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Review

Characterization and remediation of soils contaminated with uranium

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ABSTRACT

Environmental contamination caused by radionuclides, in particular by uranium and its decay products is a serious problem worldwide. The development of nuclear science and technology has led to increasing nuclear waste containing uranium being released and disposed in the environment.

The objective of this paper is to develop a better understanding of the techniques for the remediation of soils polluted with radionuclides (uranium in particular), considering: the chemical forms of uranium, including depleted uranium (DU) in soil and other environmental media, their characteristics and concentrations, and some of the effects on environmental and human health; research issues concerning the remediation process, the benefits and results; a better understanding of the range of uses and situations for which each is most appropriate.

The paper addresses the main features of the following techniques for uranium remediation: natural attenuation, physical methods, chemical processes (chemical extraction methods from contaminated soils assisted by various suitable chelators (sodium bicarbonate, citric acid, two-stage acid leaching procedure), extraction using supercritical fluids such as solvents, permeable reactive barriers), biological processes (biomineralization and microbial reduction, phytoremediation, biosorption), and electrokinetic methods. In addition, factors affecting uranium removal from soils are furthermore reviewed including soil characteristics, pH and reagent concentration, retention time.

Contents

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1. Radionuclides in soil

Radionuclides are found in the soil as a consequence of some pathways [1]:

- as a part of Earth's layer (primordial radionuclides);
- generated and deposited by cosmic ray interactions;
- as a result of anthropogenic activities.

Artificial radionuclides are also introduced into the environment following nuclear power plant accidents or nuclear weapons tests, nuclear energy activities, scientific and other uses [2–5]. In addition, soil may interact with low-level radioactive waste materials that have been buried for disposal [6–9]. Radionuclides can travel around the world on air streams. Their weight and weather determine their deposition to the ground. Also, the heavy rains can bring the radioactive particles to the ground [10]. Soils possess sorbent and complexing capacities which contribute to the immobilization of radionuclides from water in the underlying layers, after they were displaced from complexes or adsorption sites.

Radionuclides existing in soil can be dissolved in solution, or ion exchanged in reaction, complexed with soil organics or precipitate as pure or mixed solids. They can move into the water, air and the food supply.

The immobility of these radioactive elements in uppermost soil layers represents a problem for environment and human health, since they can be easily integrated in the food chain [2,11,12]. A scheme for radionuclides movement in soil was proposed by Igwe et al. [7] (Fig. 1). Consequently, the major part of radionuclides released into the environment will finally accumulate in either the upper layer of soils or interstitial system of sediments in aquatic systems. As a consequence, a risk for ecosystems, agro-systems and health could be induced.

In particular, uranium mining and milling have caused enormous damage to the environment by means of abandoned waste accumulation and improper disposal of the radioactive material, waste dump after uranium prospections, other workings, especially in the last 60 years since the end of the Second World War. Large amounts of uranium-containing (both high- and low-level) waste are generated from activities such as fuel fabrication, fuel reprocessing, research and development (R&D). All these negative impacts influenced the quality of the environment and affected mainly surface and ground waters, soils and simultaneously polluted great areas of land and endangered the catchments of drinking water. Also, uranium generates an important issue against public perception on the risk that the environmental contamination poses to the environmental and human health [14]. Therefore, it is strongly evident that the contamination caused by uranium has severe negative biological effects on important groups of the soil food web [3].

The potential risk of uranium soil contamination is a global problem as about every country can be affected by one or more activities mentioned above. Depleted, enriched and natural uranium contamination in soil and water has been identified at many sites worldwide, so that measures for preventing their assimilation by plants should be considered a preliminary step towards the remediation of contaminated areas [2,13–17]. For a long period of time uranium was leached commercially in a large number of deposits using different *in situ* technologies [18–20], either alkaline leaching using solutions containing carbonate and hydrocarbonate ions, or acid leaching [21,22].

The solubility of uranium in soil is dependent on several factors such as: pH, redox potential, temperature, soil texture, organic and inorganic compounds, moisture and microbial activity [23]. Soluble forms can migrate with soil water, be uptaken by plants or aquatic organisms or volatilized [7].

Several years ago, all commercial-scale operations for uranium leaching were stopped due to a complex of different political, economical and environmental reasons [24]. However, regardless of some preventive and remedial actions during the uranium recovery, many natural ecosystems were heavily polluted with radioactive elements, mainly through the seepage of acid drainage waters [25–27]. Such waters are still a persistent environmental problem at many abandoned mine sites, while soils around the water flow path are polluted with radioactive elements becoming unsuitable for agricultural use, so that soil remediation has to be considered [11,28].

Another problem is the contamination of soil and water with depleted uranium, which has increased public health concerns due to the chemical toxicity of DU at elevated dosages [29–33]. For this reason, there is great interest in developing methods for U removal from contaminated sources.

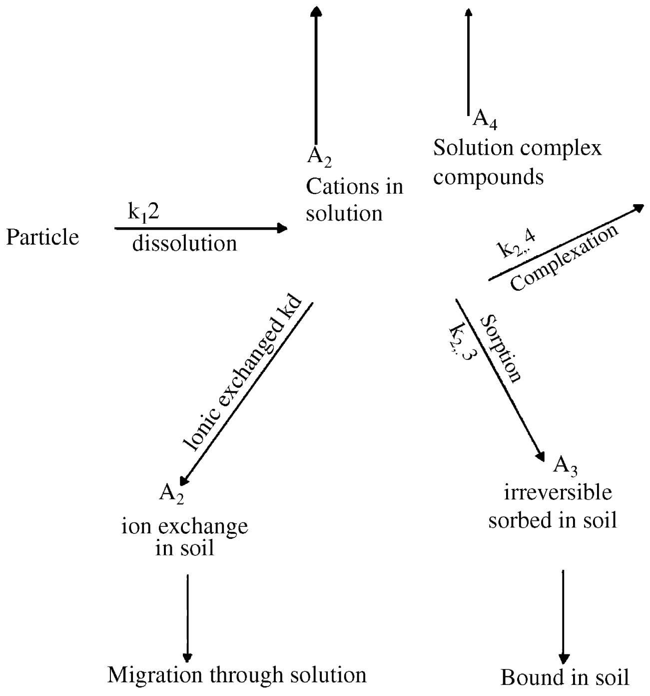


Fig. 1. Radionuclide transformation processes in soil (k_i—reaction rate) [7].

Various methods for remediation of soils contaminated with radioactive elements are known but only few of them have been applied under field conditions. The excavation and transportation of the heavily polluted soils to specific depositories is still a common practice in most countries [34].

The aim of this article is to provide an overview on the main aspects concerning the presence of uranium in the environment, in particular in soil, as well as on techniques for remediation of polluted soil together with recent advances in the application of these processes to the detoxification of uranium contamination.

2. Characteristics and concentrations of uranium in the environment

2.1. Uranium properties

Uranium can be characterized as a heavy, ductile and slightly paramagnetic metal, silver-white in color and pyrophoric when finely divided and in this form it can react with cold water [23,35,36]. It is the first element, with the atomic number 92, which was found by Henry Becquerel (in 1896) to possess the property to be radioactive [37]. As a naturally occurring element, it contributes to low levels of natural background radiation in the environment. Uranium is found in all rock types in varying, but usually small concentrations [12,38]. Uranium is widely dispersed in the earth's crust, rocks and soils at a level of about 2–4 ppm by weight [12,37,39]. The natural concentration of uranium in the earth crust is about 10^{-6} g/g. Also, the uranium concentration in ocean water, plants, and animal organisms is around 10^{-7} g/g, as a result of the solubility of U(VI) compounds in water [40].

Volcanic eruption is another natural phenomenon that may increase the concentration of natural uranium in the soil. The redistribution of uranium and uranium progeny to both soil and water occurs often naturally in environmental circuit.

Uranium is in fact more abundant than gold, silver, mercury, antimony or cadmium, and more or less as common as tin, cobalt, lead, molybdenum and arsenic [4,41]. It is an extremely dense metal (at 19 g/cm^3, about twice as heavy per unit volume as lead), being the heaviest chemical element to be found in the nature. Natural uranium exists in three different forms (isotopes), all of which are radioactive [41,42]. The two most abundant isotopes, uranium 235 (0.72%) and uranium-238 (99.27%), have radioactive half-lives of about 7×10^8 and 4.4×10^9 years, respectively [12,43]. An important characteristic is its toxicity [4,37].

Uranium is found in virtually all rock and soil (being derived from erosion of the rocks), it is essentially everywhere in groundwater [43–45]. Lower concentrations of uranium are found in basic rocks, while acidic rocks contain higher uranium concentrations [46,47]. As Table 1 shows, the average radioactivity in soils is similar to that in the rocks, usually bedrock, from which it derives [46]. The average radioactivity in soil of ^{234}U from Table 1 is 0.6–1 pCi/g. Since the activity of ^{234}U accounts for approximately one-half of the total activity in natural uranium, the value in Table 1 may be multiplied by two to obtain the total uranium radioactivity in soils (approximately 1.2 pCi/g) [46,47]. However, there are wide variations from the values presented in the table, particularly in areas where uranium minerals are more concentrated [4,37,51–55].

Table 2
Radioactive characteristics of natural uranium [51]

Characteristic	Uranium series		Actinium series
	238	234	235
Nuclide half-life (years)	4.46×10^9	245.5×10^3	704×10^6
Natural abundance (%)	99.2742	0.0054	0.7204
Type of emission	Alpha	Alpha	Alpha
Decay energy (MeV)	4.270	4.859	4.679
% of α-activity	0.0123	0.0127	0.0006
Total % of α-activity	0.0256		

The mineralogy of uranium-containing minerals has been described by Frondel [48]. In essentially all geological environments, +4 and +6 are the most important oxidation states of uranium [49–51]. The characteristics of naturally occurring uranium are shown in Table 2.

Primordial uranium consists of three isotopes, ^{238}U and ^{234}U from the uranium series and ^{235}U from the actinium series. In nature, an imbalance between ^{234}U and ^{238}U may exist due to alpha particle withdraw from the decay of ^{238}U that increases the availability of ^{234}U for transport through geological processes.

Almost all uranium as found in nature is the isotope ^{238}U. It undergoes radioactive decay into a long series of 13 different radionuclides before finally reaching a stable state in ^{206}Pb. These radionuclides emit *alpha* or *beta* radiation and some also emit *gamma* radiation of widely varying energies [4,37,55]. The ratio of ^{234}U to ^{238}U would be expected to be unity as long as the uranium stays locked inside undisturbed crustal rock in secular equilibrium with its progeny, but measurements show that the ratio is typically different than unity [55–57]. This disequilibrium occurs when the rock is disturbed by chemical or physical changes involving water. These processes can change the uranium isotope ratios in air, soil and water.

Table 1
Average radioactivity of uranium in several types of rocks and soils [46]

Material	^{238}U (pCi/g)	Series equilibrium radioactivity		
		Total alpha emission	Total beta emission	Total gamma emission
Ingenious rocks				
Basalt	0.2–0.3	1.6–2.4	1.2–1.8	0.6–0.9
Mafic	0.2–0.3	1.6–2.4	1.2–1.8	0.6–0.9
Salic	1.3–1.6	10.4–12.8	7.8–9.6	3.9–4.8
Granite	1.0	8.0	6.0	3.0
Sedimentary rocks				
Shale	1.0	8.0	6.0	3.0
Sandstones	1.0	8.0	6.0	3.0
Clean quartz	0.2–0.3	1.6–2.4	1.2–1.8	0.6–0.9
Dirty quartz	1.0	8.0	6.0	3.0
Arkose	0.3–0.7	2.4–5.6	1.8–4.2	0.9–2.1
Beach sands	1.0	8.0	6.0	3.0
Carbonate rocks	0.7	5.6	4.2	2.7
Soils	0.6	4.8	3.6	1.8

Table 3
Normalized uranium effluent discharges from various activities involving uranium [58]

Uranium-238	Curies per GWy(e)
Atmospheric releases	
Minning	–
Milling	1.8×10^{-2}
Mill tailings	1.9×10^{-5}
Conversion	2.0×10^{-3}
Enrichment	9.9×10^{-4}
Fabrication	2.0×10^{-5}
Liquid releases	
Conversion	2.2×10^{-2}
Enrichment	9.9×10^{-3}
Fabrication	9.9×10^{-3}

The uranium present in the rocks and soil as a natural constituent represents natural background levels. Natural processes of wind and water erosion, dissolution, precipitation, and volcanic action acting on natural uranium in rock and soil redistribute far more uranium in the total environment than the industries in the nuclear fuel cycle. However, those industries may release large quantities of uranium in specific locations, mainly in the form of solids placed on tailings piles, followed by liquids released to tailings ponds and then airborne releases, both directly from the facilities and by wind erosion of the tailings piles [55–58] (Table 3).

A major localized source of enhanced natural uranium can result from mining and milling operations (Table 3). As part of nuclear fuel cycle, uranium conversion, uranium enrichment and fuel fabrication facilities also release small amounts of uranium to the atmosphere [55–60] (Table 3 and Fig. 2)

Contamination of the soil can occur either from deposition of uranium originally discharged into the atmosphere, or from waste products discharged directly into or on the ground (e.g., water containing uranium from either underground or open-pit mines). Examples of industrial activities that may result in soil deposition include uranium mining and milling, uranium processing, phosphate mining, heavy metal mining, coal use and inappropriate waste disposal (Fig. 2).

The contamination could be specific for various locations, depending on the contamination source and this lead to unambiguous and significant effort for conditioning, treatment, storage and safe disposal of nuclear waste at the repository [58]. Available data on concentrations of uranium in different places confirm these conclusions and reveals the fact that efforts have to be devoted for remediation and for public health preservation. Some American contaminated sites are relevant from this perspective [1,10,44,45,56,58] (http://www.atsdr.cdc.gov/toxprofiles/tp150-c5.pdf; http://www.epa.gov/superfund/sites/npl/nar1605.htm):

- concentrations of uranium in Louisiana soils ranged from 2.35 to 3.98 μg/g (average radioactivity 1.6–2.7 pCi/g);
- uranium concentrations in phosphate rocks in north and central Florida ranged from 6.8 to 124 μg/g (4.5–83.4 pCi/g);
- soil samples adjacent to Los Alamos, NM, taken during 1974–1977 contained total uranium in the range of 0.1–5.1 μg/g (0.067–3.4 pCi/g), with a mean concentration of 2.4 μg/g (1.6 pCi/g);
- the concentrations of uranium in soils adjacent to the Hanford Fuel Fabrication Facility near Richland, WA, that were collected during 1978–1981 ranged from 0.76 to 4.6 μg/g (0.51–3.1 pCi/g), with a median value of 1.8 μg/g (1.2 pCi/g);
- the control samples for the Hanford Fuel Fabrication Study contained uranium at concentrations of 0.32–1.128 μg/g (0.21–0.86 pCi/g), with a median value of 0.73 μg/g (0.49 pCi/g);
- uranium in the soil of the Paducah Gaseous Diffusion Plant in Kentucky ranged from 4.9 to 7.1 μg/g (3.3–4.8 pCi/g), whereas off-

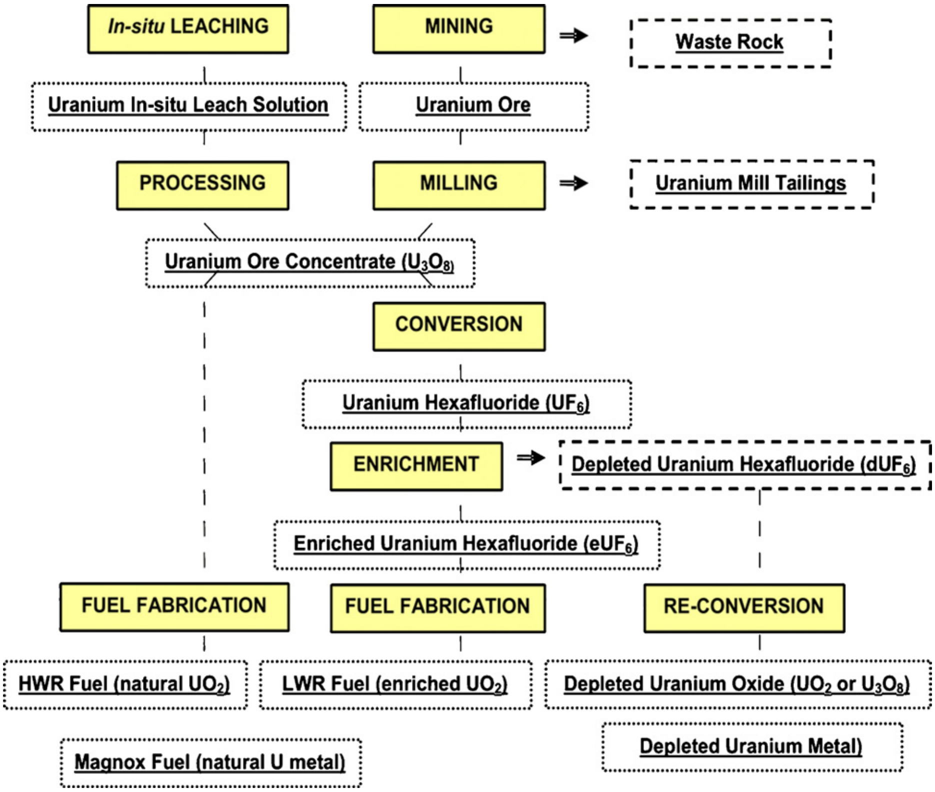


Fig. 2. Activities with impact on soil contamination with uranium and uranium compounds [55–60].

site samples taken as far as 12 miles away contained uranium at levels of 6.4–9.0 μg/g (3.8–6.0 pCi/g);
- soil monitoring data from the area surrounding the Feed Material Production Center at Fernald, OH, showed that the uranium concentrations within an 8 km^2 area were between 4.5 and 34 μg/g (3–23 pCi/g) compared to a mean of 3.3 μg/g (2.2 pCi/g) for natural background levels;
- uranium levels in surface soils at the Fernald site as high as 50 times natural background levels.

