

MAY 13 1988

Dr. Charles G. Interrante, Program Manager
Metallurgy Division - Corrosion Section
National Bureau of Standards
U.S. Department of Commerce
Gaithersburg, MD. 20899

Dear Dr. Interrante:

We have reviewed the draft report, "Corrosion Behavior Of Low Carbon Steel in High pH Aqueous Media", and have indicated our comments on the enclosed markup. Some are editorial in nature, but others are intended to focus attention on our interest in more specificity as to findings, conclusions and recommendations. Thus:

1. Will A27 ASTM grade 60-30 low carbon steel passivate under any circumstances, and in particular under those at the Nevada site?
2. Can pitting corrosion for this steel be dismissed as a potential failure mechanism?
3. Would it be of value to determine what substances were present in the thick corrosion films?
4. If pitting does not occur in this steel, how can there be modelling studies of pit propagation? Should the Isaacs work be reviewed to determine whether it is consistent with the current work?

For the immediate future, however, it would seem any experimental work should concentrate on the materials proposed for the tuff site, such as stainless steels. What questions have been identified as having major importance to our ability to assess DOE proposals for waste package design?

MAY 13 1988

Actions resulting from this letter are considered to be within the scope of FIN A-4171. No changes in costs or delivery of contracted products are authorized. Please notify me immediately if you feel this letter will result in additional costs or delay in delivery of contracted products.

Sincerely,

Charles H. Peterson
Materials Engineering Section
Technical Review Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure:
As stated

cc: Dr. Neville Pugh, Director
Metallurgy Division

Dr. Dale Hall, Group Leader
Corrosion Group, Metallurgy Division

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Should add some words that this work was in progress at the time
2 of the potential sites were deleted. It was decided Complete DRAFT
rather than discard what had been done. Should also add text showing
how it fits into total work.

Corrosion Behavior of Low Carbon Steel in High pH Aqueous Media

Anna C. Fraker and Jonice S. Harris

Introduction

The purpose of this work was to study the corrosion behavior and local corrosion susceptibility of low carbon steel in simulated ground water at a pH of 9.75 and a temperature of 95 C. These studies were conducted as part of a program to evaluate materials for long term nuclear waste storage. The canister storage materials should remain intact for 300 to 1000 years as part of a design which would limit release of radionuclides at all times ~~up to 10,000 years~~, to no more than one part in 10^5 of a 1000 year inventory. The test conditions used in the present study typify those of a basalt repository in the state of Washington, but selected aspects of the results are applicable to low carbon steels in other environments of similar composition.

after the
containment
period

Previous studies of low carbon steel in this environment indicated that pits were occasionally found after testing but stated that pitting would not develop in repository conditions¹. In general, pitting would not be expected in low carbon steel in aqueous media due to the absence of surface passivation^{2,3,4}. Other reports on corrosion of low carbon steel in aqueous media indicated uneven attack over the specimen surface but did not indicate pitting attack⁵.

Modelling studies⁶ of pit propagation in low carbon steel showed that pit depth propagation increased with the presence of inert or nonreactive pit walls. It has not been determined that sufficient pit depth and corrosion product accumulation would develop to produce this protective effect assumed in the model.

Seems obvious that if the walls are inert, only the pit floor will corrode and therefore will corrode faster.

Modelling of pitting has been discussed⁷, and pitting was related to galvanic corrosion with two distinct electrodes in contact where the pit dissolves rapidly and the rest of the metal is passive and dissolves slowly. The rates of electrochemical processes within the pit and on the surface must be known as well as how these rates are affected by solution composition, temperature, current path and other environmental factors. Most of this information is accessible experimentally⁷.

Still another consideration in studying pitting in metals which do not passivate under specified conditions is pitting at cathodic potentials. Pitting at cathodic potentials has been reported for austenitic stainless steel⁸ and for passivated iron^{9,10}. The latter work concluded that the pitting potential was a mixed potential with a cathodic dissolution process,



and an anodic dissolution process, $\text{Fe} > \text{Fe}^{2+} + 2e^-$. Other work indicated that reactions in local cells during anodic and cathodic polarization would be the same¹¹. This discussion concluded with the analysis that localized corrosion at cathodic potentials could occur but that it was rare and would not cause serious problems⁴.

