Environmental chemistry of uranium

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Abstract

Uranium as a lithophilic element of not negligible chemical toxicity and in the same time as a natural radioactive component of the environment occurs in the Earth's crust reaching an average concentration almost $4 \cdot 10^{-4}$ percent by mass. In spite of these facts the existence of uranium did not bring about significant environmental impacts – in whole of their context – until uncontrolled militarization and nuclear weapon testing have been realized in the middle of the last century. While the indefectible operation of the world's more then four hundred energetic nuclear reactors including the related radioactive waste management comprise a consequential issue, processes and facilities designated for spent nuclear fuel reprocessing represent a special piece of the problem depicted. All of the pertinent activities are connected to uranium exploitation and may contribute to devastation of the environment. Furthermore, a large deal of activities in question disturb the natural balance between uranium and its daughter radionuclides in germane locations. In recent time the related problems are discussed even more frequently because of constantly rising uranium prices, which in the last 20 years have increased more than 10-times and the latest progress in the area of technologies utilized for obtaining and exploitation of uranium from its less abundant ores should be considered as well. The mentioned facts give reasons to possess an overview of uranium's environmental features including the most efficient methods recently used for uranium detection - the need of fast, sensitive and reliable determination of uranium in various concentrations in waters, sediments and soil samples providing its trouble-free monitoring is out of question. This paper intends to highlight the most important characteristics of uranium controlling its behaviour in the environment and so closely connected to its physicochemical and toxicological properties.

1 Introduction

Approximately five percent of all known minerals contain uranium as an essential structural constituent. Therefore uranium minerals display a remarkable structure and chemical diversity. They are excellent indicators of geochemical environments, which are closely related to geochemical element cycles. The oxidation and dissolution of uranium minerals leads to growth of its concentration in hydrothermal as well as meteoric fluids. Under reducing conditions, uranium transport is likely to be measured in fractions of centimetre. Where conditions are sufficiently oxidizing to stabilize the uranyl ion (UO_2^{2+}) and its complexes, uranium can migrate many kilometres from its source in altered rocks and then precipitate into uranium minerals [29].

Uranium, thorium and potassium are the main elements contributing to natural terrestrial radioactivity. Uranium of natural isotopic composition consists of three isotopes: $^{238}\mathrm{U}$, $^{235}\mathrm{U}$ and $^{234}\mathrm{U}$, all of them are radioactive. $^{238}\mathrm{U}$ is an alpha emitter, decaying through the 18-member uranium natural decay series into $^{206}\mathrm{Pb}$. The decay series of $^{235}\mathrm{U}$ (the actinouranium series) has 15 members that ends in stable $^{207}\mathrm{Pb}$. This series includes only two long lived ($>$ several days) radioactive members, namely $^{231}\mathrm{Pa}$ ($T = 3.28\mathrm{years}$) and $^{227}\mathrm{Ac}$ ($T = 21.77\mathrm{days}$). Only $^{235}\mathrm{U}$ is a valuable fuel for electricity production. During the manufacture of nuclear fuel, the concentration of $^{235}\mathrm{U}$ is commonly increased from about 0.71% to about $3-4\%$. The residue of depleted uranium, which contains about 0.2% $^{235}\mathrm{U}$, is used chiefly in armor piercing shells and for counterweights because of its pyrophoric

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properties and its high density. Uranium is fast acquiring notoriety as a radiological hazard. In fact, its radiotoxicity is known to be low. However, its chemical toxicity should not be ignored. Generally, only dissolved uranium is chemically toxic. In its most common and bioavailable forms uranium exists as a uranyl ion and shares many chemical and biological properties with the alkaline earth ions [66, 68, 82].

Uranium is a very reactive element readily combining with many elements to form a variety of complexes. The oxygen containing uranium compounds as well as the uranyl ion can combine easily with Cl^-, Na_3^-, SO_4^{2-} and CO_3^{2-}. In aerated aqueous solutions at $pH \leq 2.5$, the uranyl ion is very stable. Near pH 7, uranyl ion forms stable complexes with phosphate and carbonate. The information concerning the uranium ion species actually present in the water supply is critical for the selection of the treatment process and its successful operation [78].

Numerous methods are available for the determination of uranium, depending on experimental objectives and the type of analysis attempted. In addition to conventional methods such as fluorometric analysis, various other techniques are available, based on the radioactivity of uranium. These methods should effectively measure its radioactivity, which is not always proportional to the total mass concentration of uranium [53].

The purpose of uranium mining is to produce fuel for civilian nuclear power plants and for military programs. Extraction of uranium ores, milling and chemical processing to prepare a uranium concentrate, known as yellow cake (U_3O_8), are accompanied by the production of large amounts of solid and liquid residues. They contain hazardous elements, including uranium and daughter products of uranium decay chains, which may occur in the groundwater in concentration exceeding relevant protection standards. Environmental impact and health risks related to uranium mill tailing occur by two main processes. One is surface soil/water contamination by erosion and wind dispersion of radioactive material and air pollution by radon emission. The other is contamination of the subsurface including groundwater due to leaching and leaking of radioactive and hazardous metals (Cd, Cu, Pb, Zn) from the tailings [1].

2 Properties of uranium in respect of environmental protection

Uranium is a chemical element with atomic number 92. As mentioned above, natural uranium is a mixture of three isotopes, ^{238}U (99.276%), ^{235}U (0.718%) and ^{234}U (0.004%). Uranium is a naturally occurring, ubiquitous, lithophilic metal found in various chemical forms including abiotic and biotic environmental forms, e.g. in soils, rocks, seas, oceans and microorganisms [36].

Uranium is a heavy, silvery-white, ductile, weakly radioactive, strongly electropositive and slightly paramagnetic metal exhibiting poor electrical conductivity. It is an easily oxidizable element, which in the air becomes coated with a layer of oxide. Thus in nature uranium mainly occurs in oxidized forms. The abundance of uranium in the Earth's crust roughly corresponds with that of Mo and As and in the same time it is more plentiful than Cu, Sb, W and Cd. Uranium metal powder is autopyrophoric and can burn spontaneously at room temperature in the presence of air, oxygen and water. At $200 - 400°C$ uranium powder may self-ignite in atmospheres of CO_2 and N_2. Oxidation of uranium under certain conditions may generate sufficient energy to cause a chemical explosion [4, 12, 35]. At laboratory temperature uranium is malleable. After heating it becomes fragile and by increasing the temperature uranium behaves as a plastic material [14]. It may exist in three allotropic modifications, namely in *orthorhombic*, *tetragonal* and in *body-centered cubic* ones [28]. Uranium exhibits a high melting point ($1132°C$) and it is one of the heaviest naturally occurring elements. The density of uranium ($19.05\ g\ cm^{-3}$) is 65% higher than that of lead [12, 14].