2.2. Depleted uranium

Depleted uranium results as a byproduct during the processing of natural uranium, which makes it suitable for use as fuel in nuclear power plants or as a component in nuclear weapons [4,61]. Studies on the radiological and chemical properties of depleted uranium showed that they can be compared to those of natural uranium, which is all over present in soil. Natural uranium has the same chemotoxicity, but its radiotoxicity is 60% higher [35,61]. Some studies revealed that the external exposure to radiation from depleted uranium is generally not major concern, so that depleted uranium is not a significant health hazard if it is not taken into the body. Natural and depleted uranium is much more likely to be chemical than radiation hazardous [35,39,54,55,62,63]. Some studies have however shown that exposure to intact depleted uranium weapons systems, both munitions and armor, pose very little risk from external radiation [39]. Also, it was found that the ^{234}U that remains in depleted uranium emits a small amount of low-energy gamma radiation [32,35]. Even if allowed to enter the body, depleted uranium, like natural uranium, has the potential for both chemical and radiological toxicity, with the two important target organs being the kidneys and the lungs [35,42,64]. Some published data refer to the toxic effects of depleted uranium on reproduction and development, as well as on risk of leukemia and central nervous system [65–69]. The relative contribution of each pathway to the total uptake into the body depends on the physical and chemical nature of the uranium, as well as the level and duration of exposure [32,53,70,71].

2.3. Chemical forms of uranium

Uranium can be found in soil as sorbed (both on soil particles and pore water), complexed, precipitated and reduced forms, all of which have various impacts on its mobility and fate in the soil environment [72]. It can exist in many chemical forms [4,37,54,55,61,69,73,74].

In nature, uranium is generally found as an oxide, such as in the olive-green-colored mineral pitchblende, which contains triuranium octaoxide (U_3O_8). In soil, uranium is typically in an oxidized form, and in water, it is usually present as a uranyl hydroxyl carbonate complex [37,75,76]. Uranium in ores can be extracted and chemically converted into uranium dioxide (UO_2) or other chemical forms usable in industry. When refined, uranium is a silvery-white metal with very high density (being 65% denser than lead).

Uranium dioxide (UO_2) is the chemical form most often used for nuclear reactor fuel. Uranium–fluorine compounds are also common in uranium processing, with uranium hexafluoride (UF_6) being the form used in the gaseous diffusion enrichment process. Uranium tetrafluoride (UF_4) is frequently produced as an intermediate in the processing of uranium. As noted above, in its pure form, uranium is a silver-colored metal. Because several of these compounds might be used or produced during the conversion process, a brief description of the physical and chemical properties is provided below.

The mobility of uranium in soil and its vertical transport (leaching) to groundwater depend on properties of the soil such as pH, oxidation–reduction potential, concentration of complexing anions, porosity of the soil, soil particle size and sorption properties, as well as the amount of water available [57,77]. Retention of uranium by the soil may be due to adsorption, chemisorption, ion exchange or a combination of mechanisms [77]. Any soil property that alters the sorption mechanism will also alter the mobility of uranium in the soil.

Complexation and redox reactions control the mobility of uranium in the environment [78]. Uranium can exist in the +3, +4, +5 and +6 oxidation states. In aqueous media only U(IV) and U(VI) are stable. The primary abiotic and biological processes that transform uranium in soil are oxidation–reduction reactions that convert U(VI) (soluble) to U(IV) (insoluble) [79]. Further abiotic and biological processes that can transform uranium in the environment are the reactions that form complexes with inorganic and organic ligands.

Some compounds, such as UCI_4, decompose in aqueous media to the U(VI). In acid solution and in the body, the oxygen-containing cation $UO_2{}^{2+}$, where uranium has the oxidation state VI, is the predominant form. In general, hexavalent uranium compounds are the most soluble.

The reduction of U(VI) to U(IV) by abiotic and biotic processes, as well as its re-oxidation has received considerable attention because the oxidation state of uranium has a significant effect on its mobility in the natural environment. Uranium exists in solution predominantly as $UO_2{}^{2+}$ and as soluble carbonate complexes $(UO_2)_2CO_3(OH)_3{}^-$, $UO_2CO_3{}^\circ$, $UO_2(CO3)_2{}^{2-}$, $UO_2(CO_3)_3{}^{4-}$ and possibly $(UO_2)_3(CO_3)_6{}^{6-}$ [80–82]. Between pH 4.0 and 7.5, the pH range of most soils, U(VI) exists primarily in hydrolyzed forms. Uranium(VI), i.e., uranyl, uranium will exist in the +6 oxidation state under oxidizing to mildly reducing environments. Uranium(IV) is stable under reducing conditions and is considered relatively immobile because U(IV) forms sparingly soluble minerals, such as uraninite (UO_2). Dissolved U(III) easily oxidizes to U(IV) under most reducing conditions found in nature. The U(V) aqueous species (UO^{3+}) readily disproportionates to U(IV) and U(VI). Under reducing conditions, the speciation of U(IV) is dominated by the neutral aqueous species $U(OH)_4{}^0$ (aq) at pH values greater than 2 [83,84].

The estimates of the solubilities and the speciation of uranium (nature and concentration species) are predicted from thermodynamic data, taking into account the presence of inorganic ligands in the groundwaters studied, mainly $[OH]^-$, $[HCO_3]^-$, $[CO_3]^{2-}$, $[H_2PO_4]^-$ $[HPO_4]^{2-}$, $[PO_4]^{3-}$, $[SO_4]^{2-}$ (in case of disposal in rock-salt formation) and the properties of these waters (redox potential) [85].

Eh–pH-diagrams show the thermodynamic stability areas of different species in an aqueous solution. Stability areas are presented as a function of pH and electrochemical potential scales. Usually the upper and lower stability limits of water are also shown in the diagrams with dotted lines. Traditionally these diagrams have been taken from different handbooks [Pourbaix Atlas Handbook]. In most handbooks these diagrams are available only for a limited number of temperatures, concentrations and element combinations [83,84,86,87].

The distribution of uranium species at 25 °C as a function of pH for both oxidizing and moderately reducing conditions is illustrated in Fig. 3, which further emphasizes that hydrolysis species and carbonate complexes are of primary importance. The major oxidation of U(IV) and U(V) as states of uranium is also apparent.

Uranium (IV) is very insoluble forming uraninite (UO_2) or a mixed valence oxide phase like $UO_{2.25}$ or $U0_{2.33}$. Uranium(VI) is much more soluble and mobile. Uranium(VI) also forms soluble

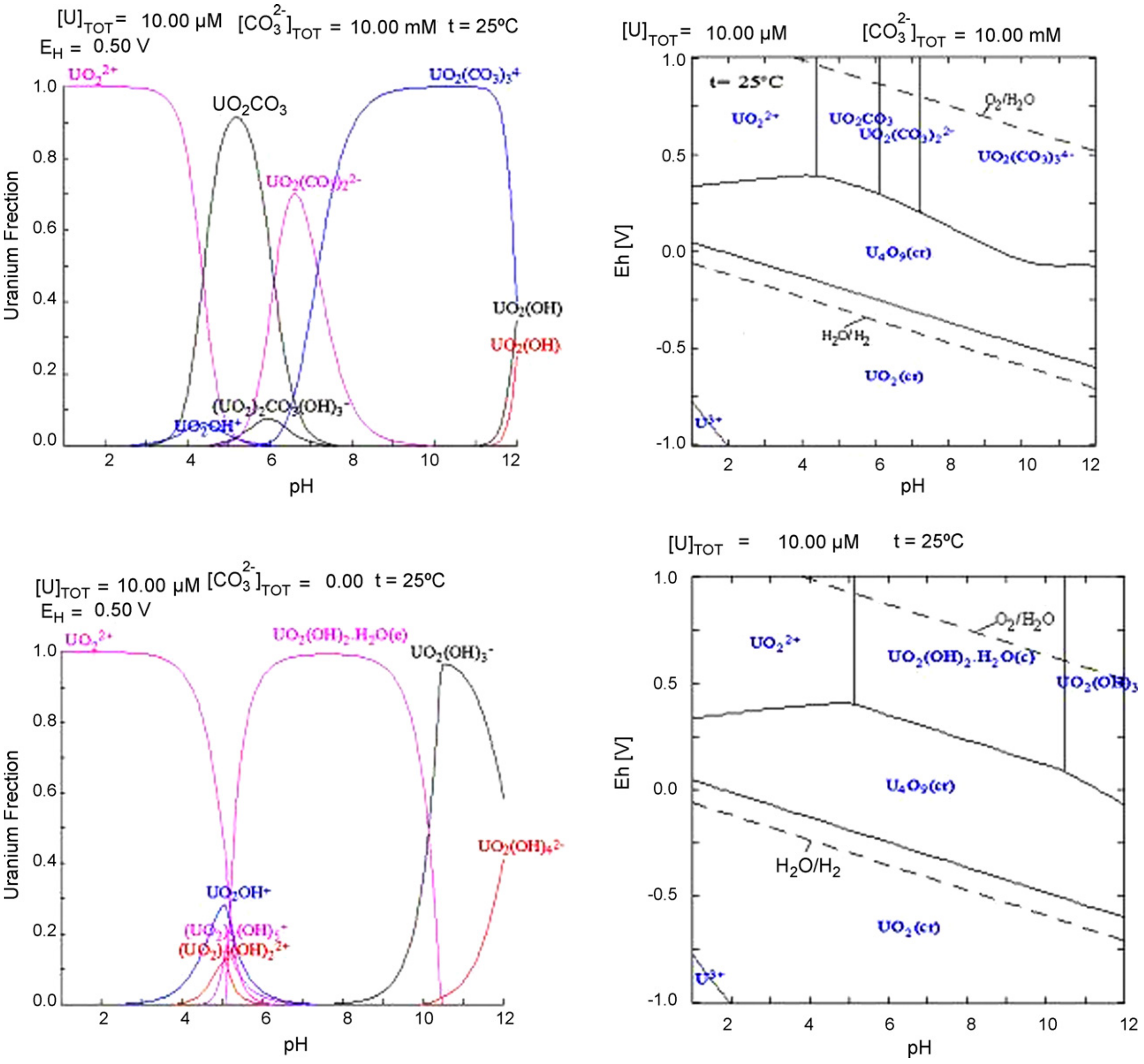


Fig. 3. Eh–pH and uranium species distributions as a function on pH for oxidizing and mildly reducing conditions (adapted upon [88,89]).

complexes with carbonate anions in natural waters. The aqueous speciation of U(VI) in carbonate-containing waters at near neutral and basic higher pH values is dominated by a series of strong anionic aqueous carbonate complexes [e.g., $UO_2CO_3{}^0$ (aq), $UO_2(CO3)_2{}^{2-}$ and $UO_2(CO_3)_3{}^{4-}$]. Fig. 3 shows that the aqueous complex $[UO_2(CO_3)_2]^{2-}$ is the predominant form of uranium between pH 7 and 8 in an oxidized environment. Numerous investigations of the adsorption of uranium on soils and minerals have shown that carbonate complexing appreciably reduces adsorption of uranium leading to its release from soils [90–93]. Eh–pH diagram for uranium shows the presence of solid phase at low Eh and predominance of dissolved uranium carbonate complexes at high Eh values. The upper diagonal dashed line is the superior stability limit of water and represents oxidizing conditions, while the lower diagonal dashed line represents the inferior limit of water stability under reducing conditions. When Eh values are above 0.25 V and pH between 7 and 8, uranium will be in the oxidized valence state (VI). Also, when Eh values are higher than 0.25 V (usually for pH ranging between 1 and 5), uranium is in the valence state (VI), as uranyl ion $[UO]^{2+}$. In alkaline medium, carbonate is the most significant ligand (in natural water) and the greater solubility of the U(VI) ion is in part due to its tendency to form anionic carbonate complexes [78,90–93].

The dependency of the speciation distribution on pH and carbon dioxide concentration in a closed system is shown in Fig. 4. The formation of carbonate complexes can change the stability field of U(VI). These U(VI) complexes may exist in alkaline conditions and high carbonate concentrations even in reducing conditions [94–96].

Uranyl hydroxy complexes such as $UO_2(OH)^+$ and $(UO_2)_3(OH)_5{}^+$ are also formed, but generally in smaller amounts except at high temperature or in carbonate-depleted alkaline water. In reducing water, the U(IV) hydrolysis leads to $U(OH)_4{}^0$ [83,84]. The solubility of reduced uranium is low and it has a strong tendency to hydrolyse, forming colloids, especially when environmental conditions change. High concentration of inorganic salts hinders the formation of colloids, while colloids already present may coagulate [95,97].

In dolomitic water Eh–pH diagram for uranium (0.01–0.5 mg U/L) is more complicated due to the presence of calcium

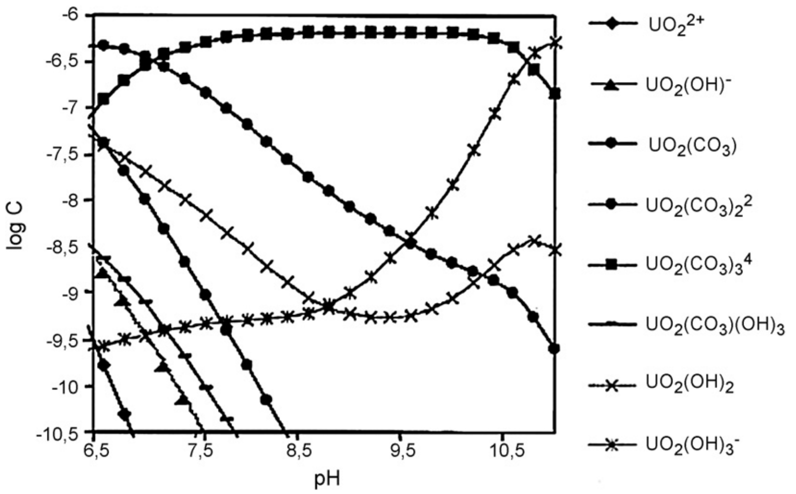


Fig. 4. The effect of pH and concentration of carbon dioxide (log *C*) on the speciation of uranium in ground water assumed as a closed system [94].

and magnesium ions, and other possible complex with sulfate [98–100]. A diagram for a real dolomitic system is presented in Fig. 5.

pH-drop below 6 (under normal oxidizing conditions) might allow for uranium to stay in solution as $[(UO_2)_3OH]^{5+}$ instead of precipitation as a carbonate [99,100].

In addition to dissolved carbonate, uranium can also form stable complexes with other naturally occurring inorganic and organic ligands such as phosphate complexes $[UO_2HPO_4{}^0$ (aq) and $UO_2PO_4{}^-]$ (Fig. 6) [101]. Complexes with sulfate (Fig. 7) [102], fluoride and possibly chloride are potentially important uranyl species where concentrations of these anions are high. However, their stability is considerably less than the carbonate and phosphate complexes [82].

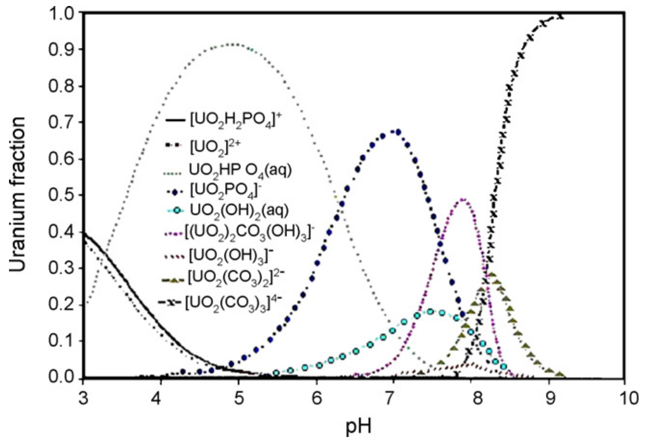


Fig. 6. Calculated uranium speciation in the system UO_2–PO_4–CO_3–OH–H_2O at over-saturation at *t* = 25 °C [101].

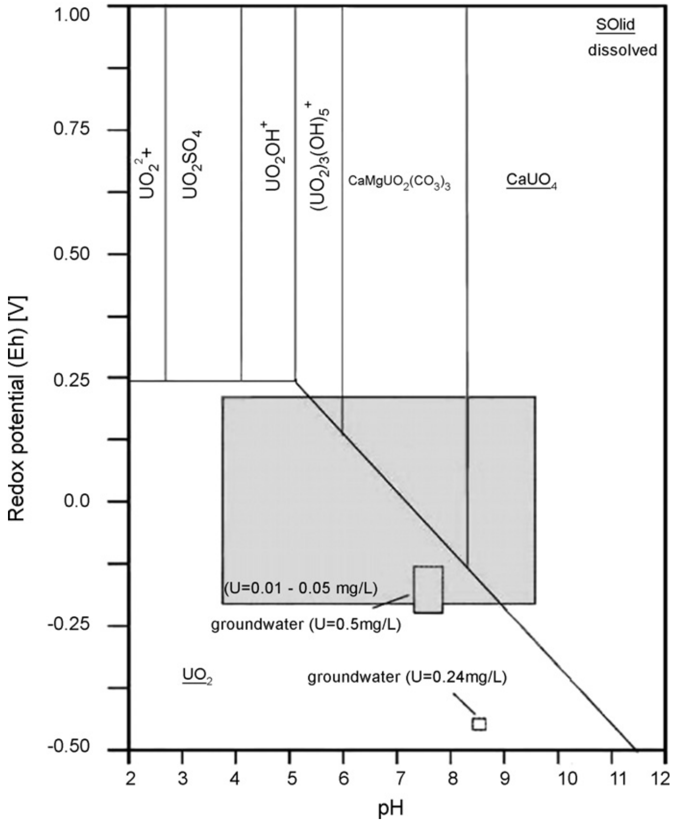


Fig. 5. Eh–pH diagram for uranium (0.01–0.5 mg U/L) in dolomitic water (adapted upon [100]).

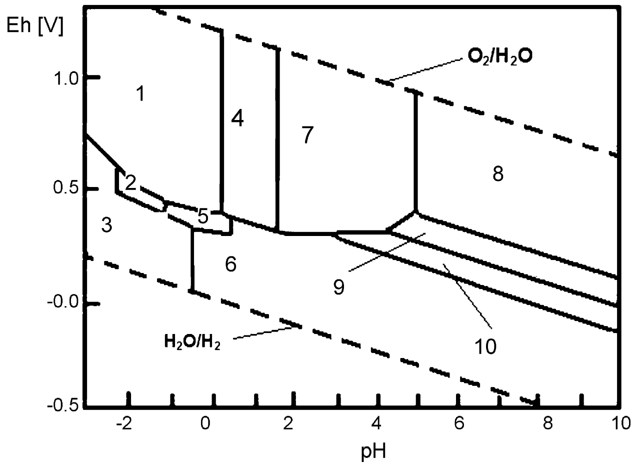


Fig. 7. Eh–pH diagram and uranium speciation in present of sulfates at *t* = 25 °C (concentrations of U-ions: 0.01 mg/L; concentrations of sulfate-ions: 0.1 mg/L) [102]. (1) UO_2^{2+}; (2) $U(SO_4)^{2+}$; (3) U^{4+}; (4) $UO_2(SO_4)^0$; (5) $U(SO_4)_2^0$; (6) UO_2; (7) $UO_2(SO)^{2-}$; (8) $UO_2(OH)_2H_2O$; (9) U_3O_8; (10) U_4O_9.

