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Chemical and mineralogical transformations caused by weathering in anti-tank DU penetrators (“the silver bullets”) discharged during the Kosovo war

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Abstract

A depleted-uranium penetrator, shot in 1999 at Djakovica, Western Kosovo, and there collected in June 2001, shows evident alteration processes, perceivable as black and yellow coatings. XRD indicates that the black coating mostly consists of uraninite, UO_2 , with possible presence of other more oxidized uranium forms, such as U_3O_8 . The yellow material is mostly amorphous, with variable weak diffraction lines, due to minor embedded uraninite grains, or possibly to schoepite, $\text{UO}_3 \times 2\text{H}_2\text{O}$.

SEM-EDS reveals only uranium. Whereas uraninite does not show any crystal shape, the yellow material recrystallizes to flattened pseudo-hexagonal prisms, approximately 2–10 μm wide and 1–4 μm long. Raman spectra of the yellow material have peaks at 3474 and 3222 cm^{-1} , indicative for OH groups, plus at 812 and 744 cm^{-1} , indicative for UO_2^{2+} uranyl ions.

Based on the different data, the yellow material covering the depleted-uranium dart is an oxidized corrosion product, containing uranyl ions and hydroxyls and/or water molecules, akin to schoepite. Therefore, the Djakovica dart shows evident oxidation and leaching processes, progressively releasing mobile uranium forms. As uranium will be progressively dispersed far from the impact sites, at a rate controlled by the presence of effective fixing mechanisms, we feel necessary to maintain long term geochemical control of water pollution within the battlefield surroundings.

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1. Introduction

The use of depleted uranium (DU) anti-tank munitions by NATO forces to strike Serbian armoured troops, during the 1999 Kosovo conflict, raised many

polemics, especially over the public opinion of countries sending soldiers to the Balkans (e.g., Murray et al., 2002). Even the idea to employ depleted uranium to construct tips able to pierce the armor of battle tanks was criticized, since other materials (i.e., tungsten) might be used to produce very high density penetrators having good ballistic properties.

Actually, until 1970 piercing tips of anti-armor ammunition were commonly made by tungsten.

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However, at that time NATO was decidedly troubled by the overwhelming number of tanks of the Warsaw Pact (3–1 ratio was estimated), as well as by their continuously improving performance. To maintain the traditional deterrence strategy, NATO was constrained to provide the best anti-armor ammunition, able to deal effectively with the Warsaw Pact tanks. From the strictly military point of view, the use of anti-tank ammunitions equipped with DU penetrators (actually, a uranium alloy named “staballoy”, containing 0.75 wt.% titanium) was appropriate. Huge quantities of DU were available at low cost and DU penetrators revealed to be incomparably better than any other material. For instance, whereas the tungsten penetrators acquire a mushroom-shaped head on impact, the DU penetrators display a “self-sharpening” aptitude. In other words, the “silver bullets” slice through tanks like a hot knife through butter.

Another crucial quality of DU ammunitions is offered by their pyrophoric behaviour, making them decidedly lethal against armored targets. While penetrating through the armor, the DU dart becomes overheated and burns, violently reacting with atmospheric oxygen. This triggers either fuel combustion and shot-magazine explosion which completely destroy the tank (Fig. 1).

Following a request by the United Nations General Secretary, NATO informed that approximately 30000

DU rounds were shot by the A-10 anti-tank aircrafts in Spring 1999 in Kosovo. As they weigh 300 g each, a total of nine uranium tons were added to the natural uranium content of the hit areas (UNEP, 2001). NATO estimated that 70–90% of the shot rounds missed the target and penetrated into the ground, at a depth depending from the substratum nature. This fact raised some worries because of possible uranium transfer to the food chain and groundwater pollution. In fact, although the radioactivity levels proved to be generally not significant (e.g., UNEP, 2001), uranium is a toxic heavy element with adverse effects upon kidneys and, possibly, lungs. Incidentally, we observe that the Kosovo uranium waste is a small percentage with respect to the 320 uranium tons (or more) deposited on the Iraqi soil in 1991, and, most probably, with respect to the still larger amount there discharged in 2003.