Uranium can be prepared from its oxide via reduction by calcium or magnesium. This metal reacts with almost all non-metallic elements as well as with their compounds increasing its reactivity with temperature [28, 50].

Depleted uranium (DU) is the major waste product of uranium enrichment. In typical DU the content of ^{235}U is about one-third of its original value ($0.2 - 0.3\%$). DU was used in three recent conflicts in the form of DU projectiles: in Iraq and Kuwait (1991), in Bosnia-Herzegovina (1995) and in Kosovo (1999). The radiological and chemical properties of DU can be compared to those of natural uranium, both they have very similar chemical toxicity. The presence of DU has been recorded in urine, faeces, hair and nails [12].

Uranium can exist in five oxidation states: $+2$, $+3$, $+4$, $+5$ and $+6$. However, only the $+4$ and $+6$ states are stable enough to be of practical importance. *Tetravalent uranium* is reasonably stable and forms *hydroxides, hydrated fluorides* and *phosphates* of low solubility. *Hexavalent uranium* is the most stable state and the most commonly occurring form is U_3O_8. Major compounds of uranium include oxides, fluorides, carbides, nitrates, chlorides, acetates and others [28, 50]. The synthesis of new uranium-containing complexes continues targeted first of all to study of covalent behaviour of uranium and to gain more information concerning uranium coordination chemistry in general. A number of uranium-containing complexes have been shown to be useful in applications such as catalysis, ion and neutral molecule sensing and small molecule activation [76].

Table 1: Solubility of selected uranium compounds in various solvents [4]

Uranium compound	**Solubility**	
	Water	**Other solvents**
Uranium (U)	Insoluble	soluble in acids
Uranium dioxide (UO_2)	Insoluble	soluble in HNO_3
Uranium trioxide (UO_3)	Insoluble	soluble in HNO_3, HCl
Triuranium octaoxide (U_3O_8)	Insoluble	soluble in HNO_3, H_2SO_4
Uranium tetrafluoride (UF_4)	very slightly soluble	soluble in concentrated acids and alkalis
Uranium hexafluoride (UF_6)	Decomposes	soluble in CCl_4 and chloroform
Uranium tetrachloride (UCl_4)	Soluble	soluble in ethanol
Uranyl fluoride (UO_2F_2)	Soluble	soluble in ethanol
Uranyl acetate dehydrate ($UO_2(CH_3COO_2)_2 \cdot 2H_2O$)	$7.7 g/100\ cm^3$ at $15°C$	soluble in ethanol
Uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$)	miscible in water at $15°C$	soluble in ethanol
Ammonium diuranate ($(NH_4)_2U_2O_7$)	practically insoluble	soluble in acids
Uranium peroxide (UO_4)	Decomposes	no data available

Uranium metal heated from 250 to $300°C$ reacts with hydrogen to form *uranium hydride*. Even higher temperatures will reversibly remove the hydrogen. Two crystal modifications of uranium hydride exist: the *α form* (obtained at low temperatures) and the *β form* (the formation temperature is above $250°C$). Both, *uranium carbides* (UC, UC_2, U_2C_3) and *uranium nitrides* (UN, UN_2, U_2N_3) are relatively inert semimetallic compounds. They exhibit minimal solubility in acids, react with water and can ignite in air to form U_3O_8. All *uranium fluorides* (UF_3, UF_4, UF_6) can be produced using uranium tetrafluoride. UF_4 itself is prepared by hydrofluorination of uranium dioxide. *Bromides* and *iodides* of uranium are formed by direct reaction of bromine and iodine respectively with uranium or by adding UH_3 to the relevant element's acids. *Uranium oxyhalides* are water-soluble and include UO_2F_2, $UOCl_2$, UO_2Cl_2 and UO_2Br_2. The stability of these compounds decreases as the atomic weight of the component halide increases [38].

Uranium is a relatively *mobile element* in the near surface zone owing to the stability of U(VI) aqueous complexes. However, it may be precipitated by reduction to U(IV) or in the form of uranium minerals, principally *phosphates, silicates, arsenates, vanadates* and *oxyhydroxides*, several of which may occur simultaneously at the same locality. The amount of uranium released to ground- or surface waters from these secondary sources will depend on the solubility and dissolution rate of the phases as a function of *pH and water composition* [15]. Therefore, information about the solubility of uranium compounds is crucial because of their potential migration in the environment (Table 1).

Uranyl species are less prone to hydrolysis than U(IV) and consequently colloids play a less significant role in the near surface transport of uranium than thorium. An important exception to this general rule occurs in organic-rich environments, such as peat bogs. Organics of high molecular weight (humic acids) possess a strong affinity towards uranium and spectroscopic studies indicate that it is bound in the U(VI) state [47, 69]. Uranium sulphate and carbonate complexes are soluble and migrate with the groundwater. U(VI) can be complexed by humic acids associated with peat under acidic to alkaline pH conditions. This may retard U(VI) migration by adsorption of the complex U(VI) – humic acid onto aquifer material. Investigation of uranium mine water samples from Germany resulted in knowledge that uranium speciation strongly depends on their pH values. It was found the following uranium species: $Ca_2UO_2(CO_3)_3$ (aq.) at $pH = 7.1$ in carbonate and Ca-containing mine water, $UO_2(CO_3)_3^{4-}$ at $pH = 9.8$ in carbonate-containing and Ca-poor tailing water, UO_2SO_4 (aq.) at $pH = 2.6$ in sulphate-rich mine water [1].

The role and importance of *redox reactions* in determining actinide subsurface mobility are beyond question. In the subsurface, redox control is often established by the iron mineralogy and associated aqueous chemistry. The mechanisms by which redox control is established are a key aspect of remediation and immobilization strategies for actinides when they are present as subsurface contaminants. The important effects of redox-active minerals and microbial processes on subsurface redox processes are not mutually exclusive [70].

Variations in temperatures, pressure and solution composition (pH, oxidation-reduction potential, ionic strength

Table 2: Classification of uranium compounds in respect of their solubility in organism [12]

Type F (fast)	Type M (medium)	Type S (slow)
Uranium hexafluoride (UF_6) Uranium tetrachloride (UCl_4) Uranyl fluoride (UO_2F_2) Uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$)	Uranium tetrafluoride (UF_4) Uranium trioxide (UO_3)	Uranium dioxide (UO_2) Triuranium octaoxide (U_3O_8)

and the presence of complex-forming ligands) mean that scores of aqueous actinide species can be involved in a diverse array of geochemical and environmental processes. Attention paid to aqueous speciation of uranium makes it possible to construct oxidation potential-pH diagram. Among these, Eh (oxidation potencial), pe (negative base ten logarithm of the activity of the aqueous electron), fO_2 (fugacity of oxygen) and fH_2 (fugacity of hydrogen) are in common usage. Hydrolysis constants and redox relations among aqueous uranium species can be used to generate oxidation potential-pH diagrams at various temperatures and pressures [60].

