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MEMORANDUM FOR: Robert J. Wright
High-Level Waste Technical Development Branch
Division of Waste Management

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FROM: Michael B. McNeil
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SUBJECT: CORROSION FAILURES IN BWIP WASTE CONTAINERS

I concur in Bob Cook's view that using the waste containers proposed by Rockwell for the BWIP site presents unacceptable risks of failure because of the vulnerability of the weldments to pitting corrosion and related failure mechanisms if we assume that resaturation occurs quickly.

My reasoning is as follows. There is considerable chloride in the groundwater, as well as considerable carbonate. The chloride in particular may be concentrated because the heat of the containers in the immediate post-emplacement period will tend to concentrate solutes by evaporating some of the groundwater. I agree that this is a conjecture and that Bob and I have no experimental proof; but it is a very reasonable conjecture.

The steels which were proposed in the SCR were alloy steels which are likely to produce hard and chemically inhomogeneous welds and heat affected zones. I believe that these will be attacked by the chloride-containing groundwater with the production of extensive pitting. This pitting can cause failure in two ways: first, pits may penetrate the container by simply growing. Bob has done an analysis, based on work done by Atomics International, which indicates that this is a serious risk. The analysis is not conclusive (we are hoping to build on it to develop a more accurate analysis of pitting statistics), but it is based on plausible reasoning and cannot be disregarded. Furthermore, there will be considerable stresses in the containers due not only to residual stresses from fabrication (these will be worst at the welds, which are the most vulnerable areas anyway), but also from differential expansion, from geological effects, and from changes in the specific volume of the backfill. In the presence of carbonate ions and radiolytic hydrogen, steels are vulnerable to stress corrosion cracking and hydrogen

embrittlement; pits will increase local stresses and increase the vulnerability of the containers to both these failure mechanisms. Incidentally, the UKAEA Harwell group regard stress corrosion cracking and hydrogen embrittlement as the most worrisome failure mechanisms because once they start they are very rapid (the time scale for total failure once cracking starts being in focus rather than years) and because they have the potential to shatter parts of the container rather than just boring holes, so radionuclide release after such a failure would be much more rapid.

DOE appears to have given very little consideration to stress corrosion cracking and hydrogen embrittlement. They presented three independent arguments as to why their designs were relatively safe against pitting corrosion: first, that resaturation will occur very slowly an that there will be no aqueous corrosion until the cesium and strontium are gone. There may be merit to this argument, but as I understand NMSS's reading of 10 CFR 60, we are required to assume for waste package design purposes that resaturation is very rapid. Second, that the groundwater will be very reducing. This is based on the correct observation that freshly cracked basalt surfaces are very reducing. However, the relevance of this observation is diminished by the observation (cited in the SCA) that deep groundwaters have substantial oxygen concentrations and that groundwaters in general have pH values at which the water ought not to be stable in contact with clean fresh basalt surfaces. The answer to this apparent contradiction is probably that groundwater passes through cracks and holes whose surfaces have long since been oxygenated. It is true that mining will produce much new basalt surface, but the surface will be produced in the presence of air and water vapor and will probably be thoroughly oxidized before the repository is closed. DOE's third defense is to use pitting factors; that is, to measure the average general corrosion rate and estimate the depth of the average pit as some multiple (say 10) of the average depth of general corrosion. This has some merit where general corrosion is fairly rapid and the part in question is homogeneous chemically. It is not appropriate when the average general corrosion rate is measured on bulk material and the pits we are worried about are in a weldment; it is not appropriate when the bulk has passivated, and it does not tell us how deep the deepest pit is, or what fraction of the pits have reached some specified depth (say the thickness of the container).

Examples of design requirements which I think would be useful in judging:

1. The system (including welds and heat-affected zones) should be chemically homogeneous and clean (i.e., free of inclusion insofar as possible). This requirement is not quantifiable at present, but will be after successful completion of RES' proposed manufacturing research project.

2. The welds should be sought be soft and (if the container is ferrous) purely ferritic.

3. The container should have minimal residual and thermal stresses and, if at all possible, the local stress at any point exposed to carbonate-containing water should be less than 150 megapascals. This is a very demanding criterion and may not be achievable.

4. The alloy chemistry should be such that vulnerability to pitting is minimized.

5. The alloy chemistry and container design should be such that vulnerability to hydrogen embrittlement is minimized.

There is one other restriction which may be necessary. It has long been known that if a ferrous alloy containing carbon (e.g., a carbon steel) is placed in an environment rich in hydrogen at high temperatures, methane is formed at the grain boundaries and leads to damage of the structure. Beth Hall, Bob Cook and I examined this phenomenon last year and concluded that at the temperatures we are concerned with the effect was negligible. Since then I have learned that a group at BNL, under DOE sponsorship, has been examining this issues and that our disregard of the effect may have been premature. It may, in fact, be necessary to set a low carbon spec on containers which are not self-shielded. This is ongoing unpublished work and I hope to have more extensive information in a month or so. RES is undertaking a research project which will leave us in a much better position to set quantitative requirements in the area of material specs, but no results will be available for at least a year.

In summary, I feel that the proposed BWIP package design, in the saturated environment we are supposed to assume, incurs a number of risks that add up to a very considerable probability of failure for a typical container within 300 years, which is the shortest period of acceptable containment I have heard suggested. I am not prepared to quantify the risk precisely, but I would say that the probability of such failure is on the general order of magnitude of even odds.

Many of the risks, however, appear to be assumed quite unnecessarily. For example, if DOE would only adopt a pure iron container, 15 cm thick and electron beam welded (which is entirely practical) the risks would be radically reduced. Even better might be a self-shielded pure iron container, though in this case the closure problem would require more careful consideration. THere are several grades of "pure iron." The simplest is transformer iron, often called Armco iron after the major U. S. supplier. I have discussed the probably cost of 15 cm thick Armco iron containers with Dr. James Fulton of DOE, who is a retired Assistant Vice President of Allegheny Ludlum Steel Company. Dr. Fulton believes that while Armco iron is expensive now because it is a "carriage trade" item sold in small quantities, and that if it were ordered in large quantities such as would be required for the repository, it would be little more expensive than carbon steel. A better grade is "Ferrovac," a very pure vacuum remelted grade. Vacuum remelted metals are inherently more expensive than ordinary steels, but again the question of economics of scale need to be considered and it should not be disregarded as a candidate material. I could think of at least one other alternative (thixocast pseudowrought iron), but the above are the obvious ones and the safest from the standpoint of availability of data on past performance.

I hope that this has clarified my position. Bob Cook and I have minor divergences of view due to one or the other of use placing more or less emphasis on particular issue, but I think that we are in general agreement that Rockwell's proposed design should be rejected as incurring large and unnecessary risks.

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