Because of the thermodynamic instability of metallic uranium with respect to oxidized forms, weathering processes may progressively corrode the DU metal pieces. New U-rich mineral phases may form at the reactive surface, while some uranium may be lost in solution as very mobile UO_2^{2+} uranyl and reach groundwater. Alteration rate and equilibrium stability of newly-formed assemblages will ultimately control uranium spreading in the environment. As contamination levels in food and drinking water could rise after some years, they should be monitored when there is a reasonable possibility of significant quantities of DU entering the ground water or food chain (WHO, 2001a,b).

During a sampling survey in Western Kosovo (June 2001), done to assess the environmental impact of DU discharged in heavily hit areas, we found a DU penetrator implanted into a concrete platform in front of a Serbian garrison, near Djakovica. The DU surface clearly showed intense alteration processes, perceivable even by naked eye as variously coloured spots and coatings. In what follows, we describe the chemical and mineralogical details of transformations occurred after two years permanence at the finding place. Although we presently deal with a Kosovo DU penetrator, we recall the even larger quantities of DU ammunition used elsewhere (i.e., the Gulf Wars). In the latter case, DU has been questioned to contribute to the increased occurrence of cancer, renal disease and congenital malformations, possibly together with other causes that led to an “epidemiological nightmare” (Abbott, 2001).

2. Sampling and methods

As previously stated, the DU penetrator studied was found driven deep into a 30 cm thick concrete platform at a garrison of the former Yugoslavian Army (VJ) in Djakovica. The garrison, used for armored vehicles storage and as ammunition repository, has an area of

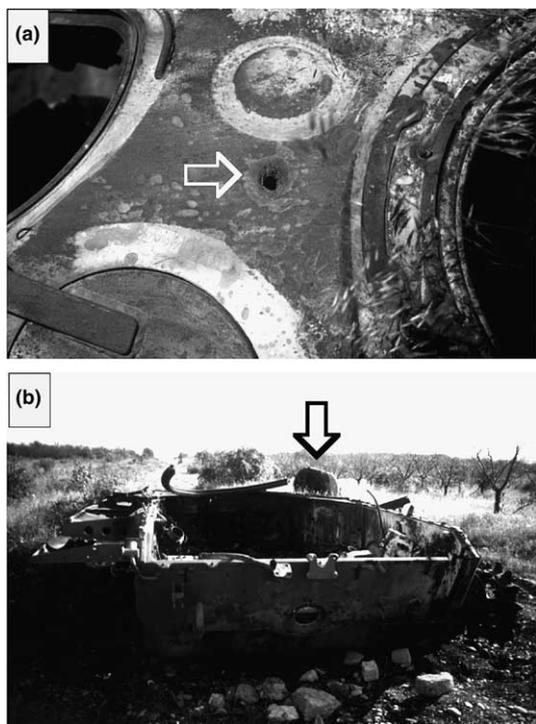


Fig. 1. (a) Hole in the armor of a Serbian tank made by a DU dart. (b) The dramatic effect of the DU dart on the same tank.

approximately 100×200 m (Fig. 2) and was attacked by NATO aircraft on May 14, 1999 which fired about 300 DU rounds.

The dart, once singled out by β/γ radiation survey, was taken out by cutting a slab (40×40 cm) of the concrete containing the object. The concrete piece was transferred to our laboratories in Italy where the DU penetrator was carefully released (even if not completely) and slices were taken for analytical work (Fig. 3).

After optical observations done using a stereomicroscope, individual particles were extracted and submitted to further morphological, structural and chemical determinations.

2.1. ICP-MS spectrometry

The DU bullet was inspected for plutonium and other transuranic species and $^{235}\text{U}/^{238}\text{U}$ ratio was measured by an ICP-MS Perkin Elmer-Sciex 6100 spectrometer. Three slices of the inner bullet were cut away and dissolved by a mixture of $\text{HNO}_3 + \text{HCl} + \text{HClO}_4$ at 280°C and a pressure of 55 bars in a Milestone Ethos 900 microwave lab-station. The instrumental conditions were analogous to those reported by the U isotopes determination method of ASTM (2001). Analytical quality was checked by analyzing the Standard Reference Material NBS U-005a, having a nominal $^{235}\text{U}/^{238}\text{U}$ wt.% ratio of 0.005025.

2.2. X-ray diffraction

Diffraction data were collected using the copper $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) emitted by a ceramic micro-focus X-ray tube, powered at 40 kV and 25 mA. Single

particles, in the order of one to two hundreds μm in size, were glued to a glass fiber and mounted in a 114.6 mm Gandolfi camera. The pattern was accumulated for 6–10 h using X-ray film (see Gandolfi, 1967).