Eh–pH diagram from Fig. 7 shows that, if the pH of uranium-bearing aqueous medium is increased, an insoluble uranate precipitate (namely "yellow cake") is formed. Also, this diagram represents a useful guideline regarding the regions of pH and oxidation potential in which simple uranium oxide, ions in solutions and insoluble uranates exist [102].

Organic complexes may also be important to uranium aqueous chemistry, thereby increasing their solubility and mobility in soil. The uncomplexed uranyl ion has a greater tendency to form complexes with fulvic and humic acids than many other metals with a +2 valence [103]. In particular, the presence of organic substances and/or colloids in the groundwater increases the complexity of the system. Humic substances formed by the degradation of plants and animals constitute a heterogeneous category of compounds with a complex forming capacity due to the presence of carboxylic, hydroxy and phenolic groups [4]. Dissolved humic substances (humic and fulvic acids) proved to be strong complexing agents for many trace metals in the environment, forming also stable complexes or chelates with radionuclides [104,105]. These substances can be found as dissolved in surface waters as well as in groundwaters, in concentrations ranging from less than 1 mg (TOC)/L to more than 100 mg (TOC)/L. It has been shown that the binding of metals to humic acid apparently occurs at binding sites with relatively well-defined complex formation constants [104]. Uranium mineral precipitation and co-precipitation processes may also be important during remediation for some environmental conditions, and several uranium (co)precipitates may form, depending on the geochemical conditions [106,107]. Solubility processes may also be particularly important for the environmental behavior of U(VI) under oxidizing conditions in those soils that become partially saturated with water or completely dry, when the concentration of uranium in the residue pore fluids may exceed the solubility limits for U(VI)-containing [84].

2.3.1. Uranium oxides

The most common forms of uranium oxide are U_3O_8 and UO_2. Both oxide forms are solids with a low solubility in water and relatively stable over a wide range of environmental conditions [61,108]. U_3O_8 is the most stable form of uranium and is the form found in nature. The most common form of U_3O_8 is *yellow cake*, a solid named for its characteristic color that is produced during the uranium mining and milling process. UO_2 is a solid ceramic material and is the form in which uranium is most commonly used as a nuclear reactor fuel [4]. At ambient temperatures, UO_2 will gradually convert to U_3O_8. Uranium oxides are extremely stable in the environment and are thus generally considered the preferred chemical form for storage or disposal [61].

2.3.2. Uranium hexafluoride

UF_6 is the chemical form of uranium, which is used during the uranium enrichment process [65]. Within a reasonable range of temperature and pressure, it can be solid, liquid or gaseous [109]. At ambient conditions, UF_6 is a volatile, white, crystalline solid. Solid UF_6 is readily transformed into the gaseous or liquid states by the application of heat. All three phases – solid, liquid and gas – coexist at 64 °C (the triple point). Only the gaseous phase exists above 230 °C, the critical temperature, at which the critical pressure is 4.61 mPa. The vapor pressure above the solid reaches 0.1 mPa at 56 °C, the sublimation temperature.

Solid UF_6 is a white, dense, crystalline material that resembles rock salt. UF_6 does not react with oxygen, nitrogen, carbon dioxide or dry air, but it does react with water or water vapor (including humidity in the air) [110]. When UF_6 comes into contact with water, such as water vapor in the air, the UF_6 and water react, forming corrosive hydrogen fluoride (HF) and a uranium–fluoride compound called uranyl fluoride (UO_2F_2). For this reason, UF_6 is always handled in leak-tight containers and processing equipment. Although very convenient for processing, UF_6 is not considered a preferred form for long-term storage or disposal because of its relative instability [61].

2.3.3. Uranium tetrafluoride

UF_4 is often called *green salt* because of its characteristic color. It is generally an intermediate in the conversion of UF_6 to U_3O_8, UO_2 or uranium metal because it can be readily converted to any of these forms. UF_4 is a solid composed of agglomerating particles with a texture similar to baking soda. It is non-volatile, non-hydroscopic, but only slightly soluble in water [61]. After exposure to water, UF_4 slowly dissolves and undergoes hydrolysis, forming any of several possible uranium compounds and hydrogen fluoride [110]. The time for hydrolysis can be lengthy. Although not as stable as the uranium oxides, several recent studies have indicated that UF_4 may be suitable for disposal.

2.3.4. Uranium metal

Uranium metal is heavy, silvery white, malleable, ductile and softer than steel. It is one of the most dense materials known (19 g/cm^3), being 1.6 times more dense than lead [37]. Uranium metal is not as stable as U_3O_8 or UO_2 because it is subject to surface oxidation. It blurs in air, with the oxide film preventing further oxidation of bulk metal at room temperature. Water attacks uranium metal slowly at room temperature and rapidly at higher temperatures. Uranium metal powder or chips will ignite spontaneously in air at ambient temperature [111].

Some characteristics of uranium compounds, most of them determinant for choosing the remediation technique, are summed up in Table 4 [4,37,61,71,112–117].

2.4. Uranium compounds toxicity

The toxic effects generated by uranium exposure are based on its chemical and radioactive characteristics. Toxicity is closely related to solubility, i.e., the more soluble the uranium compound is, the more toxic it becomes [118].

The permissible levels for soluble compounds are based on chemical toxicity, whereas the permissible body level for insoluble compounds is based on radiotoxicity.

Several possible health effects are associated with human exposure to radiation from uranium. Because all uranium isotopes mainly emit alpha particles that have little penetrating ability, the main radiation hazard from uranium occurs when uranium compounds are ingested or inhaled [118–120].

The less water-soluble compounds (uranium trioxide, sodium diuranate, ammonium diuranate) were of moderate-to-low toxicity, while the insoluble compounds (uranium tetrafluoride, uranium dioxide, uranium peroxide, triuranium octaoxide) were primarily pulmonary toxicants. Soluble uranium compounds are toxic both when breathed or ingested. Generally, hexavalent uranium, which forms soluble compounds, is more likely to be a systemic toxicant than the less soluble tetravalent uranium [98]. The most soluble uranium compounds are UF_6, $UO_2(NO_3)_2$, UO_2Cl_2, UO_2F_2 and uranyl acetates, sulfates and carbonates. Some moderately soluble compounds are UF_4, UO_2, UO_4, $(NH_4)_2U_2O_7$, UO_3 and uranyl nitrates. The rapid passage of soluble uranium compounds through the body tends to allow relatively large amounts to be absorbed. Soluble uranium compounds may (also) be absorbed through the skin. The least soluble compounds are high-fired UO_2, U_3O_8, and uranium hydrides and carbides. The high toxicity effect of insoluble compounds is largely due to lung irradiation by inhaled particles. This

Table 4
Physical characteristics of uranium compounds [61]

Compound		Melting point (°C)	Density (g/cm^3)		Properties
			Crystal particle	Bulk	
UF_6	Uranium hexafluoride	64.1	4.68	4.6	Soluble in water, decomposes to UO_2F_2 high chemically toxic
UF_4	Uranium tetrafluoride	960 ± 5	6.7	2.0–4.5	Very slightly soluble in water at ambiental temperature
UO_2F_2	Uranyl fluoride	Decomposes to U_3O_8 at 300	6.37	~2.6	Soluble in water at ambiental temperature
UO_2Cl_2	Uranyl chloride	Decomposes			Decomposes in the presence of light, exhibits fluorescence, highly toxic
U_3O_8	Triuranium octaoxide	Decomposes to UO_2 at 1300	8.30	1.5–4.0	Very stable, has a low solubility in water
UO_2	Uranium dioxide	2878 ± 20	10.96	2.0–5.0	Insoluble in water, highly toxic and spontaneously flammable, used in weapons in place of lead in the Gulf War (also called uranium oxide, uranitite)
UO_3	Uranium trioxide	~200–650	8.0	5.5–8.7	Insoluble in water, poisonous, decomposes when heated (also called uranyl oxide)
$UO_2(NO_3)_2 \cdot 2H_2O$	Uranium nitrate	118 (decomposes)		2.81	Dissolves in water to form a weak solution of nitric acid, the reaction is not hazardous, oxidizing and highly toxic compound
Uranium metal		1132	19.05	19	Insoluble

material is transferred from the lungs of animals quite slowly (http://web.ead.anl.gov/uranium/guide/ucompound/health/index.cfm).

Of the most important uranium compounds used industrially, UF_6 and $UO_2(NO_3)_2 \cdot 6H_20$ are the most toxic, whereas UO_3 is only moderately toxic, and UO_2, U_30_8 and UF_4 are considered low in toxicity.

A variety of materials on radiation effects, obtained from animal experiments and studies in humans were published [3,119–121]. As it has already highlighted above, from literature data it results that all uranium mixtures, natural, depleted or enriched, are considered chemical toxins that may result in nephrotoxic effects [3,122,123]. The majority of the uranium deposited in the kidney is removed with a biological halftime of 6 days and the remainder with a 1500 d half-time. No permanent effects have been observed in any exposure case [3].

The presence of high levels of uranium (U) compounds in the human body has been reported to affect renal functions and, at very high concentrations, lead to kidney failure [124,125]. The primary pathways of U entrance into the human body are inhalation of contaminated dust or ingestion of contaminated water. The chemical toxicity of uranium as a heavy metal has raised public health concerns, especially in areas where contamination of local soils and groundwater from radioactive material has taken place. As a result, there is strong interest in remediation of uranium and depleted uranium laden areas [125].

3. Methods and techniques for uranium removal

3.1. General description

The objective of any remedial action is to reduce the risks to human health, environment and property to acceptable levels by removing or reducing the source of contamination or by blocking exposure pathways. Once the decision has been made that some remedial action is necessary, there are various potential options for achieving that objective [5,9,126,127].

Radionuclides and heavy metals are retained by soil in three ways [11,128,129]:

- adsorption onto the surface of mineral particles;
- complexation by humic substances in organic particles;
- precipitation reaction.

As was highlighted above, the mobility of uranium in soil is mainly controlled by complexation and redox reactions [78,130,131]:

- complexation leads to mobile species or precipitation of U-bearing minerals;
- redox reactions change the solubility between the two major oxidation states: U(IV)–U(VI):
  - o reduction of U(VI) to U(IV) immobilizes uranium;
  - o oxidation of U(IV) to U(VI) mobilizes uranium because of the dissolution of U(IV) bearing minerals.

These reactions are the basis for certain remediation technologies, their combination determining the mobility and fate of uranium. Furthermore, the techniques and methods for uranium removal from soil are selected according to the type of contaminants present, the behavior of the contaminants in the environment and the exposure pathways [5,9]. For sites with mixed contamination, it is often necessary to use several remediation technologies, sometimes in series, i.e., treatment trains, to effectively address risk from the radioactive, chemical and physical hazards that could be present. In addition, sites may have contamination in different media [17]. It is not uncommon, for example, to have also groundwater contamination on sites with extensive soil contamination, so that a range of technologies is needed for remediation of the various contamination problems [5,132].

There are three basic options for any intended remedial actions: *monitored non-intervention*, *containment* or *removal*, summarized in Table 5 and various techniques/technologies are associated, such as:

- separation;
- concentration and/or volume reduction;
- immobilization/sequestration.

In contrast with organic compounds, radionuclides in general and uranium in particular, cannot be commonly destroyed or degraded.

Each one of the above fundamental technical choices will direct decision makers to substantially different paths with regard to their subsequent choices, actions and potential results, making available significantly different technological options for application, within a remediation program, which involves multidisciplinary environ-

Table 5
Basic options for remediations of uranium-contaminated soils [3,133–140]

Option for remediation	Main actions involved	Requirements and characteristics	Technique	Goals	Technology	Description	Application
Monitored non-intervention	Establishing a monitoring scheme to determine the evolution of the site, while it is maintained undisturbed and an alternative can be initiated if required	In certain cases the radionuclide(s) present may have a sufficiently short half-life, allowing it/them first to decay to a level below that of concern, i.e., applying monitored non-intervention, before treating the other contaminants, thus reducing the problem to a so-named conventional contamination problem		Monitoring wells and/or infiltration monitoring systems	Dilution	Radioactive materials are discharged routinely into the air and surface waters, both fresh and marine, from nuclear facilities worldwide	*In situ*
						The effectiveness of dilution in aqueous media is critically dependent on the speciation of the radioelement under the prevailing environmental conditions	For long-lived radionuclides and metals, dilution may be the only process decreasing potential releases which might occur with remobilization
						This will control factors such as solubility, adsorption to surfaces, bioavailability and toxicity	May lower contaminant levels to the point where they are acceptable in a regulatory sense, though there has been no net reduction in contaminant mass
					Natural attenuation	Requires adequate monitoring, owing to the evolution of natural systems with time and our incomplete understanding of the processes operating	*In situ* Physical processes (radioactive decay, filtration, volatilization) Chemical processes (precipitation, co-precipitation, sorption, complexation by organics) Biological processes Constitutes the least invasive approach to environmental restoration
Containment	Immobilizing the contaminants inside the area where they already exist, that is containing or restricting the mobility of the radioactive contaminants	Aiming to reduce the potential for further migration or entry into active pathways for exposure	Isolation	Attempt to prevent the transport of contaminants by containing them within a designated area	Capping	Provide an impermeable barrier to surface water infiltration to contaminated soil for prevention of further release of contaminants to the surrounding surface water or groundwater (simple single-layer caps and more complex multi-layer systems)	Is the preferred remedial method for sites having low levels of wastes with low toxicity and low mobility, or wastes that have been pretreated to obtain these characteristics; used as a temporary measure to reduce the mobility of wastes that pose a high risk until a permanent remedy is selected and implemented

	Relatively simple and rapid implementation often at lower cost than alternatives that require excavation; ability to treat large areas and volumes of waste; potential for successful containment as the final action at the site					Selected for a number of sites with low levels of contamination
				Subsurface barriers	Reduce the movement of contaminated groundwater from the site, or to restrict the flow of uncontaminated groundwater through the contaminated site	Are commonly used to restrict the lateral flow of groundwater. For effective isolation of the contaminated matrix, the barrier should extend and key into a continuous, low-permeability layer, such as clay or competent bedrock, below the contaminated area Can prevent the escape of contamination from the site by using an infiltration barrier and collection system to create a hydraulic gradient in the inward direction
		Immobilization	Reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix	Solidification/ stabilization	Solidification involves the formation of a solidified matrix that physically binds the contaminated material	*In situ*
					Stabilization referred to as fixation, usually utilizes a chemical reaction to convert the waste to a less mobile form	*Ex situ*
						In-place mixing is similar to *ex situ* area mixing except that the soil is not excavated prior to treatment. The *in situ* process is useful for treating surface or shallow contamination
				Vitrification	Decreases mobility of metal contaminants by high-temperature treatment of the contaminated area that results in the formation of vitreous material, usually an oxide solid	*In situ* processes are preferred due to the lower energy requirements and cost typical stages in *ex situ* vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product

Table 5 (*Continued*)

Option for remediation	Main actions involved	Requirements and characteristics	Technique	Goals	Technology	Description	Application
Removal	Applying an appropriate treatment scheme for contaminants elimination	Aiming to extract, concentrate and then safely dispose of the contaminants at another location	Toxicity and/or mobility reduction	Chemical and/or biological processes can be used to alter the form of metal contaminants in order to decrease their toxicity and/or mobility	Chemical treatment	Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of contaminants (oxidation, reduction, and neutralization)	Can be performed *ex situ* or *in situ*
							Is often used as pretreatment for S/S and other treatment technologies
					Permeable treatment walls	Remove contaminants from groundwater by degrading, transforming, precipitating or adsorbing the target solutes as the water flows through permeable trenches containing reactive material within the subsurface (elemental iron, limestone barriers)	*In situ*
					Biological treatment	Exploits natural biological processes that allow certain plants and microorganisms to aid in the remediation of uranium (occur through a variety of mechanisms, including adsorption, oxidation and reduction reactions, and methylation) (bioaccumulation, phytoremediation, phytoextraction, phytostabilization, rhizofiltration, bioleaching, biochemical processes	*In situ*; *ex situ*
			Physical separation	Attempts to separate the contaminated material from the rest of the soil matrix by exploiting certain characteristics of uranium and soil; can operate based on particle size, particle density, surface and magnetic properties of the contaminated soil	Screening	Physical separation techniques are available that operate based on particle size, particle density, surface and magnetic properties of the contaminated soil	*Ex situ*
					Classification		Is often used as a form of pretreatment in order to reduce the amount of material requiring subsequent treatment
					Gravity Concentration Magnetic separation Froth flotation		

	Extraction	Can be achieved by contacting the contaminated soil with a solution containing extracting agents (soil washing and *in situ* soil flushing) or by electrokinetic processes. The contaminated fraction of soil and/or process water is separated from the remaining soil and disposed or treated	Soil washing	Requires soil excavation prior to treatment; chemical treatment involves addition of extraction agents that react with the contaminant and leach it from the soil; physical treatment is achieved by particle size separation technologies adapted from mineral processing to concentrate the contaminant in a particular size fraction (involves preliminary screening, secondary screening, chemical treatment, physical treatment, dewatering, water treatment	*Ex situ*
			Pyrometallurgical extraction	Use elevated temperature extraction and processing for removal of metals from contaminated soils Is usually preceded by physical treatment to provide optimum particle size	Most applicable to large volumes of highly-contaminated soils (metal concentrations >5–20%, especially when contaminant recovery is expected
			In situ soil flushing	Mobilize metals by leaching contaminants from soils so that they can be extracted without excavating the contaminated materials	*In situ* The applicability of *in situ* soil flushing technologies depends largely on site-specific properties, such as hydraulic conductivity, that influence the ability to contact the extractant with contaminants and to effectively recover the flushing solution with collection wells
			Electrokinetic treatment	Apply a low density current to contaminated soil in order to mobilize contaminants in the form of charged species	*In situ* *Ex situ* Is most applicable to saturated soils with low ground-water flow rates and moderate to low permeability The efficiency of removal by this process is influenced by the type and concentration of contaminant, the type of soil, soil structure, and interfacial chemistry of the soil

