2.2 LABORATORY STUDIES OF THE CORROSION AND MECHANICAL PROPERTIES OF TITANIUM GRADE-12 UNDER WIPP REPOSITORY CONDITIONS

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I intend to review some of the laboratory work that has been performed at the Sandia Laboratories. We have done very little in the laboratory over the last few years, our activities being mainly in support of the in situ program. Most of the work we have done has been performed in brine close in composition to that observed at the WIPP site.

There are a number of areas I would like to review. The first one is the effect of gamma radiation. There are two aspects we have investigated: (i) the effect of gamma radiation on corrosion and mechanical properties; and (ii) the extent of hydrogen uptake in the presence of gamma irradiation. Figure 1 shows the effect of gamma radiation on general

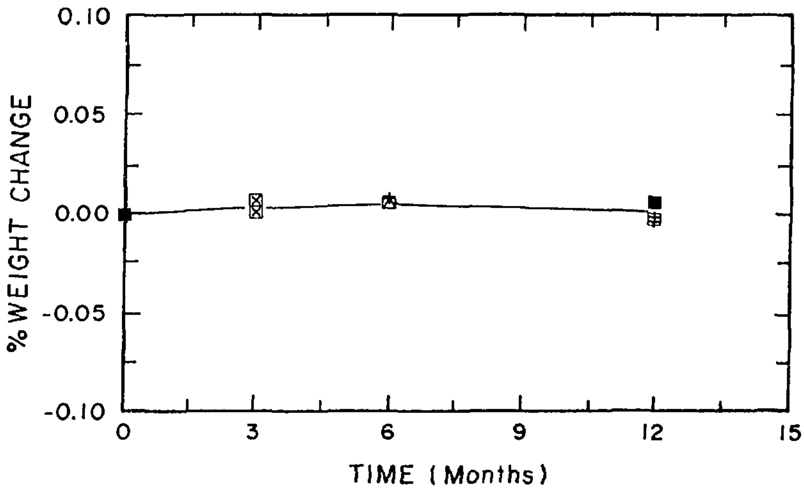


FIGURE 1: Impact of γ Irradiation (10^4 rad•h^{-1}) on the General Corrosion of Titanium Grade-12 in a Brine Solution at 90°C

corrosion, expressed as a weight change, for an exposure period of up to one year. As you can see, there is no real effect of irradiation on general corrosion. If we look at the Charpy impact energy, we see a very slight decrease in mechanical properties with exposure time, Figure 2. This decrease is probably within experimental error. We see a similar lack of effect of radiation if we measure the tensile properties using the slow strain rate technique, Figure 3. If you look at the total elongation, the uniform elongation, and the reduction in area, you see that, again, gamma radiation really does not change the mechanical properties significantly. All these results were obtained in a radiation field of 10^4 rad•h^{-1} at 90°C.

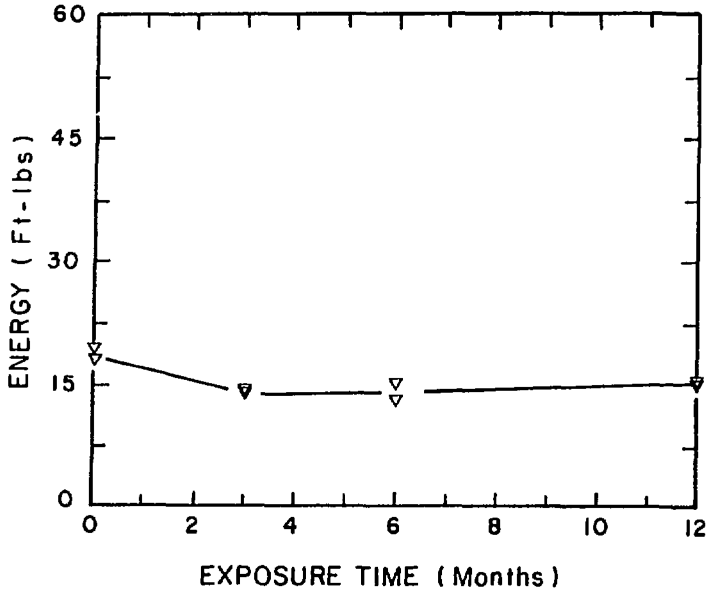


FIGURE 2: Charpy Impact Energy of Titanium Grade-12 as a Function of Exposure Time to Brine at 90°C in the Presence of a γ-Radiation Field of 10^4 rad•h^{-1}

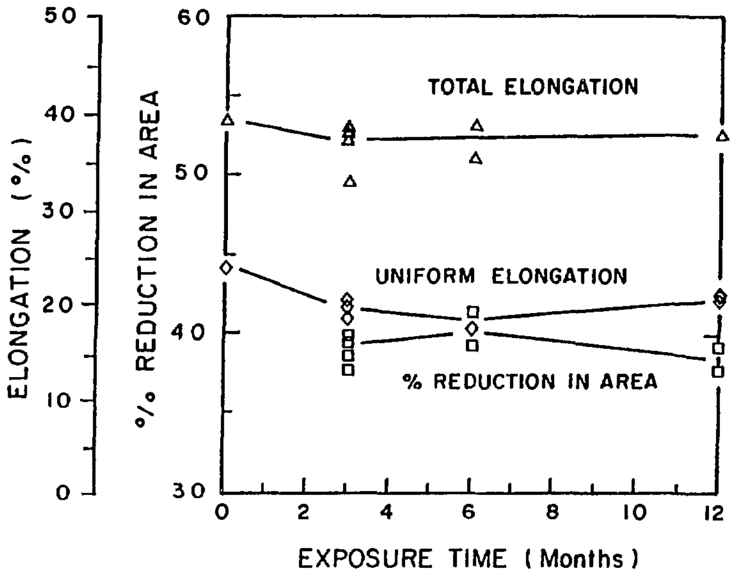


FIGURE 3: Tensile Properties of Titanium Grade-12 in γ-Irradiated Brine Solutions (90°C, 10^4 rad•h^{-1}) Obtained by the Slow Strain Rate Technique

INTERRANTE There is a significant change. Are you saying that these changes are insignificant when considering the use of this material in the construction of a waste container?

