APPENDIX D
BRINE/CEMENT INTERACTIONS

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Concern about potentially deleterious constituents in the Waste Isolation Pilot Plant (WIPP) brines were initially raised when evidence of some minor concrete deterioration in the waste shaft key was noted. The cause is geochemical alteration of the concrete shaft liner and shaft grout by the brine present at the Rustler-Salado contact. Chemical constituents detected in brine samples included both organic and inorganic compounds that probably originated from dissolution of the concrete liner and grout materials used in the shaft construction. The presence of large amounts of organics that likely originated from the chemical grout appeared to have complexed the calcium present in the brine, interfering with the inorganic chemistry of the naturally occurring brine. The brines in contact with the waste shaft key were also found to be significantly higher in both chlorides and magnesium than the Salado Formation brine. These factors probably resulted in a Rustler/Salado brine chemistry more aggressive than that of the naturally occurring Salado brines that may contact the panel barrier.

Lankard Materials Laboratory (LML) (1992) concluded that there has been both a "physical attack" component and a "chemical attack" component acting upon the waste shaft key by brines. A "worst-case" scenario proposed by LML indicated that deterioration from both chemical and physical factors could result in a loss of material on the shaft side of the concrete liner at a rate of approximately 12 centimeters (5 inches) over a 50-year period.

The very local deterioration of the waste shaft key concrete resulted in some reduction in its load-bearing capacity and some increase in its permeability to brine infiltration. In addition, exposure of chemical residue deposits to the air within the shaft may have created a spalling effect that also facilitated local concrete deterioration on the interior (shaft opening) side of the liner.

Sandia National Laboratories/New Mexico (SNL/NM) studied the effect of high-magnesium brine interactions on various candidate barrier materials (SNL/NM, 1994). High-magnesium brines are characteristic of the Rustler-Salado contact, which is the location of the waste shaft key. The study was intended to evaluate chemical impacts to mass-concrete barriers in the WIPP panels and to the Salado Formation. However, the results of the study were also used to evaluate the cause of the deterioration of the waste shaft key. IT Corporation (IT) (1994), in a separate study, also evaluated the geochemistry of brines associated with the waste shaft key near the Rustler-Salado Formation contact.

Both studies concluded that the brines have chemically reacted with the constituents in the concrete and grouts used in the waste shaft key liner. The SNL/NM (SNL/NM, 1994) study theorized that the loss of the liner's strength was facilitated by the loss of calcium from the concrete liner. SNL/NM noted that the magnesium present in the brine replaced calcium in the concrete, but the replacement process occurred as a delayed reaction. Magnesium replacement did not occur until after the structural integrity of the waste shaft key liner was already impacted negatively by the loss of calcium, which increased the porosity of the liner. This resulted in a more open and permeable microstructure not attributable solely to a weakening effect from magnesium replacement. Both the IT and SNL/NM studies supported the conclusion that the waste shaft key liner deterioration occurred only locally and in the outermost reaction zone of the liner, so that the structural integrity of the liner as a whole was not significantly impacted. SNL/NM proposed that further deterioration of the liner may be limited only to areas of the concrete liner that develop stress fractures.

Wakeley et al. (1993) studied salt-saturated concrete and grout emplaced in the floor of the WIPP repository six years before its retrieval. The concrete and grout used in the study were cementitious, rather than organic. In retrieving the concrete and grout plugs, the plugs were overcored to also retrieve some host rock.

The study concluded that little to no deterioration occurred to the concrete or grout and that general compressive strengths of the concrete and grout increased over time. The lowest compressive strength values were observed in samples taken from the disturbed rock zone. Reaction rims with increased permeability were noted on anhydrite surrounding the plugs, suggesting interaction between the grout or concrete and host rock. However, comparable evidence of a reaction with the concrete or grout was not seen. There was also evidence of dissolution of halite in the anhydrite zone near the plugs; however, the evidence also indicates that the presence of the halite facilitated better bonding between the grout or concrete and the host rock. Crystallization of new phases was also noted on free surfaces, indicating that strongly ionic magnesium-bearing fluids were present and moving. The fluid movement appeared to have no effect on the host rock other than to improve bonding.

The differences in the appearances, strengths, and phase assemblages between the grout/concrete plugs in the study discussed above and the waste shaft key liner concrete are different enough that two extremely different service environments can be inferred. The magnesium level and fluid transport are apparently much greater in the waste shaft key location, facilitating a greater degree of deterioration of the waste shaft key concrete than was noted in the plugs studied by Wakeley et al. (1993). The waste shaft key concrete liner was also composed of organic constituents, which appeared to be more reactive with the brine chemistry. The main concrete barrier will be located in a service environment similar to that studied by Wakeley et al. (1993), where very minor amounts of brine would contact the main concrete barrier.

References

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