These facts correspond to others mentioned below in Table 2, where data concerning the solubility of selected uranium compounds in the body fluids are presented. Generally, the major uranium oxides generated are U_3O_8, UO_2 and UO_3. These three compounds are relatively insoluble, dissolving only slowly in organism.

3 Uranium toxicological profile

Uranium is a metal whose biological effects are very similar to other heavy metals (Pb, Hg, Cd). It has been identified as a nephrotoxine. Its nephrotoxic effects are more likely due to its chemical properties rather than its radioactivity, although ingested uranium may have a radiological effect on other tissues of deposition [51].

As it was mentioned, the chemical toxicity of soluble uranium compounds can even surpass the potential radiotoxic effects. The general population may be exposed to low level of uranium by inhalation or through the diet. Uranium may be also introduced into drinking water supplies through the mining and milling of uranium ores [23]. Although the biokinetics, metabolism and chemical toxicity of uranium, including its toxic effects on kidney function, are well established, there was a lack of published observations regarding uranium-induced reproductive and developmental toxic effects [22]. The latest experimental studies in mammals have demonstrated that during pregnancy, maternal stress may enhance the metal-induced adverse effects on embryo/fetal and postnatal development [24]. Even if the kidney is a critical organ for uranium toxicity, the brain could also be a target organ after uranium exposure. Central effects were observed, even though uranium brain levels were very low [52]. Many isolated studies were published on the mechanism for the toxic effects of uranium at moderate to high acute doses on experimental animals. However, from the ethical point of view, only a few works were done on the bioeffects of chronic uranium intakes by human [11].

Depleted uranium is a low-level radioactive waste product of natural uranium enrichment with ^{235}U for reactor fuels or nuclear weapons. The radiological hazard of depleted uranium is less than that from natural or enriched uranium. However, depleted uranium is also a heavy metal with toxicity being a function of route of exposure, particle solubility, contact time and route of elimination. Consequently, depleted uranium exposure can result in both chemical toxicity and toxicity from radioactivity. The first one (mainly on kidney) occurs in general at lower exposure levels than the radiological toxic effects. One conception is inhalation exposure to insoluble uranium compounds, about which the main concern is increased cancer risk from the internal exposure to radioactivity. In contrast, insoluble compounds are poorly absorbed from the gastrointestinal tract and generally have low toxicity [4, 16, 23].

3.1 Mechanism of uranium toxicity and toxicokinetics

The renal and respiratory effects from exposure of humans and animals to uranium are usually attributed to its *chemical properties*, while theoretically potential excess cancers are usually attributed to its *radiation properties* [6, 21, 26]. In general, large doses of ionizing radiation have the actual or theoretical potential of being carcinogenic, teratogenic and mutagenic. DNA has been found to be the most radiosensitive biological molecule, and ionizing radiation has been observed to damage individual chromosomes. The main result from low level ionizing radiation exposure is DNA damage or fragmentation. Viable cells repair the damage but these errors can result in production gene mutation or chromosomal aberrations. The latest mentioned following large radiation doses have been demonstrated in humans and in research animals, showing that ionizing radiation can both initiate and promote carcinogenesis, and interfere with reproduction and development [58, 73, 83, 85].

The most sensitive indicator of uranium toxicity to mammals, and perhaps humans, is nephrotoxicity. While acute high level exposure to uranium compounds can clearly cause *kidney diseases* in humans, the evidence for similar toxicity as the result of long-term lower level occupational exposure is equivocal [64, 92]. Epidemiologic studies have not noted an increase in deaths from urogenital or renal diseases following occupational exposure to uranium [13, 17]. Most studies of *respiratory diseases* reported for uranium involve noncancerous damage of alveolar epithelium cell. These changes are characterized by interstitial inflammation of the alveolar epithelium leading eventually to serious diseases, which reduce respiratory function of lungs [26, 89].

Biokinetics of uranium depends strongly on the chemical form administrated or the route of exposure. On the other hand, its uptake and retention by the kidney and skeleton depends on age, gender and the mass uranium input [49]. The human body naturally contains approximately $56\ \mu$g of uranium, $32\ \mu$g (56%) are in the skeleton, $11\ \mu$g in muscle tissue, $9\ \mu$g in fat, $2\ \mu$g in blood and less than $1\ \mu$g in lung, liver and kidneys [30].

Absorption of uranium is low by all exposure routes (inhalation, oral and dermal). Absorption of inhaled uranium compounds takes place in the respiratory tract via transfer across cell membranes. The deposition of inhaled uranium dust particles in the lungs depends on the particle size and its following absorption used to be effected by its solubility in biological fluids [41, 42]. Estimates of systemic absorption from inhaled uranium-containing dusts in occupational settings based on urinary excretion of uranium range from 0.76 to 5%. Gastrointestinal absorption of uranium can vary from < 0.1 to 6% depending on the solubility of the uranium compound. Studies in volunteers indicate that approximately 2% of the uranium from drinking water and dietary sources is absorbed in humans. Another comprehensive review shows that the absorption is 0.2% for insoluble compounds and 2% for soluble hexavalent compounds [42, 48, 79].

Concerning dermal absorption, toxicity experiments in animals indicate that water soluble uranium compounds are the most easily absorbed ones. Once in the blood, uranium is distributed to the organs of the body. Uranium in body fluids generally exists as the uranyl ion complexed with anions such as citrate and bicarbonate. Uranium preferentially distributes to bone, liver and kidney. Half-times for retention of uranium are estimated to be 11 days in bone and $2 - 6$ days in the kidney. The uranium burden of human body is approximately $90\ \mu$g. The large majority of uranium ($> 95\%$) that enters the body is not absorbed and is eliminated via the feces. Excretion of absorbed uranium is mainly via the kidney as it has been mentioned above [55].

3.2 Inhalation and ingestion

Both inhalation and ingestion of uranium compounds have been shown to produce renal injury in laboratory animals characterized by damage to the glomerulus and proximal epithelium [84].

The toxicity of uranium compounds to the lungs and distal organs varies when exposed by the inhalation route. In general, more soluble compounds ($\mathrm{UO_2F_2}$, $\mathrm{UCl_4}$, $\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$) are less toxic to the lungs but more toxic systematically by the inhalation route due to easier absorption from the lungs into the blood and transportation to distal organs [80].

The maximal dosage just failing to be lethal for rats in a 30-day feeding test was about 0.5% uranium compound in the diet for the three compounds ($\mathrm{UO_2(NO_3)_2 \cdot 6H_2O}$, $\mathrm{UO_2F_2}$, $\mathrm{UCl_4}$) and 20% uranium compound for the three insoluble uranium compounds ($\mathrm{UO_2}$, $\mathrm{UO_3}$ a $\mathrm{U_3O_8}$) tested. No amount of insoluble uranium compound acceptable to rat was lethal. Dietary levels of $1-4\%$ soluble uranium compound caused 50% mortality in 30 days. The marked difference in the toxicity of soluble and insoluble uranium compounds is attributable to the easy of absorption and, thus the dose that reaches the target organs [25, 63].