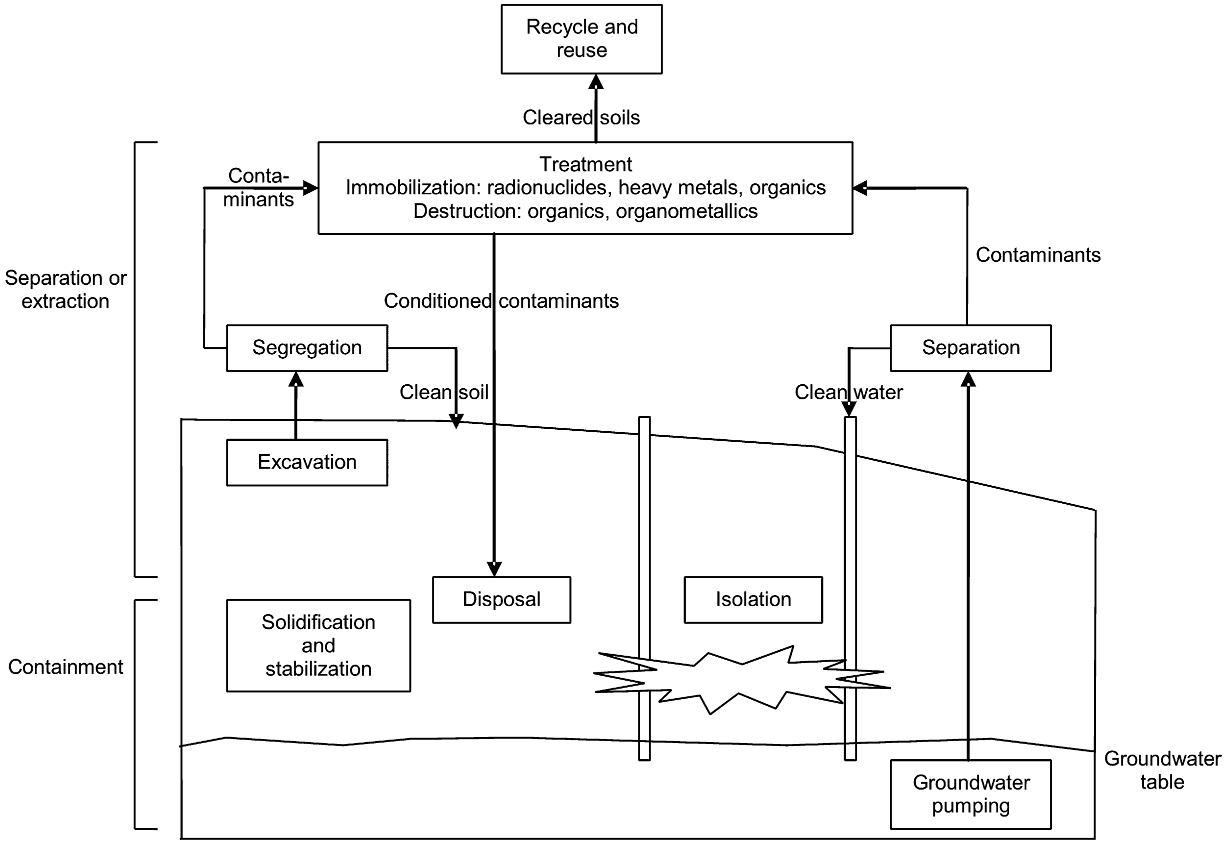


Fig. 8. Classification of remediation techniques by function [133].

mental research on characterization, monitoring, modelling and technologies for remediation (Fig. 8).

Any measurable remediation objective has to consider several factors, which could induce an impact on the decision making process have to be considered, like basic evaluation criteria that include engineering and non-engineering reasons for ensuring the achievability of the “cheaper, smarter and cleaner” soil remediation philosophy, such as [20,28,132,141–143]:

- cleanup goals;
- form and concentration of pollutants;
- volume and physical/chemical properties of the polluted soils;
- remediation effectiveness;
- designated use of the cleaned site;
- cost associated with the remediation program;
- occupational safety and health risks associated with the technology;
- potential secondary environmental impacts (collateral damage);
- prior experience with the application of the technology;
- sustainability of any necessary institutional control;
- socio-economic considerations.

Fig. 9 is a schematic representation of the relations between evaluation of remediation alternatives and remediation aims and options as a support for decisions making about implementation, so that the remediation performances be fulfilled.

The costs for implementing available technologies will vary significantly between sites because costs are influenced by a wide variety of factors. Fig. 10 represents the ranges of operating costs that have been observed for remediation of metals-contaminated soils by a number of techniques.

Remediation technologies available for treating uranium contaminated soils and groundwater could be applied as either *ex situ* or *in situ* techniques [132,144–146].

In situ techniques are generally preferred because they cause less site disturbance, less contaminant exposure to the environmental professionals and public in the vicinity, and they are often less complicated and more economical [141–146]. Also, because radionuclides are not destroyed, *ex situ* remediation requires sites for waste disposal, which have to meet special acceptance criteria and are limited [147].

A series of bench-scale studies were conducted to evaluate the influence of some factors affecting uranium removal from soils, such as soil characteristics, time, temperature, attrition scrubbing, pH and reagent concentrations, oxidizing and reducing chemical environments [143–145,148].

Soil characteristics affect the remediation process, since soil behaves as a complex sorbent. Uranium preferentially adheres to soil particles, with a soil concentration typically about 35 times higher than that in the interstitial water. Concentration ratios are usually much higher for clay soils (e.g., 1600). The concentrations and distributions of uranium among particle size fractions of the soils vary significantly, as is shown in Table 6. Data in Table 6 are for particle size fractions of the some soils after wet sieving and separation of the clay fractions −0.002 mm diameter following methods according to some authors [148–150].

When mining soils are remediated, it is necessary to discern that uranium mining wastes comprise several types of waste [134]:

- overburden (soil and rock that is covering a deposit of ore, such as uranium. It usually contains at least trace amounts of the ore plus radioactive decay products);

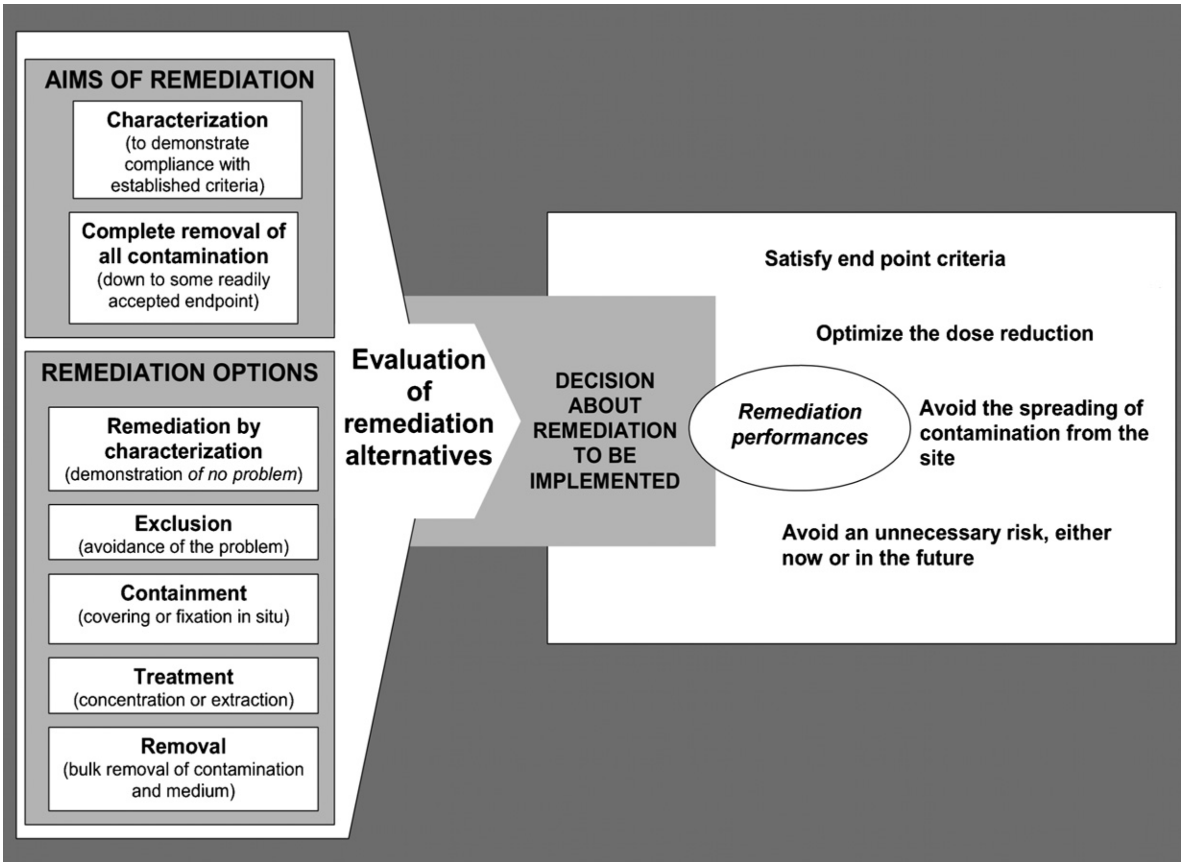


Fig. 9. Remediation alternative evaluation in relation with aims and performance [adapted upon 139–143].

- unreclaimed, subeconomic ores (ores that have too little uranium to be profitable, called “protores);
- “barren” rock (rock containing no ore);
- drill cuttings.

The Eh–pH diagrams (Figs. 3–7) indicate that sorption onto soil can be strongly influenced by the pH of the soil solution and, to a lesser extent, by the presence of calcium, suggesting specific chemical interactions between U(VI) and the soil matrix, so that the remediation process will depend on the same factors like those influencing uranium solubility [151,152]. Therefore, soil remediation techniques will be chosen considering sorption, complexation and redox reactions as the dominant mechanisms responsible for the reduction of mobility, toxicity or bioavailability of radionuclide contaminants [10,78,130,131,153,154].

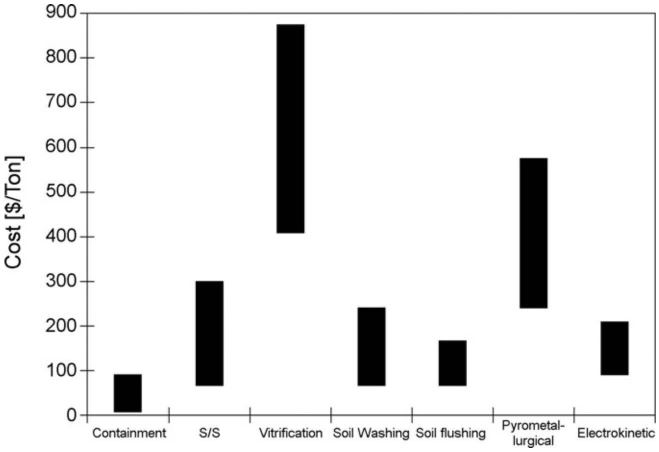


Fig. 10. Estimated operating costs of some available remediation technologies for contaminated soils (http://www.clu-in.org/download/toolkity/metals.pdf).

The sorptive phases that could control U(VI) sorption onto the soil are the iron and manganese oxide coatings and the clay fraction. Specifically, hydroxyl groups on the oxide surface, –SOH, are expected to be the dominant sorption sites [155].

Hydroxylated groups (–SiOH and –AlOH) situated along the edges of clay minerals can also be significant sorption sites [156]. Sorption onto such variable charge sites depends on the pH of the soil solution.

Some authors reported adsorption edges at pH 4–5 working with sorbents as goethite and ferrihydrite [90,157,158]; the lower sorption edge could be caused by the heterogeneity of the soil: iron and manganese oxides, clays and a small fraction of organic matter are all present.

The pH dependence of the sorption process indicates that protons (H^+) compete with U(VI) for sorption sites (surface hydroxyl groups, –SOH); at low pH, H^+ is the key sorbing species, forming positively charged diprotonated sites ($-SOH_2^+$). As the pH increases, U(VI) ions displace H^+ and bind to OH groups on the surface. The U(VI) reaction with those surface hydroxyl groups is similar to the hydrolysis reaction observed in aqueous solution only.

Sorption of U(VI)–CO_3^{2-} complexes is responsible for the large degree of U(VI) removal from the aqueous solution observed near neutral pH [98–100]. The identity of these U(VI)–carbonate surface species was analyzed by several authors: Hsi and Langmuir [158] have discussed sorption of $[UO_2(CO_3)SO_3]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$ onto goethite; Payne and Waite [159] have suggested UO_2CO_3,

Table 6
Concentrations dry weight basis and distribution of uranium in soils [149,150]

Soil, uranium concentration (mg kg^{-1})	Size fraction (mm)	Particle size distribution (wt%)	Uranium concentration (mg kg^{-1})	Uranium contribution by size fraction (wt%)
Y-12 landfarm	>2.00	1.8	442	4.3
	2.00–0.075	17.5	361	33.8
	0.075–0.020	34.1	31	5.8
	0.020–0.002	30.4	180	29.3
	–0.002	16.2	312	26.9
Incinerator soil-538	2.00–0.053	12.5	1033	27
	0.53–0.002	73.9	286	44
	–0.002	13.6	1019	29
Minning soil-446	2.00–0.053	22.6	117	7
	0.053–0.002	56.5	239	37
	–0.002	20.9	983	56

$[UO_2(CO_3)_2]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$ sorption onto amorphous ferric oxyhydroxide ($Fe_2O_3{\cdot}H_2O$); Waite et al. [90] have proposed sorption of UO_2CO_3 onto ferrihydrite; Duff and Amrhein [81] have found that $[(UO_2)_2CO_3(OH)_3]^-$ is the sorbing species in the presence of goethite. There is a number of spectroscopic studies that provide direct evidence for the formation of ternary U–carbonato species $[SO_2UO_2(CO_3)_x$ on mineral surface such as hematite and silica [160,161].

Several investigations on the removal of uranium from artificially contaminated soils as well as from anthropogenic sources, such as mine tailings and DU processing facilities, revealed that the application of any remedial technology for soils contaminated with uranium must take into account the potential of exposure to workers (as a consequence of the presence of radionuclides and the type and energy of radiation emitted) and the need to keep the exposure as low as reasonable achievable [147,162–164]. The ultimate goal is to develop technologies that can further reduce risks, reduce cleanup costs and reduce the volume of remaining contaminated soil [15]. These involve technologies assessment based on some reasons, which can include [15,141,146,147]:

- accounting of contaminant distribution, soil characteristics and adhesion/absorption characteristics of contaminants on soil particles;
- evaluation of physical, chemical and biological processes that should have potential to remediate radioactive contaminated soils;
- ranking of technologies based on technical value, potential experience and facility of implementation;
- engineering evaluation of technologies to determine scale-up potential and cost effectiveness;
- identification of secondary waste treatment needs for full-scale implementation;
- identification of difficulties and research needed to overcome technology limitations.

3.2. Natural attenuation

The long-term restorations of ecosystems and contaminated sites have been attributed to natural attenuation processes.

Natural attenuation is the process by which the concentration of environmental pollution is reduced to an acceptable level by natural processes. According to the USEPA [47], natural attenuation is the “use of natural processes to contain the spread of the contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites”. It can also be termed as intrinsic remediation, bio-attenuation and intrinsic bioremediation [164,165,166]. Natural attenuation is considered to be the least invasive approach to environmental remediation. Generally, these processes occur in soil, groundwater, and surface water systems at all sites at varying rates and degrees of effectiveness to decrease the concentrations of organic and inorganic contaminants [152,166,167,168]. The efficiency of this mode of remediation will vary based on the biological and chemical nature of the contaminated site. The physical, chemical and biological processes, the rate and extent to which these natural attenuation processes occur are different for each contaminant and site hydrologic and geochemical conditions. Under certain conditions (e.g., through sorption or oxidation–reduction reactions), natural attenuation could effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil [169].

Natural attenuation of radionuclides can occur through a number of sorption processes, including incorporation of contaminants into a mineral in the soil or an aquifer or by being entrapped in a rock pore [170]. Whereas natural attenuation of organic contaminants means breakdown and elimination by microorganisms, natural attenuation of radionuclides involves their encasing in a mineral where they will not escape unless chemical conditions change dramatically [135,152,166,170,171].

A number of investigations were performed concerning the natural attenuation of uranium in a tailings disposal site, which revealed that a number of radionuclides exhibit significant migration potential in the presence of aqueous, low molecular weight organic compounds immobile organic matter in the form of peat or organic-rich horizons in soils and sediments that may provide excellent substrates for radionuclide retention [168,172–176]. When uranium is dissolved in groundwater, it can be attracted to natural iron coatings located on walls of rocks through which the water is flowing, and bind to the iron coating and then move into microscopic rock pore and then incorporated into the iron coating [176,177,178].

The monitoring of the process involves the study of the rate and extent of irreversible adsorption of uranium, the fraction of uranium in aquifers associated with the phenomenon, and the degree of irreversible adsorption of uranium required to reduce the amount of uranium under the safety levels [179,180]. Microorganisms appear to be excellent indicators of soil health because they respond to changes in the soil ecosystem quickly [181].

Phytostabilization strategies may be suitable to reduce the dispersion of uranium and the overall risks of U-contaminated soils. Plants grown in soils with high carbonate–U fractions can accumulate the most U in shoot sand roots, while in clay soils with high Fe, Mn anorganic fractions this process is low [148]. Macrophytes in natural and constructed wetlands can influence uranium immobilization either directly by uptake and accumulation and/or indirectly (biomass production—litterfall and root turnover decomposition).

A number of investigations on the natural attenuation of the uranium (U) load in the surface water in various environmental conditions (for example, within a humid forest in Japan) were performed [15,176,178,180,182]. Surface water and sediments that had accumulated behind dams in the area were investigated in terms of their mineralogy and chemistry. The results of this investigation indicate that U, which within the study area is derived from pegmatites at a mine, is attenuated by uptake onto the surface of organic material as well as by amorphous material that forms over time within the dammed sediments. In most cases costs only occur in connection with monitoring [177,179].

3.3. *Physical processes*

Physical processes include soil capping, soil washing, soil aeration and heat flow, water storage and drainage, solidification, solubilization and solute transport [28,183,184].

Landfilling of radionuclides is difficult and expensive and land disposal restrictions have to be taken into account, as well as other national and international regulations [147,185,186].

