides, even if it were desired to utilize the endurance test results in NH_4NCS for service life predictions, this would hardly be feasible at present. For that, it would be necessary to know the acceleration factor, i.e., the factor by which the actual service life of the wire is speeded up (i.e., shortened) when it is tested to endurance fracture in the NH_4NCS solution. This factor is not known, nor can it be determined within the foreseeable future, because there are too few instances of fracture in actual practice for which the circumstances of their occurrence are known and because hitherto hardly any endurance tests have been performed in advance on prestressing steel that subsequently fractured. Instead of basing oneself on the results of observations on actual structures, it might be possible to make use of the results of tests in simulated practical solutions, more particularly those performed in solution “a” (saturated $Ca(OH)_2$ with 2% $CaCl_2$). For that purpose, however, it would first be necessary to achieve sufficiently reproducible fracturing behaviour which is something we have not yet accomplished and which, in our opinion, will not be quickly accomplished either. Cathodic polarization is sometimes recommended to solve this problem. Improvement of reproducibility can indeed be reached in this way, but only by sacrificing the passivating action of the concrete medium, i.e. by establishing conditions that deviate from practice.

Determining the hydrogen embrittlement susceptibility by means of a reproducible standardized test (such as the NH_4NCS test) therefore remains important, however, because such testing will provide the *relative* data concerning an intrinsic steel property which plays a part in determining the service life of the steel under investigation when such steel is used in concrete.

References

1. A. A. Seyes, M. J. Brabers and A. A. van Haute: Analysis of the influence of hydrogen on pitting corrosion and stress corrosion of austenitic stainless steel in chloride environment. Corrosion (NACE), 1974 (30) 47.
2. Micro-electrodes for corrosion research:
   A. P. Doig and J. W. Edington: Use of micro-electrodes in the study of SCC in aged Al 7.2 wt% Mg and Al 4.4 wt% Cu alloys. Brit. Corr. J. (Quarterly) 1974 (No. 2) 88.
   B. H. J. Clearly: Micro-electrodes for corrosion study. Corrosion (NACE), 1968 (24) 159.
   C. Use of micro reference electrodes for the measurement of local potential differences. See ref. 1 (Seyes et al.) who measured a difference of 800 mV between the bottom of an artificial pit and the surface of the steel. Others (see ref. 20) measured a difference of 150 mV in an acid environment.
   D. H. W. Pickering and R. P. Frankenthal: On the mechanism of localized corrosion of iron and stainless steel. J. Electrochem. Soc. 1972 (119) 1297.
3. Sodium tungsten bronze electrodes:
   A. A. G. Kokshrov and V. F. Ust-Kachkintsev: Electrode properties of sodium tungsten bronzes. Uch. Zap. Permsk. Gos. Univ. 1964 (No. 111) 63. (Translated from Russian into English by A. J. Gay).
   B. J. P. Randin, A. K. Vijh and A. B. Glughtai: Electrochemical behaviour of sodium tungsten bronze electrodes in acidic media. J. Electrochem. Soc. 1974 (120) 1174.
4. CUR Report 49: Cases of damage due to corrosion of prestressing steel. Netherlands Committee for Concrete Research, July 1971.
5. Stress corrosion of prestressing steel. ("De Bilderberg", Oosterbeek, The Netherlands).
   A. First Symposium on 8–9 Sept. 1971, Proceedings Parts 1 & 2.
   B. Second Symposium on 20–21 Sept. 1973, Proceedings.
6. P. Pequin, M. Rubaud, P. Longuel and A. Zelwer: L'étude de la corrosion des aciers et métaux dans le béton. Cahiers du Centre Scientifique et Technique du Bâtîment, No. 130, June 1972, Cahier 1109.
7. H. Grafen: Das Spannungsrisskorrosionsverhalten von unlegierten, niedriglegierten und hochlegierten Baustählen. Z. f. Wirtsch. Fertigung 1974 (9) 425.
8. B. Cox: A correlation between acoustic emission during SCC and fractography of cracking of the zircalloys. Corrosion (NACE) 1974 191.
9. Mme M. Brachet, E. Duffaut and P. Lacombe: Influence de la structure superficielle de fils d'acier à haute résistance pour béton précontraint sur leur tenue à la corrosion sous tension en atmosphère humide. Mémoires Scientifiques Rev. Metallurg. 1967 (LXIV No. 7/8) 607.
10. E. Riecke: Über den wasserstoffinduzierten Sprödbruch hochfester Stähle Arch. Eisenhüttenwes. 1973 (44) 647. See also: Über den wasserstoffinduzierten Sprödbruch hochfester Stähle. Kommission der Europäischen Gemeinschaften. Abschlussbericht Max-Planck-Institut, Düsseldorf. Forschungsvertrag No. 6120-42 (1) 011, (1-7-1968/30-6-1973). EUR 5250d (3. Teil) 1975.
11. A. Asphahani and H. H. Uhlig: Stress corrosion cracking of 4010 high strength steel in aqueous solutions. J. Electrochem. Soc. 1975 (122) 174.
12. H. Bohni: Die Wasserstoffversprödung bei Spannstählen. Werkst. und Korrosion 1975 (26) 199.
13. J. C. Charbonnier, B. Marandet and H. Margot-Marette: Etude de l'influence de quelques facteurs physico-chimiques sur les phénomènes de corrosion sous contrainte d'un acier à très haute résistance, en milieux aqueux. Irsid RE 272-15 Dec. 1974 (Cos 74/156-95.42.07.03).