4 Analytical determination of uranium

Uranium is unique in that it is one of few naturally occurring radionuclides and can be determined by direct radiometric counting techniques. These techniques, however, are limited in their applicability due to the low specific activity of uranium and low concentrations at which it is typically found in nature. It is frequently necessary to preconcentrate and extract uranium in order to reduce the volume of solution and increase the uranium concentration. It can be achieved by *coprecipitation, liquid-liquid extraction, liquid membranes, ion-exchange, extraction chromatography, flotation, adsorptive accumulation, solid phase extraction* or *ion imprinting polymers* [67, 90].

As uranium is a relatively mobile element in many surface or near surface environment, its geochemical exploration methods require the measurement of the trace quantities of metal ion in water samples along with that in plants, soil and rocks [34].

The techniques which can be used for trace analysis generally have sensitivity but are complex and costly, require skilled technicians and large laboratory-based instrumentation. Long analysis time, extensive sample handling with multiple washing steps and transportation and storage prior to detection and quantification are other limitation [44].

Knowledge of the uranium content in the environment is important mainly because of its high chemical toxicity. Table 3 summarizes several analytical methods used for uranium determination in various environmental samples. Among the most frequently used techniques belong: *spectrophotometry, radiometric methods* (α - spectrometry, γ - spectrometry), *techniques of neutron activation* analysis (INAA - instrumental neutron activation analysis, RNAA - radiochemical neutron activation analysis, FTA - fission track analysis), *atomic spectrometric techniques* (AAS - atomic absorption spectrometry, AES - atomic emission spectrometry, ICP - AES - inductively coupled plasma - atomic emission spectrometry, XRF - X - ray fluoresce), *mass spectrometry, gas chromatography, complexometric titration and numerous electrochemical methods* [27, 34, 86, 90].

ICP-MS is an interesting alternative method for uranium determination. This method has several advantages, e.g. short duration of the analysis, low detection limits (ng per dm^3), low sample consumption and minimum of spectral interferences [27].

Voltammetric techniques are known to show unique advantages both economical (low initial and running costs) and strictly analytical (the ability to determine low levels of metal in different matrixes). In particular, stripping techniques are perfectly suited for trace and ultratrace metal determination [57]. Adsorptive cathodic stripping voltammetry (ACSV) is based upon adsorptive accumulation of metal ion complex with a suitable ligand at the electrode and then scanning the potential of the electrode in the negative direction. Several complexing reagent already have been applied to determine uranium by ACSV such as *catechol, mordant blue, oxine, cupferron, DTA, propyl galate, 2-TT-TBP, xylidyl blue, TTA, triphosphineoxide, potassium hydrogen phthalate, chloranilic acid, aluminon, PAR and salicylidenimine* [34].

Uranium (VI) forms a complex with dipicolinic acid (2, 6-pyridinedicarboxylic acid), which can be highly sensitive and selective determined by ACSV using a hanging mercury drop electrode [34]. This technique was also applied for determination of Ni, Co, Rh and U in the lake water samples. Very good precision and accuracy were achieved, e.g. relative percentage of standard deviation varied from 2 to 5% [57]. The simultaneous ACSV determination of Mo, Sb, V and U as their chloranilic acid (2, 5-dichloro-4, 6-dihydroxy-1, 3-benzoquinone) complexes have been investigated as well. A pH of $2.3-3$, for sweet or sea water, a chloranilic acid concentration of 1×10^{-4} mol dm^{-3}, and accumulation potential of $+50$ mV were chosen for the analysis [72].

Table 3: Overview of analytical methods for uranium determination in environmental samples [4]

Sample matrix	Analytical method	Detection limit	Accuracy
Air	ICP-MS (total uranium)	$0.1\ \mu\mathrm{g\ dm}^{-3}$ in final solution	———
	α-spectrometry	5.55×10^{-4} Bq	———
	INAA	$0.03\ \mu\mathrm{g}$ on filter	———
Rainwater	α-spectrometry (isotope quantification)	0.02 dpm dm^{-3} for $^{238}\mathrm{U}$ in solution	68%
Drinking water	fluorometry (total uranium)	$< 20\ \mu\mathrm{g\ dm}^{-3}$ (directly); $0.1\ \mu\mathrm{g\ dm}^{-3}$ (pure)	104% (cleaned)
	gross α-counting (total uranium)	$0.037\ \mathrm{Bq\ dm}^{-3}$	92.60%
	laser inductive fluorometry	$0.08\ \mu\mathrm{g\ dm}^{-3}$	100% from $1\ \mu\mathrm{gdm}^{-3}$
Natural waters	spectrophotometry (total uranium)	$0.1\ \mu\mathrm{g\ dm}^{-3}$	100% from $1\ \mu\mathrm{g\ dm}^{-3}$
Water	fluorometry (total uranium)	$5\ \mu\mathrm{g\ dm}^{-3}$	117.5% at $6.3\ \mu\mathrm{g\ dm}^{-3}$
	α-spectrometry (isotope quantification)	0.02 dpm dm^{-3}	$97.7-108\%$ $0.028-0.044\ \mathrm{Bq\ dm}^{-3}$
	α-spectrometry (isotope quantification)	0.02 dpm dm^{-3} for $^{238}\mathrm{U}$ in solution	———
	NAA (total uranium)	$3\ \mu\mathrm{g\ dm}^{-3}$	$> 80\%$

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Sample matrix	Analytical method	Detection limit	Accuracy
	pulse laser phosphorimetry	0.05 ppb	103% (average)
Groundwater	FI-ICP-MS (isotopic quantification)	3 ng dm^{-3} for $^{238}\mathrm{U}$	$\pm 1.8\%$
	spectrometry (total uranium)	$1.2\ \mu\mathrm{g\ dm}^{-3}$	———
Water and waste	ICP-MS (total uranium)	$0.1\ \mu\mathrm{g\ dm}^{-3}$	$105-110\%$
Sea water	X-ray fluorescence (total uranium)	$0.56-0.64\ \mu\mathrm{g\ dm}^{-3}$	———
	cathodic stripping voltammetry (total uranium)	$0.02-0.2\ \mathrm{nmol\ dm}^{-3}$	
Soil, sediment and biota	α-spectrometry (isotope quantification)	$0.3\ \mu\mathrm{g/sample}$	67%
Minerals	laser fluorometry	———	———
Building materials and lichens	α-spectrometry (determination of isotopic amount)	$0.3\ \mu\mathrm{g/sample}$	$54-73\%$
Vegetation	ICP-MS (total uranium)	$0.1\ \mu\mathrm{g\ dm}^{-3}$	———
	laser fluorometry (total dissolved uranium)	$0.05\ \mathrm{mg/kg}$ in plant ash	———
Process water	laser fluorometry (total dissolved uranium)	$0.01\ \mu\mathrm{g\ dm}^{-3}$	———
	ion chromatography, spectrophotometric determination of U(VI)	$0.04\ \mathrm{mg\ dm}^{-3}$	
Rocks minerals, biological material	spectrophotometric	$0.062\ \mathrm{mg\ dm}^{-3}$ (with back extraction)	$99-103\%$
Coal ash	ICP	$29\ \mu\mathrm{g\ dm}^{-3}$	98%
Sediment, pore water	ICP-MS	$40\ \mathrm{pg\ cm}^{-3}$	99%
Field survey	scintillation detector	200-500 dpm/100 cm^2	———