Soil capping is a strategy of radioactive waste containment, when buried waste is capped with layers of materials (even impermeable) mainly to prevent surface water infiltrations, although it does not fully solve the contamination problem and does not change the waste's toxicity [184,187–191]. In fact, caps are covers placed over landfills and other waste areas, and are intended to isolate the waste.

Impermeable caps could be single of multi-layer clays, topped by plastic sheets, soil, etc. [184,187]. Capping process can be structured in four phases [184,188–190]:

- *mobilization* (preparation of site for cap construction);
- *operational* (actual cap construction);
- *closure* (installation of monitoring wells, decontamination and demobilization of equipment);
- *post-closure* (monitoring and long-term maintenance).

Capping technology has the advantage of little disturbance of contaminants as well as lower costs [184]. Some disadvantages refer to caps degradation by cracking (especially in environments with freeze and thaw cycles) or weakening by penetration of plant roots, landfill setting, etc. [191].

Soil-washing or *soil-flushing* systems are designed to treat soils where the majority of the contaminants are concentrated in the finer-grained materials or on the surfaces of the larger soil particles. Soil washing entails extraction of unwanted contaminants from soil with liquids, generally aqueous solution, when the contaminants are separated from the soil matrix and transferred to the washing solution and then the washing solution is extracted from the soil. Water or liquid solutions, whether injected or infiltrated into the contaminated area, mobilize the contaminant and are then collected and brought to the surface for disposal, recirculation, on-site treatment or reinjection [178]. Some operational and performance criteria were used for this analysis, such as [192,193]:

- removal efficiency, as the ratio of uranium activity in the treated soil to that in contaminated soil;
- ability to meet the standards;
- possibility to achieve the smallest volume of the treated soil so as to ensure off-site disposal.

The majority of soil-washing processes involve screening processes in order to separate the fine contaminated particles [28,183].

Solidification—the binding of a waste/soil into a solid mass can reduce its contaminant leaching potential. This process involves the generation of blocks of waste, where the radionuclides are kept mechanically within a solid matrix [147]. Vitrification of molten glass is another solidification method which uses heat of up to 1200 °C to melt and convert waste into crystalline products. Also, *stabilization* reduces the solubility and/or chemical reactivity of a waste/soil. Usually, it entails the addition of various binders (cement, silicates) in order to limit the solubility and/or mobility of radionuclides [147]. Both can be done *in situ* or *ex situ* on excavated materials by processing at a staging area either on site or off-site [28]. Physical treatment processes can be sequenced in a treatment queue, such as: excavation, transportation to a vitrification site and vitrification/sequestration [109].

3.4. *Chemical methods*

Chemical processes for remediation of radionuclide polluted soils include chemical degradation/transformation, volatilization, oxidation/reduction, solubility processes and adsorption/desorption.

A variety of chemical remediation techniques are available for remediation of radionuclide-contaminated soils that can be grouped as

- chemical conversion into a water-soluble form;
- chemical immobilization.

Research has shown that there are at least three different forms of uranium in the contaminated soil:

- uranium(VI) phosphate minerals;
- reduced U(IV) phases;
- complexed U(VI) with soil organic matter;
- a small fraction of U(VI) sorbed onto soil minerals [72].

These methods are often expensive to apply and lack the specificity required to treat target metals against a background of competing ions [27,194,195]. In addition, such approaches are not applicable to cost-effective remediation of large-scale subsurface contamination *in situ*. Also, the extraction media and procedures designed for a selective uranium removal have to preserve the physico-chemical characteristics of soils and avoid the generation of secondary waste forms, difficult to manage or dispose.

The removal procedures must guarantee a good mobility of uranium so that it would pass from the environmental component into another system [183,195]. Four approaches to increase metal mobility in heavy metal and radionuclide polluted soils have been suggested: change in acidity, change in ionic strength, change in redox potential and formation of mobile complexes [27,28,196]. They are discussed in the following paragraphs.

Table 7 highlights some chemical processes used for extracting U from contaminated soils indicating that several highly efficient choices exist for the extraction of U from contaminated soils and other materials [197]. Under ambient oxidizing conditions, U(VI) should be easily removed using bicarbonate, a strong inorganic acid or a weak organic acid (ascorbic, citric). Ebbs et al. [198] have examined the role of acidification and chelating agents in the solubilization of uranium (U) from contaminated soil and compared the two methods.

3.4.1. *Chemical extraction*

The chemical extraction process from contaminated soils involves the conversion of uranium into a water-soluble form, which is then extracted from the soil. An adequate uranium extraction can be achieved if certain conditions are met [195,199,200]:

Table 7
Selected DU chemical soil extraction methods [197]

Total DU removed	U content (mg/kg)	Material	Extraction method	Overall percentage	Reference
420	1320	Contaminated soil and ash	0.1–0.5 M $NaHCO_3$	80	[138]
95	708[a]	Acid/mixed/alkaline tailings, contaminated soil	0.1 M $NaHCO_3$	20–94	[162]
449	732	Contaminated soil	0.2–0.6 M citric acid	85–99	[163]
–	2629	Radioactive waste	4 M HNO_3 + 0.05 M H_3BO_3	>99	[164]

[a] Values interpolated from publication.

- uranium solubilization by exposing it to the solution which contains the chelating ions (citrate, carbonate);
- availability of complexing anions, by controlling the solution chemistry, chemical environment and conditions (pH, time, temperature) and early uranium precipitation;
- uranium oxidation to the hexavalent state (in the presence of carbonate).

Using chelating agents to extract uranium from contaminated soils is considered to be a chemical treatment method [201–205].

U(VI) cationic complexes are abundant from low to alkaline pH (about pH 8) (Eqs. (1)–(5)):

$$4H^+ + UO_2{}^{2+} + 2e^- \rightarrow 2H_2O_{(l)} + U^{4+} \tag{1}$$

$$UO_2{}^{2+} + 2e^- \rightarrow UO_{2(s)} \tag{2}$$

$$UO_2{}^{2+} + H_2O_{(l)} \rightarrow H^+ + UO_2OH^+ \tag{3}$$

$$3UO_2{}^{2+} + 5H_2O_{(l)}(5H^+ + [(UO_2)_3(OH)_5]+ \tag{4}$$

$$3UO_2{}^{2+} + 7H_2O_{(l)}(7H^+ + [(UO_2)_3(OH)_7]- \tag{5}$$

Chelating agents may be either organic or inorganic compounds. A number of inorganic chelators have been investigated for remediation and some of complexation constants for those chelators are now available [78,90–93,99–102,201]. Polyphosphates are considered as the most efficient inorganic chelators. Their annual consumption is higher than that of organic chelating agents [200,201,202]. Chelating compounds may be represented either using conventional empirical and structured formulas or some type formula as shown in Table 8 .

The strong chelators with target metals will have much greater solubility and stability (i.e., stability constant p*K*) than other reactions with metals in the aqueous phase [200–203]. This strength can be shown as p*K* chelators/p*K* natural ligands. The greater this ratio, the stronger this chelator will be. The stability of chelates is influenced by a number of parameters. Several of the stability factors common to all chelate systems are the size and number of rings, substituents on the rings, and the nature of the metal and donor atoms. The role of acidification and chelating agents in the solubilization of uranium (U) from contaminated soil was examined in a series of experiments.

3.4.1.1. Method(s) using sodium carbonate/bicarbonate. Carbonate/bicarbonate ions could lead to a rapid and greatly increased leaching and mobilization of U(VI) from a contaminated soil, depending on site-specific conditions [72,162,197].

Sodium bicarbonate has been used in the mining industry to extract U from carbonate bearing ore material. The bicarbonate ion forms strong aqueous complexes with U(VI) according to reactions (6) and (7) and enhances the dissolution of $UO_2{}^{2+}$.

$$UO_2{}^{2+}{}_{(aq)} + 2HCO_3{}^-{}_{(aq)} \rightarrow [UO_2(CO_3)_2]^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \tag{6}$$

$$[UO_2(CO_3)_2]^{2-}{}_{(aq)} + HCO_{3(aq)} \rightarrow [UO_2(CO_3)_3]^{4-}{}_{(aq)} + H^+{}_{(aq)} \tag{7}$$

This stable water-soluble complex forms easily under ambient conditions. Fig. 11 presents the dominating complexes of $UO_2{}^{2+}$ as a function of $[CO_3]^{2-}$ [206–208].

Mason et al. [138] used $NaHCO_3$ solution as an alkaline treatment for U contaminated soils from a processing facility in OH, USA. The authors were able to recover 80% of the total DU in the aqueous phase. Residual DU in the soil was determined to be comprised of relatively insoluble minerals, including meta-autunite ($Ca(UO_2)_2(PO_4)_2{\cdot}xH_2O$, $\log K_{sp(25\,^\circ C)} = -48.5$), uranium metaphosphate ($U(PO_3)_4$) and uraninite (UO_2). It was considered that the autunite was formed because the local soil had high phosphate content from prior pollution to the site. Mason et al. [138] indicated that efficiencies of 75–90% corresponding approximately to the percentage of uranium in the oxidized state were achieved for the removal of uranium from contaminated soils (Ohio in USA) using 0.5 M sodium bicarbonate as the dominant reagent.

Sodium peroxide, Na_2O_2, was also added to the leaching process to promote oxidation of U(IV) by the following reactions:

$$Na_2O_2 + 2H_2O_{(l)} \rightarrow 2NaOH + H_2O_2 \tag{8}$$

$$UO_2(s) + H_2O_2 + 2H^+ \rightarrow UO_2{}^{2+} + 2H_2O_{(l)} \tag{9}$$

Use of sodium peroxide (oxidizing agent), improved uranium removal due to oxidation of U(IV), enhancing the solubility of the uranium [28]. The oxidation of U(IV) to U(VI) occurred by a two electron transfer from U(IV) to H_2O_2 [209]. The resulting uranyl ion ($UO_2{}^{2+}$) was then available for subsequent complexation with HCO_3 ions by reaction (1). A 10:1 molar ratio of oxidant to U enhanced the extraction of DU by 20% [206].

Phillips et al. [162] applied a process for concentrating uranium from contaminated soils in which uranium is first extracted with bicarbonate and then the extracted uranium is precipitated with U(VI)-reducing microorganisms. Their results demonstrate that bicarbonate extraction of uranium from soil followed by microbial U(VI) reduction might be an effective mechanism for concentrating uranium from some contaminated soils.

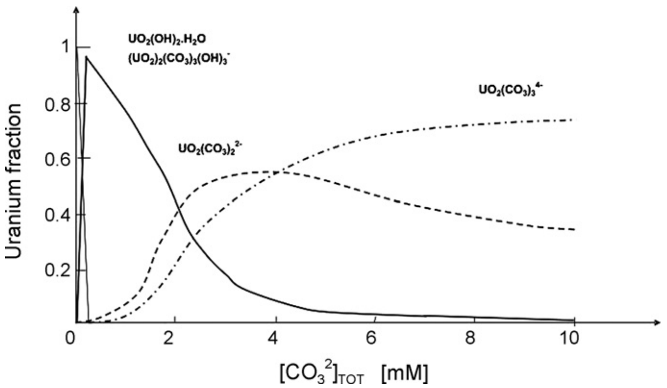


Fig. 11. Speciation of uranium depending on $CO_3{}^{2-}$ concentration (adapted upon [204–206]).

Table 8
Examples of different types of chelating compounds for uranil and corresponding chelats [55,201,202]

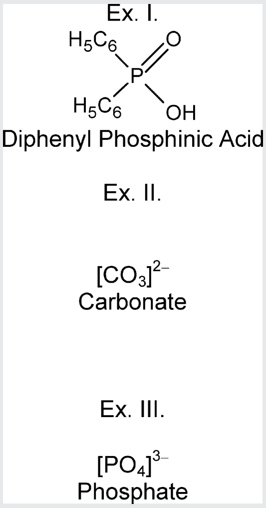
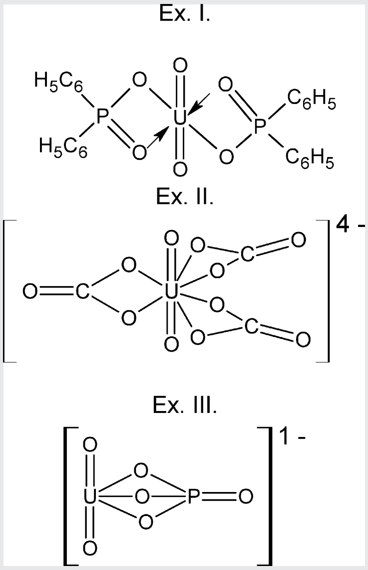
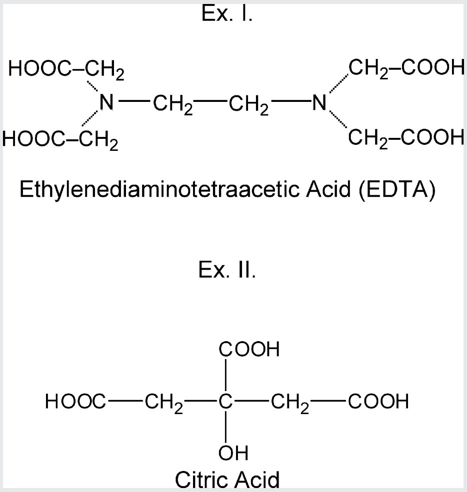
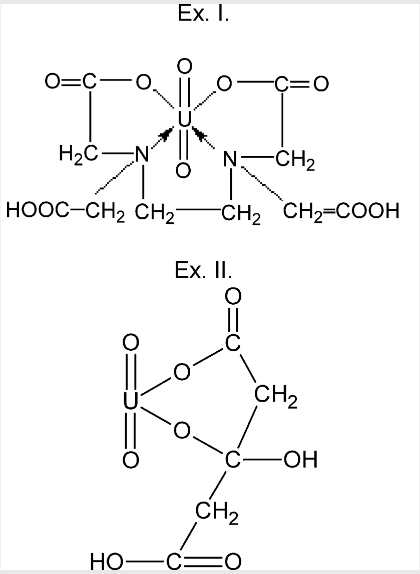
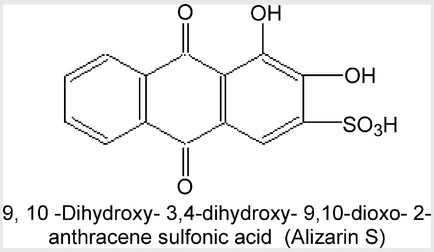
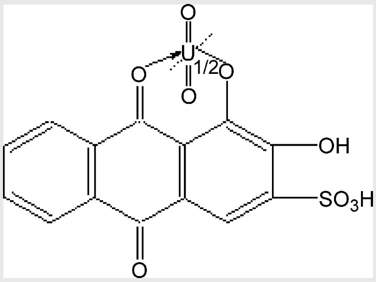
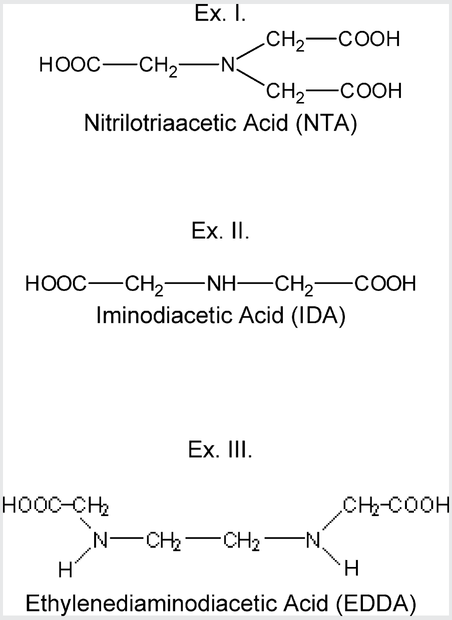
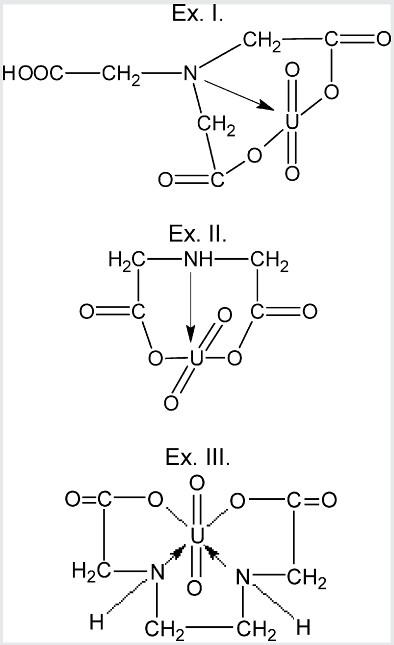
Active group in chelators	Chelator agents	Corresponding chelats
Proton acid groups		
Partially dissociated acid		
Alcohol/phenol groups that lose protons		

Table 8 (*Continued*)

Active group in chelators	Chelator agents	Corresponding chelats
Entire multidentate ligand molecule or a donor atom that lose protons	 Ex. I. Nitrilotriaacetic Acid (NTA) Ex. II. Iminodiacetic Acid (IDA) Ex. III. Ethylenediaminodiacetic Acid (EDDA)	 Ex. I. Ex. II. Ex. III.

Bench scale experiments described by Kulpa and Hughes [197] showed that a certain soil could be treated effectively using a 0.2 M sodium bicarbonate solution at a temperature of approximately 320 °C and a retention time of 1.5 h and concluded that chemical treatment using carbonate extraction achieved removal efficiencies of up to 90%. A pilot plant designed to process 2-ton batches of contaminated soil indicated that chemical extraction soil washing would result in contaminant removal efficiencies of approximately 82% and volume reductions of 95% [197].

Based on these results, a soil washing facility of 10 ton/h production *was* designed and constructed, leading to important cost savings comparative to shipment and disposal procedure. A block diagram of this system is presented in Fig. 12. This process which uses a relatively mild concentration of sodium carbonate to form a carbonate complex with uranium is approximately 85–95% effective depending on properties of the soil and source term of the uranium material contained in the soil.

The feasibility of the carbonate extraction process in a full-scale operation designed to leach uranium from contaminated soils using sodium carbonate/bicarbonate solution was also determined by several researchers [192,210,211].

3.4.1.2. Method using citric acid. Weak organic acids or their salts can be used as environmentally compatible compounds. Citrate is used as a complexing agent to mobilize sorbed and precipitated uranium in both *in situ* and *ex situ* extraction of soils and nuclear reactor components. Various researches revealed that citric acid is highly effective in uranium mobilization and the efficiency of extraction from contaminated soils increased with the acid concentration [202,213]. However, care should be taken with the quantity of citric acid used in such systems, because additional quantities may result in uranium migration which contaminates groundwater.

