THE ROYAL SOCIETY

The health hazards of depleted uranium munitions, part II

Annexe G: Corrosion of DU and DU alloys: a brief discussion and review

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G1 Introduction

Corrosion is the general name given to a wide range of complex physical and chemical processes that result in detrimental changes to the fabric and structure of a given metal, and is analogous in many ways to natural weathering processes.

The rate by which a given substance or alloy corrodes may be expressed in a number of different ways depending upon the nature or type of experiment. Under controlled laboratory conditions, the corrosion rate is usually characterised in terms of a reaction rate constant *k*. This constant may be related either to the weight gain of the specimen per unit area per unit time or the amount of metal reacted per unit area by an equation with the general form

$$\frac{\Delta W}{A} = kt^n \qquad (1)$$

where

W	=	weight gain of the specimen or the mass of metal reacted
A	=	reacting surface area of the specimen
k	=	reaction rate constant
t	=	time
n	=	an exponential factor which is determined empirically

It is generally considered that the empirical term *n* will be ½ for parabolic oxide growth and unity (1) for linear oxide growth. Parabolic growth kinetics are characteristic of diffusion-controlled growth of a coherent oxide film, whilst linear kinetics can be characteristic of reaction rate controlled growth, diffusion-controlled growth through a coherent oxide film of constant thickness, or transformation of one reaction product to another.

In the case of the majority of studies of DU-Ti alloys (eg Table G1) it has been assumed by the investigators that *n* = unity and that *W* is expressed as weight of metal reacted. Therefore *k* can be expressed as a constant for given conditions with units of g cm^{-2} $year^{-1}$ or alternatively as cm $year^{-1}$ by multiplying the rate in mg cm^{-2} $year^{-1}$ by the reciprocal of the metal's density.

G2 Corrosion mechanisms

From a mechanistic and theoretical viewpoint the corrosion and dissolution of metallic DU (uranium) can be considered to be in two stages (each of which can be divided into a number of sub-stages):

(a) oxidation of zero-valent metallic uranium to U(IV)

(b) oxidation of U(IV) to U(VI)

From a thermodynamic perspective the first stage in this process will be favourable under all earth surface conditions; corrosion rates for pure uranium under a variety of conditions have been reviewed and compiled by Totemeier (1995). The second stage in this process is dependent on the prevailing local redox and pH conditions, whether this be in soil, air or water (Erikson et al 1990). Under reducing or poorly oxidising conditions U(IV) minerals are likely to dominate and favour the production of low solubility corrosion products, whilst in oxidising environments U(VI) minerals such as Schoepite and aqueous U(VI) species predominate generally favouring corrosion products of significantly higher solubility (see also Annexe F).

From a more applied perspective, metallic uranium or DU may corrode through a number of processes (eg galvanic corrosion, crevice corrosion, pitting corrosion), the majority of which are controlled by the local chemical environment in which the metallic uranium or uranium alloy resides. For example, corrosion may occur in air, water or in contact with the water- and air-filled porosity of soils and sediments. In addition to understanding the pure thermodynamics and kinetics of corrosion reactions, it is also essential to consider the removal (or mass transport) of reaction products, such as oxides, which may be less reactive than the initial pure metal phases forming a 'passive' barrier through which both reactant and reaction product must pass.

G2.1 Corrosion and primary reactions

Three factors primarily control corrosion reactions under environmental conditions:

(1) The physical form of DU (ie alloy density (the percentage of alloy metal compared with parent material, in this case DU), surface area available for reaction, microstructure, crystal structure of fired DU) (see Figure G1)

(2) the chemical composition of the DU which is in contact with the environment (ie nature of the alloy, composition of DU dusts, etc) (see Figure G2)

(3) the chemical composition and physical state of environmental reactants with which the uranium metal may be in contact (ie fluid or gas composition, local Eh conditions) (see Figure G3).

Figure G1. The effects of microstructure and crystal structure on corrosion rates and environmental sensitivity of uranium alloys (adapted from Metals Handbook 1987, 1991). Note that initial unpublished data from the USA indicates that fired penetrators made of U-0.75Ti may corrode slower than unfired penetrators (C Toque, DSTL, personal communication)

