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QUESTIONS & ANSWERS

WHERE IS THE HYDROGEN COMING FROM IN THE LOWER MARINE RISER PACKAGE IN SLIDE 10?

Hydrogen can be produced in the sea from different sources, such as the reaction of carbon dioxide with seawater. However, the hydrogen produced in this failure was attributed to Zinc coated bolting. The hydrogen is generated by the Zinc's reaction with the seawater in the water chemical breakdown.

WHAT WAS THE EXACT HARDNESS OF THE BOLTS OF THE THREE BOLT FAILURES?

For the riser connector failure, the bolts had an HRC between 35 and 39. For the LMRP failure, the hardness was also higher than HRC 35. For the BOP flange failure, the HRC varied from 28 to 44 due to segregation of Molybdenum and Nickel.

WHAT IS THE EXTERNAL PRESSURE DIFFERENCE BETWEEN THE RISER CONNECTION, THE LOWER MARINE RISER, AND THE BOP?

We are not very sure about the pressure, but we know the depth. The connector failure occurred at 3200 ft below sea level, and the LMRP and BOP failures happened at the bottom of the sea at around 6000 ft. We can get an estimated value if we consider that the pressure increases one bar every 33 ft of depth according to the National Oceanic and Atmospheric Administration.

WHERE IS THE ATMOSPHERIC PRESSURE INVOLVED IN THE DIAGRAM OF SLIDE 14?

The atmospheric pressure is part of the environment, generated by the depths of the ocean. This high pressure can facilitate the penetration of hydrogen into the steel.

IS THE MECHANISM SHOWN IN SLIDE 15 THE SAME IN PRESENCE OF SCALES OR MIC?

The mechanism in slide 15 is a broad explanation of the de-cohesion mechanism combined with the hydrogen-enhanced localized plasticity mechanism. It does not intend to describe them, it's just a graphic description of these mechanisms. Microorganisms do not generate a specific mechanism; their presence accelerates certain reactions by modifying the environment. For example, the sulfate-reducing bacteria is known for reducing the hydrogen recombination to hydrogen gas. This will increase the presence of atomic hydrogen that can lead to permeation into the steel.

DOES THE MECHANISM ON SLIDE 15 ALSO EXPLAIN LIQUID METAL EMBRITTLEMENT?

No. Liquid metal embrittlement is not an electrochemical process. It occurs when a susceptible material enters into contact with a liquid metal such as galvanized steel. The steel loses ductility and becomes brittle. This also may occur when the operation temperature is close to the melting temperature of the coating.

DO WE NEED A STRESS CONCENTRATOR TO INDUCE BREAKING AS IT IS SHOWN IN SLIDE 15?

In real life, an artificial stress concentrator is not needed to induce breaking. The breakdown can occur in cracks naturally formed inside the material. The stress concentrator in slide 15 shows an experimental sample with a higher probability of cracking.

SO YOUR VENN DIAGRAM INCLUDES HARDNESS AS THE CRITICAL MATERIAL PROPERTY. WE ARE ALSO CONCERNED ABOUT HIGH STRENGTH AS WELL, CORRECT? I REALIZE THAT THERE ARE CORRELATIONS BETWEEN UTS AND HARDNESS. I GUESS MY QUESTION IS THAT WE ARE CONCERNED BASED ON UTS, NOT JUST HARNESS?

Hardness, in this case, causes the material's susceptibility. The load (torque) that is applied to the bolts is what causes stress. In regards to the latter, we are concerned with the material's mechanical strength and keeping a constant stress when torque is applied. The depletion of sacrificial coatings causes changes in the bolt stress since some material is physically gone, leading to inconsistent performance and no two bolts being the same. Nickel-Cobalt keeps the stress constant (K factor) and allows the bolting to behave uniformly, avoiding overtorque and providing a homogeneous grip around the flange.

IN THE ASTM F519, ARE THE SAMPLES BAKED AFTER BEING COATED AS WELL AS THE BOLTS?

