International Workshop

On Long-Term Extrapolation of Passive Behavior

July 19-20, 2001 Washington

Question 1: On the effects of long-term passive dissolution

-Since commercial alloys are being used to manufacture the waste packages and due to „atmospheric" corrosion conditions in the repository it has to be assumed that most of the effects described in the speculative scenarios (defect sweeping, vacancy build up, debris accumulation, potential ennoblement) do not necessarily occur uniformly over the whole passive surface of a WP (Waste Package). Therefore if these effects are really occuring during the long-term exposure, and if these are also effective to promote passive metal dissolution, they will lead to some degree of inhomogeneous metal loss. In case of oxide spalling it is assumed that repassivation occurs fast enough and no localized corrosion takes place.

-According to our experience from exposure tests in long-range alpine road tunnels in Switzerland and in France up to 25 years, we never observed this scenarios on passive metal surfaces. Instead external debris accumulation from environmental influences occurs much faster and may lead in case of hindered repassivation to enhanced localized corrosion processes. These debris accumulations are not necesssarily conected to the passive state of the materials but are rather caused by the environment in the repository.

-Our results from the field tests in the Mont-Blanc Tunnel lasting for approximately 8 years show, that the nickel-base alloys (Inconel 2.4856, Hastelloy C4 2.4610) do not corrode at all in this heaviliy contamintaed atmosphere of long-range alpine road tunnels contrary to 304 and 316 SS which show severe corrosion already after 1 year. (Pollution: Chlorides, sulphates, sulfides, nitrates, RL ≥78 %, T ≤ 35°C)

NOTES: BOHNI PULLED OUT OF WORKSHOP AT LAST MINUTE (3 DAYS BEFORE) BUT PROVIDED THESE NOTES.
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Question 2: On the long-term preservation of conditions preventing localized corrosion.

a)

-Critical pitting potentials quoted in the literature are usually treshold potentials at or above which stable pit growth occurs. Pit initiation processes followed by metastable pitting may already occur at much lower potentials. This leads to the concept of „metastable pitting". Therefore question 2 should be rewritten more precisely: What is the lowest potential where metastable pits can be transformed into stable pits under certain given environmental conditions. (in case of Ni in highly conc. $NiCl_2$ - solutions this potential is approx. -50 – -100 mV_{SCE} at RT)

-If the the transformation from metastable to stable pitting is mainly controlled by the chemical composition of the pit or crevice electrolyte the pit or crevice geometry of the initial pits and crevices together with the mass transport in the bulk electrolyte are of decisive importance. High Cl^- concentrations (saturation) in the water films strongly promote this transition and decrease the corresponding critical pitting potential. Therefore the expected environmental conditions in the repository including temperature play a key role with respect to the critical pit growth potential. It is important to consider these surface conditions as function of time. Our experience in long-range road tunnel investigations indicate that we get a gradual increase in concentration over the years.

-The open circuit potential is mainly influenced by the oxidizing conditions in the repository, in the present case probably air or eventually products from radiation.

b)

-Transition from metastable to stable pit growth depends on many paramerters such as potential, pH, temperature crevice or pit geometry etc. Some of them may not be directly related to E_{crit}. Therefore the necessary conditions for stable pitting always results from the behavior of the whole system. It also has to be looked at from stochastic point of view.

c)

-Corrosion tests and surface analytical investigation of worst case repository consitions.