SORENSON That is correct. However, if you look at the scatter in the data, it's not even clear that there is any statistically significant change in the mechanical properties. Also, we can see no structural changes induced by gamma irradiation when we examine the samples by SEM or TEM. We have seen no evidence of crevice corrosion or stress corrosion cracking (U-bend samples) for either irradiated or unirradiated specimens. This is in contrast to the published results of Westerman (PNL/SRP-SA-14323). His experiments were, however, performed at a higher temperature (150°C). In the absence of irradiation, our tests on titanium Grade-12 at 250°C have shown no evidence of crevice corrosion after 5 years of exposure. A significant difference between our tests and those of Westerman is in the type of crevice used. He used an alumina crevice spacer, whereas we used metal-to-metal crevices and metal-to-Teflon crevices. Whether such differences can account for the observed differences in behaviour is not clear.

SHOESMITH What is your criterion for saying that you don't have crevice corrosion? Is it based on a visual examination?

SORENSEN Yes. We look at the sample to see if there is any evidence of crevice corrosion. With Grade-2 titanium we see crevice corrosion in several areas. With Grade-12, all we have seen is a thickening of the oxide within the crevice. We infer this from the interference colours we see.

SHOESMITH Is the crevice wet before you start?

SORENSEN Yes, it is.

Oriani and co-workers at the University of Minnesota have studied the effect of irradiation on hydrogen uptake (Y.J. Kim and R.A. Oriani, Corrosion 43(2), 85-92 (1987)). They observed, Figure 4, that the hydrogen concentration in the material increased with exposure time irrespective of whether gamma radiation was present. Radiation actually reduces the extent of hydrogen uptake. If we look at the open circuit potential of Grade-12 titanium both with and without radiation, Figure 5, we see that the potential is increased in the presence of radiation. This can be attributed to the presence of radiolytically produced oxidizing species in the solution. Figure 6 shows the X-ray diffraction patterns observed on titanium Grade-12 samples after immersion in brine with and without gamma irradiation. With gamma radiation present, we see an increase in the anatase (A) to rutile (R) ratio. The reduction in the amount of hydrogen uptake, Figure 4, can therefore be attributed to the formation of the more protective anatase film.

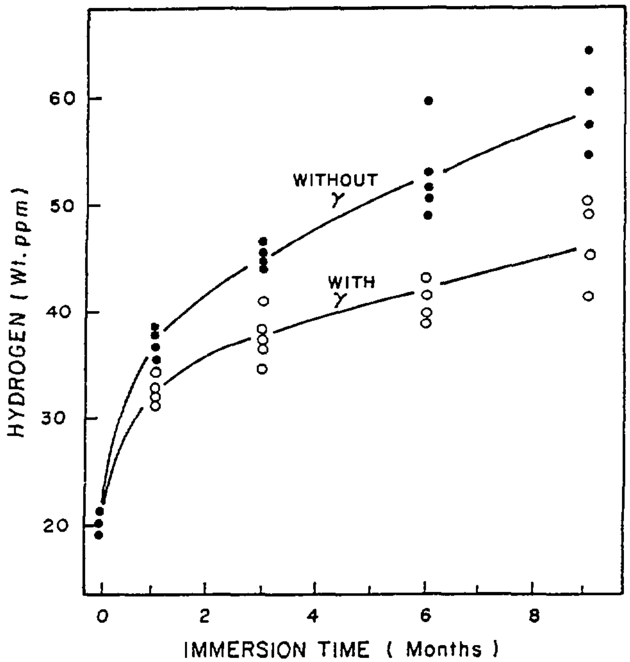


FIGURE 4: Hydrogen Content of As-Received Titanium Grade-12 as a Function of Immersion Time in Unirradiated and Irradiated (~ 10^5 rad•h^{-1}) Brine (pH = 6.5 to 6.8) at 250°C

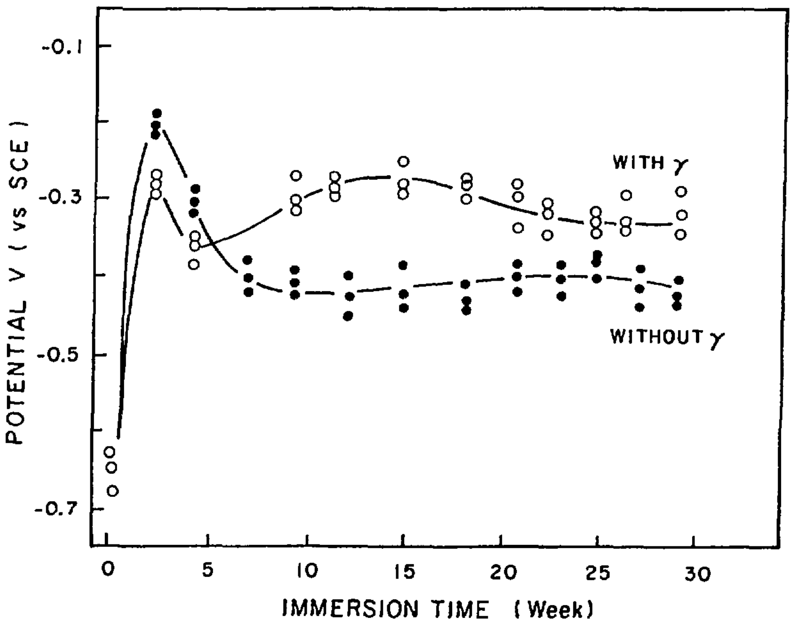


FIGURE 5: Open-Circuit Potential of As-Received Titanium Grade-12 as a Function of Immersion Time in Unirradiated and Irradiated (~ 10^5 rad•h^{-1}) Brine (pH = 6.5 to 6.8) at 108°C