$\Delta G = ?$
Source of $4e^-$?
Some of Fe_2O_3 ?
Needs more description.

Overall equation could be: $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{H} + \text{Fe} \rightarrow 3\text{Fe}(\text{OH})_2$
but where did the Fe_2O_3 come from?

Some studies have been conducted of corrosion behavior of carbon steels in tuff repository environments¹². These studies indicated that AISI 1020 - 1025 and ASTM A-36 did not suffer excessive corrosion in the tuff environment but that more data, increased testing times and studies of galvanic effects were needed.

Roman nails, with a composition similar to A216 low carbon steel which had been buried for 2000 years in Inchtuthil, Perthshire were unearthed and found to be heavily corroded with the remaining material being ferrite with only a small amount of pearlite near the edge¹³. There were areas of localized corrosion but the origin could not be determined due to the overall gross corrosion attack. Approximately 900 nails were found at the burial site, but it is not known whether there were more and some had disintegrated.

Usefulness? what conclusion can be drawn?

The present investigation applied conventional electrochemical techniques to study pitting susceptibility of low carbon steel, and procedures and results are discussed. Electrochemical measurements indicated that pitting would not be occurring. Microscopic examination of corroded specimens indicated overall general uneven surface corrosion with some shallow local attack in the ferritic phase. Since the specimen never passivated, the localized attack was related to preferential surface sites, and not to the usual electrode potential difference and current densities for producing pits of unknown depth and damage. These results indicate that pitting, as classically defined, does not occur in this low carbon steel. The overall general corrosion, thick surface films, and nonpassivating conditions resulted in limited and shallow localized attack.

and if not classically defined?

Materials and Methods

The A 27 (ASTM grade 60-30) low carbon steel sheet material was obtained from the Pacific Northwest Laboratory. The composition of A27 steel is given in Table 1.

what is the classical definition?

Table 1. Composition of A 27, ASTM Grade 60-30 Steel

C	Mn	Si	P	S	Mo	Cr	Ni	Fe
0.245	0.69	0.59	0.016	0.018	0.04	0.43	0.20	Bal.

nominal? as analyzed? variability or tolerance?

Specimens were cut with a diamond saw. Some specimens were placed in permanent mounts for etching and photographing, and others were mounted in temporary mounts for polishing in preparation for corrosion testing. All specimens were polished through 300 to 600 grit SiC papers and then with 6 um and 1 um diamond paste with a final polish in 0.05 um Al₂O₃. Ethanol was used as a wetting agent in the final polish since the steel corroded or etched when water was used for the polishing. Specimens were prepared immediately before testing or were kept in a desiccator for a few days. Specimens for microscopic study were etched with a mixture of 9 parts ethanol to 1 part nitric acid, washed, dried and then studied using the light microscope.

This is in carbon particles system. Are they all removed?

Is all the Al₂O₃ removed? (2)

The Grande Ronde No. 4 water was prepared using previously established methods and compositions¹⁴. The composition of this water was based on ground water samples which previously were collected and analyzed. The pH was adjusted to a value of 9.75 using either 0.10 M HCl or 0.10 M NaOH. Stock solutions are prepared and later diluted as needed for use. The compositions of the stock solutions are given in Tables 2 and 3. One liter of synthetic Grande Ronde No. 4 water is prepared by adding 25 ml of stock solution A and 25 ml of stock solution B to 900 ml water. After the pH is adjusted, water is added to bring the water level 1 L. The water was placed in the testing flask and brought to a temperature of 95 C before inserting the specimen.

Table 2. Composition of Grande Ronde 4 Basic Stock Solution A?

<u>Compound</u>	<u>Amount (g)</u>
Na ₂ SiO ₃ · 9H ₂ O	18.2
Na ₂ CO ₃	6.40
Na ₂ SO ₄	0.239
NaF	1.76
NaOH (50 % solution)	23.0
Water	(Add water to bring volume to 1 liter.)

Table 3. Composition of Grande Ronde 4 Acid Stock Solution B?