For the test, no. We want them to be susceptible to hydrogen during testing to evaluate whether or not our process produces it, so the samples are not baked to keep the HRC above 50.

THE THREE FAILURES JIM DESCRIBED ALL HAPPENED AROUND HOLIDAYS. DID THIS HAVE ANY EFFECT ON CAUSE OR RESPONSE TO THE FAILURES?

The failures did not occur around holidays, and holidays are not a necessary occurrence to produce hydrogen embrittlement failure. All the case studies were found in the bolting with no holidays.

HOW IS THE POTENTIAL VALUE DEFINED FOR THE SWEET SPOT?

This is the thermodynamic protection potential, or immunity potential, where iron is protected. The calculation considers iron's standard electrochemical potential (-0.44 V vs SHE), a very low concentration of iron ions in solution (10-5 M), and the Ag/AgCl (seawater) reference electrode. By using the Nernst equation and by introducing the standard electrochemical potential and the iron concentration, a potential protection value of -0.588 V vs SHE is obtained. By converting this value to the reference electrode scale (+0.266V), a value of -0.854 V vs Ag/AgCl (seawater) is obtained.

IN SLIDE 19 YOU MENTION THAT NO ELECTRONS ARE EXCHANGED, BUT HOW CAN YOU STOP THE ELECTRON FLOW IF YOU ARE APPLYING CATHODIC POLARIZATION?

The flow of electrons is not stopped. We meant to say that no electrons are involved in corrosion reactions. Electrons are still flowing from the external supply, or sacrificial anode, and they produce hydrogen, but they are not involved in corrosion reactions.

HOW IS THE Y-AXIS NORMALIZED IN SLIDE 20?

There was an initial crack in the samples and the experiment measured the crack propagation when applying a small load. The normalization was applied by comparing the crack propagation with the initial length.

IN SLIDE 22, IS NICKEL-COBALT CATHODIC TO STEEL?

Nickel-Cobalt is thermodynamically cathodic to steel. However, the kinetics of Nickel-Cobalt are so slow that they do not form a galvanic couple. In the specific case of hydrogen production, this "coupling" is not going to form hydrogen. We have performed tests where the coating is removed, exposing the steel to the environment, and we have not found any hydrogen production. Also, the corrosion rate is not different for steel.

WHAT IS THE RELATIONSHIP BETWEEN HYDROGEN EMBRITTLEMENT, STRESS CORROSION CRACKING, AND H2S CORROSION CRACKING? ARE THEY ALL CAUSED FROM THE SAME GENERATION OF HYDROGEN IONS AND HYDROGEN GAS FROM WATER THAT IS CAUSED BY SEA WATER AND H2S IN THE ENVIRONMENT AROUND STEEL BOLTS?

They are different in several aspects. Not all of them need the presence of hydrogen. The stress corrosion cracking (SCC) mechanism involves crack propagation by anodic dissolution, so hydrogen is not a requirement for having SCC. Hydrogen embrittlement and hydrogen sulfide corrosion cracking (H2S) both involve hydrogen and they are cathodic processes, but the mechanisms are different. The generation of hydrogen in hydrogen embrittlement, as we said in the webinar, is due to cathodic potential or overpotential. In H2S, the S2- acts as a poison for hydrogen recombination. Hydrogen remains uncombined, it accumulates, and penetrates into the material. To clarify, H2S corrosion cracking is also considered hydrogen embrittlement, but a clear separation in the mechanism causes it to be considered differently.

IN THE DIAGRAM OF SLIDE 24, HOW DOES THE PRESSURE AND SEAWATER MODIFY THE WATER STABILITY REGION?

Slightly. By increasing the pressure, the values of potential for hydrogen reaction drop around 60 mV every 100 bar. Chlorides expand the water stability region, but also the iron equilibrium in the different regions of the diagram. These changes do not affect the damage produced by sacrificial alloys, which are still in the hydrogen production zone.