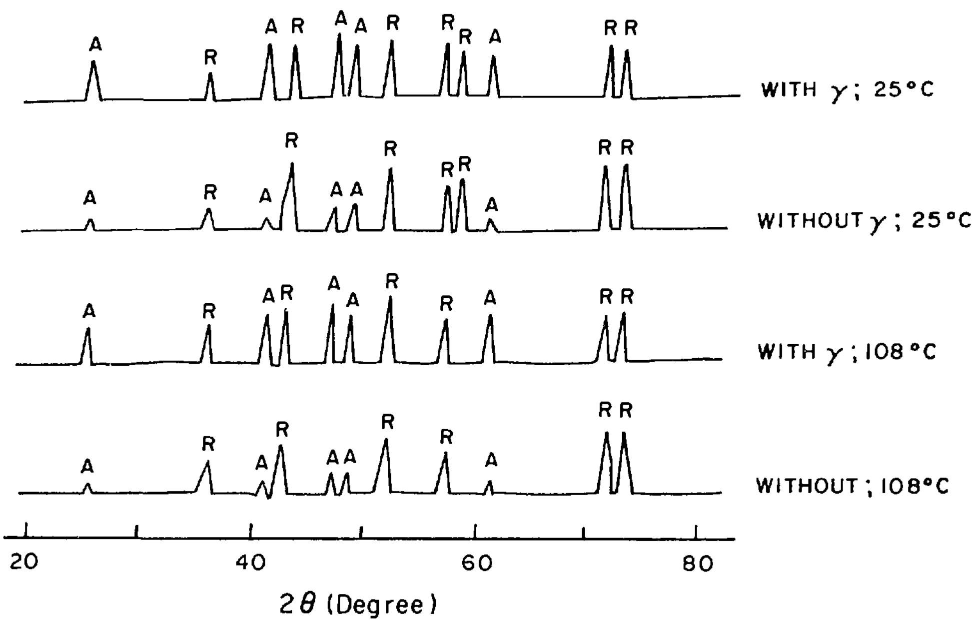


FIGURE 6: X-Ray Diffraction Patterns Observed on Titanium Grade-12 Samples After Immersion in Brine With (10^5 rad•h^{-1}) and Without γ Irradiation. R represents the rutile and A the anatase form of titanium oxide.

IKEDA Were these tests done under naturally aerated conditions?

SORENSEN I don't remember.

Oriani and co-workers also showed that the addition of H_2O_2 to their solutions had the same effect as the presence of radiation.

INTERRANTE When you rely on the presence of an oxide film to prevent hydrogen uptake, the prediction of long-term behaviour will be very difficult.

SORENSEN Yes, it will be very difficult to predict the failure mode for a corrosion-resistant material. That is the argument used by those who favour the use of a corrosion allowance material. It also depends on the type of localized attack your material will support, pitting, crevice corrosion, or stress corrosion cracking. If we look just at pitting, there are two important aspects: pit initiation and pit propagation. Pit propagation can be modeled but pit initiation is very difficult to model. Consequently, if we adopt a corrosion-resistant material, we will have to concede that we cannot model the failure process. However, we can still understand the mechanisms by which it may fail, measure their rate, and hence predict a lifetime for a container.

SHOESMITH We think we have a criterion for crevice corrosion. In our experiments we force initiation of crevice corrosion to occur, and then demonstrate that it cannot propagate under certain circumstances. For this to be the case the system must be naturally repassivating.

SORENSEN Even those experiments will not enable us to predict when our container will fail.

Since titanium is a known hydride former, the second area that I'd like to address is environmental cracking by processes such as stress corrosion cracking or hydrogen embrittlement. Figure 7 shows that anodic

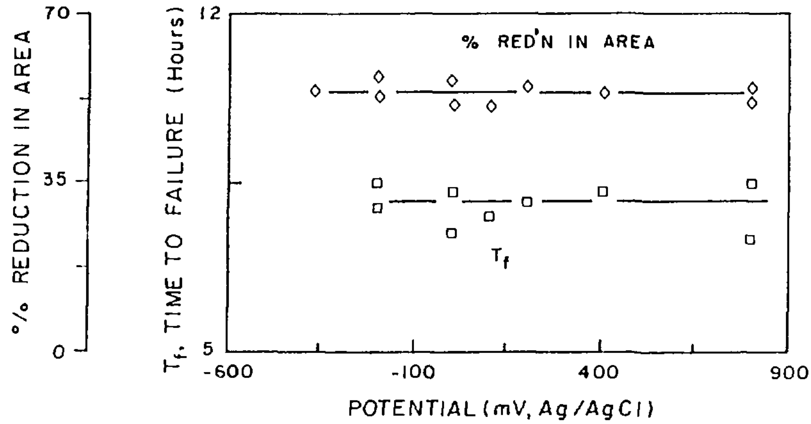


FIGURE 7: Impact of Anodic Polarization on the Mechanical Properties of Titanium Grade-12 as Determined from Slow Strain Rate Experiments; Brine A at 150°C; Strain Rate of 10^{-7} in•s^{-1}

polarization does not affect the mechanical properties as determined by slow strain rate experiments. Both the time to failure (T_f) and the percent reduction in area (% RA) are independent of the applied potential. Figure 8 compares the fracture surfaces obtained in air with those obtained in brine solutions with applied anodic potentials. There are no observable differences in fracture mode. Consequently, stress corrosion cracking is unlikely to occur. On the other hand, if we cathodically polarize the sample to a high enough overpotential in a slow strain rate test, we see a decrease in both the time to failure and the percent reduction in area, Figure 9.

The fracture surfaces shown in Figure 10 show that extensive cathodic polarization induces brittle fracture. Also, secondary cracking is observed along the gauge length and on the fracture surface.

SHOESMITH Have you measured a threshold potential for embrittlement?

SORENSEN No. The threshold potential is very dependent on the strain rate used.

