

Stress corrosion cracking of rock bolts: an examination of the metallurgical and environmental factors behind preliminary rock bolt failure

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SCHOOL OF MATERIAL SCIENCE AND
ENGINEERING

FACULTY OF SCIENCE

*STRESS CORROSION CRACKING OF ROCK BOLTS: AN
EXAMINATION OF THE METALLURGICAL AND
ENVIRONMENTAL FACTORS BEHIND PRELIMINARY ROCK
BOLT FAILURE*

by

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Thesis submitted as a requirement for the degree
PhD. of Engineering (Failure Analysis)

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ABSTRACT

Rock bolting is a form of ground support that is widely used in engineering for supporting underground excavations and to improve slope stability. In particular, it is widely used in the mining industry, where rock bolts have become the primary form of ground support for roadway development in underground coal mines. However, stress corrosion cracking (SCC) of rock bolts began to be observed in the 1990s compromising the integrity of rock bolting.

The work presented in this thesis is part of a broader study of stress corrosion cracking of rock bolts in underground mines. It has focused on understanding the environment in which failures occur and the mechanism behind failure. SCC tests which could be used in-situ in underground mines were also evaluated and validated in the laboratory.

An investigation into the ground water was conducted for two mines (Mines A and B) which were known to have undergone a substantial number of SCC failures. From this investigation, it was concluded that mine water chemistry can vary significantly from place to place however both mine waters were found to be alkaline and corrosive. The alkalinity in both mines was almost exclusively due to the presence of bicarbonate ions, with the bicarbonate levels in Mine A being substantially higher than in Mine B. An investigation into the presence of microbiological organisms was also carried out as part of this work and showed that water from Mine B contained both iron- and sulphur-reducing microorganisms.

An investigation into the failure mechanism in rock bolts retrieved from these two mines was also conducted. This indicated that SCC in underground coal mines can occur by two different mechanisms. In high alkalinity mine water, SCC occurs by an anodic mechanism involving carbonate/bicarbonate cracking, whereas in low alkalinity mine water, a cathodic mechanism occurs involving hydrogen induced cracking. The two different SCC mechanisms are similar to the high pH carbonate/bicarbonate SCC and the near-neutral pH hydrogen induced SCC observed in buried pipelines. The occurrence of carbonate/bicarbonate SCC has not however been reported previously.

The use of a pin-loaded slotted coupon test was examined which was suitable for use in rock bolt bore holes while also retaining the physical and metallurgical features present at the surface of rock bolts. The test methodology was validated in the laboratory using an acidified sodium chloride sodium sulphide solution. Laboratory testing was

subsequently conducted for 3 months in ground water extracted from Mine B using the pin-loaded specimen. Alternating 8 hour wet/8 hour dry cycling was used for the tests. No SCC failures were observed within the test duration. This may indicate that microorganisms, which did not survive when the water was removed from the mine, may be involved in the in-situ SCC process.

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I dedicate this thesis to everyone who supported and inspired me along the way:

To my colleagues, Damon Vandermat and Peter Craig. Although the journey to this point has been tedious and exhausting it has also been one which was invigorating and I could not have asked for better people to have shared this life experience with and would like to Deepak Chopra to sum up our journey

“No single decision you ever made has led in a straight line to where you find yourself now. You peeked down some roads and took a few steps before turning back. You followed some roads that came to a dead end and others that got lost at too many intersections. Ultimately, all road are connected to all other road”

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Hebrews 13:21 "May God make you perfect in every good work to do his will, working in you that which is wellpleasing in his sight, through Jesus Christ; to whom be glory forever and ever"

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LIST OF ABBREVIATIONS AND ACRONYMS

AEM	Analytical Electron Microscopy
ARC	Australian Research Council
ASTM	American Society for Testing and Material
AT	Australian Technology
CIS	Corrugated Irregular Surface
EBSD	Electron Back Scattered Diffraction
EPS	Extracellular Polimeric Substances
HELP	Hydrogen Enhanced Localised Plasticity
HISCC	Hydrogen Induced Stress Corrosion Cracking
ICP	Inductively Coupled Plasms
IGSCC	Intergranular Stress Corrosion Cracking
kN	Kilonewtons
kPa	Kilopascal
L	Liters
LIST	Linearly Increasing Stress Test
LME	Liquid Metal Embrittlement
LSI	Langelier Saturation Index
mL	Millilitre
Mm	Millimeter
MPa	Megapascal
MVC	Micro Void Coalescence
ORP	Oxidation Reduction Potential
OTUs	Operational Taxonomic Units
PTFE	Polytetrafluroethylene
SCC	Stress Corrosion Cracking

SRB	Sulphate Reducing Bacteria
TTF	Time to Failure
TTS	Tearing Topography Surface
UTS	Ultimate Tensile Strength
WASM	Western Australian School of Mines

1 INTRODUCTION

1.1 Background

Rock bolting is a form of ground support that is widely used in engineering for supporting underground excavations and to improve slope stability. In particular it is widely used in the mining industry, where rock bolts have become the primary form of ground support for roadway development in underground coal mines^[1]. Figure 1-1 shows a series of rock bolts reinforcing the strata in the roof of an underground mine.

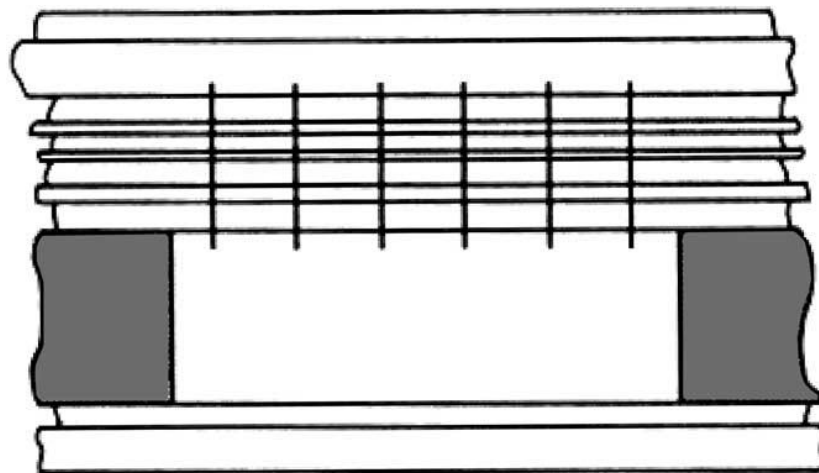


Figure 1-1: Schematic diagram showing rock bolts reinforcing the roof strata in an underground mine^[2].

The rock bolts used in Australian mines are known as chemical bolts. They are lengths of steel bar, typically 2.4 m long and 22 mm in diameter which are inserted into predrilled holes in the strata and then bonded into the holes using polyester resin grout (referred to as a chemical fixative). The polyester resin grout is contained in a cartridge which is

placed at the tip of the bolt. When the rock bolt reaches the end of the bolt hole, the cartridge ruptures and the grout is extruded back along the annular cavity between the bolt and the hole, bonding the bolt to the strata. The bolts contain embossed helical ribs, which aid in the bonding process, while the bottom end of the bolt is threaded.

Once the bolt is inserted and bonded, an end plate is placed on the threaded end, and an end nut fitted to the thread. A domed washer is used between the end plate and the nut. The nut is torqued to give a preload of 10-14 tonnes.

The technique described above is known as Australian Technology (AT) rock bolting and is also used in several other countries. An installed rock bolt is shown in Figure 1-2.

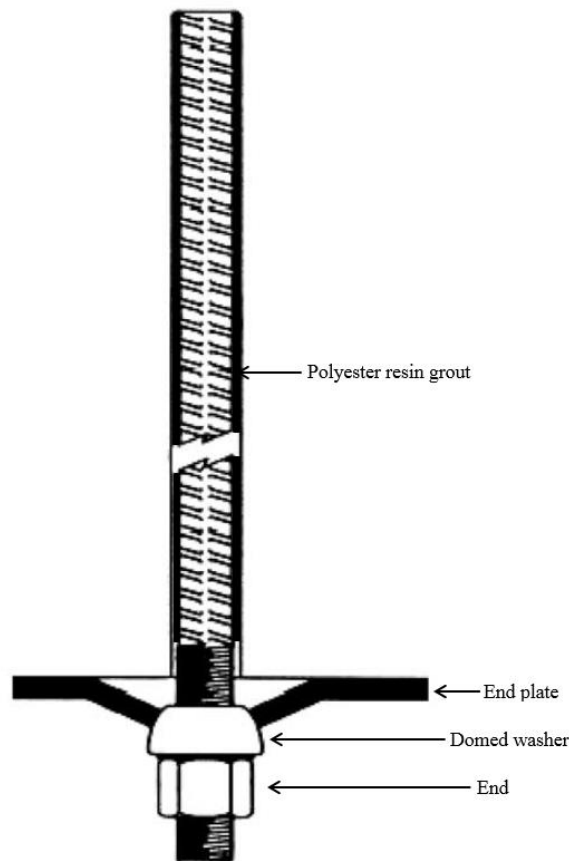


Figure 1-2: Schematic diagram showing installed rock bolt reinforcing the roof strata in an underground mine.^[2]

Rock bolts were first used in Australia in the 1940's, when pioneering work was done on the Snowy Mountains Scheme. Shortly after this, they were trialled at Elrington Colliery as a means of supplementing the timber supports that were used at that time^[3].

Since then, the technologies associated with rock bolting have progressed from simple hand-drilled holes and mechanical shell point anchored rock bolts, to highly automated

drilling, resin injected, fully encapsulated systems^[1]. Over time, stronger grades of steel have also been introduced to meet the increased demand placed on rock bolts as mines become deeper.

When excessive loads are experienced by the rock bolting system, failure can occur either by rupture of the rock bolt or by failure of the anchor system. When rock bolt rupture occurs, the bolt fails in a ductile manner with significant plastic deformation occurring in the form of localised necking at the point of rupture.

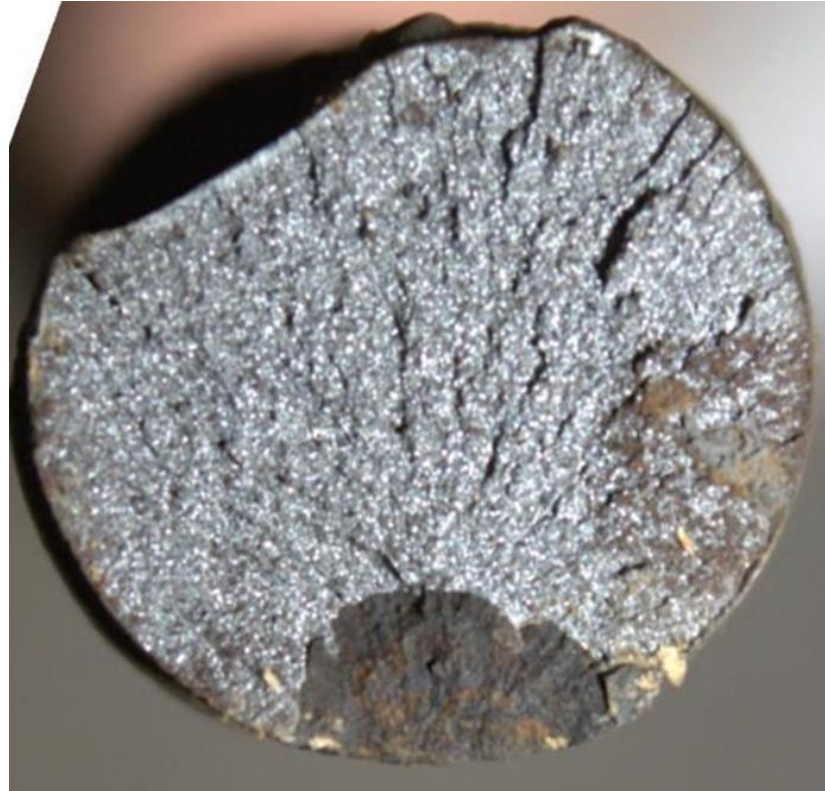


Figure 1-3: Typical SCC fracture surface of a rock bolt. The dark thumbnail shaped region at the bottom of the image is the SCC region. The bright specular region is the region of overload failure.

However, during the 1990s, brittle failure of rock bolts began to be observed in underground coal mines. The rock bolts were found to have fractured perpendicular to their axis without any noticeable plastic deformation. The fracture surface of the failed bolts was characterised by a small dark thumbnail shaped region extending from the surface of the bolt, with the remainder of the fracture being bright and specular in appearance^[4]. An example is shown in Figure 1.3. These failures were subsequently identified as being due to stress corrosion cracking induced by the groundwater in the mines^[4-6].

At the time of these studies a variety of grades of steel and processing techniques were used in the manufacture of rock bolts in Australia. The study undertaken by Crosky et al.^[5] showed that all were susceptible to SCC. It was, however, noted that the rock bolts generally had a low Charpy impact toughness and that this adversely affected to length to which SCC cracks could grow before catastrophic failure occurred. Accordingly, there was a move to the use of a single tougher grade of steel (a silicon-bearing, vanadium-microalloyed steel known as HSAC 840). This substantially reduced the incidence of failure for several years but failures of this steel eventually began to occur. This resulted in renewed interest in rock bolt failures, with a view to developing a permanent solution, and a further study was commenced under the sponsorship of the Australian Research Council (ARC) and a consortium of industry partners. The work presented in this thesis is a part of that study. It involved examination of service failures, development of a method for laboratory testing for rock bolt SCC, and analysis of mine groundwater.

1.2 Thesis Structure and Research Methodology

This thesis is presented over six chapters as detailed below.

- **Chapter 1 – Introduction:** This chapter provides a background to the project and an outline of the work undertaken in this thesis.
- **Chapter 2 – Literature Review:** This chapter presents a review of the relevant literature. It begins with a review of stress corrosion cracking, with particular emphasis on SCC of steel induced by groundwater. A detailed review of prior studies of rock bolt SCC is then given.
- **Chapter 3 – Environmental Classification:** This chapter provides an analysis of mine water collected from several locations in two different underground coal mines in terms of both ionic species and microbiological organisms. The results are examined in terms of their effect on SCC.
- **Chapter 4 – Examination of Service Failed Rock Bolts:** This chapter provides a detailed study of failed rock bolts retrieved principally from the two mines for which the water analyses were made. Most of the failed bolts were manufactured from HSAC 840 steel which has replaced the grades of steel previously used. The findings are analysed in terms of the results from the water analyses.

- **Chapter 5 – Coupon Testing:** This chapter presents some preliminary work undertaken on SCC testing using coupon samples cut from rock bolts. Coupon specimens rather than full scale specimens were used since these were easier to place in mines
- **Chapter 6 – Conclusion and Recommendations:** This chapter summarises the findings of the work and gives recommendations for future research.

1.3 Publications

1. Elias, E, Vandermat, D, Craig, P, Chen, H, Crosky, A G, Saydam, S, Hagan, P, Hebblewhite, B, 2013. Metallurgical examination of rockbolts failed in service due to stress corrosion cracking, in Proceedings 7th Internal Symposium on Ground Support in Mining and Underground Construction, Australian Centre for Geomechanics, Perth, pp. 473-484, presented at 7th International Symposium on Ground Support in Mining and Underground Construction, Perth, 13 – 15 May 2013
2. Elias, E, Vandermaat, D, Craig, P, Crosky, A G, Saydam, S, Hagan, P and Hebblewhite, B, 2013. Environmental characterisation of the stress-corrosion cracking of rockbolts in underground coal mines via laboratory and in-situ testing, in Rock Mechanics for Resources, Energy, and Environment (EUROCK 2013), CRC Press/Balkema, London, pp. 261 - 266, presented at EUROCK 2013, The 2013 ISRM International Symposium, Wroclaw, Poland, 23 – 26 September 2013.
3. Craig, P, Saydam, S, Hagan, P, Hebblewhite, B, Vandermaat, D, Crosky, A, and Elias, E. (2014) Investigation into the corrosive environments to which underground coal mine rock bolts are exposed, in AusRock2014: Proceedings 3rd Australasian Ground Control in Mining Conference, 4 – 5 November, 2014, Sydney.
4. Vandermat, D, Elias, E, Craig, P, Saydam, S, Crosky, A, Hagan, P and Hebblewhite, B, 2012. Experimental Protocol for Examining Street Corrosion Cracking of Rockbolts, in Coal 2012: Proceedings 12th Coal Operators Conference, Wollongong, Australia (eds. Aziz N, Kinnimoth B). pp. 130 – 137 (Institute of Mining and Metallurgy: Wollongong).
5. Vandermat, D, Elias, E, Tang, Z, E, Craig, P, Saydam, S, Crosky, A, Hagan, P and Hebblewhite, B, 2012. Coupon Testing for Field Assessment of Stress Corrosion Cracking of Rock Bolts, in Proceedings 31st International Conference on Ground Control in Mining, Morgantown, United States of America (eds. Barczak T, and Tadolini S) pp. 157 – 165.

6. Crosky, A G, Smith, B, Elias, E, Chen, H, Craig, P, Hagan, P, Vandermaat, D, Saydam, S and Hebblewhite, B, 2012. Stress corrosion cracking failure of rockbolts in underground mines in Australia, in Proceedings 7th International Symposium Rockbolting and Rock Mechanics in Mining, Aachen, Germany. pp. 335 – 348 (BBK: Institute of Mining Engineering).

2 LITERATURE REVIEW

2.1 Stress Corrosion Cracking

2.1.1 Introduction

Stress corrosion cracking is defined as slow, progressive crack growth under the application of a sustained load (applied and/or residual) in a mildly corrosive environment^[7]. The failure occurs in a brittle manner below the ultimate tensile strength of the material. The observed crack propagation is the result of the combined and synergistic interaction of mechanical stress and corrosion reactions and, accordingly, requires the interaction of a susceptible material, a specific environment and a sustained load. All three requirements must be met simultaneously in order for SCC to occur. This is illustrated schematically in Figure 2-1. by the region defined by the intersection of the three requirement circles.

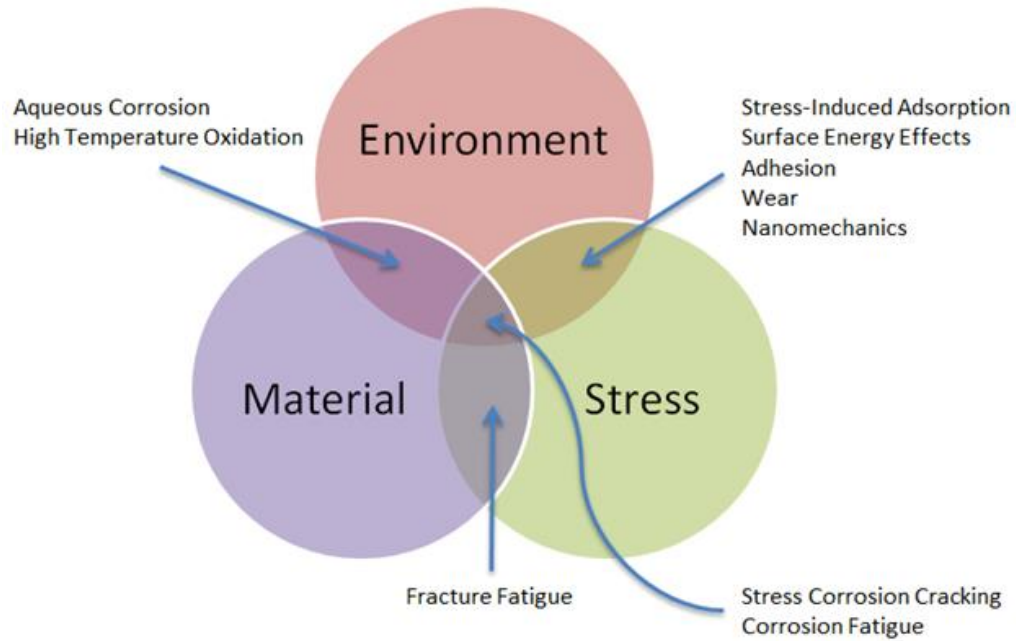


Figure 2-1: Schematic diagram showing the SCC region in material / environment / stress space^[8].

SCC cracks can initiate at surface flaws that either preexist or are formed during service by corrosion, wear or other related processes. These cracks then propagate in either a transgranular or intergranular mode. In some cases both transgranular and intergranular crack propagation can occur^[4].

As SCC is a delayed failure process, the cracks in the material initiate and propagate at slow rates (for example 10^{-9} to 10^{-6} m/s^[7]) until the stress in the remaining ligament of metal exceeds the fracture strength. The main stages leading up to SCC of a material are as follows^[7]:

- crack initiation and stage 1 propagation
- stage 2 or steady state crack propagation
- stage 3 crack propagation or final failure

One common misconception is that SCC is the result of the stress concentration (defined by the stress intensity factor, K) at corrosion generated surface flaws, when a critical value of stress concentration, K_{crit} , is reached and mechanical fracture of the material results^[9]. However, even though stress corrosion does initiate at the surface flaws, the stress concentration is found to be below the critical value which is required to cause catastrophic overload failure^[10]. This is demonstrated by the fact that precorrosion,

followed by continuous loading in an inert environment, will not produce any noticeable crack propagation^[7]. However, simultaneous environmental exposure and application of stress on the material will cause subcritical crack propagation. Due to the combined simultaneous interactions of both the mechanical and chemical effects causing crack propagation, and the fact that neither factor acting independently would yield the same effects, this process is known as ‘synergy’.

The stresses required to cause SCC are usually small, i.e., significantly lower than the yield stress of the material, and are tensile in nature^[7]. These stresses can be either residual or externally applied. Residual stresses alone can often be sufficient to cause SCC failure. However it is only tensile residual stresses that are detrimental; compressive residual stresses can be used to prevent SCC. Static loading is usually considered to be responsible for SCC, while environmentally induced crack propagation due to cyclic loading is usually considered to be corrosion fatigue. The distinction can become blurred and corrosion fatigue is often considered as a subset of SCC. However, both corrosion fatigue and SCC should be considered separately as the environments which give rise to these two processes are not always the same^[7].

It is noted that the term SCC is commonly used to describe failure that occurs in metals. However, other classes of material are also subject to delayed failures by environmentally induced crack propagation. For example, ceramics exhibit environmentally induced crack propagation and polymeric materials frequently exhibit environmentally-induced craze cracking. For a long period of time, it was believed that pure metals were immune to SCC, but recent studies have proven this to be incorrect^[11].

Environments that cause SCC are usually aqueous and can be either condensed layers of moisture or bulk solutions. SCC is alloy/environment specific, that is, for a given alloy, SCC can only occur when a specific chemical species is present in the environment. As a result, an environment that causes SCC in one alloy may not cause it in another. Changing the temperature, the degree of aeration and/or the concentration of ionic species in solution may change a harmless environment into one that has the potential to cause SCC failure. Similarly, different heat treatments may make the same alloy either immune or susceptible to SCC. There are a wide variety of alloy/environment combinations that can cause SCC. The more common combinations are listed in Table 2-1.

Table 2-1: Alloy / Environment system exhibiting SCC^[12].

Alloy	Environment
Carbon steel	Hot nitrate, hydroxide, carbonate/bicarbonate solution
High strength steel	Aqueous electrolytes, particularly when containing H ₂ S
High nickel alloys	High purity steam
Magnesium alloys	Aqueous Cl ⁻

2.1.2 Characteristics of Stress Corrosion Cracking

SCC failures are macroscopically brittle, i.e., failure occurs without any significant macroscopic plastic deformation. Microscopically, the cracks are either intergranular, or transgranular and cleavage like. In duplex microstructures, where two phases are present in comparable proportions, one phase often cracks more easily than the other. This results in characteristic cracking patterns along the fracture surface. It must also be noted that plastic deformation always accompanies crack growth and plays a key role in most cracking mechanisms, as discussed in Section 2.1.3.3. When the fracture surface shows evidence of stepwise (discontinuous) crack propagation, transgranular SCC is often observed. However, intergranular SCC can also be observed depending on the mechanism involved.

In some cases, intact ligaments are present behind the crack tip and these shield the tip from some of the applied stress intensity. The presence of ligaments results in a very characteristic type of fracture surfaces since the ligaments produce crack arrest markings on the fracture surface.

2.1.3 Stages of Stress Corrosion Cracking

SCC involves both an initiation stage and a propagation stage. These two stages are different but related processes.

2.1.3.1 Initiation of Stress Corrosion Cracking

2.1.3.1.1 Crack Initiation at Surface Discontinuities

Preexisting surface features, such as grooves, laps (seams caused by folding over metal or sharp corners, followed by rolling or forging) and burrs (also caused by the fabrication process) are places where SCC frequently initiates. Figure 2-2, illustrates both the lap (Figure 2-2(a)) and burr (Figure 2-2(b)) surface features which were generated in the

preparation of a joint for welding during the grinding process^[7]. These features can then act as a crevice for ions to concentrate, thus accelerating the rate of corrosion.

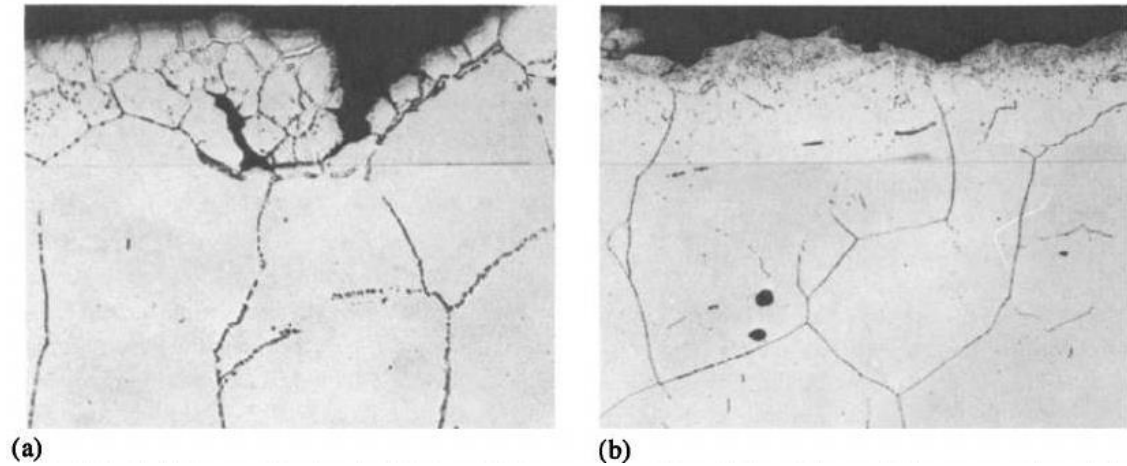


Figure 2-2: Optical micrographs showing defects on the inner surface of type 304 stainless steel pipe near a weld root showing (a) a lap and (b) a burr^[7].

2.1.3.1.2 Crack Initiation at Corrosion Pits

Stress corrosion cracks can also initiate at pits that have formed during exposure to service environments or during cleaning operations. These pits can form at inclusions (non-metallic impurity particles) that intersect the free surface, or by localised breakdown of the protective film as illustrated in Figure 2-3. Breakdown of the protective oxide film is brought about by either mechanical damage or chemical attack by aggressive ions, such as Cl^- . However, a pit will only form when the electrochemical potential equals or exceeds that of the pitting potential.

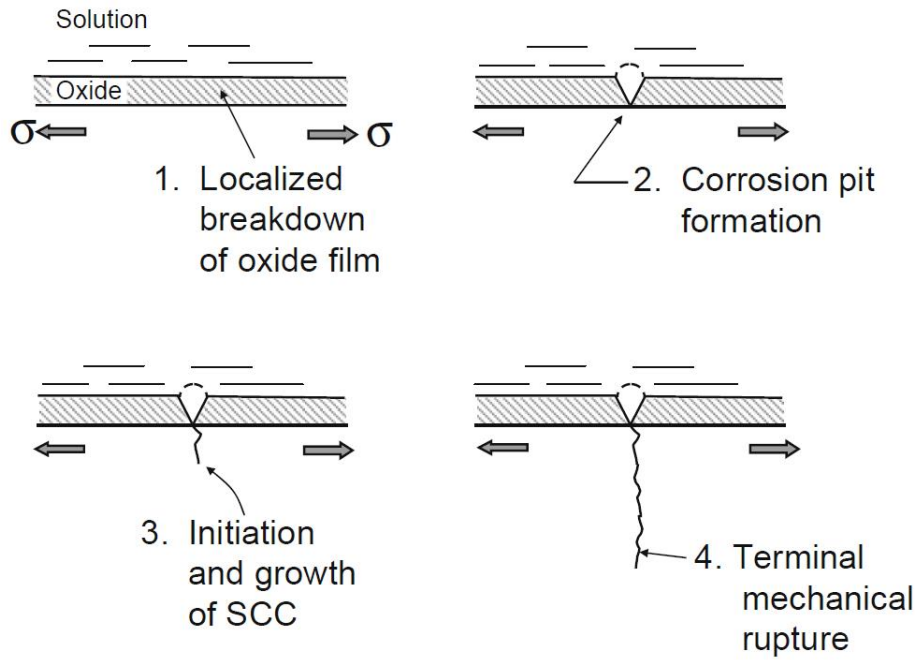


Figure 2-3: Stages in the initiation of stress-corrosion cracking^[8].

The following parameters play an important role in the transition from pitting to cracking and, as such, must be taken into account:

- electrochemistry at the base of the pit
- pit geometry
- chemistry of the material
- stress or strain at the base of the pit

The precise relationship between these parameters and crack initiation has not, however, been fully established due to the inability to measure crack initiation. Nevertheless, some general comments can be made as follows^[7]:

- The aspect ratio between the penetration and the lateral corrosion of a pit must be greater than about 10 (1000 is typically observed for SCC) before the pit acts as a crack initiation site. The pit walls must exhibit some passive film forming capability in order for this to happen
- A change in the corrosive environment and potential within a pit may also be necessary for a pit to act as a crack initiator
- Although the local stresses and strain rates at the base of the pit play a role in SCC initiation, there are examples where preexisting pits have not initiated stress

corrosion cracks. This observation has led to the conclusion that the electrochemistry of the pit is more important than the local stress.

2.1.3.1.3 Crack Initiation by Intergranular Corrosion or Slip Dissolution

The initiation of stress corrosion cracks can also occur in the absence of both surface discontinuities and corrosion pits by either intergranular corrosion or a slip-dissolution processes. Cracks which initiate via intergranular corrosion require that the local grain-boundary chemistry is different from the bulk chemistry. This condition occurs with the segregation of impurities such as phosphorus, sulphur or silicon in a variety of materials. On the other hand, cracks which initiate via slip dissolution result from local corrosion at emerging slip planes and occur primarily in low stacking fault materials. In carbon manganese (C-Mn) or low-alloy steels, intergranular corrosion occurs along segregated zones rich in carbon, nitrogen or phosphorous. This provides a stress concentration which helps to achieve the critical stress intensity factor, K_{ISCC} , required for stress corrosion cracking to initiate.

It is noted that subsequent growth of cracks which have initiated by either of these methods can, however, be easily hindered because of changes in grain-boundary orientation, crack angle, or electrochemistry, after they have grown to about one grain diameter.

2.1.3.2 Propagation of Stress Corrosion Cracking

As noted earlier, two modes of crack propagation can occur, these being intergranular and transgranular. In intergranular SCC the crack propagates along grain boundaries, whereas transgranular cracks occur through the grains.

Intergranular SCC can result from either grain-boundary precipitation or grain-boundary segregation. Grain-boundary precipitation includes carbide precipitation in austenitic stainless steels and nickel-base alloys, which causes depletion of chromium adjacent to the grain boundary, and intermetallic precipitation in aluminium alloys, which causes the grain boundary to be anodically active. Grain boundary segregation of impurities such as phosphorus, sulphur, carbon and silicon can produce a grain boundary that consists of up to 50% impurity atoms within a region 1 to 2 nm thick. These impurity atoms can alter the corrosion and mechanical properties of the grain boundary and can therefore cause cracking by anodic dissolution and, in some cases, simple mechanical fracture^[7].

Transgranular SCC can be affected by numerous metallurgical factors. These factors include crystal structure, grain size and shape, anisotropy, dislocation density and

geometry, yield strength, composition, stacking-fault energy, ordering and phase composition^[13].

2.1.3.3 Crack Propagation Mechanisms

There have been many different mechanisms proposed to explain the synergistic stress/corrosion interactions that occur at the crack tip. The proposed mechanisms have been classified into two basic categories as outlined below:

- dissolution models
- mechanical fracture models

It is generally considered that no single model can be “universal” in view of the multiplicity of mechanisms observed. While in many cases the atomistic mechanism is unknown, cracking can often be controlled or predicted through an understanding of the localized corrosion process that precedes SCC.

2.1.3.3.1 Dissolution Models

According to models of this type, a crack advances by preferential dissolution at its tip. A number of models have been proposed to account for this process. For example, preferential dissolution at the crack tip has been attributed to the presence of active paths in the material, stresses at the crack tip, and chemical-mechanical interactions. However, research has essentially eliminated all but the film rupture model from serious consideration, and attention is now focused on the details of this model^[14, 15].

2.1.3.3.1.1 Film Rupture

This model assumes that the stress acts to rupture the protective oxide film and open the crack. Two investigators, working independently, first postulated that localized plastic deformation at the crack tip ruptures the passivating film, exposing the bare metal^[16]. This bare metal then dissolves rapidly, resulting in crack extension, until the passivating film is reformed, whereupon the cycle repeats itself. Some investigators assume that once propagation starts, the crack tip remains bare because the rate of film rupture at the crack tip is greater than the rate of repassivation, as shown in Figure 2-4(a). On the other hand, others assume that the crack tip repassivates completely and is periodically ruptured by the emergence of slip steps, as shown in Figure 2-4(b)^[7].

The film rupture model is not well accepted for transgranular SCC because fracture surfaces are flat, crystallography oriented and opposing fracture surfaces match topographically, indicating little dissolution during crack advance^[17].

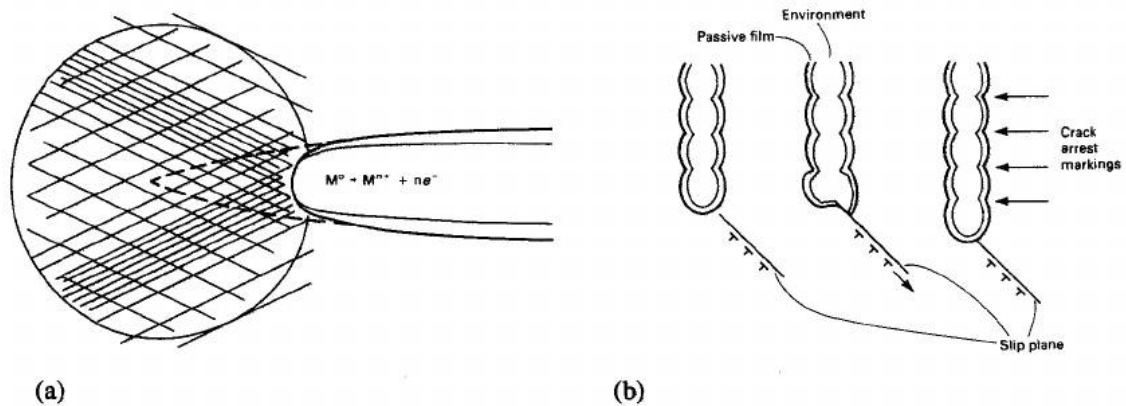


Figure 2-4: Schematic representation of crack propagation by the film rupture model^[7].

2.1.3.3.1.2 Active Path Intergranular SCC (Anodic Dissolution)

According to this model SCC follows a preferential pre-existing reactive path. For example, chemical segregation at grain boundaries could cause preferential corrosion at the grain boundary, causing the crack to propagate along the grain boundary^[7]. The crack propagation is self-sustaining, as an unstable electrochemical cell is formed at the tip, which is often referred to as an occluded corrosion cell. The tip of the crack is the anode, with the surrounding material acting as the cathode. The crack then propagates into the material following the path of least resistance, which is along the grain boundaries. This continuous process continues until the remaining cross sectional area of the material is unable to sustain the applied tensile load, whereupon catastrophic failure occurs.

2.1.3.3.2 Mechanical Fracture Models

Mechanical fracture models originally assumed that stress concentration at the base of corrosion pits or slots increased to the point of ductile deformation and fracture. These early proposals assumed that the crack essentially propagated by dissolution and that the remaining ligaments then failed by mechanical fracture, either in a ductile or brittle manner. A refinement of this approach has been proposed and is known as the corrosion tunnel model.

2.1.3.3.2.1 Corrosion Tunnel Model

This model assumes that a fine array of small corrosion tunnels form at emerging slip steps. These tunnels grow in length and diameter and length until the material in between the tunnels can no longer bear the applied load, and the ligaments separating the individual tunnels then undergo a ductile tearing process, as illustrated in Figure 2-5(a)^[7]. As a result, the cracks propagate by alternating tunnel growth and ductile fracture. The model predicts that the resulting fracture surface should be grooved with evidence of microvoid coalescence on the peaks of the grooves. However this type of fracture surface is not observed and the model has therefore been modified.

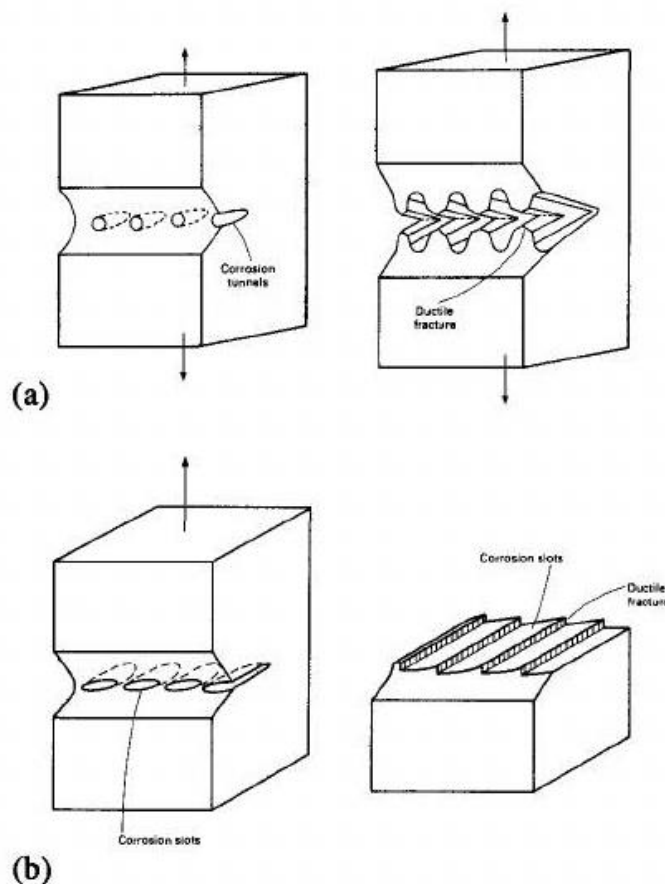


Figure 2-5: Corrosion tunnel models^[7].

The modified model envisages that the application of a tensile stress results in a change in the morphology of the corrosion damage from tunnels to thin, flat slots. This concept is illustrated in Figure 2-5(b). Transgranular SCC can then be explained in terms of the formation and subsequent mechanical separation of corrosion slots.

2.1.3.3.2.2 Adsorption Models

There are two chemical models that have been proposed to deal with the adsorption of chemical species at the crack tip, as discussed below. The two models are similar in that they rely on the adsorption of a chemical species, however one deals with the nucleation of voids while the other concentrates on the weakening of the atomic bonds in the matrix.

Adsorption Enhanced Plasticity

Studies which have been carried out by Lynch^[18], in the area of fracture processes of liquid-metal embrittlement (LME), hydrogen embrittlement and SCC led him to conclude that similar processes occur in each case. Since chemisorption is common to all three failure modes, this process was believed to be responsible for environmentally induced crack propagation^[19].

Fractographic studies have indicated that cleavage fracture is not an atomically brittle process, but occurs by alternate slip at the crack tip, in conjunction with the formation of very small voids ahead of the crack. It was proposed that chemisorption of an environmental species facilitated nucleation of dislocations at the crack tip, thus promoting the shear processes responsible for brittle, cleavage-like fractures.

Adsorption Induced Brittle Fracture

This model, which is illustrated in Figure 2.6, is based on the hypothesis that adsorption of environmental species lowers the interatomic bond strength. As a result, the stress at the crack tip is sufficient to rupture the bonds allowing the crack to advance. However, this mechanism depends on the concept that the surface energy of a solid is reduced by chemisorption of a solution species and that the stress required for fracture is given by the Griffith criterion of crack formation in brittle solids. For a crack in a thin plate, the stress required for brittle fracture is given by Equation (2-1)^[8],

$$\sigma_F = \sqrt{\frac{2\gamma E}{\pi a}} \quad (2-1)$$

where:

- σ_F is the stress required for brittle fracture
- E is Young's modulus
- γ is the surface free energy of the solid
- a is the crack length

This mechanism proposes that the crack velocity is dictated by the rate at which species are transported to the crack tip. The model also predicts that cracks should propagate in a continuous manner. However, it fails to explain how the cracks maintain an atomically sharp tip in a normally ductile material, as it does not include a provision for limiting deformation in the plastic zone. In addition, it cannot explain the discontinuous nature often observed for the crack propagation process.

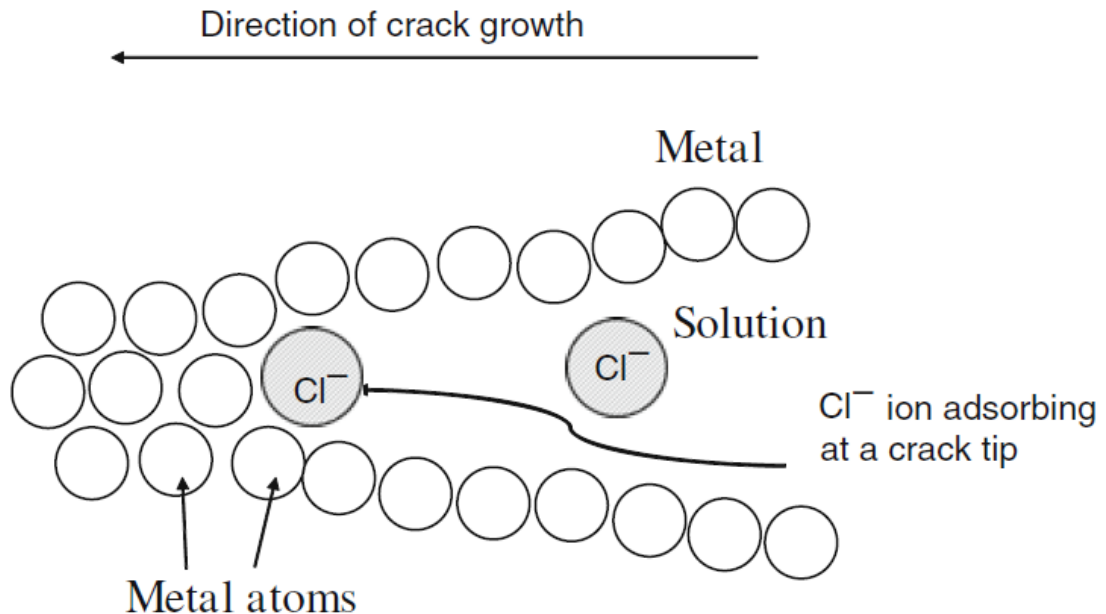


Figure 2-6: Schematic diagram of the adsorption induced brittle fracture model^[8].

2.1.3.3.2.3 The Tarnish Rupture Model

The tarnish-rupture model, illustrated in Figure 2-7, was first developed to explain transgranular SCC, however after significant research the model has been modified to also explain intergranular SCC. In the original model, a brittle surface film is considered to form on the metal and then fracture due to the applied stress^[7]. Consequently, the metal is exposed, and rapidly reacts with the environment to re-form the surface film. The crack propagates by alternating film growth and fracture, which is illustrated in Figure 2-7(a). While initially based on the assumption that the oxide film penetrates along the grain boundary ahead of the crack tip, as illustrated in Figure 2-7(b), the model was subsequently modified to explain intergranular SCC^[7]. Crack propagation is achieved by alternating periods of film growth and brittle-film fracture. It must be noted that film growth requires transport of species across the film^[20]. Consequently, the thickness of the film is limited in the absence of stress.

This model predicts crack-arrest markings on intergranular fracture surfaces and discontinuous acoustic emissions during crack propagation, both of which are not always observed during intergranular SCC. The model also assumes penetration of the film into the grain boundary ahead of the crack tip, but this is not the case for all systems.

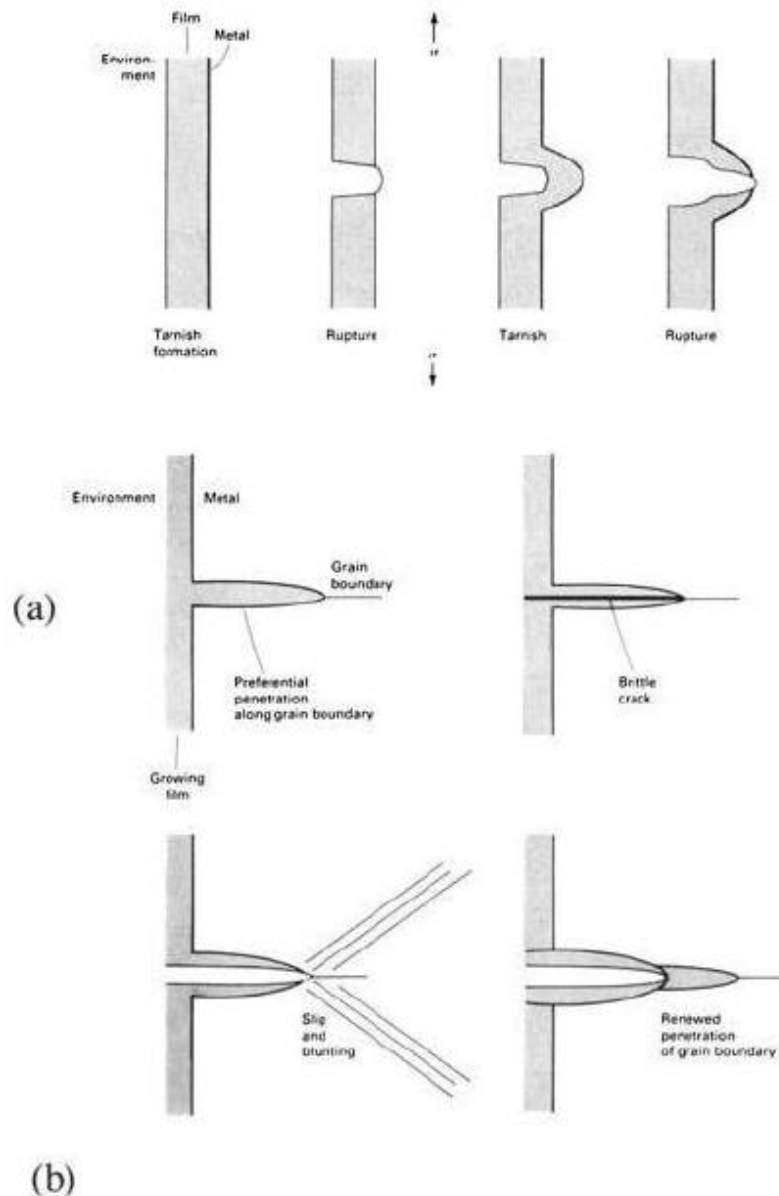


Figure 2-7: Tarnish rupture models^[7].

2.1.3.3.2.4 Film Induced Cleavage Model

The film induced cleavage model was developed based on the hypothesis that a surface film could induce cleavage fracture. This model envisages the process to be as follows^[7]:

- a thin film or layer forms on the surface
- a brittle crack initiates in this layer

- the brittle crack crosses the film/metal interface with little loss in velocity
- once in the ductile metal, the brittle crack will continue to propagate in a brittle manner
- the crack will eventually blunt and arrest, after which the entire process repeats itself.

This model can explain the crack arrest markings, the cleavage like facets present on the fracture surface, and the discontinuous nature of the crack propagation process. It must be noted that the hypothesis that a brittle crack will propagate after it has entered the normally ductile metal is a critical point since it requires that a thin surface layer can induce brittle crack propagation over a distance much greater than the film thickness. However, it was concluded that this would be possible if the crack was sharp and was propagating at high velocity before it entered the ductile metal^[21].

2.1.3.3.2.5 Surface Mobility Model

This model, developed by Galvele, proposes that cracks grow by surface diffusion of metal atoms (possibly combined with ions or molecules from the environment) from a very sharp crack tip to the crack walls. This leaves vacancies at the crack tip, thereby producing crack tip advancement. This model is illustrated in Figure 2-8.

Formation of surface compounds with low melting points promotes SCC by increasing the surface self-diffusivity of the metal. The details of the crack tip and its interaction with the environment (i.e., electrochemistry) are considered to be secondary factors that contribute by maintaining the critical surface compound^[19]. The model has been applied to liquid metal embrittlement as well as SCC and is reported to have considerable predictive capability^[19].

One of the key factors which led Galvele to develop the surface mobility model was his view that slip-dissolution could not work in the restricted geometry of a crack, as the crack is not a one dimensional slot and the crack opening angle permits very high anodic current densities in cracks without saturation of metal salts or very high IR potential drops. According to Galvele's model, the crack velocity, v , is given by Equation (2-2),

$$v = \frac{D_s}{L} \left(e^{\frac{\sigma a^3}{kT}} - 1 \right) \quad (2-2)$$

where:

- D_s is the surface self-diffusion coefficient
- L is a characteristic diffusion length
- σ is the elastic surface stress at the crack tip
- a^3 is the volume of a vacancy

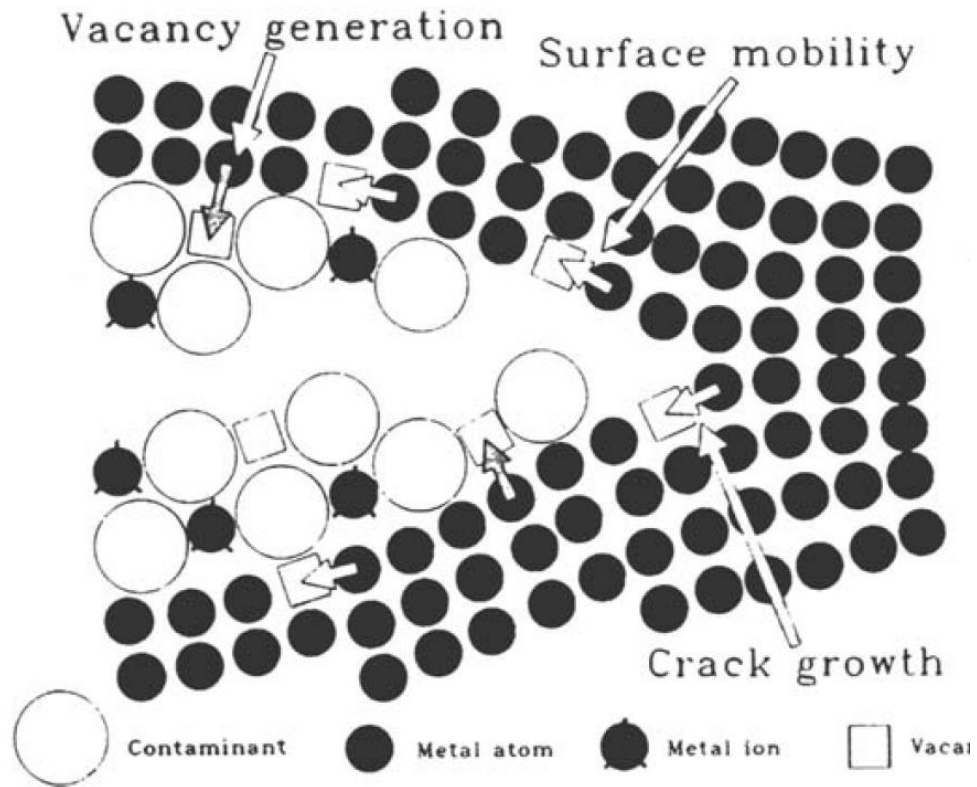


Figure 2-8: Galvele's surface mobility model for SCC^[19].

Sieradzki and Friedersdorf^[22] examined the model and noted that the treatment of the diffusion process is greatly simplified. However, they considered the main flaws in the analysis to be:

- The equilibrium vacancy concentration in a plane can be increased by the normal tensile stress, but Galvele applied the relevant equation to the crack tip where this stress is zero. In view of this, small second-order effects would need to be invoked.
- Proper accounting of the chemical potential of the vacancies must include a capillary term of the form $+\frac{\gamma a^3}{r}$ (γ is the surface energy and r is the crack-tip radius). This prevents the crack from attaining very low r values, yet the surface mobility mechanism assumes an atomically sharp crack.

Sieradzki and Friedersdorf concluded that the crack velocities attainable by surface mobility (with the blunt crack tip just mentioned) are 10^8 to 10^{14} times lower than those calculated by Galvele. Their expression for crack velocity is given by Equation (2-3).

$$v = \frac{D_s N_s \Omega^2}{kT} \times \frac{2}{\pi} \times \frac{1}{r^2} \times \left(\frac{\sigma_{yy}^2}{2E} - \gamma \kappa \right) \quad (2-3)$$

where:

- N_s is the number of lattice sites per unit area
- Ω is the atomic volume (a^3)
- k is the curvature, which is just $1/r$ for the crack tip

2.1.3.3.2.6 Hydrogen Induced Cracking

Hydrogen induced cracking, is believed to be the main mechanism for SCC of steels. The work carried out by Mukhopadhyay et al.^[23], suggests that when hydrogen enters a steel matrix it can reduce the bond strength of the metal atoms thus resulting in embrittlement. When the hydrogen concentration reaches a critical level, a crack can propagate through the embrittled region at a stress that is much lower than the material's yield strength^[24]. The process is often referred to as hydrogen embrittlement but the term hydrogen induced stress corrosion cracking (HISCC) is preferred here.

During corrosion, the anodic reaction is metal dissolution as shown in Equation (2-4),



In an acid solution, the cathodic reaction is hydrogen evolution. The hydrogen so produced can then enter the steel as atomic hydrogen. Since the species responsible for cracking is generated by the cathodic reaction, hydrogen induced SCC is referred to as cathodic SCC.

Ductile fracture in metals occurs by a process involving localized nucleation of microvoids and their subsequent coalescence. This requires a relatively high level of stress. In contrast, local subcritical crack advance can occur at a much lower stress if the material in front of the crack has a critical hydrogen concentration. This means that the speed of the crack propagation can be dictated by the speed with which hydrogen is transported to the region in front of the crack tip.

There are two principal mechanisms that have been proposed to explain how hydrogen gets transported to the region in front of the crack tip, these being lattice diffusion and dislocation drag^[24].

The lattice diffusion mechanism considers that atomic hydrogen produced at the metal surface diffuses to the region ahead of a crack tip due to the driving force produced by the triaxial stress state ahead of the crack tip. The process is facilitated by the relatively fast diffusion rate of hydrogen in steel which results from the small size of the hydrogen atom in the steel lattice.

The dislocation dragging (or dislocation sweeping) mechanism considers that hydrogen atoms become bound to moving dislocations which then drag them into the region ahead of the crack tip. However, Toribio and Kharin^[25] have shown that the hydrogen affected area exceeded the plastic zone and was thus larger than the region in which dislocations could move. This suggests that although dislocation transport is known to be a hydrogen transport mechanism it cannot account fully for the depth of hydrogen absorption observed.

The level of hydrogen uptake can be affected by other factors. As shown later, the atomic hydrogen produced by the cathodic reaction can form molecular hydrogen which then escapes into the atmosphere. However, certain species can inhibit the conversion of atomic hydrogen to molecular hydrogen. As a result, these species, known as hydrogen recombining poisons, enhance the uptake of cathodic hydrogen. For example, tin (Sn) and antimony (Sb) grain boundary impurities have been postulated to enhance hydrogen uptake in nickel, as shown schematically in Figure 2-9. A review of the combined effects of impurity segregation and HIC concluded, however, that grain boundary impurities enhance crack growth due to grain boundary embrittlement but not by enhanced hydrogen uptake^[7].

In contrast to enhancement, hydrogen transport is hindered by the trapping of hydrogen at lattice imperfections such as point defects, precipitates, and grain boundaries. As a result the speed at which the hydrogen concentration increases in the region ahead of the crack tip is dependent on the balance between hydrogen transport and hydrogen trapping.

It is worth noting that HIC tends to be particularly severe at temperatures around 300K^[7] which corresponds to the service temperature of rock bolts.

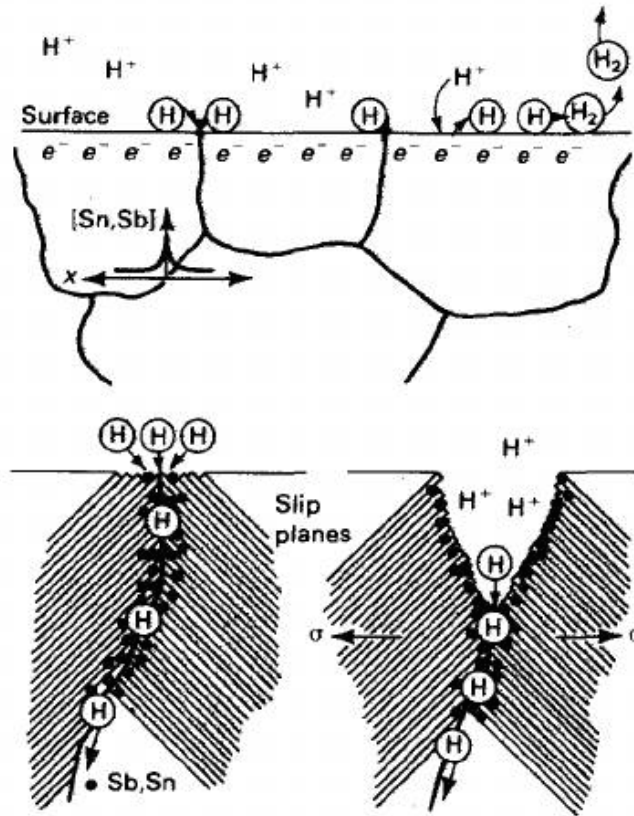


Figure 2-9: Schematic diagram showing the effect of some impurities on mechanism by which intergranular embrittlement of nickel is presumed to occur at cathodic potentials^[7].

Sources of Hydrogen

The most obvious source of hydrogen is the cathodic reaction of the corrosion process that balances the anodic reaction of metal dissolution. In this process, hydrogen atoms (H_{ads}) are produced by the reduction of hydrogen ions en route to the evolution of hydrogen gas (H_2). The first step is as follows:



Followed by either:



Or



Equation (2-5) followed by Equation (2-6) is called the combination mechanism of hydrogen evolution, while Equation (2-5) together with Equation (2-7) is called the

electrochemical mechanism of hydrogen evolution^[26]. Both of these mechanisms result in the removal of atomic hydrogen, however some can enter the metal (causing HIC) rather than participating in Equations (2-6) and (2-7).

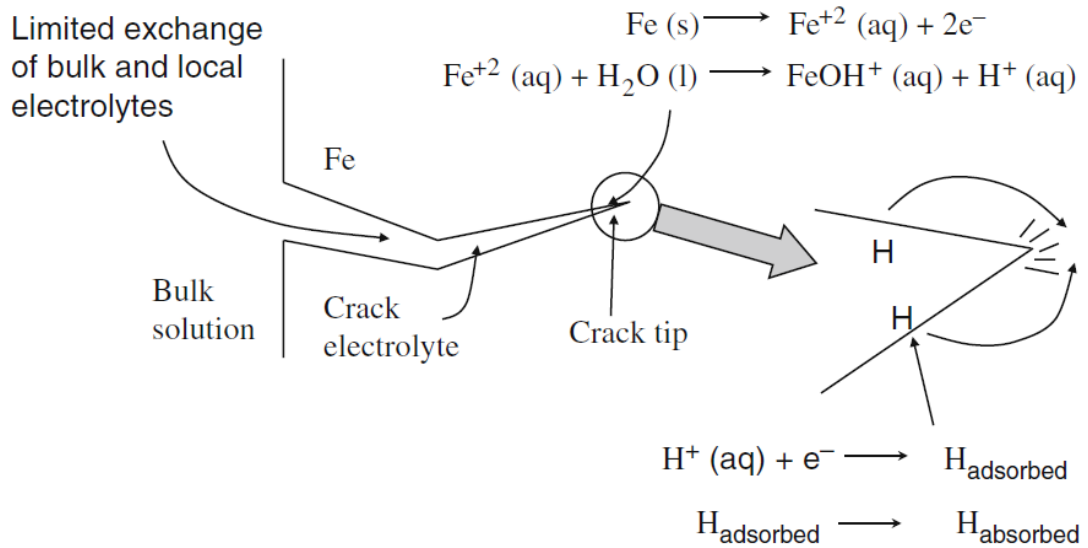
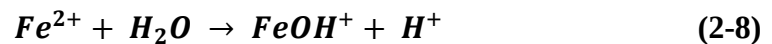


Figure 2-10: An illustration of how crack tip reactions can produce hydrogen atoms available for migration into the metal at stressed regions ahead of the crack tip^[7].

In SCC, the narrow confines of the stress corrosion crack limit the exchange of dissolved metal ions with the bulk electrolyte, as illustrated in Figure 2-10. Thus, metal cations, in this case Fe^{2+} ions, accumulate within the stress corrosion crack and can then be hydrolysed with the attendant production of hydrogen ions, as shown in Equation (2-8).



The hydrogen ions then react with the steel to generate hydrogen atoms which can either combine to form H_2 or migrate into the stressed region.

Another source of hydrogen is from microbial action. Microorganisms, especially bacteria, can accelerate corrosion by several mechanisms, the simplest being by altering their immediate environment due to their metabolic by-products, such as organic and inorganic acids. For example, sulphuric acid is produced from sulphides by sulphur oxidizing bacteria in aerobic conditions and the work of Podesta, Estrella and Estes^[27] has shown that such actions have resulted in HIC. Another common example is sulphate reducing bacteria (SRB). SRB often form colonies on the metal surface under anaerobic conditions because the presence of oxygen can be lethal to SRB^[8]. The anaerobic conditions are often formed under a biofilm that is usually formed by other aerobic microorganisms that can be commonly found close to SRB. SRB reduce sulphate to

hydrogen sulphide, H_2S , which can liberate hydrogen at the metal surface, as illustrated in Equation (2-9).



This can then cause HIC. Further discussion of the role of microorganisms on the SCC of rock bolts is given in Chapter 3.

2.1.4 Controlling Parameters

Several different reactions and processes are required for SCC to occur. The slowest of these events will be the rate limiting step and will determine the maximum rate at which the crack can develop. Potential rate limiting steps are shown in Figure 2-11 and are as follows^[7]:

- mass transport along the crack to or away from the crack tip
- reactions in the solution near the crack
- surface adsorption at or near the crack tip
- surface diffusion
- surface reactions
- adsorption into the material
- diffusion into the plastic zone ahead of the advancing crack tip
- chemical reactions in the material
- interatomic bond rupture

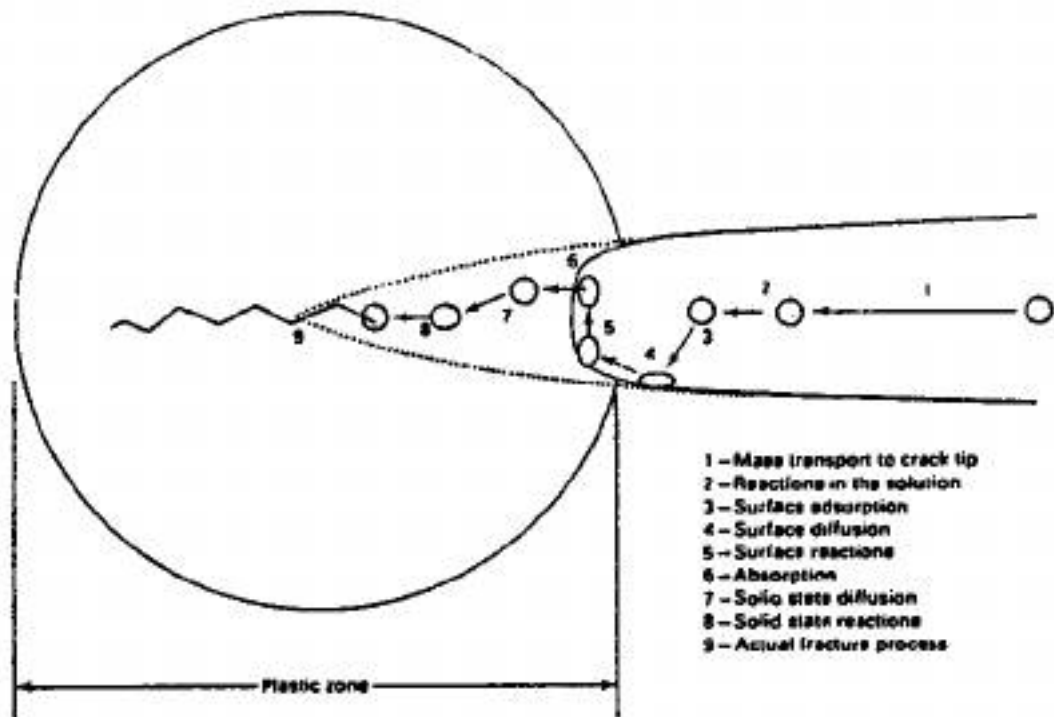


Figure 2-11: Schematic of crack tip processes that may be the rate determining step in environmentally assisted crack propagation^[7].