Laboratory and bench-scale experiments were conducted by Kantar and Honeyman [212] to determine the efficiency of citric acid as an agent to mobilize and extract uranium from contaminated soils. Some results indicated that citric acid is highly effective in removing uranium, and that the extraction efficiency increases with increasing citric acid concentration, especially under slightly acidic to alkaline conditions [212,214,215].

The enhanced U(VI) desorption in the presence of citrate may be explained through several processes, including the complexation of U(VI) with citrate and extraction of secondary coatings (e.g., Fe), together with the liberation of Fe–citrate complexes into solution [212,215–217]. In batch washing systems, the presence of 10^{-3} M citric acid enhances the extraction of uranium 2.8 times greater than water alone for the conditions of the experiment. Huang et al. [218] found a close correlation between the U and the Fe and Al concentrations in the soil solution after the addition of citric acid was found, explained by the dissolution of Fe and Al sesquioxides and hence release of U from soil material to the soil solution. For example, a removal efficiency of up to 98% was achieved with 10 mL of 10^{-3} M citric acid in batch systems, whereas it is required 150 mL of 0.1 M citric acid to accomplish similar extraction efficiencies in column soil flushing systems [212].

Citric acid ($C_6H_8O_7$, H_3Cit) has also been used to treat DU contaminated soil from various locations (OH, USA, Serbia) with removals efficiencies ranging from 85 to 99% [125,163,217]. The acid formed an aqueous complex with U(VI) under acidic conditions (below pH 5.0) by the reaction (10) [219]:

$$UO_2^{2+} + Cit^{3-} \rightarrow UO_2Cit^- \qquad (10)$$

An important advantage of U–citrate complexes for remediation accomplishments is their biodegradability. This may depend on the pH of the system, initial *U:citrate* molar ratios, contact time. For example, Huang et al. [218] and Gramss et al. [213] have found that, in solutions buffered at pH 6–7, limited biodegradation of citrate occurred within 10 days with initial *U:citrate* molar ratios ranging from 1:2 to 1:8, while over 99% of the citrate is biodegraded

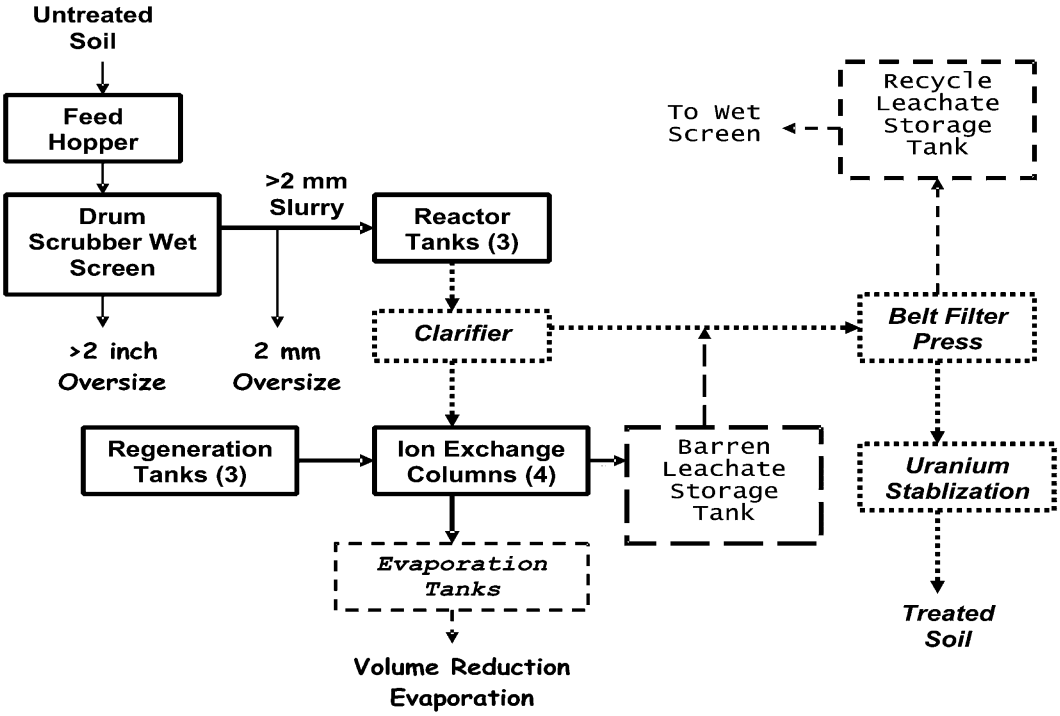


Fig. 12. Soil washing process simplified flow diagram [195].

rapidly at pH 8–9. They explained this behavior by the fact that the increase of pH shifted the equilibrium speciation of uranium from (UO_2–citrate) to $(UO_2)_3(OH)_7$ and, consequently, the bioavailability of citrate was increased. At pH 6–7, a significant amount of uranium is also observed to associate with biomass, whereas only a negligible amount is observed at pH 8–9 [218]. The biodegradability of U–citrate complexes is an important control over the potential migration of residual uranium after the extraction process is complete [216]. The experimental results of Huang et al. [218] show that the residual concentration of uranium–citrate complexes left in the treated soils can be reduced rapidly if the soil water pH ranged between 8 and 9 after the extraction process. The biodegradation of U–citrate complex does not cause uranium release [220].

3.4.1.3. Two-stage acid leaching procedure. Another method of DU extraction was reported by Jonathan et al. [221] and Nirdosh [164]. A two-stage acid leaching procedure was developed for treatment of radioactive soil waste or aqueous system containing around 2.1×10^{-4} M (50 mg/L) U.

In the two-stage leaching procedure, uranium is first removed from the particulate matter by forming coarse particulate slurry in an aqueous medium containing acid, hydrogen peroxide and iron. The coarse particulate matter is separated from the slurry and processed for subsequent release to the environment. Residual uranium is further leached from the remaining fine particulate fraction in a second-stage leaching by forming slurry of the fine particulate fraction in an aqueous medium containing acid, hydrogen peroxide and iron. The fine particulate matter is separated from the slurry and processed for subsequent release to the environment as clean soil [221,222].

Uranium is recovered from the leaching-steps' supernatant solutions in either a two-stage precipitation or by passage over an ion-exchange resin. Water recovered from the uranium removal steps is recycled for use in the upstream processing steps. In particular, the water requirements are reduced by utilizing a closed loop system for process water which is reclaimed, clarified and recirculated [221]. The overall processing scheme of the method is shown in Fig. 13.

3.4.1.4. Extraction with solvents and supercritical fluids. A variety of hazardous organic solvents could be replaced with supercritical fluids, which are hybrid solvents with properties between those of gases and liquids, with a low viscosity, high diffusion rates and no surface tension [221,223,224], CO_2 and water are the best known solvents applied for extraction in supercritical conditions [225–227].

By changing the temperature and pressure and, perhaps, adding small amounts of co-solvents, these two environmentally benign compounds can span a remarkably wide range of solvating power [226,228,229]. Supercritical CO_2 (SC-CO_2) can be used with chelating agents to replace organic solvents for the extraction of uranium from aqueous solutions produced in the processing of the ore, as well as for the removal of heavy metals from soils and sludges [225,226,228]. The removal of uranium from acidic waste solutions in the nuclear industry using solvent extraction is currently performed with tri-butylphosphate (TBP) [230]. There are numerous published papers which highlight the use of supercritical fluids for uranium extraction [226,229,231–235]. Direct dissolution of recalcitrant uranium oxides using nitric acid and metal-complexing agents in supercritical fluid carbon dioxide has also been reported [236–238].

Meguro et al. [229] applied a new method referred to as supercritical CO_2 fluid leaching (SFL), which is based on selective dissolution of uranium oxides with the supercritical CO_2 fluid containing the HNO_3–tri-*n*-butylphosphate complex, has been developed for the removal and recovery of uranium from solid wastes contaminated by uranium oxides. A similar technique was applied by Chiu et al. [239] to extract uranium from mixed wastes in contaminated soils, also containing PCBs. The contaminated soil was first extracted with neat supercritical CO_2 at 150 °C and 200 atm to remove PCBs. Subsequently, complexing agents, tri-*n*-butylphosphate and thenoyltrifluoroacetylacetone (HTTA), were

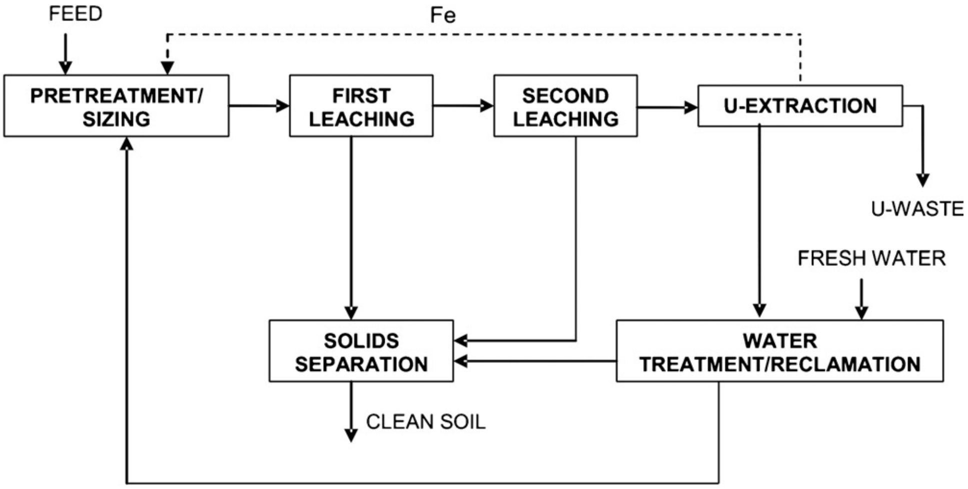


Fig. 13. A simplified process flow diagram which illustrates methods of uranium removal in the two-stage leaching procedure [218].

added to remove uranium from the contaminated soils. This method allowed for the removal of all PCBs and 75% of uranium, after multiple extractions. The authors recommend this extraction method for treating various mixed wastes [239].

Shimada et al. [240] studied the decontamination nature of the reactive extraction of uranium in the presence of some metal chemicals using a single-phase mixture of HNO_3, H_2O and tri-*n*-butylphosphate in supercritical carbon dioxide. They measured the decontamination factors (DFs) of the metals from their mixture with U, as a function of the molecular ratio of U to TBP in the extracted complex. Dilution by SC-CO_2 effectively increased the DFs.

The supercritical fluid extraction (SFE) method using CO_2 as a medium with an extractant of HNO_3–tri-*n*-butylphosphate complex was applied by Dung et al. [241] to extract uranium from several uranyl phosphate compounds and simulated uranium ores. They found that uranium could be efficiently extracted from both the uranyl phosphates and simulated ores. Also, it was thus demonstrated that the SFE method using CO_2 is useful as a pretreatment method for the analysis of uranium in ores.

Extraction of uranium with SC-CO_2 containing modifier solvent (methanol, tri-*n*-octyl phosphine oxide (TOPO) and tri-*n*-butylphosphate) was studied by Kumar et al. [239,242,243]. The extraction behavior of the $UO_2(NO_3)_2{\cdot}2TOPO$ complex loaded on tissues matrix was also investigated. Supercritical carbon dioxide modified with methanol alone was found to extract a maximum of about 76% uranium from tissue matrix [242].

Agrawal [244] has investigated Uranium(VI) extraction with *N*-phenyl-(1,2-methano-fullerene C_{60})61-formohydroxamic acid, PMFFHA, in dichloromethane by supercritical carbon dioxide–dichloromethane (modifier) medium. The uranium was determined in human blood serum, natural water, seawater, standard samples and also in monazite sand. The PMFFHA has been successfully used as carrier for the selective and efficient transport of uranium(VI). The feed comprised of a solution of uranium(VI) and aqueous solution of diverse cations and anions in pH 4.5, while 1 M HNO_3 was also used as a stripping agent in the receiving compartment of permeated cell [244].

Lin et al. [245] have analyzed the feasibility of using sulfur-containing organophosphorus reagents for the chelation-supercritical fluid extraction of toxic heavy metals and uranium from acidic media, using a specially designed flow-through liquid extractor. All the studies evidenced the fact that supercritical CO_2 fluid extraction proved to be an attractive method, where traditional solvent extraction systems could be successfully replaced.

3.4.2. Permeable reactive barriers (PRBs)

PRB are a relatively new technology for groundwater remediation: a trench arranged downstream of the contaminant source and filled with reactive material allows the treatment of contaminated groundwater passing slowly through [15,117,244,246,247]. They are in fact permeable walls that are installed across the flow path of a contaminant plume. USEPA defined PRB as: *a zone of reactive material which extends below the water table to intercept and treat contaminated groundwater* (http://www.epa.gov/ahaazuuc/topics/prb.html).

The wall is designed to be at least as permeable as the surrounding aquifer material. The PRBs contain a zone of reactive material that is designed to act as an *in situ* treatment zone for specific contaminants as groundwater flows through it [248–250]. The feasibility of using low-cost organic materials within a permeable reactive barrier to treat uranium contaminated environmental components was also investigated, because a permeable reactive barrier is considered an innovative, green engineering approach used for soil and groundwater remediation. The results showed that it has a high potential to threat shallow aquifer at a lower cost than pump-and-treat methods, but its cost-effectiveness has not yet been proven, due to a lack of long-term data [249–253]. Schad and Gratwohl [253] have calculated that the cost of remediation using PRB is 50% less than the pump-and-treat technique, while human exposure is reduced.

Radionuclides can be incorporated (*immobilized*) in the mineral structures of soil, so that a long-term fixation may be expected. The attenuation of pollutant concentrations using PRBs involves the use of a wide range of materials, suitable for various processes [117,254]:

- adsorption: porous and/or high surface area materials (activated carbon);
- chemical reduction: elemental metals;
- bioremediation;
- ionic exchange (resin-based materials), etc.

Fuller et al. [255] and Arey et al. [256] investigated the mechanisms of U(VI) removal by apatite and hydroxyapatite in laboratory studies and in samples recovered from the bone-char apatite PRB, in order to evaluate the feasibility of apatite-based *in situ* permeable reactive barriers. It was found that hydroxyapatite, illite and zeotite, alone or in combination, are also able to chemically immobilize uranium in contaminated soils and sediments with various organic contents [256,257].

Fine-grained zero-valent iron (ZVI) was used to study the mechanism of uranium immobilization, i.e., either by reductive precipitation or by adsorption onto reactive surfaces such as ferric oxyhydroxides, by means of batch experiments using different compositions of synthetic groundwater-containing uranium, at different levels of HCO_3^-, NO_3^-, SO_4^{2-} and humic acids [258]. The experimental results indicated that uranium is immobilized by reductive precipitation of U(VI) to insoluble U(IV). Very fine-grained zero-valent iron proved to be most effective with a uranium removal efficiency of more than 99.9% for carbon-rich and carbon-poor groundwater. However, PRBs do not provide a permanent solution as the precipitated uranium could potentially reoxidize (in the case of a reductive barrier like zero-valent or ferrous iron) [259].

PRBs may offer a cost-effective alternative to other soil remediation methods, but they are limited to shallow/near surface contamination or shallow groundwater. While the installation costs are typically low, the ongoing costs of replacing reactant and disposing of spent reactant may drive these costs into the medium range [259].

They could be applied as permanent, semi-permanent or replaceable units installed across the flow direction of narrow contaminant plumes, to be cost effective for deployment and monitoring.

3.5. Biological methods

3.5.1. Background

Biotechnological options have been proposed to improve or substitute traditional technologies for the remediation of contaminated wastes to levels that are difficult to achieve by standard physico-chemical treatments alone. With references around the globe, the value of this new approach is also recognized by industry worldwide [260]. Generally, there are three classifications of bioremediation processes [139,146,261,262]:

- *biotransformation*: the alteration of contaminant molecules into less or no hazardous molecules;
- *biodegradation*: the breakdown of organic substances in smaller organic or inorganic molecules;
- *biomineralization*: is the complete biodegradation of organic materials into inorganic constituents such as CO_2 or H_2O_4.

These three types of bioremediation can principally occur either *in situ* (at the site of contamination) or *ex situ* (contaminant taken out of the site of contamination and treated elsewhere). Strategies suggested for removal of metals and radionuclides from contaminated environments include microbial leaching, microbial surfactants (biosurfactants), volatilization and bioaccumulation/complexation [28].

Nevertheless, bioremediation provides a technique for cleaning up pollution by enhancing the same biodegradation processes that occur in nature. Depending on the site and its contaminants, bioremediation may be safer and less expensive than alternative solutions such as incineration or landfilling of the contaminated materials (http://ei.cornell.edu/biodeg/bioremed/). In this context, bioremediation of radionuclides/radioactive wastes, besides natural attenuation, has proven to be an inevitable necessity that has been strived using biotransformations, bioaccumulation, biosorption, biostimulation, bioaugmentation, biodegradation of chelators, volatilization, as well as treatment trains [54,262,263]. These treatment options could provide an attractive alternative for cleanup of radionuclides from soils, which also minimize the disruption to the environment caused by excavation [140,260,264–266]. They include phytoremediation, which means the use of plants for *in situ* remediation of contaminated soil through contaminant removal, degradation or containment and bioremediation which involves the use of microbes to sequester contaminants or transform them into a less-toxic state in soil, water and activated sludge systems. Many such processes exploit microorganisms with key roles in the biogeochemical cycling of toxic metals and radionuclides [265,266].

Microorganisms can interact with these contaminants and transform them from one chemical form to another by changing their oxidation state through the addition of (reduction) or moving (oxidation) of electrons [267]. The increasing body of information addressing microbially mediated mechanisms for uranium removal from solutions refers mainly to [54,268–272]:

- enzymatic reduction of soluble U(VI) to insoluble U(IV);
- precipitation of U(VI) after reactions with inorganic ligands;
- biosorption of U(VI) through complexation with cell surface groups.

Bioremediation can be accelerated in surface soils by the symbiotic relationship between soil and microbes, owing to ability of plants to stimulate soil microorganisms through the release of nutrients from and the transport of oxygen to their roots [28]. The rhizosphere, as the zone of soil closely associated with the plant root has much higher numbers of metabolically active microorganisms than unplanted soil, since it is characterized by an increased microbial activity and biomass at the root–soil interface [28,273,274].

Emerging procedures rely on injecting organic carbon (OC) into contaminated sediments in order to stimulate direct or indirect microbial U(VI) reduction to U(IV) solids [172,275,276].