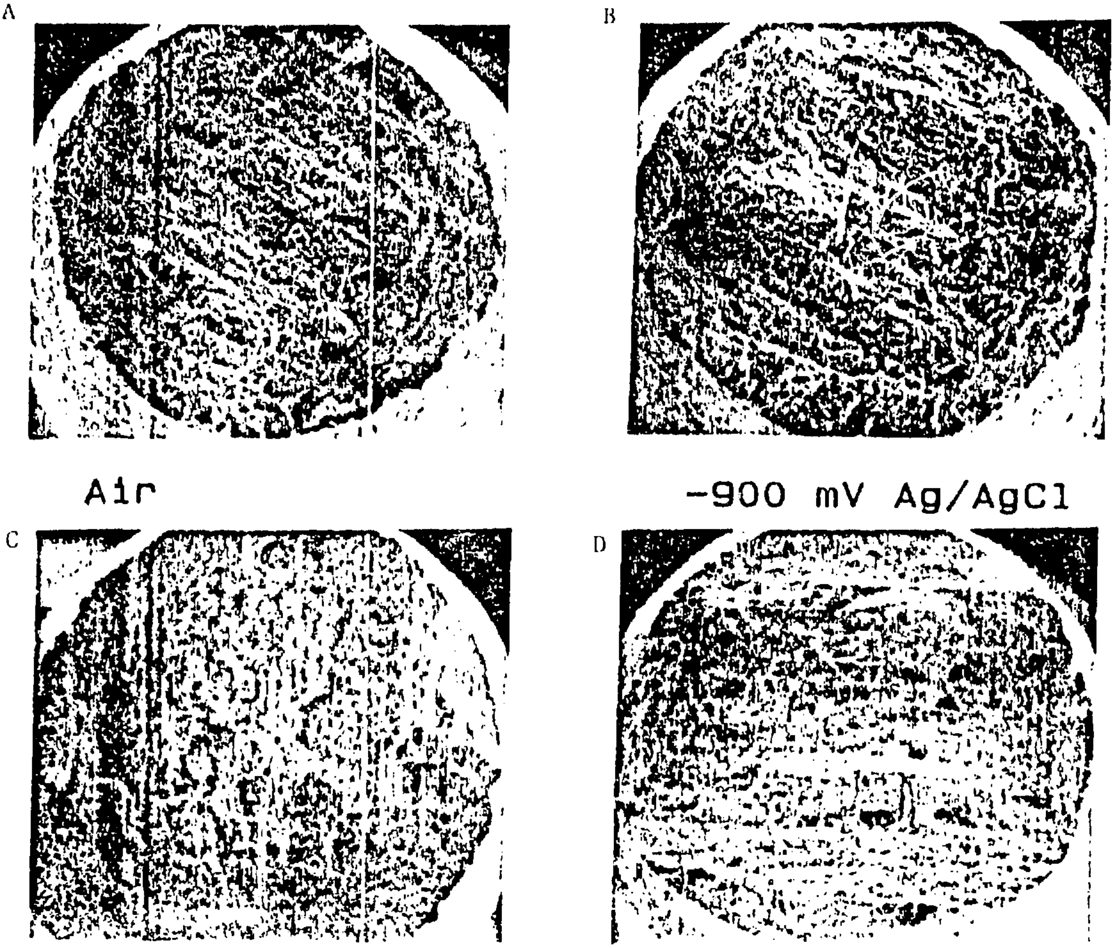


FIGURE 8: Fracture Surface Obtained in Air (A) Compared to Those Obtained Under Anodic Polarization in Brine A at 150°C; (B) -900 mV (vs Ag/AgCl); (C) 800 mV; (D) 0 mV

We have looked at the effect of hydrogen on the microstructure of Grade-12 titanium and we see an interesting change in microstructure with the addition of hydrogen, Figure 11. Hydrogen goes mainly into the beta phase, Grade-12 titanium being an alpha-beta alloy. The impurities are contained almost entirely in the beta phase, shown as the dark phase in these micrographs. With the addition of hydrogen we see a change in microstructure from the equilibrium-type microstructure to a microstructure where we have alternating layers of alpha and beta phase. The beta phase is actually transformed on the addition of hydrogen. Associated with this change in microstructure we see a slight decrease in mechanical properties with the addition of hydrogen. The extent of this effect depends somewhat on the alloy chemistry. We have measured the change in mechanical

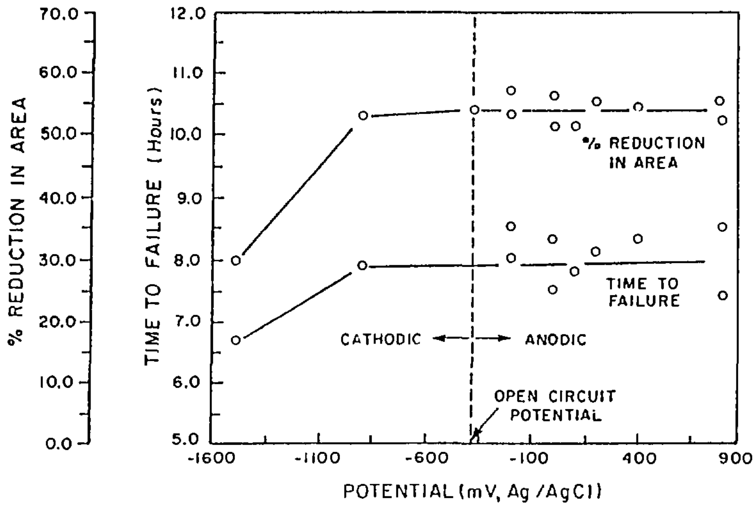


FIGURE 9: The Effect of Applied Cathodic Potentials on the Tensile Properties of titanium Grade-12 in Brine A at 150°C Obtained by the Slow Strain Rate Technique