WHEN YOU'RE TALKING ABOUT POTENTIAL AND CURRENT IN VARIOUS COATINGS, IS THIS RELATED TO THE COATING PROCESS OR WHILE IN SERVICE?

We refer to the service conditions. Either sacrificial coatings or cathodic protection produce a potential difference that is the driving force for the metal's protection. The current we measured is also related to service conditions.

THIS MECHANISM IS NOT THE SAME AS IRON CARBIDE PRECIPITATION AT GRAIN BOUNDARIES, IS IT?

This also causes embrittlement and cracking. Here they use Niobium or Titanium additives to tie up the Carbon and prevent the FeC formation. It is correct, but not the same. Hydrogen embrittlement starts electrochemically and hydrogen doesn't necessarily go to the grain boundary. Instead, hydrogen atoms are attracted to the crack tips and move along with slip planes in an almost symbiotic relationship. The presence of hydrogen induces planes to move, and this movement attracts more hydrogen atoms.

WHY DID YOU CHOOSE NICKEL-COBALT OVER TITANIUM AS THE TEST COATING METAL. WAS THIS A COST CHOICE OR THE BEST OPTION?

Looking at the chart, it seems that Titanium would be the better choice.

Titanium cannot be electrodeposited in regular aqueous baths. Its reactivity requires baths which make the plating process impractical. If there was such a possible aqueous bath process, hydrogen would be reduced before titanium and cause the titanium plating to induce more hydrogen into the base material during production, leading to embrittlement. There are other options for titanium coatings, such mechanical (cladding) or vapor deposition. However, cladding has issues with shapes and vapor deposition is elaborate and costly.

IS (1) XYLON 1052 COATING ACCEPTABLE OR A USE OF A ZINC PHOSPHATE BATH AT 200 F FOLLOWED BY A XYLAN/TEFLON COATING BAKED AT 450 F - BOLTS ARE A193 B7 NUTT A194 GR 2H A PROBLEM?

What we highlight here is that, regardless the type of Zinc coating used, it will produce hydrogen in service conditions. We did not mean to discard or recommend using any coating, but the problem we are targeting is hydrogen production and likelihood of hydrogen embrittlement. In any circumstance, Zinc coatings will produce hydrogen.

DID YOU DO ANY OF YOUR COMPARISON TESTS (SLIDE 32) ON A GRADE THAT IS RELEVANT TO THE SUBSEA INDUSTRY?

The fastener grade in F519 is very high hardness and tensile strength compared to grades such as L7. The idea of ASTM F519 is to test the material in the worst-case scenario, which is why it considers a very susceptible material and not the ones in service. If there is no damage caused by the test to the susceptible material, then the probability of having a damage in service conditions with real materials will be very low.

WAS THERE ANY POTENTIODYNAMIC OR PERMEATION TESTING DONE WITH THE NICKEL-COBALT DAMAGED AND EXPOSING BARE STEEL?

Yes, both cases. In addition, we also did galvanic coupling tests. The potentiodynamic plots showed no further corrosion activity on the exposed steel and the galvanic coupling did not induce a higher corrosion rate on the steel. In the permeation tests, we damaged 7.5% of the exposed surface and the hydrogen formed on the bare steel either did not produce . I invite you to review our whitepaper on galvanic corrosion studies, which we will post on our website son.

WE ALSO HAVE HYDROGEN EMBRITTLEMENT IN PETROLEUM REFINING. ONE SPECIFIC EXAMPLE IS IN DEETHANIZER DISTILLATION COLUMNS IN AN UNSATURATED GAS PLANT, SUCH AS IN AN FCC GAS PLANT. I WOULD HAVE TO CHECK MY FILES AS TO WHAT METALLURGICAL SAFEGUARDS ARE USED TO COMBAT THIS. I'M NOT SURE IF THESE MECHANISMS ARE THE SAME AS THE ONES HERE.

The hydrogen source is different in refineries and that may change the mechanisms. It would be very interesting to have the information about materials and chemistry of the environment in order to propose a likely mechanism.