2.3. Scanning electron microscopy (SEM)

SEM observations were obtained from chips mounted over stubs covered with conductive carbon-coated adhesive tape; the specimen was covered by a light carbon film. Observations were led using either secondary or backscattered electrons, within a Philips XL30 SEM. The microscope was equipped with a thin-window Energy Dispersive Spectrometer (EDS), capable to detect all the elements with atomic number higher than six (carbon).

2.4. μ -Raman spectroscopy

Tiny fragments of the yellow corrosion product (some tens of μm in size) were selected under the stereomicroscope and deposited within a Petridish. Raman spectra were collected using a Dilor Raman microspectrometer, with attached microscope, using an Ar laser with wavelength of 514 nm (see Hope et al., 2001 and references therein).

3. Results

3.1. Macroscopic appearance

The DU dart is strongly implanted within concrete. Only the tail (approximately one third of the whole dart)

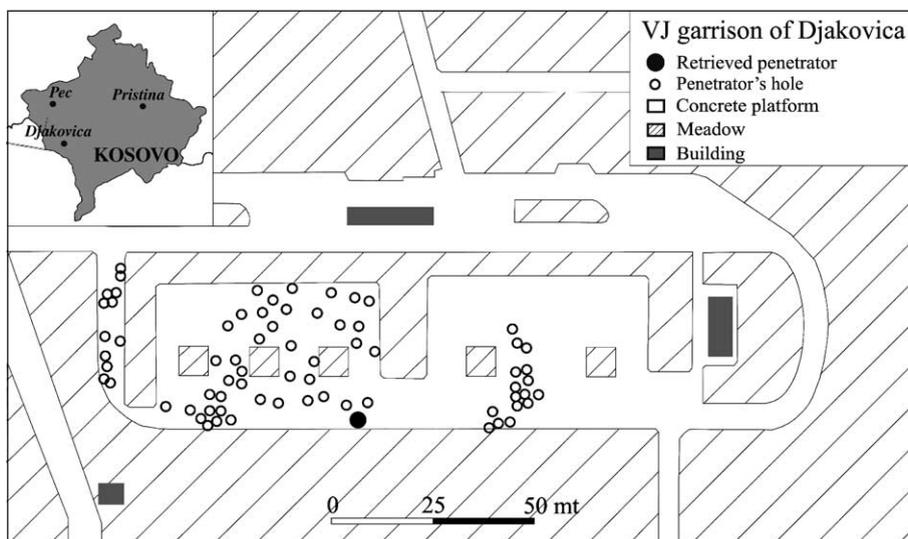


Fig. 2. Schematic map of the Djakovica garrison where the DU dart was found embedded in concrete.