In aqueous solution, it would be expected that the rate limiting step would be mass transport along the crack to or away from the crack tip, since the rate of adsorption and of surface reaction should both be fast^[7]. The effect of environmental parameters on the rate limiting step must also be considered. The main environmental parameters are^[7]:

- temperature
- pressure
- solute species
- solute concentration and activity
- pH
- electrochemical potential
- microbiological species

If any one (or more) of these parameters is altered the rate of crack propagation may be accelerated or retarded. Moreover, the environment at the crack tip (occluded site) can differ significantly from the bulk solution^[7]. If the bulk solution has the capacity to yield a critical SCC environment at the crack tip then crack propagation will occur. However,

if the bulk solution yields an unfavourable environment at the crack tip, such as one which is too corrosive, then crack propagation will not occur.

Other factors may also influence the rate of crack propagation. These include^[8]:

- the magnitude of the applied stress or the stress–intensity factor
- the stress state, including;
 - o plane stress
 - o plane strain
- the loading mode at the crack tip
- the alloy composition, including;
 - o nominal composition
 - o exact composition
 - o impurity or tramp element content
- the metallurgical conditions, including;
 - o strength level
 - o second phases present in matrix and at the grain boundaries
 - o composition of phases
 - o grain size
 - o grain boundary segregation
 - o residual stresses
- crack geometry, including;
 - o length, width and aspect ratio
 - o crack opening and crack tip closure

2.2 Stress Corrosion Cracking of Low Strength Carbon and Low Alloy Steels (Yield Strengths less than 1241 MPa)

Steels are conventionally divided into low strength steels and high strength steels based on their yield strength. As in Jones^[12], steels with yield strengths less than 1241 MPa (180 ksi) will be considered here as low strength steels. The steels used in Australia for rock

bolts have yield strengths of ~450-800 MPa^[5], and are therefore considered as low strength steels. Accordingly, the following discussion is restricted to low strength steels.

Of particular relevance to this thesis, is the extensive literature on SCC of buried steel natural gas pipelines, since the environment responsible for SCC was found to be groundwater^[28], as is the case for rock bolts. As for rock bolts, the pipeline steels were low strength steels, in this case with yield strengths of 241 MPa (35 ksi) to 483 MPa (70 ksi). Like rock bolt steels, they are ferritic-pearlitic steels although their pearlite content is lower due to their lower carbon content (typically 0.2% compared with 0.4-0.55% for rock bolts). Table 2-2 gives measured compositions and mechanical properties for samples from three common pipeline steels. It is noted that X60 and X65 are both microalloyed steels, as are some rock bolt steels.

Table 2-2: Composition and mechanical properties of pipeline steels^[29].

Element	X52	X60	X65
Carbon	0.22	0.06	0.13
Manganese	0.96	1.63	1.54
Phosphorous	<0.005	0.013	0.009
Sulphur	0.013	<0.005	<0.002
Silicon	0.02	0.27	0.28
Nickel	0.09	0.14	0.02
Chromium	0.04	0.09	0.06
Molybdenum	0.018	0.198	0.005
Copper	0.22	0.37	0.02
Niobium	<0.01	0.075	0.04
Aluminium	<0.005	0.028	0.033
Mechanical Properties			
0.2% YS (MPa)	383	489	531
UTS (MPa)	556	616	626
Elongation (%)	31.2	34.3	31.0

The service conditions for pipelines are, however, somewhat different to those for rock bolts. Firstly, gas pipelines are subject to small fluctuating stresses due to small pressure fluctuations arising from the pumping process. This kind of stress fluctuation is not experienced by rock bolts.

Pipelines are also protectively coated, with various materials having been used, including asphalt and coal tar, polyethylene tape, fusion bonded epoxy, and extruded polyethylene. However, gaps, breaks and disbonds can occur in the coatings, locally exposing the underlying metal to the environment, and thus, potentially, to SCC. Rock bolts are also

coated by virtue of being encapsulated in resin but full encapsulation to the bottom of the rock bolt is not generally achieved.

The pipelines are also cathodically protected in order to prevent corrosion from taking place. However, the cathodic protection current does not always penetrate through the coating allowing corrosion, and potentially SCC, to occur at disbands in the coating where groundwater has ingressed^[28]. It is noted that cathodic protection is not used for rock bolts due to the hazards faced in underground coal mines.

Despite the differences given above, it is considered that the work on SCC of gas pipelines is of considerable relevance to SCC of rock bolts.

The research on pipelines established that two different types of SCC were occurring. These were termed “high pH” and “near-neutral pH” SCC (sometimes referred to as “low-pH SCC”) due to the different environments in which each occurred. High pH SCC was identified first and was attributed to carbonate/bicarbonate cracking. This mode of SCC was found to be intergranular with the cracks occurring between, or around, the ferrite grains^[30]. Near-neutral pH SCC was identified later and was attributed to hydrogen induced cracking. In this case cracking was transgranular. This cracking occurred in a dilute bicarbonate environment.

High pH (carbonate-bicarbonate) SCC is discussed in the following section, while near-neutral pH (dilute bicarbonate) SCC is discussed in the subsequent section.

2.2.1 High pH (Carbonate / Bicarbonate) Stress Corrosion Cracking

A number of different chemical species were initially considered as possible causative agents for SCC of pipelines. These included hydroxides, nitrates and phosphates. All these species are passivating agents and were known to cause SCC of carbon steels. However, pH values high enough to cause caustic cracking were never detected in electrolyte samples taken from beneath coatings at failure sites and there was no evidence for concentration of nitrates or phosphates above the low levels found in ground water^[10]. Subsequently, it was discovered that concentrated carbonate-bicarbonate solutions could cause SCC of pipeline steels and such solutions were detected at the pipe surface in the vicinity of SCC^[31]. Table 2-3 shows the composition of the liquid found underneath the coatings of pipelines in the United States near the location of SCC^[10].

Table 2-3: Composition of liquids found under coatings near the locations of stress corrosion cracks^[10].

State	Amount in Solution (%)*					
	pH	CO ₃ ²⁻	HCO ₃ ⁻	OH ⁻	Cl ⁻	NO ₃ ⁻
Alabama	9.7	0.5	0.5	-	-	-
Arizona	12.3	1.0	N	0.1	0.01	0.007
Mississippi	10	1.4	0.5	N	0.12	0.004
Mississippi	10	0.9	0.8	N	0.12	<0.01
Mississippi	9.6	0.5	0.6	N	N	-
North Carolina	10.5	0.7	0.4	N	-	N

*N = none detected

In view of these findings, it was concluded that a concentrated carbonate-bicarbonate solution was responsible for the SCC observed on pipelines and a mechanism for the development of the environment was proposed^[10]. It was considered that the cathodic protection applied to the pipelines caused an increase in pH of the natural ground water at the pipe surface. As a result, hydroxyl ions are generated and accumulated on the pipeline surface, according to Equations (2-10) and (2-11), causing the pH to increase^[32].



Conversion of bicarbonate to carbonate ions also occurs over time. The high concentration of carbonate/bicarbonate ions, leads to a tendency for the solution to passivate the steel surface, and intergranular SCC can then occurs^[32].

The extent that the pH increases is dependent on the partial pressure of carbon dioxide (CO₂). In the absence of CO₂, the pH increases to 11 – 12. The solution consists of nearly all carbonate ions, and the passive film characteristics and electrochemistry are not conducive to SCC. However, if there is an appropriate partial pressure of CO₂, CO₂ is rapidly absorbed by the high pH solution. The solution then becomes buffered because of an equilibrium between bicarbonate and carbonate ions, and the pH remains in the vicinity of 9. Researchers have simulated this environment in laboratory tests using a 1N NaHCO₃ – 1N Na₂CO₃ solution, which has a pH of approximately 9.3^[11]. Intergranular SCC (IGSCC) was found to occur when the potential is in the range, marked as IGSCC in Figure 2-12.

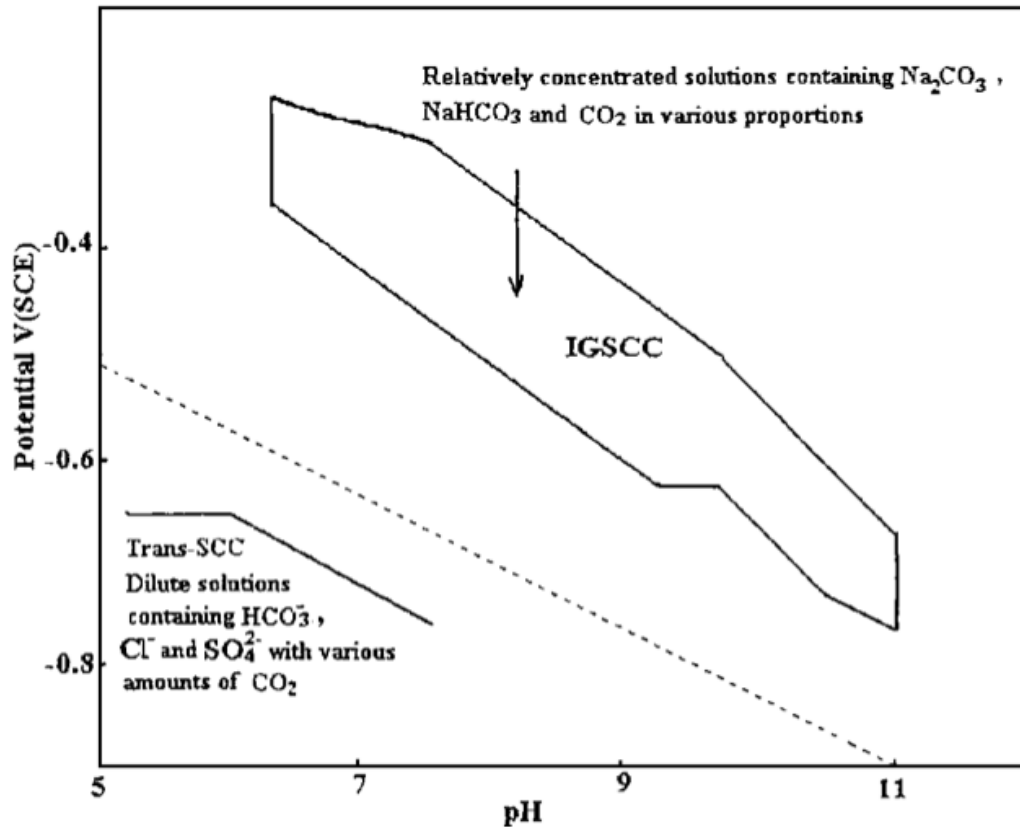


Figure 2-12: Potential pH diagram showing the regimes for intergranular SCC and transgranular SCC at 24°C in solutions containing different amounts of CO_3^{2-} , HCO_3^- and CO_2 to achieve different pH values^[33].

Confirmation that a concentrated carbonate-bicarbonate environment was responsible for pipeline SCC was obtained from laboratory SCC testing in a carbonate-bicarbonate environment since the characteristics developed were consistent with most of the field observations. These included the intergranular mode of cracking, the temperature, potential and stress dependence of cracking, the initiation of multiple cracks on pipeline samples, and the presence of magnetite (Fe_3O_4) on the intergranular fracture surfaces. Beavers et al. later reported that iron carbonate (FeCO_3) as well as magnetite (Fe_3O_4) was present on the fracture surfaces^[34].

SCC of pipeline steels in the high pH environment was found to occur only over a very limited potential range, about 100 mV wide, which is centred around about -720 mV Cu/CuSO₄ (CSE) at 75°C and moves in the positive (noble) direction with decreasing temperature^[10]. This potential range corresponds to the transition between active corrosion and strong passivity, as shown in Figure 2-13. In this respect, the behaviour is similar to that observed for steel in both nitrate and hydroxide solutions^[35]. It also occurs

over a limited pH range, centred near a pH of 9, as shown in Figure 2-14. At pH values above 10, the solution is primarily composed of carbonate and, as noted above, the passive film characteristics and electrochemistry are not conducive to SCC. At pH values below 8, the solution is dominated by the bicarbonate anion, which is not highly soluble unless cations other than Na^+ , e.g. NH_4^+ , are present. This is not the case for groundwater where the dominant cation is Na^+ .

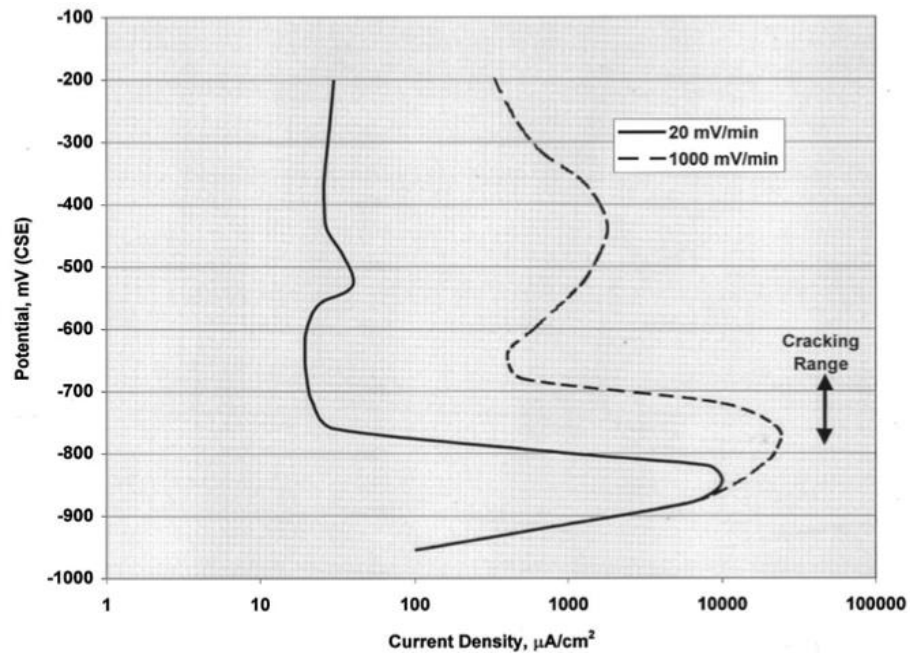


Figure 2-13: Potentiodynamic polarization curves for mild steel at 90°C in 1N Na_2CO_3 – 1N NaHCO_3 at two scan rates, showing the potential range over which SCC occurs^[10].

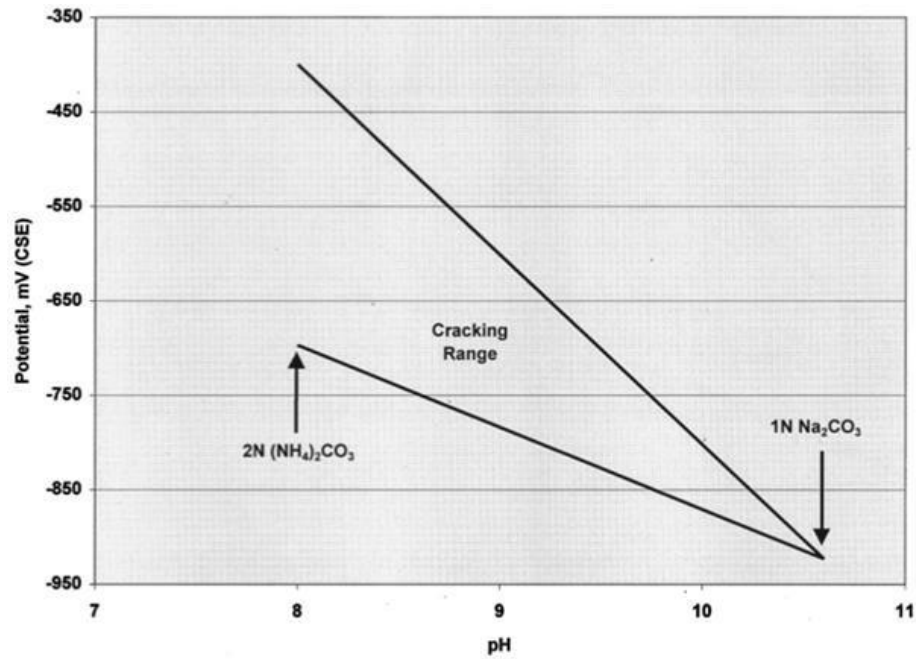


Figure 2-14: Potetial – pH region where SCC was found for pipeline steels in carbonate-bicarbonate solutions at 75°C^[10].

The temperature range reported for carbonate SCC is about 22 to 88°C^[31]. Cracking is also sensitive to strain rate^[35], as illustrated in Figure 2-15. This is attributed to the effect of strain rate on repassivation.

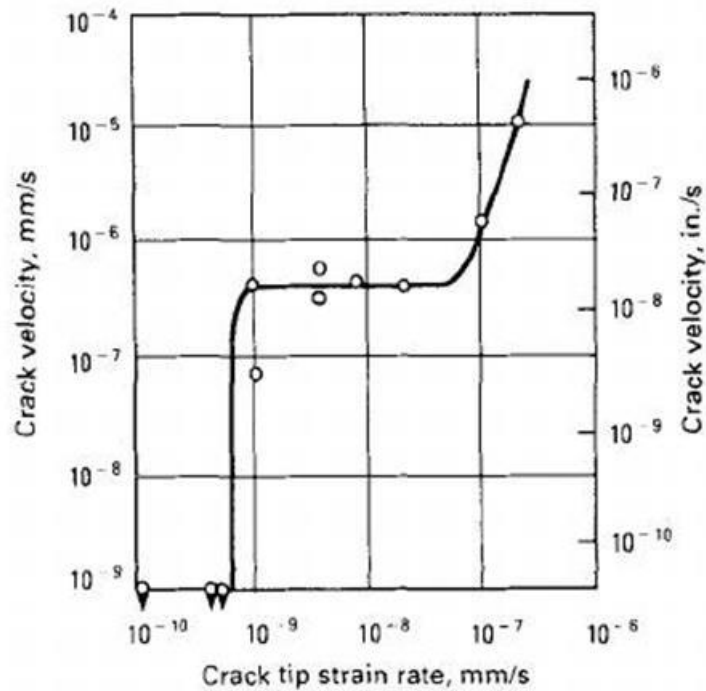


Figure 2-15: Effect of strain rate on SCC of carbon-manganese steel in carbonate solution^[35].

As noted in the previous section, high pH SCC has been found to occur intergranularly by propagation along the ferrite:ferrite grain boundaries. When the crack tip meets a pearlite colony, it is either deflected or, alternatively, propagates through the pearlite colony in a transgranular manner^[35]. The cracks produced are narrow and tight^[35] and can also be branched^[34]. Examples of unbranched and branched high pH SCC cracks are shown in Figure 2.16.

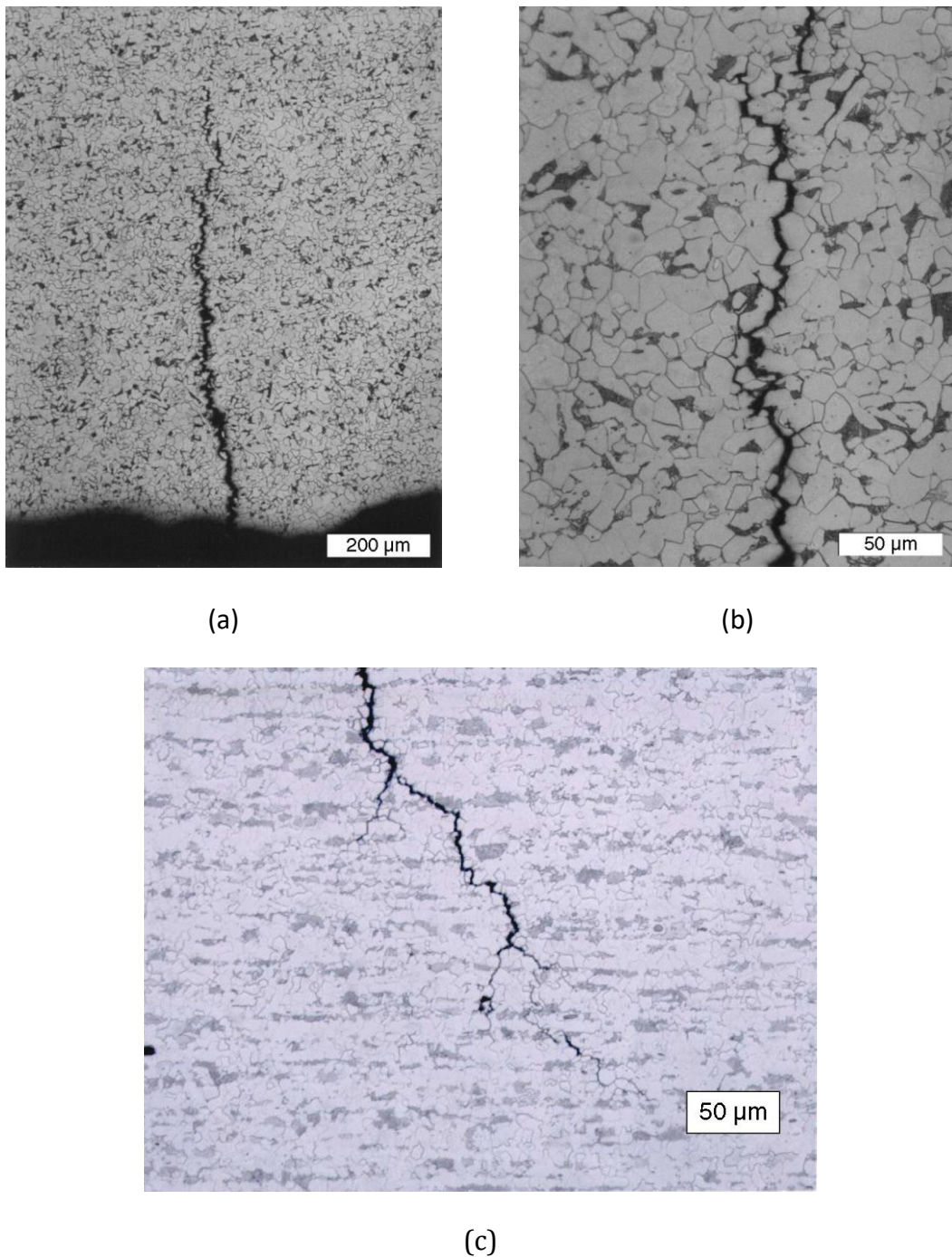


Figure 2-16: High pH SCC cracks in pipeline steels (a) unbranched crack; (b) higher magnification view of crack in (a); (c) branched crack^[36].

In the early 1970s, an extensive field survey was performed on high pH SCC of natural gas pipelines in an attempt to correlate its occurrence with metallurgical, environmental and operating parameters^[10]. SCC was found to occur on pipelines having a variety of diameters, wall thicknesses, pipeline grades, compositions, manufacturers and joining techniques. Moreover, the range of compositions in which SCC was found covered the range of almost all pipeline steels used at the time of the survey.

Laboratory studies were subsequently conducted to examine more closely the metallurgical variables with a view to identifying cracking resistant steels. It was found that additions of chromium, nickel and molybdenum in the range 2-6% reduced susceptibility^[37] but such steels were considered prohibitively expensive and their production was not pursued. Asahi et al. examined the effect of microstructure on X52, X65 and X80 grade pipeline steels by varying the processing treatment^[38]. They found that thermomechanical controlled processed and quenched and tempered steels, with uniform microstructures (fine-grained bainite or acicular ferrite), were more resistant to intergranular SCC than controlled rolled steels with mixed microstructures (ferrite-pearlite). The results indicated that initiation was more difficult in the uniform microstructures structures although it was found that the subsequent crack propagation rate was not affected by microstructure. Kimura et al.^[39] showed that susceptibility to near- neutral pH SCC was also higher for ferrite-pearlite structures than for uniform structures (as in quench and tempered steels), further indicating that homogeneous structures have a higher resistance to SCC.

When pipeline steel is exposed to high pH solutions, grain boundaries undergo preferential dissolution. If a stress of an appropriate magnitude is not present the dissolution does not penetrate far^[32]. The propensity for such intergranular attack was initially thought to be related to the presence of carbon, sulphur or phosphorus segregated to the grain boundaries in ferritic steel^[40-43]. Wang et al.^[44] measured the grain boundary compositions for X-65 and X-52 pipeline steels using analytical electron microscopy (AEM). The results showed that there was no segregation at ferrite:ferrite grain boundaries, indicating that phosphorous and sulphur are not responsible for preferential dissolution of grain boundaries during intergranular SCC^[44-46]. A similar result has been reported for X-42 steel^[32].

It was not possible to establish the distribution of carbon using AEM due to experimental limitations of the technique^[47]. However, there is other evidence linking carbon to

intergranular SCC of ferritic steels. For example, removal of carbon by wet hydrogen decarburization stops intergranular SCC in steels^[48]. In addition, Long and Uhlig^[40] showed that there was no intergranular SCC in carbon steels with carbon levels of less than 0.002 wt.%. Furthermore, the addition of carbon to pure iron induced intergranular SCC^[30, 43]. Parkins^[42] concluded that the experimental results are consistent with Fe₃C particles, and probably C in interstitial solution, acting as efficient cathodes for cathodic discharge, accelerating dissolution of the adjacent ferrite.

While high pH SCC is generally intergranular it has been reported that transgranular cracking can occur when the cracks become relatively deep or are subject to relatively high stress levels or high fluctuating stresses^[38].

2.2.2 Near-Neutral pH Stress Corrosion Cracking (Hydrogen Induced Cracking)

Research into high pH SCC has been in progress since the 1970s but research into near-neutral pH SCC is more recent. Because of the differences between the two types of cracking, the findings from high pH SCC were not generally transferable to near-neutral pH SCC. The characteristics of near-neutral pH and high pH SCC are compared in Table 2-4.

Table 2-4: Characteristics of high pH and near neutral pH SCC in pipelines^[28].

Factor	Near-Neutral pH SCC (Non-Classical)	High pH SCC (Classical)
Temperature	- No apparent correlation with temperature of pipe - Appears to occur in colder climates where CO₂ concentration in groundwater is higher	- Growth rate decreases exponentially with temperature decrease
Associated Electrolyte	- Dilute bicarbonate solution with a neutral pH in the range of 5.5 to 7.5	- Concentrated bicarbonate or carbonate-bicarbonate solution with an alkaline pH greater than 9.3
Electrochemical Potential	- At free corrosion potential: -760 to -790 mV (Cu/CuSO₄) - Cathodic protection does not reach pipe surface at SCC sites	- At free corrosion potential: -600 to -750 mV (Cu/CuSO₄) - Cathodic protection is effective to achieve these potentials
Crack Path and Morphology	- Primarily transgranular - Wide cracks with evidence of substantial corrosion of crack side wall - Associated with iron carbonate and magnetite films	- Primarily intergranular - Narrow tight cracks with no evidence of secondary corrosion of the crack walls - Associated with iron carbonate and magnetite films
Temperature Dependence	- Not Established	- Arrhenius Behaviour

Electrochemical studies of pipeline steels clearly demonstrated that the near-neutral pH environments do not promote the active-passive transitions that are observed with the high pH cracking environment^[10]. This can be seen when comparing Figure 2-13 and Figure 2-17.

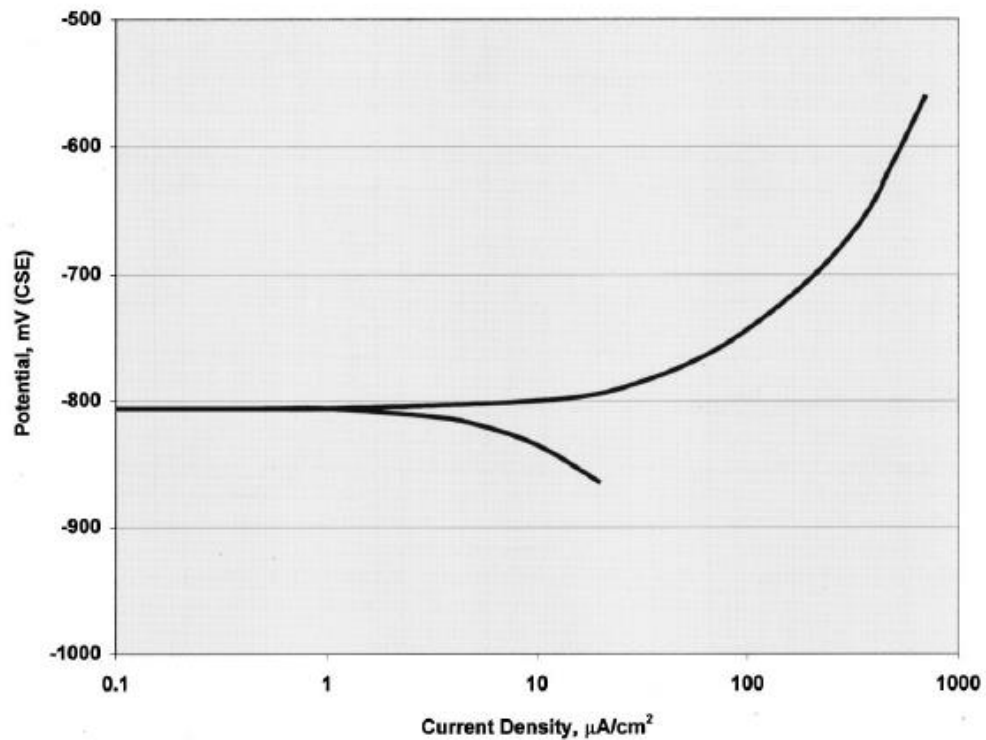


Figure 2-17: Anodic potentiodynamic polarization curve for X-65 pipeline steel at 35°C in a simulated near-neutral pH cracking electrolyte sparged with gas containing 5 percent CO₂, 95 percent N₂; scan rate 0.17mV/s^[10].

Initial attempts to reproduce near-neutral pH SCC in the laboratory used test techniques that were similar to those that had been developed for the evaluation of high pH SCC but achieved only limited success^[10]. However, significant advances were subsequently made. Parkins^[13] reported that environmentally induced cracks could be initiated in the surface of pipeline steels in near-neutral pH environments under cyclic loading conditions. The cracks initiated most readily on natural, corroded, mill-scaled surfaces. However, the cyclic-load conditions (stress ranges, frequencies and number of cycles) required to obtain crack initiation in a reasonable length of time were generally more severe than those encountered in the field. Harle et al.^[49] produced transgranular crack propagation in a near-neutral pH environment using precracked compact tension specimens of pipeline steels. The fractographic features were very similar to those observed in field failures and the crack propagation rates were consistent with field observations.

In the report of the inquiry into SCC in Canadian oil and gas pipelines^[28], Parkins suggested that the mechanism of crack growth involved both dissolution of the steel and ingress of hydrogen into the steel. The hydrogen then facilitated crack growth by

promoting reduced ductility. He noted that the corrosion observed on the sides of cracks, both in service and in laboratory tests, provided evidence that dissolution occurred within the cracks. However, the observed growth rates were markedly greater than could be accounted for by the rate of dissolution in near-neutral pH environments and it was concluded that hydrogen was involved. The role of hydrogen is discussed in more detail in the following section.

The factors contributing to the development of near-neutral pH cracking were considered to include^[28]:

- Initiation of cracks at pits on the steel surface wherein a localized environment is generated with a pH low enough to produce atomic hydrogen in the pit
- The presence of carbon dioxide in the groundwater assisting in creating near-neutral pH levels
- Entry of some of the atomic hydrogen produced into the steel, degrading the mechanical properties locally so that cracks are initiated or grown by a combination of dissolution and hydrogen embrittlement
- Continuing anodic dissolution in the crack assisted by hydrogen entry into the steel

It was noted that the role of stress may not be solely to fracture the embrittled steel but may also be to rupture the protective film, so as to allow hydrogen to reach, and then penetrate into, the steel.

Parkins' view that near-neutral pH SCC crack growth involves both dissolution and hydrogen production is supported by subsequent work by Leis, Wilmott and Jack, Lambert and Plumtree, and Beavers^[28].

The cracks produced by near-neutral pH SCC were quite different to those observed for high pH SCC, being generally transgranular, and exhibiting substantial corrosion of the sidewalls. As a result, the cracks appeared much wider than high pH SCC cracks. However, the cracks generally became narrower as they deepened. An example of near-neutral pH cracks is shown in Figure 2-18. As with high pH SCC the fracture surfaces of near-neutral pH SCC were found to contain both Fe_3O_4 and FeCO_3 ^[28].

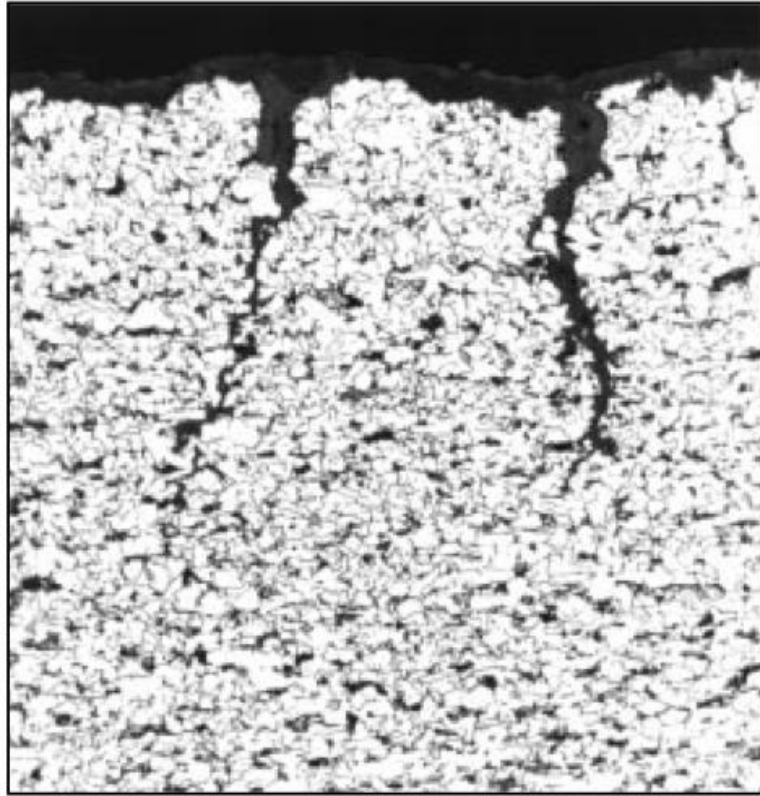


Figure 2-18: Metallographic section of near-neutral pH SCC (Magnified 250 times)^[28].

As noted earlier, coatings are applied to the pipelines and, as a result, the conditions at the pipe surface may be different to those in the surrounding soil. Accordingly, the environment responsible for SCC must be considered as that at the pipe surface. From both laboratory research and field experience it was found that the environment for near-neutral pH SCC consisted of low concentrations of carbonic acid and bicarbonate ions with the presence of other species, including chloride, sulphate and nitrate ions.

The carbonic acid results from the combination of carbon dioxide (CO_2) in the soil with ground water. The lower the groundwater temperature, the higher the solubility of CO_2 and the lower the pH, with the range being 5.5–7.5. The carbonic acid concentrations were measured where service failures had occurred and were found to be relatively dilute and, therefore, not strongly corrosive^[28].

The environment for the near-neutral pH SCC can only develop in pipelines after damage to, or disbondment of, the pipe coating. As noted earlier, cathodic protection is used in pipelines and if the cathodic current reaches the pipe surface in the presence of groundwater containing CO_2 , a carbonate/bicarbonate environment will form with a pH in the range of 9 to 13 and near-neutral pH SCC will not occur. However, some types of

pipe coating, when disbonded, act as a barrier to cathodic protection. The high resistivity of the soil may also prevent the cathodic current from reaching the pipe surface. In these instances, if the groundwater and CO₂ are present at the pipe surface, a carbonic acid environment forms, with a pH in the range of 5.5 to 7.5, i.e., the range associated with near-neutral pH SCC.

For near-neutral pH SCC, the following factors have been suggested as influencing crack initiation^[32]:

- inclusions
- aligned surface defects
- persistent slip bands produced by mechanical pre-treatment of the steel
- pre-existing defects on the pipeline surface
- coating disbondment.

As for high pH SCC, near-neutral pH SCC has been observed in a number of different grades of pipeline steel having a number of different yield strengths.

2.2.3 Mechanistic Understanding of High and Near-Neutral pH Stress Corrosion Cracking

Since the identification of high pH SCC on pipeline steel, researchers have studied high pH pipeline SCC extensively and its mechanism, caused by preferential dissolution at the grain boundaries, is well accepted. For intergranular SCC, i.e., high pH SCC, Parkins showed that the crack rate for a variety of alloys in various environments can be evaluated from the dissolution current densities measured on bulk specimens under the same environmental conditions^[42]. The crack propagation rate can be calculated according to Faraday's law:

$$CPR = \frac{i_a \times M}{z \times F \times d} \quad (2-12)$$

where:

- CPR is the crack propagation rate
- i_a is the anodic current density
- M is the atomic weight
- z is the valency of solvated species

- F is Faraday's constant
- d is the density of the metal

It has been found that the calculated propagation rate is in agreement with the estimated one^[32, 40]. Accordingly, the mechanism of high pH SCC is attributed to anodic dissolution resulting from selective dissolution at the grain boundaries and repeated rupture of passivating films that form over the crack tip.

Figure 2-12 shows that there is no gradual transition from intergranular to transgranular SCC. Instead there is a discontinuity between the two forms with the potential range for transgranular SCC being lower than that for intergranular SCC. This implies that they have different mechanisms. If the mechanism for near-neutral pH SCC were anodic dissolution, then SCC in the pH 5.8 solution extends to lower potential from about -0.67 V (SCE), the highest potential for transgranular cracking in Figure 2-12. Figure 2-19 shows that the current density is about 1×10^{-4} A/cm² at -0.67 V (SCE). The CPR is then about 4×10^{-8} mm/s according to Equation (2-12), which corresponds to the observed stress corrosion crack velocity in the field and in laboratory tests. However, when the potential is below -0.67 V (SCE), the current density is reduced according to Figure 2-19, and the CPR should also be reduced. When the potential is lowered below the open circuit potential, the CPR would be very small, possibly not detectable, or even cease. However, this is not the case. Transgranular SCC can occur near the open circuit potential especially below the free corrosion potential and the CPR calculated from Equation (2-12) is found to be lower than the measured CPR. A dissolution mechanism is therefore not supported. Research on X-65 pipeline steel (65 ksi (450 MPa) yield strength), reported in by Beavers and Harle^[10], revealed that typical anodic current densities were of the order of $20 \mu\text{A}/\text{cm}^2$ in a near-neutral pH SCC environment that was sparged with 5 percent CO₂. This current density corresponded to a crack velocity of about 7×10^{-9} mm/s. In contrast, Beavers and Harle^[10] observed that crack velocities were at least two orders of magnitude higher in constant displacement rate testing of precracked specimens of pipeline steels in this near-neutral pH cracking environment.

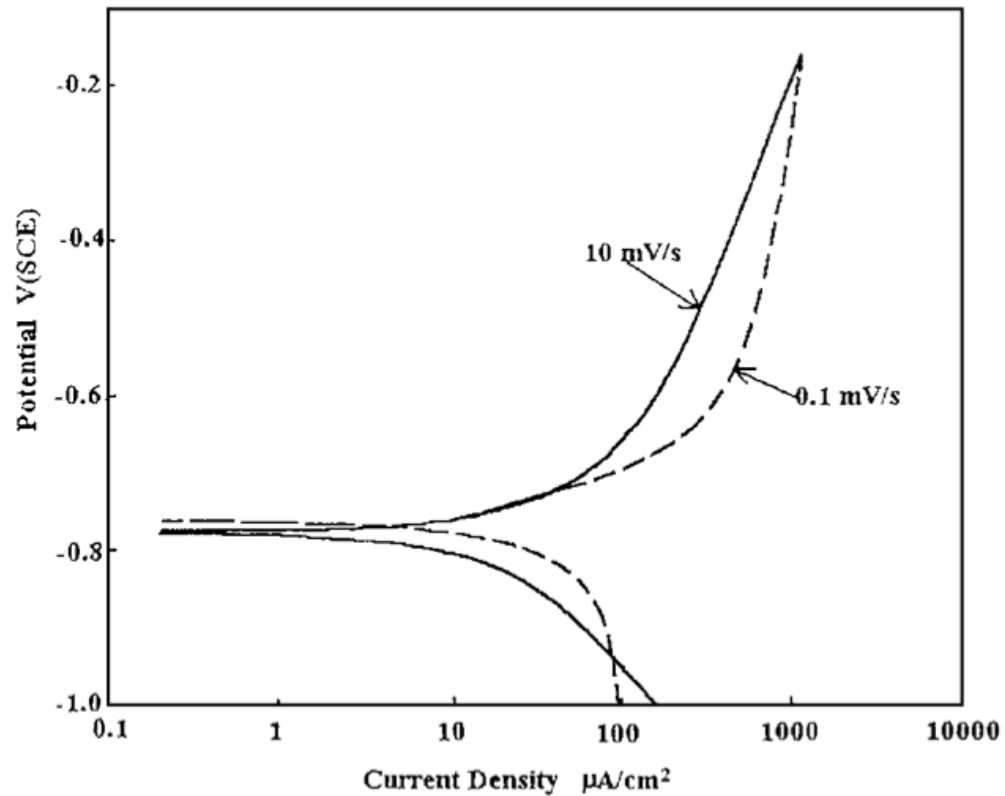


Figure 2-19: Fast and slow sweep rate polarization curves at 24°C for a pipeline steel in simulated ground water saturated with CO₂ with a pH of 5.8.

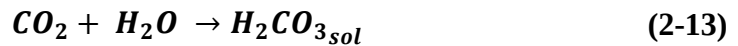
The lack of specificity of the conditions for crack propagation in the near-neutral pH environment is also not consistent with an anodic dissolution mechanism for crack propagation. For example, near-neutral pH cracking appears to be relatively less sensitive to potential than high pH SCC with the severity of near-neutral pH SCC not appearing to increase with increasing negative potential in bulk solutions^[13]. In more recent work^[10], evidence of environmental cracking has also been observed in deionized water in which carbon dioxide was bubbled. In contrast, the potential range for cracking in the concentrated carbonate-bicarbonate environment is very narrow as previously described. In the high pH environment, both carbonate and bicarbonate species must be present and cracking occurs over a limited range of pH and potential, as shown in Figure 2-14. Finally, evidence of crack propagation was not detected in constant load and interrupted constant displacement rate tests on pipeline steels in a near-neutral pH cracking environment^[10]. In contrast, alloy environment systems where the anodic dissolution mechanism is thought to operate all exhibit crack growth under constant load or constant displacement conditions. Nevertheless, dissolution does occur within the crack for near-neutral pH SCC as evidenced by the heavy lateral corrosion on the crack side.

The characteristics of near-neutral pH SCC also do not appear to be consistent with a film-induced cleavage (FIC) mechanism^[10]. This mechanism requires the presence of a brittle coherent oxide film, dealloyed layer, or some other brittle film or layer but there is currently no evidence that a film or layer with the required properties is present.

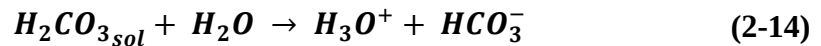
In view of the above it is concluded that there is some process other than dissolution or FIC involved in the crack propagation in solutions with near-neutral pH. Figure 2-12 includes the line for equilibrium discharge of hydrogen. The potential range for transgranular SCC is below this line. This indicates that in the lower pH range, hydrogen discharge is possible, so the mechanism for near-neutral pH SCC may be related to hydrogen. Gu^[50, 51] deduced an equation for the synergistic effect of hydrogen and stress on the anodic dissolution rate and suggested the following mechanism for near-neutral pH SCC. As the anodic potential comes closer to E_{corr} , local dissolution or pitting occurs, generating H^+ , which results in local acidification within individual pits. The acidification could facilitate the crack initiation and propagation process. As a result, Gu suggested that near-neutral pH SCC is dominated by the mechanism of hydrogen facilitated anodic dissolution. At cathodic potentials, it is suggested that, when the hydrogen concentration reaches a critical value, hydrogen induced cracking controls the cracking process.

While there is considerable evidence that hydrogen plays a critical role in the near-neutral pH SCC^[13, 52], the precise mechanism responsible for producing cracking is still contentious. A number of effects of hydrogen at the crack tip have been postulated, including reduction in the cohesive strength of the lattice, the pinning of dislocations, and hydrogen enhanced localized plasticity (HELP)^[52].

The most likely source of hydrogen in near-neutral pH SCC is carbonic acid, formed by the dissolution of carbon dioxide in the groundwater^[53, 54]



The carbonic acid can further react with water to produce a hydronium ion and a bicarbonate ion



The hydronium ion is then reduced to generate hydrogen at the metal surface.



Schmitt^[53, 54] also identified a second mechanism for hydrogen generation involving adsorbed species on the metal surface. Corrosion potential measurements^[10] are

consistent with this mechanism for hydrogen generation. Typical corrosion potentials for X-65 steel in a simulated dilute groundwater solution, known as NS₄, containing 5 percent CO₂ (pH of about 6.75), are -785 mV CSE (-485 mV SHE). The composition of this, and other solution used for laboratory SCC testing of pipeline steels is given in Table 2-5. On a Pourbaix diagram for CO₂, the pH and potential given above lie slightly below the hydrogen reduction line.

Table 2-5: Composition of simulated near-neutral pH cracking electrolytes^[13].

Substance	NS1	NS2	NS3	NS4
KCl	0.149	0.142	0.037	0.122
NaHCO ₃	0.504	0.031	0.559	0.483
CaCl ₂ ·2H ₂ O	0.159	0.073	0.008	0.181
MgSO ₄ ·7H ₂ O	0.106	0.254	0.089	0.131

It is well known that hydrogen can reduce the ductility of the steel without producing multiple cracks, but the same amount of hydrogen in the steel held below the yield stress may not have any noticeable effect^[13]. Normally, when severe SCC occurs, the reduction in area during tensile testing is low, but the embrittling effect of hydrogen can confuse the issue. Parkins^[13] showed that in some slow strain rate specimens held near E_{corr} in the near-neutral pH environment, the reduction in area (RA) at failure decreased from 70 percent to 30 percent even in the absence of secondary cracking.

Some investigators consider that the magnitude of the reduction in area correlates with the rate of hydrogen absorption^[50]. Others consider that hydrogen can reduce the yield strength of the steel, then promote the onset of plastic deformation, or can lower the total deformation that can be tolerated by the steel before fracture^[55-57].

Recently, Colwell and Leis postulated that the underlying drivers for near-neutral pH SCC were based simply on the CO₂ – H₂O system^[58, 59]. This mechanism for the pipeline environment accounts for hydrogen production as well as the formation of FeCO₃ without changes in the solution pH. Figure 2-20 shows the results of calculations that provide the regions of predominance for the three equilibrium species that can exist when CO₂ dissolves in water. The nature of the species is a function of the pH of the solution. The lines on Figure 2-20 are calculated from the equilibrium constants for reactions (2-16) and (2-17)^[59]



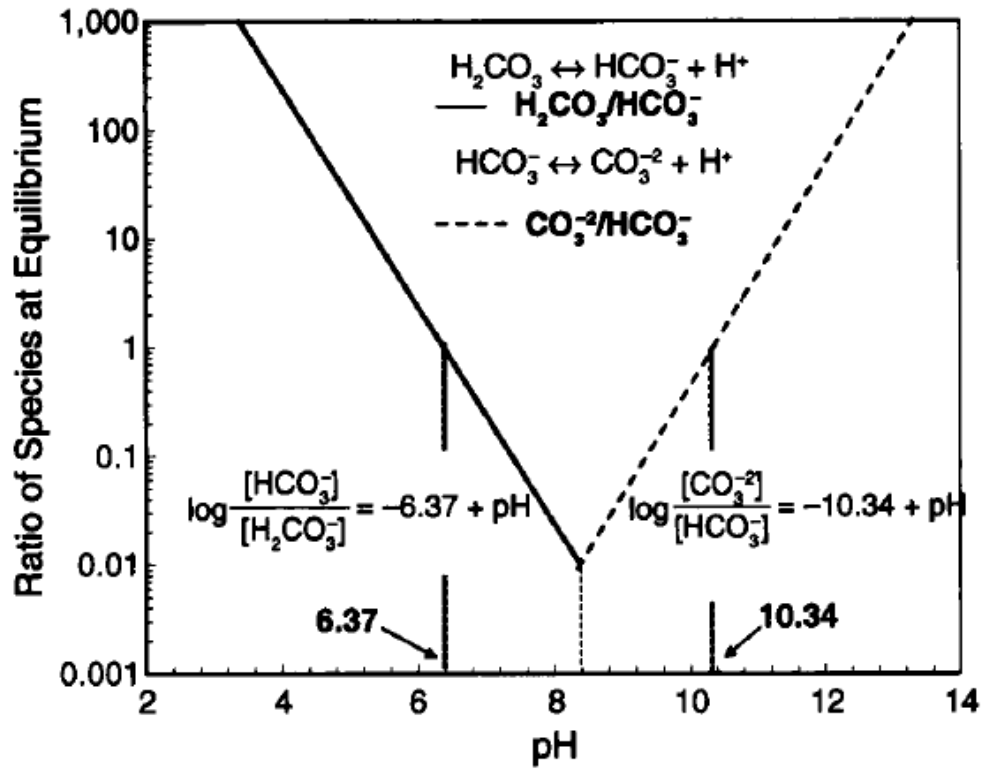


Figure 2-20: Calculated equilibrium constant values as a function of the ratio of species at equilibrium and pH^[59].

The equilibrium of these species is determined from the equilibrium constants shown, respectively, for each reaction in Equations (2-18) and (2-19)^[59]

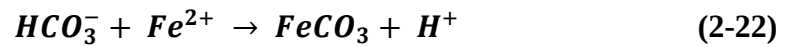
$$\log \left(\frac{\text{HCO}_3^-}{\text{H}_2\text{CO}_3} \right) = -6.37 + \text{pH} \quad (2-18)$$

$$\log \left(\frac{\text{CO}_3^{2-}}{\text{HCO}_3^-} \right) = -10.33 + \text{pH} \quad (2-19)$$

At a ratio of one, the species are in equal molar amounts, and the solution is effectively buffered. This corresponds to a pH of 6.4. At pH values between 6.4 and 10.3, the bicarbonate ions predominate. The minimum in Figure 2-20, at a pH value of 8.4, represents the point of concentrated bicarbonate. At more acidic values, carbonic acid forms, and at more basic values, carbonate ions predominate. The pH of the solution found near transgranular SCC failure of pipelines was reported to be approximately 6.4, where the H_2CO_3 and bicarbonate ion concentration is roughly equal. The pH will remain at 6.4 as long as the species for the reaction are available in the solution^[58]. As shown in Figure 2-20, the changing environments can account for both intergranular and

transgranular SCC of pipeline steels. It is noted that both types of cracking have been reported to occur on the same section of pipelines^[60]. The presence of other ions in the solution may also affect the SCC mechanism.

The Colwell–Leis mechanism uses this information to account for the release of hydrogen and formation of Fe_2CO_3 in simple bicarbonate solutions as explained by the following steps^[59]:



The hydrogen released from the reaction of bicarbonate with the metal ion, and the hydrogen formed from the dissolution of H_2CO_3 , can ingress into the steel. This method of hydrogen generation does not change the pH of the solution. H_2CO_3 is further formed by the dissolution of CO_2 in groundwater. The production of FeCO_3 would account for the FeCO_3 found on the fracture surfaces.

In the above discussion, no distinction has been made between SCC initiation and SCC propagation. For many of the systems where the anodic dissolution mechanism is thought to operate, it is generally considered that both initiation and propagation occur by the same mechanism. Some exceptions exist, such as situations where stress corrosion cracks initiate at pits.

For hydrogen-related SCC, it is probable that the initiation and growth mechanisms are different^[58-61]. In the case of near-neutral pH SCC, possible initiation mechanisms include fatigue, pitting, or even high pH SCC and a number of the features of near-neutral pH SCC suggest that such mechanisms may be involved. Near-neutral pH SCC is frequently associated with features on the pipe surfaces such as pits, gouges and welds^[10]. Where near-neutral pH SCC occurs in the pipe body away from these features, the appearance of the crack colonies is nearly identical with high pH colonies, suggesting that they may have similar origins, at least in some cases. In the laboratory, it is very difficult to initiate colonies of near-neutral pH cracks in the absence of stress concentrators and fatigue loading^[13].

In summary, whilst the mechanism of high pH SCC is almost universally accepted, there is less agreement on the mechanism of near-neutral pH SCC.

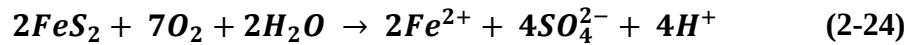
2.2.4 Environmental Effects

2.2.4.1 Effect of Coal

Steel structures that come into contact with coal can undergo significant corrosion. Consequently, it is useful to have an understanding of how corrosion proceeds in the presence of coal.

Experimental work investigating the corrosion of mild steel by coal has focused on extracted coal, rather than on corrosion of steel when embedded in the coal. Nonetheless, the work is still of interest here. The studies have been focused mainly on the corrosivity of the fluid that resides within the media, or has been in contact with the media, for example, minewaters. These studies have shown the corrosion rate to increase with increasing chloride and sulphate concentration and decreasing electrolyte pH levels.

Gardiner and Melchers (2002) investigated the influence of particle size and quantity of moisture on corrosivity of mild steel. It was found that the corrosion rate increased as the mean particle size decreased. Additionally, it was found that the corrosion rate was dependent on the moisture content of the coal. The materials used in this investigation had neutral pH free moisture. However, the free moisture in some types of coal can be acidic. The pH level of free moisture in coal is a function of the relative supply of pyrite (FeS_2) and carbonates (mostly CaCO_3) from the coal and is dependent on the relative rates of both the acid and alkali forming reactions, given in Equations (2-24) and (2-25), respectively:



When the pH is neutral the reduction of oxygen becomes the cathodic reaction in the corrosion process. This is shown in Equation (2-26).



Corrosion studies of neutral pH underground minewaters^[62] did not reveal a correlation between corrosion rate and chloride and sulphate concentration. This was to be expected as the mild steel samples examined were immersed in stagnant solutions such that the corrosion rate was low and controlled by the diffusion of oxygen. However, when

immersed in aerated minewaters, the corrosion rate increased with increased chloride and sulphate concentrations before decreasing as the concentration increased further. The peak was attributed to the increasing salt concentration reducing the solubility of oxygen in the solution.

The existence of a maximum corrosion rate at a critical moisture content suggests that there must be a ratio of water in the media at which corrosion reactions are maximized. This has been explained in terms of the continuity of the fluid and air phases and their subsequent influence on the magnitude of the electrical conductivity and oxygen diffusion coefficient. At low levels of moisture the air phase is continuous within a coal sample and the underlying steel is sufficiently aerated such that the diffusion of oxygen to the corroding surface does not limit the rate of corrosion. The influence of the ohmic overpotential then dominates and the corrosion rate is a function of the electrical conductivity of the sample. This in turn is related to the concentration of chloride and sulphate ions within the free moisture. Alternatively, at high levels of moisture, a continuous water phase is established and the corrosion rate becomes limited by the cathodic reduction of oxygen. The concentration of chloride and sulphate ions then has minimal influence. In summary, for coal with approximately neutral pH, the corrosion rate is a function of the quantity of moisture and the particle size, while at low moisture levels, the concentration of chlorides and sulphate anions also affects the corrosion rate.

When the free moisture is acidic the cathodic reaction is the hydrogen evolution reaction, shown in Equation (2-27).



Due to the consumption of hydrogen ions in the cathodic reaction it may be expected that the rate of corrosion is dependent on the pH level. Spero and Flitt^[63] measured the corrosion rate of mild steel immersed in de-aerated acidic coal leachates and found the following relationship between corrosion rate, current (I) and pH:

$$\log(I) = a - bpH \quad (2-28)$$

where, a and b are constants.

The corrosion rate increased with increasing chloride and sulphate concentration in a manner that could be represented by a bi-logarithmic equation.

2.2.5 Metallurgical Effects

2.2.5.1 Effect of Decarburisation

Beavers et al. noted that low carbon steels are more susceptible to anodic SCC than steels with higher carbon contents, and on this basis, suggested that surface decarburization (which is characteristic of hot rolled steel) should increase susceptibility to high pH SCC^[34]. They found that SCC crack growth depths increased with increasing depth of decarburization and considered this to be confirmation of the detrimental effect of decarburization. Asahi et al. also reported that decarburization reduced the resistance of some pipeline steels to carbonate/bicarbonate SCC^[38].

2.2.5.2 Effect of Grit Blasting / Shot Peening (Surface Roughness)

Shot peening produces a compressive residual stress in the surface of the peened article and this is beneficial to SCC resistance^[64]. Grit blasting also has a similar effect but the blasting media consists of angular particles rather than spherical shot. Grit blasting therefore produces rougher surface features than shot peening and this results in higher stress concentrations being present on the grit blasted surface^[34, 60, 65].

Kentish^[60] investigated the effect of grit blasting on SCC resistance of X70 grade (70 ksi (490 MPa) yield) pipeline steel. They used a single class of grit blast but varied the surface roughness levels. Unblasted samples and shot peened samples were also examined.

SCC testing was conducted using a 1N sodium carbonate plus 1 N sodium bicarbonate solution at 75°C with a potential of -0.65 V (SCE) and a strain rate of approximately $7 \times 10^{-7} \text{ s}^{-1}$. SCC performance was evaluated as the ratio of the time to failure in the carbonate/bicarbonate solution to that in an inert environment.

Both grit blasting and shot peening improved the fatigue performance compared to that of the untreated (referred to as “as formed”) material, Figure 2-21. However there was a marked reduction in the level of improvement as the surface roughness decreased. This was attributed to an increased level of stress concentration with increased surface roughness.

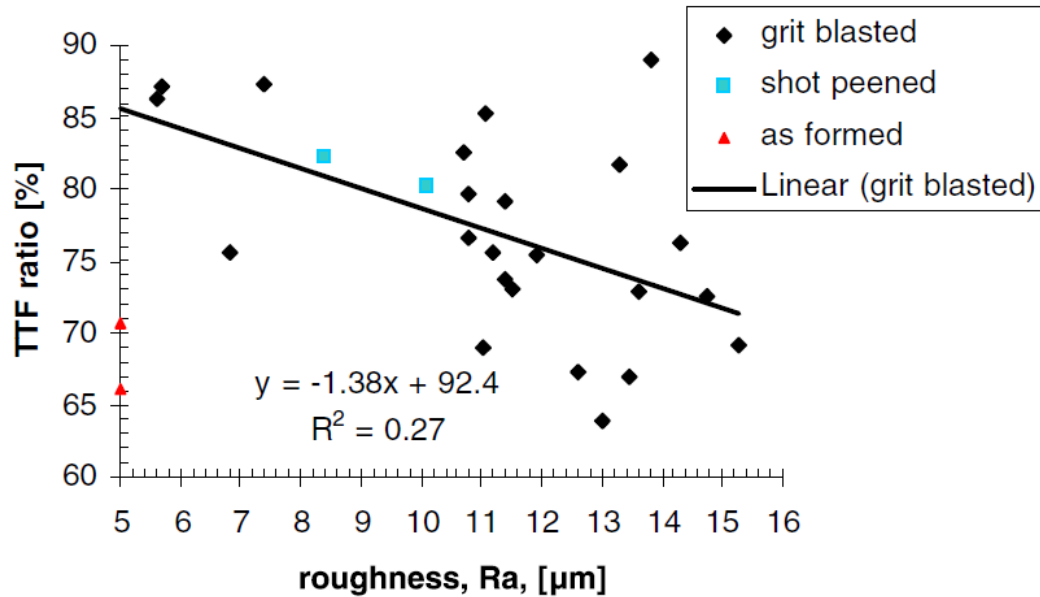


Figure 2-21: Effect of roughness on time to failure (TTF) for all grit blasted samples^[60].

Kentish noted that the stress concentrations associated with the higher surface roughnesses may be similar to, if not higher than, those associated with corrosion pits. However, it was considered that the closer proximity of the surface irregularities for grit blasted surfaces, compared to that for corrosion pits, may reduce the overall effect due to interaction. This is supported by the work of Li et al.^[66] who found that the stress concentration was relaxed by 20% as a result of surface rounding in shot peened dents when investigating the effects of multiple indentations. Although this work involved the smoother shot peened surfaces, similar, but probably less, relaxation would be expected for the grit blasted surfaces due to the greater angularity and extent of the roughness^[60].

Kentish also measured the crack density and found a progressive decrease with increasing surface roughness^[60], as can be seen in Figure 2-22. Interestingly, the crack density was substantially lower for the untreated (as formed) samples than for the grit blasted samples having low surface roughness, even though the time to failure was lower.

Surface profiles for two different surface roughnesses are shown in Figure 2-23. The sample with the lower surface roughness ($R_a = 8.9$), which was achieved by using smaller grit sizes, had more closely spaced, and generally shallower surface damage, but the sharpness of the roughness profiles was similar in the two cases. It was considered that the more closely spaced damage seen for the sample with lower surface roughness could promote increased crack initiation^[60]. However a greater concentration of cracks tends to

lead to crack dormancy whilst more sparsely spaced cracks tend to encourage propagation^[60]. In view of this, it was considered that the rougher surfaces with lower crack densities may result in reduced SCC resistance^[60].

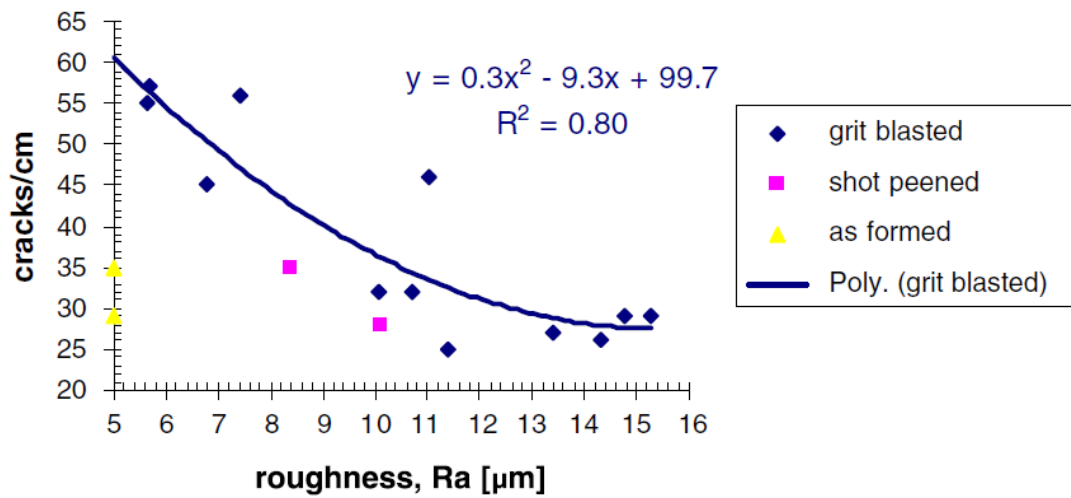


Figure 2-22: Effect of roughness on crack concentration, laboratory blasted samples^[60].

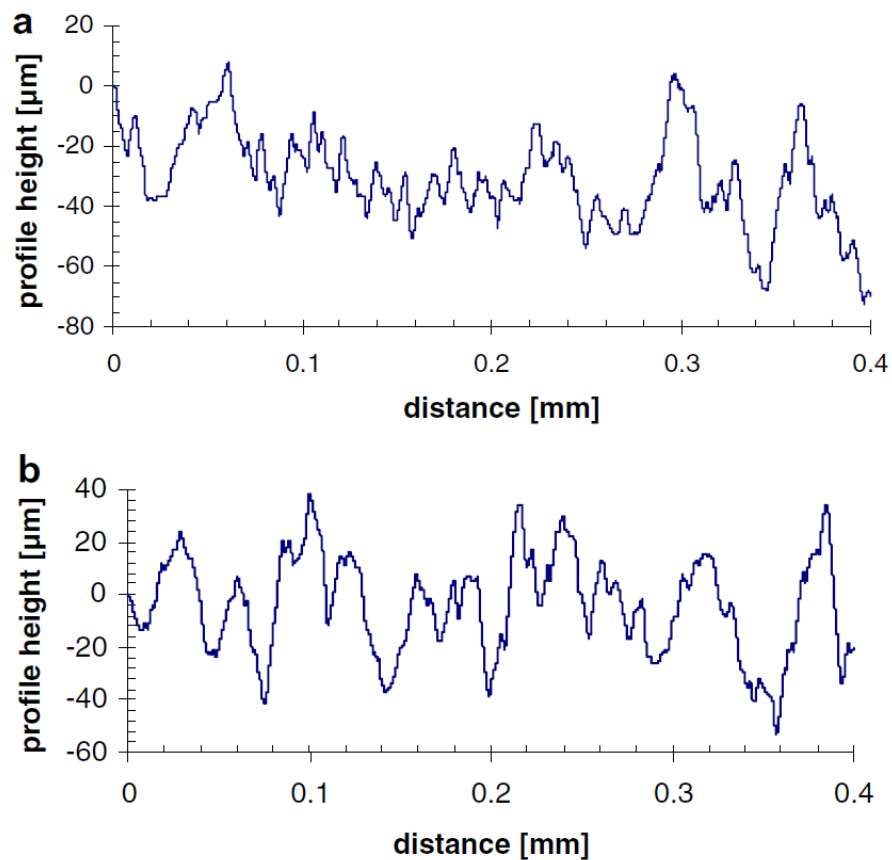


Figure 2-23: Surface profiles of grit blasted surface with a of R_a roughness of (a) 8.9 and (b) 12.7 μm ^[60].