<u>Compound</u>	<u>Amount</u>
KCl	1.05g
CaCl ₂ · 2H ₂ O	0.323g
HCl	219 ml of 2.0 M HCl
Water	(Add water to bring volume to 1 liter.)

The Cohasset Flow basalt rock and Wyoming bentonite clay were supplied by the Brookhaven National Laboratory. The basalt rock had been collected as large pieces and had to be crushed. This was difficult because the rock was hard and also there was concern regarding contamination by the crushing device. The rock was crushed by a motorized steel rock crusher. Prior to crushing, the rock crusher was washed consecutively with water, acetone and and alcohol. There was no apparent contamination of the crushed rock by the crusher. ^{15g} How determined? _{0 p.p.m.?}

The corrosion testing involved making cyclic anodic polarization measurements measurements of the A 27 low carbon steel specimens in Grande Ronde No. 4 water at a temperature of 95 C. The pH was approximately 9.75. Some tests were made in Grande Ronde No. 4 water containing a mixture of 75 percent basalt and 25 percent bentonite. The basalt and

bentonite mixture were to fill one half of the testing flask, but the bentonite expanded upon becoming wet and the mixture filled approximately two thirds of the volume of the flask. The solution and mixture were held at temperature for one hour prior to inserting the specimen and beginning the test.

The specimen was placed in the 95 C solution and left at open circuit potential for fifteen minutes prior to making the polarization measurements. The potentiostatic polarization measurements were made by applying a potential to the specimen at the rate of 0.01 V/ 15 sec. All voltages are in reference to a saturated calomel electrode (S.C.E.).

why?

standard?

Results and Discussion

Results of this work showed that the A27 steel was continuously corroding and did not undergo passivation. Specimens showed effects of corrosion in distilled water and in laboratory air. Susceptibility to pitting can be determined for metals which passivate by using a stimulation test such as the test described in the American Society for Testing and Materials (ASTM) F 746, Standard Test Method for Pitting or Crevice Corrosion of Surgical Implant Materials⁶. It was not possible to apply the stimulation test to the A27 low carbon steel. Some results of the tests which were conducted are given.

slow observed? Describe.

why?

Passivity. Representative results of the initial open circuit potential and the potential after fifteen minutes are given in Table 4 for exposure in Grande Ronde No. 4 (GR-4) water (Test A) and for GR-4 water plus basalt and bentonite (Test B).

Table 4. Open Circuit Potentials for A27 Low Carbon Steel

Test	Time, min.	Media	pH _i	pH _f	Temp. C	Pot., V
A	0	GR-4 water	9.75		95	-0.46
A	15	GR-4 water	9.75	9.2	95	-0.59
B	0	GR-4 water, basalt, bentonite	8.3		95	-0.769
B	15	GR-4 water, basalt, bentonite	8.3	7.7	95	-0.787

} Seems very low. Would these be likely in the repository

As indicated by the open circuit potential for test A, the A27 steel did not passivate in GR-4 water. The open circuit potential dropped from -0.46 upon immersion to -0.59 after fifteen minutes. This drop in potential occurred due to the absence of a passive film on the surface. The steel also did not passivate in GR-4 water plus basalt and bentonite

gradually or step wise? If gradually, proper decrease to dropped. (4)

as shown in the even lower potentials of -0.769 V initially and -0.787 V after 15 minutes.

Solution pH and Effects of Temperature and Basalt and Bentonite. The initial pH (pH_1) of the GR-4 water was set at 9.75 at 22 C, and decreased with the increasing temperature. The final pH (pH_2) of this water after the anodic polarization test and after the temperature had dropped to at 60 C was 9.2. The pH of GR-4 water plus the basalt and bentonite was lower both at low and high temperatures. The pH of the GR-4 water mixed with the basalt and bentonite was 9.75, and after combining 500 ml of this GR-4 water with 150 g of basalt and 50 g of bentonite, the pH_1 of the mixture was 8.3. After completion of the anodic polarization measurements, the pH of this mixture at 60 C was 7.7.

Significance?

Two readily observable effects of adding basalt and bentonite to the test media were an expansion of the test media and a lowering of the pH. The mixture of GR-4 water and basalt and bentonite was made and held at temperature approximately 1 hour prior to running the test. The crushed basalt provided a high surface area ratio/unit Gr-4 water. Environmental effects resulting from this mixture could change over a longer period of time.

how?
in what direction?