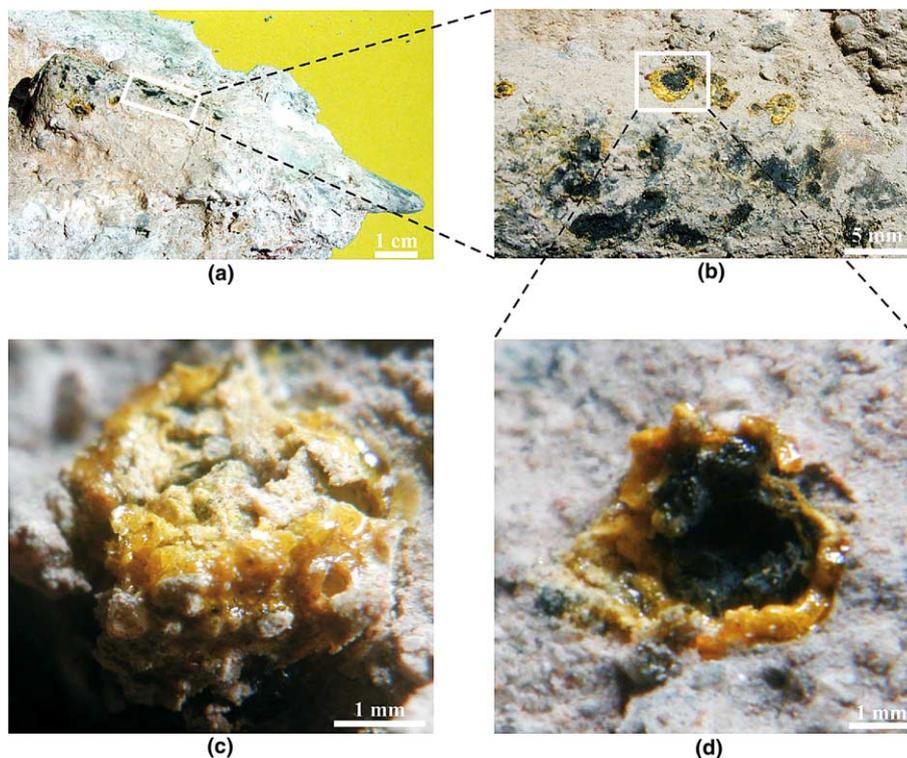


Fig. 3. (a) The DU dart before extraction from the concrete. The whole dart is 95 mm long. There is a black uraninite coating on all of the dart's tail (approximately 1/3 of the dart), with yellow incrustations in some places. (b) Tail of the dart, showing almost continuous black uraninite coating over the uranium alloy; in some areas, the black coating is weathered to yellow incrustations. (c) Round particle of the yellow uranium mineral. (d) Black uraninite coating, with the rim replaced by a continuous layer of the yellow uranium mineral.

is now exposed to external atmosphere (Fig. 3(a)). Apparently, weathering phenomena did not produce any major corrosion. In fact, the dart keeps its length of 95 mm and its diameter of 16 mm. However, the dart tail is covered by a discontinuous black coating (Fig. 3(b)). Locally, yellow spots surround the black coating, appearing as yellow crust replacing the black material (Fig. 3(c) and (d)). No crystal shape was recognized under both naked eye and stereomicroscope. Whereas the black material appears as a discrete, pulverulent particulate consisting of tiny particles, the yellow one appears compact and resinous. Based on the yellow colour, we may expect that the latter one is a corrosion product containing U^{6+} .

3.2. ICP-MS spectrometry

Five replicate analyses performed on each of the three DU penetrator slices gave a range of $^{235}U/^{238}U$ ratio values spanning from 0.001969 to 0.002021. The presence of plutonium and americium nuclides was also checked and the relative readings resulted below the instrumental detection limit of 1 pg/g.

3.3. XRD

Several tiny particles of black and yellow coatings were examined by X-ray diffraction. Both the black and yellow coatings produced poor diffraction patterns, consisting of very weak and broad lines over a very strong background, due to both poor crystallinity and self-absorption in the heavy matrix. However, in the case of the black coating a few diffraction lines may be observed, at quite constant angles from particle to particle (Table 1). The observed lines mostly match the patterns reported for uraninite, UO_2 , although the poor diffraction data do not exclude the possible occurrence of more oxidized uranium forms, such as U_3O_8 . This possibility deserves to be considered because we know that (in the case of depleted uranium particles in soils from Ceja Mountain, Kosovo) only 50% of particles consist of UO_2 , and the remainder is constituted by U_3O_8 , or variable mixtures of the two oxidation states (Salbu et al., 2003).

Conversely, in the case of the yellow material, we did not observe any evident diffraction pattern. From particle to particle, very weak diffraction lines occur in

Table 1
X-ray diffraction lines from the black coating, compared with the JCPDS data

Observed	5–550	9–206	13–225	20–1344	41–1422
	UO ₂	UO _{2.25}	UO ₂	UO _{2.25}	UO ₂
3.129	3.103	3.157	3.12	3.14	3.153
2.673	2.673	2.735	2.71	2.723	2.733
1.932	1.913	1.934	1.918	1.926	1.933
1.627	1.627	1.649	1.636	1.645	1.647

variable positions. In a few cases, they correspond to uraninite again. Sometimes, other lines seemed to match schoepite, UO₃ × 2H₂O. Actually, schoepite is a uranyl-hydroxy-hydrate, known to form as a corrosion product of uraninite. Recently, schoepite was also observed in weathered depleted uranium ammunition (Schindler et al., 2002). However, in the present case we did not achieve any conclusive XRD identification. Therefore, we conclude that the yellow material is mostly amorphous, in keeping with the colloidal appearance under the stereomicroscope; it may enclose very minor uraninite grains, as well as other grains, possibly related with the hydrated uranium oxide schoepite.