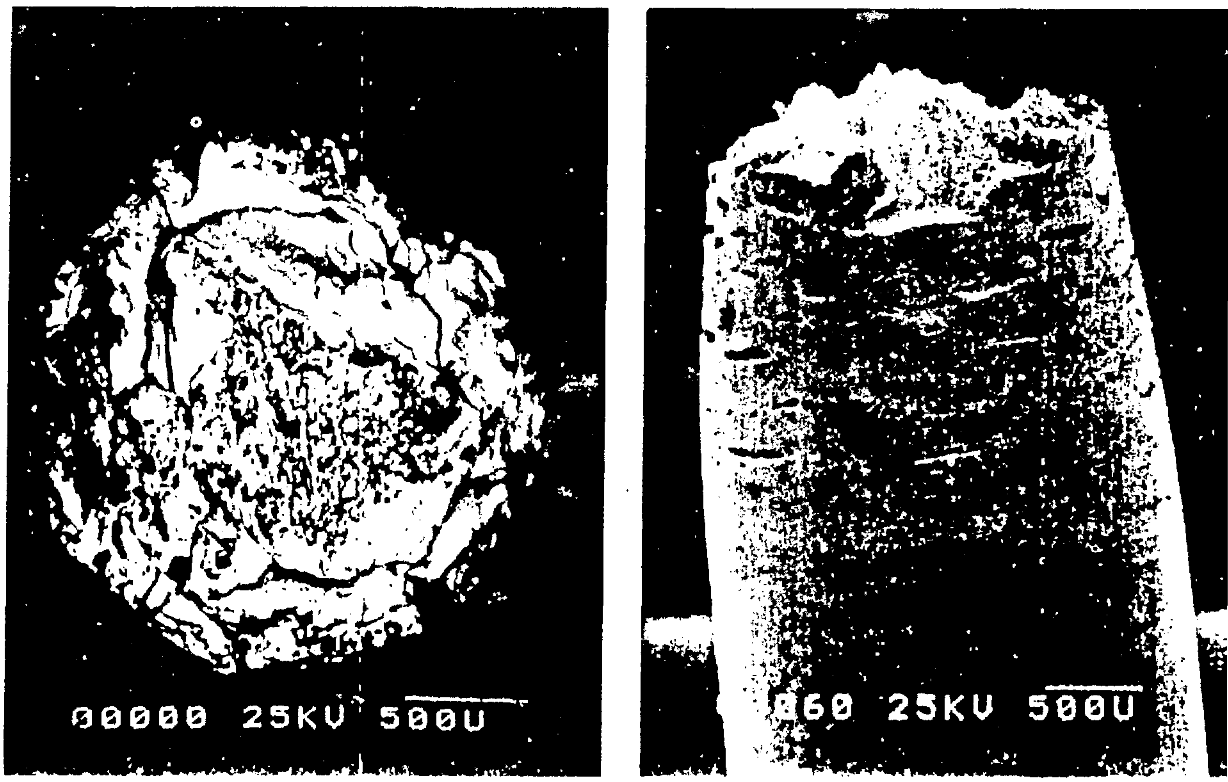


FIGURE 10: Fracture Surfaces of a titanium Grade-12 Specimen Strained to Failure at a Cathodic Potential of -1500 mV (vs Ag/AgCl) in Brine A at 150°C

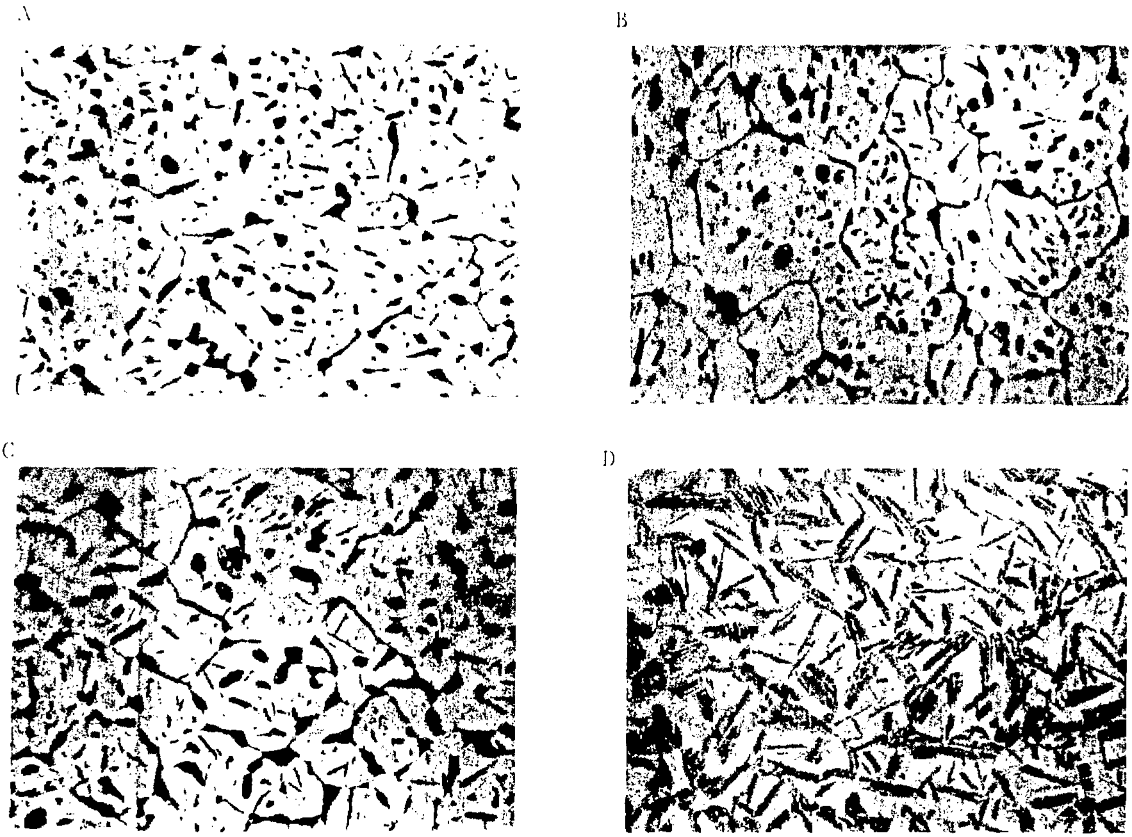


FIGURE 11: The Effect of Hydrogen Content on the Microstructure of Titanium Grade-12: (A) 140 ppm H; (B) 225 ppm; (C) 445 ppm; (D) 975 ppm

properties for about 10 different compositions of Grade-12 titanium, and some are more susceptible to mechanical degradation than others. Figure 12 shows the time to failure for titanium Grade-12 (heat 5980), the readily available material. The change in mechanical properties is evident at all temperatures, from 25°C up to 150°C and there appears to be no effect of environment, i.e., it doesn't matter whether the tests are run in brine or in air. For this particular alloy, very little change in mechanical properties is observed for hydrogen contents up to ~ 500 ppm. At higher hydrogen levels, up to 975 ppm in this case, we observe only a small change in mechanical properties, Figure 12. This decrease in time to failure appears to be associated with the observed change in microstructure to the transformed beta phase, Figure 11. It would be interesting to see what effect hydrogen has on the Grade-2 titanium, since that is an alpha alloy.