Anodic Polarization. An example of a cyclic anodic polarization curve is shown in Figure 1 where the log of the current density is plotted versus the applied potential. This is an example of the test labeled "A" in Table 4. Arrows on the curve indicate the direction of the applied potential during the test.

This curve shows that no passivation occurred and that the current density increased from the beginning. The current levels off somewhat at high currents due to the presence of a thick film which limits diffusion. This film is constantly breaking up and falling off of the specimen causing sudden rises in the current. This is not a protective film. The reversal of the potential does not show the hysteresis in the current. The increased current in the remaining portion of the curve may be due to increased specimen area as a result of the corrosion during the test.

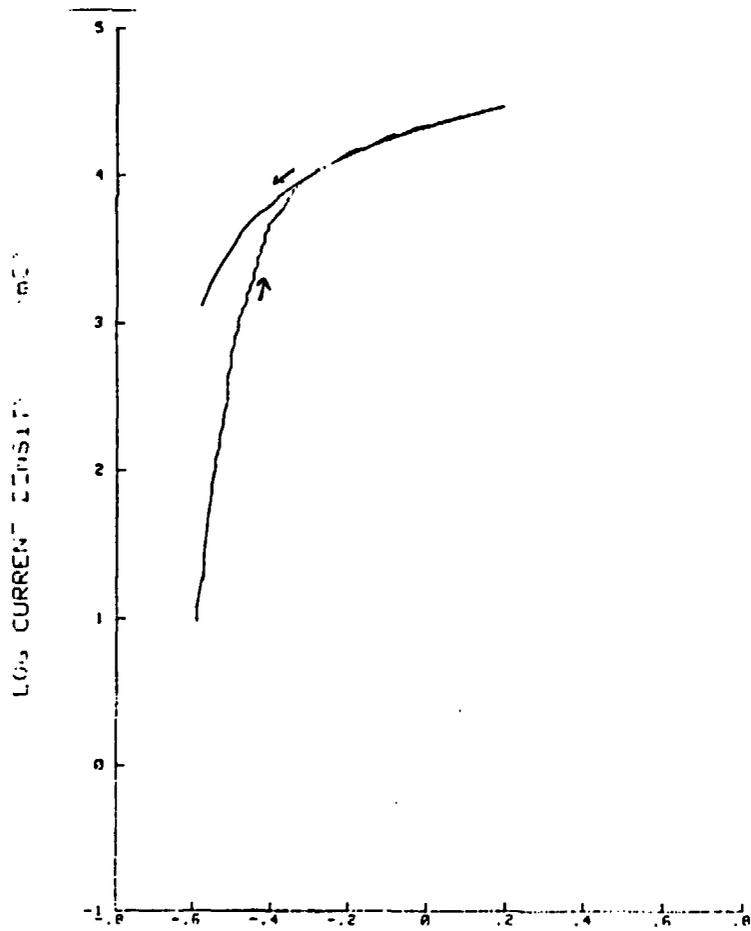
opinion?
of what?
with same smooth.