Beavers et al.^[34] also reported that shot peening and grit blasting could be highly beneficial to SCC resistance of pipeline steel.

2.2.5.3 Effects of Alloy Chemistry

As noted in Section 2.2.1, additions of chromium, nickel and molybdenum in the range 2-6% reduced the susceptibility of pipeline steels to high pH SCC^[37], while carbon, sulphur or phosphorus segregated to the ferrite grain boundaries was initially thought to be detrimental^[40-43]. It was, however, found that sulphur and phosphorous were not present at the grain boundaries while results for carbon were inconclusive^[30, 44-46].

The effect of individual alloying elements on the SCC behaviour of steels has been examined in various other environments and has been found to be quite complex, as discussed below.

Increasing carbon content is reported to decrease resistance to SCC in aqueous chlorides, with the effect being greatest in the 0.2 to 0.4% range^[67, 68]. However, no clear influence of carbon on SCC resistance has been found in aqueous hydrogen sulphide with some researchers reporting that it causes a slight improvement, while others have reported it to have a slightly detrimental effect^[35].

The resistance of mild steel to SCC in nitrate solutions is determined primarily by carbon content, with the steels being susceptible to SCC for carbon contents in the range 0.001-0.018% but being resistant outside this range^[41]. SCC susceptibility is thought to be largely due to carbide morphology and distribution. SCC resistance of alloy steels appears to be independent of carbon content^[61, 69].

Susceptibility of plain carbon steels to SCC in hydroxide solutions (caustic cracking) increases with increasing carbon content up to about 0.2%, beyond which a beneficial effect has been reported^[35].

The presence of manganese increases susceptibility to chloride SCC in medium carbon steels, but not in their low carbon counterparts^[68]. Increases in the manganese content of steel are also reported to be detrimental to SCC resistance in hydrogen sulphide environments, possibly due to segregation effects^[35]. The resistance of carbon steels to SCC in nitrate solutions is also adversely affected by increased manganese content, especially when the steel is annealed at high temperatures for extended periods^[70, 71].

Nickel contents above 1% have been reported by some workers to reduce the SCC resistance of steels in hydrogen sulphide containing environments^[72], but other workers

have not observed a significant effect. No effect of nickel on SCC in nitrate solutions has been reported^[73].

Chromium contents below about 1.4% have been reported to be beneficial to SCC in aqueous hydrogen sulphide, however, above this level detrimental effects are generally observed^[35]. A similar beneficial effect of chromium on SCC resistance in nitrate solutions has been reported up to about 1.0%^[70, 71, 73].

Molybdenum and vanadium are all considered to increase SCC resistance to hydrogen sulphide^[74]. Titanium additions also increase SCC resistance provided they are low enough to avoid second-phase titanium carbonitride precipitation which increases susceptibility^[75]. A beneficial effect of titanium on SCC resistance in nitrate solutions has also been reported^[40, 71].

Copper has been reported to increase susceptibility of steel to SCC in nitrate solutions^[73] but silicon appears to have a beneficial effect^[40]. Silicon contents greater than 1.6% have been reported to also decrease SCC propagation rates in chloride solutions.

Aluminium has been reported to increase SCC resistance to hydrogen sulphide in the range 0.3 to 0.6%^[35]. Improvements in SCC resistance in nitrate solutions are reported at levels above about 0.3%. A possible beneficial effect of aluminium on caustic cracking has also been reported^[73].

High sulphur and phosphorous contents have been found to reduce the SCC resistance of steels in hydrogen sulphide and can also affect SCC in nitrate solutions^[76]. No influence of oxygen and nitrogen has been reported for SCC in hydrogen sulphide solutions^[40]. Nitrogen levels below 0.01% promote SCC of steels in nitrate solutions, but higher levels appear to be beneficial^[35].

2.2.5.4 Effect of Manganese Sulphide Inclusions

Hydrogen induced stress corrosion cracking (HISCC) in H₂S environments is known to be associated with the presence of non-metallic inclusions, especially manganese sulphide (MnS), and also with banded microstructures^[77]. The interface between large MnS inclusions and/or the banded structure and matrix usually act as sinks for hydrogen. Hydrogen tends to diffuse to these interfaces and reach the critical value required for cracking. Since the cracks initiate at the elongated MnS particles, HISCC susceptibility increases with increasing MnS content, which, in turn, increases with increasing sulphur

content in the steel. Steel rolling at lower temperature increases the HISCC susceptibility by elongating the sulphide inclusions^[77].

Several studies have examined the effect of MnS inclusions in steel exposed to water at elevated temperatures. Such temperatures are not experienced by rock bolts but the rock bolt steels do contain MnS inclusions and a review of this work is therefore included.

Hurst et al.^[78] reported that MnS inclusions act as starting points for SCC in low-alloy steel in high-temperature oxygenated water (288°C). However, they did not clarify their role in SCC initiation.

The sulphur content of low-alloy steel has also been found to affect the corrosion fatigue crack growth behavior of the steel in high-temperature oxygenated water (288°C)^[79]. It was considered that this was associated with the level of MnS inclusions in the steel. Dissolution of MnS inclusions would be expected to change the water chemistry in crevices left from MnS dissolution, making it more aggressive and accelerating the corrosion fatigue crack growth rate. The same mechanism may apply in SCC.

Kuniya, Anzai and Masaoka^[80] performed an investigation of the effect of MnS inclusions on the SCC initiation in low-alloy steel using slow strain rate tensile tests for steels with different sulphur contents at different dissolved oxygen concentrations in high-temperature (288°C) water. From this investigation, the following was found;

- MnS inclusions acted as the starting points of SCC as well as pitting corrosion. In 288°C water containing high concentrations of dissolved oxygen (8 ppm), SCC initiated from both MnS inclusions and pitting corrosion. On the other hand, in water containing a low-dissolved oxygen (0.2 ppm) concentration, SCC initiation from MnS inclusions became dominant
- SCC initiation depended on the probability of MnS existing on the specimen surface in contact with the high-temperature water. The number of SCC starting points in intermediate sulphur content material (about 0.015 wt.%S) was larger than that in low-sulphur content material (about 0.004 wt.%S)
- The existence of MnS inclusions had only a small effect on SCC propagation in 288°C water containing 8 ppm dissolved oxygen. On the other hand, they acted as the starting points of secondary propagation in 288°C water containing low-dissolved oxygen (0.2 ppm)

2.2.5.5 Effect of Microstructure

Steels of potential interest for rock bolting can be divided into two main microstructural types, these being ferritic-pearlitic and quenched and tempered (martensitic or bainitic)^[35, 75]. As discussed in Section 2.2.1, steels with homogenous structures, such as bainite, have been found to have higher resistance to both high pH and near neutral pH SCC than those with mixed ferritic-pearlitic structures. Quenched and tempered 1040 grade steel produced by the Tempcore process has been used for rock bolts in the past but its use was discontinued due to problems with rib shaving which was required prior to rolling the thread on the end of the bolts^[5]. Currently, only ferritic-pearlitic steels are used. None the less it is useful to include quench and tempered steels in the following discussion.

Quenched and tempered steels have been shown to have superior SCC resistance in aqueous hydrogen sulphide, compared with normalized steels of similar strength levels^[75]. Indeed, martensitic microstructures have been found to generally give the best SCC resistance at a given strength level^[76]. Bainitic microstructures have approximately equivalent SCC resistance. The presence of untempered martensite is considered detrimental. Coarse or globular carbides that result from slow cooling and tempering produce an intermediate level of SCC resistance. In nitrate solutions, steels with pearlitic microstructures are superior in SCC resistance compared with steels having fine spheroidised carbides^[81].

Fine grain size has been shown to increase the SCC resistance of quenched and tempered steels in hydrogen sulphide solutions^[72]. Similar effects have been observed for carbon steels in nitrates, where increased austenitizing temperature, resulting in grain growth, has adversely affected SCC resistance^[82]. Increased cooling rate after austenitising has also been shown to decrease SCC resistance in nitrate environments^[35].

Manganese segregation in tempered steels can produce localized regions of increased hardness. This results in a preferential path for SCC in aqueous hydrogen sulphide and a corresponding drop in SCC resistance^[75].

Grain boundary segregants can significantly influence the SCC of steels in environments in which intergranular cracking predominates. These effects have been systematically studied in elevated temperature nitrate solutions^[83-85]. Following aging treatments to promote segregation, enhanced SCC susceptibility of steels to calcium nitrate was attributed to locally high phosphorus and sulphur levels at grain boundaries^[83]. Somewhat mixed results been reported for silicon and tin in similar environments^[85]. In ammonium

nitrate solutions, phosphorus, sulphur, arsenic, tin and antimony, present with silicon, germanium, selenium, tellurium and bismuth, strongly promoted intergranular SCC^[84].

Inclusions in steels act as SCC initiation sites and accelerate crack propagation in the direction of elongated inclusions such as sulphides^[86, 87]. Resultant anisotropy of hydrogen sulphide SCC has been reported in both plate and tubular products^[35, 75].

2.2.5.6 Effect of Cold Working

The increases in strength, hardness and residual stresses that result from cold working can significantly influence the SCC behavior of steels unless the materials are adequately stress relieved by thermal treatment^[35].

In aqueous chlorides, plastic prestrain to about 5% has been reported to have little effect on the SCC of low and medium strength steels, but as little as 1% prestrain can adversely affect higher strength steels^[35]. Plastic prestrain can, however result in compressive residual stresses. In such cases, SCC resistance increases due to the beneficial effect of compressive residual stress on SCC initiation. Accordingly, cold drawn wires (which have surface compressive residual stresses) have been found to have better SCC resistance than heat treated wires (without surface compressive residual stresses) having the same strength levels^[7].

In hydrogen sulphide environments, cold working as little as 1% has been found to have a strong detrimental effect on SCC resistance^[35, 88]. As shown in Table 2-6, cold working can impart SCC susceptibility to even low strength steels that would not otherwise exhibit SCC. Such effects are believed to be due to increases both in available sites for SCC initiation and in hydrogen solubility^[89].

Table 2-6: Effect of cold work on SCC of 130 and 80 grade pipeline steel tested in 5% NaCl saturated with hydrogen sulphide^[35].

Prestrain (% elongation)	Applied stress (% yield strength)	
	130	80
0	No SCC	No SCC
1	No SCC	No SCC
2	No SCC	No SCC
3	SCC	No SCC
4	SCC	No SCC

For low carbon steels, cold working reportedly improves SCC resistance in nitrates^[35, 90]. At intermediate carbon levels, from 0.09 to 0.19%, SCC resistance initially decreases and

then increases with increased amounts of cold work. Introduction of residual compressive stresses by shot peening improves the nitrate SCC resistance of steels^[91]. Plastic straining appears to be a prerequisite for SCC in hydroxide environments.

The effect of cold work on rock bolt steels is discussed further in Section 2.3.

2.2.5.7 Effect of Strength Level

Strength level has a very substantial influence on the SCC resistance of steels under a variety of conditions, with resistance decreasing as strength level is increased^[28].

Steels with yield strengths of less than 1240 MPa are considered resistant to SCC in aqueous chlorides when not highly stressed, but the maximum yield strength level was found to be reduced to 1030 MPa for more highly stressed notched specimens^[35]. Indeed, SCC has been reported in precracked steel specimens with yield strengths as low as 760 MPa.

Steels with yield strengths below 930 MPa resisted SCC in ambient temperature 15% HCl solutions^[92] but steels with yield strengths above 1282 MPa exhibited SCC.

Although a clearly defined yield strength threshold for SCC in aqueous chlorides is not apparent, it can be generalized that steels with yield strengths of less than 689 MPa (100 ksi) are resistant^[35]. Above this value, SCC in aqueous chlorides can occur, with SCC resistance decreasing with increased yield strength. This strength level corresponds to a threshold stress intensity for SCC of about $110 \text{ MPa}\sqrt{\text{m}}$ ^[35].

Resistance of steels to SCC in environments containing hydrogen sulphide also decreases with increasing strength level^[76] with the threshold stress for cracking often being well below the yield strength of the steel. SCC in aqueous hydrogen sulphide has been reported at yield strength levels down to 296 to 414 MPa in laboratory tests^[35].

Steels with yield strengths below about 1030 MPa are reportedly resistant to SCC in sulphuric acid solutions, but SCC was observed above this level^[92].

2.2.5.8 Effect of Fracture Toughness

Steels with good fracture toughness are generally more resistant to SCC. A good correlation between fracture toughness and SCC resistance has been reported for steels with strengths of 700 to 1380 MPa in synthetic seawater. However, no significant correlation between toughness and SCC resistance was found for 4xxx series steels in aqueous hydrogen sulphide^[35].

Fracture toughness also has a pronounced effect on SCC life since the critical crack length a (length of SCC crack at point of final catastrophic failure) is proportional to the square of the fracture toughness K_{IC} , as can be seen from the following equation:

$$\sigma = \frac{K_{IC}}{Y\sqrt{\pi a}} \quad (2-29)$$

where σ is the applied stress and Y is the shape factor. Thus, as pointed out by Crosky et al.^[5], doubling the fracture toughness would increase the time to failure fourfold (assuming the method used for increasing fracture toughness does not alter the SCC crack growth rate).

2.2.5.9 Effect of Stress

The tensile stress experienced by a material is of major importance in stress corrosion cracking with a number of physical processes being dependent on stress level. These include the fracture strain for a passive film rupture mechanism, the critical resolved shear stress for a slip dissolution mechanism, the fracture stress for a brittle film induced cleavage mechanism and a critical crack tip opening for transport of species in the crack^[12]. As noted earlier, the stress level includes residual, as well as applied, stresses. While the effects of environmental and metallurgical factors vary widely for different SCC mechanisms many similarities are seen for the effect of stress^[12].

In particular, the subcritical crack growth behaviour is similar for many material/environment combinations. A typical subcritical crack propagation rate versus stress intensity relationship is shown in Figure 2-24. The behaviour is characterised by a threshold stress intensity, below which observable crack growth does not occur. The threshold stress intensity is generally considered to be associated with development of a plastic zone at the crack tip^[12].

The stress intensity is a function of both stress and crack length. In some cases, stress only is considered and the stress required for observable crack growth is correspondingly referred to as the threshold stress. Because of the difficulty in providing a precise definition of observable crack growth, varying definitions of threshold stress have evolved. These include the stress above which cracks initiate and grow to failure, the stress level that will grow a crack to a specific depth and the stress level required to give a specific crack growth rate^[28].

Considerable work has been carried out on the effect of stress in pipeline steels for both high pH and near-neutral pH SCC. A substantial hoop stress is generated in the pipe wall due to the internal operating pressure of the pipeline. This is supplemented by residual stresses from the pipe manufacturing process as well as small fluctuating stresses resulting from pressure fluctuations arising from the pumping process.

For high pH SCC it has been found that the threshold stress approaches the yield stress of the material on machined surfaces^[93]. However, it is significantly reduced on actual pipe surfaces due to the presence of mill scale and corrosion pits on the pipe surface^[93]. For mill scaled surfaces, the threshold stress has been found to be typically 60-70% of the yield stress (taken as the minimum specified yield strength of the material) although significant scatter was observed. The scatter has been attributed to variation in the level of residual stress in the pipe wall^[93].

The cyclic stresses associated with pipeline operation were found to reduce the threshold stress. This has been attributed to the occurrence of cyclic creep which is considered to facilitate rupture of the passive films^[93].

Service failures were found to occur at 46-76% of the yield stress. The lower minimum threshold stress observed for service failures than for laboratory tests probably reflects the effect of the fluctuating stresses.

High pH SCC cracks have often been found in areas containing pits in both service failures and laboratory tests. The pits cause stress concentration, particularly when they are relatively deep. High pH crack nucleation appears to increase with increasing pit density^[93].

The effect of stress on near-neutral pH SCC of pipeline steels has also been studied extensively. While cracking could be produced in the laboratory in slow strain rate testing (although only under extreme loading conditions)^[13], it could not be produced in constant load and constant displacement testing without the superposition of cyclic stresses^[93]. Accordingly, much of the work has involved the application of a component of cyclic loading. It is noted however that crack growth could be produced without cyclic loading in precracked specimens^[94].

Parkins examined the effect of stress on crack initiation in X65 (448 MPa) pipeline steel^[28]. He used a superimposed cyclic loading and found that at an R ratio (ratio of minimum stress to maximum stress) of 0.5 a minimum stress level of 69% of the yield stress was required to produce cracks. A minimum stress level of 72% of the yield stress

was required when an R ratio of 0.85 was used. Beavers and Harle deduced that the threshold stress for service failure was about 65% of the yield stress^[93].

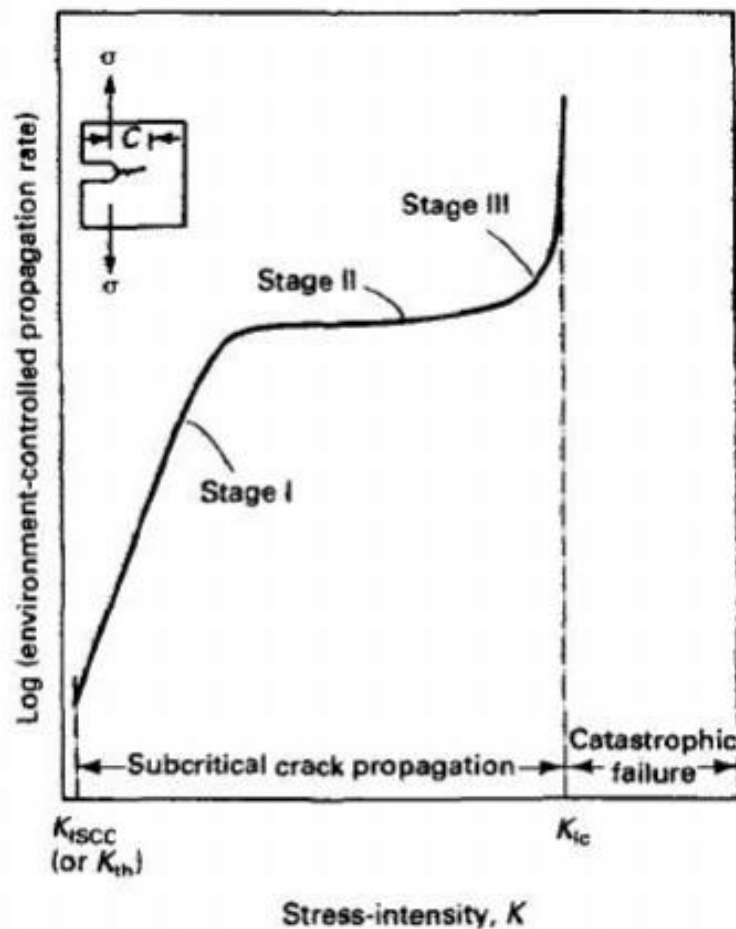


Figure 2-24: Typical subcritical crack-propagation rate versus stress-intensity relationship^[12].

The effect of stress on crack growth has also been examined. Parkins conducted laboratory tests on X65 grade steel at stresses ranging from 360 MPa (80% of yield stress) to 483 MPa (108% of yield stress) with R-ratios of 0.5, 0.70 and 0.85. The tests were carried out using a weak carbonic acid environment representative of that found in the field (NS4 solution, Table 2-5). The results are shown in Figure 2-25^[28]. It can be seen that the crack growth rate increases with increasing stress level but that the effect reduces as the R ratio increases.

Crack growth rate was also found to increase in the NS4 solution with increasing strain rate^[30].

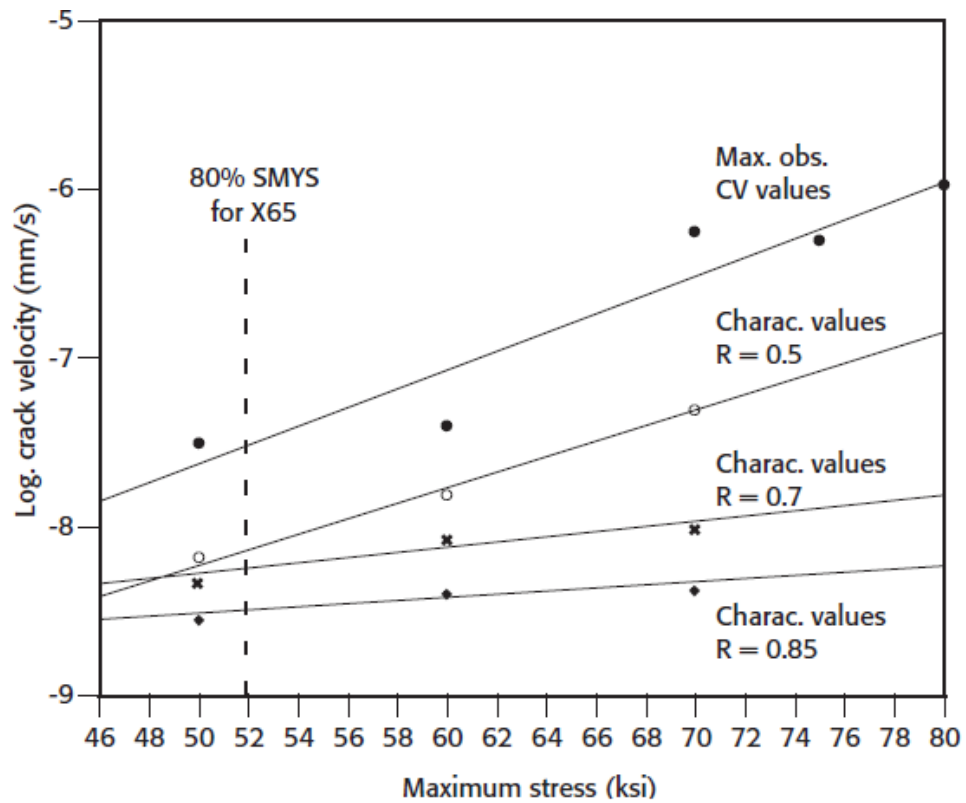


Figure 2-25: Near-neutral pH SCC growth rates as a function of stress amplitude and maximum stress for an X65 steel in TransCanada's 36 inch pipeline^[28].

2.2.5.10 Effect of Temperature

The influence of temperature depends on the nature of the process at the SCC crack tip. A higher temperature may mean a higher corrosion rate since there is more energy available to speed up any thermally activated processes. In the case of pipeline SCC, the crack growth rate at high pH SCC follows Arrhenius behaviour^[36] as given by the Arrhenius Equation below,

$$k = Ae^{-\frac{E}{RT}} \quad (2-30)$$

where:

- k is the rate constant
- A is the frequency factor
- E is the activation energy
- R is the universal gas constant
- T is the temperature in kelvin

The rate constant k gives the temperature dependent component of the crack growth rate. The resulting exponential increase in crack growth rate with temperature indicates that the rate controlling step is thermally activated.

In contrast, no obvious effect of temperature on crack growth rate has been found for near-neutral SCC^[36]. Parkins^[13] carried out slow strain rate tests but the results showed no significant differences for crack growth rates at temperatures of 5°C and 45°C. However, field investigations have found that near-neutral pH SCC does not occur where the soil temperature surrounding the pipe was in the region of 10°C or lower^[28].

Beavers suggests that the absence of a correlation between high soil temperatures and near-neutral pH SCC may result from the increasing solubility of CO₂ in water at lower temperatures^[28]. As more CO₂ dissolves in groundwater, the ability of the cathodic protection system to raise the pH at the pipe surface is greatly reduced.

2.3 Rock Bolt Corrosion and Stress Corrosion Cracking

2.3.1 Rock Bolt Corrosion

Rock bolt corrosion is a common problem that has largely been ignored by the mining industry until recently. Villaescusa et al.^[95, 96] developed a corrosivity classification for the hard rock mining (metalliferous) industry in Australia. More recently, work has been done by Spearing, et al.^[97, 98], as well as by Hadjigeorgiou, et al.^[99] to classify corrosion in US and Canadian mines. In Europe, the German standard DIN 50929 has been used by a number of industries to classify the severity of ground water conditions on metal structures. However there is not a clear relationship between the classifications given in the standard and observed corrosion rates^[100].

The work of Villaescusa et al.^[95, 96] focused on analyses of water collected from a number of mines across Australia and Western Australia. They concluded that the existing corrosion classification standards were not appropriate in the Australian hard rock mining context. Similar work was later carried out on Canadian and US mines by Hadjigeorgiou, et al.^[99] and Spearing et al.^[97, 98].

Hadjigeorgiou et al. examined the progressive corrosion of ground support from a number of mines, collating this data with the age of the support and the ground water conditions. They found a relationship between these factors with the corrosion rates in ground support structures ranging from 0.07 to 1.4 mm/year.

Spearing et al. investigated the effect of corrosion on the serviceability of rock bolts. They devised a testing facility which stimulated the in situ conditions rock bolts were typically exposed too. Over the course of the test, the environment was left stagnant and not regularly replenished. As a result, chemical species were consumed during the corrosion process and excessive Fe^{2+} ions began to build up in the solution. Hence, the chemical composition of the testing medium migrated away from the initial testing conditions. This work highlighted the importance of either using a steady stream of flowing testing solution or refreshing the testing solution at regular intervals to maintain chemical stability.

2.3.2 Stress Corrosion Cracking Failures of Rock Bolts in Underground Coal Mines

SCC failure of rock bolts was first reported by Gray^[4] in 1998 following the observation of brittle fractures at stresses below the ultimate strength in underground coal mines in Australia. Subsequently, Crosky et al. carried out a study of 44 bolts, which had failed in a brittle manner, from 4 different underground coal mines in Australia^[28]. Only the section of bolt from the fracture to the protruding end (i.e., the threaded end was available for examination, since the rest of the bolt remained embedded in the roof of the mine. All but one of the bolts were 22 mm in diameter. Additionally, all bolts except for one had failed in the shank, with the remaining bolt having failed in the threaded end. It is noted that a preload of 10-14 tonnes is applied on installation of the rock bolts in Australian mines. This corresponds to a stress of approximately 260-370 MPa.

The failed bolts had been made from a range of different grades of steels, these being AISI 1040, AISI 1050, AISI 1355, AISI 5152, and a silicon manganese 0.4%C vanadium-microalloyed steel known as HSAC 840 (840 MPa UTS). These represented essentially the full range of grades that were in use at the time. The chemical compositions of the rock bolts examined are given in Table 2-7.

The rock bolts had also been made by a range of different processes, namely hot rolling to the final profile (including rib pattern), cold rolling of the rib pattern onto hot rolled bars, and hot rolling to the final profile then surface hardening on cooling using the Tempcore process.

Despite the range of compositions and processing methods, all of the failed bolts were found to have the following similarities:

- A fracture surface perpendicular to the axis of the bolts

- An absence of significant necking in the vicinity of the fracture
- Slight bending (usually) in the vicinity of the fracture
- Nucleation of the fracture at the base of a rib
- A discoloured region at the fracture origin.

Table 2-7: Chemical composition of rock bolts examined by Crosky et al^[5].

Bolt ID	Bolt Type	Steel Grade	%C	%Mn	%Si	%Ni	%Cr	%Mo	%S	%P	%Cu	%Nb	%V	%Ti	%Al	%B
1	HPC ¹	1340 ²	0.41	1.83	0.21	0.01	0.02	<0.01	0.120	0.026	0.01	0.01	0.12	0.01	0.01	0.003
2	HPC	840	0.38	1.60	1.08	0.01	0.03	<0.01	0.015	0.017	0.01	0.01	0.06	0.01	0.01	0.001
3	HPC	840	0.38	1.59	1.05	0.01	0.03	<0.01	0.014	0.016	0.01	0.01	0.06	0.01	<0.01	0.001
4	Thread	1050	0.49	0.67	0.19	0.07	0.19	<0.01	0.026	0.008	0.24	<0.01	0.01	<0.01	<0.01	<0.001
5	Thread	1050	0.52	0.67	0.20	0.07	0.19	<0.01	0.031	0.011	0.25	<0.01	0.01	<0.01	<0.01	<0.001
6	Thread	1050	0.52	0.67	0.19	0.07	0.19	<0.01	0.030	0.011	0.25	<0.01	0.01	<0.01	<0.01	<0.001
7	AVH	5150	0.49	0.76	0.23	0.06	0.80	0.01	0.016	0.008	0.14	<0.01	0.01	0.01	<0.01	<0.001
8	AVH	5150	0.50	0.83	0.21	0.05	0.83	0.01	0.020	0.011	0.11	<0.01	0.01	0.01	<0.01	<0.001
9	AVH	5150	0.48	0.79	0.19	0.05	0.80	0.01	0.017	0.010	0.10	<0.01	0.01	<0.01	<0.01	<0.001
10	AVH	5150	0.49	0.78	0.24	0.05	0.82	0.02	0.024	0.011	0.10	<0.01	0.01	<0.01	<0.01	0.001
11	AX	1355	0.54	1.70	0.25	0.09	0.10	0.02	0.032	0.012	0.28	<0.01	0.01	0.01	<0.01	0.001
12	AVH	5150	0.48	0.81	0.26	0.04	0.73	<0.01	0.020	0.012	0.11	<0.01	0.01	<0.01	<0.01	<0.001
13	AVH	5150	0.50	0.82	0.19	0.06	0.73	<0.01	0.016	0.007	0.10	<0.01	0.01	<0.01	<0.01	<0.001
14	AVH	5150	0.51	0.79	0.20	0.04	0.81	<0.01	0.018	0.011	0.11	<0.01	0.01	0.01	<0.01	0.001
15	AVH	5150	0.50	0.70	0.22	0.02	0.81	0.03	0.019	0.007	0.07	<0.01	0.01	<0.01	<0.01	<0.001
16	AVH	5150	0.53	0.75	0.27	0.03	0.85	0.04	0.023	0.009	0.08	<0.01	0.01	0.01	<0.01	0.001
17	AVH	5150	0.53	0.72	0.25	0.03	0.83	0.03	0.022	0.009	0.07	<0.01	0.01	0.01	<0.01	0.001
18	AVH	5150	0.52	0.72	0.24	0.03	0.82	0.03	0.019	0.008	0.07	<0.01	0.01	<0.01	<0.01	<0.001
19	AXR	1355	0.55	1.36	0.20	0.11	0.08	0.03	0.016	0.007	0.25	0.01	0.01	0.01	<0.01	0.001
20	AXR	1355	0.51	1.36	0.26	0.08	0.10	0.02	0.012	0.009	0.18	0.01	0.01	0.01	<0.01	0.001
21	AXR	1355	0.60	1.38	0.28	0.08	0.11	0.02	0.022	0.012	0.21	0.01	0.01	0.01	0.01	0.002
22	AXR	1355	0.52	1.50	0.28	0.12	0.16	0.03	0.028	0.027	0.24	0.01	0.01	0.01	<0.01	0.001

23	AXR	1355	0.53	1.31	0.26	0.09	0.17	0.03	0.019	0.019	0.15	0.01	0.01	0.01	<0.01	0.002
24	Wriggle	1040	0.40	0.67	0.15	0.08	0.10	0.02	0.019	0.014	0.24	<0.01	<0.01	<0.01	<0.01	0.001
25	AXR	1355	0.53	1.41	0.27	0.08	0.16	0.02	0.026	0.033	0.25	0.01	0.01	0.01	<0.01	0.002
26	AXR	1355	0.53	1.38	0.25	0.08	0.15	0.02	0.023	0.032	0.25	0.01	0.01	0.01	<0.01	0.001
27	AXR	1355	0.54	1.41	0.25	0.08	0.14	0.02	0.027	0.021	0.17	<0.01	0.01	0.01	<0.01	0.002
28	X ¹	1050	0.50	0.68	0.19	0.01	0.02	<0.01	0.014	0.018	0.02	<0.01	0.01	<0.01	0.03	0.001
29	Unknown	1355	0.55	1.44	0.27	0.11	0.11	0.02	0.028	0.025	0.25	0.01	0.01	0.01	<0.01	0.002
30	Unknown	1355	0.53	1.53	0.27	0.11	0.11	0.03	0.028	0.024	0.22	0.01	0.01	0.01	<0.01	0.002
31	Unknown	1355	0.56	1.52	0.29	0.08	0.13	0.02	0.018	0.022	0.18	0.01	0.01	0.01	<0.01	0.002
32	X ¹	1050	0.51	0.72	0.21	0.01	0.04	0.01	0.020	0.017	0.01	<0.01	0.01	<0.01	0.03	0.001
33	X	1355	0.54	1.68	0.27	0.07	0.06	0.02	0.003	0.010	0.27	0.01	0.01	0.01	<0.01	0.002
34	X	1355	0.51	1.62	0.27	0.08	0.06	0.02	0.025	0.010	0.27	0.01	0.01	0.01	<0.01	0.002
35	X	1355	0.53	1.60	0.26	0.07	0.06	0.02	0.025	0.010	0.26	0.01	0.01	0.01	<0.01	0.002
36	X	1355	0.53	1.62	0.27	0.08	0.06	0.02	0.027	0.011	0.27	0.01	0.01	0.01	<0.02	0.002
37	X	1355	0.54	1.68	0.28	0.08	0.07	0.02	0.028	0.013	0.23	0.01	0.01	0.01	<0.03	0.002
38	X	1355	0.53	1.56	0.27	0.09	0.08	0.02	0.022	0.008	0.21	0.01	0.01	0.01	<0.04	0.002
39	X	1355	0.50	1.50	0.26	0.08	0.07	0.02	0.020	0.008	0.20	0.01	0.01	0.01	<0.01	0.002
40	X	1355	0.53	1.56	0.28	0.09	0.08	0.03	0.020	0.009	0.20	0.01	0.01	0.01	<0.01	0.002
41	X	1355	0.55	1.57	0.27	0.09	0.08	0.02	0.022	0.009	0.21	0.01	0.01	0.01	<0.01	0.002
42	X	1355	0.55	1.75	0.32	0.07	0.08	0.02	0.026	0.012	0.21	0.01	0.01	0.01	0.01	0.002
43	X	1355	0.54	1.73	0.32	0.07	0.08	0.02	0.024	0.012	0.22	0.01	0.01	0.01	<0.01	0.002
44	AVH	5150	0.47	0.79	0.19	0.05	0.65	0.02	0.009	0.006						

¹Tempcore

²Resulphurised grade



Figure 2-26: Subcritical (secondary) cracks along the base of some ribs of a failed rock bolt, as revealed by magnetic particle inspection^[5].

Magnetic particle inspection frequently revealed a series of small secondary (subcritical) cracks along the base of some of the ribs. An example is shown in Figure 2-26.

Examples of the fracture surfaces seen on the failed rock bolts are shown in Figure 2-27. All are characterized by small thumbnail-shaped dark discoloured regions at the fracture origin. The depth of the thumbnail-shaped region was $\sim 1\text{-}7$ mm. In many cases, more than one of these dark thumbnail-shaped regions was present, sometimes overlapping and sometimes discrete, Figure 2-27.

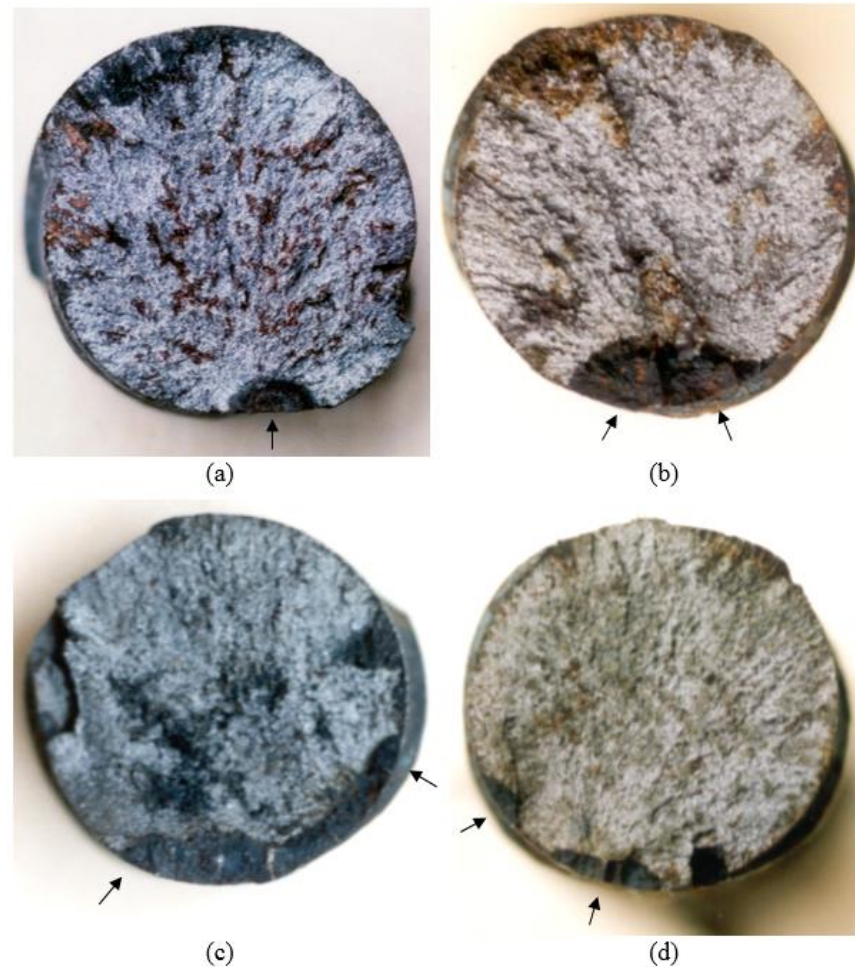


Figure 2-27: Examples of fracture surfaces showing thumbnail-shaped dark discoloured regions (arrowed) at fracture origin (a) single dark region, (b) two overlapping dark regions, (c) multiple overlapping dark regions (between arrows) and (d) discrete dark regions^[5].

Fractographic studies of the broken rock bolts showed that the discoloured region of the fracture surface was consistent with SCC, while the region beyond the SCC zone had failed by brittle cleavage, Figure 2-28. Metallographic examination of subcritical cracks often revealed branching.

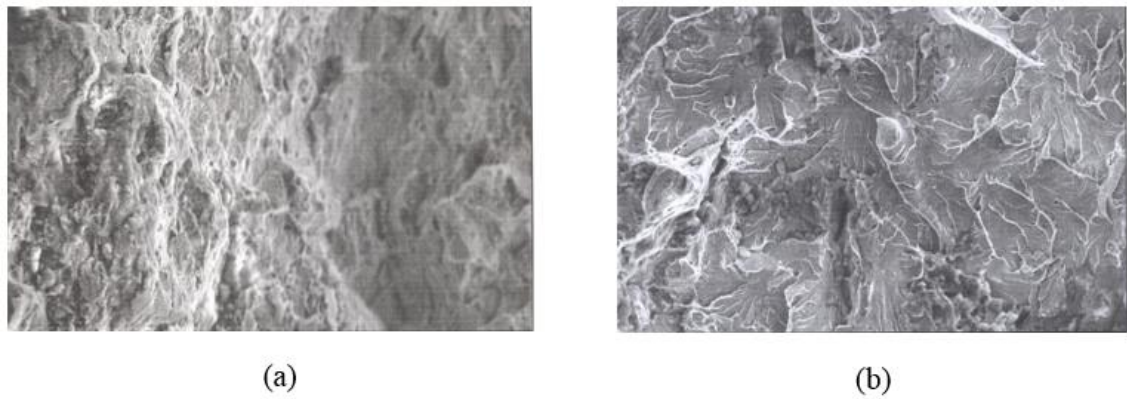


Figure 2-28: SEM fractographs of typical fracture surface showing (a) SCC region and (b) overload region

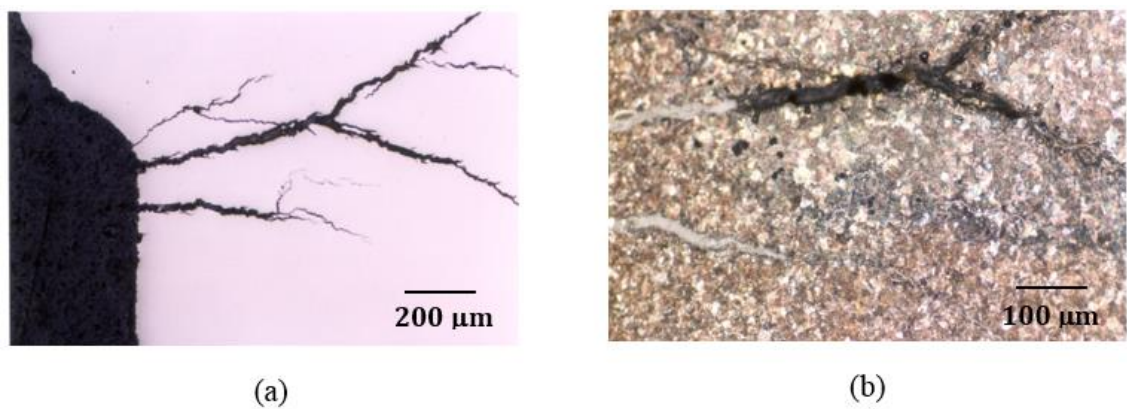


Figure 2-29: Optical micrograph of subcritical cracks in a failed rock bolt (a) unetched and (b) corresponding region at higher magnification after etching in 2% Nital.

The failed Australian rock bolts, had essentially three different microstructures:

- A predominantly pearlitic microstructure with small amounts of ferrite (1050, 1355 and 5152 steel)
- A mixed pearlitic/ferritic microstructure (840 grade steel)
- Tempered martensite outer layer with a pearlitic core (Tempcore processed steel)

The rock bolts also exhibited a decarburized surface layer which resulted from the hot rolling used in their manufacture.

It was found that the rock bolts generally had low Charpy impact toughness with the values being in the range 4-9 Joules except for the Tempcore processed bolts which had values of 14-16 Joules^[101].

Most of the failed bolts showed evidence of a slight bend near the location of the fracture, with the fracture origin being located on the tension side of the bend.

Rock bolt failures also occurred in a number of underground coal mines in the United Kingdom (UK), where Australian Technology (AT) rock bolts were also being used^[102]. A detailed review of these failures is given in Crosky et al.^[5]. As in Australia, the rock bolts were 22 mm in diameter.

As for the failed rock bolts from Australian mines, the UK rock bolts had failed in a brittle manner perpendicular to their axes. However, unlike the Australian rock bolts, only a single steel chemistry was used in the UK. Additionally, a preload of less than 2 tonnes was used when installing the rock bolts^[103] compared with 10-14 tonnes in Australia.

The steel used in the UK bolts was a 0.3% carbon vanadium-microalloyed steel with a microstructure consisting of approximately 75% ferrite and 25% pearlite^[104], as is typical of hot rolled steel of this composition in the normalized condition^[105]. The steel exhibited a similar low impact toughness to that found for the majority of the Australian bolts^[102]. A water analysis taken from the vicinity of rock bolt failures in one of the UK mines is given in Table 2-8^[106]. The water had a neutral pH (7.1) but a very high salinity (142,000 mg/l) which was several times that of seawater.

Table 2-8: Analysis of minewater sample taken from vicinity of rock bolt failures in one of the UK mines^[106].

Analysis	Value
pH	7.1
Total Hardness	7441 mg/l
Total Alkalinity	157 mg/l
Total Iron	6.5 mg/l
Calcium	22100 mg/l
Magnesium	4100 mg/l
Barium	1510 mg/l
Strontium	1050 mg/l
Sodium	67200 mg/l
Carbonate	94 mg/l
Sulphate	28 mg/l
Chloride	142000 mg/l

In one case, a roof failure occurred permitting the full length of the rock bolts to be retrieved and it was found that the rock bolts had been bent into a flattened S-shape, with the fracture occurring at the corners of the bend, as shown in Figure 2-30. The retrieved rock bolts are shown in Figure 2-31.

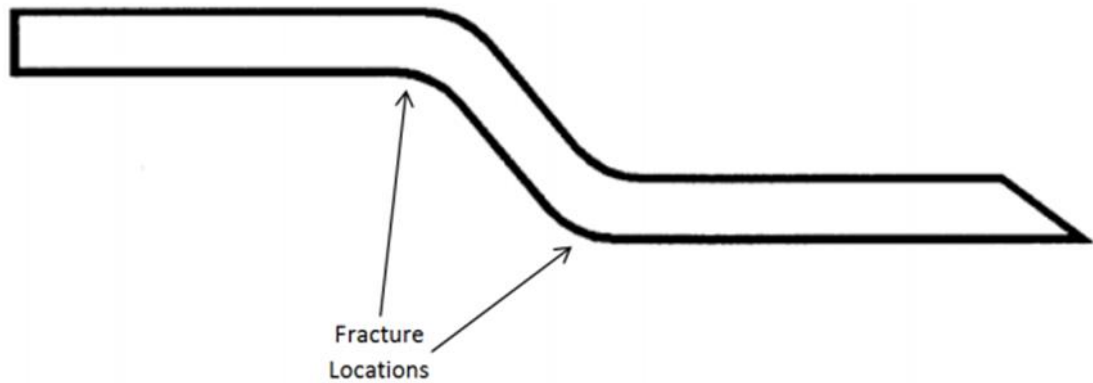


Figure 2-30: Bending of rock bolts prior to failure^[102].

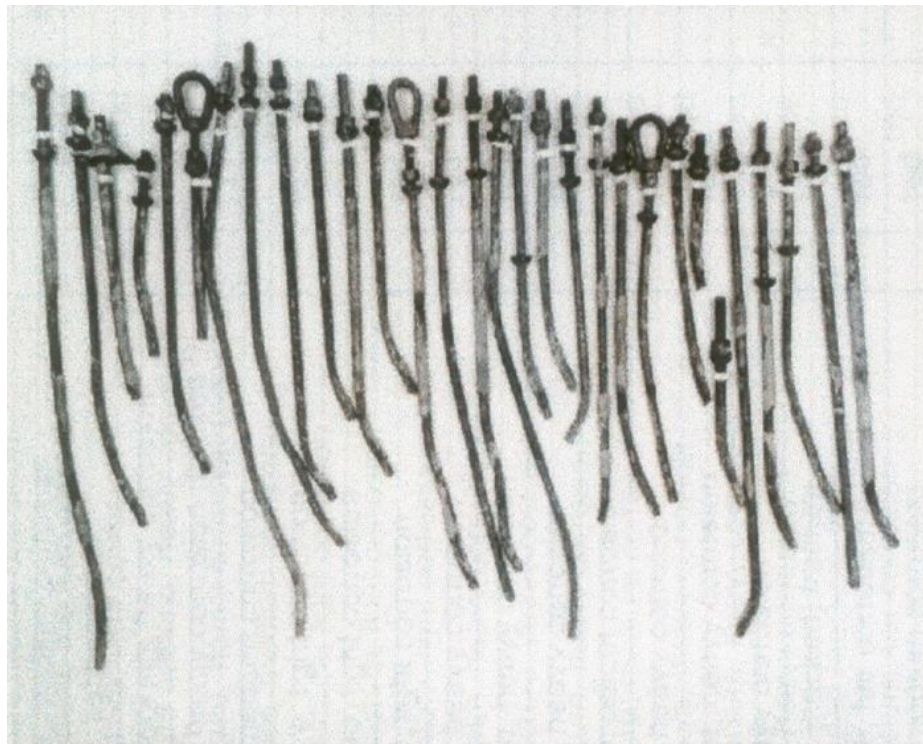


Figure 2-31: Failed rock bolts retrieved from UK mine after roof failure^[106].

Of the 30 fractured rock bolts retrieved from the failed roof and a further 10 from other mines, only one appeared to have failed by SCC. For the remainder, failure was considered to have been initiated by stress concentrators produced by corrosion pitting. Only two of the 40 bolts had failed in the threaded region at the end of the bolt.

The rock bolt which had failed by SCC showed a very dark region (the SCC region) which extended to a depth of 0.75 mm. The fracture surface in this region was reported to be intergranular in nature, with the remainder of the fracture being brittle transgranular cleavage. Additional transverse cracks were observed near the fracture surface and sections through these cracks revealed that they were branched and intergranular, Figure 2-32^[106].

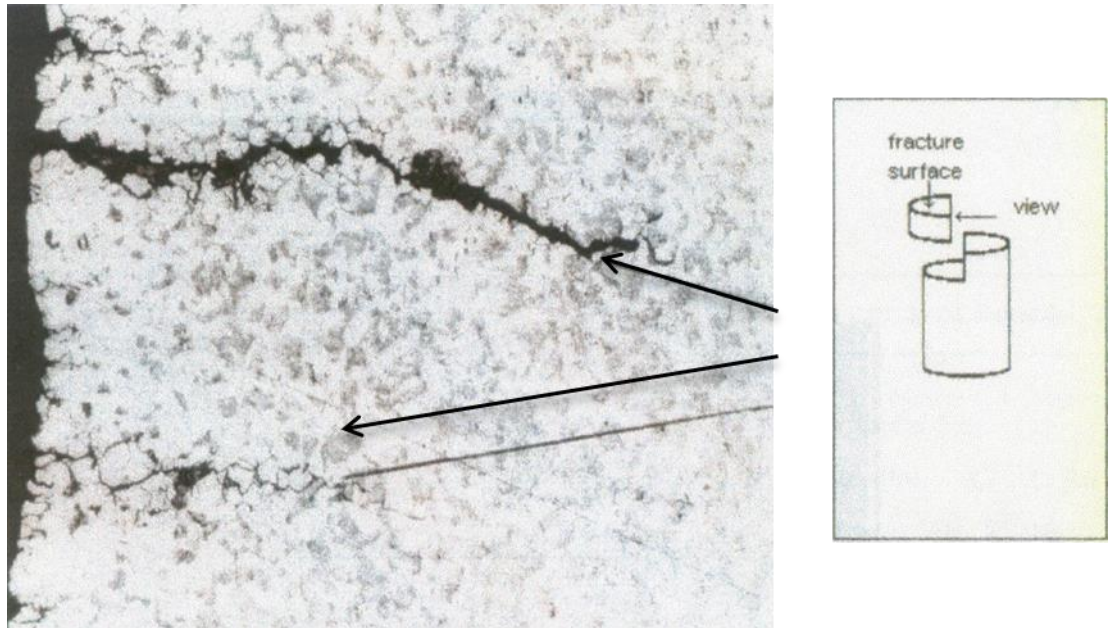


Figure 2-32: Branched intergranular cracks (arrowed) near fracture surface of UK rock bolt which failed by SCC at 100x magnification^[106].

Three of the bolts considered to have failed from the stress concentration resulting from corrosion pitting were sectioned and limited evidence was seen of intergranular cracking originating from some of the corrosion pits in at least one of these bolts. Figure 2-33^[106]. All of the additional cracks were reported to have initiated on the tension side of the bend, as was also found in Australia.

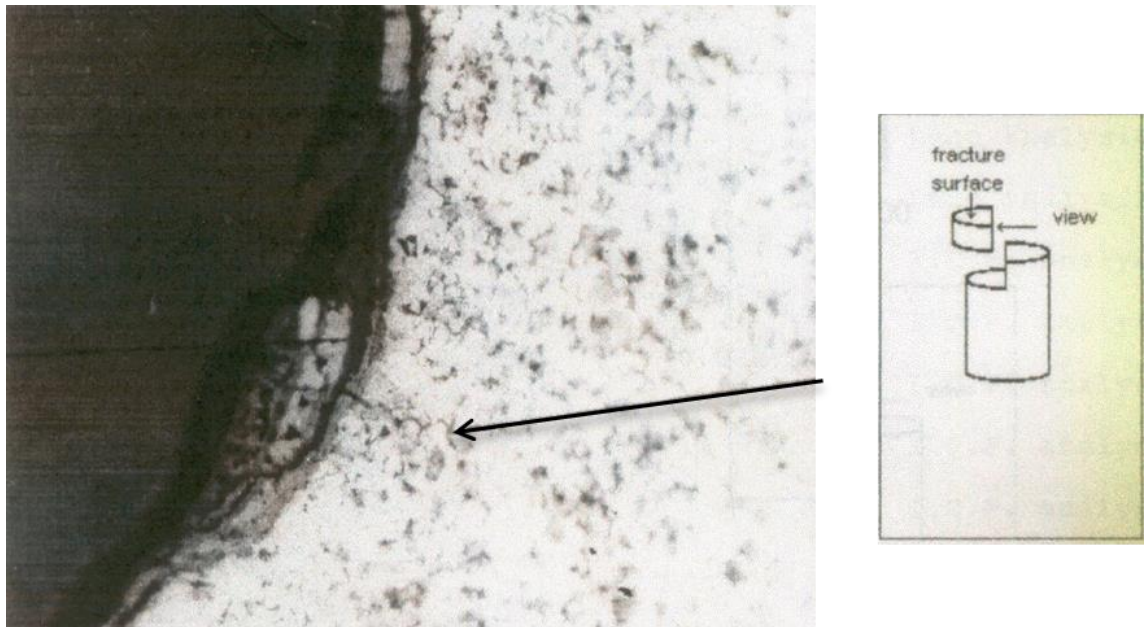


Figure 2-33: Intergranular crack (arrowed) originating from corrosion pit in failed UK rock bolt at 100x magnification^[106].

All the failed rock bolts showed some degree of corrosion, but some of the fracture surfaces were heavily corroded, indicating that these rock bolts had failed a considerable time before the roof collapsed^[102].

The findings from the UK study led to the conclusion that the rock bolt failures were induced by strata shear in the roof of the mine which produced the S-shape bending^[102]. It was considered that the bending of the rock bolts caused the brittle polyester grout to crack at the bend allowing an ingress of ground water to this now highly stressed region of the rock bolt, thereby facilitating SCC^[103]. It was noted that in some cases the grouting may not have extended the full length of the bolt providing direct access for the mine water in the ungrouted region.

The failed bolts from the Australian mines examined by Crosky et al.^[5] all failed below the resin encapsulation (also referred to as the grouted horizon). However, these bolts had been retrieved after falling from the roof. Bolts which fail within the encapsulation length should generally remain anchored within the roof, so that the only bolts which fall from the roof (and are thus available for examination) are those which fail below the resin encapsulation.

Two bolts were, however, obtained in a later study^[107] that had failed within the encapsulation length^[107]. One of these is shown in Figure 2-34, Figure 2-35 and Figure 2-36. A bend is present in the rock bolt about one third of the distance between the fracture

and the protruding end, Figure 2-34. Cracking and spalling of the grout can be seen in this region, Figure 2-34 and Figure 2-36, confirming Shutter et al.'s^[103] proposal that cracking of the grout occurs exposing the underlying metal when the rock bolts are bent as result of strata shear. Cracking and spalling of the grout is also evident in the vicinity of the fracture in this bolt, Figure 2-35.



Figure 2-34: Bolt broken in grouted region. The bolt contains a bend (arrowed) about one third of the way between the fracture and the protruding end^[107].



Figure 2-35: Close up view of fracture in bolt shown in Figure 2-34^[107].

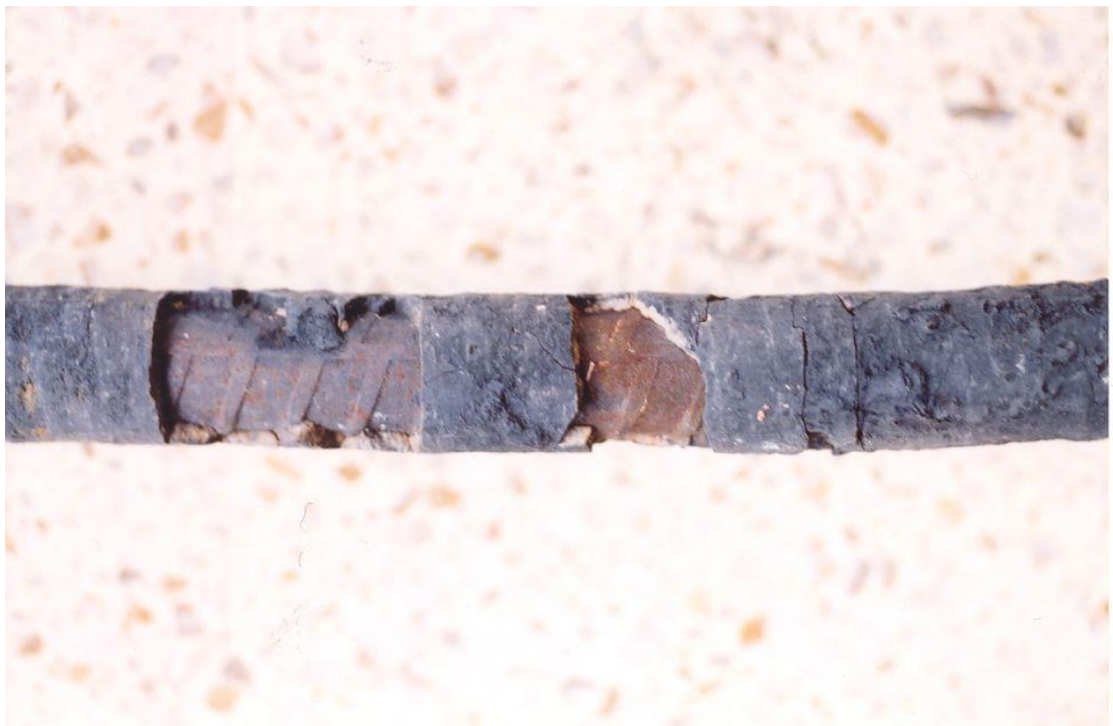


Figure 2-36: Close up view of cracking and associated spalling of grout at bend arrowed in Figure 2-34^[107].

For the low toughness steel used in the UK rock bolts it was demonstrated that a pit 1 mm deep with an aspect ratio of 6 was sufficient to initiate failure in a rock bolt when loaded to its yield strength^[102]. Accordingly, the toughness of rock bolt steel was increased

substantially (which as shown in Section 2.2.5.8, increases the depth to which a defect can grow before causing catastrophic failure) with a minimum requirement of 27 Joules, and the incidence of failure decreased enormously^[108]. It is, however, noted that a significant failure again occurred in 2011, although the precise details are not available.

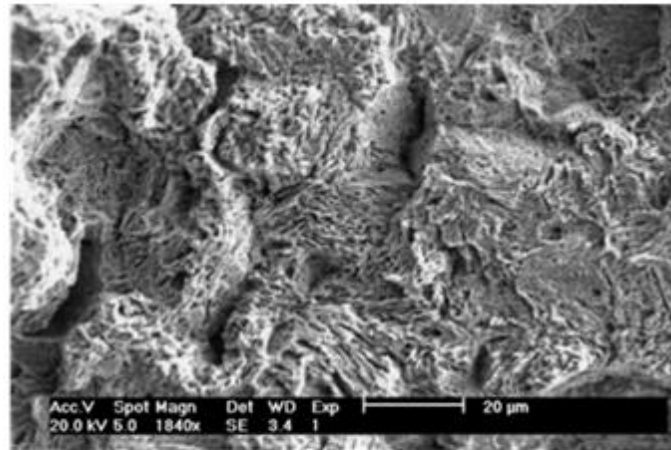
In Australia, there was also a change to tougher steel, with the grades of steel previously used being replaced by HSAC 840 steel with a toughness of 18-20 Joules. This initially had considerable success but eventually failures again began to be reported.

Prior to the change to a single tougher grade of steel, Gamboa and Atrens^[6] undertook a fractographic analysis of failed rock bolts from four Australian coal mines. In a subsequent publication, Villalbo and Atrens^[109] indicated that the rock bolts were made from AISI 1355 steel^[109]. However, it is evident from Reference 24 that only three of the six rock bolts were examined by Gamboa were AISI 1355 with the others being AISI 5152 (one bolt) and HSAC 840 (two bolts). One of the bolts was found to contain secondary (subcritical) cracks at the base of the ribs^[24] as was also observed in some of the bolts examined by Crosky et al.^[101]

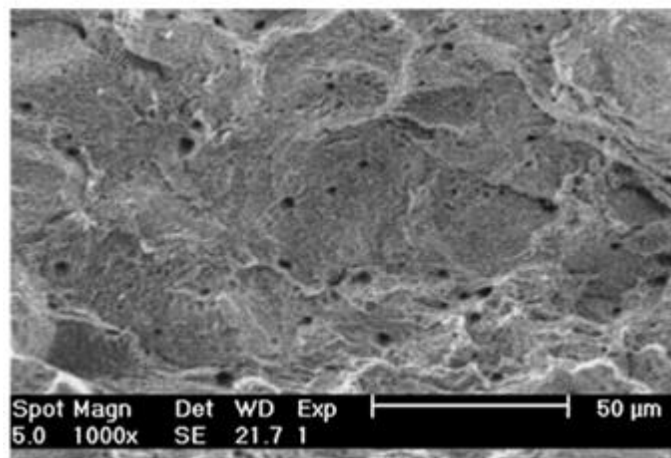
As found by Crosky et al.^[101], the fracture surfaces of all but one of the six bolts consisted of a small thumbnail-shaped SCC region surrounded by a brittle catastrophic failure region. The remaining rock bolt was considered to have failed by corrosion fatigue induced by a fan suspended from the rock bolt and was not examined further^[24].

From their study, Gamboa and Atrens concluded that the SCC fracture surfaces consisted of three different fracture morphologies, tearing topography surfaces (TTS), corrugated irregular surface (CIS), and micro void coalescence (MVC)^[6]. These are shown in Figure 2-37. Gamboa reported that the fracture surfaces had the same features for all three grades of steel.

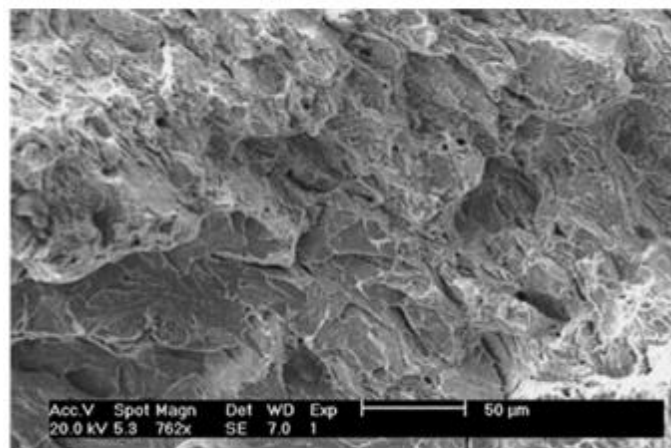
TTS occurred closest to the surface of the rock bolts, while MVC was mainly located at the end of the SCC zone (i.e., adjacent to the catastrophic overload fracture region). No evidence of any additional morphologies was seen in the transition regions between the three different fracture morphologies. Gamboa and Atrens also reported that the fracture features bore no association with the underlying microstructure^[6].



(a)



(b)



(c)

Figure 2-37: Scanning electron fractographs showing the three different fracture modes (a) tearing topography surface (TTS), (b) corrugated irregular surface (CIS) and (c) micro void coalescence (MVC). A region of the final catastrophic brittle cleavage failure can be seen in the bottom right hand side of (c)^[6].

The terminology used by Gamboa and Atrens was based on that used by Toribio and coworkers^[110, 111] to describe the fractographic features they observed in hydrogen-charged notched and precracked eutectoid pearlitic steel. They reported that there was a gradual change from TTS to MVC (which they termed quasi-MVC) but didn't report the presence of the intermediate CIS morphology seen by Gamboa and Atrens.

Toribio and coworkers^[110, 111] considered that the TTS morphology represented the fracture morphology for hydrogen induced failure in pearlitic steels. It was proposed that quasi-MVC was a precursor to TTS and occurred ahead of the growing crack tip where the hydrogen concentration was insufficient for hydrogen induced cracking. They considered that microvoids are nucleated in this only weakly hydrogenated region, by a hydrogen assisted nucleation mechanism, and then subsequently grow. As the hydrogen content increases more microvoids are nucleated. The now closely spaced microvoids link up under a stronger hydrogen influence to progressively form the TTS topography. They considered that the mechanism of hydrogen-enhanced void growth was different to that in the absence of hydrogen^[111].

Based on the above, the quasi-MVC topography was considered to be a mixture of hydrogen-induced microvoids and regions of cleavage produced in the material which remained between the voids when final overload failure occurred^[111].

In view of the similarity between the fracture features seen on rock bolts and those seen on hydrogen charged pearlitic steels, Gamboa and Atrens proposed that SCC failure of rock bolts also occurred by a hydrogen-assisted mechanism^[6]. They postulated that as the corrosion reaction occurs, hydrogen released at the crack tip diffuses to the triaxial region ahead of the crack tip, embrittling the steel once it reaches a critical concentration. They considered that the region ahead of the crack tip having the critical hydrogen concentration was flame shaped due to the combined effects of the concentration gradient and the triaxial stress state ahead of the crack tip as is shown in Figure 2-38.

