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MEMORANDUM FOR: Kien Chang,
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SUBJECT: GEOCHEMICAL MEASUREMENT PROBLEMS IN DOE CORROSION TESTING
 AT BWIP

The electrochemical potential is a critical experimental variable in corrosion testing; for one thing, if conditions are too reducing, the metal cannot be oxidized. One of the major concerns at BWIP has been the uncertainty in the electrochemical potential. As measured relative to the standard hydrogen electrode, DOE's experimental values have varied from -200 millivolts to +300 millivolts.

As you know, DOE presented arguments for more reducing (more negative) values but, as Dave Brooks and I have repeatedly pointed out, none of the theoretical arguments are very convincing; certainly none of them are so convincing that we would be tempted to discard all the existing experimental measurements in favor of estimates from theory.

The point of this memorandum is to direct your attention to the practical consequences of the experimental scatter in terms of uniform and localized corrosion.

Analyses of the stability of various phases permits one to describe the basic corrosion characteristics of metals. In regions where the metal is immune, it will not corrode; in regions where it is active, it will corrode; and in areas where it is passive, it will not corrode uniformly but is likely to display pitting and crevice corrosion.

If the true redox state of the system is within the range of the experimental data given in the EA, then pure iron at 25°C is in a region of active corrosion for pH less than a number between 6 and 9 (the exact figure depends on the E_H), and in a passive region for higher pH (M. Pourbaix, Lectures in Electrochemical Corrosion, Plenum Press, 1973; p17).

For copper, on the other hand, the range of experimental data includes large areas of immunity at believable pH for tests at 25°C; for example, at pH = 7 copper is immune below 60 millivolts, and only under very basic conditions (pH

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= 12) does copper become active at $E_H = -200$ mv; to see the full importance of this observation, one should consider that with DOE's contractors' experimental techniques, it is easy to get too high a value for E_H (by contaminating the samples with atmospheric oxygen), but very difficult to get too low a value. Consequently, the true value of E_H , assuming the spread in DOE's values is due to experimental error rather than variation in groundwaters, is likely to be much closer to -200 millivolts than +300.

If this is the case, DOE may well be able to argue a plausible case for the geochemistry being such as to make copper immune. If they can do so, proving containment integrity will be relatively easy, especially as copper does not show hydrogen embrittlement under normal conditions and stress corrosion cracking of pure copper occurs under fairly specialised condition. Pure copper (use of which would avoid grain-boundary degradation problems) has very poor mechanical strength, but its use in combination with some steel components would have real advantages and may have something to do with DOE's present flurry of activity on copper.


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