5 Uranium occurrence in the environment

Uranium is a component of practically all rocks and therefore it is classified as a lithophilic element. Its relative abundance compares to silver, gold and the light rare earths elements and it is more common than tin, mercury and lead. It occurs in numerous minerals and is also found in lignite, monazite sands, phosphate rock and phosphate fertilizers, in which the uranium concentration may reach as much as $200\ \mathrm{mg\ kg}^{-1}$. Uranium is usually present in minerals either as a *major* or as a *minor component* (Table 4). The *primary uranium minerals* are generally black or dark brown, noticably heavy and often have a shiny or pitch-like luster.

There are only three known primary uranium ore minerals (*uraninite* ($\mathrm{UO_2}$), *pitchblende* ($\mathrm{U_3O_8}$) and *davidite* ($(\mathrm{Fe,\ Ce,\ U})_2(\mathrm{Ti,\ Fe,\ V,\ Cr})_5\mathrm{O}_{12}$). Sometimes they are altered to form the bright-coloured *secondary uranium minerals* (complex oxides, silicates, phosphates, vanadates). Also *specific micas* contain uranium in the form of sulphates, phosphates, carbonates and arsenates, which are products of the weathering of original uranium ores [12, 18, 56, 59, 62].

Uranium is found at an average concentration of $\sim 0.0003\%$ in the Earth's crust. The levels of uranium in natural igneous rocks and sedimentary rocks may vary from 0.5 to $4.7\ \mu\mathrm{g\ g}^{-1}$. In carbonate rocks, the average

Table 4: Overview of selected uranium minerals [29]

Minerals with uranium as an essential component		**Minerals with uranium as a minor component**	
Name	*Formula*	*Name*	*Formula*
Uraninite	$(U^{4+}_{1-x-y-z}U^{6+}_{x}REE^{3+}_{y}M^{2+}_{z})O_{2+x-y-z}$	Betafite	$(Ca, Na, U)_2(Ti, Nb, Ta)_2O_6(OH)$
Coffinite	$USiO_4 \cdot nH_2O$	Brabantite	$Ca(Th, U)(PO_4)_2$
Brannerite	$(U, Ca, Y, Ce)(Ti, Fe)_2O_6$	Davidite	$(Ce, La)(Y, U, Fe^{2+})(Ti, Fe^{3+})_{20}(O, OH)_{30}$
Orthobrannerite	$(U^{6+}, U^{4+})(Ti, Fe)_2O_6(OH)$	Ekanite	$Ca_2(Th, U)Si_8O_{20}$
Ianthinite	$U^{4+}(U^{6+}O_2)O_4(OH)_6(H_2O)_9$	Huttonite	$(Th, U)SiO_4$
Ishikawaite	$(U, Ca, Y, Ce)(Nb, Ta)O_4$	Kobeite-(Y)	$(Y, U)(Ti, Nb)_2(O, OH)_6$
Lermontovite	$U(PO_4)(OH)(H_2O)_n$	Mckelveyite-(Y)	$Ba_3Na(Ca, U)Y(CO_3)_6(H_2O)_3$
Moluranite	$H_4U(UO_2)_3(MoO_4)_7(H_2O)_{18}$	Monazite-(REE)	$(La - Sm)PO_4$
Mourite	$UMo_5O_{12}(OH)_{10}$	Plumbobetafite	$(Pb, U, Ca)(Ti, Nb)_2O_6(OH, F)$
Ningyoite	$(U, Ca, Ce, Fe)_2(PO_4)_2 \cdot 1 - 2H_2O$	Plumbomicrolite	$(Pb, U, Ca)_2Ta_2O_6(OH)$
Petschekite	$UFe^{2+}(Nb, Ta)_2O_8$	Plumbopyrochlore	$(Pb, U, Ca)_{2-x}Nb_2O_6(OH)$
Sedovite	$U(MoO_4)_2$	Samarskite-(Y)	$(Y, REE, U, Fe^{3+}, Fe^{2+})(Nb, Ta)O_4$
Uranomicrolite	$(U, Ca, Ce)_2(Ta, Nb)_2O_6(OH, F)$	Thorianite	$(Th, U)O_2$
Tyuyamunite	$Ca(UO_2)_2(V_2O_8)(H_2O)_8$	Thorite	$(Th, U)SiO_4$
Carnotite	$K_2(UO_2)_2(V_2O_8)(H_2O)_3$	Thorogummite	$(Th, U)(SiO_4)_{1-x}(OH)_{4x}$
Torbernite	$Cu[(UO_2)(PO_4)]_2(H_2O)_8$	Tristramite	$(Ca, U^{4+}, Fe^{3+})(PO_4, SO_4)(H_2O)_2$
Autunite	$Ca[(UO_2)(PO_4)]_2(H_2O)_{10-12}$	Yttrobetafite-(Y)	$(Y, U, Ce)(Ti, Nb, Ta)_2O_6(OH)$
Vyacheslavite	$U(PO_4)(OH)(H_2O)_{2,5}$	Yttrocrasite-(Y)	$(Z, Th, Ca, U)(Ti, Fe^{3+})_2(O, OH)_6$

Note: REE – Rare Earth Element

level is 2.0 μg g^{-1}. Unconsolidated beach sands contain an average concentration of 3.0 μg g^{-1} of uranium. The uranium content in soil is related to the bedrock from which the soil is formed. The average concentration of uranium in soils is about 1.8 μg g^{-1}. Taking the typical pH range of natural aqueous systems between pH 4 and pH 9 and the relative atmospheric CO_2 partial pressure of 0.03% a highly mobile carbonated species of uranium is formed. Thus, uranium is eluted from soils to rivers and lakes. Continental surface waters contain from 0.1 to 500 μg dm^{-3} of uranium. The uranium concentrations in rivers have been already studied several times and range from 0.2 to 0.6 μg kg^{-1}. However, a major deposit of uranium represents seawater with the concentration about 3.0 μg g^{-1} [12, 43, 46, 56].