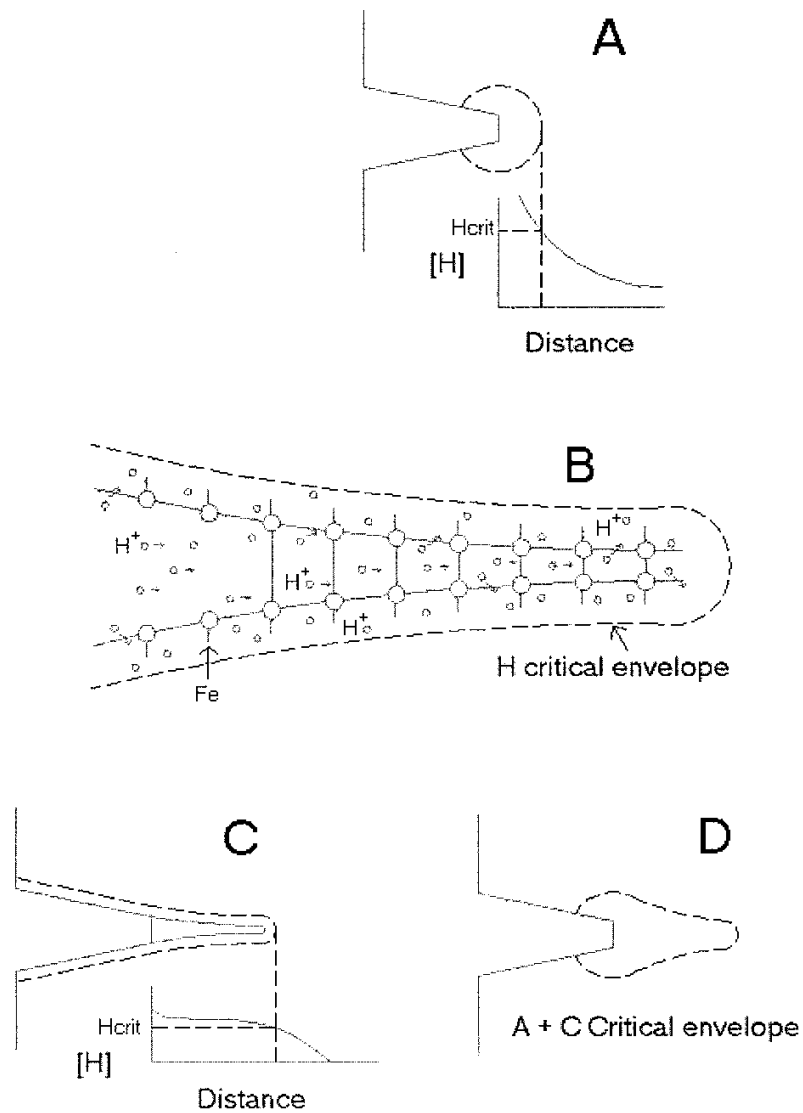


Figure 2-38: Embrittled region ahead of crack tip as proposed by Gamboa and Atrens^[6].

It was considered that a crack could grow in any direction within the embrittled flame-shaped region. However, cracks not parallel to the flame axis would eventually reach the perimeter of the embrittled region, where there was now insufficient hydrogen for continued propagation. At this point, the crack would turn back into the embrittled region and then continue to grow. The process is shown schematically in Figure 2-39. Gamboa and Atrens considered that the fractographic features observed by them were consistent with this mechanism^[6].

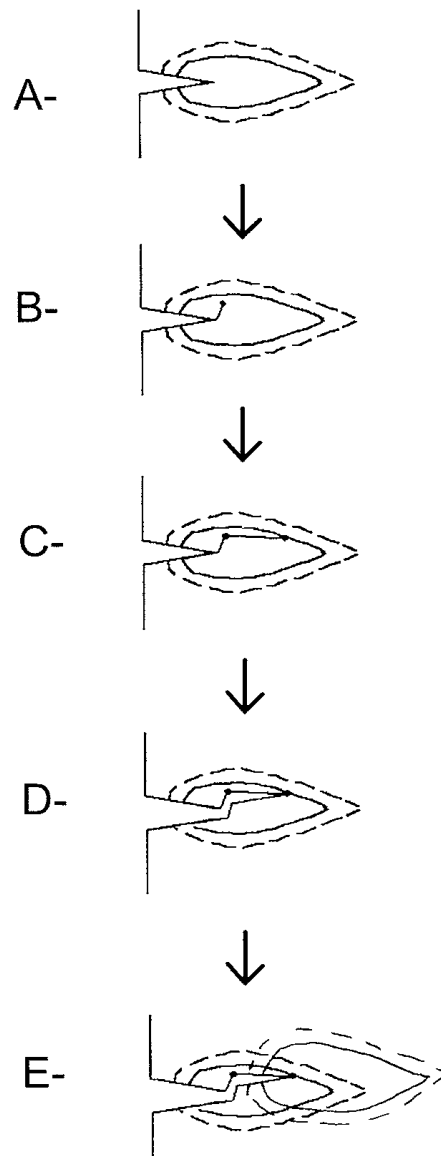


Figure 2-39: Proposed mechanism for crack propagation^[6].

Recently, Kang et al.^[112] reported SCC failure of rock bolts in underground coal mines in China. The rock bolts were again Australian Technology rock bolts and, as in Australia and the UK, they were resin anchored bolts 22 mm in diameter. The rock bolts were hot rolled ribbed bolts with a yield strength of 600 MPa. The chemical composition of the bolts was not reported. High pretension was used when installing the bolts^[112].

Kang et al. reported that in China the rock bolts can be point anchored, partially anchored, or fully anchored, depending on the resin encapsulation length. The most commonly used bolt is a partially anchored bolt with an anchor length of 1-1.5 metres^[112].

Kang et al. focused on partially anchored bolts and reported that these failed mainly in the threaded region at the end of the bolt and their study was restricted to such failures.

The present study excludes thread failures, since they represent only a few percent of the failures seen in Australia, and, accordingly, the work in this area is not considered here.

Kang et al. did, however, note that some bolt failures occurred within the shank of the bolt and reported that such failures occurred, in some cases at the interface between the free and anchored part of the bolt, but in other cases within the anchored part of the bolt at intersections with a geological parting. They reported that for fully anchored bolts, fracture generally occurred within the anchored region and only occasionally at the threaded end^[112].

They also examined bolts from a collapsed roof and reported that these were bent in several locations, Figure 2-40. This is consistent with the UK finding of bending from strata shear.



Figure 2-40: Bent rock bolts obtained from a collapsed roof in Chinese coal mine^[112].

Kang et al.^[112] suggested a number of methods to remedy rock bolt failure. These included improving the toughness of the steel (as has been done in Australia and the UK), as well as reducing the residual stress in the bolts.

Anecdotal evidence from the international mining community has indicated that SCC failure of rock bolts has also occurred in several other countries. The problem thus appears to be of international significance.

2.3.3 Laboratory Investigation into Rock Bolt Stress Corrosion Cracking

2.3.3.1 Slotted Coupon Testing

The first reported laboratory testing of SCC in rock bolts was that conducted by Parrott^[104] after the roof failure in the UK. He used specimens taken from rock bolts into which a central slot had been cut, as shown in Figure 2-41. A tensile stress was generated in the two sides of the specimen by inserting a 15 mm diameter round mandrel at the mid-point. It was found, from examination of untested specimens after removal of the mandrel, that the tensile stress in the sides of the specimen was slightly above yield.

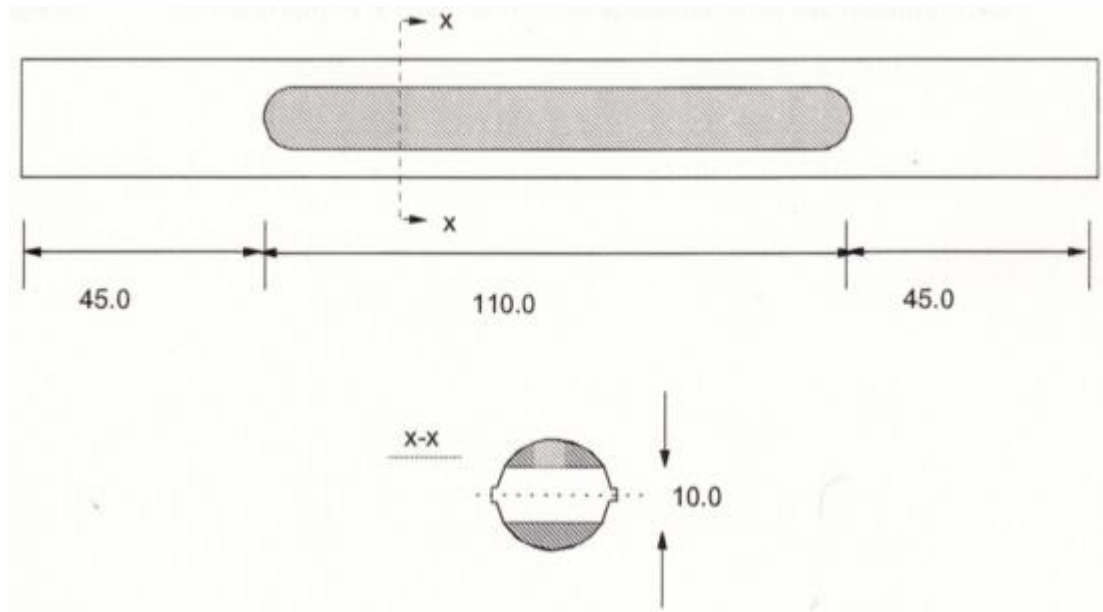


Figure 2-41: Diagram giving the dimensions of the stress corrosion specimens^[104].

Prior to testing, the outer surface of each side of the specimen was masked with tape and the entire specimen then dipped in paraffin wax. The masking tape was then removed from the outer surfaces of the specimen sides so that corrosion was confined to these areas.

Four replicate specimens were then immersed in each of the following solutions at ambient temperature:

- acidified 3.5% sodium chloride solution containing hydrogen sulphide
- 3.5% sodium chloride solution
- minewater collected from the site of the roof failure

The test period was 1000 hours for the acidified sodium chloride solution containing hydrogen sulphide and 12 weeks for the remaining solutions. Each specimen was

removed once every 24 hours and examined visually for evidence of cracking. The results of the stress corrosion tests in the three solutions are given in Table 2-9, Table 2-10 and Table 2-11. Three of the four specimens exposed to the acidified sodium chloride solution containing hydrogen sulphide underwent failure but the specimens exposed to the other solutions did not.

Table 2-9: SCC test results for specimens placed in an acidified 3.5% sodium chloride solution containing hydrogen sulphide solution^[104].

Specimen ID	Time to Failure / Hours	Position of fracture
1	804	Through one side at center of rib
2	522	Through one side following rib
3	216	Through one side at center of rib
4	Unbroken after 1000	-

Table 2-10: SCC test results for specimens placed in a 3.5% sodium chloride solution^[104].

Specimen ID	Time to Failure / Weeks	Observations
5	Unbroken after 12 weeks	Heavy rusting
6	Unbroken after 12 weeks	Heavy rusting
7	Unbroken after 12 weeks	Heavy rusting
8	Unbroken after 12 weeks	Heavy rusting

Table 2-11: SCC test results for specimens placed in minewater^[104].

Specimen ID	Time to Failure / Weeks	Observations
9	Unbroken after 12 weeks	Heavy rusting
10	Unbroken after 12 weeks	Heavy rusting
11	Unbroken after 12 weeks	Heavy rusting
12	Unbroken after 12 weeks	Heavy rusting

The three failed specimens are shown in Figure 2-42, while a low magnification image of the fracture surface of one of the specimens is shown in Figure 2-43. The cracking was reported to be intergranular, Figure 2-44, as in the service failed bolt.



Figure 2-42: Specimens which failed in acidified 3.5% sodium chloride solution containing hydrogen sulphide solution^[104].

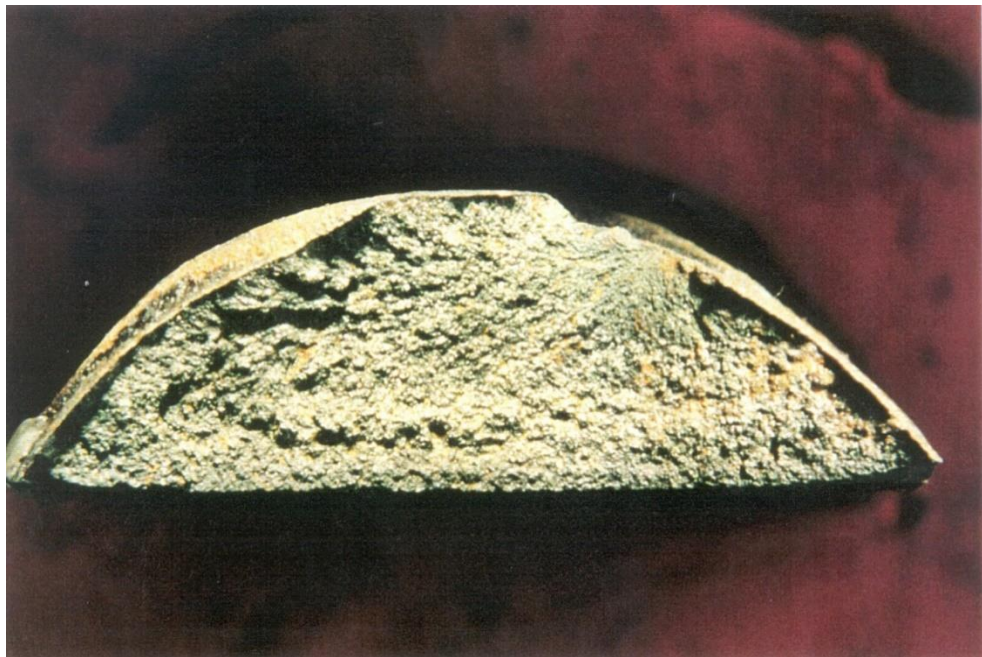


Figure 2-43: Fracture surface of bolt sample failed during stress corrosion cracking testing^[104].



Figure 2-44: Section through fracture surface showing intergranular nature of cracking at 400x magnification^[104].

2.3.3.2 Linearly Increasing Stress Testing

An extensive laboratory investigation into SCC of rock bolt steels has been carried out by Atrens and co-workers^[2, 109, 113-115] using the linearly increasing stress test (LIST)^[116]. In this test, small-scale specimens, as shown in Figure 2-45 were placed vertically in a load frame, Figure 2-46, and loaded using a weight and lever mechanism. In order to apply the increasing stress, the weight was moved slowly away from the fulcrum to increase the load. A chemical cell was attached to the gauge section of the test specimen to allow exposure to the test environment. The chemical cell was made from Pyrex glass and had an inlet for gas purging and a condenser for cooling the water vapour. The specimen was sealed inside the cell with two O-rings, seated in grooves machined into the specimen to ensure that only the gauge section of the specimen was exposed to the test environment^[116].



Figure 2-45: LIST test specimens (a) standard specimen, (b) specimen with original surface containing transverse ribs, (c) specimen with original surface containing both transverse and longitudinal ribs.

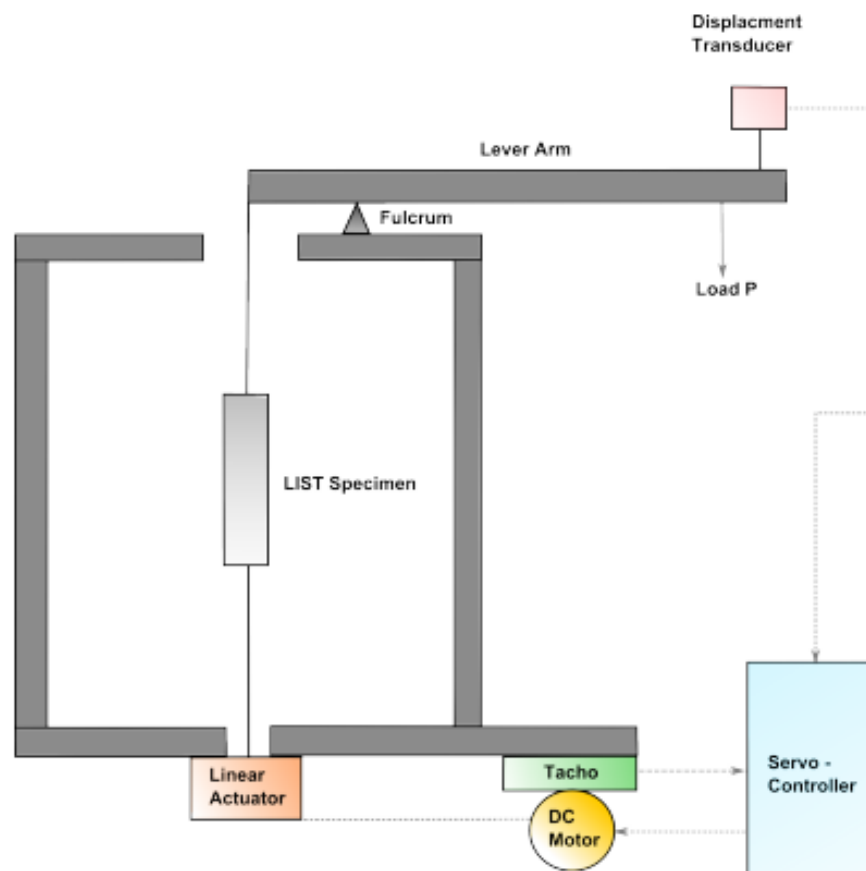


Figure 2-46: LIST testing apparatus.

Specimens were machined from four different grades of commercial rock bolt having the chemistries shown in Table 2-12 and designated by Gamboa and Atrens as Steels A-D. Steel A was AISI 1355^[109, 113], Steel B was the improved toughness carbon silicon vanadium microalloyed steel (HSAC 840) used in Australia, Steel C was the improved toughness carbon manganese vanadium-microalloyed steel used in the UK^[101] and Steel D was AISI 5152^[109]. As noted by Gamboa and Atren^[113], the microalloyed steels were controlled rolled to produce a fine grain size while 5152 was cold worked 10%. The mechanical properties of the four different steels are given in Table 2-13.

Table 2-12: Chemical Composition of Steels Studied by Gamboa and Atrens^[2].

Grade	%C	%Si	%Mn	%P	%S	%Ni	%Cr	%Mo	%Al	%V
Steel A	0.54	0.26	1.63	0.017	0.027	0.09	0.08	0.03	0.004	0.003
Steel B	0.37	1.05	1.46	0.013	0.009	0.01	0.02	0.01	0.004	0.043
Steel C	0.25	0.36	1.32	0.016	0.027	0.07	0.05	0.03	0.005	0.21
Steel D	0.54	0.10	0.90	0.015	0.025	0.35	0.9	0.1	-	-

Table 2-13: Mechanical Properties of Steels Studied by Gamboa and Atrens^[2].

Grade	Yield strength (MPa)	UTS (MPa)	Elongation (%)	Reduction in area (%)	Charpy impact energy (J)
Steel A	622	954	18.0	37.9	6
Steel B	635	873	22.2	50.3	18
Steel C	689	838	21.4	52.2	29
Steel D	745	890	12.0	-	-

Initial SCC testing was conducted on Steel A using the linearly increasing stress test (LIST) with the sample exposed to a sulphate solution with a pH of 2.1^[2]. The applied stress was increased at a rate of 0.019 MPa s⁻¹^[2]. The fractographic features (i.e., the features observed on the fracture surfaces) of samples failed in this way were considered to be essentially identical to those seen on rock bolts failed in service and, on this basis, it was concluded that the test carried out under these conditions could be considered representative of in-service rock bolt SCC.

In subsequent work a chloride solution with a pH of 1.8 was also examined^[2]. It is noted that both solutions were made up from the same four constituents, sulphuric acid (H₂SO₄), sodium chloride (NaCl), sodium carbonate (Na₂CO₃) and distilled water. However, the amount of NaCl was varied so that the sulphate was more predominant in the "sulphate solution" and the chloride more predominant in the "chloride solution", as shown

in Table 2-14. The free corrosion potential for both solutions was reported to be -350 mV vs SHE^[2].

Table 2-14: Formulation of Sulphate and Chloride solutions^[2].

Solution	pH	Sulphate (ppm)	Chloride (ppm)	Carbonate (ppm)
Sulphate	2.1	300	100	100
Chloride	1.8	300	1400	100

Gamboa and Atrens considered that the two standard solutions given in Table 2-14 "might be characteristic of two different chemistries that might be found in underground water samples at mine sites"^[2]. Chemical analyses of the two standard solutions are compared with mine water samples from eight metalliferous mines and one colliery in Figure 2-47. Gamboa and Atrens considered that the chemical composition of the laboratory solutions had similarities to the mine water samples, particularly to three of the samples (EC4, EC8 and EC9) which included the colliery sample (EC8), although they noted that no SCC failures had occurred in any of the mines from which the mine water samples were obtained. While the sodium levels and chloride levels in the mine waters might be a reasonable match, the mine waters are near neutral with pHs ranging from 6.8-8.3, whereas the standard laboratory solutions used by Gamboa and Atrens were highly acidic with pHs of 1-8-2.1.

Sample ID		pH	EC (mS)	Ca (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	S (mg/l)	Cu (mg/l)	TDS (mg/l)	Cl (mg/l)	NO3 (mg/l)	Alkalinity (mg/l) CaCO ₃
EC1	Dam 1	7.61	50.5	835	99	1188	14839	2090	0.015	47221	23600	2.12	312
EC2	Dam 2	7.23	48.8	809	98	1092	13382	1925	0.014	42161	22600	0.05	347
EC3	2K3	8.13	1.88	155	13	109	117	157	0.017	1508	1082	1.24	396
EC4	213	8.32	1.42	91	17	108	96	132	0.018	1183	636	7.95	334
EC5	13DA	6.84	15.3	488	164	4100	831	5854	0.024	30436	83	1.45	211
EC6	13DB	7.12	15.4	489	165	4100	831	5760	0.029	31215	57	7.30	209
EC7	13DC	7.74	16.4	489	189	4420	938	6148	0.004	30480	84	3.09	176
EC8	New entry	7.86	4.39	113	9	165	750	179	0.018	3006	1736	0.99	968
EC9	Pajingo	7.69	4.05	423	9	56	546	464	0.035	3322	1434	0.14	182
	Sulphate	2.1	—	Nil	Nil	Nil	388	540	Nil	—	100	—	100
	Chloride	1.8	—	Nil	Nil	Nil	1942	540	Nil	—	1400	—	50

Figure 2-47: Analyses for Mine Water and Standard Sulphate and Chloride Solutions^[2].

Various modifications of the two standard solutions were also examined. These were as follows:

- Carbon dioxide (CO₂) gas bubbled through the standard sulphate and chloride solutions for the duration of the testing (to examine the effect of deaeration)

- Air bubbled through the standard sulphate and chloride solutions for the duration of the testing with a sample of coal attached to the test piece (to examine the effect of a more positive corrosion potential)
- Standard sulphate solution concentrated 10x, 100x and 1000x with pH unchanged.
- Standard chloride solution concentrated 100x with pH unchanged.
- Standard sulphate solution with modified pH values of 4.2, 6.3 and 9.4.
- Standard chloride solution with modified pH values of 3.1, 7.7 and 10.7.
- Standard sulphate solution with applied potentials of +100, +150, -100 and -300 mV.
- Standard sulphate solution concentrated 100x with modified pH value of 6.1
- Standard sulphate solution concentrated 100x with modified pH value of 6.6 and applied corrosion potentials of -300 and -500 mV
- Standard sulphate solution with modified pH value of 6.2.
- Standard sulphate solution with modified pH value of 7.3 and applied corrosion potential of -300 mV.
- Standard sulphate solution with modified pH value of 7.5 and applied corrosion potential of -570 mV.

The results of testing in these solutions using the LIST procedure are summarised in Figure 2-48. The tests appear to have been carried out principally using Steel A (AISI 1355). It can be seen that SCC occurred for the two standard solutions (LIST 24 and LIST 26) and the modified solutions with the same pH, (LIST 38, 42-44 and LIST 39, 40 and 46) but not for the solutions with less acidic pH values, i.e., the standard solutions with modified pH values (LIST 28, 29 and 34 and LIST 31, 37 and 36). Gamboa and Atrens reported that hydrogen bubbling was observed in the two standard solutions which was considered to indicate that a hydrogen-induced SCC mechanism was involved^[2].

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Sample	Environment	Potential mV vs SHE	SCC
LIST 24	S pH 2.1	-350	Yes
LIST 41	S pH 2.1 and CO ₂	-	Yes
LIST 38	S pH 2.1 and coal, aerated	-	Yes
LIST 44	S pH 2.0, ×10 conc	-	Yes
LIST 43	S pH 2.0, ×100 conc	-	Yes
LIST 42	S pH 2.0, ×1000 conc	-	Yes
LIST 28	S pH 4.2	-350	No
LIST 29	S pH 6.3	-350	No
LIST 34	S pH 9.4	-350	No
LIST 47	S pH 2.1 E_{corr}	-350	Yes
LIST 48	S pH 2.1 E_{corr} + 100 mV	-250	No
LIST 50	S pH 2.1 E_{corr} + 150 mV	-200	No
LIST 49	S pH 2.1 E_{corr} - 100 mV	-450	Yes
LIST 51	S pH 2.1 E_{corr} - 300 mV	-650	Yes
LIST 52	S pH 6.2 E_{corr}	-350	No
LIST 53	S pH 7.27 E_{corr} - 300 mV	-650	No
LIST 54	S pH 7.46 E_{corr} - 570 mV	-920	Yes
LIST 45	S pH 6.16, ×100 conc, E_{corr}	-420	No
LIST 64	S pH 6.6, ×100 conc, E_{corr} - 300 mV	-720	No
LIST 66	S pH 6.6, ×100 conc, E_{corr} - 500 mV	-1120	Yes
LIST 68	S pH 9.7, E_{corr} - 900 mV	-1350	Yes
LIST 85	S pH 1.2, E_{corr} - 150 mV	-350	Yes
LIST 87	S pH 1.2, E_{corr} + 100 mV	-150	Yes
LIST 88	S pH 11.8, E_{corr} 1180 mV	-1300	Yes
LIST 26	C pH 1.8	-350	Yes
LIST 39	C pH 1.8 and CO ₂	-	Yes
LIST 40	C pH 1.8 and coal, aerated	-	Yes
LIST 46	C pH 1.8, ×100 conc	-	Yes
LIST 31	C pH 3.1	-350	No
LIST 37	C pH 7.7	-350	No
LIST 36	C pH 10.7	-350	No

Figure 2-48: Environments and Test Results for LIST Tests^[2].

As noted earlier, the pH of the solutions in which SCC was successfully produced (1.8-2.1) is much lower than that of the near neutral pH (6.8-8.2) mine water samples given by Gamboa and Atrens^[2]. The pH of the mine water sample from the UK was also neutral with a value of 7.1, Table 2-8. Gamboa and Atrens address this discrepancy by suggesting that the local pH conditions at a SCC initiation point (for example, a pit) could be lowered sufficiently by microorganisms in the water^[2].

SCC failure was produced in the modified pH solutions in four cases (LIST 54, 66, 68 and 88) but these all had substantial applied corrosion potentials (i.e., applied anodic potentials) which would not be experienced in underground collieries.

2.3.3.3 Threshold Testing

Gamboa and Atrens also examined the threshold stress for SCC for the four steels given in Table 2-12^[2]. This was done by loading each of the steels to progressively higher stresses until a stress corrosion crack was developed. The steels were held at each of the stress levels for three days. The absence or presence of a stress corrosion crack was determined by cryogenic fracturing each sample to expose any subcritical cracks (cracks that had not grown to a sufficient length to produce catastrophic failure). The specimens

were also examined for corrosion pitting since it was considered that pits could act as initiation sites for SCC cracks. The standard sulphate solution (pH = 2.1) was used for the tests.

Table 2-15: SCC Threshold Stress^[2].

Steel	Yield strength (MPa)	UTS (MPa)	Stress not causing SCC (MPa)	Stress causing SCC (MPa)	Threshold stress (MPa)
Steel A	622	954	770 (NP) ¹ 861 (NP) 885 (NP)	922	900
Steel B	635	873	700 (P-27h) ² 800 (P-30h)	850	850
Steel C	689	838	700 (P-1.3h) 800 (P-50h)	830	815
Steel D	745	890		No SCC failure ³	No SCC failure

¹ NP = no pitting.

² P = pitting - time in hours for pits to develop is also given.

³ Failed by ductile overload without development of any SCC.

The results are given in Table 2-15. The yield strength and ultimate tensile strength (UTS), as given in Table 2-13, are also shown. Stress corrosion cracking was produced in Steels A, B and C, but not in Steel D. The threshold stresses for the 3 steels which did produce SCC were very high, being above the yield strength in all cases. This is consistent with the view of Shutter et al. that failure occurs at bends in the rock bolts produced by strata shear since the stress in the bolts would then be above yield.

However, as noted above, Steel D (5152) did not undergo SCC which is contrary to service experience, with 12 of the 44 bolts examined by Crosky et al.^[5] being of this chemistry. In contrast Steel B, (HSAC 840) which gave greatly improved performance in Australia, and Steel C, which gave very good performance in the UK, both underwent SCC failure in the tests. These inconsistencies cast doubt on the validity of using low pH solutions to represent the in-service local SCC environment.

In view of the inability to obtain SCC failure of the AISI 5152 rock bolts in the threshold tests, Villalbo and Atrens postulated that, since these rock bolts are cold worked 10%, cold working might be beneficial to SCC resistance^[115]. They examined this by measuring the applied potential to cause SCC in AISI 5152 samples containing no cold work, 10% cold work and 55% cold work, respectively. The applied potential required to cause SCC increased with the amount of cold work, consistent with their hypothesis.

2.3.3.4 Crack Propagation Rates

Gamboa and Atrens used the results from both the LIST tests and the threshold stress tests to calculate the SCC crack growth velocity for Steels A-C^[2]. For the LIST tests, the crack growth rate was determined by dividing the crack length at failure by the total time from the start of the test. As noted by Gamboa and Atrens this assumes that crack initiation starts right at the beginning of the test and may therefore underestimate that actual crack growth rate. In the constant load tests, the crack growth rate was determined from the threshold specimens by dividing the crack length by the time under load.

Table 2-16: Crack Growth Velocities^[2].

Steel	Crack Growth Velocity					
	Constant Load Test			Standard LIST Test		
	Time at constant stress (h)	SCC crack size (mm)	SCC crack velocity (m s ⁻¹)	LIST test duration (h)	SCC crack size (mm)	SCC crack velocity (m s ⁻¹)
Steel A	5.3	0.5	2.6×10^{-8}	14.8	1.3	2.4×10^{-8}
				15.0	1.1	2.1×10^{-8}
Steel B	70.8	0.5	5.5×10^{-9}	14.0	1.0	1.9×10^{-8}
Steel C	50	1.0	2.0×10^{-9}	12.3	1.0	2.2×10^{-8}

The crack growth velocities obtained by the two methods are shown in Table 2-16. These range from $\sim 10^{-8}$ - 10^{-9} m.s⁻¹. Gamboa and Atrens note that, at such rates, a rock bolt would fail “within hours of it reaching the threshold stress provided that the local environment is conducive to SCC.”

2.3.3.5 Surface Features

The specimens used by Gamboa and Atrens in the work reviewed above were machined from the interior of rock bolts so that the surface features of an actual rock bolt, such as mill scale, decarburization and surface residual stresses, all produced during hot rolling, were not retained. In addition, the stress concentration produced by the ribs was not reproduced.

To allow these features to be taken into account modified test specimens, as shown in Figure 2-45 (b) and (c) were tested^[114]. The first specimen (Figure 2-45(b)) contained only the transverse ribs while the second specimen (Figure 2-45(c)) additionally contained one of the two longitudinal ribs which are present at diametrically opposite positions along the length of rock bolts. The samples were manufactured from AISI 1355

rock bolts and again tested using the LIST method. It was concluded that the surface features did not have a direct impact on SCC resistance of rock bolts^[114].

3 ENVIRONMENTAL CLASSIFICATION

3.1 Introduction

This chapter gives the results of the analyses of mine water samples. The analyses were conducted on several samples collected from two underground coal mines which had experienced numerous SCC failures of rock bolts in recent years. The two mines are referred to as Mines A and B. Failed rock bolts retrieved from these two mines (4 from each) are examined in the following chapter, together with rock bolts from 4 other mines (1 from each).

Both chemical and biological species were analysed. Biological species were included in the study since it had been suggested by Gambao and Atrens^[2] that microorganisms in the mine water might be contributing to SCC.

3.2 Experimental Methods

3.2.1 Sample Collection for Chemical Analysis

Mine water samples were collected from ten different locations in Mine A and eleven different locations in Mine B. The locations were chosen as being ones where bolt failure had occurred. The samples were collected in glass bottles made of Duran borosilicate glass, Type 3.3, except those taken for trace element analysis. In these cases polytetrafluoroethylene (PTFE) bottles were used instead to avoid contamination from species which might leach from the glass. PTFE liners were used on the caps of all bottles.

Sampling was performed by collecting water that was dripping from rock bolts installed in the roof. After obtaining the samples they were kept as cool as possible, without freezing them, to avoid volatilization or biodegradation, and to retard biological action and hydrolysis of chemical compounds such as complexes. This was done by packing the sample bottles in crushed ice as soon as the samples were obtained. Once the samples had been transported to the testing laboratory they were stored in a refrigerator at 4°C.

The analyses were performed by either the UNSW Analytical Laboratory or ALS Environmental Services, Smithfield, NSW, Australia. The analytical procedures used were from established internationally recognised procedures such as those published by the USEPA, APHA, AS and NEPM. In house developed procedures were employed by ALS in the absence of documented standards. The analyses were carried out within 24 hours of the samples being collected. The samples were kept at 4°C for the duration of the analysis.

In addition to testing for dissolved ionic species, several other parameters were measured. These included pH, alkalinity, conductivity, total solids, dissolved oxygen and hardness. The carbonate and bicarbonate levels expressed as mg/l CO_3^{2-} and HCO_3^- , respectively, were determined by converting the carbonate and bicarbonate alkalinity, expressed in mg/l CaCO_3 , using their respective molar masses. This gave conversion factors of 1.22 for bicarbonate and 0.6 for carbonate.

3.2.2 Sample Collection for Biological Analysis

Samples for microbiological analysis were collected from 2 separate locations in Mine B, designated L12 and L13, and analysed for the presence of iron and sulphur oxidising and reducing bacteria which are known to have a link to the corrosion of steel^[117, 118]. Mine B was selected for this part of the analysis since it was considered to be the more susceptible to microbial-induced SCC. The water samples were again collected from dripping ground water into glass bottles made of Duran borosilicate glass. A swab from a brown/orange substance that had accumulated on the surface of the rock bolts and roof-mesh was also collected and placed into the same type of bottle. This location is designated L14. The collection bottles were wrapped in cloth to exclude light and kept cold during transportation to UNSW. Water which drained from the swab was analysed separately to the swab.

Water samples were filtered and extracted in triplicate using the PowerWater DNA isolation kit (Mobio) following the manufacturer's instructions. The presence of DNA

was confirmed via spectrometry, gel electrophoresis and 16S rRNA gene amplification. Fungal PCRs with 18S (small sub unit primers), however, showed no amplification and thus the fungal assay was not performed. A total genomic DNA was extracted in duplicate from the Swab Sample using FastDNA™ Spin Kit for Soil DNA Isolation Kit (MP Biomedicals) as per the manufacturer's instructions. DNA samples from both the water and the swab were sent to RTL Genomics (<http://rtlgenomics.com/services-home/>), Lubbock, Texas, USA, for pyrosequencing. The sequencing was carried out using a Roche 454 FLX Genome Sequencer optimising for 3000 reads. The procedure used was confidential and the details were not disclosed by the laboratory.

The primers and assays used to amplify sample DNA for pyrosequencing are shown in Table 3-1.

Table 3-1: Primers and assays used to amplify sample DNA for pyrosequencing.

Target Organisms	Primer	Assay Name
Bacteria	28F	Assay b.2
	519R	
Achaea	349R	Assay a.1
	806R	

An open source software, Mothur v 1.25, was used for processing, cluster analysis and classification of the raw sequence data^[119]. Sequences were trimmed of barcodes and the forward primer and reduced to unique sequences for subsequent computational ease. Sequences were aligned to SILVA database^[120] and screened for poor sequence quality. Chimeras were detected and removed. Sequences were then grouped into operational taxonomic units (OTUs) based on 0.05 (genus) cut-off levels and classified against NCBI nucleotide database.

3.3 Results

3.3.1 Chemical Analysis

The results of the analyses conducted on the 10 samples from Mine A and the 11 samples from Mine B are given in Table 3-2 and Table 3-3, respectively, while the averages and range of values are given in Table 3-4. It can be seen from Table 3-2 that the sample from location L1 had an exceptionally high sulphate level compared to the other samples from Mine A (81764 mg/l compared with an average of 0.5 mg/l for the remainder), while the sodium, carbonate and bicarbonate levels were also substantially higher (1334, 200 and

3273 mg/l, respectively, compared with average values of 439, 25 and 1179 mg/l, respectively, for the remainder). The analysis from location L1 has therefore been omitted when determining the average values and ranges for Mine A in order to avoid excessively skewing the averages.

It can be seen from Table 3-4 that, the range of values is generally noticeably smaller for Mine B than for Mine A, (even excluding the values for L1 in Mine A) indicating a greater level of consistency in the Mine B ground water.

Of the ionic species, sodium and bicarbonate are the most prominent with average levels of ~200- 1200 mg/l, Table 3-4, while all other species had average levels of < 40 mg/l. It can also be seen from Table 3-4 that the average levels of sodium and bicarbonate are higher for Mine A than for Mine B, with the values being 439 and 1179 mg/l, respectively, for Mine A, and 177 and 484 mg/l, respectively, for Mine B. The alkalinity, conductivity and hardness are also substantially higher for Mine A than for Mine B, with values of 990, 1823 and 104, respectively, for Mine A, compared with 399, 846 and 39, respectively, for Mine B. It is noted that the total alkalinity is dominated by the bicarbonate ions with the bicarbonate alkalinity being 97.6 of the total alkalinity in Mine A and 99.5% in Mine B.

The average pH was somewhat higher for Mine A than for Mine B (8.1 compared with 7.8), although the pH at location L1 (not included in the averages) was 9.1.

Table 3-2: Water analysis from Mine A.

Location	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
Depth of cover (m)	400	400	400	400	400	400	400	400	400	400
Flowing (Yes/No)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Flowrate mL/min	30	N	170	N	N	30	N	170	N	N
Temperature °C	22	20	23	20	20	23	23	23	23	23
Total Alkalinity as CaCO ₃ (mg/l)	2883	554	1820	681	553	1840	1100	454	1340	570
Hydroxide Alkalinity as CaCO ₃ (mg/l)	0	<1	<1	<1	<1	<1	<1	<1	<1	<1
Carbonate Alkalinity as CaCO ₃ (mg/l)	200	6	15	36	10	41	70	32	<1	10
Carbonate Alkalinity as CO ₃ ²⁻ (mg/l)	120	4	9	22	6	25	42	19	<1	6
Bicarbonate Alkalinity as CaCO ₃ (mg/l)	2683	549	1805	646	543	1799	1030	422	1340	560
Bicarbonate Alkalinity as HCO ₃ ⁻ (mg/l)	3273	670	2202	788	662	2195	1257	515	1635	683
Conductivity (µS/cm)	8260	1080	3340	1340	1140	3320	1960	875	2190	1160
Total Solids Dried (mg/l)	3227	643	2310	840	682	2190	N	N	N	N
Total Dissolved Solids (mg/l)	497	616	1930	775	671	2060	N	N	N	N
Total Suspended Solids (mg/l)	0.39	12	130	5	5	44	N	N	N	N
Ratio Between TDS and Conductivity	0.1	0.6	0.6	0.6	0.6	0.6	N	N	N	N
pH	9.11	8.33	7.52	8.5	8.33	7.8	8.04	8.51	7.7	8.46
Dissolved Oxygen (mg/l)	6.7	10.1	6.6	10.1	6.8	N	N	N	N	N
Basic Oxygen Demand (mg/l)	0	2	7	2	6	N	N	N	N	N
Hardness (mg/l)	99	22	281	61	31	296	107	18	113	9
Calcium, Ca (mg/l)	16	4	58	8	6	64	23	4	24	2
Copper, Cu (mg/l)	0.05	0	0	0	0	0	0	0	0	0
Iron, Fe (mg/l)	0.78	0.47	2.21	0.05	0.06	0.84	0.05	0.05	0.05	0.05

Potassium, K (mg/l)	7	4	18	8	4	19	6	4	7	2
Magnesium, Mg (mg/l)	14.5	3	33	10	4	33	12	2	13	1
Sodium, Na (mg/l)	1334	260	797	322	264	789	486	218	540	273
Zinc, Zn (mg/l)	0.04	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.04
Fluoride, F (mg/l)	0	0.3	0.1	0.6	0.2	0.1	0.2	0.4	0.3	1.8
Chloride, Cl (mg/l)	15	26	28	22	26	27	21	20	20	21
Carbonate (mg/l)	200	6	15	36	10	41	70	32	1	10
Bicarbonate (mg/l)	3273	670	2202	788	662	2195	1257	515	1635	683
Phosphate, PO ₄ (mg/l)	0.81	0.01	0.02	0.01	0.01	0.02	0.04	0.01	0.01	0.03
Sulphate, SO ₄ (mg/l)	81764	0	0	0	0	1	1	0.22	1	1
N-nitrate & nitrite (mg/l)	29.4	0.01	6.13	2.04	0.01	0.06	0.01	0.76	0.01	0.01

N = Not Analysed

Table 3-3: Water analysis from Mine B

Location	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11
Depth of cover (m)	400	400	400	400	400	400	400	400	400	400	400
Flowing (Yes/No)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Flowrate mL/min	N	100-200	N	N	N	N	N	N	N	N	N
Temperature °C	N	20	N	N	N	N	N	N	N	N	N
Total Alkalinity as CaCO ₃ (mg/l)	N	355	471	484	302	572	201	308	485	401	406
Hydroxide Alkalinity as CaCO ₃ (mg/l)	N	0	<1	<1	<1	<1	<1	<1	<1	<1	<1
Carbonate Alkalinity as CaCO ₃ (mg/l)	N	0	<1	<1	<1	20	<1	<1	<1	<1	<1
Carbonate Alkalinity as CO ₃ ²⁻ (mg/l)	N	0	<1	<1	<1	12	<1	<1	<1	<1	<1
Bicarbonate Alkalinity as CaCO ₃ (mg/l)	N	355	471	484	302	552	201	308	485	401	406
Bicarbonate Alkalinity as HCO ₃ ⁻ (mg/l)	N	434	575	590	368	673	245	376	592	489	495
Conductivity (µS/cm)	837	820	935	962	580	1160	466	619	1020	957	952
Salinity	0.2	N	N	N	N	N	N	N	N	N	N
Total Solids Dried (mg/l)	465	456	600	596	378	680	286	374	582	702	688
Total Dissolved Solids (mg/l)	465	398	618	598	350	636	261	270	556	522	506
Total Suspended Solids (mg/l)	0	40	5	5	18	46	5	12	6	9	8
Ratio Between TDS and Conductivity	0.6	0.5	0.7	0.6	0.6	0.5	0.6	0.4	0.5	0.5	0.5
pH	7.43	7.76	7.95	7.96	8.15	8.46	7.85	7.52	7.91	7.51	7.55
Dissolved Oxygen (mg/l)	4.5	5.9	7.2	6.6	9.6	10.2	10.2	7.9	9	5.5	6.3
Basic Oxygen Demand (mg/l)	0	1.1	2	2	2	2	2	2	2	2	2
Hardness (mg/l)	3.4	4.9	11	6.6	0	0	72	136	148	24	24
Calcium, Ca (mg/l)	0.5	0.9	1	1	1	1	14	28	28	3	3
Copper, Cu (mg/l)	0	0.01	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001

Iron, Fe (mg/l)	1.0	1.4	0.95	0.96	0.51	1.3	1.4	2.9	3.0	3.4	3.5
Potassium, K (mg/l)	6.2	5.3	0.02	0.01	4	5	32	37	38	24	24
Magnesium, Mg (mg/l)	0.5	0.6	2	1	1	1	9	16	19	4	4
Sodium, Na (mg/l)	190	182	247	260	148	290	52	60	120	194	199
Zinc, Zn (mg/l)	0	0.009	0.005	0.005	0.005	0.007	0.005	0.005	0.005	0.006	0.005
Fluoride, F (mg/l)	0.4	0.4	0.5	0.6	0.4	1	0.5	0.8	1.2	0.3	0.3
Chloride, Cl (mg/l)	7	7	8	9	8	7	7	9	9	6	6
Carbonate (mg/l)	N	0	<1	<1	<1	20	<1	<1	<1	<1	<1
Bicarbonate (mg/l)	N	434	575	590	368	673	245	376	592	489	495
Nitrite, NO ₂ (mg/l)	0	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Bromide, Br (mg/l)	0	0	0	0	0	0	0	0	0	0	0
Nitrate, NO ₃ (mg/l)	0	0	0.04	0.04	0.04	0.01	0.01	0.08	0.02	0.02	0.01
Phosphate, PO ₄ (mg/l)	0	0	0.02	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01
Sulphate, SO ₄ (mg/l)	90	81	39	42	1	1	7	4	4	71	69
N-NH ₄ (mg/l)	0.5	0.4	0	0	0	0	0	0	0	0	0
N-NO ₃ (mg/l)	0.005	0	0	0	0	0	0	0	0	0	0
N-NO ₄ (mg/l)	0.001	0	0	0	0	0	0	0	0	0	0

N = Not Analysed

Table 3-4: Average values and range of values for ground water from Mines A and B.

Analysis	Mine A*	Mine B	Mine A*	Mine B
	Average	Average	Range	Range
Total Alkalinity as CaCO ₃ (mg/l)	990	399	553-1840	201-572
Hydroxide Alkalinity as CaCO ₃ (mg/l)	<1	<1	0-1	0-1
Carbonate Alkalinity as CaCO ₃ (mg/l)	25	2	1-70	0-20
Carbonate Alkalinity as CO ₃ ²⁻ (mg/l)	17	2	1-42	0-12
Bicarbonate Alkalinity as CaCO ₃ (mg/l)	966	397	422-1805	201-552
Bicarbonate Alkalinity as HCO ₃ ⁻ (mg/l)	1179	484	515-2202	245-673
Conductivity (µS/cm)	1823	846	875-3340	466-1020
Salinity	N	0.0	N	0.00-0.02
Total Solids Dried (mg/l)	741	528	0-2190	286-688
Total Dissolved Solids (mg/l)	672	471	0-2060	261-618
Total Suspended Solids (mg/l)	22	15	0-130	5 - 46
Ratio Between TDS and Conductivity	0.3	0.6	0-0.6	0.4-0.7
Dissolved Oxygen (mg/l)	3.7	7.5	0-10	5-10
Biochemical Oxygen Demand (mg/l)	1.9	1.7	2-7	0-2
Hardness (mg/l)	104	39	9-296	0-148
pH	8.1	7.8	7.5-8.5	7.4-8.5
Calcium, Ca (mg/l)	21	7.4	2-58	0.5-28
Copper, Cu (mg/l)	0.0	0.0	0	0-0.002
Iron, Fe (mg/l)	0.4	1.8	0.05-2.2	0.5-3.5
Potassium, K (mg/l)	8.0	16.0	2-19	0.01-38
Magnesium, Mg (mg/l)	12	5.3	1-33	0.5-19
Sodium, Na (mg/l)	439	177	218-797	52-290
Zinc, Zn (mg/l)	0.0	0.0	0.01-0.04	0-0.009
Fluoride, F (mg/l)	0.4	0.6	0-1.8	0.03-1.2
Chloride, Cl (mg/l)	23	7.6	20-28	6 to 9
Phosphate, PO ₄ (mg/l)	0.0	0.0	0.01-0.04	0-0.04
Carbonate (mg/l)	25	2	0-70	0.20
Bicarbonate (mg/l)	1179	484	515-2202	245-673
Sulphate, SO ₄ (mg/l)	0.5	37	0-1	1 to 90

* Excludes L1

3.3.2 Microbiological Analysis

3.3.2.1 Bacteria

The percentage of sequences identified as corrosive bacterial genera detected in the swab sample from Location L14, and the associated water sample, are given in Table 3-5.

Table 3-5: Percentage of sequences identified as corrosive bacterial genera detected in swab and associated water sample.

Genus	Water	Swab
<i>Betaproteobacteria</i>	19.35	9.36
<i>Hydrogenophaga</i>	13.04	0.67
<i>Methylophilus</i>	8.90	0.45
<i>Methylocaldum</i>	6.89	18.61
<i>Zoogloea</i>	4.86	0.14
<i>Chlorobi</i>	1.33	0.72
<i>Unclassified Bacteria</i>	1.03	6.35
<i>Rhodocyclaceae</i>	0.93	0.64
<i>Terrimonas</i>	0.83	0.06
<i>Sphingomonas</i>	0.63	0.59
<i>Denitratisoma</i>	0.61	0.06
<i>Acidobacterium</i>	0.59	26.02
<i>Azospirillum</i>	0.58	0.45
<i>Methylibium</i>	0.57	0.53
<i>Rhodobacter</i>	0.56	0.17
<i>Rhodoferrax</i>	0.54	0.22
<i>Opitutus</i>	0.42	0.61
<i>Bacteroidetes</i>	0.42	0.28
<i>Roseateles</i>	0.21	0.89
<i>Erythromicrobium</i>	0.16	0.45
<i>Methylococcus</i>	0.13	4.96
<i>Caulobacter</i>	0.11	0.64
<i>Segetibacter</i>	0.11	0.14
<i>Pleomorphomonas</i>	0.10	0.08
<i>Polyangiaceae</i>	0.06	0.25
<i>Xanthobacter</i>	0.04	0.45
<i>Hyphomicrobium</i>	0.02	0.50
<i>Rhodocyclus</i>	0.02	0.11
<i>Pedomicrobium</i>	0.01	0.11
<i>Laribacter</i>	11.59	-
<i>Methylocystis</i>	-	9.56
<i>Methylosoma</i>	7.90	-
<i>Thiobacillus*</i>	7.42	-

<i>Nitrospira</i>	-	5.63
<i>Nordella</i>	-	1.95
<i>Flavobacterium</i>	1.64	-
<i>Dechloromonas</i>	1.18	-
<i>Methylobacter</i>	1.04	-
<i>Pelomonas</i>	0.85	-
<i>Haliscomenobacter</i>	0.83	-
<i>Methylosinus</i>	-	0.81
<i>Solirubrobacter</i>	-	0.81
<i>Rhodospirillaceae</i>	-	0.78
<i>Desulfarculus</i>	0.68	-
<i>Acidobacteria</i>	-	0.67
<i>Bradyrhizobium</i>	-	0.64
<i>Methylocella</i>	-	0.61
<i>Desulfovibrio</i> *	0.55	-
<i>Acidovorax</i>	0.51	-
<i>Altererythrobacter</i>	-	0.45
<i>Aquiflexum</i>	-	0.45
<i>Asticcacaulis</i>	0.38	-
<i>Sphingobacteriales</i>	0.38	-
<i>Lactobacillus</i>	-	0.31
<i>Myxococcaceae</i>	-	0.31
<i>OP10</i> [#]	-	0.28
<i>Staphylococcus</i>	0.25	-
<i>Deltaproteobacteria</i>	0.21	-
<i>Phenylobacterium</i>	0.21	-
<i>Roseospira</i>	-	0.20
<i>Magnetobacterium</i>	-	0.17
<i>Nocardiaceae</i>	-	0.17
<i>Blastochloris</i>	-	0.14
<i>Limibacter</i>	-	0.14
<i>Methylomonas</i>	-	0.14
<i>Desulfotomaculum</i> *	0.13	-
<i>Buchnera</i>	-	0.11
<i>Pseudoruegeria</i>	-	0.11
<i>Sideroxydans</i>	-	0.11
<i>Sphingosinicella</i>	-	0.11
<i>Anaerophaga</i>	0.09	-
<i>Cryptanaerobacter</i>	0.09	-
<i>Oleomonas</i>	0.09	-
<i>Arenibacter</i>	-	0.08
<i>Conexibacter</i>	-	0.08
<i>Coriobacteriaceae</i>	0.08	-

<i>Propionivibrio</i>	0.08	-
<i>Coenonia</i>	0.07	-
<i>Geobacter</i>	0.07	-
<i>Sulfurospirillum</i>	0.07	-
<i>Victivallis</i>	0.07	-
<i>Ectothiorhodospiraceae</i>	-	0.06
<i>Chloroflexi</i>	0.06	-
<i>Spirochaetaceae</i>	0.06	-
<i>Acidobacteriaceae</i>	-	0.06
<i>Actinosynnemataceae</i>	-	0.06
<i>Arsenophonus</i>	-	0.06
<i>Defluviibacter</i>	-	0.06
<i>Gallionella</i> *	-	0.06
<i>Gemmatimonas</i>	-	0.06
<i>Meganema</i>	-	0.06
<i>Mesorhizobium</i>	-	0.06
<i>Planctomyces</i>	-	0.06
<i>Seionella</i>	-	0.06
<i>Verrucomicrobia</i>	-	0.06
<i>Desulfomonile</i>	0.04	-
<i>Methylosarcina</i>	0.04	-
<i>Odyssella</i>	0.04	-
<i>Acetobacterium</i>	0.03	-
<i>Crenothrix</i>	0.03	-
<i>Pelotomaculum</i>	0.03	-
<i>Treponema</i>	0.03	-
<i>Hyphomicrobiaceae</i>	-	0.03
<i>Bellilinea</i>	0.02	-
<i>Caenispirillum</i>	0.02	-
<i>Nevskia</i>	0.02	-
<i>Alistipes</i>	0.01	-
<i>Dysgonomonas</i>	0.01	-
<i>Emticicia</i>	0.01	-
<i>Janthinobacterium</i>	0.01	-
<i>Pseudomonas</i> *	0.01	-

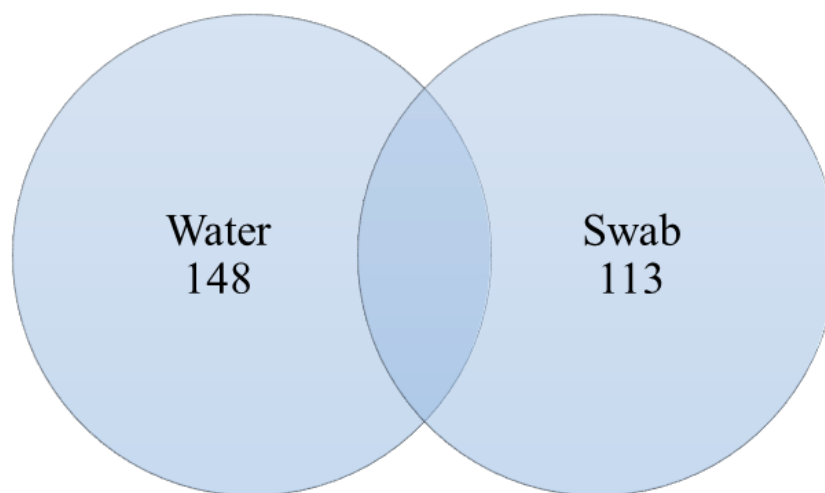


Figure 3-1: Venn diagram showing the number of species present in, and common to, the water sample and the swab sample.

The water and swab communities shared about 10% of the same sequences, as shown in Figure 3-1. Both the water and swab samples were dominated by betaproteobacteria (~55% and 25% of sequences, respectively), followed by gammaproteobacteria, alphaproteobacteria and deltaproteobacteria, as shown in Figure 3-2. It was found that more of the bacteria sequences *Thiobacillis*, *Desulfovibrio*, *Desulfotomaculum*, *Gallionella* and *Pseudomonas*, which are known to be corrosive^[117], were present in the water sample than in the swab, Table 3.5.

The results from the two water samples from locations L12 and L13 are shown in Figure 3-2 and Figure 3-3. The bacterial sequences from L12 were again dominated by betaproteobacteria which comprised ~97% of the sequences, followed by unidentified environmental sequences (2% of sequences) and gammaproteobacteria (1% of sequences). The majority of betaproteobacteria were identified as bacterial species involved with iron oxidation (i.e. *Rhodospirillum rubrum*, *Gallionella*, *Thiobacillus* and *Limnobacter*) and nitrogen cycling (i.e. *Denitratisoma*, *Nitromonas*)^[121, 122].

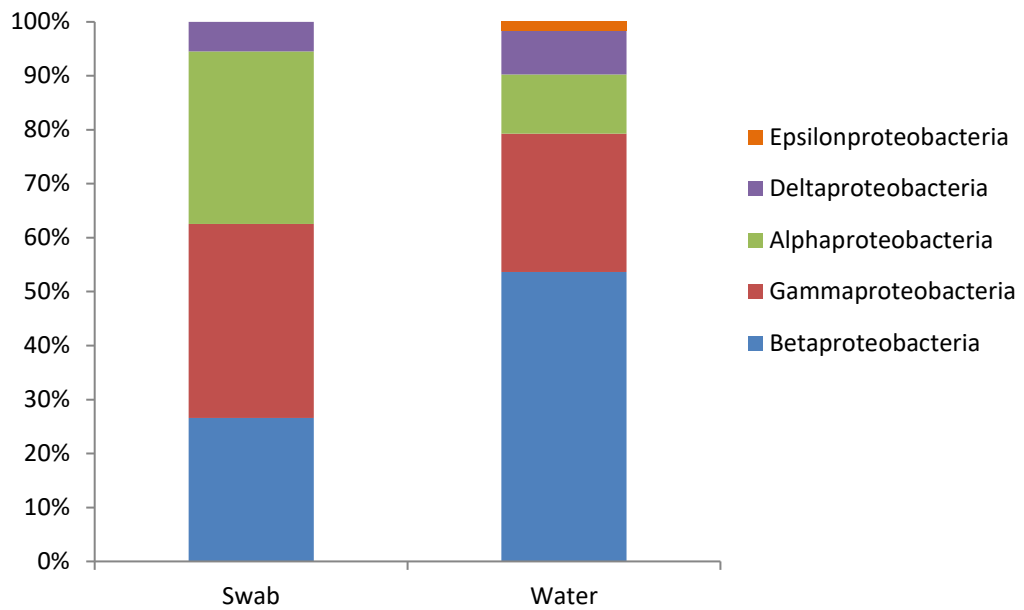


Figure 3-2: Distribution of bacterial sequences at Phylum level for swab and water samples.

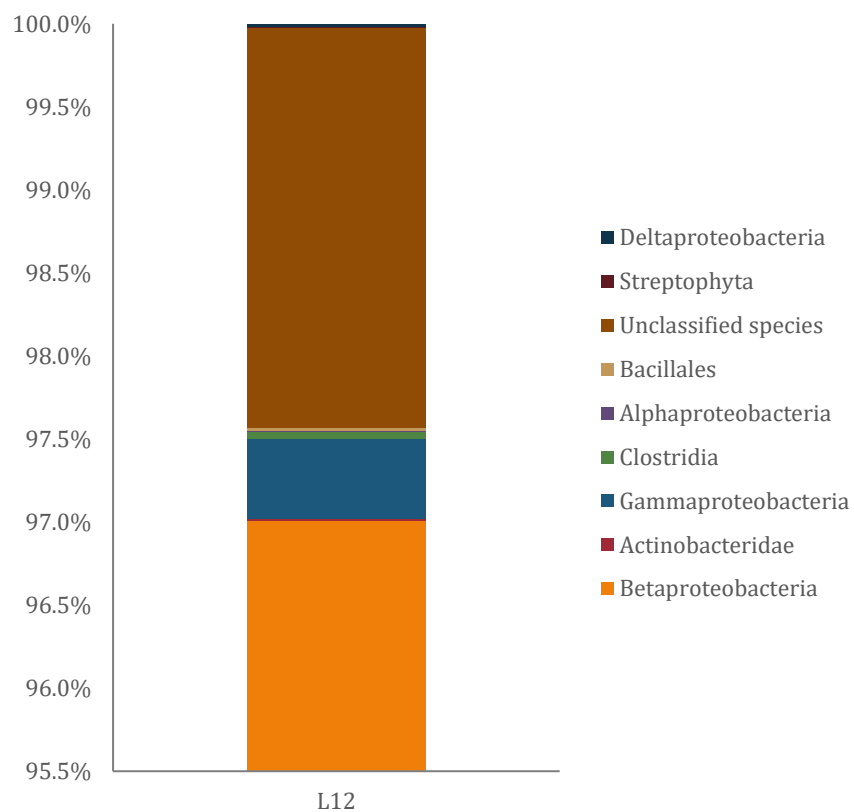


Figure 3-3: Distribution of bacterial sequences at Phylum level for sample from location L12.

The bacterial sequences were from Location 2 were quite different being dominated by gammaproteobacteria, (87% of sequences) followed by betaproteobacteria (11% of

sequences), Figure 3-4. The majority of gammaproteobacteria sequences had matches to *Acinetobacter* and *Pseudomonas* species that occur commonly in soil environments. Other gammaproteobacteria species identified are known to perform iron oxidation (i.e. *Crenothrix*) and reduction (i.e. *Shewanella*) while others were Halotolerant/phillic (i.e. *Halotalia*, *Halomonas*, *Kushneria*).

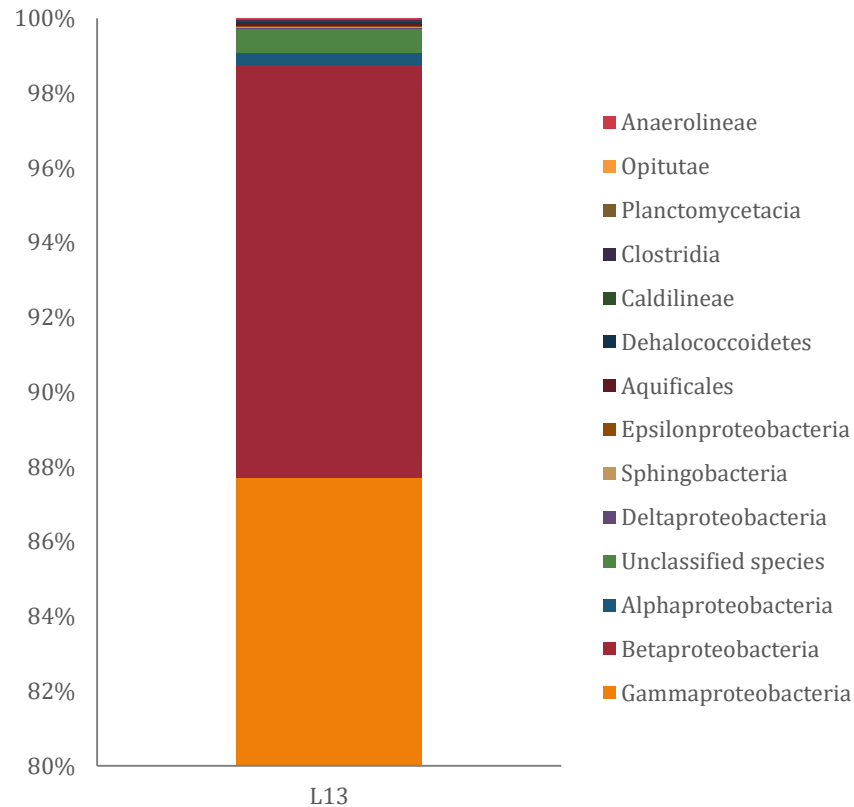


Figure 3-4: Distribution of bacterial sequences at Phylum level for sample from Location L13.

3.3.2.2 Achaea

Achaea data was generated for the swab sample, Figure 3-5 and the two water samples taken from locations L12, Figure 3-6 and L13, Figure 3-7. The two water samples had >3000 sequences, but the data was still processed for comparison with Achaea identified on the swab.

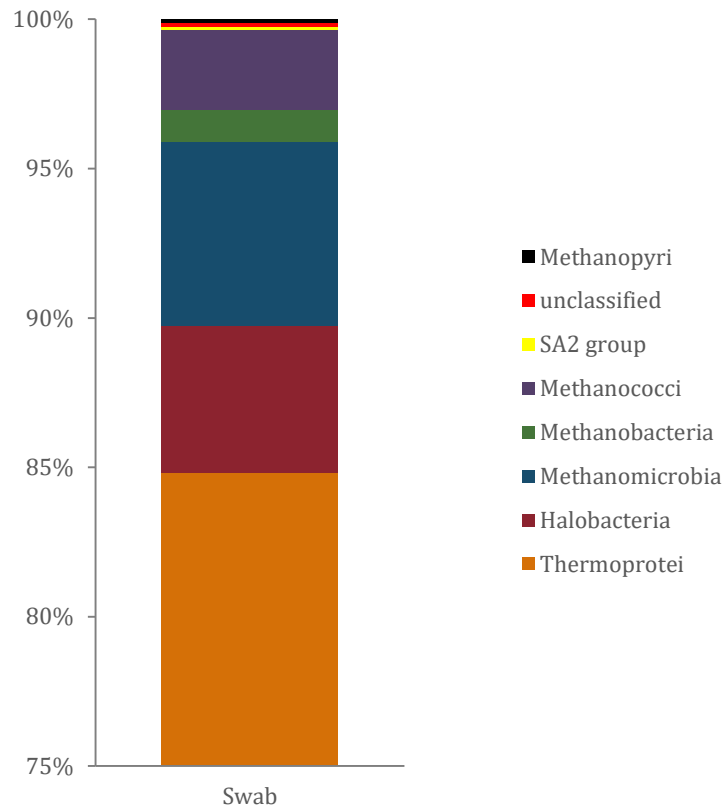


Figure 3-5: Distribution of Achaean sequences at Order level for swab.