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WHAT HAPPENS TO THE HYDROGEN PERMEATION IF THE NICKEL-COBALT PLATING IS DAMAGED?

In the permeation tests, we damaged 7.5% of the coating surface and the hydrogen formed on the bare steel did not produce a detectable current. The amount of hydrogen is not enough to reach a threshold and generate a harmful situation.

HOW SUSCEPTIBLE IS THE NICKEL-COBALT PLATING TO MECHANICAL DAMAGE?

It is not susceptible. It can be damaged, of course, but its hardness and adherence make it a tough material. One of the main characteristics shown by Nickel-Cobalt is that, when it is damaged, the damage does not grow or extend even after exposure to corrosive environments.

AT WHAT HARDNESS DOES A MATERIAL BECOME SUSCEPTIBLE?

According to different materials testing and recommendation organizations such as ASTM, API, NACE, susceptibility occurs at hardness higher than HRC 34.

ARE CERTAIN THREAD LUBRICANTS BETTER SUITED FOR USE WITH NICKEL-COBALT PLATING?

Yes, performance did improve using certain lubricants. If you go to the whitepaper section of our website, you can download our study “K-factor and Durability Evaluation of Coated Bolts” which we produced in collaboration with Jet-Lube and Whitmore. We used two types of lubricants and compared Nickel-Cobalt to other coating systems.

WHY DO YOU SHOW ONLY THE ULTIMATE STRESS IN SLIDE 34? WHAT HAPPENS WITH THE OTHER PARAMETERS?

The samples we used to test the hydrogen susceptibility caused by cathodic protection had a notch that acted as a stress concentrator. This shape allows little to no elongation of the material. The fracture occurs right after the material starts stretching and the measured parameter is the ultimate stress, or rupture stress.

WHAT STRESSES, AS A PERCENTAGE OF UTS, ARE AT RISK FOR HYDROGEN EMBRITTLEMENT FAILURES?

That is hard to know in real systems. Since bolt failure can occur through a combination of events, the stress may vary widely. The ASTM F519 standard recommends using the 75% of the ultimate tensile strength (UTS) for testing in a controlled system.

HOW EFFECTIVE IS THE NICKEL-COBALT PLATING AS A PROTECTIVE COATING WITHOUT CATHODIC PROTECTION, E.G. TOPSIDE APPLICATIONS? SINCE IT IS NOT SACRIFICIAL, DOES IT PROTECT?

Nickel-Cobalt is extremely effective in topside applications, even without cathodic protection. The fasteners we electroplate with Nickel-Cobalt have an estimated 21 years of life expectancy, and we have a warranty that guarantees five years with no seizing issues. As far as we’re concerned, Nickel-Cobalt offers the best protection for the base metal.

ARE YOU RECOMMENDING THAT DOXSTEEL ALLOWS THE USE OF A HIGH STRENGTH MATERIAL WITH KNOWN SUSCEPTIBILITY? FOR EXAMPLE, WOULD NICKEL-COBALT PLATING ALLOW THE SAFE USE OF 4140 WITH HRC 45?
In critical bolting environments, it is best to have multiple layers of protection. Anything can happen in real world applications, so it is our mission to account for as many variables as possible. One of the ways we do this is by complying with API 20E specifications, which recommend that fasteners do not exceed HRC 34. However, to make sure that our coating and processes will stand up to adverse conditions, we perform hydrogen embrittlement tests such as ASTM F519 intentionally using fasteners with higher HRC values. This allows us to test the performance and resiliency of the coating, to make sure that our process does not produce hydrogen, and to make sure that our coating will continue to act as a barrier to hydrogen in the field. Nickel-Cobalt will protect harder materials from hydrogen, but the best recommendation is to use fasteners with a hardness that does not exceed HRC 34. With multiple layers of protection, you can considerably reduce the risk of bolt failure.