Uranium mobility in soil and its vertical transport to groundwater depends on soil properties (pH, redox potential, soil matrix porosity, particle size, amount of available water) [9]. Retention of uranium in soil is a result of several processes such as adsorption, chemisorption, ion exchange or their combination [2]. The uranium sorption rate of soils with abundant clay and Fe content is generally high. Therefore, normally uranium does not reach the groundwater level [77]. Concentration of uranium in the air is effected by concentration and its particle size, which may have dimensions from 1 to 10 μm [10].

Two main groups of deposits are recognized, those of igneous plutonic or volcanic association, including metamorphic deposits and those of sediment/sedimentary basin association (Table 5). On the basis of geological setting and in order of economic importance the classes of uranium deposits are: (1) *Unconformity related*, (2) *Sandstone*, (3) *Quartz-pebble conglomerate*, (4) *Veins*, (5) *Breccia complex*, (6) *Intrusive*, (7) *Phosphorite*, (8) *Collapse breccia*, (9) *Volcanic*, (10) *Surficial*, (11) *Metasomatite*, (12) *Metamorphic*, (13) *Lignite* and (14) *Black shale* [66].

Deposits of economic interest consist of a variable number of veins ranging in size from short and hairlike stringers to those several kilometres long and as much as several metres thick. Vein uranium deposits are epigenetic concentrations of uranium minerals, typically pitchblende and coffinite, in fractures shear zones and stockworks. The uranium minerals are either the *sole metallic* constituents in the *veins* or in *polymetallic veins*, which are accompanied by other metals, such as Bi, Co, Ni, As, Ag and Cu. The deposits are hosted by: (i) granitic or syenitic rocks (*intragranitic veins*), (ii) rocks surrounding granitic plutons (*perigranitic or peribatholithic veins*), or (iii) sheared or mylonitized, usually metamorphosed, sedimentary or igneous complexes (*veins in shear and fault zones*). Classification of the uranium vein deposits, based on their geological setting, takes into account

Table 5: Classification of uranium deposits [66]

A. IGNEOUS PLUTONIC AND VOLCANIC ASSOCIATION	1. Igneous Plutonic Association	1.1 Magmatic uranium deposits – formed by different of evolved uraniferous magmas	1.1.1 Alkaline complex deposits
		1.2 Formed as a result of high-to-low temperature hydrothermal activity associated with high-level granite magmatism	1.2.1 Granite associated deposits including vein-type deposits
			1.2.2 Perigranitic vein deposits
			1.2.3 Metasomatite deposits
	2. Igneous Plutonic and Volcanic Association	2.1 Deposits associated with granite magmatism and acid volcanic and volcaniclastic sequences in anorogenic setting	2.1.1 Breccia complex deposits
	3. Igneous Volcanic Association	3.1 Formed as a result of high-to-low temperature hydrothermal activity associated with high-level mainly felsic volcanics	3.1.1 Volcanic deposits
B. METAMORPHIC ASSOCIATION	1. Formed by metamorphic fluids probably derived from igneous or sedimentary rocks previously enriched in uranium	1.1 Synmetamorphic deposits	———
		1.2 Vein deposits in metamorphic rocks	———
C. SEDIMENT/SEDIMENTARY BASIN ASSOCIATION	1. Continental	1.1 Associated with late post-orogenic sedimentary basins having mainly clastic fill - formed or modified in some cases by intra-basinal fluid flow	1.1.1 Quartz-pebble conglomerate deposits
			1.1.2 Unconformity-related deposits
			1.1.3 Sandstone deposits
			1.1.4 Sediment-hosted vein deposits
			1.1.5 Collapse breccia deposits
			1.1.6 Lignite deposits
		1.2 Penecontemporaneous with sedimentation or formed by surface weathering	1.2.1 Surficial deposits
	2. Marine	2.1 Oceanic	Phosphorite deposits
		2.2 Epicontinental	Black shale deposits

structural and lithological controls in their localization. *Intragranitic uranium veins* are known to occur in France (*La Crouzille area, Vendée area*), in Portugal (*Beira uranium district*), in Canada (*Millet Brook area, Nova Scotia, Crackingstone Peninsula, Lake Athabasca, Saskatchewan*), in China (*Xiazhuang ore field*) and in Czech Republic (*western part of Bohemia*). Perigranitic uranium veins are known from Czech Republic (*Příbram district*), from Spain (*Ciudad Rodrigo*) and from Portugal (*Beiras and Alto Alentejo districts*). Polymetallic deposits in perigranitic environments have been an important source of uranium in the past. This type of deposit is in Czech Republic (*Jáchymov*), in Germany (*Aue area*), in Canada (*Port Radium deposit at Great Bear Lake*) and in China (*Chanziping*) [71].

Many uranium deposits worldwide contain daughter isotopes in disequilibrium with their parents. Chemical fractionation is the main factor responsible for this. The chemical fractionation includes preferential leaching, selective solubility, adsorption and emplacement processes [19].

6 Uranium ores mining and its environmental impacts

The steps necessary to produce uranium for its various uses include *mining, milling, conversion to uranium hexafluoride, enrichment, reduction* to metal or *oxidation* to uranium oxide, and *fabrication* into the desired shape. Open-pit mining, in situ leaching and underground mining are three techniques that have been used for mining uranium-containing ores. The two most common used mining methods are open-pit and underground mining. The choice of method is influenced by factors such as the size, shape, grade, depth and thickness of the ore deposits. In situ leaching involves dissolving uranium from the host rock with liquids without removing the rock from the ground and can only be carried out on unconsolidated sandstone uranium deposits located below the water table in a confined aquifer [4, 37].

A wide range of uranium-bearing minerals are being mined and processed commercially. Ore extraction and processing may lead to enhanced levels of naturally occurring radionuclides (NORs) in products, by-products and waste as well as in surroundings and installations of the facility. Uranium mining and milling belong to the nine major categories, which were identified on the basis of the probability of occurrence of high levels of NORs [87]. The chief hazard in uranium mining is from radiation, the emission of alpha particles from uranium, radon gas and its particulate daughters (^{218}Po (RaA) and ^{214}Bi (RaC)) [88].

Australia has a long history of uranium mining. Most of the early production came from *Rum Jungle* (North Territory) and *Mary Kathleen* (Queensland). The second generation of uranium mines *Ranger, Nabarlek* and *Olympic Dam* came on line in the 1970s and 1980s. In the early days of uranium mining, only little attention was given to environmental matters and considerable pollution and environmental degradation occurred. For the second generation mines, waste management and environmental protection were given high priority at the initial planning stages resulting in reductions in environmental impact and in rehabilitation costs. The current generation of mines and ore processing plants in Australia has achieved even lower environmental impacts because of *improved water management, maximum consolidated densities and minimum rehabilitation time, returning of tailings to the mine as well as minimising radon release and long-term erosion* [39].