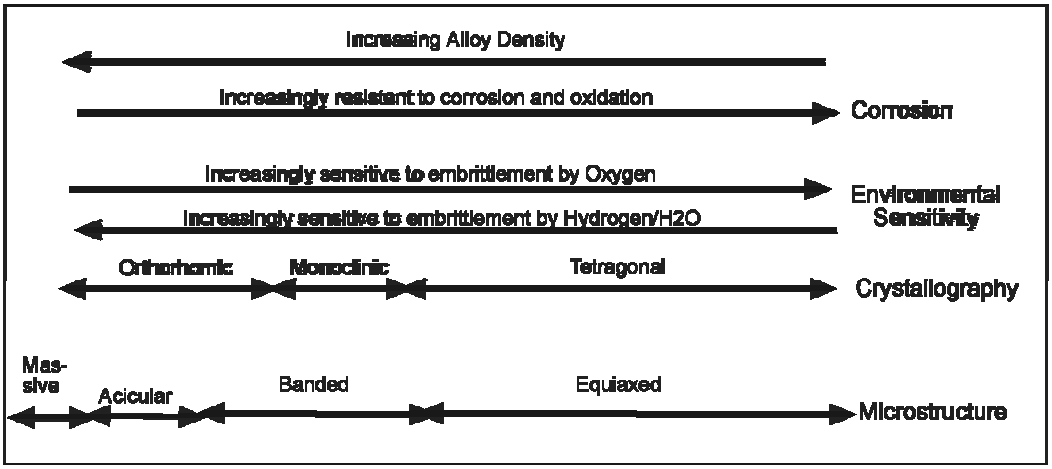


Figure G2 The effect of the chemical composition of various U alloys on average corrosion rates in hot humid air (Metals Handbook 1991). Specimens were tested at 74ºC and 75% relative humidity except for U-6Nb which was tested at 75ºC and 50% relative humidity. U-0.75Ti is uranium alloyed with 0.75% titanium as used in DU penetrators.

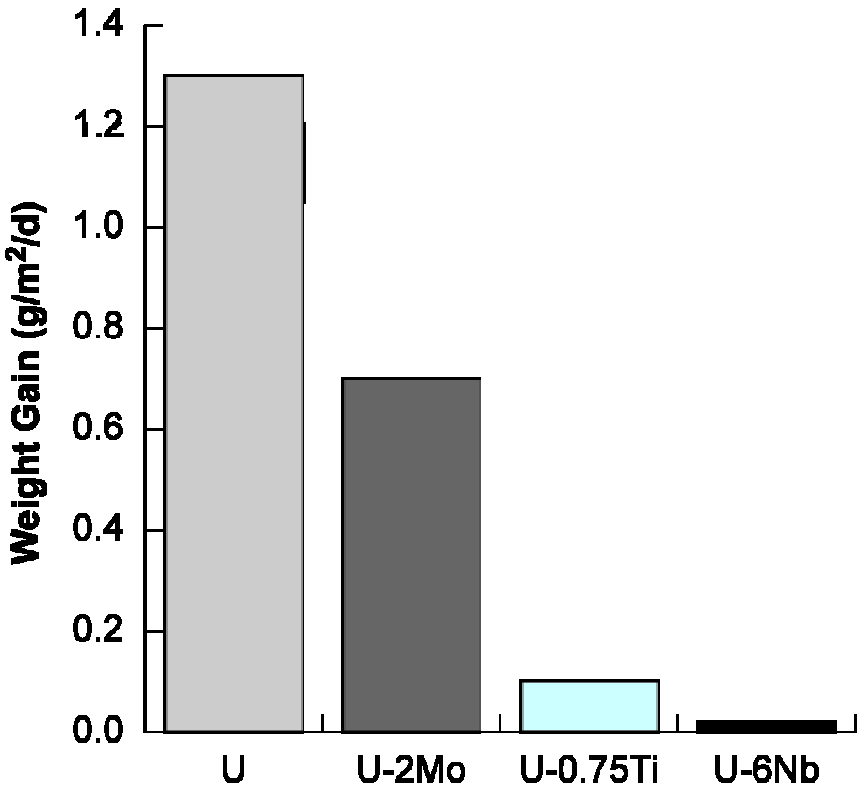
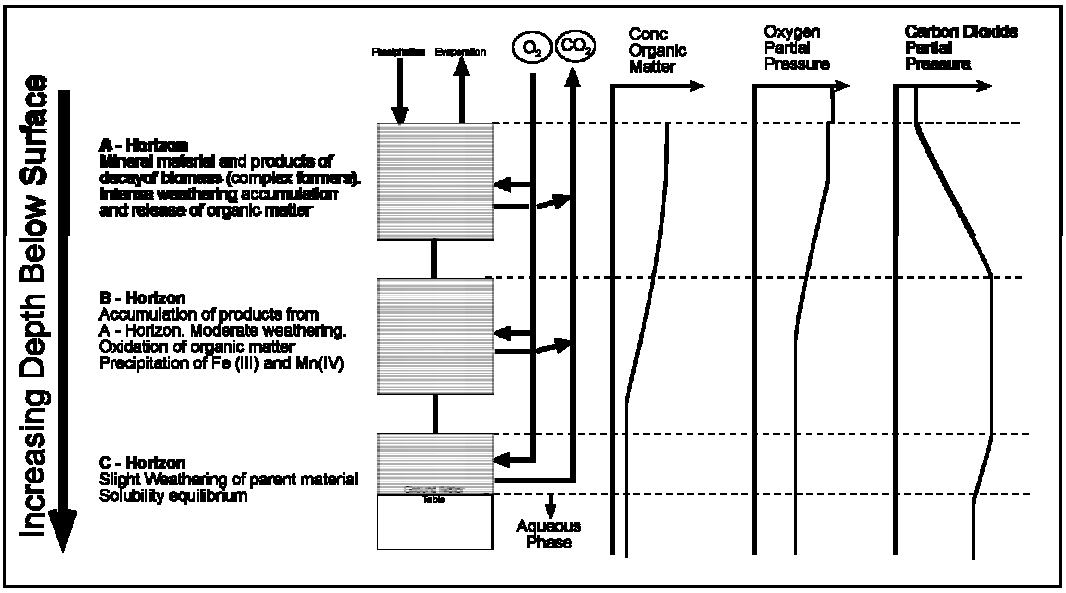