3.4. SEM-EDS

The black material (uraninite, from XRD) appears as a pressed powder, with no evidence for any crystal shape. SEM-EDS X-ray spectrometry reveals only well evident U-lines.

The yellow material is more compact, but still containing only uranium. Locally, it hosts vugs and fractures covered by tiny crystals (Fig. 4), apparently formed by recrystallization of the surrounding mass. Individual crystals appear as sub-rounded, flattened pseudo-hexagonal prisms, approximately 2–10 μm wide and 1–4 μm long. Recrystallization processes are well known for uranyl-hydroxy hydrate minerals; for instance, during weathering cycles primary hydrated schoepite, UO₃ × 2H₂O, transforms to a more stable dehydrated schoepite, UO₃ × 0.8H₂O (Mutter et al., 2002).

3.5. μ-Raman

Fig. 5 reports the Raman spectra obtained from the yellow material. The most important information derives from the presence of peaks at 3474 and 3222 cm⁻¹, indicative for the presence of OH bonds, with two well different vibration frequencies. Moreover, two other intense peaks occur at 812 and 744 cm⁻¹. This spectral region is indicative for symmetric stretch vibration of the UO₂²⁺ uranyl ion, with frequency shift depending from the local bonding situation (Amme et al., 2002). For instance, synthetic schoepite shows a doublet close to 855 and 843 cm⁻¹, and variable depend-

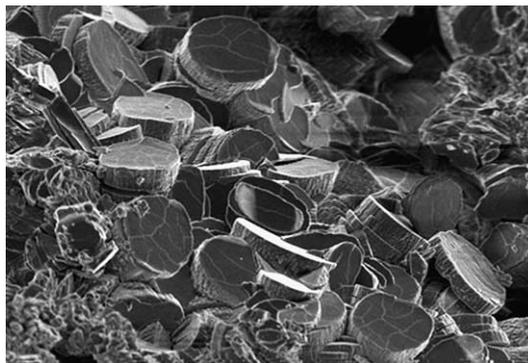


Fig. 4. Prismatic pseudo-hexagonal crystals, approximately 2–10 μm wide, formed by recrystallization of the surrounding yellow mass (top right and bottom left).

ing upon the hydration state. Similarly, studtite UO₄ × 4H₂O shows a couple of peaks at 870 and 820 cm⁻¹. Other uranyl minerals systematically have a peak in the 790–840 range. Experimental corrosion tests yielded yellow products that produce sharp peaks at 817 cm⁻¹ (Amme et al., 2002).

Therefore, we conclude from the Raman spectra that the yellow spots occurring in the Djakovica dart actually correspond to an oxidized corrosion product, containing uranyl ions and hydroxyls and/or water molecules.

4. Discussion and conclusions

The corrosion behaviour of DU has been recently reviewed by Smith (2002). Basically, corrosion rate depends from both the material characteristic and the environmental conditions. For instance, in hot humid air, the U–0.75Ti staballoy used in DU penetrators shows weight gain (after oxidation) one order of magnitude lower than pure uranium. Apparently, fired penetrators made by staballoy corrode slower than unfired penetrators. Factors such as the concentration of O₂, CO₂, HCO₃⁻, NaCl, soil pH and organic carbon content explain the wide range of corrosion rates observed in soils.

According to Smith (2002), experimental corrosion studies under different environmental conditions result