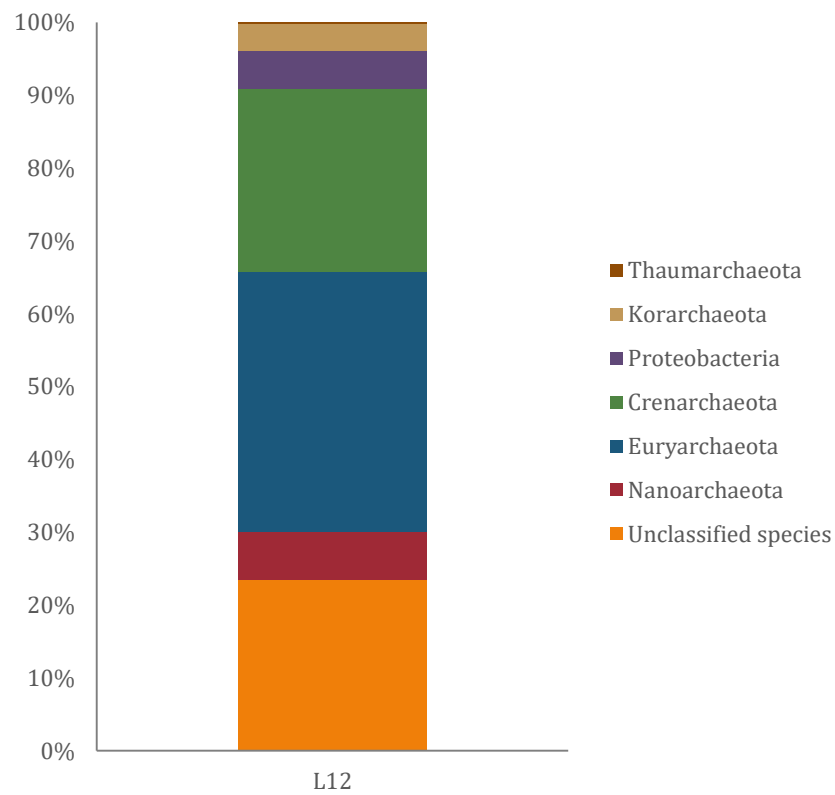


Figure 3-6: Distribution of Archaeal sequences at Phylum level for water sample from location L12.

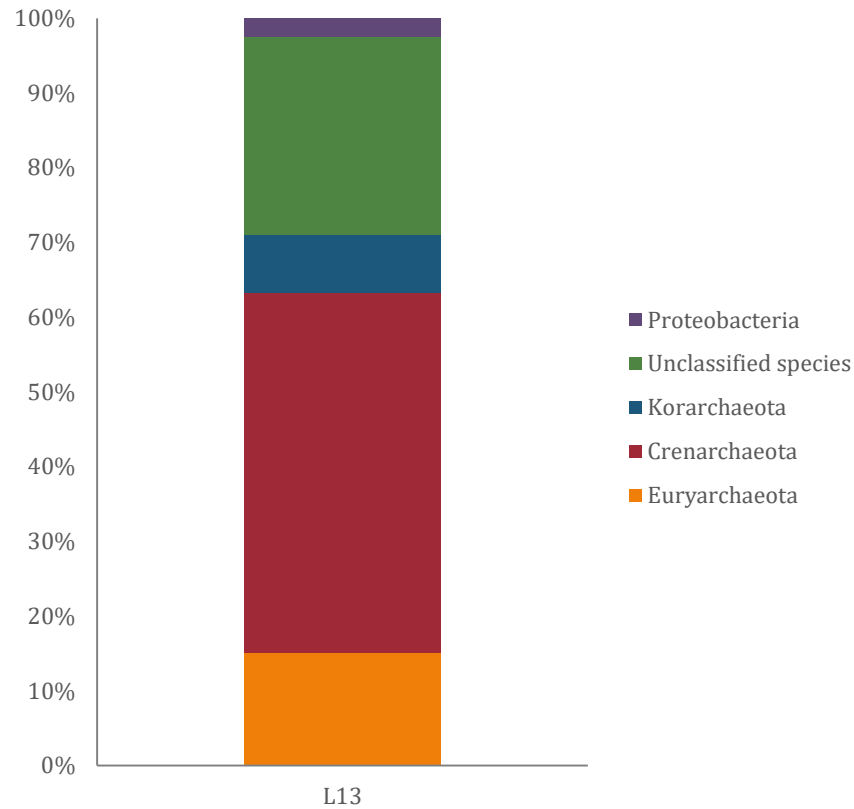


Figure 3-7: Distribution of Archaeal sequences at Phylum level for water sample from location L13.

The water samples from both locations L12 and L13 are dominated predominately by the same archaea species, these being *Korarchaeota*, *Crenarchaeota* and *Euryarchaeota*. However there are no common species between those found within the swab and the water. This suggests that the environmental conditions within the crust which forms on the steel are vastly different to those of the water flowing within the strata.

3.4 Discussion

3.4.1 Chemical Species

The water analyses indicated that the principal ionic species present were sodium and bicarbonate, Table 3-2 to Table 3-4, with average levels ranging from ~200-400 mg/l and 500-1200 mg/l, respectively, (neglecting the higher values obtained from location L1 in Mine A).

The average sodium and bicarbonate levels were ~2½ times higher for Mine A than for Mine B, as also were the alkalinity, conductivity and hardness. The alkalinity was

dominated by the bicarbonate ions in both mines with bicarbonate alkalinity being 97% of the total alkalinity in Mine A and 99% in Mine B.

The data from Mine A showed more variability than that from Mine B. Moreover, in one location in Mine A (L1) an extremely high sulphate concentration was recorded, being three orders of magnitude higher than in any other location in either mine, while the sodium and bicarbonate levels were also higher by a factor of 3. The results from this location, in particular, indicates the variability in water chemistry that can occur from place to place in a mine.

The pH varied from 7.4-9.1, with the average value being somewhat higher (8.2 including value from L1) in Mine A than Mine B (7.8). The highest value of 9.1 was also recorded in Mine A.

Water analyses from two underground coal mines from two coalfields in India (Jharia and Raniganj), published by Singh^[123], are given for comparison in Table 3-6 and Table 3-7. The ionic concentrations are given in ppm, which is equivalent to mg/l assuming the constituents in the mine water do not change the density of water. The average values and range of values are also given in these two tables and are compared with the corresponding values from Mine A (including location L1) and Mine B in Table 3-8.

There is again considerable variability in the data for the individual samples from both the Indian mines, as can be seen from the ranges given in Table 3-6 and Table 3-7. On the other hand, the average values from the two Indian mines are generally quite similar, Table 3-8. In contrast, the average values from the Australian mines are generally lower, but still within the ranges reported for the two Indian mines. Obvious exceptions are the values for alkalinity and sulphate levels for Mine A, which in Table 3-8, include the unusually high values for the sample from location L1. If this sample is excluded the averages for Mine A become 990 and 0.5 respectively. The alkalinity is still approximately twice the maximum value found in the two Indian mines, but the sulphate is now marginally below the minimum values. As noted above, the alkalinity level in the two Australian mines is dominated by bicarbonate alkalinity. It is not known whether the same is true of the Indian mines, but in any event, it is clear that the bicarbonate is high in comparison to that in the Indian coal mines (and also that in Mine B).

Singh subsequently published water analyses from a third coalfield, Assam, in India^[124]. The analyses, were from 4 underground coal mines, Lido (Tirap) Jeypore, Baragolai and Tipong 3-6 analyses being reported for each mine. The analyses are given in Table 3-9,

while the average and range of values are compared with those for the other 2 Indian mines, and also the two Australian mines, in Table 3-10.

Table 3-6: Water analysis from Jharia coalfield.

Mine Site	Sample Number	pH	Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (ppm)	Dissolved Solids (ppm)	Sulphate (ppm)	Chloride (ppm)	Iron (ppm)
Jharia Coalfields	1	7.9	1000	102.2	180.91	271.2	429.33	704.48	14.97	1570
Jharia Coalfields	2	8.1	830	120.24	128.64	304.8	112	457.31	37.43	12.5
Jharia Coalfields	3	8	820	124.24	123.78	222	1212	549.48	19.65	15
Jharia Coalfields	4	8	685	110.22	99.49	206.4	1040	420	30.88	8.7
Jharia Coalfields	5	8.1	570	80.16	89.81	294	914.66	236.74	31.81	9.2
Jharia Coalfields	6	8.2	558	101.8	73.84	176.8	781.3	325.63	31.35	4
Jharia Coalfields	7	7.9	505	74.14	77.67	177.6	926.66	316.3	24.33	17
Jharia Coalfields	8	7.4	500	74.14	76.45	158.4	817.33	330.57	38.37	18.5
Jharia Coalfields	9	8.3	450	126.2	32.68	90.84	1374	73.65	52.82	10.5
Jharia Coalfields	10	8.2	434	74.96	60	304.3	563.9	118.1	33.37	9.2
Jharia Coalfields	11	8	405	62.12	60.67	276	549.33	129.21	28.07	6.4
Jharia Coalfields	12	7.3	326	59.08	43.38	188.7	790.6	84.49	85.51	24
Jharia Coalfields	13	8.2	238	49.68	27.69	329.8	734.6	80.1	29.45	14.2
Jharia Coalfields	14	7.6	9	16.27	12	93.5	194.6	45.26	20.9	21.3
Jharia Coalfields	15	7.8	75	12.82	10.43	510	798.66	14.81	38.37	7
Jharia Coalfields	16	8.4	572	136.24	56.3	35.7	980	535.4	23.75	11
Jharia Coalfields	17	6.3	1060	116.67	94.16	8.5	2001	1070.9	304.84	4.96
Average		7.9	532	85	73	215	836	323	50	104
Range		6.3-8.4	9-1060	13-136	10-181	36-510	112-2001	15-1071	15-304	4-1570

Table 3-7: Water analyses from Raniganj coalfield.

Mine Site	Sample Number	pH	Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (ppm)	Dissolved Solids (ppm)	Sulphate (ppm)	Chloride (ppm)	Iron (ppm)
Raniganj Coalfield	1	8.1	382	68	53	420	570	75	35	1
Raniganj Coalfield	2	7.0	780	162	98	410	990	376	29	16
Raniganj Coalfield	3	7.8	665	118	90	335	880	368	150	15
Raniganj Coalfield	4	8.0	380	84	39	85	756	270	41	10
Raniganj Coalfield	5	8	753	156	101	353	949	436	176	19
Raniganj Coalfield	6	7.4	1248	216	180	448	1622	789	22	28
Raniganj Coalfield	7	7.4	897	162	125	390	1210	500	18	22
Raniganj Coalfield	8	8	50	16	5	400	576	15	48	15
Raniganj Coalfield	9	8.2	132	26	17	395	408	30	78	1
Raniganj Coalfield	10	7.3	92	19	11	130	286	28	26	5
Average		7.7	538	103	72	337	825	289	62	13
Range		7.0-8.2	50-1248	16-216	5-180	85-448	408-1210	15-789	18-176	1-28

Table 3-8: Comparison of water analyses from Jharia and Raniganj coalfields with those from Mine A and Mine B.

Mine Site	pH	Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (ppm)	Dissolved solids (ppm)	Sulphate (ppm)	Chloride (ppm)	Iron (ppm)
Jharia Average	7.9	532	85	73	215	836	323	50	104
Jharia Range	6.3-8.4	9-1060	13-136	10-181	36-510	112-2001	15-1071	15-304	4-1571
Raniganj Average	7.7	538	103	72	337	825	289	62	13
Raniganj Range	7.0-8.2	50-1248	16-216	5-180	85-448	408-1210	15-78	18-176	1-28
Mine A Average ¹	8.2	104	21	13	2882 (990) ²	672	8777 (0.5) ²	23	0.4
Mine A Range ¹	7.5-9.1	9-296	2-58	1-33	553-1840	0-2060	0-81764	15-28	0-2
Mine B Average	7.8	39	7	5	362	471	37	8	2
Mine B Range	7.4-8.5	0-148	1-28	1-19	201-572	261-618	1-90	6-9	1-4

¹ Includes values from location L1² Value in brackets excludes result from location L1

Table 3-9: Water analyses from Assam coalfield.

Mine Site	Sample Number	pH	Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Acidity (ppm)	Dissolved Solids (ppm)	Sulphate (ppm)	Fluoride (ppm)	Iron (ppm)
Lido (Tirap)	1	2.7	2300	104	108	2040	2518	3050	1.1	350
	2	2.7	1800	98	78	2100	3180	2500	0.6	358
	3	5.3	990	125	63	95	1662	1662	0.6	120
	4	3.1	3300	245	74	1230	4200	2880	1.1	670
	5	2.5	1130	116	75	980	3060	3210	1.6	136
	Average	3.3	1904	138	80	1289	2924	2660	1.0	327
	Range	2.5-5.3	990-3300	98-245	63-108	95-2040	1662-4200	1662-3210	0.6-1.6	120-670
Jeypore	1	2.9	2900	85	66	1090	4210	2420	1.4	545
	2	2.8	3170	60	100	1185	3816	3100	1.3	760
	3	2.5	2120	42	84	2350	2680	3110	1.2	388
	4	2.5	1930	58	49	2110	4066	2956	1.2	385
	5	2.3	1490	50	58	2480	2600	3030	1.6	192
	6	5.9	590	320	104	88	1190	1156	0.8	100
	Average	3.2	2033	103	77	1551	3094	2629	1.3	395
	Range	2.3-5.9	590-2900	42-320	49-104	88-2480	1190-4210	1156-3110	0.8-1.6	100-760
Baragolai	1	8.4	415	250	112	-	750	607	0.6	22
	2	4.0	900	222	96	190	1200	984	1.0	60
	3	4.5	790	126	59	144	874	1110	0.9	120
	4	4.1	595	288	78	160	1180	329	1.1	56
	Average	5.3	675	222	86	165	1001	758	0.9	65
	Range	4.0-8.4	415-900	126-288	59-96	0-190	750-1200	329-1110	0.6-1.1	22-120

Tipong	1	3.9	570	98	68	210	814	611	1.1	39
	2	8.2	605	504	110	-	780	500	0.7	16
	3	4.1	890	400	112	100	936	984	1.5	45
	Average	5.4	688	334	97	155	843	698	1.1	33
	Range	3.9-8.2	570-890	98-540	68-112	0-250	780-936	500-984	0.7-1.5	16-39

Table 3-10: Comparison of water analysis from Welbeck mine with analyses from Mine A and Mine B.

Mine Site	pH	Hardness (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Total Alkalinity (mg/l)	Sulphate (mg/l)	Chloride (mg/l)	Iron (mg/l)
Welbeck	7.1	7441	22100	4100	67300	157	28	14200	6.5
Mine A Average ¹	8.2	104	21	13	528 (439) ²	2882 (990) ²	8777 (0.5) ²	23	0.4
Mine A Range ¹	7.5-9.1	9-296	2-58	1-33	218-1334	553-1840	0-81764	15-28	0-2
Mine B Average	7.8	39	7	5	177	362	37	8	2
Mine B Range	7.4-8.5	0-148	1-28	1-19	52-290	201-572	1-90	6-9	1-4

¹ Includes values from location L1² Value in brackets excludes result from location L1

Contrary to the results for the other two Indian coalfields, and those for the two Australian mines, the pH values were all <7 , except for Baragolai Sample 1 which had a pH of 8.4 and Tipong Sample 2 which had a pH of 8.2, Table 3-9. Moreover, the pH values from the Lido and Jeypore mines were all in the range 2.3-3.3, except for one result for each mine which was in the range 5.3-5.9. The pH was somewhat higher for the Baragolai and Tipong mines, being in the range 3.9-4.5, except for the two samples mentioned above.

Singh attributed the generally acidic nature of the mine waters to dissolution of oxidised pyritic materials in the coal and associated strata during the mining operations. This is consistent with the high levels of sulphate and iron found in the acidic mine waters, especially those with the lower pH values, Table 3-9.

The results from Assam coal field are considered to be of limited significance to the present study since the mine waters in the present study were all alkaline, not acidic. However, the results serve to illustrate the variability that can occur, even in a single mine. They also demonstrate that the pH of mine water can, in some cases, approach the value of 2.1 used by Gamboa and Atrens^[2] in their SCC tests on rock bolt samples.

A water analysis has also been reported by Galloway^[106] for Welbeck Colliery in the UK. This mine underwent a roof fall with at least one bolt having experienced SCC, as discussed in Chapter 2. The mine water was obtained from a location near the site of the rock bolt failures. The water analysis is compared with the values from the present study in Table 3-11. The metal ion levels and also the chloride levels are orders of magnitude higher than for Mines A and B and also for the Indian mines. The pH of 7.1 was significantly lower than the average values for Mines A and B (8.2 and 7.7, respectively) and those for the mines from the Jharia and Raniganj coal fields (7.9 and 7.7), but not for the Assam coal fields. The total alkalinity of 157 mg/l was also lower than the average for Mine B and the Jharia and Raniganj coal field mines, but essentially within the ranges for these 3 mines/minesfields. However, it was substantially below the average value for Mine A (even excluding the result for L1) and in fact substantially below the minimum value of 553 mg/l. The lower alkalinity of the Welbeck mine compared to that in Mine A means that bicarbonate level is also correspondingly lower.

A water analysis has also been reported by Gamboa and Atrens for an underground coal mine in Australia^[2]. They noted that no SCC failures of rock bolts had occurred in that mine at the time the water sample was taken.

The mine water analysis is given in Table 3-11 where it is compared with the results of the present study. The chloride levels are about 2 orders of magnitude higher than in the present study although still 2 orders of magnitude lower than in the Welbeck mine water. The metal ions are also generally substantially higher than in the present study. The alkalinity of 968 mg/l is similar to that for Mine A when the value for location L1 is omitted, but it is not known to what extent this value reflects the bicarbonate level in the mine water.

The above results indicate that the chemistry of mine waters can vary significantly even within a single mine, making it difficult to establish the exact environment responsible for the rock bolt failures examined in the next chapter. It is also noted that the analyses conducted in the present study were made subsequent to the rock bolts failing. It is known that mine water chemistry can vary over time and the water chemistry, even if representative of the mine water at the failure locations at the time the analyses were made, may not be representative of the local mine water chemistry while the bolts were in service.

Notwithstanding the uncertainties discussed above, there are clearly some differences between the mine water from Mine A and that from Mine B. Of particular interest is the substantially higher bicarbonate level in Mine A and the somewhat higher pH, as will be discussed in the following chapter.

Table 3-11: Comparison of water analysis published by Gamboa and Atrens with analyses from Mine A and Mine B.

Mine Site	pH	Hardness (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Alkalinity (mg/l)	Dissolved Solids (mg/l)	Sulphate (mg/l)	Chloride (mg/l)	Iron (mg/l)
Australia [G & A]	7.9	N	113	165	750	968	3006	N	1736	N
Mine A Average ¹	8.2	104	21	13	528 (439) ²	2882 (990) ²	672	8777 (0.5) ²	23	0.4
Mine A Range ¹	7.5-9.1	9-296	2-58	1-33	218-1334	553-2882	0-2060	0-81764	15-28	0-2
Mine B Average	7.8	39	7	5	177	362	471	37	8	2
Mine B Range	7.4-8.5	0-148	1-28	1-19	218-797	201-572	261-618	1-90	6-9	1-4

¹ Includes values from location L1² Value in brackets excludes result from location L1

N = Not Analysed

3.4.2 Corrosivity

As discussed in Chapter 2, the occurrence of SCC is generally restricted to only mildly corrosive environments since strongly corrosive environments cause excessive corrosion of the crack walls leading to crack tip blunting^[7]. Nonetheless it is of interest to compare the corrosivity for the waters from the two mines.

The corrosivity classifications as given by DIN 50929 and the Western Australian School of Mines (WASM) Index in Reference 125 are given for Mines A and B in Table 3-12 and Table 3-13.

Table 3-12: Corrosivity of groundwater from Mine A as indicated by the classifications given in DIN 50929 and by the Western Australian School of Mines (WASM) Index.^[125]

Location	pH	Dissolved Oxygen (mg/l)	Total Dissolved Solids (mg/l)	DIN 50929 Pitting Corrosion	DIN 50929 General Corrosion	WASM Uniform Corrosion
1	9.11	6.7	497	High	Medium	> 0.2 mm/yr
2	8.33	10.1	616	Very low	Very low	> 0.2 mm/yr
3	7.52	6.6	1930	Very low	Very low	> 0.2 mm/yr
4	8.5	10.1	7756	Very low	Very low	> 0.2 mm/yr
5	8.33	6.87	671	Very low	Very low	> 0.2 mm/yr
6	7.8	0	2060	Very low	Very low	Low
7	8.04	0	0	Very low	Very low	Low
8	8.51	0	0	Very low	Very low	Low
9	7.7	0	0	Very low	Very low	Low
10	8.46	0	0	Very low	Very low	Low

Table 3-13: Corrosivity of groundwater from Mine B as indicated by the classifications given in DIN 50929 and by the Western Australian School of Mines (WASM) Index.^[125]

Location	pH	Dissolved Oxygen (mg/l)	Total Dissolved Solids (mg/l)	DIN 50929 Pitting Corrosion	DIN 50929 General Corrosion	WASM Uniform Corrosion
1	7.43	4.5	465	Medium	Small	0.2 mm/yr
2	7.76	6.0	398	Small	Very low	> 0.2 mm/yr
3	7.95	7.2	618	Very low	Very low	> 0.2 mm/yr
4	7.96	6.6	598	Very low	Very low	> 0.2 mm/yr
5	8.15	9.6	350	Very low	Very low	> 0.2 mm/yr
6	8.46	10.2	636	Very low	Very low	> 0.2 mm/yr
7	7.85	10.2	261	Very low	Very low	> 0.2 mm/yr
8	7.52	7.9	270	Very low	Very low	> 0.2 mm/yr
9	7.91	9	556	Very low	Very low	> 0.2 mm/yr
10	7.51	5.5	522	Very low	Very low	> 0.2 mm/yr
11	7.55	6.3	506	Very low	Very low	> 0.2 mm/yr

Table 3-14: Langelier Saturation Index for Mine A.

Location	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
Langelier Saturation Index (LSI) at 25°C	1.5	-0.18	0.55	0.35	-0.0081	0.88	0.56	0.013	0.34	-0.28

Table 3-15: Langelier Saturation Index for Mine B.

Location	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11
Langelier Saturation Index (LSI) at 25°C	-5.7	-1.6	-1.2	-1.2	-1.1	-0.64	-0.58	-0.34	0.16	-1.3	-1.2

According to the DIN 50929 classification pitting corrosion is very low in Mine A, except at location L1 where it is high. Similarly, general corrosion is very low, except at location L1 where it is medium. For Mine B, the DIN 50929 pitting corrosion and general corrosion are low, except for locations L1 and L2 where pitting corrosion is medium at L1 and small at L2, while general corrosion is small at L1. In contrast, the WASM Index indicates a high general corrosion rate of >0.2 mm/year at Locations L1-L5 in Mine A and at all locations other than L1 in Mine B where it is 0.2 mm/year. These contradictory results indicate the very different corrosion predictions given by the two different classification methods.

The Langelier Saturation Index (LSI) was also calculated in accordance with ASTM D3739-94. This index is used to determine the need for scale control due to calcium carbonate precipitation in water sources containing a total dissolved solids concentration of less than 10,000 mg/l (as in the present study). ASTM D3739-94 gives the Langelier Saturation Index as:

$$LSI = pH + \log \left(\frac{K_a * \gamma_{Ca^{2+}} * [Ca^{2+}] * \gamma_{HCO_3^-} * [HCO_3^-]}{\gamma_{H^+} * K_{sp}} \right) \quad (3-1)$$

where:

- pH is the pH value of the water being assessed;
- γ_{H^+} is the activity coefficient of hydrogen ion;
- $\gamma_{CO_3^{2-}}$ is the activity coefficient of carbonate;
- $\gamma_{Ca^{2+}}$ is the activity coefficient of calcium;
- $[H^+]$ is the concentration of hydrogen ion;
- $[CO_3^{2-}]$ is the concentration of carbonate;
- $[Ca^{2+}]$ is the concentration of calcium; and
- K_a and K_{sp} are equilibrium constants

Water with an LSI value more negative than -0.5 is described as “aggressive.” An aggressive water will not deposit a protective film or layer of calcium carbonate. Instead it will dissolve such a film where one exists. This leaves any exposed metallic surfaces unprotected and open to corrosion resulting from phenomena like galvanic differences,

low pH, or significant concentrations of sulphate or chloride ions. In contrast, a water with a positive LSI will deposit a protective film or layer.

The LSI values for the water samples from Mine A and Mine B are shown in Table 3-14 and Table 3-15, respectively. Ways of interpreting the LSI data are given in Table 3-16^[126] and Table 3-17^[127].

Table 3-16: Interpretation of LSI values.

LSI Value	Interpretation
LSI < 0	Water is undersaturated with respect to calcium carbonate. Undersaturated water has a tendency to remove existing calcium carbonate protective coatings in pipelines and equipment.
LSI = 0	Water is considered to be neutral. Neither scale-forming nor scale removing.
LSI > 0	Water is supersaturated with respect to calcium carbonate (CaCO ₃), and scale formation may occur

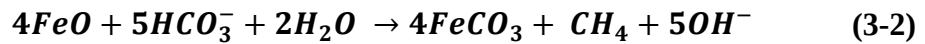
Table 3-17: Alternative interpretation of LSI values.

LSI Value	Interpretation
2.0	Scale forming, but non-corrosive
0.5	Slightly scale forming and corrosive
0	Balanced, but pitting corrosion possible
-0.5	Slightly corrosive, but not scale forming
-2	Serious corrosion

On average Mine A has an LSI value greater than zero whereas Mine B has a value less than zero. Table 3-16 and Table 3-17 indicate that the water from both mines is corrosive, however, as Mine A has an LSI value greater than zero, it has the potential to form a calcium carbonate film or layer during the corrosion process which can lead to bicarbonate SCC.

3.4.3 Biological Species

Methane producing archaea can cause direct corrosion if metallic iron is the only source of reducing equivalents in their habitat. Dinh et al.^[128] isolated a new archaea, *Methanobacterium* sp, that produced methane with iron using methanogens at a faster rate than that for hydrogen production. The methanogens then bypass the slow abiotic H₂ formation on iron by faster direct use of the electrons. The resulting reaction is^[129, 130]:



The process may play a significant role in microbial iron corrosion because methanogenic archaeae may take advantage of electroconductive FeS precipitated by the co-occurring sulphate reduction reaction. Furthermore, if sulphate becomes limiting and though the sulphate reducing bacteria (SRB), these lithotrophic methanogenic archaea could even be favoured in growth and activity contributing to the corrosion^[128]. Methanogenic species were found in the microbial community of the water indicating the potential for the occurrence of methanogenic iron corrosion at the crack tip.

Microbiological corrosion is frequently linked to the activity of bacteria (particularly SRB), with far less attention being paid to the impact of iron-reducing bacteria and methane producing archae on the corrosion process.

SRB represented the most predominant bacterial fraction of the total bacterial community with the proportion of *δ-Proteobacteria*, generally consisting of *Desulfovibrio* sp., *Desulfobulbus* sp. and *Desulfuromonas* sp. SRB have been considered to be the major bacterial group involved in microbiologically influenced corrosion of various metals including carbon steels, stainless steels and copper alloys^[121, 122]. For example, the *Desulfovibrio* species (e.g. *D. desulfuricans*, *D. vulgaris*, *D. salexigens*), are regarded as the main initiator of anaerobic corrosion with their capacity to consume hydrogen very effectively^[131-133]. Furthermore, their activity often occurs in biofilms developed on the surfaces of metals^[121, 134] resulting in a tendency to pit the metal^[135]. The microbial colonization of the metal surfaces drastically changes the electrical interface commonly used in inorganic corrosion, e.g. ions, pH, oxidation reduction potential (ORP)^[136, 137].

Desulfovibrio species also have the ability to produce extracellular polymeric substances (EPS) which are used in the reduction of sulphate to hydrogen sulphide^[133, 135]. This might be an important feature considering that hydrogen sulphide is the most important agent in the corrosive action of SRB^[132, 138].

3.5 Conclusions

1. The ground water in both mines was alkaline and not acidic
2. The ground water was substantially different in the two mines. In particular, the alkalinity was much higher in Mine A than in Mine B. The alkalinity in Mine A was also substantially higher than in mines in three Indian coalfields and in the Welbeck mine in the UK.
3. The alkalinity in both mines was almost exclusively due to the presence of bicarbonate ions. Accordingly, the bicarbonate level was substantially higher in Mine A than in Mine B. It was also substantially higher than in the Indian and UK mines.
4. The pH for Mine A was higher than for Mine B, in one case being as high as 9.1.
5. The ground water from both mines was classified as being corrosive, however, the Langelier saturation index indicated that the water from Mine A had the potential to form a calcium carbonate film or layer during the corrosion process which can then lead to bicarbonate SCC.
6. Mine water chemistry can vary significantly from place to place in a mine and also from one mine to another.
7. Microbacterial species which are known to influence corrosion were detected in the ground water.

4 EXAMINATION OF SERVICE FAILED ROCK BOLTS

4.1 Introduction

This chapter gives the results of a study of failed rock bolts retrieved from underground coal mines in Australia. Most of these bolts were manufactured from HSAC 840 steel which has replaced the grades of steel previously used.

4.2 Experimental Methods

4.2.1 Materials

Twelve failed rock bolts from six different coal mines in Australia, designated Mines A, B, C, D, E and F, were obtained for the study. Water analyses for Mines A and B are given in Chapter 3. Rock bolts 2, 4, 7, and 11 were from Mine A, Rock bolts 1, 3, 6 and 8 were from Mine B, Rock bolt 5 was from Mine C, Rock bolt 9 was from Mine D, Rock bolt 10 was from Mine E and Rock bolt 12 was from Mine F. Only the section of bolt from the fracture to the threaded end was provided in each case, since the remainder of the bolt was still embedded in the rock. The retrieved sections varied from approximately 100 – 1500 mm in length. Most of the bolts showed a discernible bend directly adjacent to the location of the fracture, as can be seen in Figure 4-1. Otherwise, the retrieved section was essentially straight in most cases. All bolts had a diameter of 22 mm.



Figure 4-1: Failed rock bolt recovered from mine site. A slight bend can be seen (arrowed) adjacent to the position of the fracture.

On receipt, a section about 10 mm in length was cut from the threaded end of each bolt and chemically analysed using optical emission spectroscopy. The analyses were carried out by Quality Castings, Revesby, NSW and the results are given in Table 4-1. The analyses showed that the failed rock bolts were of four different chemical types, namely:

- HSAC 840 (0.4%C, 1%S microalloyed steel) – Bolts 1, 5-9, 11-12
- Low silicon HSAC 840 (0.4%C, 0.35%S microalloyed steel) – Bolt 2
- AISI 1355 (1.5% manganese steel) – Bolts 3, 10
- AISI 5152 (0.5%C chromium steel) – Bolt 4.

It is noted that the low silicon HSAC 840 steel was an interim grade used only for a short time when the standard HSAC 840 was not available. Thus only a very small number of these bolts went into service.

Table 4-1: Chemical composition of service failed rock bolt.

Sample	%C	%Mn	%Si	%Ni	%Cr	%Mo	%S	%P	%Cu	%V	%W	%Ti	%Al
1	0.37	1.49	1.09	0.02	0.03	<0.001	0.013	0.021	0.006	0.037	0.023	0.001	0.008
2	0.40	1.44	0.35	0.05	0.06	0.01	0.027	0.015	0.180	0.048	0.020	0.001	0.004
3	0.54	1.65	0.25	0.10	0.09	0.02	0.020	0.013	0.202	0.002	0.016	0.001	0.003
4	0.56	0.81	0.25	0.03	0.76	0.005	0.018	0.029	0.010	0.008	0.023	0.002	0.027
5	0.39	1.55	1.04	0.02	0.02	<0.001	0.015	0.019	0.014	0.039	0.015	0.002	0.006
6	0.37	1.51	1.06	0.03	0.03	0.001	0.014	0.017	0.030	0.036	0.018	0.002	0.006
7	0.38	1.55	1.13	0.02	0.03	0.002	0.018	0.024	0.010	0.037	0.019	0.002	0.005
8	0.38	1.54	1.02	0.02	0.02	<0.001	0.015	0.018	0.004	0.036	0.026	0.002	0.005
9	0.38	1.51	1.01	0.03	0.03	<0.001	0.016	0.019	0.018	0.04	0.024	0.001	0.005
10	0.58	1.61	0.23	0.07	0.07	0.01	0.043	0.024	0.233	0.002	0.026	0.001	0.003
11	0.39	1.49	1.03	0.02	0.03	0.001	0.015	0.024	0.010	0.041	0.019	0.002	0.004
12	0.37	1.55	1.10	0.03	0.02	0.001	0.012	0.014	0.007	0.025	0.018	0.003	0.004

4.2.2 Crack Detection

All twelve rock bolts were crack detected using the wet continuous magnetic particle method with the magnetization in the longitudinal direction of the bolts. An Ardrex electromagnetic yoke was used to magnetise the rock bolts. Ardrex 8910 W white background lacquer and Ardrex 800/3 black magnetic ink were used as the crack detection consumables. The fracture surface, and the immediately adjacent region, were masked during crack detection to avoid contamination of the fracture surface from the background lacquer.

As in the earlier study by Crosky et al.^[5], only some of the 12 bolts were found to contain cracks. Examples are shown in Figure 4-2 (Rock bolt 2) and Figure 4-4 (Rock bolt 7). In some cases, cracks could be seen without the aid of magnetic particle inspection, Figure 4-4 (Rock bolt 1). As can be seen from Figure 4-2 to Figure 4-4, the cracks ran in the transverse direction and were present along the base of several of the ribs, again consistent with the earlier findings^[5]. The cracks shown in Figure 4-2 and Figure 4-3 have not grown to a sufficient length to cause rupture and are therefore referred to as subcritical cracks. Such cracks are sometimes referred to as secondary cracks^[64] but the term subcritical cracks is preferred here.



Figure 4-2: Subcritical cracks revealed in Rock bolt 2 by magnetic particle inspection



Figure 4-3: Subcritical cracks revealed in Rock bolt 7 by magnetic particle inspection.



Figure 4-4: Cracks (arrowed) visible in Rock bolt 1 without the aid of magnetic particle inspection.

4.2.3 Fractographic Examination

Seven rock bolts from the twelve given in Table 4-1 were selected for fractographic examination. These were chosen as bolts which showed the least post-failure corrosion, as evidenced by lack of rusting of the overload region of the fracture surface. The HSAC 840 bolts were of most interest since, unlike the 1355 and 5152 bolts, they had not been examined extensively during the earlier studies by Crosky et al.^[5] and Gamboa and

Atrens^[24]. Accordingly, four standard HSAC 840 bolts (Rock bolts 1 and 5-7) bolts and one low silicon HSAC 840 bolt (Rock bolt 2) were selected. One 1355 bolt (Rock bolt 3) and one 5152 bolt (Rock bolt 4) were also examined.

Each of the rock bolts was sectioned approximately 10 mm below the fracture surface to enable examination by optical microscopy. Optical microscopy was carried out using an Olympus SZ-STU2 low power stereo optical microscope.

Rock bolts 5 and 6 (both HSAC 840), were selected for further examination by scanning electron microscopy since their fracture surfaces showed post-failure corrosion. The fracture surfaces were first examined after ultrasonic cleaning in a water-detergent mixture. However, this did not adequately remove the corrosion product on the SCC region and this prevented detailed examination and the fracture surfaces. Accordingly, the specimens were subsequently ultrasonically cleaned for 15 seconds in Ajax inhibited hydrochloric acid to remove the corrosion product. This procedure had been previously shown by Chen to remove the corrosion product in rock bolts without significantly attacking the underlying material^[139]. Cleaning in 5% EDTA, as used by Gamboa and Atrens^[24] was also tried but adequate cleaning was not achieved. The fracture surfaces were examined uncoated using a Hitachi S3400-I scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV.

4.2.4 Hardness Testing

A transverse section approximately 10 mm thick was cut from each of the rock bolts for hardness testing. The section was then metallographically polished on the transverse face to a 1 μm diamond finish. Hardness testing was conducted on the polished face using a Struers Duramin-A300 hardness tester with a load of 1 kg and an indentation time of 15 seconds. The hardness was determined as the average of three measurements made midway between the surface and the centre of the rock bolts, with each point being equally spaced around the specimen.

4.2.5 Microstructural Examination

A piece was cut from the transverse section used for hardness testing for Rock bolts 1-4 and hot mounted in Bakelite at 180°C using a Struers ProntoPress-20, then ground progressively using 120, 320, 800 and 1200 SiC emery papers using a Struers Labopol-5, then polished on a 3 micron diamond pad and finished using a 1 micron diamond pad,

using a Struers DAP-2. The samples were then etched in 5% Nital and examined using a Nikon Ephiphot 200 inverted optical microscope. Images were captured using a Nikon DXM 1200 digital camera utilising Nikon ACT-1 software.

4.2.6 Examination of Crack Path

As shown in Figure 4-2 to Figure 4-4, some of the rock bolts contained short transverse subcritical cracks at the base of some of the ribs. These cracks are considered to be shorter variants of the cracks which had led to catastrophic failure in these bolts. Accordingly, a number of the subcritical cracks seen in Rock bolts 1, 2 and 7 (all HSAC 840) were sectioned to examine the crack profile and crack path. These rock bolts were from mines which had near-neutral pH (Rock bolt 1 – Mine B) and high pH (Rock bolt 2 and 7 – Mine A). The ground water analyses for these mines are given in Chapter 3. While 2 rock bolts with subcritical cracks were obtained from Mine A, only a single bolt was available from mine B.

Each of the rock bolts was sectioned longitudinally at the locations shown in Figure 4-5 to Figure 4-7. The sections were then mounted in Bakelite and metallographically polished to a 1 μm diamond finish using the procedure described in Section 4.2.3. The specimens were ground and polished several times to provide a good overview of the nature of the cracks. In the case of Rock bolt 2, the polished sections were etched in 5% Nital to establish the relationship between the crack path and the microstructure.

Where appropriate, electron backscattered diffraction (EBSD) was used to determine the grain orientation on either side of the crack to establish whether the crack was running through a single grain or along the boundary between two adjoining grains. EBSD was carried out using a Carl Zeiss Auriga CrossBeam Workstation fitted with a NordlysF EBSD system, operated at an accelerating voltage of 15 kV.

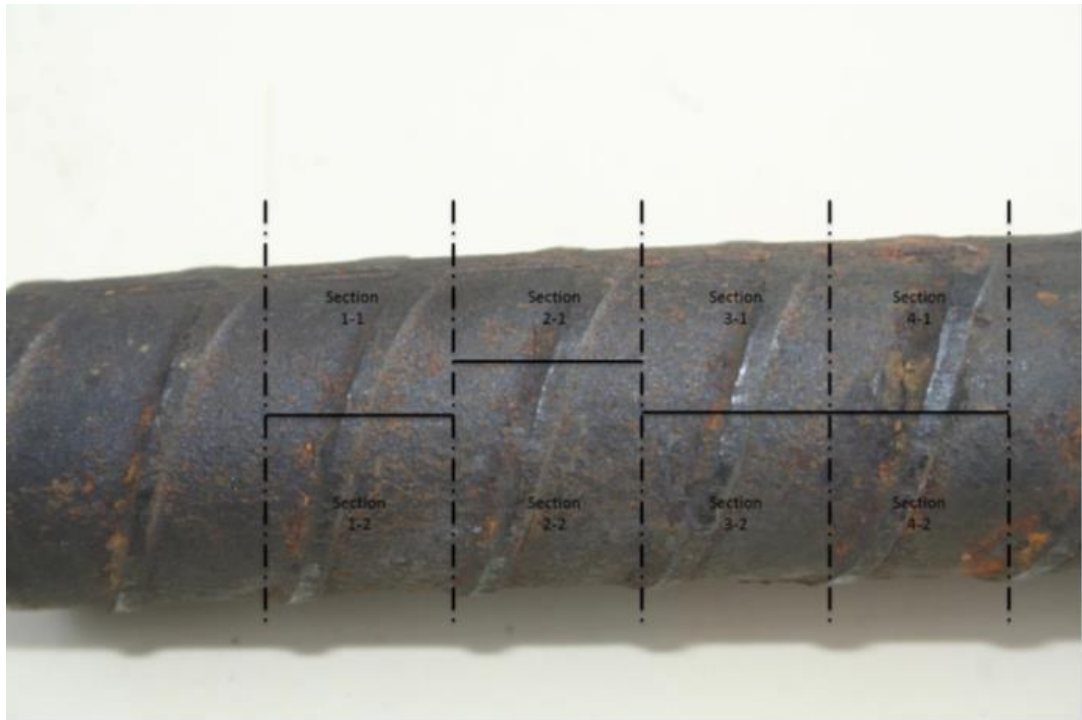


Figure 4-5: Location of sections made in Rock bolt 1.

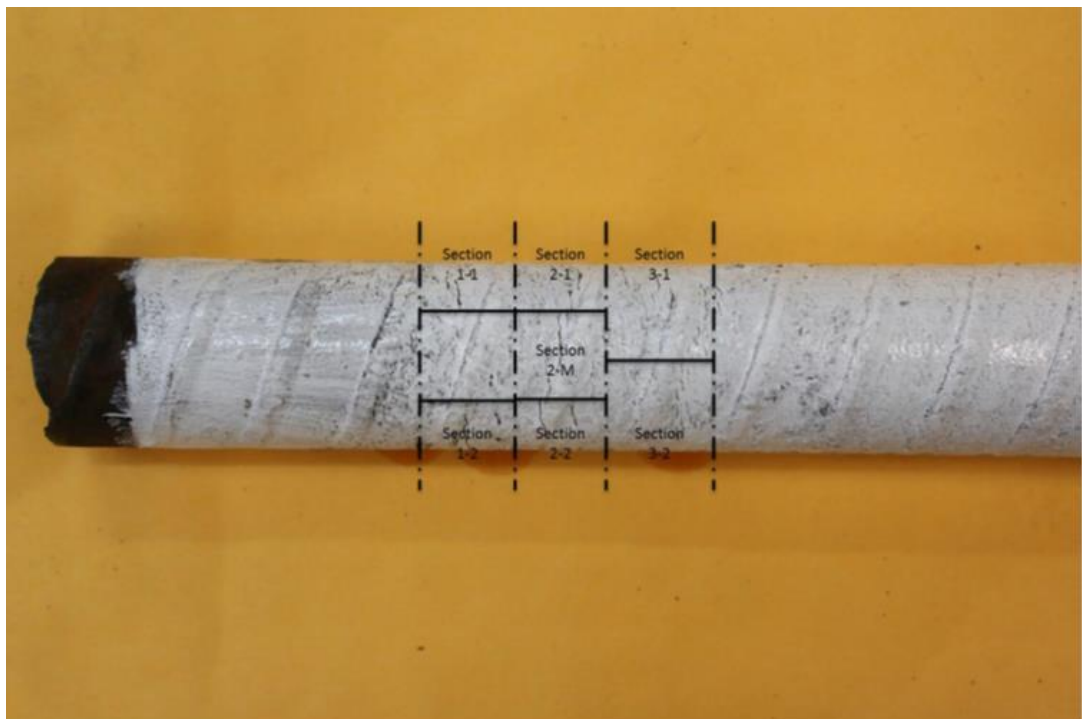


Figure 4-6: Location of sections made to Rock bolt 2.

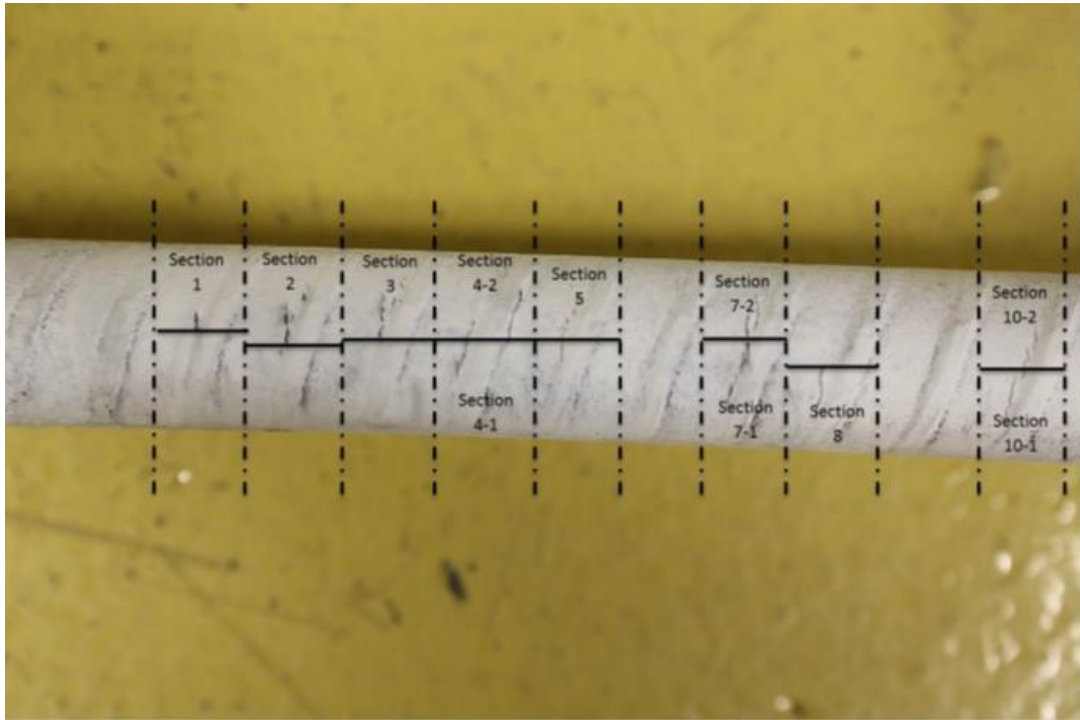


Figure 4-7: Location of sections made in Rock bolt 7.

4.2.7 Analysis of Corrosion Product

The corrosion product present in subcritical cracks was analysed for Rock bolts 1 and 2. As noted above, these bolts came from mines with quite different water chemistries. The analyses were carried out on longitudinally sectioned samples prepared in the manner described above excluding the etching step. The corrosion product present in the cracks was analysed using a Renishaw inVia laser Raman microscope using 514 nm (green) excitation. Care was taken to avoid heating of the corrosion product by the beam during the analysis since this can cause temperature-induced changes to the corrosion product.

4.3 Results

4.3.1 Microstructure Examination

The transverse microstructure of failed rock bolts from the four different steel grades is shown at the surface and in the centre of each bolt in Figure 4-8 to Figure 4-15. The HSAC 840 steel (Rock bolt 1) is shown in Figure 4-8 and Figure 4-9, the low silicon HSAC 840 steel (Rock bolt 2) in Figure 4-10 and Figure 4-11, the 1355 steel in (Rock bolt 3) in Figure 4-12 and Figure 4-13 and the 5152 steel (Rock bolt 4) in Figure 4-14 and Figure 4-15. All rock bolts showed surface decarburisation which had resulted from the hot rolling process used in their manufacture. The HSAC 840 steel had a mixed

ferrite/pearlite structure, with a similar microstructure also being observed in the low silicon HSAC 840 steel. The AISI 1355 steel had a mostly pearlitic structure with just a small amount of ferrite at the prior austenite grain boundaries, while the AISI 5152 steel was almost fully pearlitic. All steels contained manganese sulphide inclusions, as is characteristic of air melted steels.

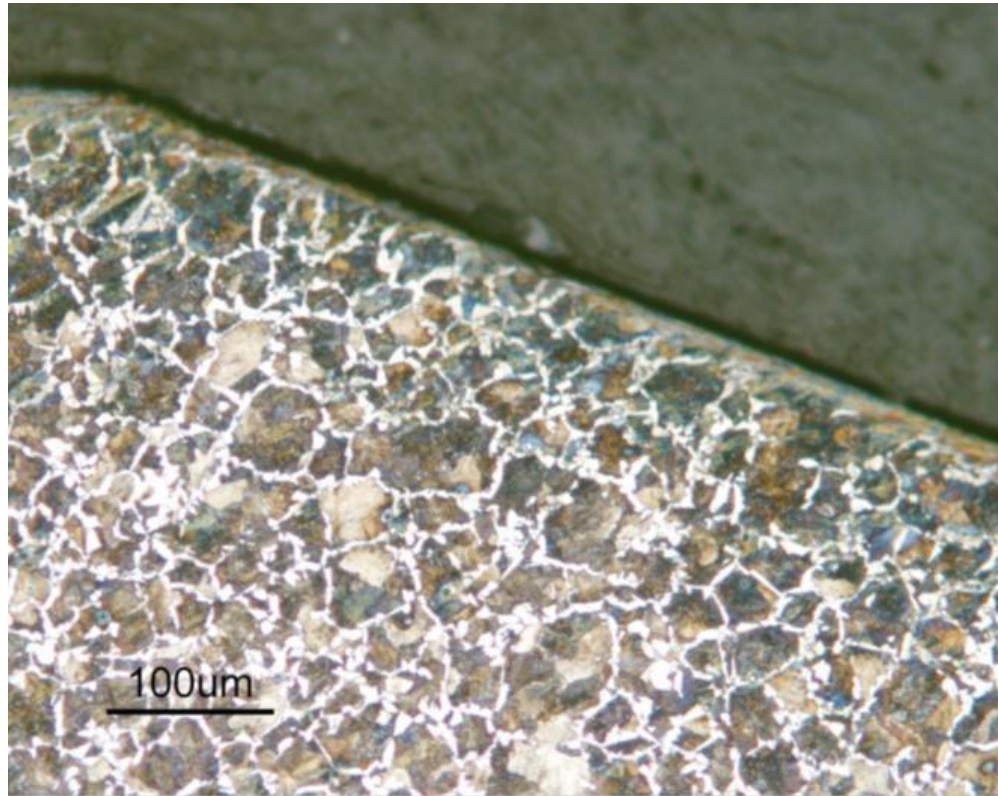


Figure 4-8: Transverse microstructure at surface of service failed HSAC 840 rock bolt (Rock bolt 1).

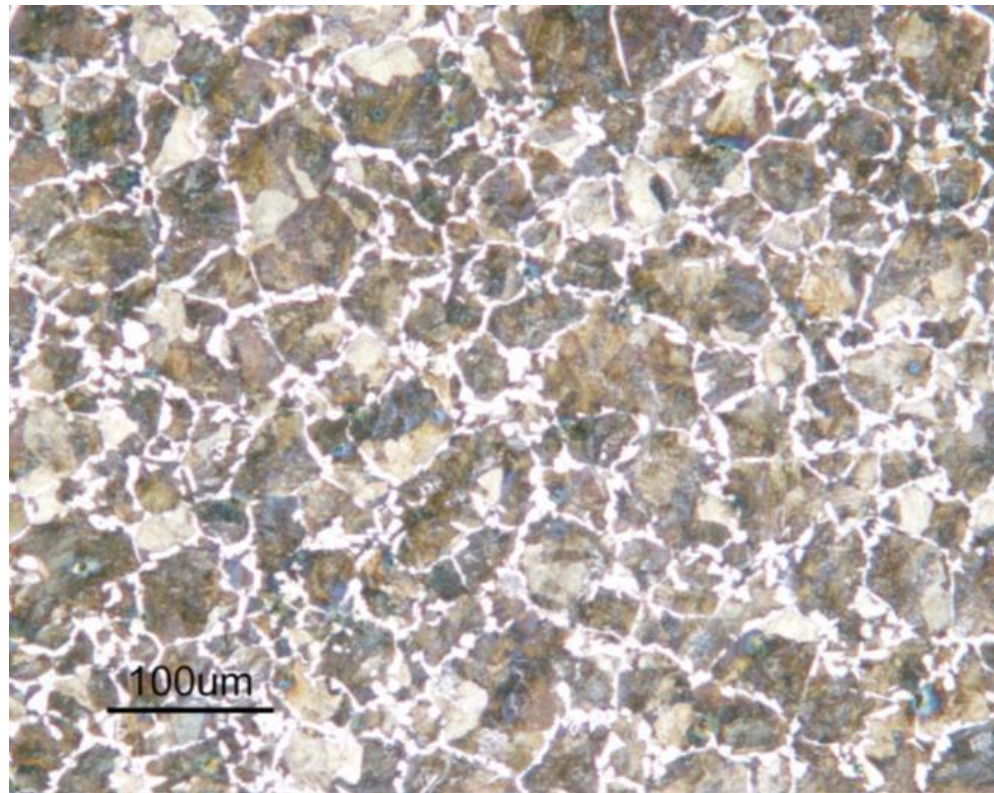


Figure 4-9: Transverse microstructure at the centre of service failed HSAC 840 rock bolt (Rock bolt 1).

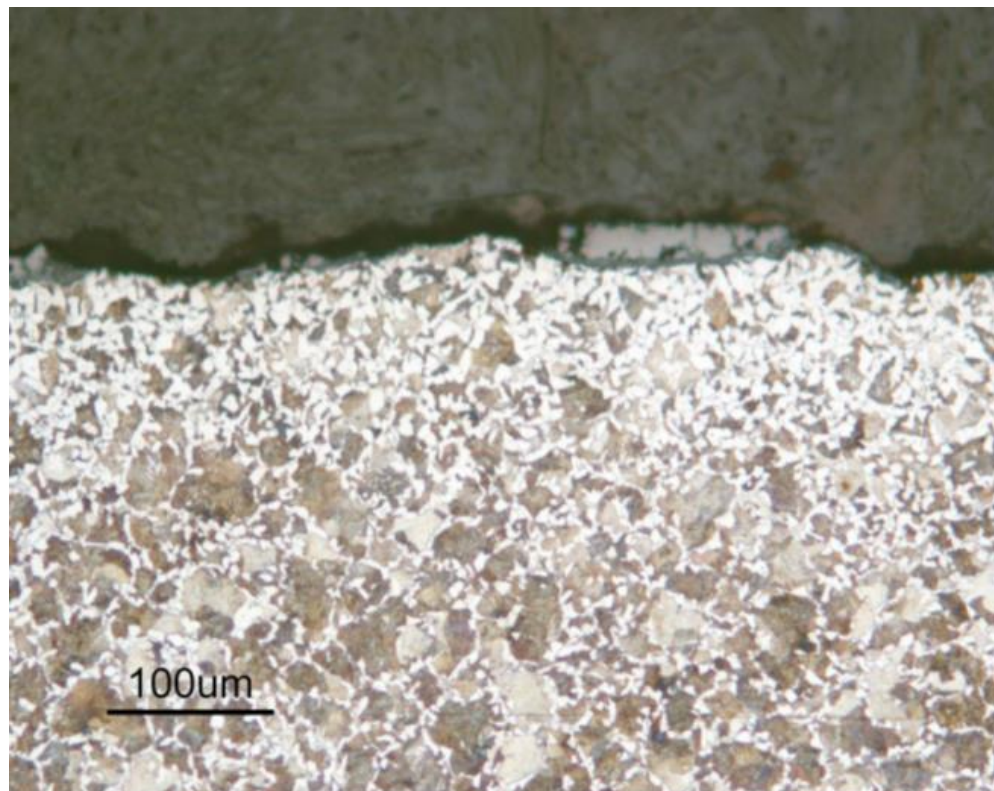


Figure 4-10: Transverse microstructure at the surface of service failed low Si HSAC 840 rock bolt (Rock bolt 2).

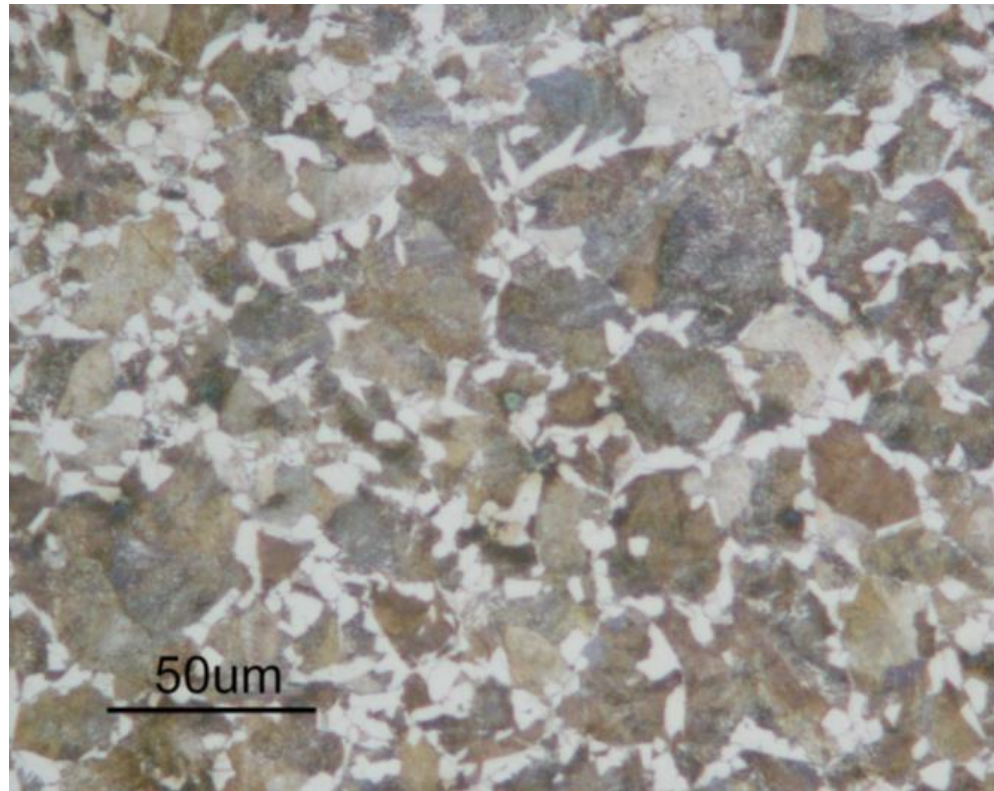


Figure 4-11: Transverse microstructure at the centre of service failed low Si HSAC 840 rock bolt (Rock bolt 2).

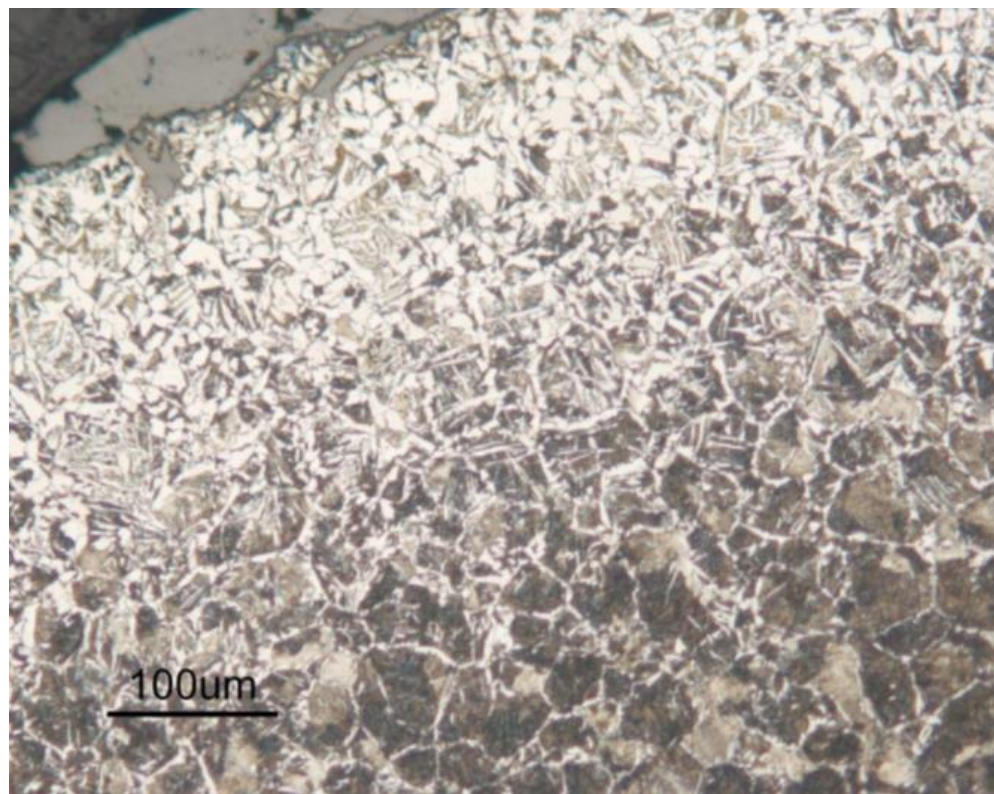


Figure 4-12: Transverse microstructure at the surface of service failed 1355 rock bolt (Rock bolt 3).

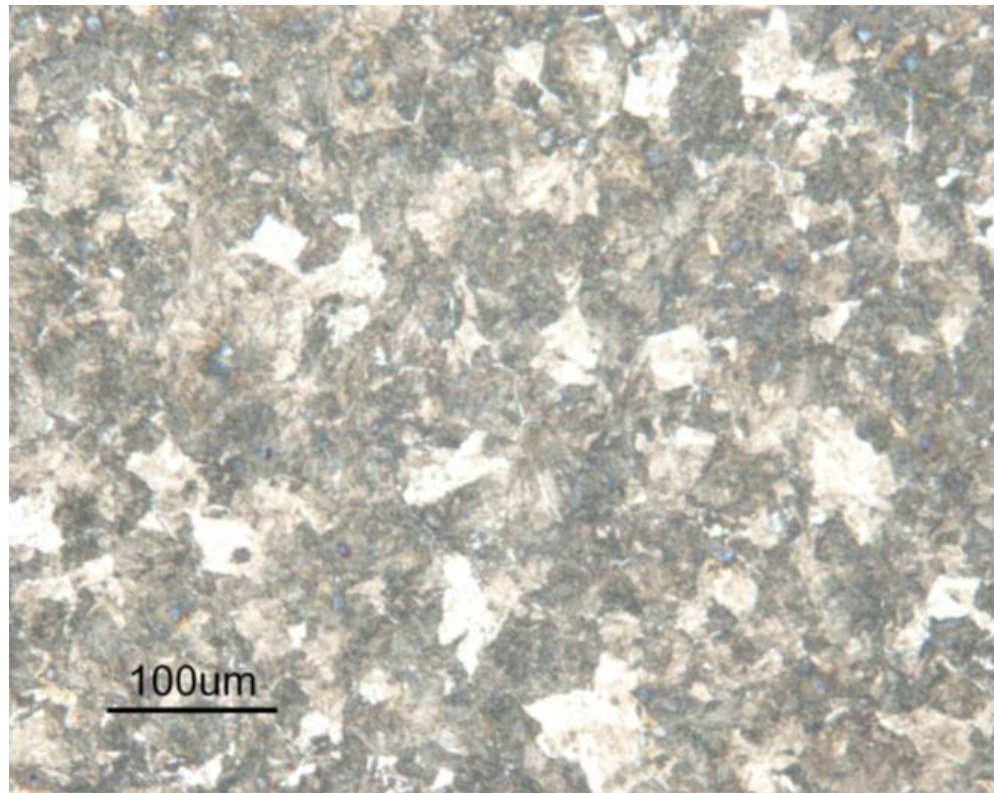


Figure 4-13: Transverse microstructure at the centre of service failed 1355 rock bolt (Rock bolt 3).

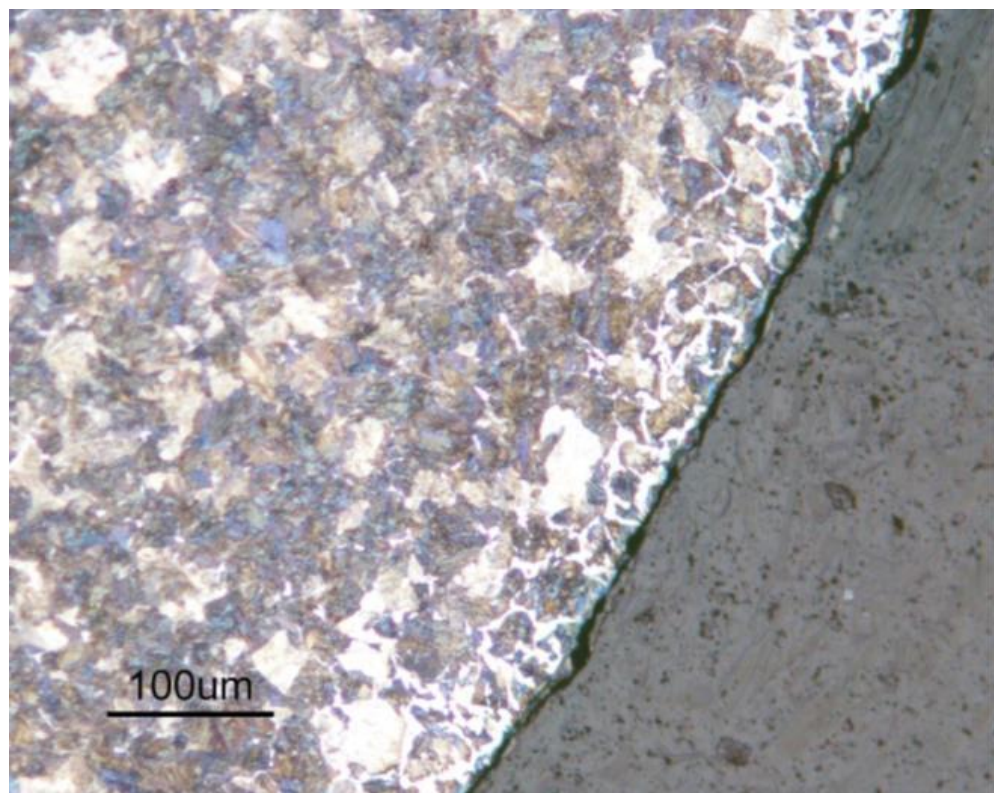


Figure 4-14: Transverse microstructure at the surface of service failed 5152 rock bolt (Rock bolt 4).

