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Impact of Zr Content on Radionuclide Release Rates in Metal Waste Forms

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Reference alloy waste forms (RAW) underwent hybrid corrosion/immersion testing to parameterize the ANL analytical oxidative-dissolution model to enable the calculation of fractional release rates. The waste forms tested at SRNL were variations of the RAW-3 formulation that uses HT9 as the main alloy component, and are meant to enable evaluation of the impact of Zr:U ratio on the release rates of actinides and Tc-99. The test solutions were air saturated alkaline and acidic brines, representing potential repositories with those conditions. The testing approach consisted of 4 major steps; 1) bare surface corrosion measurements, 2) hybrid potentiostatic hold/exposure measurements, 3) measurement of radionuclide concentrations and relations to anodic current from potentiostatic holds, and 4) identification of corroding phases using SEM/EDS of electrodes.

The RAW-3 alloys possessed a depleted uranium content of ~1 % (by atom, or 4 % by mass) as a surrogate for enriched uranium and actinides, while Zr concentrations varied from ~0.3%-2% (atomic). The waste forms were labeled per their U:Zr ratio as 1U:2Zr, 1U:1Zr, and 3U:1Zr. A total of 6 hybrid experiments were undertaken in FY15, with each experiment lasting about 5 weeks in length. The FY15 tests, combined with earlier work, allow for a more definitive understanding of constituents beneficial to alloy stability in corrosive environments, and prediction of radionuclide release rates.

Figure 1 (lower left) shows the anodic current from a 5 week hybrid test with a fixed electrode potential of 50 mV vs. SCE for the 1U:2Zr alloy electrode. The top right of Figure 1 shows the specific alloying elements of interest that have leached into the test solution, and shows negligible U, Mo or Re (surrogate for Tc) release beyond 2 days. The anodic current is directly proportional to the net dissolution rate, and shows about two orders of magnitude decrease within 2 weeks. EIS was used to probe the surface stability of the electrode during the hybrid tests and detected the formation of a passivating layer within 2 weeks with increasing surface stability over the testing period (not shown). Based on this evidence, it is concluded the corrosion potential (E_{corr}) for the 1U:2Zr alloy electrode has risen above the imposed potential. SEM and EDS analysis of the electrode surface proved that the surface was corrosion resistant, with minimal oxidation, and no evident localized corrosion (not shown).

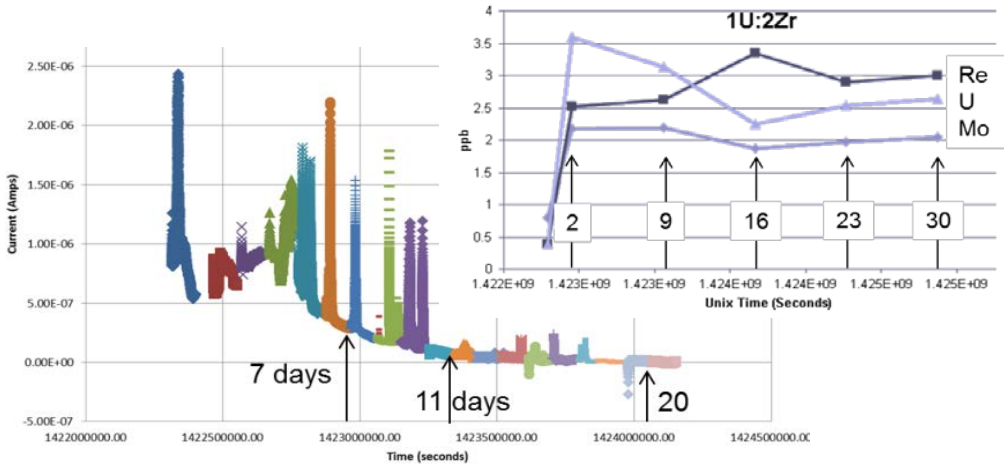


Figure 1 Current as a function of time for the 1U:2Zr alloy shows a steadily decreasing current after the first 4 days exposure in an alkaline brine. While the concentration of U. Mo, and Re (Tc-99 surrogate), show negligible release from the alloy waste form after the initial exposure.