Figure G3. Effect of soil profile properties on the composition of the aqueous and gas phases likely to be encountered during the environmental corrosion of DU in soils (after Stumm and Morgan 1981). Note: (a) A-Horizon, B-Horizon and C-Horizon represent characteristic zones within a generic soil profile; (b) the partial pressures of gases in soil profiles are highly variable and may be grossly affected by the presence or absence of microbial activity (often related to temperature). However, in temperate environments the partial pressure of oxygen typically ranges from 0.1 to 0.2 atm whilst that of CO_2 varies from 10^{-4} to 10^{-2} atm.



G2.2 Experimental studies of DU corrosion focussing on DU penetrator alloys

Despite the recent interest in DU-Ti alloys, very few recent studies have been undertaken to determine experimentally the corrosion rate of these alloys across a variety of environmental conditions. Data from a selection of studies identified during the course of this work are summarised and identified in Tables G1 and G2.

Table G1. Studies of DU and uranium corrosion under environmental conditions

Study	Authors	Matrix	Rate (cm year^{-1})	Comments
(1)	Chang et al (1991)	DU-Ti - 3.5% NaCl	Not determined	Corrosion products Severe pitting Black corrosion product over all specimen, UO_2 or UH_3 Al and Zn coatings showed yellow deposits UO_3
(2)	Trzaskoma (1982)	DU-Ti - air 30 days	<0.00061	Black products formed believed to be UO_2, hydrated uranium oxides
(2)	Trzaskoma (1982)	DU-Ti - H_2O	0.0038	
(2)	Trzaskoma (1982)	DU-Ti - 3.5% NaCl	0.021	
(3)	McIntyre et al (1988)	DU-Ti - 5% NaCl, 12 days	0.077	

Study	Authors	Matrix	Rate (cm year^{-1})	Comments
(4)	Winkel and Childs (1983)	Pure ^{238}U	0.069	
(4)	Winkel and Childs (1983)	DU-Ti	0.023	
(5)	AEPI (1995)	DU-Ti - soil	0.05-0.10	Higher in soils with elevated presence of carbonate minerals Potential demonstration of oxidative reaction with CO_2
(6)	Weirick and Douglass (1976)	DU-Ti - 50 mg/litre NaCl	0.0020	Eruptions of yellow corrosion products
(6)	Weirick and Douglass (1976)	DU-Ti - moist air (110% humidity)	0.00034	
(7)	Catherine Toque, DSTL (personal communication)	DU-Ti - Kirkcudbright soil, up to 18 months exposure	0.25	60% weight loss for a 275 g billet Difficult to estimate rate because of severe weight loss Higher rates noted for grooved rather than smooth DU billets
(7)	Catherine Toque, DSTL (personal communication)	DU-Ti - Eskmeals soil, up to 18 months exposure	0.013	3% weight loss for a 275 g billet Difficult to estimate rate because of severe weight loss
(8)	Kindlimann and Greene (1967)	Pure ^{238}U - 4M HNO_3	Not determined	Dissolution rate decreases with increasing acidity
(8)	Kindlimann and Greene (1967)	Pure ^{238}U - NaOH	Not determined	Dissolution rate slow
(8)	Kindlimann and Greene (1967)	Pure ^{238}U - Cl	Not determined	Higher dissolution rates in presence of Cl with non-uniform and insoluble products formed
(9)	Schroeder et al (1959)	Pure ^{238}U - air at 100 °C and 60 °C, 50 days	1.44	After 50 days at 60 °C concentration in water (11,900 mg/litre) higher than predicted solubility of $U(OH)_4$ probably due to the formation of complexes Concluded that corrosion product formed at approximately 100 °C does not produce a protective layer
(10)	Ward and Waber (1962)	Pure ^{238}U - complexing anions (Cl, HCO_3, etc)	Not determined	Vigorous corrosion produced by complexing anions, especially in the presence of oxygen

Experimental studies summarised in Table G1 have employed a wide variety of techniques to determine corrosion rates, from simple recording of weight loss against time for sequentially sacrificed samples, to more detailed studies in which the nature and adhesion characteristics of corrosion products have been studied. From these studies it is clear that the physical and chemical form of the alloy and environmental reactants play an important role in the corrosion and ultimate dissolution of metallic uranium and DU-Ti alloys, and that experimental data support the generalised two-step process described earlier in this annexe.