APPENDIX

Memorandum on the effect of some properties of steel on the stress corrosion susceptibility of prestressing steel

The following properties are discussed:

1. Effect of chemical composition
2. Effect of structure and heat treatment
3. Effect of mechanical properties:
   a. Tensile strength
   b. Toughness
4. Effect of surface condition.

Re 1 *Effect of chemical composition*

The effect, executed by an increase of the mentioned chemical element in promoting (+) or retarding (–) the endurance time to fracture in stress corrosion tests with prestressing wires, is indicated in the following table: (0 denotes: no notable influence):

	effect on	
element	patented colddrawn wire	quenched and tempered wire
C	–	–
Mn	0	?
Si	–	+
Cr	0	0
Si+Cr	–	+
S	–?	–?
Al	+	0?
N	0/+	?
Al+N	+	?

Carbon often has an indirect effect in that a higher carbon content usually brings about a higher tensile strength. Varying the Mn content is found to have no effect (on drawn wire anyway). Increasing the Si content has an unfavourable effect on drawn wire, whereas it results in better endurance times in quenched and tempered wire. Cr in a content of up to 0.5–0.7% has no effect. Combinations of Si and Cr produce an unfavourable effect in drawn wire, but a favourable one in quenched and tempered wire. It has been asserted that a relatively high content of S increases the susceptibility of steel to hydrogen embrittlement. (This is attributed to the effect of sulphides in retarding $2H^+ \rightarrow H_2$ and thus increasing the risk of hydrogen being absorbed into the steel). Aluminium, possibly in combination with an increased content of N, would appear to have a favourable effect because of its grain-refining action.

Re 2 *Effect of structure and heat treatment*

A cold-drawn troostite structure with a 70–85% reduction of cross-sectional area is found to attain relatively long endurance times in stress corrosion tests. With reductions of area < 70% shorter endurance times are obtained, despite the lower tensile strength of the steel. This has tentatively been attributed to the less elongated (fibre-like) structure of the steel. For reductions of area > 85–90% there is a risk of overstreching the wire (micro-cracks at which brittle fracture is possibly initiated).

It was found that drawn wires which had been patented at 400 °C and were completely bainitic attained, shorter endurance times in stress corrosion tests than did wires patented at 450 °C and 500 °C (which were wholly or largely troostitic).

Tempered martensite in carbon steel with the same chemical composition and tensile strength as a patented drawn wire has a relatively short endurance time in comparison with the latter. With modified chemical composition, however, a quenched and tempered steel may also posses substantial resistance to stress corrosion.

Heat treatment of cold-drawn wire often increases its resistance to stress corrosion. More particularly, artificial ageing and stabilizing are envisaged here. The effect is perhaps attributable to a reduction of internal stresses.

Re 3 *Effect of mechanical properties*

a. Effect of tensile strength

For quenched and tempered wire it has been very clearly established that with increasing tensile strength the endurance time in stress corrosion tests becomes shorter (for wire stressed to the same proportion of its tensile strength, e.g., to $0.7\sigma_B$. See Fig. D14.