WHAT ABOUT MAKE AND BREAK CONNECTIONS THAT MAY REMOVE THE COATING? HOW TENACIOUS IS THE COATING?
Nickel-Cobalt is a tough alloy. It can be damaged, but its hardness and adherence make it difficult. Once the coating is damaged, however, the damage does not extend or grow. Even after exposure to highly corrosive environments, the damage does not grow.

WHAT IS THE COMPARATIVE EFFECTIVENESS OF NICKEL-COBALT VS. HOT DIP GALVANIZED (HDG) ZINC ON THE GENERAL GALVANIC CORROSION?
Nickel-Cobalt and Hot Dip Galvanized (HDG) Zinc behave differently in terms of galvanic corrosion, so it is hard to measure them with the same ruler. When using HDG, its galvanic coupling with steel is the most important issue, as this process produces hydrogen and leaves the steel at risk of hydrogen embrittlement. With Nickel-Cobalt, the galvanic coupling does not occur, so it will not produce hydrogen while acting as a barrier to corrosion and hydrogen from the environment.

THE EFFECT OF CATHODIC PROTECTION ON RESISTANCE APPEARS TO BE VERY DRAMATIC. IS THERE ANY BACKGROUND/SUPPORTING DOCUMENTATION ON THIS?
There are several publications showing the effect of polarizing cathodically to form hydrogen and its effect on mechanical properties and crack propagation. It is common practice to study crack propagation and embrittlement at different cathodic potentials. However, the direct relationship between cathodic protection by sacrificial coatings or impressed current and mechanical properties is not that common. The reason for this is that cathodic protection has not been considered the direct cause of hydrogen embrittlement, but the source of hydrogen that leads to this phenomenon.

SINCE THE NICKEL-COBALT PLATING IS CATHODIC TO STEEL, WHAT HAPPENS TO THE STEEL AT THE LOCATION OF DAMAGE TO THE PLATING OR TO LOCATIONS (E.G. THREAD ROOTS) WHERE THE PLATING MAY NOT BE PERFECT? DOESN'T THE STEEL BECOME ANODIC TO THE PLATING, AND WITH AN UNFAVORABLE SURFACE AREA RATIO

LEADING TO RAPID DISSOLUTION/PITTING AT THE LOCATION OF THE HOLIDAY?

The steel does not suffer further corrosion other than the exposure to the environment. The Nickel-Cobalt is rather inactive to corrosion on steel. The surface ratio of Nickel-Cobalt to steel is not indicative of the extent of corrosion and it does not show any big cathode/small anode effect, so it does not form localized corrosion. The damage extends neither around the holiday nor underneath the coating around the holiday. We have tested non-perfect studs with seawater and we have not found an indication of higher corrosion on steel caused by the Nickel-Cobalt plating.

HAVE YOU APPLIED THIS MATERIAL TO ITEMS OTHER THAN FASTENERS, SUCH AS SEALING MANDRELS, ETC.?

Yes. When we discovered Nickel-Cobalt, it was being used by NASA and the military as a coating with many applications. Although our production is for fasteners, we have done special plating on other materials and applications with outstanding results. However, we are focused on producing the best fastener for the market.

ARE HYDROGEN EMBRITTLEMENT FAILURES SEEN IN COATED PRESSURE VESSELS IN NON-MARINE ENVIRONMENTS?

There are documented cases of failure by hydrogen in pressure vessels and pipelines, but they are not limited or specific to hydrogen embrittlement. They may be hydrogen-induced cracking or other types of hydrogen-related failure. The source of hydrogen for these cases can also be, but are not limited to, cathodic overprotection. The mechanisms vary depending on the environment.

HOW FAR CAN IMPRESSED CURRENT FROM THE SHIP TRAVEL DOWN THE RISER LINE?

Cathodic protection can be applied by either sacrificial anodes or impressed current to the whole riser. When using impressed current, the signal extent will depend on the direct current source, but in either case the signal range will depend on the anodic distribution. Anodic distribution is quite important. Since homogeneous protection is required, the marine environment and scales interfere with this cathodic protection, creating unprotected areas or the opposite, overprotection.