As we can see from Figure 13, the hydrogen does not change the deformation characteristics, only the fracture mode, i.e., the early part of this curve shows no effect of hydrogen. However, once deformation starts, failure occurs as opposed to continuing deformation. Note, this effect is only

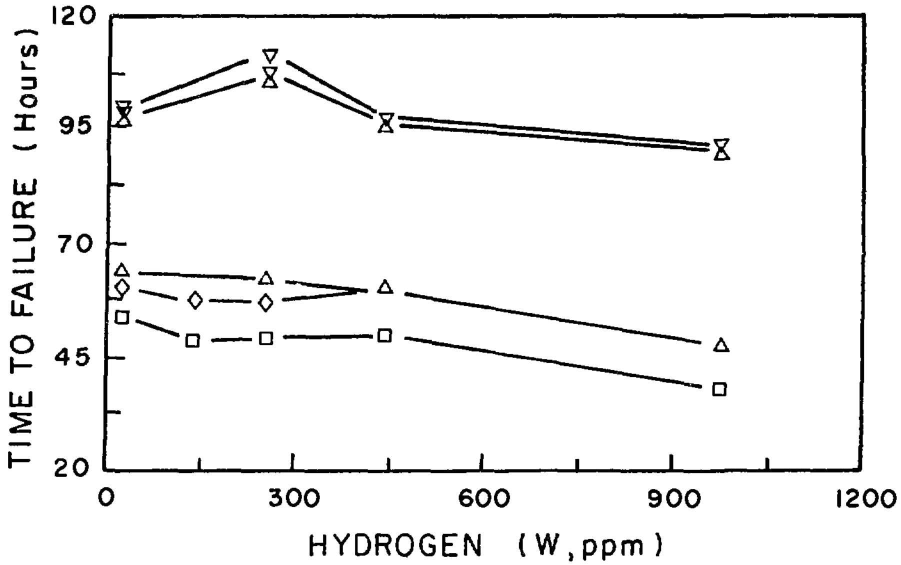


FIGURE 12: Time to Failure of Titanium Grade-12 (Heat 5980) Under Slow Strain Rate Conditions in Air and Brine at Various Temperatures; Air, 25°C; < Air, 85°C; Δ Brine, 85°C; X Air, 150°C; ∇ Brine, 150°C

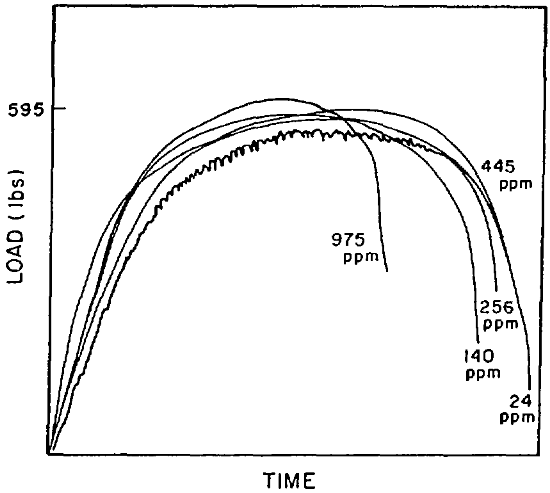


FIGURE 13: Slow Strain Rate Curves for Titanium Grade-12 Containing Various Amounts of Hydrogen in Air at 25°C and a Strain Rate of 10^{-7} in•s^{-1}

observed at hydrogen levels > 500 ppm. Figure 14 shows the reduction in area (from slow strain rate experiments) as a function of hydrogen content for a series of different Ti-Grade-12 heats. The hydrogen levels were achieved using gas phase charging at the Sandia Laboratories. We see the same type of behaviour as before. When we increase the hydrogen concentration, we observe a decrease in the reduction in area. This happens regardless of the alloy. Although different alloys have different strengths to begin with, all of them behave in a similar fashion.

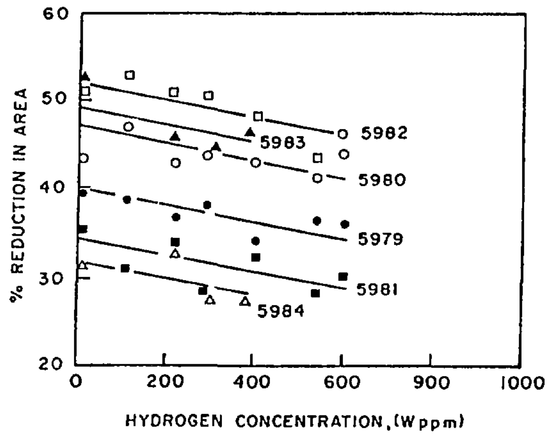


FIGURE 14: Reduction in Area (from Slow Strain Rate Experiments) for Different Titanium Grade-12 Heats (5979 to 5984) Containing Various Amounts of Hydrogen

In Figure 15, the time to failure as a function of hydrogen content is shown for two Grade-12 materials, one high in alloying additions and one low. The high iron/nickel/molybdenum alloy (0.4% Fe, 0.9% Ni, 0.4% Mo, 0.25% O) is more susceptible to hydrogen, i.e., we observe a decrease in

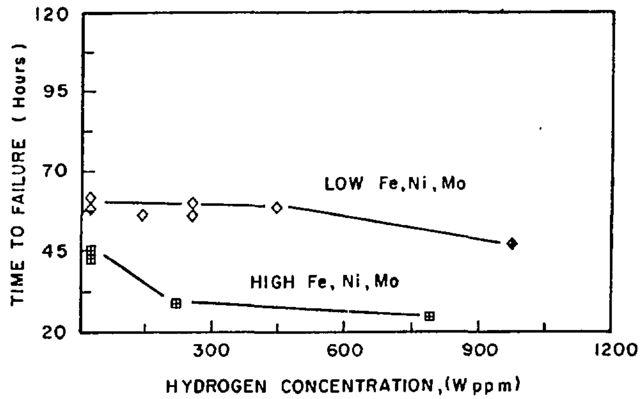


FIGURE 15: Time to Failure (From Slow Strain Rate Experiments) for Two Titanium Grade-12 Specimens in Air and Brine at 85°C as a Function of Hydrogen Concentration; Strain Rate 10^{-7} in•s^{-1}

mechanical properties at a lower hydrogen concentration than we do with a cleaner alloy containing less iron/nickel/molybdenum (0.05% Fe, 0.6% Ni, 0.2% Mo, 0.1% O). The time to failure is also sensitive to sample orientation, Figure 16. The material appears to be more susceptible to cracking in the transverse mode. The fracture surfaces of Figure 17 show evidence of secondary cracking with the transverse section but not with the longitudinal section.