For drawn wire this is not necessarily always so, since it depends to some extent on how the higher tensile strength has been obtained. If the strength has been increased only as a result of a higher degree of drawing reduction (in cold drawing) this need by no means result in a shortening of the endurance time (provided that the reduction is not too great). On the other hand, the endurance time is shortened when the strength increase is due, for example, to a higher carbon content or higher strength after patenting or inadequate or not very suitable heat treatment.

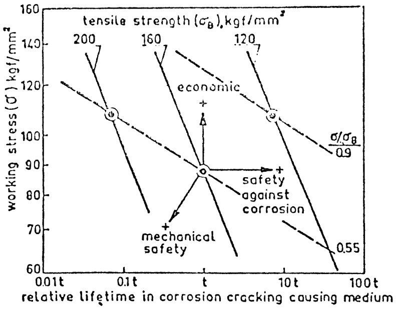


Fig. D14. Economic and safe design with prestressing steel.

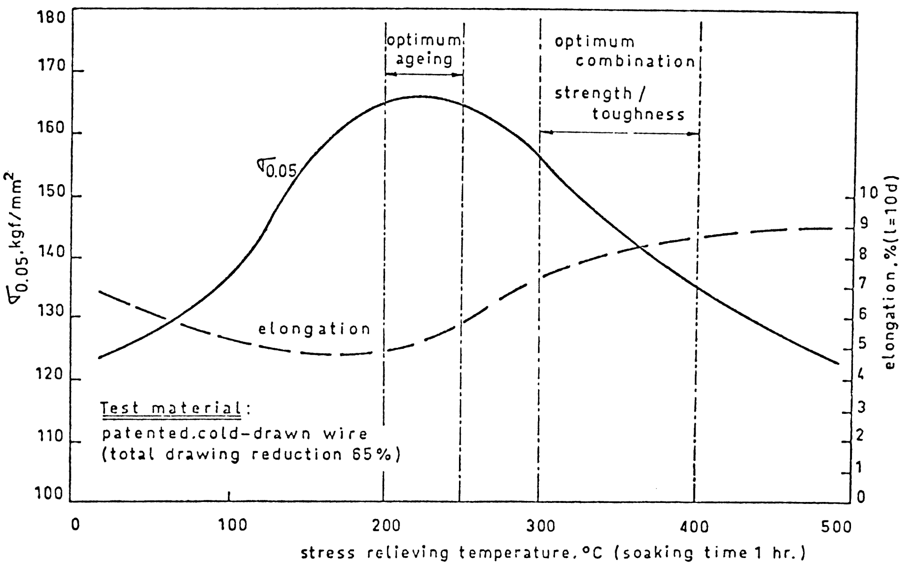


Fig. D15. Influence of stress relieving on the properties of prestressing steel (schematically).

b. Effect of thoughness

A tougher steel will in general possess somewhat higher resistance to the spread of stress corrosion cracks and to brittle fracture. This may account for the favourable effect of heat treatment (provided that this is of sufficiently long duration and/or at sufficiently high temperature; see Fig. D15. Also, changes in chemical composition and changes in the structure of the steel which increase its toughness similarly have a favourable effect. Influencing factors which have as yet been little investigated are, for example, the effects of nickel (for which it has been shown that an amount of as little as 0.5% can increase the toughness of prestressing steel) and the effects of (re)melting processes which considerably improve the purity of the steel.

For quenched and tempered steel used for making machinery components it has been found that remelting processes which improve the purity of the steel may reduce its susceptibility to hydrogen embrittlement.

Re 4 *Effect of surface condition*

The following should be avoided:

- surface defects due to manufacture (small cracks, laps, mechanical damage, etc.);
- deviating structure at the surface (decarburization, martensitic edge zones, etc.);
- "foreign" substances on the surface (dirt, particles of other metals, rust, traces of drawing grease, etc.).

The following may have a corrosion-retarding effect:

- removal of the above-mentioned surface films and particles liable to have an adverse effect;

- mechanical treatments such as shotblasting and polishing, causing any surface cracks to be closed up and/or a compressive stress to be produced at the surface;
- plastics coatings;
- chemical coatings (phosphates, etc.);
- metallic coatings (e.g., zinc; the favourable effect supposed to be obtained in this way is highly disputable, however).