The former German Democratic Republic was the third largest producer of uranium until 1991 when uranium production in the *Erzgebirge area* (Saxony) was halted. It was a major source of uranium for Soviet nuclear programs between 1945 and 1989. The concentration of uranium in the ores was approximately from 0.04 to 0.11%. The total amount of mined materials (ores and tailings) was 1200 million tons. 200 million tons were transported to processing plants. The remaining 1000 million tons were dumped in nature, partly forming new landscapes. As a result of the uranium mining more than 8000 tailings, deposits and shafts remained in Saxony. Dumping occurred without protection for ground and surface water, leaching by rain or distribution of uranium-bearing dust by wind. In this region inhabitants are permanently exposed to an elevated level of natural radioactivity. Additionally, the radiation exposure was increased, sometimes drastically, by mining and processing the uranium ore [45, 56]. The other former *Königstein uranium mine* (Saxony) in Germany was used as a case study for reactive transport modelling as a tool for evaluating mine decommissioning and rehabilitation options. The area consists of a series of sandstone aquifers separated by clay-rich aquitards. From 1950 through to the end of 1990, uranium ore (0.03 wt.$\%$ of uranium) was extracted here by means of an underground in situ leaching process. It involved passing a sulphuric acid leaching solution through isolated blocks of the ore body. The metal-containing solution was then collected at the base of the mine for processing at surface. The simulation results of the modelling show that at low pH and high pe values, uranium is predominantly in the mobile oxidized state (U(VI)). At lower pe value, reduced U(IV) is dominant and the mobility of uranium is limited by the solution of uraninite. The movement of uranium is sensitive to the presence of carbonate minerals, Fe- and Al-oxyhydroxides and sulphides in the aquifer. Where carbonates or gibbsite are present, the precipitation of Fe(III) as $Fe(OH)_3$ limits the extent of uranium depletion. The uraninite mass in the aquifer is also important, because the total uranium flux out depends on the mass of uraninite available. Reducing conditions predominate and they lead to the reduction of infiltrating dissolved U(VI), the precipitation of uraninite and the removal of uranium from solution [5].

The *Mina Fe uranium ore deposit* is the most important in the Spanish Iberian massif (Salamanca). In this area the schist-graywacke complex rocks consist mainly of a metamorphosed sequence, in part turbiditic, of carbonaceous pelitic and fine-grained psammitic rocks, in which sedimentary textures are frequently observed. The uranium mineralization was the result of a hydrothermal three main steps process. It has been intensively eroded and oxidised as well as covered in place by continental Tertiary and Quaternary sediments. Numerous secondary uranium minerals such as yellow gummites, ianthinite, epi-ianthinite, alpha uranotyle, autunite, metaautunite, torbernite, saleeite and uranopilite were formed as a result of the weathering processes. The geochemical behaviour of Fe, U and Mn under acid and oxidising conditions at this site can be summarised as follows: (i) in the oxidising zone the conditions were predominantly acid and the water became abundant in sulphate until all pyrite was consumed, (ii) consequently, uranium was mobilised, Fe(III) and Mn(IV) partially precipitated as oxyhydroxides and (iii) some significant amounts of trace metals (W, Cu, Ni, Co, Zn, Cu) were retained. The study also illustrates the well-known stability of natural UO_2 in the reduced zone [65].

Uranium mining activities in *Cunha Baixa* (Portugal) were extensive between 1967 and 1993, with high production of poor ore. The underground mine pit was filled with poor ore and flooded with sulphuric acid to extract uranium. The extraction of ore left a temporary pond, which floods the underground exploration pit. Ore exploitation left millions of tons of tailings in the surrounding area, close to human houses. Contamination of the area (water and soil compartment) presently represents a serious hazard to human and wildlife. Therefore, the evaluation of the acute toxicity of water and sediments from a pond that floods a uranium mine pit, in two period (spring and autumn) have been studied. Results showed that the sediments were non-toxic, unlike the superficial water. Water toxicity was higher in the autumn, when the effluent was more acidic [3].

The secondary uranium ore of *Um Ara mining area* (Egypt) is composed mainly of uranophane and β-uranophane. They occur in the oxidized zone as idiomorphic crystals filling cavities and as coating on the fracture surface of the alkali-feldspar and albitized granites. The formation of these secondary uranium deposits is manily attributed to the action of oxic groundwater on previously corroded primary uranium minerals present in the host granitic rocks. The uranyl silicate crystals seem to be precipitated from the groundwater by evaporation [19].

In most countries the *geochemical aspects* such as the stability of pile *slopes, dikes and retaining dams* are made in relevant building or mining regulations, while *environmental* and *radiological impacts* have often been neglected. Typical environmental problems arising from mill tailings are: radon emanation, windblown, dust dispersal and the *leaching of contaminants* (including radionuclides, heavy metals and arsenic) into surface and groundwater. The radon from waste material can reach the ambient atmosphere where its free circulation is possible. Emissions to water bodies occur when infiltration of precipitation is unhindered, bottom-liners are absent and no collection of drainage waters is installed [40].

Most *uranium mining* and subsequent *milling* of ores resulted in large volumes of radioactive sand-like residues called mill tailings. These *contain radioactive elements* such as U, Th, Ra, Rn and non-radioactive heavy metals in low concentrations. What is important mill tailings typically *contain about* 85% *of the radioactivity present in unprocessed ore*. They constitute a *potential hazard to public health for very long periods* of time. Uranium mill tailings are of particular environmental concern also because they contain a range of biotoxic heavy metals and other compounds. They may contain sulfidic minerals and thus prone to generate acid mine drainage, the large surface area of the tailings deposits adversely affects large areas of land and renders potentially valuable land unfit for other uses. On the other hand, uranium deposits can be weathered also naturally by oxidizing groundwater flowing through fractured rock and infiltrating from the surface [1, 40, 91].

In countries where the annual rate of precipitation is higher than the evaporation rate (e.g. Germany, Canada), uranium tailing are frequently close to groundwater that connects with creeks, rivers and lakes. Therefore, leaching of uranium can contaminate large volumes of waters. In countries with arid to semi-arid weather (e.g. Australia, western USA) groundwater contamination is a serious problem as well because of the limited quantities of water available for aquatic fauna, for irrigation and as drinking water [1].

Inappropriate conditioning and disposal of tailings waste permit the contamination to spread into the air, soil, sediment, surface water as well as groundwater. Under aerobic and anaerobic conditions, dissolution or immobilization of uranium is affected or can be affected by one or more of the following processes [31]:

- *changes in pH and redox* that result in *changes of the speciation* and/or oxidation state,
- *complexation* such as chelation by siderophore and other microbial products and by inorganic species such as carbonate and phosphate,

- *bioaccumulation*, movement and release due to *remineralization* elsewhere in the environment.

The extent and direction of uranium migration are determined by factors such as the rate and direction of groundwater flow, and the extent to which mineral assemblages of host rocks adsorb uranium from solution [74].

