Uranium corrosion in grout: Lateral expansion trials

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Completed on behalf of SDP, Sellafield Ltd.

Introduction

Part of the ongoing programme of work to assist the SDP project in resolving process issues and underpin the encapsulated product involves demonstrating that the SDP products incorporating metallic uranium and associated corrosion products can meet the acceptable requirements for manufacture, interim storage and ultimate disposal. In order to support this objective, it is necessary to assess the effect of the corrosion rates of the aforementioned reactive metals on the lifetimes of SDP products with respect to the expansive forces imparted on to the container from the corroding wasteform and the ability of the package to accommodate the resultant stresses.

Trial methodology and background

To support the SDP project and aid understanding of uranium metal / encapsulant interactions and resultant expansive forces generated, trials have been set-up using two grout mix recipes that are representative of the proposed SDP process.

Mix 1: 1:1 GGBS/CEM I with additional Sludge matrix, equating to 1.075t of powders added to 1200L sludge (Typical SDP mix).

Mix 2: 1:1 PFA/OPC with additional Sludge matrix, equating to 1.075t of powders added to 1200L sludge (A potential back-up grout system).

In each trial a metal penny is encapsulated in one of the grout mix recipes, within either an acrylic or stainless steel tube vessel that is placed within the measurement rig set-up. The rig allows the corrosion rate to be determined from pressure increases due to hydrogen gas evolution, and stresses from the encapsulant grout (induced stress) using a load cell set-up. The rigs are held in water baths in order to maintain a constant temperature of 50°C.

The corrosion of the metal pennies in the grout/sludge matrices results in a corrosion product that occupies a greater volume than the parent metal that has corroded. Consequently, expansive forces are exerted on the grout matrix which generates an induced stress that causes the matrix to crack when the compressive and tensile strength of the matrix is exceeded.

The diagram on the right shows the experimental vessel set-up used to measure the lateral expansion forces generated through the corrosion of the encapsulated metal penny (left hand side). The diagram on the right hand side shows the regions of strain within the grout monolith and the induced stress measured using the experimental set-up.

Results

Induced stress measurements taken over a 175 day period highlight an initial linear growth related to time. Small horizontal and vertical cracks formed in the grout over the first 14 days of the trials, these cracks increased in frequency and opened up over the 175 day period.

Two of the vessels using the PFA:OPC started to show induced stress relief after approximately 40 and 100 days, this was associated with the formation of vertical cracks extending to the grout upper surface.

The plot and images on the right show the development of induced stress with time for PFA:OPC encapsulated samples, and the cracking of trial 6 (a PFA:OPC encapsulant trial) during this period.

The corrosion rate for the trials was observed to decrease from an initial peak rate, shown in the table on the right.

The induced stress and cumulative corrosion for trials that exhibited no induced stress relief over the 175 day period show a linear relationship. However the two trials that showed induced stress relief at approximately 40 and 100 days showed a reduction in the rate of increase of induced stress as the cumulative corrosion increased.

The plots below show the induced stress plotted with cumulative corrosion for vessels 1 and 3, which saw no induced stress relief, and vessels 5 and 6 which experienced induced stress relief at approximately 40 and 100 days.

Observations

Characteristic cracking is observed in both grout systems with uranium pennies: Two horizontal cracks, one either side of the penny location. This is a result of the induced stress in the grout reaching values greater than the grout/sludge tensile strength. The horizontal cracks are then joined by vertical cracks, which increase in number with increasing cumulative corrosion. These cracks are linked to the compressive and tensile strength of a thin layer of grout surrounding the edge of the metal penny in a hoop shape. The measurement of stress in this region was not part of this trial.

PFA/OPC/Sludge and GGBS/CEM I/Sludge matrices in stainless steel holders show that the induced stress reached is in agreement, yet the cumulative corrosion in the two matrices differ. By percentage corrosion the rate of induced stress increase is greater in PFA/OPC/Sludge than in GGBS/CEM I/Sludge, as shown below.

Conclusions

With both grout systems the initial high uranium corrosion rate appears to reduce over a 175 day period. The observed corrosion rates are in reasonable agreement with rates measured in previous studies.

Vertical cracks form, joining the horizontal cracks to the nearest grout surface, resulting in relief of the induced stress in the grout/sludge matrix. These cracks form when the induced stress is greater than the compressive strength of the grout/sludge matrix. This is affected by the percentage voidage and void size in the grout, creating areas of localised high stress that may overcome the compressive strength of the matrix. Vertical strain relieving cracks do not form until the induced stress is greater than the compressive strength of the grout/sludge matrix.

When the induced stress is higher than the compressive strength of the grout matrix stress relieving cracking occurs to limit the rate of increase of the induced stress, continued cracking further retards the rate. The increasing induced stress causes fragmentation of the grout matrix, this fragmentation would likely reduce the total force exerted on an external container.