Rates from studies summarised in Table G2 show a surprising degree of consistency between different studies, and are broadly compatible with observations of the condition of DU-Ti alloy penetrators made following the Kosovo conflict by UNEP and other national and multinational agencies. The wide range of relatively rapid corrosion rates observed in soils demonstrates the importance of factors such as the concentration of O_2, CO_2 and bicarbonate, and soil pH and organic carbon content in this heterogeneous environment (see Figure G3). It is also clear that the corrosion of DU-Ti alloy is enhanced in solutions containing NaCl and this sensitivity has proved to be a hindrance in the storage of such ammunitions on board ship. Such data are obviously also of direct relevance where DU-Ti alloys have been introduced into the marine environment (eg Kirkcudbright in Scotland).

Table G2. Summary of corrosion rates in the literature (cm/year) for DU-Ti(0.75) alloy (for comparison the corrosion rate of metallic DU in 3.5% NaCl was determined to be 0.069 cm/year[4])

Air	Distilled water	Soil	50 ppm NaCl	3.5% NaCl	5% NaCl
<0.001[2]	0.004[2]	0.050[5]	0.002[6]	0.021[2]	0.077[3]
0.00034[6]		0.100[5]		0.023[4]	
		0.25[7a]			
		0.013[7b]			

Data presented in Table G2 have been used to estimate the quantities of DU released into the environment under a variety of conditions through corrosion of the two most common types of penetrator used by the military. In doing this it has been assumed that corrosion occurs at a linear rate for at least the first year. This assumption is likely to be conservative and is also consistent with unpublished data from recent MOD studies (Catherine Toque, DSTL, personal communication). Within this context it should also be noted that Schroeder et al (1959) concluded that corrosion products formed when uranium is exposed to air at approximately 100 °C did not produce a protective layer.

Table G3. Calculated initial corrosion rates (g uranium released by corrosion per year) for a typical DU-Ti(0.75) alloy rod of similar dimensions to a 30 mm armour piercing round, using corrosion rates given in Table G2 (initial r = 0.55, l = 15, density = 19 g/cm^3, weight = 270 g)

Air	Distilled water	Soil	3.5% NaCl	5% NaCl
<1[2]	4[2]	47[5]	20[2]	71[3]
0.29[6]		90[5]	22[4]	

Table G4. Calculated initial corrosion rates (g uranium released by corrosion per year) for a typical DU-Ti(0.75) alloy rod of similar dimensions to a 120 mm armour piercing round, using corrosion rates given in Table G2 (initial r = 1.59, l = 32.5, density = 19 g/cm^3, weight = 4850 g)

Air	Distilled water	Soil	3.5% NaCl	5% NaCl
<6[2]	25[2]	300[5]	130[2]	460[3]
2[6]		600[5]	140[4]	

In assessing the rates of DU released from 30 mm armour piercing rounds (Table G3) it has been assumed that the penetrator has been completely separated from its aluminium jacket assembly. Data from UNEP (2001) and MOD (2001) suggest that penetrators fired in actual conflict situations can either completely lose or retain their associated fairing, although the relative frequency of such events is currently unknown.

G2.3 Transport of corrosion product from the immediate vicinity of penetrators

Following corrosion, DU may migrate away from the penetrator's local environment. Such migration may occur either within the solid phase as a result of bioturbation or other physical disturbance of the penetrator and its local environment (such as ploughing) or wind erosion of penetrators lying on the surface of the soil), or alternatively through dissolution and subsequent transport in soil pore fluids. In the latter case transport is dependent on the solubility (from both a thermodynamic and kinetic perspective) of corrosion products.

In all cases the relative dominance of transport mechanisms outlined above depends upon the depth to which the penetrator has been buried, the amount of dust produced during the initial impact and the degree of weathering. In the majority of cases where small calibre DU munitions have been used in strafing attacks against poorly armoured targets, it is likely that that dissolution and transport within the soil zone are the dominant transport pathways. Factors predominantly controlling migration dissolution are discussed elsewhere in the main text and in Annexe F.

In the case of large calibre munitions used against heavily armoured targets, resuspension of dusts and weathered DU initially represent the dominant transport pathway until such dusts have themselves become dissolved and/or physically become transported into environments where resuspension is unlikely.

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