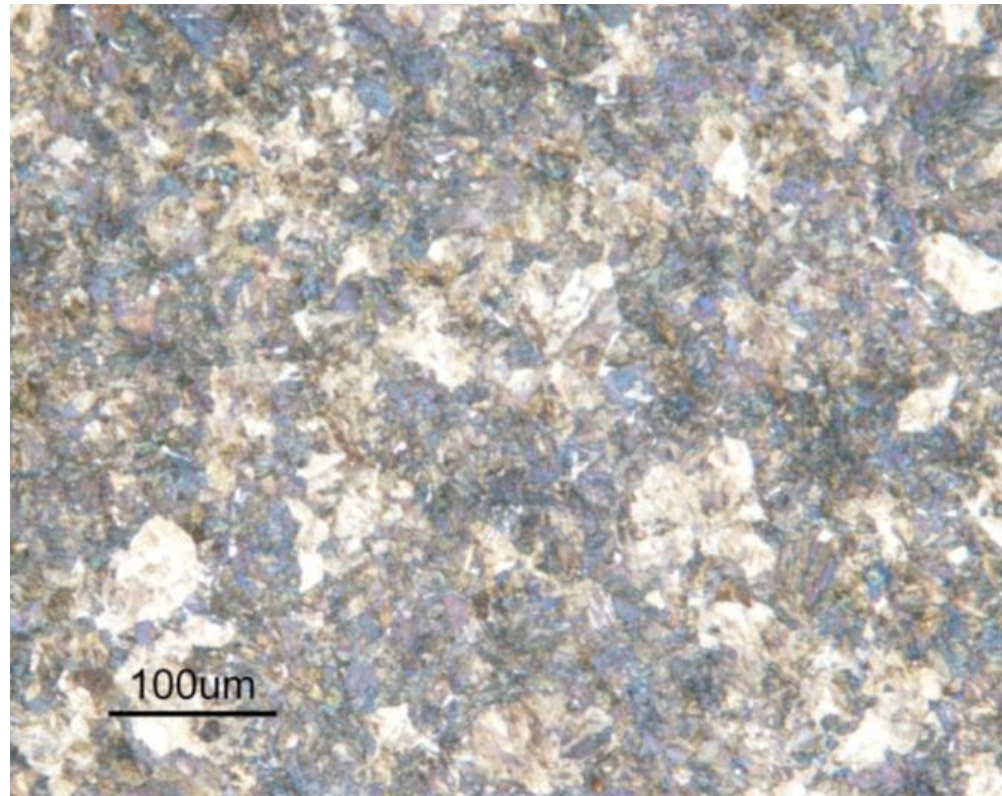


Figure 4-15: Transverse microstructure at the centre of service failed 5152 rock bolt (Rock bolt 4).

4.3.2 Hardness

The hardness of the twelve rock bolts is given in Table 4-2. The values range from 250 – 336 HV₁ which correspond to tensile strengths of approximately 820-1090 MPa^[64].

Table 4-2: Hardness values of failed rock bolts.

Sample ID	Steel Grade	Hardness HV ₁
1	840	314
2	840 (low Si)	259
3	1355	316
4	5152	333
5	840	300
6	840	272
7	840	284
8	840	261
9	840	283
10	1355	336
11	840	285
12	840	250

4.3.3 Fractography

The fracture surfaces of Rock bolts 1-12 are shown in Figure 4-16 to Figure 4-27, while examples of the broken bolts side on are shown in Figure 4-28 to Figure 4-34. All bolts fractured in a brittle manner with the fracture being planar and perpendicular to the axis of the bolt, as shown in Figure 4-28 to Figure 4-34.

The fracture surfaces showed a thumbnail shaped discoloured region (at bottom of each image), as is characteristic of stress corrosion cracking, followed by a bright region which had resulted from final overload fracture of the bolt, as shown in Figure 4-16 to Figure 4-27. These features are the same as those reported in the earlier study by Crosky et al.^[5].

In some cases, there was a single thumbnail shaped SCC region (eg, Rock bolt 5) in others two overlapping thumbnail shaped SCC regions (eg, Rock bolt 6), while in others there were multiple overlapping thumbnail shaped SCC regions (eg, Rock bolt 2). This is again consistent with the findings of Crosky et al.^[5].

The depth of the SCC region was measured for the 12 rock bolts, as illustrated by the dotted line in Figure 4-16 to Figure 4-27, and the results are given in Table 4-3. The crack depth varied considerably ranging from 1 mm to 11 mm in the 22 mm diameter of the rock bolts. The variation was independent of rock bolt chemistry with the SCC region for the eight HSAC 840 rock bolts varying over the full extent of this range.



Figure 4-16: Fracture surface of Rock bolt 1.



Figure 4-17: Fracture surface of Rock bolt 2.

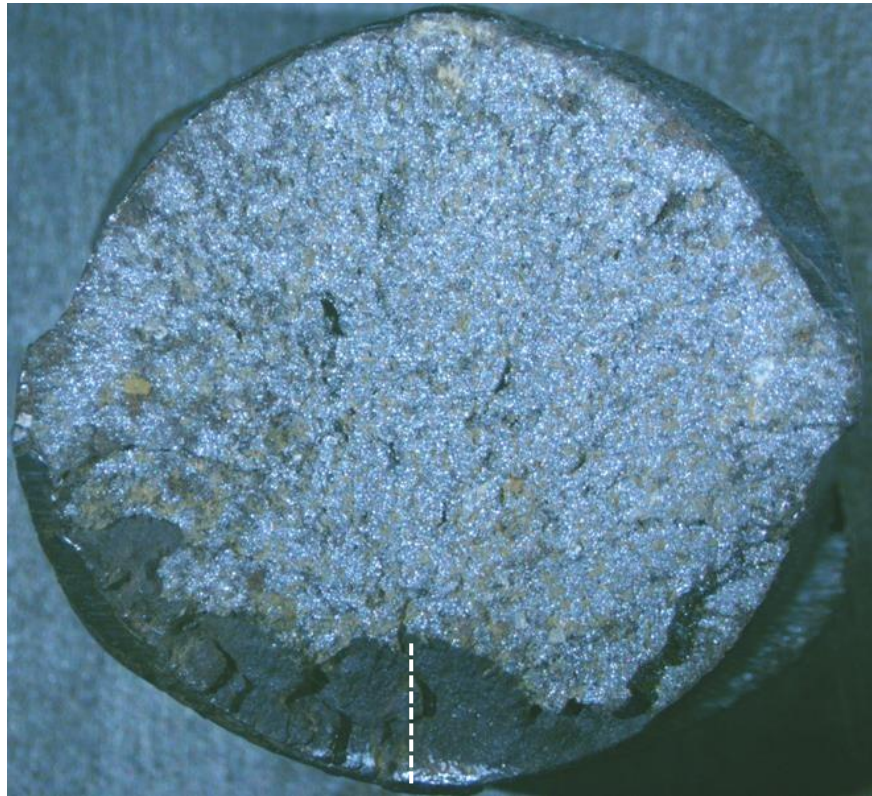


Figure 4-18: Fracture surface of Rock bolt 3.



Figure 4-19: Fracture surface of Rock bolt 4.



Figure 4-20: Fracture surface of Rock bolt 5.



Figure 4-21: Fracture surface of Rock bolt 6.



Figure 4-22: Fracture surface of Rock bolt 7.



Figure 4-23: Fracture surface of Rock bolt 8.



Figure 4-24: Fracture surface of Rock bolt 9.



Figure 4-25: Fracture surface of Rock bolt 10.

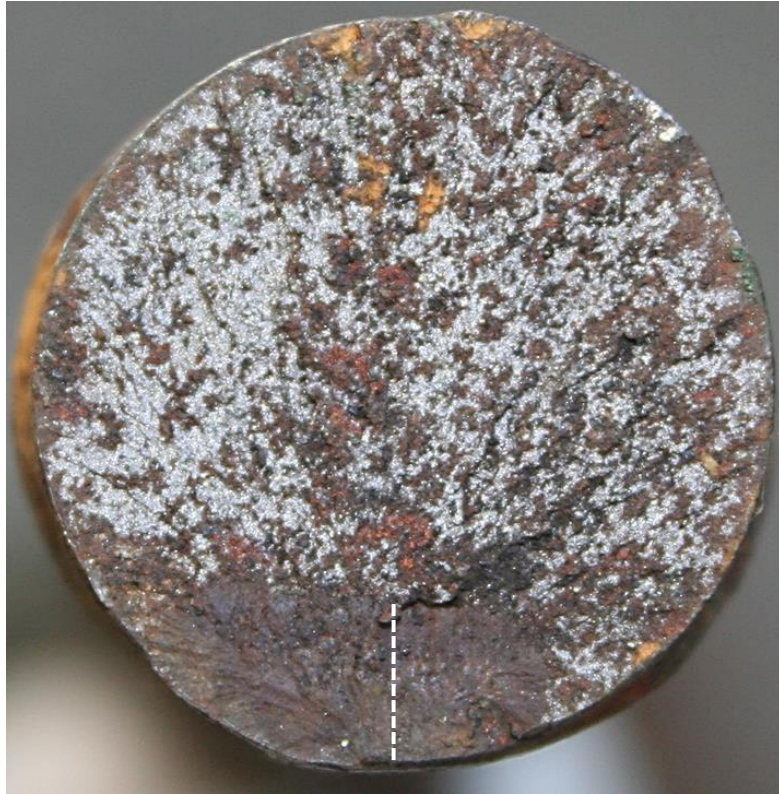


Figure 4-26: Fracture surface of Rock bolt 11.



Figure 4-27: Fracture surface of Rock bolt 12.



Figure 4-28: Rock bolt 1 profile.



Figure 4-29: Rock bolt 2 profile.



Figure 4-30: Rock bolt 3 profile.



Figure 4-31: Rock bolt 4 profile.



Figure 4-32: Rock bolt 7 profile.

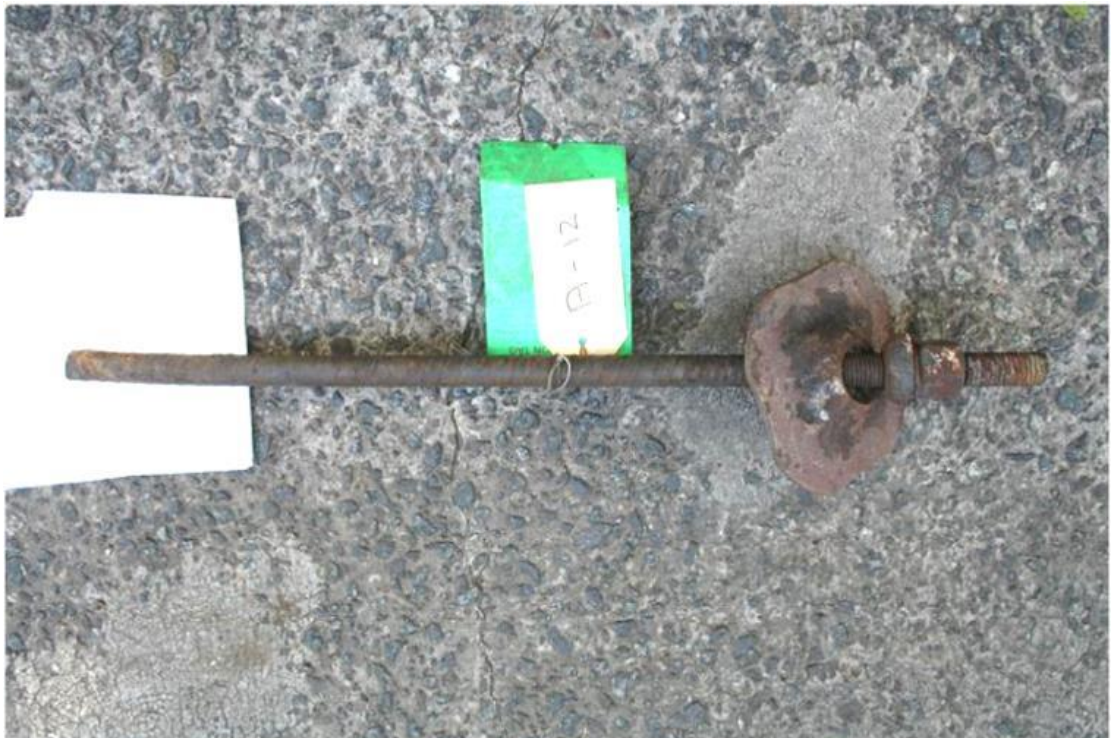


Figure 4-33: Rock bolt 11 profile.



Figure 4-34: Rock bolt 12 profile.

Table 4-3: Measured SCC crack depth.

Rock bolt	Steel Grade	Specimen Diameter / mm	Crack Depth / mm
1	840	22.1	3.8
2	840 (low Si)	22.2	7.3
3	1355	22.0	4.3
4	5152	21.6	9.9
5	840	22.0	1.3
6	840	22.0	3.1
7	840	22.1	11.3
8	840	22.0	2.5
9	840	22.0	9.0
10	1355	22.0	1.1
11	840	21.9	5.1
12	840	22.1	5.1

Low magnification SEM fractographs of Rock bolt 5 (an HSAC 840 rock bolt from Mine C) are shown in Figure 4-35 and Figure 4-36. The thumbnail shaped SCC region at the origin is clearly visible and, in this case, extends inwards to a depth of 1.3 mm (Table 4-3). Beyond the thumbnail shaped region the fracture topography can be seen to be quite different. This region corresponds to the bright region of the fracture surfaces seen in Figure 4-20.

The appearance of the fracture surface in the thumbnail-shaped region is shown at higher magnification in Figure 4-37 and Figure 4-38. The fracture surface shows features characteristic of tearing topography surface (TTS), which, as discussed in Section 2.3.2, is observed in steels which have undergone stress corrosion cracking. This is considered to confirm that this part of the fracture has occurred by stress corrosion cracking.

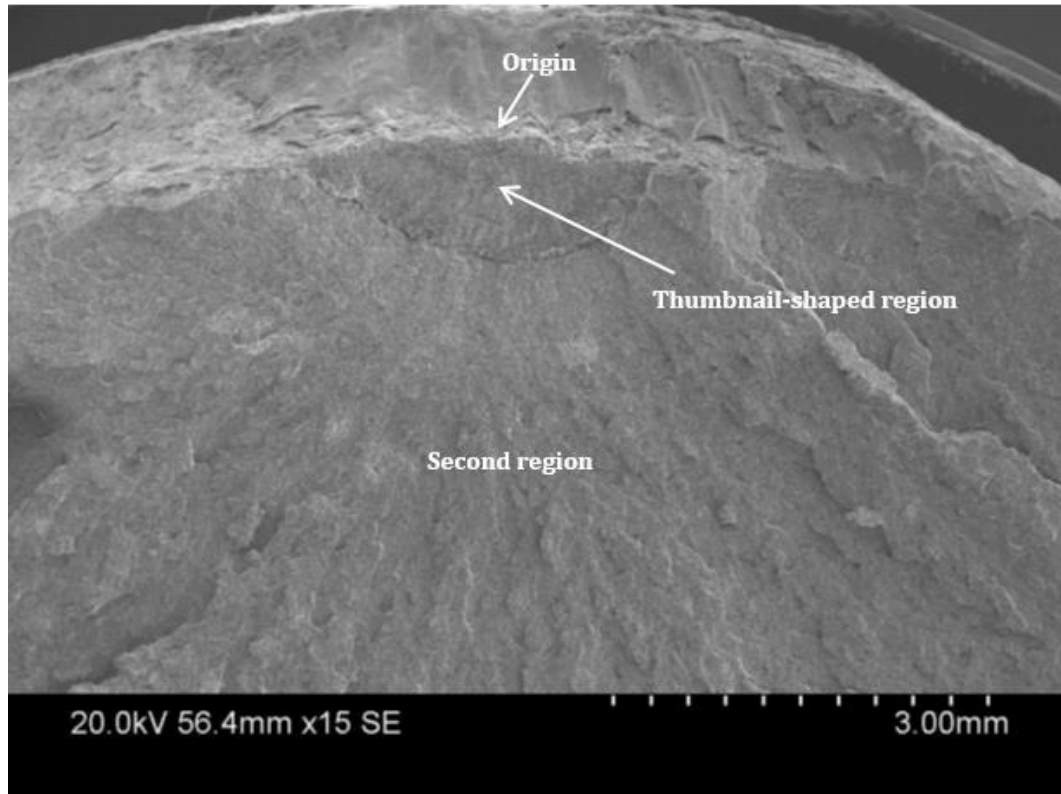


Figure 4-35: Low magnification SEM fractograph of Rock bolt 5. The approximate position of the fracture origin is indicated.

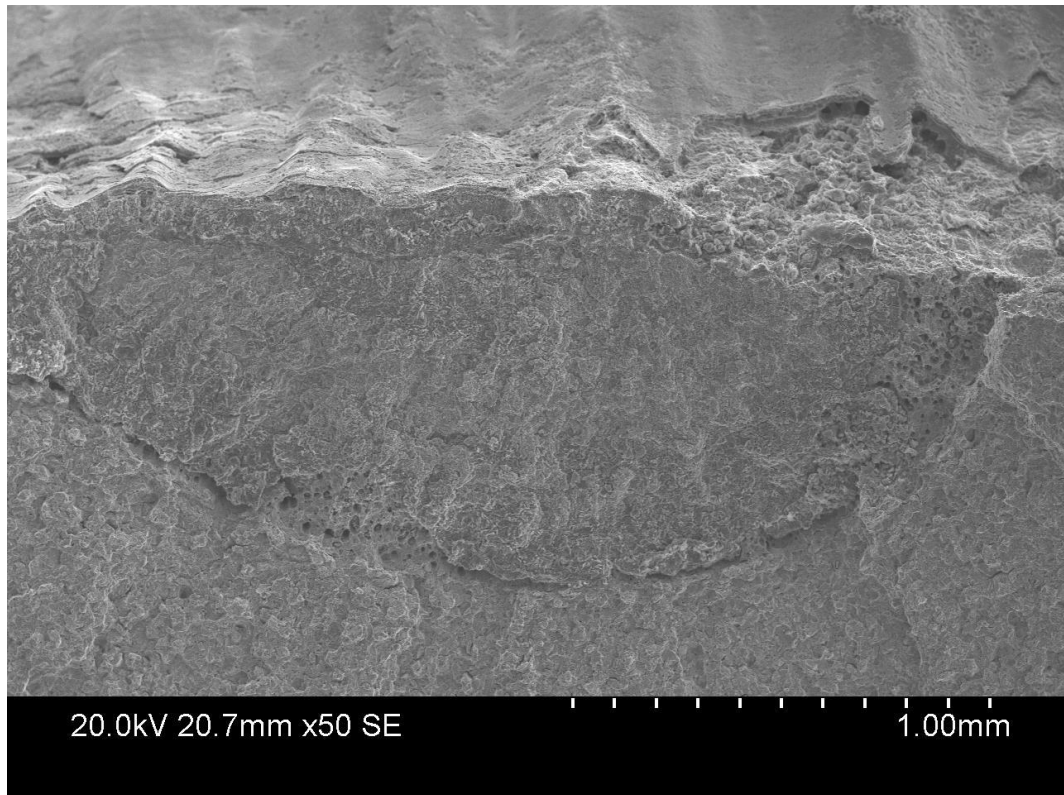


Figure 4-36: SEM image showing an overview of the thumbnail shaped region in Rock bolt 5.

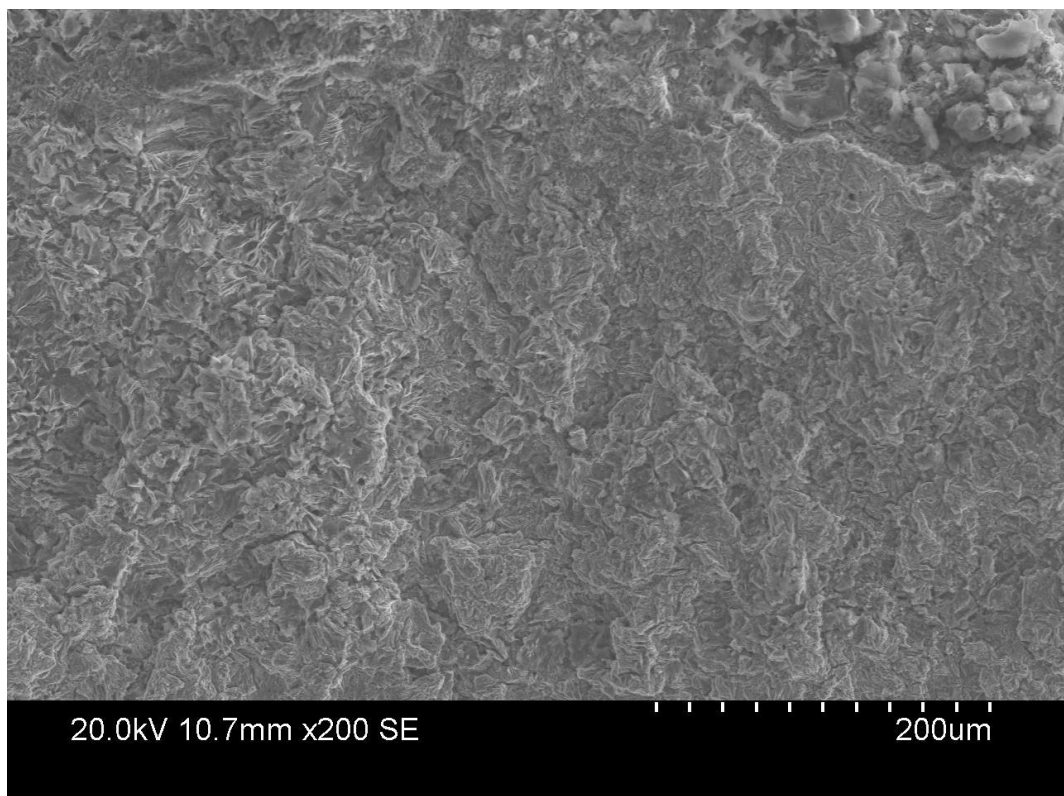


Figure 4-37: SEM fractograph of Rock bolt 5 in thumbnail shaped region.

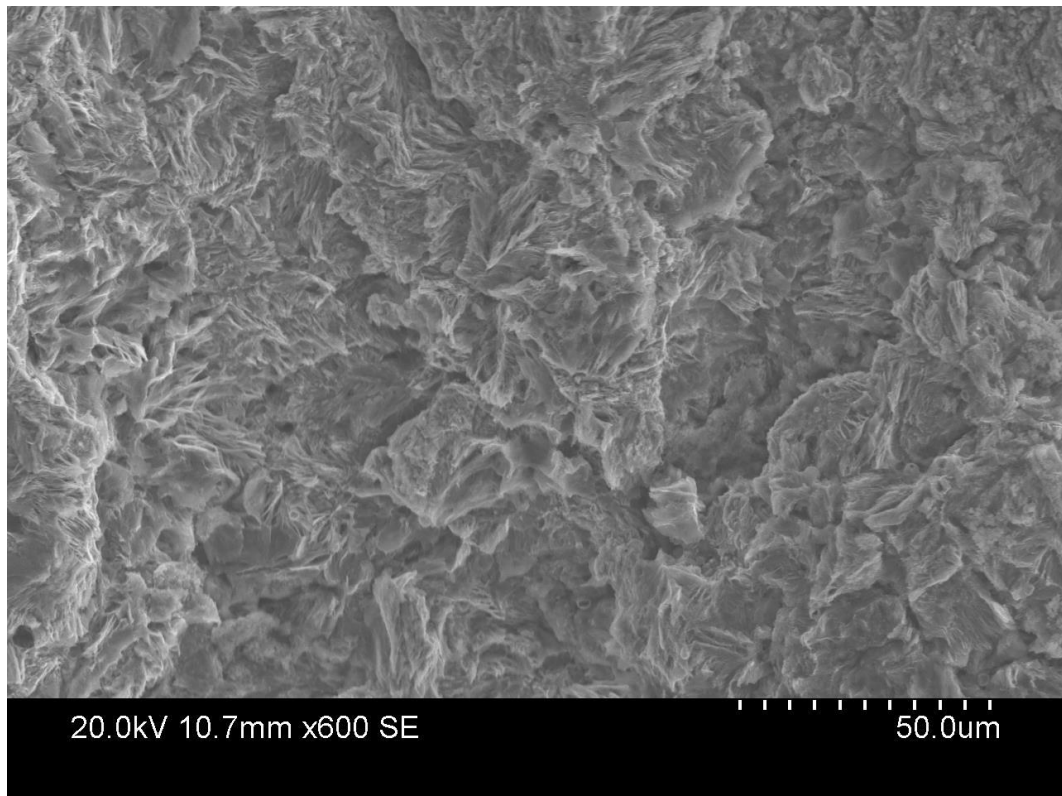


Figure 4-38: Higher magnification SEM fractograph of region shown in Figure 4-37.

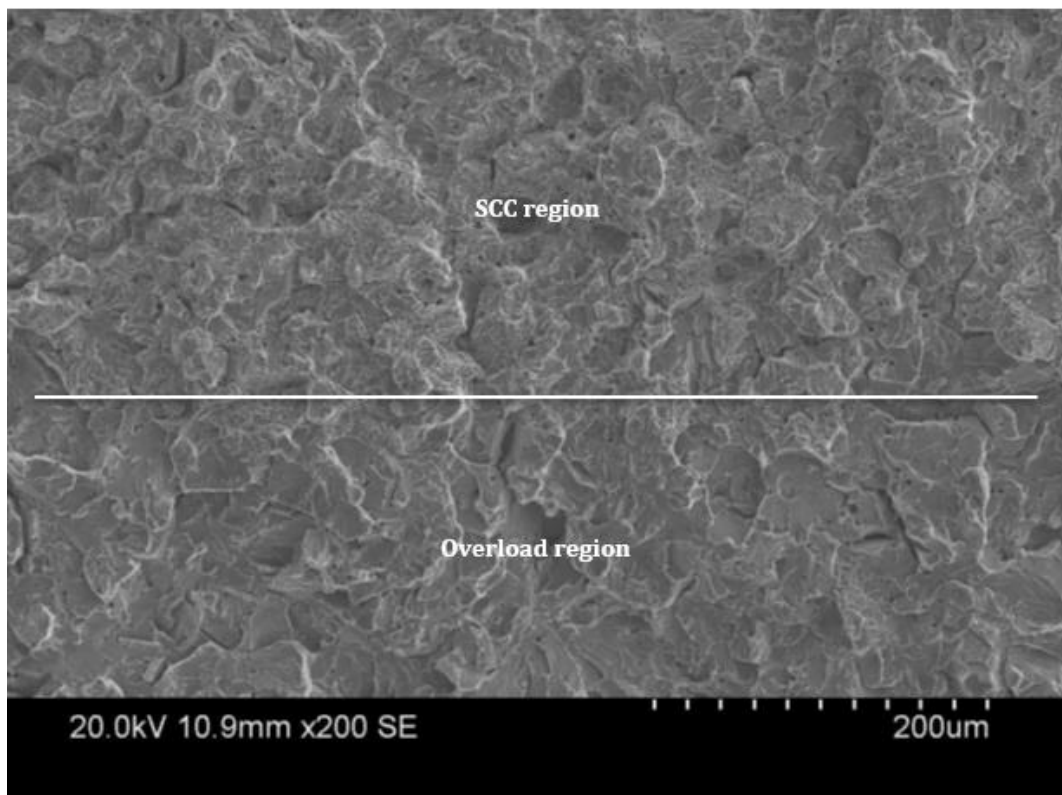


Figure 4-39: SEM fractograph of Rock bolt 5 showing the transition from SCC to overload failure.

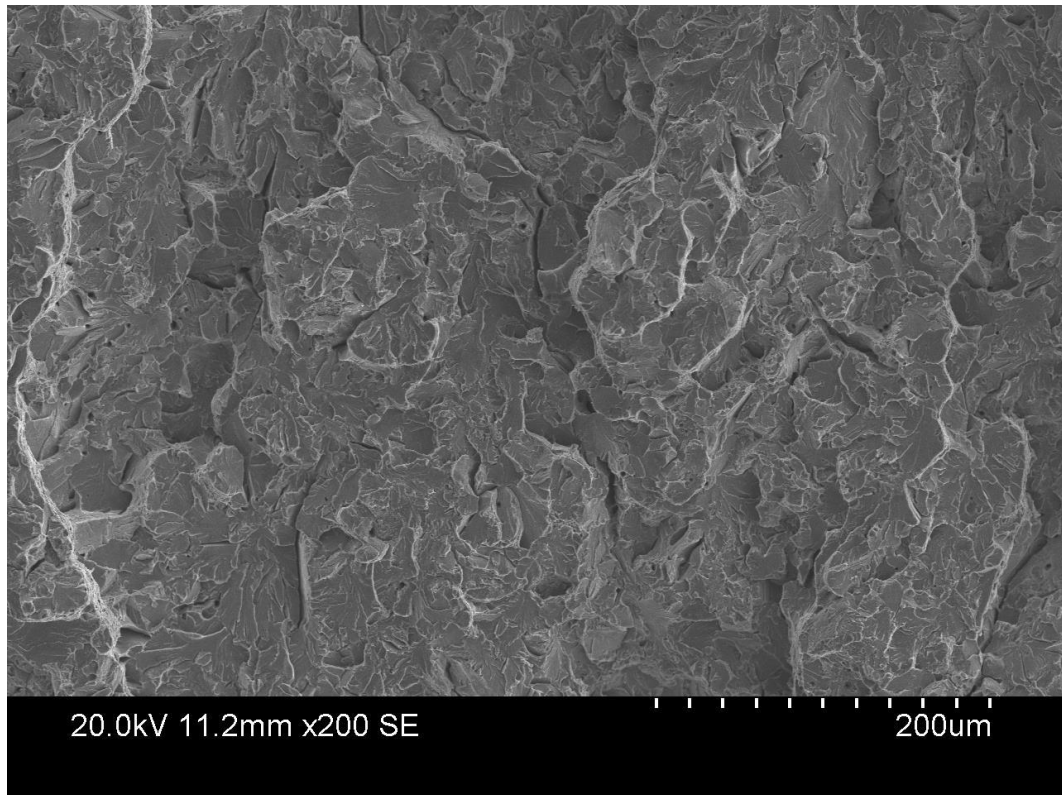


Figure 4-40: SEM fractograph of Rock bolt 5 showing the overload region.

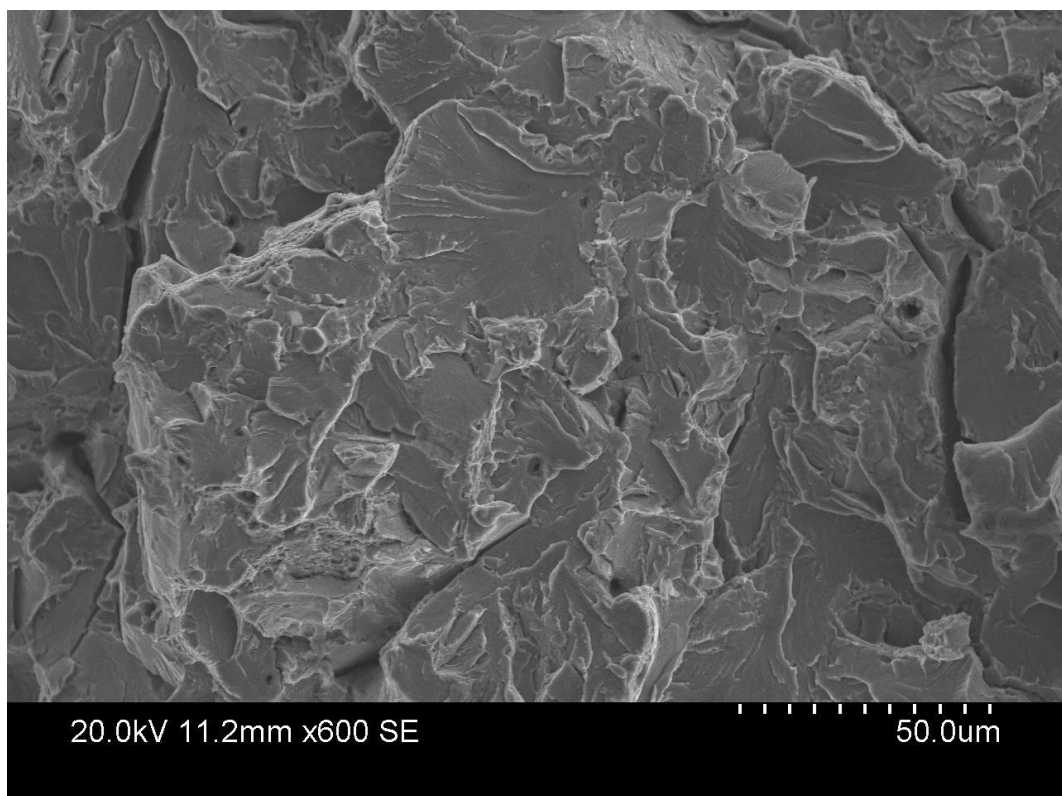


Figure 4-41: Higher magnification SEM fractograph of region shown in Figure 4-40.

The transition between the SCC region and the remainder of the fracture is shown in Figure 4-39. A sharp demarcation is evident between the SCC region, delineating the

transition from SCC to overload. The overload region beyond the transition is shown in Figure 4-40 and at higher magnification in Figure 4-41. The fracture surface has the characteristic appearance of transgranular cleavage which is typical of brittle overload failure.

SEM fractographs of a second HSAC 840 bolt, (Rock bolt 6), from a different mine (Mine B) are shown in Figure 4-42 to Figure 4-47. In this case, there are two adjoining thumbnail shaped SCC regions. These are marked A and B in Figure 4-42, and shown separately at somewhat higher magnification in Figure 4-43 and Figure 4-44, respectively. The SCC region B is shown at higher magnification in Figure 4-45, with the transition from SCC to overload being shown in Figure 4-46, and the overload region in Figure 4-47. The features of the SCC and overload regions can be seen to be similar to those in Rock bolt 5.

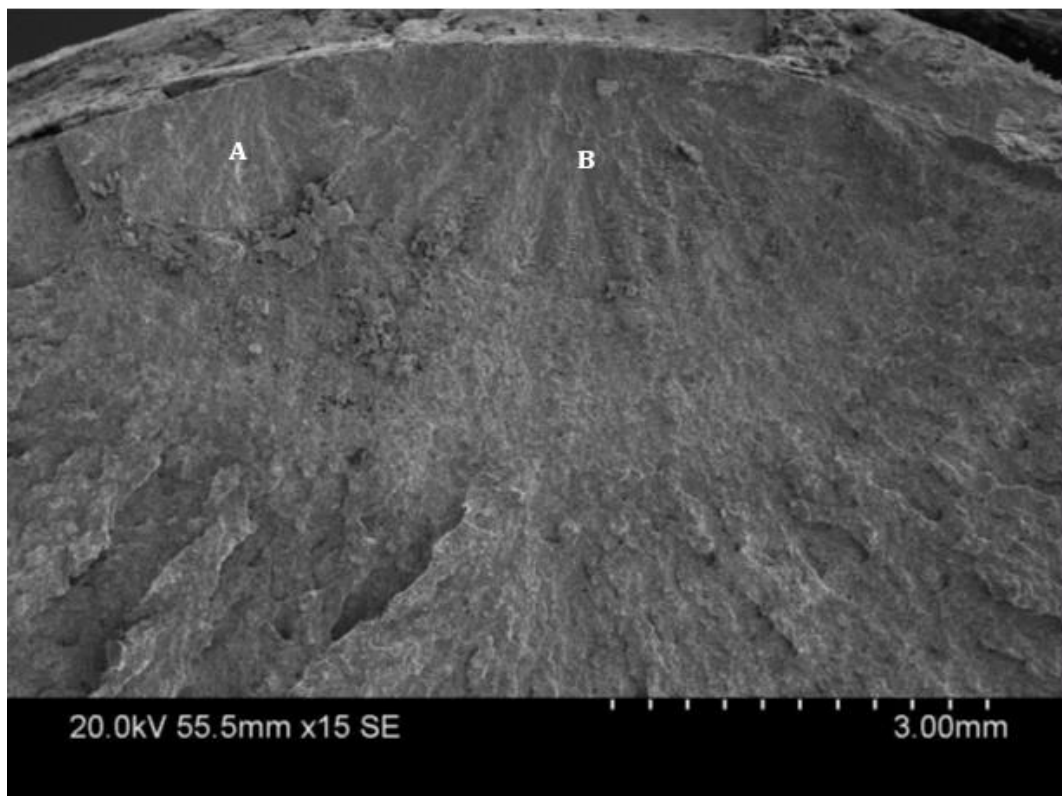


Figure 4-42: Low magnification SEM fractograph of Rock bolt 6. The two separate SCC regions are marked A and B.

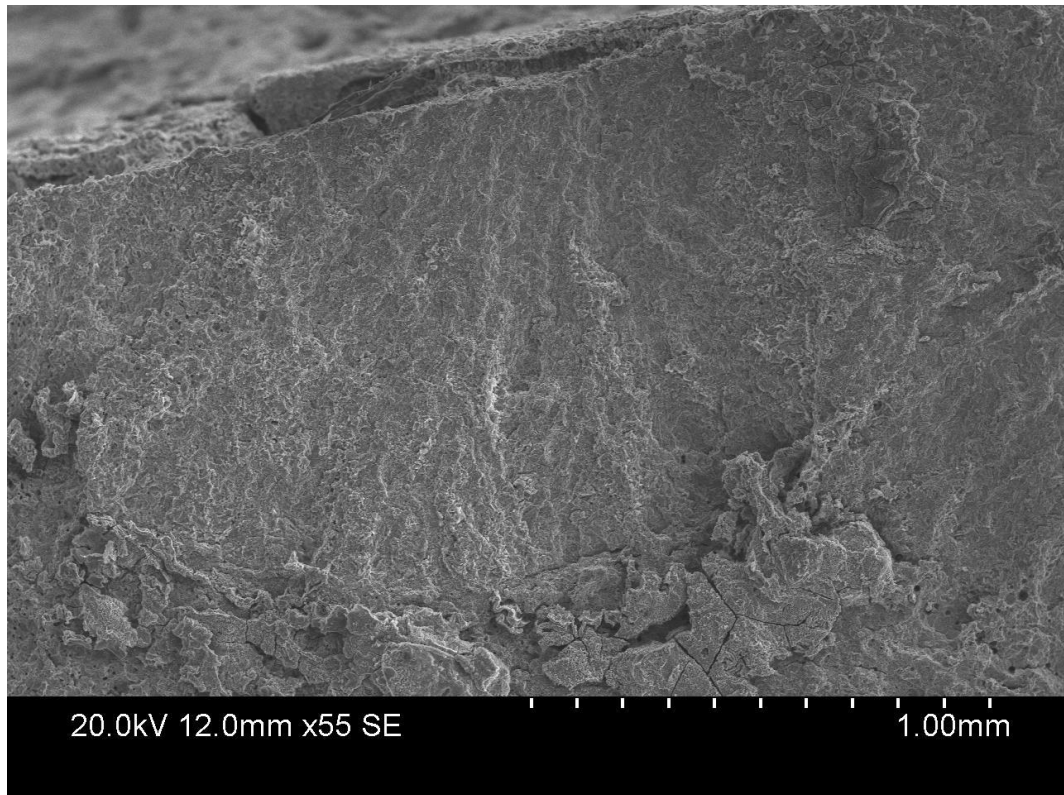


Figure 4-43: SEM fractography of Rock bolt 6 showing SCC region marked A in Figure 4-42.

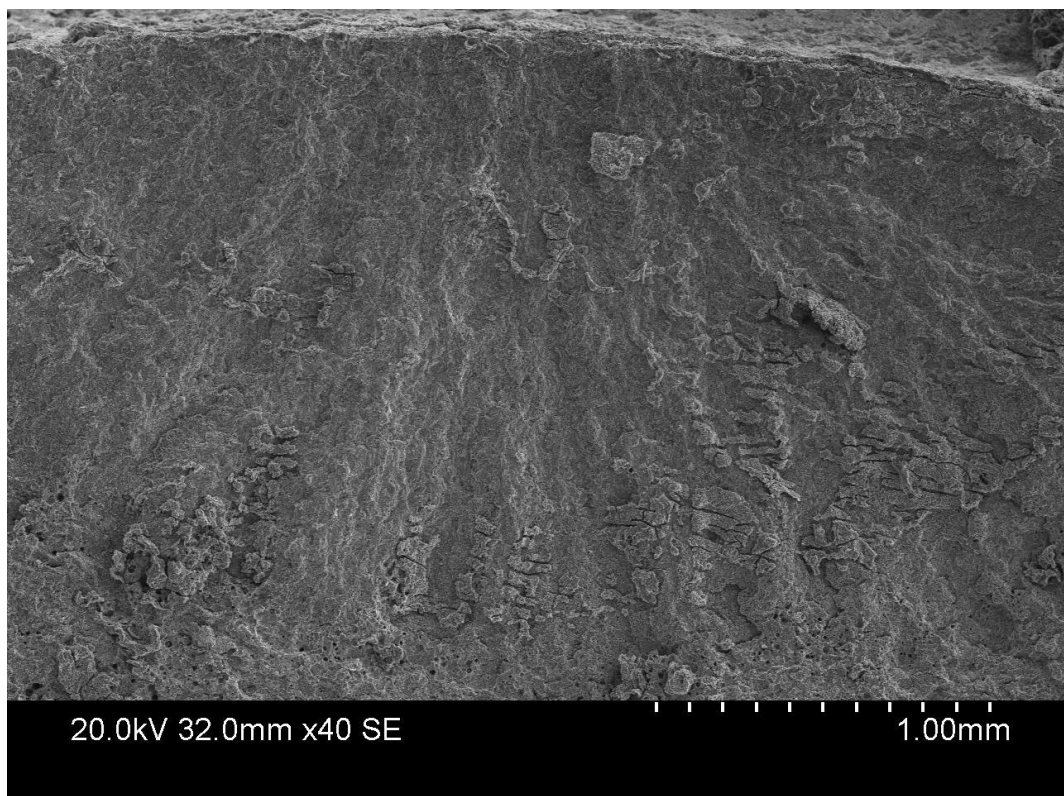


Figure 4-44: SEM fractography of Rock bolt 6 showing SCC region marked B in Figure 4-42.

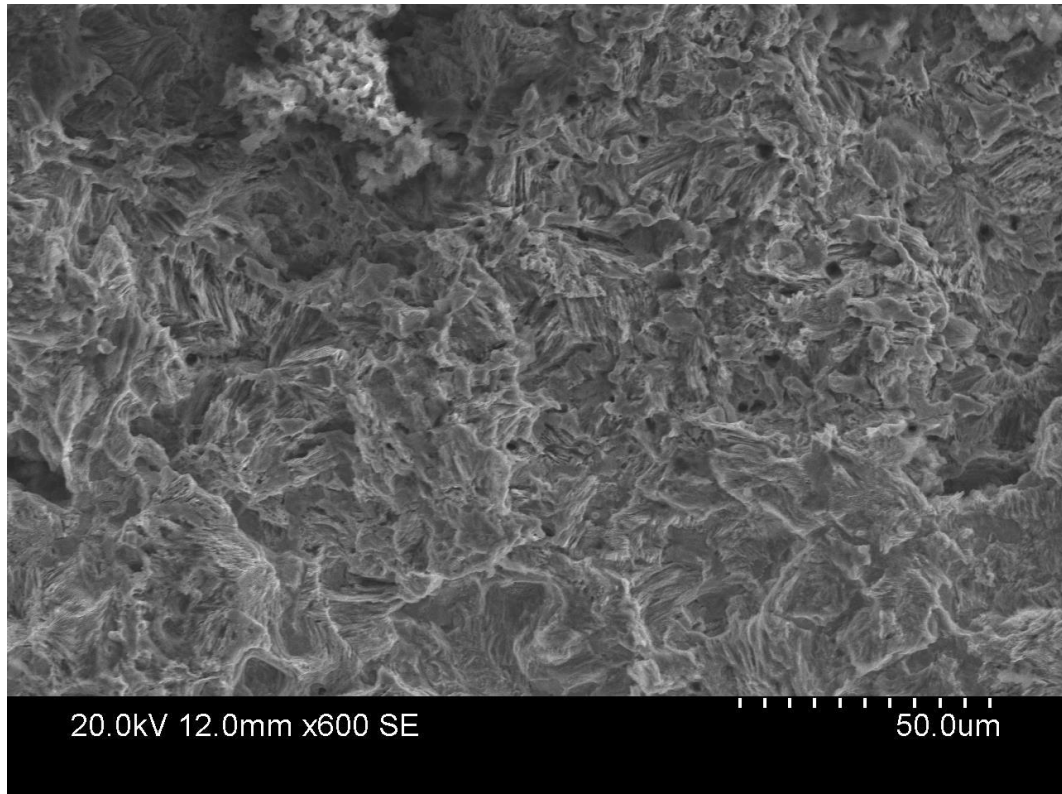


Figure 4-45: Higher magnification SEM of Rock bolt 6 showing region B.

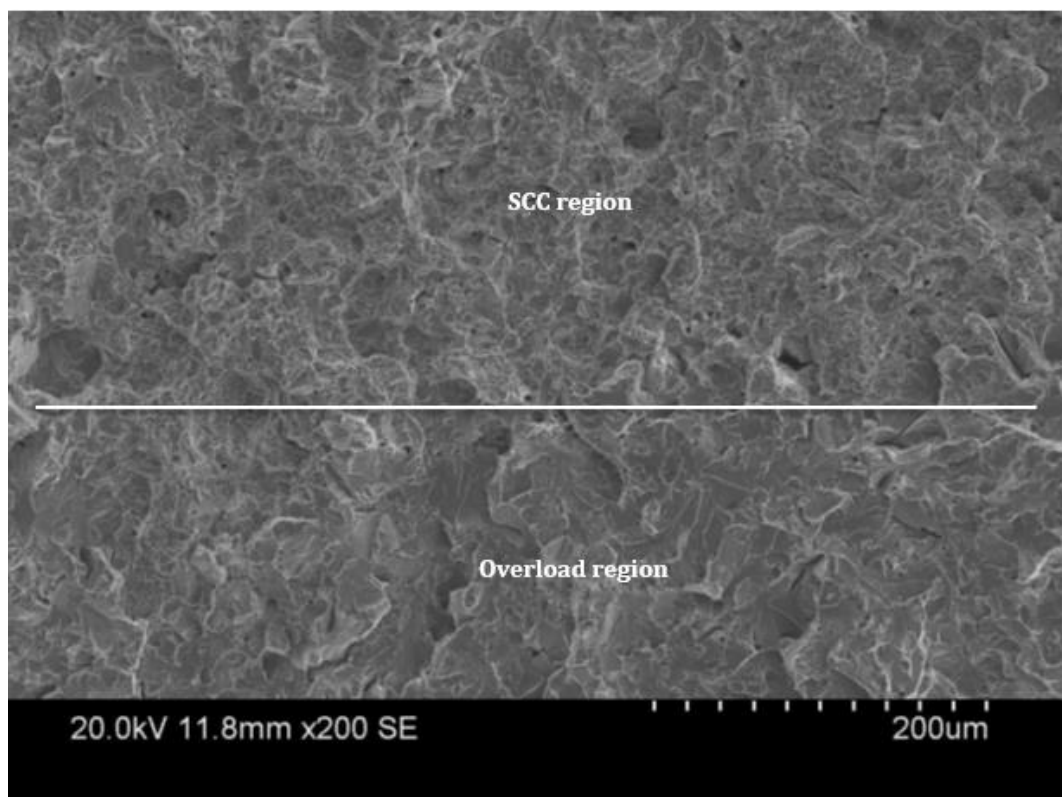


Figure 4-46: SEM fractography of Rock bolt 6 showing transition from SCC to overload failure.

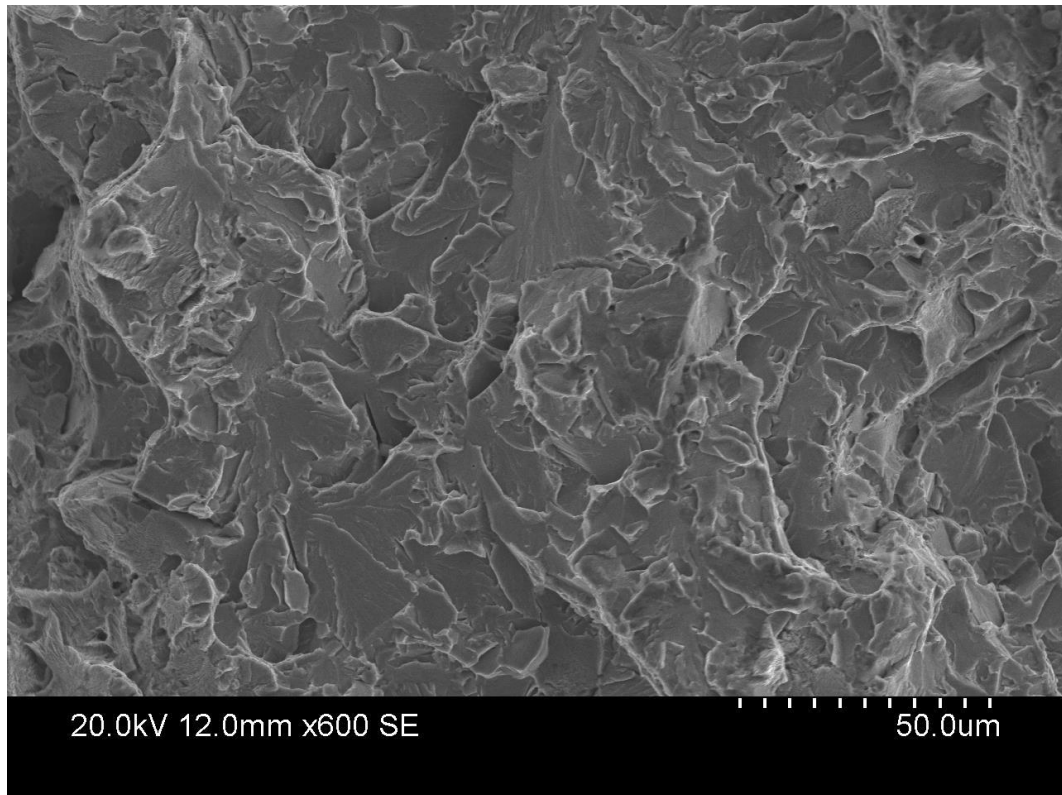


Figure 4-47: SEM fractography showing overload failure region in Rock bolt 6.

4.3.4 Subcritical Cracks

4.3.4.1 Crack Morphology

Metallographically sectioned subcritical cracks were examined in Rock bolts 1, 2 and 7. As noted earlier, these rock bolts had been retrieved from two mines having quite different ground water chemistries. Rock bolt 1 came from mine B while Rock bolts 2 and 7 came from Mine A. Typical examples of the cracks seen in the three rock bolts are shown in Figure 4-48 and Figure 4-49 (Rock bolt 1), Figure 4-50 (Rock bolt 2) and Figure 4-51 (Rock bolt 7). The cracks in Rock bolt 1 (Mine B) were found to be quite different to those in Rock bolts 2 and 7 (both Mine A) with those in Rock bolt 1 being wide and gaping, but with a narrow tip, Figure 4-48 and Figure 4-49 while those in Rock bolts 2 and 7 were narrow and tight with some branching. The crack morphology was found to be consistent for all the cracks examined in Rock bolt 1, Figure 4-48 and Figure 4-49 while the same was true for all the cracks examined in both Rock bolts 2 and 7.

All cracks were found to contain corrosion product.

Careful examination of the surface of the sections through Rock bolt 1 revealed small cracks extending into the rock bolt from cracks present in the mill scale, as shown in Figure 4-52. This was not however observed in the sections through Rock bolt 2

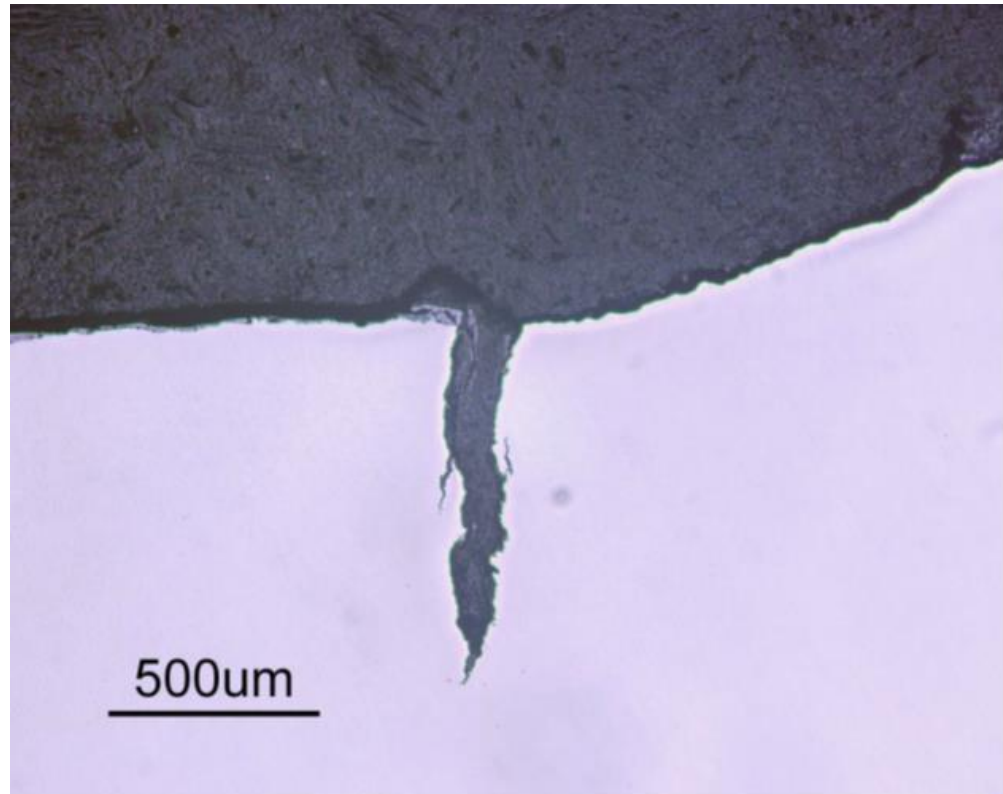


Figure 4-48: Transverse section showing typical crack morphology in Rock bolt 1.

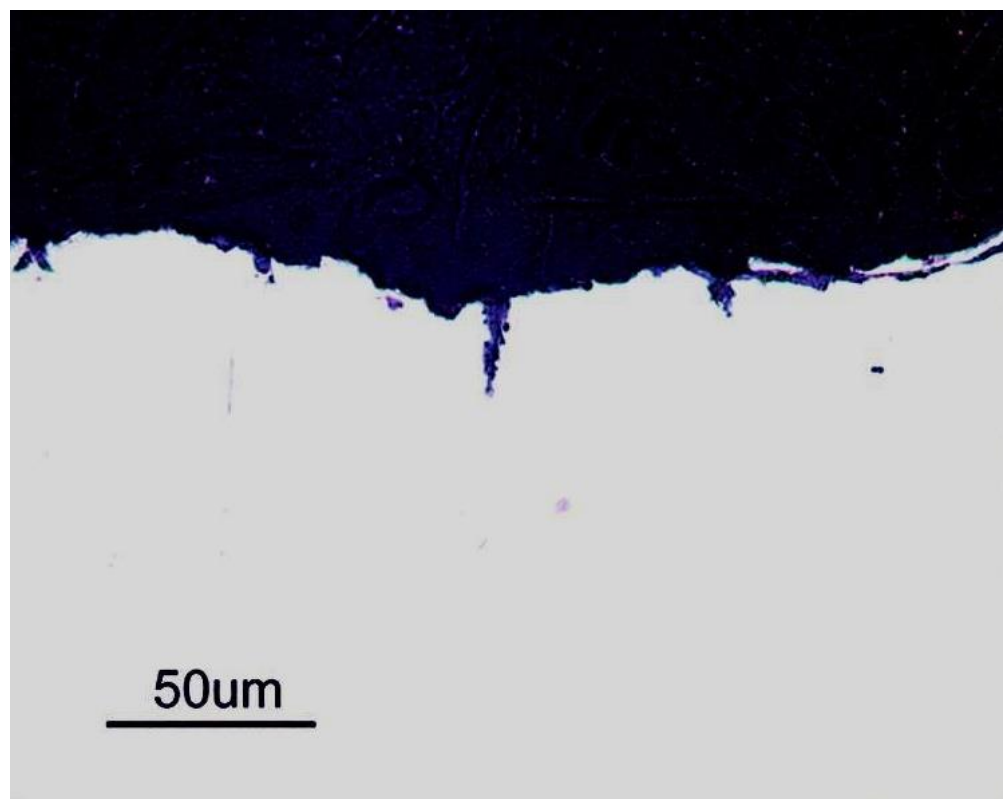


Figure 4-49: Transverse section showing typical crack morphology in Rock bolt 1.

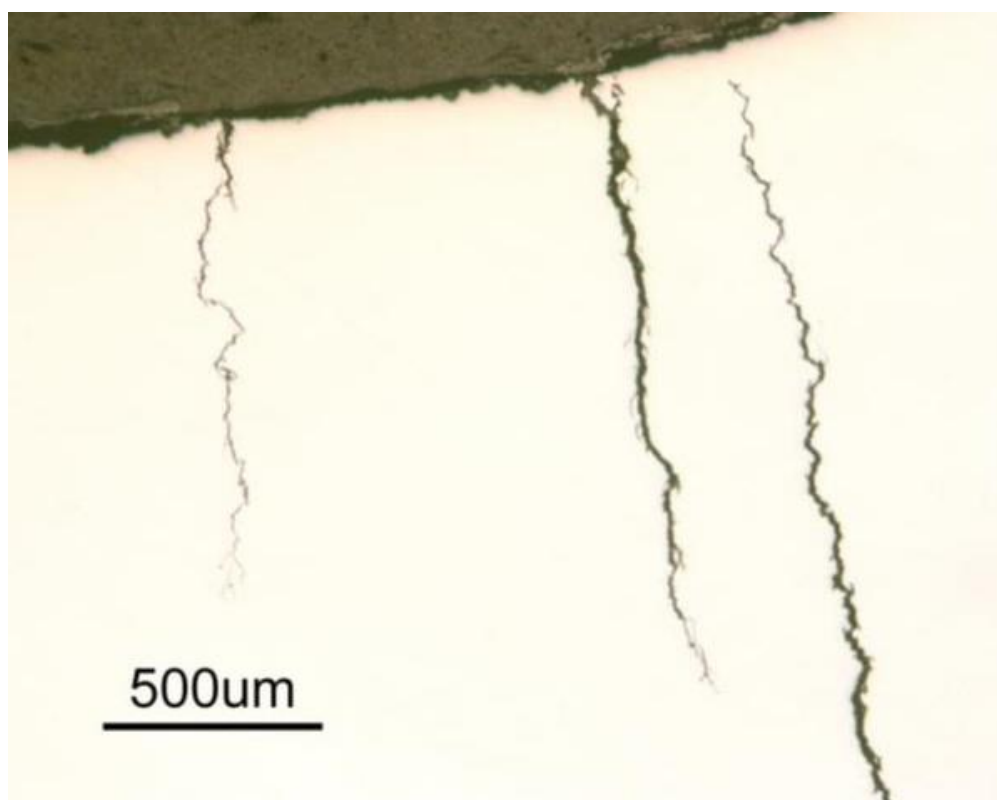


Figure 4-50: Transverse section showing typical crack morphology in Rock bolt 2.

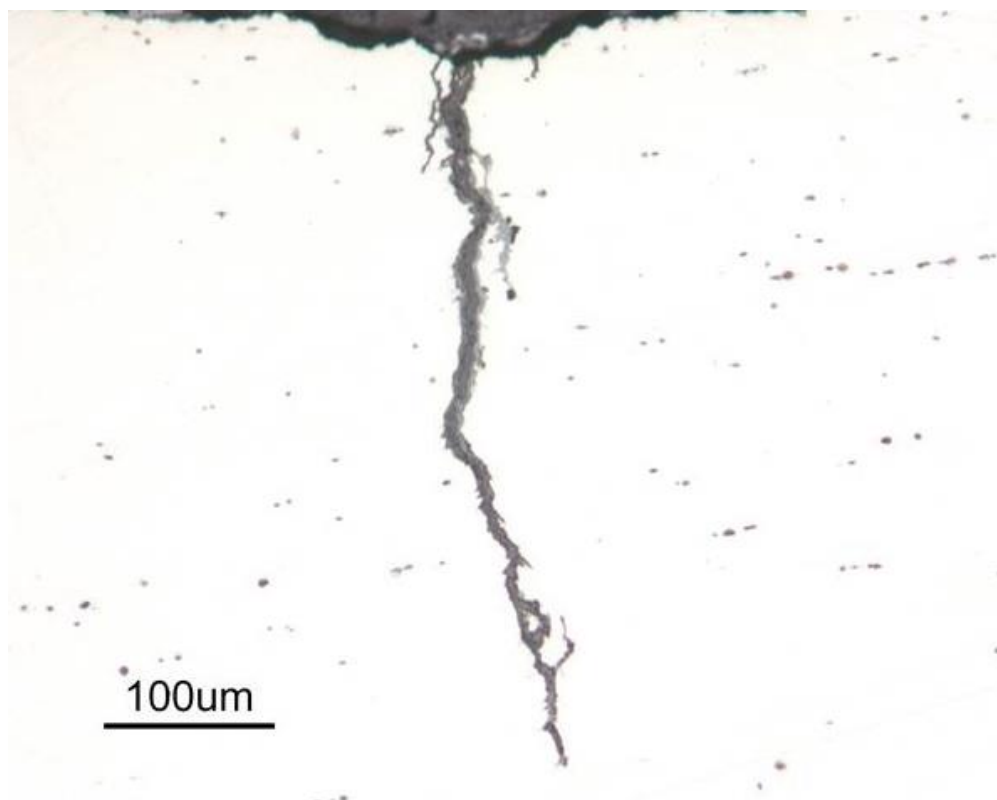


Figure 4-51: Transverse section showing typical crack morphology in Rock bolt 7.