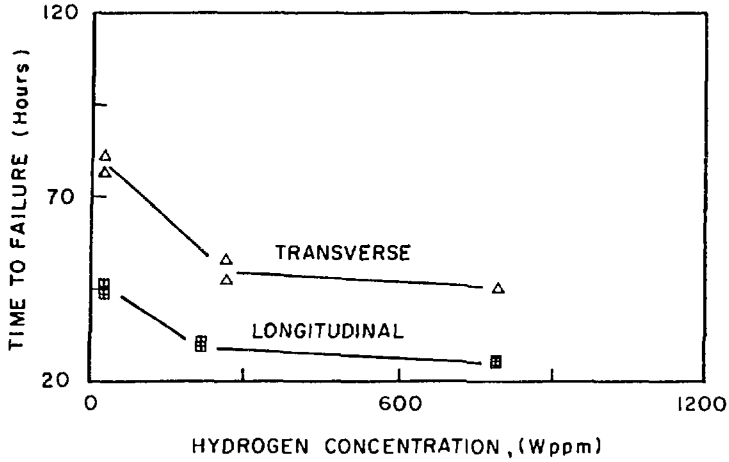
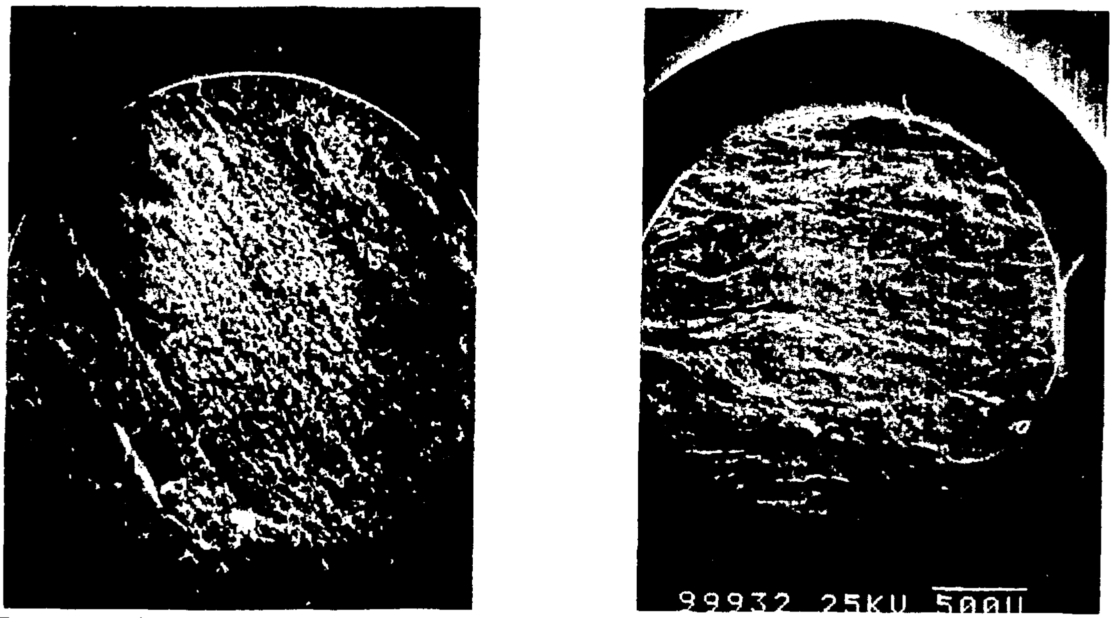


FIGURE 16: Time to Failure for Two Sample Orientations of Titanium Grade-12 as a Function of Hydrogen Content in Air and Brine at 85°C; Strain Rate = 10^{-7} in•s^{-1}

A sensitizing heat treatment has very little effect on the mechanical properties, Figure 18. We have also studied the effect of welding on mechanical properties. We observe no degradation in mechanical properties for either TIG- or EB-welded samples when tested in air and in brine,, Figure 19.

Transverse Sample | Longitudinal Sample



Severe Secondary Cracking | No Secondary Cracking

FIGURE 17: Fracture Surfaces for Two Orientations of Titanium Grade-12 Strained to Failure under the Conditions Noted in the Legend to Figure 16

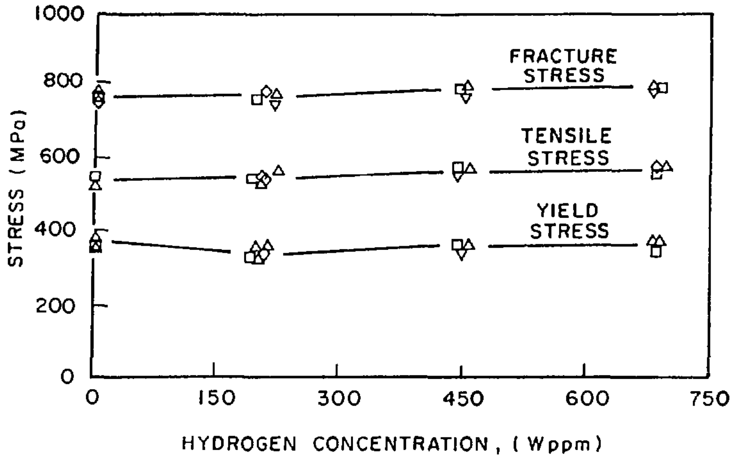


FIGURE 18: The Effect of Sensitizing Heat Treatments on the Mechanical Properties of Titanium Grade-12 as a Function of Hydrogen Content; □ - 675°C for 0.5 h; <> - 675°C for 4 h; Δ - 675°C for 32 h