not a dent

the explanation

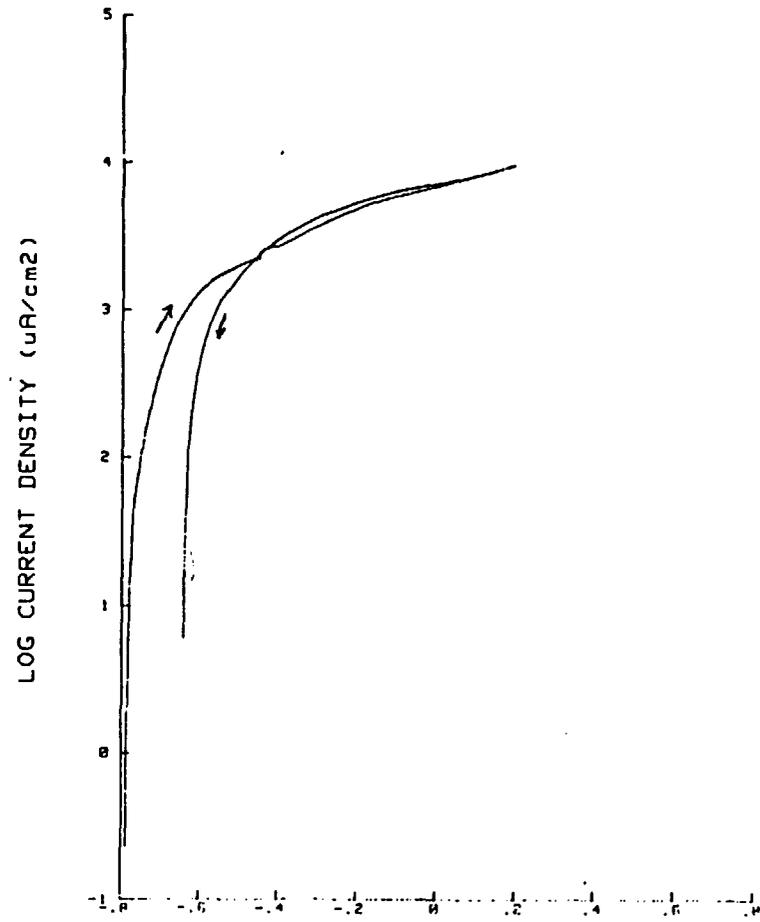
Figure 2 is a cyclic anodic polarization curve for the test represented by "B" in Table 4. This curve starts from a lower corrosion potential and also shows that no passivation occurred. Here, as in the test of Figure 1, with increasing applied potential, the current reaches a level where it levels off due to the formation of a thick film and limited diffusion. The current level in the remaining portion of the curve is different from that of Figure 1 and is lower. This may indicate increased protectiveness of the film or some reaction of the film with the basalt, bentonite and water mixture.

opinion?
should reconcile with Fig 1 explanation



APPLIED POTENTIAL (V vs SCE)

Figure 1. Cyclic anodic polarization curve for A27 steel in GR-4 water at 95°C.



APPLIED POTENTIAL (V vs SCE)

Figure 2. Cyclic anodic polarization curve for A27 steel in GR-4 water with basalt and bentonite at 95°C.

Microstructures. Examples of the microstructure of two uncorroded specimens are shown at two different magnifications in the micrographs of figures 3 and 4. This microstructure consists of areas of ferrite (labeled f) and pearlite (labeled p). After anodic polarization, the specimen surface becomes uneven and three dimensional in appearance due to the corrosive attack. The pearlite is attacked more severely than the ferrite, as shown in Figure 5. Figure 6 shows an area with some localized attack. These areas, which could be identified as pits, are shallow and crystallographic, but these are not pits in the normal sense of the term.

can't see in picture

define pit.



Fig. 3. A27 steel, uncorroded.

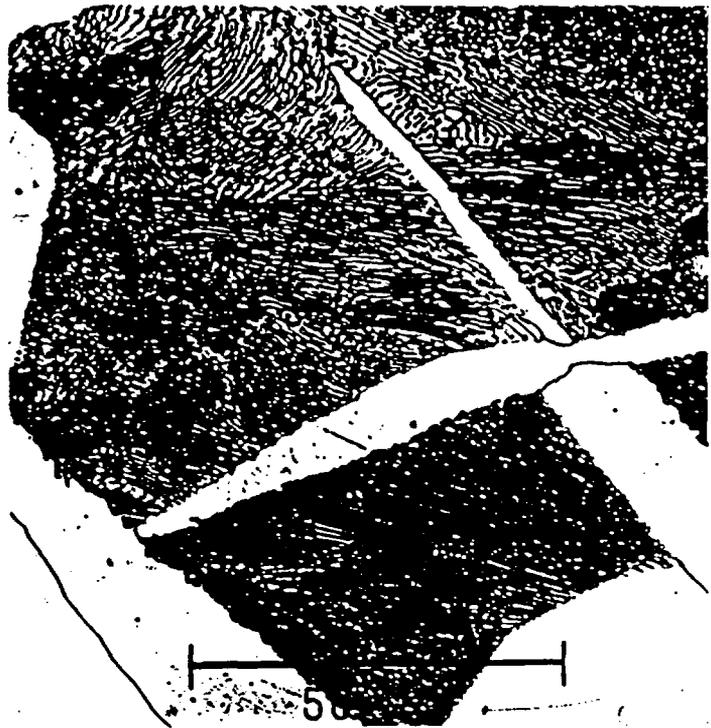


Fig. 4. A27 steel, uncorroded.



