

COMPARISON OF SURFACE AND DOWNHOLE ELECTROCHEMICAL MEASUREMENTS
IN RESEARCH AREA GROUNDWATERS ON THE CANADIAN SHIELD

by

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ABSTRACT

A study of the pH and redox conditions in deep groundwaters in plutonic rocks of the Canadian Shield has been performed as part of the geosciences research for the Canadian Nuclear Fuel Waste Management Program. Four instrumented systems have been employed to assess the pH and redox conditions of groundwaters in crystalline rocks to depths approaching 1000 m and to compare measurements made down-borehole with those made on groundwater pumped to the surface. The systems were AECL's Mark I and Mark II downhole hydrogeochemical probes, the Swedish Chemlog downhole multiple sensor and a standard AECL flowcell for measurements at the surface. The Chemlog system was also subjected to a series of calibration tests in an artificial borehole test facility to determine the effects of pressure and temperature on the pH and redox measurements.

Both Eh and pH sensors in the Chemlog were found to respond to temperature changes, by up to 15 mV (-0.25 pH units), whereas only the pH sensor was pressure-sensitive (up to 0.2 pH units at 8.3 MPa). Field testing of the AECL and Chemlog probes showed that pH was up to 0.5 pH units lower downhole than at the surface. Significant differences were observed between surface and downhole Eh measurements, but they did not form a consistent pattern. The Chemlog system gave downhole Eh values that were higher than measurements at the surface, whereas both AECL probes generally indicated lower (by up to 300 mV) values downhole. The short times allowed for equilibration of the Chemlog sensors, poor electrochemical poisoning of the groundwaters tested, and the possibility of contamination by O₂ from the pump drive-gas, flowcell and sensor materials are probable causes of these differences.

The results indicate, however, that in adequately poised groundwaters, Eh is best measured downhole, with more than one sensor and, preferably, with different types of inert metal electrodes so that nonequilibrium or kinetic effects can be distinguished. Measurements at the surface are acceptable if the flowcell system is well sealed from the atmosphere, if groundwater pump rates are high enough to minimize effects of O₂ diffusion from the atmosphere, and if measurements are of a sufficient duration. Redox conditions can be established qualitatively, therefore, for most Shield groundwaters by electrode measurements. The higher salinity groundwaters encountered at depth in the Canadian Shield, while not having a dominant, natural, electro-active species, do appear to have a more readily definable redox state than dilute, shallow groundwater.