Supporting Information

Time-dependent surface modification of uranium oxides exposed to water plasma

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Simulation of the kinetics of plasma-induced oxidation of UO_2

Reactions included:

O + U(IV) → U(V)	(1)
O + U(V) → U(VI)	(2)
H + U(V) → U(IV)	(3)
H + U(VI) → U(V)	(4)
H + U(VI) → U(Vb)	(5)
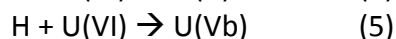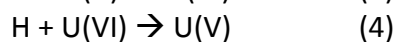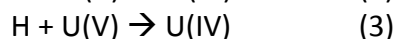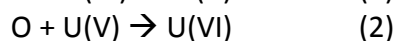
Reaction (5) describes the formation of U(V) deeper in the oxide film.

The oxide surface is exposed to a continuous flux of a low-pressure plasma of fixed composition. This simplifies the rate expressions. For reaction (1) we would normally write: $-d[U(IV)]/dt = k_{(1)}[O][U(IV)]$ for a truly homogeneous reaction (without a continuous supply of reactants) but given the nature of the plasma exposure we can simplify this to $-d[U(IV)]/dt = k^*[U(IV)]$ where k^* is a constant that accounts for the flux of O as well as the rate constant for the reaction between O and U(IV). The constants, k^*, for reaction (1)-(5) that gives a reasonable fit to experimental data are the following:

Table S1. Operational rate constants

Reaction	k^* (s^{-1})
(1)	8.6×10^{-7}
(2)	8.6×10^{-7}
(3)	1.0×10^{-7}
(4)	1.0×10^{-7}
(5)	1.0×10^{-8}

The above constants should be used for calculation where the concentration of U(IV), U(V) and U(VI) are given as fractions, i.e., the maximum concentration is 1.

The system of differential equations that originate from the reaction mechanism taking the constants in Table S1 into account can be solved using a number of different softwares. In this work we used the software MAKSIMA[1] to solve the system of differential equations as a function of exposure time. MAKSIMA is a code for simulating radiation chemistry in homogeneous systems but it can easily be adapted for the kind of simulation performed here.

References

1. M. B. Carver, D. V. Hanley and K. R. Chaplin, MAKSIMA-CHEMIST a program for mass action kinetics simulation by automatic chemical equation manipulation and integration using stiff techniques. *AECL*, *Technical Report*, Ontario, 1979.