Biological remediation offers the potential for a highly selective removal of toxic metals coupled with considerable operational flexibility; they can be used both *in situ* and *ex situ* in a range of bioreactor configurations, which can correspond to any vessel or container consisting of basic devices, such as lined depressions in the ground to advanced metal containers, where biological degradation of contaminants is isolated and controlled, and environmental conditions can be monitored and controlled [194,260,265,274,277].

Unfortunately, biological remediation is not a viable option for every site. An initial site characterization is highly recommended to determine whether biological remediation will be an effective treatment of choice [140]. Also, biodegradation which converts organic contaminants in CO_2 and water cannot disintegrate radionuclides, so that bioremediation of uranium and other radionuclides is different from that applied to toxic organic substances [54,278].

Some aspects regarding bacteria participation in facilitating complete extraction of uranium and other radionuclides from contaminated soils and sediments are discussed and reviewed, so that two mechanisms of bacteria action were highlighted [278,279]:

- *an indirect mechanism*, which involves the production of proton and oxidant (Fe^{3+} for example play a very important role in metal leaching);
- *a direct mechanism*, responsible for metal dissolution, when bacteria interact with minerals and contribute to their dissolution with a higher rate than that of chemical leaching.

Various tests performed in laboratory experiments with soil samples taken from contaminated lands revealed that an efficient natural bioremediation of the soils could be achieved *in situ* based on the activity of the indigenous soil microflora. The treatment was connected with the dissolution of the contaminants in the upper soil horizons and their transfer into the deeply located soil horizons, where they were immobilized as different insoluble compounds as the result of the action of some aerobic microorganisms [34,142]. Also, the immobilization was ascribed to the anaerobic sulfate-reducing bacteria. Suitable changes in the levels of some essential environmental factors such as water, oxygen and nutrient contents in the soil enhanced the activity of these microorganisms. For example, Groudev et al. [34] have been found that, within 8 months of treatment, the contents of radioactive elements and toxic heavy metals in the soil were decreased below the relevant permissible levels. These processes are enhanced when the radionuclides are solubilized, so that different chemolithotrophic and heterotrophic microorganisms are able to leach uranium and other radioactive elements from different mineral raw materials in both acidic and alkaline water solutions [34,54,162,280–282]. Bacterial processes for the reduction of radionuclides and metals such as uranium, selenium, manganese, etc. have also proven to offer great potential for cleanup of groundwater streams, as was also highlighted above [260].

Various fungi were also applied for bioremediation. Fomina et al. [267] have used a complex methodological approach involving advanced solid state speciation and scanning electron microscopy to study the ability of saprotrophic, ericoid and ectomycorrhizal fungi to transform uranium trioxide (UO_3) and triuranium octaoxide (U_3O_8) considered as model oxides. The study has revealed that fungi exhibit a high uranium oxide tolerance, and possess the ability to solubilize UO_3 and U_3O_8 and to accumulate uranium within the mycelium to over 80 mg (g dry weight)$^{-1}$ biomass. Some biotic activity (e.g., burrowing) can contribute to the turnover of bulk material (and hence re-contamination) within soil.

In optimal conditions biological remediation methods can be quite effective, but a site characterization is necessary, which should include the following aspects [139,140,146,283]:

- nutrient sources availability (such as nitrates, phosphates, carbon source, minerals) to support the microbial or plant species;
- characterization of existing site biological activity (plants and microbes) and plume delineation;
- bioavailability of the pollutant for effective treatment;
- soil acidity/alkalinity to determine the need for fertilizers and
- aeration;
- chemical form of the radioactive species;
- half-life of the radionuclide;
- plant or microbial species the best suited for site decontamination;
- plume delineation.

3.5.2. *Biomineralization, formation of insoluble metal sulphides and phosphates*

A number of microorganisms possess the ability to transform uranium from contaminated soils and sediments to less soluble and less toxic chemical state [54,264,282,284–288]. This potential is considered very attractive for establishing certain remediation strategies because of its low cost, as well as of short-term studies supporting its feasibility [54,282,289–291].

The uranyl ion $[UO_2]^{2+}$, the common, soluble form of this element in the environment can be immobilized by microbes in several ways, three of which are shown in Fig. 14. While the chemical reduction of uranium is inhibited by the formation of negatively charged U(VI)–CO_3 complexes that are present in nature, microbes are capable of enzymatically reducing these species to form U(IV)-bearing minerals such as hydrated uraninite, highly insoluble [54,131,286]. Numerous experimental studies demonstrated that various dissimilatory metal and sulfate-reducing bacteria such as *Shewanella*, *Geobacter* and *Desulfovibrio* species act as oxido-reduction agents by coupling the oxidation of organic matter and H_2 to the reduction of mobile U(VI), resulting in immobile U(IV) and the subsequent precipitation of uranitite (UO_2) [54,281,282,284–286,290,292–294]. The *Desulfovibrio vulgaris* bacteria and other organisms can carry out the reduction [295,296]. Reaction A in the middle branch of Fig. 6 can be carried out by *Deinococcus radiodurans* [284,297]. The uranyl ion can also be precipitated as cell-bound hydrogen uranyl phosphate without a change in the oxidation state of the uranium, as shown in the right pathway branch in Fig. 14. This reaction is facilitated by acid phosphatase N from *Citrobacter* sp. [91].

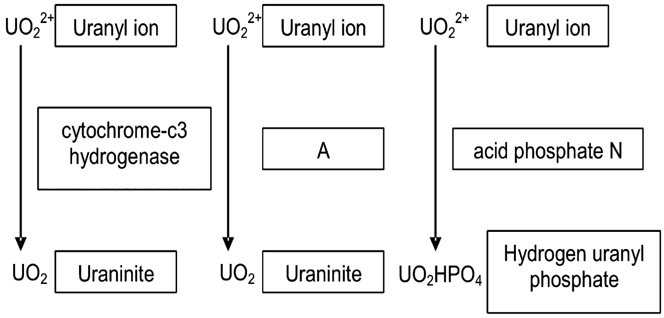


Fig. 14. Pathways for uranium transformation in the presence of enzymes [91].

Dissimilatory iron-reducing bacteria (DIRB—*Geobacter* and *Pyrobaculum* species) have an important role in oxidizing organic contaminants (e.g., aromatic hydrocarbons) in the subsurface as well as in immobilizing uranium and playing also possible roles in the formation of uranium deposits and magnetite in hydrothermal environments [54,298–300].

U(VI) is also reduced by microbes in suspensions or in biofilms that contain organic or inorganic ligands or electron acceptors such as Fe(III) oxides, sulfate or selenate [162,294,301,302]. A simplified scheme of uranium bioreduction is illustrated in Fig. 15.

Remediation of U(VI) by applying the microbial process, followed by immobilization can be further improved by the addition of organic electron donors (acetate, ethanol), which also enhance the growth of Fe(III)—reducing bacteria [54,269,302]. When unperturbed by influxes of highly oxidizing terminal electron acceptors (TEAs), U(IV) is commonly assumed to be stable in reducing sediments [275].

However, Wan et al. [275] have observed that, although previous short-term experiments on microbially mediated U(VI) reduction have supported the possibility of immobilizing the toxic metal through formation of insoluble U(IV) minerals, longer-term laboratory study performed along 17 months showed that microbial reduction of U can be transient, even under sustained reducing conditions. Uranium was first reduced during 3 months, but later it was reoxidized and solubilized, even assisted by a persistent microbial community capable of reducing U(VI). This behavior was considered as the result of the effect of some key factors, which favorize the reactions presented in Table 9 [275]:

- oxidation of organic carbon, which caused increases in (bi)carbonate concentrations and formation of very stable uranyl carbonate complexes, thereby increasing the thermodynamic favorability of U(IV) oxidation (Eqs. (I)–(III));
- the presence of calcium, originated from calcite in sediments, which is effective in releasing U(VI) into solution through formation of calcium complexes at near-neutral pH (Eqs. (IV)

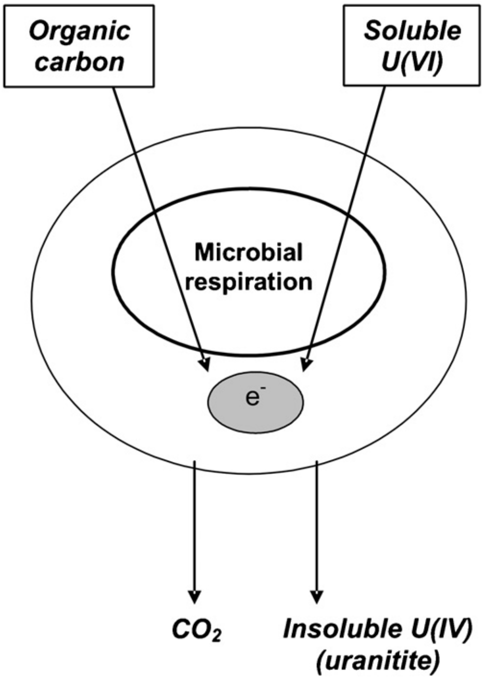


Fig. 15. Microbial reduction of U(VI) to U(IV) (adapted upon Ginder-Vogel et al. [292]).

and (V)) much less susceptible to bioreduction and sorption [275,303–306];

- the potentials for the dominant U redox reactions under various partial pressure of CO_2, dependent on experimental conditions the experimental conditions ($Eh^{a,b,c}$) (Table 9).

Re-oxidation of U(IV) is thermodynamically favorable in reducing soils.

Thermodynamic calculations on amorphous uranitite, UO_2(am) solubility based on equations in Table 9, performed by Wan et al. [275] indicated that concentrations of U(VI)aq increase by orders of magnitude when CO_2 partial pressure increases (for example from $10^{-3.5}$ to $10^{-1.5}$ atm (other conditions constant). This is also evident in (Fig. 16), where the equilibrium between $U(VI)_{aq}$ and amorphous uraninite, UO_2(am) is described by Eh–pH diagrams [272]. Increasing PCO_2 shifts the U(VI)aq/U(IV)S equilibrium towards lower redox potentials. Furthermore, comparison of the graph a (without Ca^{2+}) and b (equilibrium with calcite), illustrates the large shift in U(VI)aq/U(IV)S redox equilibrium boundaries to lower potentials in systems containing calcite, especially for pH < 8.0 [275].

The need to optimize bioremediation procedures in order to ensure a sustainable, effective remediation in the presence of other contaminants (complexing anions, toxic metals, organics, chelators) is very actual as well as the assessment of suitable remediation end-points [268].

3.5.3. *Phytoremediation*

USEPA has defined phytoremediation *as the use of plants for containment, degradation or extraction of xenobiotics from water or soil substrates* [307]. Phytoremediation involves the use of plants to extract, sequester and/or detoxify the pollutants present in soil,

Table 9
Redox reactions and potentials [275]

Reactions	Eh^a (mV)	Eh^b (mV)	Eh^c (mV)
I. $UO_2CO_3 + 6H^+ + 2e^- \rightarrow UO_2(s) + HCO_3^-$	278	−62	−121
II. $UO_2(CO_3)_2^{2-} + 2H^+ + 2e^- \rightarrow UO_2(s) + 2HCO_3^-$	366	−78	−197
III. $UO_2(CO_3)_3^{4-} + 3H^+ + 2e^- \rightarrow UO_2(s) + 3HCO_3^-$	531	−17	−195
IV. $Ca_2UO_2(CO_3)_3 + 3H^+ + 2e^- \rightarrow UO_2(s) + 3HCO_3^- + 2Ca^{2+}$	278	−181	−240
V. $CaUO_2(CO_3)_3^{2-} + 3H^+ + 2e^- \rightarrow UO_2(s) + 3HCO_3^- + Ca^{2+}$	427	−76	−195
VI. $Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	976	−78	−78
VII. MnO_2 (pyrolusite) + $4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1220	1180	1180

[a] Standards redox potentials.

[b] Reduction potential under conditions: $PCO_2 = 10^{-3.5}$ atm, pH 7.4, $\Sigma U(VI)_{(aq)} = 10^{-8}$ M, $Fe^{2+} = 4.5 \times 10^{-5}$ M, $Mn^{2+} = 3.5 \times 10^{-5}$ M, $Ca^{2+} = 10^{-1.5}$ M.

[c] Reduction potential under experimental conditions: $PCO_2 = 10^{-1.5}$ atm, pH 7.4, $\Sigma U(VI)_{(aq)} = 10^{-8}$ M, $Fe^{2+} = 4.5 \times 10^{-5}$ M, $Mn^{2+} = 3.5 \times 10^{-5}$ M, $Ca^{2+} = 10^{-3.5}$ M. Note that $[Ca^{2+}]$ is a dependence of PCO_2.

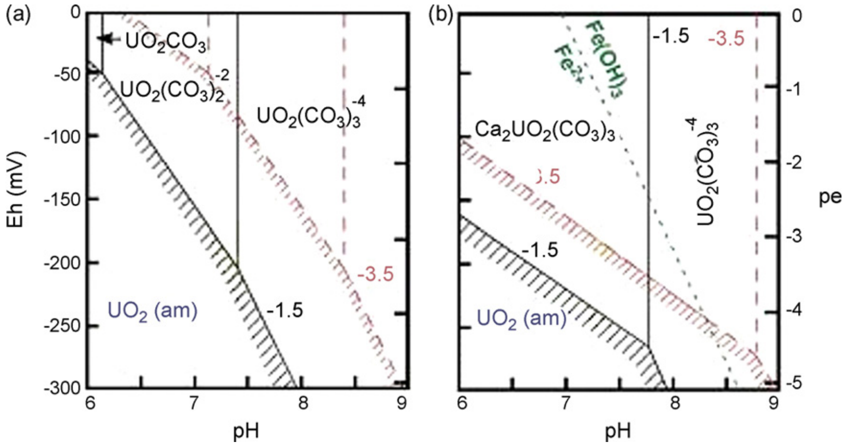


Fig. 16. Eh–pH diagram of $U(VI)_{aq}$ equilibrium with UO_2(am) without Ca^{2+} (a) and with calcite (b) (for $\Sigma U(VI)aq = 10^{-8}$ M, at $\log PCO_2 = -3.5$ and $\log PCO_2 = -1.5$; for comparisons, the $Fe(OH)3/Fe^{2+}$ ($Fe^{2+} = 10^{-4}$ M) redox transition is shown as a dotted line) [272].

water and air [308,309]. For long-time projects and adequate pollutants, phytoremediation is considered as the cheaper and simplest option available for soil cleanup [308,309].

Plants are used increasingly as tools in controlling or remediating environmental contamination, because it was found that they have the ability to absorb and accumulate metals and radionuclides in an efficient way if they are adapted to a wide range of environmental conditions. These are tolerant plants, having heavy metal hyper accumulation potential, which could be beneficial in phytoremediation for cleanup of soil and water; on the other hand tolerant food crops, if exposed to heavy metals in their growth medium, may be dangerous as carriers of toxic metals in the food chain leading to food toxicity [16,148,154,310]. Mathematical models related to plant characteristics (e.g., biomass and planting density) to predict a long-term U-removal rate from the soil were also developed [310].

Plant-assisted remediation of soil can generally occur through one or more of the following mechanisms [139,274,311]:

- *phytostabilization*: involves the use of plants to contain or immobilize contaminants in the soil by:
  - o absorption and accumulation by roots;
  - o adsorption onto root surface;
  - o precipitation within the root zone.
- *phytodegradation/phytotransformation*: involves the breakdown of contaminants through:
  - o metabolic processes(internally);
  - o release of enzymes into the soil.
- *phytovolatilization*: the uptake and transpiration into the atmosphere of a contaminant by a plant;
- *rhisodegradation*: involves the breakdown of the contaminants in the soil due to microbial/root/soil interaction;
- *phytohydraulics*: involves the use of plants to control the migration of contaminants.

Radionuclide bioavailability mostly depends on [311]:

- type of radionuclide deposition;
- time of deposition;
- soil characteristics.

The mechanisms of phytoremediation depend on the type and location of the contaminant [274,312]. Phytoextraction seems to be the most applied phytoremediation procedure, especially when the availability of uranium from soil to plants is improved by applying some methods such as chelation (for example adding citrate), complexation aiming to solubilize, detoxify and enhance U accumulation by plants [148,274,312,313].

The transfer of radionuclides from soils to plants is dependent on three classes of factors [129,214,314]:

- quantity factor (that is the total amount of potentially available elements);
- intensity factor (the activity, the ionic ratios of elements in the soil solution, presence of other species (nitrogen, phosphorous));
- reaction kinetics (the rate of element transfer from solid to liquid phases and to plant roots).

Uranium phytoextraction, as an emerging technology may provide an environmentally friendly alternative for the cleanup of U-contaminated soils.

Considering the effects of various soil amendments on uranium desorption from soil to soil solution, a number of authors investigated the physiological characteristics of uranium uptake and accumulation in plants, and developed techniques to trigger uranium hyperaccumulation in plants [313,314]. Their studies indicate that soil organic matter sequestered uranium, rendering it largely unavailable for plant uptake [265].

Also, the uranyl ($UO_2{}^{2+}$) cation is the chemical species of U most readily accumulated in plant shoots [198]. Furthermore, adding the organic acid citrate to soils greatly increases both the solubility of uranium and its bioavailability for plant uptake and translocation [214].

Some studies have shown that the proportion of retained uranium with plant biomass can be smaller than expected, since a larger part of this U is turned over in organic matter to downstream receptors. Determining the importance of organic matter turnover to the fate of uranium represents an important aspect to understanding the long-term efficacy of some phytoremediation techniques applied for contaminated sites and water.

Phytoremediation of radionuclides offers some advantages [44,311,315,316]:

- the soil is treated *in situ*, further disruption to the soil dynamics being avoided;
- plants remain for consecutive harvest on the land;
- exposure times for workers are reduced;
- can be used as a long-term treatment.

3.5.4. *Biosorption*

Biosorption was developed as a remediation way that could help to recover heavy metals [317]. Non-viable biomass which exhibits metal-sequestering properties can offer a basis for a new approach to remove heavy metals when they occur at low concentrations [270,318–320]. Although biosorptive uptake of some heavy metals was well documented, radionuclide sorption is a research area with several non-elucidated aspects. Various biosorbents were applied for uranium biosorption directly from soil or after it was transferred in water [321]. Also, large efforts have been concentrated especially on studying the uranium sorption by different microorganisms such as bacteria [250,322–328], actinomycetes [328,329], fungi [330–332], yeasts [332] or algae [333–335].