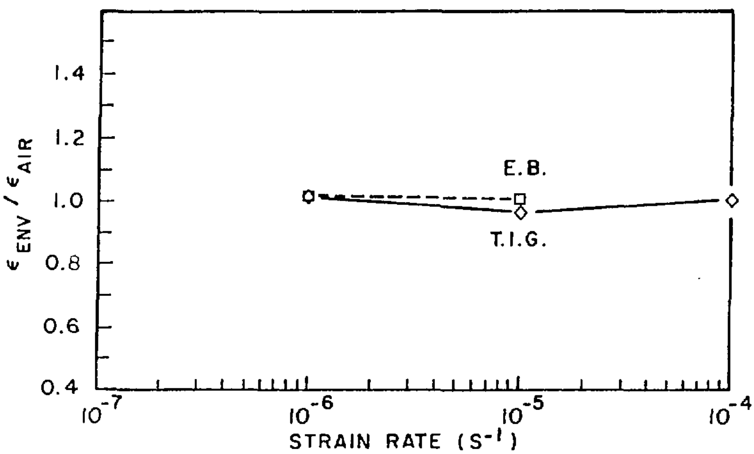


FIGURE 19: The Effect of TIG and EB Welding on the Ratio of Mechanical Properties for Titanium Grade-12 as a Function of Strain Rate in Brine Compared to Air

Since there are documented cases of pitting of titanium Grade-2 due to smeared iron contamination, we have looked for a similar effect with Grade-12. We have observed no degradation in either corrosion or mechanical properties due to the presence of smeared iron.

SUMMARY

(1) The Effects of Irradiation

(a) Absorption of hydrogen continues with increasing exposure times.

(b) The presence of radiation retards the uptake of hydrogen.

(c) Radiation increases the corrosion potential.

(d) The oxidizing species formed by the radiolytic decomposition of water lead to the formation of a more protective film. This film contains a larger proportion of anatase (compared to rutile) than that formed in the absence of radiation.

(2) The Effects of Hydrogen Absorption

(a) Hydrogen absorption at levels > 500 ppm causes a change in microstructure in titanium Grade-12. This change is from the equilibrium microstructure to a microstructure with alternating layers of alpha and beta phase.

(b) Severe cathodic polarization causes embrittlement.

(c) High internal concentrations of hydrogen (> 500 ppm) cause a small loss in ductility.

(d) Titanium-12 is more susceptible to cracking in the transverse, as opposed to longitudinal, mode.

(e) High levels of Ni, Mo, Fe increase the susceptibility to cracking as the amount of absorbed hydrogen increases.

(f) All alloys exhibit good resistance to cracking.

(g) No susceptibility to stress corrosion cracking has been observed.

CONCLUSIONS

Our results indicate that titanium Grade-12 is a viable canister material. We only observe a degradation in mechanical properties with high applied cathodic currents or very high internal hydrogen concentrations (i.e., 975 ppm). I should add that it is not easy to force nearly 1000 ppm into this material. A series of four charging and annealing cycles was required. Without this repetitive annealing we would simply build up a layer of hydride on the surface of the material.

GARISTO It isn't clear to me why you use a radiation field of 10^4 rad•h^{-1}. Since we have to extrapolate from short-term data to make long-term predictions, would it not be better to use a much higher radiation field to increase the total dose absorbed by the system. We could then claim that this was equivalent to a smaller dose accumulated over a much longer exposure period.

MOLECKE Unfortunately, we don't expect the corrosion rate to be a linear function of radiation dose rate. The kind of species produced, as well as their concentration, will vary with dose rate.

STAHL Someone questioned whether it was important to differentiate between air-saturated and deaerated solutions. It will be important because different radiolytic species will be produced in the two situations.

BREHM At fields as high as 10^7 rad•h^{-1}, would you not affect the morphology and electronic properties of the oxide? Will the film be adherent and protective under these conditions?

INTERRANTE Your results show that hydrogen uptake only influences the mechanical properties of Ti Grade-12 at high levels. You claim that such levels would require very long exposure times. At such long times, would you not expect the hydride already present to slow down the rate of the adsorption process? If this is so, are you able to predict a limiting value for the hydrogen uptake?

SORENSEN I don't think that is the case. There is no evidence to suggest that the presence of a hydride layer prevents further ingress of hydrogen. In our charging experiments, we used high charging current densities. Under these conditions, we did form a surface layer of hydride. At lower charging rates, the hydrogen has time to diffuse into the titanium and you do not observe a surface layer of hydride. In Oriani's work, for example, there were no indications that hydride was present. He obtained levels of 60 ppm after two years of exposure to radiation. His data are probably the most realistic in terms of hydrogen uptake. Hydrogen uptake appears to be leveling off, but unfortunately his exposure times were too short to show whether a limiting concentration would be reached.

SHOESMITH Does heat treating have any significant effect on the microstructure or on the distribution of the alloying elements? If so, do these changes affect the rate of hydrogen uptake?

SORENSEN When you sensitize by heat treating you decompose the beta phase and form Ti_2Ni.

SHOESMITH Does the Ti_2Ni absorb hydrogen as readily as the initial beta phase? If hydrogen uptake is through the beta phase, would your heat treatment not lead to less hydrogen uptake?

SORENSEN I don't know.

DEBRUYN I would like to comment on the work of Westerman's that you mentioned. He observed crevice corrosion under alumina spacers. We also used alumina spacers when studying crevice corrosion of titanium, but did not observe any metal attack. Perhaps that is because we used clay water at 90°C.

SORENSEN There are many differences between Westerman's experiments and ours. We will attempt experiments to determine which is the most important variable and what it is that causes the crevice corrosion in his case.

INTERRANTE Did you both use the same water?

SORENSEN No. They are similar, but not exactly the same. That is one difference between the two experiments. However, there are others, such as the type of crevice, the temperature, etc.

KASS What are the differences in the water?

WESTERMAN We used a magnesium concentration of about 48,000 ppm, which makes our magnesium content considerably higher than in the Sandia experiments. Our sodium, potassium and calcium levels are about the same.

SHOESMITH Is the effect of magnesium to reduce the pH due to its high-temperature hydrolysis, or does it also destroy the passive film on the titanium?

WESTERMAN For Ti Grade-12, I suspect we would have observed similar behaviour in sodium chloride solutions without any magnesium. The magnesium content of the brine certainly affects the corrosion of mild steel, but for titanium we have no evidence to say it causes crevice corrosion.

SORENSEN There are too many differences in our experiments to ascribe the effect to any one variable.