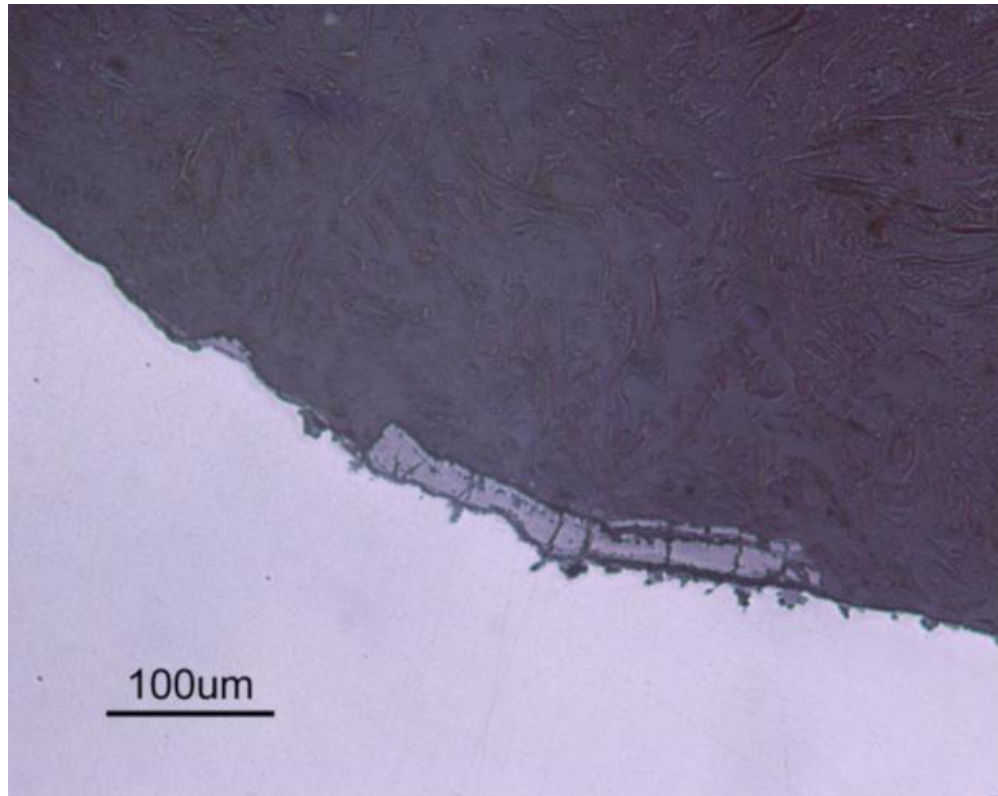
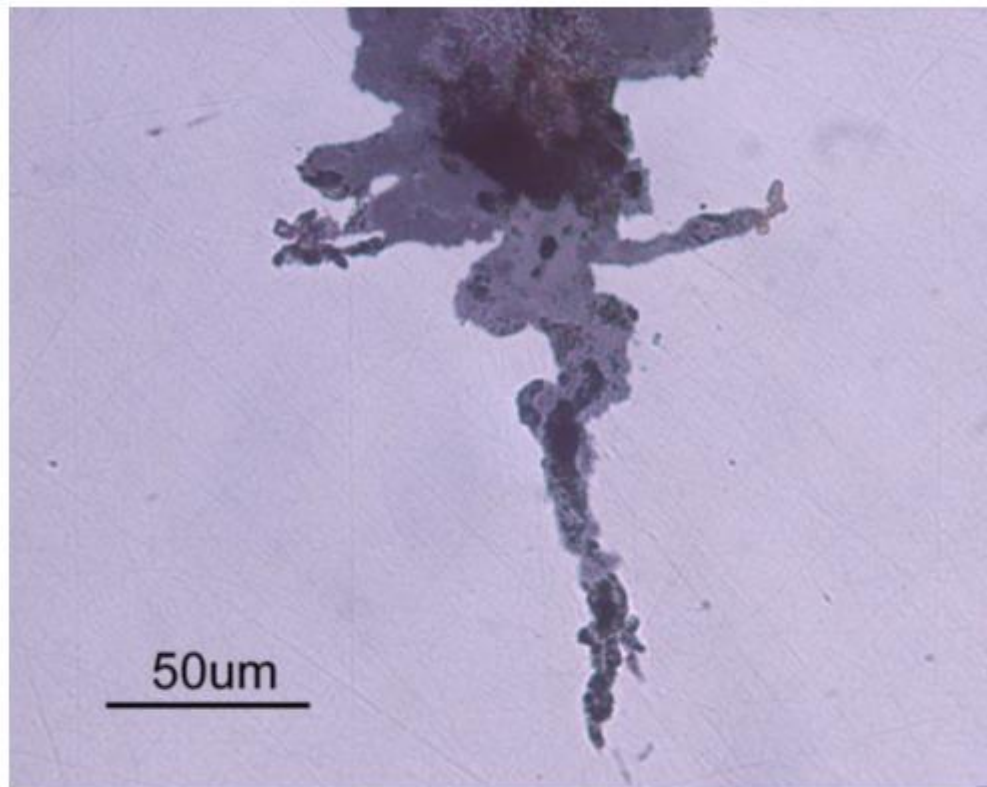


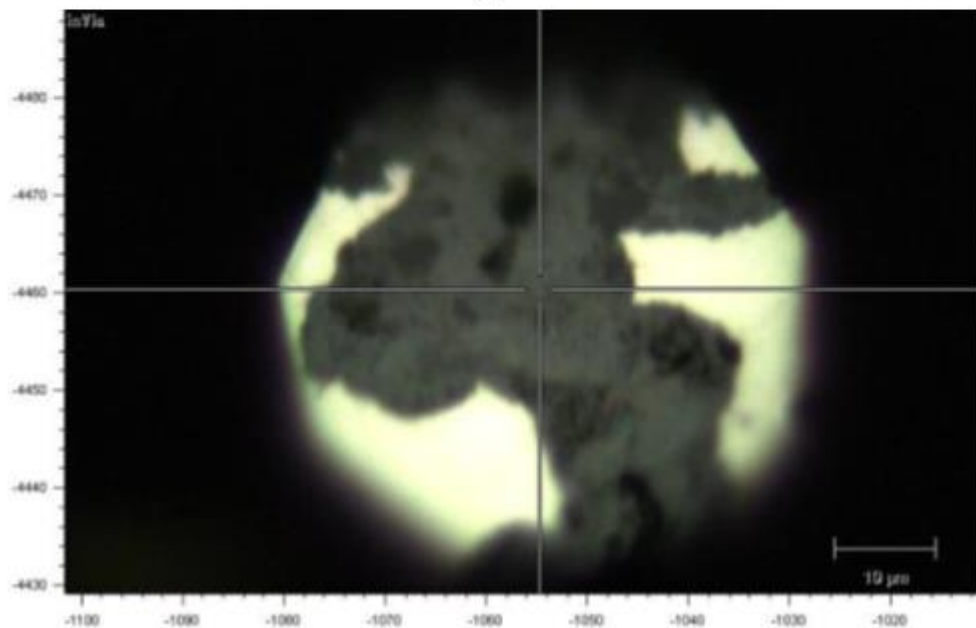
Figure 4-52: Transverse section through Rock bolt 1 showing cracks developing from cracks in the mill scale.

4.3.4.2 Corrosion Product

MicroRaman spectroscopy was used to analyse the corrosion product in sectioned subcritical cracks in Rock bolts 1 and 2. The crack examined in Rock bolt 1 is shown Figure 4-53, while that examined in Rock bolt 2 is shown in Figure 4-54.

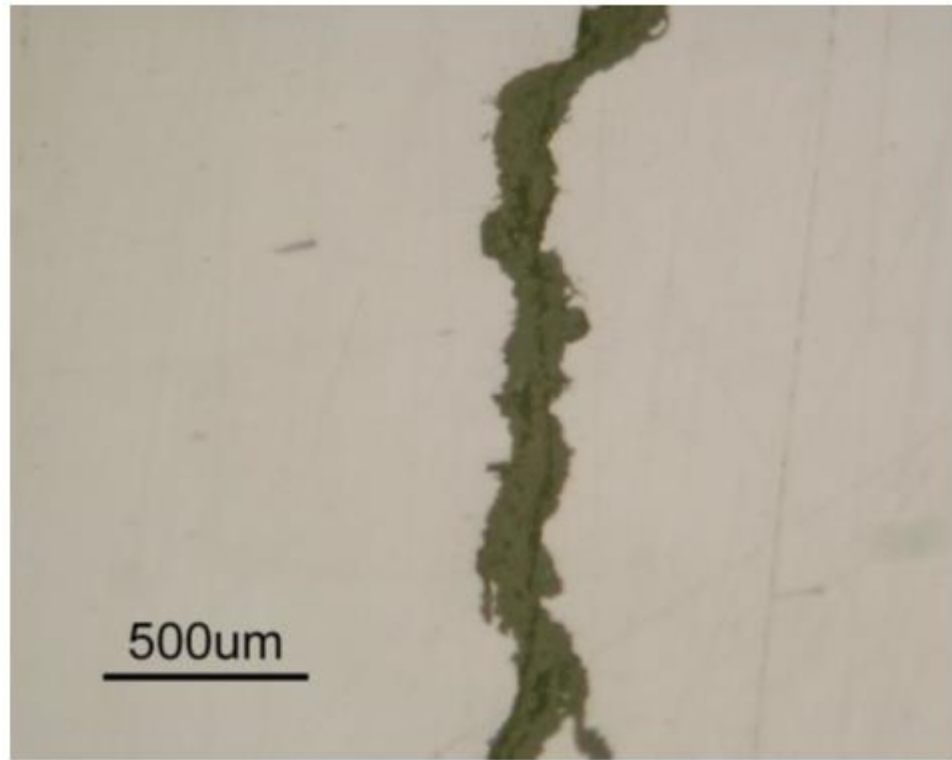


(a)

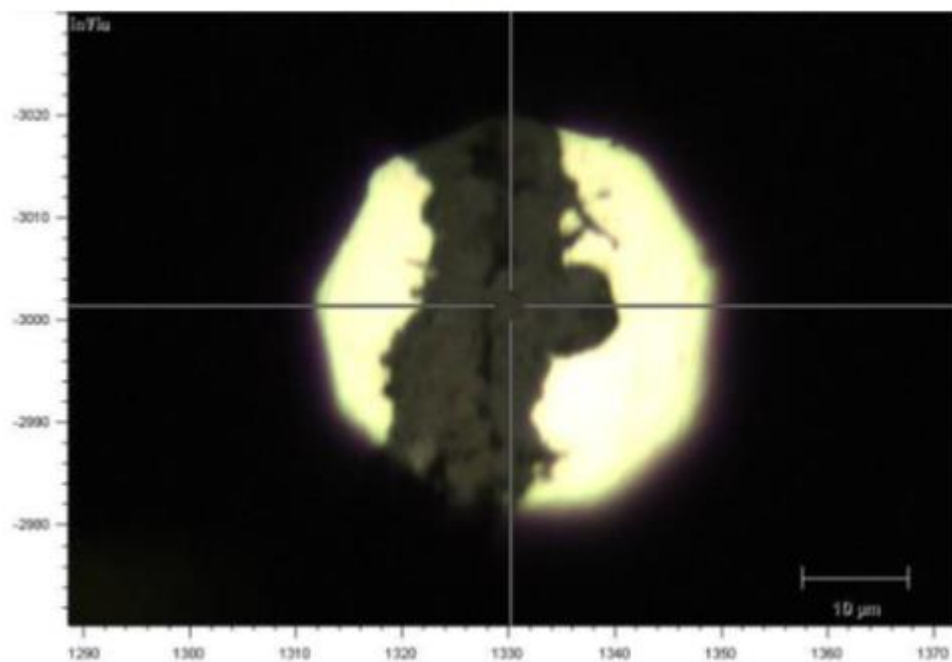


(b)

Figure 4-53: Transverse section through Rock bolt 1 (a) overview of crack in which corrosion product (grey coloured material) was analysed and (b) location of analysis (centre of cross hairs).



(a)



(b)

Figure 4-54: Transverse section through Rock bolt 2 (a) overview of crack in which corrosion product (grey coloured material) was analysed and (b) location of analysis (centre of cross hairs).

The spectra obtained from the two specimens are shown in Figure 4-55 and Figure 4-56. It can be seen that the two spectra are quite different. Comparison with the library spectra

provided by the equipment supplier (Renishaw) indicated that the main component in the corrosion product in Rock bolt 1 was Fe_3O_4 (magnetite) while the main component in Rock bolt 2 was FeCO_3 (siderite).

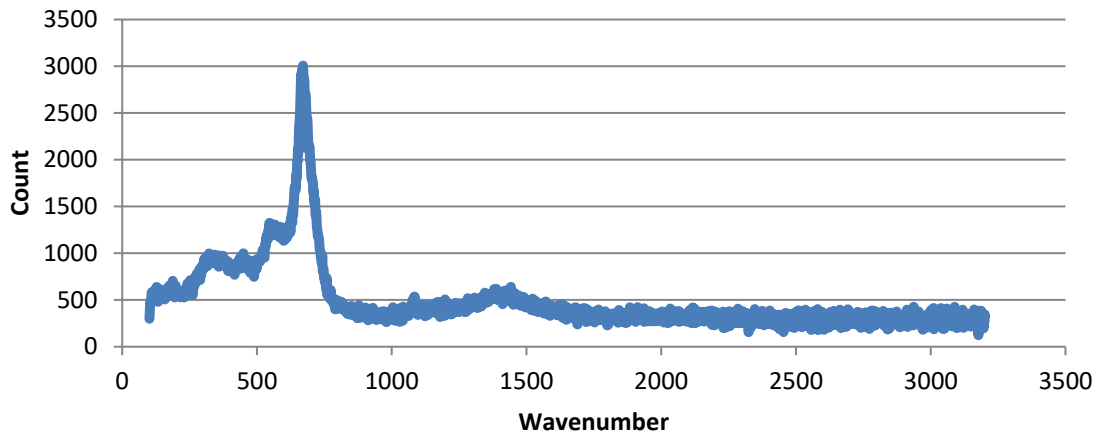


Figure 4-55: Raman spectrum from corrosion product in subcritical crack in Rock bolt 1.

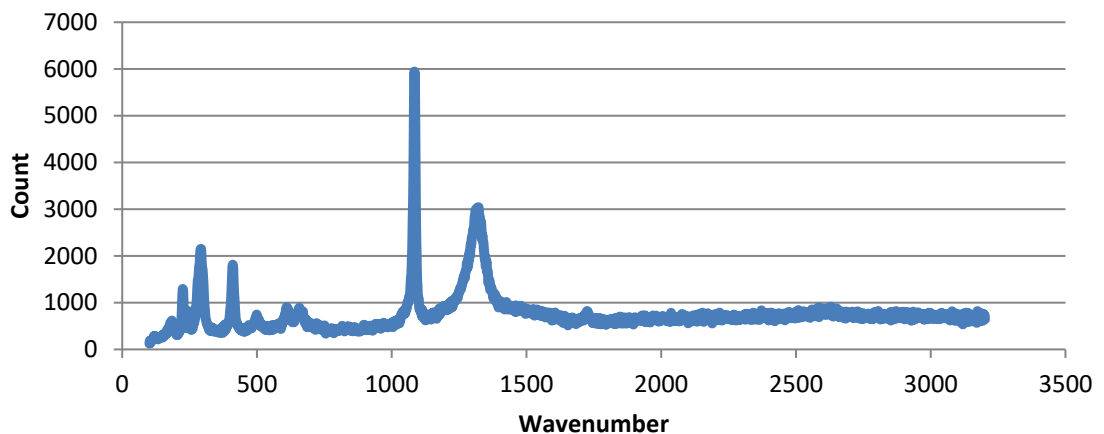


Figure 4-56: Raman spectrum from corrosion product in subcritical crack in Rock bolt 2.

4.3.4.3 Crack Path

An SEM micrograph showing a section of a crack in Rock bolt 2 is given in Figure 4-57. The boxed regions A and B are shown at higher magnification in Figure 4-58 and Figure 4-59 while a third region of the crack (which is not present in the field of view of Figure 4-57) is shown at the same magnification in Figure 4-60. The pearlite colonies through which the crack traverses in Figure 4-58 and Figure 4-59 have their lamellae oriented approximately parallel to the macroscopic crack direction and the crack can be seen to be cutting through these colonies along the boundaries between the individual lamellae (i.e.,

along the boundary between the alternating ferrite and carbide lamellae which constitute the pearlite structure). However, where the lamellae are oriented more nearly perpendicular to the macroscopic crack direction, the crack again runs along the boundaries between the lamellae, (eg, the colony marked X-X in Figure 4-60) or, more commonly, avoids cutting through the colony altogether, instead preferring to propagate along the boundary with an adjoining colony (eg, the colonies marked Y and Z in Figure 4-60). Propagation of the crack along the ferrite/pearlite boundaries also occurred in some places, as can be seen in Figure 4-57, Figure 4-58 and Figure 4-59.

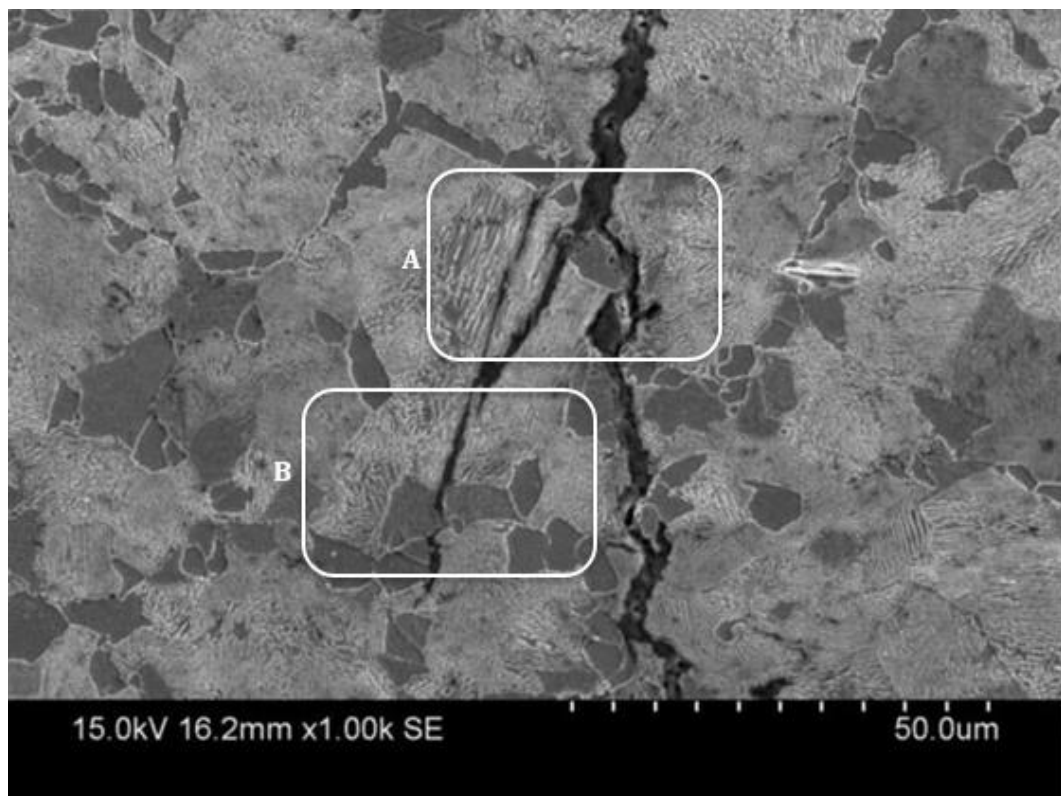


Figure 4-57: SEM micrograph showing crack path in transverse section of Rock bolt 2.

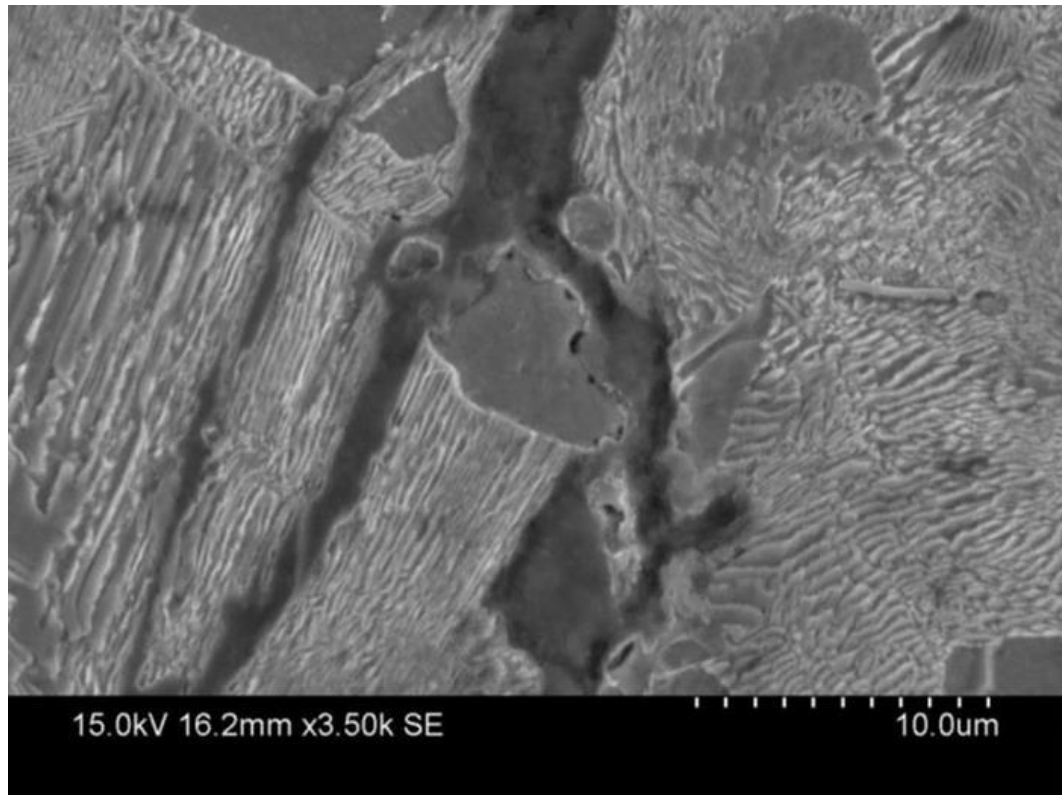


Figure 4-58: Higher magnification SEM micrograph showing region marked A in Figure 4-57.

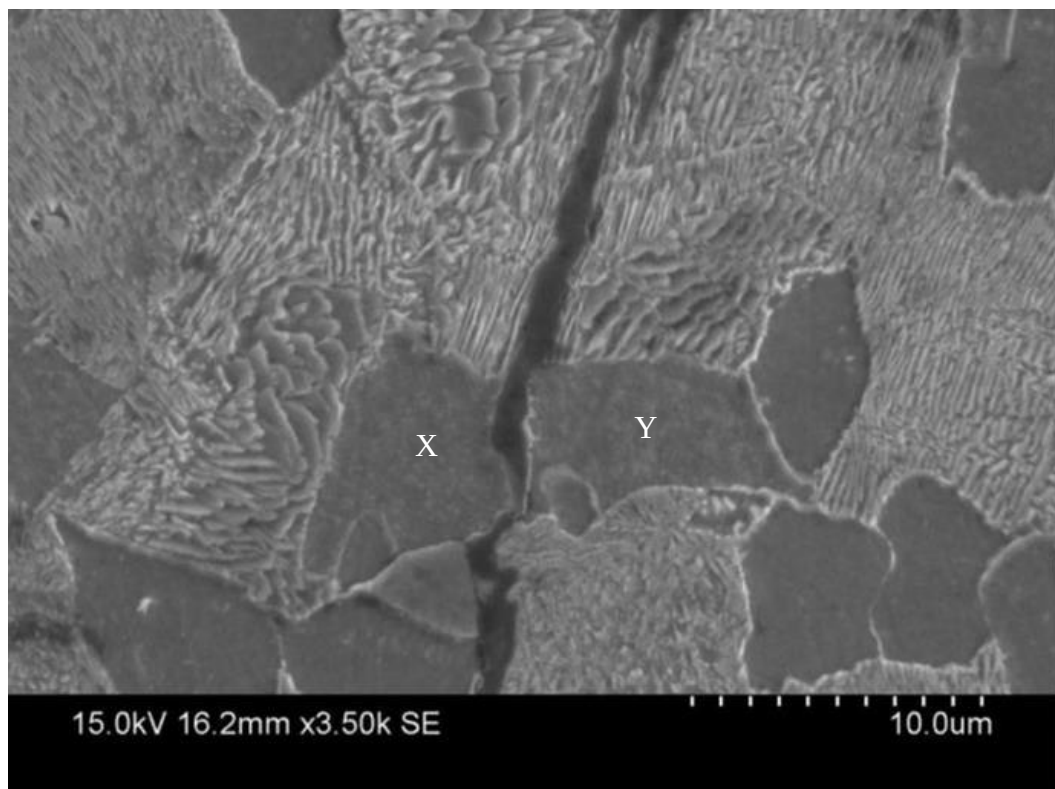


Figure 4-59: Higher magnification SEM micrograph showing region marked B in Figure 4-57.

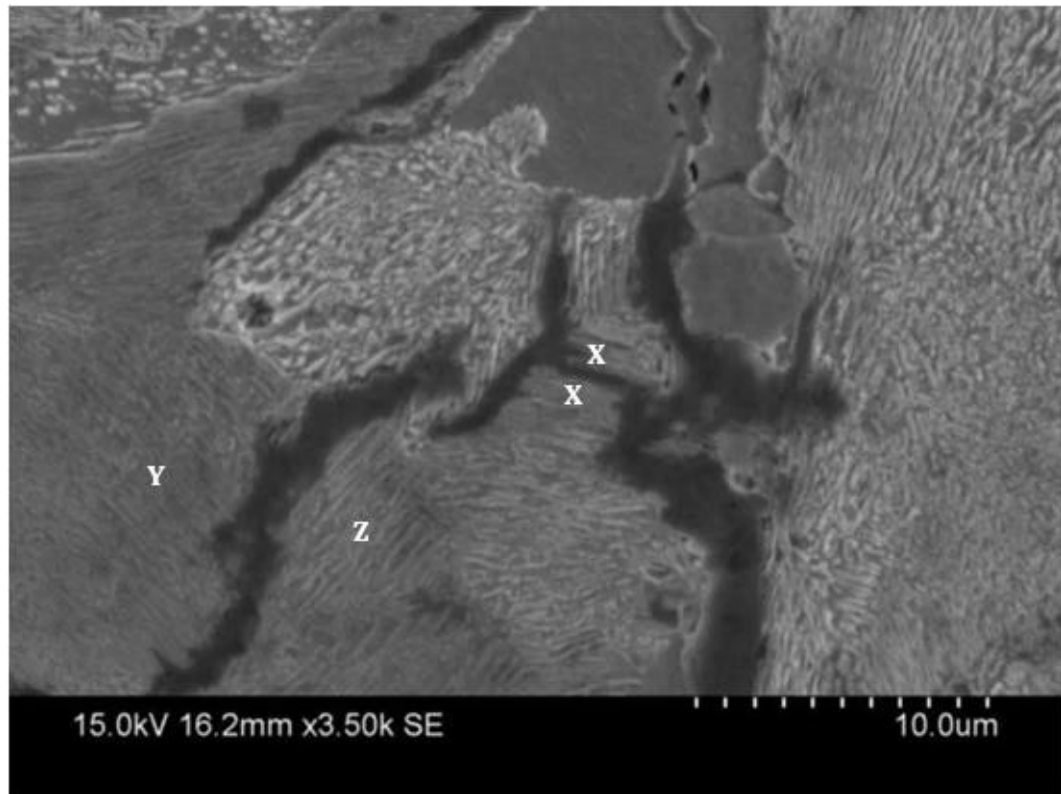


Figure 4-60: SEM micrograph showing a third region of the crack in Rock bolt 2.

A part of the crack shown in Figure 4-59 passes through two adjoining regions of ferrite labelled X and Y in this figure. This part of the crack is shown again in Figure 4-61 together with an electron back scattered diffraction (EBSD) image of the same area. The EBSD image indicates that the two adjoining regions of ferrite have the same orientation (as revealed by their identical colouring in the EBSD image), thus establishing that the crack is cutting through a ferrite grain, and not running along the boundary between two adjoining ferrite grains.

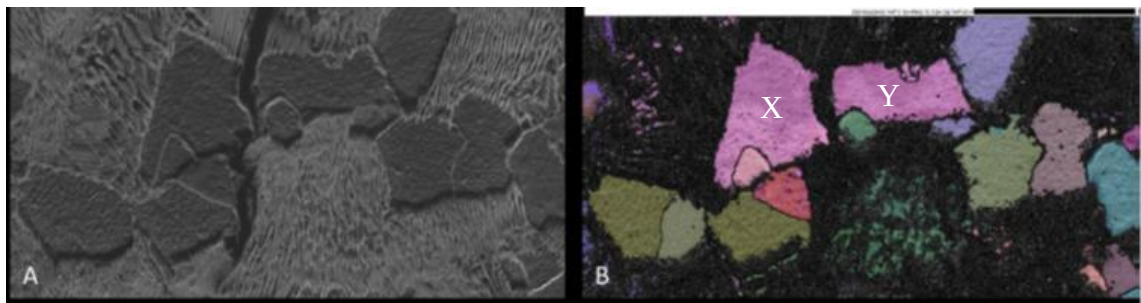


Figure 4-61: (a) SEM micrograph and (b) corresponding EBSD image of region of crack running through two adjoining regions (marked X and Y) of ferrite in Rock bolt 2.

4.4 Discussion

4.4.1 Crack Depth

The depths of the SCC cracks in Rock bolts 1-12 varied from 1-11 mm. These values are in reasonable agreement with the values of 1-7 mm reported by Crosky et al.^[101] from measurements made on 29 bolts, Table 4-4, and 1-8 mm reported by Gambao^[24] from measurements made on 5 bolts, Table 4-5. The rock bolts examined by Crosky et al. included eighteen AISI 1355 grade and eight AISI 5152 grade steels, but no HSAC 840 grade bolts, while three AISI 1355 grade, one AISI 5152 and one HSAC 840 grade bolts were examined by Gambao.

Table 4-4: SCC crack depths reported by Crosky et al.^[101]

Bolt ID	Steel Grade	SCC Crack Depth (mm)
7	5152	3.8
10	5152	2
11	1355	2.2
12	5152	4.4
14	5152	3
15	5152	~1
17	5152	2.0
18	5152	<1
19	1355	4.1
20	1355	2.0
21	1355	4.0
22	1355	4.1
23	1355	7
24	1040	5
25	1355	1.3
26	1355	1.5
28	1050	5.0
30	1355	~1
32	1050	~7
33	1355	5.0
35	1355	5.5
37	1355	4.0
38	1355	3.1
39	1355	4.6
40	1355	3.7
41	1355	2.4
42	1355	2.0
43	1355	2.6
44	5152	2.0

Table 4-5: SCC crack depths reported by Gamboa*^[24].

Rock bolt	Steel Grade	Mine	SCC Crack Depth (mm)
1	1355	1	1.9
2	1355	1	1.3
3	1355	2	1.1
4	840	3	8.0
5	5152	4	3.1

* Gamboa also examined a second HSAC bolt but considered this to have failed by corrosion fatigue.

It is difficult to make comparisons between the different steel grades from the results of the present study since, while nine HSAC 840 grade bolts were examined, only two AISI 1355 and one AISI 5152 bolt were studied. However, the more substantial data of Crosky et al., given in Table 4-4, gives an average crack depth of 3.3 mm for the eighteen AISI 1355 bolts and 2.4 mm for the eight AISI 5152 bolts. The average value for the nine HSAC 840 grade bolts from the present study is substantially larger, being 5.4 mm. Similarly, the HSAC 840 grade bolt examined by Gamboa had a larger crack depth than the other 4 bolts.

The increased crack depth for the HSAC 840 bolts is to be expected since the toughness is substantially higher for this grade of steel than for the other 2 grades (average Charpy impact value of 15 J compared with 5 J for AISI 1355 and 6 J for AISI 5152^[101]). As noted in Chapter 2, and given by Equation (2-29), the critical crack depth is dependent on toughness, so that tougher materials can tolerate deeper cracks before undergoing catastrophic failure. This was, in fact, the reason for replacing the lower toughness grades with the tougher HSAC 840 in the early 2000s.

4.4.2 Stress at Fracture

The critical crack depth is also dependent on the applied load, as is also evident from Equation (2-29). Conversely, the stress at failure of the rock bolts can be calculated from the SCC crack depth. Valiente and Elices^[140] have used linear elastic fracture mechanics to predict the stress at failure in circular section prestressed steel tendons containing a transverse thumbnail shaped surface crack. The tendons had a diameter of 36 mm and were made from a 0.65%C vanadium-microalloyed steel with a yield strength of 1143 MPa, a tensile strength of 1285 MPa and a fracture toughness of 33 MPam^{1/2}. They compared their predictions with service data from two tendons, containing cracks of known depth, which had failed in a macroscopically brittle manner, and also two

specimens which had been precracked in the laboratory by fatigue loading. They obtained excellent agreement between the predicted and actual rupture loads, as shown in Figure 4-62 and considered therefore that the linear elastic fracture mechanics approach was valid.

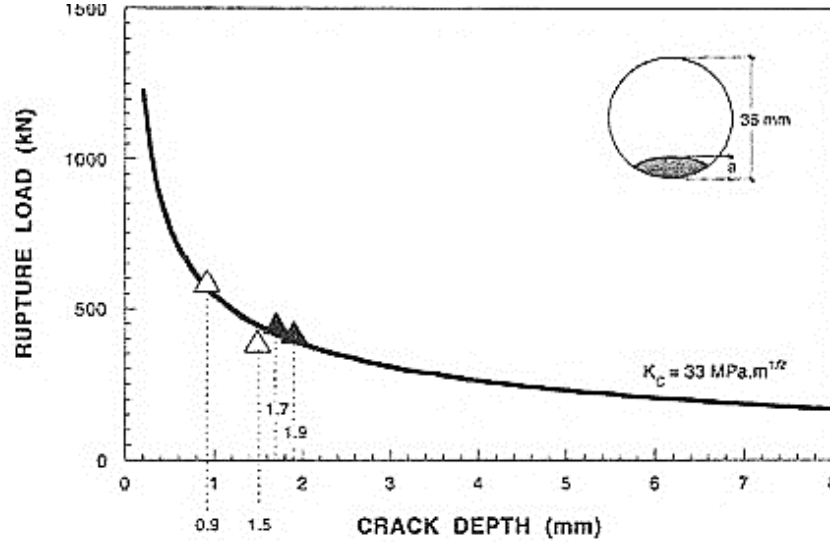


Figure 4-62: Comparison of calculated rupture load vs crack depth with service failures (filled triangles) and fatigue precracking specimens (unfilled triangles)^[140].

In their analysis, they modelled the thumbnail shaped crack as an elliptical crack with semi-axes a and b , as shown in Figure 4-63. For small values of a/b the rupture load P is given by:

$$P = \frac{D\sqrt{\pi D}}{4} K_{IC} \cdot M\left(\frac{a}{D}\right) \quad (4-1)$$

where D is the diameter of the circular bar, K_{IC} is the fracture toughness and $M(a/D)$ is non-dimensional function which is rewritten below as $M(\xi)$. For small values of a/b , $M(\xi)$ can be approximated by:

$$M(\xi) = \xi^{-0.5} \cdot (1.0806 + 0.6386\xi - 2.4445\xi^2 + 13.463\xi^3)^{-1} \quad (4-2)$$

It is noted that the function $M(\xi)$ varies with crack length a in the same way as shown for Equation (4-1) in Figure 4-62, i.e., it decreases progressively with increased crack length.

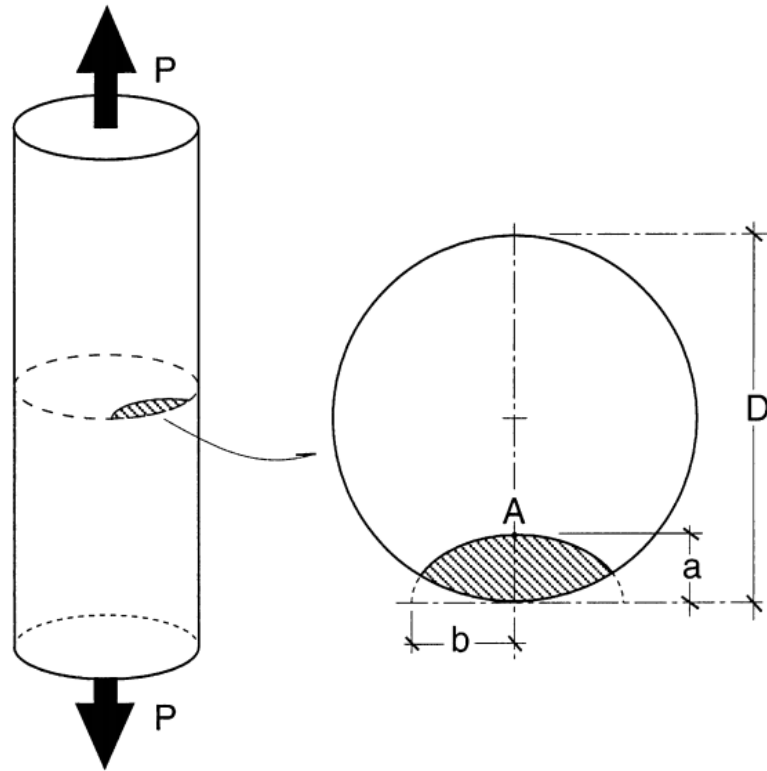


Figure 4-63: Geometry and notation of surface crack.

The procedure used above should also be applicable to rock bolts but requires a knowledge of the fracture toughness. While no measurements of fracture toughness were made, data was available for the Charpy impact toughness, as indicated above. Shutter et al.^[103] have determined a correlation between Charpy impact toughness C_v and fracture toughness using three UK rock bolt steels with Charpy values ranging from 4-40 J. Their data is shown in Figure 4-64 and gave the correlation as:

$$K_{IC} = 17.4 (C_v)^{0.46} \quad (4-3)$$

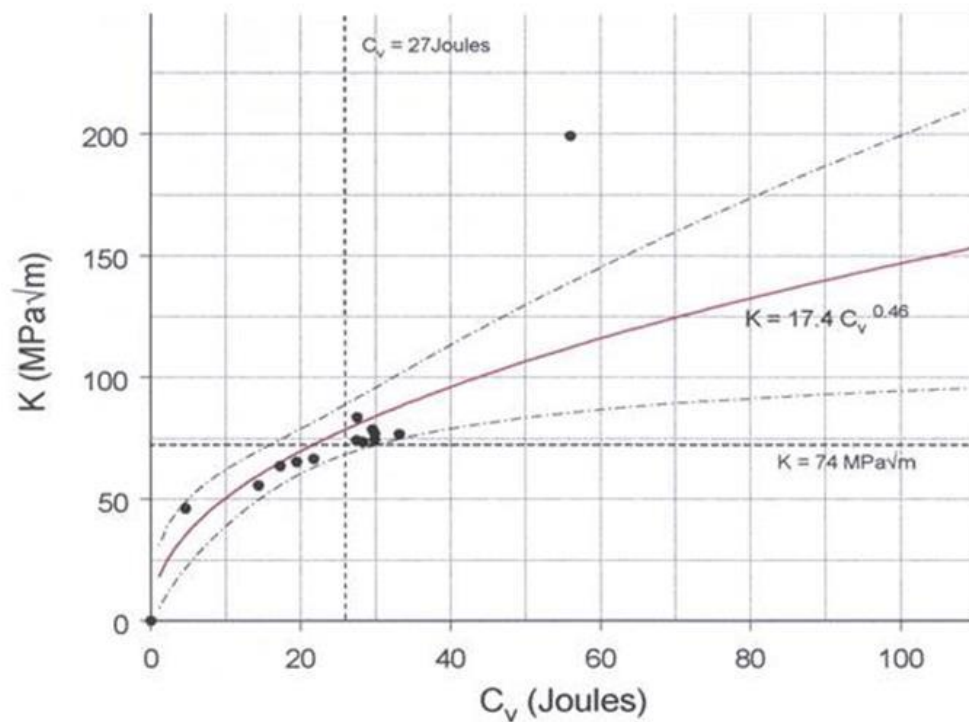


Figure 4-64: Correlation curve for converting Charpy impact toughness C_v and fracture toughness K .^[103]

Based on this correlation, the fracture toughness was determined using the average Charpy values of 5, 6 and 15 J given above for the AISI 1355, the AISI 5152 and the HSAC 840 rock bolts, respectively, and used to calculate the stress at fracture using the procedure of Valiente and Elices. The results are given in Table 4-6. The minimum specified yield strength is also given Table 4-6. The HSAC 840 and 1355 rock bolts have a minimum specified yield strength of 600 MPa while the 5152 bolts (which receive some cold work) have a minimum specified yield strength of 745 MPa.

Table 4-6: Calculated fracture stress for Rock bolts 1 – 12.

Rock Bolt	Steel Grade	Specimen Diameter mm	C _v J	K _{IC} MPam ^{1/2}	Crack Depth mm	Yield Strength MPa	Fracture Stress MPa
1	840	22.1	15	60.5	3.8	600	470
2	840 (low Si)	22.2	15	60.5	7.3	600	264
3	1355	22.0	5	36.5	4.3	600	258
4	5152	21.6	6	39.7	9.9	745	104
5	840	22.0	15	60.5	1.3	600	845
6	840	22.0	15	60.5	3.1	600	527
7	840	22.1	15	60.5	11.3	600	126
8	840	22.0	15	60.5	2.5	600	600
9	840	22.0	15	60.5	9.0	600	193
10	1355	22.0	5	36.5	1.1	600	565
11	840	21.9	15	60.5	5.1	600	380
12	840	22.1	15	60.5	5.1	600	381

The calculated fracture stresses vary from 104 MPa to 845 MPa and, except for two of the HSAC bolts (Rock bolts 5 and 8), are all below the minimum specified yield strength. Moreover, for Rock bolts 4 (AISI 5152), and 7 and 9 (both HSAC 840), the calculated fracture stress is, in fact, below the minimum pretensioning stress of 260 MPa (10 tonne) applied to the bolts on installation. This may indicate that some stress relaxation can occur in service in some cases.

From Equation (4-1), the maximum calculated crack depth for failure above the yield strength would be approximately 0.75 mm for the AISI 5152 bolts, 0.95 mm for AISI 1355 bolts and 2.5 mm for the HSAC 840 bolts. This would mean that, at best, only two of the eight AISI 5152 bolts and only one of the eighteen AISI 1355 bolts examined in the earlier work by Crosky et al.^[101] would have failed above their yield strength.

From examination of Table 4-5 it can also be seen that none of the five bolts examined by Gamboa would have failed above their yield strength. This is supported by estimates of the stress at failure reported by Gamboa for the bolts listed as Bolts 1 and 5 in Table 4-5. The estimates were made from the level of deformation in the end plates and were 270-400 MPa for Bolt 1, and 145 MPa for Bolt 5. The fracture stress calculated using Equation (4-1) was somewhat higher in both cases, being 415, and 347 MPa, respectively (but still below the yield strength). This may indicate that determination of the fracture stress from the level of end plate deformation may underestimate the true value.

The material used by Valiente and Elices to validate their procedure had a fracture toughness of $33 \text{ MPam}^{1/2}$. The fracture toughness calculated using Equation (4-1) was $36.5 \text{ MPam}^{1/2}$ for AISI 1355 and $39.7 \text{ MPam}^{1/2}$ for AISI 5152 and these values are considered sufficiently close to the toughness of the material used by Valiente and Elices for their validation to hold. However, the same may not be true for the HSAC 840 bolts which had a calculated toughness of $60.5 \text{ MPam}^{1/2}$. The higher toughness would increase the level of plasticity at the crack tip and could result in the stress at failure being underestimated.

It is also noted that the condition that a/b is small, which is assumed by Valiente and Elices, is not satisfied for some of the bolts (notably Rock bolts 2, 4, 7 and 9) while in others the assumption of an elliptical crack (notably Rock bolt 2) is incorrect. In these cases there would also be expected to be some error in the calculated values.

Notwithstanding the deficiencies mentioned above, the results of the present study, coupled with those of Crosky et al.^[5, 101] and Gambao^[24] are inconsistent with the minimum stress required to cause SCC determined by Gamboa and Atrens^[6, 113] from their threshold stress testing, as given in Table 2-15. The minimum stresses obtained from their testing were 900 MPa for AISI 1355 and 850 MPa for HSAC 840, while SCC could not be produced at all in AISI 5152. The inconsistency of these results with the failure stresses calculated above casts further doubt on the validity of using low pH solutions (pH=2.1) to represent the in-service local SCC environment.

The stresses at failure calculated above are also inconsistent with the view of Shutter et al.^[103] and Crosky et al.^[101] that the stress responsible for failure is produced by localised plastic bending of the bolt resulting from strata shear. Their view is supported by the observation of Shutter et al. of S-bends in rock bolts from a collapsed mine and the observation by Crosky et al. of a small localised bend on the tension side of the failure in most of the bolts examined by them, as was also found in the present study. Such bending would result in the elastic stress (which drives SCC) being above the original yield strength due to the work hardening produced at the bend. However, the calculated stresses at failure are generally below the yield stress. This may mean that some elastic relaxation occurs after the plastic bend has been produced.

Vandermaat et al.^[141] also estimated the stress at failure for 22 AISI 1355 and 23 HSAC840 rock bolts, which had failed in service, from measurement of the rib spacing after failure. They used this to calculate the plastic strain which they then converted to stress using the stress strain curves for each of the steels. Their results gave stresses of

600-900 MPa, which are equal to or above the minimum specified yield strength of both steels (600 MPa), but generally below the threshold stresses determined by Gamboa and Atrens.

It is noted that the analysis of Vandermaat et al. assumed that the full elastic stress at the time the plastic strain occurred was still present in the bolt at the time of failure. This would not have been the case if, as suggested above, some elastic relaxation had occurred subsequent to the production of the plastic strain and, in such cases, the elastic stress could well be below the yield strength

4.4.3 Fracture Surface

The two fracture surfaces examined in detail in the present study were both from HSAC 840 bolts. One contained a single SCC region (Rock bolt 5) while the second contained two adjoining SCC regions (Rock bolt 6). The presence of multiple SCC regions was also observed by Crosky et al.^[101], though not by Gamboa^[24]. The presence of multiple SCC regions in some bolts is considered to be consistent with the observations of multiple cracks along the base of the ribs of some bolts. These would be expected to be propagating simultaneously and some may then link up laterally prior to final failure.

SEM examination of the fracture surfaces revealed similar features in the two bolts. These features were similar to those reported by Gamboa and Atrens^[6], with the SCC regions exhibiting features similar to what they reported as tearing topography surface (TTS) and the overload region displaying cleavage-like features. It is noted that Gamboa reported that the fine scale fracture features, as observed by SEM, were similar in the rock bolts made from all three grades of steel (AISI 1355, AISI 5152 and HSAC 840). This is despite the difference in microstructures; AISI 1355 is essentially fully pearlitic, AISI 5152 is also essentially fully pearlitic but receives 10% cold work, while HSAC 840 has a substantial amount of proeutectoid ferrite in addition to pearlite.

Interestingly, the bolts studied here, together with those examined by Gamboa, showed no evidence of intergranular fracture in the SCC region, unlike the rock bolt which failed by SCC in the UK^[106] and those that failed by SCC in the UK laboratory tests^[104]. However, Crosky has recently observed intergranular SCC failure in a rock bolt which was retrieved from an underground coal mine in Australia which was not a part of the present study.

4.4.4 Subcritical Cracks

4.4.4.1 Introduction

Subcritical cracks (often referred to as secondary cracks) were found in three of the rock bolts examined. Such cracks are widely accepted as having the same origin as the cracks which produce catastrophic failure, but are at an earlier stage in their development^[64]. Accordingly, several cracks in each of these bolts were sectioned to examine their morphology and their relationship with the microstructure. Corrosion product in these cracks is more protected from post-fracture exposure and contamination than that on the fracture surfaces. As a result, analysis of the corrosion product in the cracks should allow more reliable identification of the species involved.

4.4.4.2 Crack Morphology

The rock bolts which contained subcritical cracks (Rock bolts 1,2 and 7) came from two different mines (Mines A and B) which, as shown in the previous chapter, had quite different ground water chemistries. In particular, the alkalinity was much higher in Mine A than in Mine B with average values of 1179 mg/l and 399 mg/l, respectively. One location in Mine A (L1) had a distinctly higher alkalinity than the other locations, Section 3.3.1, but even excluding this result the average alkalinity was 990 mg/l which is still very much higher than for Mine B. Accordingly, the cracking observed in these two mines will be referred to as high alkalinity and low alkalinity SCC, respectively. As noted in Chapter 3, the alkalinity is due almost exclusively to the presence of bicarbonate ions.

The subcritical cracks were also quite different in the rock bolts from the two different mines, despite all three bolts examined being made from the same steel, HSAC 840. Rock bolts 2 and 7 had narrow tight cracks with some branching, while Rock bolt 1 had broad cracks with a narrow tip.

The narrow tight cracks are similar to those observed by Crosky et al.^[101] and shown in Figure 4-50. While the bolts examined here were HSAC 840, with a mixed ferrite/pearlite structure, the bolt shown in Figure 4-50 is an AISI 1355 bolt, with an essentially fully pearlitic structure, indicating that the same type of cracking is occurring despite the difference in microstructure and chemistry of the two grades of steel.

The tight narrow cracks are also similar to the high pH cracks seen in the SCC failures of pipelines, as shown in Figure 2-16, which were found to occur in concentrated bicarbonate solutions, Table 2-3. The similarity between the pipeline cracks and those observed in the two rock bolts from Mine A is not surprising since the water in this mine

also had a high bicarbonate level. The bicarbonate level was in fact higher in the Mine A water than in the samples of water taken from under the coating of pipelines near the locations of stress corrosion cracks, for which values of 0.4-0.8% were reported, Table 2-3.

It is noted that the pH in Mine A was lower than the values of 9.6-12.3 reported for the pipeline water samples, Table 2-3, although in one location in Mine A a value of 9.1 was obtained. It may be that the local pH at the site of SCC failures in rock bolts is higher than the global value in the mine.

In the pipeline studies, it was considered that the high concentration of carbonate/bicarbonate ions, led to a tendency for the solution to passivate the steel surface, resulting in the occurrence of SCC, Section 2.2.1. SCC then occurs by a dissolution process and, accordingly, by an anodic mechanism, Section 2.2.1. The Langelier index for Mine A indicates that the water is generally film forming, consistent with this mechanism.

The cracks seen in the rock bolt from Mine B are more reminiscent of the wide cracks seen in pipeline steels which had undergone near neutral pH SCC, as shown in Figure 2-18. Near neutral pH cracking occurs in dilute bicarbonate solutions, Table 2-4, as was more the case for the ground water from Mine B. As discussed in Section 2.2.2, near neutral pH pipeline SCC is considered to occur by a hydrogen induced mechanism. The cathodic reaction is considered to occur at the crack tip resulting in evolution of hydrogen which diffuses into the steel causing the metal ahead of the crack tip to become embrittled so as to undergo consequent cracking. The anodic reaction takes place on the crack walls behind the crack tip, resulting in metal dissolution and, consequently, substantial widening of the crack, Section 2.2.2.

It is clear that the wide cracks present in the rock bolt from Mine B, shown in Figure 4-48 and Figure 4-49, had undergone substantial corrosion of the sidewalls, while the thin region of crack, at and near the crack tip, is consistent with the crack propagating by hydrogen induced cracking. This follows since the anodic reaction with, its consequent sidewall dissolution, occurs after the embrittlement crack has formed. Thus, a newly formed region of the embrittlement crack should be narrow and tight, while the pre-existing region behind the newly formed crack should be wide as a result of subsequent sidewall dissolution. The morphology of the subcritical cracks seen in the rock bolt from Mine B are consistent with such a process. In view of the crack morphology, and the

comparatively low bicarbonate level in the ground water, it is considered that the cracking seen in Rock bolt 1 is due to hydrogen induced SCC.

Atrens and coworkers also considered that rock bolt SCC occurs by a similar hydrogen induced mechanism^[6, 109], as discussed in Section 2.2. However this conclusion was not based on examination of subcritical cracks, but instead on the similarity between the fracture features on failed bolts and those produced in the laboratory in low pH solutions where hydrogen evolution occurred. They also considered the fracture features to be similar to those produced by Toribio and coworkers^[111, 142] in hydrogen charged pearlitic steels, where the fracture was clearly hydrogen induced.

4.4.4.3 Crack Path

The only prior study of the SCC crack path known to the author was that reported by Galloway^[106] from examination of failed bolts from Welbeck colliery in the UK. As discussed in Section 2.1.2, only one of the 40 rock bolts examined in the UK studies appeared to have failed by SCC with failure of the remainder being attributed to stress concentration resulting from corrosion pits. However, subcritical SCC cracks were found in some of the other bolts examined from Welbeck colliery, as shown in Figure 2-32 and Figure 2-33, and these were found to be intergranular, Section 2.1.2, consistent with the reported nature of the fracture surface seen on the bolt which had failed by SCC. The steel used in the UK was a 0.3% carbon steel and had a lower pearlite content than the HSAC 840 steel (0.4% carbon) examined in the present study, as can be seen from examination of Figure 2-32 and Figure 2-33. The cracks clearly appear to be propagating around the ferrite grains but it is difficult to tell whether they are propagating along ferrite/ferrite boundaries, ferrite/pearlite boundaries or through the pearlite colonies which can frequently be seen at the ferrite boundaries. It is noted that the ground water in Welbeck colliery had a pH of 7.1 while the bolt in which the crack path was examined in the present study (Rock bolt 2) was from Mine A which had an average pH of 8.2.

The crack examined in the present study propagated through the pearlite colonies along the ferrite/carbide boundary (i.e., between the ferrite and carbide lamellae which constitute the pearlite structure) when the lamellae were oriented approximately parallel to the macroscopic crack growth direction, but ran around the colonies, either along the boundary between two pearlite colonies or along the boundary between a pearlite colony and a ferrite grain, when the lamellae were oriented at a more oblique direction. In one case, the crack was seen traversing two adjacent regions of ferrite and it was established

that these two regions were not a pair of adjacent ferrite grains but instead a single grain which had been bisected by the crack. This indicates that when failure occurs in a region of ferrite it is transgranular and not intergranular. It is noted that no evidence of intergranular fracture was seen on the fracture surfaces of the two bolts examined by SEM (Rock bolts 5 and 6) although it is noted that neither of these bolts was from Mine A.

The crack examined in the present study was from the high alkalinity mine, and as discussed earlier, its macroscopic features were similar to those for high pH SCC in pipeline steels. However, high pH SCC in pipeline steels is considered to be intergranular^[30, 44, 46]. Li et al.^[143] examined the crack path in X52 pipeline steel that contained colonies of service-induced subcritical cracks. The steel examined was a 0.3%C-1.3% Mn steel with a ferrite/pearlite microstructure. Again the lower carbon content resulted in a higher ferrite content than in the HSAC 840 rock bolts. Moreover, the HSAC 840 rock bolts were accelerated cooled which further increases the pearlite content (with a correspondingly reduced ferrite content). Thus the ferrite content was substantially higher (approximately 50%) in the pipeline steel than in HSAC 840 rock bolts. As a result, there were many adjoining ferrite grains in the pipeline steel, the microstructure of which is shown in Figure 4-65 (a). A crack is arrowed in Figure 4-65 (b).

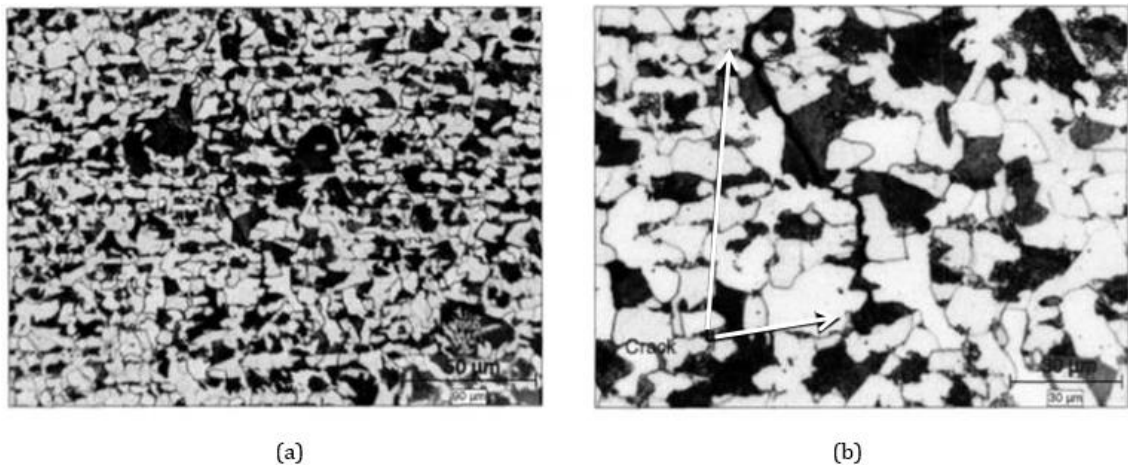


Figure 4-65: (a) microstructure of section cut from X52 steel pipeline (b) microstructure in (a) at higher magnification. A crack is arrowed in (b)^[143].

High magnification images of the crack path are shown in Figure 4-66. Li et al. found that the cracks propagated along the ferrite/ferrite grain boundaries when there were no neighbouring pearlite colonies. When a pearlite colony was encountered, the crack travelled through the colony if the lamellae were approximately parallel to the crack

direction, Figure 4-66 (d) but around the colony if the lamellae were more normal to the crack direction, Figure 4-66 (b). It is noted that where the crack travelled around a pearlite colony it travelled along the boundary between adjoining pearlite colonies in some cases and along the pearlite/ferrite boundaries in others, Figure 4-66 (b). The nature of the crack propagation associated with the pearlite colonies is identical to that found in the present study.

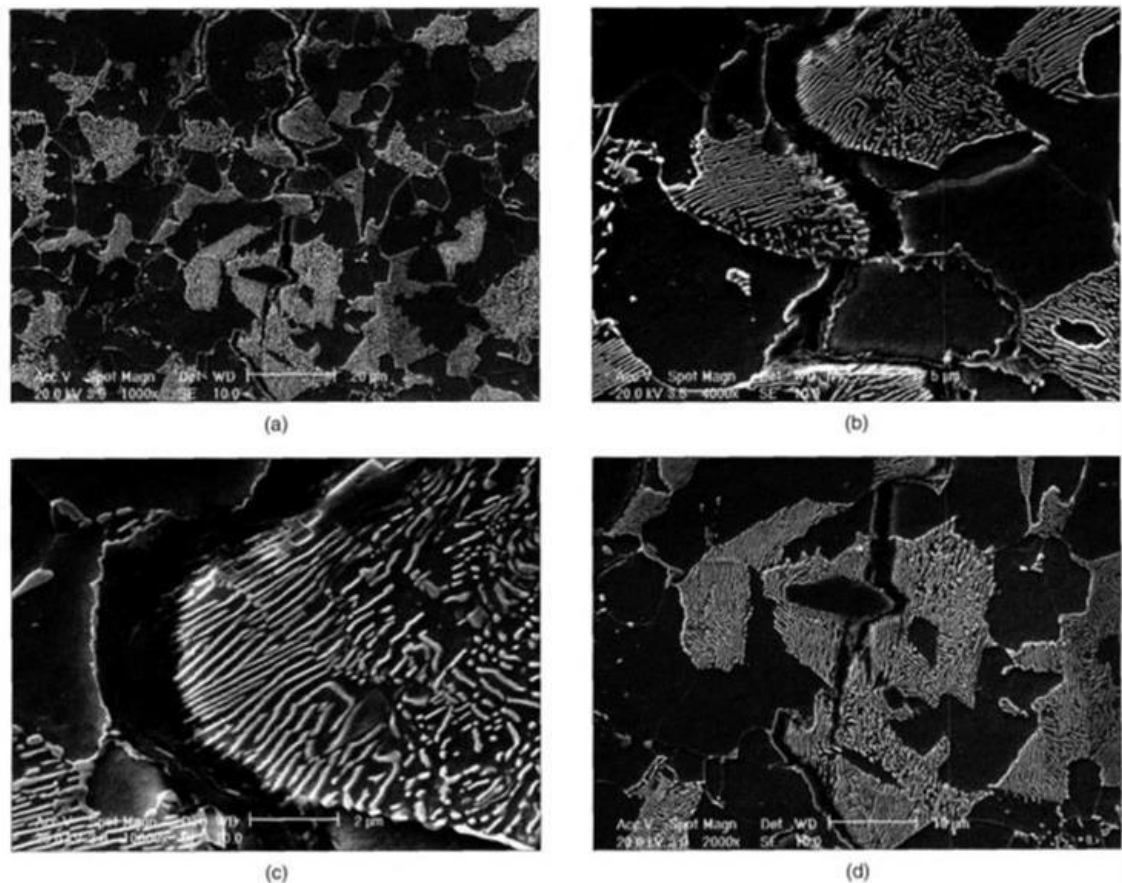


Figure 4-66: SEM images showing crack path^[143].

Li et al. noted that the pearlitic structure is relatively strong and should resist crack propagation, even when the lamellae are parallel to the crack growth direction, and postulated that crack propagation through the pearlite could be related to the electrochemical potential difference between the ferrite and the carbide phases in the pearlite. It was considered that, within the pearlite, the carbide phase would be cathodic to the ferrite, and this would facilitate dissolution of the ferrite within the pearlite due to the development of a galvanic cell. Thus, when the lamellae were approximately parallel to the macroscopic crack direction, SCC would be facilitated by dissolution of the ferrite in the pearlite along the boundary with the adjacent carbide lamella, allowing the crack

to cut through the pearlite colony. They considered therefore that fracture through the pearlite was transgranular, in contrast to the intergranular cracking observed in the ferrite regions.

It is noted that, contrary to the findings of Li et al., crack propagation along the ferrite/ferrite boundaries was not observed in the present study. To a large extent this would be due to the substantially lower ferrite content in the HSAC 840 steel, see for example Figure 4-57, which resulted in a substantially reduced number of adjoining ferrite grains and, accordingly, a substantially reduced number of ferrite/ferrite boundaries. Moreover, because of the substantially higher quantity of pearlite, it was possible for the crack to travel through, or around, the pearlite colonies with minimal necessity for traversing regions of ferrite, as can be seen in Figure 4-57.

In contrast, substantial pearlite-free regions were present in the X52 steel, as can be seen from Figure 4-66. As a result, the crack would need to traverse substantial regions containing only ferrite.

As discussed above, the single example seen in the present study of a crack traversing a region of ferrite involved the crack cutting through a ferrite grain rather than travelling along a ferrite/ferrite boundary. It is considered likely that the ferrite grain was left as a ligament bridging the crack after the crack had advanced, and then fractured subsequently. This follows since, because of the high amount of pearlite in the HSAC 840 steel, it is probable that there would be a continuous path through the pearlite above (and/or below) the plane of the section shown in Figure 4-66. This would then allow the crack to be able to advance beyond the ferrite grain by travelling through the underlying (or overlying) pearlite.

The similarity between the findings from the present study of the crack path and those by Li et al. for a high pH SCC crack provides further evidence that the failure mechanism is similar in the two cases.

As discussed earlier, the rock bolts from Mine B are considered to have undergone a different SCC mechanism which is similar to that for near neutral pH SCC of pipeline steels. The crack path was not examined in these bolts since most of the crack had undergone extensive lateral corrosion.

4.4.4.4 Corrosion Product

The corrosion product in the crack in the rock bolt from the high alkalinity mine (Rock bolt 2, Mine A) was principally iron carbonate (FeCO_3) while that for the rock bolt from the low alkalinity mine (Rock bolt 1, Mine B) was principally magnetite (Fe_3O_4). No other studies of the corrosion product in SCC cracks have been reported previously for rock bolts or pipeline steels, but, as discussed in Sections 2.2.1 and 2.2.2, both iron carbonate and magnetite have been reported to be present together on the fracture surfaces of both high pH and near neutral pH SCC failures in pipeline steels. The level to which each was present in each case was not however given.

Since high pH SCC of pipelines was found to occur in a concentrated carbonate/bicarbonate environment, Section 2.2.1, while near neutral pH SCC occurred in a dilute carbonate/bicarbonate, Section 2.2.2, it would be expected that iron carbonate would be present in larger quantities on the fracture surface (and also in subcritical cracks) of high pH SCC failures than on that of near neutral pH SCC failures. It is concluded therefore that the presence of predominantly iron carbonate in the subcritical crack in Rock bolt 3 is further indication that the rock bolt failures from high alkalinity mines, such as Mine A, are occurring through a similar mechanism to high pH pipeline SCC. This is in contrast to the lack of prominence of iron carbonate in the subcritical crack in Rock bolt 1 which is considered to indicate that a different SCC mechanism is operating in the low alkalinity mines, such as Mine B, with the mechanism now being similar to that for near neutral pH pipeline SCC.

4.4.4.5 Crack Growth Rate

As discussed in Section 2.3.3.4, Gambao and Atrens determined SCC crack growth rates at the threshold stress (minimum stress to cause SCC) for both AISI 1355 and HSAC 840 grade steels on samples taken from rock bolts^[6, 113]. The rates ranged from $\sim 10^{-8} - 10^{-9} \text{ ms}^{-1}$. They noted that at these rates a rock bolt would fail within only hours (later stated to be a few days) once stressed to the threshold stress. This seems to be inconsistent with service experience where rock bolts typically survive several years before failure. To explain this anomaly Gambao and Atrens proposed that the strata shear that produces the stress which drives SCC must have occurred just a few days before catastrophic failure. However, it is generally considered that strata movement is most likely to occur shortly after installation of the bolts. In view of this it is considered that the crack growth rates reported by Gambao and Atrens are unlikely to be representative of those that occur in service.

4.4.5 Acidic (low pH) Stress Corrosion Cracking of Rock Bolts

Parrott^[104] and Gambao and Atrens^[113] have been able to produce SCC cracks in the laboratory in samples taken from rock bolts, both with and without the surface features of the rock bolts, as discussed in Chapter 2. Parrott used an acidified sodium chloride solution containing hydrogen sulphide. The pH was not specified, although the solution was clearly acidic. Gamboa and Atrens used both sulphate and chloride solutions with a range of pH values. SCC was produced in the sulphate solution at a pH of 2.1 but not at values of 4.2 or higher, and in the chloride solution at a pH value of 1.8, but not at values of 3.1 or higher, Figure 2-35. As discussed in Chapter 3, some mine waters have been found to have pHs in the range 2-3. However, the mine waters examined in the present study, as well as those reported by Parrott had pHs of 7 or above. Despite producing SCC under acidic conditions, Parrott was unable to produce SCC in the laboratory in the same types of specimen using samples of mine water.

Gamboa and Atrens also reported that the Australian mine waters analysed by them had pH levels of 7 or more. They suggested that the failure to produce SCC at the pH levels found for these mine waters might indicate that microorganisms, which could lower the pH locally, might be responsible for the SCC failures. Accordingly, the ground water from Mine B was analysed for microorganisms in the present study. Mine B was chosen since it was considered that microorganism-induced SCC was more likely in the low alkalinity waters.

The environment in Mine B is known to contain iron- and sulphur-reducing microorganisms. These organisms act to create localised 'biomes' known as tubercles on the surface of metal substrates. The structure of these tubercles can facilitate the growth and development of anaerobic bacteria in otherwise aerobic solution conditions. The environment within these structures can also very acidic.