6.1 Former uranium mining sites and their remediation

An important factor to be considered during the operation and decommissioning of a mine site is the potential for contamination of adjacent aquifers and surface-water bodies. Previous research at mine drainage sites indicates that a complex sequence of acid-base, redox and dissolution-precipitation reactions occur simultaneously as plume water advances through the mine working, tailings and aquifer [5].

European uranium mining and milling was mainly carried out in *Germany, Czech Republic, France, Bulgaria, Romania, Hungary* and *Spain*. Most mining and milling sites in France and Spain are closed and remediated or their remediation is in progress. There are many abandoned sites in Eastern Europe. Many of them pose serious problems because preservation and protection of the environment has often been neglected and in many cases they are located close to human settlements. The most prominent case of environmental contamination is due to mining activities in former Eastern Germany, where in total 220 kt uranium were produced (48 major ore dumps, 14 tailling ponds). The Czech Republic is second, with a uranium production of 118 kt (100 uranium mining sites and 10 mills) [87].

In the context of bioremediation, solubilization of metal contaminants provides a means of removal from solid matrices, such as soils, sediments, dumps and other solid industrial wastes. Alternatively, immobilization processes may enable metals to be transformed in situ and are particularly applicable to removing metals from aqueous solution. Chemical aspects of bioremediation of water contaminated by uranium are widely discussed. As it was mentioned earlier in acid waters and in soil uranium primarily occurs in the form of soluble salts as uranyl ion. Its solubility decreases by reduction to U (IV) form what results in immobilization of uranium in the environment [33].

The mineral uraninite is highly insoluble. Microbes can reduce uranyl ion to hydrated uraninite. The reduction can be carried out by a cytochrome-c3 hydrogenase from *Desulfovibrio vulgaris* [54] and by *Deinococcus radiodurans* R1 in the laboratory with concomitant oxidation of the humic acid analog anthranhydroquinone-2,6-disulfonate (AQDSH2) to its quinone [32]. Uranyl ion can be precipitated as cell-bound hydrogen uranyl phosphate without change in oxidation state of the uranium. This reaction is facilitated by acid phosphatase N from *Citrobacter* sp. N14 [8]. On the other hand, some microorganisms are able to dissolve uranium from soil and ores. Certain microorganisms (e.g. *Thiobacillus ferrooxidans*) can facilitate the oxidation Fe^{2+} to Fe^{3+}. The Fe^{3+} ion, in turn, can convert insoluble UO_2 to soluble UO_2^{2+} ions. This reaction enhances the mobility of uranium in soil from mining and milling wastes [7, 20, 75]. Uranium may be removed from the pore water of sediments under sulphate reduction conditions, microbes may control this process indirectly [7].

7 Current state of uranium exploitation in the world

Finally, to enable the partial quantification of the environmental aspects concerning the utilization of uranium - as the governing nuclear fuel for electricity production - we present some important data of its recent exploitation.

In 2006 the world electric energy consumption represented $15.45.10^{12}$ kWh [81]. Simultaneously, according to the latest NEA & IAEA report, 435 commercial nuclear reactors were running at this period of time with overall 370 GW_e capacity requiring 66500 tons of uranium. For the year 2030 the nuclear capacity of the world is projected to grow between 509 GW_e (low demand case) and 663 GW_e (high demand case). The world reactor-related per annum U-requirements in connection with the projected rise, represents 93775 tons and 121955 tons of uranium respectively [61].

Uranium resources are generally classified as follows: **Identified resources** (comprising *Reasonably assured resources* and *Inferred resources*) refer to uranium deposits delineated by sufficient direct measurement to conduct prefeasibility and sometimes feasibility studies. For *Reasonably assured resources* high confidence in estimates of grade and tonnage are compatible with mining decision making standards. *Inferred resources* are not defined with such a high degree of confidence and generally require further direct measurements prior to making a decision to mine. **Undiscovered resources** (*Prognosticated resources* and *Speculative resources*) refer to resources that are expected to occur based on geological knowledge of previously discovered deposits and regional geological mapping. *Prognostigated resources* refer to those expected to occur in known uranium provinces, generally supported by some direct evidence. *Speculative resources* refer to those expected to occur in geological provinces that may

Table 6: Recent changes in uranium Identified resources category [61]

Resource category	**kilotons** in 2005	**kilotons** in 2007	**changes** in %
Total identified resources	11293	12894	+14.18
$<$ USD 130/kgU	4743	5469	+15.31
$<$ USD 80/kgU	3804	4456	+17.14
$<$ USD 40/kgU	2746	2970	+8.16
Reasonably assured resources	7887	7702	-2.35
$<$ USD 130/kgU	3297	3338	+1.24
$<$ USD 80/kgU	2643	2598	-1.7
$<$ USD 40/kgU	1947	1766	-9.3
Inferred resources	3406	5192	+52.43
$<$ USD 130/kgU	1446	2130	+47.3
$<$ USD 80/kgU	1161	1858	+60.03
$<$ USD 40/kgU	799	1204	+50.69

host uranium deposits. Both *Prognostigated resources* and *Speculative resources* require significant amounts of exploration before their existence can be confirmed and grades and tonnages can be defined [61].

In 2007 the total **Identified resources** of uranium including the $<$ USD 40/kgU category, the $<$ USD 80/kgU category and the $<$ USD 130/kgU category increased to about $12,894,000$ tons. The same reading for 2005 has been $11,293,000$ tons. These data represent an increase of 11.4% in period of two years. The recent changes in Identified resources of uranium in more details are indicated in Table 6.

7.1 The world's recent nuclear electricity generating capacity

At the end of 2006 in altogether 30 countries a total of 435 commercial nuclear reactors were operating. In addition to these running reactors 27 ones have been under construction with a net projected performance reaching 21.4 GW_e. The most important data connected with the nuclear electricity generating capacity of selected countries are presented in Table 7 [61].

Table 7: Nuclear electricity generating capacity of the world's most involved countries in comparison of V4 countries [61]

COUNTRY	**Operating reactors**	**2006 Uranium requirements [tU]**	**2006 NPP capacity [GWe]**	**2006 NPP electricity [TWh]**
Canada	18	1800	12.5	94.0
China & Chinese Taipei	16	2030	12.47	90.10
Czech Republic	**6**	**665**	**3.49**	**24.50**
France	59	7185	63.26	428.70
Germany	17	3710	20.34	158.70
Hungary	**4**	**380**	**1.78**	**12.66**
India	16	445	3.78	15.59
Japan	55	7940	47.10	291.50
Poland	**0**	**0**	**0**	**0**
Republic of Korea	20	3200	17.45	141.18
Russian Federation	31	4000	21.74	156.40
Slovak Republic	**5**	**490**	**2.03**	**16.60**
Sweden	10	1600	9.03	65.05
Ukraine	15	2480	13.80	84.90
United Kingdom	19	2165	10.50	69.40
United States	103	22890	100.10	787.00
World Total	435	66500	370.23	2675.08

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