



Stress corrosion testing of copper in near neutral sulfide solutions

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Copper is the intended canister material for the disposal of spent nuclear fuel in Sweden. At repository depth the groundwater may contain dissolved sulfide.

Copper rods were tested for stress corrosion cracking in chloride solutions with different sulfide concentrations. The pH of the test solution was kept near neutral by addition of 10 mM phosphate buffer of pH 7.2. Slow strain rate tests were performed at 90°C and at 60°C. The extension rate was $5 \times 10^{-7} \text{ s}^{-1}$ until rupture for most tests whereas some were interrupted after a few days of testing. Cross sections of the specimens were investigated with SEM.

Results showed intergranular corrosion in the shape of cracks at a level of 1 mM sulfide at 60°C and at 90°C. Tests under similar conditions with 0.02 mM sulfide did not result in such intergranular corrosion but only an uneven surface. Stress-strain curves do not reveal any signs of stress corrosion cracking. The time to final rupture and the elongation at rupture were independent of the test conditions used.

Intergranular corrosion in the shape of cracks developed early during the test. Tests interrupted after 2 or 4 days of strain revealed a number of cracks preferentially located towards the ends of the gauge length of the test rod. At final rupture of the test rods, after about 14 days of continuous strain, the cracks were more evenly distributed along the test rod. Necking and final rupture occurred close to the middle of the gauge length and not at the location where the first cracks appeared. The maximum depth of the cracks was estimated to about 10-20 μm . The maximum depth of cracks found after final rupture did not significantly exceed that found after 2 or 4 days.

Results are discussed in terms of intergranular corrosion with a possible spatial separation between anodic and cathodic sites. One role of the strain is suggested to be cracking of a layer of corrosion products that otherwise would be protecting. Another role of stress and strain would be to aggravate intergranular corrosion at sites where gaps in the protective layer coincide with a susceptible grain boundary.

Intergranular corrosion seems to produce dissolved copper sulfide species as primary corrosion products. The more stable $\text{Cu}_2\text{S}(\text{s})$ forms outside the cavities, initially. The rate of propagation is then limited by the rate of diffusion of soluble corrosion products from the front of the cavity to the mouth of the cavity. Eventually, solid Cu_2S forms also inside the cavity. The Cu_2S is predicted to form in increasing proportions, inside the cavity, as more surface become available for crystal growth. Because of the volume increase when copper metal is corroded to Cu_2S , the cavity will tend to fill up with Cu_2S . Finally, the cavity will be filled with solid corrosion products and unless continued strain creates new aqueous volume in the cavity, propagation will stop.

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