Results of a literature review and the cation exchange capacity measurements performed by England [250] suggest that other organic materials, such as peat, can be used to remove soluble uranium from contaminated water. Natural peat deposits remove and sequester uranium from soils and groundwater under certain geochemical conditions while several species of bacteria, including *Desulfovibrio desulfuricans* precipitate soluble uranium from solution [250]. Some factors which influence the biosorption performance were also investigated [324,333,336], such as:

- co-existing cations (potassium, ammonium, magnesium, heavy metals);
- co-existing anions (nitrate, sulfate, thiosulfate, chloride, fluoride);
- sorbent type and amount;
- pH of the solution;
- contact time.

For example, when uranium binding by a *P. aeruginosa* strain was investigated by Hu et al. [271], they found that the rate of uranium adsorption increased following permeabilization of the outer and/or cytoplasmic membrane by organic solvents such as acetone. Also, uranium loading capacity increased with increasing pH under acidic conditions, actually due to uranium speciation and the H^+ competition at some binding sites even in an immobilized state on polymeric materials, including calcium alginate, polyacrylamide, polysulfone and polyurethane [325].

Basic aspects of uranium adsorption by peat have been investigated during batch experiments, when the influence of different experimental parameters such as final solution pH, adsorbent dosage, sorption time, temperature and various concentrations of uranium on uptake were evaluated [336]. It was observed that maximum uranium adsorption occurred in the pH range 4.0–6.0. Psareva et al. [337] presented the effect of the pretreatment of cork biomass with a hydrochloric acid solution on its sorption affinity towards uranium. The increase of the concentration of strong acidic and weak acidic groups on cork biomass surface led to an increase in the sorption capacity towards uranium more than twice. Alga biomass modified by protonation was found to sequester uranyl ions from aqueous solution at various levels of pH [336]. An algae-clay composite adsorbent was tested by Donat and Aytas [338] for its ability to recover U(VI) from diluted aqueous solutions. Macro marine algae (*Ulva* sp.) and clay (Na bentonite) were used to prepare composite adsorbent, which proved to be suitable as sorbent material for recovery and biosorption/adsorption of uranium ions from aqueous solutions.

Some viable and non-viable fungi proved to be good biosorbents and the biosorption process showed to be pH dependent as well. Uranium uptake by dried roots of *Eichhornia crassipes* was rapid and the biomass could remove 54% of the initial uranium present, also dependent on pH value [339].

Compared with other (conventional) treatment methods, biosorption as a biomass-based system is considered as cost-effective and flexible in detoxification of very dilute effluents [327].

3.6. *Electrokinetic methods*

As a process applied for separation and extraction of contaminants such as heavy metals, radionuclides or organic contaminants, electrokinetics was reported to be a feasible alternative for remediation of saturated or unsaturated soils, sludge and sediments contaminated with uranium (both anionic: $(UO_2(CO_3)_2)^{2-}$ or cationic: $(UO_2{}^{2+})$ forms [340–344].

Two main phenomena can be present [340,344]:

1. dissolved ionic species in the soil-water solution migrate toward the opposite-charged electrode, at a rate which depends on the local potential gradient, as well as charge and mobility of ions.
2. a bulk flow of soil-water is induced toward the cathode, at a rate which depends on the local potential gradient and zeta potential of soil.

Electrokinetic methods are based on two phenomena (*electromigration* and *electroosmosis*) and began to be used within the last few decades for the remediation of uranium contaminated soils and/or groundwater, being also known as electrokinetic remediation, electroremediation, electrorestoration, electroreclamation, electrochemical decontamination or electromigration [340,341,344–348]. The transport of the contaminant induced during electrochemical treatment is based on the well-known electrokinetic processes that take part in wet porous medium under an electric field (electrophorersis, electroosmosis, electromigration), which can simultaneous change the electrokinetic properties of soil particles and the chemistry of pore fluid [349,350]. The resulting soil–chemical interactions may enhance or inhibit the extractability of contaminants by electrokinetics, as various electrochemical processes are dynamic, reversible, and interdependent [351–354]. Acar et al. [346] have defined the electrokinetic remediation as a controlled application of electrical migration and electroosmosis together with the electrolysis reactions at electrodes.

Electrophoresis is mostly applicable for unrestrained particle transport in poorly consolidated systems, which compact the soil to anode and disintegrate it on cathode [342].

Electrophoresis of clay colloids could still plays an important role if chemical species of interest are adsorbed at migrating colloids [342,355]. The separation of uranium(VI) and lanthanides was investigated by Macka et al. [356] which applied capillary electrophoresis (CE) to the form of anionic complexes with arsenazo III in aqueous background electrolytes. They established that the process performance depends strongly on the chemistry of the surface of the internal wall capillary. Also, the capillary electrophoresis and time-resolved laser-induced fluorescence (TRLIF) was found to be a good method to characterize the different complexes of uranium [357,358].

When a low intensity current is applied across pairs of electrodes planted in the ground on each site of contaminated soil, it causes electroosmosis and ion migration toward the electrodes [340]. When electroosmosis occurs, non-ionic species will be transported along with the induced water flow [340,343]. This transport, together with sorption, precipitation and dissolution reactions covers the fundamental mechanisms which affect the electrokinetic remediation process [341]. Electroosmosis is the dominant process where a direct current can generate an accelerated flow of water in the soil [359].

Electromigration is the main mechanism for the electrochemical process, when the contaminants are ionic or surface charged. It defines the movement of ions and ion complexes across the porous media. The average mobility of the ions is of about 10 times greater than that of electroosmotic ability, but is superimposed or tied to the movement induced by electroosmosis, complementing each other [350,360].

Sediment typically has a negative surface charge. The metal ions are used to bind with negatively charged sediment. In an electric field, the metal ions move towards the cathode by leaving the surface of the sediment. This process accelerates by the primary reactions of electrochemical processes by acidification the sediment at the anode. The hydrogen ions can replace the metal ions from the sediment surface (relation (11)) [341,342].

$$nH^+ + \equiv (\text{sediment})^{n-}M^{n+} = \equiv (\text{sediment})^{n-}nH^+ + M^{n+} \qquad (11)$$

Speciation and precipitation are major factors in mobilization and transport of heavy metal constituents by ion-migration component. The speciation is dependent upon a number of fairly well understood parameters including pH, redox potential and ion concentration [342,346,347]. These same factors influence the equilibrium conditions relating to both the sediment and contaminants. In the electric field, metal ions could be oxidized by forming a redox barrier. The concept of redox barrier is that of a permeable reactive barrier driven by low voltage DC current. This is accomplished by installing closely spaced permeable electrodes transverse to flow through a targeted plume sequential oxidizing and reducing conditions are generated about positive and negative electrodes, respectively.

The electrochemical ions might gain electrons at cathode to form solid metals. Due to pH barrier, metal ions might combine with OH^- or carbonate ions to precipitate. The most probable cases are the last two equations ((14) and (15)).

$$4M^{n+} + 4H^+ + O2 = 4M^{(n+1)+} + 2H_2O\,(\text{redox barrier}) \qquad (12)$$

$$M^{n+} + ne^- = M(s) \qquad (13)$$

$$M^{n+} + nOH^- = M(OH)_n\downarrow\ (\text{pH-barrier}) \qquad (14)$$

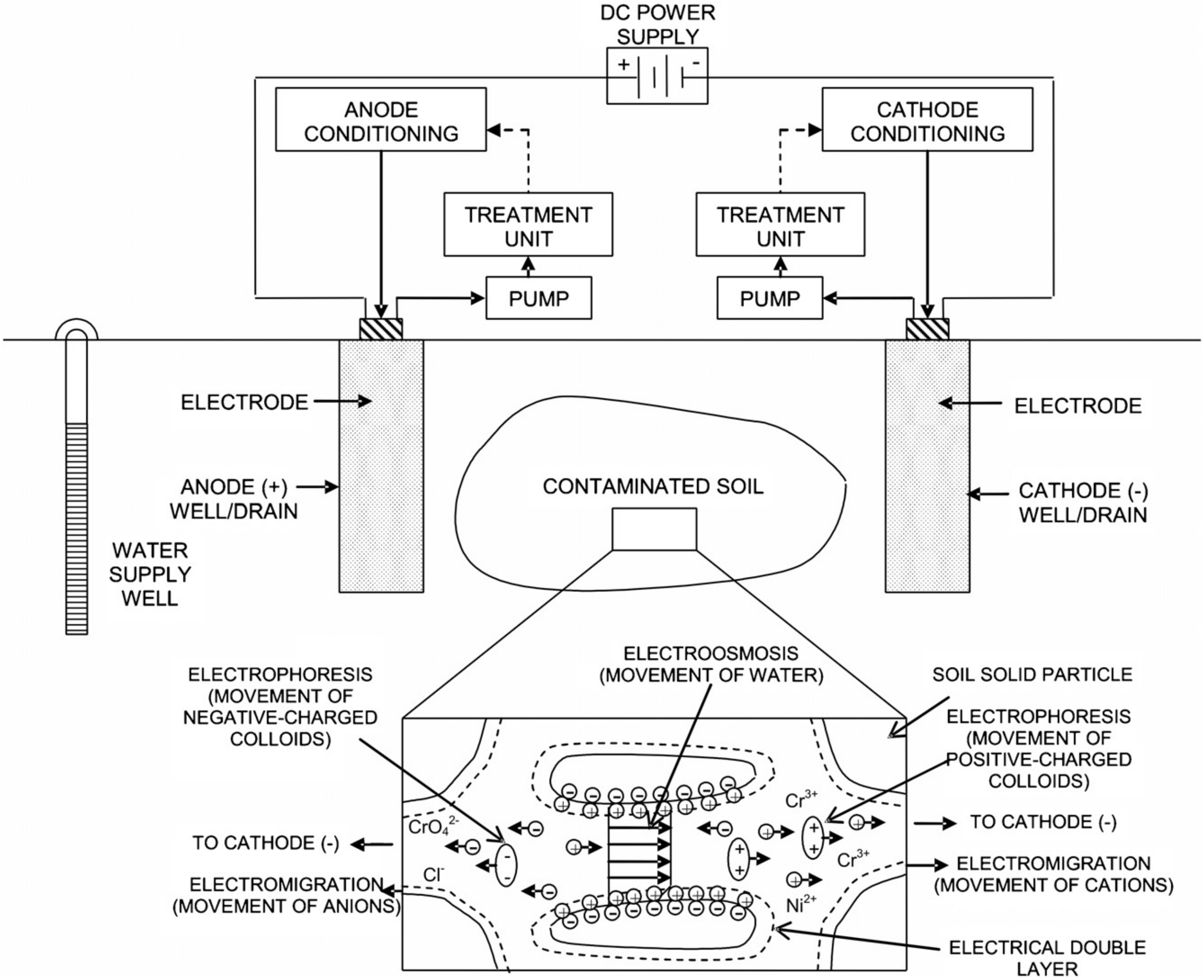


Fig. 17. Schematic *in situ* electrokinetic remediation system [349].

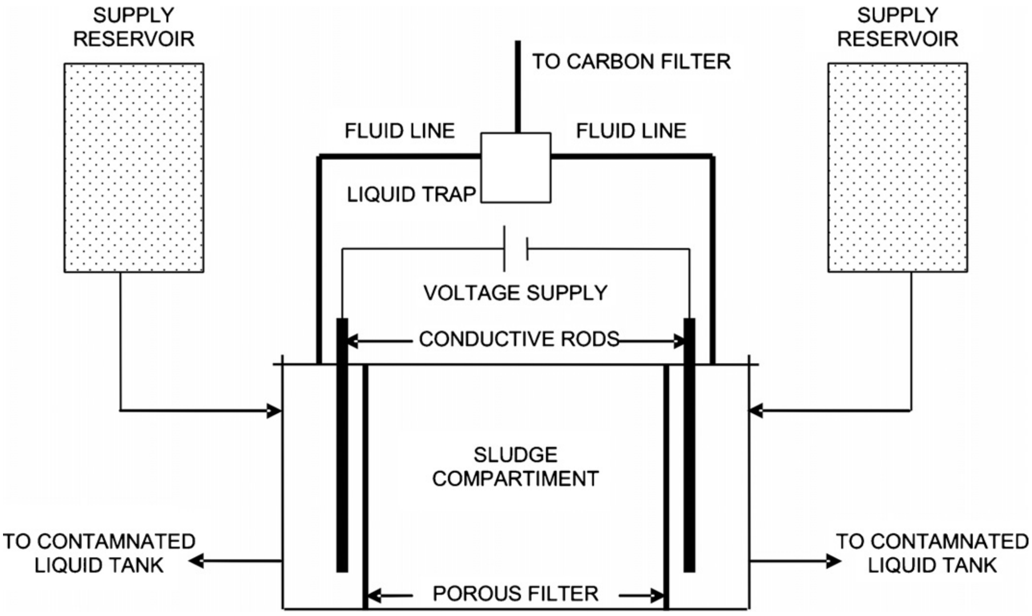


Fig. 18. Schematic *ex situ* electrokinetic remediation system [349].

$$M^{2+} + HCO_3^- + OH^- = MCO_3\downarrow + H_2O \qquad (15)$$

Me denotes a metal.

The application of a low direct current or a low potential gradient through electrodes can create an acidic front at the anode and a basic front at the cathode by primary electrochemical reactions (Eqs. (16) and (17)) [342,349]. The voltage distribution between the electrodes is affected by pH, which also influence the solubility, desorption and mobility of radionuclides removed from soil [346,347,351,352,362].

$$2H_2O - 4e- = O_2\uparrow + 4H^+ \,(\text{anode}) \qquad (16)$$

$$4H_2O + 4e- = 2H_2\uparrow + 4OH^- \,(\text{cathode}) \qquad (17)$$

$E_0 = -0.828\,V$

Therefore, H^+ ions are generated at the anode and OH^- ions at the cathode. Low pH values in soil are favorable for desorption and dissolution of uranium, but high pH facilitates the sorption and precipitation [349,361].

The *in situ* generation of acidic conditions favorizes the mobilization of sorbed contaminants for transportation to the collection system at the cathode [344,348,349,356].

As a result of the application of this electric field, contaminants may be mobilized, concentrated at the electrodes and extracted from the sediment [346,347,352]. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. Also, mobilizing reagents may be introduced at the electrodes to enhance contaminant removal rates [340,341,346,362]. These compounds must be selective for the targeted contaminant, as well as biodegradable, but a careful control and their complete postremediation have to be ensured [344].

A number of studies revealed that electrokinetic remediation technique requires the presence of a pore fluid in the soil pores, which is able to conduct the electrical field and also to transport the species injected to or extracted from the polluted soil mass [346,352,353,363]. In addition, the electrokinetic methods have to be applied after a number of laboratory and field tests have been performed, in order to gather information about [341,342,346]:

- field electrical conductivity;
- pH;
- electrical conductivity of water from soil pores;
- chemical composition of pore water (especially dissolved anions, cations, concentration of contaminants);
- chemical composition of soil (buffering capacity, geochemistry).

A typical *in situ* electrokinetic remediation system is shown schematically in Fig. 17 [345]. Essentially, electrokinetics involves the installation of electrodes into the subsurface surrounding the contaminated region. After the electrodes are in place, a low electrical potential is applied across the anode(s) (positively charged electrode) and the cathode(s) (negatively charged electrode). As a result of the electrical gradient, different physico-chemical reactions occur and contaminant transport occurs due to various mechanisms within the soil and groundwater.

Electrokinetics can also be used as an *ex situ* treatment technology by employing a reactor similar to the one shown schematically in Fig. 18. A similar setup was used by Reddy et al. [345] for electrokinetic treatment of soils contaminated with heavy metals, at laboratory scale. The setup consists of an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source, and a multimeter.

Electrokinetic remediation has the advantage that a high degree of control of flow direction can be achieved [347]. It has been driven by the demand for technologies that are cost effective and will eliminate the long-term liability [364]. However, there are still problems in the field demonstration in a large scale due to some issues as control of contaminant movement, ability of cleanup goals. The efficiency of electrokinetic methods depends on particle size, ion mobility, contaminant concentration and the type of species, their solubility in the specific soil, their electrical charge, total ionic concentration, their location and form in the soil, availability of organic matter in the soil [341,346,347]. Uranium was efficiently removed from low permeability soils such as clay, while adding some adjuvants such as acetic acid enhanced the process, resulting in the prevention of the precipitation of uranium ions in the cathode region [365].

Hence, electrokinetic soil remediation is considered to be one of the most promising soil decontamination processes because it has high removal efficiency and time effectiveness in low permeability soils, such as clay [362].

4. Conclusions

The presence of uranium in soil generates an important issue against public perception on the risk which the contamination poses to the environmental and human health. In spite of some preventive and remedial actions during the uranium recovery, many natural ecosystems were heavily polluted with radioactive elements.

Various methods for remediation of soils contaminated with radioactive elements are known but only few of them have been applied under large-scale conditions. Each one will direct decision makers to substantially different paths with regard to their subsequent choices, actions and potential results, making available significantly different technological options for application. Basic evaluation criteria include engineering and non-engineering considerations.

Natural attenuation of radionuclides involves enclosing the radionuclides in a mineral where they will not escape unless chemical conditions change dramatically. Chemical approaches are available for metal and radionuclide remediation, but are often expensive to apply and lack the specificity required to treat target metals against a background of competing ions. Microbial processes are beginning to be used in the cleanup of radioactive and metallic contaminants of soils and sediments through biotransformation, biodegradation and biomineralization. Biological approach offer the potential for the highly selective removal of toxic metals coupled with considerable operational flexibility; they can be used both *in situ* and *ex situ*. Electrokinetics became more and more applied for the remediation of contaminated soils and/or groundwater. This technique has been called electrokinetic remediation, electroremediation, electrorestoration, electroreclamation, electrochemical decontamination or electromigration.

The costs for implementing available technologies vary significantly between sites because costs are influenced by a wide variety of factors. The influence of time, temperature, attrition scrubbing, pH and reagent concentrations, and the effects of oxidizing and reducing chemical environments on the removal of uranium from the soil have to be considered during remediation. Application of special remediation techniques is correlated with a successful soil testing, which depends upon the relation between remediation alternatives and remediation aims and options, as a support for decisions making about implementation. Suitable accounting for all factors affecting the result of an environmental remediation project enables to evaluate and compare the versatility, efficiency and economics of various technologies that may be combined into systems for the characterization and remediation of uranium contaminated soils, as well as finding an optimum solution for a given knowledge base that will satisfy the societal goals and add value to the project itself.

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