HAVE YOU MEASURED THE HARDNESS OF FAILED COMPONENTS AFTER HYDROGEN EMBRITTLEMENT?

There are different methodologies depending on the size and shape of the material and the relevant information regarding the case of hydrogen embrittlement. Usually, Rockwell Hardness is measured to obtain an overall knowledge of material's hardness. However, other types of hardness such as microhardness and Vickers are used to identify banding, segregation, or the effect of specific phases in the steel.

YOU MENTIONED SOFT AND HARD PHASES IN THE BOLTS. HOW DO WE CONTROL THIS? IS IT IMPROPER HEAT TREATMENT PRACTICE?

An improper heat treatment may cause phase segregation or banding in the microstructure which can lead to the creation of weak areas more susceptible to hydrogen induction. By following the API 20E specifications, we make sure that every single bolt comes with the proper heat treatment before and after plating to create extra layers of protection.

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DO I UNDERSTAND THAT HIGHER ATMOSPHERIC PRESSURE ACTUALLY DRIVES THE HYDROGEN INTO THE STEEL BOLT?

Yes. The atmospheric pressure pushes the hydrogen inside the steel. The pressure itself does not produce more hydrogen, but it complicates the chemical hydrogen recombination and forces the hydrogen into the material. This is why an effective coating that does not produce hydrogen and acts as a barrier to environmental hydrogen is so critical.

COULD SUCH COATING BE APPLICABLE IN SOUR SERVICE APPLICATIONS AS PER NACE 103?

NACE 103, Section 16 for bolting does mention that Zinc/Cadmium coatings should not be used due to hydrogen production enhancement, but it also mentions that metallic coatings are not allowed for prevention of sulfide stress corrosion cracking. We believe in Nickel-Cobalt plating for these applications, and one of our goals is to have Nickel-Cobalt included in the permitted plated coatings for H2S-SCC. Our preliminary results show outstanding performance in this environment. We have not found any drawback so far, but we will continue to conduct research in this extremely important subject.

DOES MAXIMUM HARDNESS LIMITED TO HRC 34 SOLVE ALL PROBLEMS?

It can considerably reduce the risk, but it is not the only factor that contributes to hydrogen embrittlement. Preventing hydrogen from being induced in production and using a non-sacrificial coating that acts as a barrier to hydrogen in the field also have a major impact on reducing risk. If you can remove the hydrogen, you can eliminate the risk of hydrogen embrittlement.

WHAT ARE THE LIMITS ON HARDNESS ON HIGH STRENGTH BOLTS ABOVE WATER?

According to ASTM A193 and ASTM A320, the maximum hardness for bolting of high temperature, high pressure services and other special applications should not exceed HRC 35.

CAN YOU SHARE THIS PRESENTATION SO I CAN SHARE FURTHER WITHIN MY OFFICE?
CAN WE GET A COPY OF THE SLIDES BY EMAIL, OR CAN WE DOWNLOAD THEM FROM YOUR WEBSITE?

The webinar is available on our website: **doxteel.com**.

DO YOU ISSUE PDH CERTIFICATES FOR P.E. CONTINUING EDUCATION FOR THIS WEBINAR?

Unfortunately, no. Our intention with our webinar series is to expand the knowledge of the industry and to improve communication and knowledge sharing between verticals on a variety of topics. In addition, we want to make sure those in the office are connected to those in the field. We will make sure to send out an email to register for our next webinar when it comes closer, and we'll also post that update on our website and in our social media channels. We encourage you to join our LinkedIn group, The Cost of Bolt Failure, where we hold ongoing discussions about how fasteners can help companies save time, money and lives. We also host Lunch and Learn's, so if you are interested in bringing in your teams to our offices to talk more on these subjects, please feel free to reach out via our website, **doxsteel.com**, and follow our company page on LinkedIn.

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