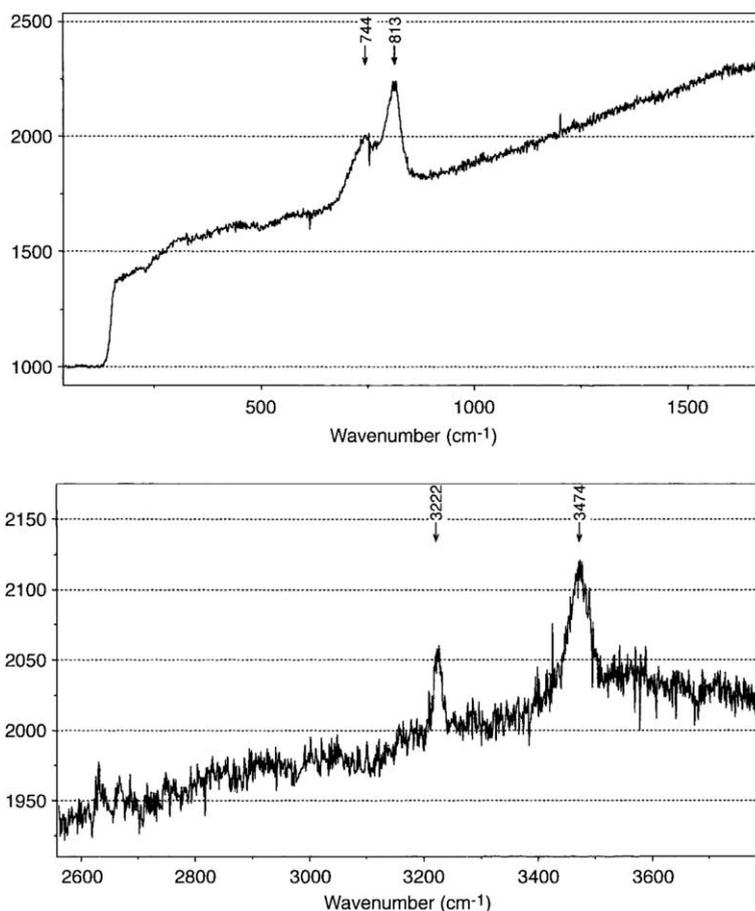


Fig. 5. Raman spectra of the yellow material replacing the uraninite, in the region 2600–3880 and 200–1600 cm^{-1} .

into features such as the occurrence of black corrosion products, yellow deposits, hydrated uranium oxides, eruptions of yellow corrosion products. These results match quite well the corrosion state observed within the real Djakovica dart, after two years from shooting. This dart stood for two years within a perhaps uncommon situation (a concrete platform). Probably most of the shots that missed the target penetrate deeper within the ground, where they undergo corrosion effects under acidic and humid conditions. These conditions may largely differ from the ones expected for the concrete platform (dry and basic). Furthermore, the specific physical state of the DU waste may strongly control the uranium leaching. In fact, dissolution kinetics strongly increases with the increasing flow rate and surface area (Pierce et al., 2002).

Current estimates indicate that most of the rounds remain buried in the soil, with very limited possibility of recovery. As shown by the Djakovica round, they will inevitably undergo oxidation and leaching, progressively releasing mobile uranium forms, such as the observed UO_2^{2+} uranyl ions. The corrosion rate will largely depend

upon the physical state of the given uranium-bearing material (particles or bulk metal), as well as upon the local chemical conditions of the site where uranium waste is deposited (humidity, pH, temperature, and so on). Most probably, the metallic Djakovica round, embedded within cement, was weathering more slowly than the uranium fog consisting of fine dispersed uranium oxide particles produced during firing and impact.

Up to now, measurements from the battlefields seem to indicate that contamination occurs as hotspots, located close to the impact sites (e.g., Murray et al., 2002). Similar conclusions were drawn by authors who studied bio-monitors such as lichens (Loppi et al., 2003) and earthworms (Di Lella et al., 2003a,b) to investigate the environmental impact of DU in this area.

However, we may expect that uranium may be progressively dispersed far from the impact sites, at a rate controlled by the local presence, or absence, of mechanisms capable to fix uranium (Daff et al., 2002, and references therein). Therefore, we feel necessary to maintain a long term geochemical control of water pollution within the areas surrounding the battlefield.

Indeed a monitoring of the groundwaters of Djakovica area, performed in autumn 2001, by the determination of U content in 247 wells, gave a range values of $0.001\text{--}27.8\ \mu\text{g l}^{-1}$, while $1.5\ \mu\text{g l}^{-1}$ was the average value and $0.3\ \mu\text{g l}^{-1}$ the median (still unpublished data). These figures are quite compatible with the natural uranium values in groundwaters; more specifically, they pertain to the low uranium rank. For instance, the allowed maximal uranium concentration in drinkable water has been established in EU as high as $100\ \mu\text{g l}^{-1}$ (EU, 1998).

Assuming that the weathering state of the Djakovica dart may be considered representative of the general situation, we also conclude that most of the corrosion must still occur. Therefore, the available geochemical determinations, done in the Djakovica wells since 2001, represent a good estimate of the natural uranium background in the area, before the Kosovo war.

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