4.5 Conclusions

1. The results indicate that SCC in underground coal mines can occur by two different mechanisms. Only one mechanism has been proposed previously.
2. In high alkalinity mine water, SCC occurs by an anodic mechanism involving carbonate/bicarbonate cracking, similar to that observed for high pH SCC of pipeline steels.
3. In low alkalinity mine water, a cathodic mechanism occurs involving hydrogen induced cracking, similar to that observed for near neutral pH SCC of pipeline steels.
4. Iron- and sulphur-reducing microorganisms were found in the ground water from Mine B and this may indicate that such organisms are involved in low alkalinity SCC of rock bolts, as suggested by Gamboa and Atrens.
5. The SCC region of the fracture surfaces of failed rock bolts was transgranular and exhibited a tearing topography surface, as found previously by Gamboa and Atrens
- 6.. High alkalinity cracks propagated through pearlite colonies when the pearlite lamellae were oriented approximately parallel to the macroscopic crack direction, but around the colonies when the lamella were oriented at a more oblique angle. This is consistent with the findings of Li et al. for high pH pipeline SCC.
7. The depth of the SCC cracks prior to catastrophic failure of the rock bolts varied considerably even amongst bolts with the same toughness. This is to be expected since the loading produced by strata shear should vary from place to place within a mine.
8. Determination of the load at failure from the depth of the SCC cracks indicated that the load was generally below the yield stress. This is in contrast to estimates made based on plastic strain in failed bolts and the frequent observation of some permanent bending in the vicinity of the fracture surface of failed bolts. This may indicate that some relaxation of the elastic stress that drives SCC occurs subsequent to the plastic deformation

5 COUPON TESTING PROTOCOL

5.1 Introduction

This chapter presents some preliminary work undertaken on SCC testing using coupon samples cut from rock bolts. Coupon specimens rather than full scale specimens were used since these were easier to place in mines and also easier to test in the laboratory. The work was intended to provide a basis for subsequent testing by other researchers working in the project.

5.2 Experimental Methods

Testing was initially conducted in-situ in Mine B using a modified version of the ASTM G39 bent beam SCC specimen. Subsequently, testing was conducted in the laboratory using a pin-loaded slotted coupon specimen, as used previously by Parrott^[104] and discussed in Section 2.3.3.1. Bar loaded specimens which were capable of producing a greater stress were also examined. The in-situ testing was conducted using samples taken from HSAC 840 rock bolts since these are the predominant type of rock bolt currently installed in mines. In subsequent testing using the slotted coupon specimens, the samples were taken from both HSAC 840 and AISI 1355 bolts since these were considered to span the range of steels that have been used for rock bolts.

5.2.1 Bent Beam Stress Corrosion Cracking Testing

5.2.1.1 Test Configuration

The bent beam test was selected from the substantial range of SCC tests that have been developed^[7] since it was considered to best replicate in-service conditions. Both three and four-point bend tests were used. In the three-point bend test, the tensile stress on the outer fibers of the specimen ranges from zero at the outer support pins to a maximum at the central loading nose, where the peak stress is experienced. In the four-point test, the stress develops from zero at the outer support pins, to a maximum between the two loading noses, where the peak stress is constant^[7].

5.2.1.2 Test Specimens

The specimens used in the tests were taken from the surface of the rock bolts so as to enable surface features, i.e., ribs, mill scale and decarburization, to be retained. The specimens were first cut longitudinally from the surface of the rock bolts using a band saw fitted with a guide to ensure that the top and bottom sides of the specimen were parallel. The coupons so produced were 10 mm thick and 200 mm long (4 point bend) or 120 mm long (3 point bend). The coupons were then ground on the underside with a surface grinder to a final thickness of 4 mm. This resulted in the specimens being 17.3 mm wide. The thickness was chosen as 4 mm to allow the specimens to be bent manually with relative ease using a loading screw. A test specimen is shown in Figure 5-1.



Figure 5-1: Bent beam specimen shown from topside and underside.

ASTM G39 utilises a rectangular section specimen as shown in Figure 5-2 (a). However it was not possible to retain the surface features of the rock bolt in such a specimen and a

modified specimen with a segment-shaped cross section was used instead, as shown in Figure 5-2 (b). The specimens were loaded with the original surface of the rock bolt being on the tension side of the bend and located in the test fixture such that a rib was at the centre of the bend. It was noted in Chapter 4 that rock bolts which had failed by SCC commonly showed a small bend at the location of failure while failure invariably initiated at the base of the ribs. The test methodology was intended to replicate these features

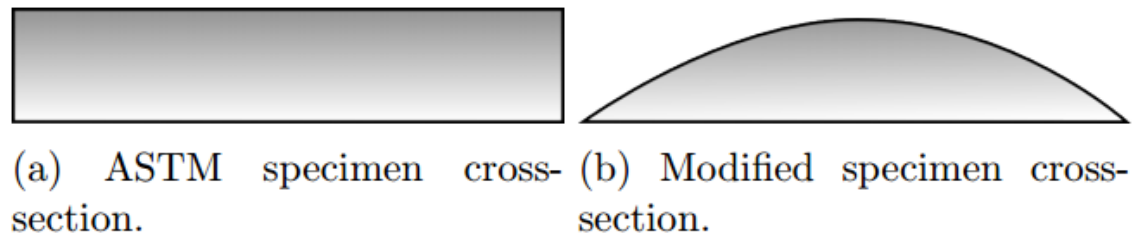


Figure 5-2: Cross section of bent beam specimen (a) as specified in ASTM G39 (b) as used in present study.

5.2.1.3 Test Fixtures

Since the bend tests were to be conducted in-situ in a mine it was necessary to use purpose built fixtures for the testing. The three-point bend fixture is shown in Figure 5-3 while the four-point fixture is shown in Figure 5-4. Schematic drawings of the two fixtures are shown in Figure 5-5 and Figure 5-6, respectively. For The span for the three-point bend tests was 75 mm. For the four-point test the span was 150 mm while the distance between the two loading noses was 75mm. Both fixtures were manufactured from stainless steel.

The test specimens were loaded using a loading screw attached to the loading nose(s), Figure 5-3 to Figure 5-6. Teflon tape was applied to the support pins and loading noses to prevent galvanic coupling between the test specimen and the fixture. Bitumen paint was applied to the ground face of the specimen to ensure that only the part of the specimen containing the original rock bolt surface was exposed to the environment.

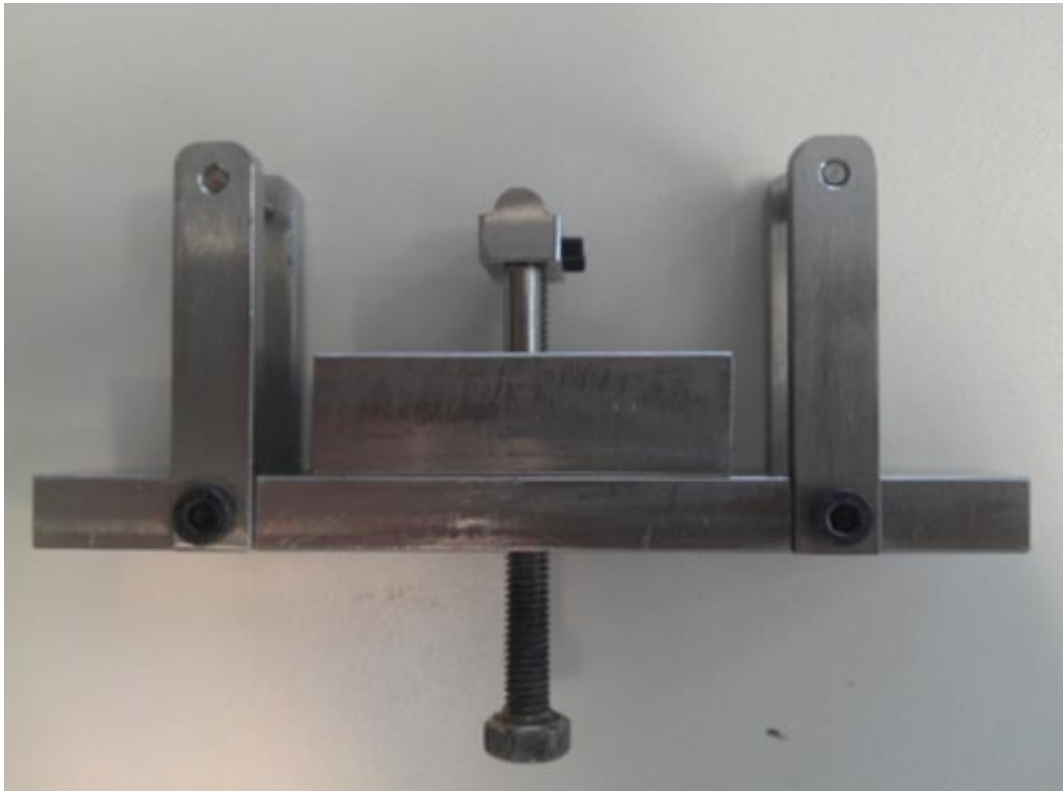


Figure 5-3: Three-point bend fixture.

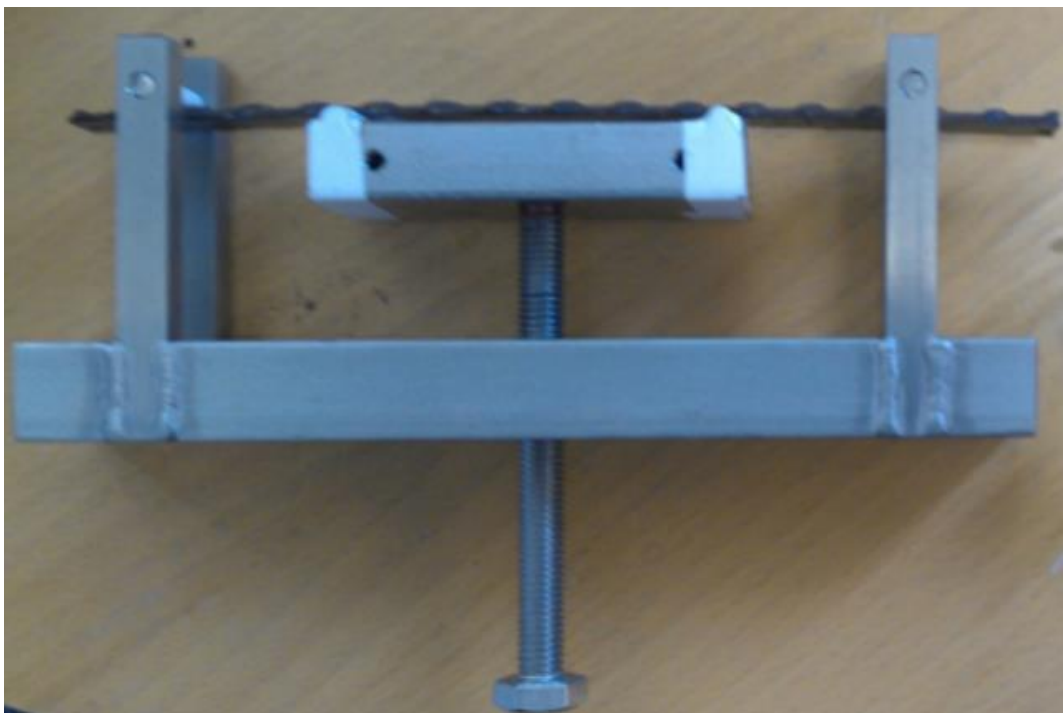


Figure 5-4: Four-point bend fixture.

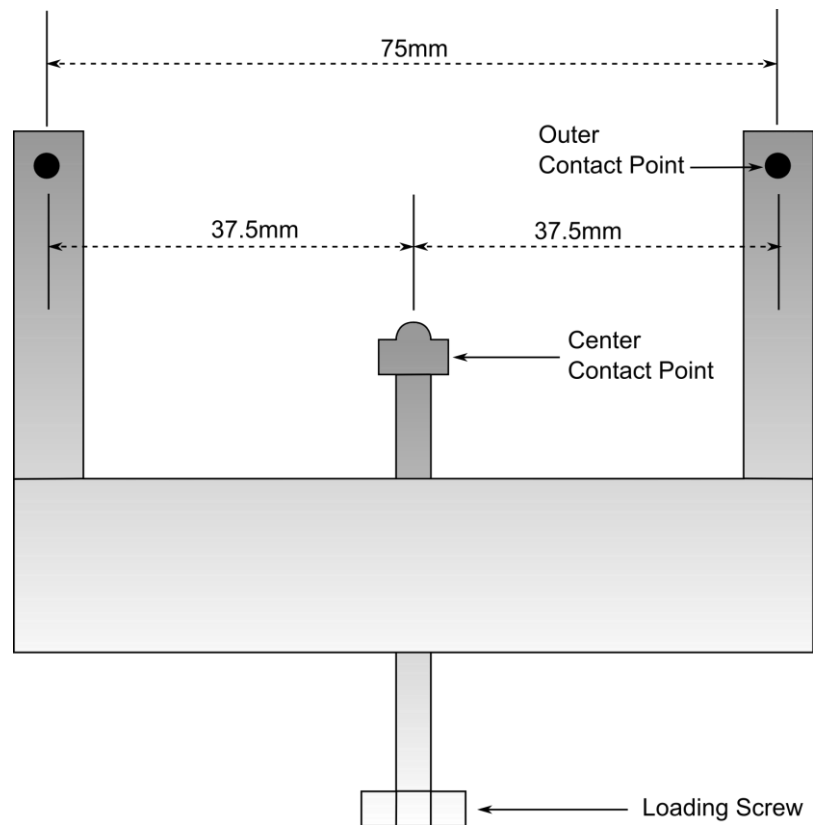
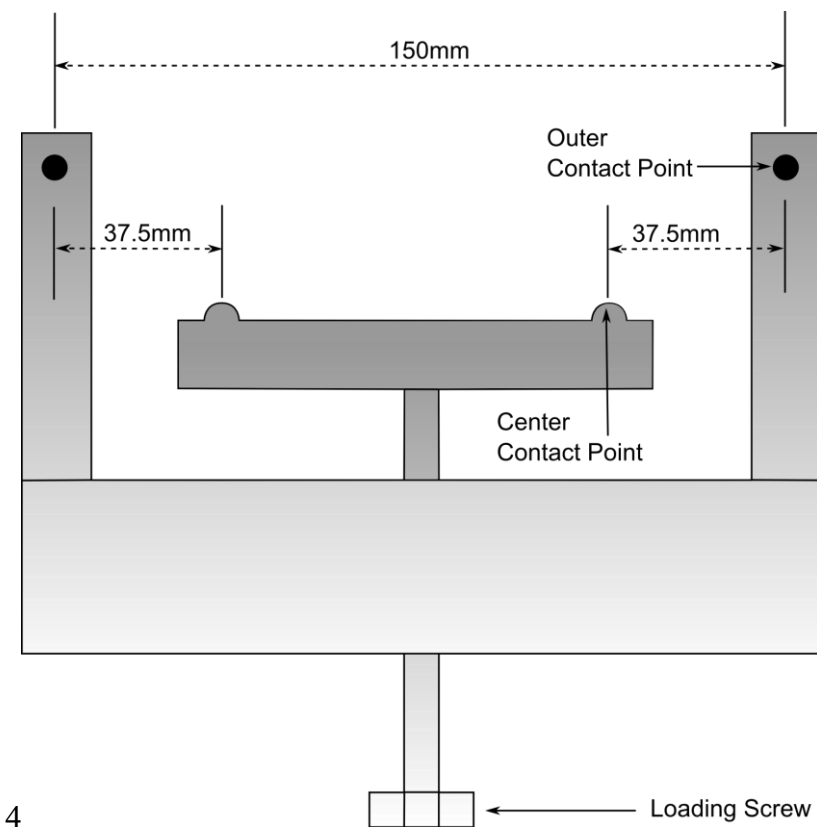


Figure 5-5: Schematic drawing of three-point bend fixture.



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Figure 5-6: Schematic drawing of four-point bend fixture.

ASTM G39 gives equations to calculate the stress on the outer fibre on the tension side of the bend test specimens. These are given below for three point and four point bend configurations as Equations (5-1) and (5-2), respectively.

$$\sigma = \frac{6Ety}{H^2} \quad (5-1)$$

$$\sigma = \frac{12Ety}{3H^2 - 4A^2} \quad (5-2)$$

where:

- σ is the stress in the outer fiber (MPa)
- E is Young's modulus of the material (230 GPa for rock bolt steel)
- t is the specimen thickness (mm)
- d is the distance from the neutral axis to the extreme fibre (mm)
- y is the maximum deflection between outer supports (mm)
- H is the distance between outer supports (mm)
- A is the distance between the inner supports in the four point bend test (mm)

These equations are, however, for rectangular section specimens, whereas the specimens used here had a segment-shaped cross section. Modified equations were therefore derived to take into account the change in the second moment of inertia of the specimens. The modified equations based on a 4 mm segment taken from the surface of a 21.6 mm rock bolt, and noting that for the four point bend test $A = \frac{H}{2}$, are given as Equations (5-3) and (5-4) below.

$$\sigma = \frac{12Edy}{H^2} \quad (5-3)$$

$$\sigma = \frac{24Edy}{2.75H^2} \quad (5-4)$$

5.2.1.4 Testing

The specimens were placed in the test fixtures and loaded to a deflection of 5 mm using the loading screw. The stress in the outer fibre calculated using Equations (5-3) and (5-4) was 580 MPa for the three-point bend specimen and 290 MPa for the four-point bend specimen. The two loaded test specimens were then installed in Mine B, at a heading characterized by poor ground conditions and a heavy inflow of groundwater, where a

substantial number of SCC affected rock bolts had been found. The fixtures were attached to the roof meshing with plastic cable ties to ensure that the specimens were electrically isolated so as to avoid any galvanic action. The specimens were located under a stream of dripping water flowing from the end a rock bolt. A flow rate of ~50 ml/min was recorded at the test locations prior to installation of the test specimens. The specimens were left in the mine for 97 days. It is probable that the flow rate would have varied over this time.

5.2.2 Slotted Coupon Stress Corrosion Testing

5.2.2.1 Test Configuration

The three- and four-point bend tests required a separate loading fixture for each test specimen and this greatly limited the number of specimens that could be tested. An alternative method which was much simpler was subsequently identified, which had been developed by Parrott^[104] specifically for SCC testing of rock bolts. As discussed in Section 2.3.3.1, this test involved cutting a relatively short coupon from a rock bolt and then machining a longitudinal slot in the middle of the coupon at the centre of its width. An oversized pin (15 mm diameter) was then inserted into the slot causing the material on either side of the slot to be bent outwards so as to produce a tensile stress at the surface of the coupon. It is noted that this method again allows the surface features of the rock bolt to be retained. Parrott demonstrated that SCC could be produced using this test in an acidified 3.5% sodium chloride solution containing hydrogen sulphide^[104].

In view of the relative simplicity of the slotted coupon test, the bend tests were discontinued and this test adopted instead. The work done in the present thesis involved testing in the laboratory. In-situ testing in boreholes in the roof of mines was conducted by another investigator as a separate part of the overall project.

5.2.2.2 Sample Preparation

The slotted coupon specimens were manufactured from both HSAC 840 and AISI 1355 rock bolts since, as discussed earlier, these were considered to span the range of steels that have been used for rock bolts. Coupons 200 mm long were cut from the rock bolts and a 10 mm wide slot then milled along the axis of the coupon for the middle 100 mm, as shown in Figure 5-7. The slot was cut along the ‘spine’ of the rock bolt, so that the rib profiles were left intact. The coupons were cut from the rock bolts such that a rib was present at the centre of the slot and thus at the location of the loading pin/bar.

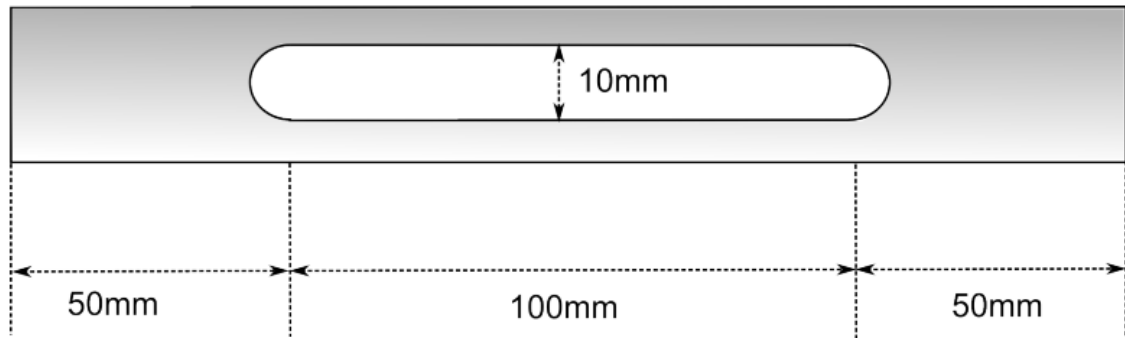


Figure 5-7: Dimensions of slotted coupon specimens.

Two different levels of loading were used. In the first case an oversized pin (18 mm diameter) was inserted into the slot while in the second case a stressing bar was used which produced a substantially greater amount of bending in the sides of the specimen. In the first method, the pin was tapered at one end, Figure 5-8, and then inserted, tapered end first, into the centre of the slot using a hydraulic ram, forcing the two sides of the slot apart. An 18 mm pin diameter was chosen, since this was found to produce visible permanent deformation of the sides of the specimen, indicating that the stress was above yield. Vandermaat determined the peak stress in the specimen using finite element analysis and obtained a value of 898 MPa^[144]. This is similar to the calculated stress at failure for Rock Bolt 5 given in Table 4-6. In practice, slight inaccuracies in alignment of the slot and the pin led to an asymmetry in the amount of deflection experienced by each side of the specimen and thus variation in the applied stress. The pins were machined from the same rock bolts as the slotted coupons to avoid galvanic action.



Figure 5-8: Slotted specimen with loading pin.

The stressing bar, Figure 5-9, was used to produce substantially higher stress in the sides of the specimen than could be obtained using an oversize pin. Rock bolt steels show substantial work hardening and this effect could be exploited to substantially increase the level of elastic strain in the sample. As for the loading pins, a tapered design was used for the loading bar. The bar was initially parallel sided with a width of 67 mm, but then tapered outward to a second parallel sided region, 75 mm in width, Figure 5-9. The width of the second parallel sided region was selected such that the steel would be loaded to just below its ultimate strength when the stressing bar was inserted to its full width. To insert the stressing bar, the slotted specimen was loaded in compression. This caused the two ligaments on either side of the slot to buckle outwards, inducing a large tensile strain in the outer radius of the bends. Once the desired width was reached, the load was paused and the small end of the tapered bar inserted into the specimen. The specimen was then unloaded, during which elastic springback occurred causing the specimen to clamp onto the loading bar. A hydraulic press was then used to push the tapered loading bar into the specimen to its full width. This ensured that the elastic strain lost during springback was fully reintroduced back into the test specimen.

Once the loading pin or bar was inserted, the specimens were cleaned using acetone and paper towels to remove any oil deposited in the manufacturing process. The central slot was then coated with paraffin wax to ensure that only the surface of the rock bolt was exposed to the test environment.



Figure 5-9: Slotted specimen with tapered stressing bar.

5.2.2.3 Testing

Testing of both the pin-loaded and bar-loaded specimens was conducted initially by immersing one specimen of each configuration from both steels in an acidified sodium chloride sodium sulphide solution to validate the procedure. The composition of the solution is shown in Table 5-1. Testing was conducted in a sealed container at 21°C with the solution being refreshed twice weekly. The samples were left in the solution for up to one month or until failure, whichever occurred first.

Table 5-1: Makeup of acidified sodium chloride sodium sulphide solution.

Component	Amount
Sodium chloride	70 g
Sodium sulphide	2 g
Glacial acetic acid	60 ml
Distilled water	1940 ml
pH	2.8

Subsequently a more detailed study was undertaken in which the specimens were exposed to ground water collected from Mine B. A parallel set of test was conducted using distilled water as a control. The compositions of the mine water and the distilled water, determined using inductively coupled plasma (ICP) spectroscopy, are given in Table 5-2 and Table 5-3.

Table 5-2: Composition of ground water from Mine B.

Temperature °C	pH	Conductivity (mS/m)	Na (mg/l)	Cl (mg/l)	Fe (mg/l)	SO ₄ (mg/l)	K (mg/l)
20	7.76	820	182.3	7.4	1.4	80.5	5.3

Table 5-3: Distilled water analysis.

Temperature °C	pH	Na (mg/l)	Cl (mg/l)	Fe (mg/l)	S (mg/l)	K (mg/l)
20	7	1.2	0	0	0.03	0.18

It was suggested by Shutter et al.^[102] and also Crosky et al.^[101] that improved resistance to SCC might be achieved by galvanizing the rock bolts. As discussed in Section 2.2.5, shot peening is also considered to be beneficial to SCC resistance. Accordingly, these two treatments were also evaluated by testing in both the mine water and the distilled water. It was decided to use just the pin-loaded specimen for these tests since the bar-loaded-specimen proved unsuitable, as is discussed later.

The tests were conducted using a custom built rig that cycled the specimens through wet and dry conditions using an 8 hour wet/8 hour dry cycle. This was done since alternate wetting and drying is known to accelerate corrosion. Additionally, at least some rock bolts would be expected to experience alternating wet and dry conditions in service. The rig used for the testing is shown in Figure 5-10.



Figure 5-10: Test rig used for cycling test specimens through alternating wetting and drying cycles.

A total of 36 specimens was examined. The test matrix is given in Table 5-4. Testing was conducted in a controlled environment of 21°C and 50% relative humidity for a period of 90 days after which they were examined for cracking using an Olympus SZ-STU2 low power stereo optical microscope.

All test specimens were also weighed before and after testing to determine the level of corrosion that had taken place during the tests. Prior to weighing the specimens post-testing, they were cleaned of corrosion product by immersion in Ajax inhibited hydrochloric acid for 60 seconds followed by wire brushing. The cleaning step in inhibited hydrochloric acid solution was omitted for the galvanized specimens to avoid dissolution of the galvanizing.

Table 5-4: Test matrix.

Specimen	Treatment	Solution	Grade
A-1	Normal	Distilled Water	840
A-2	Normal	Distilled Water	840
B-5	Normal	Distilled Water	840
I-4	Normal	Distilled Water	1355
J-3	Normal	Distilled Water	1355
I-3	Normal	Distilled Water	1355
A-3	Normal	Mine Water	840
A-4	Normal	Mine Water	840
A-5	Normal	Mine Water	840
I-1	Normal	Mine Water	1355
I-2	Normal	Mine Water	1355
I-5	Normal	Mine Water	1355
Q-3	Shot Peened	Distilled Water	840
Q-7	Shot Peened	Distilled Water	840
R-1	Shot Peened	Distilled Water	840
R-5	Shot Peened	Distilled Water	1355
R-10	Shot Peened	Distilled Water	1355
Q-2	Shot Peened	Mine Water	840
Q-4	Shot Peened	Mine Water	840
R-2	Shot Peened	Mine Water	1355
R-3	Shot Peened	Mine Water	1355
R-4	Shot Peened	Mine Water	1355

The results were used to determine the corrosion rate using the following equation:

$$\text{Corrosion Rate (mm/yr)} = \frac{K \times W}{A \times T \times D} \quad (5-5)$$

where:

- K is the corrosion rate constant, equal to 8.76×10^4 mm/y
- W is the loss of specimen mass (g)
- A is the original surface area (cm²)
- T is the exposure time (h)
- D is the density of steel which is 7.89 g/cm³

5.2.3 Fractographic Examination

The fracture surfaces of failed specimens were examined using an Olympus SZ-STU2 low power stereo optical microscope and a Hitachi S3400-I scanning electron microscope (SEM) as described in Section 4.2.3. Prior to SEM examination, the fracture surfaces were cut from the failed specimen approximately 10 mm below the fracture and cleaned in Ajax inhibited hydrochloric acid, as described in Section 4.2.5.

5.3 Results

5.3.1 Ben Beam Stress Corrosion Cracking Testing

The three- and four-point bend test specimens are shown, immediately after being installed in Mine B, in Figure 5-11 and Figure 5-12.



Figure 5-11: Three-point bend test specimen in place in Mine B.



Figure 5-12: Four-point bend test specimen in place in Mine B.

At the time of installation a thick, brown/orange, gelatinous substance was observed to have accumulated on the mesh and rock bolts protruding from the roof. The substance was similar to that for which a swab analysis was made, the results of which are given in Section 3.3.2. Inspection of the test pieces after they had been in the mine for one week revealed that the brown/orange substance had also begun to accumulate on the surface of the specimens and loading fixtures. After three months, this substance was found to have engulfed the samples, as can be seen in Figure 5-13 and Figure 5-14.



Figure 5-13: Three-point bend specimen after 1 week in Mine B.



Figure 5-14: Three-point bend specimen after 3 month in Mine B.

After 97 days in-situ, the test specimens were collected and returned to the laboratory for analysis. However, no evidence of SCC was detected in either specimen.

5.3.2 Slotted Coupon Stress Corrosion Testing

5.3.2.1 Testing in Acidified Sodium Chloride Sodium Sulphide Solution

The bar-loaded specimens from both the AISI 1355 and the HSAC 840 steels, and also the AISI 1355 pin-loaded specimen, failed within 24 hours of being placed in the acidified sodium chloride sodium sulphide solution. The exact time for failure was not established since all the three specimens failed some time between the first inspection at 2 hours and the next inspection at 24 hours. This indicates that the failure time was somewhere between 2 and 24 hours. In contrast, the HSAC 840 pin loaded specimen showed no sign of SCC even after one month.

The AISI 1355 pin-loaded specimen and the HSAC 840 bar-loaded specimen are shown in Figure 5-15 and Figure 5-16, respectively. The pin-loaded specimen failed across a rib at the location of the pin but both the bar loaded specimens failed at the end of the slot. The bar-loaded specimens also showed visible cracks at the inside corners at the opposite end of the slot, indicating that in these specimens failure had initiated from the inside of the slot and not from the rock bolt surface. This is to be expected since the tensile stress is on the inside at this location. The stress is also concentrated at the end of the slot. To minimise this, the end of the slots were rounded, as illustrated in Figure 5-7.

Low power optical microscope images of the fracture surfaces are shown in Figure 5-17 and Figure 5-18. Both specimens showed the characteristic thumbnail shaped SCC region seen on the service failed rock bolts (Section 4.3) followed by a final overload region. The SCC region had initiated from the original rock bolt surface in the pin-loaded specimen. However, two separate SCC regions were seen on the fracture surface of the bar-loaded specimen and these were located at each corner of the internal slot, indicating that, in this specimen, SCC was initiated from the milled surface of the slot and not from the original surface of the rock bolt. In both specimens, the overload region was quite discoloured due to secondary corrosion which had occurred as result of the specimens remaining in the test solution for a period of time after failure.

SEM fractographs showing the fracture surface at approximately the centre of the SCC region and at the transition between the SCC and overload regions are shown for both specimens in Figure 5-19 to Figure 5-22. The SCC regions show the tearing topography surface (TTS) characteristic of SCC while the overload region shows transgranular brittle cleavage. These features are in accordance with those seen on the fracture surfaces of the

service failed bolts, Section 4.3, and are considered to confirm that failure had occurred as a result of stress corrosion cracking.



Figure 5-15: AISI 1355 pin-loaded specimen after failure.



Figure 5-16: AISI 1355 bar loaded specimen after failure.

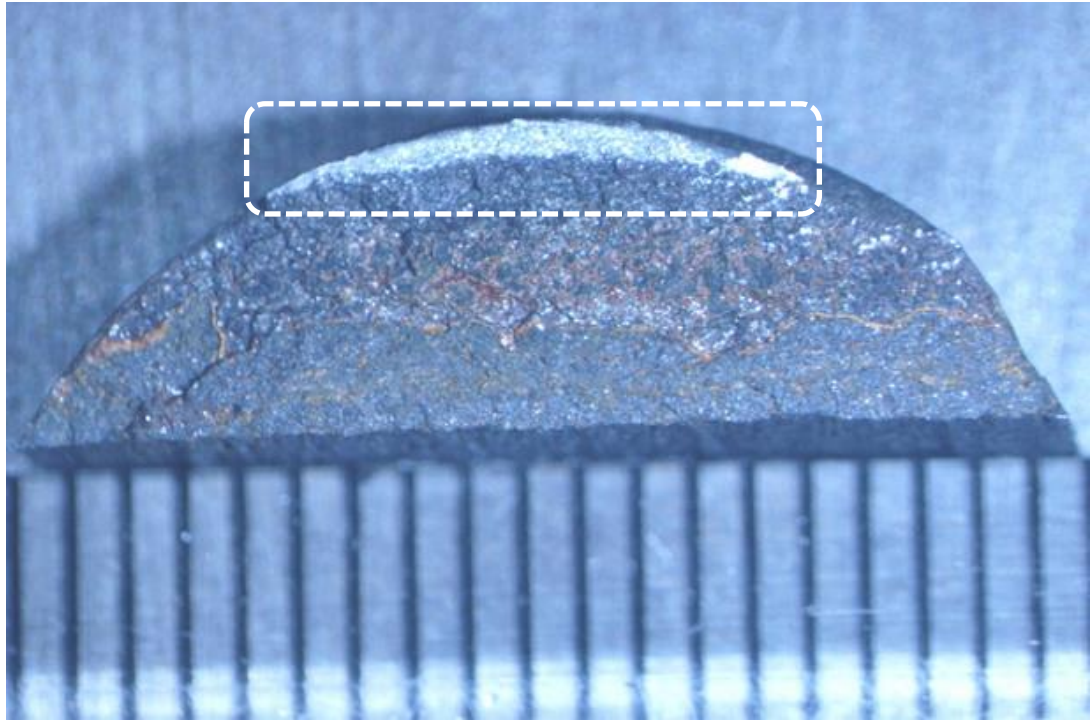


Figure 5-17: Fracture surface of AISI 1355 pin loaded specimen after failure. Graduations are in mm. The extent of the SCC region is indicated by the dashed line.

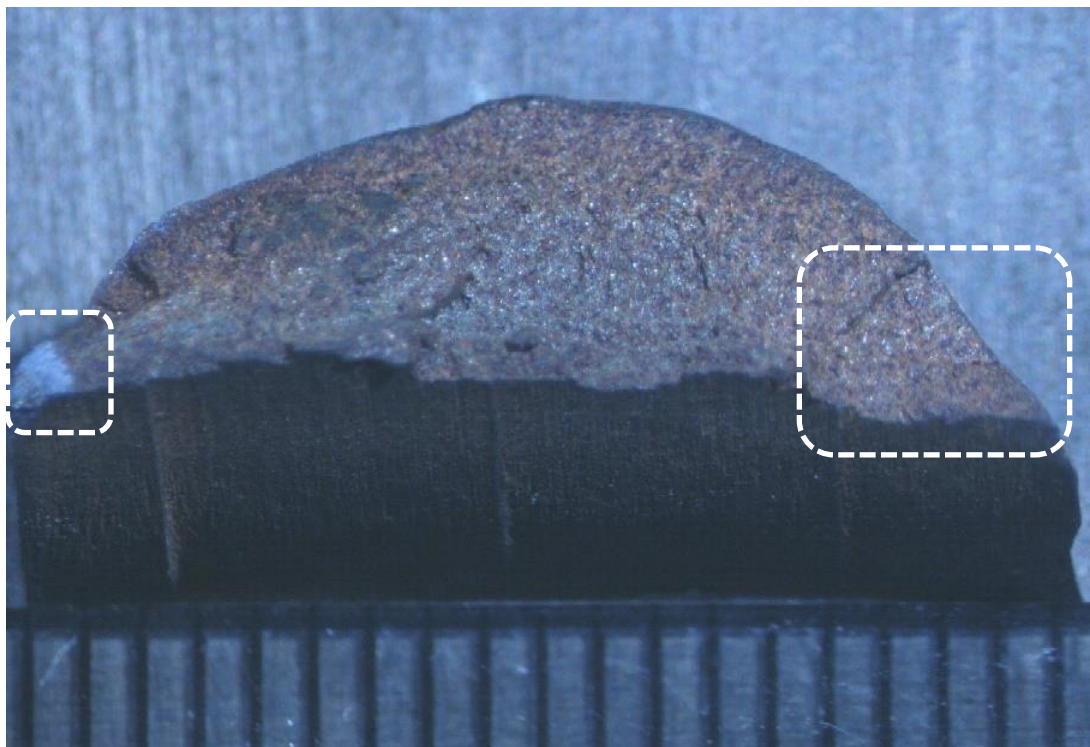


Figure 5-18: Fracture surface of AISI 1355 bar loaded specimen after failure. Graduations are in mm. SCC regions are present at both corners of the specimen. The extent of the SCC region is indicated by the dashed lines.

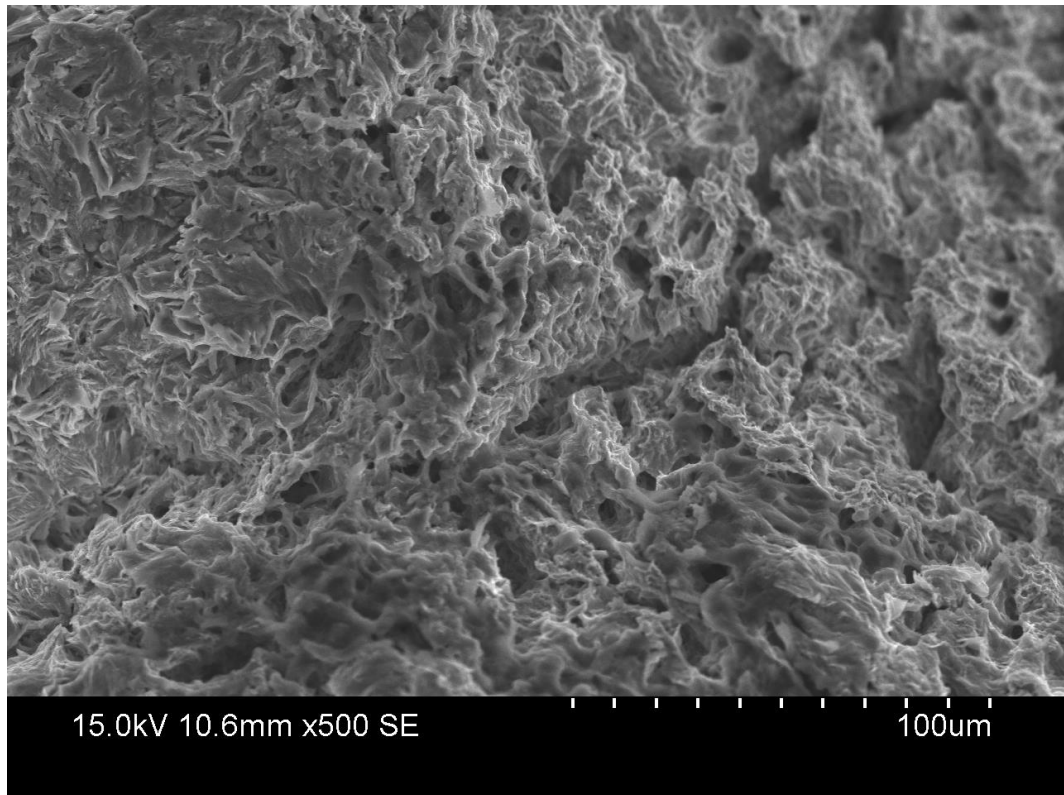


Figure 5-19: SEM fractography at approximately the centre of SCC region of the AISI 1355 pin loaded specimen.

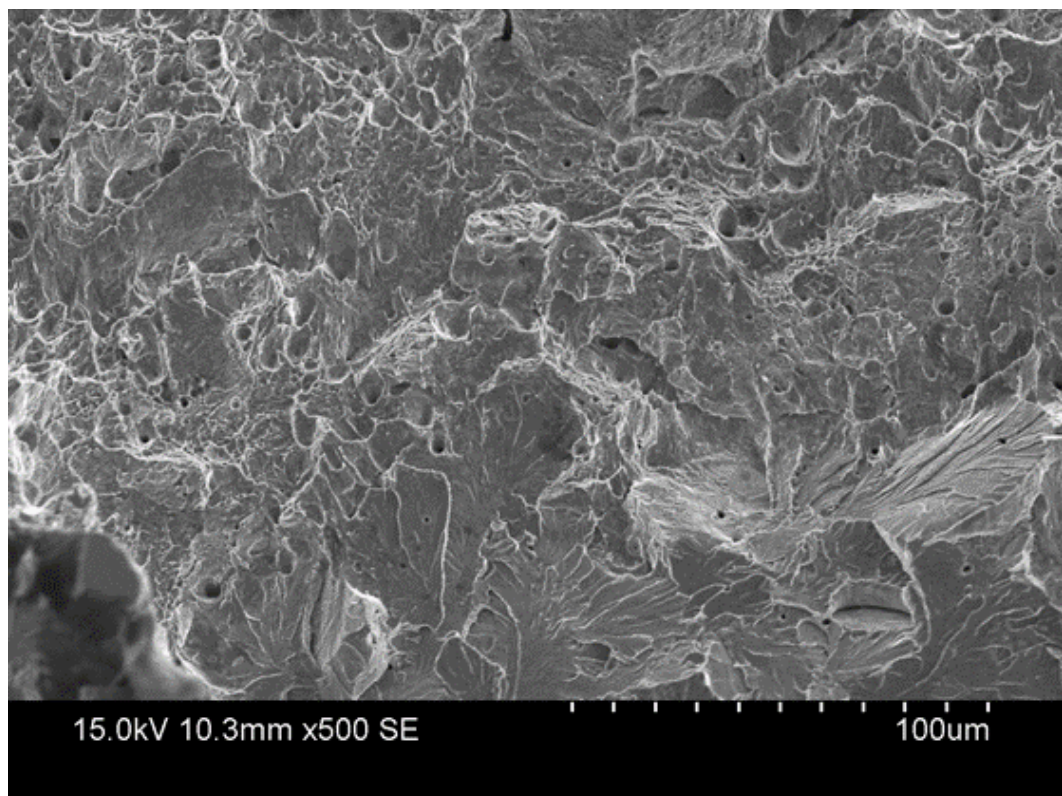


Figure 5-20: SEM fractography showing transition from SCC to overload failure in AISI 1355 pin loaded specimen.

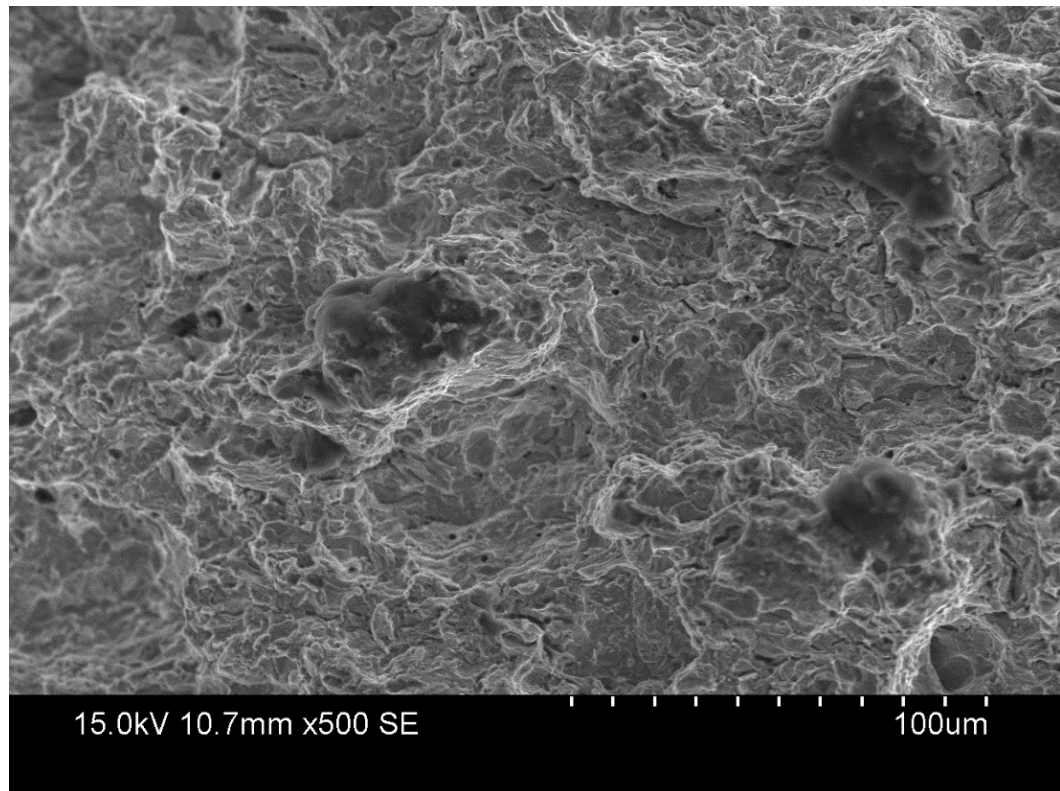


Figure 5-21: SEM fractograph at approximately the centre of the right hand side SCC region of the AISI 1355 bar loaded specimen.

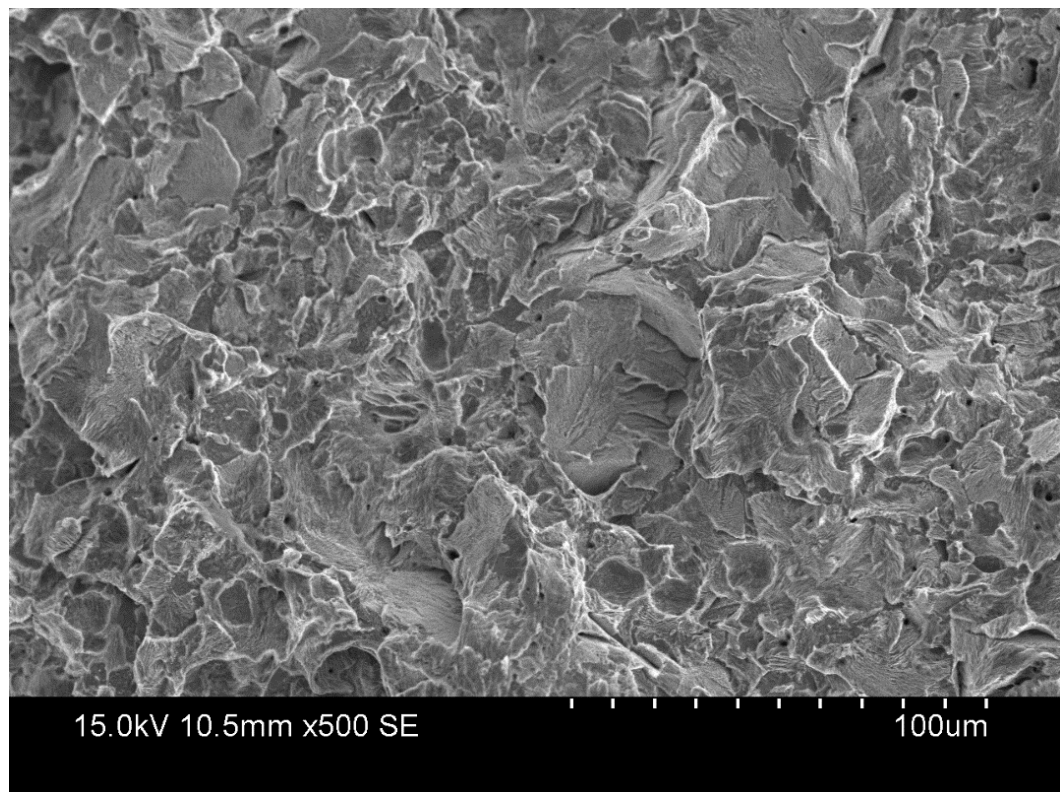


Figure 5-22: SEM fractography showing transition from SCC to overload failure in AISI bar loaded specimen.

5.3.2.2 Testing in Mine Water

Alternate wet/dry cycling in ground water from Mine B, and also a distilled water control solution, was conducted on loaded coupon specimens made from untreated rock bolts, shot peened rock bolts and galvanized rock bolts. The results given in the previous section indicated that the bar loaded specimens cracked from the machined slot rather than from the original rock bolt surface. This was considered undesirable since failure was intended to start from the original surface of the rock bolt where the surface features were still retained. Accordingly, only the pin loaded specimens, which failed from the original surface, were used for this part of the study.

Testing of the pin-loaded slotted coupon specimens failed to produce any SCC cracking over the testing period of 90 days. However, the results did provide some information on the relative corrosion performance of the different treatments for the two different steels in the two different environments. The weight loss measurements after removal of the corrosion product are given in Table 5-5 while the corrosion rates are given in Table 5-6. In contrast to the other specimens, the galvanised specimens underwent a small weight gain of approximately 4 g. This is considered to be due to incomplete removal of the corrosion layer on the galvanised surface. Since no corrosion of the steel occurred, no data is given for these specimens in Table 5-5.

In general, corrosion was more rapid in the mine water than in distilled water, with the average corrosion rates being 4.0×10^{-4} and 2.3×10^{-4} , respectively, Table 5-6. This is to be expected in view of the substantially higher concentration of ionic species in the mine water, Table 5-2 and Table 5-3. In the distilled water, the shot peened samples corroded at approximately the same rates as the untreated samples while the rates of corrosion were also similar for the two steels. However, in the mine water, the shot peened samples corroded approximately an order of magnitude faster than the untreated samples for the HSAC 840 steel, but the reverse was true for the AISI 1355 grade. It is uncertain whether this is a real effect or a result of experimental error.

Table 5-5: Weight loss measurements after removal of the corrosion product.

Specimen	Treatment	Solution	Grade	Weight Before	Weight After
A-1	Normal	Distilled Water	840	366.7	364.9
A-2	Normal	Distilled Water	840	423.4	420.7
B-5	Normal	Distilled Water	840	408.8	406.7
I-4	Normal	Distilled Water	1355	441.3	439.9
J-3	Normal	Distilled Water	1355	391.7	389.9
I-3	Normal	Distilled Water	1355	381.1	379.4
A-3	Normal	Mine Water	840	419.5	418.2
A-4	Normal	Mine Water	840	420.2	418.8
A-5	Normal	Mine Water	840	423.8	422.5
I-1	Normal	Mine Water	1355	402.5	400.6
I-2	Normal	Mine Water	1355	405.4	403.9
I-5	Normal	Mine Water	1355	402.1	396.9
Q-3	Shot Peened	Distilled Water	840	398.7	408.3
Q-7	Shot Peened	Distilled Water	840	417.0	394.0
R-1	Shot Peened	Distilled Water	840	410.8	409.2
R-5	Shot Peened	Distilled Water	1355	401.0	399.9
R-10	Shot Peened	Distilled Water	1355	407.4	406.1
Q-2	Shot Peened	Mine Water	840	412.4	401.9
Q-4	Shot Peened	Mine Water	840	410.1	406.4
R-2	Shot Peened	Mine Water	1355	412.8	412.3
R-3	Shot Peened	Mine Water	1355	408.4	408.2
R-4	Shot Peened	Mine Water	1355	408.1	407.9

Table 5-6: Corrosion for slotted specimens exposed to alternating wetting and drying cycles.

Grade	Treatment	Distilled Water (mm/yr)	Mine Water (mm/yr)	Average (mm/yr)
840	Untreated	3.1×10^{-4}	1.8×10^{-4}	2.43×10^{-4}
	Shot Peened	2.2×10^{-4}	9.8×10^{-4}	5.98×10^{-4}
	Galvanised	-	-	-
1355	Untreated	2.2×10^{-4}	4.0×10^{-4}	3.11×10^{-4}
	Shot Peened	1.7×10^{-4}	0.4×10^{-4}	1.06×10^{-4}
	Galvanised	-	-	-
Average (mm/yr)		2.3×10^{-4}	4.0×10^{-4}	

5.4 Discussion

5.4.1 Bent Beam Stress Corrosion Cracking Testing

The three-point and four-point bent beam specimens failed to show any evidence of stress corrosion cracking after being installed in Mine B for 97 days under a flow of mine water. This indicates that either the time was too short or the mine water at the location used was not conducive to SCC. The time used was short in comparison to the failure times experienced in service which are typically a number of years. However, it was considered that detectable subcritical cracks might start to develop within the time used for the tests, but this was not the case. The specimens were intentionally placed in a location where a substantial number of SCC failures had been found to occur. However, this does not necessarily guarantee that the mine water was conducive to SCC since its chemistry can vary from place to place and also over time.

It is also noted that the stresses used of 580 MPa for the three-point specimen and 290 MPa for the four point specimen are well below the threshold stress of 850 MPa reported by Gambao and Atrous^[6, 113] for SCC of HSAC 840 rock bolts and, on this basis, SCC would not be expected. However, as discussed in Section 4, the testing done by these workers may not be representative of the SCC conditions which exist in underground coal mines.

It is noted that Vandermaat^[144] has been able to obtain SCC failures at 580 MPa in both the three-point and four-point specimens using the acidified sodium chloride sodium sulphide solution given in Table 5-1. This indicates that the load of 580 MPa applied to the in situ three-point bend specimen is sufficient to produce SCC. It also indicates that the threshold stress can be below 850 MPa.

The bent beam test configuration has the advantage over the slotted coupon test configuration of providing more accurate and reproducible loading during the test. This is in contrast to the slotted coupon specimen for which any inaccuracy in machining will result in the load being different to the ideal value. However, each bent beam specimen requires a dedicated test fixture and this becomes prohibitively expensive if a substantial number of in-situ tests are to be conducted simultaneously. In contrast, the slotted coupon specimens are cheap to produce and are therefore readily suited to large scale in-situ installation. In addition, while the bent beam specimens can be easily hung from the roof of a mine, as in the present study, it is more desirable to locate them in the roof of the mine in order to fully replicate the environment experienced by failed bolts and this would

require an unrealistically large bore hole. The slotted coupon specimens, on the other hand, are only marginally wider than a rock bolt and can be inserted into standard size bore hole.

5.4.2 Slotted Coupon Stress Corrosion Cracking Tests

5.4.2.1 Testing in Acidified Sodium Chloride Sodium Sulphide Solution

The bar-loaded slotted coupon tests failed within 24 hours for both the AISI 1355 coupons and the HSAC 840 ones when exposed to the acidified sodium chloride sodium sulphide solution. Failure also occurred within the same time for the AISI 1355 pin-loaded specimen but the HSAC 840 pin loaded specimen remained unfailed after 30 days.

The pin-loaded slotted coupon specimen failed from the original surface of the rock bolt and the test therefore included any effect of the surface features of rock bolts (ribs, mill scale and decarburisation). Failure of this specimen is therefore considered to validate the testing methodology.

In contrast, the two bar-loaded specimens both failed from the milled surface of the internal slot and were not, therefore, representative of the in-service failures since the rock bolt surface features were not present at the location where cracking initiated. For this reason, use of this specimen was discontinued.

The failure of the AISI 1355 pin-loaded specimen within 24 hours, and the absence of failure in the pin-loaded HSAC 840 specimen after 30 days, suggest that the HSAC 840 bolts are more resistant to SCC, as was expected when the change to HSAC 840 bolts was made. This was confirmed in subsequent testing by Vandermaat^[144], using pin-loaded slotted coupon specimens exposed to the acidified sodium chloride sodium sulphide solution given in Table 5-1, which showed that the SCC life of AISI 1355 rock bolts was only half that of HSAC 840 bolts.

As noted earlier, the pin-loaded slotted coupon specimen is well suited to in-situ testing in the roof of mines to replicate the in-service SCC condition. In recent work, Craig inserted pin loaded coupon specimens in bore holes in the roof of Mine B and observed SCC cracking in an AISI 1355 specimen when it was inspected after 203 days^[145]. Cracking was observed in a second AISI 1355 specimen when inspected after 566 days^[145]. As discussed above, the tests conducted in the acidified sodium chloride sodium sulphide solution validated the pin-loaded slotted coupon test methodology. Craig's results have now validated the test methodology in-situ in a mine.

In earlier work, Gamboa and Atrens^[6, 113] proposed that rock bolts should fail within hours (or at most a few days) of being loaded at a sufficiently high stress to cause SCC (i.e., the threshold stress). The specimens used by Craig were loaded before installation and were therefore exposed to SCC for the full duration of the test. The SCC cracks found by Craig had not grown to a sufficient depth to cause catastrophic failure indicating that the time required for catastrophic failure would have been even greater than the 200 plus days duration of his tests. This, in turn, indicates that the crack growth rates are orders of magnitude slower than proposed by Gamboa and Atrens, and that the SCC lifetime should be of the order of years, in keeping with the in-service data. This further suggests that the tests conducted by Gamboa and Atrens were not representative of the in-service conditions experienced by rock bolts.

It is noted that the test specimens used by Craig were 1.2 m long and contained five equally spaced pin-loaded slots so as to allow testing for SCC at different locations within the bore hole in the roof of the mine. For each of the two test specimens that showed SCC cracking, the cracking was restricted to just one of the pin loaded slots, with no evidence of cracking in the remainder^[145]. This suggests that the ground water chemistry might vary from place to place even in a single bore hole.

Craig installed HSAC 840 test specimens at the same locations as the two AISI 1355 test specimens that showed SCC cracking, but no cracks were detected in HSAC 840 specimens. This is consistent with the HSAC 840 bolts having greater resistance to SCC, as discussed early. The change to HSAC 840 was based on fracture mechanics which indicates that doubling the toughness of the bolts quadruples the depth to which an SCC crack must grow in order to produce catastrophic failure. Assuming that the crack growth rate remains unchanged, doubling the toughness should likewise quadruple the time to failure. The failure to obtain any detectable cracking in the HSAC 840 test specimens examined by Craig may simply be due to differences in local water chemistry. However, it may alternatively indicate that SCC crack initiation and/or growth is slower in HSAC 840 bolts than in AISI 1355 ones.

5.4.2.2 Testing in Mine Water

Tests were conducted in ground water from Mine B using the pin-loaded slotted coupon specimens subjected to alternate 8 hour wet and 8 hour dry cycling to accelerate corrosion. Shot peened and galvanized specimens were tested as well as standard untreated specimens. Both AISI 1355 and HSAC 840 specimens were examined.

No failures were observed in any of the specimens. The test duration of 90 days was relatively short in comparison to the SCC service life of rock bolts but, as discussed earlier, it was anticipated that detectable subcritical cracks would develop in this time. The absence of such cracks indicates that either the mine water was not conducive to SCC or that the crack initiation and subsequent growth to a detectable size was too slow.

It is noted that Craig observed SCC cracking in his in-situ specimens after 203 days which is only about twice the duration of the tests conducted here. On this basis, some evidence of cracking might be expected in the present tests. The absence of cracks may therefore indicate that the test water was not conducive to SCC.

As noted in Chapter 4, slotted coupon tests conducted by Parrott^[104] for 12 weeks (84 days) in mine water extracted near the location of failed bolts also failed to produce any evidence of SCC. This, together with the present findings, may indicate that microbacterial species, such as the sulphate reducing bacteria found in the ground water from Mine B, might be instrumental in the SCC process. This has been suggested previously by Gambao and Atrens^[6, 113] to explain their inability to produce SCC of rock bolts in their laboratory tests at pHs $> \sim 2$. Sulphate reducing bacteria usually grow in anaerobic conditions and are therefore unlikely to survive when the groundwater is removed from the mine^[131]. This could explain why failure did not occur in the extracted mine water.

As discussed above, the slotted coupon test, developed and validated in this thesis, and subsequently extended by Craig to provide multiple test sites in the one test piece, has now been validated by him in-situ in an underground coal mine. The test thus provides a simple and validated tool for evaluating the potential for rock bolt SCC at any location in an underground mine

5.5 Conclusions

1. In-situ testing was undertaken for three months in Mine B at a location where several SCC failures had occurred. Three- and four-point bent beam specimens cut from HSAC 840 rock bolts so as to retain the surface features on the tension side of the specimens were used. However, no evidence of stress corrosion cracking was observed. This is considered to be either because the test duration was too short, the applied stress was too low, or the mine water at the specific location used was not conducive to SCC.
2. Pin-loaded slotted coupon tests made from both HSAC 840 and AISI 1355 rock bolts with the surface features retained were tested in the laboratory at 21°C using an acidified sodium chloride sodium sulphide solution. The AISI 1355 specimen failed by SCC within 24 hours, validating the test procedure. The test procedure has subsequently been validated in-situ in Mine B in another part of the overall project.
3. The pin-loaded HSAC 840 slotted coupon test remained unfailed after 30 days. This suggests that HSAC 840 rock bolts are more resistant to SCC than AISI 1355 bolts, as has been confirmed subsequently by Vandermaat^[144] in another part of the overall project.
4. HSAC 840 and AISI 1355 bar-loaded slotted coupon specimens stressed to a higher level than the pin-loaded specimens were also tested in the acidified sodium chloride sodium sulphide solution. The specimens from both steels underwent SCC failure within 24 hours. However, both specimens failed from the inside of the slot, rather than from the original surface of the rock bolt, and the test was therefore considered unsuitable.
5. Pin-loaded slotted coupon tests were conducted in the laboratory using extracted mine water. The tests were conducted for both HSAC and AISI 1355 specimens under ambient conditions using alternating wetting and drying cycles. No SCC failures were observed within the 3 month test duration. This may indicate that microorganisms which did not survive when the water was removed from the mine may be involved in the in-situ SCC process.
6. Corrosion occurred more rapidly in mine water than in distilled water. This is to be expected due to the higher concentration of ionic species in the mine water.

6 CONCLUSIONS AND RECOMMENDATIONS

The work presented in this thesis is part of a broader study of stress corrosion cracking of rock bolts in underground coal mines. This part of the project has focused on understanding the environment in which failures occur and the mechanism behind failure. SCC tests which could be used in-situ in underground mines were also evaluated and validated in the laboratory.

In order to classify the environment present, an investigation into the ground water was conducted for two mines, referred to as Mines A and B, which were known to have undergone a substantial number of SCC failures. From this, it was concluded that mine water chemistry can vary significantly from place to place, however both mine waters were found to be alkaline and corrosive. The alkalinity in both mines was almost exclusively due to the presence of bicarbonate ions, with the bicarbonate levels in Mine A being substantially higher than in Mine B. Biological analysis of the water from Mine B revealed that it contained both iron- and sulphur-reducing microorganisms.

An investigation into the failure mechanism at these two mines indicated that SCC in underground coal mines can occur by two different mechanisms. In high alkalinity mine water, SCC occurs by an anodic mechanism involving carbonate/bicarbonate cracking, whereas in low alkalinity mine water, a cathodic mechanism occurs involving hydrogen induced cracking. The two different SCC mechanisms are similar to the high pH carbonate/bicarbonate SCC and the near-neutral pH hydrogen induced SCC observed in

buried pipelines. In previous work, Gamboa and Atrens have proposed that rock bolt SCC occurs by a cathodic hydrogen induced mechanism but no reports of an anodic carbonate/bicarbonate mechanism have been made previously.

Examination of the depth of the SCC cracks in failed rock bolts revealed that there was considerable variability, even amongst bolts having the same toughness, as would be expected from variability in the level of strata shear. Fracture mechanics analysis indicated that the load was generally below the yield stress of the material at the time of final overload failure. This is in contrast to estimates made based on plastic strain in failed bolts and the frequent observation of some permanent bending in the vicinity of the fracture surface of failed bolts. This may indicate that some relaxation of the elastic stress that drives SCC occurs subsequent to the plastic deformation.

A pin-loaded slotted coupon test was identified which was well suited to in-situ testing for rock bolt SCC in underground mines, while also allowing the physical and metallurgical surface features of rock bolts to be retained. The test methodology was validated in the laboratory using an acidified sodium chloride sodium sulphide solution. The test methodology has subsequently been validated in-situ in an underground coal mine by another researcher working on a different part of the broader research project and the test now provides a practical tool for evaluating the propensity for rock bolt SCC anywhere in an underground mine.

Pin-loaded slotted coupon tests were conducted in the laboratory for both HSAC 840 and AISI 1355 specimens using ground water collected from Mine B. The tests were conducted using alternating 8 hour wet/8 hour dry cycling. However, no SCC failures were observed within the 3 month test duration. This may indicate that microorganisms, which did not survive when the water was removed from the mine may be involved in the in-situ SCC process.

The following are some areas that are considered to be useful avenues for further research:

1. Additional mines

Only 2 mines were examined in detail in the present study. It is considered that extension of the work to cover a larger number of mines, including metalliferous as well as coal mines, should be undertaken.

2. Clay bands

Crosky et al.^[107] reported that there appeared to be a link between SCC of rock bolts and the presence of clay bands in the strata. It was not possible to examine this within the scope of the present study but it is considered that further work is required to properly classify the mineralogy within the bolting horizon and its links to SCC.

3. Effect of micro-organisms

This study found that the mine water contained iron- and sulphur-reducing micro-organisms. As noted above, the inability to produce SCC in extracted mine water may mean that these microorganisms are instrumental in the in-situ SCC process. It is recommended that tests be conducted in the laboratory in solutions containing these microorganisms. It is understood that the microorganisms can be grown, and will survive, under laboratory conditions if appropriate nutrients are used.

4. Mill scale

Small cracks extending into the surface of a rock bolt were seen extending from cracks in the mill scale, suggesting that the mill scale may crack under load and aid in the initiation of SCC cracks. This may be due to the stress concentration produced at the cracks in the mill scale. In addition, it has been reported that mill scale is cathodic to steel^[146] and this may then also assist in SCC nucleation. In this respect, it is of interest to note that Beavers and Harle^[10] have reported the SCC threshold stress was significantly reduced in pipeline steel by the presence of mill scale. In view of these findings, it is considered that a more detailed examination of the role of mill scale on SCC of rock bolts could be beneficial.

5. Reduction of susceptibility of rock bolts to SCC

The use of shot peening and also galvanising of the bolts were examined as part of the present study but useful results were not obtained since, while no failures were observed for the treated specimens, no failures were observed either for the untreated ones. Shot peening and galvanising have been examined further in other parts of the project and have not been found to be beneficial. A very significant area for future research would be to examine other treatments. Now that a validated in-situ SCC test has been developed, a variety of strategies could readily be examined.

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