Fig. 5. A27 steel, anodically polarized, (cyclic).

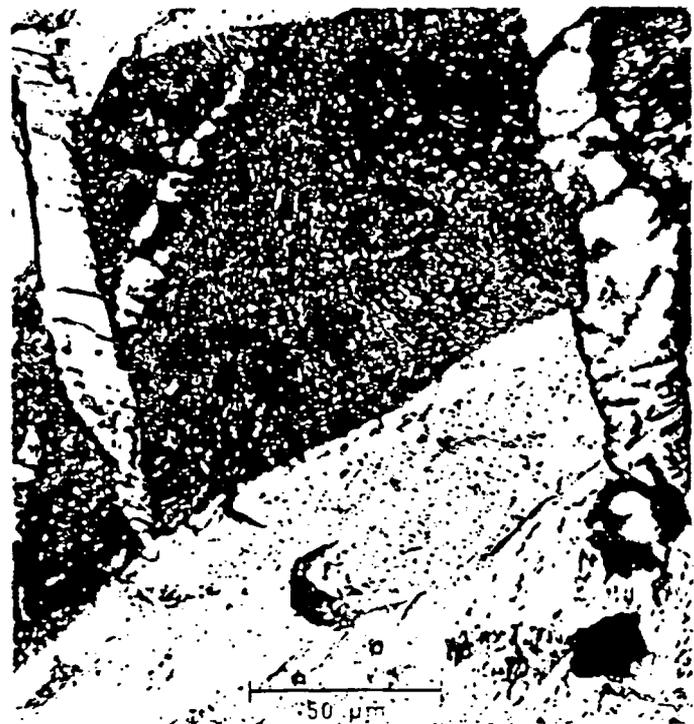


Fig. 6. A27 steel, cathodically polarized.

Conclusions

Anodic polarization tests were conducted with A27 (ASTM grade 60-30) low carbon steel exposed in 95 C simulated Grande Ronde No. 4 water which had a solution pH ranging from 7.7 to 9.75. The following conclusions can be made from this investigation.

1. A27 ASTM grade 60-30 low carbon steel corrodes to some degree in laboratory air and in distilled water. *describe*
2. A27 ASTM grade 60-30 low carbon steel does not passivate in simulated Grande Ronde No. 4 and would not be expected to exhibit pitting corrosion as it is normally defined. *therefore?*
3. Electrochemical electrode potential measurements showed that the open circuit potential decreased after immersion. This indicates that a passive film is not forming and that general (uniform) corrosion was occurring. *become more negative*
4. Localized attack was observed. The localized ^{pp} corroded areas appeared to be crystallographic and were shallow. These areas of localized corrosion are not pits in the classical sense because they are not the result of the local breakdown of a passive film. The exact cause of these features is not known. *decreased in absolute value?*
5. Thick corrosion product films formed on the surface and occasionally, dropped off. Observation of surfaces under the films revealed an uneven and irregular morphology with preferential attack in the pearlitic regions (grains) of the A27 steel. *analysis? grain boundaries?*
6. Effects of adding basalt and bentonite to the simulated Grande Ronde No. 4 water were to increase the volume of the mixture and lower the pH. There may have been additional ions released into the mixture but this was not determined.
7. Increasing temperature lowers the pH of the simulated Grande Ronde No. 4 water. *2nd of dry water.*

Recommendation

what to find?
Additional studies of low carbon steel in various media and for longer times would be useful for determining the materials durability. The irregular surface attack during the general corrosion should be more fully described as well as effects of varying amounts of pearlite in the microstructure, effects of varying ionic species and changing solution pH. The amount and distribution of elements, such as Si, S and P, also should be considered.

The effect of
This section should be more specific.

Specific Recommendation?

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