Figure 2 (bottom left) shows the 5 week evolution of the anodic current from the hybrid test of the 3U:1Zr alloy. The anodic current indicates the corrosion rate doubles within the first week of exposure. The lower Zr content in the 3U:1Zr alloy, about 17 % of the Zr content (atomic) of the 1U:2Zr alloy, leads to less surface stability, as indicated by EIS Bode plots indicating constant polarization resistance throughout test with active corrosion. Solution concentrations shown in Figure 2 (top right) further indicate constant Re release rate throughout test (surrogate for Tc). Based on this evidence, it can be concluded that the waste form composition with the 3U:1Zr ratio has insufficient Zr to form durable host phases, with the corrosion potential lying below the imposed potential of 50 mV. This is especially notable for Re release as Re mostly reports to non Zr bearing phases.

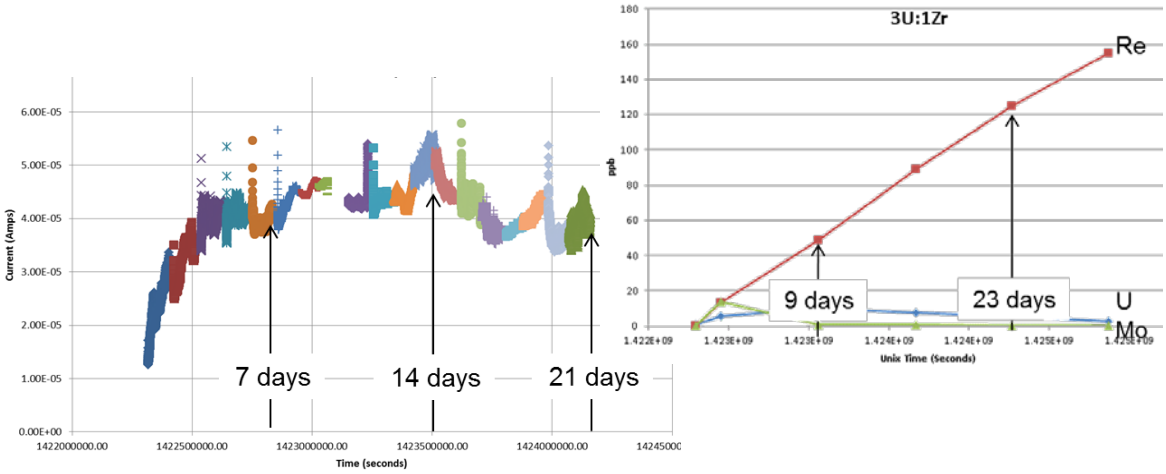
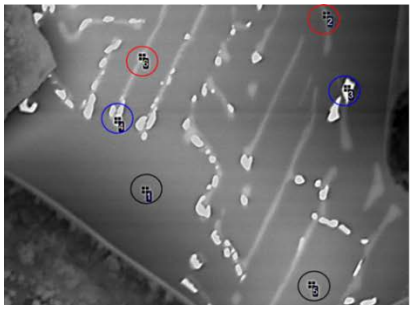


Figure 2 Bottom left: current as a function of time for the 3U:1Zr alloy shows an initial increase in current after the first 4 days exposure in alkaline brine, and then remains relatively steady. Top right: the concentration of Re (Tc-99 surrogate), shows a constant increase in concentration, corresponding throughout the testing period.

Figure 3 shows an SEM micrograph and EDS of points of interest on the 3U:1Zr alloy waste form surface after the hybrid testing, showing that the corrosion that was observed was general corrosion. Evident on the lower left and upper right of the image is a surface oxide. Point 1 and 5 represent the primary steel phase in the alloy consisting mostly of Fe and Cr, and is where the majority of the Re reports. Point 2 and 6 show a Zr rich phase that is not identified with U sequestration. Points 3 and 4 represent a Pd-Fe-U rich phase to which the U primarily reports to.



EDS Point Measurements (atomic %)	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	14.4	0.0	81.4	1.2	0.0	1.4	0.5	0.5	0.0	0.5	0.0
5	15.6	0.0	80.8	1.0	0.0	1.9	0.0	0.0	0.0	0.8	0.0
2	10.5	0.0	46.3	0.4	39.5	2.2	0.0	0.0	0.0	0.3	0.7
6	13.7	0.0	67.5	0.6	15.4	2.1	0.0	0.0	0.0	0.6	0.0
3	10.6	0.0	45.9	0.7	0.0	1.2	1.5	7.9	23.1	0.4	8.7
4	11.8	0.3	62.5	1.1	1.3	0.9	0.6	4.5	12.1	0.5	4.4

Figure 3 SEM of 3U:1Zr waste form surface under a freshly spalled oxide cover and EDS analysis of circled points.